



Quantum Mechanical / Molecular Mechanics Study of Electronically Excited states and Assessment of Methods for Calculating Vertical Excitation Energies

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Mario Ramos da Silva Junior

The present work is a cumulative dissertation
according to § 4 Sec. 1 from the Promotionsordnung der Mathematisch-
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This doctoral thesis is based on seven original articles either published or submitted in international peer-reviewed journals. It covers two major topics in the field of computational photochemistry and photobiology. The first part addresses the benchmarking of theoretical methods for computing electronically excited states, including the derivation of theoretical best estimates for vertical excitation energies that should be useful for the validation of existing methods and as reference data for the parametrization of new approximate methods. The second part reports an application of QM/MM methodology to electronically excited biomolecules, with an investigation of the photoinduced processes in two artificial flavin derivatives inserted into the YtvA protein.

In the following the articles that form this thesis are listed, together with the tasks I performed in every publication:

M. Schreiber, *M. R. Silva-Junior*, S. P. A. Sauer, W. Thiel “Benchmarks for electronically excited states: CASPT2, CC2, CCSD and CC3”, *J. Chem. Phys.*, **128**, pp. 134110/1–25, 2008.

I carried out the extensive literature survey of the benchmark molecules and was involved in the assignment of states. In addition, I produced part of the Supporting Information.

M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer, W. Thiel “Benchmarks for electronically excited states: Time-dependent Density Functional Theory and Density Functional Theory Based Multireference Configuration Interaction”, *J. Chem. Phys.*, **129**, pp. 104103/1–14, 2008.

I performed the TD-DFT calculations together with the assignment of the TD-DFT and DFT/MRCI results. I also carried out the statistical evaluations for the excitation energies and one-electron properties and provided the literature survey.

S. P. A. Sauer, M. Schreiber, *M. R. Silva-Junior*, W. Thiel “Benchmarks for electronically excited states: A comparison of noniterative and iterative triples corrections — CCSDR(3) versus CC3”, *J. Chem. Theor. Comput.*, **5**, pp. 555–563, 2009. In this paper I supported the assignment of the states and produced some of the figures.

M. R. Silva-Junior and W. Thiel “Benchmark of electronically excited states for semiempirical methods: MNDO, AM1, PM3, OM1, OM2, OM3, INDO/S and INDO/S2”, *J. Chem. Theor. Comput.*, **6**, pp. 1546–1564, 2010.

All calculations and statistical evaluations were done by myself.

M. R. Silva-Junior, S. P. A. Sauer, M. Schreiber and W. Thiel “Basis set effects on coupled cluster benchmarks for electronically excited states: CC3, CCSDR(3) and CC2”, *Mol. Phys.*, **108**, pp. 453–465, 2010.

The CC2 calculations and the assignment of all coupled-cluster results were my main tasks in this publication. I also provided the statistical results and their discussion.

M. R. Silva-Junior, S. P. A. Sauer, M. Schreiber and W. Thiel “Benchmarks of electronically excited states: Basis set effects on CASPT2 results”, *J. Chem. Phys.*, **133**, pp. 174318/1–13, 2010.

I performed part of the CASPT2 calculations and all statistical evaluations. I also contributed to the discussion of the results.

M. R. Silva-Junior, M. Mansurova, W. Gärtner, W. Thiel “Photophysics of structurally modified flavin derivatives in the blue light photoreceptor Ytva: A combined experimental and theoretical study”, submitted.

I carried out all the theoretical calculations and the analysis of the theoretical results.

In addition, during the period of my doctoral studies, the following article has been published, which is not included in this thesis:

S. Salzmann, *M. R. Silva-Junior*, W. Thiel, C. M. Marian “Influence of the LOV domain on low-lying excited states of flavin: A combined quantum-mechanics molecular-mechanics investigation”, *J. Phys. Chem. B*, **113**, pp. 15610–15618, 2009.

The support of the QM/MM system setup and of the geometry optimizations were my main tasks in this contribution.

Abstract

A systematic and extensive benchmark of theoretical methods for computing electronically excited states is presented in the first part of this dissertation. The chosen reference set comprised 28 organic molecules and diverse types of singlet and triplet valence excited states. Using the same ground-state geometries and the medium-sized TZVP basis set, MS-CASPT2 and coupled-cluster CC3 calculations were carried out and compared with high-level theoretical work in the literature. Generally there was excellent agreement between the results from these *ab initio* calculations, especially when the weight of singles excitations was higher than 90% which is usually the case for triplet and low-lying singlet excitations. On the basis of these own calculation and high-level literature results, a set of theoretical best estimates (TBE) for vertical excitation energies was derived. Subsequently, basis set effects were analyzed both at the MS-CASPT2 and the coupled cluster level. Basis set extension from TZVP to aug-cc-pVTZ led to a rather small and systematic lowering of the computed vertical excitation energies, which prompted a minor update in the recommended TBE values.

The *ab initio* benchmark data were used to evaluate the performance of methods based on density functional theory (DFT) and of semiempirical methods. Time-dependent density functional theory (TD-DFT) gave different accuracies for singlet and triplet states; among the three functionals studied, B3LYP yielded the lowest mean absolute deviations, whereas BP86 (BHLYP) tended to underestimate (overestimate) the reference excitation energies. The DFT/MRCI method performed uniformly well for singlet and triplet states and was the best among the tested DFT-based approaches. Among the semiempirical methods, the orthogonalization-corrected approaches (OM1, OM2, and OM3) were ranked as best, almost comparable in performance with TD-DFT/B3LYP. The most popular ground-state semiempirical methods (AM1, PM3, and MNDO) were found not suitable for the treatment of excited states, since they systematically gave much too low excitation energies. The spectroscopy-parametrized INDO/S method performed well for low-lying singlet excited states, but less so for triplet states and for high-lying singlet states above 7 eV.

In the second part of this dissertation, the photoinduced processes in a blue-light photoreceptor with artificial chromophores were studied using combined quantum mechanics / molecular mechanics (QM/MM) methods. This work was motivated by experimental findings that the insertion of the chromophores 1- and 5-deaza flavin mononucleotide (1DFMN and 5DFMN) into the binding pocket of

the LOV domain of the YtvA protein leads to unexpected and different behavior: 1DFMN-YtvA does not undergo any photoinduced reactions, whereas 5DFMN-YtvA forms a photoadduct in a triplet reaction (similar to the parent FMN chromophore) followed by photochemical dark state recovery. The QM/MM calculations reproduced the observed spectral shifts of the protein-incorporated 1DFMN-YtvA and 5DFMN-YtvA reasonably well. For 1DFMN-YtvA, they identified a radiationless deactivation channel along a hydrogen transfer pathway from the active-site cysteine residue to the flavine that might be responsible for the lack of photochemical activity. For 5DFMN-YtvA, they provided a comprehensive mechanistic scenario that is compatible with the available experimental evidence. According to the calculations, photoexcitation of 5DFMN-YtvA into the bright S_1 state is followed by relaxation, intersystem crossing to the triplet manifold, hydrogen transfer on the T_1 surface via a moderate barrier to yield a biradical, intersystem crossing to the ground state, and recombination in the biradical to form an adduct with a S–C4a covalent bond. Photoexcitation of this adduct triggers cleavage of this bond in the S_1 state, and the resulting biradical can return to the ground state via another hydrogen transfer in the T_1 state. Alternative photoadducts with a S–C5 bond are found more difficult to generate and do not offer an easily accessible path for the photochemically induced dark state recovery.

Zusammenfassung

Im ersten Teil dieser Dissertation wird ein systematischer und umfassender Vergleichstest theoretischer Methoden zur Berechnung elektronisch angeregter Zustände präsentiert. Zunächst wurde ein Vergleichssatz ausgewählt, bestehend aus 28 organischen Molekülen mit verschiedenen Typen angeregter Singulett- und Triplett-Zuständen. Unter Verwendung identischer Molekülgeometrien und des mittelgroßen TZVP Basissatzes wurden MS-CASPT2 und Coupled Cluster CC3 Rechnungen durchgeführt und deren Ergebnisse mit denen hoch-genauer *ab initio* Rechnungen aus der Literatur verglichen. Dabei wurde generell eine ausgezeichnete Übereinstimmung zwischen diesen Resultaten gefunden, insbesondere wenn die Beiträge von Einfachanregungen mehr als 90 % betrug, was normalerweise bei Triplett-Zuständen und bei niedrig liegenden Singulett-Zuständen der Fall ist. Auf der Grundlage der eigenen Rechnungen und einer Analyse der Literaturdaten wurde ein Satz von besten Referenzwerten für die vertikalen Anregungsenergien erstellt. In der Folge wurden Basissatzeffekte auf die MS-CASPT2 und Coupled Cluster Ergebnisse untersucht. Die Erweiterung des Basissatzes von TZVP zur größeren aug-cc-pVTZ Basis führte zu einer relativ geringen und systematischen Erniedrigung der berechneten vertikalen Anregungsenergien, die in einer Anpassung der empfohlenen Referenzwerte berücksichtigt wurde.

Die *ab initio* Benchmarkdaten wurden benutzt, um die Genauigkeit von Methoden der Dichtefunktionaltheorie (DFT) und von semiempirischen Methoden für elektronisch angeregte Zustände zu evaluieren. Die zeitabhängige Dichtefunktionaltheorie (TD-DFT) lieferte unterschiedlich genaue Ergebnisse für Singulett- und Triplett-Zustände; von den drei getesteten Funktionalen ergab B3LYP die kleinsten mittleren absoluten Abweichungen, während mit BP86 (BHLYP) eher zu kleine (zu große) Anregungsenergien erhalten wurden. Die DFT/MRCI Methode lieferte einheitlich gute Ergebnisse für Singulett- und Triplett-Zustände, mit den insgesamt kleinsten mittleren Abweichungen. Von den untersuchten semiempirischen Methoden schnitten die Methoden mit Orthogonalisierungskorrekturen (OM1, OM2 und OM3) am besten ab, fast vergleichbar in der Qualität mit TD-DFT/B3LYP. Die Standardmethoden AM1, PM3 und MNDO erwiesen sich als nicht geeignet zur Behandlung angeregter Zustände, weil die berechneten Anregungsenergien systematisch viel zu klein waren. Die speziell für spektroskopische Rechnungen parametrisierte INDO/S Methode ergab gute Resultate für niedrig liegende angeregte Singulett-Zustände, allerdings auch größere Fehler für Triplett-Zustände und hoch liegende Singulett-Zustände oberhalb von 7 eV.

In dem zweiten Teil der Dissertation wurden photoinduzierte Prozesse in einem Blaulicht-Photorezeptor mit künstlichen Chromophoren mit kombinierten quantenmechanischen / molekülmechanischen (QM/MM) Verfahren untersucht. Diese Arbeiten waren motiviert durch experimentelle Befunde, nach denen der Einbau der Chromophore 1- und 5-Deazaflavin-Mononukleotid (1DFMN und 5DFMN) in die Bindungstasche der LOV-Domäne des YtvA-Proteins zu einem unterschiedlichen und unerwarteten Verhalten nach UV-Bestrahlung führt: Bei 1DFMN beobachtet man keinerlei photochemische Reaktion, während 5DFMN in einer Triplett-Reaktion ein Photoaddukt bildet (ähnlich wie FMN), welches dann photochemisch wieder in den Dunkelizustand zurückgeführt werden kann. Die QM/MM Rechnungen reproduzierten die beobachteten spektralen Verschiebungen beim Einbau der Chromophore in das Protein gut. Beim 1DFMN-YtvA gelang es, einen strahlungslosen Deaktivierungspfad zu identifizieren, der mit einem Wasserstofftransfer von einem benachbarten Cystein zum Flavin einhergeht und der für die fehlende photochemische Reaktivität verantwortlich sein könnte. Beim 5DFMN-YtvA konnte aufgrund der QM/MM Rechnungen ein detaillierter Mechanismus vorgeschlagen werden, der mit den derzeit bekannten experimentellen Befunden vereinbar ist. Demzufolge relaxiert 5DFMN-YtvA nach Photoanregung zunächst in dem S_1 Zustand, gefolgt von einem Intersystem Crossing (ISC) zum Triplett, einem Wasserstofftransfer in dem T_1 Zustand unter Bildung eines Biradikals, einem erneuten ISC zum Grundzustand und anschließender Rekombination des Biradikals, wobei ein Addukt mit einer kovalenten S–C4a Bindung entsteht. Die Photoanregung dieses Addukts führt zum Bruch der S–C4a Bindung im S_1 Zustand, das so gebildete Biradikal kann dann über einen erneuten Wasserstofftransfer im T_1 Zustand zum Dunkelizustand zurückkehren. Alternative Photoaddukte mit einer S–C5 Bindung sind schwieriger zu erzeugen, und es wurde bei ihnen außerdem kein leicht zugänglicher Reaktionsweg zur photochemischen Regenerierung des Dunkelizustands gefunden.

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Chapter 1

Introduction

1.1 Reference data for electronically excited states

Benchmark sets of molecules with reliable reference data are essential tools for the validation of existing computational methods and for the parameterization of improved approximate methods. For ground-state molecules, such sets are available, for example the G2 and G3 sets [1–3] which collect a large number of small and medium-sized molecules with accurate experimental thermochemical data. These sets have been used extensively to assess the accuracy of quantum-chemical methods in thermochemistry.[3–5]

Corresponding representative benchmarks have been missing for electronically excited states. Traditionally, the primary target of theoretical work in this area has been the calculation of vertical excitation energies and oscillator strengths to predict the electronic spectra, both for small molecules and for medium-sized chromophores that are important in organic photochemistry. It is hard and often even impossible to obtain reliable and accurate experimental reference data for these target properties, due to various well-known reasons: The observed band maxima do not exactly match the vertical excitation energies, bands are often found to overlap, spectral assignments may be uncertain, and spectra may be available only in solution and not in the gas phase. These problems are most pronounced for larger chromophores which are often most interesting with regard to photochemistry.

1.1.1 CASPT2 and coupled-cluster methods

Given this situation, one may turn to high-level *ab initio* theory and generate the required reference data computationally. Unfortunately, theoretical calculations with very high accuracy such as full CI are still restricted to systems containing

up to 4-6 atoms, [6] and are thus prohibitive for most organic chromophores of interest. During the past two decades, CASPT2 (complete-active-space second-order perturbation theory) [7–9] has emerged as the standard *ab initio* method for calculating excited-state properties of medium-sized molecules, and it has been widely applied, e.g., for the assignment of absorption spectra. There are many examples in the literature that illustrate the ability of this multireference method to properly describe all types of excitations. The introduction of the multi-state CASPT2 (MS-CASPT2) approach [10] has alleviated the problems with intruder states and improved the description of states of the same symmetry with strong valence-Rydberg mixing which had been troublesome in the original CASPT2 approach.

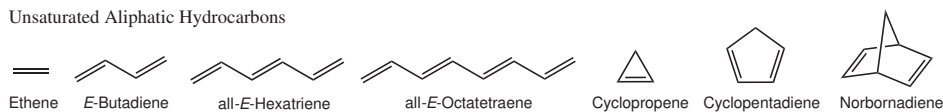
Alternatively, there are methods based on CC (coupled cluster) theory such as CC2, CCSD, CC3, and CCSDT [11–18] which have been proposed more recently and have thus been applied less extensively than CASPT2. Recent developments for CC2 such as the use of the resolution of identity [19] as well as a spin-component scaled version [20] make this methodology suitable for applications on large chromophores. In the literature, there has been some debate about the relative merits of CASPT2 and CC-based methods, but a balanced assessment has been difficult because of technical differences in the published work. Since the coupled-cluster methods derive the excited-state properties from linear response theory, the valence-Rydberg mixing is intrinsically considered and can thus not be decoupled.

After an extensive survey of the literature, a benchmark set of 28 medium-sized organic molecules was defined, and the properties of their valence excited states (with emphasis on vertical excitation energies) were computed using MS-CASPT2, CC2, CCSD, and CC3 at a uniform level (MP2/6-31G* ground-state equilibrium geometries, TZVP basis set, standard CASPT2 conventions). These benchmark molecules cover the most important chromophores found in organic photochemistry (see Figure 1.1). The focus on valence states assures that the chosen setup is appropriate to obtain a realistic description of the character and the properties of the excited states studied. Based on a careful comparison of results presented in this work and published high-level *ab initio* results from the literature, theoretical best estimates of the excitation energies are derived for the benchmark molecules.

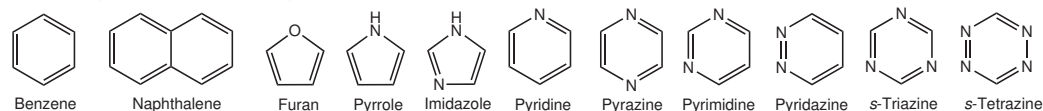
1.1.2 TD-DFT and DFT/MRCI

The application of accurate *ab initio* methods such as MS-CASPT2 and CC3 is still limited in practice to rather small molecules, and there is clearly a need for reliable approximate methods that can deal with larger systems. Over the past decade, time-dependent density functional theory (TD-DFT) [21] has become one of the most prominent methods for calculating excited states. [22] A major ad-

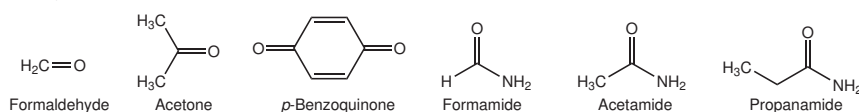
Unsaturated Aliphatic Hydrocarbons



Aromatic Hydrocarbons and Heterocycles



Aldehydes, Ketones and Amides



Nucleobases

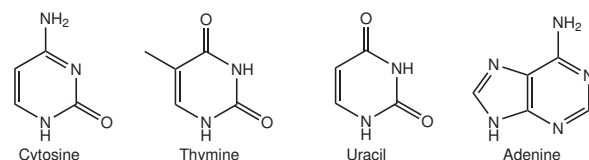


Figure 1.1: Benchmark set of molecules considered in this study.

vantage of TD-DFT is its low computational cost, [23] roughly comparable with single excitation theories based on the Hartree-Fock (HF) ground state such as configuration interaction with singles or the random phase approximation. Since the commonly used adiabatic approximation represents the response of a molecule in terms of single excitations, TD-DFT is best suited for excited states that are dominated by single excitations. TD-DFT calculations can be easily standardized and are thus user-friendly (without the need to define an active space or to select reference configurations).

Evaluations of TD-DFT performance have been reported for various density functionals. [24–33] Most of these studies have compared TD-DFT vertical excitation energies either with experimental results or with published CASPT2 calculations. Generally speaking, these evaluations are less comprehensive and less systematic than desirable.

An alternative DFT-based method for electronically excited states arises from the use of Kohn-Sham (KS) orbitals in a multi-reference configuration interaction (MRCI) framework. [34] In this ansatz, the major part of dynamic electron correlation is captured by the KS-DFT treatment, and static correlation effects are introduced by the MRCI technique which is also flexible enough to properly describe states with double excitation character. The DFT/MRCI configuration state

functions (CSFs) are built from KS rather than HF orbitals. The method has been tested for a number of organic chromophores [34, 35] and applied to the simulation of gas phase UV/Vis spectra (see for example [36–45]) and CD spectra. [46] Although these previous applications indicate a promising performance, DFT/MRCI has not been used as widely as TD-DFT, and further validation is desirable.

A systematic benchmark of TD-DFT with three functionals (BP86, B3LYP and BHLYP) and DFT/MRCI is presented using the set of accurate *ab initio* reference data previously established (see above). The same molecular geometries and basis sets are employed as in the previous CASPT2 and coupled-cluster calculations to allow for a direct comparison between the results. Statistical evaluations and general assessments of performance will be given that highlight the merits and shortcomings of each method.

1.1.3 Semiempirical methods

Another promising and pragmatic approach for large molecules is provided by semiempirical molecular orbital (MO) methods such as MNDO, [47] AM1, [48] and PM3 [49] coupled with a configuration interaction (CI) procedure. These methods are based on the NDDO (neglect of diatomic differential overlap) integral approximation and have been parametrized against ground-state properties, in particular heats of formation and geometries. They have been widely applied in computational studies of ground-state processes (for reviews, see refs. [50–52]). Applications to electronically excited states [53] are rare, however, mainly because these standard methods normally underestimate their energies strongly, as result of the integral approximations and the ground-state parametrization. A straightforward remedy for this shortcoming would be a system-specific reparametrization [54] for a given application (see for example ref. [55]) which is however cumbersome in practice and also unsatisfactory from a conceptual point of view.

Among the semiempirical approaches designed to describe excited-state processes, the INDO/S [56–58] method has become the standard procedure. In combination with CIS (configuration interaction with single excitations), it has been widely used for organic molecules, [59–61] transition metals [62, 63], and even lanthanides. [64] The lack of higher excitations in the INDO/S CIS treatment restricts applications to states dominated by single excitations. Another limitation is the focus on vertical processes: by its design, INDO/S targets spectroscopy rather than photochemistry, and it is thus not made for the exploration of excited-state potential energy surfaces (PES).

Semiempirical methods using orthogonalization corrections (OM1 [65, 66], OM2 [67, 68] and OM3 [69]) offer a better description of virtual orbitals and their

energies. [65] For ground state-properties, they are superior in performance to standard NDDO methods like AM1 and PM3. [5] Despite the fact that they have been parametrized with regard to ground-state reference data, they also provide encouraging results in case studies on vertical excitation energies, [68, 70, 71] conical intersections, [72] and semiclassical excited-state dynamics. [73] However, a thorough benchmark on the performance of semiempirical methods for electronically excited states has been missing. Such a systematic evaluation is reported here for the standard NDDO-based semiempirical methods (MNDO, AM1, PM3), the commonly used INDO-based approaches (INDO/S, INDO/S2), and the orthogonalization-corrected methods (OM1, OM2, OM3). Reference data are again taken from the previous benchmark work outlined in the Section 1.1.1. The discussion addresses some specific troublesome cases, followed by statistical evaluations and an outlook with comments that may guide future reparametrizations.

1.2 QM/MM applications on electronically excited biomolecules

For very large molecular systems with hundreds of atoms, all the methods outlined above become prohibitively expensive. An alternative that has been used progressively is the combined Quantum Mechanics / Molecular Mechanics (QM/MM) approach. The system is divided into an inner region, which is treated with a quantum-chemical method as accurately as needed (e.g., *ab initio* or DFT), and an outer region, which is described by a less accurate classical force field.

Recently, Senn and Thiel [74, 75] reviewed the QM/MM methodology and surveyed QM/MM applications for many diverse types of biomolecular systems. The great majority (above 90%) of these studies address processes that occur on the ground-state potential energy surface (PES). QM/MM investigations of excited-state processes are still relatively rare, although they have become more feasible in recent years due to the development of analytical excited-state gradients in several QM codes.

1.2.1 Photoreceptors

Photoreceptors are a special class of biomolecules that undergo excited-state processes which control biological activity and mediate diverse physiological responses to light irradiation. This class includes xanthopsins, phytochromes, and cryptochromes, BLUF (Blue-Light Using Flavin) proteins and LOV (light-oxygen-

voltage) sensors. [76, 77] The function of these photoreceptors requires the presence of a chromophore, namely 4-hydroxycinnamic acid (in xanthopsins), tetrapyrrol derivatives (in phytochromes), flavin adenine dinucleotide FAD (in cryptochromes, BLUF), and flavin mononucleotide FMN (LOV domains).

The phototropins were the first LOV proteins identified in plants. They normally contain two LOV domains that are bound to a serine/histidine kinase. They control a variety of biological processes such as phototropism, chloroplast relocation and stomatal opening. [78, 79] Based on sequence homology to these plant phototropins, a prokaryotic YtvA protein was found in the bacterium *Bacillus subtilis*, which contains a single LOV domain, attached to a STAS domain. [80] When this protein is activated by blue-light irradiation, it mediates environmental stress, [81, 82] in a manner similar to phototropins. However, there is still limited knowledge about this signalling mechanism which has been the subject of active research in the last decade (for a review see [83]). In order to understand these systems at a molecular level, two main strategies have been followed experimentally: modifications of the protein through site-directed mutagenesis and, more recently, modifications of the chromophore in recombinant systems. Here the focus is on the latter strategy.

1.2.2 Modifying the chromophore

LOV sensors undergo specific sequences of reactions after blue-light irradiation. In isolated LOV domains (LOV₄₄₇) irradiation triggers a photocycle, with the formation of a blue-shifted FMN-cysteine C4a-thiol adduct (LOV₃₉₀) [84] that slowly reverts to LOV₄₄₇ in the dark. [76] There is experimental [85, 86] and theoretical [38, 87–89] evidence that a reactive flavin triplet state plays a fundamental role in the adduct formation, at an intermediate step of the mechanism. Dark state recovery occurs thermally, but rather slowly, with kinetics up to hours in bacterial LOV proteins. [90]

Recently experimental methods have been developed to incorporate modified cofactors into photoreceptors [91] and thus to help in the design of recombinant proteins with specially tailored chromophores inside the binding pocket. Particularly, two modified flavin derivatives have raised the interest of experimentalists due to their exotic photochemistry compared with the parent FMN compound, namely 1- and 5-deaza-flavin mononucleotide (1DFMN and 5DFMN, see Figure 1.2). They have been recently investigated in aqueous solution using spectroscopic measurements and theoretical calculations. [92, 93] 1DFMN shows a strong bathochromic shift of its first absorption band, and there is no evidence of a triplet state being formed. By contrast, 5DFMN exhibits a significant hypsochromic shift, with formation of triplet states detected by transient absorption spectroscopy and confirmed by the theoretical calculations. An obvious question

is whether the photophysical behavior of such molecules changes when inserted into a LOV domain.

QM/MM calculations of these two modified cofactors incorporated into the LOV domain of the YtvA protein will be presented and discussed. On this basis a comprehensive mechanism of the photophysics will be outlined for each system and compared with recent experimental findings.

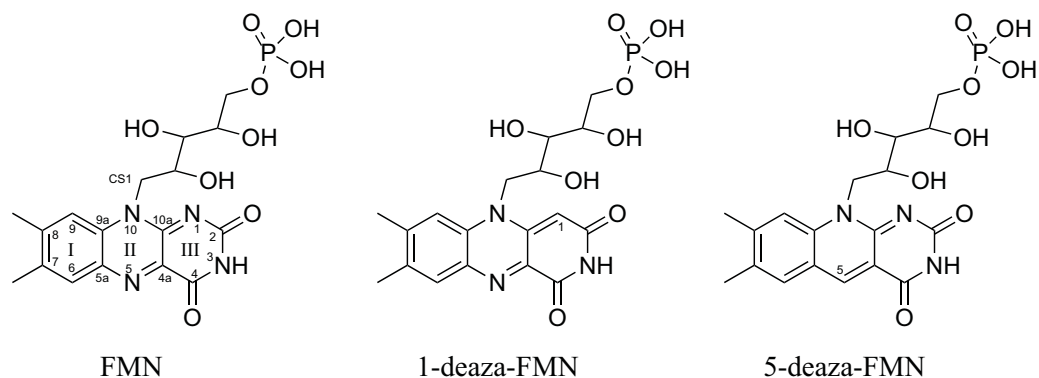


Figure 1.2: Flavin mononucleotide (FMN, left) and its 1-deaza, 1DFMN (center) and 5-deaza, 5DFMN (right) derivatives. The ribityl-5'-phosphate chain is shown for all compounds.

Chapter 2

Methods

This section presents a brief overview of the methods employed in this study. For more detailed descriptions the reader is advised to consult either the original publications or book references where the entire formalism is derived. This section is divided into five major parts covering the following methods: (a) CASSCF (complete-active-space self-consistent field) and CASPT2 (multiconfigurational second-order perturbation theory); (b) methods derived from coupled-cluster theory (CC2, CCSD, CCSDR(3), and CC3); (c) methods based on density functional theory (TD-DFT and DFT/MRCI); (d) semiempirical methods, with emphasis on orthogonalization-corrected approaches (OM1, OM2, and OM3); and (e) combined quantum mechanics / molecular mechanics (QM/MM).

2.1 CASSCF / CASPT2

The description of these methods is derived from ref. [9], with detailed formalism found in the references [94, 95]. CASSCF is a variant of the general MC-SCF (multiconfigurational self-consistent field) approach. A multiconfigurational wavefunction can be written as follows:

$$\Psi = \sum_I^M c_I \Phi_I = c_1 \Phi_1 + c_2 \Phi_2 + \cdots + c_M \Phi_M, \quad (2.1)$$

where c_I is the coefficient associated with configuration Φ_I and the summation extends over all possible M configurations Φ_I , each of which is normally written as a linear combination of Slater determinants. This expansion includes only those configurations which have the same spatial and spin symmetry as the state of interest. Such configurations are called configuration state functions (CSFs). The final wavefunction is obtained by optimizing both the CI coefficients c_I and the molecular orbitals (MOs) used to generate the electronic configurations Φ_I . The

expression for the energy of a multiconfigurational wavefunction (Eq. 2.1) is given by:

$$\begin{aligned}
 E &= \left\langle \sum_I c_I \Phi_I | \hat{\mathbf{H}} | \sum_j c_j \Phi_j \right\rangle \\
 &= \sum_{tu} \sum_{IJ} c_I c_J d_{tu}^{IJ} h_{tu} + \frac{1}{2} \sum_{tuvw} \sum_{IJ} c_I c_J D_{tuvw}^{IJ} (tu|vw) \\
 &= \sum_{tu} d_{tu} h_{tu} + \frac{1}{2} \sum_{tuvw} D_{tuvw} (tu|vw),
 \end{aligned} \tag{2.2}$$

where $\hat{H}$ is the electronic Hamiltonian operator (within the Born-Oppenheimer approximation), h_{tu} and $(tu|vw)$ are one- and two-electron integrals, respectively, and d_{tu} and D_{tuvw} are the one- and two-electron density matrices, respectively. Usually, the electronic energy is expressed as a function of the variational parameters of the wavefunction, namely the CI and MO coefficients. In order to optimize the wavefunction one needs to find the stationary energy point (Eq. 2.2), based on the variation of the coefficients c_I and of the molecular orbitals ϕ_t , with the constraints:

$$\sum_I c_I^2 = 1, \tag{2.3}$$

$$\langle \phi_t | \phi_u \rangle = \delta_{tu}, \tag{2.4}$$

which ensure wavefunction normalization (Eq. 2.3) and the orthonormality of the MOs (Eq. 2.4). Two common approaches to optimize the wavefunction are: (a) the use of Lagrange multipliers together with a Taylor expansion of the energy, iterated using the Newton-Raphson procedure, or (b) the application of a super-CI approach. These methodologies are explained in detail in the references given at the beginning of this section. Within the MCSCF formalism, many diverse types of wavefunction can be constructed. In the most popular CASSCF variant, the orbital set (occupied and virtual) is divided into four subsets:

1. Core: Internal orbitals that are assumed to remain unaltered during excitation/deexcitation of valence electrons;
2. Inactive: Orbitals that do not participate in these processes, but should still be reoptimized to improve the description of the system;
3. Active: Orbitals that are directly involved in the processes mentioned in item 1 and thus must be reoptimized;

4. Virtual (or secondary): Orbitals that are not be occupied and remain unchanged.

With these four subsets defined, the configuration generation with the CASSCF method is as follows: The core orbitals are always doubly occupied and maintained in their original form (e. g., as obtained from an initial standard SCF calculation - this is frequently called the frozen-core approach). The inactive orbitals are also always doubly occupied, but are reoptimized during the CASSCF calculation. The active orbitals are optimized both with regard to their form and their occupation number, normally starting from initial occupations of zero, one or two. The virtual (secondary) orbitals remain empty. After choosing the orbitals that will be part of each subset, all possible CSFs within the active space are generated (full CI, FCI). The CASSCF wavefunction is the FCI solution built from these configurations.

One major challenge in CASSCF applications is exactly how to choose these orbital subsets. Unfortunately there is not a straightforward and unique way to define the active space for a given system. Through the years, however, a consensus approach has developed, with construction of a standard active space as starting point. For organic molecules, for example, the whole π -system (π and π^* orbitals) is usually considered the minimal active space that should be selected when $\pi \rightarrow \pi^*$ transitions are studied. The size of the active space is normally the main limiting factor in CASSCF calculations. The number of CAS configurations is given by the Weyl-Robinson equation [96]:

$$N_{CAS} = \frac{2S+1}{n+1} \binom{n+1}{N/2-S} \binom{n+1}{N/2+S+1}, \quad (2.5)$$

where n is the number of active orbitals, N is the number of active electrons, and S is the total spin. In practice, the number of orbitals in the active space is usually still limited to 12-15, with a similar or smaller number of electrons. In CASSCF calculations of excited states, one often encounters a “root flipping”: during optimization of the wavefunction for a given excited state, the ground-state energy grows gradually and, at a certain point, becomes lower than the energy of the excited state in question. A remedy for this problem is the use of a common set of orbitals for all states during the optimization process, through the so-called state-averaged CASSCF (SA-CASSCF) method. [97, 98] The mean energy value is defined as weighted sum over the energies of each state considered in the averaging, and the density matrix for a single state is likewise substituted by mean density matrices (see Equation 2.2). One thus obtains a mean set of MOs (state-averaged MOs) and a CASSCF wavefunction for every state included. This method has many advantages over the single-state approach: one computes several states in a single job, the wavefunction generally converges faster, and the orthogonality

between the states is ensured which facilitates the calculation of transition properties.

The CASSCF method has the intrinsic flexibility to properly describe diverse electronic states of different character. However, it recovers only part of the correlation energy arising from the so-called static (non-dynamical) correlation, and therefore one needs to also account for the remaining dynamical correlation when aiming at accurate results. One popular method for this purpose is CASPT2 [7–9] which applies second-order perturbation theory to the multiconfigurational zero-order CASSCF wavefunctions, similar in spirit to the second-order Møller-Plesset (MP2) treatment on top of a single-reference Hartree-Fock wavefunction. The zero-order Hamiltonian for CASPT2 can be written in different ways, the commonly chosen analogue to Møller-Plesset perturbation theory has the form:

$$\hat{H}_0 = \hat{P}_0 \mathbf{F} \hat{P}_0 + \hat{P}_{SD} \mathbf{F} \hat{P}_{SD} + \hat{P}_X \mathbf{F} \hat{P}_X, \quad (2.6)$$

with the CASSCF wavefunction as eigenfunction ($|\Phi_0\rangle$). The configuration space is divided into different subspaces: 0 (the reference configuration space), SD (all CSFs singly and doubly excited with respect to the CAS space, i. e., the interacting configuration space V_{SD}), and X (the space of the remaining configurations that do not interact with the reference function). The symbols $\hat{P}_i$ represent the corresponding projection operators, and F denotes the generalized Fock operator. The first-order CASPT2 wavefunction is composed of CAS wavefunctions that belong to V_{SD} :

$$|\Psi_1\rangle = \sum_{j=1}^M C_j |\Psi_j\rangle, |\Psi_j\rangle \in V_{SD}, \quad (2.7)$$

$$|\Psi_1\rangle = \sum_{p,q,r,s} C_{pqrs} |pqrs\rangle = \sum_{pqrs} \mathbf{E}_{pq} \mathbf{E}_{rs} |\Psi_0\rangle, \quad (2.8)$$

In the expressions above, $\mathbf{E}_{pq}$ denotes an excitation operator, defined as the product of the creation operator $a_p^\dagger$ and the annihilation operator a_q . The indexes p, q, r, s are general indexes for the orbitals. More specifically, there are three categories: $i, j, k, \dots$ refer to the inactive orbitals; $t, u, v, \dots$ to the active orbitals; and $a, b, c, \dots$ to the secondary orbitals. V_{SD} represents the first-order interaction space, and $\{C_j = 1, \dots, M\}$ is the solution of the linear equations:

$$\sum_{i=1}^M C_j \langle \Psi_i | \hat{F} - E_0 | \Psi_j \rangle = -\langle \Psi_i | \mathbf{H} | \Psi_0 \rangle. \quad (2.9)$$

The configurations belonging to the interaction space V_{SD} can be classified into eight categories, according to the number of electrons created in the virtual space:

- Internal (no electron in the virtual space):

$$\mathbf{E}_{ti}\mathbf{E}_{uv}|\Psi_0\rangle$$

$$\mathbf{E}_{ti}\mathbf{E}_{uj}|\Psi_0\rangle$$

- Semi-internal (one electron in the virtual space):

$$\mathbf{E}_{at}\mathbf{E}_{uv}|\Psi_0\rangle$$

$$\mathbf{E}_{ai}\mathbf{E}_{tu}|\Psi_0\rangle \text{ and } \mathbf{E}_{ti}\mathbf{E}_{au}|\Psi_0\rangle$$

$$\mathbf{E}_{ti}\mathbf{E}_{aj}|\Psi_0\rangle$$

- External (two electrons in the virtual space):

$$\mathbf{E}_{at}\mathbf{E}_{bu}|\Psi_0\rangle$$

$$\mathbf{E}_{ai}\mathbf{E}_{bt}|\Psi_0\rangle$$

$$\mathbf{E}_{ai}\mathbf{E}_{bj}|\Psi_0\rangle$$

The energy, correct to second order, is given by:

$$E_2 = \langle \Psi_0 | \mathbf{H} | \Psi \rangle. \quad (2.10)$$

and the normalized wavefunction, correct to first order, is:

$$|\Psi\rangle = \sqrt{\omega}|\Psi_0\rangle + \sqrt{1-\omega}|\Psi_1\rangle, \quad (2.11)$$

where ω is the weight of the CAS reference wavefunction and $|\Psi_1\rangle$ is the first-order normalized wavefunction. This completes the outline of the basic CASPT2 method.

The extensive use of the CASPT2 method over the years revealed several shortcomings that arise from the use of a multiconfigurational wavefunction and a truncated active space. Examples of artifacts are the appearance of so-called intruder states and the strong mixing of valence and Rydberg states. Such problems are explained in more detail in the following, together with strategies to overcome them. Because CASPT2 is a perturbative method, its proper use requires the perturbation to be small. Therefore, it is essential to include into the reference wavefunction Ψ_0 all configurations which have high coefficients. In other words, when the weight of the reference wavefunction (ω) is small in a CASPT2 calculation, the active space should be expanded.

When several states of a given symmetry are calculated, it is important that all of them have similar values of ω to ensure a balanced treatment of the correlation effects. If any state has a very low value of ω , this indicates problems with “intruder states”, which belong to the first-order interaction space V_{SD} .

There are two ways to treat the problems with an intruder state. If this state interacts strongly with the reference wavefunction, the contribution to the energy from this state can not be ignored. One remedy is to increase the active space, in order to include the orbitals which cause the appearance of intruder states (through small energy denominators in the perturbation treatment). When the intruder state interacts only weakly with the other states included in the reference wavefunction (large coefficients, but small energy contributions), the level-shift technique [99] can be applied to remove the intruder state. In this technique, the Hamiltonian H_0 is substituted by a shifted Hamiltonian ($\hat{H}_0 + \epsilon \hat{P}_I$), where ϵ is a small positive number and $\hat{P}_I$ is a projector operator to the first-order interaction space. When using this technique, one must apply an a posteriori correction to the second-order energy which is now dependent on the parameter ϵ . This is done by testing different values of ϵ and comparing the corresponding CASPT2 energies with and without the shift (which will be different when an intruder state is present and equal otherwise).

Another relevant issue to be considered is the form of the generalized Fock operator. The diagonal matrix elements of the one-electron generalized Fock operator are related either to ionization potentials (occupied orbitals) or electron affinities (empty orbitals). For orbitals with an occupation number of one, the corresponding diagonal Fock matrix element is the average of the ionization potential and the electron affinity. [100] This implies that the energy denominators in the expression for second-order energy correction can become very small in such cases, causing a systematic underestimation of computed excitation energies. Ghigo *et al.* [100] proposed a new definition for the zero-order Hamiltonian, called IPEA shift, which depends on an average shift parameter ϵ . After some calibration with atomic data, they proposed an ϵ value of 0.25 a.u., which has now become the default in CASPT2 calculations.

Finally, there are cases when the SA-CASSCF wavefunction is not a good starting point for the CASPT2 calculation, for instance, when states of the same symmetry and of different character (valence, Rydberg) lie close in energy and contribute to similar extent to the final wavefunction. Dissociation paths near avoid crossing regions also suffer from this deficiency. Such problems have largely been overcome in the multistate CASPT2 (MS-CASPT2) method [10] which is now an established standard procedure in CASPT2 calculations. It is based on the construction of an effective Hamiltonian whose diagonal elements correspond to the CASPT2 energies, whereas the off-diagonal elements represent the coupling terms between the relevant roots up to second order of the dynamic correlation

energy. This effective Hamiltonian is diagonalized first before performing the perturbation treatment.

2.2 Coupled-cluster methods

This section provides a brief general description of coupled-cluster (CC) theory, highlighting the methods used in this study, namely CC2, CCSD, CCSDR(3), and CC3. Details of the methodology are found in the original publications [12, 13, 101–103], with derivation here following the recent review [104]. The coupled-cluster ansatz is given by:

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_{HF}\rangle \quad (2.12)$$

where $|\Psi_{HF}\rangle$ denotes the Hartree-Fock reference wavefunction and $\hat{T}$ is the so-called cluster operator:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_n = \sum_{i=1}^n \sum_{\mu_i} t_{\mu_i} \tau_{\mu_i}. \quad (2.13)$$

In this section, the following notation is used. Electrons are promoted from occupied orbitals $i, j, k, \dots$ to unoccupied orbitals $a, b, c, \dots$. Excitation operators in second quantization are written as $a_a^\dagger a_i$ for single excitations, $a_a^\dagger a_b^\dagger a_i a_j$ for double excitations, and so on. These operators can be denoted by τ_{μ_i} , for i -tuple excitations. Thus the index i corresponds the level of excitation and μ stands for a particular index set ($ai, aibj, \dots$ etc). Referring back to equation 2.13, the number of electrons in the system is n and t_{μ_i} refers to the cluster amplitudes. When the CC wavefunction ansatz is introduced into the time-independent Schrödinger equation and pre-multiplied with $e^{-\hat{T}}$ one obtains:

$$e^{-\hat{T}} \mathbf{H} e^{\hat{T}} |\Psi_{HF}\rangle = E_{CC} |\Psi_{HF}\rangle, \quad (2.14)$$

The expression for the CC energy is derived by projecting on the Hartree-Fock reference space:

$$E_{CC} = \langle \Psi_{HF} | \mathbf{H} e^{\hat{T}} | \Psi_{HF} \rangle \quad (2.15)$$

since the $e^{-\hat{T}}$ operator drops out due to the condition: $\tau_{\nu_j} |\Psi_{HF}\rangle = 0$.

$$e_{\mu_i} = \langle \mu_i | e^{-\hat{T}} \mathbf{H} e^{\hat{T}} | \Psi_{HF} \rangle = 0 \quad (2.16)$$

These are the central equations of coupled cluster theory. Truncations of the cluster operator $\hat{T}$ formally define a particular method: $T = T_1$ (CCS), $T_1 + T_2$ (CCSD), $T_1 + T_2 + T_3$ (CCSDT), etc. Starting from this hierarchy of methods,

one can derive approximate approaches that include higher excitations via a perturbative framework, and thus reduce the scaling of the computational effort with respect to the number of orbitals, without significant loss of accuracy. The most popular such methods for treating excited states by CC theory are CC2 [12, 15] and CC3 [13, 14, 18], which can be characterized as follows.

CC2 is an approximation to CCSD where the singles equations are treated in the same manner as CCSD, whereas the doubles equations for the nonlinear ground-state amplitudes as well as for the linear response are approximated by the first-order terms only. The singles excitation operator (T_1) is treated as zeroth order, since the response of the singles excitations to an external one-electron perturbation, such as electromagnetic radiation, is of zeroth order. The equations for the ground-state doubles amplitudes are almost identical to expressions of the MP2 method, apart from the fact that the two-electron integrals are transformed with T_1 . Concerning excited electronic states, singles dominated excitations are corrected through second order, whereas pure double excitations are only correct to zeroth order. CC3 is an approximation to full CCSDT in a similar manner as CC2 is an approximation to CCSD. The triples equations in CC3 are approximated by the second-order terms following the condition that the singles excitations are treated again as zeroth order, whereas the CCSDT singles and doubles equations are kept unchanged. Singles (doubles) dominated excitations are now correct to third (second) order. CCSDR(3) is based on a pseudoperturbation theory expansion of the CC3 eigenvalue problem and thus includes essentially only a non-iterative triples correction which is added to the CCSD excitation energy, scaling formally also as N^7 with the number of orbitals N .

2.3 Time-dependent DFT and DFT/MRCI

This section starts with a brief overview of time-dependent density functional theory (TD-DFT). The derivation outlined here follows the reference [105]. For a detailed description and derivation of the main equations, see [22, 106–108].

Let us consider an N -electron system that is initially found at time $t = t_0$ in its ground state $|\Phi_0\rangle$. At times $t > t_0$, a time-dependent perturbation $\lambda\hat{U}(t)$ is applied. The electric dipole part (μ) of this perturbation, when considering a monochromatic radiation field, is given by the expression:

$$\lambda\hat{U}(t) = -\mu E e^{-i\omega t} \quad (2.17)$$

oscillating with frequency ω at a (constant) field strength E . The linear response of an observable is defined as the first variation of the expectation value with respect to the scalar variable λ . Considering the Fock operator $\hat{F}$, written as a functional of the first order density matrix γ , we have:

$$\hat{F}[\gamma](t) = \hat{h}[\gamma](t) + \nu_H[\gamma](t) - \nu_{xc}[\gamma](t) + \lambda \hat{U}(t), \quad (2.18)$$

where h is the one-electron part of the Hamiltonian, the index H denotes the two-electron Coulomb part, and v_{xc} represents the exchange-correlation potential. The linear response of the mean-field density matrix then has the form:

$$\gamma^{(1)}(t) = \frac{d}{d\lambda} \gamma(t)|_{\lambda=0} \quad (2.19)$$

By a Fourier transformation to the frequency domain and after expansion into the complete set of Kohn-Sham one-electron eigenstates, one obtains the following equation:

$$\gamma^{(1)}(\omega) = \sum_i \sum_a \left(\frac{u_{ai}(\omega)}{\omega - (\varepsilon_a - \varepsilon_i)} |i\rangle\langle a| \right) - \left(\frac{u_{ai}^*(\omega)}{\omega + (\varepsilon_a - \varepsilon_i)} |a\rangle\langle i| \right), \quad (2.20)$$

where i and a are occupied and virtual orbitals, respectively; ε denotes their energies and u_{ia} the matrix elements of the perturbation in the basis of the orbitals. After some algebraic manipulations and insertion of equation 2.20 into 2.18, one obtains a non-hermitian eigenvalue problem. This should be solved with the constraint $\omega = \Delta E$. It has the form:

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Delta E \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (2.21)$$

with X and Y as the solution vectors of the single particle-hole (excitations, $|i\rangle\langle a|$) and hole-particle (deexcitations, $|a\rangle\langle i|$) amplitudes, respectively; A and B are related to the Hamiltonian matrices between the single (de)excitations that are constituted of one-particle eigenvalues and the Coulomb and exchange integrals over molecular orbitals. The matrix elements can be expressed as:

$$\begin{aligned} A_{ia\sigma,jb\tau} = & \delta_{\sigma\tau} \delta_{ij} \delta_{ab} (\epsilon_{a\sigma} - \epsilon_{i\tau}) + (i_{\sigma} a_{\sigma} | j_{\tau} b_{\tau}) \\ & - \delta_{\sigma\tau} c_{\text{HF}} (i_{\sigma} j_{\sigma} | a_{\tau} b_{\tau}) + (1 - c_{\text{HF}}) (i_{\sigma} a_{\sigma} | f_{\sigma\tau} | j_{\tau} b_{\tau}) \end{aligned} \quad (2.22)$$

$$\begin{aligned} B_{ia\sigma,jb\tau} = & (i_{\sigma} a_{\sigma} | b_{\tau} j_{\tau}) - \delta_{\sigma\tau} c_{\text{HF}} (i_{\sigma} b_{\sigma} | a_{\tau} j_{\tau}) \\ & + (1 - c_{\text{HF}}) (i_{\sigma} a_{\sigma} | f_{\sigma\tau} | b_{\tau} j_{\tau}) \end{aligned} \quad (2.23)$$

where σ and τ are the spin variables. The parameter c_{HF} denotes the amount of Hartree-Fock exchange in hybrid functionals. The last terms in equations 2.22 and 2.23 are defined by:

$$(i_{\sigma}a_{\sigma}|f_{\sigma\tau}|j_{\tau}b_{\tau}) = \iint i(r_1)a(r_1)f_{\sigma\tau}^{xc}(r_1, r_2)j(r_2)b(r_2)dr_1dr_2. \quad (2.24)$$

The time-dependent exchange-correlation kernel $f_{\sigma\tau}^{xc}$, when derived from the time-independent ground-state functional, defines the so-called adiabatic approximation, having the form:

$$f_{\sigma\tau}^{xc}(r_1, r_2) = \frac{\delta^2 E_{xc}}{\delta\rho_{\sigma}(r_1)\delta\rho_{\tau}(r_2)} \quad (2.25)$$

This approximation should work best when $\omega \rightarrow 0$, i. e., for energetically low-lying excited states. This concludes the description of fundamental aspects of the TD-DFT methodology.

The TD-DFT calculations reported in this work were performed with the TURBOMOLE program (version 5.7.1). [109] Three functionals were investigated: the gradient corrected BP86 functional, [110, 111] the hybrid Becke3-Lee-Yang-Parr (B3LYP) functional [110, 112, 113] with 20 % of HF exchange, and the Becke-half-and-half-Lee-Yang-Parr (BHLYP) functional [112, 114] with 50 % of HF exchange. In the BP86 case, the resolution of identity (RI) method was employed to evaluate the two-electron integrals, making use of auxiliary basis sets from the TURBOMOLE library. [115, 116] Calculations of vertical excitation energies [23, 117–120] were done in the adiabatic approximation. [23, 121] For every state symmetry, the energies, dipole moments and oscillator strengths were computed at least for the five lowest states. [120, 122–124]

Another DFT-based method for describing electronically excited states is the combination of DFT and configuration interaction (CI). Grimme [125] initially proposed such a combination with a CIS treatment involving only single excitations. This was later extended and generalized to a multireference singles and doubles CI treatment (DFT/MRCI) [34, 126] which is briefly outlined in the following.

The general idea behind the DFT/MRCI method is to capture dynamical electron correlation by standard DFT and the nondynamical effects by a rather small CI expansion. Considering the fact that the electronic Hamiltonian in a CI method can be written in terms of a one-electron Fock operator and the SCF energy of a particular parent configuration, any matrix element can be formulated in terms of its difference from the SCF result. [125] Denoting the occupation number of the i th MO in the parent configuration by $\bar{n}_i$, the Fock operator, the Hartree-Fock (HF) energy, and the Hamiltonian are given by:

$$\hat{F}_{ij}^{HF} = \hat{h}_{ij} + \sum_k \bar{n}_k [(ij|kk) - 1/2 (ik|jk)] \quad (2.26)$$

$$E^{HF} = \sum_i \bar{n}_i \hat{F}_{ii}^{HF} - \frac{1}{2} \sum_{ij} \bar{n}_i \bar{n}_j [(ii|jj) - 1/2 (ij|ij)] \quad (2.27)$$

$$\begin{aligned}\hat{H} = & \sum_{ij} F_{ij}^{HF} \hat{E}_i^j - \sum_{ijk} [(ij|kk) - 1/2 (ik|jk)] \bar{n}_k \hat{E}_i^j \\ & + \frac{1}{2} \sum_{ijkl} (ij|kl) [\hat{E}_i^j \hat{E}_k^l - \delta_{jk} \hat{E}_i^l],\end{aligned}\quad (2.28)$$

where the two-electron integrals are written in Mulliken notation and $\hat{E}_k^l$ is the single-particle (de)excitation operator. Defining the occupation number vector v for the space part and the spin-specific coupling pattern w , the Hamiltonian matrix elements between two CSFs $\langle wv|\hat{H}|w'v'\rangle$ can be divided into four classes: [34, 126]

- Ia Same space part, same spin-coupling (diagonal);
- Ia Same space part, different spin-coupling (off-diagonal);
- Ib Space part differs by one-electron excitation (off-diagonal);
- Ib Space part differs by two-electron excitation (off-diagonal).

The key approximation of the DFT/MRCI method is to introduce empirical corrections of the exact Kohn-Sham matrix elements and scaled two-electron integrals, to avoid double counting of correlation effects and to be able to tune the results. The diagonal elements of the effective DFT/CI Hamiltonian $\hat{H}^{DFT}$ have the form:

$$\begin{aligned}\langle wv|\hat{H}^{DFT} - E^{DFT}|wv\rangle = & \langle wv|\hat{H} - E^{HF}|wv\rangle - \sum_c^{n_{exc}} (F_{cc}^{HF} - F_{cc}^{KS}) + \\ & \sum_a^{n_{exc}} (F_{aa}^{HF} - F_{aa}^{KS}) + \frac{1}{n_{exc}} \sum_a^{n_{exc}} \sum_c^{n_{exc}} p_J (aa|cc) - p[N_o] (ac|ac)\end{aligned}\quad (2.29)$$

where F_{ij}^{KS} is a matrix element of the Kohn-Sham Fock operator of the parent state and E^{DFT} is the pure DFT energy of the parent determinant $|\bar{w}\bar{v}\rangle$. The indices c and a refer to creation and annihilation operators, and n_{exc} is the excitation level with respect to the space part of the parent determinant. $p[N_o]$ has different forms for singlet and triplet states: ${}^1p[N_o] = p[0] + N_o^1\alpha$ and ${}^3p[N_o] = N_o^3\alpha$. The off-diagonal elements are obtained by an appropriate scaling of the exact matrix elements:

$$\langle wv|\hat{H}^{DFT}|w'v'\rangle = \langle wv|\hat{H}|w'v'\rangle p_1 e^{-p_2 \Delta E_{ww'}^4} \quad (2.30)$$

where p_1 and p_2 are scaling factors and $\Delta E_{ww'}$ is the energy difference between the diagonal elements of the two CSFs. This damping is necessary to avoid an overestimate of electron correlation effects, which are already partly included in the diagonal term. The parameters p_J , $p[0]$ and α are obtained by a least-squares fit of calculated excitation energies against experimental data of selected reference

Table 2.1: DFT/MRCI parameters for BH-LYP functional for singlet and triplet states.

Multiplicity	Parameter				
	p_1	p_2	p_J	$p[0]$	α
singlet	0.619	3.27	0.510	0.595	0.106
triplet	0.619	3.27	0.493	–	0.056

molecules, using BHLYP as DFT functional. The final DFT/MRCI parameters are shown in Table 2.1.

In the DFT/MRCI calculations reported in this work, two-electron integrals were evaluated using the RI approximation [115, 127] with the optimized RI-MP2 basis sets from the TURBOMOLE library. Calculations were carried out using the mrci program. [34] The adopted energy threshold value of 1.0 hartree always yielded converged results for the excitation energies. Initial reference configurations were generated by promoting up to two (active) electrons out of ten electrons in ten active orbitals. The corresponding number of reference configurations varied between 14 for cyclopentadiene and 244 for *s*-tetrizine. The oscillator strengths were calculated in the dipole length representation. This standard DFT/MRCI procedure was applied to all benchmark molecules.

2.4 Semiempirical methods

This section reviews the basic formalism of semiempirical quantum-chemical methods. Detailed derivations are available in several reviews. [50, 58, 128–130] Semiempirical methods are formulated in the framework of Hartree-Fock molecular orbital (MO) theory. They employ a minimal value basis set and make use of rather drastic integral approximations to speed up the calculations. The most important interactions are retained, and the corresponding integrals are represented by parametric functions that are parametrized against experimental data. The MOs ψ_i are expressed as a linear combination of atomic orbitals ϕ_i , with expansion coefficients and energies obtained from the solution of the secular equations 2.32:

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}, \quad (2.31)$$

$$0 = \sum_{\nu} (F_{\mu\nu} - S_{\mu\nu} \epsilon_i) c_{\nu i}, \quad (2.32)$$

where $S_{\mu\nu}$ is the overlap integral. The Fock matrix elements $F_{\mu\nu}$ are defined as:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \left[(\mu\nu, \lambda\sigma) - \frac{1}{2}(\mu\lambda, \nu\sigma) \right]. \quad (2.33)$$

$H_{\mu\nu}$ and $P_{\lambda\sigma}$ are elements of the one-electron core Hamiltonian and the density matrix, respectively, and $(\mu\lambda, \nu\sigma)$ is a two-electron integral. The total energy E_{tot} of a molecule is the sum of its electronic energy E_{el} and the nuclear repulsion V_{NN} :

$$E_{el} = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}), \quad (2.34)$$

$$E_{tot} = E_{el} + V_{NN}. \quad (2.35)$$

The chosen integral approximations characterize a semiempirical method. Usually most of the integrals are neglected, whereas many of the remaining ones are parametrized against experimental data or derived from analytical expressions (see below). Most semiempirical methods employ the zero-differential-overlap (ZDO) approximation:

$$\mu(1)\nu(1)d\tau(1) = \delta_{\mu\nu}\mu(1)\nu(1)d\tau(1). \quad (2.36)$$

As a consequence, all three-center and four-center two-electron integrals vanish, i.e. the computation of these integrals scales with N^2 . For the calculation of the Fock matrix, only the one- and two-center terms remain for the one- and two-electron integrals. Historically, further approximations in this equation have been introduced, defining three classes of methods. The first scheme is the complete neglect of differential overlap (CNDO) [131, 132] which assumes:

$$\mu^A(1)\nu^B(1)d\tau(1) = \delta_{\mu\nu}s^A(1)s^A(1)d\tau(1), \quad (2.37)$$

where the subscripts assign an atomic orbital (AO, μ or ν) to an atom (A or B) and s^A denotes a spherically symmetric s AO at atom A . This implies that all non-vanishing two-electron integrals for a given pair $A - B$ are identical in CNDO. An improved scheme is the so-called intermediate neglect of differential overlap (INDO) [133] where all integrals from CNDO are considered, plus all one-center two-electron integrals. A modified version of INDO combined with a singles CI treatment (CIS) was parametrized by Ridley and Zerner (INDO/S) [56, 57] for calculating electronic spectra, particularly vertical excitation energies at a given ground-state geometry. The best ZDO-based integral approximation is the neglect of diatomic differential overlap (NDDO) which requires

$$\mu^A(1) \nu^B(1) d\tau(1) = \delta_{AB} \mu^A(1) \nu^B(1) d\tau(1) \quad (2.38)$$

during integral evaluation. This NDDO scheme retains the heterogeneity of the two-center two-electron integrals and thus improves on the INDO or CNDO models that use a common value for all these integrals.

The most widely used semiempirical methods are based on the NDDO scheme, e.g., MNDO, [47] AM1, [48] and PM3. [49] They use of a minimal valence basis set which contributes to their computational efficiency. In the following the main equations of the MNDO model are presented, with differences between AM1 and PM3 methods outlined thereafter:

$$0 = \sum_{\nu} (F_{\mu\nu} - \delta_{\mu\nu} \varepsilon_i) c_{\nu i}, \quad (2.39)$$

$$\begin{aligned} F_{\mu^A \nu^A} = & H_{\mu^A \nu^A} + \sum_{\lambda^A} \sum_{\sigma^A} P_{\lambda^A \sigma^A} \\ & \times \left[(\mu^A \nu^A | \lambda^A \sigma^A) - \frac{1}{2} (\mu^A \lambda^A | \nu^A \sigma^A) \right] \\ & + \sum_B \sum_{\lambda_B} \sum_{\sigma_B} P_{\lambda_B \sigma_B} (\mu^A \nu^A | \lambda^B \sigma^B), \end{aligned} \quad (2.40)$$

$$F_{\mu^A \nu^B} = H_{\mu^A \nu^B} - \frac{1}{2} \sum_{\lambda^A} \sum_{\sigma^B} P_{\lambda^A \sigma^B} (\mu^A \lambda^A | \nu^B \sigma^B), \quad (2.41)$$

$$E_{\text{tot}} = E_{\text{el}} + \sum_{A < B} \sum E_{AB}^{\text{core}}. \quad (2.42)$$

This model includes the following interactions and energy terms:

- one-center one-electron energies $U_{\mu\mu}$ (which are part of $H_{\mu\mu}$);
- one-center two-electron repulsion integrals $(\mu^A \nu^A | \lambda^A \sigma^A)$;
- two-center one-electron resonance integrals $\beta_{\mu\nu} = H_{\mu^A \nu^B}$;
- two-center one-electron integrals $(\mu^A \nu^A | B)$ representing electrostatic core-electrons (part of $H_{\mu^A \nu^A}$);
- two-center two-electron repulsion integrals $(\mu^A \nu^A | \lambda^B \sigma^B)$;
- two-center core-core repulsions E_{AB}^{core} .

MNDO differs from the other two methods (AM1 and PM3) mainly in the treatment of core-core repulsion term:

$$E_{AB}^{core} = Z_A Z_B (s_A s_A | s_B s_B) [1 + e^{-\alpha_a R_{AB}} + e^{-\alpha_b R_{AB}}], \quad (2.43)$$

The extra exponential terms (with parameters $\alpha_{a(b)}$) are introduced to account for Pauli repulsion and to better model repulsive interactions at smaller interatomic distances. The core-core repulsion terms are modified in AM1 and PM3 by adding further Gaussian correction terms:

$$\begin{aligned} E_{AB} = & Z_A Z_B (s_A s_A | s_B s_B) [1 + e^{-\alpha_a R_{AB}} + e^{-\alpha_b R_{AB}}] \\ & + \frac{Z_A Z_B}{R_{AB}} \sum_{i=1}^4 \{ a_i(A) \exp [-b_i(A)(R_{AB} - c_i(A))^2] \\ & + a_i(B) \exp [-b_i(B)(R_{AB} - c_i(B))^2] \}, \end{aligned} \quad (2.44)$$

with further adjustable parameters $a_i(A)$, $b_i(A)$, and $c_i(A)$. PM3 differs from AM1 and MNDO also in that it treats the one-center, two-electron integrals as pure parameters, instead of deriving them from atomic spectroscopy.

A new generation of semiempirical methods arises from the explicit inclusion of orthogonalization corrections in the semiempirical NDDO-MO scheme. All one-electron integrals are strongly affected by these orthogonalization corrections. Conceptually, the inclusion of these corrections in the Fock matrix is expected to improve the description of virtual orbitals which are shifted to higher energies. In OM2 (Orthogonalization Model 2) the Fock matrix elements are given by:

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\nu}^A P_{\nu\nu} \left[(\mu\mu|\nu\nu)^s - \frac{1}{2}(\mu\nu|\mu\nu)^s \right] \sum_{B \neq A}^B \sum_{\lambda}^B \sum_{\sigma}^B P_{\lambda\sigma} (\mu\mu|\lambda\sigma)^s, \quad (2.45)$$

$$F_{\mu\nu} = H_{\mu\nu} + \frac{1}{2} P_{\mu\nu} [3(\mu\nu|\mu\nu)^s - (\mu\mu|\nu\nu)^s] \sum_{B \neq A}^B \sum_{\lambda}^B \sum_{\sigma}^B P_{\lambda\sigma} (\mu\nu|\lambda\sigma)^s, \quad (2.46)$$

$$F_{\mu\lambda} = H_{\mu\lambda} - \frac{1}{2} \sum_{\nu}^A \sum_{\sigma}^B P_{\nu\sigma} (\mu\nu|\lambda\sigma)^s. \quad (2.47)$$

The matrix elements of the core-electron Hamiltonian are:

$$H_{\mu\mu} = U_{\mu\mu} + \sum_B [Z_B(\mu\mu|ss)^s + V_{\mu\mu,B}(PI) + V_{\mu\mu,B}(ORT) + V_{\mu\mu,B}(ECP)], \quad (2.48)$$

$$H_{\mu\nu} = \sum_B [Z_B(\mu\nu|ss)^s + V_{\mu\nu,B}(PI) + V_{\mu\nu,B}(ORT) + V_{\mu\nu,B}(ECP)], \quad (2.49)$$

$$H_{\mu\lambda} = \beta_{\mu\lambda} + \sum_C V_{\mu\lambda,C}(ORT). \quad (2.50)$$

Explicit formulas for the terms in equations 2.45–2.50 are listed below:

$$(\mu\nu|\lambda\sigma)^s = f_{KO}(\mu\nu|\lambda\sigma)^a, \quad (2.51)$$

$$f_{KO} = \frac{(ss|ss)^s}{(ss|ss)^a}, \quad (2.52)$$

$$\beta_{\mu\lambda} = \pm \frac{1}{2}(\beta_\mu^A + \beta_\lambda^B) \sqrt{R_{AB}} e^{-(\alpha_\mu^A + \alpha_\lambda^B)} R_{AB}^2, \quad (2.53)$$

$$V_{\mu\nu,B}(PI) = [V_{\mu\nu,B}^a - Z_B(\mu\nu|ss)^a] f_{KO}, \quad (2.54)$$

$$\begin{aligned} V_{\mu\nu,B}(ORT) = & -\frac{1}{2}F_1^A \sum_{\lambda}^B (S_{\mu\lambda}\beta_{\lambda\nu} + \beta_{\mu\lambda}S_{\lambda\nu}) \\ & + \frac{1}{8}F_2^A \sum_{\lambda}^B S_{\mu\lambda}S_{\lambda\nu} (H_{\mu\mu}^{loc} + H_{\nu\nu}^{loc} - 2H_{\lambda\lambda}^{loc}), \end{aligned} \quad (2.55)$$

$$\begin{aligned} V_{\mu\lambda,C}(ORT) = & -\frac{1}{2}G_1^{AB} \sum_{\rho}^C (S_{\mu\rho}\beta_{\rho\lambda} + \beta_{\mu\rho}S_{\rho\lambda}) \\ & + \frac{1}{8}G_2^{AB} \sum_{\rho}^C S_{\mu\rho}S_{\rho\lambda} (H_{\mu\mu}^{loc} + H_{\lambda\lambda}^{loc} - 2H_{\rho\rho}^{loc}), \end{aligned} \quad (2.56)$$

$$G_x^{AB} = \frac{1}{2}(G_x^A + G_x^B), x = 1, 2 \quad (2.57)$$

$$V_{\mu\nu,B}(ECP) = -(S_{\mu\alpha}G_{\alpha\nu} + G_{\mu\alpha}S_{\alpha\nu} - S_{\mu\alpha}S_{\alpha\nu}F_{\alpha\alpha}), \quad (2.58)$$

$$G_{\mu\alpha} = \frac{1}{2}(\beta_{\mu}^A + \beta_{\alpha}^B)\sqrt{R_{AB}}e^{-(\alpha_{\mu}^A + \alpha_{\alpha}^B)}R_{AB}^2. \quad (2.59)$$

The subscripts s and a on the integrals refer to their semiempirical [134, 135] and analytical forms, and their ratio defines the Klopman-Ohno factor (f_{KO}). The parameters F_x^A and G_x^{AB} control the amount of correction that is taken into account for the resonance integrals.

There are two other two semiempirical methods with such orthogonalization corrections (OM1 and OM3) which can be considered as variants of OM2. The OM1 method [65, 66] does not contain the extra term that takes into account interactions of non-neighbor atoms ($V_{\mu\lambda,C}(ORT)$); in addition, it makes use of *ab initio* pseudopotentials in the term $V_{\mu\nu,B}(ECP)$ that are then scaled by the Klopman-Ohno factor. The OM3 method [69] neglects some small contributions to the corrections $V_{\mu\nu,B}(ORT)$ and $V_{\mu\lambda,C}(ORT)$, by setting F_2^A and G_2^{AB} equal to zero.

In the semiempirical calculations on electronically excited states reported in this work, a standard closed-shell SCF treatment was followed by a CI calculation to determine the excited-state properties. For six of the investigated methods (MNDO, AM1, PM3, OM1, OM2 and OM3), MRCI (multireference configuration interaction) calculations were carried out using the GUGA (graphical unitary group approach) implementation in our semiempirical code [136]; these calculations utilized a standard active space and all configurations up to an excitation level of four (CISDTQ). In addition, INDO/S and INDO/S2 (an oxygen-reparametrized version of INDO/S [137]) computations were performed using the ZINDO-MN [138] program and a standard CIS treatment.

2.5 QM/MM methods

This final section presents a brief introduction to quantum mechanics / molecular mechanics (QM/MM) methods. Comprehensive reviews on the methodology and detailed surveys of applications of biological relevance are available in the recent literature. [74, 75]

The central concept of the QM/MM scheme is to divide a large system into an inner region, treated quantum-mechanically (called QM region or I), and an outer region, which is described by a force field (called MM region or O). The total energy of the system is not simply the sum of the energies from the inner and outer regions, since these regions interact strongly. The boundary between the subsystems must be treated carefully, especially when it crosses covalent bonds. The simplest and most popular strategy is the link-atom approach, where an additional hydrogen atom is placed in the covalent bond being cut. This atom is included in

the QM treatment, while the covalent bond between the QM and MM regions is described at the MM level.

There are two types of QM/MM energy expression in the literature, i.e., a subtractive scheme and an additive scheme. The former can be regarded as a MM approach, in which a certain region has been cut out and replaced by a higher-level treatment. One major shortcoming of this approach is the need to have MM parameters for the whole system, which are often cumbersome to obtain for electronically demanding QM regions. By contrast, in the additive scheme, the MM calculation is performed only for the outer MM region which alleviates the need for extra MM parameters. The energy expression of the additive scheme is given by:

$$E_{\text{QM/MM}} = E_{\text{MM}}(\mathbf{O}) + E_{\text{QM}}(\mathbf{I} + \mathbf{L}) + E_{\text{QM/MM}}(\mathbf{I}, \mathbf{O}). \quad (2.60)$$

The coupling term $E_{\text{QM-MM}}(\mathbf{I}, \mathbf{O})$ collects all the interaction terms between the inner and outer region and includes the electrostatic, van der Waals, and bonded interactions between the atoms in the QM and MM regions:

$$E_{\text{QM/MM}}(\mathbf{I}, \mathbf{O}) = E_{\text{QM/MM}}^{\text{el}} + E_{\text{QM/MM}}^{\text{vdW}} + E_{\text{QM/MM}}^{\text{b}}. \quad (2.61)$$

The last two terms of equation 2.61 are handled purely at the MM level. The first term determines the type of embedding used in the calculation (mechanical or electrostatic or polarized embedding). The commonly applied electrostatic embedding takes into account the polarization of the QM region due to MM point charges. The QM Hamiltonian has the following form:

$$\hat{H}_{\text{QM/MM}}^{\text{el}} = - \sum_i^{\text{electrons}} \sum_{M \in \mathcal{O}} \frac{q_M}{|r_i - R_M|} + \sum_{\alpha \in \mathcal{I} + \mathbf{L}} \sum_{M \in \mathcal{O}} \frac{q_M Z_\alpha}{|R_\alpha - R_M|} \quad (2.62)$$

where q_m denotes the MM point charges and Z_α is the nuclear charge of the QM atoms. The index i runs over all electrons, M over the point charges, and α over the QM nuclei.

Chapter 3

Benchmarking electronically excited states

3.1 Initial considerations

In this section, high-level *ab initio* results from CASPT2 and coupled-cluster calculations are presented. The choice of the medium-sized basis set TZVP is explained, followed by a brief discussion of general trends observed in the results. Together with an extensive survey of the literature of high-level *ab initio* values for the molecules contained in the benchmark set, guidelines for the definition of theoretical best estimates are established. The developed procedure is exemplified for four molecules: Ethene, naphtalene, furan, and adenine. Statistical results for singlet and triplet states are outlined and briefly discussed. For one-electron properties, such as oscillator strengths, results are listed and commented. Finally basis-set effects on CASPT2 and coupled cluster methods are evaluated, improving the definition of theoretical best estimates to some extent.

In the MS-CASPT2 calculations for $\pi \rightarrow \pi^*$ states, the active space comprised all π and π^* orbitals; for $n(\sigma) \rightarrow \pi^*$ states, the relevant $n(\sigma)$ orbitals were also included. This active space is denoted as (n,m) , with n electrons in m orbitals. It is the smallest reasonable choice one can take. Additional orbitals were added, when more flexibility in the active space was needed or when one had to avoid intruder states. Multistate CASPT2 energies as well as one-electron properties such as oscillator strengths and excited-state dipole moments were computed with the program MOLCAS (version 6.4). [139] All linear response coupled-cluster calculations were performed with the Dalton 2.0 [140] program. The same geometries and basis set were employed as for CASPT2 calculations.

3.2 Coupled-cluster and MS-CASPT2 results

A central issue for comparison of vertical excitation energies obtained by different methods consists of intrinsic details and common features of how the calculations were set up. The use of the same ground-state equilibrium geometries (MP2/6-31G*) and medium-sized basis set (TZVP) contributes mostly for this consistency. Moreover, for CASPT2, other parameters such as the active space as well as the use of a single-state or multi-state treatment play a role for the final excitation energy. However, it is important to analyse how the quality of the results depends of the setup employed.

In order to address the basis set dependence, CASPT2, CCSD, and CC3 results are obtained with the TZVP basis and 12 different correlation-consistent basis sets [141, 142] (up to augmented polarized quintuple-zeta) for the $\pi \rightarrow \pi^*$ transitions in ethene, illustrated in Figure 3.1. The triplet state (1^3B_{1u} , lower panel) is a well-characterized low-lying state, dominated by a single excitation. Consequently, variations of less than 0.1 eV are found, with TZVP results sufficiently accurate for CCSD and CC3 methods. In contrast, the high-lying singlet state (1^1B_{1u} , top panel), which is known to be rather diffuse and susceptible to valence-Rydberg mixing, shows a large basis set dependence: An extension of basis in the cc-pVXZ series (X=D,T,Q,Z) significantly lowers the excitation energy by ca. 0.6 eV, and the TZVP result is much too high (by more than 0.4 eV). Augmented basis sets with added diffuse functions are surely most appropriate for this singlet state, confirmed by the fast convergence observed in the aug-cc-pVXZ series. In this context, another methodological aspect is worth to be mentioned (see Figure 3.1): The single-state (SS) CASPT2 treatment with a (2,2) active space, even using extended basis sets such as in the aug-cc-pVXZ series, overestimates the excitation energy to the 1^1B_{1u} state by more than 0.5 eV compared to the CC3 method or a multistate (MS) CASPT2 treatment [143] with a (8,20) active space. Previous results [144] have already pointed out the tendency of this procedure to exaggerate valence-Rydberg mixing, which is corrected by MS-CASPT2. [143]

In the following, the singlet and triplet excitation energies of the benchmark set are addressed, collected in the Tables 3.1 and 3.2, respectively. These tables contain previous CASPT2 results from the Roos group, [143–161] the current MS-CASPT2, CC2, CCSD, CCSDR(3) (only for singlet states) and CC3 results with the TZVP basis, and a set of theoretical best estimates (TBE) based on the current calculations together with a survey of literature data (references [13, 15, 16, 28, 37, 41, 43, 141, 143–277]).

Looking at the computational results in the first five data columns of Tables 3.1 and 3.2, general trends are observed: (a) The excitation energies from the current CASPT2 calculations are often about 0.2 eV higher than the previously published CASPT2 values, consistent with the inclusion of the IPEA shift [100]

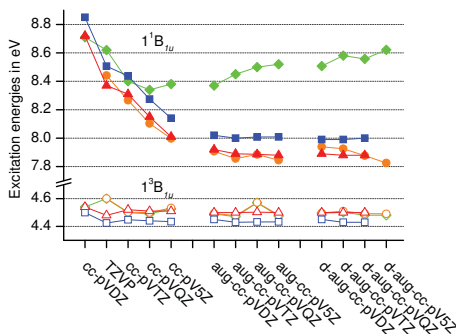


Figure 3.1: Basis set dependence of the 1^1B_{1u} (filled symbols, top) and the 1^3B_{1u} (open symbols, bottom) state of ethene with different methods: CCSD (squares, blue), CC3 (triangles, red), CASPT2 with 2,2 (diamonds, green) and 8,20 (circles, orange) active space.

in the present calculations. (b) The deviations between the current and previous CASPT2 results tend to be larger for high-lying excited states. This is expected since the current calculations use the TZVP basis without diffuse functions whereas the previous CASPT2 studies normally included diffuse functions in their basis to take into account valence-Rydberg mixing effects. The current use of the MS-CASPT2 approach [143] is expected to reduce the effects of valence-Rydberg mixing, but the lack of diffuse functions in the TZVP basis will still cause problems for high-lying valence states. (c) Among the coupled cluster results, the singlet excitation energies from the most reliable coupled cluster method (CC3) are normally lower than those from CC2 and always lower than those from CCSD using the TZVP basis set. CCSDR(3), on the other hand, yields results virtually identical to CC3. (d) For excited states that are dominated by single excitations (single excitation weight - T_1 - above 90%, see Table 3.1), the current CASPT2 and CC3 results are generally very close to each other (within 0.1 eV). Such excellent agreement is found particularly often for triplet states.

Table 3.1: Vertical singlet excitation energies ΔE (eV) of all statistically evaluated molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (% T_1) ^d	CCSDR(3) ^c	CC3 ^c (% T_1) ^d	TBE ^d
Ethene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.98	8.62	8.40	8.51 (97.2)	8.36	8.37 (96.9)	7.8
<i>E</i> -Butadiene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	6.23	6.47	6.49	6.72 (95.5)	6.56	6.58 (93.7)	6.18
	2^1A_g ($\pi \rightarrow \pi^*$)	6.27	6.63	7.63	7.42 (85.8)	6.95	6.77 (72.8)	6.55
all- <i>E</i> -Hexatriene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	5.01	5.31	5.41	5.72 (95.0)	5.56	5.58 (92.6)	5.10
	2^1A_g ($\pi \rightarrow \pi^*$)	5.20	5.42	6.67	6.61 (84.7)	6.04	5.72 (65.8)	5.09
all- <i>E</i> -Octatetraene	2^1A_g ($\pi \rightarrow \pi^*$)	4.38	4.64	5.87	5.99 (85.4)	5.40	4.97 (62.9)	4.47
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	4.42	4.70	4.72	5.07 (94.7)	4.93	4.94 (91.9)	4.66
Cyclopropene	1^1B_1 ($\sigma \rightarrow \pi^*$)	6.36	6.76	6.96	6.96 (94.5)	6.89	6.90 (93.0)	6.76

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Table 3.1 – Continued

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CCSDR(3) ^c	CC3 ^c (%T ₁) ^d	TBE ^f
Cyclopentadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.45	7.06	7.17	7.24 (96.3)	7.10	7.10 (95.5)	7.06
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.27	5.51	5.69	5.87 (95.7)	5.72	5.73 (94.3)	5.55
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.31	7.05	7.05 (89.4)	6.76	6.61 (79.3)	6.31
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.89	8.52	8.86	8.95 (95.8)	8.72	8.69 (93.1)	
Norbornadiene	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	5.28	5.34	5.57	5.80 (95.3)	5.65	5.64 (93.4)	5.34
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.20	6.11	6.37	6.69 (94.5)	6.51	6.49 (91.9)	6.11
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.48	7.32	7.65	7.87 (95.5)	7.65	7.64 (93.8)	
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	7.36	7.44	7.66	7.87 (95.0)	7.73	7.71 (93.0)	
Benzene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.84	5.05	5.27	5.19 (90.5)	5.12	5.07 (85.8)	5.08
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.30	6.45	6.68	6.74 (95.6)	6.70	6.68 (93.6)	6.54
	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	7.03	7.07	7.44	7.65 (94.5)	7.45	7.45 (92.2)	7.13
	2 ¹ E _{2g} ($\pi \rightarrow \pi^*$)	7.90	8.21	9.03	9.21 (84.9)	8.71	8.43 (65.6)	8.41
Naphthalene	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	4.03	4.24	4.45	4.41 (90.5)	4.34	4.27 (85.2)	4.24
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.56	4.77	4.96	5.21 (94.3)	5.08	5.03 (90.6)	4.77
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.39	5.90	6.22	6.23 (90.1)	6.09	5.98 (82.2)	5.90
	1 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	5.53	6.00	6.21	6.53 (91.4)	6.26	6.07 (79.6)	6.00
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	5.54	6.07	6.25	6.55 (93.9)	6.35	6.33 (90.7)	6.07
	2 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	5.87	6.48	6.82	6.97 (93.8)	6.81	6.79 (91.3)	6.48
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.93	6.33	6.57	6.77 (93.8)	6.60	6.57 (90.5)	6.33
	3 ¹ A _g ($\pi \rightarrow \pi^*$)	6.04	6.71	7.34	7.77 (88.4)	7.29	6.90 (70.0)	6.71
	3 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.16	8.18	8.46	8.77 (93.5)	8.53	8.44 (87.9)	
	3 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	7.18	7.76	8.85	9.03 (84.1)	8.50	8.12 (58.7)	
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.04	6.43	6.75	6.80 (94.9)	6.64	6.60 (92.9)	6.32
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.16	6.52	6.87	6.89 (90.8)	6.71	6.62 (84.9)	6.57
Furan	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.66	8.22	8.78	8.83 (94.2)	8.57	8.53 (90.7)	8.13
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	5.92	6.31	6.61	6.61 (91.2)	6.47	6.40 (86.0)	6.37
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.00	6.33	6.88	6.87 (94.2)	6.74	6.71 (91.6)	6.57
Pyrrole	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.46	8.17	8.44	8.44 (93.7)	8.20	8.17 (90.2)	7.91
	1 ¹ A''($n \rightarrow \pi^*$)	6.52	6.81	6.86	7.01 (92.4)	6.87	6.82 (87.6)	6.81
	2 ¹ A'($\pi \rightarrow \pi^*$)	6.72	6.19	6.73	6.80 (92.0)	6.64	6.58 (87.2)	6.19
Imidazole	3 ¹ A'($\pi \rightarrow \pi^*$)	7.15	6.93	7.28	7.27 (93.1)	7.15	7.10 (89.8)	6.93
	2 ¹ A''($n \rightarrow \pi^*$)	7.56	7.91	8.00	8.15 (93.3)	7.98	7.93 (89.4)	
	4 ¹ A'($\pi \rightarrow \pi^*$)	8.51	8.15	8.62	8.70 (92.7)	8.49	8.45 (88.8)	
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	4.84	5.02	5.32	5.27 (90.6)	5.20	5.15 (85.9)	4.85
Pyridine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.91	5.14	5.12	5.25 (92.8)	5.12	5.05 (88.1)	4.59
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.17	5.47	5.39	5.73 (92.4)	5.55	5.50 (87.7)	5.11
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.42	6.39	6.88	6.94 (95.3)	6.88	6.85 (92.8)	6.26
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.23	7.46	7.72	7.94 (94.2)	7.72	7.70 (91.5)	7.18
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.48	7.29	7.61	7.81 (93.5)	7.61	7.59 (89.7)	7.27
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.96	8.70	9.00	9.45 (89.5)	9.00	8.68 (74.1)	
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.95	8.62	9.37	9.64 (84.4)	9.09	8.77 (65.2)	
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	3.63	4.12	4.26	4.42 (93.4)	4.31	4.24 (89.9)	3.95
	1 ¹ A _u ($n \rightarrow \pi^*$)	4.52	4.70	4.95	5.29 (92.7)	5.11	5.05 (88.4)	4.81
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.75	4.85	5.13	5.14 (90.8)	5.07	5.02 (86.2)	4.64
Pyrazine	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.17	5.68	5.92	6.02 (92.1)	5.86	5.74 (85.0)	5.56
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.13	6.41	6.70	7.13 (90.8)	6.86	6.75 (83.8)	6.60
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.70	6.89	7.10	7.18 (95.6)	7.10	7.07 (93.3)	6.58
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.57	7.79	8.13	8.34 (93.9)	8.09	8.06 (90.9)	7.72
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.70	7.65	8.07	8.29 (93.2)	8.08	8.05 (89.7)	7.60
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	8.19	8.47	9.42	9.75 (83.5)	9.16	8.77 (61.1)	
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	8.26	8.61	9.26	9.55 (89.1)	9.04	8.69 (74.2)	
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	3.81	4.44	4.49	4.70 (92.7)	4.56	4.50 (88.4)	4.55
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.12	4.81	4.84	5.12 (92.6)	4.97	4.93 (88.2)	4.91
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	4.93	5.24	5.51	5.49 (90.5)	5.42	5.36 (85.7)	5.44
Pyrimidine	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.72	6.64	7.12	7.17 (94.8)	7.10	7.06 (92.2)	6.95
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.32	7.64	8.08	8.24 (93.8)	8.02	8.01 (90.7)	
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.57	7.21	7.79	7.97 (93.5)	7.77	7.74 (89.7)	
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	3.48	3.78	3.90	4.11 (93.1)	3.99	3.92 (89.0)	3.78
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	3.66	4.32	4.40	4.76 (92.0)	4.57	4.49 (86.6)	4.32
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	4.86	5.18	5.37	5.35 (90.2)	5.28	5.22 (85.2)	5.18
Pyridazine	2 ¹ A ₂ ($n \rightarrow \pi^*$)	5.09	5.77	5.81	6.00 (92.1)	5.84	5.74 (86.6)	5.77
	2 ¹ B ₁ ($n \rightarrow \pi^*$)	5.80	6.52	6.40	6.70 (92.0)	6.49	6.41 (86.6)	
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.61	6.31	7.00	7.09 (94.7)	6.99	6.93 (90.7)	
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.39	7.29	7.57	7.79 (93.8)	7.58	7.55 (90.2)	
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.50	7.62	7.90	8.11 (93.8)	7.86	7.82 (90.5)	
	1 ¹ A''($n \rightarrow \pi^*$)	3.90	4.60	4.70	4.96 (92.3)	4.81	4.78 (88.0)	4.60

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Table 3.1 – Continued

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CCSDR(3) ^c	CC3 ^c (%T ₁) ^d	TBE ^f
<i>s</i> -Tetrazine	1 ¹ A ₂ ''(n → π*)	4.08	4.66	4.80	4.98 (92.5)	4.83	4.76 (88.0)	4.66
	1 ¹ E''(n → π*)	4.36	4.71	4.77	5.01 (92.5)	4.87	4.81 (88.1)	4.71
	1 ¹ A ₂ '(π → π*)	5.33	5.79	5.82	5.84 (90.2)	5.76	5.71 (85.1)	5.79
	2 ¹ A ₁ '(π → π*)	6.77	7.25	7.52	7.51 (93.7)	7.44	7.41 (90.8)	
	2 ¹ E''(n → π*)	7.15	7.72	8.04	8.19 (90.9)	7.95	7.80 (88.1)	
	1 ¹ E'(π → π*)	8.16	7.49	8.06	8.28 (93.7)	8.07	8.04 (88.8)	
	2 ¹ E'(π → π*)	8.03	8.99	9.93	10.24 (91.2)	9.89	9.44 (74.3)	
	1 ¹ B _{3u} (n → π*)	1.96	2.24	2.47	2.71 (93.2)	2.61	2.53 (89.6)	2.24
	1 ¹ A _u (n → π*)	3.06	3.48	3.67	4.07 (92.2)	3.88	3.79 (87.5)	3.48
	1 ¹ B _{1g} (n → π*)	4.51	4.73	5.10	5.32 (91.7)	5.15	4.97 (82.5)	4.73
	1 ¹ B _{2u} (π → π*)	4.89	4.91	5.20	5.27 (90.0)	5.20	5.12 (84.6)	4.91
	1 ¹ B _{2g} (n → π*)	5.05	5.18	5.53	5.70 (90.7)	5.51	5.34 (80.7)	5.18
	1 ¹ B _{3g} (n, n → π*, π*)	5.16	5.79					5.79
	2 ¹ A _u (n → π*)	5.28	5.47	5.50	5.70 (92.5)	5.56	5.46 (87.4)	5.47
	2 ¹ B _{2g} (n → π*)	5.48	6.07	6.32	6.76 (90.1)	6.43	6.23 (79.2)	
	2 ¹ B _{1g} (n → π*)	5.99	6.38	6.91	7.25 (91.1)	6.98	6.87 (84.7)	
	3 ¹ B _{1g} (n → π*)	6.20	6.74	7.64	8.36 (86.9)	7.60	7.08 (63.2)	
	2 ¹ B _{3u} (n → π*)	6.37	6.77	6.70	6.99 (93.2)	6.77	6.67 (86.7)	
	1 ¹ B _{1u} (π → π*)	7.13	6.96	7.60	7.66 (94.9)	7.54	7.45 (91.0)	
	2 ¹ B _{1u} (π → π*)	7.54	7.43	7.75	8.06 (93.4)	7.83	7.79 (90.2)	
Formaldehyde	2 ¹ B _{2u} (π → π*)	7.94	8.15	8.65	8.88 (93.2)	8.58	8.51 (87.7)	
	2 ¹ B _{3g} (π → π*)	8.12	8.32	8.97	9.44 (84.3)	8.86	8.47 (63.6)	
	1 ¹ A ₂ (n → π*)	3.91	3.98	4.09	3.97 (93.4)	3.94	3.95 (91.2)	3.88
	1 ¹ B ₁ (σ → π*)	9.09	9.14	9.35	9.26 (93.4)	9.19	9.18 (90.9)	9.1
Acetone	2 ¹ A ₁ (π → π*)	9.77	9.31	10.34	10.54 (94.4)	10.43	10.45 (91.3)	9.3
	1 ¹ A ₂ (n → π*)	4.18	4.42	4.52	4.43 (93.4)	4.39	4.40 (90.8)	4.40
	1 ¹ B ₁ (σ → π*)	9.10	9.27	9.29	9.26 (93.8)	9.17	9.17 (91.5)	9.1
	2 ¹ A ₁ (π → π*)	9.16	9.31	9.74	9.87 (93.5)	9.66	9.65 (90.1)	9.4
<i>p</i> -Benzoquinone	1 ¹ A _u (n → π*)	2.50	2.80	2.92	3.19 (91.7)	3.01	2.85 (83.0)	2.80
	1 ¹ B _{1g} (n → π*)	2.50	2.78	2.81	3.07 (92.0)	2.90	2.75 (84.1)	2.78
	1 ¹ B _{3g} (π → π*)	4.19	4.25	4.69	4.93 (92.7)	4.69	4.59 (87.9)	4.25
	1 ¹ B _{1u} (π → π*)	5.15	5.29	5.59	5.89 (92.5)	5.65	5.62 (88.4)	5.29
	1 ¹ B _{3u} (n → π*)	5.15	5.60	5.69	6.55 (91.0)	6.09	5.82 (75.2)	5.60
	2 ¹ B _{3g} (π → π*)	6.34	6.98	7.36	7.62 (91.0)	7.36	7.27 (83.8)	6.98
	2 ¹ B _{1u} (π → π*)	7.08	7.91	8.31	8.47 (91.7)	8.10	7.82 (68.6)	
	1 ¹ A''(n → π*)	5.61	5.63	5.76	5.66 (93.6)	5.65	5.65 (90.7)	5.63
Formamide	2 ¹ A'(π → π*)	7.41	7.44	8.15	8.52 (92.9)	8.30	8.27 (87.9)	7.44
	3 ¹ A'(π → π*)	10.50	10.54	11.24	11.34 (92.7)	11.06	10.93 (86.6)	
	1 ¹ A''(n → π*)	5.54	5.80	5.77	5.71 (93.5)	5.69	5.69 (90.6)	5.80
Acetamide	2 ¹ A'(π → π*)	7.21	7.27	7.66	7.85 (92.8)	7.69	7.67 (89.1)	7.27
	3 ¹ A'(π → π*)	10.08	10.09	10.71	10.77 (93.0)	10.56	10.50 (88.7)	
	1 ¹ A''(n → π*)	5.48	5.72	5.78	5.74 (93.6)	5.71	5.72 (90.6)	5.72
Propanamide	2 ¹ A'(π → π*)	7.28	7.20	7.56	7.80 (93.0)	7.64	7.62 (89.2)	7.20
	3 ¹ A'(π → π*)	9.95	9.94	10.33	10.34 (93.3)	10.13	10.06 (89.0)	
	2 ¹ A'(π → π*)	4.39	4.68	4.80	4.98 (91.6)			4.66
Cytosine	1 ¹ A''(n → π*)	5.00	5.12	5.43	5.45 (92.5)			4.87
	2 ¹ A''(n → π*)	6.53	5.54	5.01	5.99 (92.6)			5.26
	3 ¹ A'(π → π*)	5.36	5.54	5.71	5.95 (91.1)			5.62
	4 ¹ A'(π → π*)	6.16	6.40	6.65	6.81 (92.3)			
	5 ¹ A'(π → π*)	6.74	6.98	6.94	7.23 (91.9)			
	6 ¹ A'(π → π*)	7.61	8.23	8.45	8.69 (92.1)			
	1 ¹ A''(n → π*)	4.39	4.94	4.94	5.14 (92.5)			4.82
Thymine	2 ¹ A'(π → π*)	4.88	5.06	5.39	5.60 (93.0)			5.20
	3 ¹ A'(π → π*)	5.88	6.15	6.46	6.78 (90.9)			6.27
	2 ¹ A''(n → π*)	5.91	6.38	6.33	6.57 (93.3)			6.16
	4 ¹ A'(π → π*)	6.10	6.52	6.80	7.05 (92.5)			6.53
	4 ¹ A''(n → π*)	6.15	6.86	6.73	7.67 (91.6)			
	5 ¹ A''(n → π*)	6.70	7.43	7.18	7.87 (91.6)			
	5 ¹ A'(π → π*)	7.13	7.43	7.71	7.90 (91.8)			
Uracil	1 ¹ A''(n → π*)	4.54	4.90	4.91	5.11 (92.4)			4.80
	2 ¹ A'(π → π*)	5.00	5.23	5.52	5.70 (92.6)			5.35
	3 ¹ A'(π → π*)	5.82	6.15	6.43	6.76 (90.6)			6.26
	2 ¹ A''(n → π*)	6.00	6.27	6.73	7.68 (91.5)			6.10
	3 ¹ A''(n → π*)	6.37	6.97	6.26	6.50 (93.3)			6.56
	4 ¹ A'(π → π*)	6.46	6.75	6.96	7.19 (92.5)			6.70
	5 ¹ A''(n → π*)	6.95	7.28	7.12	7.74 (91.7)			

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Table 3.1 – Continued

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CCSDR(3) ^c	CC3 ^c (%T ₁) ^d	TBE ^f
Adenine	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.00	7.42	7.66	7.81 (91.8)			
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.13	5.20	5.28	5.37 (91.3)			5.25
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.20	5.30	5.42	5.61 (92.9)			5.25
	1 ¹ A'' ($n \rightarrow \pi^*$)	6.15	5.21	5.27	5.58 (92.6)			5.12
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.86	5.97	5.91	6.19 (92.9)			5.75
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.24	6.35	6.58	6.83 (92.3)			
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.72	6.64	6.93	7.17 (91.8)			
	6 ¹ A' ($\pi \rightarrow \pi^*$)	6.99	6.88	7.49	7.72 (91.9)			
	7 ¹ A' ($\pi \rightarrow \pi^*$)	7.57	7.56	8.04	8.47 (91.1)			

^aData from publications by the Roos group in the 1990s. References [13, 15, 16, 28, 37, 41, 43, 141, 143–277].^bCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.^cCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.^dWeight of the single excitations in the coupled cluster calculations.^eTheoretical best estimates from *ab initio* calculations. See text for details.

Table 3.2: Vertical triplet excitation energies ΔE (eV) of all statistically evaluated molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CC3 ^c (%T ₁) ^d	TBE ^e
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.39	4.60	4.52	4.42 (99.4)	4.48 (99.3)	4.50
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	3.20	3.34	3.40	3.25 (98.9)	3.32 (98.5)	3.20
	$1^3A_g (\pi \rightarrow \pi^*)$	4.89	5.16	5.25	5.15 (99.1)	5.17 (98.9)	5.08
all- <i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	2.55	2.71	2.78	2.62 (98.6)	2.69 (98.0)	2.40
	$1^3A_g (\pi \rightarrow \pi^*)$	4.12	4.31	4.40	4.28 (98.9)	4.32 (98.4)	4.15
all- <i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	2.17	2.33	2.40	2.23 (98.5)	2.30 (97.6)	2.20
	$1^3A_g (\pi \rightarrow \pi^*)$	3.39	3.69	3.76	3.62 (98.7)	3.67 (98.1)	3.55
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	4.18	4.35	4.44	4.30 (99.2)	4.34 (99.1)	4.34
	$1^3B_1 (\sigma \rightarrow \pi^*)$	6.05	6.51	6.65	6.66 (98.5)	6.62 (98.1)	6.62
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.15	3.28	3.36	3.18 (98.9)	3.25 (98.5)	3.25
	$1^3A_1 (\pi \rightarrow \pi^*)$	4.90	5.10	5.22	5.07 (99.0)	5.09 (98.7)	5.09
Norbomadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	3.42	3.75	3.76	3.67 (99.0)	3.72 (98.7)	3.72
	$1^3B_2 (\pi \rightarrow \pi^*)$	3.80	4.22	4.25	4.09 (99.2)	4.16 (99.0)	4.16
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.89	4.17	4.31	3.94 (99.0)	4.12 (98.7)	4.15
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	4.49	4.90	5.14	4.97 (97.9)	4.90 (97.0)	4.86
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	5.49	5.76	6.08	6.00 (98.6)	6.04 (98.2)	5.88
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.12	7.41	7.99	7.73 (97.6)	7.49 (94.9)	7.51
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.10	3.20	3.27	2.99 (98.2)	3.11 (97.3)	3.11
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	3.89	4.29	4.38	4.27 (97.9)	4.18 (93.2)	4.18
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.23	4.55	4.64	4.44 (97.4)	4.47 (96.9)	4.47
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.30	4.71	4.88	4.67 (98.6)	4.64 (97.8)	4.64
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	4.45	5.00	5.11	5.10 (97.8)	5.11 (96.8)	5.11
	$1^3A_g (\pi \rightarrow \pi^*)$	5.27	5.57	5.76	5.57 (97.7)	5.52 (96.5)	5.52
	$2^3B_{1g} (\pi \rightarrow \pi^*)$	5.71	6.25	6.44	6.79 (98.3)	6.48 (97.6)	6.48
	$2^3A_g (\pi \rightarrow \pi^*)$	5.83	6.42	6.83	6.81 (98.5)	6.47 (97.9)	6.47
	$3^3A_g (\pi \rightarrow \pi^*)$	5.91	6.63	6.94	6.96 (97.3)	6.79 (95.0)	6.79
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	6.23	6.67	7.23	7.04 (97.3)	6.76 (94.0)	6.76
Furan	$1^3B_2 (\pi \rightarrow \pi^*)$	3.99	4.17	4.38	4.10 (98.9)	4.17 (98.5)	4.17
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.15	5.49	5.67	5.48 (98.7)	5.48 (98.2)	5.48
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	4.27	4.52	4.68	4.41 (98.8)	4.48 (98.4)	4.48
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.16	5.53	5.72	5.54 (98.4)	5.51 (97.8)	5.51
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.49	4.65	4.89	4.62 (98.8)	4.69 (98.4)	4.69
	$2^3A' (\pi \rightarrow \pi^*)$	5.47	5.74	6.01	5.83 (98.5)	5.79 (97.9)	5.79
	$1^3A'' (n \rightarrow \pi^*)$	6.07	6.36	6.44	6.43 (98.3)	6.37 (97.4)	6.37
	$3^3A' (\pi \rightarrow \pi^*)$	6.53	6.44	6.74	6.56 (98.4)	6.55 (97.9)	6.55
	$4^3A' (\pi \rightarrow \pi^*)$	7.08	7.43	7.68	7.54 (98.0)	7.42 (97.1)	
	$2^3A'' (n \rightarrow \pi^*)$	7.15	7.51	7.52	7.76 (97.6)	7.51 (96.0)	
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	4.05	4.27	4.46	4.07 (99.0)	4.25 (98.6)	4.06
	$1^3B_1 (n \rightarrow \pi^*)$	4.41	4.55	4.54	4.61 (98.1)	4.50 (97.1)	4.25
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.56	4.72	5.07	4.91 (98.0)	4.86 (97.2)	4.64
	$2^3A_1 (\pi \rightarrow \pi^*)$	4.73	5.03	5.33	5.13 (97.9)	5.05 (97.0)	4.91
	$1^3A_2 (n \rightarrow \pi^*)$	5.10	5.48	5.35	5.67 (97.5)	5.46 (95.8)	5.28
	$2^3B_2 (\pi \rightarrow \pi^*)$	6.02	6.02	6.52	6.41 (98.3)	6.40 (97.8)	6.08
	$3^3B_2 (\pi \rightarrow \pi^*)$	7.28	7.88	8.39	8.12 (97.4)	7.83 (94.4)	
	$3^3A_1 (\pi \rightarrow \pi^*)$	7.34	7.56	8.18	7.90 (97.7)	7.66 (95.3)	
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.45	1.56	1.86	1.99 (98.1)	1.89 (97.2)	1.89
	$1^3A_u (n \rightarrow \pi^*)$	2.81	3.26	3.43	3.74 (97.7)	3.52 (96.3)	3.52
	$1^3B_{1g} (n \rightarrow \pi^*)$	3.76	4.14	4.30	4.31 (98.2)	4.21 (97.1)	4.21
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.25	4.36	4.62	4.05 (99.0)	4.33 (98.5)	4.33
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	4.29	4.56	4.81	4.57 (98.1)	4.54 (97.4)	4.54
	$1^3B_{2g} (n \rightarrow \pi^*)$	4.67	4.93	5.03	5.09 (98.0)	4.93 (96.4)	4.93
	$2^3A_u (n \rightarrow \pi^*)$	4.85	5.02	5.05	5.20 (97.8)	5.03 (96.6)	5.03
	$1^3B_{3g} (n, n \rightarrow \pi^*, \pi^*)$	5.08	5.50				
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.09	5.40	5.67	5.48 (97.5)	5.38 (96.5)	5.38
	$2^3B_{2g} (n \rightarrow \pi^*)$	5.30	5.97	6.05	6.51 (96.8)	6.04 (93.0)	
	$2^3B_{1g} (n \rightarrow \pi^*)$	5.68	6.31	6.72	7.11 (96.9)	6.60 (92.3)	
	$2^3B_{3u} (n \rightarrow \pi^*)$	6.14	6.54	6.52	6.80 (97.5)	6.53 (95.8)	
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	6.81	7.10	7.65	7.46 (97.7)	7.36 (96.8)	
Formaldehyde	$1^3A_2 (\pi \rightarrow \pi^*)$	3.48	3.58	3.57	3.52 (98.6)	3.55 (98.1)	3.50
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.99	5.84	6.08	5.78 (99.3)	5.83 (99.2)	5.87
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	3.90	4.08	4.08	4.03 (98.4)	4.05 (97.9)	4.05

Continued on Next Page...

Table 3.2 – Continued

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CC3 ^c (%T ₁) ^d	TBE ^e
<i>p</i> -Benzoquinone	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.98	6.03	6.27	5.94 (99.1)	6.03 (98.9)	6.03
	1 ³ B _{1g} ($n \rightarrow \pi^*$)	2.17	2.63	2.47	2.71 (97.9)	2.51 (95.9)	2.51
	1 ³ A _u ($n \rightarrow \pi^*$)	2.27	2.68	2.59	2.83 (97.8)	2.62 (95.7)	2.62
	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	2.91	2.99	3.12	2.89 (98.5)	2.96 (97.8)	2.96
	1 ³ B _{3g} ($\pi \rightarrow \pi^*$)	3.19	3.31	3.50	3.42 (98.6)	3.41 (98.0)	3.41
Formamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.34	5.40	5.39	5.32 (98.4)	5.36 (97.8)	5.36
	1 ³ A' ($\pi \rightarrow \pi^*$)	5.69	5.58	5.94	5.67 (98.7)	5.74 (98.4)	5.74
Acetamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.24	5.53	5.42	5.39 (98.4)	5.42 (98.3)	5.42
	1 ³ A' ($\pi \rightarrow \pi^*$)	5.57	5.75	6.06	5.83 (98.7)	5.88 (98.3)	5.88
Propanamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.28	5.44	5.44	5.41 (98.4)	5.45 (97.7)	5.45
	1 ³ A' ($\pi \rightarrow \pi^*$)	5.94	5.79	6.07	5.84 (98.7)	5.90 (98.3)	5.90

^aData from publications by the Roos group in the 1990s. References [13, 15, 16, 28, 37, 41, 43, 141, 143–277].^bCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.^cCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.^dWeight of the single excitations in the coupled cluster calculations.^eTheoretical best estimates from *ab initio* calculations. See text for details.

Theoretical best estimates for the vertical excitation energies were adopted from published highly correlated *ab initio* studies with large basis sets, when available (in November 2007). In the absence of such literature data, these estimates were derived from the present calculations using the following guidelines: CC3/TZVP values were taken for the triplet states with single excitation weights of typically more than 95 %. MS-CASPT2/TZVP values were favored for the singlet excited states because there is normally at least one singlet state in each benchmark molecule with a CC3 single excitation weight of less than 90 %. Given the limitations of the TZVP basis outlined previously, CC3/TZVP or CASPT2/TZVP energies were usually not accepted as best estimates if they exceed 7 eV or if there is reason to assume that diffuse basis functions are essential for a given state. To illustrate how the current results were analysed together with the literature survey, a discussion of all valence states is presented for ethene, naphthalene, furan, and adenine.

Ethene (D_{2h}). As already mentioned in the beginning of this Section, the energy of the 1¹B_{1u} state depends strongly on the basis set and on the active space, in the case of CASPT2. Using the TZVP basis and the standard (2,2) active space gives a rather high SS-CASPT2 excitation energy of 8.62 eV. Increasing the active space lowers this value by about 0.2 eV and brings it close to the CC3 result of 8.37 eV with the TZVP basis. Further improvements require the addition of diffuse functions. Doing so at the SS-CASPT2 level with suitably chosen active spaces, one obtains excitation energies that converge to 8.44 eV, consistent with the published values of 8.40 eV [144] and 8.45 eV. [10] As pointed out previously, a MS-CASPT2 treatment is advantageous in states with significant valence-Rydberg mixing, and a MS-CASPT2 calculation with a reasonably large basis set and active space indeed yields a much lower excitation energy of 7.98 eV. [143] After further extending the basis set up to d-aug-cc-pV5Z and the active space - up to (8,20) - we arrive at a converged MS-CASPT2 value of 7.83 eV (see Fig-

ure 3.1). At the coupled cluster level the basis set dependence is smaller, but still substantial (CC3/TZVP 8.37 eV, converged CC3 value of 7.88 eV).

The 1^1B_{1u} state of ethene has been subject of many high-level *ab initio* studies. Its accurate description is challenging because of the pronounced valence-Rydberg mixing between the qualitatively different configurations arising from $\pi \rightarrow \pi^*$ and $\pi \rightarrow 3d\pi$ excitations. The best MS-CASPT2 values for the vertical excitation energies (see above) lie in the same range as other multireference perturbation results. [235, 253] Equation-of-motion coupled cluster methods give values between 7.74 and 7.99 eV (EOM-CCSDT-3: 7.89 eV). [211] An earlier CC3 study with a basis set containing diffuse functions arrives at 7.87 eV, [278] in close agreement with the results using an extended basis set (aug-cc-pV5Z or d-aug-cc-pVQZ). Extensive multireference configuration interaction and related calculations (MRCI-SD+Q, MR-AQCC) converge to a recommended value of 7.7 eV, [180] while SORCI/aug-cc-pVTZ calculations yield 7.79 eV. [257] On the experimental side, the band maximum is observed at 7.66 eV, [279] but the inclusion of corrections for zero-point and non-adiabatic effects leads to somewhat higher estimates for the vertical excitation energy of 7.8 eV [280] and 8.0 eV, [281–283] respectively. Based on these data it is concluded that the vertical excitation energy of the 1^1B_{1u} state can still not be assigned precisely, but should lie between 7.7 and 8.0 eV. Finally, a best estimate of 7.8 eV is chosen.

The 1^3B_{1u} triplet state is dominated by a single excitation and is thus easier to handle theoretically. Calculated vertical excitation energies include 4.49 eV (MS-CASPT2/d-aug-cc-pV5Z) and 4.50 eV (CC3/d-aug-cc-pVQZ or aug-cc-pV5Z), which lies in the same range as the literature results: 4.39 eV (CASPT2) [144] and 4.47 eV (SORCI/aug-cc-pVTZ). [257] An extensive MR-CI study yields values in a narrow range between 4.47 and 4.53 eV. [180] Experimental values from electron impact and optical spectroscopy are 4.36 eV [284] and 4.6 eV, [285] respectively. A value of 4.50 eV is adopted as best estimate.

Naphthalene (D_{2h}). The present CASPT2 excitation energies are generally blue shifted when compared with previous CASPT2 results, [150] typically by 0.2–0.4 eV for low-energy singlet and triplet states that are dominated by single excitations. Larger blue shifts are encountered for singlet states with strong contributions from doubly excited configurations (2^1A_g , 1^1B_{1g} , 3^1A_g , 3^1B_{3u}) and also more generally for states with large perturbation corrections (2 eV or more) to the CASSCF excitation energies (2^1B_{3u} , 2^1B_{1g} , 3^1B_{2u}). The CC2 excitation energies are even more blue shifted, especially in these problem cases. The CC3/TZVP energies are also slightly higher than the CASPT2/TZVP values, but they are rather close for the lower excited singlet and all triplet states.

The experimental studies often focus on the 0-0 bands. Experimental vertical excitation energies are known from optical and electron impact spectra for the following singlet states: 4.0 eV (1^1B_{3u}), [286] 4.7 eV (1^1B_{2u}), [286] 5.89 eV

(2^1B_{3u}), [287] 6.14 eV (2^1B_{2u}), [287] and 7.6 eV (3^1B_{2u}). [286] Additional data come from two-photon absorption spectroscopy [288]: 5.22 eV (1^1B_{1g}), 5.52 eV (2^1A_g), and 6.05 eV (3^1A_g). The most intense peak for the lowest triplet state (1^3B_{2u}) is found in a gas-phase energy loss spectrum at 3.0 eV. [289] Triplet-triplet excitations are observed at 2.25 eV (1^3A_g), [290] 2.93 eV (3^3A_g), [290] and 3.12 eV (2^3B_{1g}). [290] The latter value corresponds to the most intense peak, whereas the former two values refer to the onset of the band.

The previous [150] and present CASPT2 results enclose the quoted experimental values in most cases and show comparable deviations. Therefore, the current CASPT2/TZVP values below 7 eV are selected as reference data for the singlet states. Following the defined guidelines, CC3/TZVP results are taken as reference data for the triplet states, which are rather close to previous [150] and current CASPT2 calculations.

Furan (C_{2v}). The current CASPT2/TZVP approach gives the three lowest singlet valence excited states at 6.43 eV (1^1B_2), 6.52 eV (2^1A_1) and 8.22 eV (3^1A_1), i.e., about 0.4-0.5 eV higher than in the early CASPT2/ANO study [147] and about 0.1-0.3 eV lower than in CC3/TZVP. The 1^1B_2 state is red-shifted to 6.25 eV when the active space in CASPT2/TZVP is enlarged by two more orbitals. The current CASPT2/TZVP results agree well with recent high level MRCI data [233] (1^1B_2 : 6.44 eV, 2^1A_1 : 6.53 eV) and CC3/ANO data [182] (1^1B_2 : 6.35 eV, 2^1A_1 : 6.61 eV and 3^1A_1 : 8.35 eV). We adopt the CC3 results with basis set correction as best estimates [191] (1^1B_2 : 6.32 eV, 2^1A_1 : 6.57 eV and 3^1A_1 : 8.13 eV). The valence bands in the experimental optical spectrum are quite broad and show maxima at 6.06 eV, 6.47/6.61 eV, and 7.79 eV. [291]

In the case of the two lowest triplet states, calculations at the CASPT2/TZVP and CC3/TZVP level of theory yield virtually identical excitation energies which are about 0.2-0.3 eV higher than those from the early CASPT2/ANO study. [147] The two maxima in the electron impact spectra lie at 3.99 eV and 5.22 eV. [291] Following the guidelines, the present CC3/TZVP results are adopted as reference data (1^3B_2 : 4.17 eV, 1^3A_1 : 5.48 eV).

Adenine (C_s). An early CASPT2 study [161] gave excitation energies of more than 6 eV for the $n \rightarrow \pi^*$ states, about 1 eV higher than all more recent studies which place both the lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ state around 5 eV. These two states ($1^1A''$ and $2^1A'$) are virtually degenerate (within 0.05 eV) in the current CASPT2/TZVP and CC2/TZVP calculations as well as at the CASPT2/6-31G*, [241] SAC-CI/cc-pVDZ, [212] and CIPSI/cc-pVDZ levels, [194] while the $1^1A''$ state is slightly lower, by about 0.1 eV, in DFT-MRCI/TZVPP, [41] CC2/aug-cc-pVTZ, [248] and CASPT2/6-31G(d,p). [228]

The computed splitting between the two lowest $\pi \rightarrow \pi^*$ states ($2^1A'$ and $3^1A'$) states usually lies between 0.1 and 0.2 eV, both in the present calculations (0.09 eV CASPT2/TZVP, 0.20 eV CC2/TZVP) and in the published work (0.19 eV, [228])

0.11 eV, [241] 0.14 eV, [171] 0.14 eV [41]), whereas the two states are degenerate at the CC2/aug-cc-pVTZ level. [248]

CC3/TZVP results could not be obtained due to their computational demands. CC2/aug-cc-pVTZ results [248] are adopted as reference data. The differences between the CC2/aug-cc-pVTZ and CASPT2/TZVP excitation energies for adenine are less than 0.1 eV in most cases.

3.2.1 Statistical evaluation

Statistical comparisons between the present CASPT2 and coupled-cluster (CC2, CCSD, and CC3) results are outlined in this section. They covers a total of 223 excited states, i.e., the 152 singlets from Table 3.1 and the 71 triplets from Table 3.2.

For the purpose of statistical evaluation, the current CASPT2/TZVP results are used as reference, for the following reasons: Coupled-cluster results suffer from low single excitation weights for a number of states (see Table 3.1) and CC3 calculations were not feasible for the nucleobases. Moreover, the CASPT2/TZVP and CC3/TZVP results for the triplets are generally quite close to each other (see Table 3.2), making this choice of reference data less critical.

Earlier CASPT2 results from the Roos group [143–161] are available for all benchmark molecules (see Tables 3.1 and 3.2). Although these were obtained with different basis sets and geometries, it is still instructive to compare them with the present results, and they are thus included in the statistical evaluation. However, a comparison with the available experimental data was avoided, although vertical excitation energies from the earlier CASPT2 work are often quite close to the absorption maxima of the experimental spectra.

Singlet states

Statistical results for the vertical excitation energies of the singlet excited valence states are given in Table 3.3, which lists the mean, absolute mean, standard, and maximum deviations with respect to the CASPT2/TZVP results. Figure 3.2 shows the corresponding correlations between the CC/TZVP and CASPT2/TZVP results with the associated correlation coefficients r .

It is clearly seen from Figure 3.2 that CC/TZVP excitation energies are generally higher than those from CASPT2/TZVP, typically by 0.3 eV for CC2, 0.5 eV for CCSD, and 0.2 eV for CC3. It is also observed that the mean and absolute mean deviations for these methods have only a small difference, indicating a rather systematic deviation between the methods. By contrast, the earlier CASPT2 results tend to be lower than the present CASPT2/TZVP values, on average by more than 0.2 eV.

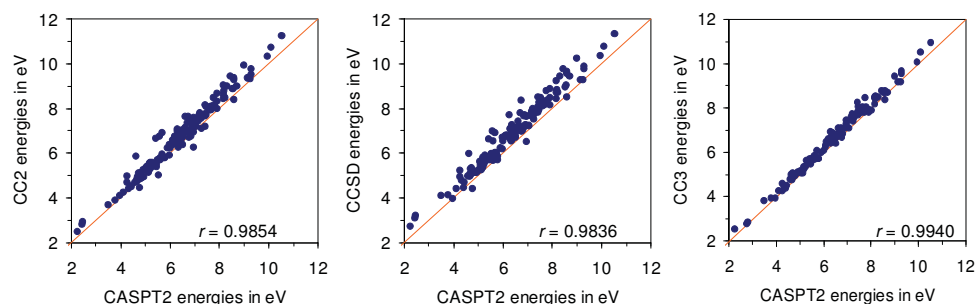


Figure 3.2: Correlation plots for all calculated singlet excited states: CC/TZVP vs CASPT2/TZVP vertical excitation energies.

Table 3.3: Deviations in excitation energies of singlet excited states of all 28 benchmark molecules with respect to CASPT2/TZVP.

	Method			
	CC2	CCSD	CC3	CASPT2 ^a
Count ^b	152	152	121	152
Mean	0.29	0.49	0.20	-0.23
Abs. Mean	0.32	0.50	0.22	0.35
Std. Dev.	0.41	0.58	0.27	0.42
Maximum	1.25	1.62	0.83	1.02

^aData from publications by the Roos group in the 1990s collated and discussed on section 3.2.

^bTotal number of considered states.

One should note that the highest-level coupled-cluster results (CC3) agree with the CASPT2 reference data best. CC2 outperforms CCSD in comparisons with CASPT2 and CC3. In general, CCSD seems to overestimate the excitation energies significantly (on average at least 0.2 eV higher than with any of the other methods).

It is also important to emphasize that CC2 and CCSD are not expected to be reliable for states with considerable double excitation character, and high deviations are indeed found for such singlet excited states. For example, in the case of CC2/TZVP, the three largest deviations from CASPT2/TZVP occur for the 2^1A_g states of all-*E*-hexatriene (+1.25 eV), all-*E*-octatetraene (+1.23 eV), and *E*-butadiene (+1.00 eV). For these states with strong double excitation contributions, the deviations are similarly large for CCSD/TZVP, and much reduced for

CC3/TZVP (see Table 3.1). Excluding such problematic states is thus expected to improve the performance of CC2 and CCSD.

Triplet states

A statistical comparison for 71 excited triplet states is summarized in Table 3.4. It is noteworthy that there is excellent agreement between the coupled-cluster and CASPT2/TZVP results, especially for the CC3 method (mean absolute deviation of 0.08 eV). In contrast, the earlier CASPT2 energies are systematically lower, on average by almost 0.3 eV (see Table 3.4).

Table 3.4: Deviation in excitation energies of triplet excited states of 19 benchmark molecules with respect to CASPT2/TZVP.

	Method			
	CC2	CCSD	CC3	CASPT2 ^a
Count ^b	71	71	71	71
Mean	0.18	0.08	0.03	-0.28
Abs. Mean	0.19	0.16	0.08	0.28
Std. Dev.	0.24	0.22	0.11	0.32
Maximum	0.62	0.80	0.38	0.72

^aData from publications by the Roos group in the 1990s collated and discussed on section 3.2.

^bTotal number of considered states.

Large deviations between the present CASPT2/TZVP and CC/TZVP results for the triplets are rare. The maximum deviation with CC3 concerns the 2^3B_2 state of pyridine (+0.38 eV), and there are four deviations exceeding 0.2 eV in the case of *s*-tetrazine. These are exceptions, however, since the agreement is better than 0.1 eV for the vast majority of states.

3.2.2 Oscillator strengths

It would clearly be desirable to have reference data not only for vertical excitation energies, but also for oscillator strengths of dipole-allowed vertical transitions. Table 3.5 collects the corresponding results from the present CASPT2, CC2, and CCSD calculations with the TZVP basis. It also contains the earlier CASPT2 results from the Roos group [143–161] and the range of published values from other *ab initio* studies.

Contrary to the case of excitation energies, derivation of best estimates for oscillator strengths is still not straightforward for the following reasons: Literature

values using high-level *ab initio* methods are scarce, and several studies deliver accurate excitation energies but do not even quote oscillator strengths. Furthermore, the results found in the literature span a wide range and, even when comparing with the current CASPT2 and coupled-cluster calculations, deviations seems too large to define realistic best estimates. Therefore the current results are merely listed, and only some qualitative comments are given.

Table 3.5: Oscillator strengths f for allowed vertical singlet transitions in the benchmark molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c	Lit. values ^d
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.360	0.513	0.431	0.410	0.358–0.494
<i>E</i> -Butadiene	$1^1B_u (\pi \rightarrow \pi^*)$	0.686	0.783	0.809	0.776	0.52–0.803
all- <i>E</i> -Hexatriene	$1^1B_u (\pi \rightarrow \pi^*)$	0.85	1.045	1.272	1.213	0.655–1.154
all- <i>E</i> -Octatetraene	$1^1B_u (\pi \rightarrow \pi^*)$	1.832	1.299	1.757	1.665	1.382
Cyclopropene	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.010	0.010	0.001	0.001	
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.101	0.234	0.086	0.083	
Cyclopentadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.148	0.144	0.110	0.097	0.099–0.157
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.000	0.001	0.011	0.008	0.001–0.019
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.442	0.965	0.658	0.648	0.225–0.538
Norbornadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.008	0.092	0.023	0.029	
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.343	0.393	0.185	0.187	
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.000	0.000	0.000	0.000	
Benzene	$1^1E_{1u} (\pi \rightarrow \pi^*)$	0.82	0.847	0.694	0.686	0.323–1.33
Naphthalene	$1^1B_{3u} (\pi \rightarrow \pi^*)$	0.001	0.001	0.000	0.000	0.000
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.050	0.137	0.094	0.083	0.082
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	1.337	1.548	1.450	1.461	1.326
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.313	0.402	0.272	0.294	0.268
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	0.848	0.708	0.548	0.538	0.840
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	0.048	0.008	0.010	0.014	0.067
Furan	$1^1B_2 (\pi \rightarrow \pi^*)$	0.154	0.199	0.172	0.159	0.144–0.185
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.002	0.008	0.003	0.001	0.000–0.011
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.416	0.793	0.506	0.501	0.194–0.494
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	0.020	0.031	0.006	0.005	0.000–0.036
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.125	0.205	0.182	0.166	0.099–0.99
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.326	0.613	0.532	0.527	0.176–0.706
Imidazole	$1^1A'' (n \rightarrow \pi^*)$	0.011	0.010	0.003	0.005	
	$2^1A' (\pi \rightarrow \pi^*)$	0.126	0.229	0.088	0.088	0.080
	$3^1A' (\pi \rightarrow \pi^*)$	0.143	0.062	0.085	0.081	0.070
	$2^1A'' (n \rightarrow \pi^*)$	0.013	0.019	0.006	0.004	
	$4^1A' (\pi \rightarrow \pi^*)$	0.594	0.555	0.406	0.420	
Pyridine	$1^1B_2 (\pi \rightarrow \pi^*)$	0.018	0.044	0.025	0.022	0.023–0.040
	$1^1B_1 (n \rightarrow \pi^*)$	0.009	0.009	0.005	0.006	0.005–0.01
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.005	0.004	0.021	0.015	0.006–0.021
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.82	0.849	0.498	0.590	0.513–0.67
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.64	0.691	0.549	0.548	0.407–0.65
	$4^1A_1 (\pi \rightarrow \pi^*)$	0.03	0.000	0.000	0.002	
	$3^1B_2 (\pi \rightarrow \pi^*)$	0.158	0.089	0.012	0.014	
Pyrazine	$1^1B_{3u} (n \rightarrow \pi^*)$	0.01	0.012	0.007	0.008	0.01
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.07	0.123	0.070	0.067	0.08

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Table 3.5 – Continued

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c	Lit. values ^d
Pyrimidine	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.08	0.107	0.096	0.074	0.06
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.76	0.774	0.424	0.458	0.37
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.66	0.622	0.400	0.423	0.33
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	0.00	0.000	0.000	0.000	
	$2^1A_g (\pi \rightarrow \pi^*)$	0.00	0.000	0.000	0.000	
	$1^1B_1 (n \rightarrow \pi^*)$	0.02	0.013	0.006	0.007	0.007–0.01
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.001	0.049	0.023	0.022	0.01–0.026
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.05	0.164	0.062	0.038	0.017–0.03
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.58	0.540	0.446	0.461	
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.79	0.768	0.476	0.470	0.41–0.499
Pyridazine	$3^1B_2 (\pi \rightarrow \pi^*)$	0.06	0.000	0.000	0.000	
	$4^1A_1 (\pi \rightarrow \pi^*)$	0.14	0.000	0.000	0.000	
	$1^1B_1 (n \rightarrow \pi^*)$	0.01	0.010	0.006	0.007	
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.009	0.027	0.014	0.014	
	$2^1B_1 (n \rightarrow \pi^*)$	0.008	0.008	0.005	0.005	
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.003	0.115	0.009	0.006	
<i>s</i> -Triazine	$2^1B_2 (\pi \rightarrow \pi^*)$	0.75	0.603	0.489	0.459	
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.50	0.742	0.444	0.494	
	$1^1A_2'' (n \rightarrow \pi^*)$	0.015	0.021	0.017	0.018	0.02–0.027
<i>s</i> -Tetrazine	$1^1E' (\pi \rightarrow \pi^*)$	0.61	0.680	0.441	0.437	0.92
	$2^1E' (\pi \rightarrow \pi^*)$	0.21	0.044	0.000	0.000	
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.013	0.013	0.007	0.009	0.007–0.012
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.045	0.110	0.046	0.047	0.052–0.095
	$2^1B_{3u} (n \rightarrow \pi^*)$	0.017	0.021	0.011	0.012	0.01–0.018
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.001	0.136	0.017	0.003	0.00–0.054
Formaldehyde	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.687	0.496	0.376	0.381	0.39–0.630
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.733	0.588	0.368	0.333	0.45–0.755
	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.01	0.013	0.079	0.074	0.000–0.001
Acetone	$2^1A_1 (\pi \rightarrow \pi^*)$	0.28	0.451	0.368	0.374	0.063–0.100
	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.010	0.011	0.000	0.000	0.003
<i>p</i> -Benzoquinone	$2^1A_1 (\pi \rightarrow \pi^*)$	0.326	0.358	0.298	0.256	0.255
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	0.000	0.000	0.000	0.000	
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.616	0.638	0.538	0.558	0.636–0.704
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.000	0.000	0.000	0.001	0.000
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.022	0.016	0.000	0.000	
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.624	0.660	0.544	0.509	0.693
	$3^1B_{1u} (\pi \rightarrow \pi^*)$	0.030	0.079	0.000	0.000	
Formamide	$1^1A'' (n \rightarrow \pi^*)$	0.001	0.001	0.001	0.001	0.000–0.001
	$2^1A' (\pi \rightarrow \pi^*)$	0.371	0.479	0.385	0.371	0.149–0.338
	$3^1A' (\pi \rightarrow \pi^*)$	0.131	0.163	0.010	0.102	
Acetamide	$1^1A'' (n \rightarrow \pi^*)$	0.001	0.001	0.001	0.001	
	$2^1A' (\pi \rightarrow \pi^*)$	0.292	0.424	0.199	0.223	
	$3^1A' (\pi \rightarrow \pi^*)$	0.179	0.263	0.279	0.299	
Propanamide	$1^1A'' (n \rightarrow \pi^*)$	0.001	0.001	0.000	0.000	
	$2^1A' (\pi \rightarrow \pi^*)$	0.346	0.405	0.138	0.180	
	$3^1A' (\pi \rightarrow \pi^*)$	0.205	0.275	0.189	0.150	
Cytosine	$2^1A' (\pi \rightarrow \pi^*)$	0.061	0.093	0.049	0.058	0.052–0.080
	$1^1A'' (n \rightarrow \pi^*)$	0.005	0.003	0.001	0.002	0.001–0.002
	$3^1A' (\pi \rightarrow \pi^*)$	0.108	0.352	0.165	0.178	0.138–0.181
	$4^1A' (\pi \rightarrow \pi^*)$	0.863	0.623	0.632	0.608	
	$2^1A'' (n \rightarrow \pi^*)$	0.001	0.002	0.002	0.000	0.001–0.003
	$5^1A' (\pi \rightarrow \pi^*)$	0.147	0.366	0.168	0.159	
	$6^1A' (\pi \rightarrow \pi^*)$	0.239	0.132	0.223	0.112	

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42 CHAPTER 3. BENCHMARKING ELECTRONICALLY EXCITED STATES

Table 3.5 – Continued

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c	Lit. values ^d
Thymine	1 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.17	0.334	0.197	0.222	0.18
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.17	0.067	0.080	0.071	0.04
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.15	0.356	0.250	0.285	0.18
	3 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	4 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.85	0.672	0.515	0.361	
Uracil	6 ¹ A' ($\pi \rightarrow \pi^*$)	0.00	0.004	0.000	0.000	
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.19	0.320	0.197	0.224	0.18–0.26
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.08	0.047	0.058	0.061	0.04–0.05
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.001	
	3 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.29	0.249	0.188	0.209	0.035–0.17
	4 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
Adenine	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.76	0.804	0.547	0.430	0.51
	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.070	0.146	0.037	0.002	0.004–0.03
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.370	0.201	0.276	0.297	0.17–0.36
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.001	0.000	0.000	0.001–0.007
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.851	0.538	0.496	0.513	0.51
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.159	0.001	0.085	0.070	
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.002	0.000	0.000	0.003–0.005
	6 ¹ A' ($\pi \rightarrow \pi^*$)	0.565	0.010	0.320	0.286	
	7 ¹ A' ($\pi \rightarrow \pi^*$)	0.406	0.037	0.177	0.122	

^aData from publications by the Roos group in the 1990s. References [13, 15, 16, 28, 37, 41, 43, 141, 143–277].

^bCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.

^cCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.

^dRange of *ab initio* literature values.

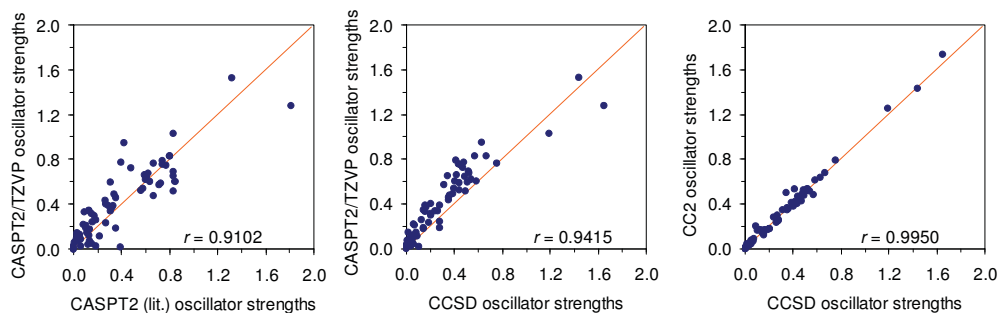


Figure 3.3: Correlation plots for all dipole allowed oscillator strengths: CASPT2 (literature) vs CASPT2/TZVP, CCSD/TZVP vs CASPT2/TZVP and CCSD/TZVP vs CC2.

Inspection of Table 3.5 shows that all methods give the same qualitative picture for the distribution of the oscillator strength. Weak transitions with almost vanishing

intensity are identified consistently, and the computed intensity order is usually the same for a given molecule.

Figure 3.3 shows the correlations between the oscillator strengths from CASPT2 (Roos group versus this work) and coupled-cluster calculations. Comparing the results with each other, CC2/TZVP and CCSD/TZVP generally yield quite similar oscillator strengths, with no noticeable trend for systematic deviations. In addition, earlier CASPT2 values from the Roos group lie in the same range as those from the present CASPT2 results, although deviations scatter more than for CC2 and CCSD (see Figure 3.3). Finally the CASPT2/TZVP oscillator strengths are higher than the coupled cluster results in most cases.

3.3 Assignment of theoretical best estimates

Theoretical best estimates for the vertical excitation energies were selected for 104 singlet excited states and 63 triplet excited states in 28 benchmark molecules. For singlet states, the MS-CASPT2/TZVP results were chosen for 43 states, together with CC3/TZVP (3) as well as MRCI (9), MRMP (4) and coupled-cluster (45) results from the literature obtained with larger basis sets (and also with geometries optimized at a higher level of theory). For the triplet states, most of which are well described by single excitations, CC3/TZVP results have been taken as best estimates for most of the states (44), together with MRCI (9), MRMP (4) and coupled-cluster (6) results from the literature.

Although the proposed best estimates show some heterogeneity with regard to the methodology used, it is strongly believed that this reference set is useful for validating approximate methods for electronically excited states. It should be emphasized at this point that this has been an initial attempt to derive a reference set for electronically excited states. And without any doubt this set can be improved by further higher-level calculations (see the discussion in chapter 7) and by adding more benchmark molecules.

In contrast to vertical excitation energies, it has not been possible to derive best estimates for one-electron properties such as oscillator strengths and dipole moments from the current results and collated literature data. The main problem in this regard is the lack of convergence studies for these properties and the strong scatter of the values computed by different high-level methods.

Chapter 4

Assessment of TD-DFT and DFT/MRCI methods

4.1 Initial considerations

In this section the performance of the DFT-based methods TD-DFT (with BP86, B3LYP and BHLYP functionals) and DFT/MRCI is evaluated using accurate *ab initio* reference data (see the preceding chapter). The same ground-state equilibrium geometries (MP2/6-31G*) and the same basis set (TZVP) are employed as in the reference calculations to ensure a consistency that is essential for benchmarking purposes. A proper evaluation requires the correct assignment of all excited states – a major task which is sometimes nontrivial. A state ordering based on a linear correspondence of energies is not sufficient for a reliable assignment of states. Pure gradient-corrected functionals (like BP86) give usually rather low orbital energy gaps, and hence relatively low transition energies, [118] whereas an increased admixture of HF exchange in hybrid functionals leads to blue-shifted excitation energies and, occasionally, even to an inversion of the ordering. [292] Therefore, the excited state wavefunction composition as well as one-electron properties (such as oscillator strengths and state dipole moments) were inspected in each case to arrive at a reliable assignment.

The following discussion focuses on the statistical evaluation of the DFT-based results for vertical excitation energies and one-electron properties. Results for individual molecules from the benchmark set will not be discussed, unless particularly high deviations are encountered for some method.

4.2 Statistical evaluation

During the statistical evaluation of excitation energies, the present DFT-based results are compared with four sets of reference data that have been assembled in the preceding section: the earlier CASPT2 results from the Roos group, followed by the MS-CASPT2/TZVP and CC3/TZVP data, and the proposed theoretical best estimates. For one-electron properties such as oscillator strengths, however, the reference data for the oscillator strengths come from the published CASPT2 as well as the own MS-CASPT2 and CC2 calculations. Finally, dipole moments are compared against published CASPT2 and own MS-CASPT2 results.

Singlet state energies

Table 4.1 summarizes the statistical evaluation for the singlet excited states in the benchmark set. Given are the number of states considered, the mean deviation (MD), the mean absolute deviation (MAD), and the standard and maximum deviations among each set. The number of states differs somewhat between the different reference sets: Available are 146 singlet state energies from the published CASPT2 and the own MS-CASPT2 calculations, but only 116 CC3 energies and 104 theoretical best estimates.

When using the published CASPT2 data as reference, DFT/MRCI gives the lowest mean absolute deviation (0.29 eV), followed by TD-DFT/B3LYP (0.37 eV), TD-DFT/BP86 (0.44 eV) and TD-DFT/BHLYP (0.73 eV). Positive (negative) mean deviations indicate that the calculated energies tend to be blue-shifted (red-shifted) with respect to the reference values. The DFT/MRCI results (MD of 0.02 eV) thus scatter around the literature CASPT2 data. The excitation energies from TD-DFT/BP86 are lower on average (MD of -0.27 eV), while those from TD-DFT/B3LYP and TD-DFT/BHLYP are slightly and considerably higher on average (MD of 0.10 and 0.65 eV, respectively). The largest deviations for the four DFT-based methods are found for the $1^1A''$ state of *s*-triazine (0.79 eV, DFT/MRCI), the 3^1B_{3u} state of naphthalene (0.82 eV, TD-DFT/BP86; 1.47 eV, TD-DFT/B3LYP), and the 3^1B_{1g} state of *s*-tetrazine (3.00 eV, TD-DFT/BHLYP), the latter marking the largest overall deviation.

Results from section 3.2.1 show that singlet excitation energies from the MS-CASPT2 and CC3/TZVP calculations are on average about 0.2 and 0.4 eV higher than the published CASPT2 values. Thus a change in the reference set to MS-CASPT2/TZVP and CC3/TZVP causes corresponding shifts in the mean deviations of the TD-DFT and DFT/MRCI results (Table 4.1). Now the DFT-based excitation energies appear generally red-shifted with respect to the *ab initio* data, except for TD-DFT/BHLYP. The TD-DFT/BP86 results show the worst agreement with the reference data (MD of -0.48 and -0.61 eV compared to MS-CASPT2 and

CC3, respectively), whereas TD-DFT/B3LYP and DFT/MRCI perform similarly well.

The most relevant comparisons involve the theoretical best estimates as reference data. Here DFT/MRCI and TD-DFT/B3LYP outperform TD-DFT/BP86 and TD-DFT/BHLYP: The mean absolute deviation is smallest for DFT/MRCI (0.22 eV) followed rather closely by TD-DFT/B3LYP (0.27 eV) and much ahead of TD-DFT/BP86 (0.52 eV) and TD-DFT/BHLYP (0.50 eV). Both DFT/MRCI and TD-DFT/B3LYP tend to give singlet excitation energies that are slightly too low (MD of -0.13 and -0.07 eV).

Triplet state energies

Statistical results for the triplet states are listed in Table 4.2 and visualized in Figure 4.1. The number of states considered varies for the different reference sets: 71 states are available from the earlier CASPT2 as well as the own MS-CASPT2 and CC3 calculations, and there are theoretical best estimates for 63 of these states (See Section 3.2.1).

It is evident at first sight that the DFT-based methods systematically underestimate the *ab initio* reference triplet excitation energies. With one minor exception (MD of 0.02 eV of DFT/MRCI with respect to the published CASPT2 results as reference), all MDs are negative. DFT/MRCI generally fares best, for example with respect to the theoretical best estimates (MD of -0.24 eV compared with values between -0.45 eV and -0.54 eV for the three TD-DFT approaches); likewise, DFT/MRCI has by far the lowest MAD (0.25 vs 0.45–0.60 eV, see Table 4.2). Noteworthy is also the close correspondence between DFT/MRCI and the published CASPT2 results (MD of 0.02 eV and MAD of 0.17 eV).

One-electron properties

Contrary to the excitation energies, theoretical best estimates could not yet be derived from the benchmark study presented in section 3.2. Nevertheless, correlation plots between the oscillator strengths from the DFT-based calculations and from the CASPT2, MS-CASPT2/TZVP and CC2/TZVP calculations are illustrated in Figure 4.2. The statistical data are summarized in Table 4.3.

Consistent with previous results, [293] the TD-DFT methods tend to underestimate the *ab initio* oscillator strengths to some extent (more so for CASPT2 or MS-CASPT2 than for CC2): The mean deviations are all negative and of similar magnitude as the corresponding MAD values (Table 4.3). The DFT/MRCI oscillator strengths are spread around the published CASPT2 reference data (MD of -0.003); they tend to be somewhat lower than the MS-CASPT2/TZVP results (MD of -0.019) and somewhat higher than the CC2/TZVP results (MD of 0.039).

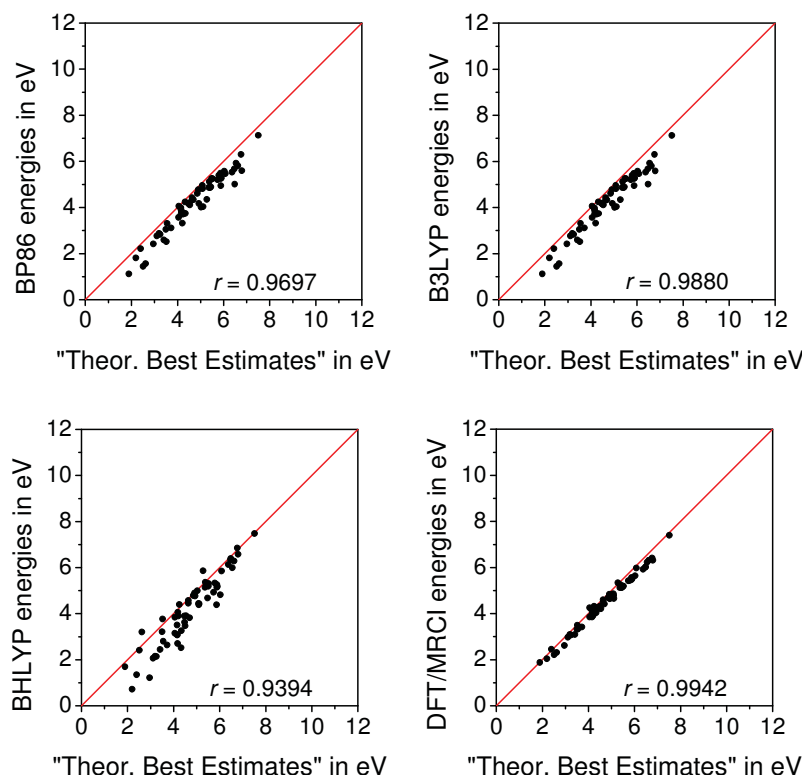


Figure 4.1: Correlation plots for all calculated triplet excited states: TD-DFT (BP86, B3LYP, BHLYP) and DFT/MRCI vs theoretical best estimates for vertical excitation energies.

Considering the overall deviations in Table 4.3, DFT/MRCI fares best in the comparisons with the CASPT2 and MS-CASPT2/TZVP reference data, and performs similar to TD-DFT/B3LYP with respect to the CC2/TZVP reference data set.

Table 4.4 presents the statistical evaluations for state dipole moments using previous CASSCF results and the own MS-CASPT2/TZVP results as reference. The mean absolute deviations of the DFT-based state dipole moments from the *ab initio* results are generally in the range between 0.6 and 0.8 D, while the corresponding mean deviations are considerably lower in magnitude (indicating significant scattering).

The mean deviations in Table 4.4 are all negative, suggesting a tendency of DFT-based methods to give lower state dipole moments than the *ab initio* reference methods. This is deceptive insofar as the MD values are affected by a few pronounced negative outliers that occur in the excited states of the nucleobases, with deviations above 4 Debye. However, the majority of the DFT-based state dipole

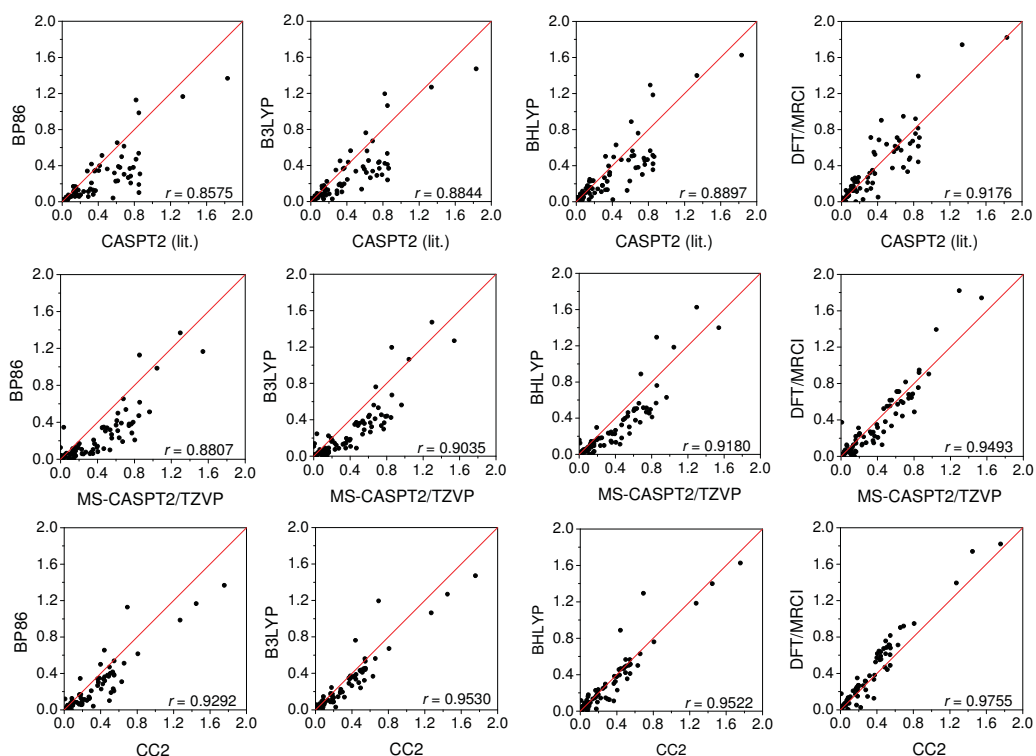


Figure 4.2: Correlation plots of oscillator strengths for all dipole-allowed excited states using earlier CASPT2, MS-CASPT2/TZVP and CC2/TZVP results as reference data.

moments are actually larger than their *ab initio* counterparts. For example, 57, 60, 61, and 57 % of the state dipole moments from TD-DFT/BP86, TD-DFT/B3LYP, TD-DFT/BHLYP, and DFT/MRCI, respectively, are larger by 0–1 D than the MS-CASPT2/TZVP values.

Table 4.1: TD-DFT and DFT/MRCI deviations of vertical excitation energies (eV) for singlet excited states with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASPT2 results ^a				
Count ^b	146	146	146	146
Mean	-0.27	0.10	0.65	0.02
Abs. Mean	0.44	0.37	0.73	0.29
Std. Dev.	0.58	0.48	0.90	0.39
Max. (+) dev.	0.82	1.47	3.00	0.79
Max. (−) dev.	2.04	1.42	0.95	1.37
MS-CASPT2/TZVP results ^c				
Count ^b	146	146	146	146
Mean	-0.48	-0.11	0.44	-0.19
Abs. Mean	0.56	0.30	0.52	0.26
Std. Dev.	0.68	0.38	0.67	0.33
Max. (+) dev.	0.63	1.05	2.47	0.75
Max. (−) dev.	1.77	0.94	0.85	0.97
CC3/TZVP results ^c				
Count ^a	116	116	116	116
Mean	-0.61	-0.29	0.20	-0.39
Abs. Mean	0.65	0.39	0.44	0.39
Std. Dev.	0.73	0.46	0.57	0.46
Max. (+) dev.	0.34	0.82	2.12	—
Max. (−) dev.	1.89	1.28	1.13	1.26
Theoretical best estimates ^c				
Count ^a	104	104	104	104
Mean	-0.44	-0.07	0.43	-0.13
Abs. Mean	0.52	0.27	0.50	0.22
Std. Dev.	0.62	0.33	0.62	0.29
Max. (+) dev.	0.65	1.02	1.73	0.75
Max. (−) dev.	1.37	0.75	0.56	0.90

^aData from publications by the Roos group in the 1990s collated and discussed on section 3.2.^bTotal number of states considered.^cSee Section 3.2.

Table 4.2: TD-DFT and DFT/MRCI deviations of vertical excitation energies (in eV) for triplet excited states with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASPT2 results ^a				
Count ^b	71	71	71	71
Mean	-0.30	-0.18	-0.19	0.02
Abs. Mean	0.32	0.27	0.58	0.17
Std. Dev.	0.40	0.33	0.75	0.22
Max. (+) dev.	0.26	0.65	1.85	0.69
Max. (−) dev.	0.85	0.81	1.74	0.53
MS-CASPT2/TZVP results ^c				
Count ^b	71	71	71	71
Mean	-0.56	-0.43	-0.45	-0.24
Abs. Mean	0.56	0.43	0.58	0.25
Std. Dev.	0.63	0.47	0.75	0.27
Max. (+) dev.	–	–	1.16	0.27
Max. (−) dev.	1.21	0.80	1.86	0.44
CC3/TZVP results ^c				
Count ^b	71	71	71	71
Mean	-0.60	-0.48	-0.49	-0.28
Abs. Mean	0.60	0.48	0.60	0.28
Std. Dev.	0.68	0.51	0.76	0.30
Max. (+) dev.	–	–	0.93	0.01
Max. (−) dev.	1.48	0.94	1.81	0.49
Theoretical best estimates ^c				
Count ^b	63	63	63	63
Mean	-0.53	-0.45	-0.55	-0.24
Abs. Mean	0.53	0.45	0.60	0.25
Std. Dev.	0.61	0.49	0.76	0.28
Max. (+) dev.	–	–	0.58	0.19
Max. (−) dev.	1.48	0.93	1.82	0.49

^aData from publications by the Roos group in the 1990s collated and discussed on section 3.2.^bTotal number of states considered.^cSee Section 3.2 for details.

Table 4.3: TD-DFT and DFT/MRCI deviations of oscillator strengths (in length representation) of optically allowed states with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASPT2 results ^a				
Count ^b	109	109	109	109
Mean	-0.096	-0.075	-0.050	-0.003
Abs. Mean	0.112	0.101	0.095	0.078
Std. Dev.	0.200	0.175	0.160	0.141
Max. (+) dev.	0.307	0.375	0.473	0.543
Max. (−) dev.	0.751	0.611	0.496	0.409
MS-CASPT2/TZVP results ^c				
Count ^b	109	109	109	109
Mean	-0.112	-0.092	-0.067	-0.019
Abs. Mean	0.128	0.113	0.096	0.069
Std. Dev.	0.195	0.169	0.146	0.113
Max. (+) dev.	0.309	0.339	0.437	0.522
Max. (−) dev.	0.597	0.471	0.392	0.325
CC2/TZVP results ^c				
Count ^b	109	109	109	109
Mean	-0.054	-0.034	-0.009	0.039
Abs. Mean	0.075	0.055	0.044	0.062
Std. Dev.	0.127	0.098	0.094	0.098
Max. (+) dev.	0.433	0.501	0.599	0.290
Max. (−) dev.	0.396	0.286	0.257	0.242

^aData from publications by the Roos group in the 1990s collated and discussed on section 3.2.^bTotal number of states considered.^cSee Section 3.2.

Table 4.4: TD-DFT and DFT/MRCI deviations of state dipole moments (in D) with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASSCF results ^a				
Count ^b	138	138	138	138
Mean	-0.45	-0.39	-0.28	-0.31
Abs. Mean	0.86	0.77	0.66	0.60
Std. Dev.	1.38	1.25	1.05	1.09
Max. (+) dev.	2.39	2.11	1.96	1.67
Max. (−) dev.	7.11	6.39	4.80	5.86
MS-CASPT2/TZVP results ^c				
Count ^b	138	138	138	138
Mean	-0.17	-0.12	-0.01	-0.04
Abs. Mean	0.75	0.59	0.61	0.58
Std. Dev.	1.12	0.92	0.96	0.92
Max. (+) dev.	3.42	2.80	4.13	3.37
Max. (−) dev.	4.83	4.25	4.23	4.66

^aData from publications by the Roos group in the 1990s collated and discussed on section 3.2.

^bTotal number of states considered.

^cSee Section 3.2.

Chapter 5

Assessment of semiempirical methods

5.1 Initial considerations

Following the same guidelines in the case of the DFT-based methods, the performance of eight semiempirical methods was evaluated against the reference sets discussed in section 3.2. Two different CI approaches were used: The GUGA-CI method with up to quadruple excitations (CI-SDTQ) and a standard active space, similar to the CASSCF/CASPT2 setup, was chosen for MNDO, AM1, PM3, OM1, OM2, and OM3. By contrast, a CI singles treatment was applied for INDO/S and its variant INDO/S2, which have been parameterized at this level against spectroscopic reference data.

5.2 Statistical evaluations

This section summarizes the statistic evaluation of vertical excitation energies and one-electron properties for all semiempirical methods considered. The derived theoretical best estimates (see section 3.3) serve as reference for vertical excitation energies. For oscillator strengths as well as for dipole moments, however, only qualitative comments are made because of the lack of best estimates for these properties.

5.2.1 Vertical excitation energies

Table 5.1 contains statistical results for singlet excited states (separated by classes of compounds based on atom type) against theoretical best estimates (TBEs) as

Table 5.1: Deviations of vertical excitation energies (in eV) for singlet states with respect to theoretical best estimates.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^a	INDO/S2 ^a
CH-containing molecules								
Count ^b	25	25	25	25	25	25	25	25
Mean	-1.68	-1.36	-1.29	-0.27	-0.29	-0.25	-0.20	-0.20
Abs. Mean	1.68	1.36	1.29	0.42	0.41	0.40	0.42	0.42
Std. Dev.	1.89	1.55	1.48	0.52	0.51	0.49	0.47	0.47
Max. (+) dev.	—	—	0.04	0.76	0.66	0.72	0.81	0.81
Max. (−) dev.	3.95	3.30	3.21	1.34	1.22	1.19	0.84	0.84
CHN-containing molecules								
Count ^b	43	43	43	43	43	43	42	42
Mean	-1.11	-1.01	-1.43	-0.27	-0.21	-0.09	-0.34	-0.34
Abs. Mean	1.22	1.13	1.43	0.38	0.45	0.46	0.48	0.48
Std. Dev.	1.41	1.27	1.53	0.49	0.54	0.57	0.63	0.63
Max. (+) dev.	0.69	0.85	—	0.37	1.42	1.76	0.92	0.92
Max. (−) dev.	3.00	2.60	2.58	1.16	1.09	1.08	1.45	1.45
CHO and CNOH-containing molecules								
Count ^b	36	36	36	36	36	36	36	36
Mean	-1.27	-1.09	-1.46	-0.47	-0.55	-0.35	-0.12	0.22
Abs. Mean	1.29	1.14	1.48	0.57	0.62	0.47	0.62	0.61
Std. Dev.	1.44	1.25	1.63	0.64	0.69	0.52	0.88	1.04
Max. (+) dev.	0.18	0.42	0.19	0.56	0.58	0.60	2.79	4.24
Max. (−) dev.	3.04	2.61	2.53	1.19	1.39	1.06	1.37	0.90
All molecules								
Count ^b	104	104	104	104	104	104	103	103
Mean	-1.30	-1.12	-1.40	-0.34	-0.36	-0.22	-0.23	-0.11
Abs. Mean	1.35	1.19	1.41	0.45	0.50	0.45	0.51	0.51
Std. Dev.	1.55	1.34	1.55	0.55	0.59	0.54	0.70	0.77
Max. (+) dev.	0.69	0.85	0.19	0.76	1.42	1.76	2.79	4.24
Max. (−) dev.	3.95	3.30	3.21	1.34	1.39	1.19	1.45	1.45

^aINDO/S (as well as INDO/S2) results performed using ZINDO-MN [138] program.^bTotal number of states considered.

reference data. Generally, the semiempirical Hamiltonians MNDO, AM1 and PM3 yield vertical excitation energies that are systematically lower values than the reference data, with mean absolute deviations (MAD) above 1.0 eV. In the case of the hydrocarbons, the errors are largest for MNDO (MAD of 1.68 eV), while AM1 and PM3 perform slightly better (MAD of 1.36 and 1.29 eV respectively).

The results are much improved for methods with orthogonalization corrections (OM1, OM2, OM3). Overall, MADs around 0.50 eV are found; the computed vertical excitation energies are underestimated roughly by 0.3 eV compared with the best estimates. When classes of compounds are analyzed separately, one finds deviations for oxygen-containing species with OM1 and OM2 that are slight higher, by about 0.1 eV, than in other classes of compounds (MAD of 0.57 and 0.62 eV, respectively). OM3 yields similar MAD values for all classes of compounds (around

0.45 eV).

Overall, INDO/S and the oxygen-reparametrized INDO/S2 variant yield MAD values for singlet excited states comparable with OM2; the computed vertical excitation energies are again slightly underestimated compared with the best estimates (mean deviations of -0.23 and -0.11 eV, respectively). The number of states considered for INDO/S and INDO/S2 is lower than for the other methods because the CIS treatment does not properly describe states with significant double excitation character and many high-lying states – such cases were identified by wavefunction analysis and discarded. The deficiency of INDO/S to reproduce the excitation energies for oxygen-containing molecules [61] is also seen in the present results (MAD of 0.62 eV). However, the claimed improvement of the oxygen-reparametrized INDO/S2 variant of Li *et. al.* [137] is not confirmed.

The statistical results for the triplet states are collected in Table 5.2. Overall, the MAD values resemble those of the singlet states. The mean deviations become more negative for all semiempirical methods but INDO/S (by about 0.2 eV for MNDO/AM1/PM3 and 0.1 eV for OM1/OM2/OM3). If classes of compounds are examined separately, the highest deviations are found either for hydrocarbons (MNDO/AM1/PM3) or for oxygen-containing compounds (all other methods, with MAD values at least 0.1 eV higher than overall). Surprisingly, the MAD value for oxygen-containing molecules is larger for INDO/S2 than its parent INDO/S version (1.02 versus 0.72 eV), contrary to previous claims. [137]

Finally, Figure 5.1 provides a visual summary in the form of a histogram plot for the deviations of the computed vertical excitation energies from the TBE values of all states below 6 eV. On the basis of these histograms and the statistical data presented in this section, it is possible to rank the semiempirical methods investigated here according to their overall performance to describe excitation energies. The OMx methods are clearly the best choice, with minor differences in the performance of the three variants, with a slight edge of OM2 and OM3 over OM1. INDO/S and INDO/S2 also perform reasonably well on average, especially for low-lying states, but show a considerably wider error distribution. Finally, the MNDO, AM1 and PM3 methods that are well established and widely used for ground states are least suitable for electronically excited states in their standard ground-state parametrization.

5.2.2 One-electron properties

The semiempirical results for oscillator strengths and state dipole moments are compared to three sets of reference data, namely published earlier CASSCF/CASPT2 results and the own MS-CASPT2/TZVP and CC2/TZVP results. For oscillator strengths, Figure 5.2 illustrates one of these comparisons, with MS-CASPT2/TZVP results as reference data. Similar patterns are found when other reference data are

Table 5.2: Deviations of vertical excitation energies (in eV) for triplet states with respect to theoretical best estimates.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^a	INDO/S2 ^a
CH-containing molecules								
Count ^b	27	27	27	27	27	27	27	27
Mean	-1.79	-1.51	-1.44	-0.42	-0.37	-0.35	-0.38	-0.38
Abs. Mean	1.92	1.67	1.44	0.45	0.42	0.41	0.57	0.57
Std. Dev.	2.05	1.84	1.55	0.55	0.54	0.52	0.74	0.74
Max. (+) dev.	1.73	2.12	—	0.36	0.55	0.54	0.85	0.85
Max. (−) dev.	3.70	3.90	2.98	1.31	1.21	1.17	1.63	1.63
CHN-containing molecules								
Count ^b	20	20	20	20	20	20	20	20
Mean	-1.24	-1.10	-1.44	-0.39	-0.27	-0.05	-0.43	-0.43
Abs. Mean	1.29	1.16	1.44	0.43	0.44	0.49	0.70	0.70
Std. Dev.	1.50	1.32	1.55	0.56	0.52	0.56	0.92	0.92
Max. (+) dev.	0.54	0.47	—	0.19	0.64	1.08	0.86	0.86
Max. (−) dev.	2.63	2.28	2.43	1.05	0.92	0.87	2.01	2.01
CHO and CNOH-containing molecules								
Count ^b	16	16	16	16	16	16	16	16
Mean	-1.35	-1.07	-1.34	-0.57	-0.53	-0.39	-0.04	0.60
Abs. Mean	1.38	1.15	1.37	0.62	0.60	0.49	0.72	1.02
Std. Dev.	1.54	1.29	1.56	0.73	0.70	0.57	0.96	1.44
Max. (+) dev.	0.14	0.39	0.20	0.41	0.59	0.61	2.49	4.30
Max. (−) dev.	2.63	2.26	2.40	1.04	1.03	0.89	1.54	1.48
All molecules								
Count ^b	63	63	63	63	63	63	63	63
Mean	-1.50	-1.27	-1.41	-0.45	-0.38	-0.26	-0.31	-0.15
Abs. Mean	1.58	1.37	1.42	0.49	0.47	0.45	0.65	0.72
Std. Dev.	1.77	1.56	1.55	0.61	0.58	0.54	0.86	1.01
Max. (+) dev.	1.73	2.12	0.20	0.41	0.64	1.08	2.49	4.30
Max. (−) dev.	3.70	3.90	2.98	1.31	1.21	1.17	2.01	2.01

^aINDO/S (as well as INDO/S2) results performed using ZINDO-MN [138] program.^bTotal number of states considered.

used. An inspection of Figure 5.2 shows that the results scatter over a wide range, the largest deviations being found for high-lying states. The correlation coefficients between the semiempirical and MS-CASPT2/TZVP oscillator strengths are therefore smaller than in the case of the excitation energies, but still distinctive enough to allow a ranking (see Figure 5.2): OM1, OM2, and OM3 fare best (correlation coefficients of 0.9512, 0.9409, and 0.9266) followed by INDO/S and INDO/S2 (0.9280 and 0.9107), while MNDO, AM1, and PM3 show the least satisfactory correlation (0.8177, 0.8643 and 0.8775).

Table 5.3 presents the statistical evaluation of all non-zero state dipole moments in the benchmark set. It is evident that the semiempirical results often differ rather strongly from the *ab initio* data. The performance of OMx (MAD 0.68–0.71 D)

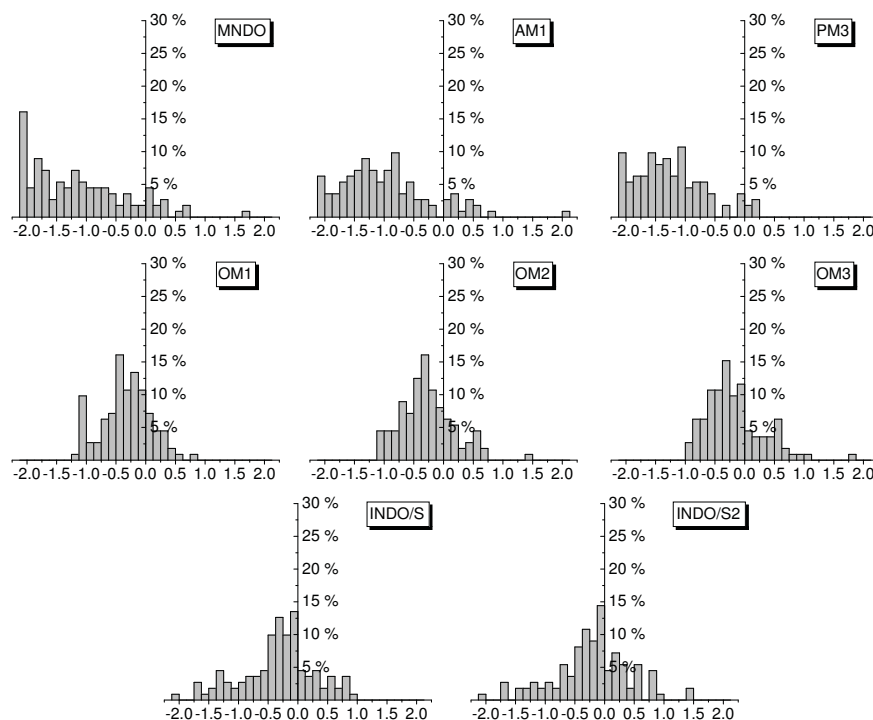


Figure 5.1: Correlation plots of vertical excitation energies for all states with reference values (theoretical best estimates) under 6 eV considered in this study.

and MNDO/AM1/PM3 (MAD 0.66–0.76 D) is similar in this case and better than that of INDO/S and INDO/S2 (MAD 1.08–1.19 D). The overall mean errors suggest that state dipole moments tend to be underestimated by OMx (on average by 0.10–0.23 D) and somewhat more by MNDO/AM1/PM3 (on average by 0.27–0.37 D), while INDO/S and INDO/S2 tend to overestimate them (on average by 0.40–0.49 D). These trends are also apparent from the correlation plots.

Summarizing the statistical evaluations for the oscillator strengths and state dipole moments, the OMx methods show the best overall performance for these one-electron properties, without any pronounced preference for one of the three variants. One should note that the OMx deviations from the *ab initio* reference data are rather similar to what has been found for DFT-based methods, both for oscillator strengths (MAD: TD-B3LYP 0.113, DFT/MRCI 0.069, OMx 0.077–0.094) and for state dipole moments (MAD: TD-B3LYP 0.59 D, DFT/MRCI 0.58 D, OMx 0.68–0.71 D).

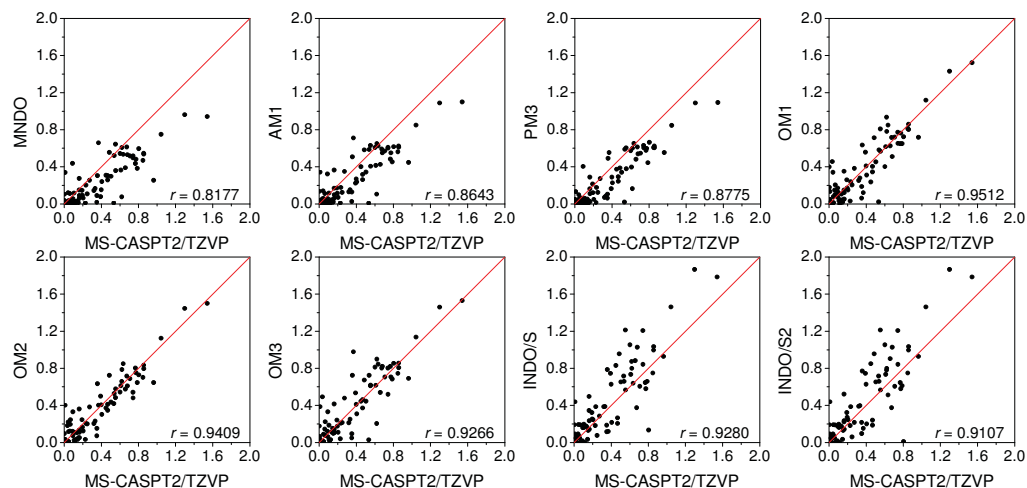


Figure 5.2: Correlation plots of oscillator strengths for all dipole-allowed excited states using MS-CASPT2/TZVP results as reference data.

Table 5.3: Deviations of state dipole moments (in D) for the semiempirical hamiltonians studied with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^a	INDO/S2 ^a
Published CASPT2 results ^b								
Count ^c	142	142	142	142	142	142	104	104
Mean	-0.61	-0.58	-0.51	-0.47	-0.11	-0.34	0.11	0.20
Abs. Mean	0.93	1.03	1.02	0.94	0.86	0.92	1.25	1.35
Std. Dev.	1.44	1.53	1.54	1.44	1.38	1.43	2.16	2.26
Max. (+) dev.	2.37	3.81	2.98	5.22	5.75	5.49	9.73	9.92
Max. (-) dev.	7.17	7.28	7.21	6.58	5.82	6.10	4.92	5.08
MS-CASPT2/TZVP results ^b								
Count ^c	142	142	142	142	142	142	104	104
Mean	-0.37	-0.34	-0.27	-0.23	-0.13	-0.10	0.40	0.49
Abs. Mean	0.66	0.76	0.72	0.68	0.68	0.71	1.08	1.19
Std. Dev.	0.91	1.05	1.00	1.00	1.07	1.07	2.03	2.11
Max. (+) dev.	3.52	3.73	3.98	5.97	5.64	5.38	10.01	9.81
Max. (-) dev.	4.91	4.60	4.91	4.25	4.68	4.37	4.90	4.30

¹Ground state as well as singlet states considered using CM2 model [137].

²See Section 3.2.

³Total number of states considered.

Chapter 6

Improvement of best estimates

6.1 Effect of basis set extension

In chapter 3, CASPT2 and coupled-cluster results have been discussed for vertical excitation energies obtained with the TZVP basis set, which was considered sufficiently flexible for the low-lying valence excited states contained in the benchmark set. However, since the TZVP basis lacks diffuse functions, it is less appropriate for high-lying valence states and for states which are spatially extended and have (partial) Rydberg character. The situation is less clear-cut for coupled cluster methods based on linear response, where valence-Rydberg mixing can not intrinsically be decoupled like in multistate CASPT2. In any event, one may expect a general improvement by an extension of the basis set that offers the flexibility to describe spatially extended valence states.

In the basis set convergence tests on the ethene molecule discussed in section 3.2, the augmented basis set aug-cc-pVTZ yields very small deviations (less than 0.1 eV) compared with the most extended basis. Although this basis set is not the best choice for studying Rydberg states, it should be appropriate for high-lying valence states, where the diffuse character of the basis set plays an important role. In the following, basis set effects are discussed for coupled-cluster and CASPT2 results, together with their implications for the theoretical best estimates of vertical excitation energies.

6.1.1 Coupled-cluster methods

The basis set dependence was investigated for the coupled cluster methods CC2, CCSDR(3) and CC3. For this study, CCSDR(3) and CC3 calculations were carried out using the Dalton 2.0 [140] program, whereas CC2 calculations were done using the resolution-of-identity approximation, [294, 295] as implemented

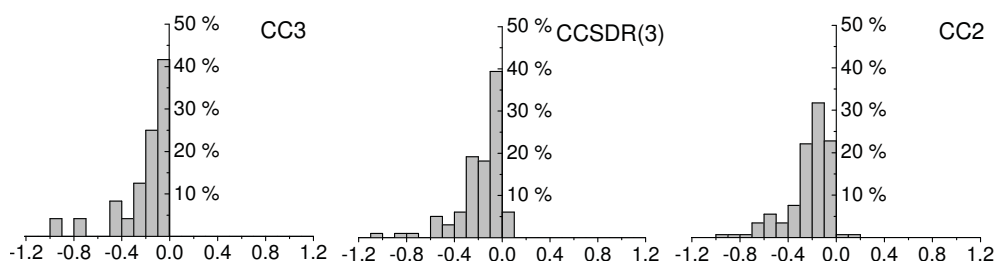


Figure 6.1: Histograms (in %) of the deviations between aug-cc-pVTZ and TZVP vertical excitation energies (eV) of singlet excited states at the CC3, CCSDR(3), and CC2 levels.

in the program RICC2 [19, 296–298] from the TURBOMOLE package (version 5.10). [299]

The results were compared with previously obtained CC/TZVP excitation energies (listed in section 3.2). Due to the high computational demands of CCSDR(3) and particularly CC3, only a subset of the benchmark molecules could be calculated with these methods, yielding results for 22 singlet states with CC3 and 99 singlet states with CCSDR(3). The efficient parallel implementation of the RICC2 method in the TURBOMOLE program allowed the computation of all the 143 singlet excited states from the original benchmark set at the CC2 level. Histograms for the deviations of the aug-cc-pVTZ from the TZVP results are shown in Figure 6.1, and the corresponding statistical data are given in Table 6.1.

Table 6.1: Deviations in excitation energies (eV) of singlet excited states obtained with the aug-cc-pVTZ basis set with respect to TZVP results^a.

	CC2	CC2 ^b	CCSDR(3)	CC3
Count ^c	143	99	99	22
Mean	-0.22	-0.22	-0.18	-0.18
Abs. Mean	0.23	0.22	0.18	0.18
Std. Dev.	0.29	0.28	0.26	0.25
Maximum (+)	1.34	1.34	1.05	0.75

^aTZVP results from Section 3.2.

^bIncluding only the same subset of states as in the CCSDR(3) calculations.

^cTotal number of considered states.

Inspection of the histograms in Figure 6.1 immediately reveals a systematic lowering of the excitation energies when going from the TZVP to the larger aug-cc-pVTZ basis, for each of the three coupled cluster methods. The mean and absolute

Table 6.2: Deviations in the vertical excitation energies (eV) of singlet excited states: CC3/TZVP-based estimates with CC2 and CCSDR(3) basis set corrections vs. CC3/aug-cc-pVTZ results.

	CC3 with CC2 correction ^a	CC3 with CCSDR(3) correction ^b
Count ^c	22	22
Mean	-0.02	0.01
Abs. Mean	0.08	0.02
Std. Dev.	0.15	0.02
Maximum (−)	0.42	0.03
Maximum (+)	0.32	0.04

^aEstimated CC3/aug-cc-pVTZ = CC3/TZVP + CC2/aug-cc-pVTZ − CC2/TZVP.

^bEstimated CC3/aug-cc-pVTZ = CC3/TZVP + CCSDR(3)/aug-cc-pVTZ − CCSDR(3)/TZVP.

^cTotal number of considered states.

mean deviations in Table 6.1 are of essentially the same magnitude (about 0.2 eV) for all three coupled cluster methods. This confirms that the basis set effects are systematic. Looking at the details in Table 6.1, it is possible to note that the basis set dependence is slightly more pronounced for CC2 than for CCSDR(3) and CC3, both for the full set of CC2 results as well as for the subset of states that is shared between CC2 and CCSDR(3). Comparing CCSDR(3) and CC3, the statistical data in Table 6.1 indicate an essentially identical basis set dependence of the computed vertical excitation energies. This suggests an incremental scheme where expensive CC3 calculations that may only be feasible with a smaller basis set (such as TZVP) are augmented with a basis set correction obtained at the cheaper CC2 or CCSDR(3) level.

For the 22 states where CC3/aug-cc-pVTZ results are available, this correction scheme has been tested, with statistical results listed in Table 6.2. For the estimates obtained from the CC3/TZVP results plus the CCSDR(3) correction, the agreement with the CC3/aug-cc-pVTZ results is almost perfect, with negligible mean and absolute mean deviations of 0.01 and 0.02 eV, respectively, and a maximum deviation of only 0.04 eV. The CC2 correction performs not quite so well: The mean and absolute mean deviations are still quite low (-0.02 and 0.08 eV, respectively), but there are outliers for states with a low CC3/TZVP single excitation weight (maximum deviation of -0.42 eV for 2^1A_g of butadiene and 1^1E_{2g} of benzene, % R_1 below 70%).

For the CC2 method we have also computed vertical triplet excitation energies as well as one-electron properties such as oscillator strengths and dipole moments. Statistical evaluations for the differences between the results obtained with the aug-cc-pVTZ and TZVP basis sets are shown in Table 6.3, together with the cor-

Table 6.3: Deviations between the CC2/aug-cc-pVTZ and CC2/TZVP results for the vertical excitation energies (eV) of singlet and triplet excited states and for the oscillator strengths and dipole moments (D) of singlet excited states: Statistics for all 28 benchmark molecules.

	CC2/aug-cc-pVTZ			
	Singlet states	Triplet states	Osc. strength	Dipole moment
Count ^a	143	71	95	128
Mean	-0.22	-0.08	-0.032	-0.12
Abs. Mean	0.23	0.10	0.047	0.57
Std. Dev.	0.29	0.14	0.088	0.97
Maximum (–)	1.34	0.54	0.287	3.51
Correl. coef. ^b	0.9951	0.9977	0.9659	0.8325

^aTotal number of considered states. Some data has been discarded whose assignment was considered unreliable.

^bCorrelation coefficient.

responding results for the singlet states. For the triplet excited states, significantly smaller mean and absolute mean deviations of -0.08 and 0.10 eV are found, confirming the quality of the previous TZVP results and the small basis set dependence of excited triplet states (compared with singlet states). The largest deviation is encountered for the 3^3B_2 state of pyridine (-0.54 eV) which has large contributions of high-lying and doubly excited CSFs (as in the case of the corresponding singlet state).

The situation is less clear-cut for one-electron properties (oscillator strengths and excited state dipole moments), which are often affected in a quite different way by the addition of diffuse and polarization functions. While there is usually a slight decrease in the computed excitation energies, the one-electron properties change more randomly. In this context, it is important to note the distinction in combination rules when diffuse functions are included: Two states which are composed of $+/-$ combinations of CSFs, giving bright/dark states, can evolve into two states with moderate intensity after increasing the basis set – this change in the composition of the CI wavefunctions will necessarily affect the one-electron properties quite strongly. Overall, the extension of the basis from TZVP to aug-cc-pVTZ tends to lower both the oscillator strengths and the dipole moments, see Table 6.3. The correlation coefficients of 0.9659 for the oscillator strengths and 0.8325 for excited-state dipole moments are still reasonably large, but clearly much smaller than those for the vertical excitation energies.

6.1.2 CASPT2 results

In contrast to linear-response methods, basis set extensions in CASSCF/CASPT2 calculations face more difficulties than just the higher computational demand. For instance, the use of a “standard” active space is no longer appropriate in this case, mainly because it often leads to convergence problems in the CASSCF wavefunction as well as low reference weights of the states calculated. Therefore, the active space had to be extended by additional orbitals and optimized for each individual molecule. In the state-averaged (SA) CASSCF reference functions that are used in the subsequent CASPT2 calculations, significantly more states had to be included in the SA procedure when going from the TZVP to the aug-cc-pVTZ basis, because many Rydberg states now appear lower in energy than some high-lying valence states during the CASSCF calculation.

The number of states considered in the CASPT2/aug-cc-pVTZ study is almost the same as in the preceding CASPT2/TZVP work. Despite all technical difficulties, only two high-lying states could not be identified during the SA-CASSCF calculations with the aug-cc-pVTZ basis set ($6^1A'$, Cytosine and $5^3A'$, Imidazole). Generally, the assignment of states was mainly based on the CI wavefunction composition of each root and on the expectation value $\langle r^2 \rangle$.

Histograms of the deviations between CASPT2/aug-cc-pVTZ and CASPT2/TZVP results for all 151 singlet and 70 triplet vertical excitation energies are illustrated in Figure 6.2. An initial visual inspection of these plots indicates a narrow distribution of the deviations with a tendency of a constant shift towards smaller values, since most of the deviations are negative (78 and 80% for singlet and triplet states, respectively). These observations corroborate the statistical results listed in the Table 6.4: The mean deviations are negative, with mean absolute deviations of the same magnitude (about 0.1 eV). It is noteworthy that these deviations are even smaller than those found for the coupled-cluster methods (Section 6.1.1). For the singlet case, the highest deviations occur for the $4^1A'$ state of cytosine (0.80 eV) and the 3^1B_{3u} state of naphthalene (-1.05 eV): both states lie high in energy (above 6.5 eV), and their wavefunctions are highly multiconfigurational and contain large contributions from double excitations. Consequently, the augmented basis set should describe these states better than the TZVP basis set. In the case of triplet states, the largest negative deviation is found for the 3^3A_1 state of pyridine (-1.45 eV) which is also characterized by large contributions from double excitations.

In analogy to the coupled cluster results, the one-electron properties (oscillator strengths and dipole moments) do not change in a systematic manner in the CASPT2 calculations upon basis set extension. The statistical data in Table 6.4 indicate fairly random changes for these properties, with a slight trend to lower values. As already mentioned in the preceding section, these properties are more

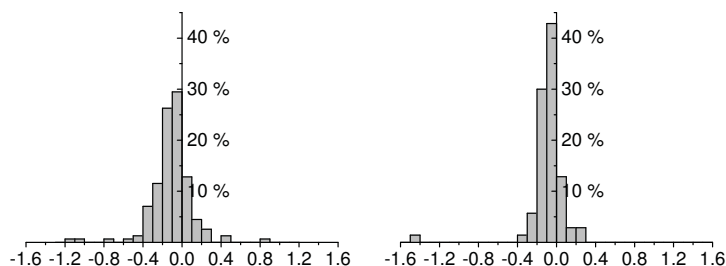


Figure 6.2: Histograms (%) of the deviations between CASPT2/aug-cc-pVTZ and CASPT2/TZVP vertical excitation energies (eV) of singlet (left) and triplet (right) excited states.

strongly affected by the addition of diffuse and polarization functions. For oscillator strengths, the order of magnitude is preserved for most of the states considered, with the largest changes occurring for intense transitions. For dipole moments, the situation is less clear, but similar to what is found in the coupled-cluster CC2 calculations: the mean deviation is close to zero (-0.01 D), but some high-lying states have the dipole moments changed by more than 3 D upon basis set extension (cyclopentadiene 3^1A_1 : +3.97 D; propanamide $2^1A'$: -3.19 D). The correlation coefficient for the dipole moments is reasonably high (0.8871), but still significantly lower than for the vertical excitation energies.

6.2 Theoretical best estimates

In chapter 3, a reference set of theoretical best estimates for vertical excitation energies was presented (called TBE-1 in the following). TBE-1 values were adopted for 104 singlet excited states and 63 triplet excited states. They were taken, when available, from published highly correlated *ab initio* calculations with large basis sets at the multi-reference configuration interaction (MRCI), multi-reference perturbation theory (MRMP), or coupled cluster (CC) level. In the absence of such literature data, own CC3/TZVP as well as CASPT2/TZVP values were used for triplet and singlet states, respectively, following well-defined guidelines (see chapter 3).

An obvious question is whether these theoretical best estimates should be upgraded in view of the new results with the larger aug-cc-pVTZ basis (see sections 6.1.1 and 6.1.2), in order to derive an improved set of reference data (called TBE-2). The previously adopted *ab initio* values from the literature were checked, and

Table 6.4: Deviations between the CASPT2/aug-cc-pVTZ and CASPT2/TZVP results for vertical excitation energies (eV) of singlet and triplet excited states and for the oscillator strengths and dipole moments (D) of singlet excited states: Statistics for all 28 benchmark molecules.

	Singlet states	Triplet states	Osc. strength	Dip. Moment
Count ^a	151	70	106	138
Mean	-0.11	-0.09	-0.039	-0.01
Abs. Mean	0.16	0.12	0.063	0.52
Std. Dev.	0.22	0.21	0.115	0.85
Maximum (+)	0.80	0.23	0.334	3.97
Maximum (−)	1.05	1.45	0.479	3.19
Correl. Coef. ^b	0.9899	0.9899	0.9469	0.8871

^aTotal number of considered states.

^bCorrelation coefficient.

it was found that they can generally be retained. In several cases, the results using with the aug-cc-pVTZ basis are of similar quality and numerically close to the literature values, but in the absence of significant improvements, it seems better to keep the TBE-1 values of these states, for the sake of consistency.

On the other hand, the TBE-1 values taken from the previous CASPT2/TZVP and CC3/TZVP calculations should be replaced by the new results with the aug-cc-pVTZ basis. However, a slight different guideline has been adopted: coupled-cluster results (CC/aug-cc-pVTZ) are now used both for singlet and triplet states, except for states with CC3/TZVP single excitation weights (see section 3.2.1) of less than 80 %, where the MS-CASPT2/aug-cc-pVTZ values are preferred. The main shift is the preference for coupled-cluster over MS-CASPT2 results also for the singlet states. This is motivated by two observations. First, the MS-CASPT2 calculations with the aug-cc-pVTZ basis are less standardized than those with the TZVP basis due to the need to choose individually optimized active spaces and state averaging procedures, and second, it seems difficult to avoid occasional outliers in the MS-CASPT2/aug-cc-pVTZ results when using such molecule-specific procedures. The CC/aug-cc-pVTZ results appear to be more robust in general.

The TBE-1 and TBE-2 values do not differ much, as can be seen from the statistical evaluation in Table 6.5. The mean and mean absolute deviations below 0.1 eV confirm the high quality of the earlier TBE-1 values both for the singlet and triplet states. As expected, they are of the same order as the typical changes in the vertical excitation energies upon basis set extension.

Table 6.5: Deviations in the theoretical best estimates of vertical excitation energies (eV): TBE-1 versus TBE-2.^a

	Singlet states	Triplet states
Count ^b	104	63
Mean	0.00	-0.05
Abs. Mean	0.08	0.06
Std. Dev.	0.12	0.10
Maximum (+)	0.33	0.18
Maximum (−)	0.50	0.36

^aFor the definition of TBE-1 and TBE-2 reference sets, see text.^bTotal number of considered states.

6.3 Assessment of approximate methods

In chapters 4 and 5, statistical evaluations of DFT-based and semiempirical methods were discussed with respect to the first set of theoretical best estimates (TBE-1). For the sake of consistency, an update of these statistical evaluations with respect to the new TBE-2 reference data is presented in Tables 6.6 and 6.7 for the singlet and triplet states, respectively. As anticipated, there are only minor differences between the two sets of statistical data. For the DFT-based methods, independent of the reference set used, DFT/MRCI still fares best, followed by TD-DFT/B3LYP, whereas TD-DFT/BP86 (TD-DFT/BHLYP) yield excitation energies that generally tend to be too low (too high). The semiempirical methods show similar behavior against all three reference sets: the widely applied semiempirical methods MNDO, AM1 and PM3 strongly underestimate the reference excitation energies, the NDDO-based orthogonalization-corrected methods (OM1, OM2, and OM3) give typical errors in the range of 0.41–0.47 eV both for singlet and triplet states, and the INDO/S method, parametrized for spectroscopical purposes, performs reasonably well with typical errors of 0.5 eV for excited singlet and 0.65 eV for triplet states. The correlation coefficients are always similar for both reference sets. Therefore, all the conclusions outlined in the preceding chapters regarding the ranking and performance of the evaluated methods remain valid.

Table 6.6: Deviations of vertical excitation energies (eV) for singlet excited states from DFT and semiempirical methods with respect to theoretical best estimates.

	TD-BP86	TD-B3LYP	TD-BHLYP	DFT/MRCI	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S
TBE-1 reference ^a											
Count ^b	104	104	104	104	104	104	104	104	104	104	103
Mean	-0.44	-0.07	0.43	-0.13	-1.30	-1.12	-1.40	-0.34	-0.36	-0.22	-0.23
Abs. Mean	0.52	0.27	0.50	0.22	1.35	1.19	1.41	0.45	0.50	0.45	0.51
Std. Dev.	0.62	0.33	0.62	0.29	1.55	1.34	1.55	0.55	0.59	0.54	0.70
Max. (+) dev.	0.65	1.02	1.73	0.75	0.69	0.85	0.19	0.76	1.42	1.76	2.79
Max. (-) dev.	1.37	0.75	0.56	0.90	3.95	3.30	3.21	1.34	1.39	1.19	1.45
Correl. coef.	0.9566	0.9716	0.9444	0.9823	0.7850	0.8404	0.8678	0.9456	0.9342	0.9319	0.9145
TBE-2 reference											
Count ^b	104	104	104	104	104	104	104	104	104	104	103
Mean	-0.45	-0.08	0.41	-0.13	-1.31	-1.12	-1.41	-0.34	-0.35	-0.22	-0.23
Abs. Mean	0.53	0.27	0.48	0.20	1.34	1.17	1.41	0.43	0.47	0.41	0.52
Std. Dev.	0.63	0.33	0.60	0.26	1.53	1.32	1.54	0.52	0.55	0.49	0.70
Max. (+) dev.	0.64	0.78	1.57	0.79	0.78	0.71	0.10	0.73	1.28	1.62	2.78
Max. (-) dev.	1.37	0.71	0.40	0.64	3.69	3.04	2.95	1.19	1.33	1.09	1.41
Correl. coef.	0.9583	0.9740	0.9476	0.9862	0.7942	0.8503	0.8748	0.9525	0.9431	0.9420	0.9157

^a Statistical evaluations for DFT-based and semiempirical methods discussed in the sections 4.2 and 5.2, respectively.^b Total number of states considered.

Table 6.7: Deviations of vertical excitation energies (eV) for triplet excited states from DFT and semiempirical methods with respect to theoretical best estimates.

	TD-BP86	TD-B3LYP	TD-BHLYP	DFT/MRCI	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S
TBE-1 reference ^a											
Count ^b	63	63	63	63	63	63	63	63	63	63	63
Mean	-0.53	-0.45	-0.55	-0.24	-1.50	-1.27	-1.41	-0.45	-0.38	-0.26	-0.31
Abs. Mean	0.53	0.45	0.60	0.25	1.55	1.30	1.42	0.49	0.47	0.45	0.65
Std. Dev.	0.61	0.49	0.76	0.28	1.72	1.44	1.55	0.61	0.58	0.54	0.86
Max. (+) dev.	—	—	0.58	0.19	0.55	0.47	0.20	0.41	0.64	1.08	2.49
Max. (−) dev.	1.48	0.93	1.82	0.49	3.66	3.06	2.98	1.31	1.21	1.17	2.01
Correl. coef.	0.9697	0.9880	0.9394	0.9942	0.7639	0.8346	0.8801	0.9505	0.9425	0.9246	0.8442
TBE-2 reference											
Count ^b	63	63	63	63	63	63	63	63	63	63	63
Mean	-0.48	-0.40	-0.50	-0.19	-1.47	-1.22	-1.37	-0.40	-0.33	-0.22	-0.26
Abs. Mean	0.48	0.40	0.57	0.20	1.50	1.26	1.38	0.47	0.46	0.44	0.64
Std. Dev.	0.55	0.44	0.74	0.23	1.67	1.40	1.50	0.57	0.55	0.52	0.84
Max. (+) dev.	—	—	0.59	0.19	0.56	0.49	0.21	0.42	0.67	1.23	2.45
Max. (−) dev.	1.12	0.83	1.85	0.57	3.66	3.06	2.98	1.31	1.21	1.17	1.97
Correl. coef.	0.9738	0.9888	0.9341	0.9945	0.7563	0.8283	0.8709	0.9438	0.9365	0.9193	0.8440

^aStatistical evaluations for DFT-based and semiempirical methods discussed in the sections 4.2 and 5.2, respectively.

^bTotal number of states considered.

Chapter 7

QM/MM study of LOV domains

7.1 Structurally modified flavines

This chapter summarizes the results of a quantum mechanics / molecular mechanics (QM/MM) study of two modified flavines, 1DFMN and 5DFMN, incorporated into the LOV domain of the YtvA protein. The QM/MM calculations address the mechanism of the photophysical and photochemical processes that occur in and around these chromophores after blue-light irradiation. They provide information on the structures and the spectra of intermediates, the reaction reaction pathways on the excited singlet and triplet surfaces, and the radiationless relaxation to the ground state. The QM/MM results are discussed with reference to recent experimental results.

Starting from the X-ray structure of the FMN-containing YtvA protein [300] (PDB: 2PR5, A), preparatory QM(SCC-DFTB)/MM(CHARMM) molecular dynamics (MD) simulations were carried out using the CHARMM (version 31b1) program. The initial coordinates from FMN served as template for building the artificial chromophores in the binding pocket of the protein. The MD runs were preceded by a standard protocol of adding the missing hydrogen atoms and solvating the protein in a 35 Å water sphere. Random snapshots were selected from the MD production run as starting points for subsequent further QM(DFT)/MM geometry optimizations. For this purpose, the Chemshell [301] package was used, with optimizations carried out in hybrid delocalized internal coordinates (HDLC) by the HDLC optimizer. [302] The MM part was always represented by the CHARMM22 force field using the DL_POLY driver as implemented in ChemShell. In the ground-state optimizations with the TURBOMOLE (version 5.9.1) program, [109, 303] the QM region was described by the B3LYP [110, 112, 113] functional and the TZVP basis set. [238] In the excited-state optimizations of singlet (S_1) states, time-dependent density functional theory (TD-

DFT) [23, 117–119] was applied at the same level (B3LYP/TZVP) making use of the analytical gradient code in TURBOMOLE. For the T_1 state, unrestricted DFT (UB3LYP/TZVP) was used due to triplet instabilities in the TD-DFT approach. An electrostatic embedding scheme was adopted and no cutoffs were imposed for the nonbonding QM/MM interactions. Hydrogen link atoms were used at the QM/MM boundary with the charge shift model.

After visual inspection of the binding pocket of the YtvA LOV protein with the incorporated artificial chromophore, the QM region was defined (38 atoms), consisting of the isoalloxazine ring (cut at the ribityl chain, see Figure 1.2) and the side chain of CYS62 residue. To obtain detailed information on the mechanism of adduct formation, reaction paths on the excited-state PES were investigated through QM/MM restrained geometry optimizations along suitably defined reaction coordinates. For a more accurate evaluation of energies of ground and excited states, the DFT-based multireference configuration interaction (DFT/MRCI) method [34] was used as QM component at optimized QM/MM geometries.

In the following, the spectroscopy and photophysics of the 1DFMN and 5DFMN chromophores bound noncovalently to the YtvA-LOV domain are discussed separately.

7.2 1DFMN-YtvA-LOV

The photocycle of the 1-deaza-1-carba-FMN chromophore in the YtvA-LOV domain is summarized on the left side of Figure 7.1. In the protein environment, the vertical excitation energies of 1DFMN show a strong red-shift with respect to the parent FMN compound. The excitation wavelength to the first bright singlet excited state lies at 475 nm according to DFT/MRCI calculations (2.61 eV, average over four optimized snapshots), in reasonable agreement with the experimental maximum (505 nm). This transition corresponds to a HOMO $\rightarrow$ LUMO excitation, involving two orbitals of π character that are localized at the flavin moiety. Only one triplet state is found energetically below the first singlet excited state, with a mean excitation wavelength of 650 nm and the same $\pi \rightarrow \pi^*$ character.

Excited-state geometry optimization of the S_1 state lengthens the bonds in rings II and III of the isoalloxazine core and leads to an energy lowering of about 0.5 eV (10.7 kcal/mol). At the optimized S_1 geometry, an emission wavelength of 630 nm (1.97 eV) is computed, with a large oscillator strength (0.16). For this system, triplet formation is not seen experimentally. The QM/MM calculations indicate that an intersystem singlet-triplet crossing is unlikely because of large energy gaps: at its minimum geometry, the S_1 state lies 0.74 eV above the T_1 state and 0.49 eV below the T_2 state.

Starting from the S_1 minimum structure, QM(TD-B3LYP)/MM restrained geome-

try optimizations on the S_1 surface were carried out to trace the hydrogen transfer from the thiol group of CYS62 residue to the N5 atom of flavin, followed by DFT/MRCI single-point energy evaluations. This hydrogen transfer is facilitated by the increased proton affinity of N5 in the excited state. [93] An energy barrier of 11 kcal/mol could be estimated from these calculations, via a transition state characterized by the migrant hydrogen atom being equidistant to N5 and sulfur of CYS62 (1.50 Å). Electronically, this transition state is a biradical with one electron localized at the sulfur atom of CYS62 and a second one mainly localized at the flavin atoms N5 and C4a. Further optimization along the hydrogen transfer pathway leads to a S_1/S_0 conical intersection, with the migrating hydrogen atom already roughly in the flavin plane and almost bound to the N5 atom (1.12 Å distance), as illustrated on the right side of Figure 7.1. Energetically, this conical intersection lies 18.0 kcal/mol below the S_1 minimum and, as expected, ground-state QM/MM geometry optimization of this structure leads to dark state recovery. The internal conversion mechanism outlined above offers a tentative explanation for the very short fluorescence lifetime of 1DFMN in the YtvA-LOV domain. As a cautionary comment, one should point out, however, that the calculated barrier on the S_1 surface seems quite high for a very fast internal conversion process in the ps range. To further support the feasibility of such a mechanism, one should perform higher-level calculations to check the computed barrier height as well as dynamical simulations starting from the Franck-Condon region to see whether the conical intersection on the hydrogen transfer path is dynamically accessible.

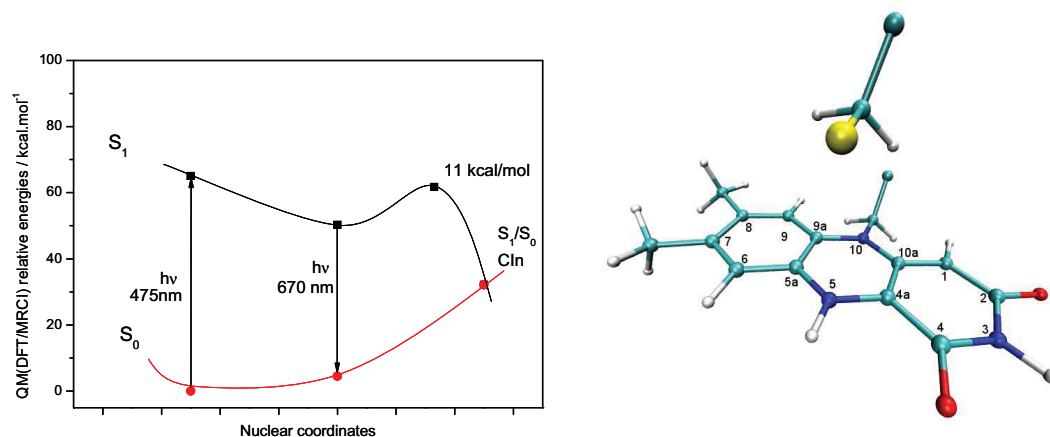


Figure 7.1: Schematic representation of 1DFMN-YtvA-LOV photophysics (left), with details on the geometry of S_1/S_0 conical intersection (right). Only atoms included in the QM region are shown.

7.3 5DFMN-YtvA-LOV

The initial MD simulations indicate that the substitution of the N5 atom by a CH group directly affects the structure of the binding pocket. Contrary to the case of the 1DFMN-YtvA-LOV, this system undergoes a photocycle with photoadduct formation. Figure 7.2 provides a schematic view of the complete photocycle and shows the reaction intermediates and the photoadduct. Also given are the QM(DFT/MRCI)/MM relative energies (in kcal/mol) and the vertical excitation wavelengths averaged over three snapshots. In the following, we discuss every step of this mechanism in more detail.

Vertical excitation energies were first computed for the dark state structure. The first two singlet excited states at 396 and 329 nm have large oscillator strengths. They are characterized by $\pi \rightarrow \pi^*$ excitations localized on the flavin ring, with some charge-transfer contribution (from CYS62 to flavin) in the second transition. The first two triplet states are both computed to lie energetically below the S_1 state (excitation wavelengths of 473 and 422 nm, respectively), and are also characterized by $\pi \rightarrow \pi^*$ excitations.

Population of the S_1 state leads to a slight geometry relaxation, with some lengthening of the bonds in the pterin moiety of the isoalloxazine core. Fluorescence from the S_1 minima yields emission wavelengths in the range of 430–460 nm, and the calculated oscillator strengths of 0.1–0.2 translate into fluorescence lifetimes in the range of 10–90 ns. Along the S_1 relaxation pathway (between the Franck-Condon point and the minimum) there is an energetically accessible crossing between S_1 and T_2 . At the S_1 minimum geometry, the energy gap between these two states is only 0.05 eV, which readily allows for an intersystem crossing to the T_2 state. According to Kasha's rule, there will be a very fast internal conversion $T_2 \rightarrow T_1$. Geometry optimization of the T_1 state yields a structure similar to the S_1 state, as expected, since the wave function of both states is dominated by a singly excited $\pi \rightarrow \pi^*$ configuration. DFT/MRCI vertical triplet-triplet excitations were computed for the T_1 optimized QM(U-B3LYP)/MM geometries. Transitions with moderate intensity (above 0.05) are found in the range of 450–525 nm, resembling the experimental transient spectra (maximum peak at 500 nm). The T_1 minimum lies about 11 kcal/mol lower than the S_1 minimum and 53 kcal/mol above the dark state.

The T_1 species is taken as the starting point for studying the reaction mechanism. In view of the compact binding pocket and the proximity of the thiol group to the flavin, hydrogen transfers from SH(CYS62) either to the C5 or C4a atoms of flavin would seem possible (see figure 7.2). Restrained QM(UB3LYP)/MM geometry optimizations were performed on the T_1 surface, with subsequent DFT/MRCI single-point energy evaluations. The difference of distances $d(S-H) - d(H \cdots C)$ was taken as reaction coordinate (with $C = C5$ or $C4a$). For both reaction path-

ways, a transition state was found, characterized by a pyramidal carbon atom and a H–C bond already partially formed. However, the energy barriers for this process on the T_1 surface differ considerably, depending on which hydrogen acceptor is considered: While the hydrogen transfer to the C5 atom needs to overcome an energy barrier of 16.3 kcal/mol, the barrier for transfer to C4a is 11.4 kcal higher (27.7 kcal/mol). Following the pathway with the lowest barrier, a T_1/S_0 intersystem crossing (ISC1) is found, with concomitant formation of a neutral biradical and an increased charge-transfer character of the T_1 state. Ground-state geometry optimization starting from ISC1 yields an adduct (called adduct 1) with a covalent S–C4a bond and an sp^3 carbon atom C5 that carries two hydrogen atoms. Energetically this adduct lies 28.2 kcal/mol higher than the dark state. By contrast, the alternative pathway that considers hydrogen transfer to the C4a atom yields an adduct (called adduct 2, see Figure 7.2) with a covalent S–C5 bond and hydrogen attached to the C4a position. Energetically this adduct 2 lies 32.3 kcal/mol above the dark state.

It is reasonable to assume that adduct 1 is the major photoproduct based on the magnitude of the energy barriers, although adduct 2 can not conclusively be ruled out. Hence, the photophysics and photochemistry of these two photoproducts were investigated to model the experimentally observed photochemical recovery of the parent state. The main results are summarized in the following.

Vertical photoexcitation into the S_1 state of adduct 1 (with a covalent S–C4a bond) is calculated to occur at 3.60 eV (wavelength: 344 nm). Geometry optimization of this S_1 state leads to S–C4a bond cleavage and formation of neutral biradical, with the S–C4a distance increasing from 1.9 Å in the S_0 ground state to 2.4 Å in the S_1 state. This can be understood from the molecular orbital picture: the transition corresponds to a HOMO→LUMO excitation, with the HOMO (LUMO) orbital having some bonding (antibonding) character along the S–C4a bond. Considering the large spin-orbital matrix elements between the S_1 state and higher triplet states ($S_1-T_3 = 197 \text{ cm}^{-1}$), two pathways can be expected for the S_1 biradical: dark state recovery may occur through hydrogen abstraction or the triplet state is populated via intersystem crossing. Optimization of the T_1 state again yields a biradical species, but with a much larger S–C4a distance (3.57 Å, average value) and an almost planar isoalloxazine moiety (with two C5–H bonds). Energetically, this minimum lies 28 kcal/mol above the S_0 ground state of adduct 1. Dark state recovery can then be achieved by hydrogen abstraction on the T_1 surface, through the same transition state as found for the forward reaction (see Figure 7.2).

Turning to adduct 2 with a covalent S–C5 bond, it is reasonable to assume that it may have been formed in small amounts by the alternative reaction mechanism considered for the T_1 state. Figure 7.3 gives a schematic overview of possible photocycle. One path to be considered is the vertical excitation to the bright S_1 state, with an associated wavelength of 327 nm. Geometry relaxation of the S_1

state yields an expansion of rings I and II and a slight elongation of the S–C5 bond by 0.02 Å (relative to ground-state), but no bond is broken. Considering the proximity of the S_1 minimum and the T_2 state (0.1 eV) as well as the heavy-atom effect, intersystem crossing might take place. Following the same arguments as described for the forward reaction, decay to the T_1 state is expected. Geometry optimization of this state yields a similar structure to S_1 , with minor changes in bond distances and angles, and the S–C5 bond remains intact. Therefore it is hard to believe that a possible hydrogen abstraction from the C4a atom can be the driving force for S–C5 bond breakage. Hence, the flavin remains covalently bound to the protein in each case so that there is no evidence for photochemical dark-state recovery via adduct 2. Instead, there should be fluorescence from the S_1 minimum (average emission wavelength of 443 nm and oscillator strength of 0.213).

Rearrangement of adduct 2 on the ground-state surface could yield another adduct 3 by hydrogen transfer to the N1 atom (adduct 3, see Figure 7.3). It has been suggested on the basis of circular dichroism and ^{13}C NMR measurements that this adduct 3 with the covalent S–C5 bond and a N1–H bond could be the main photoproduct when 5DFMN is incorporated into a LOV domain. [304] Our QM/MM calculations for adduct 3 predict a strong UV vertical excitation to the bright S_1 state at a wavelength of 302 nm. Geometry optimization of this excited state, however, does not lead to a minimum, but reaches a S_1/S_0 conical intersection that is similar to the low-energy conical intersection in 1DFMN-LOV. Hence, there will be a fast internal conversion back to the ground state of the adduct, and consequently the dark state of the parent chromophore will not be recovered easily by photoexcitation of adduct 3. These results argue against the proposed mechanism for the photoreaction that involves adduct 3. [304]

On the basis of this analysis of all possible adducts, it is reasonable to conclude that adduct 1 is the main photoproduct and that the dark state can only be recovered by photoexcitation of this adduct. Other conceivable photoproducts (adduct 2 or 3) do not allow for photochemical dark state recovery.

In summary, these theoretical findings help to explain the available experimental data for these modified flavin chromophores incorporated into the LOV domain of the YtvA protein – the proposed mechanism for the photoinduced processes are consistent with the available experimental evidence.



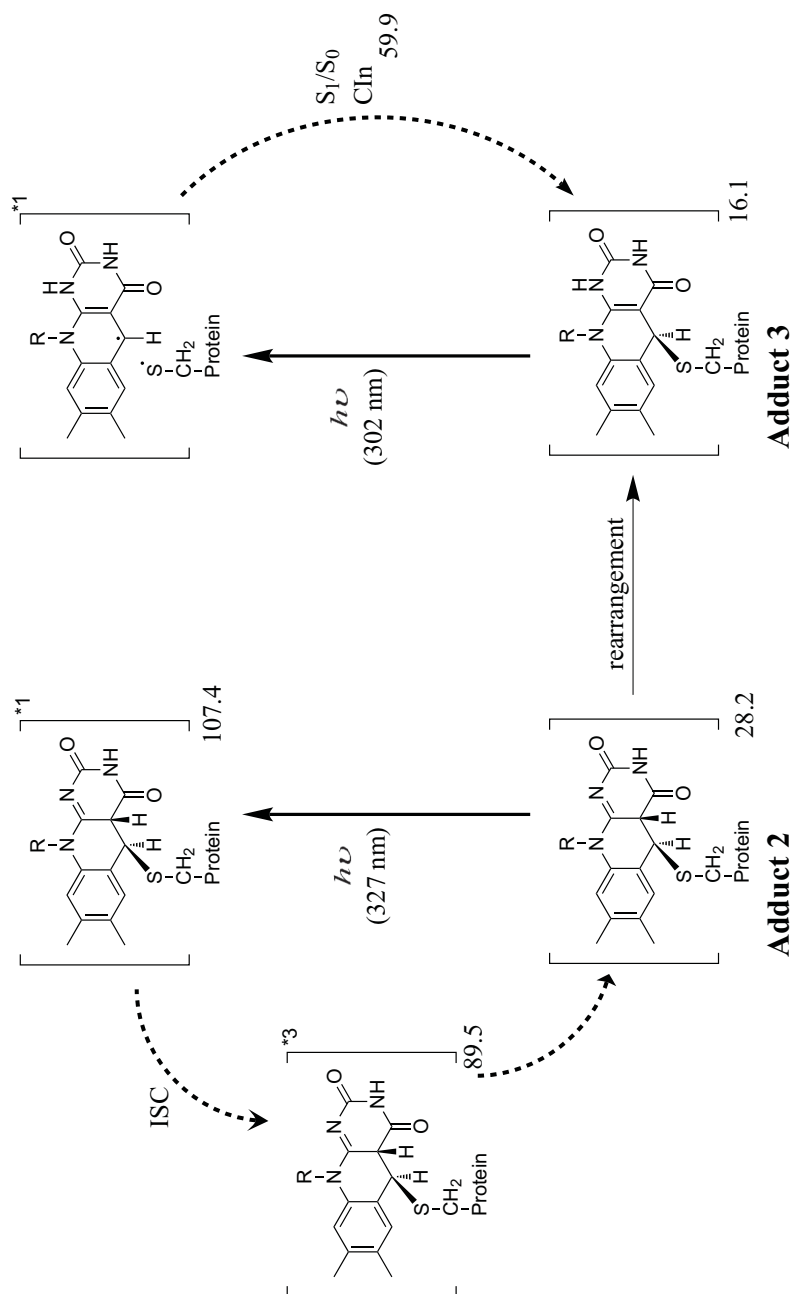


Figure 7.3: Schematic photocycle of adduct 2, a possible side product from blue-light irradiation, with possible intermediates. QM(DFT/MRCI)/MM relative energies are given in kcal/mol (averaged over three snapshots).

Table 7.1: Relative energies of 5-deaza-DFMN-YtvA-LOV calculated at the QM(DFT/MRCI)/CHARMM level of theory for some selected snapshots. Values in kcal/mol.

	snap 3	snap 4	snap 5	Average
S ₀	0.0	0.0	0.0	0.0
S ₁ vertical	73.5	73.0	71.1	72.5
S ₁ minimum	66.1	65.1	59.3	63.5
T ₁ minimum	54.3	54.7	49.2	52.7
T ₁ TS1 / ISC1 ^a			65.5/46.8	
T ₁ TS2 / ISC2 ^a			76.9/51.8	
Adduct1 (S ₀)	32.2/32.2 ^b	31.2/35.7 ^b	21.1/23.4 ^b	28.2/30.4 ^b
Adduct1 (S ₁ vert.)	115.0	113.4	104.8	111.1
Adduct1 (S ₁ min.)	90.0	87.3	78.1	85.1
Adduct1 (T ₁ min.)	60.9	58.6	48.9	56.1
Adduct1 (TS)			65.5	
Adduct2 (S ₀)	46.2/43.6 ^b	29.1/31.6 ^b	21.6/21.1 ^b	32.3/32.1 ^b
Adduct2 (S ₁ vert.)	134.8	118.0	108.3	119.9
Adduct2 (S ₁ min.)	121.6	107.0	98.4	107.4
Adduct2 (T ₁ min.)	106.9	90.5	79.5	89.5
Adduct3 (S ₀)	21.5/38.1 ^b	18.5/29.5 ^b	8.4/0.1 ^b	16.1/22.6 ^b
Adduct3 (S ₁ /S ₀ CIn)	74.3	58.5	49.5	59.9

^aTransition states and intersystem crossing points for the reaction mechanisms illustrated in Figure 7.2.

^bB3LYP/CHARMM values using a larger QM region that includes neighboring residues and three water molecules close to the flavin ring.

Chapter 8

Conclusions

This dissertation addresses two relevant topics in theoretical photochemistry: the benchmarking of theoretical methods for computing electronically excited states and QM/MM investigations of excited-state processes in biomolecules.

Extensive benchmarks of electronically excited states have been carried out for 28 molecules that are representative examples of the most common organic chromophores. In the first step, multistate CASPT2 and coupled cluster (CC2, CCSD and CC3) calculations were performed using a consistent setup (same TZVP basis set, same ground-state MP2 geometries, and standard CASPT2 conventions). The MS-CASPT2/TZVP and CC3/TZVP vertical excitation energies are found to be in very good agreement, with mean absolute deviations of 0.20 eV for the singlet states and 0.08 eV for the triplet states calculated. The performance of the other coupled-cluster methods (CC2, CCSD) against CASPT2 results is also satisfactory, especially when considering only states with single excitation character higher than 90 % (mean absolute deviations for singlet states of 0.22 and 0.37 eV for CC2 and CCSD, respectively). When comparing with previously published CASPT2 results from the Roos group and others, the present MS-CASPT2 vertical excitation energies are typically higher by about 0.2 eV due to the use of the multistate approach with the IPEA shift. A detailed analysis of our own MS-CASPT2 and CC3 results as well as other high-level *ab initio* data collated from the literature allowed us to propose theoretical best estimates (TBE-1) for the vertical excitation energies of 104 singlet and 63 triplet valence excited states. This benchmark set is designed mainly for the following two purposes: the validation of existing theoretical methods through performance analysis and the development of new approximate methods by parametrization against reliable and accurate reference data.

Having defined theoretical best estimates for vertical excitation energies, time-dependent density functional theory (TD-DFT) using three functionals (BP86, B3LYP and BHLYP) as well as a DFT-based multireference configuration in-

teraction method (DFT/MRCI) were evaluated with regard to their performance. Among these methods, DFT/MRCI performs best, giving the lowest mean absolute deviations. Within TD-DFT, B3LYP is clearly superior to BP86 and BHLYP. The computed excitation energies are usually in the order $\text{TD-DFT/BP86} < \text{DFT/MRCI} \approx \text{TD-DFT/B3LYP} < \text{TD-DFT/BHLYP}$, with the systematic trend that TD-DFT/BP86 (TD-DFT/BHLYP) generally underestimates (overestimates) the TBE-1 values. For the triplet states, all studied DFT-based methods tend to give vertical excitation energies that are lower than the theoretical best estimates, with the smallest deviations for DFT/MRCI. It should be emphasized in this context that the reference data set does not include charge transfer or Rydberg states, so that the TD-DFT results do not reflect the well-known qualitative deficiencies of TD-DFT for these types of excitation. However, the reference set does contain some states with double excitation character (like the A_g states of polyenes) which are problematic for TD-DFT and other single-reference approaches.

Furthermore, eight semiempirical methods (MNDO, AM1, PM3, OM1, OM2, OM3, INDO/S, and INDO/S2) were evaluated against the proposed TBE-1 set of theoretical best estimates. In these calculations, electron correlation was treated explicitly by configuration interaction methods (CIS for INDO/S and its variant INDO/S2; GUGA-CISDTQ otherwise), and a standard setup was used (same geometries and analogous active spaces as in the CASPT2/TZVP calculations). The conventional semiempirical methods (MNDO, AM1, PM3) strongly and systematically underestimate the vertical excitation energies, with mean deviations of more than 1.0 eV. The orthogonalization-corrected semiempirical methods (OM1, OM2, OM3) perform well overall, especially for low-lying singlet and triplet states, with deviations only slightly higher than those from TD-DFT/B3LYP; somewhat larger deviations are found in the case of high-lying states and oxygen-containing compounds, which should be targeted in any re-parametrization. Finally, the well-known INDO/S method performs reasonably well for low-lying singlet states, but shows deficiencies for high-lying singlet and triplet states. The oxygen-reparametrized INDO/S2 variant improves the results for low-lying singlet states to some extent, but seems even worse than INDO/S for high-lying singlets and for triplet states and can thus not be recommended because of its unbalanced performance.

The benchmark study was completed by developing a second-generation set of theoretical best estimates (TBE-2) using coupled-cluster and MS-CASPT2 calculations with the augmented correlation-consistent aug-cc-pVTZ basis set. Going from the TZVP to the larger aug-cc-pVTZ basis leads to a systematic lowering of the computed vertical excitation energies, typically by 0.2 eV at the coupled cluster level and by about 0.1 eV at the MS-CASPT2 level. CC3/aug-cc-pVTZ calculations are computationally very demanding and thus often not feasible for larger molecules, but an additive correction scheme allows us to obtain coupled cluster

results close to CC3/aug-cc-pVTZ quality from CC2/aug-cc-pVTZ, CC2/TZVP, and CCSDR(3)/TZVP calculations. An improved set of theoretical best estimates (TBE-2) was generated by incorporating some of the new *ab initio* results obtained with the aug-cc-pVTZ basis. A re-evaluation of DFT-based and semiempirical methods with respect to the TBE-2 values leads to only minor shifts in the statistical data, without any change in the qualitative conclusions and the ranking of the evaluated methods.

In an application of QM/MM methods to electronically excited biomolecules, the photophysical and photochemical properties of 1- and 5-deaza flavin mononucleotide (1DFMN and 5DFMN) were characterized in the LOV domain of the blue-light photoreceptor YtvA from *Bacillus subtilis*.

Experimentally, the protein-incorporated 1DFMN does not show any photochemical activity. According to the QM/MM calculations, photoexcitation of 1DFMN-YtvA populates the bright S_1 state, which after geometry relaxation may decay to the ground state either by fluorescence or by internal conversion through a S_1/S_0 conical intersection with biradical character (18 kcal/mol below the S_1 minimum). On the radiationless deactivation pathway along a hydrogen transfer pathway, the system has to cross a barrier of about 11 kcal/mol (relative to the S_1 minimum). In the absence of dynamical calculations, it is not clear whether the conical intersection can be reached from the Franck-Condon region fast enough to explain the experimental observation of a very short-lived fluorescence peak in 1DFMN-YtvA.

Experimentally, the behavior of 5DFMN-YtvA is less straightforward. This flavin derivative is the first compound identified so far that generates a thermally stable, photochemically reversible photoadduct in a LOV domain. The QM/MM calculations suggest the following mechanism. After photoexcitation to the S_1 state, there is an efficient intersystem crossing near the S_1 minimum to the T_2 state, which quickly relaxes to the T_1 state. On the T_1 surface, a hydrogen atom can be transferred from the CYS62 thiol group to the C5 atom of the flavin, via a biradicaloid transition state with a barrier of 16 kcal/mol, and the thus formed biradical can undergo another intersystem crossing to the ground state which triggers the barrierless formation of a photoadduct with a covalent S-C4a bond. The photochemical dark state recovery proceeds by photoexcitation of this adduct which causes immediate formation of a S_1 biradical with an essentially broken S-C4a bond, followed by intersystem crossing to the triplet state, from which the dark state can be regenerated. Alternative photoadducts with a S-C5 bond are more difficult to generate and lack easily accessible paths for the photochemically induced dark state recovery. The mechanistic scenario derived from the QM/MM calculations on 5DFMN-YtvA is consistent with the experimental findings provided that the reactions involve a photoadduct with a covalent S-C4a bond.

Chapter 9

Outlook

Considering the benchmark part of this work, it is obvious that the proposed set of theoretical best estimates for vertical excitation energies can be further improved. This can be done by extending the reference data base through addition of further reference molecules and by providing more accurate reference energies through higher-level calculations. Furthermore, it is highly desirable to generate theoretical best estimates also for other excited-state properties such as oscillator strengths and dipole moments, which will require careful convergence studies for these properties.

Concerning the evaluation of approximate methods, this work motivates further systematic investigations of DFT/MRCI performance, especially for cases such as charge-transfer and Rydberg transitions where standard TD-DFT approaches are known to fail. The insights gained in the evaluation of the semiempirical methods should help to set up strategies for their improvement, in particular in the case of the orthogonalization-corrected methods (OM1, OM2, OM3). The proposed theoretical best estimates can be used as excited-state reference data in future reparametrizations, particularly for oxygen-containing compounds which show somewhat larger deviations.

Finally, considering the QM/MM study of LOV domains, excited-state dynamics simulations for the 1DFMN-YtvA system would be desirable to see whether the proposed radiationless deactivation pathway is dynamically accessible. The QM/MM calculation of additional spectroscopic parameters for intermediates in the proposed photocycle of 5DFMN-YtvA could guide experimentalists in attempts to detect these species, for example by vibrational or NMR spectroscopy.

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Chapter 10

Appendix

Paper I

*Benchmarks for electronically excited states:
CASPT2, CC2, CCSD, and CC3*

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Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3

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A benchmark set of 28 medium-sized organic molecules is assembled that covers the most important classes of chromophores including polyenes and other unsaturated aliphatic compounds, aromatic hydrocarbons, heterocycles, carbonyl compounds, and nucleobases. Vertical excitation energies and one-electron properties are computed for the valence excited states of these molecules using both multiconfigurational second-order perturbation theory, CASPT2, and a hierarchy of coupled cluster methods, CC2, CCSD, and CC3. The calculations are done at identical geometries (MP2/6-31G*) and with the same basis set (TZVP). In most cases, the CC3 results are very close to the CASPT2 results, whereas there are larger deviations with CC2 and CCSD, especially in singlet excited states that are not dominated by single excitations. Statistical evaluations of the calculated vertical excitation energies for 223 states are presented and discussed in order to assess the relative merits of the applied methods. CC2 reproduces the CC3 reference data for the singlets better than CCSD. On the basis of the current computational results and an extensive survey of the literature, we propose best estimates for the energies of 104 singlet and 63 triplet excited states. © 2008 American Institute of Physics. [DOI: 10.1063/1.2889385]

I. INTRODUCTION

Benchmark sets of molecules with reliable reference data are essential tools for the validation of existing computational methods and for the parameterization of improved approximate methods. For ground-state molecules, such sets are available, for example the G2 and G3 sets^{1–3} which collect a large number of small and medium-sized molecules with accurate experimental thermochemical data. These sets have been used extensively to assess the accuracy of quantum-chemical methods in thermochemistry.^{3–5}

Corresponding representative benchmarks are missing for electronically excited states. Traditionally, the primary target of theoretical work in this area has been the calculation of vertical excitation energies and oscillator strengths to predict the electronic spectra, both for small molecules and for medium-sized chromophores that are important in organic photochemistry. It is hard and often even impossible to obtain reliable and accurate experimental reference data for these target properties, due to various well-known reasons: the observed band maxima do not exactly match the vertical excitation energies, bands are often found to overlap, spectral assignments may be uncertain, and spectra may be available only in solution and not in the gas phase. These problems are most pronounced for larger chromophores which are often most interesting with regard to photochemistry.

Given this situation, one may turn to high-level *ab initio* theory and generate the required reference data computationally. During the past two decades, CASPT2 (complete-active-space second-order perturbation theory^{6–8}) has emerged as the standard *ab initio* method for calculating

excited-state properties of our target molecules, and many such CASPT2 data are available in the literature. As an alternative, there are methods based on CC (coupled cluster) theory such as CC2, CCSD, CC3, and CCSDT^{9–16} which have been proposed more recently and have thus been applied less extensively than CASPT2. In the literature, there is some debate about the relative merits of CASPT2 and CC-based methods, but a balanced assessment is difficult because of technical differences in the published work.

In the present article, we define a benchmark set of 28 medium-sized organic molecules and compute the properties of their valence excited states (with emphasis on vertical excitation energies) using CASPT2, CC2, CCSD, and CC3 at a uniform level (same geometries, same basis set, standard CASPT2 conventions). This allows us to check the consistency of the results from these methods and their performance for different types of excited states. Based on the insight gained in this manner, we derive reference data for an excited-state benchmark set. In this endeavor, we use our own current results as well as published data from other high-level *ab initio* calculations.

II. BENCHMARK MOLECULES

The selected benchmark set of 28 organic molecules comprises unsaturated aliphatic hydrocarbons (including polyenes and cyclic compounds), aromatic hydrocarbons and heterocycles, carbonyl compounds, and nucleobases (see Fig. 1). It is intended to cover the most important chromophores in organic photochemistry. The ground-state geometries of these molecules were optimized at the MP2 level (Møller-Plesset second-order perturbation theory with the 6-31G* basis¹⁷) using the GAUSSIAN program package.¹⁸ The highest

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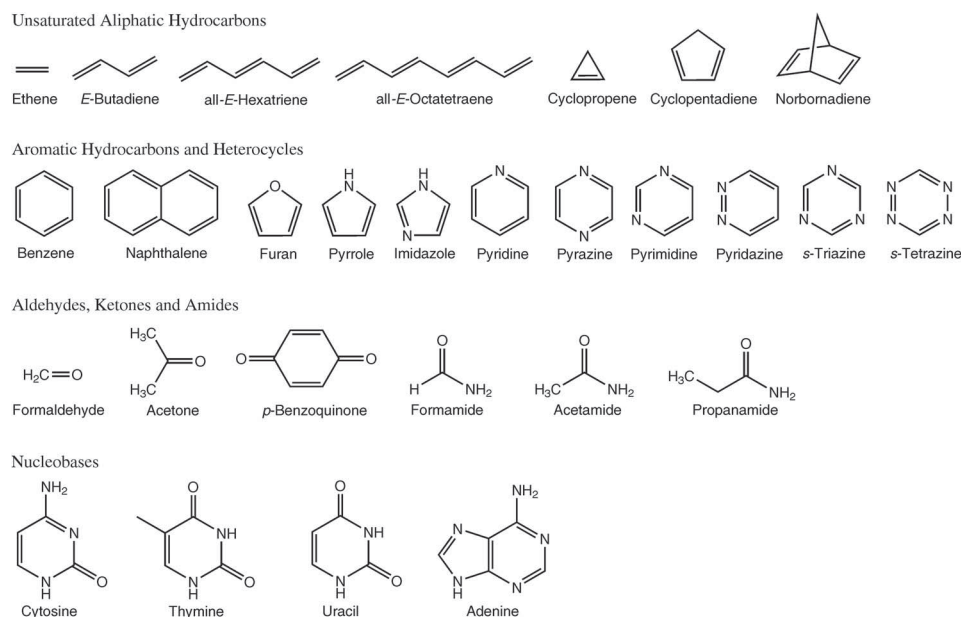


FIG. 1. Benchmark set of molecules considered in this study.

possible point group symmetry was imposed during the optimization (as specified below). The optimized geometries are deposited in the Supporting Information.²⁸⁷ All computational results in this article refer to these geometries. The states of interest were chosen individually for each benchmark molecule (see below).

III. COMPUTATIONAL METHODS

A. General considerations

As already stated, our goal is to treat the valence excited states of all benchmark molecules at a uniform level, and hence with the same standard basis set. Obviously, this requires a compromise between accuracy and cost. We consider basis sets of at least polarized triple-zeta quality as being necessary in terms of accuracy. Such basis sets are affordable for all of the chosen benchmark molecules in the case of CASPT2, CC2, and CCSD, and for most of them in the case of CC3. Among these methods, CC3 is by far the most expensive, and its inclusion prevents the general use of larger basis sets in this study. We have therefore selected the TZVP basis set¹⁹ as our standard in this work. All calculations were done with this basis unless noted otherwise.

It should be emphasized that the TZVP basis set does not contain diffuse functions. It will thus be insufficient for those excited states that are spatially extended and have (partial) Rydberg character. Our main interest is in the low-lying valence excited states with a compact electron density where the TZVP basis should be adequate. However, we shall also consider a number of higher-lying states where basis set deficiencies must be taken into account and need to be discussed specifically.

To illustrate these issues we address the basis set dependence of the computed vertical excitation energies for the $\pi \rightarrow \pi^*$ transitions in ethene. The CASPT2, CCSD, and CC3 results obtained with the TZVP basis and 12 different correlation-consistent basis sets^{20,21} (up to augmented polarized quintuple-zeta) are plotted in Fig. 2. The triplet case

(lower panel, 1^3B_{1u} state) is typical of low-lying valence states that are dominated by a single excitation: the basis set dependence is very minor, with variations of less than 0.1 eV, and the TZVP basis gives sufficiently accurate results, especially for CCSD and CC3. The situation is quite different for the high-lying singlet state (top panel, 1^1B_{1u}) which is known to be rather diffuse and susceptible to valence-Rydberg mixing: extending the basis in the cc-pVXZ series ($X=D,T,Q,5$) significantly lowers the excitation energy (by about 0.6 eV), and the TZVP result is much too high (by more than 0.4 eV). Augmented basis sets with added diffuse functions are of course more appropriate for this singlet state, as can be seen from the fast convergence of the computed excitation energies in the aug-cc-pVXZ series. One further methodological aspect is noteworthy in this context (see Fig. 2, top panel): when using extended basis sets, e.g., in the aug-cc-pVXZ series, the single-state (SS) CASPT2 treatment with a (2,2) active space overestimates

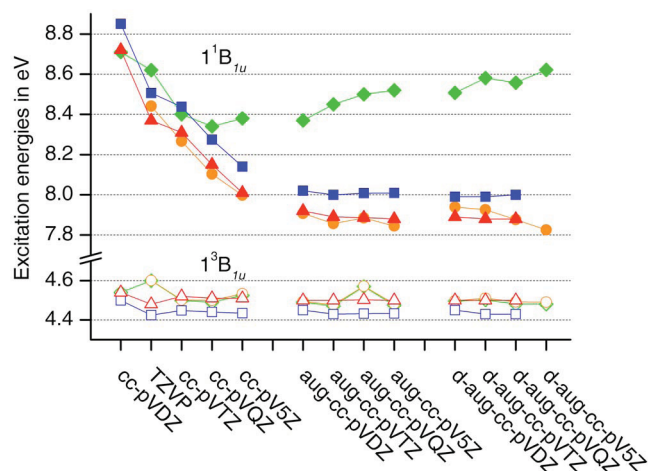


FIG. 2. (Color online) Basis set dependence of the 1^1B_{1u} (filled symbols, top) and the 1^3B_{1u} (open symbols, bottom) state of ethene with different methods: CCSD (squares, blue), CC3 (triangles, red), CASPT2 with 2,2 (diamonds, green) and 8,20 (circles, orange) active space.

the excitation energy to the 1^1B_{1u} state considerably (by more than 0.5 eV) compared to the CC3 method or a multi-state (MS) CASPT2 treatment²² with a (8,20) active space. This is in line with previous experience²³ that SS-CASPT2 tends to exaggerate valence-Rydberg mixing in such situations which is corrected by MS-CASPT2.²² The CC-based methods do not suffer from such problems.¹¹

CC3 excitation energies have previously been calculated for many of our benchmark molecules, mostly with larger basis sets than in the present study.^{11,14,24–35} Compared with these results, the TZVP basis set gives CC3 excitation energies which are normally slightly too large, by 0.02–0.15 eV, with a few exceptional cases where the deviations range up to 0.3 eV. Such deviations are probably at least partly due to differences in the chosen geometries. It should be stressed, however, that the deviations between the results of the various correlated methods are much less affected by the differences in basis set and geometry. For example, the triples corrections, i.e., the differences between the CC3 and CCSD results, obtained in the present study deviate by only a few hundredths of eV from the literature values.

B. CASPT2 calculations

Our benchmark set covers $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $\sigma \rightarrow \pi^*$ excitations. The active space for the calculation of the CASSCF (complete-active-space self-consistent-field) reference function^{36,37} of any given molecule generally included all π and π^* orbitals as well as any n and σ orbitals involved. The number of active electrons was the total number of π electrons plus two electrons for each n and σ orbital included. This type of active space represents the smallest reasonable choice and will be denoted as “standard.” Extensions of this active space were tested for each individual molecule to assess the effect of more variational freedom in the reference function and, if necessary, to handle intruder states. The CASSCF reference functions were then determined using state averaging (SA) with equal weights for all desired states of a given symmetry. In case of artificial configurational mixing, additional states were considered in the SA procedure to overcome this problem. The resulting CASSCF reference functions were used in the subsequent MS-CASPT2 perturbation treatment.^{6,7,22} The occurrence of intruder states was checked by inspecting the weight of the reference function in the perturbation treatment, and if necessary, a level shift was applied to avoid intruder state problems.^{38,39} The reported CASPT2 excitation energies are based on the MS-CASPT2 excited-state energies. For transitions from the singlet ground state (S_0) to singlets of the same symmetry, the excitation energies refer to the MS-CASPT2 ground-state energy, otherwise to the separately computed SS-CASPT2 ground-state energy. Electric transition dipole moments were calculated from the perturbatively modified wave functions and combined with the MS-CASPT2 energies to obtain the oscillator strengths.^{40,41}

This standard CASPT2 procedure was applied to all benchmark molecules. As indicated above, it may become necessary in some cases to deviate from the standard procedure (e.g., with regard to the definition of the active space,

the number of states included in the SA procedure, or the handling of intruder states). Such deviations will be discussed individually.

CASPT2 results have been published previously for all our benchmark molecules (mostly by the Roos group in the 1990s). Apart from obvious differences in the chosen setup (e.g., concerning geometries and basis sets) there are two important conceptual differences: (a) Our excitation energies refer to MS-CASPT2 energies rather than SS-CASPT2 energies as in the previous work (which was mostly published before the introduction of the MS-CASPT2 approach²² in 1998). The MS-CASPT2 treatment has the advantage that it avoids an exaggerated mixing of valence and Rydberg states, and also of nearly degenerate covalent and ionic states. Hence it often improves the description of higher-lying excited states compared with SS-CASPT2. (b) Our calculations employ the recommended default option in the current MOLCAS code⁴² to include the so-called IPEA shift.⁴³ This empirical parameter has been introduced to compensate for systematic errors in CASPT2 ionization potentials (IP) and electron affinities (EA). Its application typically increases the computed CASPT2 excitation energies by about 0.1–0.3 eV and corrects for the known tendency of CASPT2 to slightly underestimate excitation energies.

The CASPT2 calculations were carried out with the MOLCAS program (version 6.4).⁴²

C. Coupled cluster calculations

In state-specific approaches such as CASPT2 excitation energies are calculated as the difference between the energies of specific states. Physical insight is necessary in order to identify the excited states and to choose the active spaces properly. In the polarization propagator^{44–47} or response function methods,⁴⁸ on the other hand, the excitation energies are obtained directly as poles of the linear response function, and the transition moments as the corresponding residues, without having to calculate the wave functions and energies of the involved states separately.

Approximate response functions are available for multi-configurational,^{48–50} Møller–Plesset perturbation theory^{51–55} (MPPT) and CC wave functions.^{9–11,13–16,56–60} The CC response approaches are “black box” methods, which are fully specified by the chosen CC model and one-electron basis set, independent of the system to be studied. They provide a hierarchy of methods (CCS, CC2, CCSD, CC3, CCSDT, etc.) where the accuracy is improved in each step due to the increasing completeness of the cluster expansion from singles (S) over singles and doubles (SD) to singles, doubles and triples (SDT), and so forth. The computational effort also increases in each step, because CC2 formally scales as N^5 with the number of orbitals N , CCSD as N^6 , and CC3 as N^7 . The excitation energies and transition moments are calculated in CC response theory by solving the linear response eigenvalue problem,⁶¹ although the optimization of the ground-state energy requires the solution of a non-linear set of equations. This is in contrast to the nonlinear optimization of all required states in the state-specific approaches such as CASPT2.

CC2 (Refs. 10 and 13) is an approximation to CCSD in the sense that the doubles equations for the nonlinear ground-state amplitudes and for the linear response are approximated by the first-order terms only, whereas the singles equations are kept unchanged. The singles excitation operator T_1 is treated as zeroth order, since the response of the singles excitations to an external one-electron perturbation, such as electromagnetic radiation, is of zeroth order. Furthermore, this provides an approximate description of orbital relaxation to electron correlation and the external perturbation. The equations for the ground-state doubles amplitudes in CC2 are almost equal to the MP2 expressions, except that the two-electron integrals are transformed with T_1 . Hence, the pure double-double excitation block of the CC2 Jacobian is of only zeroth order, i.e., it is diagonal and consists of only orbital energy differences. Singles dominated excitations are thus correct through second order in CC2, whereas pure double excitations are only correct to zeroth order.

The excitation energies obtained in CCSD linear response theory^{9,14,56,59,62} are identical to those obtained from the equation-of-motion coupled cluster approach (EOM-CCSD).⁶³ Singles dominated excitations are still only correct through second order in CCSD but doubles dominated excitations are now correct to first order.

CC3 (Refs. 11, 12, and 16) is an approximation to CCSDT,¹⁶ in a similar manner as CC2 is an approximation to CCSD. The triples equations in CC3 are approximated by the second-order terms under the condition that the singles excitations are treated again as zeroth order, whereas the CCSDT singles and doubles equations are kept unchanged. Singles (doubles) dominated excitations are now correct to third (second) order. Finally, in CCSDT linear response theory, which again gives identical excitations as the corresponding EOM-CCSDT method, singles (doubles) dominated excitation energies are correct to fourth (third) order.

CC response theory methods are expected to give excitation energies of high accuracy for systems where the ground state is well described by a single determinant and the excited states are dominated by single excitations (weight of 90% or more). Multireference systems where the ground state consists of several determinants with large weights are not suitable for CC methods and need to be described by multiconfigurational methods. On the other hand, excited states which consist of several determinants with large weights pose no problem as long as they are dominated by single excitations.

According to benchmark calculations on small molecules with comparison to full CI results,^{11,16,28,62,64–69} the mean absolute (maximum) errors for singles dominated singlet excitations are around 0.46(1.08) eV at the CC2 level, 0.12(0.23) eV at the CCSD level, 0.016(0.047) eV at the CC3 level, and 0.029(0.083) eV at the CCSDT level. For the singles dominated triplet excitation energies, the corresponding errors are 0.40(0.69) eV at the CC2 level, 0.12(0.26) eV at the CCSD level, 0.016(0.071) eV at the CC3 level, and 0.025(0.050) eV at the CCSDT level. For both type of excitations the error is reduced by about a factor of 3 with each step up to CC3, but CC3 and CCSDT perform more or less equally on average, i.e., no further improvement is obtained

at the CCSDT level (due to fortuitous error cancellation in CC3). Singlet and triplet excitation energies are computed with similar accuracy if single excitations contribute with similar weight to the excited state. However, single excitations normally dominate more in triplet than in singlet excited states, and therefore triplet excitation energies tend to be better described by CC response theory methods than singlet excitation energies. For doubles dominated excitations, the errors relative to the full CI results can be as large as 1–2 eV for CCSD and 0.3–0.8 eV for CC3. Since the coupled cluster response theory methods are size extensive and general (i.e., without special adaptation to the particular system under study), the errors should not depend on system size.

All CC linear response calculations were carried out with the DALTON 2.0 program package.⁷⁰

IV. RESULTS AND DISCUSSION

The results of our CASPT2, CC2, CCSD, and CC3 calculations are documented in the Supporting Information (Tables VIII–XXXVII). There is one table for each benchmark molecule which contains, for each state considered, the computed vertical excitation energy, oscillator strength, dipole moment, and expectation value of $\langle z^2 \rangle$ as a measure of its spatial extent with respect to a suitable Cartesian coordinate z . Experimental data (Refs. 71–158) and previous CASPT2 results from the literature (Refs. 22, 23, and 159–175) are also given with the corresponding references. The footnotes in Tables VIII–XXXVII specify computational details of our CASPT2 calculations, especially in cases where nonstandard options have been used.

A. Vertical excitation energies of the benchmark molecules

In the following, we first address the singlet and triplet excitation energies of our benchmark set which are collected in Tables I and II, respectively. These tables contain previous CASPT2 results from the Roos group,^{22,23,159–175} the current CASPT2, CC2, CCSD, and CC3 results with the TZVP basis, and a best estimate based on our current calculations and a survey of literature data. The latter are summarized in the Supporting Information for each benchmark molecule (Tables XXXVIII–LXXI, Refs. 11, 13, 14, 20, 22–24, 26, 27, 29–34, 40, 76, 131, 156, and 159–282).

Looking at the computational result in the first five data columns of Tables I and II, there are some general trends. (a) The excitation energies from the current CASPT2 calculations are often about 0.2 eV higher than the previously published CASPT2 values, consistent with the inclusion of the IPEA shift⁴³ in the present work (see Sec. III B). (b) The deviations between the current and previous CASPT2 results tend to be larger for high-lying excited states. This is expected since our current calculations use the TZVP basis without diffuse functions whereas the previous CASPT2 studies normally included diffuse functions in their basis to account for Rydberg states and valence-Rydberg mixing. The current use of the MS-CASPT2 approach²² is expected to reduce the effects of valence-Rydberg mixing, but the lack of

TABLE I. Vertical singlet excitation energies ΔE (eV) of all statistically evaluated molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (% T_1) ^d	CC3 ^c (% T_1) ^d	Best est. ^e
Ethene	1 $^1B_{1u}$ ($\pi \rightarrow \pi^*$)	7.98	8.62	8.40	8.51(97.2)	8.37(96.9)	7.8
<i>E</i> -Butadiene	1 ^1B_u ($\pi \rightarrow \pi^*$)	6.23	6.47	6.49	6.72(95.5)	6.58(93.7)	6.18
	2 ^1A_g ($\pi \rightarrow \pi^*$)	6.27	6.83	7.63	7.42(85.8)	6.77(72.8)	6.55
all- <i>E</i> -Hexatriene	1 ^1B_u ($\pi \rightarrow \pi^*$)	5.01	5.31	5.41	5.72(95.0)	5.58(92.6)	5.10
	2 ^1A_g ($\pi \rightarrow \pi^*$)	5.20	5.42	6.67	6.61(84.7)	5.72(65.8)	5.09
all- <i>E</i> -Octatetraene	2 ^1A_g ($\pi \rightarrow \pi^*$)	4.38	4.64	5.87	5.99(85.4)	4.97(62.9)	4.47
	1 ^1B_u ($\pi \rightarrow \pi^*$)	4.42	4.70	4.72	5.07(94.7)	4.94(91.9)	4.66
Cyclopropene	1 $^1B_1$ ($\sigma \rightarrow \pi^*$)	6.36	6.76	6.96	6.96(94.5)	6.90(93.0)	6.76
	1 $^1B_2$ ($\pi \rightarrow \pi^*$)	7.45	7.06	7.17	7.24(96.3)	7.10(95.5)	7.06
Cyclopentadiene	1 $^1B_2$ ($\pi \rightarrow \pi^*$)	5.27	5.51	5.69	5.87(95.7)	5.73(94.3)	5.55
	2 $^1A_1$ ($\pi \rightarrow \pi^*$)	6.31	6.31	7.05	7.05(89.4)	6.61(79.3)	6.31
	3 $^1A_1$ ($\pi \rightarrow \pi^*$)	7.89	8.52	8.86	8.95(95.8)	6.69(93.1)	
Norbornadiene	1 $^1A_2$ ($\pi \rightarrow \pi^*$)	5.28	5.34	5.57	5.80(95.3)	5.64(93.4)	5.34
	1 $^1B_2$ ($\pi \rightarrow \pi^*$)	6.20	6.11	6.37	6.69(94.5)	6.49(91.9)	6.11
	2 $^1B_2$ ($\pi \rightarrow \pi^*$)	6.48	7.32	7.65	7.87(95.5)	7.64(93.8)	
	2 $^1A_2$ ($\pi \rightarrow \pi^*$)	7.36	7.44	7.66	7.87(95.0)	7.71(93.0)	
Benzene	1 $^1B_{2u}$ ($\pi \rightarrow \pi^*$)	4.84	5.05	5.27	5.19(95.0)	5.07(85.8)	5.08
	1 $^1B_{1u}$ ($\pi \rightarrow \pi^*$)	6.30	6.45	6.68	6.74(95.6)	6.68(93.6)	6.54
	1 $^1E_{1u}$ ($\pi \rightarrow \pi^*$)	7.03	7.07	7.44	7.65(94.5)	7.45(92.2)	7.13
	2 $^1E_{2g}$ ($\pi \rightarrow \pi^*$)	7.90	8.21	9.03	9.21(84.9)	8.43(65.6)	8.41
Naphthalene	1 $^1B_{3u}$ ($\pi \rightarrow \pi^*$)	4.03	4.24	4.45	4.41(90.5)	4.27(85.2)	4.24
	1 $^1B_{2u}$ ($\pi \rightarrow \pi^*$)	4.56	4.77	4.96	5.21(94.3)	5.03(90.6)	4.77
	2 ^1A_g ($\pi \rightarrow \pi^*$)	5.39	5.90	6.22	6.23(90.1)	5.98(82.2)	5.90
	1 $^1B_{1g}$ ($\pi \rightarrow \pi^*$)	5.53	6.00	6.21	6.53(91.4)	6.07(79.6)	6.00
	2 $^1B_{3u}$ ($\pi \rightarrow \pi^*$)	5.54	6.07	6.25	6.55(93.9)	6.33(90.7)	6.07
	2 $^1B_{1g}$ ($\pi \rightarrow \pi^*$)	5.87	6.48	6.82	6.97(93.8)	6.79(91.3)	6.48
	2 $^1B_{2u}$ ($\pi \rightarrow \pi^*$)	5.93	6.33	6.57	6.77(93.8)	6.57(90.5)	6.33
	3 ^1A_g ($\pi \rightarrow \pi^*$)	6.04	6.71	7.34	7.77(88.4)	6.90(70.0)	6.71
	3 $^1B_{2u}$ ($\pi \rightarrow \pi^*$)	7.16	8.18	8.46	8.77(93.5)	8.44(87.9)	
	3 $^1B_{3u}$ ($\pi \rightarrow \pi^*$)	7.18	7.76	8.85	9.03(84.1)	8.12(53.7)	
Furan	1 $^1B_2$ ($\pi \rightarrow \pi^*$)	6.04	6.43	6.75	6.80(94.9)	6.60(92.6)	6.32
	2 $^1A_1$ ($\pi \rightarrow \pi^*$)	6.16	6.52	6.87	6.89(90.8)	6.62(84.9)	6.57
	3 $^1A_1$ ($\pi \rightarrow \pi^*$)	7.66	8.22	8.78	8.83(94.2)	8.53(90.7)	8.13
Pyrrole	2 $^1A_1$ ($\pi \rightarrow \pi^*$)	5.92	6.31	6.61	6.61(91.2)	6.40(86.0)	6.37
	1 $^1B_2$ ($\pi \rightarrow \pi^*$)	6.00	6.33	6.83	6.87(94.2)	6.71(91.6)	6.57
	3 $^1A_1$ ($\pi \rightarrow \pi^*$)	7.46	8.17	8.44	8.44(93.7)	8.17(90.2)	7.91
Imidazole	1 $^1A''$ ($n \rightarrow \pi^*$)	6.52	6.81	6.86	7.01(92.4)	6.82(87.6)	6.81
	2 $^1A'$ ($\pi \rightarrow \pi^*$)	6.72	6.19	6.73	6.80(92.0)	6.58(87.2)	6.19
	3 $^1A'$ ($\pi \rightarrow \pi^*$)	7.15	6.93	7.28	7.27(93.1)	7.10(89.8)	6.93
	2 $^1A''$ ($\pi \rightarrow \pi^*$)	7.56	7.91	8.00	8.15(93.3)	7.93(89.4)	
	4 $^1A'$ ($\pi \rightarrow \pi^*$)	8.51	8.15	8.62	8.70(92.7)	8.45(88.6)	
Pyridine	1 $^1B_2$ ($\pi \rightarrow \pi^*$)	4.84	5.02	5.32	5.27(90.6)	5.15(85.9)	4.85
	1 $^1B_1$ ($n \rightarrow \pi^*$)	4.91	5.14	5.12	5.25(92.8)	5.05(88.1)	4.59
	2 $^1A_2$ ($n \rightarrow \pi^*$)	5.17	5.47	5.39	5.73(92.4)	5.50(87.7)	5.11
	2 $^1A_1$ ($\pi \rightarrow \pi^*$)	6.42	6.39	6.88	6.94(95.3)	6.85(92.8)	6.26
	3 $^1A_1$ ($\pi \rightarrow \pi^*$)	7.23	7.46	7.72	7.94(94.2)	7.70(91.5)	7.18
	2 $^1B_2$ ($\pi \rightarrow \pi^*$)	7.48	7.29	7.61	7.81(93.5)	7.59(89.7)	7.27
	4 $^1A_1$ ($\pi \rightarrow \pi^*$)	7.96	8.70	9.00	9.45(89.5)	8.68(74.1)	
	3 $^1B_2$ ($\pi \rightarrow \pi^*$)	7.95	8.62	9.37	9.64(84.4)	8.77(65.2)	
Pyrazine	1 $^1B_{3u}$ ($n \rightarrow \pi^*$)	3.63	4.12	4.26	4.42(93.4)	4.24(89.9)	3.95
	1 ^1A_u ($n \rightarrow \pi^*$)	4.52	4.70	4.95	5.29(92.7)	5.05(88.4)	4.81
	1 $^1B_{2u}$ ($\pi \rightarrow \pi^*$)	4.75	4.85	5.13	5.14(90.8)	5.02(86.2)	4.64
	1 $^1B_{2g}$ ($n \rightarrow \pi^*$)	5.17	5.68	5.92	6.02(92.1)	5.74(85.0)	5.56

TABLE I. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CC3 ^c (%T ₁) ^d	Best est. ^e
	1 ¹ B _{1g} (<i>n</i> → π^*)	6.13	6.41	6.70	7.13(90.8)	6.75(85.8)	6.60
	1 ¹ B _{1u} (π → π^*)	6.70	6.89	7.10	7.18(95.6)	7.07(93.3)	6.58
	2 ¹ B _{1u} (π → π^*)	7.57	7.79	8.13	8.34(93.9)	8.06(90.9)	7.72
	2 ¹ B _{2u} (π → π^*)	7.70	7.65	8.07	8.29(93.2)	8.05(89.7)	7.60
	1 ¹ B _{3g} (π → π^*)	8.19	8.47	9.42	9.75(83.5)	8.77(61.1)	
	2 ¹ A _g (π → π^*)	8.26	8.61	9.26	9.55(89.1)	8.69(74.2)	
Pyrimidine	1 ¹ B ₁ (<i>n</i> → π^*)	3.81	4.44	4.49	4.70(92.7)	4.50(88.4)	4.55
	1 ¹ A ₂ (<i>n</i> → π^*)	4.12	4.81	4.84	5.12(92.6)	4.93(88.2)	4.91
	1 ¹ B ₂ (π → π^*)	4.93	5.24	5.51	5.49(90.5)	5.36(85.7)	5.44
	2 ¹ A ₁ (π → π^*)	6.72	6.64	7.12	7.17(94.8)	7.06(92.2)	6.95
	2 ¹ B ₂ (π → π^*)	7.32	7.64	8.08	8.24(93.8)	8.01(90.7)	
	3 ¹ A ₁ (π → π^*)	7.57	7.21	7.79	7.97(93.5)	7.74(89.7)	
Pyridazine	1 ¹ B ₁ (<i>n</i> → π^*)	3.48	3.78	3.90	4.11(93.1)	3.92(89.0)	3.78
	1 ¹ A ₂ (<i>n</i> → π^*)	3.66	4.32	4.40	4.76(92.0)	4.49(86.6)	4.32
	2 ¹ A ₁ (π → π^*)	4.86	5.18	5.37	5.35(90.2)	5.22(85.2)	5.18
	2 ¹ A ₂ (<i>n</i> → π^*)	5.09	5.77	5.81	6.00(92.1)	5.74(86.6)	5.77
	2 ¹ B ₁ (<i>n</i> → π^*)	5.80	6.52	6.40	6.70(92.0)	6.41(86.6)	
	1 ¹ B ₂ (π → π^*)	6.61	6.31	7.00	7.09(94.7)	6.93(90.7)	
	2 ¹ B ₂ (π → π^*)	7.39	7.29	7.57	7.79(93.8)	7.55(90.2)	
	3 ¹ A ₁ (π → π^*)	7.50	7.62	7.90	8.11(93.8)	7.82(90.5)	
<i>s</i> -Triazine	1 ¹ A ₁ ' (<i>n</i> → π^*)	3.90	4.60	4.70	4.96(92.3)	4.78(88.0)	4.60
	1 ¹ A ₂ ' (<i>n</i> → π^*)	4.08	4.68	4.80	4.98(92.5)	4.76(88.0)	4.66
	1 ¹ E'' (<i>n</i> → π^*)	4.36	4.71	4.77	5.01(92.5)	4.81(88.1)	4.71
	1 ¹ A ₂ ' (π → π^*)	5.33	5.79	5.82	5.84(90.2)	5.71(85.1)	5.79
	2 ¹ A ₁ ' (π → π^*)	6.77	7.25	7.52	7.51(93.7)	7.41(90.8)	
	2 ¹ E'' (<i>n</i> → π^*)	7.15	7.72	8.04	8.19(90.9)	7.80(88.1)	
	1 ¹ E' (π → π^*)	8.16	7.49	8.06	8.28(93.7)	8.04(88.8)	
	2 ¹ E' (π → π^*)	8.03	8.99	9.93	10.24(91.2)	9.44(74.3)	
<i>s</i> -Tetrazine	1 ¹ B _{3u} (<i>n</i> → π^*)	1.96	2.24	2.47	2.71(93.2)	2.53(89.6)	2.24
	1 ¹ A _u (π → π^*)	3.06	3.48	3.67	4.07(92.2)	3.79(87.5)	3.48
	1 ¹ B _{1g} (<i>n</i> → π^*)	4.51	4.73	5.10	5.32(91.7)	4.97(82.5)	4.73
	1 ¹ B _{2u} (π → π^*)	4.89	4.91	5.20	5.27(90.0)	5.12(84.6)	4.91
	1 ¹ B _{2g} (<i>n</i> → π^*)	5.05	5.18	5.53	5.70(90.7)	5.34(80.7)	5.18
	1 ¹ B _{3g} (<i>n</i> , <i>n</i> → π^* , π^*)	5.16	5.79				5.79
	2 ¹ A _u (<i>n</i> → π^*)	5.28	5.47	5.50	5.70(92.5)	5.46(87.4)	5.47
	2 ¹ B _{2g} (<i>n</i> → π^*)	5.48	6.07	6.32	6.76(90.1)	6.23(79.2)	
	2 ¹ B _{1g} (<i>n</i> → π^*)	5.99	6.38	6.91	7.25(91.1)	6.87(84.7)	
	3 ¹ B _{1g} (<i>n</i> → π^*)	6.20	6.74	7.64	8.36(86.9)	7.08(63.2)	
	2 ¹ B _{3u} (<i>n</i> → π^*)	6.37	6.77	6.70	6.99(93.2)	6.67(86.7)	
	1 ¹ B _{1u} (π → π^*)	7.13	6.96	7.60	7.66(94.9)	7.45(91.0)	
	2 ¹ B _{1u} (π → π^*)	7.54	7.43	7.75	8.06(93.4)	7.79(90.2)	
	2 ¹ B _{2u} (π → π^*)	7.94	8.15	8.65	8.88(93.2)	8.51(87.7)	
	2 ¹ B _{3g} (π → π^*)	8.12	8.32	8.97	9.44(84.3)	8.47(63.6)	
Formaldehyde	1 ¹ A ₂ (<i>n</i> → π^*)	3.91	3.98	4.09	3.97(93.4)	3.95(91.2)	3.88
	1 ¹ B ₁ (σ → π^*)	9.09	9.14	9.35	9.26(93.4)	9.18(90.9)	9.1
	2 ¹ A ₁ (π → π^*)	9.77	9.31	10.34	10.54(94.4)	10.45(91.3)	9.3
Acetone	1 ¹ A ₂ (<i>n</i> → π^*)	4.18	4.42	4.52	4.43(93.4)	4.40(90.8)	4.40
	1 ¹ B ₁ (σ → π^*)	9.10	9.27	9.29	9.26(93.8)	9.17(91.5)	9.1
	2 ¹ A ₁ (π → π^*)	9.16	9.31	9.74	9.87(93.5)	9.65(90.1)	9.4
<i>p</i> -Benzoquinone	1 ¹ A _u (<i>n</i> → π^*)	2.50	2.80	2.92	3.19(91.7)	2.85(83.0)	2.80
	1 ¹ B _{1g} (<i>n</i> → π^*)	2.50	2.78	2.81	3.07(92.0)	2.75(84.1)	2.78
	1 ¹ B _{3g} (π → π^*)	4.19	4.25	4.69	4.93(92.7)	4.59(87.9)	4.25
	1 ¹ B _{1u} (π → π^*)	5.15	5.29	5.59	5.89(92.5)	5.62(88.4)	5.29
	1 ¹ B _{3u} (<i>n</i> → π^*)	5.15	5.60	5.69	6.55(91.0)	5.82(75.2)	5.60
	2 ¹ B _{3g} (π → π^*)	6.34	6.98	7.36	7.62(91.0)	7.27(88.8)	6.98
	2 ¹ B _{1u} (π → π^*)	7.08	7.91	8.31	8.47(91.7)	7.82(68.6)	

TABLE I. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CC3 ^c (%T ₁) ^d	Best est. ^e
Formamide	1 ¹ A'' ($n \rightarrow \pi^*$)	5.61	5.63	5.76	5.66(93.6)	5.65(90.7)	5.63
	2 ¹ A' ($\pi \rightarrow \pi^*$)	7.41	7.44	8.15	4.52(92.9)	8.27(87.9)	7.44
	3 ¹ A' ($\pi \rightarrow \pi^*$)	10.50	10.54	11.24	11.34(92.7)	10.93(86.6)	
Acetamide	1 ¹ A'' ($n \rightarrow \pi^*$)	5.54	5.80	5.77	5.71(93.5)	5.69(90.6)	5.80
	2 ¹ A' ($\pi \rightarrow \pi^*$)	7.21	7.27	7.66	7.85(92.8)	7.67(89.1)	7.27
	3 ¹ A' ($\pi \rightarrow \pi^*$)	10.08	10.09	10.71	10.77(93.0)	10.50(88.7)	
Propanamide	1 ¹ A'' ($n \rightarrow \pi^*$)	5.48	5.72	5.78	5.74(93.6)	5.72(90.6)	5.72
	2 ¹ A'' ($\pi \rightarrow \pi^*$)	7.28	7.20	7.56	7.80(93.0)	7.62(89.2)	7.20
	3 ¹ A' ($\pi \rightarrow \pi^*$)	9.95	9.94	10.33	10.34(93.3)	10.06(89.0)	
Cytosine	2 ¹ A' ($\pi \rightarrow \pi^*$)	4.39	4.68	4.80	4.98(91.6)		4.66
	1 ¹ A'' ($n \rightarrow \pi^*$)	5.00	5.12	5.13	5.45(92.5)		4.87
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.53	5.54	5.01	5.99(92.6)		5.26
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.36	5.54	5.71	5.95(91.1)		5.62
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.16	6.40	6.65	6.81(92.3)		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.74	6.98	6.94	7.23(91.9)		
	6 ¹ A' ($\pi \rightarrow \pi^*$)	7.61	8.23	8.45	8.69(92.1)		
Thymine	1 ¹ A'' ($n \rightarrow \pi^*$)	4.39	4.94	4.94	5.14(92.5)		4.82
	2 ¹ A' ($\pi \rightarrow \pi^*$)	4.88	5.06	5.39	5.60(93.0)		5.20
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.88	6.15	6.46	6.78(90.9)		6.27
	2 ¹ A'' ($n \rightarrow \pi^*$)	5.91	6.38	6.33	6.57(93.3)		6.16
	4 ² A' ($\pi \rightarrow \pi^*$)	6.10	6.52	6.80	7.05(92.5)		6.53
	4 ¹ A'' ($n \rightarrow \pi^*$)	6.15	6.86	6.73	7.67(91.6)		
	5 ¹ A'' ($n \rightarrow \pi^*$)	6.70	7.43	7.18	7.87(91.6)		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.13	7.43	7.71	7.90(91.8)		
Uracil	1 ¹ A'' ($n \rightarrow \pi^*$)	4.54	4.90	4.91	5.11(92.4)		4.80
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.00	5.23	5.52	5.70(92.6)		5.35
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.82	6.15	6.43	6.76(90.6)		6.26
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.00	6.27	6.73	7.68(91.5)		6.10
	3 ¹ A'' ($n \rightarrow \pi^*$)	6.37	6.97	6.26	6.50(93.3)		6.56
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.46	6.75	6.96	7.19(92.5)		6.70
	5 ¹ A'' ($n \rightarrow \pi^*$)	6.95	7.28	7.12	7.74(91.7)		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.00	7.42	7.66	7.81(91.8)		
Adenine	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.13	5.20	5.28	5.37(91.3)		5.25
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.20	5.30	5.42	5.61(92.9)		5.25
	1 ¹ A'' ($n \rightarrow \pi^*$)	6.15	5.21	5.27	5.58(92.6)		5.12
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.86	5.97	5.91	6.19(92.9)		5.75
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.24	6.35	6.58	6.83(92.3)		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.72	6.64	6.93	7.17(91.8)		
	6 ¹ A' ($\pi \rightarrow \pi^*$)	6.99	6.88	7.49	7.72(91.9)		
	7 ¹ A' ($\pi \rightarrow \pi^*$)	7.57	7.56	8.04	8.47(91.1)		

^aData from publications by the Roos group in the 1990s. See Supporting Information for references.^bCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.^cCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.^dWeight of the single excitations in the coupled cluster calculations.^eBest estimate from *ab initio* calculations. See text for details.

diffuse functions in the TZVP basis will still cause problems for high-lying valence states. (c) Among the coupled cluster results, the singlet excitation energies from the most reliable CC3 method are normally lower than those from CC2 and always lower than those from CCSD. (d) For excited states that are dominated by single excitations, the current CASPT2 and CC3 results are generally very close to each other (within 0.1 eV). Such excellent agreement is found particularly often for triplet states.

Best estimates for the vertical excitation energies were adopted from published highly correlated *ab initio* studies with large basis sets. In the absence of such literature data, these estimates were derived from the present calculations using the following guidelines: CC3/TZVP values were taken for the triplet states (with single excitation weights of typically more than 95%). CASPT2/TZVP values were favored for the singlet excited states because there is normally at least one singlet state in each benchmark molecule with a

TABLE II. Vertical triplet excitation energies ΔE (eV) of all statistically evaluated molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (% T_1) ^d	CC3 ^c (% T_1) ^d	Best est. ^e
Ethene	1 $^3B_{1u}$ ($\pi \rightarrow \pi^*$)	4.39	4.60	4.52	4.42(99.4)	4.48(99.3)	4.50
<i>E</i> -Butadiene	1 ^3B_u ($\pi \rightarrow \pi^*$)	3.20	3.44	3.40	3.25(98.9)	3.32(98.5)	3.20
	1 ^3A_g ($\pi \rightarrow \pi^*$)	4.89	5.16	5.25	5.15(99.1)	5.17(98.9)	5.08
all- <i>E</i> -Hexatriene	1 ^3B_u ($\pi \rightarrow \pi^*$)	2.55	2.71	2.78	2.62(98.6)	2.69(98.0)	2.40
	1 ^3A_g ($\pi \rightarrow \pi^*$)	4.12	4.31	4.40	4.28(98.9)	4.32(98.4)	4.15
all- <i>E</i> -Octatetraene	1 ^3B_u ($\pi \rightarrow \pi^*$)	2.17	2.33	2.40	2.23(98.5)	2.30(97.6)	2.20
	1 ^3A_g ($\pi \rightarrow \pi^*$)	3.39	3.69	3.76	3.62(98.7)	3.67(98.1)	3.55
Cyclopropene	1 $^3B_2$ ($\pi \rightarrow \pi^*$)	4.18	4.35	4.44	4.30(99.2)	4.34(99.1)	4.34
	1 $^3B_1$ ($\sigma \rightarrow \pi^*$)	6.05	6.51	6.65	6.66(98.5)	6.62(98.1)	6.62
Cyclopentadiene	1 $^3B_2$ ($\pi \rightarrow \pi^*$)	3.15	3.28	3.36	3.18(98.9)	3.25(98.5)	3.25
	1 $^3A_1$ ($\pi \rightarrow \pi^*$)	4.90	5.10	5.22	5.07(99.0)	5.09(98.7)	5.09
Norbornadine	1 $^3A_2$ ($\pi \rightarrow \pi^*$)	3.42	3.75	3.76	3.67(99.0)	3.72(98.7)	3.72
	1 $^3B_2$ ($\pi \rightarrow \pi^*$)	3.80	4.22	4.25	4.09(99.2)	4.16(99.0)	4.16
Benzene	1 $^3B_{1u}$ ($\pi \rightarrow \pi^*$)	3.89	4.17	4.31	3.94(99.0)	4.12(98.7)	4.15
	1 $^3E_{1u}$ ($\pi \rightarrow \pi^*$)	4.49	4.90	5.14	4.97(97.9)	4.90(97.0)	4.86
	1 $^3B_{2u}$ ($\pi \rightarrow \pi^*$)	5.49	5.76	6.08	6.00(98.6)	6.04(98.2)	5.88
	1 $^3E_{2g}$ ($\pi \rightarrow \pi^*$)	7.12	7.41	7.99	7.73(97.6)	7.49(94.9)	7.51
Naphthalene	1 $^3B_{2u}$ ($\pi \rightarrow \pi^*$)	3.10	3.20	3.27	2.99(98.2)	3.11(97.3)	3.11
	1 $^3B_{3u}$ ($\pi \rightarrow \pi^*$)	3.89	4.29	4.38	4.27(97.9)	4.18(93.2)	4.18
	1 $^3B_{1g}$ ($\pi \rightarrow \pi^*$)	4.23	4.55	4.64	4.44(97.4)	4.47(96.9)	4.47
	2 $^3B_{2u}$ ($\pi \rightarrow \pi^*$)	4.30	4.71	4.88	4.67(98.6)	4.64(97.8)	4.64
	2 $^3B_{3u}$ ($\pi \rightarrow \pi^*$)	4.45	5.00	5.11	5.10(97.8)	5.11(96.8)	5.11
	1 ^3A_g ($\pi \rightarrow \pi^*$)	5.27	5.57	5.76	5.57(97.7)	5.52(96.5)	5.52
	2 $^3B_{1g}$ ($\pi \rightarrow \pi^*$)	5.71	6.25	6.44	6.79(98.3)	6.48(97.6)	6.48
	2 ^3A_g ($\pi \rightarrow \pi^*$)	5.83	6.42	6.83	6.81(98.5)	6.47(97.9)	6.47
	3 ^3A_g ($\pi \rightarrow \pi^*$)	5.91	6.63	6.94	6.96(97.3)	6.79(95.0)	6.79
	3 $^3B_{1g}$ ($\pi \rightarrow \pi^*$)	6.23	6.67	7.23	7.04(97.3)	6.76(94.0)	6.76
Furan	1 $^3B_2$ ($\pi \rightarrow \pi^*$)	3.99	4.17	4.38	4.10(98.9)	4.17(98.5)	4.17
	1 $^3A_1$ ($\pi \rightarrow \pi^*$)	5.15	5.49	5.67	5.48(98.7)	5.48(98.2)	5.48
Pyrrole	1 $^3B_2$ ($\pi \rightarrow \pi^*$)	4.27	4.52	4.68	4.41(98.8)	4.48(98.4)	4.48
	1 $^3A_1$ ($\pi \rightarrow \pi^*$)	5.16	5.53	5.72	5.54(98.4)	5.51(97.8)	5.51
Imidazole	1 $^3A'$ ($\pi \rightarrow \pi^*$)	4.49	4.65	4.89	4.62(98.8)	4.69(98.4)	4.69
	2 $^3A'$ ($\pi \rightarrow \pi^*$)	5.47	5.74	6.01	5.83(98.5)	5.79(97.9)	5.79
	1 $^3A''$ ($n \rightarrow \pi^*$)	6.07	6.36	6.44	6.43(98.3)	6.37(97.4)	6.37
	3 $^3A'$ ($\pi \rightarrow \pi^*$)	6.53	6.44	6.74	6.56(98.4)	6.55(97.9)	6.55
	4 $^3A'$ ($\pi \rightarrow \pi^*$)	7.08	7.43	7.68	7.54(98.0)	7.42(97.1)	
	2 $^3A''$ ($n \rightarrow \pi^*$)	7.15	7.51	7.52	7.76(97.6)	7.51(96.0)	
Pyridine	1 $^3A_1$ ($\pi \rightarrow \pi^*$)	4.05	4.27	4.46	4.07(99.0)	4.25(98.6)	4.06
	1 $^3B_1$ ($n \rightarrow \pi^*$)	4.41	4.55	4.54	4.61(98.1)	4.50(97.1)	4.25
	1 $^3B_2$ ($\pi \rightarrow \pi^*$)	4.56	4.72	5.07	4.91(98.0)	4.86(97.2)	4.64
	2 $^3A_1$ ($\pi \rightarrow \pi^*$)	4.73	5.03	5.33	5.13(97.9)	5.05(97.0)	4.91
	1 $^3A_2$ ($n \rightarrow \pi^*$)	5.10	5.48	5.35	5.67(97.5)	5.46(95.8)	5.28
	2 $^3B_2$ ($\pi \rightarrow \pi^*$)	6.02	6.02	6.52	6.41(98.3)	6.40(97.8)	6.08
	3 $^3B_2$ ($\pi \rightarrow \pi^*$)	7.28	7.88	8.39	8.12(97.4)	7.83(94.4)	
	3 $^3A_1$ ($\pi \rightarrow \pi^*$)	7.34	7.56	8.18	7.90(97.7)	7.66(95.3)	
<i>s</i> -Tetrazine	1 $^3B_{3u}$ ($n \rightarrow \pi^*$)	1.45	1.56	1.86	1.99(98.1)	1.89(97.2)	1.89
	1 ^3A_u ($n \rightarrow \pi^*$)	2.81	3.26	3.43	3.74(97.7)	3.52(96.3)	3.52
	1 $^3B_{1g}$ ($n \rightarrow \pi^*$)	3.76	4.14	4.30	4.31(98.2)	4.21(97.1)	4.21
	1 $^3B_{1u}$ ($\pi \rightarrow \pi^*$)	4.25	4.36	4.62	4.05(99.0)	4.33(98.5)	4.33
	1 $^3B_{2u}$ ($\pi \rightarrow \pi^*$)	4.29	4.56	4.81	4.57(98.1)	4.54(97.4)	4.54
	1 $^3B_{2g}$ ($n \rightarrow \pi^*$)	4.67	4.93	5.03	5.09(98.0)	4.93(96.4)	4.93
	2 ^3A_u ($n \rightarrow \pi^*$)	4.85	5.02	5.05	5.20(97.8)	5.03(96.6)	5.03

TABLE II. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c (%T ₁) ^d	CC3 ^c (%T ₁) ^d	Best est. ^e
	1 ³ B _{3g} (<i>n</i> , <i>n</i> → π^* , π^*)	5.08	5.50				
	2 ³ B _{1u} (π → π^*)	5.09	5.40	5.67	5.48(97.5)	5.38(96.5)	5.38
	2 ³ B _{2g} (<i>n</i> → π^*)	5.30	5.97	6.05	6.51(96.8)	6.04(93.0)	
	2 ³ B _{1g} (<i>n</i> → π^*)	5.68	6.31	6.72	7.11(96.9)	6.60(92.3)	
	2 ³ B _{3u} (<i>n</i> → π^*)	6.14	6.54	6.52	6.80(97.5)	6.53(95.8)	
	2 ³ B _{2u} (π → π^*)	6.81	7.10	7.65	7.46(97.7)	7.36(96.8)	
Formaldehyde	1 ³ A ₂ (π → π^*)	3.48	3.58	3.57	3.52(98.6)	3.55(98.1)	3.50
	1 ³ A ₁ (π → π^*)	5.99	5.84	6.08	5.78(99.3)	5.83(99.2)	5.87
Acetone	1 ³ A ₂ (<i>n</i> → π^*)	3.90	4.08	4.08	4.03(98.4)	4.05(97.9)	4.05
	1 ³ A ₁ (π → π^*)	5.98	6.03	6.27	5.94(99.1)	6.03(98.9)	6.03
<i>p</i> -Benzoquinone	1 ³ B _{1g} (<i>n</i> → π^*)	2.17	2.63	2.47	2.71(97.9)	2.51(95.9)	2.51
	1 ³ A _u (<i>n</i> → π^*)	2.27	2.68	2.59	2.83(97.8)	2.62(95.7)	2.62
	1 ³ B _{1u} (π → π^*)	2.91	2.99	3.12	2.89(98.5)	2.96(97.8)	2.96
	1 ³ B _{3g} (π → π^*)	3.19	3.31	3.50	3.42(98.6)	3.41(98.0)	3.41
Formamide	1 ³ A'' (<i>n</i> → π^*)	5.34	5.40	5.39	5.32(98.4)	5.36(97.8)	5.36
	1 ³ A' (π → π^*)	5.69	5.58	5.94	5.67(98.7)	5.74(98.4)	5.74
Acetamide	1 ³ A'' (<i>n</i> → π^*)	5.24	5.53	5.42	5.39(98.4)	5.42(98.3)	5.42
	1 ³ A' (<i>n</i> → π^*)	5.57	5.75	6.06	5.83(98.7)	5.88(98.3)	5.88
Propanamide	1 ³ A'' (<i>n</i> → π^*)	5.28	5.44	5.44	5.41(98.4)	5.45(97.7)	5.45
	1 ³ A' (π → π^*)	5.94	5.79	6.07	5.84(98.7)	5.90(98.3)	5.90

^aData from publications by the Roos group in the 1990s. See Supporting Information for references.^bCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.^cCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.^dWeight of the single excitations in the coupled cluster calculations.^eBest estimate values from *ab initio* calculations. See text for details.

CC3 single excitation weight of less than 90%. Given the limitations of the TZVP basis, CC3/TZVP or CASPT2/TZVP energies were usually not accepted as best estimates if they exceed 7 eV or if there is reason to assume that diffuse basis functions are essential for a given state.

After these general remarks, we now discuss the individual benchmark molecules, without commenting again on the general trends and rules outlined above.

1. Unsaturated aliphatic hydrocarbons

Ethene (*D*_{2h}, Tables VIII, IX, and XXXVIII). As already discussed in Sec. III A the energy of the 1 ¹B_{1u} state depends strongly on the basis set (diffuse functions) and on the active space (in CASPT2). Using the TZVP basis and the standard (2,2) active space with two electrons occupying the π and π^* orbital gives a rather high SS-CASPT2 excitation energy of 8.62 eV. Increasing the active space lowers this value by about 0.2 eV and brings it close to the CC3 result of 8.37 eV for the TZVP basis. Further improvements require the addition of diffuse functions. Doing so at the SS-CASPT2 level with suitably chosen active spaces, we obtain excitation energies that converge to 8.44 eV, consistent with the published values of 8.40 eV (Ref. 23) and 8.45 eV.²⁸³ As pointed out previously, an MS-CASPT2 treatment is advantageous in states with significant valence-Rydberg mixing, and an MS-CASPT2 calculation with a reasonably large basis set and active space indeed yields a much lower excita-

tion energy of 7.98 eV.²² After further extending the basis set (up to d-aug-cc-pV5Z) and the active space [up to (8,20)], we arrive at a converged MS-CASPT2 value of 7.83 eV (see Fig. 2 and Table IX). At the coupled cluster level the basis set dependence is smaller, but still substantial (CC3/TZVP 8.37 eV, converged CC3 value of 7.88 eV).

The 1 ¹B_{1u} state of ethene has been the subject of many high-level *ab initio* studies. Its accurate description is challenging because of the pronounced valence-Rydberg mixing between the qualitatively different configurations arising from π → π^* and π → 3d π excitations. The best MS-CASPT2 values for the vertical excitation energies (see above) lie in the same range as other multireference perturbation results.^{243,262} Equation-of-motion coupled cluster methods give values between 7.74 and 7.99 eV (EOM-CCSDT-3: 7.89 eV).²²¹ An earlier CC3 study with a basis set containing diffuse functions arrives at 7.87 eV,⁶² in close agreement with our extended basis set (aug-cc-pV5Z or d-aug-cc-pVQZ) results in Table IX. Extensive multireference configuration interaction and related calculations (MRCI-SD+Q, MR-AQCC) converge to a recommended value of 7.7 eV,¹⁹² while SORCI/aug-cc-pVTZ calculations yield 7.79 eV.²⁶⁶ On the experimental side, the band maximum is observed at 7.66 eV,⁹⁰ but the inclusion of corrections for zero-point and nonadiabatic effects leads to somewhat higher estimates for the vertical excitation energy of 7.8 eV (Ref. 71) and 8.0 eV,^{92,126,149} respectively. We con-

clude on the basis of these data that the vertical excitation energy of the 1^1B_{1u} state can still not be assigned precisely, but should lie between 7.7 and 8.0 eV. Our best estimate is 7.8 eV.

The 1^3B_{1u} triplet state is dominated by a single excitation and is thus easier to handle theoretically. Calculated vertical excitation energies include 4.49 eV (MS-CASPT2/d-aug-cc-pV5Z, this work), 4.50 eV (CC3/d-aug-cc-pVQZ or aug-cc-pV5Z, this work), 4.39 eV (CASPT2),²³ and 4.47 eV (SORCI/aug-cc-pVTZ).²⁶⁶ An extensive MR-CI study yields values in a narrow range between 4.47 and 4.53 eV.¹⁹² Experimental values from electron impact and optical spectroscopy are 4.36 eV (Ref. 158) and 4.6 eV,¹⁵⁴ respectively. We adopt 4.50 eV as best estimate.

Butadiene (C_{2h} , Tables X and XXXIX). The first excited singlet state (1^1B_u) is dominated by a single excitation (HOMO $\rightarrow$ LUMO, weight of 99% in CASPT2) (HOMO denotes highest occupied molecular orbital and LUMO denotes lowest unoccupied molecular orbital). It is influenced by valence-Rydberg mixing²³ and thus somewhat more diffuse than the ground state ($\langle z^2 \rangle$ values of 26 versus 22 a.u.),²¹¹ whereas our MS-CASPT2/TZVP calculations without diffuse functions give a similar spatial extent for these two states (22–23 a.u.). The MS-CASPT2 vertical excitation energy of 6.47 eV obtained with our standard conventions is reduced to 6.25 eV upon extension of the active space and averaging over additional roots in the SA procedure (see Table X). The wave function of the second excited singlet state (2^1A_g) contains large contributions not only from single excitations (HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1), but also from the HOMO $\rightarrow$ LUMO double excitation. This mixing is well described at the CASPT2 level. However, the CC2 and CCSD methods fail in such situations, and the computed vertical excitation energy for the 2^1A_g state indeed drops dramatically when going from CC2 and CCSD to CC3. Both MS-CASPT2 and CC3 predict the 1^1B_u below the 2^1A_g state, with an energy gap of 0.16 and 0.19 eV, respectively.

In the literature, the ordering of the first two excited singlets has been controversial. A comprehensive survey²⁸⁴ shows that most of the high-level *ab initio* methods place the 1^1B_u state slightly below the 2^1A_g state. Recent extensive MR-CI and related calculations (MR-CISD+Q and MR-AQCC with complete basis set extrapolation²¹¹) lead to best vertical excitation energies of 6.18 eV (1^1B_u) and 6.55 eV (2^1A_g). Other recent values come from SAC-CI (6.33 and 6.56 eV) (Ref. 248) and SORCI (6.29 and 6.37 eV) (Ref. 266) studies. The early CASPT2 results (6.23 and 6.27 eV) (Ref. 23) appear to be reasonable for 1^1B_u , but somewhat too low for 2^1A_g . We adopt as best theoretical estimates the MR-CI-based values of 6.18 eV (1^1B_u) and 6.55 eV (2^1A_g).²¹¹ Experimentally, the band maximum of the bright 1^1B_u state is found at 5.92 eV,^{94,102,155} i.e., 0.26 eV below our best estimate of the vertical excitation energy which might suggest a nonvertical character of this transition. We also note that an experimental estimate of valence-Rydberg mixing in conjugated dienes leads to an “unperturbed” energy of 6.25 eV for the 1^1B_u valence state.²⁸⁵ There appear to be no reliable experimental data on the precise location of the dark 2^1A_g state.

The two lowest triplet states of butadiene are less controversial. Recent SAC-CI calculations²⁴⁸ yield vertical excitation energies of 3.20 eV (1^3B_u) and 5.08 eV (1^3A_g) which are slightly lower than the values from SORCI/aug-cc-pVTZ (3.32 and 5.27 eV),²⁶⁶ MS-CASPT2/TZVP (3.34 and 5.16 eV), and CC3/TZVP (3.32 and 5.17 eV), see Table II. The early CASPT2 results (3.20 and 4.89 eV) (Ref. 23) again seem reasonable for 1^3B_u and on the low side for 1^3A_g . We adopt the recent SAC-CI values as the currently best theoretical estimates (even though the chosen basis is not very large). The experimental band maxima in the electron impact spectra are found at 3.22 and 4.91 eV.^{94,104,155}

Hexatriene (C_{2h} , Tables XI and XL). CASPT2 calculations for the 1^1B_u state with our standard conventions overestimate the vertical excitation energy severely (6.39 eV) when the CASSCF reference is obtained for a single 1^1B_u state in this case. Inclusion of the second-lowest state of this symmetry in the SA-CASSCF treatment lowers the computed energy to 5.31 eV. The 2^1A_g state is calculated slightly above the 1^1B_u state, with an energy gap of 0.11 eV (CASPT2/TZVP) and 0.14 eV (CC3/TZVP).

For hexatriene and higher polyenes, not so many high-level *ab initio* studies are available as for ethene and butadiene. CASPT2 calculations²³ place the 1^1B_u and 2^1A_g states at 5.01 and 5.20 eV, respectively, while more recent multi-reference perturbation (MRMP) calculations with a large active space and basis-set corrections²⁴³ arrive at best estimates of 5.10 and 5.09 eV. We adopt these latter values. Experimentally, the optical absorption intensity maximum for the 1^1B_u state is at 4.93 eV, while the electron impact intensity maximum is at 5.13 eV.¹⁰³ The precise location of the 2^1A_g state is not known experimentally.

For the 1^3B_u and 1^3A_g triplet states, we have virtually identical results from CASPT2/TZVP (2.71 and 4.31 eV) and CC3/TZVP (2.69 and 4.32 eV) which are somewhat higher than previous CASPT2 results (2.55 and 4.12 eV) (Ref. 23) and the extrapolated MRMP data (2.40 and 4.15 eV).²⁴³ We again adopt the MRMP values which are rather close to the experimental values (2.61 and 4.11 eV) from electron impact.¹⁰³

Octatetraene (C_{2h} , Tables XII and XLI). It is known experimentally that the 2^1A_g state lies below the 1^1B_u state in octatetraene and longer polyenes. The present and past¹⁵⁹ CASPT2 calculations reproduce the inversion, but the computed energy gap is quite small in both cases (0.04 and 0.06 eV). The CC2 and CCSD methods do not treat the doubly excited 2^1A_g state properly and thus yield an unreasonable gap, as in the case of butadiene and hexatriene. CC3/TZVP calculations on octatetraene, however, reduce the gap to 0.03 eV, predicting the 1^1B_u (4.94 eV) below the 2^1A_g state (4.97 eV).

Vertical excitation energies for the 1^3B_u , 2^3A_g , 1^1B_u , and 2^1A_g states are available from previous CASPT2 work (2.17, 3.39, 4.38, and 4.42 eV) (Ref. 159) and from MRMP calculation with basis set extrapolation (2.20, 3.55, 4.66, and 4.47 eV).²⁴³ They are quite close to the published electron-impact values for the triplets (2.10 and 3.55 eV) (Ref. 151)

and the optical absorption maximum for the bright 1^1B_u state (4.41 eV).^{96,119} We take the MRMP values as theoretical reference data.

Cyclopropene (C_{2v} , Tables XIII and XLII). In the electronic spectrum of cyclopropene, the first band corresponds to a valence $\sigma \rightarrow \pi^*$ transition, which lies well below the valence $\pi \rightarrow \pi^*$ transition (by 0.7 eV according to the optical gas-phase spectrum¹²⁷). Our current calculations reproduce this ordering, but give a smaller energy difference of 0.2–0.3 eV at all levels applied (CASPT2, CC2, CCSD, CC3), whereas the previous CASPT2 calculations¹⁶⁰ overestimate this difference (giving 1.1 eV) due to exaggerated valence-Rydberg mixing involving the upper state. The two lowest valence triplet states show the reverse order as expected ($\pi \rightarrow \pi^*$ below $\sigma \rightarrow \pi^*$ by about 2 eV).

Our computed vertical excitation energies for the two lowest singlet and triplet valence states are generally consistent with each other (CASPT2, CC2, CCSD, CC3) and somewhat larger than those from the earlier CASPT2 calculations,¹⁶⁰ except for the 1^1B_2 state ($\pi \rightarrow \pi^*$) where our present MS-CASPT2 treatment is more suitable than the previous SS-CASPT2 treatment for handling the valence-Rydberg mixing (see discussion for ethene above). We adopt the present MS-CASPT2 results for the singlets (1^1B_1 6.76 eV, 1^1B_2 7.06 eV) and the CC3/TZVP values for the triplets (1^3B_2 4.34 eV, 1^3B_1 6.62 eV) as reference data, even though they are somewhat higher than the available low-resolution experimental data (e.g., 1^1B_1 6.45 eV, 1^3B_2 4.16 eV).^{107,127}

Cyclopentadiene (C_{2v} , Tables XIV and XLIII). Among the valence excited singlets, the 1^1B_2 state is lowest followed by the 2^1A_1 state which lies about 1 eV higher at all levels. The 1^1B_2 state is dominated by a $\pi \rightarrow \pi^*$ single excitation, while the 1^1A_1 states contain significant contributions from double excitations and thus pose problems for CC2 and CCSD. This is reflected in the relatively large decrease of 0.44 eV (2^1A_1) and 0.26 eV (3^1A_1) in the computed excitation energies when going from CCSD to CC3. The CASPT2 results are also sensitive: state averaging over five rather than four 1^1A_1 roots reduces the doubly excited character of the 3^1A_1 state appreciably and lowers the computed dipole moment from 2.35 to 0.40 D, which indirectly affects the 2^1A_1 state whose energy decreases from 6.52 to 6.31 eV.

The vertical excitation energy of the lowest $\pi \rightarrow \pi^*$ valence transition (1^1B_2) has been studied very carefully at the coupled cluster level.³² The CCSDT-3/cc-pVTZ value of 5.70 eV is close to our CC3/TZVP value of 5.73 eV. The best estimate of 5.55(5) eV at the EOM-CCSDT level with an exhaustive basis set³² is still 0.25 eV above the experimentally observed band maximum at 5.30(2) eV.⁸⁷ Simulations of the spectrum in a vibronic coupling framework²⁸⁶ indicate that the actual absorption maximum lies 0.13 eV below the vertical excitation energy³² which accounts for part of the discrepancy. A corresponding correction of the experimental data leads to a final estimate of 5.43(5) eV.³² While this value is expected to be most realistic, our strategy is to admit only purely theoretical reference data, and hence

we adopt the best such estimate of 5.55 eV (see above) which is close to our present CASPT2/TZVP result of 5.51 eV.

The other excited states of cyclopentadiene are less well characterized. The 2^1A_1 state (not observed experimentally) has been estimated to lie around 6.2 eV based on experimental correlations, while the higher 1^1A_1 valence state is found at 7.9 eV.¹⁴⁰ For the 2^1A_1 state, the previous¹⁶¹ and the current CASPT2 calculations yield the same value (6.31 eV, adopted) which is very close to the EOM-CCSD(T) result (6.37 eV).²²¹ In the case of the higher 1^1A_1 valence state, the published CASPT2 and EOM-CCSD(T) values differ too much (7.89 versus 8.29 eV) to settle on a recommended value. For the two lowest triplet valence states, on the other hand, all computed vertical excitation energies are quite similar; we adopt our CC3/TZVP results as best estimates (3.25 and 5.09 eV).

Norbornadiene (C_{2v} , Tables XV and XLIV). The two double bonds in norbornadiene are not conjugated and can thus influence each other only by through-space and through-bond interactions. According to our CASPT2/TZVP calculations, the excited valence singlet manifold begins with the 1^1A_2 state at 5.34 eV, followed by two well separated 1^1B_2 states at 6.11 and 7.32 eV, and a second 1^1A_2 state at 7.44 eV. The MS-CASPT2 solutions for the two 1^1B_2 states are dominated by single $\pi \rightarrow \pi^*$ excitations (1^1B_2 : 94% $a_1 \rightarrow b_2$ and 2^1B_2 : 94% $b_1 \rightarrow a_2$). The CC3/TZVP calculations yield an analogous energy pattern for the singlet states, with a shift of 0.3 eV towards higher values.

In the previous CASPT2 study,¹⁶² the two 1^1A_2 states occur at similar energies as presently (5.28 and 7.36 eV), but the two 1^1B_2 states are closely spaced at 6.20 and 6.48 eV, with a separation of only 0.28 eV. It has been pointed out that these two 1^1B_2 states suffer from considerable mixing with nearby Rydberg states which will affect the computed excitation energies in the original CASPT2 work,¹⁶² but not in our present MS-CASPT2 setup. Experimentally, the singlet states are found at 5.25, 5.95, 6.65, and 7.50 eV by electron impact measurements,¹⁴² and the second of these values is also found by optical spectroscopy.⁷³ These experimental data are overall in reasonable agreement with both sets of CASPT2 results, except for the separation of the two 1^1B_2 states (0.7 eV). As best theoretical estimates for the states below 6.5 eV, we adopt the current CASPT2/TZVP results for the singlets and the CC3/TZVP results for the triplets.

2. Aromatic hydrocarbons and heterocycles

Benzene (D_{6h} , Tables XVI, XLV, and XLVI). Most of the $\pi \rightarrow \pi^*$ states considered are dominated by single excitations and can thus be handled well by all methods applied. Exceptions are the high-lying 2^1E_{2g} and the 1^3E_{2g} states which contain some HOMO $\rightarrow$ LUMO double excitation (12%–14%) and are therefore problematic for CC2 and CCSD. Generally, however, our CASPT2/TZVP results agree well with the CC3/TZVP values which tend to be slightly higher (typically by 0.2 eV), and also with the other coupled cluster results.

The published CASPT2 singlet and triplet excitation energies¹⁶³ are somewhat lower than our CASPT2 values, usually by about 0.2 eV. The available coupled cluster studies for the excited singlets^{24,213,245} and triplets²⁷ yield results that are rather close to our current CASPT2 values. We adopt the published CC3 values obtained with large basis sets^{24,27} as best theoretical estimates: 5.08 eV (1^1B_{2u}), 6.54 eV (1^1B_{1u}), 7.13 eV (1^1E_{1u}), 8.41 eV (1^1E_{2g}), 4.15 eV (1^3B_{1u}), 4.86 eV (1^3E_{1u}), 5.88 eV (1^3B_{2u}), and 7.51 eV (1^3E_{2g}). Reliable experimental vertical excitation energies are available for the first three singlets (4.90, 6.20, and 6.94 eV) (Refs. 82 and 112) and for the first three triplets (3.94, 4.76, and 5.60 eV).¹¹⁷ The positions of the fourth valence singlet and triplet are less certain, the usually quoted values are 7.8 eV (Ref. 99) and 7.24–7.74 eV,¹⁶³ respectively.

Naphthalene (D_{2h} , Tables XVII, XLVII, and XLVIII). Compared with the previous CASPT2 results,¹⁶⁴ the present CASPT2 excitation energies are generally blueshifted, typically by 0.2–0.4 eV for low-energy singlet and triplet states that are dominated by single excitations. Larger blueshifts are encountered for singlet states with strong contributions from doubly excited configurations (2^1A_g , 1^1B_{1g} , 3^1A_g , 3^1B_{3u}) and also more generally for states with large perturbation corrections (2 eV or more) to the CASSCF excitation energies (2^1B_{3u} , 2^1B_{1g} , 3^1B_{2u}). The CC2 excitation energies are even more blue shifted, especially in these problem cases. The CC3/TZVP energies are also slightly higher than the CASPT2/TZVP values, but they are rather close for the lower excited singlet and all triplet states.

The experimental studies often focus on the 0-0 bands. Experimental vertical excitation energies are known from optical and electron impact spectra for the following singlet states: 4.0 eV (1^1B_{3u}),¹⁰⁵ 4.7 eV (1^1B_{2u}),¹⁰⁵ 5.89 eV (2^1B_{3u}),¹⁴⁵ 6.14 eV (2^1B_{2u}),¹⁴⁵ and 7.6 eV (3^1B_{2u}).¹⁰⁵ Additional data come from two-photon absorption spectroscopy:¹⁵² 5.22 eV (1^1B_{1g}), 5.52 eV (2^1A_g), and 6.05 eV (3^1A_g). The most intense peak for the lowest triplet state (1^3B_{2u}) is found in a gas-phase energy loss spectrum at 3.0 eV.¹⁴⁴ Triplet-triplet excitations are observed at 2.25 eV (1^3A_g),⁸⁹ 2.93 eV (3^3A_g),⁸⁹ and 3.12 eV (2^3B_{1g}).⁸⁹ The latter value corresponds to the most intense peak, whereas the former two values refer to the onset of the band.

The previous¹⁶⁴ and present CASPT2 results bracket the quoted experimental values in most cases and show comparable deviations. We adopt the current CASPT2/TZVP values below 7 eV as reference data.

Furan (C_{2v} , Tables XVIII, XLIX, and L). Our standard CASPT2/TZVP approach gives the three lowest singlet valence excited states at 6.43 eV (1^1B_2), 6.52 eV (2^1A_1), and 8.22 eV (3^1A_1), i.e., about 0.4–0.5 eV higher than in the early CASPT2/ANO study¹⁶¹ and about 0.1–0.3 eV lower than in CC3/TZVP. The 1^1B_2 state is redshifted to 6.25 eV when the active space in CASPT2/TZVP is enlarged by two more orbitals (see Table XVIII). The current CASPT2/TZVP results agree well with recent high-level MRCI data²⁴¹ (1^1B_2 : 6.44 eV, 2^1A_1 : 6.53 eV) and CC3/ANO data¹⁹⁴ (1^1B_2 : 6.35 eV, 2^1A_1 : 6.61 eV, and 3^1A_1 : 8.35 eV). We

adopt the CC3 results with basis set correction as best estimates³⁰ (1^1B_2 : 6.32 eV, 2^1A_1 : 6.57 eV, and 3^1A_1 : 8.13 eV). The valence bands in the experimental optical spectrum are quite broad and show maxima at 6.06 eV, 6.47/6.61 eV, and 7.79 eV.⁷⁴

In the case of the two lowest triplet states, the present CASPT2/TZVP and CC3/TZVP calculations yield virtually identical excitation energies which are about 0.2–0.3 eV higher than those from the early CASPT2/ANO study.¹⁶¹ We adopt the present CC3/TZVP results as reference data (1^3B_2 : 4.17 eV, 1^3A_1 : 5.48 eV). The corresponding maxima in the electron impact spectra lie at 3.99 and 5.22 eV, respectively.⁷⁴

Pyrrole (C_{2v} , Tables XIX, LI, and LII). The spectra of pyrrole and furan are quite similar. The current CASPT2/TZVP excitation energies for the valence singlet states are blueshifted (by 0.3 eV or more) with respect to previous CASPT2 results.¹⁶¹ There have been many extensive *ab initio* studies on the electronic spectrum of pyrrole.^{31,161,176,178–180,193,198,199,206,215,220,230,267} Most of them have focused on the relative position of the 2^1A_1 and the 1^1B_2 valence states; the published results are rather inconsistent and cover a range of more than 1 eV for each state (see Tables LI and LII). The separation between these states is usually small (0.05–0.08 eV) with CASPT2 (Refs. 161 and 193) and somewhat more pronounced with coupled cluster methods (current CC3/TZVP: 0.31 eV, CC3/ANO:³¹ 0.26 eV). We adopt the CC3 results with basis set correction as best estimates³¹ (1^1A_1 : 6.37 eV, 2^1B_2 : 6.57 eV, and 3^1A_1 : 7.91 eV). It should be noted, however, that a recent MS-CASPT2 study¹⁹³ arrives at much lower values (1^1A_1 : 5.82 eV, 2^1B_2 : 5.87 eV). The experimental optical spectrum shows two broad bands with maxima around 6.0 and 7.5 eV, but their assignment is difficult^{31,193} because of the presence of several valence and Rydberg states.

For the two lowest triplet states, the current CASPT2/TZVP and CC3/TZVP calculations give very similar excitation energies (within 0.04 eV) which are blueshifted by about 0.2–0.3 eV relative to the earlier CASPT2 data.¹⁶¹ We adopt the CC3/TZVP results as reference data (1^3B_2 : 4.48 eV and 1^3A_1 : 5.51 eV). They are somewhat higher than the reported electron impact data [1^3B_2 : 4.21 eV (Ref. 74) and 5.1 eV (Ref. 86)].

Imidazole (C_s , Tables XX and LIII). The valence electronic spectrum of imidazole contains $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. As in most azabenzenes, the lowest singlet excited state is of $n \rightarrow \pi^*$ type. The $n \rightarrow \pi^*$ excitation energies from the current CASPT2/TZVP calculations ($1^1A''$: 6.81 eV, $2^1A''$: 7.91 eV) are very close to the corresponding CC3/TZVP values, and about 0.3 eV higher than those from an early CASPT2 study.²⁰⁷ The description of the $\pi \rightarrow \pi^*$ singlet states is more complicated. The previous CASPT2 study found the two lowest such states at 6.72 and 7.15 eV, respectively, with strong mixing and intensity borrowing between the HOMO $\rightarrow$ LUMO, (HOMO–1 $\rightarrow$ LUMO), and (HOMO $\rightarrow$ LUMO+1) configurations. To the contrary, the current MS-CASPT2 treatment gives two clean states: the lowest $\pi \rightarrow \pi^*$ singlet state at 6.19 eV is dominated by the HOMO $\rightarrow$ LUMO excitation, while the second one at

6.93 eV is of (HOMO-1 $\rightarrow$ LUMO)+(HOMO $\rightarrow$ LUMO + 1) character, in agreement with the CC3 results. Experimentally, the ultraviolet spectrum of imidazole has only been measured in solution (e.g., in ethanol) showing two broad bands with maxima around 6.0 and 6.5 eV, respectively, that have been assigned to the two lowest $\pi \rightarrow \pi^*$ singlet transitions.¹¹⁶ For the triplet valence states, the current CASPT2/TZVP and CC3/TZVP calculations give almost identical excitation energies which tend to be about 0.3 eV higher than the previous CASPT2 values.²⁰⁷ We adopt the current CASPT2/TZVP and CC3/TZVP results as best estimates for the singlet and triplet states below 7 eV, respectively.

Pyridine (C_{2v} , Tables XXI, LIV, and LV). The published CASPT2 results for the $\pi \rightarrow \pi^*$ singlet states¹⁶⁵ are reproduced reasonably well by the current CASPT2/TZVP calculations, normally within 0.2 eV (except for high-lying 4^1A_1 and 3^1B_2 states where the TZVP basis seems insufficient due to the lack of diffuse functions), while the CC3/TZVP values tend to be somewhat higher (e.g., in the case of the 2^1A_1 and 3^1A_1 states). Among the many published computational studies on the $\pi \rightarrow \pi^*$ singlet states in pyridine, the EOM-CCSD/ $\tilde{T}$ and SAC-CI calculations with large basis sets^{213,275} would appear to be quite accurate: their results agree within 0.2 eV or better, they are similarly close to the previous and present CASPT2 results (with a slight red shift), and they match the available experimental gas-phase excitation energies (1^1B_2 : 4.99 eV, 2^1A_1 : 6.38 eV, 3^1A_1 : 7.22 eV) (Ref. 122) quite well. In the case of the two lowest $n \rightarrow \pi^*$ singlet states, the present CASPT2/TZVP and CC3/TZVP excitation energies agree within 0.1 eV, while exceeding those from the published CASPT2, EOM-CCSD/ $\tilde{T}$ and SAC-CI work^{165,213,275} by typically 0.3 eV. The experimental $n \rightarrow \pi^*$ excitation energies (1^1B_1 : 4.59 eV, 1^1A_2 : 5.43 eV) (Refs. 122 and 209) imply a splitting of more than 0.8 eV, whereas the various *ab initio* calculations give splittings of typically 0.3–0.5 eV and thus show some deviation from experiment.

Concerning the triplet valence states, the present CASPT2/TZVP and CC3/TZVP results generally agree well (mostly within 0.1 eV) whereas the published CASPT2 (Ref. 165) and SAC-CI (Ref. 275) excitation energies tend to be slightly lower (by about 0.1–0.3 eV). The available experimental values (1^3A_1 : 4.10 eV, 1^3B_2 : 4.84 eV) (Ref. 209) lie in the range of the *ab initio* data.

Among the published high-level *ab initio* studies for pyridine, the SAC-CI calculations²⁷⁵ employed the largest basis, and therefore we adopt the SAC-CI results as reference data. Given the similar performance of different treatments, other choices could also be justified (e.g., the use of CC3/TZVP values for the triplets).

Pyrazine (D_{2h} , Tables XXII and LVI). The current CASPT2/TZVP and CC3/TZVP results for the $\pi \rightarrow \pi^*$ states are in reasonable agreement with the early CASPT2 results¹⁶⁷ and the experimental gas-phase data.¹²² The broad intense band with a maximum at 7.67 eV is caused by transitions to the 2^1B_{1u} and 2^1B_{2u} states which are not resolved experimentally,¹²² consistent with small computed splittings

of the order of 0.1 eV. These two states are derived from the E_{1u} state in benzene whose degeneracy is lifted due to the presence of the two nitrogen atoms in the pyrazine ring. In the case of the $n \rightarrow \pi^*$ states, the current CASPT2/TZVP excitation energies are higher than the previous CASPT2 values¹⁶⁷ (by 0.2–0.5 eV), and the CC3/TZVP values are still higher (especially for the 1^1A_u and 1^1B_{1g} states where the deviation from CASPT2/TZVP is larger than usual). Experimentally well characterized is only the lowest $n \rightarrow \pi^*$ band between 3.8 and 4.2 eV.¹²²

There are a number of other previous *ab initio* studies on the excited states of pyrazine^{76,166,203,213,245} which have provided generally consistent results (with few minor exceptions). We adopt the high-level coupled cluster data from an EOM-CCSD($\tilde{T}$) study²¹³ as reference data.

Pyrimidine (C_{2v} , Tables XXIII and LVII). Some of the comments on pyrazine above apply also to pyrimidine and pyridazine since these three disubstituted azabenzenes are electronically similar and thus share similar features in their electronic spectra. The singlet excitation energies from CASPT2/TZVP are somewhat smaller than those from CC3/TZVP (by 0.1–0.5 eV, the larger deviations occur for the higher $\pi \rightarrow \pi^*$ states). Among the literature data, we adopt the coupled cluster results with noniterative triples and basis set corrections³³ as best theoretical estimates: they are within 0.1 eV of the CC3/TZVP values, and consistently somewhat higher than the available experimental data^{122,123} (by 0.1–0.4 eV). Their accuracy is claimed to be 0.1 eV.³³

Pyridazine (C_{2v} , Tables XXIV and LVIII). The early CASPT2 results¹⁶⁷ seem rather low compared with the recent coupled cluster results from the literature,^{213,245} especially for the $n \rightarrow \pi^*$ states. The current CASPT2/TZVP excitation energies are overall similar to the EOM-CCSD($\tilde{T}$) values.²¹³ The CC3/TZVP values are usually slightly higher (especially for the 1^1B_2 state) and rather close to the EOM-CCSD results.²¹³ We adopt the CASPT2/TZVP values below 6 eV, even though they are uniformly higher than the available experimental data.

s-Triazine (D_{3h} , Tables XXV and LIX). The current CASPT2/TZVP and CC3/TZVP results agree well with each other (typically within 0.2 eV). They are higher than the previous CASPT2 (Ref. 167) and EOM-CCSD($\tilde{T}$) values. They reproduce the available experimental data for the $1^1A'_2$ and $1^1A''_2$ states reasonably well, but seem to overestimate those for the $2^1A'_1$ state and the two $1^1E''$ states. For the latter two $n \rightarrow \pi^*$ transitions, the reported experimental values¹²² differ significantly from all available *ab initio* results so that the tentative experimental assignment should be reconsidered. We adopt the CASPT2/TZVP results below 6 eV as reference data for *s*-triazine.

s-Tetrazine (D_{2h} , Tables XXVI, LX and LXI). The spectrum of *s*-tetrazine shows a wide variety of valence excited states, with many $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the singlet and triplet manifolds.^{78,80,101,131,153} The low-lying $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states of *s*-tetrazine resemble those of the other azabenzenes. An exception is the strongly redshifted 1^1B_{3u} state which has $n \rightarrow \pi^*$ -character and absorbs in the visible region around 2.3 eV (Refs. 78 and 101) (CASPT2/

TZVP: 2.24 eV, CC3/TZVP: 2.53 eV). Generally speaking, the previous *ab initio* calculations at the CASPT2,¹⁶⁸ MRCI,¹³¹ and coupled cluster²⁹ level as well as the current CASPT2/TZVP and CC3/TZVP calculation yield a consistent pattern of state energies, with the usual shifts of a few tenths of eV between the different approaches. In most cases, the CASPT2/TZVP and CC3/TZVP excitation energies differ by less than 0.2 eV, with some larger deviations being found especially for the $\pi \rightarrow \pi^*$ singlet states (up to 0.5 eV for the $^1B_{1u}$ state).

As pointed out previously,¹⁶⁸ doubly excited states of $n, n \rightarrow \pi^*, \pi^*$ character appear both in the singlet and triplet manifolds at relatively low energies. These states are also identified in the present CASPT2/TZVP calculations, but they cannot be found in the coupled cluster treatments which do not cover such doubly excited states. For example, the lowest $^3B_{3g}$ state is located at 5.50 eV in CASPT2/TZVP (doubly excited) and at 7.44 eV in CC3/TZVP (singly excited). An additional $^3B_{2u}$ state with $n, n \rightarrow \pi^*, \pi^*$ character has been found at 6.21 eV in CASPT2/TZVP.

Considering the similarity between the different sets of *ab initio* data and their completeness, we adopt the CASPT2/TZVP and CC3/TZVP results as reference data for the singlet and triplet states below 6 eV, respectively.

3. Aldehydes, ketones, and amides

Formaldehyde (C_{2v} , Tables XXVII, XXVIII, and LXII). The lowest singlet excited state ($1^1A_2, n \rightarrow \pi^*$) and the two lowest triplet states ($1^3A_2, n \rightarrow \pi^*$ and $1^3A_1, \pi \rightarrow \pi^*$) are described consistently by all methods applied; the corresponding CASPT2/TZVP and CC3/TZVP excitation energies differ by 0.01–0.05 eV. A basis set convergence study at the CCSD and CC3 level (see Table XXVIII) indicates fast convergence, and we adopt the CC3/aug-cc-pVQZ values as reference data: 1^1A_2 3.88 eV, 1^3A_2 3.50 eV, and 1^3A_1 5.87 eV. They are in good agreement with the available experimental data (1^1A_2 3.79 eV, 1^2A_2 3.50 eV, and 1^3A_1 5.82 eV) from electron impact,⁸¹ and also with previous CASPT2,¹⁶⁹ CC3,¹⁹⁷ and MR-AQCC²⁶¹ results.

The high-lying valence excited singlet states are more difficult. The CASPT2/TZVP calculations indicate substantial configurational mixing for the $2^1A_1 \pi \rightarrow \pi^*$ state (with the ground state and with $\pi \rightarrow \pi^*$ double excitations), and it is well known that this state and the $1^1B_1 \sigma \rightarrow \pi^*$ state are plagued by strong Rydberg-valence mixing,²⁶¹ which can only be captured when using basis sets with more diffuse functions than available in TZVP. The present CCSD and CC3 results for these two states are indeed rather sensitive to the basis set (see Table XXVIII), and our best values from CC3/aug-cc-pVQZ (1^1B_1 9.04 eV, 2^1A_1 9.29 eV) are not yet fully converged. These values are somewhat lower than previous theoretical results (see Table LXII) including those from CASPT2¹⁶⁹ and MR-AQCC.²⁶¹ In view of this situation, the adopted “best” values (1^1B_1 9.1 eV, 2^1A_1 9.3 eV) have a large uncertainty (possibly 0.3 eV). Experimentally, the vertical transition to these two states could not yet be identified because of the strong Rydberg-valence mixing.²⁶¹ Moreover, according to the coupled cluster calculations, both the 2^1A_1 state at 9.29 eV and the 3^1A_1 state at 10.22 eV

(CC3/aug-cc-pVQZ) have $\pi \rightarrow \pi^*$ character, with a larger oscillator strength for the latter, so that there is no uniquely defined $\pi \rightarrow \pi^*$ valence transition in formaldehyde.

Acetone (C_{2v} , Tables XXIX and LXIII). The situation in acetone is similar to that in formaldehyde. The lowest singlet excited state ($1^1A_2, n \rightarrow \pi^*$) and the two lowest triplet states ($1^3A_2, n \rightarrow \pi^*$ and $1^3A_1, \pi \rightarrow \pi^*$) are again well described by all methods. We adopt the CC3/TZVP values (1^1A_2 4.40 eV, 1^3A_2 4.05 eV, 1^3A_1 6.03 eV) which are within 0.03 eV of the CASPT2/TZVP results. Assuming an analogous basis set convergence behavior as in the case of formaldehyde, these CC3 values should change by less than 0.1 eV upon basis set extension. There is good agreement with the corresponding electron impact data (1^1A_2 4.38 eV, 1^3A_2 4.16 eV, 1^3A_1 5.88 eV).⁸¹

The high-lying valence excited singlet states are less well characterized. Analogous problems occur as discussed for formaldehyde, e.g., with regard to configurational mixing. In the absence of recent accurate literature data, we derive our best estimate for the excitation energies by the assumption that basis set extension from TZVP to aug-cc-pVQZ causes the same changes in the CC3 energies for formaldehyde and acetone (hence, 1^1B_1 9.1 eV, 2^1A_1 9.4 eV).

***p*-Benzoquinone** (D_{2h} , Tables XXX and LXIV). In the singlet manifold, we focus on the two lowest $n \rightarrow \pi^*$ states ($1^1A_u, 1^1B_{1g}$), the lowest dark $\pi \rightarrow \pi^*$ state (1^1B_{3g}), and the two lowest bright $\pi \rightarrow \pi^*$ states ($1^1B_{1u}, 2^1B_{1u}$). The CASPT2 wave functions for the two $n \rightarrow \pi^*$ states contain a considerable amount of double excitations (10%), and the weight of the single excitations in CC3 is below 90% in all five cases (lowest in 2^1B_{1u} with 69%). Nevertheless, the CC3/TZVP results are still within 0.05 eV of the CASPT2/TZVP results for the $n \rightarrow \pi^*$ states, while they differ by around 0.3 eV for the $\pi \rightarrow \pi^*$ states. Under these circumstances, we adopt the CASPT2/TZVP excitation energies as reference data in the first four cases (1^1A_u 2.80 eV, 1^1B_{1g} 2.78 eV, 1^1B_{3g} 4.25 eV, 1^1B_{1u} 5.29 eV). These values are uniformly somewhat higher than those from previous CASPT2 studies,^{156,171} and reasonably close to the observed band maxima (2.7, 2.7, 4.4, and 5.4 eV, respectively).¹⁵⁶ The 2^1B_{1u} state (observed around 7.3 eV) is problematic not only in CC3 (see above), but also in CASPT2 which actually gives two close-lying valence $^1B_{1u}$ states in this region: the CASPT2/TZVP calculations place them at 7.35 and 7.91 eV, with the latter being much brighter, whereas the more intense $^1B_{1u}$ transition has previously been found at 7.08 eV (Ref. 171) and 7.18 eV.¹⁵⁶ In view of these inconsistencies, we do not provide a recommended value for the 2^1B_{1u} state energy.

The four lowest triplet states are all dominated by single excitations (weights of more than 95% in CC3), and we therefore adopt the CC3/TZVP energies as reference data. They are close to CASPT2/TZVP values, and generally somewhat higher than the published CASPT2 results.^{156,171}

Formamide (C_s , Tables XXXI and LXV). The current and previous^{172,229,234,270} theoretical excitation energies for the lowest $n \rightarrow \pi^*$ singlet state ($1^1A''$) lie in a narrow range between 5.61 and 5.76 eV. In the case of the lowest $\pi \rightarrow \pi^*$ singlet state ($2^1A'$), the present coupled cluster results

are all above 8.1 eV and thus significantly higher than the CASPT2 value of 7.44 eV which is close to previous CASPT2 (Ref. 172) and MRCI (Refs. 229 and 270) results. Since the weight of the single excitations in CC3 is only 88% for $2^1A'$, we prefer the CASPT2 value in this case. No such problems occur for the two corresponding triplet states where the CASPT2 and CC3 results agree well again because of the dominance of the single excitations (CC3 weights of 98%). We thus adopt as reference data the CASPT2/TZVP values for the two singlet states and the CC3/TZVP values for the two triplet states, which are all in good agreement with the available experimental data.^{88,136}

Acetamide (C_s , Tables XXXII and LXVI) and *Propanamide* (C_s , Tables XXXIII and LXVII). The lowest excitation energies do not change much in the series of primary amides, neither experimentally nor theoretically. The current CASPT2 and CC3 results agree well with each other in the case of the lowest $n \rightarrow \pi^*$ singlet excitation and the two lowest triplet excitations, whereas CC3 gives a considerably higher energy (by 0.4 eV) than CASPT2 for the lowest $\pi \rightarrow \pi^*$ singlet in acetamide and propanamide. The situation is analogous to formamide, and we thus make the same choice for the reference data (CASPT2/TZVP for singlets, CC3/TZVP for triplets).

4. Nucleobases

CC3/TZVP calculations were not feasible for the four nucleobases considered (cytosine, thymine, uracil, adenine). Our CC2/TZVP results compare well to recent CC2/aug-cc-pVTZ results for these molecules²⁵⁷ considering the differences in basis sets and geometries: our computed excitation energies are consistently slightly higher than the published ones (by 0.03–0.27 eV, on average by 0.15 eV). We favor the latter because of the use of an augmented basis. The CASPT2/TZVP results scatter around the CC2/aug-cc-pVTZ data (mean deviation of 0.07 eV, mean absolute deviation of 0.15 eV).

Cytosine (C_s , Tables XXXIV and LXVIII). The first excited singlet state ($2^1A'$) corresponds to the HOMO $\rightarrow$ LUMO excitation (78% weight in CASSCF). The wave functions of the next two $\pi \rightarrow \pi^*$ singlet states also contain large contributions from a single excitation (74% HOMO $\rightarrow$ LUMO in $3^1A'$ and 62% HOMO $\rightarrow$ LUMO+1 in $4^1A'$ according to CASSCF). These $^1A'$ states do not have significant double excitation character, and should thus be well described at the CC2 level.

The first $\pi \rightarrow \pi^*$ singlet lies below the first $n \rightarrow \pi^*$ singlet at all theoretical levels, by at least 0.2 eV (e.g., CASPT2/TZVP 4.68 versus 5.12 eV, CC2/TZVP 4.80 versus 5.01 eV, CC2/aug-cc-pVTZ 4.66 versus 4.87 eV,²⁵⁷ SAC-CI/cc-pVDZ 4.40 versus 4.90,²²² DFT-MRCI/TZVP 4.83 versus 5.02 eV.²³⁵) The second excited $n \rightarrow \pi^*$ singlet was found in an early CASPT2 study¹⁷³ at an energy of 6.53 eV, much higher than in our and other recent theoretical work^{196,235,257} with energies in the range of 5.2–5.5 eV (and the $2^1A''$ state below the $3^1A'$ state).

We adopt as best theoretical estimates for the low-lying states the CC2/aug-cc-pVTZ values of 4.66 eV ($2^1A'$), 5.62 eV ($3^1A'$), 4.87 eV ($1^1A''$), and 5.26 eV ($2^1A''$).²⁵⁷

For the higher $\pi \rightarrow \pi^*$ states, we favor the current CASPT2 values, but we do not include them as reference data because of the lack of diffuse functions in the TZVP basis.

Thymine (C_s , Tables XXXV and LXIX). Compared with the previous CASPT2 results,¹⁷⁴ the present CASPT2 excitation energies are generally blueshifted, typically by 0.1–0.3 eV for the $\pi \rightarrow \pi^*$ ($^1A'$) states and by 0.5–0.7 eV for the $n \rightarrow \pi^*$ ($^1A''$) states. In the CASPT2 wave functions, the singly excited configurations have weights of about 70%–80% in the case of the $^1A'$ states, while the near degeneracy of the n orbitals is reflected in a moderate configurational mixing for the $^1A''$ states. The CASPT2/TZVP and CC2/TZVP state orderings are consistent with each other (with almost equal energies for the three lowest $n \rightarrow \pi^*$ states). Both CASPT2/TZVP and CC2/TZVP predict the $1^1A''$ somewhat below the $2^1A'$ state, in line with CC2/aug-cc-pVTZ²⁵⁷ and SAC-CI/cc-pVDZ,²²² but in contrast to another recent CASPT2 study.²⁴²

We adopt as reference data the available CC2/aug-cc-pVTZ values which lie between our current CASPT2 and CC2 values.

Uracil (C_s , Tables XXXVI and LXX). Uracil is formally obtained from thymine by removal of the methyl substituent which lowers the HOMO energy and thus raises the excitation energy of transitions originating from the HOMO ($2^1A'$ and $4^1A'$). Otherwise, the electronic spectra of uracil and thymine are very similar. In the CASPT2 wave functions, the $^1A'$ states are again dominated by one singly excited configuration (weight around 70%). The CASPT2/TZVP and CC2/TZVP calculations again give similar results (virtually identical for the two lowest $n \rightarrow \pi^*$ states).

All theoretical calculations place the lowest $\pi \rightarrow \pi^*$ state ($2^1A'$) above the lowest $n \rightarrow \pi^*$ state ($1^1A''$), with an energy gap of 0.34 eV (CASPT2/TZVP), 0.61 eV (CC2/TZVP), 0.59 eV (CCSD/TZVP), 0.46 eV (CASPT2/ANO),¹⁷⁴ 0.55 eV (CC2/aug-cc-pVQZ),²⁵⁷ and 0.83 eV (DFT-MRCI/TZVPP).²⁰²

As in the analogous case of thymine, we adopt as reference data the published CC2 values which are available for uracil at the CC2/aug-cc-pVQZ level and which lie again between our current CASPT2 and CC2 values.

Adenine (C_s , Tables XXXVII and LXXI). An early CASPT2 study¹⁷⁵ gave excitation energies of more than 6 eV for the $n \rightarrow \pi^*$ states, about 1 eV higher than all more recent studies which place both the lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states around 5 eV. These two states ($1^1A''$ and $2^1A'$) are virtually degenerate (within 0.05 eV) in the current CASPT2/TZVP and CC2/TZVP calculations as well as at the CASPT2/6-31G*,²⁵¹ SAC-CI/cc-pVDZ,²²² and CIPSI/cc-pVDZ levels,²⁰⁵ while the $1^1A''$ state is slightly lower, by about 0.1 eV, in DFT-MRCI/TZVPP,²⁴⁷ CC2/aug-cc-pVTZ,²⁵⁷ and CASPT2/6-31G(d,p).²³⁶

The computed splitting between the two lowest $\pi \rightarrow \pi^*$ states ($2^1A'$ and $3^1A'$) states usually lies between 0.1 and 0.2 eV, both in the present calculations (0.09 eV CASPT2/TZVP, 0.20 eV CC2/TZVP) and in the published work (0.19 eV,²³⁶ 0.11 eV,²⁵¹ 0.14 eV,¹⁸³ 0.14 eV,²⁴⁷) whereas the two states are degenerate at the CC2/aug-cc-pVTZ level.²⁵⁷

For the sake of consistency with the other nucleobases,

TABLE III. Deviations in excitation energies of singlet excited states of all 28 benchmark molecules with respect to CASPT2/TZVP.

	Method			
	CC2	CCSD	CC3	CASPT2 ^a
Count ^b	152	152	121	152
Mean	0.29	0.49	0.20	-0.23
Abs. Mean	0.32	0.50	0.22	0.35
Std. Dev.	0.41	0.58	0.27	0.42
Maximum	1.25	1.62	0.83	1.02

^aFrom the literature, see Table I and Supporting Information.^bTotal number of considered states.

we again select the available CC2/aug-cc-pVTZ results as reference data. The differences between the CC2/aug-cc-pVTZ and CASPT2/TZVP excitation energies for adenine are less than 0.1 eV in most cases.

5. Comments on best estimates

Overall, we have selected best estimates for the vertical excitation energies of 104 singlet excited states and 63 triplet excited states in 28 benchmark molecules. In the case of the singlets, these best estimates were taken from published MRCI (9), MRMP (4), and coupled cluster (45) calculations with large basis sets as well as from the current CASPT2/TZVP (43) and CC3/TZVP (3) values. In the case of the triplets, they come from MRCI (9), MRMP (4), and coupled cluster (6) literature data as well as from the present CC3/TZVP (44) calculations.

The best estimates from this work are internally consistent in the sense that they were obtained using the same basis set (TZVP) and ground-state geometries optimized at a common level (MP2/6-31G*). The best estimates from the literature are more heterogeneous, and also of higher accuracy, because they were computed with different and larger basis sets (partly also with basis set extrapolation); in addition, they are often based on more accurate ground-state geometries (from experiment or from high-level *ab initio* calculations). In spite of this heterogeneity, we believe that the proposed set of “best” vertical excitation energies for a representative selection of organic chromophores will be useful for validation purposes and for the parameterization of new approximate methods for electronically excited states.

TABLE IV. Deviations in excitation energies of singlet excited states of the benchmark set with respect to CASPT2/TZVP, for states where the T_1 (CC3) percentage exceeds 90%.

	Method			
	CC2	CCSD	CC3	CASPT2 ^a
Count ^b	57	57	45	57
Mean	0.17	0.36	0.19	-0.18
Abs. Mean	0.22	0.37	0.22	0.36
Std. Dev.	0.27	0.42	0.26	0.44
Maximum	0.64	0.81	0.49	0.99

^aFrom the literature, see Table I and Supporting Information.^bTotal number of considered states.

It is obvious that this set of theoretical reference data can be improved by future higher-level calculations, and also extended by adding more benchmark molecules. We thus consider the present best estimates as a first-generation benchmark set that will hopefully be superseded by more accurate theoretical data in the future.

B. Statistical evaluation

This section is devoted to statistical comparisons between the present CASPT2, CC2, CCSD, and CC3 results. It covers a total of 223 excited states, i.e., the 152 singlets from Table I and the 71 triplets from Table II. The goal of the statistical analysis is to quantify intrinsic differences (or similarities) between the CASPT2, CC2, CCSD, and CC3 approaches. This should be possible because the present calculations for a given molecule employ the same basis set (TZVP) and geometry (MP2/6-31G*). Given the methodological focus of this section, the statistical evaluation also includes higher-lying excited states (e.g., above 7 eV) where the TZVP results are not expected to be realistic (i.e., close to experiment) because of the lack of diffuse functions.

As discussed in the preceding sections, we normally prefer from our current work the CASPT2/TZVP results for the singlets and the CC3/TZVP results for the triplets. The CC calculations for the singlets suffer from low single excitation weights for a number of states (see Table I), and CC3 calculations were not feasible for the nucleobases, so that the CASPT2/TZVP data form our best consistent set for the singlets. Since the CASPT2/TZVP and CC3/TZVP results for the triplets are generally quite close to each other (see Table II), we have decided to adopt the current CASPT2/TZVP results throughout this section as reference data, for the purpose of statistical analysis. In addition, we also compare the CC results among themselves using CC3 as reference.

Earlier CASPT2 results from the Roos group^{22,23,159–175} are available for all benchmark molecules (see Tables I and II). Although these were obtained with different basis sets and geometries, it is still instructive to compare them with the present results, and they are thus included in the statistical evaluation. We do not attempt systematic comparisons with the available experimental data (see Tables XXVIII–LXXI), but we note that the vertical excitation energies from the earlier CASPT2 work are often quite close to the absorption maxima of the experimental spectra.

TABLE V. Deviations in excitation energies of singlet excited $n \rightarrow \pi^*$ states with respect to CASPT2/TZVP.

	Method			
	CC2	CCSD	CC3	CASPT2 ^a
Count ^b	47	47	35	47
Mean	0.09	0.38	0.10	-0.32
Abs. Mean	0.18	0.41	0.13	0.44
Std. Dev.	0.26	0.52	0.18	0.49
Maximum	0.90	1.62	0.49	0.99

^aFrom the literature, see Table I and Supporting Information.^bTotal number of considered states.

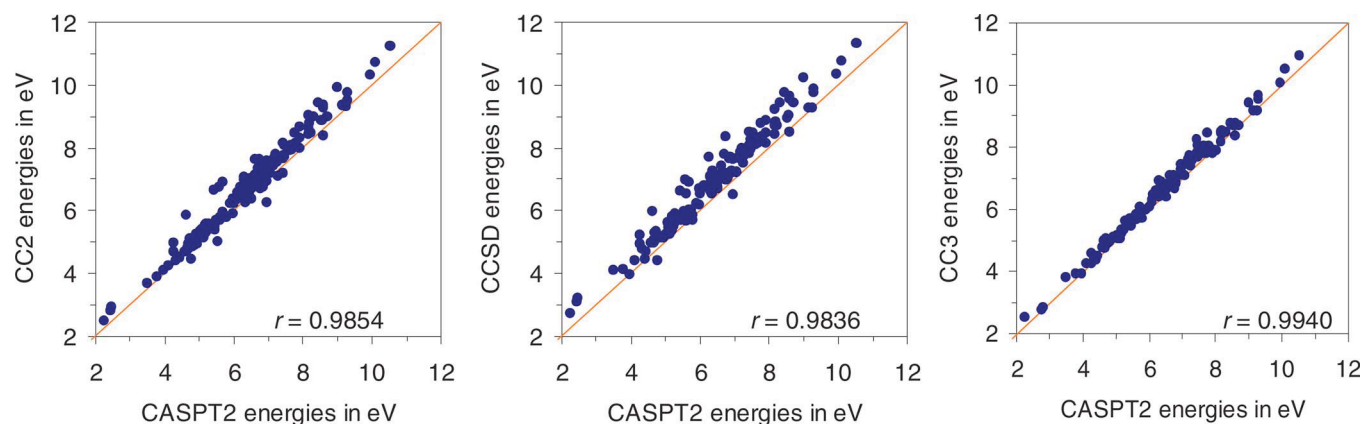


FIG. 3. (Color online) Correlation plots for all calculated singlet excited states: CC/TZVP vs CASPT2/TZVP vertical excitation energies.

1. Singlet states

The statistical results for the vertical excitation energies of the singlet excited valence states are given in Table III which lists mean, absolute mean, standard, and maximum deviations with respect to the CASPT2/TZVP results. Figure 3 shows the corresponding correlations between the CC/TZVP and CASPT2/TZVP results with the associated correlation coefficients r , and Fig. 4 provides a histogram of the deviations between CC3/TZVP and CASPT2/TZVP. The comparisons cover all available singlets (152 for CC2 and CCSD, 121 for CC3).

It is obvious from Figs. 3 and 4 that the excitation energies from CC/TZVP are generally higher than those from CASPT2/TZVP, typically by 0.3 eV for CC2, 0.5 eV for CCSD, and 0.2 eV for CC3 (see Table III, note the small difference between the mean and absolute mean deviations for these methods). By contrast, the earlier CASPT2 results tend to be lower than the present CASPT2/TZVP values, on average by more than 0.2 eV.

It is gratifying that the highest-level CC results (CC3) are closest to the CASPT2 reference data. CC2 outperforms CCSD in comparisons with CASPT2 and CC3. In general, CCSD seems to overestimate the excitation energies signifi-

cantly (on average at least 0.2 eV higher than with any of the other methods). As pointed out before, CC2 and CCSD are not expected to be reliable for states with considerable double excitation character, and particularly large deviations are indeed found for such singlet excited states. For example, in the case of CC2/TZVP, the three largest deviations from CASPT2/TZVP occur for the 2^1A_g states of all-*E*-hexatriene (+1.25 eV), all-*E*-octatetraene (+1.23 eV), and *E*-butadiene (+1.00 eV). For these states with strong double excitation contributions, the deviations are similarly large for CCSD/TZVP, and much reduced for CC3/TZVP (see Table I). Excluding such problematic states is thus expected to improve the performance of CC2 and CCSD. This is indeed found: performing the statistical analysis only for singlet excited states that are dominated by single excitations (CC3 weights of more than 90%) reduces the deviations for CC2 and CCSD strongly, without much affecting CC3 (see Table IV).

Figure 5 shows separate histograms for the deviations between CC3/TZVP and CASPT2/TZVP energies for singlet $\pi \rightarrow \pi^*$ (left) and $n \rightarrow \pi^*$ (right) excited states. It is evident that there is closer agreement for the $n \rightarrow \pi^*$ states. This is confirmed and quantified by the statistical analysis in Table

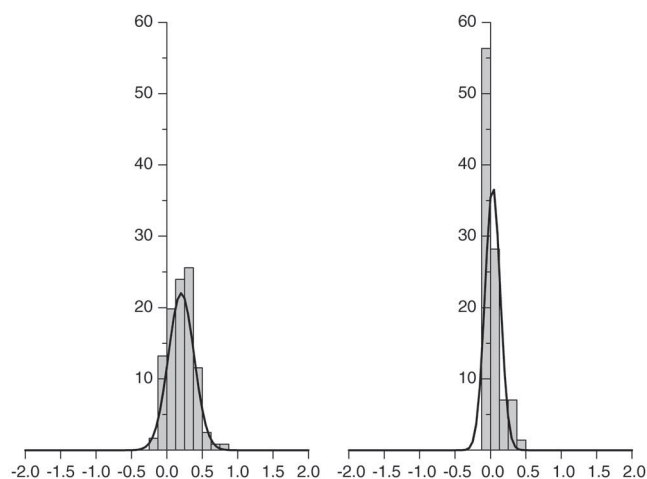


FIG. 4. Histogram for the frequency of deviation (CC3/TZVP vs CASPT2/TZVP, in%) of all calculated singlet (left) and triplet (right) excited states. The normal distribution of the deviation is also shown.

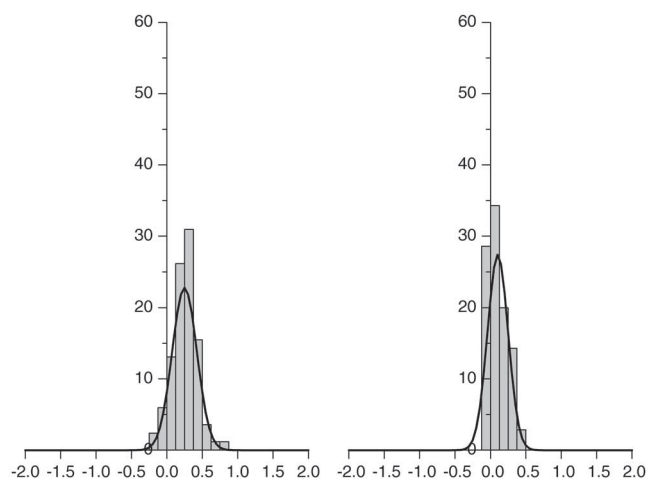


FIG. 5. Histogram of the frequency of deviation (CC3/TZVP vs CASPT2/TZVP, in%) of all calculated singlet $\pi \rightarrow \pi^*$ (left) and $n \rightarrow \pi^*$ (right) excited states. The normal distribution of the deviation is also shown.

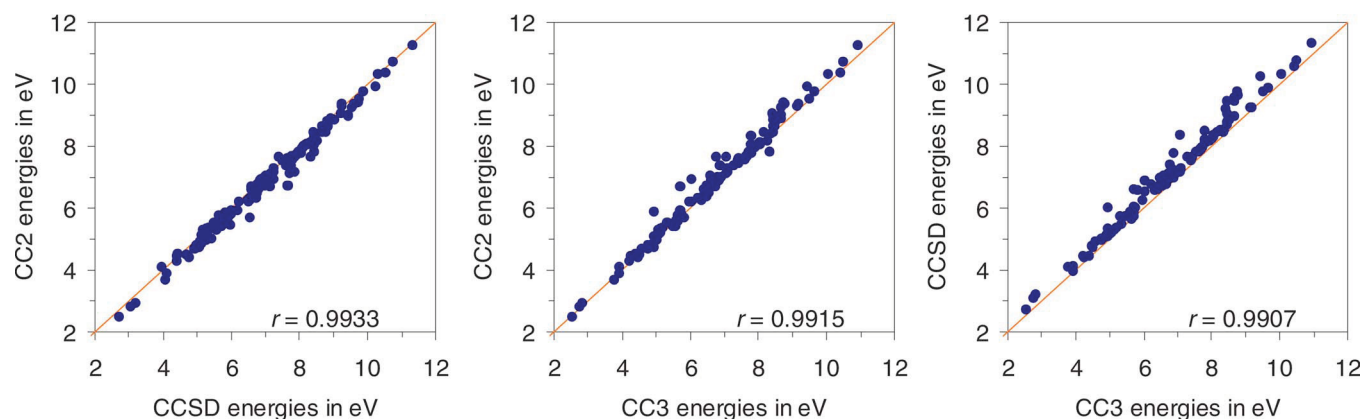


FIG. 6. (Color online) Correlation plots for all calculated singlet excited states: Coupled cluster vertical excitation energies.

V. For these states, the deviations from CASPT2/TZVP are typically 0.1–0.2 eV for CC2/TZVP, 0.4 eV for CCSD/TZVP, and only 0.1 eV for CC3/TZVP.

Figure 6 shows the correlations between the coupled cluster results. The left and the right plots emphasize again that the excitation energies from CCSD tend to be higher than those from CC2 and CC3. In the correlation between the CC2 and CC3 results (center plot) there are positive and negative deviations over the whole range. On average, the CC3 results are thus better reproduced by CC2 than by CCSD: the mean absolute deviations are 0.07 eV for CC2 and 0.25 eV for CCSD, and the individual CC2 results are closer to CC3 in 78% of the cases.

2. Triplet states

The statistical results for the 71 investigated excited triplet states are summarized in Table VI and displayed graphically in Figs. 4 and 7. It is evident at first sight that the computed vertical excitation energies are generally in excellent agreement. This holds especially for the CASPT2/TZVP and CC3/TZVP results which usually agree to better than 0.1 eV (mean absolute deviation of 0.08 eV). CCSD/TZVP and CC2/TZVP differ somewhat more from CASPT2/TZVP, but the mean absolute deviations are still quite small (0.16 and 0.19 eV, respectively). The CC3 and CCSD results scatter around the CASPT2/TZVP data, while the CC2 energies

tend to be slightly higher in general. By contrast, the earlier CASPT2 energies are systematically lower, on average by almost 0.3 eV (see Table VI).

Large deviations between the present CASPT2/TZVP and CC/TZVP results for the triplets are rare. The maximum deviation with CC3 concerns the 2^3B_2 state of pyridine (+0.38 eV), and there are four deviations exceeding 0.2 eV in the case of *s*-tetrazine. These are exceptions, however, since the agreement is better than 0.1 eV for the vast majority of states.

Comparing the coupled cluster results among themselves, one notes an internal consistency that is much more pronounced for the triplets than previously found for the singlets. This is not surprising since the triplet states in our benchmark set are all dominated by single excitations (see Table II) so that CC2 and CCSD are expected to perform well.

C. Oscillator strengths

It would clearly be desirable to have reference data not only for vertical excitation energies, but also for oscillator strengths of dipole-allowed vertical transitions. Table VII collects the corresponding results from the present CASPT2, CC2, and CCSD calculations with the TZVP basis. It also contains the earlier CASPT2 results from the Roos group^{22,23,159–175} and the range of published values from

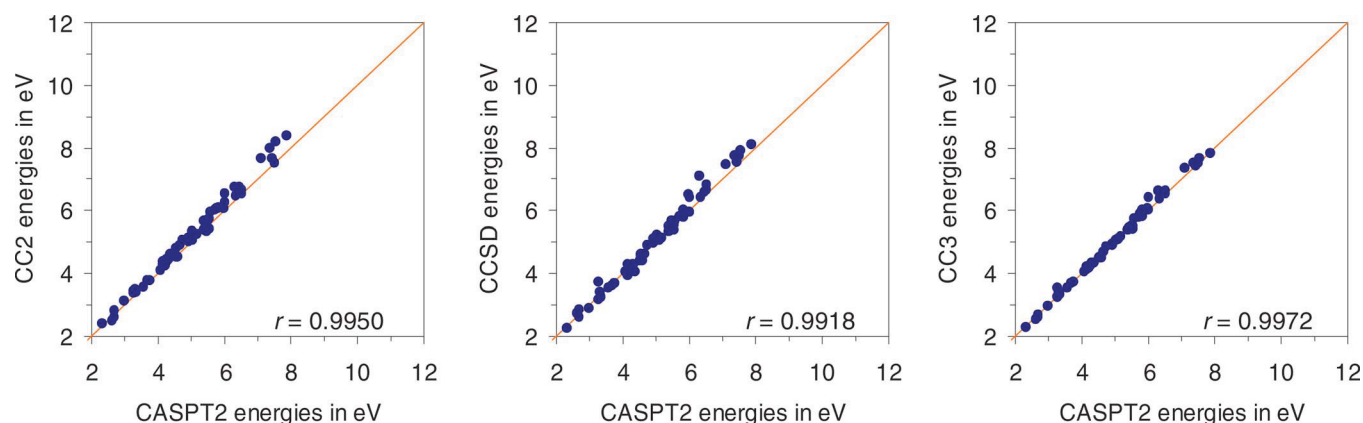


FIG. 7. (Color online) Correlation plots for all calculated triplet excited states: CC/TZVP vs CASPT2/TZVP vertical excitation energies.

TABLE VI. Deviation in excitation energies of triplet excited states of 19 benchmark molecules with respect to CASPT2/TZVP.

	Method			
	CC2	CCSD	CC3	CASPT2 ^a
Count ^b	71	71	71	71
Mean	0.18	0.08	0.03	-0.28
Abs. Mean	0.19	0.16	0.08	0.28
Std. Dev.	0.24	0.22	0.11	0.32
Maximum	0.62	0.80	0.38	0.72

^aFrom the literature, see Table II and Supporting Information.^bTotal number of considered states.

other *ab initio* work (see Tables XXXVIII–LXXI for the origin of these data and for references).

We have not attempted to derive best estimates for these oscillator strengths, for the following reasons: First, compared with excitation energies, much less effort has been spent in the literature on calculating accurate oscillator strengths. Many of the *ab initio* studies that served as source of accurate reference energies in the present work do not even quote oscillator strengths, while others provide them only at lower theoretical levels. As a consequence, the published values often span a wide range, and their convergence with regard to correlation method and basis set is rarely established for the chosen benchmark molecules. Second, in our own calculations, we find variations in the computed oscillator strengths that seem too large for defining realistic best estimates. Moreover, in the absence of a CC3 code that provides oscillator strengths, we cannot check the convergence of the coupled cluster results. Given this situation, we merely document the available data and make some qualitative comments.

Inspection of Table VII shows that all methods give the same qualitative picture for the distribution of the oscillator strength. Weak transitions with almost vanishing intensity are identified consistently, and the computed intensity order is usually the same for a given molecule.

Figure 8 shows the correlations between the oscillator strengths from the current calculations. Comparing the results with each other, CC2/TZVP and CCSD/TZVP generally

yield quite similar oscillator strengths, with no noticeable trend for systematic deviations. In the majority of cases, the CASPT2/TZVP oscillator strengths are higher than the coupled cluster results.

Comparisons with literature data are hampered by the differences in the computational methodology, especially with regard to the basis set, which are expected to affect the computed oscillator strengths strongly. Given this caveat, it is reassuring that the earlier CASPT2 values from the Roos group and the other published *ab initio* values are generally in the same range as those from our present calculations (see Table VII). The earlier CASPT2 oscillator strengths scatter around the current CASPT2/TZVP values, and there is no firm trend (see Fig. 8).

V. CONCLUSIONS

We have presented the results from extensive CASPT2 and coupled cluster calculations on the valence excited states of 28 benchmark molecules that are representative examples of organic chromophores. Comparison of these data with published results from high-level *ab initio* calculations has allowed us to propose best estimates for the vertical excitation energies of 104 singlet and 63 triplet states. We expect this benchmark set to be useful for validation and development purposes, and anticipate future improvements and extensions of this set through further high-level calculations. Analogous best estimates for oscillator strengths are desirable.

Since the current CASPT2 and coupled cluster calculations were performed with a consistent setup (same basis set and geometry, standard CASPT2 conventions) the results may be compared directly. For the 71 triplet states considered, there is excellent agreement between the CASPT2 and CC3 vertical excitation energies, with a mean absolute deviation of only 0.08 eV. The agreement is still remarkably good for the 121 singlet states with CC3 results (mean absolute deviation of 0.20 eV). In the case of the triplets, the CC3 single excitation weights are all above 90% (mostly above 95%), and hence all coupled cluster methods perform well. In the case of the singlets, there are a number of states with strong double excitation contributions in our benchmark set,

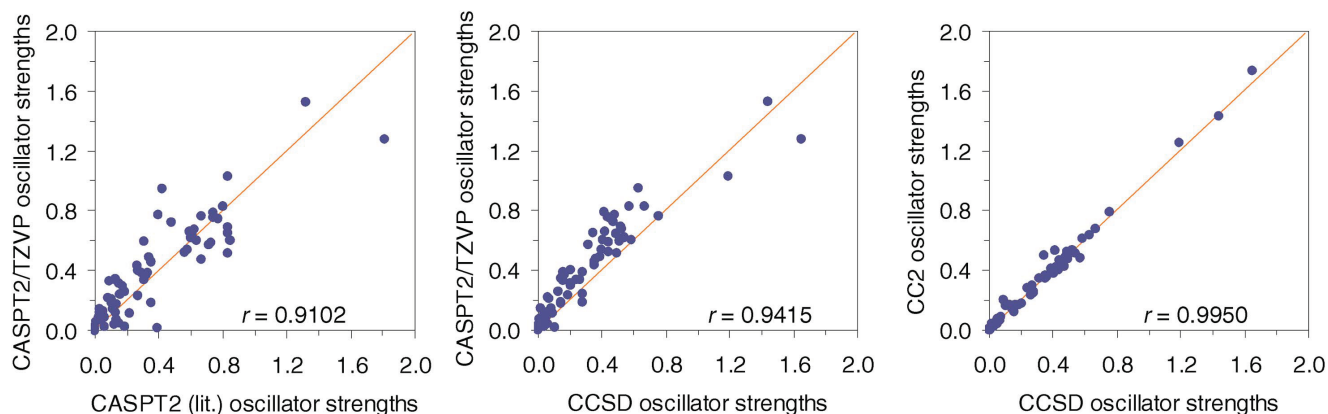


FIG. 8. (Color online) Correlation plots for all dipole-allowed oscillator strengths: CASPT2 (literature) vs CASPT2/TZVP, CCSD/TZVP vs CASPT2/TZVP and CCSD/TZVP vs CC2.

TABLE VII. Oscillator strengths f for allowed vertical singlet transitions in the benchmark molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c	Lit. ^d
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.360	0.513	0.431	0.410	0.358–0.494
<i>E</i> -Butadiene	$1^1B_u (\pi \rightarrow \pi^*)$	0.686	0.783	0.809	0.776	0.52–0.803
all- <i>E</i> -Hexatriene	$1^1B_u (\pi \rightarrow \pi^*)$	0.85	1.045	1.272	1.213	0.655–1.154
all- <i>E</i> -Octatetraene	$1^1B_u (\pi \rightarrow \pi^*)$	1.832	1.299	1.757	1.665	1.382
Cyclopropene	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.010	0.010	0.001	0.001	
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.101	0.234	0.086	0.083	
Cyclopentadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.148	0.144	0.110	0.097	0.099–0.157
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.000	0.001	0.011	0.008	0.001–0.019
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.442	0.965	0.658	0.648	0.025–0.538
Norbornadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.008	0.092	0.023	0.029	
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.343	0.393	0.185	0.187	
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.000	0.000	0.000	0.000	
Benzene	$1^1E_{1u} (\pi \rightarrow \pi^*)$	0.82	0.847	0.694	0.686	0.323–1.33
Naphthalene	$1^1B_{3u} (\pi \rightarrow \pi^*)$	0.001	0.001	0.000	0.000	0.000
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.050	0.137	0.094	0.083	0.082
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	1.337	1.548	1.450	1.461	1.326
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.313	0.402	0.272	0.294	0.268
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	0.848	0.708	0.548	0.538	0.840
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	0.048	0.008	0.010	0.014	0.067
Furan	$1^1B_2 (\pi \rightarrow \pi^*)$	0.154	0.199	0.172	0.159	0.144–0.185
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.002	0.008	0.003	0.001	0.000–0.011
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.416	0.793	0.506	0.501	0.194–0.494
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	0.020	0.031	0.006	0.005	0.000–0.036
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.125	0.205	0.182	0.166	0.099–0.99
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.326	0.613	0.532	0.527	0.176–0.706
Imidazole	$1^1A'' (n \rightarrow \pi^*)$	0.011	0.010	0.003	0.005	
	$2^1A' (\pi \rightarrow \pi^*)$	0.126	0.229	0.088	0.088	0.080
	$3^1A'' (\pi \rightarrow \pi^*)$	0.143	0.062	0.085	0.081	0.070
	$2^1A'' (n \rightarrow \pi^*)$	0.013	0.019	0.006	0.004	
	$4^1A' (\pi \rightarrow \pi^*)$	0.594	0.555	0.406	0.420	
Pyridine	$1^1B_2 (\pi \rightarrow \pi^*)$	0.018	0.044	0.025	0.022	0.023–0.040
	$1^1B_1 (n \rightarrow \pi^*)$	0.009	0.009	0.005	0.006	0.005–0.01
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.005	0.004	0.021	0.015	0.006–0.021
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.82	0.849	0.489	0.590	0.513–0.67
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.64	0.691	0.549	0.548	0.407–0.65
	$4^1A_1 (\pi \rightarrow \pi^*)$	0.03	0.000	0.000	0.002	
	$3^1B_2 (\pi \rightarrow \pi^*)$	0.158	0.089	0.012	0.014	
Pyrazine	$1^1B_{3u} (n \rightarrow \pi^*)$	0.01	0.012	0.007	0.008	0.01
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.07	0.123	0.070	0.067	0.08
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.08	0.107	0.096	0.074	0.06
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.76	0.774	0.424	0.458	0.37
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.66	0.622	0.400	0.423	0.33
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	0.00	0.000	0.000	0.000	
	$2^1A_g (\pi \rightarrow \pi^*)$	0.00	0.000	0.000	0.000	
Pyrimidine	$1^1B_1 (n \rightarrow \pi^*)$	0.02	0.013	0.006	0.007	0.007–0.01
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.001	0.049	0.023	0.022	0.01–0.026
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.05	0.164	0.062	0.038	0.017–0.03
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.58	0.540	0.446	0.461	
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.79	0.768	0.476	0.470	0.41–0.499
	$3^1B_2 (\pi \rightarrow \pi^*)$	0.06	0.000	0.000	0.000	
	$4^1A_1 (\pi \rightarrow \pi^*)$	0.14	0.000	0.000	0.000	

TABLE VII. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c	Lit. ^d
Pyridazine	1 ¹ B ₁ (<i>n</i> → π^*)	0.01	0.010	0.006	0.007	
	2 ¹ A ₁ (π → π^*)	0.009	0.027	0.014	0.014	
	2 ¹ B ₁ (<i>n</i> → π^*)	0.008	0.008	0.005	0.005	
	1 ¹ B ₂ (π → π^*)	0.003	0.115	0.009	0.006	
	2 ¹ B ₂ (π → π^*)	0.75	0.603	0.489	0.459	
	3 ¹ A ₁ (π → π^*)	0.50	0.742	0.444	0.494	
<i>s</i> -Triazine	1 ¹ A ₂ ' (<i>n</i> → π^*)	0.015	0.021	0.017	0.018	0.02–0.027
	1 ¹ E' (π → π^*)	0.61	0.680	0.441	0.437	0.92
	2 ¹ E' (π → π^*)	0.21	0.044	0.000	0.000	
<i>s</i> -Tetrazine	1 ¹ B _{3u} (<i>n</i> → π^*)	0.013	0.013	0.007	0.009	0.007–0.012
	1 ¹ B _{2u} (π → π^*)	0.045	0.110	0.046	0.047	0.052–0.095
	2 ¹ B _{3u} (<i>n</i> → π^*)	0.017	0.021	0.011	0.012	0.01–0.018
	1 ¹ B _{1u} (π → π^*)	0.001	0.136	0.017	0.003	0.00–0.054
	2 ¹ B _{1u} (π → π^*)	0.687	0.496	0.376	0.381	0.39–0.630
	2 ¹ B _{2u} (π → π^*)	0.733	0.588	0.368	0.333	0.45–0.755
Formaldehyde	1 ¹ B ₁ (σ → π^*)	0.01	0.013	0.079	0.074	0.000–0.001
	2 ¹ A ₁ (π → π^*)	0.28	0.451	0.368	0.374	0.063–0.100
Acetone	1 ¹ B ₁ (σ → π^*)	0.010	0.011	0.000	0.000	0.003
	2 ¹ A ₁ (π → π^*)	0.326	0.358	0.298	0.256	0.255
<i>p</i> -Benzoquinone	1 ¹ B _{3g} (π → π^*)	0.000	0.000	0.000	0.000	
	1 ¹ B _{1u} (π → π^*)	0.616	0.638	0.538	0.558	0.636–0.704
	1 ¹ B _{3u} (<i>n</i> → π^*)	0.000	0.000	0.000	0.001	0.000
	1 ¹ B _{2u} (π → π^*)	0.022	0.016	0.000	0.000	
	2 ¹ B _{1u} (π → π^*)	0.624	0.660	0.544	0.509	0.693
	3 ¹ B _{1u} (π → π^*)	0.030	0.079	0.000	0.000	
Formamide	1 ¹ A'' (<i>n</i> → π^*)	0.001	0.001	0.001	0.001	0.000–0.001
	2 ¹ A' (π → π^*)	0.371	0.479	0.385	0.371	0.149–0.338
	3 ¹ A' (π → π^*)	0.131	0.163	0.010	0.102	
Acetamide	1 ¹ A'' (<i>n</i> → π^*)	0.001	0.001	0.001	0.001	
	2 ¹ A' (π → π^*)	0.292	0.424	0.199	0.223	
	3 ¹ A' (π → π^*)	0.179	0.263	0.279	0.299	
Propanamide	1 ¹ A'' (<i>n</i> → π^*)	0.001	0.001	0.000	0.000	
	2 ¹ A' (π → π^*)	0.346	0.405	0.138	0.108	
	3 ¹ A' (π → π^*)	0.205	0.275	0.189	0.150	
Cytosine	2 ¹ A' (π → π^*)	0.061	0.093	0.049	0.058	0.052–0.080
	1 ¹ A'' (<i>n</i> → π^*)	0.005	0.003	0.001	0.002	0.001–0.002
	3 ¹ A' (π → π^*)	0.108	0.352	0.165	0.178	0.138–0.181
	4 ¹ A' (π → π^*)	0.863	0.623	0.632	0.608	
	2 ¹ A'' (<i>n</i> → π^*)	0.001	0.002	0.002	0.000	0.001–0.003
	5 ¹ A' (π → π^*)	0.147	0.366	0.168	0.159	
Thymine	6 ¹ A' (π → π^*)	0.239	0.132	0.223	0.112	
	1 ¹ A'' (<i>n</i> → π^*)	0.00	0.000	0.000	0.000	
	2 ¹ A' (π → π^*)	0.17	0.334	0.197	0.222	0.18
	3 ¹ A' (π → π^*)	0.17	0.067	0.080	0.071	0.04
	2 ¹ A'' (<i>n</i> → π^*)	0.00	0.000	0.000	0.000	
	4 ¹ A' (π → π^*)	0.15	0.356	0.250	0.285	0.18
	3 ¹ A'' (<i>n</i> → π^*)	0.00	0.000	0.000	0.000	
	4 ¹ A'' (<i>n</i> → π^*)	0.00	0.000	0.000	0.000	
Uracil	5 ¹ A' (π → π^*)	0.85	0.672	0.515	0.361	
	6 ¹ A' (π → π^*)	0.00	0.004	0.000	0.000	
	1 ¹ A'' (<i>n</i> → π^*)	0.00	0.000	0.000	0.000	
	2 ¹ A' (π → π^*)	0.19	0.320	0.197	0.224	0.18–0.26
	3 ¹ A' (π → π^*)	0.08	0.047	0.058	0.061	0.04–0.05

TABLE VII. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^c	CCSD ^c	Lit. ^d
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.001	
	3 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.29	0.249	0.188	0.209	0.035–0.17
	4 ¹ A'' ($n \rightarrow \pi^*$)	0.00	0.000	0.000	0.000	
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.76	0.804	0.547	0.430	0.51
Adenine	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.070	0.146	0.037	0.002	0.004–0.03
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.370	0.201	0.276	0.297	0.17–0.36
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.001	0.000	0.000	0.001–0.007
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.851	0.538	0.496	0.513	0.51
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.159	0.001	0.085	0.070	
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.002	0.000	0.000	0.003–0.005
	6 ¹ A' ($\pi \rightarrow \pi^*$)	0.565	0.010	0.320	0.286	
	7 ¹ A' ($\pi \rightarrow \pi^*$)	0.406	0.037	0.177	0.122	

^aData from publications by the Roos group in the 1990s. See Supporting Information for references.

^bCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.

^cCalculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.

^dRange of literature values. See Tables XXXVIII–LXXI in Supporting Information for details and references.

where CC2 and CCSD fail; excluding these states improves the overall agreement between the CASPT2 and coupled cluster results. According to the statistical analysis with regard to CASPT2 and CC3 reference data, CC2 outperforms CCSD in the case of the singlets, and is of similar quality for the triplets. It should be noted in this context, however, that our benchmark set, while being reasonably diverse, only consists of closed-shell organic molecules and that the behavior of CC2 may deteriorate in electronically more demanding cases such as open-shell species or transition metal complexes.

The present CASPT2 vertical excitation energies are typically 0.2–0.3 eV higher than the earlier CASPT2 values from the Roos group. This reduces the differences to the coupled cluster results appreciably that have been debated in the literature, while deteriorating the overall agreement with the observed band maxima which are generally closer to the earlier than to the present CASPT2 results.

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Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3. – Supporting Information –

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APPENDIX A: DOCUMENTATION OF OWN RESULTS: TABLES VIII TO XXXVII

1. Unsaturated Aliphatic Hydrocarbons

TABLE VIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of ethene, obtained at the ground state MP2/6-31G* equilibrium geometry.

State	Exp.	CASPT2 ^{22,23}		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle x^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)						11.6					
Singlet states											
1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.66 ^c , 7.8 ^d , 8.0 ^e	7.98	0.360	8.62	0.513	14.2	8.40	0.431	8.51	0.410	8.37
Triplet states											
1^3B_{1u} ($\pi \rightarrow \pi^*$)	4.36 ^f , 4.6 ^g	4.39		4.60	0.136	11.7	4.52		4.42		4.48

^aThe active space is (01000001)2. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Highest root included: 1^1A_g , 1^1B_{1u} , 1^3B_{1u} . Increasing the active space to (8, 11)²³ decreases the excitation energy to 8.44 eV (1^1A_g , 1^1B_{1u}).

^bExpectation value of x^2 in a.u.

^cFrom Ref.⁹⁰, band maximum in optical spectrum.

^dFrom Ref.⁷¹, with correction for zero-point effects.

^eFrom Ref.^{92,126,149}, with correction for non-adiabatic effects.

^fFrom Ref.¹⁵⁸, band maximum in electron impact spectrum.

^gFrom Ref.¹⁵⁴, Figure 14.

TABLE IX: Vertical excitation energies ΔE (eV) of the singlet and triplet B_{1u} states of ethene with different basis sets obtained at the ground state MP2/6-31G* equilibrium geometry.

Basis set	$1^1B_{1u}^a$				$1^3B_{1u}^a$			
	CASPT2 ^b	CASPT2 ^c	CCSD	CC3	CASPT2 ^b	CASPT2 ^c	CCSD	CC3
cc-pVDZ	8.71	—	8.85	8.72	4.54	—	4.50	4.54
TZVP	8.62	8.44	8.51	8.37	4.60	4.60	4.42	4.48
cc-pVTZ	8.40	8.27	8.44	8.31	4.50	4.50	4.45	4.52
cc-pVQZ	8.34	8.10	8.27	8.15	4.49	4.50	4.44	4.51
cc-pV5Z	8.38	8.00	8.14	8.01	4.53	4.53	4.43	4.51
aug-cc-pVDZ	8.37	7.91	8.02	7.92	4.49	4.49	4.45	4.50
aug-cc-pVTZ	8.45	7.86	8.00	7.89	4.47	4.48	4.43	4.50
aug-cc-pVQZ	8.50	7.88	8.01	7.89	4.57	4.57	4.43	4.50
aug-cc-pV5Z	8.52	7.85	8.01	7.88	4.47	4.48	4.43	4.50
d-aug-cc-pVDZ	8.51	7.94	7.99	7.89	4.50	4.50	4.45	4.50
d-aug-cc-pVTZ	8.58	7.93	7.99	7.88	4.50	4.51	4.43	4.50
d-aug-cc-pVQZ	8.56	7.88	8.00	7.88	4.48	4.49	4.43	4.50
d-aug-cc-pV5Z	8.62	7.83			4.48	4.49		

^aWith respect to the 1^1A_g ground state.

^bStandard active space (01000001)2. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Highest root included: 1^1A_g , 1^1B_{1u} , 1^3B_{1u} .

^cActive space (25020425)8 of symmetry as shown above. Highest root included: 1^1A_g , 3^1B_{1u} , 1^3B_{1u} .

TABLE X: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of *E*-butadiene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ²³		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)						21.8					
Singlet states											
1^1B_u (V)	5.73 ^c , 5.92 ^d	6.23	0.686	6.47 ^f	0.783	22.6	6.49	0.809	6.72	0.776	6.58
2^1A_g (V)		6.27		6.63		22.5	7.63		7.42		6.77
Triplet states											
1^3B_u	3.22 ^e	3.20		3.34		21.5	3.34		3.25		3.32
1^3A_g	4.91 ^e	4.89		5.16		21.4	5.25		5.14		5.17

^aThe active space is (0 2 2 0) 4. In parenthesis: number of active orbitals of symmetry $a_g b_g a_u b_u$, and number of active electrons. Highest root included: 3^1A_g , 2^1B_u , 1^3A_g , 1^3B_{1u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref.⁹⁷, 0-0 transition.

^dFrom Ref.^{79,94,102,104,155}, band maximum.

^eFrom Ref.^{94,104}, band maximum in electron impact spectrum.

^fDecreases to 6.25 eV when using a larger active space (0 3 3 0) 4 and averaging over three 1^1B_u states. Analogous calculation with IPEA=0: 5.94 eV.

TABLE XI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of all-*E*-hexatriene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ²³		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)						31.5					
Singlet states											
1^1B_u (V)	4.93 ^c	5.01	0.85	5.31 ^f	1.045	32.1	5.41	1.272	5.72	1.213	5.58
2^1A_g (V)	5.21 ^d	5.20		5.42		31.4	6.67		6.61		5.72
Triplet states											
1^3B_u	2.61 ^e	2.55		2.71		31.4	2.78		2.62		2.69
1^3A_g	4.11 ^e	4.12		4.31		31.3	4.40		4.28		4.32

^aThe active space is (0 3 3 0) 6. In parenthesis: number of active orbitals of symmetry $a_g b_g a_u b_u$, and number of active electrons. Highest root included: 2^1A_g , 2^1B_u , 1^3A_g , 1^3B_{1u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref.⁹⁷, 0-0 transition and band maximum in optical spectrum.

^dFrom Ref.¹⁰³, band maximum in electron impact spectrum.

^eFrom Ref.¹¹¹, two-photon absorption maximum in the liquid.

^fWith one single 1^1B_u root the CASSCF wave function has no $HOMO \rightarrow LUMO$ CSF contribution.

TABLE XII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of all-*E*-octatetraene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁵⁹		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)						41.4					
Singlet states											
2^1A_g (V)	3.59 ^c	4.38		4.64		41.5	5.87		5.99		4.97
1^1B_u (V)	4.41 ^d	4.42	1.832	4.70	1.299	41.7	4.71	1.757	5.07	1.665	4.94
2^1B_u (V)	5.88 ^e	5.83	0.010	5.74	0.003	41.5	6.91	0.001	6.89	0.002	6.06
3^1A_g (V)		6.56		6.19		41.3	6.72		6.98		6.50
4^1A_g (V)		7.14		6.57		41.5	7.01		7.05		6.81
3^1B_u (V)		8.44	0.002	8.04		41.4	7.95	0.062	8.15	0.070	7.91
Triplet states											
1^3B_u	2.10 ^f	2.17		2.33		41.3	2.40		2.23		2.30
1^3A_g	3.55 ^f	3.39		3.70		41.2	3.76		3.62		3.67

^aThe active space is (0 4 4 0) 8. In parenthesis: number of active orbitals of symmetry a_g b_g a_u b_u , and number of active electrons. Level shift 0.2 a.u. Highest root included: 4^1A_g , 3^1B_u , 1^3A_g , 1^3B_{1u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref.¹²⁵, derived from solution spectra.

^dFrom Ref.^{77,96,97,119,137,138,143,151}.

^eFrom Ref.^{77,151}.

^fFrom Ref.¹⁵¹.

TABLE XIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of cyclopropene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁶⁰			CASPT2 (current) ^a			$\langle x^2 \rangle^c$	CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f		ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			0.48			0.46		14.5					
Singlet-states													
1^1B_1 ($\sigma \rightarrow \pi^*$)	6.45 ^d	6.36	1.92	0.010	6.76	1.42	0.010	16.6	6.96	0.001	6.96	0.001	6.90
1^1B_2 ($\pi \rightarrow \pi^*$)	7.19 ^d , 7.0 ^e	7.45	0.70	0.101	7.06	1.02	0.234	16.5	7.17	0.086	7.24	0.083	7.10
Triplet-states													
1^3B_2 ($\pi \rightarrow \pi^*$)	4.16 ^e	4.18	0.65		4.35	0.02		16.5	4.44		4.30		4.34
1^3B_1 ($\sigma \rightarrow \pi^*$)	^f	6.05	1.90		6.51	1.63		14.6	6.65		6.66		6.62

^aThe active space is (0 1 1 1) 4. In parenthesis: number of active orbitals of symmetry a_1 b_2 a_2 b_1 , and number of active electrons. Highest root included: 1^1A_1 , 1^1B_1 , 1^1B_2 , 1^3B_1 , 1^3B_2 .

^bDipole moment in Debye (experimental value for the ground state is 0.46 D¹⁰⁰).

^cExpectation value of x^2 in a.u.

^dFrom Ref.¹²⁷, broad maxima in optical spectrum around 52000 and 58000 cm⁻¹.

^eFrom Ref.¹⁰⁷, from ion-impact energy-loss spectra.

^fIn Ref.¹⁰⁷, a shoulder at 6.1 eV in the ion-impact energy-loss spectra has been associated with a Rydberg transition. This feature has later been attributed to a transition to the 1^3B_1 valence state in Ref.¹⁶⁰.

TABLE XIV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of cyclopentadiene, obtained at the ground state MP2/6-31G* geometry.

		CASPT2 ¹⁶¹			CASPT2 (current) ^a				CC2		CCSD		CC3
State	Exp.	ΔE	μ^b	f	ΔE	μ	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			0.30		0.32		24.7						
Singlet states													
1^1B_2	5.30 ^d	5.27	0.57	0.148	5.51	0.50	0.144	25.7	5.69	0.110	5.87	0.097	5.73
2^1A_1	6.2 ^e	6.31	0.43	0.000	6.31	0.41	0.001	25.6	7.05	0.011	7.05	0.008	6.61
3^1A_1	7.9 ^f	7.89	1.87	0.442	8.52	0.40	0.965	25.5	8.86	0.658	8.95	0.648	8.69
Triplet states													
1^3B_2	3.1 ^g	3.15	0.14		3.28	0.09		24.7	3.36		3.18		3.25
	4.90	0.17		5.10	0.19		24.5	5.22		5.07		5.09	

^aThe active space is (0220)4. In parenthesis: number of active orbitals of symmetry $a_1 b_1 a_2 b_2$, and number of active electrons. Highest root included: 5^1A_1 , 3^1B_2 , 1^3A_1 , 1^3B_2 . State averaging over four 1^1A_1 roots results in a wave function where the 3^1A_1 state consists of nearly pure double excitations, which also influences the 2^1A_1 state. Upon state averaging over five 1^1A_1 roots, the transition energy decreases from 6.52 eV to 6.31 eV, and the double excitation is completely removed in 3^1A_1 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref.⁸⁷.

^eEstimated from experimental data in Ref.¹⁴⁰.

^fFrom Ref.¹⁴⁰.

^gFrom Ref.¹²⁸.

TABLE XV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of norbornadiene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁶²			CASPT2 (current) ^a				CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	$\langle z^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			0.12			0.01		32.3					
Singlet-states ($\pi \rightarrow \pi^*$)													
1^1A_2	$5.23^{de}, 5.25^f$	5.28	1.96		5.34	0.31		34.2	5.57		5.80		5.64
1^1B_2	$6.0^g, 5.95^{df}, 5.92^e$	6.20	1.85	0.008	6.11	0.93	0.092	33.2	6.37	0.023	6.69	0.029	6.49
2^1B_2	$6.7^g, 6.65^{ef}$	6.48	0.43	0.343	7.32	0.51	0.393	32.7	7.65	0.185	7.87	0.187	7.64
2^1A_2	7.50^f	7.36	0.55		7.44	0.16		31.7	7.66		7.87		7.71
2^1A_1		7.49	0.90	0.0002	7.97	0.10		33.5					
Triplet-states ($\pi \rightarrow \pi^*$)													
1^3A_2	$3.4^d, 3.47^e$	3.42	0.16		3.75	0.06		32.7	3.76		3.67		3.72
1^3B_2	3.9^{de}	3.80	0.12		4.22	0.05		32.1	4.25		4.09		4.16

^aThe active space is (1111)4. In parenthesis: number of active orbitals of symmetry $a_1 b_2 a_2 b_1$, and number of active electrons. Highest root included: 3^1A_1 , 2^1A_2 , 2^1B_2 , 1^3A_2 , 1^3B_2 . State averaging over three rather than two 1^1B_2 states lowers the computed excitation energies to 5.97 and 7.19 eV, respectively.

^bDipole moment in Debye.

^cExpectation value of z^2 in a.u.

^dFrom Ref.^{72,73}.

^eFrom Ref.¹⁴⁴.

^fFrom Ref.¹⁴².

^gFrom Ref.¹⁶².

2. Aromatic Hydrocarbons and Heterocycles

TABLE XVI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of benzene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷⁴		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1E_{2g})						30.1					
Singlet states											
1^1B_{2u}	4.90 ^c	4.84		5.05		30.2	5.27		5.19		5.07
1^1B_{1u}	6.20 ^c	6.30		6.44	0.001	30.2	6.68		6.74		6.68
1^1E_{1u}	6.94 ^d	7.03	0.82	7.07	0.847	30.2	7.44	0.694	7.65	0.686	7.45
2^1E_{2g}	7.8 ^e	7.90		8.21		30.1	9.03		9.21		8.43
Triplet states											
1^3B_{1u}	3.94 ^f	3.89		4.17		29.8	4.31		3.94		4.12
1^3E_{1u}	4.76 ^f	4.49		4.90		29.8	5.14		4.97		4.90
1^3B_{2u}	5.60 ^f	5.49		5.76		29.8	6.08		6.00		6.04
1^3E_{2g}	7.24-7.74 ^g	7.12		7.41		29.7	7.99		7.73		7.49

^aThe active space is (06)6. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Highest root included: $7^1A'$, $6^3A'$. The C_s CASPT2 results show minor symmetry breaking, i.e., differences of not more than 0.03 eV in the energies of states that are degenerate in D_{6h} . The CASPT2 wavefunctions of the four $HOMO \rightarrow LUMO$ -derived states are essentially linear combinations of the two respective degenerate configurations with weights of about 40 %.

^bExpectation value of z^2 in a.u.

^cFrom Ref.⁸².

^dFrom Ref.¹¹².

^eFrom Ref.⁹⁹.

^fFrom Ref.¹¹⁷.

^gFrom Ref.¹⁷⁴.

TABLE XVII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of naphthalene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁶⁴		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Singlet states											
Ground state (1^1A_g)						48.1					
1^1B_{3u}	$3.97^c, 4.0^d$	4.03	0.0005	4.24	0.0005	48.1	4.45		4.41		4.27
1^1B_{2u}	$4.45^c, 4.7^d$	4.56	0.050	4.77	0.137	48.5	4.96	0.094	5.21	0.083	5.03
2^1A_g	$5.50^e, 5.52^f$	5.39		5.90		48.0	6.22		6.23		5.98
1^1B_{1g}	$5.28^e, 5.22^f$	5.53		6.00		48.5	6.21		6.53		6.07
2^1B_{3u}	$5.63^g, 5.55^h, 5.89^c$	5.54	1.337	6.07	1.548	48.1	6.25	1.450	6.55	1.461	6.33
2^1B_{1g}		5.87		6.48		48.4	6.82		6.97		6.79
2^1B_{2u}	$6.14^c, 6.0^d$	5.93	0.313	6.33	0.402	48.5	6.57	0.272	6.77	0.294	6.57
3^1A_g	$6.01^e, 6.05^f$	6.04		6.71		48.0	7.34		7.77		6.90
3^1B_{2u}	$7.7^i, 7.6^d, 7.4^g$	7.16	0.848	8.18	0.708	48.6	8.46	0.548	8.77	0.538	8.44
3^1B_{3u}		7.18	0.048	7.76	0.008	47.9	8.85	0.010	9.03	0.014	8.12
Triplet states											
Ground state (1^3B_{2u}) ^j				3.20		47.9	3.27		2.99		3.11
1^3B_{3u}		0.80		1.05		48.3	1.12		1.28		1.08
1^3B_{1g}		1.14		1.33		48.2	1.38		1.45		1.37
2^3B_{2u}		1.20		1.50		47.9	1.61		1.69		1.53
2^3B_{3u}		1.36		1.88		48.4	1.85		2.11		2.00
1^3A_g	2.25^k	2.18	0.001	2.35	0.001	48.1	2.50		2.58		2.41
2^3B_{1g}	$3.12^l, 3.0^m$	2.61	0.097	3.26	0.123	48.3	3.17		3.80		3.38
2^3A_g	2.93^n	2.73		3.19	0.001	48.1	3.57		3.83		3.36
3^3A_g		2.81	0.001	3.55		48.2	3.67		3.97		3.69
3^3B_{1g}		3.14	0.001	3.45		47.9	3.96		4.06		3.66

^aThe active space is (0 2 0 3 2 0 3 0) 10. In parenthesis: number of active orbitals of symmetry $a_g, b_{2g}, b_{1g}, b_{3g}, a_u, b_{2u}, b_{1u}, b_{3u}$, and number of active electrons. Level shift 0.2 a.u. Highest root included: $3^1A_g, 3^1B_{1g}, 5^1B_{2u}, 4^1B_{3u}, 3^3A_g, 3^3B_{1g}, 2^3B_{2u}, 2^3B_{3u}$. The covalent 3^1B_{2u} state corresponds to a $1b_{3g} \rightarrow 3b_{1u}$ excitation which appears at 10.23 eV¹⁶⁴ and 10.38 eV, current, with CASSCF.

^bExpectation value of z^2 in a.u.

^cFrom Ref.¹⁴⁵.

^dFrom Ref.¹⁰⁵.

^eFrom Ref.¹¹³.

^fFrom Ref.¹⁵².

^gFrom Ref.¹¹⁰.

^hFrom Ref.¹¹⁴.

ⁱFrom Ref.⁸⁴.

^jThe energy of the 1^3B_{2u} state relative to the singlet ground state 1^1A_g is given in this line. The energies of the other triplet states in the following lines are given relative to the 1^3B_{2u} state.

^kFrom Ref.⁸⁹.

^lFrom Ref.¹⁵⁷.

^mFrom Ref.¹⁰⁸.

ⁿFrom Ref.⁸⁹, assigned on the basis of transition dipole moments.

TABLE XVIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of furan, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁶¹			CASPT2 (current) ^a				CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			0.93			1.09		23.9					
Singlet states													
1^1B_2	6.06 ^d	6.04	0.31	0.154	6.43	0.70	0.199	25.0	6.75	0.172	6.80	0.159	6.60
2^1A_1		6.16	1.31	0.002	6.52	1.50	0.008	24.4	6.87	0.003	6.89	0.001	6.62
3^1A_1	7.82 ^d	7.66 ^e	0.37	0.416	8.22	0.82	0.793	24.4	8.78	0.506	8.83	0.501	8.53
Triplet states													
1^3B_2	4.02 ^{df}	3.99	1.13		4.17	1.57		23.7	4.38		4.10		4.17
1^3A_1	5.22 ^f	5.15	1.34		5.49	1.37		23.7	5.67		5.48		5.48

^aThe active space is (0 3 2 0) 6. In parenthesis: number of active orbitals of symmetry $a_1 b_1 a_2 b_2$, and number of active electrons. Highest root included: 4^1A_1 , 3^1B_2 , 1^3A_1 , 1^3B_2 . The inclusion of one more b_1 and a_2 orbital into the active space (0 4 3 0/6) affects mostly the 1^1B_2 state whose excitation energy decreases from 6.43 eV to 6.25 eV.

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref.⁷⁴.

^eThe values in Table VII and Table VIII of Ref.¹⁶¹ differ.

^fFrom Ref.⁸⁶.

TABLE XIX: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of pyrrole, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁶¹			CASPT2 (current) ^a				CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			1.77			1.82		25.5					
Singlet states													
2^1A_1		5.92	1.15	0.020	6.31	1.10	0.031	25.6	6.61	0.006	6.61	0.005	6.40
1^1B_2	5.98 ^{de}	6.00	2.12	0.125	6.33	2.70	0.205	26.5	6.88	0.182	6.87	0.166	6.71
3^1A_1	7.54 ^d	7.46	2.83	0.326	8.17	3.41	0.613	25.7	8.44	0.532	8.44	0.527	8.17
Triplet states													
1^3B_2	4.21 ^{df}	4.27	0.97		4.52	0.85		25.3	4.68		4.41		4.48
1^3A_1	5.10 ^f	5.16	1.11		5.53	1.25		25.4	5.72		5.54		5.51

^aThe active space is (0 3 2 0) 6. In parenthesis: number of active orbitals of symmetry $a_1 b_1 a_2 b_2$, and number of active electrons. Highest root included: 3^1A_1 , 3^1B_2 , 1^3A_1 , 1^3B_2 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref.⁷⁴.

^eFrom Ref.⁹⁸.

^fFrom Ref.⁸⁶.

TABLE XX: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of imidazole, obtained at the ground state MP2/6-31G* geometry.

State	Exp. ^b	CASPT2 ²⁰⁷			CASPT2 (current) ^a			$\langle x^2 \rangle^d$	CC2		CCSD		CC3
		ΔE	μ^c	f	ΔE	μ	f		ΔE	f	ΔE	f	
Ground state ($1^1A'$)			3.70			3.78		24.1					
Singlet-states													
$1^1A''(n \rightarrow \pi^*)$		6.52	0.22	0.011	6.81	1.11	0.010	25.3	6.86	0.003	7.01	0.005	6.82
$2^1A'(\pi \rightarrow \pi^*)$	6.00	6.72	4.61	0.126	6.19	3.34	0.229	24.5	6.73	0.088	6.80	0.088	6.58
$3^1A'(\pi \rightarrow \pi^*)$	6.53	7.15	3.00	0.143	6.93	4.82	0.062	24.5	7.28	0.085	7.27	0.081	7.10
$2^1A''(n \rightarrow \pi^*)$		7.56	2.79	0.013	7.91	2.95	0.019	25.5	8.00	0.006	8.15	0.004	7.93
$4^1A'(\pi \rightarrow \pi^*)$		8.51	3.85	0.594	8.15	4.75	0.555	24.6	8.62	0.406	8.70	0.420	8.45
Triplet-states													
$1^3A'(\pi \rightarrow \pi^*)$		4.49	3.17		4.65	2.87		24.0	4.89		4.62		4.69
$2^3A'(\pi \rightarrow \pi^*)$		5.47	4.03		5.74	3.61		24.0	6.01		5.83		5.79
$1^3A''(n \rightarrow \pi^*)$		6.07	1.38		6.36	1.31		25.3	6.44		6.43		6.37
$3^3A'(\pi \rightarrow \pi^*)$		6.53	4.68		6.44	4.89		24.3	6.74		6.56		6.55
$4^3A'(\pi \rightarrow \pi^*)$		7.08	3.32		7.43	5.15		24.4	7.68		7.54		7.42
$2^3A''(n \rightarrow \pi^*)$		7.15	6.19		7.51	3.15		25.6	7.52		7.76		7.51

^aThe active space is (16)8. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Highest root included: $5^1A'$, $2^1A''$, $4^3A'$, $2^3A''$.

^bFrom Ref.¹¹⁶.

^cDipole moment in Debye.

^dExpectation value of x^2 in a.u.

TABLE XXI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of pyridine, obtained at the ground state MP2/6-31G* geometry.

State	Exp. ^b	CASPT2 ¹⁶⁵			CASPT2 (current) ^a			$\langle x^2 \rangle^d$	CC2		CCSD		CC3
		ΔE	μ^c	f	ΔE	μ	f		ΔE	f	ΔE	f	
Ground state (1^1A_1)						2.34		38.6					
Singlet states, $\pi \rightarrow \pi^*$													
1^1B_2 (1^1B_{2u})	4.99	4.84	2.03	0.018	5.02	2.01	0.044	38.5	5.32	0.025	5.27	0.022	5.15
2^1A_1 (1^1B_{1u})	6.38	6.42	3.28	0.005	6.39	3.26	0.004	39.2	6.88	0.021	6.94	0.015	6.85
3^1A_1 (1^1E_{1u})	7.22	7.23	2.67	0.82	7.46	1.24	0.849	39.1	7.72	0.498	7.94	0.590	7.70
2^1B_2 (1^1E_{1u})		7.48	1.83	0.64	7.29 ^e	0.79	0.691	38.5	7.61	0.549	7.81	0.548	7.59
4^1A_1 (1^1E_{2g})		7.96	1.30	0.03	8.70	3.23		39.4	9.00		9.45	0.002	8.68
3^1B_2 (1^1E_{2g})		7.95	2.57	0.158	8.62 ^e	2.15	0.089	40.2	9.37	0.012	9.64	0.014	8.77
Singlet states, $n \rightarrow \pi^*$													
1^1B_1	4.59	4.91	0.40	0.009	5.14 ^f	0.25	0.009	39.7	5.12	0.005	5.25	0.006	5.05
1^1A_2	5.43	5.17	0.93		5.47 ^f	0.86		44.4	5.39		5.73		5.50
Triplet states, $\pi \rightarrow \pi^*$													
1^3A_1	4.10	4.05	2.13		4.27	2.09		38.1	4.46		4.07		4.25
1^3B_2	4.84	4.56	2.03		4.72	2.05		38.4	5.07		4.91		4.86
2^3A_1		4.73	2.41		5.03	2.30		38.4	5.33		5.13		5.05
2^3B_2		6.02	3.79		6.02	3.19		38.5	5.07		4.91		4.86
3^3A_1		7.34	1.73		7.56	1.88		38.2	8.18		7.90		7.66
3^3B_2		7.28	1.04		7.88	1.76		39.0	8.39		8.12		7.83
Triplet states, $n \rightarrow \pi^*$													
1^3B_1		4.41	0.51		4.55 ^f	0.48		39.1	4.54		4.61		4.50
1^3A_2		5.10	0.15		5.48 ^f	0.64		38.5	5.35		5.67		5.46

^aThe active space is (0420)6. In parenthesis: number of active orbitals of symmetry a_1 b_1 a_2 b_2 , and number of active electrons. Highest root included: 4^1A_1 , 3^1B_2 , 1^1A_2 , 1^1B_1 , 3^3A_1 , 3^3B_2 , 1^3A_2 , 1^3B_1 . Extension of the active space by four b_1 and two a_2 orbitals¹⁶⁵ affects mostly the 1^1A_1 states: the energy of the 2^1A_1 and 3^1A_1 states increases by about 0.2 eV, while that of the 4^1A_1 state decreases by 0.2 eV.

^bFrom Ref.¹²².

^cDipole moment in Debye.

^dExpectation value of x^2 in a.u.

^eThe active space is (1840)8. The 2^1B_2 and 3^1B_2 excitation energies refer to this large active space to overcome an intruder state problem for the 2^1B_2 state (which has very little effect on the computed energies).

^fThe active space is (1420)8.

TABLE XXII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of pyrazine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2 ¹⁶⁶		CASPT2 (current) ^a			CC2		CCSD		CC3
			ΔE	f	ΔE	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)							26.9					
$\pi \rightarrow \pi^*$ -states												
1^1B_{2u} (1^1B_{2u})	4.81	0.062	4.75	0.07	4.85	0.123	27.3	5.13	0.070	5.14	0.067	5.02
1^1B_{1u} (1^1B_{1u})	6.51	0.10	6.70	0.08	6.89	0.107	27.8	7.10	0.096	7.18	0.074	7.07
2^1B_{1u} (1^1E_{1u})	7.67	0.72	7.57	0.76	7.79	0.774	27.7	8.13	0.424	8.34	0.458	8.06
2^1B_{2u} (1^1E_{1u})	7.67	0.72	7.70	0.66	7.65	0.622	27.4	8.07	0.400	8.29	0.423	8.05
1^1B_{3g} (1^1E_{2g})			8.19		8.47		26.6	9.42		9.75		8.77
2^1A_g (1^1E_{2g})			8.26		8.61		26.8	9.26		9.55		8.69
$n \rightarrow \pi^*$ -states												
1^1B_{3u}	3.83 ^d	0.006	3.63	0.01	4.12	0.012	28.2	4.26	0.007	4.42	0.008	4.24
1^1A_u			4.52		4.70		28.4	4.95		5.29		5.05
1^1B_{2g}	5.46 ^e		5.17 ^f		5.68		28.1	5.92		6.02		5.74
1^1B_{1g}	6.10 ^g		6.13 ^f		6.41		28.4	6.70		7.13		6.75

^aThe active space is (1 2 1 0 1 0 1 2) 10. In parenthesis: number of active orbitals of symmetry a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u} , and number of active electrons. Highest root included: 2^1A_g , 2^1A_u , 2^1B_{1g} , 1^1B_{2g} , 1^1B_{3g} , 2^1B_{1u} , 2^1B_{2u} , 1^1B_{3u} .

^bFrom Ref.¹²².

^cExpectation value of x^2 in a.u.

^d0 – 0 transition.

^eFrom Ref.⁸⁰, estimate from solution spectrum.

^fFrom Ref.¹⁶⁷.

^gAssignment uncertain.

TABLE XXIII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of pyrimidine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2 ¹⁶⁷			CASPT2 (current) ^a				CC2		CCSD		CC3
			ΔE	μ^c	f	ΔE	μ	f	$\langle x^2 \rangle^d$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			2.45			2.39			26.9					
$\pi \rightarrow \pi^*$ -states														
1^1B_2 (1^1B_{2u})	5.12	0.028	4.93	2.14	0.001	5.24	2.36	0.049	27.1	5.51	0.023	5.49	0.022	5.36
2^1A_1 (1^1B_{1u})	6.7	0.094	6.72	4.01	0.05	6.64	3.06	0.164	27.2	7.12	0.062	7.17	0.038	7.06
3^1A_1 (1^1E_{1u})	7.57	0.72	7.57	2.61	0.58	7.21	3.35	0.540	27.0	7.79	0.446	7.97	0.461	7.74
2^1B_2 (1^1E_{1u})	7.57	0.72	7.32	2.26	0.79	7.64	2.07	0.768	27.1	8.08	0.476	8.24	0.470	8.01
3^1B_2 (1^1E_{2g})			8.31	1.17	0.06	8.73	1.47		27.2					
4^1A_1 (1^1E_{2g})			7.82	2.16	0.14	9.19	2.37		27.2					
$n \rightarrow \pi^*$ -states														
1^1B_1	4.16 ^e	0.005	3.81	0.60	0.02	4.44	0.85	0.013	28.0	4.49	0.006	4.70	0.007	4.50
1^1A_2	4.62		4.12	1.05		4.81	1.24		28.2	4.84		5.12		4.93

^aThe active space is (1 1 2 4) 10. In parenthesis: number of active orbitals of symmetry a_1 b_2 a_2 b_1 , and number of active electrons. Level shift 0.1 a.u. Highest root included: 4^1A_1 , 4^1B_2 , 1^1A_2 , 1^1B_1 .

^bFrom Ref.¹²².

^cDipole moment in Debye (experimental value for the ground state is 2.33 D¹⁴⁷).

^dExpectation value of x^2 in a.u.

^e0-0 transition.

TABLE XXIV: Vertical excitation energies ΔE (eV) and other properties of the singlet states of pyridazine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2 ¹⁶⁷			CASPT2 (current) ^a				CC2		CCSD		CC3
			ΔE	μ^c	f	ΔE	μ	f	$\langle x^2 \rangle^d$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)				4.37			4.24		27.1					
$\pi \rightarrow \pi^*$ -states														
$2^1A_1(1^1B_{2u})$	$4.9^b, 5.0^e$	0.02	4.86	3.60	0.009	5.18	3.44	0.027	27.1	5.37	0.014	5.35	0.014	5.22
$1^1B_2(1^1B_{1u})$	$6.2^b, 6.5^e$	0.10	6.61	5.64	0.003	6.31	5.65	0.115	27.4	7.00	0.009	7.09	0.006	6.93
$2^1B_2(1^1E_{1u})$	$7.1^b, 7.3^e$		7.39	3.93	0.75	7.29	4.58	0.603	27.7	7.57	0.489	7.79	0.459	7.55
$3^1A_1(1^1E_{1u})$	$7.1^b, 7.3^e$		7.50	5.09	0.50	7.62	5.77	0.742	27.0	7.90	0.444	8.11	0.494	7.82
$n \rightarrow \pi^*$ -states														
1^1B_1	3.3^f	0.006	3.48	1.59	0.01	3.78	1.72	0.010	28.2	3.90	0.006	4.11	0.007	3.92
1^1A_2			3.66	1.97		4.32	1.85		28.3	4.40		4.76		4.49
2^1A_2	5.3^e		5.09	1.74		5.77	1.94		28.1	5.81		6.00		5.74
2^1B_1	$5.5\text{-}6.0^e$		5.80	1.74	0.008	6.52	2.06	0.008	28.2	6.40	0.005	6.70	0.005	6.41

^aThe active space is (1 1 2 4) 10. In parenthesis: number of active orbitals of symmetry $a_1 b_2 a_2 b_1$, and number of active electrons. Level shift 0.1 a.u. Highest root included: 4^1A_1 , 4^1B_2 , 2^1A_2 , 2^1B_1 .

^bFrom Ref.⁸⁰.

^cDipole moment in Debye (experimental value for the ground state is 4.22 D⁹³).

^dExpectation value of x^2 in a.u.

^eFrom Ref.⁷⁶.

^f0-0 transition from Ref.⁸⁰.

TABLE XXV: Vertical excitation energies ΔE (eV) and other properties of the singlet states of *s*-triazine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2 ¹⁶⁷		CASPT2 (current) ^a			CC2		CCSD		CC3
			ΔE	f	ΔE	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	
Ground state ($1^1A'_1$)							25.3					
$\pi \rightarrow \pi^*$ -states												
$1^1A'_2(1^1B_{2u})$	5.70		5.33		5.79		25.5	5.82		5.84		5.71
$2^1A'_1(1^1B_{1u})$	6.86		6.77		7.25	0.009	25.4	7.52		7.51		7.41
$1^1E'(1^1E_{1u})$	7.76	0.73	8.16	0.61	7.49	0.680	25.4	8.06	0.441	8.28	0.437	8.04
$2^1E'(1^1E_{2g})$			8.03	0.21	8.99	0.044	25.4			10.24		9.44
$n \rightarrow \pi^*$ -states												
$1^1A''_1$			3.90		4.60		26.5	4.70		4.96		4.78
$1^1A''_2$	4.59	0.013	4.08	0.015	4.66	0.021	26.5	4.80	0.017	4.98	0.018	4.76
$1^1E''$	3.97		4.36		4.71		26.5	4.77		5.01		4.81
$2^1E''$	6.15		7.15		7.72		26.5	8.04		8.19		7.80

^aThe active space is (3 6) 12. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Level shift 0.1 a.u. Highest root included: $8^1A'$, $6^1A'$.

^bFrom Ref.¹²².

^cExpectation value of x^2 in a.u.

TABLE XXVI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of *s*-tetrazine, obtained at the ground state MP2/6-31G* equilibrium geometry.

State	Exp.	CASPT2 ¹⁶⁸		CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	f	ΔE	f	$\langle x^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)						24.4					
$\pi \rightarrow \pi^*$ -singlet states											
1^1B_{2u}	5.0 ^c , 4.97 ^d	4.89	0.045	4.91	0.110	24.2	5.20	0.046	5.27	0.047	5.12
1^1B_{1u}	7.1 ^{c,d}	7.13	0.001	6.96	0.136	24.7	7.60	0.017	7.66	0.003	7.45
2^1B_{1u}	7.6 ^{c,d}	7.54	0.687	7.43	0.496	25.1	7.75	0.376	8.06	0.381	7.79
2^1B_{2u}	8.3 ^{c,d}	7.94	0.733	8.15	0.588	26.1	8.65	0.368	8.88	0.333	8.51
2^1B_{3g}		8.12		8.32		24.1	8.97		9.44		8.47
3^1A_g		8.60		8.97		24.2					
$n \rightarrow \pi^*$ - and $n, n \rightarrow \pi^*, \pi^*$ -singlet states											
$1^1B_{3u} (n \rightarrow \pi^*)$	2.25 ^e , 2.34 ^c	1.96	0.013	2.24	0.013	25.2	2.47	0.007	2.71	0.009	2.53
$1^1A_u (n \rightarrow \pi^*)$	$\approx 3.4^f$	3.06		3.48		25.5	3.67		4.07		3.79
$2^1A_g (n, n \rightarrow \pi^*, \pi^*)$		4.37		4.55		26.2					
$1^1B_{1g} (n \rightarrow \pi^*)$		4.51		4.73		25.2	5.10		5.32		4.97
$1^1B_{2g} (n \rightarrow \pi^*)$		5.05		5.18		25.2	5.53		5.70		5.34
$1^1B_{3g} (n, n \rightarrow \pi^*, \pi^*)$		5.16		5.79		26.3					
$2^1A_u (n \rightarrow \pi^*)$		5.28		5.47		25.3	5.50		5.70		5.46
$2^1B_{2g} (n \rightarrow \pi^*)$	$\approx 5.5^d$	5.48		6.07		25.3	6.32		6.76		6.23
$2^1B_{1g} (n \rightarrow \pi^*)$	5.9 ^d	5.99		6.38		25.2	6.91		7.25		6.87
$2^1B_{3u} (n \rightarrow \pi^*)$	6.6 ^c , 6.34 ^d	6.37	0.017	6.77	0.021	25.4	6.70	0.011	6.99	0.012	6.67
$3^1B_{1g} (n \rightarrow \pi^*)$		6.20		6.74		25.5	7.64		8.36		7.08
Triplet states											
$1^3B_{3u} (n \rightarrow \pi^*)$	1.69 ^{dg}	1.45		1.56		25.3	1.86		1.99		1.89
$1^3A_u (n \rightarrow \pi^*)$	2.9 ^d	2.81		3.26		25.6	3.43		3.74		3.52
$1^3B_{1g} (n \rightarrow \pi^*)$	3.6 ^d	3.76		4.14		25.3	4.30		4.31		4.21
$1^3B_{1u} (\pi \rightarrow \pi^*)$		4.25		4.36		24.2	4.62		4.05		4.33
$1^3B_{2u} (\pi \rightarrow \pi^*)$		4.29		4.56		24.2	4.81		4.57		4.54
$1^3B_{2g} (n \rightarrow \pi^*)$		4.67		4.93		25.2	5.03		5.09		4.93
$2^3A_u (n \rightarrow \pi^*)$		4.85		5.02		25.3	5.05		5.20		5.03
$1^3B_{3g} (n, n \rightarrow \pi^*, \pi^*)$		5.08		5.50		26.5					
$2^3B_{1u} (\pi \rightarrow \pi^*)$		5.09		5.40		24.2	5.67		5.48		5.38
$2^3B_{2g} (n \rightarrow \pi^*)$		5.30		5.97		25.3	6.05		6.51		6.04
$2^3B_{1g} (n \rightarrow \pi^*)$		5.68		6.31		25.1	6.72		7.11		6.60
$2^3B_{3u} (n \rightarrow \pi^*)$		6.14		6.54		25.5	6.52		6.80		6.53
$2^3B_{2u} (\pi \rightarrow \pi^*)$		6.81		7.10		24.8	7.65		7.46		7.36

^aThe active space is (12111112)12. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Level shift 0.2 a.u. Highest root included: 5^1A_g , 3^1A_u , 4^1B_{1g} , 3^1B_{2g} , 3^1B_{3g} , 3^1B_{1u} , 5^1B_{2u} , 3^1B_{3u} , 2^3A_u , 2^3B_{1g} , 2^3B_{2g} , 1^3B_{3g} , 2^3B_{1u} , 3^3B_{2u} , 2^3B_{3u} . An additional 1^1B_{2u} state with $n, n \rightarrow \pi^*, \pi^*$ character has been found lower than 2^1B_{2u} at 7.86 eV, the 2^1B_{2u} state is 5^1B_{2u} at CASSCF level.

^bExpectation value of x^2 in a.u.

^cFrom Ref.¹⁰¹.

^dFrom Ref.¹³¹.

^eFrom Ref.⁷⁸.

^fFrom Ref.⁸⁰.

^gFrom Ref.¹⁵³.

3. Aldehydes, Ketones and Amides

TABLE XXVII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of formaldehyde, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁶⁹			CASPT2 (current) ^a				CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			2.43			2.44		8.7					
Singlet states													
1^1A_2 ($n \rightarrow \pi^*$)	3.79 ^d , 4.07 ^e	3.91	1.39		3.98	1.46		10.0	4.09		3.97		3.95
1^1B_1 ($\sigma \rightarrow \pi^*$)		9.09	0.50	0.01	9.14 ^f	0.91	0.013	8.7	9.35	0.079	9.26	0.074	9.18
2^1A_1 ($\pi \rightarrow \pi^*$) ^g		9.77	0.75	0.28	9.31	2.68	0.451	9.41	10.34	0.368	10.54	0.374	10.45
Triplet states													
1^3A_2 ($n \rightarrow \pi^*$)	3.50	3.48	1.13		3.58	1.34		10.1	3.57		3.52		3.55
1^3A_1 ($\pi \rightarrow \pi^*$)	5.82	5.99	0.89		5.84	1.05		8.9	6.08		5.78		5.83

^aThe active space is (0 2 0 1) 4. In parenthesis: number of active orbitals of symmetry a_1 b_1 a_2 b_2 , and number of active electrons. Highest root included: 4^1A_1 , 1^1A_2 , 1^1B_1 , 1^3A_1 , 1^3A_2 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref.⁸¹.

^eFrom Ref.¹⁵⁰.

^fThe active space is (1 2 0 0) 4.

^gTransition 3^1A_1 with coupled cluster methods, assigned on the basis of the transition moments, see Table XXVIII for 2^1A_1 and 3^1A_1 excitation energies.

TABLE XXVIII: Vertical CCSD and CC3 excitation energies ΔE (eV) of singlet and triplet states of formaldehyde with different basis sets obtained at the ground state MP2/6-31G* equilibrium geometry.

Basis set	CCSD							CC3						
	2^1A_1	3^1A_1	1^1B_2	1^1B_1	1^1A_2	1^3A_1	1^3A_2	2^1A_1	3^1A_1	1^1B_2	1^1B_1	1^1A_2	1^3A_1	1^3A_2
cc-pVDZ	9.95	11.30	8.64	9.35	4.01	5.81	3.53	9.71	11.19	8.55	9.29	3.99	5.88	3.56
TZVP	9.77	10.54	8.45	9.26	3.97	5.75	3.52	9.53	10.45	8.34	9.18	3.95	5.83	3.55
cc-pVTZ	9.68	10.49	8.34	9.20	3.98	5.77	3.51	9.44	10.37	8.21	9.11	3.93	5.86	3.52
cc-pVQZ	9.54	10.04	8.11	9.18	3.96	5.77	3.51	9.31	9.90	7.98	9.07	3.91	5.87	3.51
aug-cc-pVDZ	9.59	10.45	7.99	9.24	3.94	5.82	3.48	9.42	10.47	8.01	9.17	3.92	5.90	3.51
aug-cc-pVTZ	9.51	10.36	8.13	9.14	3.93	5.77	3.48	9.31	10.33	8.09	9.05	3.88	5.86	3.49
aug-cc-pVQZ	9.50	10.28	8.17	9.15	3.94	5.77	3.50	9.29	10.22	8.11	9.04	3.88	5.87	3.50
d-aug-cc-pVDZ	9.19		7.83	9.22	3.93	5.81	3.47	9.17		7.86	9.16	3.92	5.89	3.50
d-aug-cc-pVTZ	9.30		8.03	9.14	3.93	5.76	3.48	9.18		8.00	9.04	3.88	5.86	3.49

TABLE XXIX: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of acetone, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷⁰			CASPT2 (current) ^a				CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	$\langle x^2 \rangle^c$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_1)			2.92			2.96		18.1					
Singlet-states													
1^1A_2 ($n \rightarrow \pi^*$)	4.38 ^d	4.18	2.27		4.42	1.49		19.1	4.52		4.43		4.40
1^1B_1 ($\sigma \rightarrow \pi^*$)		9.10	0.99	0.010	9.27	1.34	0.011	19.0	9.29		9.26		9.17
2^1A_1 ($\pi \rightarrow \pi^*$)		9.16	3.94	0.326	9.31	3.20	0.358	18.1	9.74	0.298	9.87	0.256	9.65
Triplet-states													
1^3A_2 ($n \rightarrow \pi^*$)	4.16 ^{de}	3.90	1.14		4.08	1.29		19.2	4.08		4.03		4.05
1^3A_1 ($\pi \rightarrow \pi^*$)	5.88 ^{de}	5.98	1.11		6.03	1.24		18.2	6.27		5.94		6.03

^aThe active space is (2 1 0 2) 6. In parenthesis: number of active orbitals of symmetry a_1 b_2 a_2 b_1 , and number of active electrons. Highest root included: 4^1A_1 , 1^1A_2 , 1^1B_1 , 1^3A_1 , 1^3A_2 .

^bDipole moment in Debye (experimental value for the ground state is 2.90 D¹²⁴).

^cExpectation value of x^2 in a.u.

^dFrom Ref.⁸¹.

^eFrom Ref.¹²¹.

TABLE XXX: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of *p*-benzoquinone, obtained at the ground state MP2/6-31G* equilibrium geometry.

State	Exp.	f	CASPT2 ¹⁷¹		CASPT2 (current) ^a			CC2		CCSD		CC3
			ΔE	f	ΔE	f	$\langle x^2 \rangle^b$	ΔE	f	ΔE	f	ΔE
Ground state (1^1A_g)							34.3					
Singlet states												
$1^1B_{1g} (n \rightarrow \pi^*)$	2.7 ^c , 2.49 ^d		2.50		2.78		35.5	2.81		3.07		2.75
$1^1A_u (n \rightarrow \pi^*)$	2.7 ^c , 2.48 ^d		2.50		2.80		35.5	2.92		3.19		2.85
$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.4 ^c , 4.07 ^e , 4.4 ^f	0.005	4.19		4.25		34.5	4.69		4.93		4.59
$2^1A_g (n \rightarrow \pi^*)$			4.41		4.51		36.5					
$1^1B_{2g} (n \rightarrow \pi^*)$			4.80		5.66		35.7					
$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.4 ^c , 5.12 ^e , 5.4 ^f	0.44	5.15	0.616	5.29	0.638	34.6	5.59	0.538	5.89	0.558	5.62
$1^1B_{3u} (n \rightarrow \pi^*)$			5.15		5.60		35.8	5.69		6.55	0.001	5.82
$2^1B_{2g} (n \rightarrow \pi^*)$			5.49		6.60		35.8					
$2^1B_{1g} (n \rightarrow \pi^*)$			5.76		6.15		35.5					
$2^1A_u (n \rightarrow \pi^*)$			5.79		6.05		35.5					
$3^1A_g (\pi \rightarrow \pi^*)$			5.90		6.08		34.5					
$2^1B_{3g} (\pi \rightarrow \pi^*)$			6.34		6.98		35.3	7.36		7.62		7.27
$1^1B_{2u} (\pi \rightarrow \pi^*)$			6.89	0.022	7.32	0.016	34.5					
$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.3 ^f	0.81	7.08	0.624	7.91	0.660	35.1	8.31	0.544	8.47	0.509	7.82
$3^1B_{1u} (\pi \rightarrow \pi^*)$			7.24	0.030	7.35	0.079	34.8					
$3^1B_{1g} (n \rightarrow \pi^*)$			7.36		7.90		35.3					
$3^1A_u (n \rightarrow \pi^*)$			7.39		7.90		35.3					
$4^1A_g (\pi \rightarrow \pi^*)$			7.46		8.07		34.1					
$5^1A_g (n \rightarrow \pi^*)$			7.85		8.11		36.2					
Triplet states												
$1^3B_{1g} (n \rightarrow \pi^*)$	2.28 ^g , 2.31 ^h		2.17		2.63		35.4	2.47		2.71		2.51
$1^3A_u (n \rightarrow \pi^*)$	2.32 ^g , 2.35 ^h		2.27		2.68		35.5	2.59		2.83		2.62
$1^3B_{1u} (\pi \rightarrow \pi^*)$			2.91		2.99		34.4	3.12		2.89		2.96
$1^3B_{3g} (\pi \rightarrow \pi^*)$			3.19		3.31		34.4	3.50		3.42		3.41

^aThe active space is (03111103)12. In parenthesis number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Level shift 0.2 a.u. Highest root included: 6^1A_g , $4(3)^1A_u$, $4(3)^1B_{1g}$, 3^1B_{2g} , 3^1B_{3g} , 4^1B_{1u} , 2^1B_{2u} , 3^1B_{3u} , 2^3A_u , 2^3B_{1g} , 2^3B_{3g} , 2^3B_{1u} . Two intruder states (1^1A_u and 1^1B_{1g}) have been excluded from the multi-state treatment to avoid mixing to lower-lying states which in turn, however, causes a red-shift by more than 0.4 eV. The reference weight of the respective states deviates by about 13 % from the ground state.

^bExpectation value of x^2 in a.u.

^cBand maxima from Ref.¹⁵⁶.

^d0-0 transitions from Ref.¹²⁹.

^e0-0 transitions from Ref.¹⁰⁹.

^fBand maxima from Ref.¹¹⁵.

^g0-0 transitions from Ref.¹¹⁸.

^h0-0 transitions from Ref.¹³⁵.

TABLE XXXI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of formamide, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷²			CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	ΔE	f	ΔE	f	ΔE
Ground state ($1^1A'$)			4.08			3.78						
Singlet states												
$1^1A''$ ($n \rightarrow \pi^*$)	5.5 ^c	5.61	2.12	0.001	5.63	1.98	0.001	5.76	0.001	5.66	0.001	5.65
$2^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^d	7.41	6.12	0.371	7.44	6.12	0.479	8.15	0.385	8.52	0.371	8.27
$3^1A'$ ($\pi \rightarrow \pi^*$)		10.50	5.24	0.131	10.54	5.09	0.163	11.24	0.010	11.34	0.102	10.93
Triplet states												
$1^3A''$ ($n \rightarrow \pi^*$)	5.30 ^e	5.34	1.39		5.40 ^f	1.95		5.39		5.32		5.36
$1^3A'$ ($\pi \rightarrow \pi^*$)		5.69	3.23		5.58 ^f	3.71		5.94		5.67		5.74

^aThe active space is (13)6. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Highest root included: $3^1A'$, $1^1A''$, $2^3A'$, $2^3A''$.

^bDipole moment in Debye.

^cFrom Ref.^{75,106}.

^dFrom Ref.^{88,132}.

^eFrom Ref.¹³⁶.

^fThe active space is (14)6.

TABLE XXXII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of acetamide, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷²			CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	ΔE	f	ΔE	f	ΔE
Ground state ($1^1A'$)			4.00			3.98						
Singlet states												
$1^1A''$ ($n \rightarrow \pi^*$)	5.44 ^c	5.54	2.19	0.001	5.80	1.78	0.001	5.77	0.001	5.71	0.001	5.69
$2^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^d	7.21	6.21	0.292	7.27	5.86	0.424	7.66	0.199	7.85	0.223	7.67
$3^1A'$ ($\pi \rightarrow \pi^*$)	9.9 ^e	10.08	5.15	0.179	10.09	4.52	0.263	10.71	0.279	10.77	0.299	10.50
Triplet states												
$1^3A''$ ($n \rightarrow \pi^*$)		5.24	1.61		5.53	1.70		5.42		5.39		5.42
$1^3A'$ ($\pi \rightarrow \pi^*$)		5.57	3.81		5.75	3.31		6.06		5.83		5.88

^aThe active space is (13)6. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Highest root included: $3^1A'$, $1^1A''$, $2^3A'$, $2^3A''$.

^bDipole moment in Debye.

^cFrom Ref.¹⁰⁶.

^dFrom Ref.¹³².

^eFrom Ref.⁷⁵.

TABLE XXXIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of propanamide, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷²			CASPT2 (current) ^a			CC2		CCSD		CC3
		ΔE	μ^b	f	ΔE	μ	f	ΔE	f	ΔE	f	ΔE
Ground state ($1^1A'$)			4.13			3.60						
Singlet states												
$1^1A''$ ($n \rightarrow \pi^*$)	5.44 ^c	5.48	1.90	0.001	5.72	1.73	0.001	5.78		5.74		5.72
$2^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^d	7.28	5.59	0.346	7.20	5.77	0.405	7.56	0.138	7.80	0.180	7.62
$3^1A'$ ($\pi \rightarrow \pi^*$)	9.9 ^e	9.95	4.59	0.205	9.94	4.21	0.275	10.33	0.189	10.34	0.150	10.06
Triplet states												
$1^3A''$ ($n \rightarrow \pi^*$)		5.28	1.41		5.44	1.62		5.44		5.41		5.45
$1^3A'$ ($\pi \rightarrow \pi^*$)		5.94	2.47		5.79 ^f	3.46		6.07		5.84		5.90

^aThe active space is (13)6. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Highest root included: $3^1A'$, $1^1A''$, $2^3A'$, $2^3A''$.

^bDipole moment in Debye.

^cFrom Ref.^{75,106}.

^dFrom Ref.¹³².

^eFrom Ref.⁷⁵.

^fThe active space is (14)6.

4. Nucleobases

TABLE XXXIV: Vertical excitation energies ΔE (eV) and other properties of the singlet states of cytosine, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷³			CASPT2 (current) ^a			CC2		CCSD	
		ΔE	μ^b	f	ΔE	μ	f	ΔE	f	ΔE	f
Ground state ($1^1A'$)			7.5			6.42					
$2^1A'$ ($\pi \rightarrow \pi^*$)	4.6 ^{cde}	4.39	4.7	0.061	4.68	4.58	0.093	4.80	0.049	4.98	0.058
$1^1A''$ ($n \rightarrow \pi^*$)	5.0 ^d , 5.3 ^e	5.00	4.7	0.005	5.12 ^f	2.56	0.003	5.01	0.001	5.45	0.002
$3^1A'$ ($\pi \rightarrow \pi^*$)	5.4 ^c , 5.6 ^d , 5.8 ^e	5.36	7.0	0.108	5.54	5.73	0.352	5.71	0.165	5.95	0.178
$4^1A'$ ($\pi \rightarrow \pi^*$)	6.1 ^c , 6.2 ^e , 6.4 ^d	6.16	6.2	0.863	6.40	5.92	0.623	6.65	0.632	6.81	0.608
$2^1A''$ ($n \rightarrow \pi^*$)		6.53	6.4	0.001	5.54 ^f	2.77	0.002	5.43	0.002	5.99	0.000
$5^1A'$ ($\pi \rightarrow \pi^*$)	6.7 ^c , 7.1 ^e	6.74	9.3	0.147	6.98	7.02	0.366	6.94	0.168	7.23	0.159
$6^1A'$ ($\pi \rightarrow \pi^*$)		7.61	5.0	0.239	8.23	4.66	0.132	8.45	0.223	8.69	0.112

^aThe active space is (08) 10. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.1 a.u. Highest root included: $6^1A'$, $2^1A''$.

^bDipole moment in Debye.

^cFrom Ref.¹³⁹.

^dFrom Ref.⁸³.

^eFrom Ref.⁹¹.

^fThe active space is (28) 14.

TABLE XXXV: Vertical excitation energies ΔE (eV) and other properties of the singlet states of thymine, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷⁴			CASPT2 (current) ^a			CC2		CCSD	
		ΔE	μ^b	f	ΔE	μ	f	ΔE	f	ΔE	f
Ground state ($1^1A'$)			5.0			4.12					
$1^1A''$ ($n \rightarrow \pi^*$)	4.9-5.2 ^c	4.39	3.2		4.94 ^d	2.51		4.94		5.14	
$2^1A'$ ($\pi \rightarrow \pi^*$)	4.95 ^e 4.8 ^f	4.88	6.5	0.17	5.06	5.90	0.334	5.39	0.197	5.60	0.222
$3^1A'$ ($\pi \rightarrow \pi^*$)	6.2 ^e 5.7 ^f	5.88	1.5	0.17	6.15	1.61	0.067	6.46	0.080	6.78	0.071
$2^1A''$ ($n \rightarrow \pi^*$)		5.91	4.6		6.38 ^d	3.92		6.33		6.57	
$4^1A'$ ($\pi \rightarrow \pi^*$)	6.2 ^f	6.10	7.8	0.15	6.52	6.67	0.356	6.80	0.250	7.05	0.285
$3^1A''$ ($n \rightarrow \pi^*$)		6.15	8.6		6.86 ^d	6.53		6.73		7.67	
$4^1A''$ ($n \rightarrow \pi^*$)		6.70	4.1		7.43 ^d	2.31		7.18		7.87	
$5^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^e > 6.7 ^f	7.13	3.1	0.85	7.43	3.03	0.672	7.71	0.515	7.90	0.361
$6^1A'$ ($\pi \rightarrow \pi^*$)					8.48	2.80	0.004				

^aThe active space is (09) 12. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.1 a.u. Highest root included: $6^1A'$, $4^1A''$.

^bDipole moment in Debye.

^cFrom Ref.¹²⁰.

^dThe active space is (29) 16.

^eFrom Ref.¹⁴¹.

^fFrom Ref.¹³⁴.

TABLE XXXVI: Vertical excitation energies ΔE (eV) and other properties of the singlet states of uracil, obtained at the ground state MP2/6-31G* geometry.

State	Exp. ^b	CASPT2 ¹⁷⁴			CASPT2 (current) ^a			CC2		CCSD	
		ΔE	μ^c	f	ΔE	μ	f	ΔE	f	ΔE	f
Ground state ($1^1A'$)			4.4			4.20					
$1^1A''$ ($n \rightarrow \pi^*$)	4.38 ^d 4.9-5.2 ^e	4.54	3.4		4.91 ^f	2.23		4.91		5.11	
$2^1A'$ ($\pi \rightarrow \pi^*$)	5.1	5.00	6.3	0.19	5.23	5.78	0.320	5.52	0.197	5.70	0.224
$3^1A'$ ($\pi \rightarrow \pi^*$)	6.0	5.82	2.4	0.08	6.15	2.48	0.047	6.43	0.058	6.76	0.061
$2^1A''$ ($n \rightarrow \pi^*$)		6.00	4.8		6.27 ^f	4.25		6.26		6.50	0.001
$3^1A''$ ($n \rightarrow \pi^*$)		6.37	8.7		6.97 ^f	2.14		6.73		7.68	
$4^1A'$ ($\pi \rightarrow \pi^*$)	6.6	6.46	6.9	0.29	6.75	6.52	0.249	6.96	0.188	7.19	0.209
$4^1A''$ ($n \rightarrow \pi^*$)		6.95	3.6		7.28 ^f	6.80		7.12		7.74	
$5^1A'$ ($\pi \rightarrow \pi^*$)	6.9-7.0	7.00	3.7	0.76	7.42	3.16	0.804	7.66	0.547	7.81	0.430

^aThe active space is (08) 10. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Level shift 0.1 a.u. Highest root included: $5^1A'$, $4^1A''$.

^bFrom Ref.¹³⁴.

^cDipole moment in Debye.

^dFrom Ref.¹³⁰.

^eFrom Ref.¹²⁰.

^fThe active space is (28) 14.

TABLE XXXVII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of adenine, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2 ¹⁷⁵			CASPT2 (current) ^a			CC2		CCSD	
		ΔE	μ^b	f	ΔE	μ	f	ΔE	f	ΔE	f
Ground state ($1^1A'$)			2.50			2.51					
$2^1A'$ ($\pi \rightarrow \pi^*$)	4.63 ^c	5.13	2.37	0.070	5.20	2.18	0.146	5.28	0.037	5.37	0.002
$3^1A'$ ($\pi \rightarrow \pi^*$)	4.92 ^d	5.20	2.30	0.370	5.29	2.51	0.201	5.42	0.276	5.61	0.297
$1^1A''$ ($n \rightarrow \pi^*$)	5.4 ^e	6.15	2.14	0.001	5.21 ^f	2.32	0.001	5.27		5.58	
$4^1A'$ ($\pi \rightarrow \pi^*$)	5.99 ^d	6.24	2.13	0.851	6.35	2.09	0.538	6.58	0.496	6.83	0.513
$5^1A'$ ($\pi \rightarrow \pi^*$)	6.33 ^g	6.72	4.60	0.159	6.64	3.41	0.001	6.93	0.085	7.17	0.070
$2^1A''$ ($n \rightarrow \pi^*$)		6.86	1.93	0.001	5.97 ^f	1.28	0.002	5.91		6.19	
$6^1A'$ ($\pi \rightarrow \pi^*$)	6.81 ^h	6.99	3.42	0.565	6.88	2.85	0.010	7.49	0.320	7.72	0.286
$7^1A'$ ($\pi \rightarrow \pi^*$)	7.75 ^h	7.57	6.41	0.406	7.56	0.96	0.037	8.04	0.177	8.47	0.122

^aThe active space is (010) 12. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Level shift 0.1 a.u. Highest root included: $7^1A'$, $4^1A''$.

^bDipole moment in Debye.

^cFrom Ref.⁹⁵.

^dFrom Ref.¹³⁴.

^eFrom Ref.^{85,91}.

^fThe active space is (310) 18.

^gFrom Ref.¹⁴⁶.

^hFrom Ref.¹⁴⁸.

APPENDIX B: EVALUATION OF LITERATURE RESULTS: TABLES XXXVIII TO LXXI

The Tables are arranged as follows: The columns refer to the methods used while the lines contain excitation energies and one-electron properties for a given state: the vertical excitation energies, ΔE , in eV; the dimensionless oscillator strengths, f ; the electric dipole moments, μ , in Debye; the $\langle x^2 \rangle$, $\langle y^2 \rangle$ and $\langle z^2 \rangle$ expectation values in a.u. The origin of the data can be found in the footnotes (references and number of the relevant tables in the quoted publications). The footnotes also specify technical details such as basis sets.

1. Unsaturated Aliphatic Hydrocarbons

TABLE XXXVIII: Published results for vertical excitation energies and properties of ethene.

	CASPT2 ^a	MS-CASPT2 ^b	CASSCF	MS-CASPT2 ^c	MRMP ^d	MSMRMP2 ^e	MRMP(2) ^f
1¹B_{1u} (L_a,+)							
ΔE	8.40	7.98	8.11 (-0.13) ^b	7.95	8.24	7.85	8.01
f	0.16	0.360				0.421 ^h	0.494
$\langle x^2 \rangle$	44.1	20.1					
1³B_{1u} (L_a,-)							
ΔE	4.39		4.65 (-0.26) ^c				4.36
$\langle x^2 \rangle$	11.9						
	MRMP(2)/(3) ^g	SORCI ⁱ	MR-CISD+Q ^j	MRCI/+Q ^k	(SC)2-SDCI ^l		
1¹B_{1u} (L_a,+)							
ΔE	8.61/8.87	7.79	7.69	8.02/7.80	7.59/7.99/8.09		
f		0.44					
1³B_{1u} (L_a,-)							
ΔE	4.52/4.47	4.47	4.52		3.99/4.64/4.61		
	EOM-CCSD ^m	RI-CC2 ⁿ	CC3 ⁿ	CC3 ^o	EOM-CCSD/(T)/($\tilde{T}$) ^p	QMC ^q	
1¹B_{1u} (L_a,+)							
ΔE	8.02	8.27	8.22	7.87	7.98/7.99/7.74	7.93	
f	0.36				0.358		
$\langle x^2 \rangle$					17.9		

^aCASPT2F/[TZ2P,+A]. Serrano-Andrés *et al.*²³ the PT2F results. The ΔE values and the differential dynamical correlation effects on ΔE ($\Delta\Delta E$ (dyn), in parentheses) are given in the CASSCF column. Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p2d/3s2p], plus diffuse [2s2p1d] on carbon. The one-electron properties by the CASSCF method. The results from Table II.

^bMS-CASPT2/[QZ2P/TZ2P,+A]. Finley *et al.*²² Only the ΔE values and the differential dynamical correlation effects on ΔE ($\Delta\Delta E$ (dyn), in parentheses) are given in the CASSCF column. Basis set: ANO^{181,274} 5s4p2d/3s2p] plus molecule-centered diffuse [1s1p1d]. The one-electron properties are by the PMCAS method; the excitation energies used in computing the oscillator strengths are by the MS-CASPT2 method. The results from Table 1.

^cKrawczyk *et al.*²³³ Basis set: cc-pVTZ. The results from Table II.

^dGrimme *et al.*²⁷⁷ Basis set: [4s3p1d/3s1p], of cc-pVXZ family. We added the quoted experimental value, 7.8 eV, and the provided error, 0.44 eV. The origin of the quoted CASPT2 error, 0.40 eV, is not clear, because the plausible source, Table II of Serrano-Andrés *et al.*²³ uses a different experiment-derived estimate, 8.0 eV. The results from Table 4.

^eFranz²⁶² Basis set: ANO-S²⁴⁰ (10s6p3d/7s3p)[7s6p3d/4s3p] plus molecule-centered diffuse [2s1p1d]. The results with $T_{sel}=10^{-6}$ and the V -state orbitals from Tables II and IV.

^fNakayama *et al.*²⁴³ Basis set: QZ3p, which corresponds to Dunning's cc-pVQZ basis²⁰ truncated to [5s4p3d/3s2p] contractions (higher polarization functions omitted). The QZ3p/(2, 4) results from Tables I and II.

^gWitek *et al.*²²⁴ Basis set: cc-pVTZ. MRMP: MRPT with Møller-Plesset partitioning. Number in parentheses: the order of PT. Results from Table 1.

^hConverted by $\frac{2}{3} \frac{(TDM)^2}{\Delta E}$ using the 1.48 a.u. transition dipole moment data.

ⁱSORCI/[TZPA]. Neese²⁶⁶ Basis set: aug-cc-pVTZ. The results from Table IV.

^jMR-CISD+Q/[CBS estimate]. Müller *et al.*¹⁹² the REF(12,12,1p) MR-CISD+Q/CBS estimate from Table VI.

^kBarbatti *et al.*²³² The two values given are MR-CI/MR-CISD+Q, at Level 3, SA-3-RDP/aug-cc-pVTZ, from Table I.

^l(SC)2-SDCI/[TZ2P,+A]. Pérez-Casany *et al.*²⁸² Basis set: ANO, (14s9p4d/8s4p)[4s3p2d/3s2p], plus diffuse [2s2p1d] on carbon. The three values given are calculations that used three different sets of orbitals: canonical MOs/p-dication MOs/IDDCI natural orbitals (NOs). The results from Table 1.

^mEOM-CCSD/[TZP+A/TZP]. Baeck *et al.*²⁴⁴ Basis set: PVTZ-f+R/ PVTZ-d. The results from Table 1.

ⁿHättig *et al.*²³⁹ Basis set: TZVPP, which is of (11s6p2d1f/5s2p1d)[5s3p2d1f/3s3p1d] quality. The auxiliary basis set: (8s6p5d3f1g/4s3p2d1f). The results from Table II.

^oEOM-CC3/[TZ2P+A/TZ2P]. Christiansen *et al.*¹¹ Basis set: ANO, (14s9p4d/8s4p)[4s3p2d/3s2p], plus diffuse [2s2p1d] on carbon. The results from Table III.

^pEOM-CCSD/(T)/($\tilde{T}$)/[TZ2P+A/TZ2P]. Watts *et al.*²²¹ Basis set: ANO^{181,274} [4s3p2d/3s2p], plus diffuse [2s2p1d] on carbon. Three ΔE values given are at EOM-CCSD/ EOM-CCSD(T)/EOM-CCSD($\tilde{T}$) levels. The f and $\langle x^2 \rangle$ values at EOM-CCSD level. The results from Tables I (f , $\langle x^2 \rangle$) and II (ΔE).

^qSchautz *et al.*²¹⁹ The "3body-J basis set B" Quantum Monte Carlo (QMC) results from Table I.

TABLE XXXIX: Published results for vertical excitation energies and properties of *E*-butadiene.

	CASPT2 ^a	CASSCF ^a	MRMP ^b	CASPT2 ^c	QDVPT	MRMP(2) ^d	MRMP(3) ^d	MROP(2) ^d	$H^{\nu e}$
2¹A_g (L_b,-)									
ΔE	6.27	6.64 (-0.27)	6.31	6.27	6.35 ^f	6.40	8.13	6.75	6.01
$\langle x^2 \rangle$	23.2								24.98
1¹B_u (L_a,+)									
ΔE	6.23	8.54 (-2.31)	6.21	6.06	6.39 ^g	6.10	6.71	6.18	6.01
f	0.686		0.803						0.52
$\langle x^2 \rangle$	40.9				48.1 ^g				32.62
1³A_g (L_b,-)									
ΔE	4.89	5.08 (-0.19)	4.87			4.95	5.10	5.25	4.75
$\langle x^2 \rangle$	22.0								23.27
1³B_u (L_a,-)									
ΔE	3.20	3.39	3.20		3.66 ^g	3.20	3.39	3.46	3.10
$\langle x^2 \rangle$	21.8				21.9 ^g				21.24
	RI-CC2 ^h	CCS ^h	CC3 ⁱ	EOM-CCSD/(T)/($\tilde{T}$) ^j	SORCI ^k	MR-CISD+Q ^l	MR-AQCC ^l	SAC-CI ^s	
2¹A_g (L_b,-)									
ΔE	7.57	7.47	6.76	7.23/6.92/6.76	6.37	6.59 (6.67) ^{mn}	6.58 ^p	6.56	
$\langle x^2 \rangle$				36.1		21.86 ^o	22.5 ^o		
1¹B_u (L_a,+)									
ΔE	6.37	6.57	6.26	6.42/6.36/6.13	6.29	6.32 (6.54) ^{qn}	6.18 ^r	6.33	
f			0.6585	0.651	0.6408			0.6467	
$\langle x^2 \rangle$				31.7		26.3 ^o	27.9 ^o	35.5	
1³A_g (L_b,-)									
ΔE					5.27			5.08	
1³B_u (L_a,-)									
ΔE					3.32			3.20	

^aCASPT2F/[TZP+A/DZP]. Serrano-Andrés *et al.*²³ the PT2F results in the CASPT2 column. The one-electron properties by the CASSI⁴⁰ method; the excitation energies used in computing the oscillator strengths by the CASPT2 method. Only the ΔE values and the differential dynamical correlation effects on ΔE ($\Delta\Delta E$ (dyn), in parentheses) are given in the CASSCF column. Basis set: ANO,^{181,274} (14s9p4d/8s4p)[6s3p1d/2s1p], plus diffuse [2p] on carbon. The results from Table IV.

^bMRMP/[QZ3p, no diffuse]. Nakayama *et al.*²⁴³ Basis set: QZ3p, which is the Dunning's cc-pVQZ basis²⁰ truncated to [5s4p3d/3s2p] contractions (higher polarization functions omitted). No diffuse functions. The QZ3p/(4, 8) results from Tables I and II.

^cOstojic *et al.*²³⁷ Basis set: ANO²⁷⁴ (14s9p4d3f/8s4p3d)[3s2p1d/2s1p] (it is not clear what happened with the H-*d* and non-H-*f* primitives). The results from text of page 3.

^dWitek *et al.*²²⁴ Basis set: cc-pVTZ. MRMP: MRPT with Møller- Plesset partitioning. MROP: MRPT with optimized partitioning. Number in parentheses: the order of PT. Results from Table 3.

^e[TZP+A/DZP] Chaudhuri *et al.*²⁰⁴ Basis set (10s6p1d/4s1p)[5s3p1d/2s1p] by Dunning^{20,227} plus [1p] diffuse on carbons. The 6-orbitals reference space 3rd order results from Table III.

^fLappe *et al.*²¹⁰ Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p2d/3s2p]. The Davidson-corrected "DC-MRSDCI 125/93 5x10⁻⁷" value from Table 2.

^g H^{ν} Cave *et al.*²²³ Dunning-Huzinaga (9s5p2d/4s)[4s2p2d/2s] basis, plus diffuse [2px] on carbon. The results from Table VI.

^hHättig *et al.*²³⁹ Basis set: TZVPP, which is of (11s6p2d1f/5s2p1d)[5s3p2d1f/3s3p1d] quality. The auxiliary basis set: (8s6p5d3f1g/4s3p2d1f). The results from Table III.

ⁱCC3/[TZP,+A]. Cronstrand *et al.*³⁴ The ΔE values: QR-CC3/cc-pVTZ+5 estimates from p. 2570. The oscillator strength: the CCSD/cc-pVTZ+5 value from Table 1.

^jEOM-CCSD/(T)/($\tilde{T}$)/[TZP+A/DZP]. Watts *et al.*²²¹ Basis set: ANO^{181,274} [6s3p1d/2s1p], plus diffuse [2p] on carbon. Three ΔE values given are at EOM-CCSD/ EOM-CCSD(T)/EOM-CCSD($\tilde{T}$) levels. The f and $\langle x^2 \rangle$ values at EOM-CCSD level. The results from Tables IV and V.

^kSORCI/[TZPA]. Neese²⁶⁶ Basis set: aug-cc-pVTZ. The results from Table V.

^lDallos *et al.*²¹¹

^mMR-CISD+Q/[DZPA]. The RCA2-F/MR-CISD+Q/aug-cc-pVDZ values from Table 5. The Davidson-corrected RCA3-F/MR-CISD+Q/aug-cc-pVTZ estimate from p. 23 is 6.55 eV.

ⁿThe excitation energies without Davidson correction in parentheses.

^oThe CAS(4,5)-F/aug-cc-pVTZ value from Table 6.

^pMR-AQCC/[TZPA]. The RCA3-F/MR-AQCC/aug-cc-pVTZ estimate from p. 23.

^qMR-CISD+Q/[DZPA]. The RCA2-F/MR-CISD+Q/aug-cc-pVDZ values from Table 5.

^rMR-AQCC/[CBS estimate]. The complete basis extrapolated CAS(4,5)-F/MR-AQCC+Q value from Table 6.

^sSaha *et al.*²⁴⁸ Dunning-Huzinaga [4s2p1d/2s] basis, plus diffuse [2s2p2d] for n=3 and [2s2p] for n=4. The results from Table I and II.

TABLE XL: Published results for vertical excitation energies and properties of all-*E*-hexatriene.

	CASPT2 ^a	CASPT2 ^b	MRMP ^c	CASCI-MRMP ^d	RI-CC2 ^e	CCSDR(3) ^f	H^ν ^g
2¹A_g (L_b,-)							
ΔE	5.20	4.89	5.09	5.10		6.06	5.20
$\langle x^2 \rangle$	31.8						
1¹B_u (L_a,+)							
ΔE	5.01	5.45	5.10	5.25	5.30	5.40	5.21
f	0.85	0.655	1.082			1.1540	
$\langle x^2 \rangle$	40.4						
1³A_g (L_b,-)							
ΔE	4.12		4.15				4.14
$\langle x^2 \rangle$	31.7						
1³B_u (L_a,-)							
ΔE	2.55		2.40				2.57
$\langle x^2 \rangle$	31.8						

^aCASPT2D/PT2F/[TZP+A/DZP], PT2D/PT2F. Serrano-Andrés *et al.*²³ the PT2D results in the CASPT2 column (except the value for the 2¹A_g state, which is by the PT2F CASPT2 variant). The one-electron properties by the CASSI⁴⁰ method; the excitation energies used in computing the oscillator strengths by the CASPT2 method. Basis set: ANO^{181,274} (14s9p4d/8s4p)[6s3p1d/2s1p], plus diffuse [2p] on carbon.

^bWoywod *et al.*²⁷¹ The CASPT2(g0)/ANO results from Table III. Basis set: [7s6p3d/4s3p], with some diffuse character.

^cNakayama *et al.*²⁴³ Basis set: DZp, [3s2p1d/2s], no diffuse functions. Active space (6,12). The corrected MRMP results from Tables I and II, obtained by basis set extrapolation from DZp/(6,12) to QZ3p/(6,12) using data for butadiene from Table IV. The corrected MRMP results for the triplet states seem inconsistent, since the raw data in Tables IV and VI would yield 4.04 and 2.51 eV. The uncorrected DZp/(6,12) oscillator strength from Table I.

^dKurashige *et al.*²⁶³ Basis set: cc-pVDZ. The data from Table 2.

^eHättig *et al.*²³⁹ Basis set: TZVPP. The results from Table IV.

^fCCSDR(3)/[DZP,+A]. Cronstrand *et al.*³⁴ The CCSDR(3)/cc-pVDZ+5 values from Table 2. The transition dipole moment used for calculating the f values were calculated with the EOM-CCSD method. The CCSDR(3)/CC3 ΔE values for the 2¹A_g and 1¹B_u states with the smaller 6-31++G+2 basis are 5.94/5.73 eV and 5.73/5.73 eV (Table 2).

^g H^ν /[DZP+A/DZP]. Martin *et al.*²²⁵ Basis set: II, cc-pVDZ plus diffuse [2p] on carbon. The 5V1R 3rd order results from Table 10.

TABLE XLI: Published results for vertical excitation energies and properties of all-*E*-octatetraene.

	CASPT2 ^a	MRMP ^b	CASCI-MRMP ^c	RI-CC2 ^d	CC3 ^e	MRCI ^f
2¹A_g (L_b,-)						
ΔE	4.38 (4.42) ^g	4.47	4.26		4.98	5.21 ^h
$\langle x^2 \rangle$	41.4					42.3 ^h
3¹A_g (-)						
ΔE	6.56		7.02			
$\langle x^2 \rangle$	42.3					
4¹A_g (-)						
ΔE	7.14					
$\langle x^2 \rangle$	41.3					
1¹B_u (L_a,+)						
ΔE	4.42 (4.54) ^g	4.66	4.57	4.60	5.14	4.79 ⁱ
f	1.8316	1.382				
$\langle x^2 \rangle$	43.5					44.2 ⁱ
2¹B_u (-)						
ΔE	5.83	5.30				44.2
f	0.01					
$\langle x^2 \rangle$	41.3					
3¹B_u (-)						
ΔE	8.44					
f	0.0019					
$\langle x^2 \rangle$	42.0					
1³A_g (L_b,-)						
ΔE	3.39	3.55				
$\langle x^2 \rangle$	41.3					
1³B_u (L_a,-)						
ΔE	2.17	2.20				2.45 ^h
$\langle x^2 \rangle$	41.5					42.3 ^h

^aCASPT2F/[TZP/DZP,+A]. Serrano-Andrés *et al.*¹⁵⁹ the PT2F results in the CASPT2 column. The one-electron properties by the CASSI⁴⁰ method; the excitation energies used in computing the oscillator strengths by the CASPT2 method. Basis set: (14s9p4d/8s4p)[4s3p1d/2s1p], plus molecule- centered diffuse [1s1p1d].

^bNakayama *et al.*²⁴³ Basis set: DZp, [3s2p1d/2s], no diffuse functions. Active space (8,12). The corrected MRMP results from Tables I and II, obtained by basis set extrapolation from DZp/(8,12) to QZ3p/(8,12) using data for butadiene from Table IV. The uncorrected DZp/(8,12) oscillator strength from Table I.

^cKurashige *et al.*²⁶³ Basis set: cc-pVDZ. The results from Table 2.

^dHättig *et al.*²³⁹ Basis set: TZVPP. The results from Table IV.

^eCronstrand *et al.*³⁴ The CC3/6-31++G+2 values from p. 2572.

^fCave *et al.*²⁷² Basis set: (9s5p1d/4s)[3s2p1d/2s], plus diffuse [2p] on carbon.

^gThe data in parentheses from Beljonne *et al.*²¹⁷ Basis set same as in Serrano-Andrés *et al.*¹⁵⁹. Differences from Serrano-Andrés¹⁵⁹ are due, in part, to details of the CASSCF calculations (active space, state averaging, etc).

^hThe QCI results from Table IV of Cave *et al.*²⁷²

ⁱThe CI8 results from Table II of Cave *et al.*²⁷²

TABLE XLII: Published results for vertical excitation energies and properties of cyclopropene.

	CASPT2 ^a	CASSCF ^a
1¹A₁		
μ	-0.48	
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	14.6, 12.6, 13.9	
1¹B₁		
ΔE	6.36	7.43
μ	+1.92	
f	0.0097	
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	18.3, 15.0, 12.1	
1¹B₂		
ΔE	7.45	7.77
μ	+0.70	
f	0.1007	
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	40.7, 40.0, 19.8	
1³B₁		
ΔE	6.05	6.97
μ	+1.90	
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	17.2, 14.0, 11.7	
1³B₂		
ΔE	4.18	4.65
μ	+0.65	
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	14.8, 14.0, 11.9	

^aGonzález-Luque *et al.*¹⁶⁰ the PT2F results in the CASPT2 column. The one-electron properties by the CASSI⁴⁰ method; the excitation energies used in computing the oscillator strengths by the CASPT2 method. Only ΔE values given for the CASSCF method. Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p2d/3s2p], plus molecule-centered diffuse [2s2p1d].

TABLE XLIII: Published results for vertical excitation energies and properties of cyclopentadiene.

	CASPT2 ^a	MRMP (MCQD) ^b	(SC) ² -SDCI ^c	SAC-CI ^d	SAC-CI ^e	EOM-CCSD/(T)/($\tilde{T}$) ^f	EOM-CCSD/T ^g
1¹A₁ (1¹A₁⁻)							
μ	-0.29						
$\langle x^2 \rangle$	24.8				25.51	30.8	
2¹A₁ (L_b, -, 1¹A₁⁻)							
ΔE	6.31	6.42 (6.47)	6.09	7.81	6.76	6.85/6.56/6.37	
μ	-0.42						
f	0.000	0.00391		0.0193	0.0009	0.004	
$\langle x^2 \rangle$	25.0				30.88	34.1	
4¹A₁ (B_b, +, 1¹A₁⁺)							
ΔE	7.89	8.11 (8.16)	8.36		8.17	8.54/-/8.29	
μ	-1.87						
f	0.442	0.502			0.5377	0.225	
$\langle x^2 \rangle$	26.9				61.92	63.8	
1¹B₂ (L_a, +, 1¹B₂⁺)							
ΔE	5.27	5.19 (5.27)	5.24	6.48	5.54	5.65/5.63/5.30	5.66/5.55
μ	0.572						
f	0.148	0.146		0.159	0.1305	0.099	
$\langle x^2 \rangle$	29.1				26.92	31.9	
1³A₁ (L_b, -, 1³A₁⁻)							
ΔE	4.90		4.62	5.50	5.18		
μ	-0.16						
$\langle x^2 \rangle$	24.6				25.70		
1³B₂ (L_a, -, 1³B₂⁻)							
ΔE	3.15		2.87	3.52	3.40		
μ	-0.14						
$\langle x^2 \rangle$	24.8				25.61		

^aCASPT2F/[TZP/DZP,+A]. Serrano-Andrés *et al.*¹⁶¹ the PT2F results in the CASPT2 column. Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p1d/2s1p], plus molecule-centered diffuse [2s2p2d]. The one-electron properties by the CASSI⁴⁰ method; the excitation energies used in computing the oscillator strengths by the CASPT2 method. The results from Tables II and III.

^bMRMP, MCQD/[TZP/DZP,+A]. Nakano *et al.*²⁰⁶ Basis set: valence [sp/s] functions: [cc-pVTZ/cc-pVDZ], carbon polarization functions from cc-pVDZ, plus molecule-centered diffuse [2s2p2d]. The ΔE values in parentheses are by the quasi-degenerate multi-configurational PT variant, MCQD. The results from Table II.

^c(SC)²-SDCI/[TZP/DZP,+A]. Pitarch-Ruiz *et al.*¹⁸⁵ Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p1d/2s1p], plus molecule-centered diffuse [2s2p2d] (same as in Serrano-Andrés *et al.*¹⁶¹). The results from Table 4.

^dNakatsuji *et al.*¹⁸⁰ Basis set: Huzinaga-Dunning [4s2p/2s], plus molecule-centered diffuse [2s2p1d]. The results from Tables IX and X. The excitation energy for the valence 3³A₁ state: 8.23 eV.

^eSAC-CI/[DZPA/DZP,+A]. Wan *et al.*²⁵² Basis set: aug-cc-pVDZ on carbon, cc-pVDZ on hydrogen, plus molecule-centered diffuse [3s3p3d]. The SD-R results from Table III.

^fEOM-CCSD/(T)/($\tilde{T}$)/[TZP/DZP,+A]. Watts *et al.*²²¹ Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p1d/2s1p], plus molecule-centered diffuse [2s2p2d] (same as in Serrano-Andrés *et al.*¹⁶¹). The three ΔE values refer to EOM-CCSD/EOM-CCSD(T)/EOM-CCSD($\tilde{T}$). The f and $\langle x^2 \rangle$ values at EOM-CCSD. The results from Table IX.

^gEOM-CCSD/T/[CBS estimate], experiment+EOM-CC. Bomble *et al.*³² The complete basis set estimates from p. 5238. The two ΔE values refer to EOM-CCSD and EOM-CCSDT, respectively. A best estimate of 5.43±0.05 eV for the 1¹B₂ state is derived from the experimental absorption peak maximum and a correction (0.13 eV) from a spectroscopic simulation.

TABLE XLIV: Published results for vertical excitation energies and properties of norbornadiene.

	CASPT2 ^a	EOM-CCSD ^b	STEOM-CCSD ^b	Ext-STEOM-CCSD ^b
1¹A₁ (-)				
μ	0.117			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	31.9, 28.9, 32.9			
6¹A₁ (-)				
ΔE	7.49			
μ	0.851			
f	0.0002			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	29.4, 28.5, 31.0			
1¹A₂ (+)				
ΔE	5.28	5.88	5.65	5.60
μ	1.956			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	34.5, 45.8, 47.9			
5¹A₂ (+)				
ΔE	7.36	7.58	7.47	7.41
μ	0.546			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	46.8, 52.0, 38.3			
1¹B₂ (+)				
ΔE	6.20	6.67	6.52	6.45
μ	1.847			
f	0.008			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	43.7, 53.7, 42.7			
2¹B₂ (+)				
ΔE	6.48	7.00	6.94	6.90
μ	0.434			
f	0.343			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	46.8, 47.0, 38.5			
1³A₂ (-)				
ΔE	3.42			
μ	0.160			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	31.1, 30.0, 33.4			
1³B₂ (-)				
ΔE	3.80			
μ	0.119			
$\langle x^2 \rangle, \langle y^2 \rangle, \langle z^2 \rangle$	31.8, 29.9, 32.8			

^aCASPT2/[TZP/DZP,+A]. Roos *et al.*¹⁶². Excitation energies from the PT2F variant of CASPT2; one-electron properties from the CASSI⁴⁰ method; oscillator strengths computed with the use of CASPT2 excitation energies. Basis set: ANO^{181,274} (14s9p4d/8s4p)[4s3p1d/2s1p], plus molecule-centered diffuse [1s1p1d]. The results from Table 3.

^bNooijen *et al.*²⁹ Basis set: [DZP/DZ], plus molecule-centered diffuse [2s2p2d]. The results from Table I.

2. Aromatic Hydrocarbons and Heterocycles

TABLE XLV: Published results for vertical excitation energies and properties of benzene (part 1). The two sets of symmetry labels refer to D_{6h} (D_{2h}), respectively.

	CASPT2 ^a	MRMP/ CASSCF ^b	SCF-MRMP MRMP ^c	MRMP CASSCF ^d	MRMP2/3/4(SD) ^e	MREN(2)/(3) ^f	MRMP(2)/(3)/ MROPT(2) ^g
1^1B_{1u} (B_{2u}) [$+$, $1^1B_{1u}^+$]							
ΔE	6.30	6.28/8.10	6.14/6.31	6.21/7.55	6.30/6.65/6.43	5.52/6.60	6.07/6.37/6.22
$\langle x^2 \rangle$	31.9						
1^1B_{2u} (B_{3u}) [$-$, $1^1B_{2u}^-$]							
ΔE	4.84	4.77/5.07	4.73/4.77	4.70/4.94	4.73/5.13/4.89	6.06/5.02	4.61/5.32/5.09
$\langle x^2 \rangle$	30.1						
1^1E_{1u} (B_{2u}, B_{3u}) [$+$, $1^1E_{1u}^+$]							
ΔE	7.03	6.98/9.37	6.86/7.03	6.93/8.77	7.05/7.55/7.22	5.40/8.13	6.58/9.48/ -
f	0.82			0.8912			
$\langle x^2 \rangle$	35.1						
2^1E_{2g} (A_g, B_{1g}) [$-$, $1^1E_{2g}^-$]							
ΔE	7.90	7.88/8.17	7.83/7.88	7.82/8.05		9.54/8.16	7.71/9.48/8.24
$\langle x^2 \rangle$	29.8						
1^3B_{1u} (B_{2u}) [$-$, $1^3B_{1u}^-$]							
ΔE	3.89	4.11/4.58	3.92/3.97			4.60/4.06	3.93/4.12/4.19
$\langle x^2 \rangle$	29.8						
1^3B_{2u} (B_{3u}) [$+$, $1^3B_{2u}^+$]							
ΔE	5.49	5.34/7.41	5.46/5.71			4.26/6.13	5.41/6.28/5.60
$\langle x^2 \rangle$	32.3						
1^3E_{1u} (B_{2u}, B_{3u}) [$-$, $1^3E_{1u}^-$]							
ΔE	4.49	4.81/5.62	4.54/4.58			5.01/4.90	4.43/5.02/4.90
$\langle x^2 \rangle$	30.3						
1^3E_{2g} (A_g, B_{1g}) [$-$, $1^3E_{2g}^-$]							
ΔE	7.12	7.04/7.23	7.07/7.12			8.39/7.31	6.99/8.42/7.47
$\langle x^2 \rangle$	39.3						

^aCASPT2F/[unspecified, supposedly TZP/DZP,+A]. Lorentzon *et al.*¹⁶³ the PT2F results in the CASPT2 column. Basis set: ANO^{181,274} unspecified contraction, plus molecule-centered diffuse [1s1p1d], supposedly [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. because of the reference on p. 5969 of Hald *et al.*²⁷ The results from Tables 5 and 6.

^bHirao *et al.*²⁶⁹ Basis set: cc-pVDZ, plus molecule-centered diffuse (8s8p8d)[1s1p1d]. The two ΔE values given are the MRMP and CASSCF results from Table 1.

^cNakao *et al.*¹⁹¹ Basis set: [cc-pVTZ/cc-pVDZ], plus molecule-centered diffuse (8s8p8d)[1s1p1d]. The two ΔE values given are the SCF-MRMP and MRMP results from Table 8.

^dHashimoto *et al.*²⁷⁶ Basis set: [cc- pVTZ/cc-pVDZ], plus molecule-centered diffuse (8s8p8d)[1s1p1d]. The two ΔE values given are the MRMP and CASSCF results from Table 2.

^eGrimme *et al.*²⁰⁸ Basis set: [4s3p1d/3s], plus diffuse [1p] on carbons. The three ΔE values are the MRMP2, MRMP3, and MRMP4(SD) results with $T_{sel}=0.01$ from Table 2.

^fWitek *et al.*²²⁴ Basis set: ANO (14s9p4d/8s4p)[4s3p2d/3s2p], no diffuse functions. The two ΔE values given are the MREN(2) and MREN(3) results from Table 2.

^gWitek *et al.*²²⁴ Basis set: ANO (14s9p4d/8s4p)[4s3p2d/3s2p], no diffuse functions. The three ΔE values given are the MRMP(2), MRMP(3), and MROPT(2) results from Table 2.

TABLE XLVI: Published results for vertical excitation energies and properties of benzene (part 2). The two sets of symmetry labels refer to D_{6h} (D_{2h}), respectively.

	SORCI ^a	CASSCF/ MRCI/DC ^b	CASSCF/MRCI SD/MRCISD+Q ^c	CEPA/CCI/ CASSCF ^d	SAC-CI ^e $\pi\pi + \sigma$	STEOM PT/CC3 ^f	CC2	CCSD/CC3/ CCSDR(3)	EOM- CCSD/ $(\tilde{T})$ ^g
1^1B_{1u} (B_{2u}) [$+$, $1^1B_{1u}^+$]									
ΔE	6.45		7.85/7.03/6.63	6.9/6.8/7.4	7.31/6.60	6.52/6.47	6.463 ^h	6.590/6.540/6.558 ⁱ	6.50/6.17
$\langle x^2 \rangle$					34/33				32
1^1B_{2u} (B_{3u}) [$-$, $1^1B_{2u}^-$]									
ΔE	4.96	4.97/5.17/5.21	4.97/5.09/5.10	5.4/5.6/4.9	5.25/5.25	4.96/4.81	5.232 ^h	5.189/5.078/5.120 ⁱ	5.14/4.74
$\langle x^2 \rangle$					31/31				30
1^1E_{1u} (B_{2u}, B_{3u}) [$+$, $1^1E_{1u}^+$]									
ΔE	7.19	9.41/8.32/7.90	9.30/8.16/7.51	7.4/7.4/8.3	8.25/7.47	7.20/7.15	7.070 ^h	7.166/7.132/7.150 ⁱ	7.29/6.99
f	0.77			0.523	0.61/1.03		1.049 ^j	1.067 ^j	1.33
$\langle x^2 \rangle$					62/41		42.6 ^j	41.4 ^j	36
2^1E_{2g} (A_g, B_{1g}) [$-$, $1^1E_{2g}^-$]									
ΔE	7.83		8.17/8.27/8.24	7.4/8.1/8.1		9.15/9.10	8.909 ^h	9.174/8.409/8.691 ⁱ	
1^3B_{1u} (B_{2u}) [$-$, $1^3B_{1u}^-$]									
ΔE	4.13		3.87/4.10/4.18	4.0/4.3/3.9	3.80/4.06		4.345 ^k	3.974 ^l / 4.145 ^m	
$\langle x^2 \rangle$					30/31				
1^3B_{2u} (B_{3u}) [$+$, $1^3B_{2u}^+$]									
ΔE	5.84		7.09/6.32/5.95	5.2/5.1/7.0	6.65/6.02		5.873 ^k	5.755 ^l / 5.882 ^m	
$\langle x^2 \rangle$					32/32				
1^3E_{1u} (B_{2u}, B_{3u}) [$-$, $1^3E_{1u}^-$]									
ΔE	4.75		5.00/4.96/4.90	4.0/4.3/4.9	5.05/5.02		5.058 ^k	4.903 ^l / 4.863 ^m	
$\langle x^2 \rangle$					31/31				
1^3E_{2g} (A_g, B_{1g}) [$-$, $1^3E_{2g}^-$]									
ΔE	7.00		7.20/7.42/7.47	- / - / 7.2			7.782 ^k	7.719 ^l / 7.507 ^m	

^aSORCI/[DZPA/DZ]. Neese²⁶⁶ Basis set: SV(P)+. The results from Table VI.

^bSobolewski *et al.*²⁶⁵ Basis set: DZP²⁵⁸ The three ΔE values given are the CASSCF, MRCI, and MRCI-DC (Davidson-corrected) results from Table IV.

^cWitek *et al.*²²⁴ Basis set: ANO (14s9p4d/8s4p)[4s3p2d/3s2p], no diffuse functions. The three ΔE values given are the CASSCF, MRCI, and MRCISD+Q results from Table 2.

^dMatos *et al.*²¹² Basis set: (9s8p1d/7s)[4s3p1d/3s], in which some functions on carbon supposedly are diffuse. The three ΔE values given correspond to CEPA (Table IX), CCI (Table IX), and CASSCF2 (Table VII). The f value for the 1^1E_{1u} state was calculated from $\frac{2}{3} \frac{(TDM)^2}{\Delta E}$ using the 1.70 a.u. transition dipole magnitude given in Table VIII, and the excitation energy of 7.4 eV (CEPA and CCI).

^eKitao *et al.*²¹⁶ Basis set: basis 1 in the notation of this paper, which is [4s2p/2s], plus diffuse [2p] on carbons, plus [1d] on carbons. The two ΔE and two f values shown are the 35π (before the slash) and $35\pi+45\sigma$ (after the slash) results from Table V. The two $\langle x^2 \rangle$ values shown are the 35π and $35\pi+45\sigma$ ($\langle z^2 \rangle$) results from Table VI.

^fSTEOM/[DZ2PA/DZP]. Nooijen²⁴⁵ Basis set: [Sadlej PBS/DZP]; PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). Results from Table 1.

^gEOM-CCSD/ $(\tilde{T})$ /[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values are the EOM-CCSD and EOM-CCSD/ $(\tilde{T})$ results from Table III. The f value is the EOM-CCSD result from Table III. The $\langle x^2 \rangle$ values are the $\langle z^2 \rangle$ EOM-CCSD results from Table II.

^hChristiansen *et al.*²¹⁴ Basis set: aug-cc-pVTZ-CM2, which denotes aug-cc-pVTZ plus molecule-centered diffuse [2s2p2d]. Results from Table 3.

ⁱEOM-CCSD,CC3/[TZP/DZP,+A]. Christiansen *et al.*²⁴ Basis set: ANO, (14s9p4d/8s4p)[4s3p1d/2s1p], plus molecule-centered diffuse (8s8p8d)[1s1p1d]. The three ΔE values are the CCSD/CC3/CCSDR(3) results from Table VI.

^jChristiansen *et al.*²⁶ Basis set: "ANO1", [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The CC2 and CCSD results for the 2^1E_{1u} states from Table 5.

^kHald *et al.*¹³ Basis set: aug-cc-pVTZ-CM2, which denotes aug-cc-pVTZ plus molecule-centered diffuse [2s2p2d]. Results from Table 2.

^lHald *et al.*¹⁴ Basis set: aug-cc-pVTZ-CM2, which denotes aug-cc-pVTZ plus molecule-centered diffuse [2s2p2d]. The first ΔE values given (before the slash) are the CCSD results from Table IV.

^mCC3/[supposedly TZP/DZP,+A]. Hald *et al.*²⁷ Basis set: "ANO1", supposedly [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]: the number of contracted functions, 147, coincides with that given in Footnote *b* of Table V of Christiansen *et al.*²⁶. The second ΔE values given (after the slash) are the CC3 results from Table III.

TABLE XLVII: Published results for vertical excitation energies and properties of naphthalene (part 1, singlet states). The second set of symmetry labels (in parentheses) is taken from Hashimoto *et al.*¹⁸².

	CASPT2 ^a	MRMP/CASSCF ^b	MRMP2/3/4(SD) ^c	SAC-CI $\pi\pi + \sigma$ ^d	CC2 ^e
$2^1\mathbf{A}_g$ (-, $2^1\mathbf{A}_g^-$)					
ΔE	5.39	5.65/5.86			
$\langle x^2 \rangle$	48.5				
$3^1\mathbf{A}_g$ (-, $3^1\mathbf{A}_g^-$)					
ΔE	6.04	6.44/7.04			
$\langle x^2 \rangle$	48.5				
$1^1\mathbf{B}_{2u}$ (+, $1^1\mathbf{B}_{2u}^+$)					
ΔE	4.56	4.62/6.61	4.70/5.14/4.84	6.04/5.42	4.88
f	0.0496	0.0616			
$\langle x^2 \rangle$	49.6				
$2^1\mathbf{B}_{2u}$ (+, $2^1\mathbf{B}_{2u}^+$)					
ΔE	5.93	5.95/8.12			
f	0.3127	0.2678			
$\langle x^2 \rangle$	49.6				
$4^1\mathbf{B}_{2u}$ (+, $3^1\mathbf{B}_{2u}^+$)					
ΔE	7.16	7.56/10.43			
f	0.8481	0.8398			
$\langle x^2 \rangle$	49.5				
$1^1\mathbf{B}_{3u}$ (-, $1^1\mathbf{B}_{3u}^-$)					
ΔE	4.03	4.09/4.34	3.77/4.47/4.12	4.90/4.90	4.46
f	0.0004	0.0002			
$\langle x^2 \rangle$	48.9				
$2^1\mathbf{B}_{3u}$ (+, $1^1\mathbf{B}_{3u}^+$)					
ΔE	5.54	5.62/8.21			
f	1.3365	1.3256			
$\langle x^2 \rangle$	49.5				
$4^1\mathbf{B}_{3u}$ (-, $2^1\mathbf{B}_{3u}^-$)					
ΔE	7.18	7.23/8.03			
f	0.0481	0.0671			
$\langle x^2 \rangle$	48.7				
$1^1\mathbf{B}_{1g}$ (-, $1^1\mathbf{B}_{1g}^-$)					
ΔE	5.53	5.74/6.63			
$\langle x^2 \rangle$	49.4				
$2^1\mathbf{B}_{1g}$ (+, $1^1\mathbf{B}_{1g}^+$)					
ΔE	5.87	6.14/8.61			
$\langle x^2 \rangle$	49.4				

^aCASPT2F/[DZP/DZ,+A]. Rubio *et al.*¹⁶⁴ the PT2F results in the CASPT2 column. Basis set: ANO^{181,274} (14s9p4d/8s)[3s2p1d/2s], plus molecule-centered diffuse [2s2p2d]. The singlet ΔE and f values are the results from Table 5. The $\langle x^2 \rangle$ values correspond to the $\langle z^2 \rangle$ CASSCF results from Table 3.

^bHashimoto *et al.*¹⁸² Basis set: [cc-pVDZ/cc-VDZ] (the cc-pVDZ basis without polarization functions on hydrogen atoms). No diffuse basis functions. The results from Table II.

^cGrimme *et al.*²⁰⁸ Basis set: [3s2p1d/2s]. Supposedly, no diffuse functions. The three ΔE values are the MRMP2, MRMP3, and MRMP4(SD) results with $T_{sel}=0.01$ from Table 2.

^dNakatsuji *et al.*²⁵⁹ Basis set: Huzinaga¹⁸⁸ and Dunning¹⁹⁰ [3s2p/2s], plus [2p1d] on carbon atoms. The two ΔE and two f values shown are the 58π (before the slash) and $44\pi+56\sigma$ (after the slash) results from Figure 2.

^eGrimme *et al.*¹⁸⁷ Basis set: cc-pVTZ. The results from Table 1.

TABLE XLVIII: Published results for vertical excitation energies and properties of naphthalene (part 2, triplet states). The second set of symmetry labels (in parentheses) is taken from Hashimoto *et al.*¹⁸².

	CASPT2 ^a	MRMP/CASSCF ^b
1³A_g (-, 1 ³ A _g ⁻)		
ΔE	5.28	5.27/5.55
f	0.0005	
$\langle x^2 \rangle$	48.6	
2³A_g (+, 1 ³ A _g ⁺)		
ΔE	5.83	6.07/8.13
$\langle x^2 \rangle$	49.1	
3³A_g (-, 2 ³ A _g ⁻)		
ΔE	5.91	6.13/6.51
f	0.0013	
$\langle x^2 \rangle$	48.9	
1³B_{2u} (-, 1 ³ B _{2u} ⁻)		
ΔE	3.10	3.15/3.16
$\langle x^2 \rangle$	48.6	
2³B_{2u} (-, 2 ³ B _{2u} ⁻)		
ΔE	4.30	4.40/4.65
$\langle x^2 \rangle$	48.6	
1³B_{3u} (-, 1 ³ B _{3u} ⁻)		
ΔE	3.90	3.95/4.35
$\langle x^2 \rangle$	49.1	
2³B_{3u} (+, 1 ³ B _{3u} ⁺)		
ΔE	4.46	4.58/6.46
$\langle x^2 \rangle$	49.2	
1³B_{1g} (-, 1 ³ B _{1g} ⁻)		
ΔE	4.24	4.37/4.45
$\langle x^2 \rangle$	49.0	
2³B_{1g} (+, 1 ³ B _{1g} ⁺)		
ΔE	5.71	5.86/8.18
f	0.0969	
$\langle x^2 \rangle$	49.9	
3³B_{1g} (-, 2 ³ B _{1g} ⁻)		
ΔE	6.24	6.40/6.72
f	0.0012	
$\langle x^2 \rangle$	48.7	

^aCASPT2F/[DZP/DZ,+A]. Rubio *et al.*¹⁶⁴ the PT2F results in the CASPT2 column. Basis set: ANO^{181,274} (14s9p4d/8s)[3s2p1d/2s], plus molecule-centered diffuse [2s2p2d]. The triplet ΔE values are given relative to the singlet 1¹A_g ground state, calculated using the triplet-triplet excitation energies from Table 6 and the CASSCF/CASPT2 values of 3.11/3.10 eV for $\Delta E(1^1A_g - 1^3B_{2u})$. These latter two values were computed from the total CASSCF/CASPT2 energies of the 1¹A_g and 1³B_{2u} states in Table 3 (-383.533871/-384.66179 and -383.41943/-384.548 Hartree). The f values for the transition from the lowest triplet 1³B_{2u} state are taken from Table 6.

^bHashimoto *et al.*¹⁸² Basis set: [cc-pVDZ/cc-VDZ] (the cc-pVDZ basis without polarization functions on hydrogen atoms). No diffuse basis functions. The results from Table II.

TABLE XLIX: Published results for vertical excitation energies and properties of furan (part 1).

	CASPT2 ^a	MRMP/MCQD/CASSCF ^b	MRCI ^c	MRCI DZP/DZPR ^d	MRCI ^e
1¹A₁ (-)					
μ	0.928				
$\langle x^2 \rangle$	24.1				
2¹A₁ (L_b, -)					
ΔE	6.16	6.16/6.19/7.09	6.79 - 7.08	6.024/6.63	6.53
μ	1.309				
f	0.0015	0.00349		0.011	
$\langle x^2 \rangle$	24.2				
4¹A₁ (B_b, +)					
ΔE	7.66	7.69/7.72/10.51		8.324/9.36	
μ	0.371				
f	0.4159	0.494		0.476	
$\langle x^2 \rangle$	27.0				
1¹B₂ (L_a, +)					
ΔE	6.04	5.95/5.99/8.52	7.58	6.759/6.88	6.44
μ	0.313				
f	0.1543	0.158		0.183	
$\langle x^2 \rangle$	30.2				
1³A₁ (L_b, -)					
ΔE	5.15		5.44 - 5.76	5.282/ -	
μ	1.129				
$\langle x^2 \rangle$	24.1				
1³B₂ (L_a, -)					
ΔE	3.99		4.08	3.931/ -	
μ	1.337				
$\langle x^2 \rangle$	24.0				

^aCASPT2F/[TZP/DZP,+A]. Serrano-Andrés *et al.*¹⁶¹ Basis set: ANO,^{181,274} [4s3p1d/2s1p], plus molecule- centered diffuse [2s2p2d]. The results from Table VIII (the CASPT2 ΔE values, and f). Note that the CASPT2 ΔE value for the 4¹A₁ state, 7.74 eV, given in Table VIII, does not agree with that calculated from the absolute energies given in Table VII, 7.66 eV. The origin of this discrepancy is not clear. We use the 7.66 eV value. CASPT2 is PT2F.

^bNakano *et al.*²⁰⁶ Basis set: valence [sp/s] functions: [cc-pVTZ/cc-pVDZ], carbon and oxygen polarization functions from cc-pVDZ, plus molecule-centered diffuse [2s2p2d]. The three ΔE values given come from: MRMP, quasi-degenerate multi-configurational PT variant (MCQD), and CASSCF. The f values from MRMP. All results from Table III.

^cThunemann *et al.*²³¹ Basis set: double zeta, plus bond s polarization function, plus molecule-centered diffuse [2s2p1d]. The ΔE values from Table 3 (triplet states), Table 4 (2¹A₁) and p. 318 (1¹B₂). Note that the ΔE value which is given in the text on p. 318 for the 1¹B₂ state and is presently adopted, 7.58 eV, differs from that given in the abstract, 7.54 eV.

^dPalmer *et al.*¹⁸⁴ Basis set: double zeta (DZ) plus [1d/1p] polarization (P) plus molecule-centered diffuse (Rydberg, R) [3s2p2d], denoted DZPR. The results from Table 4. The two ΔE values given were obtained with two basis sets, DZP (lacks Rydberg functions)/DZPR. The oscillator strengths seem to have been computed with the DZP basis set.

^eGromov *et al.*²⁴¹ Basis set: [aug-cc-pVDZ/cc-pVDZ], supposedly with additional [1s1p] diffuse on carbon and oxygen atoms. The MRCI results are the (internally contracted) MRCI-2 data. All results from Table I.

TABLE L: Published results for vertical excitation energies and properties of furan (part 2).

	SAC-CI ^a	SAC-CI ^b	CCS/CC2/CCSD/CCSDR(3)/CC3 ^c	EOM-CC ^d	EOM-CCSD ^e	ADC(2) ^f
1¹A₁ (-)						
μ	1.040		0.844/0.534/0.674/ - / -			
$\langle x^2 \rangle$	25					
2¹A₁ (L_b, -)						
ΔE	7.32	6.79	8.090/6.823/6.861/6.688/6.606	6.57	6.72	6.70
μ	1.500		0.834/0.869/0.966/ - / -			
f	0.0044	0.0000	0.0012/0.0020/0.0010/ - / -	0.000	0.001	0.003
$\langle x^2 \rangle$	26	26.0				
4¹A₁ (B_b, +)						
ΔE		8.34	8.953/8.387/8.559/8.399/8.349	8.13	8.16	
μ			2.122/0.737/0.653/ - / -			
f		0.4826	0.4164/0.1938/0.3440/ - / -	0.350	0.308	
$\langle x^2 \rangle$	38.4					
1¹B₂ (L_a, +)						
ΔE	7.50	6.40	6.319/6.403/6.489/6.384/6.352	6.32	6.44	6.37
μ	0.607		3.248/3.233/3.065/ - / -			
f	0.140	0.1852	0.1683/0.1494/0.1487/ - / -	0.144	0.166	0.148
$\langle x^2 \rangle$	34	42.8				
1³A₁ (L_b, -)						
ΔE	5.75	5.63				5.50
$\langle x^2 \rangle$		25.2				
1³B₂ (L_a, -)						
ΔE	4.40	4.39				4.31
$\langle x^2 \rangle$		25.0				

^aNakatsuji *et al.*¹⁸⁰ Basis set: Huzinaga-Dunning [4s2p/2s], plus molecule-centered diffuse [2s2p1d]. The results from Tables VI and VII.

^bSAC-CI/[DZPA/DZP,+A]. Wan *et al.*¹⁹⁸ Basis set: [aug-cc-pVDZ/cc-pVDZ], plus molecule-centered diffuse (3s3p3d). The results from Table III.

^cEOM-(various)CC/[TZP/DZP,+A]. Christiansen *et al.*¹⁹⁴ Basis set: ANO, [4s3p1d/2s1p], plus molecule-centered diffuse [2s2p2d], same as used by Serrano-Andrés *et al.*¹⁶¹ The EOM results from Tables V (ΔE), VI (f), and VII (μ).

^dEOM-(high-level)CC/[CBS estimate], f at EOM-CCSD/[DZP,+A]. Christiansen *et al.*³⁰ The ΔE values are the "estimated" values from Table 2, which include corrections for complete basis set extrapolation and high-order correlation effects. The f values from Table 2), presumably (by analogy with other data of this paper, see footnotes for Tables 3, 4, 6) computed at the EOM-CCSD/D+7 level; basis set D+7: cc-pVDZ plus molecule-centered diffuse.

^eEOM-CCSD/[DZPA+A/DZP]. Gromov *et al.*²⁴¹ Basis set: [aug-cc-pVDZ/cc-pVDZ], supposedly with additional [1s1p] diffuse on carbon and oxygen atoms. All results from Table I; the EOM-CCSD data from the "Opt." entry.

^fTrofimov *et al.*²⁵⁴ Basis set: cc-pVDZ, plus Rydberg [1s1p] plus molecule-centered diffuse [3s3p3d]. The second-order algebraic-diagrammatic construction, ADC(2), results from Table 5.

TABLE LI: Published results for vertical excitation energies and properties of pyrrole (part 1).

	CASPT2 ^a	MRMP/MCQD/ CASSCF ^b	MS-CASPT2 MRMP ^c	CASPT2/ CASSCF ^d	MRCI ^e	MRCI ^f	MRCI ^g	MRCI ^h	MRCISD+Q ^d
1¹A₁ (-)									
μ	1.766				1.88				
$\langle x^2 \rangle$	25.8				26		25.9	26.1	
2¹A₁ (L_b, -)									
ΔE	5.92	5.98/6.01/6.78	5.82		6.51	6.73	6.672	6.114	
μ	1.146				1.02				
f	0.0195	0.00979	0.036				0.0001	0.0012	
$\langle x^2 \rangle$	34.4				27		32.9	37.6	
6¹A₁ (B_b, +)									
ΔE	7.46	7.48/7.51/9.76					9.437	8.179	
μ	2.834								
f	0.3261	0.562					0.7060	0.4402	
$\langle x^2 \rangle$	38.9						35.8	50.7	
2¹B₂ (L_a, +)									
ΔE	6.00	6.51/6.51/8.93	5.87	5.95/7.56		7.70	6.769	6.731	6.84
μ	2.117								
f	0.1253	0.0997	0.209				0.0712	0.1599	
$\langle x^2 \rangle$	32.2						34.3	47.7	
1³A₁ (L_b, -)									
ΔE	5.16				5.45	5.71	6.220		
μ	1.113				1.35				
$\langle x^2 \rangle$	26.1				26		26.4		
1³B₂ (L_a, -)									
ΔE	4.27				4.27	4.42	4.978		
μ	0.971				0.69				
$\langle x^2 \rangle$	25.7				26		26.3		

^aCASPT2F/[TZP/DZP,+A]. Serrano-Andrés *et al.*¹⁶¹ Basis set: ANO^{181,274} [4s3p1d/2s1p], plus molecule- centered diffuse [2s2p2d]. The results from Tables IV (μ and $\langle x^2 \rangle$) and VI (the CASPT2 ΔE values, f). CASPT2 is PT2F.

^bMRMP, MCQD/[TZP/DZP,+A]. Nakano *et al.*²⁰⁶ Basis set: valence [sp/s] functions: [cc-pVTZ/cc-pVDZ], carbon and nitrogen polarization functions from cc-pVDZ, plus molecule-centered diffuse [2s2p2d]. The three ΔE values given refer to: MRMP, quasi-degenerate multi-configurational PT variant (MCQD), and CASSCF. The f values from MRMP. All results from Table IV.

^cMS-CASPT2/[TZ2P,+A]. Roos *et al.*¹⁹³ Basis set: ANO^{181,274} [4s3p2d/3s2p], plus molecule-centered diffuse [1s1p1d]. The results from Table II.

^dCelani *et al.*¹⁷⁸ Basis set: AVTZ(f,p)+, a slightly modified aug-cc-pVTZ basis. The results from Table IV.

^eTanaka *et al.*²¹⁵ Basis set: DZ [4s2p/2s], plus two diffuse p on carbon and nitrogen. The results from Table IV.

^fButscher *et al.*¹⁹⁹ Basis set: double zeta, plus five bond s polarization functions, plus molecule-centered diffuse [1s1p]. The results from Tables 4 and 5.

^gPalmer *et al.*²²⁰ Basis set: DZPR, which is DZP plus molecule-centered diffuse [3s2p2d]. The results from Tables 10 and 11.

^hMRCI/[TZP,+A]. Palmer *et al.*²⁶⁷ Basis set: TZVPR, which is TZVP plus molecule-centered diffuse [3s2p2d]. The results from Table 3. Note that the MRCI ΔE entry in Table 1 for the valence ¹B₂ state, 6.569 eV, differs from the one we adopted from Table 3, 6.731 eV.

TABLE LII: Published results for vertical excitation energies and properties of pyrrole (part 2).

	CCS/CC2/CCSD/ CCSDR(3)/CC3/estimate ^a	EOM- CCSD ^b	SAC-CI ^c	SAC-CI ^d	ADC(2) BS A/B ^e	NEVPT2 SC/PC ^f	CASSCF/NEVPT SC-2/PC-2/SC-3 ^g
¹A₁ (-)							
μ	- / - / 1.894 / - / - /		2.120				
$\langle x^2 \rangle$	- / - / 26 / - / - /		26	26			
²A₁ (L_b, -)							
ΔE	7.59/6.53/6.55/6.43/6.37/6.37		7.20	6.41	6.66/6.67	6.77/6.73	AS(0503):6.55/6.85/6.78/6.68 AS(0704):6.33/6.66/6.62/6.51 AS(0805):6.37/6.57/6.53/6.51 AS(0906):6.37/6.63/6.59/6.56
μ	- / - / 1.060 / - / - /		1.952				
f	0.0045/0.0006/0.0018/ - / - / 0.001		0.0214	0.0002			
$\langle x^2 \rangle$	- / - / 28 / - / - /		31	30	0.17/0.14		
⁶A₁ (B_b, +)							
ΔE	8.30/8.10/8.22/8.12/8.07/7.91			7.88	7.75/7.52	9.32/9.13	AS(0503):9.68/8.96/8.62/9.14 AS(0704):8.71/8.54/8.42/8.50 AS(0805):8.76/8.43/8.30/8.47 AS(0906):8.82/8.44/8.29/8.48
μ	- / - / 0.333 / - / - /						
f	0.0308/0.1763/0.2670/ - / - / 0.291			0.3252			
$\langle x^2 \rangle$	- / - / 55 / - / - /			114	1.37/1.18		
²B₂ (L_a, +)							
ΔE	6.62/6.55/6.67/6.63/6.63/6.57	6.68	7.52	6.48	6.71/7.02	7.01/6.83	AS(0503):7.94/6.66/6.43/7.07 AS(0704):7.27/7.22/7.07/7.24 AS(0805):7.23/7.11/6.96/7.12 AS(0906):7.23/7.07/6.95/7.05
μ	- / - / 6.380 / - / - /		2.077				
f	0.0273/0.0085/0.0242/ - / - / 0.033		0.0874	0.0475	0.90/0.99		
$\langle x^2 \rangle$	- / - / 59 / - / - /		47	68			
¹³A₁ (L_b, -)							
ΔE			5.84	5.60	5.55/5.72		
$\langle x^2 \rangle$				27			
¹³B₂ (L_a, -)							
ΔE			4.65	4.58	4.59/4.67		
$\langle x^2 \rangle$				27			

^aEOM-(various)CC/[TZP/DZP,+A], estimate of CC3/[large,+A]. Christiansen *et al.*³¹ Basis set used throughout except for the CC3-based estimate: ANO^{181,274} [4s3p1d/2s1p], plus molecule-centered diffuse [2s2p2d], same as used by Serrano-Andrés *et al.*¹⁶¹. The results from Tables I (ΔE) and II (μ , f , $\langle x^2 \rangle$). It seems possible that the second and the third oscillator strength subentries for the ¹B₂ state in Table II are erroneously swapped. The quoted estimates for ΔE and f are from Table VIII; the estimate for ΔE value approximates the CC3 results with a large basis.

^bCelani *et al.*¹⁷⁸ Basis set: AVTZ(f,p)+. The results from Table IV.

^cNakatsuji *et al.*¹⁸⁰ Basis set: Huzinaga-Dunning [4s2p/2s], plus molecule-centered diffuse [2s2p1d]. The results from Tables III and IV.

^dSAC-CI/[DZPA/DZP,+A]. Wan *et al.*¹⁹⁸ Basis set: [aug-cc-pVDZ/cc-pVDZ], plus molecule-centered diffuse (3s3p3d). The results from Table V.

^eTrofimov *et al.*¹⁷⁹ Two basis sets: A, cc-pVDZ, plus [2s2p] diffuse on carbon and nitrogen, plus molecule-centered diffuse [3s3p3d]; B, [4s2p/2s], plus [2s2p] diffuse on carbon and nitrogen, plus molecule-centered diffuse [2s2p1d]. The second-order algebraic-diagrammatic construction, ADC(2), results with basis sets A/B from Table 7.

^fHavenith *et al.*¹⁷⁶ Basis set: ANO^{181,274} [4s3p1d/2s1p], plus molecule-centered diffuse [2s2p2d], same as used by Serrano-Andrés *et al.*¹⁶¹. The two ΔE values given are the strongly/partially contracted results from Table VI.

^gPastore *et al.*²³⁰ Basis set: ANO^{181,274} [4s3p1d/2s1p], plus molecule-centered diffuse [1s1p1d]. All results from Table 2. The four lines contain the results with four different CASSCF active spaces. The four ΔE values given in each line refer to CASSCF, SC-NEVPT2, PC-NEVPT2, and SC-NEVPT3.

TABLE LIII: Published results for vertical excitation energies and properties of imidazole.

CASPT2 (singlet) ^a		MRCI (singlet) ^b	CASPT2 (triplet) ^a		MRCI (triplet) ^b
1¹A' (-)			1³A' (-)		
ΔE			ΔE	4.49	4.53
μ	3.70		μ	3.17	
$\langle x^2 \rangle$		61.9	$\langle x^2 \rangle$		64.5
3¹A' (L_b/L_a , +/-)			2³A' (-)		
ΔE	6.72	7.71	ΔE	5.47	6.95
μ	4.61		μ	4.03	
f	0.126	0.080			
$\langle x^2 \rangle$		112.5	$\langle x^2 \rangle$		67.9
5¹A' (L_a/L_b , +/-)			3³A' (+/-)		
ΔE	7.15	8.18	ΔE	6.53	7.22
μ	3.00		μ	4.68	
f	0.143	0.070			
$\langle x^2 \rangle$		100.0	$\langle x^2 \rangle$		64.8
8¹A' (B_b , +)			4³A' (+)		
ΔE	8.51		ΔE	7.08	7.67
μ	3.85		μ	3.32	
f	0.594				
$\langle x^2 \rangle$			$\langle x^2 \rangle$		65.5
3¹A'' (-)			2³A'' (-)		
ΔE	6.52		ΔE	6.07	
μ	0.22		μ	1.38	
f	0.011				
8¹A'' (+/-)			7³A'' (+/-)		
ΔE	7.56		ΔE	7.15	
μ	2.79		μ	6.19	
f	0.013				

^aCASPT2/[TZP/DZP,+A]. Serrano-Andrés *et al.*²⁰⁷ Basis set (called BS2 in the paper): ANO^{181,274} [4s3p1d/2s1p], plus molecule-centered diffuse [1s1p1d]. All results from Table 1. CASPT2 is supposedly PT2F.

^bMRSDCI/[DZP,+A], Machado *et al.*²²⁶ Basis set: ANO [5s4p2d/3s1p], includes augmentation. All results from Tables III and IV.

TABLE LIV: Published results for vertical excitation energies and properties of pyridine (part 1, singlet states).

	CASPT2 ^a	CASPT2/ CASSCF ^b	CASPT2/ CASSCF ^c	MRCI DZ/DZR ^d	EOM- CCSD ^e	EOM- CCSD/ $(\tilde{T})$ ^e	STEOM PT/CC ^f	STEOM PT/CC ^g	SAC-CI 35 π /35 π +50 σ ^h	SAC-CI ⁱ
1¹A₁ (-)										
μ		2.36						2.31/2.29	2.389	
2¹A₁ (B_{1u}, +/-)										
ΔE	6.42	6.35/7.48		7.422/6.990		6.70/6.36	6.68/6.62	6.69/6.62	7.64/7.04	6.26
μ	3.28	3.00						2.75/2.80	2.636/2.277	
f	0.005	0.006				0.01		0.013/0.006	0.021/0.021	0.0195
4¹A₁ (E_{1u}, +)										
ΔE	7.23	6.84/8.91		8.405/8.178				7.43/7.37	8.85/8.16	7.18
μ	2.67	2.43						1.75/1.68	5.762/1.451	
f	0.820	0.73						0.67/0.66	0.513/0.604	0.6174
3¹A₁ (E_{2g}, -)										
ΔE	7.96	7.84/8.34		9.167						
μ	1.30	1.27								
f	0.030	0.26								
1¹B₂ (B_{2u}, -)										
ΔE	4.84	4.94/5.03	4.89/5.20	5.446/4.762	5.29	5.22/4.81	5.01/4.82	5.01/4.82	5.37/5.44	4.85
μ	2.03	1.84						2.06/2.03	2.099/2.092	
f	0.018	0.04				0.03		0.026/0.023	0.023/0.038	0.0400
3¹B₂ (E_{1u}, +)										
ΔE	7.48	7.49/8.89		7.751/7.699		7.48/7.14	7.37/7.29	7.37/7.29	8.66/7.85	7.27
μ	1.83	1.19						2.69/2.69	8.850/3.091	
f	0.640	0.96				0.52		0.65/0.61	0.619/0.458	0.4072
2¹B₂ (E_{2g}, -)										
ΔE	7.95	7.78/8.14		9.259						
μ	2.57	2.31								
f	0.158	0.03								
1¹B₁ (-)										
ΔE	4.91	4.91/5.42	5.00/5.68	4.773/4.503	5.29	5.17/4.80	5.01/4.90	5.01/4.91	- /5.24	4.59
μ	0.40	0.51						1.35/1.22	- /1.184	
f	0.009	0.02				0.01		0.006/0.006	- /0.007	0.0054
1¹A₂ (+/-)										
ΔE	5.17	5.21/6.12	5.25/6.37	5.357/5.280	5.69	5.61/5.24	5.36/5.31	5.36/5.31	- /5.69	5.11
μ	0.93	0.90						1.47/1.47	- /1.451	

^aCASPT2F/[TZP/DZP,+A]. Lorentzon *et al.*¹⁶⁵ Basis set: ANO^{181,274} [4s3p1d/2s1p], plus molecule-centered diffuse [1s1p1d]. The results from Table 3. CASPT2 is PT2F.

^bFülscher *et al.*¹⁶⁷ Basis set: ANO [4s3p2d/3s2p]. No diffuse functions. The results from Table II.

^cCai *et al.*²⁰¹ Basis set: cc-pVDZ. The results from Table 3.

^dWalker *et al.*²⁰⁹ The results with two basis sets are given, [4s2p/2s] (DZ, Table 6), and DZ plus molecule-centered diffuse [3s2p2d] (DZR, Table 4).

^eEOM-CCSD/ $(\tilde{T})$ /[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values given are the EOM-CCSD and EOM-CCSD/ $(\tilde{T})$ results from Table V. The f values are the EOM-CCSD results from Table V.

^fNooijen²⁴⁵ Basis set: [PBS/DZP]; PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). Results from Table 2.

^gSTEOM/[DZ2PA/DZP]. Nooijen *et al.*²⁶⁸ Basis set: [PBS/DZP]. PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Table IV (ΔE and f) and V (μ).

^hKitao *et al.*²⁵⁵ Basis set: [4s2p/2s], plus two diffuse p_π on carbons and nitrogen, plus valence polarization d_π on carbons, plus valence polarization d on nitrogen. The results from Tables V, VII, and VIII.

ⁱSAC-CI/[TZPA/TZP,+A]. Wan *et al.*²⁷⁵ Basis set: [aug-cc-pVTZ (one f removed from carbon)/cc-pVTZ], plus molecule-centered diffuse [5s5p5d]. The SD-R results from Table II.

TABLE LV: Published results for vertical excitation energies and properties of pyridine (part 2, triplet states).

	CASPT2 ^a	CASPT2/ CASSCF ^b	MRCI ^c	EOM- CCSD ^b	STEOM PT/CC ^d	SAC-CI 35 π /35 π +50 σ ^e	SAC-CI ^f
1³A₁ (-)							
ΔE	4.05	4.10/4.08	3.946	4.06	4.07/3.73	3.94/4.34	4.06
μ	2.13					2.214/2.252	
2³A₁ (-)							
ΔE	4.73	4.77/5.25	4.932	5.12	5.07/4.90	5.17/5.32	4.91
μ	2.41					2.539/2.488	
3³A₁ (-)							
ΔE	7.34		7.637				
μ	1.73						
1³B₂ (-)							
ΔE	4.56	4.61/5.06	4.978	4.90	4.84/4.68	5.07/5.09	4.64
μ	2.03					2.021/1.983	
2³B₂ (+/-)							
ΔE	6.02		6.672		6.23/6.16	7.03/6.60	6.08
μ	3.79					3.553/3.208	
3³B₂ (-)							
ΔE	7.28		7.800				
μ	1.04						
1³B₁ (-)							
ΔE	4.41	4.37/5.09	3.870	4.63	4.43/4.32	– /4.49	4.25
μ	0.51					– /1.195	
1³A₂ (+)							
ΔE	5.10	5.22/6.36	5.427	5.62	5.36/5.31	– /5.69	5.28
μ	0.15					– /1.350	

^aCASPT2F/[TZP/DZP,+A]. Lorentzon *et al.*¹⁶⁵ Basis set: ANO^{181,274} [4s3p1d/2s1p], plus molecule-centered diffuse [1s1p1d]. The results from Table 6. CASPT2 is PT2F.

^bCai *et al.*²⁰¹ Basis set: cc-pVDZ. The results from Table 3.

^cWalker *et al.*²⁰⁹ Basis set: [4s2p/2s]. The results from Table 5.

^dSTEOM/[DZ2PA/DZP,+A]. Nooijen *et al.*²⁶⁸ Basis set: [PBS/DZP]. PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Table VI.

^eKitao *et al.*²⁵⁵ Basis set: [4s2p/2s], plus two diffuse p_π on carbon and nitrogen, plus valence polarization d_π on carbon, plus valence polarization d on nitrogen. The results from Tables V and VII.

^fSAC-CI/[TZPA/TZP,+A]. Wan *et al.*²⁷⁵ Basis set: [aug-cc-pVTZ (one f removed from carbons)/cc-pVTZ], plus molecule-centered diffuse [5s5p5d]. The SD-R results from Table I.

TABLE LVI: Published results for vertical excitation energies and properties of pyrazine.

	CASPT2 ^a	CASPT2/ CASSCF ^b	CASPT2/ PT2/PT3 ^c	EOM- CCSD/ $(\tilde{T})$ ^d	STEOM PT/CC ^e	CASSCF/ MRCI/MRCI-DC ^f	MRCI ^g
2¹A_g (E_{2g}, -)							
ΔE	8.27	8.19/8.40					
1¹B_{1u} (B_{1u}, +)							
ΔE	6.68	6.70/8.06	8.56/6.60/7.17	6.96/6.58	6.98/6.89		7.188
f	0.08	0.084/0.101		0.06			
2¹B_{1u} (E_{1u}, +)							
ΔE	7.57	7.57/9.60	10.53/7.43/8.78	8.14/7.72	8.06/7.96		11.091
f	0.76	0.722/0.916		0.37			
1¹B_{2u} (B_{2u}, -)							
ΔE	4.77	4.75/5.04	5.05/4.79/5.26	5.09/4.64	5.02/4.75	5.03/5.13/5.14	4.769
f	0.07	0.065/0.069		0.08			
2¹B_{2u} (E_{1u}, +)							
ΔE	7.75	7.70/9.48	10.03/7.28/8.72	7.93/7.60	7.88/7.75	10.0/8.98/8.55	7.887
f	0.66	0.665/0.818		0.33			
1¹B_{3g} (E_{2g}, -)							
ΔE	8.16	8.26/8.51					10.193
1¹A_u ($n \rightarrow \pi^*$, +)							
ΔE	4.37	4.52/6.33	5.92/4.36/5.33	5.20/4.81	5.02/4.93		4.928
1¹B_{1g} ($n \rightarrow \pi^*$, +)							
ΔE	6.13		7.20/6.26/6.97	7.04/6.60	6.81/6.73		6.068
1¹B_{2g} ($n \rightarrow \pi^*$, +)							
ΔE	5.17		5.91/5.50/5.99	5.97/5.56	5.85/5.68		5.356
1¹B_{3u} ($n \rightarrow \pi^*$, +)							
ΔE	3.58	3.63/5.25	4.86/3.83/4.62	4.34/3.95	4.31/4.12	4.74/4.33/4.15	3.865
f	0.01	0.010/0.014		0.01			

^aCASPT2D/[TZ2P, no diffuse], PT2D. Fulscher *et al.*¹⁶⁷ Basis set: ANO, [4s3p2d/3s2p]. No diffuse functions. The results from Table III.

^bFulscher *et al.*¹⁶⁶ Basis set: ANO, [5s4p2d/3s2p]. No diffuse functions. The results from Table 8. The CASPT2 variant used was PT2F.

^cWeber *et al.*²⁰³ Basis set: cc-pVDZ. The (10,8) active space results from Table 3.

^dEOM-CCSD/ $(\tilde{T})$ /[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values given are the EOM-CCSD and EOM-CCSD/ $(\tilde{T})$ results from Table VII. The f values are the EOM-CCSD results from Table VII.

^eSTEOM/[DZ2PA/DZP]. Nooijen²⁴⁵ Basis set: [PBS/DZP]; PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Table 5.

^fSobolewski *et al.*²⁶⁵ Basis set: DZP. The results from Table V.

^gPalmer *et al.*⁷⁶ Basis set: double zeta, plus molecule-centered diffuse [3s2p2d]. The results from Table 5.

TABLE LVII: Published results for vertical excitation energies and properties of pyrimidine.

	CASPT2 ^a	CASPT2 ^b	MRCI	CASSCF/ MRCI/+Q ^d	EOM- CCSD($\tilde{T}$) ^e	STEOM PT/CC ^f	EOM-CC ^g	CCS/CC2/ CCSD ^h	EOM- CCSD ⁱ
1¹A₁ (-)									
μ	2.45			2.427/2.460					
2¹A₁ (B_{1u}, +)									
ΔE	6.72	7.10	6.820	7.73/7.30/6.96	6.95/6.57	6.93/6.87	6.95	6.86/6.75/7.01	7.20
μ	4.01			3.927/3.309					
f	0.05			0.071/0.048	0.03		0.017		
3¹A₁ (E_{1u}, +)									
ΔE	7.57		8.488	8.54/8.15/7.67	7.73/7.35	7.51/7.44	7.65	8.72/7.48/7.73	8.10
μ	2.61			2.138/2.735					
f	0.58			0.762/0.468	0.41		0.360		
4¹A₁ (E_{2g}, +)									
ΔE	7.82			9.38/9.17/8.80					
μ	2.16			3.053/2.176					
f	0.14			0.158/0.109					
1¹B₂ (B_{2u}, -)									
ΔE	4.93	5.17	4.707	5.25/5.53/5.53	5.44/5.01	5.24/5.04	5.44		5.52
μ	2.14			2.163/2.298					
f	0.001			0.021	0.01		0.026		
2¹B₂ (E_{1u}, +)									
ΔE	7.32		8.326	8.58/8.61/8.21	8.02/7.69	7.80/7.77	8.01		8.33
μ	2.26			1.182/2.005					
f	0.79			0.993	0.41		0.490		
3¹B₂ (E_{2g}, -)									
ΔE	8.31			9.57/9.00/8.71					
μ	1.17			2.199/1.690					
f	0.06			0.008					
1¹B₁ ($n \rightarrow \pi^*$, +)									
ΔE	3.81	4.26	3.738	5.22/4.15/3.82	4.62/4.24	4.52/4.40	4.55	5.83/4.37/4.59	4.74
μ	0.60			0.818/1.159					
f	0.02			0.017	0.01		0.007		
1¹A₂ ($n \rightarrow \pi^*$, +)									
ΔE	4.12	4.49	4.191	5.83/4.61/4.22	5.03/4.74	4.77/4.72	4.91	6.68/4.88/5.16	5.10
μ	1.05			1.245/1.411					

^aCASPT2D/[TZ2P, no diffuse], PT2D. Flscher *et al.*¹⁶⁷ Basis set: ANO, [4s3p2d/3s2p]. The results from Table IV.

^bFischer *et al.*²⁶⁰ Basis set: cc-pVDZ. The results from Table 2.

^cPalmer *et al.*²⁵⁰ Basis set: double-zeta, plus molecule-centered diffuse [3s2p2d]. The results from Table 5.

^dCASSCF/MRCISD/MRCISD+Q/[TZP/DZ, no diffuse]. Malmqvist *et al.*²²⁸ Basis set: ANO, (12s8p3d/6s)[3s3p1d/2s]. The three ΔE values are the CASSCF, MRCI, and Davidson-corrected (+Q) MRCI results from Tables 1 to 6. The two μ values are the CASSCF and MRCI results from Tables 1 to 6. The two f values are the dipole length results from Table 7. Note that the Malmqvist *et al.*²²⁸ CASSCF results for the "E_{1u}" 3¹A₁ and 2¹B₂ states match rather well the Flscher *et al.*¹⁶⁷ CASSCF results for the "E_{2g}" 4¹A₁ and 3¹B₂ states, and vice versa. The state assignment in this table was chosen because the only alternative assignment would result in large positive MRCI/CASSCF $\Delta\Delta E(\text{dyn})$ for the "E_{2g}" states (for example, 9.17-8.54=0.63 eV for the 4¹A₁ state), which would be unusual. We cannot exclude the possibility, however, that the above CASSCF ΔE and f values for these two pairs of states should be swapped.

^eEOM-CCSD($\tilde{T}$)/[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values given are the EOM-CCSD and EOM-CCSD($\tilde{T}$) results from Table IX. The f values are the EOM-CCSD results from Table IX. Note that slightly different EOM-CCSD($\tilde{T}$) data are quoted in the text on p.6057: ΔE , 5.12 eV (instead of 5.01 eV) for 1¹B₂, 7.82 eV (instead of 7.69 eV) for 2¹B₂; f =0.32 (instead of f =0.41) for 2¹B₂.

^fSTEOM/[DZ2PA/DZP]. Nooijen²⁴⁵ Basis set: [PBS/DZP]; PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Table 4.

^gEOM-(high-level)CC/[CBS estimate], f at EOM-CCSD/[DZP,+A]. hrn *et al.*³³ The excitation energies given are the "best estimates" from Table 1 that are meant to approximate the exact vertical excitation energies. The f values are the EOM-CCSD results from Table 1 (basis set: cc-pVDZ plus molecule-centered diffuse [3s3p3d]).

^hEOM-CCSD/[DZ2PA]. Httig *et al.*²¹⁸ Basis set: Sadlej, [5s3p2d/3s2p]. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The EOM-CC results from Table III. We associate the 4¹A₁ state from Table III with the 3¹A₁ state in our notation because the 3¹A₁ entry in Table III is without experimental data and is likely to be diffuse. An analogous assignment was also made by Fischer *et al.*²⁶⁰ in their Table 2.

ⁱFischer *et al.*²⁶⁰ Basis set: cc-pVDZ. The results from Table 2.

TABLE LVIII: Published results for vertical excitation energies and properties of pyridazine.

	CASPT2 ^a	CASSCF ^a	MRCI	EOM- CCSD/ $(\tilde{T})^c$	STEOM PT/CC ^d	CC2 ^e	MRMP2 ^e
1¹A₁ (-)							
μ	4.37						
2¹A₁ (B_{2u}, -)							
ΔE	4.86	5.22	5.023	5.31/4.86	5.20/4.92		
μ	3.60			0.02			
f	0.009						
3¹A₁ (E_{1u}, +)							
ΔE	7.50	9.31	7.257	7.70/7.43	7.71/7.59		
μ	5.09			0.22			
f	0.50						
1¹B₂ (B_{1u}, +)							
ΔE	6.61	7.69	6.103	6.85/6.44	6.91/6.77		
μ	5.64			0.01			
f	0.003						
2¹B₂ (E_{1u}, +)							
ΔE	7.39	9.50	7.246	7.56/7.19	7.55/7.42		
μ	3.93			0.45			
f	0.75						
1¹A₂ (n $\rightarrow$ π^*, +)							
ΔE	3.66	5.35	3.274	4.68/4.28	4.57/4.46		
μ	1.97						
f							
2¹A₂ (n $\rightarrow$ π^*, +)							
ΔE	5.09	6.85	6.603	5.95/5.52	5.84/5.66		
μ	1.74						
1¹B₁ (n $\rightarrow$ π^*, +)							
ΔE	3.48	5.28	3.348	4.06/3.65	3.94/3.76	3.87	3.62
μ	1.59			0.01			
f	0.01						
2¹B₁ (n $\rightarrow$ π^*, +)							
ΔE	5.80	7.99	5.658	6.61/6.20	6.53/6.41		
μ	1.74			0.00			
f	0.008						

^aCASPT2D/[TZ2P], PT2D. Fulscher *et al.*¹⁶⁷ Basis set: ANO, [4s3p2d/3s2p]. No diffuse functions. The results from Table V.

^bPalmer *et al.*⁷⁶ Basis set: double-zeta, plus molecule-centered diffuse [3s2p2d]. The results from Table 5.

^cEOM-CCSD/ $(\tilde{T})$ /[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values are the EOM-CCSD and EOM-CCSD/ $(\tilde{T})$ results from Table XI. The f values are the EOM-CCSD results from Table XI.

^dSTEOM/[DZ2PA/DZP]. Nooijen²⁴⁵ Basis set: [PBS/DZP]; PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Table 3.

^eParac *et al.*²⁴⁹ Basis set: TZVP. The results from Table 2.

TABLE LIX: Published results for vertical excitation energies and properties of *s*-triazine.

	CASPT2 ^a	CASSCF CASPT2 ^b	MRCI ^c	EOM- CCSD($\tilde{T}$) ^d	STEOM PT/CC ^e
$2^1\mathbf{A}'_1$ [$\mathbf{A}_1$] ($\mathbf{B}_{1u}$, +)					
ΔE	6.77		7.406	7.30/6.90	7.25/7.21
$1^1\mathbf{A}'_2$ [$\mathbf{B}_2$] ($\mathbf{B}_{2u}$, -)					
ΔE	5.33	5.55/5.59	5.595	5.80/5.36	5.54/5.35
$1^1\mathbf{E}'$ [$\mathbf{A}_1+\mathbf{B}_2$] ($\mathbf{E}_{1u}$, +)					
ΔE	8.16		7.252	8.05/7.72	7.84/7.82
f	0.61			0.92	
$2^1\mathbf{E}'$ [$\mathbf{A}_1+\mathbf{B}_2$] ($\mathbf{E}_{2g}$, -)					
ΔE	8.03		10.032		
f	0.21				
$1^1\mathbf{A}''_1$ [$\mathbf{A}_2$] ($n \rightarrow \pi^*$, +)					
ΔE	3.90(3.81)	5.90/4.11	4.252	4.86/4.49	4.63/4.58
$1^1\mathbf{A}''_2$ [$\mathbf{B}_1$] ($n \rightarrow \pi^*$, +)					
ΔE	4.08(4.00)	5.11/4.30	4.139	4.95/4.54	4.84/4.74
f	0.015	0.027		0.02	
$1^1\mathbf{E}''$ [$\mathbf{A}_2+\mathbf{B}_1$] ($n \rightarrow \pi^*$, +)					
ΔE	4.36(4.24)	5.51/4.32	4.030	4.95/4.56	4.76/4.69
$2^1\mathbf{E}''$ [$\mathbf{A}_2+\mathbf{B}_1$] ($n \rightarrow \pi^*$, +)					
ΔE	7.15(7.13)		7.080	8.07/7.78	

^aCASPT2D/PT2F/[TZ2P], PT2D/PT2F. Fulscher *et al.*¹⁶⁷ Basis set: ANO, [4s3p2d/3s2p]. No diffuse functions. The results from Table VI. Note that the CASPT2 variant used was PT2D for the $\pi \rightarrow \pi^*$ states, and PT2F for the $n \rightarrow \pi^*$ states. The CASPT2D results for the $n \rightarrow \pi^*$ states are given in parentheses.

^bOliva *et al.*¹⁸⁶ Basis set: 6-31G*. The results from Table 2.

^cWalker *et al.*²⁷⁹ Basis set: double-zeta, plus molecule-centered diffuse [3s2p2d]. The results from Table 5.

^dEOM-CCSD/ $(\tilde{T})$ /[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values are the EOM-CCSD and EOM-CCSD/ $(\tilde{T})$ results from Table XIII. The f values are the EOM-CCSD results from Table XIII.

^eSTEOM/[DZ2PA/DZP]. Nooijen²⁴⁵ Basis set: [PBS/DZP]; PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Table 6.

TABLE LX: Published results for vertical excitation energies (ΔE in eV) and properties of *s*-tetrazine (part 1, dark singlet and triplet states).

state	CASPT2 ^a	MRCI ^b	CISD/ (+Q) ^c	STEOM/ Ext-STEOM ^d	EOM- CCSD($\tilde{T}$) ^d	EOM- CCSD($\tilde{T}$) ^e	FSMRCC ^f
2¹A_g ($n, n \rightarrow \pi^*, \pi^*, +$)	4.37			– /5.06			
3¹A_g ($n, n \rightarrow \pi^*, \pi^*, +$)	7.20			– /8.43			
5¹A_g ($\pi \rightarrow \pi^*, -$)	8.60	9.260					
1¹A_u ($n \rightarrow \pi^*, +$)	3.06	3.780	4.46/4.13	3.74/3.62	4.03/ –	4.03/3.59	3.44
2¹A_u ($n \rightarrow \pi^*, +$)	5.28	5.934		5.38/5.23	5.69/ –	5.69/ –	5.83
1¹B_{1g} ($n \rightarrow \pi^*, +$)	4.51	5.093	6.24/5.85	4.91/4.73	5.29/ –	5.29/ –	4.98
2¹B_{1g} ($n \rightarrow \pi^*, +$)	5.99	7.414		– /7.06			
3¹B_{1g} ($n \rightarrow \pi^*, +$)	6.20	6.567		6.86/6.73	7.20/ –	7.20/ –	7.26
1¹B_{2g} ($n \rightarrow \pi^*, +$)	5.05	5.206	7.06/6.72	5.33/5.09	5.70/ –	5.70/5.19	5.77
2¹B_{2g} ($n \rightarrow \pi^*, +$)	5.48	6.310		6.38/6.16	6.69/ –	6.69/ –	6.29
1¹B_{3g} ($n, n \rightarrow \pi^*, \pi^*, +$)	5.16			– /6.30		6.59/ –	
5¹B_{3g} ($\pi \rightarrow \pi^*, -$)	8.12	9.138					
1³A_u ($n \rightarrow \pi^*, +$)	2.81	3.141	4.21/3.89	3.47			3.14
2³A_u ($n \rightarrow \pi^*, +$)	4.85	5.383		4.89			5.30
1³B_{1g} ($n \rightarrow \pi^*, +$)	3.76	4.355	5.43/5.08	3.97			3.99
2³B_{1g} ($n \rightarrow \pi^*, +$)	5.68	6.717		6.77			7.22
1³B_{1u} ($\pi \rightarrow \pi^*, -$)	4.25	4.675	5.10/5.14	3.67			3.97
2³B_{1u} ($\pi \rightarrow \pi^*, -$)	5.09	6.021		5.31			5.74
1³B_{2g} ($n \rightarrow \pi^*, +$)	4.67	4.592	6.55/6.25	4.78			5.01
2³B_{2g} ($n \rightarrow \pi^*, +$)	5.30	6.415		6.16			6.21
1³B_{2u} ($\pi \rightarrow \pi^*, -$)	4.29	4.671	4.69/4.86	4.35			4.88
2³B_{2u} ($\pi \rightarrow \pi^*, +$)	6.81	8.457		7.36			7.82
1³B_{3g} ($n, n \rightarrow \pi^*, \pi^*, +$)	5.08						
1³B_{3u} ($n \rightarrow \pi^*, +$)	1.45	2.237	2.44/2.23	1.71			1.48
2³B_{3u} ($n \rightarrow \pi^*, +$)	6.14	6.780		6.54			6.75

^aCASPT2/[TZ2P,+A]. Rubio *et al.*¹⁶⁸ Basis set: ANO, [4s3p2d/3s2p] plus molecule-centered diffuse [1s1p1d]. The singlet results from Tables 1, 2, 4, and 6; the triplet results from Table 8. CASPT2 is supposedly PT2F (unless MS-CASPT2 is used).

^bMRCI/[DZP,+A]. Palmer *et al.*¹³¹ Basis set: DZP, plus molecule-centered diffuse [3s2p2d]. The singlet results from Table 6; the triplet results from Table 7. Note that refs.^{131,168} use different assignments for the states 2¹B_{1g} and 3¹B_{1g} (ours is based on the wave function information given in these two papers).

^cScheiner *et al.*²⁵³ Basis set: DZP. The results from Table I.

^dSTEOM, Ext-STEOM, EOM-CCSD/($\tilde{T}$)/[DZ2PA]. Nooijen¹⁸⁹ Basis set: PBS. PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The singlet results from Tables 2 and 5; the triplet results from Table 7. Note that in Table 7 one MRCI adiabatic state ($\Delta E=4.675$ eV) is put into correspondence with two CASPT2/STEOM states, 1³B_{1u} and 2³B_{1u}.

^eEOM-CCSD/($\tilde{T}$)/[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values are the EOM-CCSD and EOM-CCSD/($\tilde{T}$) results from Table XV.

^fRittby *et al.*²³⁸ Basis set: DZP. The Fock Space Multi-Reference Coupled Cluster results from Table 3 (singlets) and Table 4 (triplets).

TABLE LXI: Published results for vertical excitation energies and properties of *s*-tetrazine (part 2, bright singlet states).

	CASPT2 ^a	MRCI ^b	CISD/ (+Q) ^c	STEOM/ Ext-STEOM ^d	EOM- CCSD($\tilde{T}$) ^d	EOM- CCSD($\tilde{T}$) ^e	FSMRCC ^f
1¹B_{1u} ($n, n \rightarrow \pi^*, \pi^*, +$)							
ΔE	6.94			– /8.18			
f	0.0010						
3¹B_{1u} ($\pi \rightarrow \pi^*, +$)							
ΔE	7.13	8.346	8.27/8.10	7.31/7.14	7.41/6.95	7.41/6.95	7.91
f	0.0009	0.054		0.029		0.00	
4¹B_{1u} ($n, n \rightarrow \pi^*, \pi^*, +$)							
ΔE	7.31						
f	0.1048						
5¹B_{1u} ($\pi \rightarrow \pi^*, +$)							
ΔE	7.54	9.075		7.65/7.64	7.87/7.46	7.87/7.46	8.48
f	0.6871	0.630		0.39		0.47	
1¹B_{2u} ($\pi \rightarrow \pi^*, -$)							
ΔE	4.89	5.536	6.71/6.38	4.72/4.90	5.24/4.71	5.24/4.71	5.25
f	0.0450	0.095		0.052		0.07	
3¹B_{2u} ($n, n \rightarrow \pi^*, \pi^*, +$)							
ΔE	7.27			– /8.54			
f	0.0005						
4¹B_{2u} ($\pi \rightarrow \pi^*, +$)							
ΔE	7.94	9.769		8.44/8.28	8.70/8.20	8.70/8.20	9.21
f	0.7329	0.755		0.51		0.45	
5¹B_{2u} ($n, n \rightarrow \pi^*, \pi^*, +$)							
ΔE	8.16						
f	0.0024						
6¹B_{2u} ($n, n \rightarrow \pi^*, \pi^*, +$)							
ΔE	8.32						
f	0.0040						
1¹B_{3u} ($n \rightarrow \pi^*, +$)							
ΔE	1.96	2.862	3.11/2.89	2.38/2.22	2.68/–	2.68/2.22	2.28
f	0.0132	0.012		0.0070		0.01	
2¹B_{3u} ($n \rightarrow \pi^*, +$)							
ΔE	6.37	7.142		6.67/6.53	6.95/–	6.95/–	6.92
f	0.0165	0.018		0.014		0.01	
3¹B_{3u} ($n \rightarrow \pi^*, +$)							
ΔE	8.10	11.477					
f	0.0206	0.020					

^aCASPT2/[TZ2P,+A], supp. PT2F. Rubio *et al.*¹⁶⁸ Basis set: ANO, [4s3p2d/3s2p] plus molecule-centered diffuse [1s1p1d]. The MS-CASPT2 method was used for the 3¹B_{1u} and 5¹B_{1u} states, otherwise CASPT2 is supposedly PT2F. The results from Tables 1, 2, 4, and 6.

^bMRCI/[DZP,+A]. Palmer *et al.*¹³¹ Basis set: DZP, plus molecule-centered diffuse [3s2p2d]. The results from Table 6.

^cScheiner *et al.*²⁵³ Basis set: DZP. The results from Table I.

^dSTEOM, Ext-STEOM, EOM-CCSD/($\tilde{T}$)/[DZ2PA], f at STEOM/[DZ2PA,+A]. Nooijen¹⁸⁹ Basis set: PBS for all ΔE values, "PBS+diffuse" with the STEOM method for f values. PBS composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The results from Tables 2, 3, 5, and 6.

^eEOM-CCSD/($\tilde{T}$)/[DZ2PA]. Del Bene *et al.*²¹³ Basis set: Sadlej²⁰⁰ [5s3p2d/3s2p], denoted as POL1. Sadlej (PBS) composition is [4s2p2d] (DZ2P in the valence part) plus diffuse (1s1p/1s). The two ΔE values are the EOM-CCSD and EOM-CCSD/($\tilde{T}$) results from Table XV. The f values are the EOM-CCSD results from Table XV.

^fRittby *et al.*²³⁸ Basis set: DZP. The Fock Space Multi-Reference Coupled Cluster results from Table 3.

3. Aldehydes, Ketones and Amides

TABLE LXII: Published results for vertical excitation energies and properties of Formaldehyde.

	CASPT2 ^a	(SC) ² MR+SD (BS1/BS2) ^b	CCR(3) (BS1/BS2) ^b	EOM- CCSD ^c	EOM- CCSDT ^c	EOM- CCSD ^d	CC2/ CCSD/CC3 ^e	MR- AQCC/LRT ^f
1¹A₁								
μ	2.44					2.34		
f	8.8					20.6		8.9
1¹A₂ ($n \rightarrow \pi^*$, +)								
ΔE	3.91	4.04/4.04	4.01/3.97	3.92	3.99	3.98	4.05/4.00/3.95	3.98
μ	1.40			1.08	1.33	1.14		
$\langle z^2 \rangle$	8.3					20.9		10.5
1¹B₁ ($\sigma \rightarrow \pi^*$, -)								
ΔE	9.09	9.35/9.33	9.29/9.21	9.06	9.29	9.33		9.32
μ	0.51			0.42	0.52	0.32		
f	0.012			0.001		0.001		0.000
$\langle z^2 \rangle$	8.2					20.9		23.1
2¹A₁ ($\pi \rightarrow \pi^*$, +)								
ΔE	9.77	9.85/9.74	9.80/9.64			9.47		9.83
μ	0.76					0.29		
f	0.277					0.063		0.100
$\langle z^2 \rangle$	14.9					28.0		16.7
1³A₂ ($n \rightarrow \pi^*$, +)								
ΔE	3.48	– /3.59						
μ	1.14							
$\langle z^2 \rangle$	8.9							
1³A₁ ($\pi \rightarrow \pi^*$, +)								
ΔE	5.99	– /6.05						
μ	0.89							
$\langle z^2 \rangle$	9.6							

^aCASPT2/[TZ2P,+A], PT2F. Merchán *et al.*¹⁶⁹ Basis set: ANO, [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The results are from Table 3.

^bMR-SDCI/[DZP,+A]. Pitarchi-Ruiz *et al.*¹⁷⁷ Basis set: BS1: Same one used by Merchán *et al.* (ANO [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]); BS2: Larger ANO basis set, [6s5p3d2f/4s3p2d]. The results from Tables 3,4 and 6. No CCR(3) results for triplet states were shown.

^cEOM-CCSD/d-aug-cc-pVTZ and EOM-CCSDT/aug-cc-pVDZ. Hirata¹⁹⁵.

^dEOM-CCSD/[TZP,+A]. Gwaltney *et al.*²⁸¹ Basis set: [5s3p2d/3s2p] at CCSD/POLI1 ground state geometry. Expectations are for $\langle r^2 \rangle$ instead of $\langle z^2 \rangle$.

^eCC2/CCSD/CC3/d-aug-cc-pVQZ. Paterson *et al.*¹⁹⁷. At a B3LYP/cc-pVTZ ground state geometry. CC3 results is converged as studied.

^fMR-AQCC/LRT. Müller *et al.*²⁶¹ MR-averaged quadratic coupled cluster with a linear-response approach was used, with basis set ANO [4s3p1d/2s1p] and MINVAL active space (6,4) at experimental ground state geometry.

TABLE LXIII: Published results for vertical excitation energies and properties of acetone.

	CASPT2 ^a	EOM-CCSD ^b	SC-/PC-NEVPT ^c
1¹A₁			
μ	2.92	2.92	
$\langle z^2 \rangle$	21.3	98.9	
1¹A₂ ($n \rightarrow \pi^*$, +)			
ΔE	4.18	4.48	4.42/4.22
μ	2.29	1.48	
$\langle z^2 \rangle$	18.6	98.8	
1¹B₁ ($\sigma \rightarrow \pi^*$, -)			
ΔE	9.10	9.30	9.29/9.23
μ	0.99	0.95	
f	0.010	0.003	
$\langle z^2 \rangle$	19.0	101.4	
1¹A₁ ($\pi \rightarrow \pi^*$, +)			
ΔE	9.16	9.15	9.60/9.01
μ	3.94	2.74	
f	0.326	0.255	
$\langle z^2 \rangle$	21.3	104.8	
1³A₂ ($n \rightarrow \pi^*$, +)			
ΔE	3.90		
μ	1.14		
$\langle z^2 \rangle$	19.9		
1³A₁ ($\pi \rightarrow \pi^*$, +)			
ΔE	5.98		
μ	1.12		
$\langle z^2 \rangle$	20.6		

^aCASPT2/[TZ2P,+A], PT2F. Merchán *et al.*¹⁷⁰ Basis set: ANO, [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The results are from Table 3.

^bEOM-CCSD/[TZP,+A]. Gwaltney *et al.*²⁸¹ Basis set: [5s3p2d/3s2p]. CCSD/POLI1 ground state geometry. Expectation values for $\langle r^2 \rangle$ instead of $\langle z^2 \rangle$.

^cSC-NECPT2 and PC-NEVPT2. Angeli *et al.*²⁷⁸. SC strongly contracted, PC partially contracted. Basis set: [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d] as used in Ref.¹⁶⁹. The results from Table 8.

TABLE LXIV: Published results for vertical excitation energies and properties of *p*-benzoquinone.

	CASPT2 ^a	CASPT2 ^b	SAC-CI ^c
1¹A_u (<i>n</i> → π^* , +)			
ΔE	2.50	2.43	2.70
1¹B_{1g} (<i>n</i> → π^* , +)			
ΔE	2.50	2.39	2.51
1¹B_{3g} (π → π^* , +)			
ΔE	4.19	4.01	4.52
2¹B_{3g} (π → π^* , +)			
ΔE	6.34	6.17	
1¹B_{1u} (π → π^* , +)			
ΔE	5.15	5.09	5.47
<i>f</i>	0.616	0.636	0.704
2¹B_{1u} (π → π^* , -)			
ΔE	7.08	7.18	
<i>f</i>	0.624	0.693	
1¹B_{3u} (<i>n</i> → π^* , +)			
ΔE	5.15	4.91	
<i>f</i>	0.0002	0.0004	
1³A_u (<i>n</i> → π^* , +)			
ΔE	2.27	2.22	
1³B_{1g} (<i>n</i> → π^* , +)			
ΔE	2.17	2.16	
1³B_{3g} (π → π^* , +)			
ΔE	3.19	3.09	
1³B_{1u} (π → π^* , +)			
ΔE	2.91	2.57	

^aCASPT2/[TZ2P,+A], PT2F. Pou-Am  rigo *et al.*¹⁷¹. Basis set: ANO-L, [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The results from Table 3.

^bLS-CASPT2. Weber *et al.*¹⁵⁶. This study used the same basis set as in Ref.¹⁷¹, but employed a larger active space.

^cSAC-CI SD-R. Honda *et al.*²⁷³. Basis set: Dunning-Huzinaga [5s3p2d/3s1p]. The results from Table 2.

TABLE LXV: Published results for vertical excitation energies and properties of formamide.

	CASPT2 ^a	EOM-CCSD ^b	MRCI ^c	MRCI ^d	MR-CISD+Q ^e
1¹A'					
μ	4.08		4.56	4.46	
$\langle r^2 \rangle$	39				38.4
1¹A'' ($n \rightarrow \pi^*$, -)					
ΔE	5.61	5.71	5.86	5.76	5.72
μ	2.12		1.98	1.84	
f	0.001	0.0004	0.0003	0.000	0.001
$\langle r^2 \rangle$	38				37.9
2¹A' ($\pi \rightarrow \pi^*$, -)					
ΔE	7.41	7.66	7.94	7.40	7.60
μ	6.12		4.14	4.43	
f	0.371	0.211	0.149	0.154	0.338
$\langle r^2 \rangle$	39				59.0
3¹A' ($\pi \rightarrow \pi^*$, +)					
ΔE	10.50				
μ	5.24				
f	0.131				
$\langle r^2 \rangle$	40				
1³A'' ($n \rightarrow \pi^*$, +)					
ΔE	5.34				
μ	1.39				
$\langle r^2 \rangle$	38				
1³A' ($\pi \rightarrow \pi^*$, +)					
ΔE	5.69				
μ	3.23				
$\langle r^2 \rangle$	38				

^aCASPT2/[TZ2P,+A], PT2F. Serrano-Andrés *et al.*¹⁷². Basis set: ANO, [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The results from Table 1.

^bEOM-CCSD/[DZP, Sadlej]. Szalay *et al.*²³⁴. Basis set: PBS of Sadley ("double zeta plus polarization" quality). The results from Table 1.

^cMRCI. Hirst *et al.*²⁵⁶. Basis set: 6-31+G** with diffuse Rydberg functions (+). Active space: (9,0;16,6). The results from Tables 4 and 5.

^dMRCI. Besley *et al.*²²⁹. Basis set: d-aug-cc-pVTZ. Active space: (7 6) 6. The results from Table 2.

^eMR-CISD+Q. Antol *et al.*²⁷⁰. Basis set: d'-aug-cc-pVDZ. Energies computed using MR-CISD+Q and large active space (5 3) 8. Oscillator strengths and expectation values from MR-CISD with intermediate active space (3 3) 8.

TABLE LXVI: Published results for vertical excitation energies and properties of acetamide.

	CASPT2 ^a	MRCI ^b
1¹A'		
μ	4.00	4.64
$\langle r^2 \rangle$		
1¹A'' ($n \rightarrow \pi^*$, -)		
ΔE	5.54	6.02
μ	2.19	1.63
f	0.001	
$\langle r^2 \rangle$	50	
2¹A' ($\pi \rightarrow \pi^*$, -)		
ΔE	7.21	8.21
μ	6.21	4.48
f	0.292	0.18
$\langle r^2 \rangle$	55	
3¹A' ($\pi \rightarrow \pi^*$, +)		
ΔE	10.08	
μ	5.15	
f	0.179	
$\langle r^2 \rangle$	61	
1³A'' ($n \rightarrow \pi^*$, +)		
ΔE	5.24	
μ	1.61	
$\langle r^2 \rangle$	53	
1³A' ($\pi \rightarrow \pi^*$, +)		
ΔE	5.57	
μ	3.81	
$\langle r^2 \rangle$	58	

^aCASPT2/[TZ2P,+A], PT2F. Serrano-Andrés *et al.*¹⁷². Basis set: ANO, [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The results from Table 2.

^bMRCI. Hirst *et al.*²⁶⁴. Basis set: 6-31+G** (with spherical harmonics d functions). Active space: (12,1;16,7). The results from Table 4 and the text.

TABLE LXVII: Published results for vertical excitation energies and properties of propanamide.

	CASPT2 ^a
1¹A'	
μ	4.13
$\langle r^2 \rangle$	68
1¹A'' ($n \rightarrow \pi^*$, -)	
ΔE	5.48
μ	1.90
f	0.001
$\langle r^2 \rangle$	63
2¹A' ($\pi \rightarrow \pi^*$, -)	
ΔE	7.28
μ	5.59
f	0.011
$\langle r^2 \rangle$	66
3¹A' ($\pi \rightarrow \pi^*$, +)	
ΔE	9.95
μ	4.59
f	0.205
$\langle r^2 \rangle$	76
1³A'' ($n \rightarrow \pi^*$, +)	
ΔE	5.28
μ	1.41
$\langle r^2 \rangle$	69
1³A' ($\pi \rightarrow \pi^*$, +)	
ΔE	5.94
μ	2.47
$\langle r^2 \rangle$	64

^aCASPT2/[TZ2P,+A], PT2F. Serrano-Andrés *et al.*¹⁷². Basis set: ANO, [4s3p1d/2s1p] plus molecule-centered diffuse [1s1p1d]. The results from Table 3.

4. Nucleobases

TABLE LXVIII: Published results for vertical excitation energies and properties of cytosine.

	CASPT2 ^a	CASPT2 ^b	CC2 ^c	DFT/MRCI ^d	SAC-CI ^e
1¹A'					
μ	7.20				
2¹A'					
ΔE	4.39	4.50	4.66	4.83	4.40
μ	4.70				
f	0.061	0.065	0.052	0.080	
3¹A'					
ΔE	5.36		5.62	5.67	
μ	7.00				
f	0.108		0.138	0.181	
4¹A'					
ΔE	6.16			6.60	
μ	6.20				
f	0.863			0.694	
5¹A'					
ΔE	6.74				
μ	9.30				
f	0.147				
6¹A'					
ΔE	7.61				
μ	5.00				
f	0.239				
1¹A'' ($n \rightarrow \pi^*$, +)					
ΔE	5.00	4.88	4.87	5.02	4.90
μ	4.70				
f	0.005	0.001	0.002	0.002	
2¹A'' ($n \rightarrow \pi^*$, +)					
ΔE	6.53	5.23	5.26	5.50	
μ	6.40				
f	0.001	0.003	0.002	0.001	

^aCASPT2/TZP. Fulscher *et al.*¹⁷³. Note that states 5¹A' and 6¹A' have low reference weights.^bCASPT2/6-31G**. Merchan *et al.*¹⁹⁶. Active space: (2 7) 12.^cRI-CC2/aug-cc-pVTZ. Fleig *et al.*²⁵⁷. Ground-state geometry computed at the same level. The results from Table 5.^dDFT-MRCI/TZVP. Tomic *et al.*²³⁵. BH-LYP ground state geometry. The results from Table 2.^eSAC-CI/cc-pVDZ. Ritze *et al.*²²². The results from Table 1 (first row).

TABLE LXIX: Published results for vertical excitation energies and properties of thymine.

	CASPT2 ^a	CASPT2 ^b	CC2 ^c	SAC-CI ^d
1¹A'				
μ	5.00			
2¹A'				
ΔE	4.88	4.68	5.20	4.88
μ	6.50			
f	0.17		0.18	
3¹A'				
ΔE	5.88	5.84	6.27	
μ	1.50			
f	0.17		0.04	
4¹A'				
ΔE	6.10	6.06	6.53	
μ	7.80			
f	0.15		0.18	
5¹A'				
ΔE	7.13	6.80		
μ	3.10			
f	0.85			
1¹A'' ($n \rightarrow \pi^*$, +)				
ΔE	4.39	5.02	4.82	4.57
μ	3.20			
2¹A'' ($n \rightarrow \pi^*$, +)				
ΔE	5.91	6.55	6.16	
μ	4.60			
3¹A'' ($n \rightarrow \pi^*$, +)				
ΔE	6.15	6.95		
μ	8.60			
4¹A'' ($n \rightarrow \pi^*$, +)				
ΔE	6.70	8.44		
μ	4.10			

^aCASPT2D/ANO. Lorentzon *et al.*¹⁷⁴. CASPT2D results. Active space: (0 8) 10 for $\pi \rightarrow \pi^*$ states and (2 8) 12 for $n \rightarrow \pi^*$. The results from Table 6.

^bCASPT2/ANO-L. Perun *et al.*²⁴². Basis set: ANO-L¹⁸¹. Ground-state MP2/cc-pVDZ geometry. The results from Tables 1 and 2.

^cRI-CC2/aug-cc-pVTZ. Fleig *et al.*²⁵⁷. Ground-state geometry computed at the same level. The results from Table 3. State 4¹A' has valence-Rydberg mixing.

^dSAC-CI/cc-pVDZ. Ritze *et al.*²²². The results from Table 1 (first row).

TABLE LXX: Published results for vertical excitation energies and properties of uracil.

	CASPT2 ^a	CC2 ^b	CC2/CCSD/CC3 ^b	MRCI($\sigma\pi$) ^c	DFT/MRCI ^d
1¹A'					
μ	4.4				
2¹A'					
ΔE	5.00	5.35	5.67/5.81/5.61	5.79	5.44
μ	6.3				
f	0.19	0.18		0.19	0.26
3¹A'					
ΔE	5.82	6.26	6.63/6.91/6.51	6.31	6.15
μ	2.4				
f	0.08	0.04			0.05
4¹A'					
ΔE	6.46	6.70		6.57	6.53
μ	6.9				
f	0.29	0.17		0.035	0.16
5¹A'					
ΔE	7.00				7.39
μ	3.7				
f	0.76				0.51
1¹A'' ($n \rightarrow \pi^*$, +)					
ΔE	4.54	4.80		4.80	4.61
μ	3.4				
2¹A'' ($n \rightarrow \pi^*$, +)					
ΔE	6.00	6.10			5.95
μ	4.8				
3¹A'' ($n \rightarrow \pi^*$, +)					
ΔE	6.37	6.56			
μ	8.7				
4¹A'' ($n \rightarrow \pi^*$, +)					
ΔE	6.95				
μ	3.6				

^aCASPT2D/ANO. Lorentzon *et al.*¹⁷⁴. CASPT2D results. Active space: (2 10) 14 for $\pi \rightarrow \pi^*$ states and (2 8) 12 for $n \rightarrow \pi^*$. The results from Table 5.

^bRI-CC2/aug-cc-pVQZ. Fleig *et al.*²⁵⁷. Ground-state geometry computed at the same level. The results from Table 6. State 4¹A' has valence-Rydberg mixing. CC2/CCSD/CC3 data obtained with SV(P) basis set.

^cMRCI/cc-pVDZ. Matsika²⁸⁰. Complete active space (14, 10) plus single excitations from σ to the valence n, π space and plus all single excitations to the virtual space, denoted therein as MRCI $\sigma\pi$. The results from Table 1.

^dDFT-MRCI/TZVPP. Marian *et al.*²⁰². TZVPP basis set²⁴⁶ with 3 sets of Rydberg functions. Ground-state BH-LYP/TZVP geometry. The results from Table 1. States 4¹A' and 5¹A' have valence-Rydberg mixing.

TABLE LXXI: Published results for vertical excitation energies and properties of adenine.

	CASPT2 ^a	CASPT2 ^b	CASPT2 ^c	CASPT2 ^d	CC2 ^e	DFT/MRCI ^f	SAC-CI ^g	CIPSI ^h
1¹A'								
μ	2.50							
2¹A'								
ΔE	5.13	5.16	5.05	4.75	5.25	4.90	5.34	4.97
μ	2.37	2.46						
f	0.07	0.004	0.002	0.002	0.02	0.03		0.01
3¹A'								
ΔE	5.20	5.35	5.16	4.89	5.25	5.04		5.34
μ	2.30	4.17						
f	0.37	0.17	0.21	0.33	0.30	0.31		0.36
4¹A'								
ΔE	6.24					6.17		
μ	2.13							
f	0.851					0.51		
5¹A'								
ΔE	6.72							
μ	4.60							
f	0.159							
6¹A'								
ΔE	6.99							
μ	3.42							
f	0.565							
1¹A'' ($n \rightarrow \pi^*, +$)								
ΔE	6.15	4.96	5.01	5.00	5.12	5.01	5.31	4.96
μ	2.14	1.99						
f	0.001	0.004	0.006	0.007	0.007	0.001		0.001
2¹A'' ($n \rightarrow \pi^*, +$)								
ΔE	6.86		5.72	5.63	5.75	5.45		
μ	1.93							
f	0.001		0.005	0.005	0.003	0.003		

^aCASPT2F/[TZP+A/DZP]. Fülischer *et al.*¹⁷⁵. Active space with 10 electrons in 10 orbitals for $\pi \rightarrow \pi^*$ states. For $n \rightarrow \pi^*$ states an additional n orbital was included in the active space.

^bCASPT2/6-31G(d,p). Serrano-Andrés *et al.*²³⁶. Active space with 16 electrons in 13 orbitals. Probably (2 11) 16, as deduced from the text. The results from Table 1.

^cCASPT2/6-31G* Blancafort²⁵¹. Active space (2 12) 16.

^dCASPT2/6-311G* Chen *et al.*¹⁸³. Active space (2 9) 14. Ground-state B3LYP/6-311G* geometry. The results from Table 1.

^eRI-CC2/aug-cc-pVTZ. Fleig *et al.*²⁵⁷. Ground-state geometry computed at the same level. The results from Table 2. State 2¹A'' shows distinct valence-Rydberg mixing.

^fDFT-MRCI/TZVPP+Ryd. Marian²⁴⁷. TZVPP basis set²⁴⁶ augmented by two sets of Rydberg functions.

^gSAC-CI/cc-pVDZ. Ritze *et al.*²²². The results from Table 1 (first column).

^hCIPSI/cc-pVDZ. Mennucci *et al.*²⁰⁵

APPENDIX C: CARTESIAN COORDINATES (ÅNGSTROM) OF BENCHMARK MOLECULES

1. Unsaturated Aliphatic Hydrocarbons

ethene

H	0.000000	0.923274	1.238289
H	0.000000	-0.923274	1.238289
H	0.000000	0.923274	-1.238289
H	0.000000	-0.923274	-1.238289
C	0.000000	0.000000	0.668188
C	0.000000	0.000000	-0.668188

butadiene

H	1.080977	-2.558832	0.000000
H	-1.080977	2.558832	0.000000
H	2.103773	-1.017723	0.000000
H	-2.103773	1.017723	0.000000
H	-0.973565	-1.219040	0.000000
H	0.973565	1.219040	0.000000
C	0.000000	0.728881	0.000000
C	0.000000	-0.728881	0.000000
C	1.117962	-1.474815	0.000000
C	-1.117962	1.474815	0.000000

hexatriene

H	-0.953777	1.207691	0.000000
H	0.953777	-1.207691	0.000000
H	2.155816	0.952317	0.000000
H	-2.155816	-0.952317	0.000000
H	2.125769	3.402692	0.000000
H	-2.125769	-3.402692	0.000000
H	0.275642	3.397162	0.000000
H	-0.275642	-3.397162	0.000000
C	0.000000	0.676808	0.000000
C	0.000000	-0.676808	0.000000
C	1.204938	1.485654	0.000000
C	-1.204938	-1.485654	0.000000
C	1.203567	2.831663	0.000000
C	-1.203567	-2.831663	0.000000

octatetraene

H	0.971328	1.220141	0.000000
H	-0.971328	-1.220141	0.000000
H	-2.098090	0.984719	0.000000
H	2.098090	-0.984719	0.000000
H	-0.146884	3.418505	0.000000
H	0.146884	-3.418505	0.000000
H	-2.193473	4.766086	0.000000
H	2.193473	-4.766086	0.000000
H	-3.225698	3.230501	0.000000

H	3.225698	-3.230501	0.000000
C	0.000000	0.721498	0.000000
C	0.000000	-0.721498	0.000000
C	1.125020	-1.479523	0.000000
C	-1.125020	1.479523	0.000000
C	1.121077	-2.928812	0.000000
C	-1.121077	2.928812	0.000000
C	2.237388	-3.682282	0.000000
C	-2.237388	3.682282	0.000000

cyclopropene

H	0.912650	0.000000	1.457504
H	-0.912650	0.000000	1.457504
H	0.000000	-1.585659	-1.038624
H	0.000000	1.585659	-1.038624
C	0.000000	0.000000	0.859492
C	0.000000	-0.651229	-0.499559
C	0.000000	0.651229	-0.499559

cyclopentadiene

H	-0.879859	0.000000	1.874608
H	0.879859	0.000000	1.874608
H	0.000000	2.211693	0.612518
H	0.000000	-2.211693	0.612518
H	0.000000	1.349811	-1.886050
H	0.000000	-1.349811	-1.886050
C	0.000000	0.000000	1.215652
C	0.000000	-1.177731	0.285415
C	0.000000	1.177731	0.285415
C	0.000000	-0.732372	-0.993420
C	0.000000	0.732372	-0.993420

norbornadiene

H	0.901419	0.000000	1.967823
H	-0.901419	0.000000	1.967823
H	0.000000	2.156504	0.616597
H	0.000000	-2.156504	0.616597
H	1.924341	1.340999	-1.022814
H	-1.924341	-1.340999	-1.022814
H	-1.924341	1.340999	-1.022814
H	1.924341	-1.340999	-1.022814
C	0.000000	0.000000	1.346369
C	0.000000	1.119526	0.272221
C	0.000000	-1.119526	0.272221
C	1.235500	0.672374	-0.517602
C	-1.235500	-0.672374	-0.517602
C	-1.235500	0.672374	-0.517602
C	1.235500	-0.672374	-0.517602

2. Aromatic Hydrocarbons and Heterocycles

benzene

H	0.000000	2.484212	0.000000
H	0.000000	-2.484212	0.000000
H	2.151390	1.242106	0.000000
H	-2.151390	-1.242106	0.000000
H	-2.151390	1.242106	0.000000
H	2.151390	-1.242106	0.000000
C	0.000000	1.396792	0.000000
C	0.000000	-1.396792	0.000000
C	1.209657	0.698396	0.000000
C	-1.209657	-0.698396	0.000000
C	-1.209657	0.698396	0.000000
C	1.209657	-0.698396	0.000000

naphthalene

H	1.240557	2.492735	0.000000
H	-1.240557	-2.492735	0.000000
H	-1.240557	2.492735	0.000000
H	1.240557	-2.492735	0.000000
H	3.377213	1.246082	0.000000
H	-3.377213	-1.246082	0.000000
H	-3.377213	1.246082	0.000000
H	3.377213	-1.246082	0.000000
C	0.000000	0.716253	0.000000
C	0.000000	-0.716253	0.000000
C	1.241539	1.403577	0.000000
C	-1.241539	-1.403577	0.000000
C	-1.241539	1.403577	0.000000
C	1.241539	-1.403577	0.000000
C	2.432418	0.707325	0.000000
C	-2.432418	-0.707325	0.000000
C	-2.432418	0.707325	0.000000
C	2.432418	-0.707325	0.000000

furan

H	0.000000	2.051058	0.851533
H	0.000000	-2.051058	0.851533
H	0.000000	1.371979	-1.821224
H	0.000000	-1.371979	-1.821224
C	0.000000	1.095840	0.348301
C	0.000000	-1.095840	0.348301
C	0.000000	0.714027	-0.963274
C	0.000000	-0.714027	-0.963274
O	0.000000	0.000000	1.164881

pyrrole

H	0.000000	2.114611	0.770889
H	0.000000	-2.114611	0.770889

H	0.000000	1.358585	-1.850224
H	0.000000	-1.358585	-1.850224
H	0.000000	0.000000	2.130670
C	0.000000	1.125828	0.333870
C	0.000000	-1.125828	0.333870
C	0.000000	0.709235	-0.984789
C	0.000000	-0.709235	-0.984789
N	0.000000	0.000000	1.119862

imidazole

H	0.000000	2.119822	0.714354
H	0.000000	1.202262	-1.904898
H	0.000000	-2.104815	0.663782
H	0.000000	-0.010302	2.116597
C	0.000000	1.120107	0.305897
C	0.000000	0.635508	-0.983749
C	0.000000	-1.091835	0.283881
N	0.000000	-0.741378	-0.994001
N	0.000000	0.000000	1.104571

pyridine

H	0.000000	2.061947	1.308539
H	0.000000	-2.061947	1.308539
H	0.000000	2.156804	-1.184054
H	0.000000	-2.156804	-1.184054
H	0.000000	0.000000	-2.475074
C	0.000000	1.145417	0.721005
C	0.000000	-1.145417	0.721005
C	0.000000	1.197637	-0.673735
C	0.000000	-1.197637	-0.673735
C	0.000000	0.000000	-1.387901
N	0.000000	0.000000	1.426610

pyrazine

H	0.000000	2.068464	1.258236
H	0.000000	-2.068464	1.258236
H	0.000000	2.068464	-1.258236
H	0.000000	-2.068464	-1.258236
C	0.000000	1.135920	0.697884
C	0.000000	-1.135920	0.697884
C	0.000000	1.135920	-0.697884
C	0.000000	-1.135920	-0.697884
N	0.000000	0.000000	1.417402
N	0.000000	0.000000	-1.417402

pyrimidine

H	0.000000	2.156588	1.120200
H	0.000000	-2.156588	1.120200
H	0.000000	0.000000	-2.400385
H	0.000000	0.000000	2.440403
C	0.000000	1.186684	0.626213

C	0.000000	-1.186684	0.626213
C	0.000000	0.000000	-1.312625
C	0.000000	0.000000	1.354949
N	0.000000	1.203523	-0.717781
N	0.000000	-1.203523	-0.717781

pyridazine

H	0.000000	2.409486	-0.149325
H	0.000000	-2.409486	-0.149325
H	0.000000	1.271234	2.102647
H	0.000000	-1.271234	2.102647
C	0.000000	1.325698	-0.063084
C	0.000000	-1.325698	-0.063084
C	0.000000	0.693095	1.182948
C	0.000000	-0.693095	1.182948
N	0.000000	0.674211	-1.238929
N	0.000000	-0.674211	-1.238929

triazine

H	0.000000	0.000000	2.386083
H	0.000000	-2.066408	-1.193041
H	0.000000	2.066408	-1.193041
C	0.000000	0.000000	1.298345
C	0.000000	1.124400	-0.649173
C	0.000000	-1.124400	-0.649173
N	0.000000	0.000000	-1.379450
N	0.000000	1.194639	0.689726
N	0.000000	-1.194639	0.689726

tetrazine

H	0.000000	0.000000	-2.354794
H	0.000000	0.000000	2.354794
C	0.000000	0.000000	1.269044
C	0.000000	0.000000	-1.269044
N	0.000000	1.204572	0.670429
N	0.000000	-1.204572	0.670429
N	0.000000	1.204572	-0.670429
N	0.000000	-1.204572	-0.670429

3. Aldehydes, Ketones and Amides

formaldehyde

H	0.000000	0.934473	-0.588078
H	0.000000	-0.934473	-0.588078
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.221104

acetone

H	0.000000	2.136732	-0.112445
H	0.000000	-2.136732	-0.112445
H	-0.881334	1.333733	-1.443842
H	0.881334	-1.333733	-1.443842
H	-0.881334	-1.333733	-1.443842
H	0.881334	1.333733	-1.443842
C	0.000000	0.000000	0.000000
C	0.000000	1.287253	-0.795902
C	0.000000	-1.287253	-0.795902
O	0.000000	0.000000	1.227600

benzoquinone

H	0.000000	2.182973	1.259286
H	0.000000	-2.182973	1.259286
H	0.000000	2.182973	-1.259286
H	0.000000	-2.182973	-1.259286
C	0.000000	0.000000	1.441079
C	0.000000	0.000000	-1.441079
C	0.000000	1.266644	0.674582
C	0.000000	-1.266644	0.674582
C	0.000000	1.266644	-0.674582
C	0.000000	-1.266644	-0.674582
O	0.000000	0.000000	2.678518
O	0.000000	0.000000	-2.678518

formamide

H	-0.927427	-0.600301	0.000000
H	1.070498	-1.782390	0.000000
H	2.024514	-0.325050	0.000000
C	0.000000	0.000000	0.000000
O	0.000000	1.225060	0.000000
N	1.119392	-0.775069	0.000000

acetamide

H	1.173209	-1.735763	0.000000
H	2.035841	-0.226201	0.000000
H	-2.121189	-0.156089	0.000000
H	-1.310647	-1.472742	0.885504
H	-1.310647	-1.472742	-0.885504
C	0.000000	0.000000	0.000000
C	-1.267042	-0.831610	0.000000

O	0.000000	1.229439	0.000000
N	1.158967	-0.727718	0.000000

propanamide

H	1.171887	-1.734653	0.000000
H	2.036508	-0.225526	0.000000
H	-1.256737	-1.492368	0.877197
H	-1.256737	-1.492368	-0.877197
H	-3.420939	-0.590421	0.000000
H	-2.544313	0.678541	-0.880209
H	-2.544313	0.678541	0.880209
C	0.000000	0.000000	0.000000
C	-1.272727	-0.833216	0.000000
C	-2.523376	0.033790	0.000000
O	0.000000	1.230373	0.000000
N	1.159100	-0.726409	0.000000

4. Nucleobases

cytosine

H	-2.114860	-1.429678	0.000000
H	-0.173973	-2.806186	0.000000
H	2.073228	-1.658021	0.000000
H	3.175240	0.564335	0.000000
H	2.235202	2.033636	0.000000
C	-0.060783	-1.726152	0.000000
C	1.144884	-1.099470	0.000000
C	1.107049	0.338190	0.000000
C	-1.227573	0.430359	0.000000
O	-2.315109	0.998271	0.000000
N	0.000000	1.058130	0.000000
N	-1.201178	-0.989148	0.000000
N	2.278974	1.024187	0.000000

thymine

H	0.217481	-2.676720	0.000000
H	2.052694	0.924773	0.000000
H	-1.943101	-1.709021	0.000000
H	-3.360610	0.309754	0.000000
H	-2.616463	1.665008	0.879105
H	-2.616463	1.665008	-0.879105
C	1.356951	-0.994496	0.000000
C	0.000000	1.121102	0.000000
C	-1.214538	0.306431	0.000000
C	-1.085764	-1.041812	0.000000
C	-2.529824	1.020445	0.000000
O	2.444132	-1.558490	0.000000
O	0.023681	2.350992	0.000000
N	0.145112	-1.666249	0.000000
N	1.192460	0.382130	0.000000

uracil

H	-2.025413	-1.517742	0.000000
H	-0.021861	1.995767	0.000000
H	2.182391	-1.602586	0.000000
H	-0.026659	-2.791719	0.000000
C	-1.239290	0.359825	0.000000
C	1.279718	0.392094	0.000000
C	1.243729	-1.064577	0.000000
C	0.055755	-1.709579	0.000000
O	-2.308803	0.954763	0.000000
O	2.287387	1.092936	0.000000
N	-1.139515	-1.026364	0.000000
N	0.000000	0.978951	0.000000

adenine

H	0.974930	-3.075149	0.000000

H	2.134658	2.075802	0.000000
H	3.312010	0.776987	0.000000
H	-3.052077	-0.334232	0.000000
H	-2.711876	2.203052	0.000000
C	0.662834	-2.032900	0.000000
C	1.359313	0.172553	0.000000
C	0.000000	0.547434	0.000000
C	-0.924835	-0.500714	0.000000
C	-1.906806	1.478795	0.000000
N	-0.658577	-1.817838	0.000000
N	1.672594	-1.133202	0.000000
N	-2.150759	0.128726	0.000000
N	-0.616118	1.783396	0.000000
N	2.352763	1.090709	0.000000

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Paper II

*Benchmarks for electronically excited states:
A comparison of noniterative and iterative triples
corrections – CCSDR(3) versus CC3*

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Benchmarks for Electronically Excited States: A Comparison of Noniterative and Iterative Triples Corrections in Linear Response Coupled Cluster Methods: CCSDR(3) versus CC3

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Abstract: CCSDR(3) calculations of vertical excitation energies are reported for a set of 24 molecules and 121 excited valence singlet states from a recently published benchmark of organic molecules. The same geometries (MP2/6–31G*) and basis set (TZVP) were employed as in our previous linear response CC2, CCSD, and CC3 calculations. The CCSDR(3) results are compared against the CCSD and CC3 results. Statistical evaluation of all CCSDR(3) excitation energies gives mean absolute deviations of 0.09 eV from CC3 and 0.30 eV from CCSD. For excited states, which are dominated by single excitations, the absolute mean deviation from CC3 is reduced to 0.02 eV and the maximum deviation is 0.09 eV. CCSDR(3) is thus a very cost-effective accurate alternative to CC3.

1. Introduction

In two recent studies^{1,2} we have presented a benchmark set for the calculation of electronically excited states. This set comprises unsaturated aliphatic hydrocarbons (including polyenes and cyclic compounds), aromatic hydrocarbons and heterocycles, carbonyl compounds, and nucleobases. It consists of 28 medium size organic molecules with a total of 223 excited states (152 singlet and 71 triplet states) and is intended to cover the most important chromophores in organic photochemistry.

In the first study¹ calculations were performed with a series of linear response coupled cluster methods (CC2, CCSD, CC3)^{3–15} and with multistate complete-active-space second-order perturbation theory (MS-CASPT2).^{16–18} Based on these results and other high-level literature data, best theoretical estimates were chosen for the majority of the studied vertical excitation energies. The comparison of coupled cluster and multireference results showed that CC3 and CASPT2 excitation energies are in excellent agreement

for states which are dominated by single excitations and that CC2 performs on average better than CCSD.

In the second study² we have investigated the performance of time-dependent density functional theory (TD-DFT) with three functionals (BP86, B3LYP, and BHLYP) and DFT-based multireference configuration interaction (DFT/MRCI) methods.

Møller–Plesset perturbation theory^{19–29} and coupled cluster theory-based^{3–15,26–30} response theory methods such as CC3^{13–15} are suitable for states with low double excitation contributions. However, CC3 formally scales as N^7 with the number of orbitals N , and the high computational cost in the iterative treatment of the triple excitations in CC3 restricts its application to small systems and/or small basis sets. Looking for a computationally cheaper but comparably accurate approach, Christiansen and co-workers^{31,32} have presented the CCSDR(3) method, in which a noniterative triples correction is added to the linear response CCSD excitation energy. In this respect, CCSDR(3) is analogous to the CCSD(T) method³³ which is so successful for ground-state energies. Both methods include fourth-order terms. In CCSDR(3) the reference singles and doubles amplitudes as well as the energies of single excitation dominated states

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Table 1. Vertical Singlet Excitation Energies ΔE (eV)

molecule	state	CCSD (% R_1) ^a ref 1	CCSDR(3) (Δ) ^b this work	CC3 (% R_1) ^a ref 1
ethene	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.51 (97.2)	8.36 (−0.01)	8.37 (96.9)
<i>E</i> -butadiene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	6.72 (95.5)	6.56 (−0.02)	6.58 (93.7)
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	7.42 (85.8)	6.95 (0.18)	6.77 (72.8)
<i>all-E</i> -hexatriene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	5.72 (95.0)	5.56 (−0.02)	5.58 (92.6)
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	6.61 (84.7)	6.04 (0.32)	5.72 (65.8)
<i>all-E</i> -octatetraene	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.99 (85.4)	5.40 (0.43)	4.97 (62.9)
	1 ¹ B _u ($\pi \rightarrow \pi^*$)	5.07 (94.7)	4.93 (−0.01)	4.94 (91.9)
	2 ¹ B _u ($\pi \rightarrow \pi^*$)	6.89 (81.3)	6.91 (0.30)	6.06 (58.5)
	3 ¹ A _g ($\pi \rightarrow \pi^*$)	6.98 (92.0)	6.72 (0.23)	6.50 (71.6)
	4 ¹ A _g ($\pi \rightarrow \pi^*$)	7.05 (89.9)	7.01 (−0.05)	6.81 (92.1)
	3 ¹ B _u ($\pi \rightarrow \pi^*$)	8.15 (94.6)	7.95 (0.03)	7.91 (91.9)
cyclopropene	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	6.96 (94.5)	6.89 (−0.01)	6.90 (93.0)
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.24 (96.3)	7.10 (0.00)	7.10 (95.5)
cyclopentadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.87 (95.7)	5.72 (−0.01)	5.73 (94.3)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.05 (89.4)	6.76 (0.14)	6.61 (79.3)
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.95 (95.8)	8.72 (0.02)	8.69 (93.1)
norbornadiene	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	5.80 (95.3)	5.65 (0.01)	5.64 (93.4)
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.69 (94.5)	6.51 (0.02)	6.49 (91.9)
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.87 (95.5)	7.65 (0.01)	7.64 (93.8)
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	7.87 (95.0)	7.73 (0.02)	7.71 (93.0)
benzene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.19 (90.5)	5.12 (0.04)	5.07 (85.8)
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.74 (95.6)	6.70 (0.02)	6.68 (93.6)
	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	7.65 (94.5)	7.45 (0.00)	7.45 (92.2)
	2 ¹ E _{2g} ($\pi \rightarrow \pi^*$)	9.21 (84.9)	8.71 (0.29)	8.43 (65.6)
naphthalene	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	4.41 (90.5)	4.34 (0.07)	4.27 (85.2)
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.21 (94.3)	5.08 (0.05)	5.03 (90.6)
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	6.23 (90.1)	6.09 (0.11)	5.98 (82.2)
	1 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	6.53 (91.4)	6.26 (0.20)	6.07 (79.6)
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	6.55 (93.9)	6.35 (0.02)	6.33 (90.7)
	2 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	6.97 (93.8)	6.81 (0.02)	6.79 (91.3)
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	6.77 (93.8)	6.60 (0.03)	6.57 (90.5)
	3 ¹ A _g ($\pi \rightarrow \pi^*$)	7.77 (88.4)	7.29 (0.39)	6.90 (70.0)
	3 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.77 (93.5)	8.53 (0.08)	8.44 (87.9)
	3 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	9.03 (84.1)	8.50 (0.38)	8.12 (58.7)
furan	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.80 (94.9)	6.64 (0.04)	6.60 (92.9)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.89 (90.8)	6.71 (0.09)	6.62 (84.9)
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.83 (94.2)	8.57 (0.04)	8.53 (90.7)
pyrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.61 (91.2)	6.47 (0.07)	6.40 (86.0)
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.87 (94.2)	6.74 (0.03)	6.71 (91.6)
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.44 (93.7)	8.20 (0.04)	8.17 (90.2)
imidazole	1 ¹ A'' ($n \rightarrow \pi^*$)	7.01 (92.4)	6.87 (0.05)	6.82 (87.6)
	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.80 (92.0)	6.64 (0.06)	6.58 (87.2)
	3 ¹ A' ($\pi \rightarrow \pi^*$)	7.27 (93.1)	7.15 (0.05)	7.10 (89.8)
	2 ¹ A'' ($n \rightarrow \pi^*$)	8.15 (93.3)	7.98 (0.05)	7.93 (89.4)
	4 ¹ A' ($\pi \rightarrow \pi^*$)	8.70 (92.7)	8.49 (0.04)	8.45 (88.8)
pyridine	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.27 (90.6)	5.20 (0.05)	5.15 (85.9)
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	5.25 (92.8)	5.12 (0.07)	5.05 (88.1)
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.73 (92.4)	5.55 (0.05)	5.50 (87.7)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.94 (95.3)	6.88 (0.03)	6.85 (92.8)
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.94 (94.2)	7.72 (0.01)	7.70 (91.5)
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.81 (93.5)	7.61 (0.02)	7.59 (89.7)
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	9.45 (89.5)	9.00 (0.33)	8.68 (74.1)
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	9.64 (84.4)	9.09 (0.32)	8.77 (65.2)
pyrazine	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	4.42 (93.4)	4.31 (0.06)	4.24 (89.9)
	1 ¹ A _u ($n \rightarrow \pi^*$)	5.29 (92.7)	5.11 (0.06)	5.05 (88.4)
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.14 (90.8)	5.07 (0.05)	5.02 (86.2)
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	6.02 (92.1)	5.86 (0.12)	5.74 (85.0)
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	7.13 (90.8)	6.86 (0.11)	6.75 (83.8)
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.18 (95.6)	7.10 (0.03)	7.07 (93.3)
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.34 (93.9)	8.09 (0.03)	8.06 (90.9)
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.29 (93.2)	8.08 (0.03)	8.05 (89.7)
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	9.75 (83.5)	9.16 (0.39)	8.77 (61.1)
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	9.55 (89.1)	9.04 (0.35)	8.69 (74.2)
pyrimidine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.70 (92.7)	4.56 (0.06)	4.50 (88.4)
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.12 (92.6)	4.97 (0.05)	4.93 (88.2)
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.49 (90.5)	5.42 (0.05)	5.36 (85.7)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.17 (94.8)	7.10 (0.04)	7.06 (92.2)
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	8.24 (93.8)	8.02 (0.02)	8.01 (90.7)
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.97 (93.5)	7.77 (0.03)	7.74 (89.7)
pyridazine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.11 (93.1)	3.99 (0.07)	3.92 (89.0)
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.76 (92.0)	4.57 (0.08)	4.49 (86.6)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	5.35 (90.2)	5.28 (0.06)	5.22 (85.2)
	2 ¹ A ₂ ($n \rightarrow \pi^*$)	6.00 (92.1)	5.84 (0.10)	5.74 (86.6)
	2 ¹ B ₁ ($n \rightarrow \pi^*$)	6.70 (92.0)	6.49 (0.08)	6.41 (86.6)
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.09 (94.7)	6.99 (0.07)	6.93 (90.7)
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.79 (93.8)	7.58 (0.04)	7.55 (90.2)
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.11 (93.8)	7.86 (0.04)	7.82 (90.5)

Table 1. Continued

molecule	state	CCSD (% R_1) ^a ref 1	CCSDR(3) (Δ) ^b this work	CC3 (% R_1) ^a ref 1
s-triazine	1 ¹ A ₁ ^{''} ($n \rightarrow \pi^*$)	4.96 (92.3)	4.81 (0.04)	4.78 (88.0)
	1 ¹ A ₂ ^{''} ($n \rightarrow \pi^*$)	4.98 (92.5)	4.83 (0.07)	4.76 (88.0)
	1 ¹ E ^{''} ($n \rightarrow \pi^*$)	5.01 (92.5)	4.87 (0.05)	4.81 (88.1)
	1 ¹ A ₂ ['] ($\pi \rightarrow \pi^*$)	5.84 (90.2)	5.76 (0.06)	5.71 (85.1)
	2 ¹ A ₁ ['] ($\pi \rightarrow \pi^*$)	7.51 (93.7)	7.44 (0.03)	7.41 (90.8)
	2 ¹ E ^{''} ($n \rightarrow \pi^*$)	8.19 (90.9)	7.95 (0.15)	7.80 (88.1)
	1 ¹ E ['] ($\pi \rightarrow \pi^*$)	8.28 (93.7)	8.07 (0.02)	8.04 (88.8)
	2 ¹ E ['] ($\pi \rightarrow \pi^*$)	10.24 (91.2)	9.89 (0.46)	9.44 (74.3)
s-tetrazine	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	2.71 (93.2)	2.61 (0.08)	2.53 (89.6)
	1 ¹ A _u ($\pi \rightarrow \pi^*$)	4.07 (92.2)	3.88 (0.08)	3.79 (87.5)
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	5.32 (91.7)	5.15 (0.18)	4.97 (82.5)
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.27 (90.0)	5.20 (0.08)	5.12 (84.6)
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.70 (90.7)	5.51 (0.17)	5.34 (80.7)
	2 ¹ A _u ($n \rightarrow \pi^*$)	5.70 (92.5)	5.56 (0.10)	5.46 (87.4)
	2 ¹ B _{2g} ($n \rightarrow \pi^*$)	6.76 (90.1)	6.43 (0.20)	6.23 (79.2)
	2 ¹ B _{1g} ($n \rightarrow \pi^*$)	7.25 (91.1)	6.98 (0.11)	6.87 (84.7)
	3 ¹ B _{1g} ($n \rightarrow \pi^*$)	8.36 (86.9)	7.60 (0.52)	7.08 (63.2)
	2 ¹ B _{3u} ($n \rightarrow \pi^*$)	6.99 (93.2)	6.77 (0.10)	6.67 (86.7)
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.66 (94.9)	7.54 (0.09)	7.45 (91.0)
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.06 (93.4)	7.83 (0.04)	7.79 (90.2)
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.88 (93.2)	8.58 (0.07)	8.51 (87.7)
	2 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	9.44 (84.3)	8.86 (0.39)	8.47 (63.6)
formaldehyde	1 ¹ A ₂ ($n \rightarrow \pi^*$)	3.97 (93.4)	3.94 (0.00)	3.95 (91.2)
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	9.26 (93.4)	9.19 (0.00)	9.18 (90.9)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	10.54 (94.4)	10.43 (−0.02)	10.45 (91.3)
acetone	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.43 (93.4)	4.39 (0.00)	4.40 (90.8)
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	9.26 (93.8)	9.17 (0.01)	9.17 (91.5)
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	9.87 (93.5)	9.66 (0.01)	9.65 (90.1)
<i>p</i> -benzoquinone	1 ¹ A _u ($n \rightarrow \pi^*$)	3.19 (91.7)	3.01 (0.16)	2.85 (83.0)
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	3.07 (92.0)	2.90 (0.15)	2.75 (84.1)
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	4.93 (92.7)	4.69 (0.11)	4.59 (87.9)
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	5.89 (92.5)	5.65 (0.03)	5.62 (88.4)
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	6.55 (91.0)	6.09 (0.27)	5.82 (75.2)
	2 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	7.62 (91.0)	7.36 (0.08)	7.27 (83.8)
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.47 (91.7)	8.10 (0.28)	7.82 (68.6)
formamide	1 ¹ A ^{''} ($n \rightarrow \pi^*$)	5.66 (93.6)	5.65 (−0.01)	5.65 (90.7)
	2 ¹ A ['] ($\pi \rightarrow \pi^*$)	8.52 (92.9)	8.30 (0.03)	8.27 (87.9)
	3 ¹ A ['] ($\pi \rightarrow \pi^*$)	11.34 (92.7)	11.06 (0.13)	10.93 (86.6)
acetamide	1 ¹ A ^{''} ($n \rightarrow \pi^*$)	5.71 (93.5)	5.69 (−0.01)	5.69 (90.6)
	2 ¹ A ['] ($\pi \rightarrow \pi^*$)	7.85 (92.8)	7.69 (0.02)	7.67 (89.1)
	3 ¹ A ['] ($\pi \rightarrow \pi^*$)	10.77 (93.0)	10.56 (0.06)	10.50 (88.7)
propanamide	1 ¹ A ^{''} ($n \rightarrow \pi^*$)	5.74 (93.6)	5.71 (−0.01)	5.72 (90.6)
	2 ¹ A ['] ($\pi \rightarrow \pi^*$)	7.80 (93.0)	7.64 (0.02)	7.62 (89.2)
	3 ¹ A ['] ($\pi \rightarrow \pi^*$)	10.34 (93.3)	10.13 (0.06)	10.06 (89.0)

^a Weight of the single excitations in the coupled cluster calculations. ^b Difference between CCSDR(3) and CC3 results (in parenthesis).

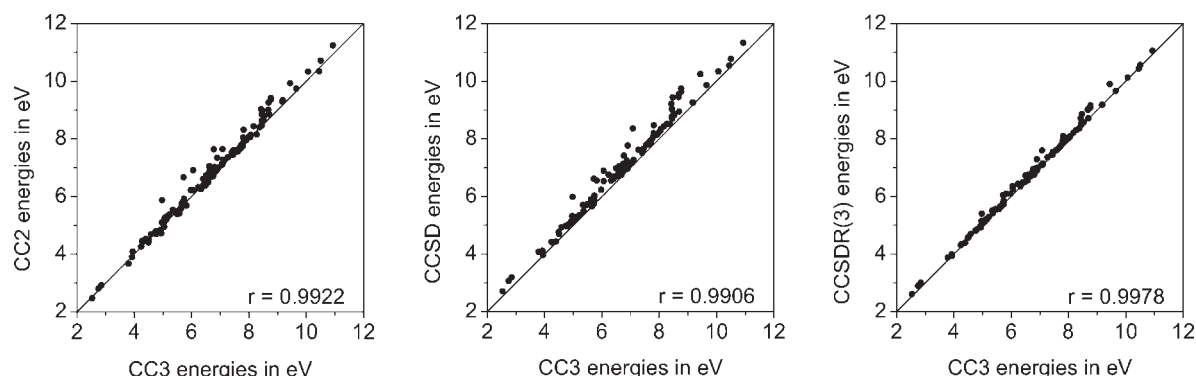


Figure 1. Correlation plots for all calculated singlet excited states: Coupled cluster vertical excitation energies.

are correct to third order whereas the reference triples amplitudes and the energies of double excitation dominated states are correct to second order exactly as in CC3.^{31,32} While the computational scaling of CCSDR(3) is of the same order as in CC3, the N^7 step is noniterative in CCSDR(3),

which implies a much smaller prefactor and therefore significant computational savings. Formally CCSDR(3) is based on a pseudoperturbation theory expansion of the CC3 eigenvalue problem and therefore bears some similarity to the CIS(D)³⁴ and RPA(D)^{21,23} methods, which are based on

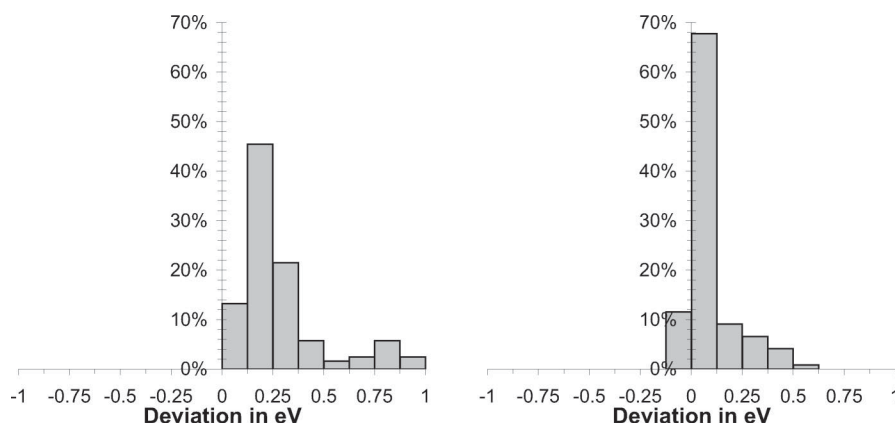


Figure 2. Histogram of the frequency of deviation (from CC3/TZVP in %) of all calculated CCSD/TZVP (left) and CCSDR(3)/TZVP (right) singlet excited states.

Table 2. Deviations in Excitation Energies of 121 Singlet Excited States with Respect to CC3/TZVP

	method		
	CC2 ^a	CCSD ^a	CCSDR(3)
mean	0.13	0.30	0.09
abs mean	0.17	0.30	0.09
std dev	0.26	0.38	0.14
maximum	0.95	1.28	0.52

^a CC2/TZVP and CCSD/TZVP results from ref 1.

the corresponding expansion of the CC2^{3,4} or second-order polarization propagator approximation (SOPPA)^{19,20,22,24,25} eigenvalue problem.

CCSDR(3) calculations have previously been carried out for a number of small^{31,32,35–37} and medium size^{36,38–45} molecules; however, a systematic comparison with CC3 and CCSD has not yet been published. In this article we present such a study for singlet excitation energies using our recently published benchmark set.¹ We have calculated CCSDR(3) excitation energies for 121 excited valence singlet states in 24 molecules, i.e. all the singlet states from the benchmark set for which CC3 results are available.¹ The new CCSDR(3) results are compared with the previously published CCSD and CC3 data. On the basis of a statistical evaluation of our results, we derive rules of thumb for the accuracy of the noniterative triples correction of CCSDR(3) relative to the iterative correction in CC3.

Although this study is only concerned with the question of how well CCSDR(3) with its noniterative triples correction is able to reproduce the results of CC3 calculations, we emphasize that CCSDR(3) is by no means the only method which includes noniterative triples corrections in the calculation of excitation energies. Several methods, EOM-CCSD(T), EOM-CCSD(T'), and EOM-CCSD($\bar{T}$), have been proposed^{46–49} that are based on the equation-of-motion coupled cluster approach (EOM-CC) developed by Bartlett and others.^{50–63} Piecuch and co-workers have extended the completely renormalized coupled-cluster theory^{64–66} to the calculation of excitation energies, by adding noniterative triples corrections to the EOM-CCSD energies in their CR-EOMCCSD(T), CR-EOMCCSD(T)_L, and r-CR-EOMCCSD(T) treatments^{65,67–71} which are based on the methods of moments of coupled cluster equations.^{67,68,72–75} Finally one

should also note in this context a recent approach⁷⁶ based on the EOM-CC(m)PT(n) methods,^{77,78} the similarity transformed EOM-CC method (STEOM)^{79–82} that implicitly includes triples excitations, the Fock space coupled cluster theory,⁸³ the SAC-CI approach of Nakatsuji,^{84,85} and the spin-flip equation-of-motion coupled cluster method by Krylov and co-workers.^{86–90}

The remaining parts of the paper are structured as follows. In Section 2 the details of the calculations are specified. In Section 3 the CCSDR(3) results are discussed in comparison with the previously published CCSD and CC3 results. Conclusions are drawn in section 4.

2. Computational Details

All calculations were carried out with the Dalton 2.0 program package.⁹¹ The same MP2/6–31G* optimized geometries^{92–95} and TZVP basis set⁹⁶ as in our previous studies were employed.^{1,2}

As discussed before,^{1,2} the TZVP basis set does not contain diffuse functions and might not be able to give a balanced description of excited states that are spatially extended and have (partial) Rydberg character. For the present study this is less important, since we are interested in a direct comparison of correlated ab initio methods in the calculation of valence excited states, which should be much less sensitive to the basis set than the absolute excitation energies. For example, the differences between the linear response CC3 and CCSD results deviate by only a few hundredths of 1 eV from the corresponding literature values^{11,13,36,38–42,44,82,97–100} obtained with mostly larger basis sets. Our absolute CC3 excitation energies, on the other hand, tend to be slightly too large, normally by 0.02–0.15 eV and sometimes by up to 0.3 eV.

3. Results and Discussion

The CCSDR(3)/TZVP results for the 121 singlet valence states are given in Table 1 together with the previously published¹ CCSD and CC3 results. 83 of these states are of $\pi \rightarrow \pi^*$ type, 35 are of $n \rightarrow \pi^*$ type and three are of $\sigma \rightarrow \pi^*$ type. Figure 1 shows correlation plots between the CC2, CCSD, and CCSDR(3) results on one side and the CC3 results on the other side for all calculated states. Figure 2

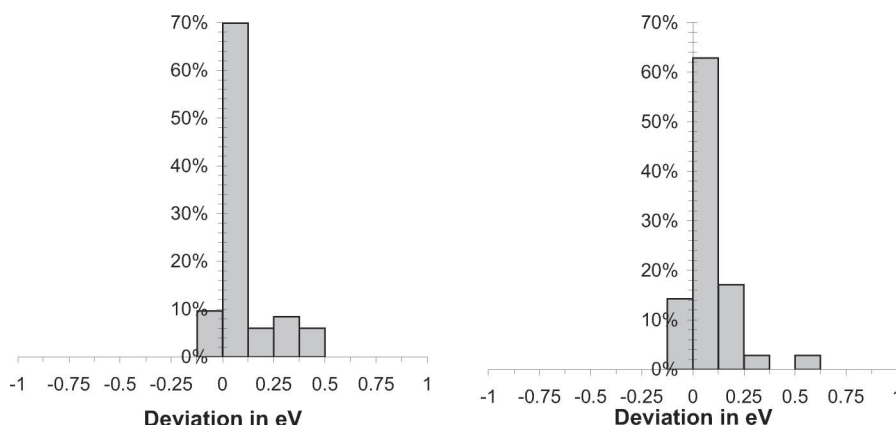


Figure 3. Histogram of the frequency of deviation (CCSDR(3)/TZVP vs CC3/TZVP, in %) of all calculated singlet $\pi \rightarrow \pi^*$ (left) and $n \rightarrow \pi^*$ (right) excited states.

Table 3. Deviations in Excitation Energies of 35 Singlet Excited $n \rightarrow \pi^*$ States with Respect to CC3/TZVP

	method		
	CC2 ^a	CCSD ^a	CCSDR(3)
mean	0.04	0.28	0.10
abs mean	0.10	0.28	0.10
std dev	0.13	0.36	0.14
maximum	0.56	1.28	0.52

^a CC2/TZVP and CCSD/TZVP results from ref 1.

Table 4. Deviations in Excitation Energies of 45 Singlet Excited States of the Benchmark Set with Respect to CC3/TZVP, for States Where the R_1 (CC3) Percentage Exceeds 90%

	method		
	CC2 ^a	CCSD ^a	CCSDR(3)
mean	0.04	0.16	0.02
abs mean	0.09	0.16	0.02
std dev	0.11	0.18	0.03
maximum	0.27	0.30	0.09

^a CC2/TZVP and CCSD/TZVP results from ref 1.

Table 5. Comparison of Relative CPU Times between CCSD, CCSDR(3), and CC3 Calculations

	molecule	
	benzene	naphthalene
basis functions	150	238
states	6 ^a	3
S+D amplitudes	≈ 515 000 ^a	3 353 467
relative CPU time		
CCSD	1	6
CCSDR(3)	22	132
CC3	1012	2706

^a Six states in four different irreducible representations were calculated in the same run: one ^1A_g state with 517029 S+D amplitudes, two $^1B_{3u}$ states with 514210 S+D amplitudes, two $^1B_{2u}$ states with 515667 S+D amplitudes and one $^1B_{1g}$ state with 514202 S+D amplitudes.

presents histograms with the frequency of deviation from CC3 for the CCSD and CCSDR(3) results. It is obvious that compared with CCSD and CC2 the noniterative triples correction in CCSDR(3) leads to a much better agreement with the CC3 results over the whole range of energies. The mean deviation from CC3 (Table 2) drops from 0.30 eV in

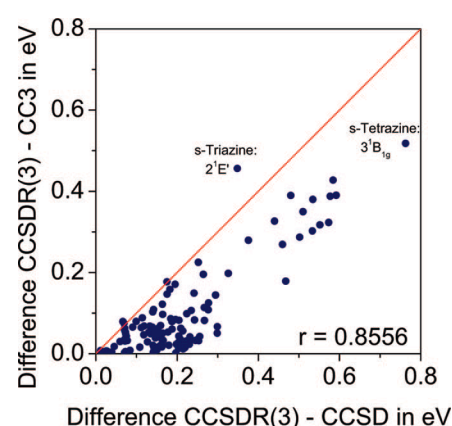


Figure 4. Correlation plot for all calculated singlet excited states: energy difference between CCSDR(3) and CC3 versus energy difference between CCSDR(3) and CCSD.

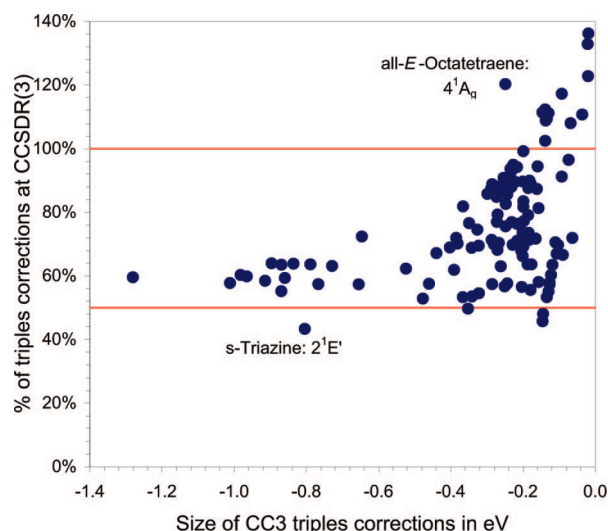


Figure 5. Correlation plot for all calculated singlet excited states: percentage of the triples correction obtained in the CCSDR(3) calculations versus the total CC3 triples correction.

CCSD to 0.09 eV in CCSDR(3). The largest deviations from CC3 are found for the $^3B_{1g}$ state of *s*-tetrazine (0.52 eV), the $2'E'$ state of *s*-triazine (0.46 eV), and the 2^1A_g state of *all-E*-octatetraene (0.43 eV), which is in each case about half

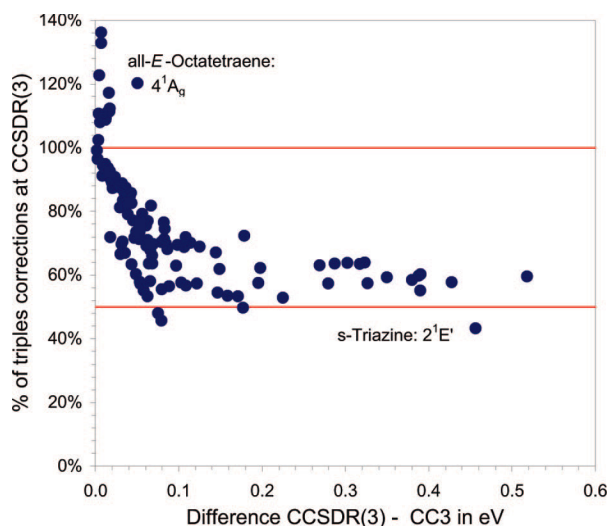


Figure 6. Correlation plot for all calculated singlet excited states: percentage of the triples correction obtained in the CCSDR(3) calculations versus the difference between CCSDR(3) and CC3.

the deviation found for CCSD. Correspondingly the standard deviation is also much smaller for CCSDR(3) than for CCSD as can be seen from Figure 2 and Table 2.

The significantly improved performance of CCSDR(3) is not restricted to a particular range of excited-state energies but holds for the whole benchmark set as illustrated in the correlation plots in Figure 1. For less than 10% of the states, CCSDR(3) predicts slightly smaller excitation energies than CC3, whereas the CCSD excitation energies in our benchmark set are always larger than the CC3 energies. We had previously found that CC2 gives excitation energies both larger and smaller than CC3 and consequently performs on average better than CCSD for our benchmark set.¹ However, compared with CCSDR(3), the spread of results is significantly larger in CC2 than in CCSDR(3). This can be seen in the correlation plots (Figure 1) and is also indicated by the standard deviations and maximum deviations in Table 2 which are about twice as large for CC2 than for CCSDR(3).

It is obvious from the histograms in Figure 3 and from the comparison of the statistical data for the $n \rightarrow \pi^*$ transitions alone (Table 3) against the data for all excited states (Table 2) that there is not much difference between the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The largest outlier with respect to CC3, i.e., the 3^1B_{1g} state of *s*-tetrazine, is a $n \rightarrow \pi^*$ transition, whereas the two next largest outliers, the $2^1E'$ state of *s*-triazine and the 2^1A_g state of *all-E*-octatetraene, are $\pi \rightarrow \pi^*$ transitions.

When restricting the statistics to states with a CC3 single excitation weight larger than 90% (called % R_1 in Table 1), the agreement between CCSDR(3) and CC3 becomes almost perfect. The mean deviation is reduced to 0.02 eV, and the maximum deviation is also less than 0.1 eV (see Table 4).

Relative CPU times for two representative calculations of excited states in benzene and naphthalene are collected in Table 5. It is gratifying to see that the necessary CPU time is dramatically reduced in CCSDR(3) compared to CC3. Nevertheless, due to the formal N^7 scaling of CCSDR(3)

these calculations are still considerably more expensive than the simpler CCSD calculations.

It would clearly be desirable to be able to estimate the remaining error of CCSDR(3) relative to CC3 based on the results of the CCSD and CCSDR(3) calculations alone. A correlation plot for the relevant energy differences (Figure 4) shows that the remaining errors in the CCSDR(3) results compared to CC3 are almost always smaller than the changes on going from CCSD to CCSDR(3) (prominent exception: the $2^1E'$ state of *s*-triazine).

Analyzing the performance of CCSDR(3) as a function of the single excitation weight in the CCSD calculations, one finds that for all states in our benchmark set with a CCSD single excitation weight smaller than 90% the difference between the CCSDR(3) and CC3 results is larger than 0.1 eV. This implies that the data from CCSD calculations allow us to pinpoint states, for which one very likely will encounter larger differences between CCSDR(3) and CC3. However, the opposite is not always true. There is one state in our benchmark set ($2^1E'$ in *s*-triazine), where the difference is 0.46 eV despite a single excitation weight of 91.2%, while there are two states in *p*-benzoquinone (1^1B_{3u} and 2^1B_{1u}) with a single excitation weight of 91–92% which differ by ≈ 0.27 eV and in total 15 states with single excitation weights of 91–93% and differences between CCSDR(3) and CC3 in the range between 0.1 and 0.2 eV.

Finally, it is important to know which fraction of the CC3 triples correction can be recovered in an CCSDR(3) calculation. This percentage is shown as a function of the size of the total CC3 triples correction in Figure 5 and as function of the remaining deviation from the CC3 results in Figure 6. It is obvious that with three exceptions (most prominent again the $2^1E'$ state of *s*-triazine) the CCSDR(3) triples correction gives at least 50% of the iterative CC3 triples correction, and on average it amounts to 78%. Even for the cases with large CC3 triple corrections (0.4 eV or more), CCSDR(3) yields about 60%. On the other hand, there are also some systems where CCSDR(3) overestimates the CC3 triples correction. However, with the exception of the 4^1A_g state of *all-E*-octatetraene, this happens only for states where the remaining difference between CCSDR(3) and CC3 is less than 0.02 eV and the total triples correction is less than 0.16 eV.

4. Conclusions

We have carried out CCSDR(3)/TZVP calculations of vertical excitation energies for 24 molecules and a total of 121 valence excited singlet states from a recently published benchmark set of organic molecules.¹ Statistical comparison of these data with the previously published linear response CC2, CCSD, and CC3 results shows that adding the noniterative triples corrections to the CCSD results leads to a substantial improvement over CC2 and CCSD for all states in this benchmark set.

Inclusion of the noniterative triples correction in CCSDR(3) often reproduces the iterative CC3 triples correction almost quantitatively, at dramatically reduced CPU times. For all states, which are dominated by single excitations (CC3 single excitation weight larger than 90%), the

CCSDR(3) results differ by at most 0.1 eV from the CC3 results. More important is that one can obtain a reasonable estimate of the accuracy of the CCSDR(3) results from the size of the triples correction in CCSDR(3) and the single excitation weight in the CCSD calculations. The remaining difference between CCSDR(3) and CC3 is in almost all cases smaller than the noniterative triples correction from CCSDR(3). CCSDR(3) normally gives at least 60% of the CC3 triples correction even if the latter is large (>0.4 eV). Furthermore one can easily identify states for which differences of more than 0.1 eV between CCSDR(3) and CC3 should be expected: for all states in our benchmark with a CCSD single excitation weight smaller than 90%, the CCSDR(3) results deviate from the CC3 results by 0.1 eV or more.

We conclude that CCSDR(3) may play a similar role for excited states as CCSD(T) does for ground states, and that an appropriate sequence of linear response-coupled cluster methods for the calculation of vertical excitation energies is CC2, CCSDR(3), CC3. However, since transition moments are not defined in CCSDR(3), the corresponding sequence for the calculation of oscillator strengths remains CC2, CCSD, CC3.

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Paper III

*Benchmarks for electronically excited states:
Time-dependent density functional theory and
density functional based multireference
configuration interaction*

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Benchmarks for electronically excited states: Time-dependent density functional theory and density functional theory based multireference configuration interaction

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Time-dependent density functional theory (TD-DFT) and DFT-based multireference configuration interaction (DFT/MRCI) calculations are reported for a recently proposed benchmark set of 28 medium-sized organic molecules. Vertical excitation energies, oscillator strengths, and excited-state dipole moments are computed using the same geometries (MP2/6-31G*) and basis set (TZVP) as in our previous *ab initio* benchmark study on electronically excited states. The results from TD-DFT (with the functionals BP86, B3LYP, and BHLYP) and from DFT/MRCI are compared against the previous high-level *ab initio* results, and, in particular, against the proposed best estimates for 104 singlet and 63 triplet vertical excitation energies. The statistical evaluation for the latter reference data gives the lowest mean absolute deviations for DFT/MRCI (0.22 eV for singlets and 0.24 eV for triplets) followed by TD-DFT/B3LYP (0.27 and 0.44 eV, respectively), whereas TD-DFT/BP86 and TD-DFT/BHLYP are significantly less accurate. The energies of singlet states with double excitation character are generally overestimated by TD-DFT, whereas triplet state energies are systematically underestimated by the currently investigated DFT-based methods. © 2008 American Institute of Physics. [DOI: 10.1063/1.2973541]

I. INTRODUCTION

In a recent study¹ we presented an *ab initio* benchmark for electronically excited states of 28 medium-sized organic molecules with a total of 223 excitations. Calculations were performed using multistate complete-active-space second-order perturbation theory (MS-CASPT2) and coupled cluster methods (CC2, CCSD, and CC3). On the basis of these results and high-level *ab initio* data from literature, we proposed best theoretical estimates for the vertical excitation energies of 104 singlet and 63 triplet excited states.

The application of accurate *ab initio* methods such as MS-CASPT2 and CC3 is still limited in practice to rather small molecules, and there is clearly a need for reliable approximate methods that can deal with larger systems. There are a number of requirements² that approximate methods for electronically excited states should ideally satisfy: generality (ability to treat arbitrary types of excited states), accuracy (small errors in excitation energies, preferably less than 0.2 eV), availability of properties (including oscillator strengths, dipole moments, and analytic nuclear gradients), minimum human effort (standardization, “black-box” character, as few technical parameters as possible), and computational efficiency (small memory and CPU demand, comparable to a corresponding ground-state calculation). While none of the currently available methods fulfills all these requirements, density functional theory (DFT) is generally considered as a promising candidate. Therefore, in this article, we evaluate

the performance of DFT-based approaches by comparison against our *ab initio* benchmark data.¹

Over the past decade, time-dependent density functional theory (TD-DFT) (Ref. 3) has become one of the most prominent methods for calculating excited states.⁴ A major advantage of TD-DFT is its low computational cost,⁵ roughly comparable with single excitation theories based on the Hartree–Fock (HF) ground state such as configuration interaction with singles or the random phase approximation. TD-DFT excitation energies are computed as poles of the frequency-dependent density matrix response.³ Since the commonly used adiabatic approximation represents this response in terms of single excitations, TD-DFT is best suited for excited states that are dominated by single excitations. TD-DFT properties are obtained from derivatives of the excited-state energy with respect to external perturbations.^{6,7} TD-DFT calculations can be standardized and are thus user-friendly (no need to define an active space or to select reference configurations).

Evaluations of TD-DFT performance have been reported for various density functionals.^{8–17} Most of these studies have compared TD-DFT vertical excitation energies either with experimental results or with published CASPT2 calculations. Generally speaking, these evaluations are less comprehensive and less systematic than desirable. The use of experimental excitation energies as reference data may be problematic because the observed band maxima do not exactly match the vertical excitation energies, bands are often found to overlap, and spectra may be available only in solution and not in the gas phase. Comparisons with published

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CASPT2 results suffer from nonuniform setup conventions in literature, e.g., with regard to geometries, basis sets, and active spaces.

An alternative DFT-based method for electronically excited states arises from the use of Kohn–Sham (KS) orbitals in a multireference configuration interaction (MRCI) framework.¹⁸ In this ansatz, the major part of dynamic electron correlation is captured by the KS-DFT treatment, and static correlation effects are introduced by the MRCI technique, which is also flexible enough to properly describe states with double excitation character. The DFT/MRCI configuration state functions are built from KS rather than from HF orbitals. The usual HF-based MRCI formalism is formally retained, but modified by incorporating five universal empirical parameters in order to alleviate problems with the double counting of dynamic electron correlation. The five DFT/MRCI parameters have been fitted to experimental data for ten reference molecules.^{18,19} Optimized values are available for singlet and triplet multiplicities¹⁸ in combination with the BHLYP hybrid exchange–correlation functional.^{20,21} The DFT/MRCI method has been tested for a number of organic chromophores^{18,22} and applied to the simulation of gas phase UV/vis spectra (see, for example, Refs. 23–32) and CD spectra.³³ Overall, however, it has been validated and used less widely than TD-DFT, in spite of its promising performance in the cited papers.

In this article, we present a systematic assessment of TD-DFT (BP86, B3LYP, and BHLYP functionals) and DFT/MRCI. We use the same geometries and basis sets as in our recent *ab initio* benchmark study¹ to ensure that the results are directly comparable. This paper is structured as follows. In Sec. II we briefly describe the computational methods used. Thereafter we discuss their performance for vertical excitation energies (Sec. III A) and one-electron properties (Sec. III B). A statistical evaluation allows us to assess the merits and shortcomings of each method in more quantitative detail (Sec. III C). We conclude with a brief summary.

II. COMPUTATIONAL METHODS

All calculations were carried out at the optimized ground-state equilibrium geometries reported previously.^{1,34} The TZVP basis was used throughout, which is of valence triple- ζ quality and augmented by polarization functions at all atoms.³⁵ As discussed before,¹ the lack of diffuse functions can compromise a balanced description of higher-lying spatially extended states. This is less relevant here, however, since the present paper focuses on the direct comparison to *ab initio* benchmark data obtained with the same basis. Further remarks on basis set dependence are found below and in literature (see, for example, Refs. 24, 27, 28, 30, and 36).

A. TD-DFT calculations

Self-consistent field (SCF) and TD-DFT calculations were performed with the TURBOMOLE program (version 5.7.1).³⁷ Three functionals were investigated: the gradient-corrected BP86 functional,^{38,39} the hybrid Becke3–Lee–Yang–Parr (B3LYP) functional^{20,38,40} with 20% of HF exchange, and the Becke-half-and-half–Lee–Yang–Parr (BH-

LYP) functional^{20,21} with 50% of HF exchange. In the BP86 case, the resolution of identity (RI) method was employed to evaluate the two-electron integrals, making use of auxiliary basis sets from the TURBOMOLE library.^{41,42} Calculations of vertical excitation energies^{5,43–46} were done in the adiabatic approximation.^{5,47} For every state symmetry, the energies, dipole moments, and oscillator strengths were computed for at least the five lowest states.^{6,7,46,48}

It is generally accepted that TD-DFT significantly underestimates excitation energies (by up to several eV) in the case of Rydberg states^{49,50} and charge transfer (CT) states,⁵¹ because of the wrong asymptotic behavior of the standard exchange functionals. Asymptotic corrections have been suggested as a remedy for Rydberg excitation energies,^{49,50} but the simultaneous description of both types of excitations remains a challenge for TD-DFT.^{5,8} It should be emphasized that the current benchmark set does not include any CT states nor any “pure” Rydberg states, and is thus not designed to document the corresponding known failures of TD-DFT.

In our previous benchmark study,¹ we checked the basis set sensitivity of the computed excitation energies for ethene and formaldehyde. We found that the results converged well for the low-lying valence states, and much more slowly for the higher-lying states with partial Rydberg character where the TZVP results were several tenths of an eV above the basis set limit. It is common wisdom that DFT calculations are less sensitive to basis set extension than *ab initio* calculations, and we thus expect qualitatively similar but quantitatively less pronounced basis set effects. This has been studied for the B3LYP and BHLYP functionals through TD-DFT calculations on formamide using the correlation-consistent basis sets cc-pVXZ as well as the augmented variants aug-cc-pVXZ and d-aug-cc-pVXZ ($X=D, T, Q, 5$).^{52,53} The results are given as Supporting Information (Table VIII).⁵⁴ They confirm our qualitative expectations. The low-lying $1\ ^1A''$ valence state is dominated by a single $n \rightarrow \pi^*$ excitation, and the computed excitation energies and one-electron properties converge quickly upon basis set extension: The TZVP excitation energy is within 0.1 eV of the basis set limit. On the other hand, the high-lying $2\ ^1A'$ state with $\pi \rightarrow \pi^*$ character suffers from considerable valence-Rydberg mixing, and consequently its energy decreases strongly upon augmentation of the basis (by 0.7–0.9 eV when going from TZVP toward the basis set limit). We emphasize again that such variations are not of primary concern in the present context since we directly compare *ab initio* and TD-DFT results obtained with the same TZVP basis set.

B. DFT/MRCI calculations

The initial KS-DFT calculations were carried out with the TURBOMOLE program (version 5.7.1).³⁷ The subsequent MRCI calculations were done with the spin-free MRCI code and the associated property program,¹⁸ which is linked to TURBOMOLE. They make use of an iterative procedure for the selection of the most important configurations. Since higher excitations (that account for dynamic correlation) are conceptually incorporated through the DFT treatment, it is justified to use an energy-based selection criterion in DFT/

MRCI and to disregard all configurations with energies above a certain configuration selection threshold. A value of 1.0 hartree yields converged results for the excitation energies and was thus adopted for all DFT/MRCI calculations. The initial reference configurations were generated from up to two (active) electrons out of ten electrons in ten active orbitals. The corresponding number of reference configurations varied between 14 for cyclopentadiene and 244 for *s*-tetrizine. The oscillator strengths were calculated in the dipole length representation. Two-electron integrals were evaluated in DFT/MRCI using the RI approximation^{41,55} with the optimized RI-MP2 basis sets from the TURBOMOLE library. This standard DFT/MRCI procedure was applied to all benchmark molecules.

III. RESULTS AND DISCUSSION

Detailed results for all excited states considered are given in Tables XI–XXXIX of the Supporting Information.⁵⁴ There is one table for each benchmark molecule that contains, for each particular state, the computed vertical excitation energy, oscillator strength, and dipole moment. The present TD-DFT (BP86, B3LYP, and BHLYP) and DFT/MRCI results are supplemented with CASPT2 results from literature as well as MS-CASPT2 results, CC3 results, and the best estimates from our previous benchmark study¹ since these enter the current statistical evaluations. In addition, selected TD-DFT results from literature are given with the corresponding references.^{5,8–13,56–65}

Our previous MS-CASPT2 calculations¹ were carried out with the inclusion of scalar relativistic effects in the one-electron Hamiltonian according to the Barysz–Sadlej–Snijders transformation⁶⁶ (MOLCAS option BSSM). Since such relativistic effects are not included in any of the other calculations, we have repeated all MS-CASPT2 calculations at the nonrelativistic level. In this paper, we present these nonrelativistic MS-CASPT2 results and use them throughout. As may have been expected, the differences between the nonrelativistic and relativistic MS-CASPT2 results for the current organic benchmark molecules (first-row only) are very small: The mean deviation (MD) for the vertical excitation energies of all 217 states is 0.00 eV, the mean absolute deviation (MAD) is 0.01 eV, and there are only few individual deviations of several hundredths of an eV. Some of the MS-CASPT2 excitation energies have been selected as best estimates in the case of singlet states,¹ and hence there are also some corresponding minor changes in these estimates (20 cases), which are included and used throughout this paper. In view of the tiny differences between the relativistic and nonrelativistic MS-CASPT2 results, all of our previous conclusions¹ remain valid.

A. Vertical excitation energies of the benchmark molecules

A total of 146 singlet and 71 triplet states have been evaluated; 147 of these are of $\pi \rightarrow \pi^*$ type, 67 are of $n \rightarrow \pi^*$ type, and three are of $\sigma \rightarrow \pi^*$ type. The results are listed in Tables I and II. Some notable trends are obvious at first sight: For the singlet states, BP86 gives the lowest TD-

DFT excitation energies, followed by B3LYP and finally BHLYP. Due to its parametrization, DFT/MRCI gives excitation energies that generally lie between those from BP86 and B3LYP, in spite of the fact that it employs KS-BHLYP orbitals.

In the following we briefly discuss the results ordered by the class of molecules studied: polyenes; unsaturated cyclic and aromatic hydrocarbons; heterocycles; aldehydes, ketones, and amides; and nucleobases. We shall focus on comparisons with the theoretical best estimates.¹ A prerequisite for such comparisons is the correct assignment of states, which is sometimes nontrivial. Pure gradient-corrected functionals (such as BP86) give usually rather low orbital energy gaps, and hence relatively low transition energies,⁴⁴ whereas an increased admixture of HF exchange in hybrid functionals leads to blueshifted excitation energies and, occasionally, to an inversion of the states.⁶⁷ It is thus often not sufficient to make assignments by analogy, but one generally needs to check the composition of every excited-state wave function as well as one-electron properties (such as oscillator strengths) to arrive at a reliable assignment.

Ethene, butadiene, hexatriene, and octatetraene (Tables XI–XIV). The simplest chromophore studied is ethene. All DFT-based results for the singlet B_{1u} state are close to the theoretical best estimate of 7.80 eV (TD-DFT/BP86 7.73 eV, TD-DFT/B3LYP 7.70 eV, TD-DFT/BHLYP 7.69 eV, and DFT/MRCI 7.96 eV). As in the case of the *ab initio* methods (MS-CASPT2 and CC with the same TZVP basis) the DFT/MRCI result is slightly blueshifted with respect to the best estimate. The triplet state energy is generally underestimated by at least 0.2 eV, with the largest deviation of about 1 eV for TD-DFT/BHLYP.

In the series of the polyenes butadiene, hexatriene, and octatetraene, the main focus lies on the right state ordering. While the *ab initio* methods usually predict close-lying A_g and B_u states, suggesting a state switch when going from hexatriene to octatetraene, the TD-DFT calculations give a sizable separation of up to 1 eV, with the B_u state distinctly lower (3.82, 4.02, and 4.29 eV) than the A_g state (4.19, 4.84, and 5.83 eV) for all functionals. The overall performance of TD-DFT appears to be poor for these A_g and B_u states (deviations of 0.28–1.57 and 0.17–0.84 eV, respectively).

DFT/MRCI gives results for the polyenes that are much closer to the trend of the theoretical best estimates. The 2^1A_g state (4.01 eV) is found below the 1^1B_u state (4.25 eV) in octatetraene. The 1^1A_g states show considerable double excitation character and are found relatively close to the best estimate value (maximum deviation of 0.37 eV for butadiene). To be more specific, the HOMO $\rightarrow$ LUMO double excitation contributes 26%, 32%, and 33% to the 2^1A_g state of butadiene, hexatriene, and octatetraene, respectively, comparable with the calculated MS-CASPT2 data¹ and other published results.⁶⁸ The deviations for the triplet state energies range from –0.23 to 0.05 eV. These results are consistent with those from an extensive recent DFT/MRCI study on polyenes.²²

Cyclopropene, cyclopentadiene, norbornadiene, benzene, and naphthalene (Tables XV–XIX). In these hydrocarbons, the largest deviations with TD-DFT (BP86) are found

TABLE I. Vertical singlet excitation energies ΔE (eV) of all evaluated molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC3 ^c	Best est. ^d	BP86	B3LYP	BHLYP	DFT/MRCI
Ethene	$1^1B_{1u}(\pi \rightarrow \pi^*)$	7.98	8.54	8.37	7.80	7.73	7.70	7.69	7.96
<i>E</i> -butadiene	$2^1A_g(\pi \rightarrow \pi^*)$	6.27	6.62	6.77	6.55	6.30	6.82	7.61	6.18
	$1^1B_u(\pi \rightarrow \pi^*)$	6.23	6.47	6.58	6.18	5.60	5.74	5.94	6.02
All- <i>E</i> -hexatriene	$2^1A_g(\pi \rightarrow \pi^*)$	5.20	5.42	5.72	5.09	5.07	5.69	6.66	4.92
	$1^1B_u(\pi \rightarrow \pi^*)$	5.01	5.31	5.58	5.10	4.50	4.69	4.93	4.95
All- <i>E</i> -octatetraene	$2^1A_g(\pi \rightarrow \pi^*)$	4.38	4.64	4.97	4.47	4.19	4.84	5.83	4.01
	$1^1B_u(\pi \rightarrow \pi^*)$	4.42	4.70	4.94	4.66	3.82	4.02	4.29	4.25
Cyclopropene	$1^1B_2(\pi \rightarrow \pi^*)$	7.45	7.06	7.10	7.06	6.13	6.31	6.50	6.74
	$1^1B_1(\sigma \rightarrow \pi^*)$	6.36	6.76	6.90	6.76	6.30	6.46	6.77	6.73
Cyclopentadiene	$2^1A_1(\pi \rightarrow \pi^*)$	6.31	6.31	6.61	6.31	6.09	6.52	7.23	6.15
	$3^1A_1(\pi \rightarrow \pi^*)$	7.89	8.52	8.69		8.04	8.15	8.29	8.16
	$1^1B_2(\pi \rightarrow \pi^*)$	5.27	5.51	5.73	5.55	4.93	5.02	5.15	5.42
Norbornadiene	$1^1A_2(\pi \rightarrow \pi^*)$	5.28	5.34	5.64	5.34	4.48	4.79	5.15	5.30
	$2^1A_2(\pi \rightarrow \pi^*)$	7.36	7.45	7.71		6.56	6.86	7.40	7.33
	$1^1B_2(\pi \rightarrow \pi^*)$	6.20	6.11	6.49	6.11	5.02	5.52	6.22	6.12
	$2^1B_2(\pi \rightarrow \pi^*)$	6.48	7.32	7.64		6.61	6.87	7.21	7.21
Benzene	$1^1B_{1u}(\pi \rightarrow \pi^*)$	6.30	6.42	6.68	6.54	6.00	6.10	6.15	6.31
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.84	5.04	5.07	5.08	5.24	5.40	5.64	5.04
	$1^1E_{1u}(\pi \rightarrow \pi^*)$	7.03	7.13	7.45	7.13	6.96	7.07	7.27	7.19
	$1^1E_{2g}(\pi \rightarrow \pi^*)$	7.90	8.18	8.43	8.41	8.28	8.91	9.70	7.51
Naphthalene	$2^1A_g(\pi \rightarrow \pi^*)$	5.39	5.87	5.98	5.87	5.85	6.18	6.63	5.65
	$3^1A_g(\pi \rightarrow \pi^*)$	6.04	6.67	6.90	6.67	6.20	6.85	7.70	6.05
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.56	4.77	5.03	4.77	4.08	4.35	4.65	4.60
	$2^1B_{2u}(\pi \rightarrow \pi^*)$	5.93	6.33	6.57	6.33	5.88	6.12	6.41	6.21
	$3^1B_{2u}(\pi \rightarrow \pi^*)$	7.16	8.17	8.44		7.53	7.87	8.45	7.84
	$1^1B_{3u}(\pi \rightarrow \pi^*)$	4.03	4.24	4.27	4.24	4.23	4.44	4.71	4.10
	$2^1B_{3u}(\pi \rightarrow \pi^*)$	5.54	6.06	6.33	6.06	5.73	5.93	6.21	5.89
	$3^1B_{3u}(\pi \rightarrow \pi^*)$	7.18	7.74	8.44		8.00	8.65	9.84	7.38
	$1^1B_{1g}(\pi \rightarrow \pi^*)$	5.53	5.99	6.07	5.99	5.04	5.58	6.28	5.53
	$2^1B_{1g}(\pi \rightarrow \pi^*)$	5.87	6.47	6.79	6.47	6.17	6.32	6.65	6.26
Furan	$2^1A_1(\pi \rightarrow \pi^*)$	6.16	6.50	6.62	6.57	6.38	6.70	7.22	6.32
	$3^1A_1(\pi \rightarrow \pi^*)$	7.66	8.17	8.53	8.13	8.16	8.25	8.43	8.21
	$1^1B_2(\pi \rightarrow \pi^*)$	6.04	6.39	6.60	6.32	6.11	6.16	6.23	6.33
Pyrrole	$2^1A_1(\pi \rightarrow \pi^*)$	5.92	6.31	6.40	6.37	6.26	6.53	6.94	6.13
	$3^1A_1(\pi \rightarrow \pi^*)$	7.46	8.17	8.17	7.91	7.85	7.96	8.15	7.88
	$1^1B_2(\pi \rightarrow \pi^*)$	6.00	6.33	6.71	6.57	6.34	6.40	6.48	6.46
Imidazole	$2^1A'(\pi \rightarrow \pi^*)$	6.72	6.19	6.58	6.19	6.29	6.45	6.65	6.29
	$3^1A'(\pi \rightarrow \pi^*)$	7.15	6.93	7.10	6.93	6.86	7.04	7.35	6.82
	$4^1A'(\pi \rightarrow \pi^*)$	8.51	8.16	8.45		8.12	8.27	8.45	8.22
	$1^1A''(n \rightarrow \pi^*)$	6.52	6.81	6.82	6.81	5.91	6.46	7.09	6.35
	$2^1A''(n \rightarrow \pi^*)$	7.56	7.90	7.93		7.18	7.45	8.16	7.63
Pyridine	$2^1A_1(\pi \rightarrow \pi^*)$	6.42	6.39	6.85	6.26	6.21	6.31	6.37	6.47
	$3^1A_1(\pi \rightarrow \pi^*)$	7.23	7.46	7.70	7.18	7.27	7.32	7.55	7.43
	$1^1B_2(\pi \rightarrow \pi^*)$	4.84	5.02	5.15	4.85	5.35	5.49	5.71	5.09
	$2^1B_2(\pi \rightarrow \pi^*)$	7.48	7.27	7.59	7.27	7.13	7.30	7.56	7.27
	$1^1B_1(n \rightarrow \pi^*)$	4.91	5.17	5.05	4.59	4.38	4.80	5.30	4.75
	$1^1A_2(n \rightarrow \pi^*)$	5.17	5.51	5.50	5.11	4.48	5.11	6.03	5.41
Pyrazine	$1^1B_{1u}(\pi \rightarrow \pi^*)$	6.70	6.89	7.07	6.58	6.41	6.50	6.55	6.71
	$2^1B_{1u}(\pi \rightarrow \pi^*)$	7.57	7.79	8.06	7.72	7.53	7.68	7.89	7.82
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.75	4.85	5.02	4.64	5.25	5.37	5.52	4.94
	$2^1B_{2u}(\pi \rightarrow \pi^*)$	7.70	7.66	8.05	7.60	7.75	7.78	8.13	7.75
	$1^1A_u(n \rightarrow \pi^*)$	4.52	4.70	5.05	4.81	4.06	4.69	5.59	5.02
	$1^1B_{1g}(n \rightarrow \pi^*)$	6.13	6.41	6.75	6.60	5.57	6.38	7.66	6.46
	$1^1B_{2g}(n \rightarrow \pi^*)$	5.17	5.68	5.74	5.56	5.11	5.55	6.02	5.26
	$1^1B_{3u}(n \rightarrow \pi^*)$	3.63	4.12	4.24	3.95	3.59	3.96	4.40	4.00
Pyrimidine	$2^1A_1(\pi \rightarrow \pi^*)$	6.72	6.63	7.06	6.95	6.46	6.58	6.67	6.69
	$3^1A_1(\pi \rightarrow \pi^*)$	7.57	7.21	7.74		7.32	7.48	7.73	7.46
	$1^1B_2(\pi \rightarrow \pi^*)$	4.93	5.24	5.36	5.44	5.59	5.74	5.98	5.35
	$2^1B_2(\pi \rightarrow \pi^*)$	7.32	7.64	8.01		7.57	7.76	7.96	7.74
	$1^1B_1(n \rightarrow \pi^*)$	3.81	4.44	4.50	4.55	3.80	4.27	4.87	4.36

TABLE I. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC3 ^c	Best est. ^d	BP86	B3LYP	BHLYP	DFT/MRCI
Pyridazine	$1^1A_2(n \rightarrow \pi^*)$	4.12	4.80	4.93	4.91	4.02	4.60	5.39	4.82
	$2^1A_1(\pi \rightarrow \pi^*)$	4.86	5.18	5.22	5.18	5.46	5.61	5.83	5.16
	$3^1A_1(\pi \rightarrow \pi^*)$	7.50	7.62	7.82		7.39	7.50	7.76	7.53
	$1^1B_2(\pi \rightarrow \pi^*)$	6.61	6.31	6.93		6.32	6.43	6.48	6.51
	$2^1B_2(\pi \rightarrow \pi^*)$	7.39	7.29	7.55		7.10	7.24	7.45	7.25
	$1^1A_2(n \rightarrow \pi^*)$	3.66	4.31	4.49	4.31	3.54	4.18	5.03	4.25
	$2^1A_2(n \rightarrow \pi^*)$	5.09	5.77	5.74	5.77	5.01	5.44	6.05	5.29
	$1^1B_1(n \rightarrow \pi^*)$	3.48	3.78	3.92	3.78	3.15	3.58	4.10	3.63
<i>s</i> -triazine	$2^1B_1(n \rightarrow \pi^*)$	5.80	6.52	6.41		5.45	6.09	6.99	6.15
	$2^1A'_1(\pi \rightarrow \pi^*)$	6.77	7.25	7.41		6.87	7.01	7.12	7.02
	$1^1A'_2(\pi \rightarrow \pi^*)$	5.53	5.79	5.71	5.79	5.95	6.14	6.45	5.70
	$1^1E'(\pi \rightarrow \pi^*)$	8.16	7.50	8.04		7.63	7.79	8.06	7.81
	$1^1A''_1(n \rightarrow \pi^*)$	3.90	4.60	4.78	4.60	3.84	4.45	5.31	4.69
	$1^1A''_2(n \rightarrow \pi^*)$	4.08	4.66	4.76	4.66	4.08	4.54	5.16	4.56
	$1^1E''(n \rightarrow \pi^*)$	4.36	4.70	4.81	4.70	3.99	4.54	5.27	4.77
	$2^1E''(n \rightarrow \pi^*)$	7.15	7.71	7.80		6.71	7.49	8.42	7.26
<i>s</i> -tetrazine	$1^1A_u(n \rightarrow \pi^*)$	3.06	3.51	3.79	3.51	2.86	3.51	4.40	3.70
	$2^1A_u(n \rightarrow \pi^*)$	5.28	5.50	5.46	5.50	4.60	5.04	5.60	5.05
	$1^1B_{1g}(n \rightarrow \pi^*)$	4.51	4.73	4.97	4.73	4.13	4.73	5.33	4.45
	$2^1B_{1g}(n \rightarrow \pi^*)$	5.99	6.45	6.87		5.87	6.64	7.73	6.00
	$3^1B_{1g}(n \rightarrow \pi^*)$	6.20	6.73	7.08		6.53	7.40	9.20	6.49
	$1^1B_{2g}(n \rightarrow \pi^*)$	5.05	5.20	5.34	5.20	4.79	5.29	5.80	4.75
	$2^1B_{2g}(n \rightarrow \pi^*)$	5.48	6.06	6.23		5.24	5.99	7.27	5.68
	$2^1B_{3g}(\pi \rightarrow \pi^*)$	8.12	8.34	8.47		8.72	9.30	9.96	7.44
	$1^1B_{1u}(\pi \rightarrow \pi^*)$	7.13	6.94	7.45		6.82	6.90	6.88	7.08
	$2^1B_{1u}(\pi \rightarrow \pi^*)$	7.54	7.42	7.79		7.36	7.48	7.70	7.53
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.89	4.93	5.12	4.93	5.46	5.58	5.74	5.07
	$2^1B_{2u}(\pi \rightarrow \pi^*)$	7.94	8.14	8.51		8.09	8.26	8.57	8.26
	$1^1B_{3u}(n \rightarrow \pi^*)$	1.96	2.29	2.53	2.29	1.85	2.24	2.72	2.35
	$2^1B_{3u}(n \rightarrow \pi^*)$	6.37	6.77	6.67		5.64	6.29	7.22	6.41
	$1^1A_2(n \rightarrow \pi^*)$	3.91	3.99	3.95	3.88	3.80	3.89	4.00	3.71
	$1^1B_1(\sigma \rightarrow \pi^*)$	9.09	9.14	9.18	9.10	8.80	8.89	9.09	8.76
Formaldehyde	$2^1A_1(\pi \rightarrow \pi^*)$	9.77	9.32	10.45	9.30	9.95	9.17	9.32	9.19
Acetone	$1^1A_2(n \rightarrow \pi^*)$	4.18	4.44	4.40	4.40	4.21	4.34	4.55	4.23
	$2^1A_1(\pi \rightarrow \pi^*)$	9.16	9.31	9.65	9.40	8.76	9.04	8.97	8.53
<i>p</i> -benzoquinone	$1^1B_1(\sigma \rightarrow \pi^*)$	9.10	9.27	9.17	9.10	8.15	8.60	9.06	8.56
	$1^1A_u(n \rightarrow \pi^*)$	2.50	2.77	2.85	2.77	2.02	2.58	2.55	2.29
	$1^1B_{1g}(n \rightarrow \pi^*)$	2.50	2.76	2.75	2.76	1.89	2.43	3.04	2.22
	$1^1B_{1u}(\pi \rightarrow \pi^*)$	5.15	5.28	5.62	5.28	4.49	4.83	5.31	5.07
	$2^1B_{1u}(\pi \rightarrow \pi^*)$	7.08	7.92	7.82		6.82	7.25	7.73	7.60
	$1^1B_{3g}(\pi \rightarrow \pi^*)$	4.19	4.26	4.59	4.26	3.36	3.73	4.25	3.99
	$2^1B_{3g}(\pi \rightarrow \pi^*)$	6.34	6.96	7.27	6.96	6.12	6.59	7.32	6.71
	$1^1B_{3u}(n \rightarrow \pi^*)$	5.15	5.64	5.82	5.64	4.39	5.43	6.80	5.81
Formamide	$1^1A''(n \rightarrow \pi^*)$	5.61	5.63	5.65	5.63	5.46	5.55	5.77	5.47
	$2^1A'(\pi \rightarrow \pi^*)$	7.41	7.39	8.27	7.39	7.90	8.13	8.84	8.14
	$3^1A'(\pi \rightarrow \pi^*)$	10.50	10.54	10.93		10.98	10.92	11.38	10.57
Acetamide	$1^1A''(n \rightarrow \pi^*)$	5.54	5.69	5.69	5.69	5.41	5.56	5.86	5.48
	$2^1A'(\pi \rightarrow \pi^*)$	7.21	7.27	7.67	7.27	7.50	7.46	8.14	7.51
	$3^1A'(\pi \rightarrow \pi^*)$	10.08	10.09	10.50		9.42	10.01	10.59	9.98
Propanamide	$1^1A''(n \rightarrow \pi^*)$	5.48	5.72	5.72	5.72	5.43	5.59	5.89	5.47
	$2^1A'(\pi \rightarrow \pi^*)$	7.28	7.20	7.62	7.20	7.28	7.76	8.09	7.46
	$3^1A'(\pi \rightarrow \pi^*)$	9.95	9.94	10.06		8.17	9.00	10.07	9.51
Cytosine	$2^1A'(\pi \rightarrow \pi^*)$	4.39	4.67		4.66	4.20	4.64	5.19	4.62
	$3^1A'(\pi \rightarrow \pi^*)$	5.36	5.53		5.62	4.92	5.42	6.16	5.43
	$4^1A'(\pi \rightarrow \pi^*)$	6.16	6.40			6.49 ^c	6.72	6.99	6.38
	$5^1A'(\pi \rightarrow \pi^*)$	6.74	6.97			6.37 ^f	6.46	7.44	6.74
	$1^1A''(n \rightarrow \pi^*)$	5.00	5.12		4.87	3.79	4.76	6.21	4.86
Thymine	$2^1A''(n \rightarrow \pi^*)$	6.53	5.53		5.26	4.49	5.11	5.64	5.32
	$2^1A'(\pi \rightarrow \pi^*)$	4.88	5.06		5.20	4.60	5.00	5.48	5.18
	$3^1A'(\pi \rightarrow \pi^*)$	5.88	6.15		6.27	5.33	5.97	6.94	5.98

TABLE I. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC3 ^c	Best est. ^d	BP86	B3LYP	BHLYP	DFT/MRCI
Uracil	4 ¹ A'($\pi \rightarrow \pi^*$)	6.10	6.53		6.53	5.85	6.31	7.03	6.42
	5 ¹ A'($\pi \rightarrow \pi^*$)	7.13	7.43			6.93	7.47	8.17	7.36
	1 ¹ A''($n \rightarrow \pi^*$)	4.39	4.95		4.82	4.09	4.70	5.30	4.48
	2 ¹ A''($n \rightarrow \pi^*$)	5.91	6.38		6.16	4.79	5.80	6.77	5.93
	3 ¹ A''($n \rightarrow \pi^*$)	6.15	6.85			5.33	6.21	7.70	6.43
	4 ¹ A''($n \rightarrow \pi^*$)	6.70	7.43			6.13	6.69	8.03	6.86
	2 ¹ A'($\pi \rightarrow \pi^*$)	5.00	5.23		5.35	4.77	5.19	5.67	5.33
	3 ¹ A'($\pi \rightarrow \pi^*$)	5.82	6.15		6.26	5.21	5.87	6.90	5.92
	4 ¹ A'($\pi \rightarrow \pi^*$)	6.46	6.74		6.70	6.01	6.50	7.21	6.56
	5 ¹ A'($\pi \rightarrow \pi^*$)	7.00	7.42			7.06	7.45	8.09	7.31
	1 ¹ A''($n \rightarrow \pi^*$)	4.54	4.91		4.80	3.97	4.63	5.27	4.41
	2 ¹ A''($n \rightarrow \pi^*$)	6.00	6.28		6.10	4.76	5.74	6.61	5.84
	3 ¹ A''($n \rightarrow \pi^*$)	6.37	6.98		6.56	5.23	6.14	7.72	6.43
	4 ¹ A''($n \rightarrow \pi^*$)	6.95	7.28			6.11	6.64	7.91	6.79
Adenine	2 ¹ A'($\pi \rightarrow \pi^*$)	5.13	5.20		5.25	4.99	5.27	5.67	4.99
	3 ¹ A'($\pi \rightarrow \pi^*$)	5.20	5.29		5.25	4.57	5.00	5.48	5.15
	4 ¹ A'($\pi \rightarrow \pi^*$)	6.24	6.34			5.84	6.32	6.87	6.29
	5 ¹ A'($\pi \rightarrow \pi^*$)	6.72	6.64			6.27	6.69	7.30	6.19
	6 ¹ A'($\pi \rightarrow \pi^*$)	6.99	6.87			6.65	7.08	7.71	7.10
	7 ¹ A'($\pi \rightarrow \pi^*$)	7.57	7.56			6.91	7.52	8.22	6.62
	1 ¹ A''($n \rightarrow \pi^*$)	6.15	5.19		5.12	4.30	4.97	5.81	5.11
	2 ¹ A''($n \rightarrow \pi^*$)	6.86	5.96		5.75	5.05	5.61	6.34	5.72

^aData from publications by the Roos group in the 1990s. For references, see Ref. 1.^bSA-CASSCF/MS-CASPT2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set. See Ref. 1 for details.^cCC3 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set. See Ref. 1 for details.^dTheoretical best estimates for vertical excitation energies. See Ref. 1 for details.^eRydberg ($n \rightarrow \sigma^*$) contamination (about 49%).^fRydberg ($n \rightarrow \sigma^*$) contamination (about 59%).

for norbornadiene (-1.09 eV, 1¹B₂), naphthalene (-0.95 eV, 1¹B_{1g}), and cyclopropene (-0.93 eV, 1¹B₂). For the B3LYP functional, the TD-DFT errors are normally in the range between -0.50 and 0.50 eV; outliers are the 1¹B₂ state in cyclopropene (-0.75 eV) and the 1¹B₂ state in norbornadiene (-0.59 eV). The TD-DFT/BHLYP results are more spread (-0.56 to 1.29 eV). The DFT/MRCI deviations are mostly between -0.32 and 0.05 eV, exceptions being the 1¹E_{2g} state in benzene (-0.90 eV) and the 3¹A_g state in naphthalene (-0.62 eV). A trend for slight systematic underestimation of triplet excitation energies is known both for TD-DFT and DFT/MRCI.¹⁹

Furan, pyrrole, imidazole, pyridine, pyrazine, pyrimidine, pyridazine, triazine, and tetrazine (Tables XX–XXVIII). In these nine heterocyclic compounds, the singlet $\pi \rightarrow \pi^*$ states are rather close to the reference data (average deviations of -0.30 , 0.02 , 0.47 , and -0.04 eV for TD-DFT/BP86, TD-DFT/B3LYP, TD-DFT/BHLYP, and DFT/MRCI, respectively). Large deviations are encountered in TD-DFT/BHLYP for the 1¹B_{1g} state in pyrazine (1.06 eV), the 1¹A₂ state in pyridine (0.92 eV), and the 1¹A_u state in pyrazine (0.78 eV). TD-DFT/BP86 tends to underestimate the excitation energies, most strongly for the $n \rightarrow \pi^*$ states. The TD-DFT/B3LYP deviations are in the range from -0.43 to 0.43 eV, with few exceptions (0.73 , 0.65 , and 0.64 eV for the 1¹B_{2u} state of pyrazine and *s*-tetrazine and for the 1¹B₂ state of pyridine, respectively). DFT/MRCI yields singlet π

$\rightarrow \pi^*$ excitation energies within 0.3 eV of the theoretical best estimates, while some $n \rightarrow \pi^*$ states show larger deviations (too small by more than 0.3 eV). Triplet state energies are again almost always underestimated by all DFT-based methods.

Formaldehyde, acetone, p-benzoquinone, formamide, acetamide, and propanamide (Tables XXX–XXXV). Excitation energies for $n \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ states from TD-DFT/BP86 and TD-DFT/B3LYP are systematically too low, while those for $\pi \rightarrow \pi^*$ states scatter considerably, with deviations ranging from -0.89 to 0.65 eV (BP86) and from -0.52 to 0.69 eV (B3LYP). TD-DFT/BHLYP, on the other hand, overestimates most excitation energies, especially of $\pi \rightarrow \pi^*$ type. DFT/MRCI is usually within -0.5 to 0.25 eV of the theoretical best estimates for all kinds of excitations, except for some high-lying states such as the 2¹A₁ state of acetone (-0.87 eV) and the 2¹A' state of formamide (0.75 eV). The average deviations for $\pi \rightarrow \pi^*$ singlet states are -0.38 , -0.12 , 0.28 , and -0.18 eV for TD-DFT/BP86, TD-DFT/B3LYP, TD-DFT/BHLYP, and DFT/MRCI, respectively. Triplet state energies are on average underestimated by TD-DFT (by about 0.6 eV for all functionals) and DFT/MRCI (by about 0.3 eV).

Cytosine, thymine, uracil, and adenine (Tables XXXVI–XXXIX). The deviations for the nucleobases are quite systematic: TD-DFT/BP86 excitation energies are strongly underestimated (on average by 0.82 eV), while the TD-DFT/BHLYP

TABLE II. Vertical triplet excitation energies ΔE (eV).

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC3 ^c	Best est. ^d	BP86	B3LYP	BHLYP	DFT/MRCI
Ethene	$1^3B_{1u}(\pi \rightarrow \pi^*)$	4.39	4.48	4.48	4.50	4.15	4.03	3.47	4.31
<i>E</i> -butadiene	$1^3A_g(\pi \rightarrow \pi^*)$	4.89	5.16	5.17	5.08	4.95	4.86	4.44	4.85
	$1^3B_u(\pi \rightarrow \pi^*)$	3.20	3.34	3.32	3.20	2.87	2.76	2.15	3.09
All- <i>E</i> -hexatriene	$1^3A_g(\pi \rightarrow \pi^*)$	4.12	4.31	4.32	4.15	3.98	3.92	3.50	3.96
	$1^3B_u(\pi \rightarrow \pi^*)$	2.55	2.71	2.69	2.40	2.21	2.09	1.35	2.45
All- <i>E</i> -octatetraene	$1^3A_g(\pi \rightarrow \pi^*)$	3.39	3.70	3.67	3.55	3.30	3.24	2.80	3.32
	$1^3B_u(\pi \rightarrow \pi^*)$	2.17	2.33	2.30	2.20	1.81	1.68	0.72	2.04
Cyclopropene	$1^3B_2(\pi \rightarrow \pi^*)$	4.18	4.35	4.34	4.34	3.74	3.70	3.25	4.03
	$1^3B_1(\sigma \rightarrow \pi^*)$	6.05	6.51	6.62	6.62	5.81	6.01	6.28	6.31
Cyclopentadiene	$1^3A_1(\pi \rightarrow \pi^*)$	4.90	5.11	5.09	5.09	4.82	4.75	4.38	4.78
	$1^3B_2(\pi \rightarrow \pi^*)$	3.15	3.28	3.25	3.25	2.82	2.71	2.14	3.07
Norbornadiene	$1^3A_2(\pi \rightarrow \pi^*)$	3.42	3.75	3.72	3.72	3.11	3.08	2.63	3.42
	$1^3B_2(\pi \rightarrow \pi^*)$	3.80	4.22	4.16	4.16	3.71	3.62	3.07	3.85
Benzene	$1^3B_{1u}(\pi \rightarrow \pi^*)$	3.89	4.17	4.12	4.15	3.93	3.77	3.08	4.13
	$1^3B_{2u}(\pi \rightarrow \pi^*)$	5.49	5.76	6.04	5.88	4.94	5.09	5.26	5.57
	$1^3E_{1u}(\pi \rightarrow \pi^*)$	4.49	4.90	4.90	4.86	4.60	4.70	4.79	4.69
	$1^3E_{2g}(\pi \rightarrow \pi^*)$	7.12	7.38	7.49	7.51	7.13	7.33	7.47	7.40
Naphthalene	$1^3A_g(\pi \rightarrow \pi^*)$	5.27	5.53	5.52	5.52	5.25	5.33	5.31	5.18
	$2^3A_g(\pi \rightarrow \pi^*)$	5.83	6.38	6.47	6.47	5.67	5.95	6.33	6.00
	$3^3A_g(\pi \rightarrow \pi^*)$	5.91	6.59	6.79	6.79	5.59	6.07	6.58	6.31
	$1^3B_{2u}(\pi \rightarrow \pi^*)$	3.10	3.16	3.11	3.11	2.76	2.69	2.06	2.97
	$2^3B_{2u}(\pi \rightarrow \pi^*)$	4.30	4.68	4.64	4.64	4.31	4.40	4.45	4.49
	$1^3B_{3u}(\pi \rightarrow \pi^*)$	3.89	4.25	4.18	4.18	3.81	3.95	4.06	3.93
	$2^3B_{3u}(\pi \rightarrow \pi^*)$	4.45	4.97	5.11	5.11	4.03	4.22	4.42	4.65
	$1^3B_{1g}(\pi \rightarrow \pi^*)$	4.23	4.51	4.47	4.47	4.19	4.17	3.90	4.25
	$2^3B_{1g}(\pi \rightarrow \pi^*)$	5.71	6.21	6.48	6.48	5.00	5.55	6.39	6.02
	$3^3B_{1g}(\pi \rightarrow \pi^*)$	6.23	6.64	6.76	6.76	6.30	6.56	6.85	6.41
Furan	$1^3A_1(\pi \rightarrow \pi^*)$	5.15	5.49	5.48	5.48	5.24	5.21	4.67	5.15
	$1^3B_2(\pi \rightarrow \pi^*)$	3.99	4.18	4.17	4.17	3.85	3.71	2.70	3.91
Pyrrole	$1^3A_1(\pi \rightarrow \pi^*)$	5.16	5.52	5.51	5.51	5.24	5.25	5.19	5.19
	$1^3B_2(\pi \rightarrow \pi^*)$	4.27	4.51	4.48	4.48	4.18	4.07	3.63	4.23
Imidazole	$1^3A'(\pi \rightarrow \pi^*)$	4.49	4.65	4.69	4.69	4.33	4.24	3.82	4.41
	$2^3A'(\pi \rightarrow \pi^*)$	5.47	5.74	5.79	5.79	5.39	5.44	5.33	5.43
	$3^3A'(\pi \rightarrow \pi^*)$	6.53	6.44	6.55	6.55	5.92	5.95	5.99	6.22
	$4^3A'(\pi \rightarrow \pi^*)$	7.08	7.44	7.42		6.76	6.93	7.21	7.14
	$1^3A''(n \rightarrow \pi^*)$	6.07	6.36	6.37	6.37	5.53	5.83	6.12	5.92
	$2^3A''(n \rightarrow \pi^*)$	7.15	7.51	7.51		6.35	6.86	7.81	7.32
Pyridine	$1^3A_1(\pi \rightarrow \pi^*)$	4.05	4.27	4.25	4.06	4.05	3.89	3.14	4.25
	$2^3A_1(\pi \rightarrow \pi^*)$	4.73	5.03	5.05	4.91	4.78	4.84	4.89	4.84
	$3^3A_1(\pi \rightarrow \pi^*)$	7.34	7.56	7.66		7.29	7.44	7.51	7.21
	$1^3B_2(\pi \rightarrow \pi^*)$	4.56	4.71	4.86	4.64	4.42	4.51	4.57	4.60
	$2^3B_2(\pi \rightarrow \pi^*)$	6.02	6.03	6.40	6.08	5.46	5.64	5.84	5.97
	$3^3B_2(\pi \rightarrow \pi^*)$	7.28	7.87	7.83		7.54	7.75	7.93	7.52
	$1^3B_1(n \rightarrow \pi^*)$	4.41	4.57	4.50	4.25	3.71	4.04	4.39	4.31
	$1^3A_2(n \rightarrow \pi^*)$	5.10	5.52	5.46	5.28	4.34	4.98	5.85	5.33
<i>s</i> -tetrazine	$1^3A_u(n \rightarrow \pi^*)$	2.81	3.28	3.52	3.52	2.52	3.10	3.76	3.50
	$2^3A_u(n \rightarrow \pi^*)$	4.85	5.04	5.03	5.03	4.00	4.43	4.99	4.84
	$1^3B_{1g}(n \rightarrow \pi^*)$	3.76	4.14	4.21	4.21	3.32	3.63	3.90	3.92
	$2^3B_{1g}(n \rightarrow \pi^*)$	5.68	6.37	6.60		5.61	6.33	7.53	6.27
	$1^3B_{1u}(\pi \rightarrow \pi^*)$	4.25	4.37	4.33	4.33	4.24	3.83	2.51	4.27
	$2^3B_{1u}(\pi \rightarrow \pi^*)$	5.00	5.40	5.38	5.38	5.12	5.24	5.36	5.26
	$1^3B_{2g}(n \rightarrow \pi^*)$	4.67	4.94	4.93	4.93	4.17	4.48	4.76	4.64
	$2^3B_{2g}(n \rightarrow \pi^*)$	5.30	5.97	6.04		4.77	5.62	6.91	5.78
	$1^3B_{2u}(\pi \rightarrow \pi^*)$	4.29	4.39	4.54	4.54	4.11	4.06	3.91	4.21
	$2^3B_{2u}(\pi \rightarrow \pi^*)$	6.81	7.08	7.36		6.42	6.63	6.94	6.94
	$1^3B_{3u}(n \rightarrow \pi^*)$	1.45	1.61	1.89	1.89	1.11	1.42	1.69	1.88
	$2^3B_{3u}(n \rightarrow \pi^*)$	6.14	6.54	6.53		5.36	5.97	6.83	6.36
Formaldehyde	$1^3A_2(n \rightarrow \pi^*)$	3.48	3.58	3.55	3.50	3.05	3.13	3.21	3.32
	$1^3A_1(\pi \rightarrow \pi^*)$	5.99	5.84	5.83	5.87	5.48	5.18	4.38	5.46
Acetone	$1^3A_2(n \rightarrow \pi^*)$	3.90	4.10	4.05	4.05	3.56	3.69	3.84	3.85

TABLE II. (Continued.)

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC3 ^c	Best est. ^d	BP86	B3LYP	BHLYP	DFT/MRCI
<i>p</i> -benzoquinone	$1^3A_1(\pi \rightarrow \pi^*)$	5.98	6.04	6.03	6.03	5.57	5.39	4.81	5.64
	$1^3A_u(n \rightarrow \pi^*)$	2.27	2.66	2.62	2.62	1.56	2.05	3.20	2.31
	$1^3B_{1g}(n \rightarrow \pi^*)$	2.17	2.62	2.51	2.51	1.44	1.92	2.42	2.21
	$1^3B_{1u}(\pi \rightarrow \pi^*)$	2.91	2.99	2.96	2.96	2.42	2.19	1.21	2.62
	$1^3B_{3g}(\pi \rightarrow \pi^*)$	3.19	3.32	3.41	3.41	2.59	2.68	2.44	3.09
Formamide	$1^3A''(n \rightarrow \pi^*)$	5.34	5.40	5.36	5.36	4.87	4.97	5.14	5.12
	$1^3A'(\pi \rightarrow \pi^*)$	5.69	5.58	5.74	5.74	5.20	5.13	4.93	5.42
Acetamide	$1^3A''(n \rightarrow \pi^*)$	5.24	5.41	5.42	5.42	4.85	5.01	5.25	5.13
	$1^3A'(\pi \rightarrow \pi^*)$	5.57	5.63	5.88	5.88	5.26	5.26	5.14	5.52
Propanamide	$1^3A''(n \rightarrow \pi^*)$	5.28	5.45	5.45	5.45	4.89	5.04	5.29	5.13
	$1^3A'(\pi \rightarrow \pi^*)$	5.94	5.80	5.90	5.90	5.27	5.28	5.18	5.51

^aData from publications by the Roos group in the 1990s cited in Ref. 1.^bSA-CASSCF/MS-CASPT2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.^cCC3 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.^dTheoretical best estimates for vertical excitation energies. See Ref. 1 for details.

results are higher than the best estimates, especially in the case of the high-lying $1^1A''$ state of cytosine (1.34 eV) and the $3^1A''$ state of uracil (1.16 eV). TD-DFT/B3LYP and DFT/MRCI results are closer to the reference data, with deviations of less than 0.40 eV.

B. One-electron properties

Theoretical studies of electronically excited states have traditionally concentrated more on the energetics rather than on one-electron properties such as oscillator strengths and dipole moments. Only relatively few studies have addressed the convergence behavior of excited-state properties, e.g., with regard to basis set or level of theory.^{5,10,59,62,64,69,70} In TD-DFT the computed oscillator strengths and excited-state dipole moments are known to depend, often quite sensitively, on the chosen functional and the basis set.^{6,57,71–73} For example, the oscillator strengths of the lowest-energy $\pi \rightarrow \pi^*$ transition in benzene and substituted benzenes are well reproduced by TD-DFT only when using hybrid functionals with a significant amount of HF exchange (BHLYP) and basis sets with diffuse functions, whereas they are strongly underestimated by pure DFT functionals.⁷² As a second example, we quote early TD-DFT studies of the excited-state dipole moments of furan and pyrrole that show a large variation (up to several Debye) with the chosen functional and basis set,⁵⁷ as well as a strong sensitivity to approximations such as neglecting orbital relaxation in the one-particle density matrix.⁷³

In analogy to the excitation energies (see Sec. II A) we have checked the basis set convergence of the computed one-electron properties at the TD-DFT level for formamide. The corresponding B3LYP and BHLYP results are documented in Table VIII of the Supporting Information.⁵⁴ As expected, we find smooth convergence for the $1^1A''$ state, which is dominated by a single $n \rightarrow \pi^*$ excitation with a weight of typically more than 90%: The oscillator strength is always close to zero, and the excited-state dipole moment decreases monotonically along the series of (augmented) correlation-consistent basis sets over a range of about 0.2 D to arrive at

converged values of 2.4 D (TD-DFT/B3LYP) and 2.2 D (TD-DFT/BHLYP). By contrast, the $2^1A'$ state shows considerable valence-Rydberg mixing, and the relative weights of the $\pi \rightarrow \pi^*$ and the Rydberg excitation vary strongly with the basis set and the amount of HF exchange in the functional: The oscillator strengths are reduced by about a factor of 2 upon basis set extension and seem to converge toward a value around 0.17, while the computed excited-state dipole moments scatter irregularly (see Table VIII). These data on formamide serve as a reminder that the one-electron properties currently calculated with the TZVP basis cannot in general be considered as converged with regard to basis set extension (especially not for the higher-lying excited states). We note again, however, that this deficiency is less relevant at present since our primary objective is the direct comparison between *ab initio* and DFT results obtained with the same TZVP basis; best estimates of excited-state one-electron properties are not yet available for our benchmark set.¹

Table IX (see Supporting Information⁵⁴) collects published *ab initio* oscillator strengths (range of values and CASPT2 data), our own MS-CASPT2, CC2, and CCSD values, and the present TD-DFT and DFT/MRCI results for all dipole-allowed vertical transitions. The majority of computed TD-DFT and DFT/MRCI oscillator strengths are in the range of the published *ab initio* values. It is obvious that most of the TD-DFT oscillator strengths (more than 85%) increase in the sequence BP86 < B3LYP < BHLYP. This is due to the increased amount of HF exchange, which leads to larger f values.⁷² For weak transitions ($n \rightarrow \pi^*$ states) such trends are not visible, of course, since the oscillator strengths are close to zero in all methods. Order-of-magnitude discrepancies between individual results from different methods are found only rarely (1^1B_2 state of pyridazine, 1^1B_{1u} state of *s*-tetrazine, and $2^1A'$ and two higher-lying $\pi \rightarrow \pi^*$ states of adenine); in these cases the MS-CASPT2 oscillator strengths deviate from the other CC- and DFT-based results because of state contamination.

Table X (see Supporting Information⁵⁴) summarizes the calculated ground-state and excited-state dipole moments

(TD-DFT and DFT/MRCI), and also includes our MS-CASPT2/TZVP results as well as published CASSCF data (see Ref. 34 for details). Despite many differences in the setup (with regard to basis set, active space, and geometry), there are only relatively few strong deviations between our MS-CASPT2/TZVP and the earlier CASSCF results: Deviations of more than 1 D are mainly found for states with strong configurational mixing, for example, the 1^1A_2 state of norbornadiene (1.64 D), the $2^1A'$, $3^1A'$, $4^3A'$, and $2^3A''$ states of imidazole (1.26, 1.82, 1.83, and 3.04 D, respectively), as well as some high-lying $\pi \rightarrow \pi^*$ states and most of the $n \rightarrow \pi^*$ states of the nucleobases (up to 5 D).

The current DFT-based calculations employ the same basis sets and geometries as the MS-CASPT2/TZVP calculations, but still yield rather different excited-state dipole moments that show quite a large spread, with strong deviations appearing throughout the whole benchmark set. For example, compared to the MS-CASPT2 reference values, much too low dipole moments are computed for the 3^3A_1 state of pyridine (0.12 D, TD-DFT/B3LYP), the 2^1B_2 state of pyrimidine (0.35 D, TD-DFT/B3LYP), the $4^1A'$ and $5^1A'$ states of cytosine (3.60 and 2.19 D, TD-DFT/BP86 with strong Rydberg contamination), and the $1^1A''$ state of adenine (0.38 D, TD-DFT/B3LYP, an $n \rightarrow \pi^*$ state unlike the preceding cases). Generally speaking, the largest deviations from the MS-CASPT2 reference data are again found for the nucleobases (see Sec. III C 4 for more details). Of course, there are also many states (especially the low-lying ones) with much better agreement. An example is the 1^1A_2 state of formaldehyde, where all theoretical values [1.39, 1.46, 1.65, 1.63, 1.57, and 1.53 D for CASSCF,⁷⁴ MS-CASPT2/TZVP, TD-DFT (BP86, B3LYP, and BHLYP), and DFT/MRCI, respectively] deviate by less than 0.20 D from the experimental value of 1.57 D.⁷⁵

C. Statistical evaluation

In the statistical evaluation for our benchmark, the present DFT-based results are related to four sets of reference data that have been assembled in our previous study: the earlier CASPT2 results from the Roos group, our own MS-CASPT2/TZVP and CC3/TZVP data, and our proposed theoretical best estimates.

1. Singlet state energies

Table III summarizes the statistical evaluation for the singlet excited states in the benchmark. Given are the number of states considered, the mean deviation (MD), the mean absolute deviation (MAD), and the standard and maximum deviations among each set. The number of states differs somewhat between the different reference sets: Available are 146 singlet state energies from the published CASPT2 and our MS-CASPT2 calculations, but only 116 CC3 energies and 104 theoretical best estimates.¹

When using the published CASPT2 data as reference, DFT/MRCI gives the lowest MAD (0.29 eV), followed by TD-DFT/B3LYP (0.37 eV), TD-DFT/BP86 (0.44 eV), and TD-DFT/BHLYP (0.73 eV). Positive (negative) MDs indicate that the calculated energies tend to be blueshifted (redshifted) with respect to the reference values. The DFT/MRCI

TABLE III. TD-DFT and DFT/MRCI deviations of vertical excitation energies (in eV) for singlet excited states with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASPT2 results ^a				
Count ^b	146	146	146	146
Mean	-0.27	0.10	0.65	0.02
Abs. mean	0.44	0.37	0.73	0.29
Std. dev.	0.58	0.48	0.90	0.39
Max. (+) dev.	0.82	1.47	3.00	0.79
Max. (-) dev.	2.04	1.42	0.95	1.37
MS-CASPT2/TZVP results ^c				
Count ^b	146	146	146	146
Mean	-0.48	-0.11	0.44	-0.19
Abs. mean	0.56	0.30	0.52	0.26
Std. dev.	0.68	0.38	0.67	0.33
Max. (+) dev.	0.63	1.05	2.47	0.75
Max. (-) dev.	1.77	0.94	0.85	0.97
CC3/TZVP results ^c				
Count ^b	116	116	116	116
Mean	-0.61	-0.29	0.20	-0.39
Abs. mean	0.65	0.39	0.44	0.39
Std. dev.	0.73	0.46	0.57	0.46
Max. (+) dev.	0.34	0.82	2.12	—
Max. (-) dev.	1.89	1.28	1.13	1.26
Theoretical best estimates ^c				
Count ^b	104	104	104	104
Mean	-0.44	-0.07	0.43	-0.13
Abs. mean	0.52	0.27	0.50	0.22
Std. dev.	0.62	0.33	0.62	0.29
Max. (+) dev.	0.65	1.02	1.73	0.75
Max. (-) dev.	1.37	0.75	0.56	0.90

^aData from publications by the Roos group in the 1990s cited in Ref. 1.

^bTotal number of states considered.

^cSee Ref. 1.

results (MD of 0.02 eV) thus scatter around the literature CASPT2 data. The excitation energies from TD-DFT/BP86 are lower on average (MD of -0.27 eV), while those from TD-DFT/B3LYP and TD-DFT/BHLYP are slightly and considerably higher on average (MDs of 0.10 and 0.65 eV, respectively). The largest deviations for the four DFT-based methods are found for the $1^1A''$ state of *s*-triazine (0.79 eV, DFT/MRCI), the 3^1B_{3u} state of naphthalene (0.82 eV, TD-DFT/BP86; 1.47 eV, TD-DFT/B3LYP), and the 3^1B_{1g} state of *s*-tetrazine (3.00 eV, TD-DFT/BHLYP), the latter marking the biggest deviation overall.

The singlet excitation energies from the MS-CASPT2 and CC3/TZVP calculations are on average about 0.2 and 0.4 eV higher than the published CASPT2 values.¹ Changing the reference set to MS-CASPT2/TZVP and CC3/TZVP will thus cause corresponding shifts in the MDs of the TD-DFT and DFT/MRCI results (Table III). Now the DFT-based excitation energies appear generally redshifted with regard to the *ab initio* data, except for TD-DFT/BHLYP. The TD-DFT/BP86 results show the worst agreement with the reference data (MDs of -0.48 and -0.61 eV compared to MS-

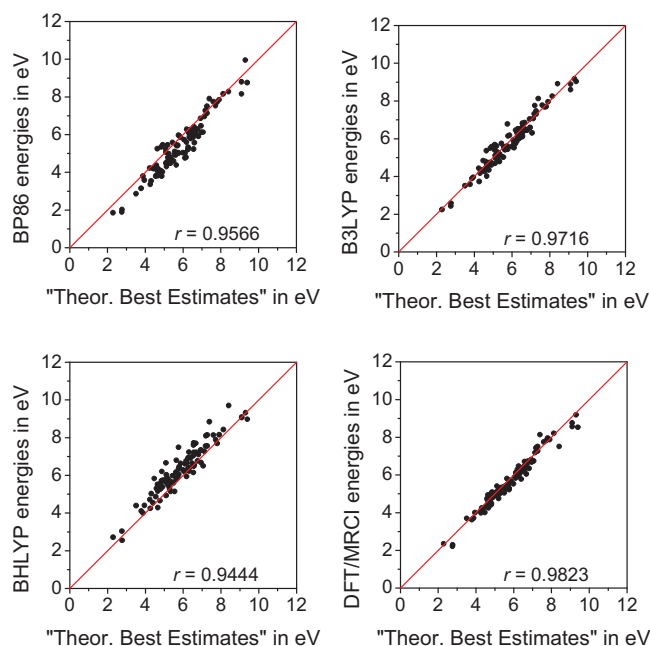


FIG. 1. (Color online) Correlation plots for all calculated singlet excited states: TD-DFT (BP86, B3LYP, and B3LYP) and DFT/MRCI vs theoretical best estimates for vertical excitation energies.

CASPT2 and CC3, respectively), whereas TD-DFT/B3LYP and DFT/MRCI perform similarly well.

The most relevant comparisons involve the theoretical best estimates as reference data. The correlation plots in Fig. 1 show immediately that TD-DFT/B3LYP and DFT/MRCI outperform TD-DFT/BP86 and TD-DFT/B3LYP. They indicate a slight edge for DFT/MRCI where the excitation energies have a smaller spread with respect to the best estimates. This is borne out by the statistical data: The MAD is smallest for DFT/MRCI (0.22 eV) followed rather closely by TD-DFT/B3LYP (0.27 eV) and much ahead of TD-DFT/BP86 (0.52 eV) and TD-DFT/B3LYP (0.50 eV). Both DFT/MRCI and TD-DFT/B3LYP tend to give singlet excitation energies that are slightly too low (MDs of -0.13 and -0.07 eV).

Figure 2 shows separate histograms for the deviations between TD-DFT/B3LYP/TZVP and theoretical best estimates of singlet $n \rightarrow \pi^*$ (left) and $\pi \rightarrow \pi^*$ (right) excited states. It is evident that there is closer agreement for the $n \rightarrow \pi^*$ states. Similar distributions are also found for the other functionals, though redshifted for TD-DFT/BP86 and blueshifted for TD-DFT/B3LYP.

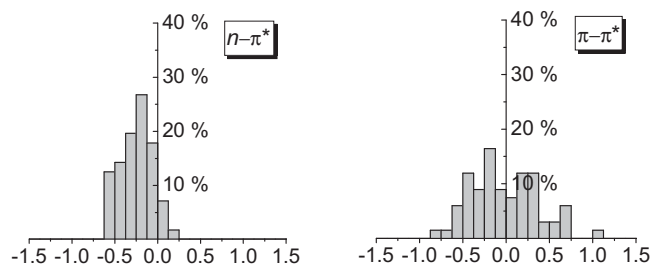


FIG. 2. Histogram of the frequency of deviation (TD-DFT/B3LYP/TZVP vs theoretical best estimates, in %) in the calculated vertical excitation energies (eV) for the singlet $n \rightarrow \pi^*$ (left) and $\pi \rightarrow \pi^*$ (right) excited states.

2. Triplet state energies

Statistical results for the triplet states are listed in Table IV and visualized in Fig. 3. The number of states considered varies for the different reference sets: 71 states are available from the earlier CASPT2 as well as from the recent MS-CASPT2 and CC3 calculations, and there are theoretical best estimates for 63 of these states.¹

It is evident at first sight that the DFT-based methods systematically underestimate the *ab initio* reference triplet excitation energies. With one minor exception (MD of 0.02 eV of DFT/MRCI with respect to the published CASPT2 results as reference), all MDs are negative. DFT/MRCI generally fares best, for example, with regard to the theoretical best estimates (MD of -0.24 eV compared with values between -0.45 and -0.54 eV for the three TD-DFT approaches); likewise, DFT/MRCI has by far the lowest MAD (0.25 versus 0.45–0.60 eV, see Table IV). Noteworthy is also the close correspondence between DFT/MRCI and the published CASPT2 results (MD of 0.02 eV and MAD of 0.17 eV).

TABLE IV. TD-DFT and DFT/MRCI deviations of vertical excitation energies (in eV) for triplet excited states with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASPT2 results ^a				
Count ^b	71	71	71	71
Mean	-0.30	-0.18	-0.19	0.02
Abs. mean	0.32	0.27	0.58	0.17
Std. dev.	0.40	0.33	0.75	0.22
Max. (+) dev.	0.26	0.65	1.85	0.69
Max. (–) dev.	0.85	0.81	1.74	0.53
MS-CASPT2/TZVP results ^c				
Count ^b	71	71	71	71
Mean	-0.56	-0.43	-0.45	-0.24
Abs. mean	0.56	0.43	0.58	0.25
Std. dev.	0.63	0.47	0.75	0.27
Max. (+) dev.	—	—	1.16	0.27
Max. (–) dev.	1.21	0.80	1.86	0.44
CC3/TZVP results ^c				
Count ^b	71	71	71	71
Mean	-0.60	-0.48	-0.49	-0.28
Abs. mean	0.60	0.48	0.60	0.28
Std. dev.	0.68	0.51	0.76	0.30
Max. (+) dev.	—	—	0.93	0.01
Max. (–) dev.	1.48	0.94	1.81	0.49
Theoretical best estimates ^c				
Count ^b	63	63	63	63
Mean	-0.53	-0.45	-0.55	-0.24
Abs. mean	0.53	0.45	0.60	0.25
Std. dev.	0.61	0.49	0.76	0.28
Max. (+) dev.	—	—	0.58	0.19
Max. (–) dev.	1.48	0.93	1.82	0.49

^aData from publications by the Roos group in the 1990s cited in Ref. 1.

^bTotal number of states considered.

^cSee Ref. 1.

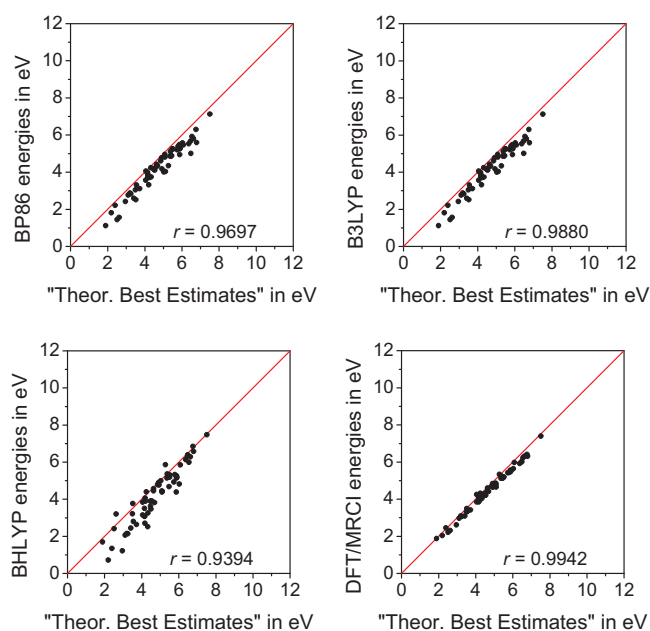


FIG. 3. (Color online) Correlation plots for all calculated triplet excited states: TD-DFT (BP86, B3LYP, and B3LYP) and DFT/MRCI vs theoretical best estimates for vertical excitation energies.

3. Excited-state energy differences

In photochemistry, the relative energies of excited states can be more important than their absolute energies. It is therefore of interest to assess the performance of the DFT-based methods also with regard to excited-state energy differences. Given their combinatorially large number, which complicates any systematic evaluation, we have decided to focus on energy differences between low-lying states that may be photochemically relevant, i.e., S_2-S_1 , T_2-T_1 , and S_1-T_1 .

Table V presents the corresponding statistical evaluation using the best estimate energy differences as reference. We find again that DFT/MRCI performs best and TD-DFT/B3LYP performs worst. The MADs of the DFT/MRCI data for the S_2-S_1 , T_2-T_1 , and S_1-T_1 gaps are between 0.1 and 0.2 eV, confirming that DFT/MRCI also provides realistic energy differences. TD-DFT/BP86 and TD-DFT/B3LYP perform comparably well for the T_2-T_1 gaps, with MADs of 0.11 and 0.16 eV, in spite of the systematic underestimation of triplet excitation energies with TD-DFT (see Table IV). The S_2-S_1 energy differences are reproduced less reliably by TD-DFT/BP86 and TD-DFT/B3LYP, with MADs of about 0.4 eV and occasional reversals in the ordering of the states (six cases with TD-DFT/BP86 and five cases with TD-DFT/B3LYP). Considering the S_1-T_1 gaps, the deviations increase in the sequence $\text{DFT/MRCI} < \text{TD-DFT/BP86} < \text{TD-DFT/B3LYP} < \text{TD-DFT/BHLYP}$.

4. One-electron properties

Figure 4 shows the correlation between the oscillator strengths from the current calculations and those from our previous *ab initio* study.¹ The statistical evaluation is summarized in Table VI for reference data taken from published CASPT2, MS-CASPT2/TZVP, and CC2/TZVP calculations.

Consistent with previous results,⁷² the TD-DFT methods

TABLE V. TD-DFT and DFT/MRCI deviations of S_2-S_1 , T_2-T_1 and S_1-T_1 energy differences (in eV) with respect to theoretical best estimates.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
S_2-S_1 ^a				
Count ^b	27	27	27	27
Mean	-0.06	-0.03	0.02	0.04
Abs. mean	0.42	0.40	0.63	0.22
Std. dev.	0.50	0.51	0.79	0.30
Max. (+) dev.	0.98	0.82	1.32	0.91
Max. (-) dev.	1.00	1.01	1.74	0.56
T_2-T_1 ^c				
Count ^b	19	19	19	19
Mean	-0.02	0.02	0.24	-0.10
Abs. mean	0.11	0.16	0.65	0.10
Std. dev.	0.17	0.18	0.71	0.12
Max. (+) dev.	0.20	0.22	1.06	—
Max. (-) dev.	0.54	0.32	1.20	0.24
S_1-T_1 ^d				
Count ^b	20	20	20	20
Mean	0.17	0.41	1.08	0.05
Abs. mean	0.26	0.41	1.08	0.14
Std. dev.	0.27	0.48	1.29	0.19
Max. (+) dev.	0.46	0.91	2.84	0.38
Max. (-) dev.	0.25	—	0.34	0.30

^aEnergy difference between the two lowest singlet excited states.

^bTotal number of molecules considered.

^cEnergy difference between the two lowest triplet excited states.

^dEnergy difference between the lowest singlet and triplet excited states.

tend to underestimate the *ab initio* oscillator strengths to some extent (more so for CASPT2 or MS-CASPT2 than for CC2): The MDs are all negative and of similar magnitude as the corresponding MAD values (Table VI). The DFT/MRCI oscillator strengths are spread around the early CASPT2 reference data (MD of -0.003); they tend to be somewhat lower than the MS-CASPT2/TZVP results (MD of -0.019) and somewhat higher than the CC2/TZVP results (MD of 0.039). Considering the overall deviations in Table VI, DFT/MRCI fares best in the comparisons with the CASPT2 and MS-CASPT2/TZVP reference data, and performs similar to TD-DFT/B3LYP with respect to the CC2/TZVP data. This is also reflected in the correlation plots (Fig. 4) where DFT/MRCI shows the best correlation among the four DFT-based methods in each case, with correlation coefficients of 0.9176, 0.9493, and 0.9755 relative to CASPT2, MS-CASPT2/TZVP, and CC2/TZVP. For the sake of completeness, we note that we tested the effect of the RI approximation on the CC2/TZVP reference data and found it to be negligibly small (generally less than ± 0.005 for oscillator strengths and ± 0.005 eV for excitation energies).

Table VII presents the statistical evaluation for state dipole moments using early CASSCF results and the current MS-CASPT2/TZVP results as reference. The MADs of the DFT-based state dipole moments from the *ab initio* results are generally in the range between 0.6 and 0.8 D, while the corresponding MDs are considerably lower in magnitude (indicating significant scatter). Deviations of more than 1 D are

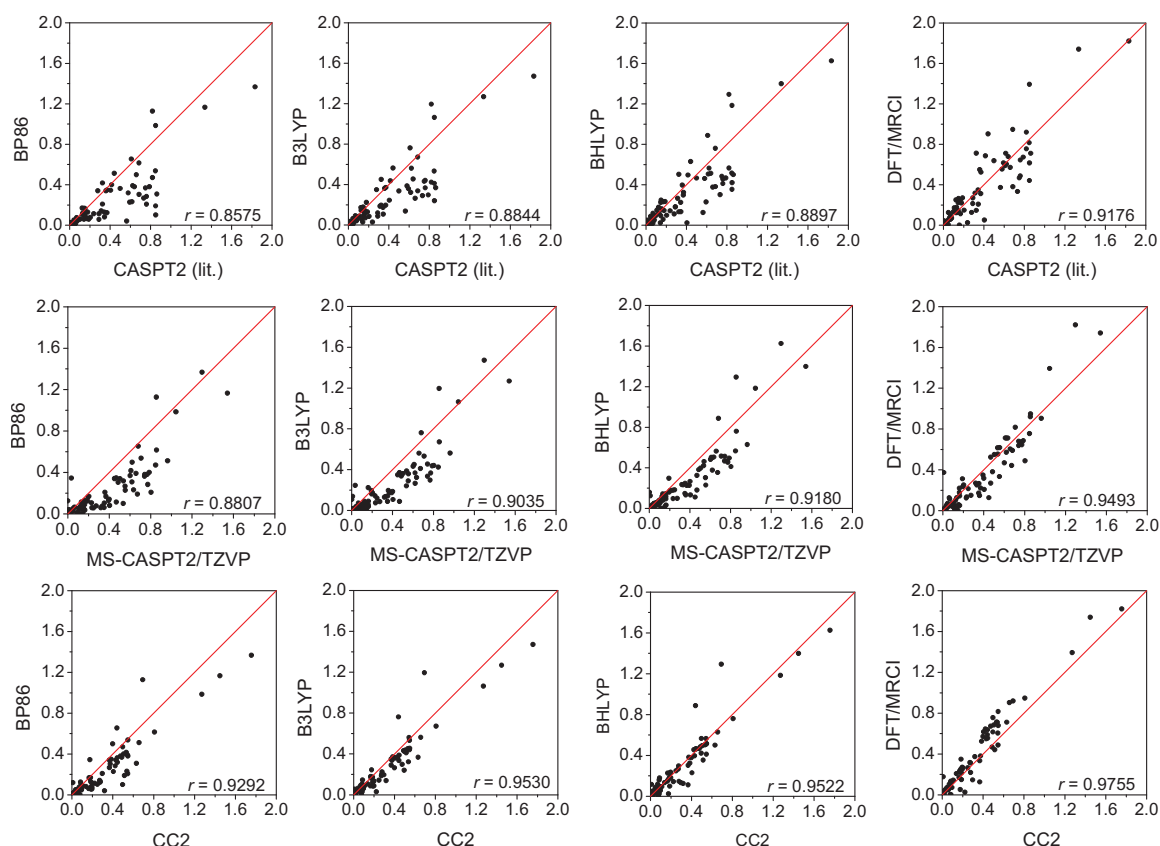


FIG. 4. (Color online) Correlation plots of oscillator strengths for all dipole-allowed excited states using earlier CASPT2, MS-CASPT2/TZVP, and CC2/TZVP results as reference data.

indeed found quite often, i.e., relative to CASSCF for 23%, 22%, 17%, and 12% of the states in TD-DFT/BP86, TD-DFT/B3LYP, TD-DFT/BHLYP, and DFT/MRCI, respectively, and relative to MS-CASPT2/TZVP for 23%, 12%, 13%, and 14% of the states (analogously).

The MDs in Table VII are all negative, which would seem to suggest that the DFT-based methods tend to give lower state dipole moments than the *ab initio* reference methods. This is deceptive insofar as the MD values are affected by a few pronounced negative outliers that occur in excited states of the nucleobases, as exemplified by the following deviations from the MS-CASPT2/TZVP dipole moments: 5 ¹A' state of cytosine, TD-DFT/BP86: -4.83 D; 3 ¹A'' state of thymine, TD-DFT/B3LYP: -4.25 D; 2 ¹A' state of formamide, TD-DFT/BHLYP: -4.23 D; and 4 ¹A'' state of uracil, DFT/MRCI: -4.66 D. Looking at histograms one finds that the majority of the DFT-based state dipole moments are actually larger than their *ab initio* counterparts. For example, 57%, 60%, 61%, and 57% of the state dipole moments from TD-DFT/BP86, TD-DFT/B3LYP, TD-DFT/BHLYP, and DFT/MRCI, respectively, are larger by 0–1 D than the MS-CASPT2/TZVP values.

The statistical evaluation for the dipole moments includes the ground states where the differences between DFT-based and *ab initio* results are generally smaller, with MADs ranging between 0.1 and 0.3 D, and a maximum overall deviation of 0.72 D (cytosine, TD-DFT/BHLYP versus MS-CASPT2/TZVP). Excluding the ground-state data from the statistics (18 out of 138 values) does not change the qualita-

TABLE VI. TD-DFT and DFT/MRCI deviations of oscillator strengths (in length representation) of optically allowed states with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASPT2 results ^a				
Count ^b	109	109	109	109
Mean	-0.096	-0.075	-0.050	-0.003
Abs. mean	0.112	0.101	0.095	0.078
Std. dev.	0.200	0.175	0.160	0.141
Max. (+) dev.	0.307	0.375	0.473	0.543
Max. (-) dev.	0.751	0.611	0.496	0.409
MS-CASPT2/TZVP results ^c				
Count ^b	109	109	109	109
Mean	-0.112	-0.092	-0.067	-0.019
Abs. mean	0.128	0.113	0.096	0.069
Std. dev.	0.195	0.169	0.146	0.113
Max. (+) dev.	0.309	0.339	0.437	0.522
Max. (-) dev.	0.597	0.471	0.392	0.325
CC2/TZVP results ^c				
Count ^b	109	109	109	109
Mean	-0.054	-0.034	-0.009	0.039
Abs. mean	0.075	0.055	0.044	0.062
Std. dev.	0.127	0.098	0.094	0.098
Max. (+) dev.	0.433	0.501	0.599	0.290
Max. (-) dev.	0.396	0.286	0.257	0.242

^aData from publications by the Roos group in the 1990s cited in Ref. 1.

^bTotal number of states considered.

^cSee Ref. 1.

TABLE VII. TD-DFT and DFT/MRCI deviations of state dipole moments (in D) with respect to *ab initio* reference data.

	Method			
	BP86	B3LYP	BHLYP	DFT/MRCI
Published CASSCF results ^a				
Count ^b	138	138	138	138
Mean	-0.45	-0.39	-0.28	-0.31
Abs. mean	0.86	0.77	0.66	0.60
Std. dev.	1.38	1.25	1.05	1.09
Max. (+) dev.	2.39	2.11	1.96	1.67
Max. (-) dev.	7.11	6.39	4.80	5.86
MS-CASPT2/TZVP results ^c				
Count ^b	138	138	138	138
Mean	-0.17	-0.12	-0.01	-0.04
Abs. mean	0.75	0.59	0.61	0.58
Std. dev.	1.12	0.92	0.96	0.92
Max. (+) dev.	3.42	2.80	4.13	3.37
Max. (-) dev.	4.83	4.25	4.23	4.66

^aData from publications by the Roos group in the 1990s cited in Ref. 1.^bTotal number of states considered.^cSee Ref. 1.

tive conclusions outlined above. We have also separately considered the statistics for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states and seen no particular trend: Most of the statistical data are similar, and the MADs remain between 0.6 and 0.8 D for both types of excited states.

IV. SUMMARY

The statistical evaluation of the present benchmark calculations shows that DFT/MRCI performs best for vertical excitation energies, giving the lowest MADs for any of the chosen *ab initio* reference data. Within TD-DFT, the B3LYP functional is clearly superior to BP86 and BHLYP. When using the proposed theoretical best estimates for 104 singlet (63 triplet) vertical excitation energies as reference data, the MADs are 0.22 (0.25) eV for DFT/MRCI, 0.27 (0.45) eV for TD-DFT/B3LYP, 0.52 (0.53) eV for TD-DFT/BP86, and 0.50 (0.60) eV for TD-DFT/BHLYP. For singlet states, the computed excitation energies are usually in the order TD-DFT/BP86 < DFT/MRCI $\approx$ TD-DFT/B3LYP < TD-DFT/BHLYP, with the systematic trend that TD-DFT/BP86 (TD-DFT/BHLYP) generally underestimates (overestimates) the best estimate values. For triplet states, all studied DFT-based methods tend to give vertical excitation energies that are lower than the theoretical best estimates, with the smallest deviations for DFT/MRCI.

Concerning one-electron properties, the current comparisons are less definitive because theoretical best estimates have not yet been established for our benchmark molecules. In an overall assessment, DFT/MRCI again seems to perform best for oscillator strengths, whereas all DFT-based methods show considerable scatter for excited-state dipole moments (compared to MS-CASPT2 values obtained with the same TZVP basis). Generally speaking, the correlations between DFT-based and *ab initio* results are better for vertical excita-

tion energies than for one-electron properties (as judged by the correlation coefficients).

The present benchmark has deliberately focused on valence excited states, such as its predecessor.¹ Low-lying valence states with double excitation character are known to be problematic for TD-DFT, and it is indeed found that the deviations for such states (e.g., in polyenes) are much larger in TD-DFT than in DFT/MRCI (which will influence but not distort the statistics). As emphasized before, the current benchmark does not include CT states and pure Rydberg states so that the statistical evaluations do not reflect the known qualitative failures of TD-DFT in these areas. It would be clearly interesting to document the performance of DFT/MRCI for these types of states, too, since the MRCI formalism should be flexible enough to treat them properly, but this is beyond the scope of the present article.

Finally, we note that a more thorough benchmarking of excited-state methods should go beyond vertical excitation spectra computed at the ground-state equilibrium geometry, by covering excited-state potential energy surfaces over a wide range of nuclear geometries (see, for example, Ref. 76). This includes proper validation of excited-state minima and conical intersections, which is essential for a reliable treatment of photochemistry. Work along these lines is in progress.

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Benchmarks for electronically excited states: TD-DFT and DFT/MRCI – Supporting Information –

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Appendix A: Numerical results discussed in the paper: Tables VIII to X

1. Basis set dependence for singlet excited states of formamide

TABLE VIII: Convergence of TD-DFT vertical excitation energies and one-electron properties of formamide for the B3LYP and BHLYP functionals^{a,b}

	$1^1A'$ μ	$2^1A'$ ΔE	f	μ	ω_π	ω_R	$1^1A''$ ΔE	f	μ	ω_n
B3LYP										
cc-pVDZ	3.82	8.45	0.342	2.52	70.0	21.9	5.59	0.001	2.54	99.8
cc-pVTZ	3.97	8.16	0.342	2.92	76.0	17.9	5.58	0.001	2.54	99.7
TZVP	4.10	8.13	0.371	2.83	72.9	18.9	5.55	0.001	2.66	99.7
cc-pVQZ	4.02	7.97	0.334	3.14	79.8	14.0	5.54	0.001	2.51	99.7
cc-pV5Z	4.03	7.78	0.320	3.44	82.9	10.0	5.49	0.001	2.48	99.5
cc-pV6Z	4.03	7.66	0.302	3.63	84.0	7.1	5.47	0.001	2.44	99.3
aug-cc-pVDZ	4.03	7.53	0.260	3.11	82.2	7.9	5.45	0.001	2.44	98.9
aug-cc-pVTZ	4.02	7.48	0.242	2.45	79.2	12.5	5.46	0.001	2.40	98.8
aug-cc-pVQZ	4.02	7.44	0.234	2.01	80.5	11.2	5.45	0.001	2.38	98.7
aug-cc-pV5Z	4.02	7.40	0.221	1.50	78.6	16.0	5.45	0.001	2.38	98.6
aug-cc-pV6Z	4.02	7.38	0.206	—	76.4	15.8	5.45	0.001	—	98.4
d-aug-cc-pVDZ	4.02	7.42	0.149	10.69	48.7	40.8	5.43	0.001	2.38	98.0
d-aug-cc-pVTZ	4.02	7.43	0.151	8.29	48.8	42.2	5.45	0.001	2.36	97.9
d-aug-cc-pVQZ	4.02	7.42	0.165	6.14	54.8	36.1	5.45	0.001	2.37	97.9
d-aug-cc-pV5Z	4.02	7.42	0.166	6.50	55.1	35.8	5.45	0.001	2.37	97.9
BHLYP										
cc-pVDZ	4.00	9.26	0.288	0.85	27.2	62.9	5.81	0.001	2.33	99.5
cc-pVTZ	4.13	8.84	0.290	1.56	32.1	63.7	5.81	0.001	2.32	99.0
TZVP	4.25	8.84	0.324	1.87	31.8	63.9	5.77	0.001	2.41	98.6
cc-pVQZ	4.16	8.55	0.279	2.74	35.6	58.8	5.79	0.001	2.30	98.5
cc-pV5Z	4.17	8.23	0.242	4.59	38.5	53.0	5.76	0.000	2.26	96.9
cc-pV6Z	4.17	8.05	0.217	5.20	40.6	52.7	5.75	0.001	2.24	94.7
aug-cc-pVDZ	4.17	8.00	0.235	3.68	52.0	38.8	5.73	0.001	2.24	96.0
aug-cc-pVTZ	4.16	7.98	0.208	4.02	44.2	45.8	5.74	0.001	2.21	93.5
aug-cc-pVQZ	4.16	7.96	0.196	4.18	39.9	53.0	5.73	0.001	2.21	90.9
aug-cc-pV5Z	4.16	7.94	0.187	4.34	36.9	54.0	5.73	0.001	2.20	86.9
d-aug-cc-pVDZ	4.16	7.90	0.180	4.59	36.6	55.2	5.72	0.001	2.21	92.4
d-aug-cc-pVTZ	4.16	7.92	0.173	4.61	34.3	56.9	5.73	0.001	2.20	89.7
d-aug-cc-pVQZ	4.16	7.92	0.172	4.59	33.0	58.4	5.73	0.001	2.20	87.7
d-aug-cc-pV5Z	4.16	7.92	0.171	4.59	31.8	59.0	5.73	0.001	2.20	85.6

^aExcitation energies ΔE in eV, dipole moments μ in Debye and oscillator strengths f in length representation.

^b ω_π , ω_R and ω_n are the weights (in %) of $\pi \rightarrow \pi^*$, Rydberg and $n \rightarrow \pi^*$ excitations in each state, respectively.

2. Oscillator strengths

TABLE IX: Oscillator strengths (in length representation) for optically allowed transitions.

Molecule	State	Lit. ^a	CASPT2 ^b	CASPT2 ^c	CC2 ^d	CCSD ^e	BP86	B3LYP	BHLYP	DFT/MRCI
Ethene	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.358–0.494	0.360	0.505	0.431	0.410	0.339	0.362	0.396	0.549
<i>E</i> -Butadiene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	0.52–0.803	0.686	0.858	0.809	0.776	0.615	0.672	0.760	0.947
all- <i>E</i> -Hexatriene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	0.655–1.154	0.850	1.045	1.272	1.213	0.984	1.063	1.184	1.393
all- <i>E</i> -Octatetraene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	1.382	1.832	1.298	1.757	1.665	1.367	1.471	1.625	1.820
Cyclopropene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)		0.101	0.234	0.086	0.083	0.058	0.074	0.097	0.133
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)		0.010	0.010	0.001	0.001	0.001	0.001	0.001	0.003
Cyclopentadiene	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.001–0.019	0.000	0.001	0.011	0.008	0.006	0.007	0.009	0.005
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.225–0.538	0.442	0.965	0.658	0.648	0.512	0.563	0.629	0.903
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.099–0.157	0.148	0.164	0.110	0.097	0.088	0.090	0.093	0.143
Norbornadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)		0.008	0.090	0.023	0.029	0.006	0.010	0.033	0.042
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)		0.343	0.394	0.185	0.187	0.128	0.173	0.226	0.349
Benzene	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	0.323–1.33	0.820	0.856	0.694	0.686	1.127	1.195	1.293	0.920
Naphthalene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.082	0.050	0.136	0.094	0.083	0.047	0.062	0.080	0.125
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.268	0.313	0.401	0.272	0.294	0.140	0.186	0.266	0.317
	3 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.840	0.848	0.709	0.548	0.538	0.537	0.532	0.514	0.816
	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	1.326	1.337	1.542	1.450	1.461	1.165	1.268	1.399	1.740
	3 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	0.067	0.048	0.008	0.010	0.014	0.002	0.010	0.002	0.005
Furan	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.000–0.011	0.002	0.007	0.003	0.001	0.000	0.000	0.000	0.000
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.194–0.494	0.416	0.788	0.506	0.501	0.399	0.437	0.496	0.685
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.144–0.185	0.154	0.196	0.172	0.159	0.162	0.162	0.159	0.235
Pyrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.000–0.036	0.020	0.031	0.006	0.005	0.001	0.001	0.003	0.004
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.176–0.706	0.326	0.611	0.532	0.527	0.417	0.451	0.503	0.712
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.099–0.99	0.125	0.205	0.182	0.166	0.168	0.173	0.174	0.250
Imidazole	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.080	0.126	0.229	0.088	0.088	0.106	0.144	0.179	0.124
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.070	0.143	0.062	0.085	0.081	0.058	0.029	0.023	0.125
	4 ¹ A' ($\pi \rightarrow \pi^*$)		0.594	0.556	0.406	0.420	0.228	0.359	0.229	0.616
	1 ¹ A'' ($n \rightarrow \pi^*$)		0.011	0.010	0.003	0.005	0.001	0.003	0.006	0.009
	2 ¹ A'' ($n \rightarrow \pi^*$)		0.013	0.020	0.006	0.004	0.008	0.005	0.000	0.007
Pyridine	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.006–0.021	0.005	0.004	0.021	0.015	0.014	0.016	0.015	0.009
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.513–0.67	0.820	0.849	0.498	0.590	0.470	0.424	0.566	0.755
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.023–0.040	0.018	0.046	0.025	0.022	0.027	0.035	0.049	0.036
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.407–0.65	0.640	0.743	0.549	0.548	0.379	0.455	0.513	0.678
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.005–0.01	0.009	0.010	0.005	0.006	0.004	0.004	0.005	0.008
Pyrazine	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.060	0.080	0.107	0.096	0.074	0.054	0.059	0.055	0.071
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.370	0.760	0.774	0.424	0.458	0.283	0.367	0.454	0.645
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.080	0.070	0.124	0.070	0.067	0.074	0.091	0.117	0.102
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.330	0.660	0.622	0.400	0.423	0.499	0.264	0.377	0.572
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	0.010	0.010	0.013	0.007	0.008	0.004	0.006	0.007	0.011
Pyrimidine	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.017–0.03	0.050	0.165	0.062	0.038	0.036	0.037	0.032	0.049
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)		0.580	0.539	0.446	0.461	0.318	0.386	0.462	0.554
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.01–0.026	0.049	0.049	0.023	0.022	0.026	0.034	0.049	0.036
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.41–0.499	0.790	0.768	0.476	0.470	0.380	0.297	0.467	0.673
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.007–0.01	0.020	0.013	0.006	0.007	0.004	0.005	0.007	0.012
Pyridazine	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)		0.009	0.027	0.014	0.014	0.016	0.022	0.033	0.024
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)		0.500	0.742	0.444	0.494	0.363	0.335	0.466	0.638
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)		0.003	0.115	0.009	0.006	0.002	0.002	0.003	0.013
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)		0.750	0.603	0.489	0.459	0.367	0.431	0.483	0.468
	1 ¹ B ₁ ($n \rightarrow \pi^*$)		0.010	0.010	0.006	0.007	0.004	0.005	0.007	0.011

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TABLE IX – Continued

Molecule	State	Lit. ^a	CASPT2 ^b	CASPT2 ^c	CC2 ^d	CCSD ^e	BP86	B3LYP	BHLYP	DFT/MRCI
<i>s</i> -Triazine	2 ¹ B ₁ ($n \rightarrow \pi^*$)		0.008	0.008	0.005	0.005	0.004	0.005	0.005	0.006
	1 ¹ E' ($\pi \rightarrow \pi^*$)	0.920	0.610	0.681	0.441	0.437	0.654	0.762	0.887	0.589
	1 ¹ A ₂ ' ($n \rightarrow \pi^*$)	0.02 –0.027	0.015	0.022	0.017	0.018	0.012	0.014	0.017	0.029
<i>s</i> -Tetrazine	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.00 –0.054	0.001	0.146	0.017	0.003	0.004	0.002	0.000	0.003
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.39 –0.630	0.687	0.487	0.376	0.381	0.303	0.337	0.382	0.381
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.052–0.095	0.045	0.109	0.046	0.047	0.050	0.064	0.088	0.047
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	0.45 –0.755	0.733	0.554	0.368	0.333	0.267	0.290	0.302	0.333
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	0.007–0.012	0.013	0.013	0.007	0.009	0.004	0.005	0.008	0.009
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	0.01 –0.018	0.017	0.020	0.011	0.012	0.008	0.010	0.012	0.012
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	0.000–0.001	0.010	0.013	0.079	0.074	0.001	0.001	0.001	0.005
Formaldehyde	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.063–0.100	0.280	0.451	0.368	0.374	0.340	0.350	0.111	0.126
Acetone	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.255	0.326	0.359	0.298	0.256	0.208	0.195	0.132	0.146
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	0.003	0.010	0.011	0.000	0.000	0.001	0.000	0.000	0.000
<i>p</i> -Benzoquinone	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.636–0.704	0.616	0.636	0.538	0.558	0.231	0.323	0.506	0.711
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.693	0.624	0.660	0.544	0.509	0.389	0.561	0.564	0.604
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.002	0.000
Formamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.149–0.338	0.371	0.469	0.385	0.371	0.347	0.371	0.324	0.524
	3 ¹ A' ($\pi \rightarrow \pi^*$)		0.131	0.163	0.010	0.102	0.119	0.055	0.116	0.176
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.000–0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Acetamide	2 ¹ A' ($\pi \rightarrow \pi^*$)		0.292	0.469	0.199	0.223	0.113	0.087	0.181	0.269
	3 ¹ A' ($\pi \rightarrow \pi^*$)		0.179	0.163	0.279	0.299	0.129	0.224	0.146	0.219
	1 ¹ A'' ($n \rightarrow \pi^*$)		0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Propanamide	2 ¹ A' ($\pi \rightarrow \pi^*$)		0.346	0.405	0.138	0.180	0.081	0.107	0.133	0.208
	3 ¹ A' ($\pi \rightarrow \pi^*$)		0.205	0.275	0.189	0.150	0.077	0.085	0.098	0.148
	1 ¹ A'' ($n \rightarrow \pi^*$)		0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.001
Cytosine	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.052–0.080	0.061	0.093	0.049	0.058	0.015	0.035	0.075	0.072
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.138–0.181	0.108	0.351	0.165	0.178	0.061	0.087	0.147	0.171
	4 ¹ A' ($\pi \rightarrow \pi^*$)		0.863	0.621	0.632	0.608	0.308	0.368	0.500	0.711
	5 ¹ A' ($\pi \rightarrow \pi^*$)		0.147	0.369	0.168	0.159	0.167	0.177	0.225	0.222
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001–0.002	0.005	0.003	0.001	0.002	0.000	0.001	0.000	0.002
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.001–0.003	0.001	0.002	0.002	0.000	0.001	0.001	0.002	0.002
Thymine	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.180	0.170	0.334	0.197	0.222	0.074	0.136	0.232	0.251
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.040	0.170	0.067	0.080	0.071	0.064	0.071	0.057	0.113
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.180	0.150	0.353	0.250	0.285	0.102	0.142	0.247	0.264
	5 ¹ A' ($\pi \rightarrow \pi^*$)		0.850	0.674	0.515	0.361	0.189	0.411	0.354	0.441
	4 ¹ A'' ($n \rightarrow \pi^*$)		0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Uracil	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.18 –0.26	0.190	0.321	0.197	0.224	0.058	0.130	0.234	0.269
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.04 –0.05	0.080	0.047	0.058	0.061	0.046	0.040	0.046	0.069
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.035–0.17	0.290	0.249	0.188	0.209	0.056	0.120	0.182	0.214
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.510	0.760	0.804	0.547	0.430	0.207	0.440	0.412	0.487
	2 ¹ A'' ($n \rightarrow \pi^*$)		0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
	4 ¹ A'' ($n \rightarrow \pi^*$)		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Adenine	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.004–0.03	0.070	0.154	0.037	0.002	0.050	0.047	0.019	0.058
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.17 –0.36	0.370	0.193	0.276	0.297	0.123	0.195	0.297	0.311
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.510	0.851	0.536	0.496	0.513	0.100	0.240	0.421	0.616
	5 ¹ A' ($\pi \rightarrow \pi^*$)		0.159	0.001	0.085	0.070	0.125	0.107	0.159	0.001
	6 ¹ A' ($\pi \rightarrow \pi^*$)		0.565	0.010	0.320	0.286	0.040	0.137	0.125	0.373
	7 ¹ A' ($\pi \rightarrow \pi^*$)		0.406	0.036	0.177	0.122	0.345	0.244	0.024	0.051
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001–0.007	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.001
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.003–0.005	0.001	0.007	0.000	0.000	0.001	0.001	0.002	0.004

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TABLE IX – Continued

Molecule	State	Lit. ^a	CASPT2 ^b	CASPT2 ^c	CC2 ^d	CCSD ^e	BP86	B3LYP	BHLYP	DFT/MRCI

^aRange of *ab initio* values collected from the literature. See Ref. 1.

^bData from publications by the Roos group in the 1990s cited in Ref. 1.

^cSA-CASSCF/MS-CASPT2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.

^dCC2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.

^eCCSD results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.

3. Dipole moments

TABLE X: State dipole moments (in Debye).

Molecule	State	CASPT2 ^a	CASPT2 ^b	BP86	B3LYP	BHLYP	DFT/MRCI
Cyclopropene	Ground State	0.48	0.46	0.45	0.45	0.46	0.42
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.70	1.02	1.67	1.25	0.84	1.04
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	1.92	1.43	1.29	1.35	1.47	2.07
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.65	0.02	0.49	0.32	0.16	0.31
	1 ³ B ₁ ($\sigma \rightarrow \pi^*$)	1.90	1.64	1.43	1.49	1.62	2.29
Cyclopentadiene	Ground State	0.30	0.31	0.55	0.50	0.47	0.43
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.43	0.40	0.62	0.60	0.62	0.44
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.87	0.46	1.20	1.01	0.89	1.46
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.57	0.32	0.23	0.22	0.13	0.31
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	0.17	0.18	0.35	0.29	0.19	0.22
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.14	0.09	0.16	0.09	0.02	0.03
Norbornadiene	Ground State	0.12	0.01	0.07	0.05	0.04	0.04
	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	1.96	0.32	0.19	0.19	0.22	0.11
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	0.55	0.16	0.71	0.52	0.37	0.62
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.85	0.93	0.53	0.58	0.70	0.76
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.43	0.52	0.64	0.25	0.15	0.07
	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	0.16	0.05	0.07	0.04	0.01	0.09
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.12	0.05	0.24	0.15	0.06	0.12
Furan	Ground State	0.93	1.01	0.62	0.71	0.80	0.86
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.31	1.41	0.72	0.80	0.83	1.21
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.37	0.69	0.35	0.46	0.55	0.07
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.31	0.22	0.87	0.97	1.09	0.76
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.13	1.51	0.60	0.82	0.93	1.11
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.34	1.28	0.96	1.15	1.48	1.42
Pyrrole	Ground State	1.77	1.82	1.96	1.95	1.96	1.89
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.15	1.10	1.70	1.71	1.77	1.27
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.83	3.40	2.17	2.24	2.33	2.97
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.12	3.47	1.78	1.71	1.62	2.14
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.11	1.25	1.53	1.46	1.51	1.37
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.97	0.85	1.36	1.21	0.88	0.89
Imidazole	Ground State	3.70	3.79	3.81	3.87	3.95	3.89
	2 ¹ A' ($\pi \rightarrow \pi^*$)	4.61	3.35	3.92	4.20	4.04	4.80
	3 ¹ A' ($\pi \rightarrow \pi^*$)	3.00	4.82	3.64	3.82	4.18	3.92
	4 ¹ A' ($\pi \rightarrow \pi^*$)	3.85	4.76	3.01	3.64	1.40	3.21
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.22	1.11	1.35	1.08	1.72	0.69
	2 ¹ A'' ($n \rightarrow \pi^*$)	2.79	2.95	2.77	3.13	2.28	3.53
	1 ³ A' ($\pi \rightarrow \pi^*$)	3.17	2.88	3.25	3.15	2.88	2.95
	2 ³ A' ($\pi \rightarrow \pi^*$)	4.03	3.61	4.84	4.87	4.88	4.45
	3 ³ A' ($\pi \rightarrow \pi^*$)	4.68	4.90	3.59	4.13	4.90	5.32
	4 ³ A' ($\pi \rightarrow \pi^*$)	3.32	5.15	4.35	4.45	4.57	4.99

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TABLE X – Continued

Molecule	State	CASSCF ^a	CASPT2 ^b	BP86	B3LYP	BHLYP	DFT/MRCI
Pyridine	1 ³ A'' ($n \rightarrow \pi^*$)	1.38	1.31	1.24	1.58	1.70	1.04
	2 ³ A'' ($n \rightarrow \pi^*$)	6.19	3.15	3.25	3.50	3.51	2.36
	Ground State	2.36	2.27	2.29	2.34	2.39	2.36
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.28	3.24	2.56	2.52	2.49	3.03
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.67	1.22	1.75	1.35	2.36	2.75
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	0.93	0.87	0.27	0.25	0.13	0.99
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.03	1.99	2.04	2.10	2.17	2.08
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.83	2.51	2.36	2.59	2.70	2.96
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.40	0.27	0.62	0.37	0.13	0.79
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	2.13	2.08	2.21	2.21	2.11	2.21
	2 ³ A ₁ ($\pi \rightarrow \pi^*$)	2.41	2.28	2.46	2.54	2.67	2.65
	3 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.73	1.87	1.62	0.12	1.82	1.67
	1 ³ A ₂ ($n \rightarrow \pi^*$)	0.15	0.65	0.27	0.24	0.10	1.13
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	2.03	2.03	1.99	2.02	2.04	2.03
	2 ³ B ₂ ($\pi \rightarrow \pi^*$)	3.79	3.17	3.05	3.26	3.67	3.73
	3 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.04	1.74	1.57	1.49	1.19	1.18
Pyrimidine	1 ³ B ₁ ($n \rightarrow \pi^*$)	0.51	0.49	0.68	0.55	0.45	1.04
	Ground State	2.45	2.40	2.39	2.44	2.49	2.47
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	4.01	3.91	3.02	2.98	2.90	3.40
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.61	1.56	1.70	2.02	2.17	2.70
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.05	1.26	1.28	1.56	2.08	1.61
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.14	2.17	2.25	2.35	2.48	2.35
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.26	1.40	2.06	0.35	2.33	1.73
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.60	0.91	0.88	0.79	0.66	0.27
Pyridazine	Ground State	4.37	4.26	4.29	4.38	4.49	4.41
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.60	3.64	3.80	3.89	4.01	3.75
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	5.09	5.73	4.00	3.66	4.68	4.96
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.97	2.15	1.91	1.93	1.99	1.56
	2 ¹ A ₂ ($n \rightarrow \pi^*$)	1.74	1.85	2.00	2.30	2.55	1.76
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.64	5.12	4.63	4.65	4.64	5.59
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	3.93	4.02	4.11	4.16	4.40	3.18
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	1.59	1.88	1.59	1.86	2.20	1.62
Formaldehyde	2 ¹ B ₁ ($n \rightarrow \pi^*$)	1.74	2.12	2.24	2.36	2.50	1.80
	Ground State	2.43	2.44	2.31	2.48	2.70	2.56
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.39	1.46	1.65	1.63	1.57	1.53
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	0.50	0.90	0.88	0.91	0.94	0.30
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.75	2.69	0.85	2.86	0.90	0.59
	1 ³ A ₂ ($n \rightarrow \pi^*$)	1.13	1.35	1.50	1.45	1.34	1.05
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	0.89	1.05	1.04	0.88	0.28	0.52
Acetone	Ground State	2.92	2.93	3.02	3.13	3.31	3.18
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.94	3.18	3.33	2.89	1.73	0.70
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	2.27	1.48	1.97	1.96	1.92	1.34
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	0.99	1.31	3.38	2.80	2.21	1.44
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.11	1.21	1.62	1.28	0.47	0.81
	1 ³ A ₂ ($n \rightarrow \pi^*$)	1.14	1.28	1.72	1.68	1.59	1.16
	Ground State	4.08	3.79	3.98	4.10	4.23	4.18
Formamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.12	6.10	3.27	2.83	1.87	1.81
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.24	5.10	2.27	2.22	4.14	4.51
	1 ¹ A'' ($n \rightarrow \pi^*$)	2.12	1.99	2.82	2.66	2.41	1.72
	1 ³ A' ($\pi \rightarrow \pi^*$)	3.23	3.71	4.45	4.22	3.38	4.14
	1 ³ A'' ($n \rightarrow \pi^*$)	1.39	1.95	2.57	2.40	2.11	1.56
	Ground State	4.00	3.77	3.95	4.06	4.22	4.15
Acetamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.21	5.87	2.16	3.61	3.56	4.52
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.15	4.53	4.09	3.76	3.75	3.93
	1 ¹ A'' ($n \rightarrow \pi^*$)	2.19	1.79	2.43	2.33	2.16	1.38

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TABLE X – Continued

Molecule	State	CASSCF ^a	CASPT2 ^b	BP86	B3LYP	BHLYP	DFT/MRCI
Propanamide	$1^3A'$ ($\pi \rightarrow \pi^*$)	3.81	3.31	4.15	3.83	2.90	3.61
	$1^3A''$ ($n \rightarrow \pi^*$)	1.61	1.70	2.19	2.08	1.89	1.25
	Ground State	4.13	3.60	3.77	3.88	4.03	3.96
	$2^1A'$ ($\pi \rightarrow \pi^*$)	5.59	5.78	4.45	4.74	3.45	4.75
	$3^1A'$ ($\pi \rightarrow \pi^*$)	4.59	4.21	1.50	2.96	4.31	3.57
	$1^1A''$ ($n \rightarrow \pi^*$)	1.90	1.70	2.29	2.21	2.07	1.26
	$1^3A'$ ($\pi \rightarrow \pi^*$)	2.47	3.47	4.15	3.84	2.94	3.49
	$1^3A''$ ($n \rightarrow \pi^*$)	1.41	1.62	2.07	1.98	1.80	1.13
Cytosine	Ground State	7.2	6.34	6.59	6.84	7.16	7.00
	$2^1A'$ ($\pi \rightarrow \pi^*$)	4.7	4.58	3.35	3.94	4.97	3.71
	$3^1A'$ ($\pi \rightarrow \pi^*$)	7.0	5.73	6.45	6.66	6.88	7.02
	$4^1A'$ ($\pi \rightarrow \pi^*$)	6.2	5.92	3.60 ^c	6.25	8.16	6.08
	$5^1A'$ ($\pi \rightarrow \pi^*$)	9.3	7.02	2.19 ^d	7.81	7.12	8.50
	$1^1A''$ ($n \rightarrow \pi^*$)	4.7	2.56	1.26	2.12	4.35	2.26
	$2^1A''$ ($n \rightarrow \pi^*$)	6.4	2.74	4.43	3.10	1.60	0.54
	Ground State	5.0	4.19	4.39	4.55	4.78	4.67
Thymine	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.5	5.92	4.65	4.94	5.25	5.90
	$3^1A'$ ($\pi \rightarrow \pi^*$)	1.5	1.61	1.30	1.58	2.54	1.78
	$4^1A'$ ($\pi \rightarrow \pi^*$)	7.8	6.66	5.65	6.43	5.85	7.50
	$5^1A'$ ($\pi \rightarrow \pi^*$)	3.1	3.05	1.34	2.51	3.07	2.89
	$1^1A''$ ($n \rightarrow \pi^*$)	3.2	2.52	1.01	1.96	2.92	3.25
	$2^1A''$ ($n \rightarrow \pi^*$)	4.6	3.92	5.08	5.65	4.59	4.98
	$3^1A''$ ($n \rightarrow \pi^*$)	8.6	6.46	4.49	2.21	6.49	5.71
	$4^1A''$ ($n \rightarrow \pi^*$)	4.1	2.27	4.14	3.16	3.72	2.64
Uracil	Ground State	4.4	4.31	4.46	4.63	4.87	4.71
	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.3	5.78	5.12	5.15	5.32	6.02
	$3^1A'$ ($\pi \rightarrow \pi^*$)	2.4	2.48	1.30	1.87	2.70	2.45
	$4^1A'$ ($\pi \rightarrow \pi^*$)	6.9	6.52	3.61	5.92	6.91	7.03
	$5^1A'$ ($\pi \rightarrow \pi^*$)	3.7	3.16	2.44	2.70	3.15	2.78
	$1^1A''$ ($n \rightarrow \pi^*$)	3.4	2.23	0.82	1.55	2.49	2.72
	$2^1A''$ ($n \rightarrow \pi^*$)	4.8	4.25	5.64	5.51	5.00	5.31
	$3^1A''$ ($n \rightarrow \pi^*$)	8.7	2.17	4.16	2.75	6.38	4.52
Adenine	$4^1A''$ ($n \rightarrow \pi^*$)	3.6	6.86	4.74	3.47	2.97	2.20
	Ground State	2.50	2.53	2.46	2.50	2.55	2.55
	$2^1A'$ ($\pi \rightarrow \pi^*$)	2.37	2.19	2.48	2.80	3.27	2.88
	$3^1A'$ ($\pi \rightarrow \pi^*$)	2.30	2.52	2.20	2.16	2.26	1.99
	$4^1A'$ ($\pi \rightarrow \pi^*$)	2.13	2.09	3.92	2.42	1.06	2.38
	$5^1A'$ ($\pi \rightarrow \pi^*$)	4.60	3.45	1.66	2.96	3.18	1.85
	$6^1A'$ ($\pi \rightarrow \pi^*$)	3.42	2.86	4.02	3.80	4.05	3.68
	$7^1A'$ ($\pi \rightarrow \pi^*$)	6.41	0.97	4.39	3.77	2.45	4.34
	$1^1A''$ ($n \rightarrow \pi^*$)	2.14	1.48	0.68	0.38	1.44	1.03
	$2^1A''$ ($n \rightarrow \pi^*$)	1.93	0.39	2.05	1.40	0.95	0.34

^aData from publications of the Roos group in the 1990s cited in Ref. 1.^bSA-CASSCF/MS-CASPT2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.^cRydberg ($n \rightarrow \sigma^*$) contamination (about 49%).^dRydberg ($n \rightarrow \sigma^*$) contamination (about 59%).

Appendix B: Results for individual molecules: Tables XI to XXXIX

The Tables are arranged as follows: The columns refer to the methods used while the lines contain excitation energies and one-electron properties for a given state: the vertical excitation energies, ΔE , in eV; the dimensionless oscillator strengths, f , and the electric dipole moments, μ , in Debye. The origin of the data can be found in the footnotes (references and number of the relevant tables in the quoted publications). The footnotes also specify technical details such as basis sets.

1. Unsaturated aliphatic hydrocarbons

TABLE XI: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet and triplet states of ethene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
1^1B_{1u} (L_a)									
ΔE	7.98	8.54	8.37	7.80	7.73	7.70	7.69	7.96	7.50 ^c , 8.05 ^d , 7.36 ^e , 7.58 ^f , 7.60 ^g
f	0.360	0.505			0.339	0.362	0.396	0.549	
Triplet States									
1^1B_{1u} (L_a)									
ΔE	4.39	4.48	4.48	4.50	4.15	4.03	3.47	4.31	3.99 ^e , 4.15 ^f , 3.94 ^g

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.².

^cB3P86/6-311(2+,2+)G**. Ref.³.

^dVignale-Kohn Functional/ET-pVQZ. Ref.⁴.

^eB3LYP/Sadlej. Ref.⁵.

^fVSXC/6-311++G(d,p). Ref.⁶.

^gPBE0/6-311++G(d,p). Ref.⁶.

TABLE XII: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet and triplet states of *E*-butadiene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
2^1A_g (L_b)									
ΔE	6.27	6.62	6.77	6.55	6.30	6.82	7.61	6.18	6.36 ^c , 6.84 ^d , 5.93 ^e , 6.46 ^f
1^1B_u (L_a)									
ΔE	6.23	6.47	6.58	6.18	5.60	5.74	5.94	6.02	5.59 ^c , 5.76 ^d , 5.59 ^f
f	0.686	0.858			0.615	0.672	0.760	0.947	0.593 ^f
Triplet States									
1^3A_g (L_b)									
ΔE	4.89	5.16	5.17	5.08	4.95	4.86	4.44	4.85	4.93 ^c , 4.81 ^d , 4.89 ^f
1^3B_u (L_a)									
ΔE	3.20	3.34	3.32	3.20	2.87	2.76	2.15	3.09	2.81 ^c , 2.67 ^d , 2.83 ^f

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.⁷.

^cVSXC/6-311++G(d,p). Ref.⁶.

^dPBE0/6-311++G(d,p). Ref.⁶.

^e“Dressed” TD-DFT. PBE0/6-311G(d,p). Ref.⁸.

^fB3LYP/6-311(2+,2+)G**. Ref.⁹.

TABLE XIII: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet and triplet states of hexatriene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
2^1A_g (L_b)									
ΔE	5.20	5.42	5.72	5.09	5.07	5.69	6.66	4.92	4.85 ^c , 5.65 ^d
1^1B_u (L_a)									
ΔE	5.01	5.31	5.58	5.10	4.50	4.69	4.93	4.95	4.64 ^d
f	0.850	1.045			0.984	1.063	1.184	1.393	1.11 ^d
Triplet States									
1^3A_g (L_b)									
ΔE	4.12	4.31	4.32	4.15	3.98	3.92	3.50	3.96	3.94 ^d
1^3B_u (L_a)									
ΔE	2.55	2.71	2.69	2.40	2.21	2.09	1.35	2.45	2.10 ^d

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.⁷.

^c“Dressed” TD-DFT. PBE0/6-311G(d,p). Ref.⁸.

^dB3LYP/6-311(2+,2+)G**. Ref.⁹.

TABLE XIV: Vertical excitation energies ΔE (eV), and oscillator strengths f of the valence singlet and triplet states of all-*E*-octatetraene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
2^1A_g ($\pi \rightarrow \pi^*$)									
ΔE	4.38	4.64	4.97	4.47	4.19	4.84	5.83	4.01	4.83 ^c
3^1A_g ($\pi \rightarrow \pi^*$)									
ΔE	6.56	6.19	6.50	6.40	5.79	6.02	6.93	5.78	
4^1A_g ($\pi \rightarrow \pi^*$)									
ΔE	7.14	6.55	6.81		5.97	6.35	8.18	6.00	
1^1B_u ($\pi \rightarrow \pi^*$)									
ΔE	4.42	4.70	4.94	4.66	3.82	4.02	4.29	4.25	3.98 ^c
f	1.832	1.298			1.367	1.471	1.625	1.820	1.56 ^c
2^1B_u ($\pi \rightarrow \pi^*$)									
ΔE	5.83	5.73	6.06	5.76	5.97	6.78	7.49	5.22	
f	0.010	0.004			0.064	0.029	0.047	0.002	
3^1B_u ($\pi \rightarrow \pi^*$)									
ΔE	8.44	8.04	7.91		7.20	7.41	8.20	7.07	
f	0.002				0.102	0.145	0.158	0.209	
Triplet States									
1^3B_u (L_a)									
ΔE	2.17	2.33	2.30	2.20	1.81	1.68	0.72	2.04	1.68 ^c
1^3A_g (L_b)									
ΔE	3.39	3.70	3.67	3.55	3.30	3.24	2.80	3.32	3.26 ^c

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹⁰.

^cB3LYP/6-311(2+,2+)G**. Ref.⁹.

TABLE XV: Vertical excitation energies ΔE (eV) dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of cyclopropene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
1 ¹ A ₁									
μ	0.48	0.46			0.45	0.45	0.46	0.42	
Singlet States									
1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)									
ΔE	6.36	6.76	6.90	6.76	6.30	6.46	6.77	6.73	
μ	1.92	1.43			1.29	1.35	1.47	2.07	
f	0.010	0.010			0.001	0.001	0.001	0.003	
1 ¹ B ₂ ($\pi \rightarrow \pi^*$)									
ΔE	7.45	7.06	7.10	7.06	6.13	6.31	6.50	6.74	6.00 ^c
μ	0.70	1.02			1.67	1.25	0.84	1.04	
f	0.101	0.234			0.058	0.074	0.097	0.133	
Triplet States									
1 ³ B ₂ ($\pi \rightarrow \pi^*$)									
ΔE	4.18	4.35	4.34	4.34	3.74	3.70	3.25	4.03	3.77 ^c
μ	0.65	0.02			0.49	0.32	0.16	0.31	
1 ³ B ₁ ($\sigma \rightarrow \pi^*$)									
ΔE	6.05	6.51	6.62	6.62	5.81	6.01	6.28	6.31	
μ	1.90	1.64			1.43	1.49	1.62	2.29	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹¹.

^cB-PW91/6-311+G**. Ref.¹².

TABLE XVI: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of cyclopentadiene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
1 ¹ A ₁									
μ	0.30	0.31			0.55	0.50	0.47	0.43	
Singlet States									
2 ¹ A ₁ (L _b)									
ΔE	6.31	6.31	6.61	6.31	6.09	6.52	7.23	6.15	6.20 ^c
μ	0.43	0.40			0.62	0.60	0.62	0.44	
f	0.000	0.001			0.006	0.007	0.009	0.005	0.005 ^c
3 ¹ A ₁ (B _b)									
ΔE	7.89	8.52	8.69		8.04	8.15	8.29	8.16	8.09 ^c
μ	1.87	0.46			1.20	1.01	0.89	1.46	
f	0.442	0.965			0.512	0.563	0.629	0.903	0.433 ^c
1 ¹ B ₂ (L _a)									
ΔE	5.27	5.51	5.73	5.55	4.93	5.02	5.15	5.42	5.02 ^c
μ	0.57	0.32			0.23	0.22	0.13	0.31	
f	0.148	0.164			0.088	0.090	0.093	0.143	0.084 ^c
Triplet States									
1 ³ A ₁ (L _b)									
ΔE	4.90	5.11	5.09	5.09	4.82	4.75	4.38	4.78	
μ	0.17	0.18			0.35	0.29	0.19	0.22	
1 ³ B ₂ (L _a)									
ΔE	3.15	3.28	3.25	3.25	2.82	2.71	2.14	3.07	
μ	0.14	0.09			0.16	0.09	0.02	0.03	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹³.

^cHCTH(AC)/TZ2P plus augmentation. Ref.¹⁴.

TABLE XVII: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of norbornadiene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI
Ground State								
1 ¹ A ₁								
μ	0.12	0.01			0.07	0.05	0.04	0.04
Singlet States								
1 ¹ A ₂								
ΔE	5.28	5.34	5.64	5.34	4.48	4.79	5.15	5.30
μ	1.96	0.32			0.19	0.19	0.22	0.11
2 ¹ A ₂								
ΔE	7.36	7.45	7.71		6.56	6.86	7.40	7.33
μ	0.55	0.16			0.71	0.52	0.37	0.62
1 ¹ B ₂								
ΔE	6.20	6.11	6.49	6.11	5.02	5.52	6.22	6.12
μ	1.85	0.93			0.53	0.58	0.70	0.76
f	0.008	0.090	0.023	0.029	0.006	0.010	0.033	0.042
2 ¹ B ₂								
ΔE	6.48	7.32	7.64		6.61	6.87	7.21	7.21
μ	0.43	0.52			0.64	0.25	0.15	0.07
f	0.343	0.394	0.185	0.187	0.128	0.173	0.226	0.349
Triplet States								
1 ³ A ₂								
ΔE	3.42	3.75	3.72	3.72	3.11	3.08	2.63	3.42
μ	0.16	0.05			0.07	0.04	0.01	0.09
1 ³ B ₂								
ΔE	3.80	4.22	4.16	4.16	3.71	3.62	3.07	3.85
μ	0.12	0.05			0.24	0.15	0.06	0.12

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹⁵.

2. Aromatic hydrocarbons and heterocycles

TABLE XVIII: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet and triplet states of benzene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
1^1B_{1u}									
ΔE	6.30	6.42	6.68	6.54	6.00	6.10	6.15	6.31	5.99 ^c , 6.04 ^d , 6.17 ^e 6.05 ^f , 6.02 ^g
1^1B_{2u}									
ΔE	4.84	5.04	5.07	5.08	5.24	5.40	5.64	5.04	5.34 ^c , 5.38 ^d , 5.50 ^e 5.39 ^f , 5.28 ^g
1^1E_{1u}									
ΔE	7.03	7.13	7.45	7.13	6.96	7.07	7.27	7.19	7.00 ^d , 6.94 ^e , 6.93 ^f , 6.94 ^g
f	0.820	0.856			1.127	1.195	1.293	0.920	
1^1E_{2g}									
ΔE	7.90	8.18	8.43	8.41	8.28	8.91	9.70	7.51	
Triplet States									
1^3B_{1u}									
ΔE	3.89	4.17	4.12	4.15	3.93	3.77	3.08	4.13	3.81 ^d , 3.64 ^e , 3.82 ^f , 4.02 ^g
1^3B_{2u}									
ΔE	5.49	5.76	6.04	5.88	4.94	5.09	5.26	5.57	5.09 ^d , 5.13 ^e , 5.05 ^f , 4.98 ^g
1^3E_{1u}									
ΔE	4.49	4.90	4.90	4.86	4.60	4.70	4.79	4.69	4.66 ^d , 4.73 ^e , 4.70 ^f , 4.66 ^g
1^3E_{2g}									
ΔE	7.12	7.38	7.49	7.51	7.13	7.33	7.47	7.40	7.20 ^d , 7.39 ^e , 7.18 ^f , 7.20 ^g

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹⁶.

^cB3LYP/aug-cc-pVTZ. Ref.⁵

^dVSXC/6-311++G(d,p). Ref.⁶.

^ePBE0/6-311++G(d,p). Ref.⁶.

^fB3LYP/6-311++G(d,p). Ref.¹⁷.

^gHCTH(AC)/TZ2P+. Ref.¹⁸.

TABLE XIX: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet and triplet states of naphthalene.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
2 ¹ A _g									
ΔE	5.39	5.87	5.98	5.87	5.85	6.18	6.63	5.65	5.96 ^c , 7.00 ^d
3 ¹ A _g									
ΔE	6.04	6.67	6.90	6.67	6.20	6.85	7.70	6.05	
1 ¹ B _{2u}									
ΔE	4.56	4.77	5.03	4.77	4.08	4.35	4.65	4.60	4.34 ^c , 4.58 ^d
f	0.050	0.136			0.047	0.062	0.080	0.125	
2 ¹ B _{2u}									
ΔE	5.93	6.33	6.57	6.33	5.88	6.12	6.41	6.21	5.81 ^c , 5.99 ^d
f	0.313	0.401			0.140	0.186	0.266	0.317	
3 ¹ B _{2u}									
ΔE	7.16	8.17	8.44		7.53	7.87	8.45	7.84	
f	0.848	0.709			0.537	0.532	0.514	0.816	
1 ¹ B _{3u}									
ΔE	4.03	4.24	4.27	4.24	4.23	4.44	4.71	4.10	4.18 ^c , 4.48 ^d
f	0.001	0.001			0.000	0.000	0.000	0.000	
2 ¹ B _{3u}									
ΔE	5.54	6.06	6.33	6.06	5.73	5.93	6.21	5.89	5.95 ^c , 6.23 ^d
f	1.337	1.542			1.165	1.268	1.399	1.740	
3 ¹ B _{3u}									
ΔE	7.18	7.74	8.44		8.00	8.65	9.84	7.38	
f	0.048	0.008			0.002	0.010	0.002	0.005	
1 ¹ B _{1g}									
ΔE	5.53	5.99	6.07	5.99	5.04	5.58	6.28	5.53	5.18 ^c , 5.62 ^d
2 ¹ B _{1g}									
ΔE	5.87	6.47	6.79	6.47	6.17	6.32	6.65	6.26	6.16 ^c , 6.35 ^d
Triplet States									
1 ³ A _g									
ΔE	5.27	5.53	5.52	5.52	5.25	5.33	5.31	5.18	5.27 ^c , 5.27 ^d
2 ³ A _g									
ΔE	5.83	6.38	6.47	6.47	5.67	5.95	6.33	6.00	5.66 ^c , 5.97 ^d
3 ³ A _g									
ΔE	5.91	6.59	6.79	6.79	5.59	6.07	6.58	6.31	5.83 ^c , 6.23 ^d
1 ³ B _{2u}									
ΔE	3.10	3.16	3.11	3.11	2.76	2.69	2.06	2.97	3.86 ^c , 2.64 ^d
2 ³ B _{2u}									
ΔE	4.30	4.68	4.64	4.64	4.31	4.40	4.45	4.49	4.15 ^c , 4.31 ^d
1 ³ B _{3u}									
ΔE	3.89	4.25	4.18	4.18	3.81	3.95	4.06	3.93	2.71 ^c , 3.99 ^d
2 ³ B _{3u}									
ΔE	4.45	4.97	5.11	5.11	4.03	4.22	4.42	4.65	4.30 ^c , 4.46 ^d
1 ³ B _{1g}									
ΔE	4.23	4.51	4.47	4.47	4.19	4.17	3.90	4.25	4.17 ^c , 4.09 ^d
2 ³ B _{1g}									
ΔE	5.71	6.21	6.48	6.48	5.00	5.55	6.39	6.02	5.15 ^c , 5.68 ^d
3 ³ B _{1g}									
ΔE	6.23	6.64	6.76	6.76	6.30	6.56	6.85	6.41	6.39 ^c , 6.24 ^d

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹⁹.

^cVSXC/6-311++G(d,p). Ref.⁶.

^dPBE0/6-311++G(d,p). Ref.⁶.

TABLE XX: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of furan.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
1 ¹ A ₁									
μ	0.93	1.01			0.62	0.71	0.80	0.86	
Singlet States									
2 ¹ A ₁ (L _b)									
ΔE	6.16	6.50	6.62	6.57	6.38	6.70	7.22	6.32	6.39 (6.42) ^c , 6.83 ^d
μ	1.31	1.41			0.72	0.80	0.83	1.21	0.93 (0.74) ^c
f	0.002	0.007			0.000	0.000	0.000	0.000	
3 ¹ A ₁ (B _b)									
ΔE	7.66	8.17	8.53	8.13	8.16	8.25	8.43	8.21	
μ	0.37	0.69			0.35	0.46	0.55	0.07	
f	0.416	0.788			0.399	0.437	0.496	0.685	
1 ¹ B ₂ (L _a)									
ΔE	6.04	6.39	6.60	6.32	6.11	6.16	6.23	6.33	6.03 (6.08) ^c , 6.10 ^d
μ	0.31	0.22			0.87	0.97	1.09	0.76	4.82 (1.69) ^c
f	0.154	0.196			0.162	0.162	0.159	0.235	
Triplet States									
1 ³ A ₁ (L _b)									
ΔE	5.15	5.49	5.48	5.48	5.24	5.21	4.67	5.15	
μ	1.13	1.28			0.60	0.82	0.93	1.11	
1 ³ B ₂ (L _a)									
ΔE	3.99	4.18	4.17	4.17	3.85	3.71	2.70	3.91	
μ	1.34	1.51			0.96	1.15	1.48	1.42	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹³.

^cHTCH/TZ2P+ (values in parenthesis using asymptotically corrected potential). Ref.²⁰.

^dPBE0/TZ2P+. Ref.²⁰.

TABLE XXI: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of pyrrole.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
1 ¹ A ₁									
μ	1.77	1.82			1.96	1.95	1.96	1.89	
Singlet States									
2 ¹ A ₁ (L _b)									
ΔE	5.92	6.31	6.40	6.37	6.26	6.53	6.94	6.13	6.01 (6.31) ^c , 6.63 ^d
μ	1.15	1.10			1.70	1.71	1.77	1.27	3.03 (1.55) ^c
f	0.020	0.031			0.001	0.001	0.003	0.004	
3 ¹ A ₁ (B _b)									
ΔE	7.46	8.17	8.17	7.91	7.85	7.96	8.15	7.88	
μ	2.83	3.40			2.17	2.24	2.33	2.97	
f	0.326	0.611			0.417	0.451	0.503	0.712	
1 ¹ B ₂ (L _a)									
ΔE	6.00	6.33	6.71	6.57	6.34	6.40	6.48	6.46	6.34 (6.48) ^c , 6.54 ^d
μ	2.12	3.47			1.78	1.71	1.62	2.14	0.38 (3.86) ^c
f	0.125	0.205			0.168	0.173	0.174	0.250	
Triplet States									
1 ³ A ₁ (L _b)									
ΔE	5.16	5.52	5.51	5.51	5.24	5.25	5.19	5.19	
μ	1.11	1.25			1.53	1.46	1.51	1.37	
1 ³ B ₂ (L _a)									
ΔE	4.27	4.51	4.48	4.48	4.18	4.07	3.63	4.23	
μ	0.97	0.85			1.36	1.21	0.88	0.89	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹³.

^cHTCH/TZ2P+ (values in parenthesis using asymptotically corrected potential). Ref.²⁰.

^dPBE0/TZ2P+. Ref.²⁰.

TABLE XXII: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of imidazole.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI
Singlet States								
1 ¹ A'								
μ	3.70	3.79			3.81	3.87	3.95	3.89
2 ¹ A' (L _b /L _a)								
ΔE	6.72	6.19	6.58	6.19	6.29	6.45	6.65	6.29
μ	4.61	3.35			3.92	4.20	4.04	4.80
f	0.126	0.229			0.106	0.144	0.179	0.124
3 ¹ A' (L _b /L _a)								
ΔE	7.15	6.93	7.10	6.93	6.86	7.04	7.35	6.82
μ	3.00	4.82			3.64	3.82	4.18	3.92
f	0.143	0.062			0.058	0.029	0.023	0.125
4 ¹ A' (B _b)								
ΔE	8.51	8.16	8.45		8.12	8.27	8.45	8.22
μ	3.85	4.76			3.01	3.64	1.40	3.21
f	0.594	0.556			0.228	0.359	0.229	0.616
1 ¹ A''								
ΔE	6.52	6.81	6.82	6.81	5.91	6.46	7.09	6.35
μ	0.22	1.11			1.35	1.08	1.72	0.69
f	0.011	0.010			0.001	0.003	0.006	0.009
2 ¹ A''								
ΔE	7.56	7.90	7.93		7.18	7.45	8.16	7.63
μ	2.79	2.95			2.77	3.13	2.28	3.53
f	0.013	0.020			0.008	0.005	0.000	0.007
Triplet States								
1 ³ A'								
ΔE	4.49	4.65	4.69	4.69	4.33	4.24	3.82	4.41
μ	3.17	2.88			3.25	3.15	2.88	2.95
2 ³ A'								
ΔE	5.47	5.74	5.79	5.79	5.39	5.44	5.33	5.43
μ	4.03	3.61			4.84	4.87	4.88	4.45
3 ³ A'								
ΔE	6.53	6.44	6.55	6.55	5.92	5.95	5.99	6.22
μ	4.68	4.90			3.59	4.13	4.90	5.32
4 ³ A'								
ΔE	7.08	7.44	7.42		6.76	6.93	7.21	7.14
μ	3.32	5.15			4.35	4.45	4.57	4.99
1 ³ A''								
ΔE	6.07	6.36	6.37	6.37	5.53	5.83	6.12	5.92
μ	1.38	1.31			1.24	1.58	1.70	1.04
2 ³ A''								
ΔE	7.15	7.51	7.51		6.35	6.86	7.81	7.32
μ	6.19	3.15			3.25	3.50	3.51	2.36

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.²¹.

TABLE XXIII: Vertical excitation energies ΔE (eV), of the singlet and triplet states of pyridine.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
μ	2.36	2.27			2.29	2.34	2.39	2.36	
Singlet States									
2^1A_1 (B_{1u})									
ΔE	6.42	6.39	6.85	6.26	6.21	6.31	6.37	6.47	6.19 ^c , 6.25 ^d , 6.42 ^e , 6.24 ^f
μ	3.28	3.24			2.56	2.52	2.49	3.03	
f	0.005	0.004			0.014	0.016	0.015	0.009	
3^1A_1 (E_{1u})									
ΔE	7.23	7.46	7.70	7.18	7.27	7.32	7.55	7.43	6.66 ^d , 7.21 ^e , 6.90 ^f
μ	2.67	1.22			1.75	1.35	2.36	2.75	
f	0.820	0.849			0.470	0.424	0.566	0.755	
1^1B_2 (B_{2u})									
ΔE	4.84	5.02	5.15	4.85	5.35	5.49	5.71	5.09	5.47 ^c , 5.48 ^d , 5.63 ^e , 5.54 ^f
μ	2.03	1.99			2.04	2.10	2.17	2.08	
f	0.018	0.046			0.027	0.035	0.049	0.036	
2^1B_2 (E_{1u})									
ΔE	7.48	7.27	7.61	7.27	7.13	7.30	7.56	7.27	7.17 ^d , 7.37 ^e , 7.25 ^f
μ	2.57	2.51			2.36	2.59	2.70	2.96	
f	0.640	0.743			0.379	0.455	0.513	0.678	
1^1B_1									
ΔE	4.91	5.17	5.05	4.59	4.38	4.80	5.30	4.75	4.76 ^c , 4.63 ^d , 4.88 ^e , 4.80 ^f
μ	0.40	0.27			0.62	0.37	0.13	0.79	
f	0.009	0.010			0.004	0.004	0.005	0.008	
1^1A_2									
ΔE	5.17	5.51	5.50	5.11	4.48	5.11	6.03	5.41	5.07 ^c , 4.77 ^d , 5.20 ^e , 5.09 ^f
μ	0.93	0.87			0.27	0.25	0.13	0.99	
Triplet States									
1^3A_1									
ΔE	4.05	4.27	4.25	4.06	4.05	3.89	3.14	4.25	3.91 ^c , 3.94 ^d , 3.80 ^e , 3.99 ^f
μ	2.13	2.08			2.21	2.21	2.11	2.21	
2^3A_1									
ΔE	4.73	5.03	5.05	4.91	4.78	4.84	4.89	4.84	4.83 ^d , 4.92 ^e , 4.91 ^f
μ	2.41	2.28			2.46	2.54	2.67	2.65	
3^3A_1									
ΔE	7.34	7.56	7.66		7.29	7.44	7.51	7.21	6.58 ^d , 7.14 ^e , 6.86 ^f
μ	1.73	1.87			1.62	0.12	1.82	1.67	
1^3B_2									
ΔE	4.56	4.71	4.86	4.64	4.42	4.51	4.57	4.60	4.47 ^c , 4.48 ^d , 4.56 ^e , 4.57 ^f
μ	2.03	2.03			1.99	2.02	2.04	2.03	
2^3B_2									
ΔE	6.02	6.03	6.40	6.08	5.46	5.64	5.84	5.97	5.61 ^d , 5.72 ^e , 5.68 ^f
μ	3.79	3.17			3.05	3.26	3.67	3.73	
3^3B_2									
ΔE	7.28	7.87	7.83		7.54	7.75	7.93	7.52	6.41 ^d , 7.01 ^e , 6.71 ^f
μ	1.04	1.74			1.57	1.49	1.19	1.18	
1^3B_1									
ΔE	4.41	4.57	4.50	4.25	3.71	4.04	4.39	4.31	4.05 ^c , 3.97 ^d , 4.09 ^e , 4.08 ^f
μ	0.51	0.49			0.68	0.55	0.45	1.04	
1^3A_2									
ΔE	5.10	5.52	5.46	5.28	4.34	4.98	5.85	5.33	4.93 ^c , 4.64 ^d , 5.04 ^e , 4.95 ^f
μ	0.15	0.65			0.27	0.24	0.10	1.13	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.²².

^cB3LYP/Sadlej. Ref.⁵.

^dVSXC/6-311++G(d,p). Ref.⁶.

^ePBE0/6-311++G(d,p). Ref.⁶.

^fB3LYP/6-311++G(d,p). Ref.¹⁷.

TABLE XXIV: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet states of pyrazine.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
1^1B_{1u} (B_{1u})									
ΔE	6.70	6.89	7.07	6.58	6.41	6.50	6.55	6.71	5.40 ^c , 6.58 ^d
f	0.080	0.107			0.054	0.059	0.055	0.071	0.10 ^c
2^1B_{1u} (E_{1u})									
ΔE	7.57	7.79	8.06	7.72	7.53	7.68	7.89	7.82	7.87 ^d
f	0.760	0.774			0.283	0.367	0.454	0.645	
1^1B_{2u} (B_{2u})									
ΔE	4.75	4.85	5.02	4.64	5.25	5.37	5.52	4.94	5.49 ^d
f	0.070	0.124			0.074	0.091	0.117	0.102	
2^1B_{2u} (E_{1u})									
ΔE	7.70	7.66	8.05	7.60	7.75	7.78	8.13	7.75	7.90 ^d
f	0.660	0.622			0.499	0.264	0.377	0.572	
1^1A_u ($n \rightarrow \pi^*$)									
ΔE	4.52	4.70	5.05	4.81	4.06	4.69	5.59	5.02	4.59 ^d
1^1B_{1g} ($n \rightarrow \pi^*$)									
ΔE	6.13	6.41	6.75	6.60	5.57	6.38	7.66	6.46	6.37 ^d
1^1B_{2g} ($n \rightarrow \pi^*$)									
ΔE	5.17	5.68	5.74	5.56	5.11	5.55	6.02	5.26	5.66 ^d
1^1B_{3u} ($n \rightarrow \pi^*$)									
ΔE	3.63	4.12	4.24	3.95	3.59	3.96	4.40	4.00	3.99 ^c , 3.99 ^d
f	0.010	0.013			0.004	0.006	0.007	0.011	0.01 ^c

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.²³.

^cB3LYP/6-31+G*. Ref.²⁴.

^dB3LYP/cc-pVDZ. Ref.²⁵.

TABLE XXV: Vertical excitation energies ΔE (eV), of the singlet states of pyrimidine.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
1 ¹ A ₁									
μ	2.45	2.40			2.39	2.44	2.49	2.47	
2 ¹ A ₁									
ΔE	6.72	6.63	7.06	6.95	6.46	6.58	6.67	6.69	6.69 ^c
μ	4.01	3.91			3.02	2.98	2.90	3.40	
f	0.050	0.165			0.036	0.037	0.032	0.049	
3 ¹ A ₁									
ΔE	7.57	7.21	7.74		7.32	7.48	7.73	7.46	7.73 ^c
μ	2.61	1.56			1.7	2.02	2.17	2.70	
f	0.580	0.539			0.318	0.386	0.462	0.554	
1 ¹ B ₂									
ΔE	4.93	5.24	5.36	5.44	5.59	5.74	5.98	5.35	5.87 ^c , 5.82 ^d
μ	2.14	2.17			2.25	2.35	2.48	2.35	
f	0.001	0.049			0.026	0.034	0.049	0.036	0.03 ^d
2 ¹ B ₂									
ΔE	7.32	7.64	8.01		7.57	7.76	7.96	7.74	7.75 ^c
μ	2.26	1.40			2.06	0.35	2.33	1.73	
f	0.790	0.768			0.380	0.297	0.467	0.673	
1 ¹ B ₁ ($n \rightarrow \pi^*$)									
ΔE	3.81	4.44	4.50	4.55	3.80	4.27	4.87	4.36	4.31 ^c , 4.30 ^e
μ	0.60	0.91			0.88	0.79	0.66	0.27	
f	0.020	0.013			0.004	0.005	0.007	0.012	
1 ¹ A ₂ ($n \rightarrow \pi^*$)									
ΔE	4.12	4.80	4.93	4.91	4.02	4.60	5.39	4.82	4.55 ^c
μ	1.05	1.26			1.28	1.56	2.08	1.61	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.²⁶.

^cB3LYP/cc-pVDZ. Ref.²⁷.

^dB3LYP/6-31+G*. Ref.²⁴.

^eB3LYP/6-31+G*. Ref.²⁸.

TABLE XXVI: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet states of pyridazine.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Ground State									
μ	4.37	4.26			4.29	4.38	4.49	4.41	
2^1A_1 ($B_{2u},-$)									
ΔE	4.86	5.18	5.22	5.18	5.46	5.61	5.83	5.16	5.66 ^c
μ	3.6	3.64			3.80	3.89	4.01	3.75	
f	0.009	0.027			0.016	0.022	0.033	0.024	0.02 ^c
3^1A_1 ($E_{1u},+$)									
ΔE	7.50	7.62	7.82		7.39	7.50	7.76	7.53	
μ	5.09	5.73			4.00	3.66	4.68	4.96	
f	0.500	0.742			0.363	0.335	0.466	0.638	
1^1B_2 ($B_{1u},+$)									
ΔE	6.61	6.31	6.93		6.32	6.43	6.48	6.51	
μ	5.64	5.12			4.63	4.65	4.64	5.59	
f	0.003	0.115			0.002	0.002	0.003	0.013	
2^1B_2 ($E_{1u},+$)									
ΔE	7.39	7.29	7.55		7.10	7.24	7.45	7.25	
μ	3.93	4.02			4.11	4.16	4.40	3.18	
f	0.750	0.603			0.367	0.431	0.483	0.468	
1^1A_2 ($n \rightarrow \pi^*,+$)									
ΔE	3.66	4.31	4.49	4.31	3.54	4.18	5.03	4.25	
μ	1.97	2.15			1.91	1.93	1.99	1.56	
2^1A_2 ($n \rightarrow \pi^*,+$)									
ΔE	5.09	5.77	5.74	5.77	5.01	5.44	6.05	5.29	
μ	1.74	1.85			2.00	2.30	2.55	1.76	
1^1B_1 ($n \rightarrow \pi^*,+$)									
ΔE	3.48	3.78	3.92	3.78	3.15	3.58	4.10	3.63	3.59 ^c , 3.54 ^d
μ	1.59	1.88			1.59	1.86	2.20	1.62	
f	0.010	0.010			0.004	0.005	0.007	0.011	<0.01 ^c
2^1B_1 ($n \rightarrow \pi^*,+$)									
ΔE	5.80	6.52	6.41		5.45	6.09	6.99	6.15	
μ	1.74	2.12			2.24	2.36	2.50	1.80	
f	0.008	0.008			0.004	0.005	0.005	0.006	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.²⁶.

^cB3LYP/6-31+G*. Ref.²⁴.

^dB3LYP/TZVP. Ref.²⁹.

TABLE XXVII: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet states of *s*-triazine.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
$2^1A'_1$ (B_{1u})									
ΔE	6.77	7.25	7.41		6.87	7.01	7.12	7.02	
$1^1A'_2$ (B_{2u})									
ΔE	5.53	5.79	5.71	5.79	5.95	6.14	6.45	5.70	6.25 ^c
$1^1E'$ (E_{1u})									
ΔE	8.16	7.50	8.04		7.63	7.79	8.06	7.81	
f	0.610	0.681			0.654	0.762	0.887	0.589	
$1^1A''_1$ ($n \rightarrow \pi^*$)									
ΔE	3.90	4.60	4.78	4.60	3.84	4.45	5.31	4.69	4.51 ^c
$1^1A''_2$ ($n \rightarrow \pi^*$)									
ΔE	4.08	4.66	4.76	4.66	4.08	4.54	5.16	4.56	4.61 ^c
f	0.015	0.022			0.012	0.014	0.017	0.029	0.015 ^c
$1^1E''$ ($n \rightarrow \pi^*$)									
ΔE	4.36	4.70	4.81	4.70	3.99	4.54	5.27	4.77	4.60 ^c
$2^1E''$ ($n \rightarrow \pi^*$)									
ΔE	7.15	7.71	7.80		6.71	7.49	8.42	7.26	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.²⁶.

^cB3LYP/6-31G*. Ref.³⁰.

TABLE XXVIII: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet states of *s*-tetrazine.^a

CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Dark Singlet States								
$1^1A_u (n \rightarrow \pi^*)$								
ΔE 3.06	3.51	3.79	3.51	2.86	3.51	4.40	3.70	3.45 ^c , 2.90 ^e
$2^1A_u (n \rightarrow \pi^*)$								
ΔE 5.28	5.50	5.46	5.50	4.60	5.04	5.60	5.05	5.32 ^c , 4.82 ^e
$1^1B_{1g} (n \rightarrow \pi^*)$								
ΔE 4.51	4.73	4.97	4.73	4.13	4.73	5.33	4.45	4.86 ^c , 4.23 ^e
$2^1B_{1g} (n \rightarrow \pi^*)$								
ΔE 5.99	6.45	6.87		5.87	6.64	7.73	6.00	7.65 ^c , 6.04 ^e
$3^1B_{1g} (n \rightarrow \pi^*)$								
ΔE 6.20	6.73	7.08		6.53	7.40	9.20	6.49	6.99 ^c , 6.65 ^e
$1^1B_{2g} (n \rightarrow \pi^*)$								
ΔE 5.05	5.20	5.34	5.20	4.79	5.29	5.80	4.75	5.66 ^c , 4.97 ^e
$2^1B_{2g} (n \rightarrow \pi^*)$								
ΔE 5.48	6.06	6.23		5.24	5.99	7.27	5.68	6.08 ^c , 5.33 ^e
$2^1B_{3g} (\pi \rightarrow \pi^*)$								
ΔE 8.12	8.34	8.47		8.72	9.30	9.96	7.44	8.86 ^e
Bright Singlet States								
$1^1B_{1u} (\pi \rightarrow \pi^*)$								
ΔE 7.13	6.94	7.45		6.82	6.90	6.88	7.08	7.11 ^c , 6.84 ^e
f 0.001	0.146			0.004	0.002	0.000	0.003	0.005 ^e
$2^1B_{1u} (\pi \rightarrow \pi^*)$								
ΔE 7.54	7.42	7.79		7.36	7.48	7.70	7.53	7.73 ^c , 7.51 ^e
f 0.687	0.487			0.303	0.337	0.382	0.381	0.253 ^e
$1^1B_{2u} (\pi \rightarrow \pi^*)$								
ΔE 4.89	4.93	5.12	4.93	5.46	5.58	5.74	5.07	5.83 ^c , 5.68 ^d , 5.54 ^e
f 0.045	0.109			0.050	0.064	0.088	0.047	0.07 ^d , 0.055 ^e
$2^1B_{2u} (\pi \rightarrow \pi^*)$								
ΔE 7.94	8.14	8.51		8.09	8.26	8.57	8.26	8.56 ^c , 8.19 ^e
f 0.733	0.554			0.267	0.290	0.302	0.333	0.252 ^e
$1^1B_{3u} (n \rightarrow \pi^*)$								
ΔE 1.96	2.29	2.53	2.29	1.85	2.24	2.72	2.35	2.23 ^c , 2.22 ^d , 1.90 ^e
f 0.013	0.013			0.004	0.005	0.008	0.009	0.01 ^d , 0.003 ^e
$2^1B_{3u} (n \rightarrow \pi^*)$								
ΔE 6.37	6.77	6.67		5.64	6.29	7.22	6.41	6.50 ^c , 5.84 ^e
f 0.017	0.020			0.008	0.010	0.012	0.012	0.007 ^e

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³¹.

^cPBE0/6-311++G(d,p). Ref.³².

^dB3LYP/6-31+G*. Ref.²⁴.

^eHCTH(AC)/TZ2P plus augmentation. Ref.¹⁴.

TABLE XXIX: Vertical excitation energies ΔE (eV) of the triplet states of *s*-tetrazine.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Triplet States									
$1^3A_u (n \rightarrow \pi^*)$									
ΔE	2.81	3.28	3.52	3.52	2.52	3.10	3.76	3.50	3.01 ^c
$2^3A_u (n \rightarrow \pi^*)$									
ΔE	4.85	5.04	5.03	5.03	4.00	4.43	4.99	4.84	4.72 ^c
$1^3B_{1g} (n \rightarrow \pi^*)$									
ΔE	3.76	4.14	4.21	4.21	3.32	3.63	3.90	3.92	3.68 ^c
$2^3B_{1g} (n \rightarrow \pi^*)$									
ΔE	5.68	6.37	6.60		5.61	6.33	7.53	6.27	6.61 ^c
$1^3B_{1u} (\pi \rightarrow \pi^*)$									
ΔE	4.25	4.37	4.33	4.33	4.24	3.83	2.51	4.27	3.92 ^c
$2^3B_{1u} (\pi \rightarrow \pi^*)$									
ΔE	5.09	5.40	5.38	5.38	5.12	5.24	5.36	5.26	5.41 ^c
$1^3B_{2g} (n \rightarrow \pi^*)$									
ΔE	4.67	4.94	4.93	4.93	4.17	4.48	4.76	4.64	4.67 ^c
$2^3B_{2g} (n \rightarrow \pi^*)$									
ΔE	5.30	5.97	6.04		4.77	5.62	6.91	5.78	5.76 ^c
$1^3B_{2u} (\pi \rightarrow \pi^*)$									
ΔE	4.29	4.39	4.54	4.54	4.11	4.06	3.91	4.21	4.22 ^c
$2^3B_{2u} (\pi \rightarrow \pi^*)$									
ΔE	6.81	7.08	7.36		6.42	6.63	6.94	6.94	6.80 ^c
$1^3B_{3u} (n \rightarrow \pi^*)$									
ΔE	1.45	1.61	1.89	1.89	1.11	1.42	1.69	1.88	1.35 ^c
$2^3B_{3u} (n \rightarrow \pi^*)$									
ΔE	6.14	6.54	6.53		5.36	5.97	6.83	6.36	6.13 ^c

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³¹.

^cPBE0/6-311++G(d,p). Ref.³².

3. Aldehydes, ketones and amides

TABLE XXX: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of formaldehyde.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
1^1A_1									
μ	2.43	2.44			2.31	2.48	2.70	2.56	
1^1A_2 ($n \rightarrow \pi^*$)									
ΔE	3.91	3.99	3.95	3.88	3.80	3.89	4.00	3.71	3.92 ^c , 3.65 ^d , 3.88 ^e 3.96 ^f , 4.10 ^g , 3.98 ^h
μ	1.39	1.46			1.65	1.63	1.57	1.53	
1^1B_1 ($\sigma \rightarrow \pi^*$)									
ΔE	9.09	9.14	9.18	9.10	8.80	8.89	9.09	8.76	9.03 ^c , 8.93 ^e , 8.34 ^g , 8.55 ^h
μ	0.50	0.90			0.88	0.91	0.94	0.30	
f	0.010	0.013			0.001	0.001	0.001	0.005	
2^1A_1 ($\pi \rightarrow \pi^*$)									
ΔE	10.08	9.32	9.53	9.30	9.95	9.17	9.32	9.19	8.98 ^c
μ	0.75	2.69			0.85	2.86	0.90	0.59	
f	0.280	0.451			0.340	0.350	0.111	0.126	
Triplet States									
1^3A_2 ($n \rightarrow \pi^*$)									
ΔE	3.48	3.58	3.55	3.50	3.05	3.13	3.21	3.32	3.04 ^d , 3.14 ^e 3.23 ^f , 3.4 ^g , 3.20 ^h
μ	1.13	1.35			1.50	1.45	1.34	1.05	
1^3A_1 ($\pi \rightarrow \pi^*$)									
ΔE	5.99	5.84	5.83	5.87	5.48	5.18	4.38	5.46	6.16 ^d , 5.32 ^e , 5.30 ^f 5.65 ^g , 5.36 ^h
μ	0.89	1.05			1.04	0.88	0.28	0.52	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³³.

^cB3P86/6-311(2+,2+)G**. Ref.³.

^dTDLDA/LDA/Sadlej+. Ref.³⁴.

^eB3LYP/Sadlej. Ref.⁵.

^fMPW1PW91/6-311++G**. Ref.³⁵.

^gVSXC/6-311++G(d,p). Ref.⁶.

^hPBE0/6-311++G(d,p). Ref.⁶.

TABLE XXXI: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of acetone.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
1 ¹ A ₁									
μ	2.92	2.93			3.02	3.13	3.31	3.18	
1 ¹ A ₂ ($n \rightarrow \pi^*$)									
ΔE	4.18	4.44	4.40	4.40	4.21	4.34	4.55	4.23	4.38 ^c , 4.44 ^g , 4.29 ^h
μ	2.27	1.48			1.97	1.96	1.92	1.34	
1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)									
ΔE	9.10	9.27	9.17	9.10	8.15	8.60	9.06	8.56	8.33 ^c , 8.19 ^h
μ	0.99	1.31			3.38	2.80	2.21	1.44	
f	0.010	0.011			0.001	0.000	0.000	0.000	0.002 ^h
2 ¹ A ₁ ($\pi \rightarrow \pi^*$)									
ΔE	9.16	9.31	9.65	9.40	8.76	9.04	8.97	8.53	7.88 ^c , 8.52 ^h
μ	3.94	3.18			3.33	2.89	1.73	0.70	
f	0.326	0.359			0.208	0.195	0.132	0.146	0.100 ^h
Triplet States									
1 ³ A ₂ ($n \rightarrow \pi^*$)									
ΔE	3.90	4.10	4.05	4.05	3.56	3.69	3.84	3.85	3.88 ^d , 3.86 ^e , 3.79 ^f , 3.86 ^g
μ	1.14	1.28			1.72	1.68	1.59	1.16	
1 ³ A ₁ ($\pi \rightarrow \pi^*$)									
ΔE	5.98	6.04	6.03	6.03	5.57	5.39	4.81	5.64	5.74 ^d , 5.52 ^e , 5.59 ^f , 5.84 ^g
μ	1.11	1.21			1.62	1.28	0.47	0.81	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³⁶.

^cB3P86/6-311(2+,2+)G**. Ref.³

^dMPW1PW91/6-311++G(3df,3pd). Ref.³⁵.

^eVSXC/6-311++G(d,p). Ref.⁶.

^fPBE0/6-311++G(d,p). Ref.⁶.

^gB3LYP/6-311++G(d,p). Ref.¹⁷.

^hHCTH(AC)/TZ2P plus augmentation. Ref.¹⁴.

TABLE XXXII: Vertical excitation energies ΔE (eV), and oscillator strengths f of the singlet and triplet states of *p*-benzoquinone.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
$1^1A_u (n \rightarrow \pi^*)$									
ΔE	2.50	2.77	2.85	2.77	2.02	2.58	2.55	2.29	
$1^1B_{1g} (n \rightarrow \pi^*)$									
ΔE	2.50	2.76	2.75	2.76	1.89	2.43	3.04	2.22	2.51 ^c
$1^1B_{1u} (\pi \rightarrow \pi^*)$									
ΔE	5.15	5.28	5.62	5.28	4.49	4.83	5.31	5.07	4.88 ^c
f	0.616	0.636			0.231	0.323	0.506	0.711	0.33 ^c
$2^1B_{1u} (\pi \rightarrow \pi^*)$									
ΔE	7.08	7.92	7.82		6.82	7.25	7.73	7.60	
f	0.624	0.660			0.389	0.561	0.564	0.604	
$1^1B_{3g} (\pi \rightarrow \pi^*)$									
ΔE	4.19	4.26	4.59	4.26	3.36	3.73	4.25	3.99	3.79 ^c
f	0.000	0.000			0.000	0.000	0.000	0.000	
$2^1B_{3g} (\pi \rightarrow \pi^*)$									
ΔE	6.34	6.96	7.27	6.96	6.12	6.59	7.32	6.71	
$1^1B_{3u} (n \rightarrow \pi^*)$									
ΔE	5.15	5.64	5.82	5.64	4.39	5.43	6.80	5.81	
f	0.000	0.000			0.000	0.000	0.002	0.000	
Triplet States									
$1^3A_u (n \rightarrow \pi^*)$									
ΔE	2.27	2.66	2.62	2.62	1.56	2.05	3.20	2.31	
$1^3B_{1g} (n \rightarrow \pi^*)$									
ΔE	2.17	2.62	2.51	2.51	1.44	1.92	2.42	2.21	
$1^3B_{1u} (\pi \rightarrow \pi^*)$									
ΔE	2.91	2.99	2.96	2.96	2.42	2.19	1.21	2.62	
$1^3B_{3g} (\pi \rightarrow \pi^*)$									
ΔE	3.19	3.32	3.41	3.41	2.59	2.68	2.44	3.09	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³⁷.

^cB3LYP/6-31+G*. Ref.²⁴.

TABLE XXXIII: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of formamide.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
1 ¹ A'									
μ	4.08	3.79			3.98	4.10	4.23	4.18	
2 ¹ A'									
ΔE	7.41	7.39	8.27	7.39	7.90	8.13	8.84	8.14	7.58 ^c , 7.67 ^d , 7.83 ^e
μ	6.12	6.10			3.27	2.83	1.87	1.81	
f	0.371	0.469			0.347	0.371	0.324	0.524	0.30 ^e
3 ¹ A'									
ΔE	10.50	10.54	10.93		10.98	10.92	11.38	10.57	
μ	5.24	5.10			2.27	2.22	4.14	4.51	
f	0.131	0.163			0.119	0.055	0.116	0.176	
1 ¹ A'' ($n \rightarrow \pi^*$)									
ΔE	5.61	5.63	5.65	5.63	5.46	5.55	5.77	5.47	5.43 ^c , 5.29 ^d , 5.52 ^e
μ	2.12	1.99			2.82	2.66	2.41	1.72	
f	0.001	0.001			0.001	0.001	0.001	0.001	0.00 ^e
Triplet States									
1 ³ A'									
ΔE	5.69	5.58	5.74	5.74	5.20	5.13	4.93	5.42	
μ	3.23	3.71			4.45	4.22	3.38	4.14	
1 ³ A'' ($n \rightarrow \pi^*$)									
ΔE	5.34	5.40	5.36	5.36	4.87	4.97	5.14	5.12	
μ	1.39	1.95			2.57	2.40	2.11	1.56	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³⁸.

^cHCTH(AC) results. Private communication with N. C. Handy cited in ref.³⁹.

^dCar-Parinello MD with LDA(AC). Ref.³⁹.

^eB3LYP/aug-cc-pVDZ. Ref.⁴⁰.

TABLE XXXIV: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strength f of the singlet and triplet states of acetamide.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States									
1 ¹ A'									
μ	4.00	3.77			3.95	4.06	4.22	4.15	
2 ¹ A'									
ΔE	7.21	7.27	7.67	7.27	7.50	7.46	8.14	7.51	7.35 ^c
μ	6.21	5.87			2.16	3.61	3.56	4.52	
f	0.292	0.469			0.113	0.087	0.181	0.269	0.07 ^c
3 ¹ A'									
ΔE	10.08	10.09	10.50		9.42	10.01	10.59	9.98	
μ	5.15	4.53			4.09	3.76	3.75	3.93	
f	0.179	0.163			0.129	0.224	0.146	0.219	
1 ¹ A'' ($n \rightarrow \pi^*$)									
ΔE	5.54	5.69	5.69	5.69	5.41	5.56	5.86	5.48	5.48 ^c
μ	2.19	1.79			2.43	2.33	2.16	1.38	
f	0.001	0.001			0.001	0.001	0.001	0.001	0.00 ^c
Triplet States									
1 ³ A'									
ΔE	5.57	5.63	5.88	5.88	5.26	5.26	5.14	5.52	
μ	3.81	3.31			4.15	3.83	2.90	3.61	
1 ³ A'' ($n \rightarrow \pi^*$)									
ΔE	5.24	5.41	5.42	5.42	4.85	5.01	5.25	5.13	
μ	1.61	1.70			2.19	2.08	1.89	1.25	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³⁸.

^cB3LYP/aug-cc-pVDZ. Ref.⁴⁰.

TABLE XXXV: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet and triplet states of propanamide.^a

	CASPT2 ^b	MS-CASPT2	CC3	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI
Singlet States								
1 ¹ A'								
μ	4.13	3.60			3.77	3.88	4.03	3.96
2 ¹ A'								
ΔE	7.28	7.20	7.62	7.20	7.28	7.76	8.09	7.46
μ	5.59	5.78			4.45	4.74	3.45	4.75
f	0.346	0.405			0.081	0.107	0.133	0.208
3 ¹ A'								
ΔE	9.95	9.94	10.06		8.17	9.00	10.07	9.51
μ	4.59	4.21			1.50	2.96	4.31	3.57
f	0.205	0.275			0.077	0.085	0.098	0.148
1 ¹ A'' ($n \rightarrow \pi^*$)								
ΔE	5.48	5.72	5.72	5.72	5.43	5.59	5.89	5.47
μ	1.90	1.70			2.29	2.21	2.07	1.26
f	0.001	0.001			0.000	0.000	0.000	0.001
Triplet States								
1 ³ A'								
ΔE	5.94	5.80	5.90	5.90	5.27	5.28	5.18	5.51
μ	2.47	3.47			4.15	3.84	2.94	3.49
1 ³ A'' ($n \rightarrow \pi^*$)								
ΔE	5.28	5.45	5.45	5.45	4.89	5.04	5.29	5.13
μ	1.41	1.62			2.07	1.98	1.80	1.13

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.³⁸.

4. Nucleobases

TABLE XXXVI: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet states of cytosine.^a

	CASPT2 ^b	MS-CASPT2	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States								
1 ¹ A'								
μ	7.2	6.34		6.59	6.84	7.16	7.00	
2 ¹ A' (L _a)								
ΔE	4.39	4.67	4.66	4.20	4.64	5.19	4.62	4.65 ^c
μ	4.7	4.58		3.35	3.94	4.97	3.71	
f	0.061	0.093		0.015	0.035	0.075	0.072	0.040 ^c
3 ¹ A' (L _b)								
ΔE	5.36	5.53	5.62	4.92	5.42	6.16	5.43	5.39 ^c
μ	7.0	5.73		6.45	6.66	6.88	7.02	
f	0.108	0.351		0.061	0.087	0.147	0.171	0.085 ^c
4 ¹ A' (B _a)								
ΔE	6.16	6.40		6.49	6.72	6.99	6.38	6.11 ^c
μ	6.2	5.92		3.60	6.25	8.16	6.08	
f	0.863	0.621		0.308	0.368	0.500	0.711	0.118 ^c
5 ¹ A' (B _b)								
ΔE	6.74	6.97		6.37	6.46	7.44	6.74	6.46 ^c
μ	9.3	7.02		2.19	7.81	7.12	8.50	
f	0.147	0.369		0.167	0.177	0.225	0.222	0.304 ^c
1 ¹ A''								
ΔE	5.00	5.12	4.87	3.79	4.76	6.21	4.86	4.76 ^c
μ	4.7	2.56		1.26	2.12	4.35	2.26	
f	0.005	0.003		0.000	0.001	0.000	0.002	0.001 ^c
2 ¹ A''								
ΔE	6.53	5.53	5.26	4.49	5.11	5.64	5.32	5.14 ^c
μ	6.4	2.74		4.43	3.10	1.60	0.54	
f	0.001	0.002		0.001	0.001	0.002	0.002	0.000 ^c

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.⁴¹.

^cB3LYP/6-311(5+,5+)G(df,pd). Ref.⁴².

TABLE XXXVII: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet states of thymine.^a

	CASPT2 ^b	MS-CASPT2	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States								
1 ¹ A'								
μ	5.0	4.19		4.39	4.55	4.78	4.67	
2 ¹ A'								
ΔE	4.88	5.06	5.20	4.60	5.00	5.48	5.18	4.96 ^c
μ	6.5	5.92		4.65	4.94	5.25	5.90	
f	0.170	0.334		0.074	0.136	0.232	0.251	0.139 ^c
3 ¹ A'								
ΔE	5.88	6.15	6.27	5.33	5.97	6.94	5.98	5.95 ^c
μ	1.5	1.61		1.30	1.58	2.54	1.78	
f	0.170	0.067		0.064	0.071	0.057	0.113	0.067 ^c
4 ¹ A'								
ΔE	6.10	6.53	6.53	5.85	6.31	7.03	6.42	6.19 ^c
μ	7.8	6.66		5.65	6.43	5.85	7.50	
f	0.150	0.353		0.102	0.142	0.247	0.264	0.116 ^c
5 ¹ A'								
ΔE	7.13	7.43		6.93	7.47	8.17	7.36	7.37 ^c
μ	3.1	3.05		1.34	2.51	3.07	2.89	
f	0.850	0.674		0.189	0.411	0.354	0.441	0.239 ^c
1 ¹ A''								
ΔE	4.39	4.95	4.82	4.09	4.70	5.30	4.48	4.69 ^c
μ	3.2	2.52		1.01	1.96	2.92	3.25	
2 ¹ A''								
ΔE	5.91	6.38	6.16	4.79	5.80	6.77	5.93	5.81 ^c
μ	4.6	3.92		5.08	5.65	4.59	4.98	
3 ¹ A''								
ΔE	6.15	6.85		5.33	6.21	7.70	6.43	6.19 ^c
μ	8.6	6.46		4.49	2.21	6.49	5.71	
4 ¹ A''								
ΔE	6.70	7.43		6.13	6.69	8.03	6.86	
μ	4.1	2.27		4.14	3.16	3.72	2.64	
f	0.000	0.000		0.000	0.000	0.001	0.000	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹⁶.

^cB3LYP/6-311(5+,5+)G(df,pd). Ref.⁴².

TABLE XXXVIII: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet states of uracil.^a

	CASPT2 ^b	MS-CASPT2	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States								
1 ¹ A'								
μ	4.4	4.31		4.46	4.63	4.87	4.71	
2 ¹ A'								
ΔE	5.00	5.23	5.35	4.77	5.19	5.67	5.33	5.17 ^c
μ	6.3	5.78		5.12	5.15	5.32	6.02	
f	0.190	0.321		0.058	0.130	0.234	0.269	0.134 ^c
3 ¹ A'								
ΔE	5.82	6.15	6.26	5.21	5.87	6.90	5.92	5.89 ^c
μ	2.4	2.48		1.30	1.87	2.70	2.45	
f	0.080	0.047		0.046	0.040	0.046	0.069	0.037 ^c
4 ¹ A'								
ΔE	6.46	6.74	6.70	6.01	6.50	7.21	6.56	6.42 ^c
μ	6.9	6.52		3.61	5.92	6.91	7.03	
f	0.290	0.249		0.056	0.120	0.182	0.214	0.117 ^c
5 ¹ A'								
ΔE	7.00	7.42		7.06	7.45	8.09	7.31	7.36 ^c
μ	3.7	3.16		2.44	2.70	3.15	2.78	
f	0.760	0.804		0.207	0.440	0.412	0.487	0.117 ^c
1 ¹ A''								
ΔE	4.54	4.91	4.80	3.97	4.63	5.27	4.41	4.66 ^c
μ	3.4	2.23		0.82	1.55	2.49	2.72	
2 ¹ A''								
ΔE	6.00	6.28	6.10	4.76	5.74	6.61	5.84	5.79 ^c
μ	4.8	4.25		5.64	5.51	5.00	5.31	
f	0.000	0.000		0.000	0.000	0.001	0.000	
3 ¹ A''								
ΔE	6.37	6.98	6.56	5.23	6.14	7.72	6.43	6.15 ^c
μ	8.7	2.17		4.16	2.75	6.38	4.52	
4 ¹ A''								
ΔE	6.95	7.28		6.11	6.64	7.91	6.79	
μ	3.6	6.86		4.74	3.47	2.97	2.20	
f	0.000	0.000		0.000	0.000	0.000	0.001	

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.¹⁶.

^cB3LYP/6-311(5+,5+)G(df,pd). Ref.⁴².

TABLE XXXIX: Vertical excitation energies ΔE (eV), dipole moment μ (D), and oscillator strengths f of the singlet states of adenine.^a

	CASPT2 ^b	MS-CASPT2	Best. Est.	BP86	B3LYP	BHLYP	DFT/MRCI	TD-DFT
Singlet States								
1 ¹ A'								
μ	2.50	2.53		2.46	2.50	2.55	2.55	
2 ¹ A'								
ΔE	5.13	5.20	5.25	4.99	5.27	5.67	4.99	5.21 ^c
μ	2.37	2.19		2.48	2.80	3.27	2.88	
f	0.070	0.154		0.050	0.047	0.019	0.058	0.035 ^c
3 ¹ A'								
ΔE	5.20	5.29	5.25	4.57	5.00	5.48	5.15	4.94 ^c
μ	2.30	2.52		2.20	2.16	2.26	1.99	
f	0.370	0.193		0.123	0.195	0.297	0.311	0.215 ^c
4 ¹ A'								
ΔE	6.24	6.34		5.84	6.32	6.87	6.29	5.93 ^c
μ	2.13	2.09		3.92	2.42	1.06	2.38	
f	0.851	0.536		0.100	0.240	0.421	0.616	0.003 ^c
5 ¹ A'								
ΔE	6.72	6.64		6.27	6.69	7.30	6.19	6.16 ^c
μ	4.60	3.45		1.66	2.96	3.18	1.85	
f	0.159	0.001		0.125	0.107	0.159	0.001	0.130 ^c
6 ¹ A'								
ΔE	6.99	6.87		6.65	7.08	7.71	7.10	
μ	3.42	2.86		4.02	3.80	4.05	3.68	
f	0.565	0.010		0.040	0.137	0.125	0.373	
7 ¹ A'								
ΔE	7.57	7.56		6.91	7.52	8.22	6.62	
μ	6.41	0.97		4.39	3.77	2.45	4.34	
f	0.406	0.036		0.345	0.244	0.024	0.051	
1 ¹ A''								
ΔE	6.15	5.19	5.12	4.30	4.97	5.81	5.11	4.93 ^c
μ	2.14	1.48		0.68	0.38	1.44	1.03	
f	0.001	0.001		0.000	0.000	0.000	0.001	0.001 ^c
2 ¹ A''								
ΔE	6.86	5.96	5.75	5.05	5.61	6.34	5.72	5.56 ^c
μ	1.93	0.39		2.05	1.40	0.95	0.34	
f	0.001	0.007		0.001	0.001	0.002	0.004	0.002 ^c

^aAll own calculations (columns MS-CASPT2, CC3, BP86, B3LYP, BHLYP, DFT/MRCI) employ MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and the TZVP basis. SA-CASSCF/MS-CASPT2 and CC3 results as well as best estimates taken from Ref.¹.

^bPublished CASPT2 result. Ref.⁴³.

^cB3LYP/6-311(3+,3+)G(df,pd). Ref.⁴².

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Paper IV

*Benchmark of electronically excited states
for semiempirical methods: MNDO, AM1, PM3,
OM1, OM2, OM3, INDO/S and INDO/S2*

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Benchmark of Electronically Excited States for Semiempirical Methods: MNDO, AM1, PM3, OM1, OM2, OM3, INDO/S, and INDO/S2

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Abstract: Semiempirical configuration interaction (CI) calculations with eight different Hamiltonians are reported for a recently proposed benchmark set of 28 medium-sized organic molecules. Vertical excitation energies and one-electron properties are computed using the same geometries as in our previous ab initio benchmark study on electronically excited states. The CI calculations for the standard methods (MNDO, AM1, PM3) and for the orthogonalization-corrected methods (OM1, OM2, OM3) include single, double, triple, and quadruple excitations (CISDTQ) using the graphical unitary group approach (GUGA) as implemented in the MNDO code. The CIS calculations for the established INDO/S method and the reparametrized INDO/S2 variant employ a modified version of the ZINDO program. As compared to the best theoretical reference data from the ab initio benchmark, all currently applied semiempirical methods tend to underestimate the vertical excitation energies, but the errors are much larger in the case of the standard methods (MNDO, AM1, PM3). Overall, the mean absolute deviations relative to the theoretical best estimates are lowest for OM3, and only slightly higher for OM1 and OM2 (in the range of 0.4–0.5 eV). INDO/S performs similar to OM2 for the vertical excitation energies of singlet states, but deteriorates considerably for triplet states. The INDO/S2 reparametrization for oxygen improves the results for low-lying singlet states of oxygen-containing compounds, but makes them worse for high-lying singlets as well as for triplets. The ab initio reference data for oscillator strengths and excited-state dipole moments are again best reproduced by the orthogonalization-corrected approaches (OM1, OM2, OM3), which thus emerge as the most favorable semiempirical methods overall for treating valence excited states of large organic chromophores.

1. Introduction

In recent years, there has been much progress in the research on electronically excited states. Elaborate experimental techniques are available to study photophysical processes in the nanosecond or femtosecond regime. Concomitantly, improved theoretical methods have been developed that allow realistic calculations on excited states and may thus provide guidance for the experimental work. On the ab initio side, MS-CASPT2 (multistate complete-active-space second-order perturbation theory)^{1–4} and

coupled cluster methods (CC2, CCSD, CC3)^{5–7} are well established and offer high accuracy for small molecules. Time-dependent density functional theory (TD-DFT)⁸ has become popular for calculations on medium-sized molecules, giving reasonable results for various (but not all) types of excited states at relatively low computational cost.^{9,10} An alternative DFT-based method makes use of Kohn–Sham orbitals in a multireference configuration interaction (MRCI) framework, modified by incorporating five universal empirical parameters to alleviate problems with the double counting of dynamic electron correlation.¹¹

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For a quantitative assessment of different theoretical approaches, reliable reference data are needed for benchmarking. Standard test sets are widely used for ground-state properties, for example, the G2 and G3 sets for thermochemistry.^{12,13} We have recently introduced an ab initio benchmark set for electronically excited states of 28 medium-sized organic molecules with a total of 223 excitations.¹⁴ On the basis of MS-CASPT2 and CC3 calculations on these molecules and of high-level ab initio data from the literature, we have proposed theoretical best estimates for the vertical excitation energies of 104 singlet and 63 triplet excited states. These reference data have been used to evaluate the performance of standard TD-DFT and DFT/MRCI approaches,¹⁵ of the coupled cluster variant CCSDR(3) with noniterative triples corrections,¹⁶ and of TD-DFT with a large number of different functionals^{17,18} including double-hybrid functionals.¹⁸

Despite recent advances, the reliable description of electronically excited states in large molecules is still a challenging problem. Accurate ab initio methods such as MS-CASPT2 and CC3 are restricted to small molecules, and the computational cost for simpler treatments such as CC2 or DFT/MRCI still rises steeply with molecular size. TD-DFT is an attractive choice because of its computational efficiency and the availability of analytical gradients, but there are a number of well-documented problems of TD-DFT,^{9,10} for example, with regard to charge-transfer states¹⁹ and singlet or triplet instabilities.²⁰ Moreover, the overall accuracy of TD-DFT is limited, with vertical excitation energies that typically show mean absolute deviations in the range of 0.3–0.5 eV from the theoretical best estimates in our benchmark set.¹⁵ Given this situation, it seems worthwhile to explore the performance of semiempirical quantum-chemical methods for electronically excited states of large organic molecules.

Standard semiempirical molecular orbital (MO) methods such as MNDO,²¹ AM1,²² and PM3²³ are based on the NDDO (neglect of diatomic differential overlap) integral approximation and have been parametrized against ground-state properties, in particular heats of formation and geometries. They have been widely applied in computational studies of ground-state processes (for reviews, see, for example, refs 24–26). Applications to electronically excited states^{27,28} are rare, however, mainly because these standard methods normally underestimate their energies strongly, as a result of the integral approximations and the ground-state parametrization. A straightforward remedy for this shortcoming would be a system-specific reparameterization²⁹ for a given application (see, for example, ref 30), which is, however, cumbersome in practice and also unsatisfactory from a conceptual point of view.

For the semiempirical calculation of vertical excitation energies, INDO/S (intermediate neglect of differential overlap for spectroscopy)^{31,32} has been the method of choice for a long time. INDO/S describes excited states by CIS (configuration interaction with single excitations) and has been parametrized at this level. It has been widely used in studies of organic molecules^{31,32} as well as transition metal complexes³³ and even lanthanides.³⁴ The INDO/S2 variant³⁵ is

a reparametrization designed to improve the results for oxygen-containing compounds. The lack of higher excitations in the INDO/S CI treatment effectively restricts applications to states dominated by single excitations. Another limitation is the focus on vertical processes: by its design, INDO/S targets spectroscopy rather than photochemistry, and it is thus not made for the exploration of excited-state potential energy surfaces (PES).

The orthogonalization-corrected OM x methods (OM1,^{36,37} OM2,^{38,39} and OM3⁴⁰) employ the NDDO integral approximation, but go beyond the standard methods (MNDO, AM1, PM3) by including additional terms in the Fock matrix that represent Pauli exchange repulsions in an approximate manner. These terms effectively raise the energy of antibonding virtual MOs and of the associated excited states.^{37,39} Therefore, one would expect an improved performance of the OM x methods not only for ground-state properties,⁴¹ but also for excited-state properties, which had not been taken into account during the OM x parametrization. The applications published so far support this view, for example, the OM2 studies on the electronically excited states of butadiene,⁴² retinal model systems,⁴³ and the rhodopsin chromophore.⁴⁴ In addition, OM2 predicts reasonable geometries for a set of 12 typical conical intersections⁴⁵ (as compared to ab initio reference data). Finally, OM2 has successfully been applied in excited-state surface-hopping dynamics calculations for several small molecules,⁴⁶ for all nucleobases,^{47–49} and for retinal models.⁵⁰ These promising indications call for a more comprehensive assessment, with detailed comparisons to established semiempirical treatments.

In this Article, we present a systematic evaluation of the performance of the standard NDDO-based semiempirical methods (MNDO, AM1, PM3), the commonly used INDO-based approaches (INDO/S, INDO/S2), and the orthogonalization-corrected methods (OM1, OM2, OM3) for electronically excited states. Reference data are taken from our previous benchmark work and comprise theoretical best estimates as well as MS-CASPT2/TZVP and CC3/TZVP data.¹⁴ This Article is structured as follows: Section 2 describes the computational methods used. Section 3 presents some general considerations on the current benchmarking. Sections 4 and 5 discuss the individual results for vertical excitation energies and one-electron properties, respectively. Section 6 is devoted to statistical evaluations, and section 7 offers a brief summary and outlook.

2. Computational Methods

All calculations were carried out at the optimized ground-state equilibrium geometries reported previously.^{14,51} The standard semiempirical Hamiltonians with default parameters were used for MNDO, AM1, PM3, OM1, OM2, and OM3, as implemented in the current version of the MNDO99 code.⁵² In the case of INDO/S, singlet states were computed using the default parameters, with $f_{\pi\pi} = 0.585$ and the Mataga–Nishimoto expression for the two-center two-electron repulsion integrals, while triplet states were treated using the recommended special parametrization and the Pariser–Parr formula for the Coulomb integrals.³² The

Table 1. OM2 Results for the Two Lowest Singlet Excited States of the Linear Polyenes with k Double Bonds, for Different Types of CI Treatment^a

threshold (%)	FCI	CISDTQ	MR-CISD ^a			
			90	85	80	75
$k = 3$						
2 ¹ A _g (eV)	4.86	4.86	4.86	4.87	4.87	4.89
1 ¹ B _u (eV)	5.33	5.33	5.33	5.33	5.33	5.32
CSFs (references) ^b	175	165	162 (10)	150 (7)	146 (6)	126 (5)
CPU time (s) ^c	0.03	0.03	0.03	0.03	0.03	0.02
$k = 4$						
2 ¹ A _g (eV)	4.19	4.20	4.21	4.22	4.25	4.25
1 ¹ B _u (eV)	4.79	4.79	4.78	4.78	4.78	4.78
CSFs (references) ^b	1764	1195	916 (12)	758 (9)	651 (6)	651 (6)
CPU time (s) ^c	0.35	0.25	0.22	0.17	0.14	0.15
$k = 5$						
2 ¹ A _g (eV)	3.68	3.72	3.74	3.75	3.78	3.79
1 ¹ B _u (eV)	4.40	4.41	4.39	4.38	4.37	4.38
CSFs (references) ^b	19 404	6601	4067 (16)	3079 (11)	2207 (7)	2003 (6)
CPU time (s) ^c	10.80	2.22	1.21	1.06	0.48	0.42
$k = 6$						
2 ¹ A _g (eV)	3.32	3.41	3.41	3.43	3.48	3.50
1 ¹ B _u (eV)	4.11	4.13	4.10	4.09	4.07	4.08
CSFs (references) ^b	226 512	28 278	13 254 (20)	8781 (13)	5931 (8)	4868 (6)
CPU time (s) ^c	446.09	17.90	6.98	4.05	2.15	1.52
$k = 7$						
2 ¹ A _g (eV)	3.06	3.20	3.19	3.22	3.27	3.30
1 ¹ B _u (eV)	3.75	3.87	3.88	3.87	3.85	3.85
CSFs (references) ^b	2 760 615	98 785	35 336 (26)	24 531 (16)	15 982 (9)	11 380 (7)
CPU time (s) ^c	144 070.91 ^d	120.37	32.42	17.01	8.30	5.10

^a See text. Active space composed of all π and π^* orbitals. Geometries optimized at the B3LYP/TZVP level. ^b Total number of configuration state functions in A_g and B_u symmetry (total number of reference configurations in MR-CISD given in parentheses). ^c Computation times refer to one AMD Opteron(tm) 845 2.8 GHz processor. ^d A semidirect algorithm is used, with all coupling coefficients being recomputed as needed.

INDO/S and INDO/S2 calculations were done with the ZINDO-MN program, version 1.2.⁵³

Consistent with the underlying parametrization procedure, the INDO/S and INDO/S2 results were obtained at the CIS level. Following standard INDO/S conventions, the active space generally included the 10 highest occupied MOs and the 10 lowest unoccupied MOs, yielding a total of 101 configuration state functions (CSF).³¹ In small molecules with less MOs, all occupied and unoccupied MOs were normally included, but high-lying states were treated with caution: when large spurious $\sigma \rightarrow \sigma^*$ contributions were encountered, the corresponding σ^* MOs were deleted from the active space. The excited-state dipole moments were computed using the recommended class IV charge model 2 (CM2).³⁵

The NDDO-based semiempirical methods considered presently (MNDO, AM1, PM3, OM1, OM2, OM3) have been parametrized against ground-state reference data at the SCF (self-consistent-field) level, so that the effects of dynamic ground-state correlation should conceptually be taken into account in an average manner through the parametrization (and through the use of damped two-electron integrals). In electronically excited states, however, there are often static (near-degeneracy) correlation effects, which call for an explicit treatment also in a semiempirical framework, using a suitably chosen (small) active space. To be as unbiased as possible, we adopted a canonical active space with m electrons in n orbitals (mn) for each molecule, in analogy to our previous MS-CASPT2 benchmark study.¹⁴

This active space includes all occupied and unoccupied π -MOs in the case of $\pi \rightarrow \pi^*$ excitations, and in addition the occupied lone-pair MOs in the case of $n \rightarrow \pi^*$ excitations. For a given active space, the least biased correlation treatment is full CI, which, however, quickly becomes too expensive even at the semiempirical level. Therefore, our standard approach in the present benchmark was chosen to be the single-reference CISDTQ treatment, which includes all single, double, triple, and quadruple excitations relative to the closed-shell SCF determinant and which is expected to provide a balanced description of all relevant states (close to the full CI limit).

To check the performance and efficiency of different CI approaches, we performed test calculations on linear polyenes with k double bonds using the CI implementation in the MNDO99 code that is based on the graphical unitary group approach (GUGA).⁵⁴ Table 1 lists the OM2 results obtained from full CI (FCI), CISDTQ, and various MR-CISD treatments (multireference CI with single and double excitations), which are approximations to CISDTQ. It is obvious that the excitation energies from FCI calculations are reproduced very well by CISDTQ; the deviations (which increase with molecular size) are mostly much smaller than 0.1 eV. At the same time, the computational costs are much reduced for CISDTQ, for example, by a factor of 25 in the case of $k = 6$ where an in-core FCI treatment is still feasible; the much larger factor for $k = 7$ is caused by the switch to a less efficient semidirect FCI algorithm in the MNDO99 code (due to the large size of the CI matrix). In the MR-CISD

Table 2. Statistical Results and Computation Times (s) for the Set of 222 Vertical Excitation Energies (in eV) Using Different Levels of Excitation in the CI Treatment for the OM1, OM2, and OM3 Methods^a

threshold (%)	FCI	CISDTQ	MR-CISD ^b			
			90	85	80	75
OM1						
count ^c		222	222	222	222	222
mean		0.01	0.03	0.03	0.03	0.03
abs. mean		0.01	0.03	0.03	0.03	0.03
std. dev.		0.01	0.05	0.05	0.06	0.06
max. (+) dev.		0.04	0.27	0.28	0.30	0.28
max. (−) dev.			0.14	0.13	0.13	0.13
CPU time (s) ^d	513.84	54.13	20.04	16.61	15.53	13.96
OM2						
count ^c		222	222	222	222	222
mean		0.00	0.02	0.02	0.03	0.03
abs. mean		0.00	0.02	0.02	0.03	0.03
std. dev.		0.01	0.04	0.04	0.05	0.05
max. (+) dev.		0.03	0.16	0.18	0.19	0.19
max. (−) dev.			0.01	0.01	0.02	0.02
CPU time (s) ^d	510.65	52.53	18.09	15.74	14.88	13.62
OM3						
count ^c		222	222	222	222	222
mean		0.00	0.02	0.02	0.02	0.03
abs. mean		0.00	0.02	0.02	0.03	0.03
std. dev.		0.01	0.04	0.04	0.05	0.05
max. (+) dev.		0.04	0.16	0.17	0.16	0.21
max. (−) dev.			0.03	0.03	0.02	0.02
CPU time (s) ^d	485.64	52.42	17.62	15.30	14.02	13.42

^a Results from a full CI within the selected active space are taken as reference. ^b See text. ^c Total number of states considered. ^d Computation times refer to one Intel Pentium 4-EMT64T 3.40 GHz processor.

calculations, the reference configurations are selected by an iterative procedure to fulfill the requirement that their combined weight in the CI wave function must exceed a given threshold value (for example, 90% or 85%); starting from a single-reference calculation, this is accomplished by adding the next most important reference configurations until this condition is satisfied (normally within one or two iterations). It is again evident that the MR-CISD results are essentially identical to the CISDTQ results and that they can be obtained at significantly less cost. This conclusion is corroborated by the corresponding data for all other benchmark molecules that are documented in the Supporting Information (see Tables S1–S6) and by the statistical data collected in Table 2. For the full set of vertical excitation energies in our benchmark, the mean absolute deviations from the OMx/FCI reference values amount to 0.00–0.01 eV for OMx/CISDTQ and to 0.02–0.03 eV for OMx/MR-CISD (thresholds 75–90%). In actual applications, it is thus perfectly legitimate to perform such semiempirical excited-state studies at the MR-CISD level; a threshold of 85% seems more than sufficient to ensure close reproduction of the CISDTQ and the FCI results. For the purposes of the present benchmark, we shall, however, rely on CISDTQ.

A final remark in this section concerns the efficiency of semiempirical CI methods relative to TD-DFT. For a direct comparison, we have computed the three low-lying ¹B₂ excited states of pyridine using the MNDO99 code for OM2/CISDTQ and the TURBOMOLE package (version 5.9.1)⁵⁵ for TDDFT-B3LYP/TZVP (starting from a previously converged SCF solution). The ratio of computation times is

1:1578 on a single-processor Intel Pentium 4-EMT64T (3.4 GHz), indicating a difference of about 3 orders of magnitude for a typical example from our benchmark suite. It is clear that the superior speed of the semiempirical CI methods will allow applications that are not feasible with TD-DFT or the even more costly ab initio methods, for example, calculations on larger chromophores or extended excited-state dynamics runs, provided that the accuracy of the semiempirical results is sufficient.

3. General Considerations

Geometries. As already mentioned, the presently used geometries are taken from our previous benchmark.¹⁴ They represent equilibrium ground-state geometries optimized at the MP2/6-31G* level in a suitable point group (assuming the highest symmetry possible). For the sake of consistency, it is obviously advantageous to adopt a common set of geometries during benchmarking, but one may still wonder by how much the results would change upon reoptimizing the geometries at the semiempirical level. One would actually expect rather small changes because semiempirical methods generally yield realistic ground-state geometries for organic molecules (see ref 41 for corresponding statistical data). Test calculations on several of the benchmark molecules confirm this view. Table S7 (Supporting Information) lists the results for a typical example, two low-lying states of pyridine obtained at geometries optimized with MP2/6-31G*, AM1, and OM2. The computed AM1 and OM2 excitation energies vary by up to 0.1 eV for the different geometries, the (small) oscillator strengths appear to be rather insensitive, and the excited-state dipole moments show variations of around 0.1 D. Overall, these changes are small enough to justify the assumption that the qualitative conclusions of the present benchmark study will remain valid also when using geometries optimized at the semiempirical level.

States. Semiempirical methods employ a minimal basis of valence orbitals and can therefore not describe Rydberg states or states with substantial valence/Rydberg mixing properly. The currently used benchmark set was designed to include only valence excited states¹⁴ and should thus be suitable for an assessment of semiempirical methods. One should keep in mind, however, that there is no clear-cut distinction between valence and other excited states in ab initio calculations, and there will be borderline cases especially for higher-lying states whose character may even change at different ab initio levels.⁵⁶ Despite these caveats, we present semiempirical results for all valence states considered previously,¹⁴ while acknowledging that it may be easier for semiempirical methods to properly describe the low-lying valence states (say, below 6 eV).

Assignments. For each benchmark molecule, the electronically excited states were first classified according to point-group symmetry. Thereafter, within a given irreducible representation, one has to establish the proper correspondence between the states obtained in the ab initio reference calculations¹⁴ and the present semiempirical calculations. This was accomplished by comparing the computed excited-state wave functions, along with the excitation energies, oscillator strengths, and excited-state dipole moments. Pro-

ceeding in this manner, a satisfactory mapping has been achieved in all cases. However, one specific problem should be pointed out. It is well-known^{38,39} that the standard NDDO-based methods (MNDO, AM1, PM3) underestimate the gap between bonding and antibonding MOs, with the latter ones being too low in energy because of the symmetric splitting of bonding and antibonding levels. This creates special problems in alternant hydrocarbons and related molecules, where two singly excited configurations strongly contribute to two excited states, which qualitatively correspond to the plus and minus combination of these configurations (for example, $\text{HOMO} \rightarrow \text{LUMO} + 1$ and $\text{HOMO} - 1 \rightarrow \text{LUMO}$ generating the L_b and B_b states in the polyenes). In the case of the standard NDDO-based methods, it is easier to populate a higher unoccupied orbital than to vacate the alternancy-related lower occupied orbital (as compared to ab initio methods). Therefore, the relative energies of the two corresponding singly excited configurations will differ, which will translate into different weights in the resulting CI wave functions of the corresponding pair of states. Such differences in the character of states have indeed been observed between standard NDDO-based and ab initio results, with the assignment based primarily on the character of the states in these cases.

4. Vertical Excitation Energies

From our previous study,¹⁴ we have MS-CASPT2 reference data for 152 singlet states and 71 triplet states, and theoretical best estimates (TBE) for the vertical excitation energies of 104 singlet states and 63 triplet states. The full set of the computed semiempirical vertical excitation energies is given in Tables 3 and 4 along with the corresponding MS-CASPT2 and TBE results. INDO/S and INDO/S2 values are listed for all molecules, although they differ only for oxygen-containing compounds (INDO/S2 reparametrization for oxygen). For the OMx methods, the vertical excitation energies obtained from FCI, CISDTQ, and MR-CISD (thresholds 75–90%) calculations are documented in more detail in the Supporting Information (Tables S1–S6). A compilation of experimental data is available from one of our previous papers.⁵¹

In the following discussion of the results, we will focus on comparisons with the TBE values, but our qualitative conclusions remain valid also when considering CASPT2 or CC3 reference data.

Ethene, Butadiene, Hexatriene, and Octatetraene. The energy of the singlet $\pi\pi^*$ state of ethene (TBE 7.80 eV) is well reproduced by the OMx methods (errors of less than 0.1 eV), but strongly underestimated by the standard MNDO-type methods (by 1.2–1.6 eV) and somewhat overestimated by INDO/S (by 0.53 eV). The energy of the triplet $\pi\pi^*$ state of ethene (TBE 4.50 eV) is underestimated by all semiempirical methods, but to a varying extent (MNDO/AM1/PM3 by 1.5–1.9 eV, INDO/S by 1.3 eV, OMx by 0.34–0.43 eV).

Butadiene is the first member of the $C_{2n}H_{2n+2}$ polyene series. The excitation energy to the bright $1^1B_u \pi\pi^*$ state (TBE 6.18 eV) is well predicted by the OMx methods (errors

of less than 0.1 eV) and also by INDO/S (too low by 0.21 eV), while the MNDO/AM1/PM3 values are again much too low (by 1.4–1.9 eV). More interesting is the dark $2^1A_g \pi\pi^*$ state, which is mainly composed of two single excitations ($\text{HOMO} \rightarrow \text{LUMO} + 1$ and $\text{HOMO} - 1 \rightarrow \text{LUMO}$) and the double excitation $\text{HOMO} \Rightarrow \text{LUMO}$ (contributing about 33% to the CISDTQ wave function of any of the NDDO-based methods). While it has been recognized early on that this state becomes the lowest excited singlet for longer polyenes,^{57,58} its position in butadiene has remained controversial for a long time. Relative to the currently adopted TBE of 6.55 eV, the excitation energies from MNDO/AM1/PM3 and from OMx are too low by 2.0–2.7 and 0.57–0.67 eV, respectively. The standard INDO/S CIS approach does not capture the double-excitation character of the 2^1A_g state and thus overestimates its energy by 0.32 eV; it has been pointed out⁵⁹ that inclusion of the doubly excited $\text{HOMO} \Rightarrow \text{LUMO}$ configuration reduces the error significantly (to 0.06 eV). This is partly fortuitous, however, because other doubly excited configurations contribute another 20% to the OMx/CISDTQ wave functions such that this state is actually dominated by double excitations. The energies of the two lowest triplet $\pi\pi^*$ states of butadiene (1^3B_u and 2^1A_g) are again underestimated by all semiempirical methods, least so by OMx (errors of 0.30–0.59 eV).

In hexatriene and octatetraene, we focus on the state ordering of the two lowest singlet excited states, 2^1A_g and 1^1B_u . The energy gap between these states is minute in hexatriene (TBE 0.01 eV) and still small in octatetraene (TBE 0.19 eV), with 2^1A_g being lower. MNDO/AM1/PM3 and OMx overestimate these gaps by 1.0–1.4 and 0.47–0.70 eV, respectively; in the case of OMx, the 1^1B_u state is described quite well (too high by 0.04–0.26 eV), while the 2^1A_g state comes out too stable (by 0.23–0.38 eV). As expected, INDO/S CIS calculations give the wrong state ordering for these two small polyenes, with 2^1A_g more than 1.0 eV above 1^1B_u (including the doubly excited $\text{HOMO} \Rightarrow \text{LUMO}$ configuration in the CI calculation does not recover the correct state ordering). The energies for the lowest 1^3B_u triplet state of hexatriene (TBE 2.40 eV) and octatetraene (TBE 2.20 eV) are well reproduced by OMx (errors of 0.11 eV or less), while those for the 1^3A_g triplet state (TBE 4.15 and 3.55 eV) are somewhat underestimated (by 0.31–0.42 eV). It should also be noted that all six NDDO-based methods predict realistic singlet–triplet energy differences (which may be important photochemically): the TBE differences $\Delta\Delta E$ ($1^1B_u - 1^3B_u$) are reproduced to within 0.17–0.28 eV for hexatriene and 0.19–0.33 eV for octatetraene, and even better in the case of the A_g states (absolute deviations of at most 0.12 and 0.21 eV, respectively).

Cyclopropene, Cyclopentadiene, Norbornadiene, Benzene, and Naphthalene. The energies of the singlet and triplet excited states of cyclopropene are generally underestimated by all NDDO-based methods. For instance, in the case of the $1^1B_2 \pi\pi^*$ state (TBE 7.06 eV), the deviations are about 1.5 eV for MNDO/AM1/PM3 and 0.47–0.67 eV for OMx. This state is rather diffuse at the CASSCF level⁶⁰ and may thus be problematic for methods using minimal basis sets.

Table 3. Vertical Singlet Excitation Energies ΔE (eV) of All Evaluated Molecules As Compared to MS-CASPT2/TZVP Results and Theoretical Best Estimates (TBE)

molecule	state	CASPT2 ^a	TBE ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
ethene	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.54	7.80	6.18	6.63	6.63	7.82	7.78	7.85	8.33	8.33
<i>E</i> -butadiene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	6.47	6.18	5.18	5.46	5.45	6.24	6.22	6.26	5.97 ^c	5.97
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	6.62	6.55	3.90	4.41	4.53	5.88	5.96	5.98	6.87 ^c	6.87
hexatriene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	5.31	5.10	4.59	4.78	4.77	5.35	5.33	5.36	4.86 ^c	4.86
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.42	5.09	3.23	3.63	3.74	4.79	4.86	4.86	5.90 ^c	5.90
all- <i>E</i> -octatetraene	2 ¹ A _g ($\pi \rightarrow \pi^*$)	4.64	4.47	2.81	3.13	3.24	4.09	4.14	4.13	5.23 ^c	5.23
	1 ¹ B _u ($\pi \rightarrow \pi^*$)	4.70	4.66	4.23	4.36	4.35	4.79	4.77	4.79	4.20 ^c	4.20
cyclopropene	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	6.76	6.76	5.22	5.35	5.67	6.33	5.75	5.93	6.92 ^d	6.92
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.06	7.06	5.58	5.54	5.58	6.59	6.42	6.39	6.90 ^d	6.90
cyclopentadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.51	5.55	4.37	4.61	4.68	5.14	5.07	5.09	5.03	5.03
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.31	3.66	4.11	4.24	5.52	5.60	5.59	6.06	6.06
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.52		6.25	6.51	6.52	7.63	7.47	7.53	7.72	7.72
norbornadiene	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	5.34	5.34	5.04	5.18	5.38	6.10	6.00	6.06	4.50	4.50
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.11	6.11	5.83	5.99	6.11	6.65	6.34	6.46	5.54	5.54
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.32		6.26	6.38	6.49	7.42	7.37	7.42	6.77	6.77
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	7.45		6.27	6.33	6.45	6.92	6.66	6.74	6.90	6.90
benzene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.04	5.08	2.71	3.13	3.19	4.41	4.48	4.51	4.71	4.71
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.42	6.54	4.49	4.84	4.90	5.98	5.94	6.03	5.96	5.96
	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	7.13	7.13	5.55	5.92	5.88	7.13	7.16	7.20	6.51	6.51
	1 ¹ E _{2g} ($\pi \rightarrow \pi^*$)	8.18	8.41	4.46	5.11	5.20	7.07	7.19	7.22	7.79	7.79
naphthalene	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	4.24	4.24	2.35	2.68	2.75	3.76	3.81	3.84	3.92	3.92
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.77	4.77	3.84	4.06	4.09	4.85	4.83	4.87	4.50	4.50
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.87	5.87	3.20	3.68	3.76	5.16	5.23	5.27	5.52	5.52
	1 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	5.99	5.99	3.80	4.24	4.33	5.67	5.74	5.76	5.65	5.65
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	6.06	6.06	4.87	5.16	5.13	6.12	6.16	6.18	5.53	5.53
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	6.33	6.33	4.70	5.05	5.06	6.22	6.23	6.28	5.96	5.96
	2 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	6.47	6.47	4.80	5.17	5.17	6.29	6.24	6.31	6.39	6.39
	3 ¹ A _g ($\pi \rightarrow \pi^*$)	6.67	6.67	3.85	4.36	4.44	5.94	6.03	6.05	6.79	6.79
	3 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	7.74		4.27	4.84	4.95	6.68	6.80	6.83	7.34	7.34
	3 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.17		6.09	6.57	6.57	8.09	8.12	8.18	7.85	7.82
furan	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.39	6.32	4.59	4.87	4.87	5.78	5.82	5.88	5.90	5.68
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.50	6.57	3.53	3.96	4.04	5.39	5.43	5.51	5.81	5.74
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.17	8.13	5.72	6.15	6.12	7.44	7.47	7.62	7.88	7.23
pyrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.37	3.37	3.77	3.79	5.21	5.28	5.29	5.38	5.38
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.57	6.57	4.42	4.65	4.55	5.77	5.86	5.94	5.16	5.16
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.17	7.91	5.31	5.65	5.53	7.10	7.18	7.16	6.57	6.57
imidazole	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.19	6.19	4.05	4.32	4.11	5.50	5.59	5.85	5.00	5.00
	1 ¹ A'' ($n \rightarrow \pi^*$)	6.81	6.81	5.25	5.24	4.48	5.87	6.00	6.08	5.36	5.36
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.93	6.93	4.62	4.84	4.70	5.95	6.04	6.16	5.65	5.65
	2 ¹ A'' ($n \rightarrow \pi^*$)	7.90		5.82	5.83	5.05	6.81	6.79	6.70	6.19	6.19
	4 ¹ A' ($\pi \rightarrow \pi^*$)	8.16		5.91	6.12	5.71	7.40	7.45	7.69	6.87	6.87
pyridine	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.02	4.85	3.01	3.38	3.35	4.56	4.65	4.83	4.76	4.76
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	5.17	4.59	4.36	4.29	3.75	4.85	4.85	4.86	4.40	4.40
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.51	5.11	4.43	4.34	3.96	5.17	5.06	4.84	5.42	5.42
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.39	6.26	4.65	5.01	5.00	6.14	6.11	6.25	6.00	6.00
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.27	7.27	5.85	6.21	6.03	7.39	7.48	7.62	6.75	6.75
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.46	7.18	5.88	6.29	6.11	7.44	7.43	7.63	6.65	6.65
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	8.60		4.76	5.33	5.32	7.09	7.20	7.44		
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.69		5.31	5.82	5.63	7.53	7.69	8.09		
pyrazine	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	4.21	3.95	3.77	3.56	3.29	3.90	3.81	4.04	3.75	3.75
	1 ¹ A _u ($n \rightarrow \pi^*$)	4.70	4.81	3.75	3.55	3.50	4.38	4.12	3.89	5.08	5.08
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.85	4.64	3.37	3.65	3.48	4.61	4.76	5.20	4.61	4.61
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.68	5.56	4.86	4.90	4.13	5.49	5.78	5.86	4.85	4.85
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.41	6.60	5.23	5.36	4.51	6.34	6.54	6.32	6.89	6.89
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.89	6.58	4.75	5.10	5.06	6.24	6.22	6.35	6.20	6.20
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.66	7.60	6.45	6.66	6.23	7.64	7.67	8.12	7.64	7.64
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.79	7.72	6.92	7.15	6.48	7.98	8.06	8.68	7.69	7.69
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	8.47		4.94	5.46	5.39	7.16	7.35	7.68	7.68	7.68
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	8.61		6.04	6.46	6.00	7.89	8.07	8.95	9.31	9.31
pyrimidine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.44	4.55	3.89	3.78	3.46	4.43	4.34	4.38	4.16	4.16
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.80	4.91	4.03	3.90	3.66	4.73	4.54	4.40	4.50	4.50
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.24	5.44	3.42	3.71	3.55	4.77	4.86	5.22	5.00	5.00
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.63	6.95	4.92	5.29	5.14	6.37	6.36	6.62	6.39	6.39
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.21		6.43	6.71	6.27	7.76	7.81	8.25	7.34	7.34
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.64		6.37	6.72	6.33	7.63	7.72	8.00	6.92	6.92
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	8.73		5.93	6.29	5.91	7.92	8.01	8.77	8.27	8.27
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	9.19		5.33	5.79	5.61	7.37	7.51	8.00	8.13	8.13
pyridazine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	3.78	3.78	4.10	4.13	3.15	4.01	4.37	4.14	3.79	3.79
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.31	4.31	4.29	4.35	3.41	4.39	4.70	4.21	4.66	4.66
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	5.18	5.18	3.25	3.56	3.41	4.63	4.74	5.08	4.95	4.95
	2 ¹ A ₂ ($n \rightarrow \pi^*$)	5.77	5.77	4.89	4.80	4.16	5.40	5.38	5.57	5.68	5.68
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.13		4.97	5.32	5.09	6.34	6.29	6.60	6.30	6.30
	2 ¹ B ₁ ($n \rightarrow \pi^*$)	6.52		5.08	5.00	4.48	5.78	5.62	5.51	6.34	6.34
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.29		6.01	6.32	6.03	7.29	7.32	7.76	7.04	7.04
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.62		6.09	6.47	6.21	7.59	7.51	7.81	7.32	7.32
s-triazine	1 ¹ A ₁ ' ($n \rightarrow \pi^*$)	4.60	4.60	4.22	4.00	3.74	4.80	4.51	4.57	4.74	4.74
	1 ¹ A ₂ ' ($n \rightarrow \pi^*$)	4.66	4.66	3.94	3.76	3.53	4.48	4.24	4.28	4.61	4.61
	1 ¹ E'' ($n \rightarrow \pi^*$)	4.70	4.70	4.08	3.89	3.61	4.66	4.40	4.45	4.44	4.44
	1 ¹ A ₂ ' ($\pi \rightarrow \pi^*$)	5.79	5.79	3.94	4.13	3.79	5.06	5.12	5.69	5.45	5.45
	2 ¹ A ₁ ' ($\pi \rightarrow \pi^*$)	7.25		5.51	5.80	5.34	6.74	6.78	7.33	6.90	6.90
	1 ¹ E' ($\pi \rightarrow \pi^*$)	7.50		6.93	7.16	6.56	7.72	7.88	8.47	7.57	7.57
	2 ¹ E'' ($n \rightarrow \pi^*$)	7.71		6.13	6.00	5.73	7.48	7.01	7.17	7.00	7.00
	2 ¹ E' ($\pi \rightarrow \pi^*$)	8.99		6.26	6.54	6.04	8.26	8.28	9.03	8.95	8.95

Table 3. Continued

molecule	state	CASPT2 ^a	TBE ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
s-tetrazine	1 ¹ B _{3u} (n → π*)	2.29	2.29	2.98	2.91	2.27	2.66	2.83	2.88	2.86	2.86
	1 ¹ A _u (n → π*)	3.51	3.51	3.80	3.65	2.99	3.53	3.55	3.08	4.43	4.43
	1 ¹ B _{1g} (n → π*)	4.73	4.73	5.09	5.58	3.69	5.08	6.15	6.49	4.38	4.38
	1 ¹ B _{2u} (π → π*)	4.93	4.93	3.62	3.84	3.50	4.71	4.88	5.74	4.84	4.84
	1 ¹ B _{2g} (n → π*)	5.20	5.20	4.42	4.41	3.87	5.02	5.33	6.11	4.94	4.94
	2 ¹ A _u (n → π*)	5.50	5.50	4.99	4.78	3.80	4.89	4.65	5.06	5.59	5.59
	1 ¹ B _{3g} (n → π*) ^e	5.86		6.54	6.41	5.07	5.93	6.28	5.88		
	2 ¹ B _{2g} (n → π*)	6.06		5.82	6.02	4.42	5.97	6.73	6.64	6.64	6.64
	2 ¹ B _{1g} (n → π*)	6.45		5.29	5.12	4.47	5.63	5.65	5.60	6.59	6.59
	3 ¹ B _{1g} (n → π*)	6.73		5.56	5.39	4.92	6.29	6.39	6.72	7.64	7.64
	2 ¹ B _{3u} (n → π*)	6.77		5.68	5.38	4.53	5.66	5.22	5.08	7.29	7.29
	1 ¹ B _{1u} (π → π*)	6.94		5.70	5.91	5.29	6.75	6.78	7.23	6.64	6.64
	2 ¹ B _{1u} (π → π*)	7.42		6.68	6.84	6.16	7.67	7.86	9.03	7.27	7.27
	2 ¹ B _{2u} (π → π*)	8.14		7.16	7.32	6.63	8.24	8.16	9.04	8.18	8.18
	2 ¹ B _{3g} (π → π*)	8.34		5.91	6.22	5.55	7.54	7.86	9.62	9.30	9.30
	1 ¹ A ₂ (n → π*)	3.99	3.88	3.21	3.07	2.87	3.71	3.55	3.59	3.62	4.09
	1 ¹ B ₁ (σ → π*)	9.14	9.10	8.46	8.68	8.63	9.30	7.93	9.01	10.95	11.36
	2 ¹ A ₁ (π → π*)	9.32	9.30	8.56	9.09	8.40	9.61	9.23	9.89	12.09	13.54
acetone	1 ¹ A ₂ (n → π*)	4.44	4.40	3.18	3.46	3.29	3.80	3.98	4.05	3.67	4.13
	1 ¹ B ₁ (σ → π*)	9.27	9.10	8.26	8.18	7.46	8.81	7.71	8.34	10.63	11.17
	2 ¹ A ₁ (π → π*)	9.31	9.40	7.97	7.86	8.28	8.33	8.08	8.51	10.87	11.79
p-benzoquinone	1 ¹ B _{1g} (n → π*)	2.76	2.76	2.79	2.88	2.72	2.62	2.64	2.58	2.67	3.00
	1 ¹ A _u (n → π*)	2.77	2.77	2.95	3.19	2.96	3.17	3.35	3.37	2.64	3.00
	1 ¹ B _{3g} (π → π*)	4.26	4.26	4.27	4.43	4.43	4.82	4.62	4.68	4.75	4.79
	1 ¹ B _{1u} (π → π*)	5.28	5.28	5.26	5.47	5.26	5.64	5.52	5.71	5.60	5.83
	1 ¹ B _{3u} (n → π*)	5.64	5.64	4.42	4.70	4.68	5.24	5.34	5.31	5.56	5.59
	2 ¹ B _{3g} (π → π*)	6.96	6.96	5.36	5.80	5.65	6.58	6.73	6.93	6.69	6.93
formamide	2 ¹ B _{1u} (π → π*)	7.92		6.28	6.66	6.65	7.81	7.79	7.87	7.41	7.45
	1 ¹ A ₂ ' (n → π*)	5.63	5.63	3.89	4.11	3.68	4.61	4.56	4.82	4.44	5.09
	2 ¹ A ₁ ' (π → π*)	7.39	7.39	5.90	5.93	5.08	6.92	6.71	7.07	7.38	7.64
	3 ¹ A ₁ ' (π → π*)	10.54		8.26	8.76	7.95	9.67	9.41	10.11	12.23	13.54
acetamide	1 ¹ A ₂ ' (n → π*)	5.69	5.69	3.83	4.23	3.79	4.59	4.75	4.98	4.36	5.00
	2 ¹ A ₁ ' (π → π*)	7.27	7.27	5.70	5.77	4.92	6.76	6.63	6.95	7.39	7.64
	3 ¹ A ₁ ' (π → π*)	10.09		7.82	8.09	7.49	8.93	8.64	9.02	11.31	12.19
propanamide	1 ¹ A ₂ ' (n → π*)	5.72	5.72	3.91	4.35	3.87	4.67	4.85	5.06	4.35	4.99
	2 ¹ A ₁ ' (π → π*)	7.20	7.20	5.69	5.77	4.92	6.78	6.64	6.94	7.46	7.71
	3 ¹ A ₁ ' (π → π*)	9.94		7.77	7.90	7.41	8.72	8.34	8.50	10.82	11.18
cytosine	2 ¹ A ₁ ' (π → π*)	4.67	4.66	3.34	3.47	3.12	4.19	4.21	4.39	4.41	4.50
	1 ¹ A ₂ ' (n → π*)	5.12	4.87	3.63	3.76	3.36	4.19	4.23	4.40	4.10	4.15
	2 ¹ A ₂ ' (n → π*)	5.53	5.26	4.05	4.32	3.83	4.76	4.83	4.95	4.73	5.33
	3 ¹ A ₁ ' (π → π*)	5.53	5.62	3.87	4.00	3.43	5.01	5.00	5.05	5.54	5.58
thymine	4 ¹ A ₁ ' (π → π*)	6.40		4.66	4.72	4.18	5.88	5.78	5.84	6.14	6.26
	5 ¹ A ₁ ' (π → π*)	6.97		4.81	4.94	4.44	6.14	5.91	5.96	6.57	6.61
	1 ¹ A ₂ ' (n → π*)	4.95	4.82	3.77	4.18	3.63	4.34	4.52	4.68	4.05	4.63
	2 ¹ A ₁ ' (π → π*)	5.06	5.20	4.02	4.09	3.63	4.97	4.81	4.81	5.07	5.17
	3 ¹ A ₁ ' (π → π*)	6.15	6.27	4.75	4.97	4.23	5.78	5.56	5.65	6.04	6.22
	2 ¹ A ₂ ' (n → π*)	6.38	6.16	4.42	4.96	4.21	5.32	5.47	5.69	4.94	5.72
	4 ¹ A ₁ ' (π → π*)	6.53	6.53	4.93	4.85	4.37	5.91	5.73	5.90	6.65	6.94
	3 ¹ A ₂ ' (n → π*)	6.85		4.95	5.41	4.91	6.07	6.08	6.08	6.50	6.78
uracil	5 ¹ A ₁ ' (π → π*)	7.43		5.67	5.78	5.08	6.71	6.50	6.73	7.35	7.67
	4 ¹ A ₂ ' (n → π*)	7.43		5.62	6.01	5.24	6.48	6.36	6.45	7.05	7.50
	1 ¹ A ₂ ' (n → π*)	4.91	4.80	3.73	4.12	3.61	4.27	4.45	4.64	4.06	4.64
	2 ¹ A ₁ ' (π → π*)	5.23	5.35	4.09	4.15	3.66	5.05	4.88	4.90	5.19	5.29
	3 ¹ A ₁ ' (π → π*)	6.15	6.26	4.80	4.96	4.24	5.78	5.68	5.86	6.31	6.51
	2 ¹ A ₂ ' (n → π*)	6.28	6.10	4.42	4.95	4.21	5.29	5.43	5.65	4.93	5.70
	4 ¹ A ₁ ' (π → π*)	6.74	6.70	4.99	5.02	4.47	6.14	5.85	5.97	6.58	6.87
	3 ¹ A ₂ ' (n → π*)	6.98	6.56	5.00	5.43	4.94	6.09	6.09	6.10	6.47	6.74
adenine	4 ¹ A ₂ ' (n → π*)	7.28		5.65	6.00	5.24	6.47	6.34	6.44	7.01	7.42
	5 ¹ A ₁ ' (π → π*)	7.42		5.70	5.78	5.11	6.72	6.50	6.75	7.20	7.42
	1 ¹ A ₂ ' (n → π*)	5.19	5.12	4.08	3.99	3.81	4.81	4.60	4.62	4.55	4.55
	2 ¹ A ₁ ' (π → π*)	5.20	5.25	3.08	3.21	2.95	4.19	4.23	4.33	4.33	4.33
	3 ¹ A ₁ ' (π → π*)	5.29	5.25	3.73	3.89	3.54	4.83	4.79	4.90	4.61	4.61
	2 ¹ A ₂ ' (n → π*)	5.96	5.75	4.36	4.32	4.09	5.10	5.05	5.16	4.69	4.69
	4 ¹ A ₁ ' (π → π*)	6.34		4.21	4.38	4.03	5.61	6.03	5.80	5.87	5.87
	5 ¹ A ₁ ' (π → π*)	6.64		4.62	4.75	4.17	6.00	5.91	6.14	5.36	5.36
	6 ¹ A ₁ ' (π → π*)	6.87		4.79	4.92	4.45	6.02	6.50	6.27	6.17	6.17
	7 ¹ A ₁ ' (π → π*)	7.56		5.14	5.25	4.69	6.49	6.64	6.74		

^a SA-CASSCF/MS-CASPT2 results using the TZVP basis and MP2/6-31G* ground-state equilibrium geometries.¹⁴ ^b Theoretical best estimates for vertical excitation energies. See ref 14 for details. ^c Including the doubly excited CSF (HOMO→LUMO) changes the energy of the 1¹B_u/2¹A_g states to 6.37/6.61 eV for butadiene, 5.14/5.29 eV for hexatriene, and 4.41/4.85 eV for octatetraene. ^d Using all orbitals in the active space yields 5.80/6.87 eV for 1¹B₁/1¹B₂. ^e Double excitation.

Cyclopentadiene has three valence excited singlet states, the lowest one being of B₂ symmetry (HOMO → LUMO transition) followed by two A₁ states (composed of combinations of HOMO − 1 → LUMO and HOMO → LUMO + 1 single excitations as well as double excitations). The semiempirical calculations again underestimate the excitation energies, for example, with OMx by 0.41–0.46 eV for 1¹B₂ (TBE 5.55 eV) and by 0.71–0.79

eV for 2¹A₁ (TBE 6.31 eV); similar deviations are found for the corresponding triplet states. The INDO/S results are reasonable for the singlet states, but much too low for the triplet states (by 1.2–1.6 eV).

Norbornadiene with its two nonconjugated double bonds seems to be described reasonably well by all six NDDO-based methods, with the energies of the two lowest singlet excited states (1¹A₂, TBE 5.34 eV; 1¹B₂, TBE 6.11 eV) being

Table 4. Vertical Triplet Excitation Energies ΔE (eV) of All Evaluated Molecules As Compared to MS-CASPT2/TZVP Results and Theoretical Best Estimates (TBE)

molecule	atate	CASPT2 ^a	TBE ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
ethene	$1^3B_{1u}(\pi \rightarrow \pi^*)$	4.48	4.50	2.58	2.98	3.05	4.07	4.14	4.16	3.23	3.23
<i>E</i> -butadiene	$1^3B_u(\pi \rightarrow \pi^*)$	3.34	3.20	1.94	2.21	2.28	2.99	3.04	3.04	2.24	2.24
	$1^3A_g(\pi \rightarrow \pi^*)$	5.16	5.08	2.82	3.25	3.32	4.49	4.56	4.59	3.71	3.71
all- <i>E</i> -hexatriene	$1^3B_u(\pi \rightarrow \pi^*)$	2.71	2.40	1.61	1.81	1.88	2.41	2.46	2.45	2.65	2.65
	$1^3A_g(\pi \rightarrow \pi^*)$	4.31	4.15	2.40	2.75	2.81	3.73	3.80	3.81	4.39	4.39
all- <i>E</i> -octatetraene	$1^3B_u(\pi \rightarrow \pi^*)$	2.33	2.20	1.44	1.59	1.66	2.09	2.12	2.11	2.20	2.20
	$1^3A_g(\pi \rightarrow \pi^*)$	3.70	3.55	2.10	2.37	2.43	3.18	3.23	3.24	3.32	3.32
cyclopropene	$1^3B_2(\pi \rightarrow \pi^*)$	4.35	4.34	2.53	2.68	2.76	3.77	3.80	3.72	3.18	3.18
	$1^3B_1(\sigma \rightarrow \pi^*)$	6.51	6.62	4.89	5.02	5.23	6.01	5.48	5.65	7.25	7.25
cyclopentadiene	$1^3B_2(\pi \rightarrow \pi^*)$	3.28	3.25	1.80	2.07	2.18	2.81	2.87	2.86	2.02	2.02
	$1^3A_1(\pi \rightarrow \pi^*)$	5.11	5.09	2.67	3.05	3.14	4.23	4.30	4.31	3.46	3.46
norbornadiene	$1^3A_2(\pi \rightarrow \pi^*)$	3.75	3.72	2.52	2.88	2.95	4.08	4.27	4.26	2.75	2.75
	$1^3B_2(\pi \rightarrow \pi^*)$	4.22	4.16	2.45	2.81	2.84	3.89	4.10	4.07	3.15	3.15
benzene	$1^3B_{1u}(\pi \rightarrow \pi^*)$	4.17	4.15	2.13	2.50	2.56	3.66	3.74	3.76	3.72	3.72
	$1^3E_{1u}(\pi \rightarrow \pi^*)$	4.90	4.86	2.85	3.25	3.31	4.48	4.54	4.57	4.83	4.83
	$1^3B_{2u}(\pi \rightarrow \pi^*)$	5.76	5.88	4.42	4.73	4.72	5.79	5.80	5.85	5.46	5.46
	$1^3E_{2g}(\pi \rightarrow \pi^*)$	7.38	7.51	3.85	4.45	4.53	6.20	6.30	6.34	6.97	6.97
naphthalene	$1^3B_{2u}(\pi \rightarrow \pi^*)$	3.16	3.11	1.76	2.01	2.07	2.84	2.89	2.90	2.95	2.95
	$1^3B_{3u}(\pi \rightarrow \pi^*)$	4.25	4.18	2.50	2.83	2.88	3.87	3.91	3.94	4.15	4.15
	$1^3B_{1g}(\pi \rightarrow \pi^*)$	4.51	4.47	2.51	2.86	2.93	4.00	4.07	4.09	4.20	4.20
	$2^3B_{2u}(\pi \rightarrow \pi^*)$	4.68	4.64	2.65	3.02	3.07	4.22	4.28	4.31	4.61	4.61
	$2^3B_{3u}(\pi \rightarrow \pi^*)$	4.97	5.11	3.91	4.09	4.09	4.95	4.95	4.99	4.61	4.61
	$1^3A_g(\pi \rightarrow \pi^*)$	5.53	5.52	3.09	3.51	3.57	4.82	4.90	4.93	5.12	5.12
	$2^3B_{1g}(\pi \rightarrow \pi^*)$	6.21	6.48	4.98	5.33	5.32	6.46	6.49	6.52	7.33	7.33
	$2^3A_g(\pi \rightarrow \pi^*)$	6.38	6.47	4.84	5.23	5.23	6.50	6.51	6.58	6.39	6.39
	$3^3A_g(\pi \rightarrow \pi^*)$	6.59	6.79	3.61	4.11	4.19	5.68	5.76	5.79	7.32	7.32
	$3^3B_{1g}(\pi \rightarrow \pi^*)$	6.64	6.76	3.66	4.17	4.23	5.71	5.79	5.83	6.63	6.63
furan	$1^3B_2(\pi \rightarrow \pi^*)$	4.18	4.17	2.18	2.47	2.50	3.40	3.50	3.53	2.79	2.95
	$1^3A_1(\pi \rightarrow \pi^*)$	5.49	5.48	2.85	3.22	3.29	4.44	4.54	4.59	3.97	4.00
pyrrole	$1^3B_2(\pi \rightarrow \pi^*)$	4.51	4.48	2.26	2.58	2.76	3.55	3.76	3.89	2.47	2.47
	$1^3A_1(\pi \rightarrow \pi^*)$	5.52	5.51	2.88	3.23	3.23	4.46	4.59	4.64	3.81	3.81
imidazole	$1^3A'(\pi \rightarrow \pi^*)$	4.65	4.69	2.46	2.77	2.89	3.70	3.95	4.06	3.04	3.04
	$2^3A'(\pi \rightarrow \pi^*)$	5.74	5.79	3.59	3.80	3.60	4.77	4.95	5.27	4.32	4.32
	$1^3A''(n \rightarrow \pi^*)$	6.36	6.37	4.89	4.84	4.14	5.43	5.60	5.70	5.42	5.42
	$3^3A'(\pi \rightarrow \pi^*)$	6.44	6.55	4.49	4.60	4.12	5.79	5.69	5.99	5.59	5.59
	$4^3A'(\pi \rightarrow \pi^*)$	7.44		4.87	4.95	4.48	6.28	6.20	6.37	7.12	7.12
	$2^3A''(n \rightarrow \pi^*)$	7.51		5.50	5.48	4.83	6.50	6.47	6.33	7.48	7.48
pyridine	$1^3A_1(\pi \rightarrow \pi^*)$	4.27	4.06	2.31	2.65	2.68	3.78	3.86	3.94	3.80	3.80
	$1^3B_1(n \rightarrow \pi^*)$	4.57	4.25	3.96	3.86	3.37	4.37	4.48	4.47	4.02	4.02
	$1^3B_2(\pi \rightarrow \pi^*)$	4.71	4.64	3.08	3.46	3.44	4.57	4.66	4.83	4.68	4.68
	$2^3A_1(\pi \rightarrow \pi^*)$	5.03	4.91	3.22	3.58	3.50	4.67	4.74	4.97	4.93	4.93
	$1^3A_2(n \rightarrow \pi^*)$	5.52	5.28	4.36	4.27	3.89	5.11	4.96	4.75	5.84	5.84
	$2^3B_2(\pi \rightarrow \pi^*)$	6.03	6.08	4.79	5.08	4.92	6.02	5.97	6.17	6.02	6.02
	$3^3A_1(\pi \rightarrow \pi^*)$	7.56		4.61	5.05	4.87	6.56	6.67	7.08		
	$3^3B_2(\pi \rightarrow \pi^*)$	7.87		4.25	4.73	4.68	6.42	6.59	6.83		
s-tetrazine	$1^3B_{3u}(n \rightarrow \pi^*)$	1.61	1.89	2.43	2.36	1.88	2.08	2.35	2.36	2.30	2.30
	$1^3A_u(n \rightarrow \pi^*)$	3.28	3.52	3.55	3.38	2.80	3.31	3.31	2.87	4.32	4.32
	$1^3B_{1g}(n \rightarrow \pi^*)$	4.14	4.21	4.23	4.30	3.14	4.12	4.85	4.78	3.72	3.72
	$1^3B_{1u}(\pi \rightarrow \pi^*)$	4.37	4.33	2.95	3.11	2.78	3.90	4.07	4.74	3.54	3.54
	$1^3B_{2u}(\pi \rightarrow \pi^*)$	4.39	4.54	3.53	3.78	3.49	4.57	4.76	5.62	3.98	3.98
	$1^3B_{2g}(n \rightarrow \pi^*)$	4.94	4.93	4.15	4.13	3.62	4.73	5.04	5.66	4.91	4.91
	$2^3A_u(n \rightarrow \pi^*)$	5.04	5.03	4.69	4.46	3.67	4.67	4.40	4.79	5.89	5.89
	$2^3B_{1u}(\pi \rightarrow \pi^*)$	5.40	5.38	3.92	4.11	3.77	4.96	5.07	6.00	5.27	5.27
	$1^3B_{3g}(n \rightarrow \pi^*)$	5.57		5.24	5.53	4.86	5.75	6.00	5.53		
	$2^3B_{2g}(n \rightarrow \pi^*)$	5.97		5.65	5.83	4.32	5.84	6.50	6.43	7.05	7.05
	$2^3B_{1g}(n \rightarrow \pi^*)$	6.37		5.43	5.38	4.85	6.16	6.29	6.65	7.37	7.37
	$2^3B_{3u}(n \rightarrow \pi^*)$	6.54		5.55	5.24	4.35	5.49	5.09	4.95	7.87	7.87
	$2^3B_{2u}(\pi \rightarrow \pi^*)$	7.08		5.76	5.87	5.22	6.69	6.73	7.43	7.23	7.23
formaldehyde	$1^3A_2(\pi \rightarrow \pi^*)$	3.58	3.50	2.92	2.74	2.57	3.40	3.23	3.24	3.14	3.68
	$1^3A_1(\pi \rightarrow \pi^*)$	5.84	5.87	4.90	5.42	5.07	5.67	5.63	6.07	6.41	8.04
acetone	$1^3A_2(n \rightarrow \pi^*)$	4.10	4.05	2.87	3.18	3.05	3.53	3.74	3.79	4.02	4.54
	$1^3A_1(\pi \rightarrow \pi^*)$	6.04	6.03	4.50	4.97	4.65	5.33	5.45	5.79	8.52	10.33
<i>p</i> -benzoquinone	$1^3B_{1g}(n \rightarrow \pi^*)$	2.62	2.51	2.61	2.71	2.57	2.46	2.50	2.42	2.74	3.09
	$1^3A_u(n \rightarrow \pi^*)$	2.66	2.62	2.76	3.01	2.82	3.03	3.21	3.23	2.81	3.24
	$1^3B_{1u}(\pi \rightarrow \pi^*)$	2.99	2.96	2.18	2.45	2.41	2.75	2.79	2.91	3.48	3.80
	$1^3B_{3g}(n \rightarrow \pi^*)$	3.32	3.41	2.33	2.63	2.68	3.38	3.32	3.34	3.49	3.64
formamide	$1^3A''(n \rightarrow \pi^*)$	5.40	5.36	3.68	3.87	3.49	4.39	4.34	4.58	4.00	4.69
	$1^3A'(\pi \rightarrow \pi^*)$	5.58	5.74	4.02	4.16	3.54	4.89	4.77	4.98	5.21	5.93
acetamide	$1^3A''(n \rightarrow \pi^*)$	5.41	5.42	3.61	4.00	3.62	4.38	4.54	4.76	4.99	5.69
	$1^3A'(\pi \rightarrow \pi^*)$	5.63	5.88	3.86	4.11	3.49	4.86	4.86	5.07	6.61	7.31
propanamide	$1^3A''(n \rightarrow \pi^*)$	5.45	5.45	3.68	4.11	3.69	4.44	4.61	4.81	5.00	5.70
	$1^3A'(\pi \rightarrow \pi^*)$	5.80	5.90	3.87	4.12	3.50	4.87	4.87	5.07	6.61	7.30

^a SA-CASSCF/MS-CASPT2 results using the TZVP basis and MP2/6-31G* ground-state equilibrium geometries.¹⁴ ^b Theoretical best estimates for vertical excitation energies. See ref 14 for details.

bracketed by the semiempirical results (with individual deviations of a few tenths of an eV). Concerning the two lowest singlet B₂ states, MNDO/AM1/PM3 predicts a significantly higher oscillator strength for the lower one, while the OMx and ab initio calculations give the opposite

trend, which is indicative of differences in the corresponding CI wave functions. The energy gap between these two singlet B₂ states is rather low in MNDO/AM1/PM3 (0.38–0.43 eV) as compared to OMx (0.77–1.03 eV) and the MS-CASPT2 reference value (1.21 eV).¹⁴

The electronic spectrum of benzene has often been studied theoretically and has served as a prototypical test case for many computational methods. There are four singlet valence $\pi\pi^*$ states in the 5–9 eV range. MNDO/AM1/PM3 underestimate their energies severely, by 1.2–3.9 eV. The OMx methods predict the first two singlet states (1^1B_{2u} , TBE 5.08 eV; 1^1B_{1u} , TBE 6.54 eV) too low by 0.51–0.67 eV, get the correct energy within 0.07 eV for the bright 1^1E_{1u} state (TBE 7.13 eV), and strongly underestimate the energy of the E_{2g} state (TBE 8.41 eV), which has significant double-excitation character, by 1.2–1.3 eV. The standard INDO/S CIS results for these $\pi\pi^*$ states suffer from $\sigma\sigma^*$ contamination, which reduces most of the excitation energies by about 0.5 eV; after excluding the corresponding σ^* MOs from the active space, the results are reasonable, with the excited singlet states in the right order and deviations of 0.37–0.62 eV from the TBE values. For the four triplet $\pi\pi^*$ states, the situation is similar as for the singlets, with an analogous performance of the different methods, which does not warrant further discussion.

In the case of naphthalene, our benchmark set includes 10 excited singlet states and 10 triplet states, which are all of $\pi\pi^*$ type. MNDO/AM1/PM3 again underestimate the excitation energies severely in general and give a partially incorrect state ordering. The OMx results are much closer to the TBE reference values, with a tendency to be too low by a few tenths of an eV, and normally produce the correct state ordering; the largest deviations from the TBE values occur for A_g states with significant double-excitation character where the OMx excitation energies are typically too low by about 0.6–0.7 eV. The INDO/S results appear to be of overall quality similar to those from OMx; the INDO/S energies for the A_g states are closer to the TBE values, which should be considered fortuitous because the INDO/S CIS calculations do not include double excitations.

Furan, Pyrrole, Imidazole, Pyridine, Pyrazine, Pyrimidine, Pyridazine, *s*-Triazine, and *s*-Tetrazine. Furan and pyrrole are isoelectronic five-ring heterocycles, which both have three singlet and two triplet $\pi\pi^*$ valence excited states. All semiempirical methods underestimate the corresponding excitation energies. The deviations from the TBE values are largest for MNDO/AM1/PM3 (1.5–3.0 eV) and still substantial for OMx (0.4–1.2 eV) and INDO/S (0.4–2.0 eV). For the first two close-lying excited singlets, the six NDDO-based methods give the reverse order for furan (like INDO/S) and the correct order for pyrrole (unlike INDO/S), while the sequence of the triplet states is always predicted correctly. INDO/S2 differs from INDO/S only in the oxygen parametrization and thus yields slightly different results for furan (surprisingly with slightly larger deviations from the TBE data).

The imidazole spectrum contains $n\pi^*$ and $\pi\pi^*$ valence transitions in the range between 6.0 and 8.5 eV.¹⁴ All semiempirical methods underestimate the $\pi\pi^*$ excitation energies in a manner similar to that in furan and pyrrole. The energies of the lowest $n\pi^*$ state in the singlet manifold ($1^1A''$, TBE 6.81 eV) and in the triplet manifold ($1^3A''$, TBE 6.37 eV) are underestimated to an extent similar to those of the $\pi\pi^*$ states (MNDO/AM1/PM3 by 1.6–2.3 eV, OMx by

0.7–0.9 eV, INDO/S by 1.0–1.5 eV), so that OMx and INDO/S give the correct order of the singlet and triplet states.

Pyridine is the first of a series of azabenzenes in our benchmark set. The introduction of one nitrogen atom lowers the symmetry and splits degenerate levels, such that the four valence $\pi\pi^*$ states in benzene correlate with six $\pi\pi^*$ states of symmetry A_1 and B_2 in pyridine. TBE values are available for the lowest four of these states both in the singlet case (4.85, 6.26, 7.18, and 7.27 eV) and in the triplet case (4.06, 4.64, 4.91, and 6.08 eV). The OMx results scatter around these reference data (typically within 0.3 eV or less), and the INDO/S results are of similar quality. There are two additional $n\pi^*$ states in the singlet manifold (1^1B_1 , TBE 4.59 eV; 1^1A_2 , TBE 5.11 eV) and in the triplet manifold (1^3B_1 , TBE 4.25 eV; 1^3A_2 , TBE 5.28 eV) whose energies are again well reproduced by OMx (typically within 0.3 eV) and also by INDO/S, even though the splitting of these two states is underestimated by OMx and overestimated by INDO/S. Overall, however, both the OMx methods and the INDO/S perform quite well for pyridine.

Similar remarks apply to the azabenzenes with two ring nitrogen atoms, that is, pyrazine, pyrimidine, and pyridazine, which are represented in our benchmark set only through their singlet excited states. The available TBE values for the eight lowest singlets in pyrazine and for the four lowest singlets in the other two molecules are generally well reproduced by the OMx methods, with typical deviations of about 0.3 eV both for $\pi\pi^*$ and $n\pi^*$ transitions and with a state ordering that is generally analogous to the one obtained from the ab initio reference calculations. The INDO/S results are generally in the same ballpark as the OMx results. Focusing on problem cases, we note that the deviations from the TBE values are larger than usual for the OMx energies of the 1^1A_u $n\pi^*$ state in pyrazine (TBE 4.81 eV, OMx too low by 0.43–0.92 eV) and for the INDO/S energy of the 1^1B_{2g} $n\pi^*$ state in pyrazine (TBE 5.56 eV, INDO/S too low by 0.71 eV); as a consequence, the splitting between these two states is overestimated by OMx and underestimated by INDO/S (where their order is actually inverted).

In the case of *s*-triazine, we focus on the four lowest singlet transitions for which TBE values have been derived. The three lowest singlet states are of $n\pi^*$ type and almost degenerate, lying within 0.1 eV (TBE 4.60–4.70 eV). The semiempirical calculations also yield three close-lying $n\pi^*$ states, typically within 0.3 eV, which appear in a similar energy range with OMx (4.3–4.8 eV) and INDO/S (4.4–4.7 eV), although their order is generally different from that found at the ab initio level. The energy of the lowest dark $\pi\pi^*$ singlet state ($1^1A'_2$, TBE 5.79 eV) is underestimated by all semiempirical methods (e.g., OMx by 0.10–0.73 eV, INDO/S by 0.34 eV). For the higher transitions above 7 eV, there is fair agreement with the available MS-CASPT2/TZVP data, with deviations roughly as expected in this energy range.

s-Tetrazine has a large number of known $n\pi^*$ and $\pi\pi^*$ states, with TBE values being available for the lowest six (eight) excited states in the singlet (triplet) manifold. Without going into detail, we note that the OMx and INDO/S methods perform about as well as anticipated from the experience

from the other azabenzenes. Given the number of close-lying states, it is inevitable, however, that there are sometimes differences in the state orderings and outliers for some of the computed excitation energies, particularly in the case of OM3.

Formaldehyde, Acetone, *p*-Benzoquinone, Formamide, Acetamide, and Propanamide. The lowest excited states of formaldehyde are $n\pi^*$ transitions, 1^3A_2 (TBE 3.50 eV) and 1^1A_2 (TBE 3.88 eV). Their energies are underestimated slightly by OMx (by 0.10–0.33 eV) and INDO/S (by 0.26–0.36 eV), and more so by MNDO/AM1/PM3 (by 0.58–1.01 eV). For the $\pi\pi^*$ triplet state (1^3A_1 , TBE 5.87 eV), the computed energies are too low for MNDO/AM1/PM3 (by 0.45–0.97 eV), while they scatter around the TBE value for OMx (within 0.2 eV) and are too high for INDO/S (by 0.54 eV) and especially for INDO/S2 (by 2.2 eV). The two remaining valence excited singlet states in our benchmark set lie above 9 eV, 1^1B_1 ($\sigma \rightarrow \pi^*$ type, TBE 9.10 eV) and 2^1A_1 ($\pi \rightarrow \pi^*$ type, TBE 9.30 eV). Their MS-CASPT2/TZVP wave functions indicate significant contributions from higher excitations in the 1^1B_1 state and some notable Rydberg-valence mixing in the 2^1A_1 state, which should only be partially recovered in semiempirical calculations; given this situation, the errors for the six NDDO-based methods of 0.2–1.2 eV are not excessive, while the INDO/S energies are too high by 1.9–2.8 eV.

The electronic spectrum of acetone is qualitatively similar to that of formaldehyde, and the performance of various semiempirical methods is also similar for both molecules, with a slight increase in the deviations from the TBE values for the lowest three states below 6 eV.

In *p*-benzoquinone, the two lowest singlet excited states are of $n\pi^*$ type. They are almost degenerate (1^1B_{1g} , TBE 2.76 eV; 1^1A_u , TBE 2.77 eV). All semiempirical methods reproduce the energy of the lowest state quite well (within 0.18 eV or less), but except for INDO/S, they compute the second state too high and thus give a sizable gap between these two dark $n\pi^*$ states (MNDO/AM1/PM3 0.16–0.31 eV, OMx 0.55–0.79 eV). The energy of the third $n\pi^*$ singlet state (1^1B_{3u} , TBE 5.64 eV) is underestimated to a different extent (MNDO/AM1/PM3 by 1.0–1.2 eV, OMx by 0.30–0.40 eV, INDO/S by 0.08 eV). The positions of the four $\pi\pi^*$ singlet states are given by OMx and INDO/S with the expected accuracy of typically 0.4 eV; for example, the first bright B_{1u} transition (TBE 5.28 eV) responsible for the first strong peak in the spectrum is calculated somewhat too high with OMx and INDO/S (by 0.24–0.43 eV). The results for the four lowest triplet states are largely analogous and will thus not be discussed in detail, except for noting that the OMx methods reproduce the TBE values to within 0.2 eV for all of these states except 1^3A_u (TBE 2.62 eV, OMx too large by 0.41–0.61 eV).

Formamide, acetamide, and propanamide have analogous valence excited states. The lowest excited singlet is an $n\pi^*$ state ($1^1A''$, TBE 5.63–5.72 eV) followed by a $\pi\pi^*$ state ($2^1A'$, TBE 7.20–7.39 eV) and another high-lying $\pi\pi^*$ state ($2^1A'$, around 10 eV or higher). The triplet manifold begins with a $n\pi^*$ state ($1^3A''$, TBE 5.36–5.45 eV) followed by a nearby $\pi\pi^*$ state ($1^3A'$, TBE 5.74–5.90 eV). The energies

of the $n\pi^*$ singlet and triplet states in these primary amides are generally underestimated by all semiempirical methods (e.g., in OMx by 0.64–1.10 eV and in INDO/S by 0.43–1.43 eV). Likewise, the energies of the $\pi\pi^*$ triplet state are underestimated in OMx by similar amounts (0.71–1.03 eV) such that the OMx triplet–triplet gaps are realistic, whereas INDO/S gives gaps that are too large. Finally, for the first $\pi\pi^*$ singlet state, the OMx and INDO/S results seem reasonable (OMx too low by 0.26–0.51 eV, INDO/S within 0.26 eV).

Cytosine, Thymine, Uracil, and Adenine. The singlet excited states of these nucleobases complete our benchmark set. We focus in the discussion on the OMx results because the MNDO/AM1/PM3 excitation energies are generally much too low as usual, whereas the INDO/S results are mostly in the same range as the OMx results but appear less regular as compared to the TBE values.

The valence excited states of cytosine consist of four $\pi\pi^*$ (A') states and two $n\pi^*$ (A'') states, which are all dominated by singly excited configurations. The OMx energies of these states are consistently lower than the available TBE values, typically by about 0.4–0.5 eV (with individual deviations in the range of 0.27–0.68 eV). Because these deviations are fairly uniform, the same state ordering is obtained from OMx as from the *ab initio* reference calculations. There is one caveat, however: according to the TBE values, the lowest excited state of cytosine is a $\pi\pi^*$ state at 4.66 eV followed by a nearby $n\pi^*$ state at 4.87 eV, whereas these two states are essentially degenerate at the OMx level (within 0.02 eV).

Thymine and uracil share the same heterocyclic ring structure and differ only in one methyl substituent, and hence their excited states are similar in character and can be discussed together. There are four $\pi\pi^*$ (A') and four $n\pi^*$ (A'') valence excited singlet states. According to the available TBE values, the state ordering is $1^1A'' < 2^1A' < 2^1A'' < 3^1A'$ in both molecules, with an $n\pi^*$ state being lowest. The same state ordering is found in the OMx calculations, which generally underestimate the excitation energies in thymine and uracil, by 0.14–0.53 eV for the lowest two states around 5 eV and by 0.40–0.85 eV for the remaining three or four states with TBE values between 6–7 eV.

In adenine, the three lowest singlet states are close in energy: the first $n\pi^*$ state ($1^1A''$, TBE 5.12 eV) is followed by two essentially degenerate $\pi\pi^*$ states ($2^1A'$ and $3^1A'$, TBE 5.25 eV) and a second $n\pi^*$ state ($2^1A''$, TBE 5.75 eV). The OMx energies are generally smaller than these TBE values, as in the case of the other nucleobases, but the deviations are less uniform. The main difference is that the two $\pi\pi^*$ states are not degenerate, but show a substantial split in OMx (by 0.56–0.64 eV). This changes the state ordering such that the lowest state in the OMx calculations is a $\pi\pi^*$ state ($2^1A'$) followed by the close-lying $1^1A''$ and $3^1A'$ states. The energy of the fourth excited state ($2^1A''$) is underestimated in OMx to a similar extent as in the other nucleobases (by 0.59–0.70 eV).

5. One-Electron Properties

Most of the benchmarking activities for electronically excited states in the literature address excitation energies, although

one-electron properties such as oscillator strengths and excited-state dipole moments could also serve as a sensitive probe for the quality of computational methods. However, as compared to excitation energies, these properties are known to converge more slowly upon basis set extension,^{14,15,61} and we have therefore not yet derived corresponding theoretical best estimates for our benchmark set. Available reference data include a range of published ab initio results as well as MS-CASPT2/TZVP and CC2/TZVP values calculated for the benchmark molecules in our previous work.¹⁴ These data can be used to evaluate the performance of our semiempirical results, which were obtained using the standard active spaces and CI treatments described in section 2 (CISDTQ for NDDO-based methods, CIS for INDO/S). Different choices for the active space and the CI treatment would affect the semiempirical results, of course, but these changes are usually rather minor for reasonable alternative choices.

5.1. Oscillator Strengths. Table S8 (Supporting Information) lists the computed oscillator strengths for all optically active states in our benchmark. It contains ab initio values previously collated from the literature,¹⁴ published CASPT2 data from the Roos group, and our own results from MS-CASPT2/TZVP and CC2/TZVP¹⁴ as well as semiempirical (MNDO, AM1, PM3, OM1, OM2, OM3, INDO/S) calculations. Generally speaking, there is broad qualitative agreement between the different sets of results, with a proper distinction between strong, medium, and weak transitions. For the low-lying excited states, the majority of the semiempirical oscillator strengths are comparable in magnitude to the MS-CASPT2 and CC2 results, while larger deviations are sometimes found for high-lying bright states where the ab initio reference data also often show some scatter. As expected, $n \rightarrow \pi^*$ transitions are normally weak and thus have low oscillator strengths both at the ab initio and at the semiempirical level. We refrain from detailed individual comparisons at this point and provide a more quantitative statistical evaluation in section 6.2.

5.2. Dipole Moments. Table S9 (Supporting Information) lists ground-state as well as excited-state dipole moments obtained from published CASPT2 work in the Roos group and from our own MS-CASPT2/TZVP,¹⁴ RI-CC2/TZVP, and semiempirical calculations. Coupled-cluster CC2 results were determined using unrelaxed densities with the RICC2^{62–65} program of the TURBOMOLE package. As pointed out before,¹⁵ the two sets of CASPT2-based results in Table S9 often differ appreciably, and the CC2 dipole moments correlate only roughly with those from the published CASPT2 and from our own MS-CASPT2/TZVP calculations (with correlation coefficients of 0.8341 and 0.8705, respectively). This scatter in the reference data calls for some caution in the assessment of the semiempirical results.

For all semiempirical methods, the computed ground-state dipole moments agree reasonably well with the ab initio results. The mean absolute deviations are around 0.3 D and thus of similar magnitude as in previous comparisons with experiment.⁴¹ The situation is much less satisfactory for the excited-state dipole moments. The MNDO, AM1, and PM3

results are reasonable for low-lying $n \rightarrow \pi^*$ states (e.g., in pyridine with deviations of less than 0.2 D), but they often also lie far away from the range spanned by the three sets of reference data (see above), especially for high-lying states where deviations up to 7 D are encountered (e.g., in uracil and thymine); in these latter cases, the composition of the excited-state wave function is different from the ab initio reference. The OMx results also scatter around the range of the reference values, but to a lesser extent. Again, there are low-lying states that are well described (e.g., in cyclopentadiene and pyrrole), while there are outliers for high-lying states especially of the nucleobases (e.g., in thymine with deviations reaching 4 D). Finally, for technical reasons, INDO/S and INDO/S2 dipole moments have been computed only for singlet states; they differ because of the use of different C_{kk} and D_{kk} parameters in the CM2 approach.³⁵ Again the INDO/S and INDO/S2 results deteriorate for the high-lying states (e.g., in thymine with deviations of 8–9 D from MS-CASPT2/TZVP). A more quantitative assessment of the semiempirical excited-state dipole moments is given in section 6.2.

6. Statistics

In the following, we present a detailed statistical evaluation of the computed vertical excitation energies and one-electron properties for all semiempirical methods studied. As reference data, we mainly use theoretical best estimates of vertical excitation energies and MS-CASPT2/TZVP oscillator strengths and dipole moments.

6.1. Vertical Excitation Energies. Table 5 summarizes statistical results for singlet excited states, both for the full set of 104 states and for three subsets (hydrocarbons, CHN compounds, CHO and CHNO compounds). The standard NDDO-based methods (MNDO, AM1, PM3) obviously underestimate the vertical excitation energies systematically and by a large margin, with mean absolute deviations (MAD) above 1.0 eV in each category. The overall MAD values are 1.35, 1.19, and 1.41 eV, respectively, with the worst performance being found in MNDO for hydrocarbons (MAD 1.68 eV) and in PM3 for CHN and oxygen-containing compounds (MAD 1.43–1.48 eV). The OMx methods (OM1, OM2, OM3) yield much better results: the vertical excitation energies are still mostly underestimated (overall on average by 0.34, 0.36, and 0.22 eV), with slightly higher mean absolute deviations (0.45, 0.50, and 0.45 eV). Looking at the three subsets separately, the OMx methods perform rather uniformly for hydrocarbons (MAD 0.40–0.42 eV) and also rather well for CHN compounds (MAD 0.38–0.46 eV), but somewhat larger errors occur for oxygen-containing compounds especially in OM1 (MAD 0.57 eV) and in OM2 (MAD 0.62 eV). Among the OMx methods, the OM3 errors appear to be most uniform, and the systematic underestimation of the energies seems least pronounced (with an overall mean error of –0.22 eV). However, one should not overemphasize this distinction from OM1 and OM2 because the three OMx methods perform quite similarly in general. Both INDO/S and its variant INDO/S2 with modified oxygen parameters yield an overall MAD value of 0.51 eV, comparable to OM2 (see above). They also tend to under-

Table 5. Deviations of Semiempirical Vertical Excitation Energies (in eV) for Singlet States with Respect to Theoretical Best Estimates

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
CH-Containing Molecules								
count ^a	25	25	25	25	25	25	25	25
mean	-1.68	-1.36	-1.29	-0.27	-0.29	-0.25	-0.20	-0.20
abs. mean	1.68	1.36	1.29	0.42	0.41	0.40	0.42	0.42
std. dev.	1.89	1.55	1.48	0.52	0.51	0.49	0.47	0.47
max. (+) dev.			0.04	0.76	0.66	0.72	0.81	0.81
max. (-) dev.	3.95	3.30	3.21	1.34	1.22	1.19	0.84	0.84
CHN-Containing Molecules								
count ^a	43	43	43	43	43	43	42	42
mean	-1.11	-1.01	-1.43	-0.27	-0.21	-0.09	-0.34	-0.34
abs. mean	1.22	1.13	1.43	0.38	0.45	0.46	0.48	0.48
std. dev.	1.41	1.27	1.53	0.49	0.54	0.57	0.63	0.63
max. (+) dev.	0.69	0.85		0.37	1.42	1.76	0.92	0.92
max. (-) dev.	3.00	2.60	2.58	1.16	1.09	1.08	1.45	1.45
CHO and CHNO-Containing Molecules								
count ^a	36	36	36	36	36	36	36	36
mean	-1.27	-1.09	-1.46	-0.47	-0.55	-0.35	-0.12	0.22
abs. mean	1.29	1.14	1.48	0.57	0.62	0.47	0.62	0.61
std. dev.	1.44	1.25	1.63	0.64	0.69	0.52	0.88	1.04
max. (+) dev.	0.18	0.42	0.19	0.56	0.58	0.60	2.79	4.24
max. (-) dev.	3.04	2.61	2.53	1.19	1.39	1.06	1.37	0.90
All Molecules								
count ^a	104	104	104	104	104	104	103	103
mean	-1.30	-1.12	-1.40	-0.34	-0.36	-0.22	-0.23	-0.11
abs. mean	1.35	1.19	1.41	0.45	0.50	0.45	0.51	0.51
std. dev.	1.55	1.34	1.55	0.55	0.59	0.54	0.70	0.77
max. (+) dev.	0.69	0.85	0.19	0.76	1.42	1.76	2.79	4.24
max. (-) dev.	3.95	3.30	3.21	1.34	1.39	1.19	1.45	1.45

^a Total number of states considered.**Table 6.** Deviations of Semiempirical Vertical Excitation Energies (in eV) for $n\pi^*$ and $\pi\pi^*$ Singlet States with Respect to Theoretical Best Estimates up to 6 eV

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
$n\pi^*$								
count ^a	33	33	33	33	33	33	32	32
mean	-0.62	-0.61	-1.08	-0.26	-0.18	-0.14	-0.31	-0.14
abs. mean	0.77	0.80	1.10	0.38	0.46	0.43	0.48	0.35
std. dev.	0.92	0.89	1.20	0.50	0.56	0.54	0.61	0.44
max. (+) dev.	0.69	0.85	0.19	0.40	1.42	1.76	0.92	0.92
max. (-) dev.	1.86	1.52	1.95	1.19	1.07	0.92	1.37	1.06
$\pi\pi^*$								
count ^a	25	25	25	25	25	25	25	25
mean	-1.42	-1.18	-1.30	-0.27	-0.26	-0.11	-0.19	-0.17
abs. mean	1.42	1.20	1.32	0.44	0.40	0.39	0.38	0.38
std. dev.	1.59	1.34	1.48	0.50	0.46	0.45	0.45	0.46
max. (+) dev.	0.01	0.19	0.17	0.76	0.66	0.81	0.81	0.81
max. (-) dev.	2.67	2.19	2.30	1.06	1.02	0.92	0.92	0.92

^a Total number of states considered.

estimate the vertical excitation energies (overall mean errors of -0.23 and -0.11 eV, respectively), but their results scatter more strongly than the OMx results (overall standard deviations of 0.70–0.77 eV as compared to 0.54–0.59 eV for OMx). Concerning the subsets, our evaluation confirms⁶⁶ that INDO/S tends to give somewhat higher errors for oxygen-containing compounds (MAD 0.62 eV), but the claimed improvement by the reparametrized INDO/S2 variant³⁵ is hardly seen in our data (MAD 0.61 eV).

The statistics in Table 5 include several singlet states above 6 eV for which TBE values are available. Because we expect in general that minimal-basis-set semiempirical calculations on valence excited states will become less appropriate the higher the energy, we have performed a

second evaluation restricted to singlet states up to 6 eV, considering $\pi\pi^*$ and $n\pi^*$ states separately. The results are shown in Table 6. It is obvious that the restriction to energies below 6 eV improves the statistics especially for MNDO, AM1, and PM3, where the MAD values for $\pi\pi^*$ states remain in the 1.2–1.4 eV range while those for the $n\pi^*$ states amount to 0.8–1.1 eV. The improvement is less pronounced for the OMx and INDO/S methods, which treat the two types of excitation in a fairly balanced manner: for example, the MAD values in OMx range from 0.39–0.44 eV for $\pi\pi^*$ states and from 0.38–0.46 eV for $n\pi^*$ states; the corresponding values for INDO/S are 0.38 and 0.48 eV. Comparison of the INDO/S and INDO/S2 statistics indicates that the reparametrization for oxygen

Table 7. Deviations of Semiempirical Vertical Excitation Energies (in eV) for Triplet States with Respect to Theoretical Best Estimates

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
CH-Containing Molecules								
count ^a	27	27	27	27	27	27	27	27
mean	-1.84	-1.50	-1.44	-0.42	-0.37	-0.35	-0.38	-0.38
abs. mean	1.84	1.50	1.44	0.45	0.42	0.41	0.57	0.57
std. dev.	1.96	1.61	1.55	0.55	0.54	0.52	0.74	0.74
max. (+) dev.				0.36	0.55	0.54	0.85	0.85
max. (-) dev.	3.66	3.06	2.98	1.31	1.21	1.17	1.63	1.63
CHN-Containing Molecules								
count ^a	20	20	20	20	20	20	20	20
mean	-1.24	-1.10	-1.44	-0.39	-0.27	-0.05	-0.43	-0.43
abs. mean	1.29	1.16	1.44	0.43	0.44	0.49	0.70	0.70
std. dev.	1.50	1.32	1.55	0.56	0.52	0.56	0.92	0.92
max. (+) dev.	0.54	0.47		0.19	0.64	1.08	0.86	0.86
max. (-) dev.	2.63	2.28	2.43	1.05	0.92	0.87	2.01	2.01
CHO and CHNO-Containing Molecules								
count ^a	16	16	16	16	16	16	16	16
mean	-1.35	-1.07	-1.34	-0.57	-0.53	-0.39	-0.04	0.60
abs. mean	1.38	1.15	1.37	0.62	0.60	0.49	0.72	1.02
std. dev.	1.54	1.29	1.56	0.73	0.70	0.57	0.96	1.44
max. (+) dev.	0.14	0.39	0.20	0.41	0.59	0.61	2.49	4.30
max. (-) dev.	2.63	2.26	2.40	1.04	1.03	0.89	1.54	1.48
All Molecules								
count ^a	63	63	63	63	63	63	63	63
mean	-1.52	-1.27	-1.41	-0.45	-0.38	-0.26	-0.31	-0.15
abs. mean	1.55	1.30	1.42	0.49	0.47	0.45	0.65	0.72
std. dev.	1.72	1.44	1.55	0.61	0.58	0.54	0.86	1.01
max. (+) dev.	0.54	0.47	0.20	0.41	0.64	1.08	2.49	4.30
max. (-) dev.	3.66	3.06	2.98	1.31	1.21	1.17	2.01	2.01

^a Total number of states considered.

has not affected the $\pi\pi^*$ states much, but has improved the energies of the $n\pi^*$ states below 6 eV (MAD 0.35 eV).

Table 7 presents the statistical results for triplet excited states, again for all states available and for three subsets (hydrocarbons, CHN compounds, CHO and CHNO compounds). The total number of states with TBE values is smaller than in the singlet case (63 vs 104), but still large enough for meaningful evaluations. As compared to the singlets, the overall performance for triplets is essentially the same for OMx (MAD 0.45–0.49 eV vs 0.45–0.50 eV), but somewhat worse for MNDO/AM1/PM3 (MAD 1.30–1.55 eV vs 1.19–1.41 eV) and also for INDO/S and INDO/S2 (MAD 0.65–0.72 eV vs 0.51 eV), but the general trends remain the same. The semiempirical excitation energies again tend to be too low, even slightly more so than in the case of the singlets (see the overall mean errors). Considering the subsets, the largest mean absolute deviations occur for the hydrocarbons in MNDO/AM1/PM3 and for the oxygen-containing compounds for OM1, OM2, INDO/S, and INDO/S2 (again in analogy to the singlets). Somewhat surprisingly, we find for the oxygen-containing compounds that INDO/S2 performs worse than INDO/S for the triplet states (MAD 1.02 eV vs 0.72 eV) despite the reparametrization, while OM3 again appears to be most balanced and performs best (MAD 0.47 eV vs 0.57–0.62 eV for OM1 and OM2).

For many photophysical and photochemical processes, the energy difference between excited states is of crucial importance. Table 8 provides a statistical evaluation for three such differences that are particularly relevant, between the

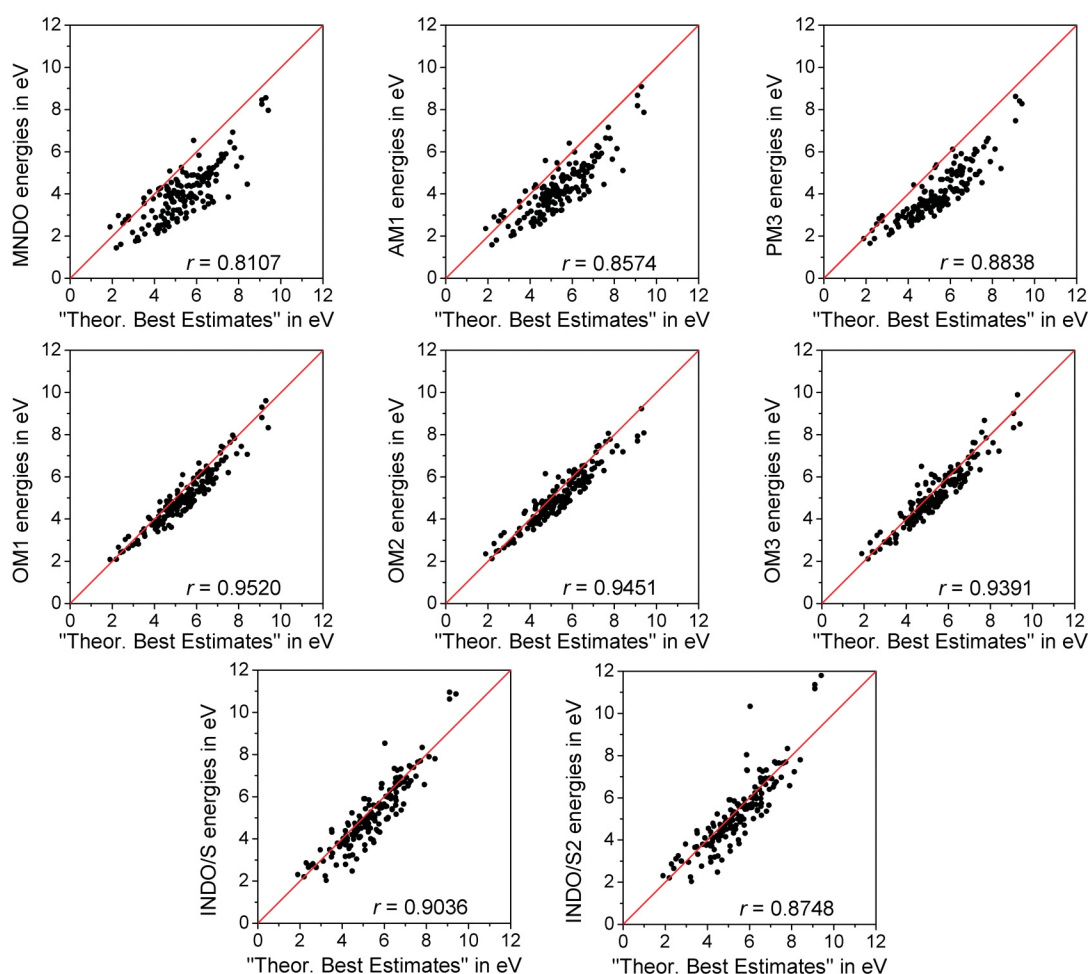
two lowest singlets, between the two lowest triplets, and between the lowest singlet and triplet states. It is obvious that the OMx methods show by far the best performance, with mean absolute deviations from the TBE values of 0.40–0.43, 0.23–0.32, and 0.20–0.21 eV for the S_2 – S_1 , T_2 – T_1 , and S_1 – T_1 energy gaps, respectively. The corresponding MAD values for the other semiempirical methods (MNDO, AM1, PM3, INDO/S, INDO/S2) are significantly higher and generally lie in the range between 0.4–0.6 eV for all three energy gaps considered. The associated mean errors indicate that these energy differences are normally underestimated in MNDO, AM1, and PM3 (on average by 0.3–0.4 eV for T_2 – T_1 and by 0.1–0.2 eV otherwise), while they are generally overestimated in INDO/S and INDO/S2 (on average by 0.4–0.6 eV for T_2 – T_1 and by 0.2–0.3 eV otherwise); by contrast, the OMx energy gaps are too low on average by only 0.1–0.2 eV for T_2 – T_1 and scatter around the TBE values for S_2 – S_1 and S_1 – T_1 (on average within 0.1 eV). These data show that the OMx methods predict the energy sequence within the excited states much better than the other semiempirical methods studied.

The overall performance for all singlet and triplet states considered can be judged from the correlation plots shown in Figure 1. The OMx results are rather close to the ideal correlation line with unit slope and yield reasonably high correlation coefficients ($r = 0.9391$ – 0.9520). The MNDO energies are generally too low and scatter considerably ($r = 0.8107$), while the AM1 and PM3 energies are also too low but more regular ($r = 0.8574$ – 0.8838). The INDO/S and INDO/S2 data also show some scatter around the TBE values

Table 8. Deviations of Semiempirical S_2-S_1 , T_2-T_1 , and S_1-T_1 Energy Differences (in eV) with Respect to Theoretical Best Estimates

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
$S_2-S_1^a$								
count ^b	27	27	27	27	27	27	27	27
mean	-0.13	-0.14	-0.24	0.04	-0.11	-0.10	0.27	0.20
abs. mean	0.64	0.52	0.57	0.42	0.40	0.43	0.64	0.55
std. dev.	0.83	0.68	0.67	0.47	0.46	0.49	0.88	0.80
max. (+) dev.	1.35	1.14	1.02	0.89	0.70	0.79	2.26	2.34
max. (-) dev.	1.65	1.42	1.29	0.75	0.97	1.02	1.22	1.22
$T_2-T_1^c$								
count ^b	19	19	19	19	19	19	19	19
mean	-0.30	-0.26	-0.37	-0.12	-0.17	-0.14	0.45	0.57
abs. mean	0.47	0.43	0.48	0.23	0.30	0.32	0.58	0.72
std. dev.	0.61	0.52	0.53	0.30	0.36	0.41	0.88	1.17
max. (+) dev.	1.46	1.02	0.50	0.46	0.60	0.70	2.52	3.81
max. (-) dev.	1.00	0.86	0.88	0.63	0.67	1.12	0.41	0.41
$S_1-T_1^d$								
count ^b	20	20	20	20	20	20	20	20
mean	-0.05	-0.06	-0.10	0.04	-0.07	-0.04	0.28	0.25
abs. mean	0.44	0.38	0.38	0.20	0.21	0.21	0.61	0.59
std. dev.	0.61	0.52	0.47	0.25	0.26	0.25	0.76	0.75
max. (+) dev.	1.52	1.11	0.81	0.54	0.46	0.39	1.80	1.80
max. (-) dev.	1.07	1.07	0.86	0.31	0.55	0.50	0.92	0.98

^a Energy difference between the two lowest singlet excited states. ^b Total number of molecules considered. ^c Energy difference between the two lowest triplet excited states. ^d Energy difference between the lowest singlet and triplet excited states.

**Figure 1.** Correlation plots of vertical excitation energies for all states considered in this study using theoretical best estimates as reference data.

($r = 0.8748-0.9036$). Similar separate correlation plots for the singlet and triplet states are presented in the Supporting Information (Figures S1 and S2).

Figure 2 provides a visual summary in the form of a histogram plot for the deviations of the computed vertical excitation energies from the TBE values of all states below

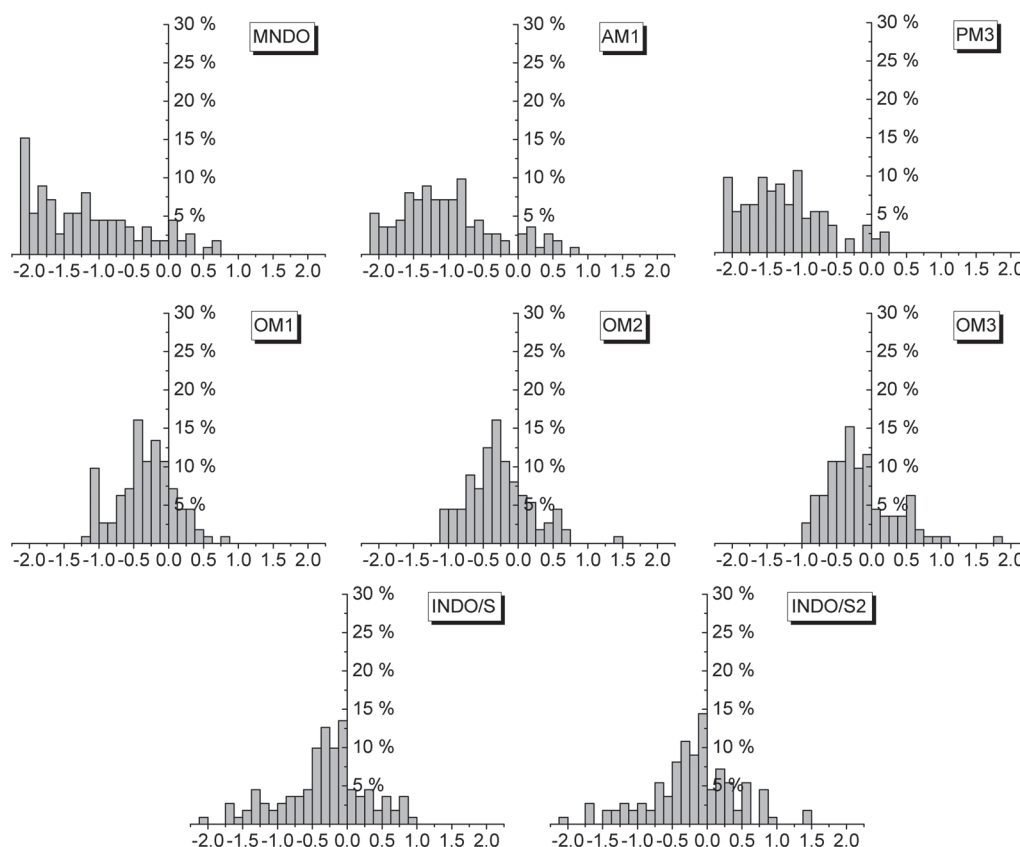


Figure 2. Histogram plots for the deviations of the calculated vertical excitation energies from the theoretical best estimates for all states below 6 eV considered in this study. In the case of MNDO, AM1, and PM3, the left-hand column collects all states whose energies are underestimated by more than 2 eV.

6 eV. Analogous histograms are given in the Supporting Information (Figures S3 and S4) separately for the $n\pi^*$ and $\pi\pi^*$ states. On the basis of these histograms and the statistical data presented in this section, it is possible to rank the semiempirical methods investigated here according to their overall performance to describe excitation energies. The OMx methods are clearly the best choice, with minor differences in the performance of the three variants, with a slight edge of OM2 and OM3 over OM1. INDO/S and INDO/S2 also perform reasonably well on average, specially for low-lying states, but show a considerably wider error distribution. Finally, the MNDO, AM1, and PM3 methods that are well established and widely used for ground states are least suitable for electronically excited states in their standard ground-state parametrization.

Among the previously studied DFT-based methods,¹⁵ TD-BP86 and TD-BHLYP show mean absolute deviations from the theoretical best estimates similar to those of the OMx methods, while TD-B3LYP and especially DFT/MRCI perform better (MAD for singlets, TD-B3LYP 0.27 eV, DFT/MRCI 0.22 eV, OMx 0.45–0.50 eV; triplets, TD-B3LYP 0.45 eV, DFT/MRCI 0.25 eV, OMx 0.45–0.49 eV). This is not unexpected in view of the computational costs, which are higher by about 3 orders of magnitude for TD-B3LYP (see section 2) and by even more in the case of DFT/MRCI. The DFT-based results have also been evaluated against other ab initio reference data.¹⁵ The corresponding statistical evaluations for the semiempirical methods are documented

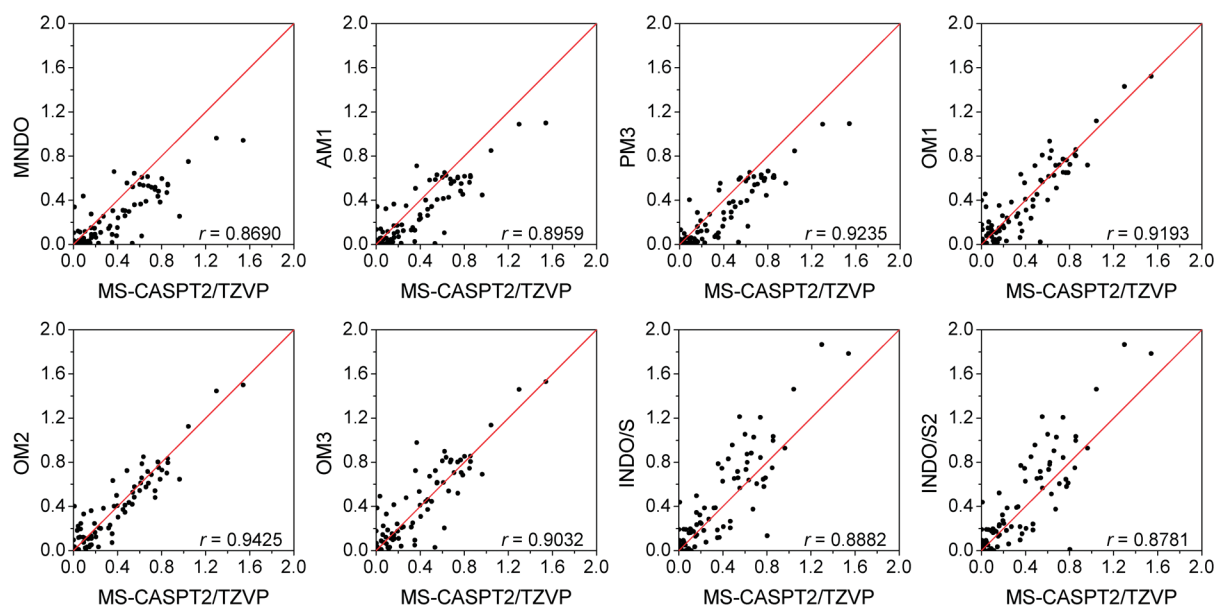
in the Supporting Information (Tables S10–S19) but will not be discussed here.

6.2. One-Electron Properties. As mentioned before, we have not yet established theoretical best estimates for the oscillator strengths and state dipole moments in our benchmark set. Therefore, we use three sets of ab initio reference data: the comparisons with our own MS-CASPT2/TZVP results¹⁴ are presented here, while those with the published CASPT2 data mainly from the Roos group and with our own CC2/TZVP data¹⁵ are given in the Supporting Information (Figures S5–S8, Tables S20 and S21). The qualitative conclusions from these comparisons are the same for each set of reference data.

Table 9 summarizes the statistical evaluation of the calculated oscillator strengths for all dipole-allowed transitions, and Figure 3 shows the corresponding correlation plots against the MS-CASPT2/TZVP reference data. Visual inspection of these plots indicates that the OMx oscillator strengths scatter around the ideal correlation line with unit slope and correlate reasonably well with the reference data ($r = 0.9032$ – 0.9425). The MNDO/AM1/PM3 oscillator strengths tend to be too low and correlate less well ($r = 0.8690$ – 0.9235), while INDO/S and INDO/S2 tend to overestimate the reference values and have low correlation coefficients ($r = 0.8781$ – 0.8882). These visual impressions are corroborated by the statistical results. For the whole set of dipole-allowed transitions considered, the mean absolute deviations from the MS-CASPT2/TZVP oscillator strengths

Table 9. Deviations of Semiempirical Oscillator Strengths (in Length Representation) of Dipole-Allowed States with Respect to *ab Initio* Reference Data

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 Results ^a								
count ^b	100	100	100	100	100	100	98	98
mean	−0.085	−0.058	−0.066	0.014	0.006	0.027	0.075	0.070
abs. mean	0.114	0.100	0.102	0.081	0.075	0.102	0.148	0.150
std. dev.	0.203	0.184	0.182	0.146	0.119	0.181	0.222	0.226
max. (+) dev.	0.511	0.564	0.406	0.309	0.307	0.831	0.707	0.707
max. (−) dev.	0.870	0.844	0.831	0.830	0.432	0.822	0.627	0.750
MS-CASPT2/TZVP Results ^a								
count ^b	100	100	100	100	100	100	98	98
mean	−0.100	−0.073	−0.081	−0.001	−0.009	0.011	0.058	0.053
abs. mean	0.131	0.113	0.105	0.086	0.077	0.094	0.134	0.137
std. dev.	0.197	0.166	0.155	0.134	0.112	0.152	0.203	0.208
max. (+) dev.	0.346	0.342	0.314	0.421	0.393	0.609	0.659	0.659
max. (−) dev.	0.711	0.529	0.516	0.515	0.320	0.507	0.671	0.794
CC2/TZVP Results ^a								
count ^b	100	100	100	100	100	100	98	98
mean	−0.035	−0.008	−0.015	0.064	0.057	0.077	0.124	0.120
abs. mean	0.092	0.087	0.084	0.102	0.082	0.118	0.151	0.150
std. dev.	0.171	0.153	0.146	0.158	0.130	0.189	0.229	0.230
max. (+) dev.	0.490	0.543	0.385	0.440	0.387	0.810	0.845	0.845
max. (−) dev.	0.795	0.670	0.670	0.475	0.312	0.467	0.414	0.537

^a See ref 14. ^b Total number of states considered.**Figure 3.** Correlation plots of oscillator strengths for all dipole-allowed transitions using MS-CASPT2/TZVP results as reference data.

are 0.077–0.094 for OM_x, 0.105–0.131 for MNDO/AM1/PM3, and 0.134–0.137 for INDO/S and INDO/S2. The overall mean deviations confirm that the OM_x oscillator strengths are on average close to the MS-CASPT2/TZVP reference data (within 0.01), while the results from MNDO/AM1/PM3 are mostly too low (on average by 0.07–0.10) and those from INDO/S and INDO/S2 mostly too high (on average by 0.05–0.06).

Table 10 presents the statistical evaluation of all nonzero state dipole moments in our benchmark set, and Figure 4 shows the corresponding correlation plots against the MS-CASPT2/TZVP reference data. It is evident that the semiempirical results often differ rather strongly from the *ab initio* data. The performance of OM_x (MAD 0.68–0.71 D) and MNDO/AM1/PM3 (MAD 0.66–0.76 D) is similar in this

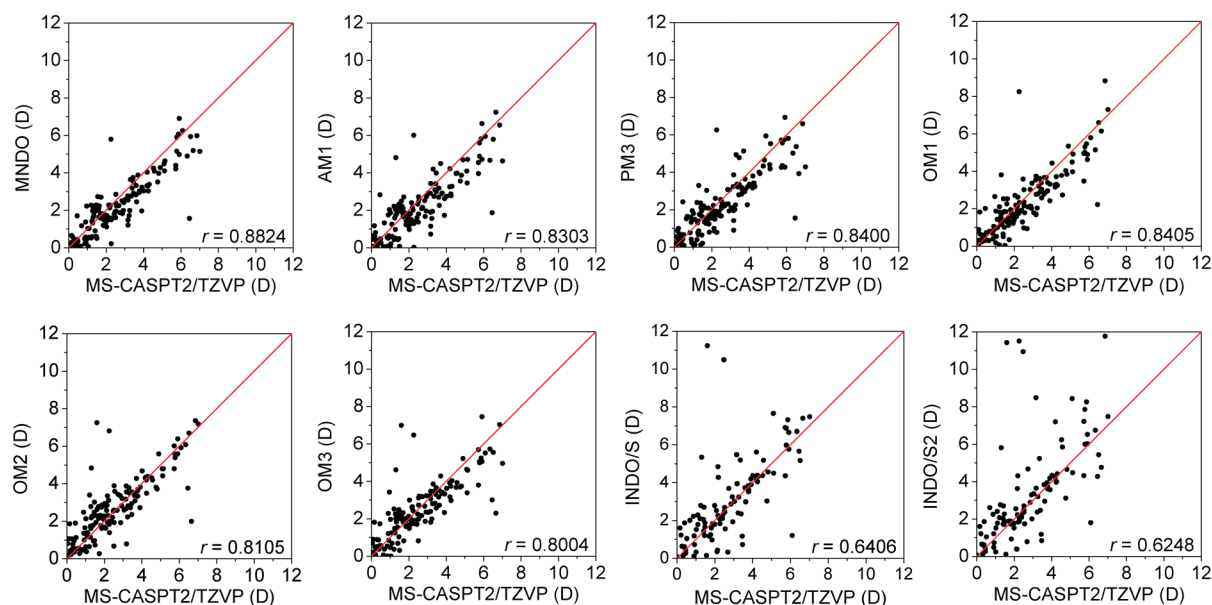
case and better than that of INDO/S and INDO/S2 (MAD 1.08–1.19 D). The overall mean errors suggest that state dipole moments tend to be underestimated by OM_x (on average by 0.10–0.23 D) and somewhat more by MNDO/AM1/PM3 (on average by 0.27–0.37 D), while INDO/S and INDO/S2 tend to overestimate them (on average by 0.40–0.49 D). These trends are also apparent from the correlation plots.

Summarizing the statistical evaluations for the oscillator strengths and state dipole moments, the OM_x methods show the best overall performance for these one-electron properties, without any pronounced preference for one of the three variants. To put the OM_x results into perspective, we note that rather similar deviations from the *ab initio* reference data have also been found for DFT-based methods, both for oscillator strengths (MAD: TD-B3LYP 0.113, DFT/MRCI

Table 10. Deviations of Semiempirical State Dipole Moments (in D) with Respect to ab Initio Reference Data^a

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 Results^b								
count ^c	142	142	142	142	142	142	104	104
mean	-0.61	-0.58	-0.51	-0.47	-0.11	-0.34	0.11	0.20
abs. mean	0.93	1.03	1.02	0.94	0.86	0.92	1.25	1.35
std. dev.	1.44	1.53	1.54	1.44	1.38	1.43	2.16	2.26
max. (+) dev.	2.37	3.81	2.98	5.22	5.75	5.49	9.73	9.92
max. (-) dev.	7.17	7.28	7.21	6.58	5.82	6.10	4.92	5.08
MS-CASPT2/TZVP Results^b								
count ^c	142	142	142	142	142	142	104	104
mean	-0.37	-0.34	-0.27	-0.23	-0.13	-0.10	0.40	0.49
abs. mean	0.66	0.76	0.72	0.68	0.68	0.71	1.08	1.19
std. dev.	0.91	1.05	1.00	1.00	1.07	1.07	2.03	2.11
max. (+) dev.	3.52	3.73	3.98	5.97	5.64	5.38	10.01	9.81
max. (-) dev.	4.91	4.60	4.91	4.25	4.68	4.37	4.90	4.30
RI-CC2/TZVP Results^b								
count ^c	140	140	140	140	140	140	103	103
mean	-0.16	-0.13	-0.07	-0.04	0.33	0.09	0.66	0.75
abs. mean	0.83	0.88	0.80	0.74	0.80	0.81	1.16	1.26
std. dev.	1.11	1.19	1.12	1.15	1.25	1.22	2.18	2.32
max. (+) dev.	4.25	4.53	4.57	6.81	5.35	5.01	10.62	9.75
max. (-) dev.	2.93	3.44	3.78	1.85	4.90	4.59	1.98	2.13

^a Ground and excited states. Only singlet states in the case of INDO/S and INDO/S2. ^b See ref 14. ^c Total number of states considered.

**Figure 4.** Correlation plots of nonzero state dipole moments (in D) for all states considered, using MS-CASPT2/TZVP results as reference data.

0.069, OMx 0.077–0.094) and for state dipole moments (MAD: TD-B3LYP 0.59 D, DFT/MRCI 0.58 D, OMx 0.68–0.71 D).¹⁵

7. Conclusions

We have performed a comprehensive validation study for eight semiempirical methods to assess their performance in describing vertical excitation energies and one-electron properties of electronically excited states. The semiempirical results were compared against ab initio reference data for a recently developed benchmark set of 28 medium-sized organic molecules, focusing on the published theoretical best estimates for excitation energies and MS-CASPT2/TZVP oscillator strengths and excited-state dipole moments.¹⁴ The benchmark set includes only valence excited states because

Rydberg states cannot be described by semiempirical methods due to the use of a minimal basis set.

The standard ground-state methods MNDO, AM1, and PM3 strongly underestimate the reference excitation energies, typically by more than 1 eV, and they often give a wrong order of the excited states because the errors are not uniform. These methods thus seem unsuitable for excited-state work unless one is prepared to undertake a system-specific reparametrization.

The INDO/S method has been parametrized for spectroscopic purposes and has often been applied to compute electronic spectra at the semiempirical level. In the current benchmark, it performs reasonably well, with typical errors of 0.5 eV for excited singlets and 0.6–0.7 eV for triplet states. By design, INDO/S does not properly account for

states with significant double-excitation character, and it is thus not surprising that the INDO/S errors are smaller for low-lying than for high-lying singlet states. The INDO/S2 variant has been reparametrized for oxygen,³⁵ which indeed improves the results for low-lying singlet states of oxygen-containing compounds, but turns out to be detrimental for the high-lying singlets and the triplet states of our benchmark molecules. Hence, INDO/S2 cannot be recommended as a general-purpose alternative to INDO/S.

The NDDO-based orthogonalization-corrected methods OM1, OM2, and OM3 show the best overall performance in the present benchmark. They give vertical excitation energies with typical errors of 0.4–0.5 eV both for valence excited singlet and for triplet states, and they predict the order of the excited states and the gaps between the low-lying states more reliably than the other semiempirical methods. The OMx/CISDTQ wave functions for valence excited states normally show a qualitatively similar composition to the corresponding ab initio CASSCF and CASPT2 wave functions (with regard to the leading configurations). The OMx methods provide reasonable one-electron properties (oscillator strengths and excited-state dipole moments), which are overall somewhat closer to the ab initio reference data than those obtained from the other semiempirical methods. The performance of the three OMx variants is generally quite similar, although OM2 and OM3 would seem to have a slight edge over OM1 in an overall assessment.

Conceptually, the OMx methods are superior to INDO/S because of the use of the more refined NDDO integral approximation, and to all other semiempirical methods considered here because of the explicit inclusion of corrections that mimic Pauli exchange repulsion and thus cause an unsymmetric splitting of bonding and antibonding levels. These advances are believed to contribute to the good OMx performance for electronically excited states, which is achieved despite the fact that the adjustable OMx parameters have been determined by calibrating purely against ground-state reference data. One may anticipate that further improvements are possible through a general-purpose reparametrization of the OMx methods that includes ground-state and excited-state reference data in a balanced manner. In such reparametrization work as well as in other applications, it seems justified to replace the CISDTQ treatment employed here by a more cost-efficient MR-CISD approach, which yields essentially the same results provided that the reference configurations dominate the CI wave functions (e.g., by requiring their combined weight to exceed 85%).

In summary, at the semiempirical level, the OMx methods appear to be the best choice for studying excited-state phenomena in large organic chromophores. While the results from the current benchmark support such applications using the existing ground-state parametrization, further improvements in the OMx description of electronically excited states may be expected from a balanced reparametrization.

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Supporting Information Available: Additional numerical results for excitation energies and one-electron properties (Tables S1–S9), additional correlation and histogram plots (Figures S1–S8), and additional statistical evaluations (Tables S10–S22). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting information for: Benchmark of electronically excited states for semiempirical methods: MNDO, AM1, PM3, OM1, OM2, OM3, INDO/S and INDO/S2

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1 Additional numerical results: Tables S 1 – S 9

1.1 Excitation energies

Table S 1: Vertical singlet excitation energies ΔE (eV) of all evaluated molecules for the semiempirical method OM1 using different approaches.^a

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	8.54	7.80	7.82	7.82	7.82	7.82	7.82	7.82
<i>E</i> -Butadiene	$2^1A_g (\pi \rightarrow \pi^*)$	6.62	6.55	5.88	5.88	5.88	5.88	5.88	5.88
	$1^1B_u (\pi \rightarrow \pi^*)$	6.47	6.18	6.24	6.24	6.24	6.24	6.24	6.24
Hexatriene	$2^1A_g (\pi \rightarrow \pi^*)$	5.42	5.09	4.79	4.79	4.79	4.80	4.81	4.82
	$1^1B_u (\pi \rightarrow \pi^*)$	5.31	5.10	5.35	5.35	5.36	5.35	5.35	5.34
all- <i>E</i> -Octatetraene	$2^1A_g (\pi \rightarrow \pi^*)$	4.64	4.47	4.07	4.09	4.09	4.09	4.10	4.11
	$1^1B_u (\pi \rightarrow \pi^*)$	4.70	4.66	4.79	4.79	4.78	4.78	4.78	4.77
Cyclopropene	$1^1B_2 (\pi \rightarrow \pi^*)$	7.06	7.06	6.59	6.59	6.59	6.59	6.59	6.59
	$1^1B_1 (\sigma \rightarrow \pi^*)$	6.76	6.76	6.33	6.33	6.33	6.33	6.33	6.33
Cyclopentadiene	$2^1A_1 (\pi \rightarrow \pi^*)$	6.31	6.31	5.52	5.52	5.52	5.52	5.52	5.52
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.52		7.63	7.63	7.63	7.63	7.63	7.63
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.51	5.55	5.14	5.14	5.14	5.14	5.14	5.14
Norbornadiene	$1^1A_2 (\pi \rightarrow \pi^*)$	5.34	5.34	6.10	6.10	6.10	6.10	6.10	6.10
	$2^1A_2 (\pi \rightarrow \pi^*)$	7.45		6.92	6.92	6.92	6.92	6.92	6.92
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.11	6.11	6.65	6.65	6.65	6.65	6.65	6.65
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.32		7.42	7.42	7.42	7.42	7.42	7.42
Benzene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.42	6.54	5.98	5.98	5.98	5.98	5.98	5.98
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.04	5.08	4.41	4.41	4.41	4.41	4.41	4.41
	$1^1E_{1u} (\pi \rightarrow \pi^*)$	7.13	7.13	7.13	7.13	7.13	7.13	7.13	7.13
	$1^1E_{2g} (\pi \rightarrow \pi^*)$	8.18	8.41	7.07	7.07	7.07	7.07	7.07	7.07
Naphthalene	$2^1A_g (\pi \rightarrow \pi^*)$	5.87	5.87	5.13	5.16	5.18	5.22	5.24	5.24

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Table S 1 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Furan	$3^1A_g (\pi \rightarrow \pi^*)$	6.67	6.67	5.91	5.94	5.96	5.99	6.02	6.02
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.77	4.77	4.84	4.85	4.84	4.83	4.82	4.83
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	6.33	6.33	6.20	6.22	6.22	6.23	6.22	6.23
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	8.17		8.06	8.09	8.11	8.12	8.12	8.13
	$1^1B_{3u} (\pi \rightarrow \pi^*)$	4.24	4.24	3.74	3.76	3.78	3.80	3.82	3.83
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	6.06	6.06	6.10	6.12	6.12	6.13	6.14	6.14
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	7.74		6.64	6.68	6.72	6.74	6.77	6.78
	$1^1B_{1g} (\pi \rightarrow \pi^*)$	5.99	5.99	5.64	5.67	5.71	5.75	5.74	5.78
	$2^1B_{1g} (\pi \rightarrow \pi^*)$	6.47	6.47	6.27	6.29	6.30	6.32	6.30	6.32
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.50	6.57	5.39	5.39	5.39	5.39	5.39	5.39
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.17	8.13	7.44	7.44	7.44	7.44	7.44	7.44
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.39	6.32	5.78	5.78	5.78	5.78	5.78	5.78
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	6.31	6.37	5.21	5.21	5.21	5.21	5.21	5.20
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.17	7.91	7.10	7.10	7.10	7.10	7.10	7.13
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.57	6.57	5.77	5.77	5.77	5.77	5.78	5.77
Imidazole	$2^1A' (\pi \rightarrow \pi^*)$	6.19	6.19	5.50	5.50	5.50	5.50	5.50	5.50
	$3^1A' (\pi \rightarrow \pi^*)$	6.93	6.93	5.95	5.95	5.95	5.96	5.96	5.96
	$4^1A' (\pi \rightarrow \pi^*)$	8.16		7.40	7.40	7.40	7.40	7.40	7.40
	$1^1A'' (n \rightarrow \pi^*)$	6.81	6.81	5.87	5.87	5.87	5.89	5.89	5.89
	$2^1A'' (n \rightarrow \pi^*)$	7.90		6.81	6.81	6.81	6.82	6.82	6.82
Pyridine	$2^1A_1 (\pi \rightarrow \pi^*)$	6.39	6.26	6.14	6.14	6.14	6.14	6.14	6.13
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.46	7.18	7.44	7.44	7.44	7.45	7.45	7.46
	$4^1A_1 (\pi \rightarrow \pi^*)$	8.69		7.52	7.53	7.54	7.54	7.55	7.55
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.02	4.85	4.56	4.56	4.56	4.58	4.58	4.57
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.27	7.27	7.39	7.39	7.39	7.41	7.41	7.40
	$3^1B_2 (\pi \rightarrow \pi^*)$	8.60		7.09	7.09	7.09	7.12	7.12	7.11

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Table S 1 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Pyrazine	$1^1B_1 (n \rightarrow \pi^*)$	5.17	4.59	4.84	4.85	4.87	4.90	4.90	4.89
	$1^1A_2 (n \rightarrow \pi^*)$	5.51	5.11	5.16	5.17	5.22	5.21	5.21	5.21
	$2^1A_g (\pi \rightarrow \pi^*)$	8.61		7.88	7.89	7.90	7.91	7.91	7.91
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.89	6.58	6.24	6.24	6.24	6.24	6.24	6.23
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.79	7.72	7.98	7.98	8.02	8.02	8.02	8.01
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.85	4.64	4.61	4.61	4.62	4.64	4.67	4.64
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	7.66	7.60	7.64	7.64	7.66	7.67	7.67	7.66
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	8.47		7.16	7.16	7.17	7.19	7.22	7.21
	$1^1A_u (n \rightarrow \pi^*)$	4.70	4.81	4.37	4.38	4.48	4.48	4.48	4.47
	$1^1B_{1g} (n \rightarrow \pi^*)$	6.41	6.60	6.33	6.34	6.39	6.39	6.56	6.55
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.68	5.56	5.48	5.49	5.52	5.57	5.57	5.72
Pyrimidine	$1^1B_{3u} (n \rightarrow \pi^*)$	4.21	3.95	3.90	3.90	4.01	4.01	4.01	4.00
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.63	6.95	6.37	6.37	6.37	6.37	6.37	6.37
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.21		7.75	7.76	7.76	7.77	7.78	7.79
	$4^1A_1 (\pi \rightarrow \pi^*)$	9.19		7.34	7.37	7.37	7.38	7.39	7.40
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.24	5.44	4.77	4.77	4.77	4.78	4.79	4.79
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.64		7.62	7.63	7.63	7.63	7.64	7.64
	$3^1B_2 (\pi \rightarrow \pi^*)$	8.73		7.92	7.92	7.93	7.93	7.94	7.94
Pyridazine	$1^1B_1 (n \rightarrow \pi^*)$	4.44	4.55	4.43	4.43	4.51	4.51	4.50	4.50
	$1^1A_2 (n \rightarrow \pi^*)$	4.80	4.91	4.73	4.73	4.81	4.81	4.80	4.80
	$2^1A_1 (\pi \rightarrow \pi^*)$	5.18	5.18	4.62	4.63	4.63	4.64	4.64	4.65
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.62		7.59	7.59	7.45	7.46	7.46	7.46
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.13		6.34	6.34	6.34	6.34	6.34	6.33
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.29		7.28	7.29	7.29	7.30	7.30	7.32
	$1^1A_2 (n \rightarrow \pi^*)$	4.31	4.31	4.39	4.39	4.40	4.45	4.45	4.44
	$2^1A_2 (n \rightarrow \pi^*)$	5.77	5.77	5.39	5.40	5.43	5.47	5.47	5.46

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Table S 1 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
<i>s</i> -Triazine	$1^1B_1 (n \rightarrow \pi^*)$	3.78	3.78	4.01	4.01	4.05	4.06	4.06	4.05
	$2^1B_1 (n \rightarrow \pi^*)$	6.52		5.78	5.78	5.82	5.83	5.83	5.82
	$2^1A'_1 (\pi \rightarrow \pi^*)$	7.25		6.74	6.74	6.75	6.75	6.75	6.75
	$1^1A'_2 (\pi \rightarrow \pi^*)$	5.79	5.79	5.06	5.06	5.06	5.06	5.07	5.07
	$1^1E' (\pi \rightarrow \pi^*)$	7.50		7.72	7.72	7.71	7.72	7.72	7.72
	$2^1E' (\pi \rightarrow \pi^*)$	8.99		8.26	8.26	8.26	8.27	8.29	8.29
	$1^1A''_1 (n \rightarrow \pi^*)$	4.60	4.60	4.80	4.80	4.89	4.90	4.90	4.89
	$1^1A''_2 (n \rightarrow \pi^*)$	4.66	4.66	4.48	4.48	4.75	4.76	4.75	4.75
	$1^1E'' (n \rightarrow \pi^*)$	4.70	4.70	4.65	4.66	4.86	4.87	4.86	4.86
	$2^1E'' (n \rightarrow \pi^*)$	7.71		7.41	7.48	7.43	7.44	7.47	7.47
<i>s</i> -Tetrazine	$1^1A_u (n \rightarrow \pi^*)$	3.51	3.51	3.52	3.53	3.57	3.66	3.66	3.64
	$2^1A_u (n \rightarrow \pi^*)$	5.50	5.50	4.89	4.89	4.94	5.02	5.02	5.00
	$1^1B_{1g} (n \rightarrow \pi^*)$	4.73	4.73	5.07	5.08	5.10	5.12	5.15	5.13
	$2^1B_{1g} (n \rightarrow \pi^*)$	6.45		5.62	5.63	5.68	5.68	5.73	5.71
	$3^1B_{1g} (n \rightarrow \pi^*)$	6.73		6.28	6.29	6.34	6.40	6.43	6.41
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.20	5.20	5.02	5.02	5.09	5.09	5.09	5.09
	$2^1B_{2g} (n \rightarrow \pi^*)$	6.06		5.96	5.97	6.04	6.04	6.03	6.02
	$1^1B_{3g} (n \rightarrow \pi^*)$	5.86		5.91	5.93	6.02	6.16	6.16	6.15
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	8.34		7.60	7.54	7.67	7.69	7.69	7.71
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.94		6.75	6.75	6.76	6.75	6.76	6.74
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.42		7.67	7.67	7.70	7.70	7.70	7.68
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.93	4.93	4.70	4.71	4.72	4.75	4.75	4.73
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.14		8.23	8.24	8.27	8.29	8.30	8.28
	$1^1B_{3u} (n \rightarrow \pi^*)$	2.29	2.29	2.65	2.66	2.76	2.76	2.76	2.74
	$2^1B_{3u} (n \rightarrow \pi^*)$	6.77		5.65	5.66	5.78	5.78	5.78	5.76
Formaldehyde	$1^1A_2 (n \rightarrow \pi^*)$	3.99	3.88	3.71	3.71	3.71	3.71	3.71	3.71

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Table S 1 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Acetone	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.14	9.10	9.30	9.30	9.30	9.30	9.30	9.30
	$2^1A_1 (\pi \rightarrow \pi^*)$	9.32	9.30	9.61	9.61	9.61	9.61	9.61	9.61
	$1^1A_2 (n \rightarrow \pi^*)$	4.44	4.40	3.80	3.80	3.80	3.80	3.80	3.80
	$2^1A_1 (\pi \rightarrow \pi^*)$	9.31	9.40	8.33	8.33	8.33	8.33	8.33	8.33
<i>p</i> -Benzoquinone	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.27	9.10	8.81	8.81	8.81	8.81	8.81	8.81
	$1^1A_u (n \rightarrow \pi^*)$	2.77	2.77	3.15	3.17	3.19	3.18	3.18	3.18
	$1^1B_{1g} (n \rightarrow \pi^*)$	2.76	2.76	2.60	2.62	2.62	2.61	2.61	2.61
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.28	5.28	5.64	5.64	5.64	5.65	5.65	5.65
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.92		7.78	7.81	7.81	7.81	7.82	7.82
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.26	4.26	4.81	4.82	4.85	4.85	4.85	4.85
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	6.96	6.96	6.57	6.58	6.65	6.65	6.65	6.64
	$1^1B_{3u} (n \rightarrow \pi^*)$	5.64	5.64	5.23	5.24	5.34	5.33	5.33	5.33
Formamide	$1^1A'' (n \rightarrow \pi^*)$	5.63	5.63	4.61	4.61	4.61	4.61	4.61	4.61
	$2^1A' (\pi \rightarrow \pi^*)$	7.39	7.39	6.92	6.92	6.92	6.92	6.92	6.92
	$3^1A' (\pi \rightarrow \pi^*)$	10.54		9.67	9.67	9.67	9.67	9.67	9.67
Acetamide	$1^1A'' (n \rightarrow \pi^*)$	5.69	5.69	4.59	4.59	4.59	4.59	4.59	4.59
	$2^1A' (\pi \rightarrow \pi^*)$	7.27	7.27	6.76	6.76	6.76	6.76	6.76	6.76
	$3^1A' (\pi \rightarrow \pi^*)$	10.09		8.93	8.93	8.93	8.93	8.93	8.93
Propanamide	$1^1A'' (n \rightarrow \pi^*)$	5.72	5.72	4.67	4.67	4.67	4.67	4.67	4.67
	$2^1A' (\pi \rightarrow \pi^*)$	7.20	7.20	6.78	6.78	6.78	6.78	6.78	6.78
	$3^1A' (\pi \rightarrow \pi^*)$	9.94		8.72	8.72	8.72	8.72	8.72	8.72
Cytosine	$2^1A' (\pi \rightarrow \pi^*)$	4.67	4.66	4.19	4.19	4.20	4.20	4.20	4.20
	$3^1A' (\pi \rightarrow \pi^*)$	5.53	5.62	5.00	5.01	5.02	5.02	5.02	5.02
	$4^1A' (\pi \rightarrow \pi^*)$	6.40		5.88	5.88	5.89	5.89	5.89	5.89
	$5^1A' (\pi \rightarrow \pi^*)$	6.97		6.13	6.14	6.15	6.15	6.15	6.15

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Table S 1 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Thymine	$1^1A'' (n \rightarrow \pi^*)$	5.12	4.87	4.19	4.19	4.21	4.22	4.25	4.25
	$2^1A'' (n \rightarrow \pi^*)$	5.53	5.26	4.76	4.76	4.78	4.79	4.81	4.81
	$2^1A' (\pi \rightarrow \pi^*)$	5.06	5.20	4.96	4.97	4.97	4.98	4.98	4.99
	$3^1A' (\pi \rightarrow \pi^*)$	6.15	6.27	5.78	5.78	5.78	5.79	5.80	5.82
	$4^1A' (\pi \rightarrow \pi^*)$	6.53	6.53	5.90	5.91	5.92	5.92	5.92	5.94
	$5^1A' (\pi \rightarrow \pi^*)$	7.43		6.71	6.71	6.72	6.72	6.72	6.74
	$1^1A'' (n \rightarrow \pi^*)$	4.95	4.82	4.34	4.34	4.35	4.34	4.35	4.37
	$2^1A'' (n \rightarrow \pi^*)$	6.38	6.16	5.31	5.32	5.32	5.32	5.33	5.34
	$3^1A'' (n \rightarrow \pi^*)$	6.85		6.07	6.07	6.08	6.08	6.10	6.12
	$4^1A'' (n \rightarrow \pi^*)$	7.43		6.47	6.48	6.48	6.48	6.48	6.52
Uracil	$2^1A' (\pi \rightarrow \pi^*)$	5.23	5.35	5.05	5.05	5.06	5.06	5.06	5.06
	$3^1A' (\pi \rightarrow \pi^*)$	6.15	6.26	5.78	5.78	5.79	5.79	5.79	5.79
	$4^1A' (\pi \rightarrow \pi^*)$	6.74	6.70	6.13	6.14	6.15	6.15	6.15	6.15
	$5^1A' (\pi \rightarrow \pi^*)$	7.42		6.71	6.72	6.73	6.73	6.73	6.73
	$1^1A'' (n \rightarrow \pi^*)$	4.91	4.80	4.27	4.27	4.27	4.27	4.27	4.27
	$2^1A'' (n \rightarrow \pi^*)$	6.28	6.10	5.28	5.29	5.29	5.29	5.29	5.29
	$3^1A'' (n \rightarrow \pi^*)$	6.98	6.56	6.09	6.09	6.10	6.10	6.10	6.10
	$4^1A'' (n \rightarrow \pi^*)$	7.28		6.46	6.47	6.47	6.47	6.47	6.47
Adenine	$2^1A' (\pi \rightarrow \pi^*)$	5.20	5.25	4.18	4.19	4.21	4.21	4.21	4.21
	$3^1A' (\pi \rightarrow \pi^*)$	5.29	5.25	4.82	4.83	4.83	4.83	4.83	4.83
	$4^1A' (\pi \rightarrow \pi^*)$	6.34		5.59	5.61	5.62	5.62	5.62	5.62
	$5^1A' (\pi \rightarrow \pi^*)$	6.64		5.98	6.00	6.02	6.02	6.02	6.02
	$6^1A' (\pi \rightarrow \pi^*)$	6.87		6.01	6.02	6.05	6.05	6.05	6.05
	$7^1A' (\pi \rightarrow \pi^*)$	7.56		6.47	6.49	6.50	6.50	6.50	6.50
	$1^1A'' (n \rightarrow \pi^*)$	5.19	5.12	4.79	4.81	4.92	4.92	4.92	4.92
	$2^1A'' (n \rightarrow \pi^*)$	5.96	5.75	5.09	5.10	5.24	5.24	5.24	5.24

^aSee main paper for notation. SDXX denotes an MR-CISD treatment with a threshold of XX%.

Table S 2: Vertical triplet excitation energies ΔE (eV) of all evaluated molecules for the semiempirical method OM1 using different approaches.^a

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.48	4.50	4.07	4.07	4.07	4.07	4.07	4.07
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	3.34	3.20	2.99	2.99	2.99	2.99	2.99	2.99
	$1^3A_g (\pi \rightarrow \pi^*)$	5.16	5.08	4.49	4.49	4.49	4.49	4.49	4.49
all- <i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	2.71	2.40	2.41	2.41	2.44	2.45	2.45	2.44
	$1^3A_g (\pi \rightarrow \pi^*)$	4.31	4.15	3.72	3.73	3.74	3.75	3.74	3.73
all- <i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	2.33	2.20	2.06	2.09	2.12	2.14	2.18	2.17
	$1^3A_g (\pi \rightarrow \pi^*)$	3.70	3.55	3.15	3.18	3.22	3.23	3.24	3.23
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	4.35	4.34	3.77	3.77	3.76	3.77	3.76	3.76
	$1^3B_1 (\sigma \rightarrow \pi^*)$	6.51	6.62	6.01	6.01	6.01	6.01	6.01	6.01
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.28	3.25	2.81	2.81	2.81	2.81	2.81	2.81
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.11	5.09	4.23	4.23	4.23	4.23	4.23	4.23
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	3.75	3.72	4.08	4.08	4.08	4.08	4.08	4.08
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.22	4.16	3.89	3.89	3.89	3.89	3.89	3.89
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.17	4.15	3.65	3.66	3.66	3.66	3.66	3.66
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	4.90	4.86	4.47	4.48	4.48	4.48	4.48	4.48
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	5.76	5.88	5.79	5.79	5.79	5.79	5.79	5.79
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.38	7.51	6.20	6.20	6.20	6.20	6.20	6.20
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.16	3.11	2.81	2.84	2.88	2.90	2.89	2.89
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	4.25	4.18	3.85	3.87	3.95	3.98	3.97	3.97
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.51	4.47	3.97	4.00	4.02	4.01	4.01	4.03
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.68	4.64	4.19	4.22	4.30	4.30	4.29	4.29
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	4.97	5.11	4.94	4.95	4.95	4.96	4.95	4.95
	$1^3A_g (\pi \rightarrow \pi^*)$	5.53	5.52	4.79	4.82	4.86	4.85	4.84	4.84

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Table S 2 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Furan	$2^3B_{1g} (\pi \rightarrow \pi^*)$	6.21	6.48	6.46	6.46	6.48	6.48	6.49	6.51
	$2^3A_g (\pi \rightarrow \pi^*)$	6.38	6.47	6.48	6.50	6.50	6.49	6.48	6.48
	$3^3A_g (\pi \rightarrow \pi^*)$	6.59	6.79	5.64	5.68	5.72	5.73	5.73	5.73
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	6.64	6.76	5.67	5.71	5.77	5.78	5.81	5.86
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.18	4.17	3.40	3.40	3.41	3.41	3.40	3.41
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.49	5.48	4.44	4.44	4.44	4.44	4.44	4.44
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	4.51	4.48	3.55	3.55	3.55	3.55	3.55	3.54
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.52	5.51	4.46	4.46	4.46	4.46	4.46	4.45
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.65	4.69	3.70	3.70	3.70	3.70	3.70	3.70
	$2^3A' (\pi \rightarrow \pi^*)$	5.74	5.79	4.77	4.77	4.77	4.77	4.77	4.77
	$1^3A'' (n \rightarrow \pi^*)$	6.36	6.37	5.43	5.43	5.43	5.44	5.44	5.44
	$3^3A' (\pi \rightarrow \pi^*)$	6.44	6.55	5.79	5.79	5.79	5.79	5.79	5.79
	$4^3A' (\pi \rightarrow \pi^*)$	7.44		6.28	6.28	6.28	6.28	6.28	6.28
	$2^3A'' (n \rightarrow \pi^*)$	7.51		6.50	6.50	6.50	6.50	6.50	6.50
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	4.27	4.06	3.77	3.78	3.78	3.78	3.78	3.77
	$1^3B_1 (n \rightarrow \pi^*)$	4.57	4.25	4.37	4.37	4.39	4.42	4.42	4.42
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.71	4.64	4.57	4.57	4.58	4.59	4.58	4.59
	$2^3A_1 (\pi \rightarrow \pi^*)$	5.03	4.91	4.67	4.67	4.67	4.67	4.69	4.69
	$1^3A_2 (n \rightarrow \pi^*)$	5.52	5.28	5.10	5.11	5.16	5.16	5.16	5.15
	$2^3B_2 (\pi \rightarrow \pi^*)$	6.03	6.08	6.02	6.02	6.02	6.03	6.03	6.02
	$3^3B_2 (\pi \rightarrow \pi^*)$	7.87		6.41	6.42	6.42	6.44	6.44	6.44
	$3^3A_1 (\pi \rightarrow \pi^*)$	7.56		6.55	6.56	6.55	6.55	6.59	6.58
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.61	1.89	2.07	2.08	2.13	2.18	2.18	2.17
	$1^3A_u (n \rightarrow \pi^*)$	3.28	3.52	3.30	3.31	3.44	3.44	3.44	3.42
	$1^3B_{1g} (n \rightarrow \pi^*)$	4.14	4.21	4.11	4.12	4.13	4.14	4.15	4.13

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Table S 2 – Continued

Molecule	State	CASPT2	TBE	OM1					
				FCI	SDTQ	SD90	SD85	SD80	SD75
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.37	4.33	3.89	3.90	3.91	3.90	3.90	3.89
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	4.39	4.54	4.57	4.57	4.60	4.60	4.60	4.58
	$1^3B_{2g} (n \rightarrow \pi^*)$	4.94	4.93	4.72	4.73	4.79	4.78	4.78	4.79
	$2^3A_u (n \rightarrow \pi^*)$	5.04	5.03	4.66	4.67	4.78	4.78	4.78	4.76
	$1^3B_{3g} (n \Rightarrow \pi^*)$	5.57		5.75	5.75	5.87	5.86	6.05	6.03
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.40	5.38	4.95	4.96	5.00	5.00	5.00	4.98
	$2^3B_{2g} (n \rightarrow \pi^*)$	5.97		5.83	5.84	5.90	5.91	5.90	5.89
	$2^3B_{1g} (n \rightarrow \pi^*)$	6.37		6.15	6.16	6.22	6.27	6.31	6.30
	$2^3B_{3u} (n \rightarrow \pi^*)$	6.54		5.48	5.49	5.55	5.61	5.61	5.59
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	7.08		6.69	6.69	6.70	6.69	6.69	6.67
Formaldehyde	$1^3A_2 (n \rightarrow \pi^*)$	3.58	3.50	3.40	3.40	3.40	3.40	3.40	3.40
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.84	5.87	5.67	5.67	5.67	5.67	5.67	5.67
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	4.10	4.05	3.53	3.53	3.53	3.53	3.53	3.53
	$1^3A_1 (\pi \rightarrow \pi^*)$	] 6.04	6.03	5.33	5.33	5.34	5.34	5.34	5.34
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	2.62	2.51	2.44	2.46	2.65	2.65	2.65	2.65
	$1^3A_u (n \rightarrow \pi^*)$	2.66	2.62	3.01	3.03	3.10	3.10	3.10	3.09
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	2.99	2.96	2.73	2.75	2.78	2.78	2.78	2.78
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	3.32	3.41	3.36	3.38	3.41	3.40	3.40	3.40
Formamide	$1^3A'' (n \rightarrow \pi^*)$	5.40	5.36	4.39	4.39	4.39	4.39	4.39	4.39
	$1^3A' (\pi \rightarrow \pi^*)$	5.58	5.74	4.89	4.89	4.89	4.89	4.89	4.89
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	5.41	5.42	4.38	4.38	4.38	4.38	4.38	4.38
	$1^3A' (\pi \rightarrow \pi^*)$	5.63	5.88	4.86	4.86	4.85	4.86	4.86	4.86
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.45	5.45	4.44	4.44	4.44	4.44	4.44	4.44
	$1^3A' (\pi \rightarrow \pi^*)$	5.80	5.90	4.87	4.87	4.87	4.87	4.87	4.87

^aSee main paper for notation. SDXX denotes an MR-CISD treatment with a threshold of XX%.

Table S 3: Vertical singlet excitation energies ΔE (eV) of all evaluated molecules for the semiempirical method OM2 using different approaches.^a

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	8.54	7.80	7.78	7.78	7.78	7.78	7.78	7.78
<i>E</i> -Butadiene	$2^1A_g (\pi \rightarrow \pi^*)$	6.62	6.55	5.96	5.96	5.96	5.96	5.96	5.96
	$1^1B_u (\pi \rightarrow \pi^*)$	6.47	6.18	6.22	6.22	6.22	6.22	6.22	6.22
Hexatriene	$2^1A_g (\pi \rightarrow \pi^*)$	5.42	5.09	4.86	4.86	4.86	4.87	4.88	4.89
	$1^1B_u (\pi \rightarrow \pi^*)$	5.31	5.10	5.33	5.33	5.34	5.34	5.34	5.33
all- <i>E</i> -Octatetraene	$2^1A_g (\pi \rightarrow \pi^*)$	4.64	4.47	4.13	4.14	4.14	4.15	4.15	4.16
	$1^1B_u (\pi \rightarrow \pi^*)$	4.70	4.66	4.77	4.77	4.76	4.76	4.76	4.76
Cyclopropene	$1^1B_2 (\pi \rightarrow \pi^*)$	7.06	7.06	6.42	6.42	6.42	6.42	6.42	6.42
	$1^1B_1 (\sigma \rightarrow \pi^*)$	6.76	6.76	5.75	5.75	5.75	5.75	5.75	5.75
Cyclopentadiene	$2^1A_1 (\pi \rightarrow \pi^*)$	6.31	6.31	5.60	5.60	5.60	5.60	5.60	5.60
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.52		7.47	7.47	7.47	7.47	7.47	7.47
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.51	5.55	5.07	5.07	5.08	5.08	5.07	5.07
Norbornadiene	$1^1A_2 (\pi \rightarrow \pi^*)$	5.34	5.34	6.00	6.00	6.00	6.00	6.00	6.00
	$2^1A_2 (\pi \rightarrow \pi^*)$	7.45		6.66	6.66	6.66	6.66	6.66	6.66
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.11	6.11	6.34	6.34	6.34	6.34	6.34	6.34
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.32		7.37	7.37	7.37	7.37	7.37	7.37
Benzene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.42	6.54	5.94	5.94	5.94	5.94	5.94	5.94
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.04	5.08	4.48	4.48	4.48	4.48	4.48	4.48
	$1^1E_{1u} (\pi \rightarrow \pi^*)$	7.13	7.13	7.16	7.16	7.16	7.16	7.16	7.16
	$1^1E_{2g} (\pi \rightarrow \pi^*)$	8.18	8.41	7.19	7.19	7.19	7.19	7.19	7.19
Naphthalene	$2^1A_g (\pi \rightarrow \pi^*)$	5.87	5.87	5.21	5.23	5.26	5.29	5.31	5.31
	$3^1A_g (\pi \rightarrow \pi^*)$	6.67	6.67	6.00	6.03	6.04	6.07	6.10	6.10
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.77	4.77	4.83	4.83	4.83	4.82	4.81	4.82

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Table S 3 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Furan	$2^1B_{2u} (\pi \rightarrow \pi^*)$	6.33	6.33	6.22	6.23	6.23	6.24	6.23	6.25
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	8.17		8.09	8.12	8.13	8.15	8.15	8.16
	$1^1B_{3u} (\pi \rightarrow \pi^*)$	4.24	4.24	3.79	3.81	3.84	3.85	3.87	3.88
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	6.06	6.06	6.14	6.16	6.17	6.17	6.18	6.18
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	7.74		6.77	6.80	6.84	6.86	6.89	6.90
	$1^1B_{1g} (\pi \rightarrow \pi^*)$	5.99	5.99	5.72	5.74	5.78	5.82	5.81	5.86
	$2^1B_{1g} (\pi \rightarrow \pi^*)$	6.47	6.47	6.22	6.24	6.25	6.27	6.26	6.26
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.50	6.57	5.43	5.43	5.44	5.44	5.44	5.43
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.17	8.13	7.47	7.47	7.47	7.47	7.47	7.50
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.39	6.32	5.82	5.82	5.82	5.82	5.82	5.81
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	6.31	6.37	5.28	5.28	5.28	5.28	5.27	5.27
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.17	7.91	7.18	7.18	7.18	7.18	7.21	7.21
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.57	6.57	5.86	5.86	5.87	5.87	5.86	5.87
Imidazole	$2^1A' (\pi \rightarrow \pi^*)$	6.19	6.19	5.59	5.59	5.60	5.60	5.59	5.59
	$3^1A' (\pi \rightarrow \pi^*)$	6.93	6.93	6.04	6.04	6.04	6.04	6.03	6.03
	$4^1A' (\pi \rightarrow \pi^*)$	8.16		7.45	7.45	7.45	7.47	7.48	7.48
	$1^1A'' (n \rightarrow \pi^*)$	6.81	6.81	6.00	6.00	6.00	6.01	6.00	6.00
	$2^1A'' (n \rightarrow \pi^*)$	7.90		6.79	6.79	6.80	6.80	6.79	6.79
Pyridine	$2^1A_1 (\pi \rightarrow \pi^*)$	6.39	6.26	6.11	6.11	6.11	6.11	6.10	6.10
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.46	7.18	7.43	7.43	7.43	7.43	7.45	7.43
	$4^1A_1 (\pi \rightarrow \pi^*)$	8.69		7.69	7.69	7.70	7.71	7.71	7.71
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.02	4.85	4.64	4.65	4.65	4.66	4.66	4.66
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.27	7.27	7.47	7.48	7.48	7.49	7.48	7.49
	$3^1B_2 (\pi \rightarrow \pi^*)$	8.60		7.20	7.20	7.20	7.22	7.21	7.21
	$1^1B_1 (n \rightarrow \pi^*)$	5.17	4.59	4.85	4.85	4.89	4.89	4.89	4.89

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Table S 3 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Pyrazine	$1^1A_2 (n \rightarrow \pi^*)$	5.51	5.11	5.05	5.06	5.09	5.09	5.09	5.09
	$2^1A_g (\pi \rightarrow \pi^*)$	8.61		8.07	8.07	8.08	8.09	8.09	8.10
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.89	6.58	6.22	6.22	6.22	6.22	6.22	6.21
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.79	7.72	8.06	8.06	8.10	8.10	8.10	8.09
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.85	4.64	4.76	4.76	4.77	4.79	4.79	4.78
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	7.66	7.60	7.67	7.67	7.69	7.70	7.70	7.70
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	8.47		7.34	7.35	7.35	7.37	7.37	7.40
	$1^1A_u (n \rightarrow \pi^*)$	4.70	4.81	4.11	4.12	4.19	4.19	4.19	4.18
	$1^1B_{1g} (n \rightarrow \pi^*)$	6.41	6.60	6.54	6.54	6.58	6.59	6.73	6.73
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.68	5.56	5.77	5.78	5.80	5.84	5.84	5.83
Pyrimidine	$1^1B_{3u} (n \rightarrow \pi^*)$	4.21	3.95	3.81	3.81	3.90	3.89	3.89	3.89
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.63	6.95	6.36	6.36	6.36	6.36	6.35	6.35
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.21		7.81	7.81	7.81	7.82	7.83	7.84
	$4^1A_1 (\pi \rightarrow \pi^*)$	9.19		7.51	7.51	7.52	7.53	7.54	7.54
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.24	5.44	4.85	4.86	4.86	4.86	4.87	4.87
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.64		7.71	7.72	7.71	7.71	7.72	7.72
	$3^1B_2 (\pi \rightarrow \pi^*)$	8.73		8.01	8.01	8.02	8.02	8.04	8.04
	$1^1B_1 (n \rightarrow \pi^*)$	4.44	4.55	4.33	4.34	4.39	4.39	4.38	4.38
	$1^1A_2 (n \rightarrow \pi^*)$	4.80	4.91	4.54	4.54	4.59	4.59	4.58	4.58
	$2^1A_1 (\pi \rightarrow \pi^*)$	5.18	5.18	4.74	4.74	4.75	4.76	4.76	4.76
Pyridazine	$3^1A_1 (\pi \rightarrow \pi^*)$	7.62		7.50	7.51	7.51	7.51	7.51	7.53
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.13		6.29	6.29	6.29	6.28	6.28	6.27
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.29		7.32	7.32	7.32	7.32	7.35	7.33
	$1^1A_2 (n \rightarrow \pi^*)$	4.31	4.31	4.70	4.70	4.74	4.73	4.73	4.72
	$2^1A_2 (n \rightarrow \pi^*)$	5.77	5.77	5.37	5.38	5.42	5.41	5.41	5.39
	$1^1B_1 (n \rightarrow \pi^*)$	3.78	3.78	4.37	4.37	4.41	4.40	4.40	4.38

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Table S 3 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
<i>s</i> -Triazine	$2^1B_1 (n \rightarrow \pi^*)$	6.52		5.62	5.62	5.65	5.65	5.65	5.63
	$2^1A'_1 (\pi \rightarrow \pi^*)$	7.25		6.78	6.78	6.78	6.78	6.77	6.77
	$1^1A'_2 (\pi \rightarrow \pi^*)$	5.79	5.79	5.12	5.12	5.12	5.13	5.14	5.14
	$1^1E' (\pi \rightarrow \pi^*)$	7.50		7.88	7.88	7.89	7.89	7.90	7.89
	$2^1E' (\pi \rightarrow \pi^*)$	8.99		8.28	8.28	8.30	8.30	8.31	8.31
	$1^1A''_1 (n \rightarrow \pi^*)$	4.60	4.60	4.51	4.51	4.53	4.54	4.53	4.53
	$1^1A''_2 (n \rightarrow \pi^*)$	4.66	4.66	4.23	4.24	4.26	4.26	4.26	4.26
	$1^1E'' (n \rightarrow \pi^*)$	4.70	4.70	4.39	4.40	4.42	4.42	4.42	4.42
	$2^1E'' (n \rightarrow \pi^*)$	7.71		7.00	7.01	7.04	7.04	7.04	7.04
<i>s</i> -Tetrazine	$1^1A_u (n \rightarrow \pi^*)$	3.51	3.51	3.55	3.55	3.64	3.63	3.63	3.63
	$2^1A_u (n \rightarrow \pi^*)$	5.50	5.50	4.65	4.65	4.74	4.73	4.73	4.72
	$1^1B_{1g} (n \rightarrow \pi^*)$	4.73	4.73	6.15	6.15	6.18	6.18	6.24	6.24
	$2^1B_{1g} (n \rightarrow \pi^*)$	6.45		5.64	5.65	5.67	5.67	5.68	5.67
	$3^1B_{1g} (n \rightarrow \pi^*)$	6.73		6.39	6.39	6.43	6.46	6.49	6.49
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.20	5.20	5.33	5.33	5.39	5.38	5.39	5.38
	$2^1B_{2g} (n \rightarrow \pi^*)$	6.06		6.73	6.73	6.78	6.77	6.77	6.76
	$1^1B_{3g} (n \Rightarrow \pi^*)$	5.86		6.26	6.28	6.42	6.42	6.42	6.41
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	8.34		7.85	7.86	7.87	7.86	7.88	7.88
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.94		6.78	6.78	6.79	6.78	6.77	6.77
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.42		7.86	7.86	7.89	7.88	7.88	7.87
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.93	4.93	4.88	4.88	4.90	4.91	4.91	4.91
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.14		8.15	8.16	8.19	8.20	8.20	8.19
	$1^1B_{3u} (n \rightarrow \pi^*)$	2.29	2.29	2.82	2.83	2.91	2.90	2.90	2.89
	$2^1B_{3u} (n \rightarrow \pi^*)$	6.77		5.21	5.22	5.30	5.29	5.29	5.28
Formaldehyde	$1^1A_2 (n \rightarrow \pi^*)$	3.99	3.88	3.55	3.55	3.55	3.55	3.55	3.55
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.14	9.10	7.93	7.93	7.93	7.93	7.93	7.93

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Table S 3 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Acetone	$2^1A_1 (\pi \rightarrow \pi^*)$	9.32	9.30	9.23	9.23	9.23	9.23	9.23	9.23
	$1^1A_2 (n \rightarrow \pi^*)$	4.44	4.40	3.98	3.98	3.98	3.98	3.98	3.98
	$2^1A_1 (\pi \rightarrow \pi^*)$	9.31	9.40	8.08	8.08	8.08	8.08	8.08	8.08
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.27	9.10	7.71	7.71	7.71	7.71	7.71	7.71
<i>p</i> -Benzoquinone	$1^1A_u (n \rightarrow \pi^*)$	2.77	2.77	3.34	3.35	3.36	3.36	3.36	3.36
	$1^1B_{1g} (n \rightarrow \pi^*)$	2.76	2.76	2.62	2.64	2.64	2.63	2.63	2.63
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.28	5.28	5.52	5.52	5.52	5.53	5.53	5.53
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.92		7.77	7.79	7.80	7.80	7.80	7.80
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.26	4.26	4.62	4.62	4.64	4.64	4.64	4.64
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	6.96	6.96	6.72	6.73	6.71	6.75	6.75	6.75
	$1^1B_{3u} (n \rightarrow \pi^*)$	5.64	5.64	5.33	5.34	5.40	5.40	5.40	5.40
Formamide	$1^1A'' (n \rightarrow \pi^*)$	5.63	5.63	4.56	4.56	4.56	4.56	4.56	4.56
	$2^1A' (\pi \rightarrow \pi^*)$	7.39	7.39	6.71	6.71	6.71	6.71	6.71	6.71
	$3^1A' (\pi \rightarrow \pi^*)$	10.54		9.41	9.41	9.41	9.41	9.41	9.41
Acetamide	$1^1A'' (n \rightarrow \pi^*)$	5.69	5.69	4.75	4.75	4.75	4.75	4.75	4.75
	$2^1A' (\pi \rightarrow \pi^*)$	7.27	7.27	6.63	6.63	6.63	6.63	6.63	6.63
	$3^1A' (\pi \rightarrow \pi^*)$	10.09		8.64	8.64	8.64	8.64	8.64	8.64
Propanamide	$1^1A'' (n \rightarrow \pi^*)$	5.72	5.72	4.85	4.85	4.85	4.85	4.85	4.85
	$2^1A' (\pi \rightarrow \pi^*)$	7.20	7.20	6.64	6.64	6.64	6.64	6.64	6.64
	$3^1A' (\pi \rightarrow \pi^*)$	9.94		8.34	8.34	8.34	8.34	8.35	8.35
Cytosine	$2^1A' (\pi \rightarrow \pi^*)$	4.67	4.66	4.21	4.21	4.21	4.21	4.21	4.21
	$3^1A' (\pi \rightarrow \pi^*)$	5.53	5.62	5.00	5.00	5.01	5.01	5.01	5.01
	$4^1A' (\pi \rightarrow \pi^*)$	6.40		5.77	5.78	5.78	5.78	5.78	5.78
	$5^1A' (\pi \rightarrow \pi^*)$	6.97		5.91	5.91	5.92	5.92	5.92	5.92
	$1^1A'' (n \rightarrow \pi^*)$	5.12	4.87	4.23	4.23	4.25	4.28	4.28	4.28

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Table S 3 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Thymine	$2^1A'' (n \rightarrow \pi^*)$	5.53	5.26	4.83	4.83	4.85	4.88	4.88	4.88
	$2^1A' (\pi \rightarrow \pi^*)$	5.06	5.20	4.81	4.81	4.82	4.82	4.82	4.83
	$3^1A' (\pi \rightarrow \pi^*)$	6.15	6.27	5.56	5.56	5.56	5.57	5.57	5.58
	$4^1A' (\pi \rightarrow \pi^*)$	6.53	6.53	5.72	5.73	5.73	5.74	5.74	5.76
	$5^1A' (\pi \rightarrow \pi^*)$	7.43		6.50	6.50	6.51	6.51	6.51	6.53
	$1^1A'' (n \rightarrow \pi^*)$	4.95	4.82	4.52	4.52	4.52	4.52	4.54	4.54
	$2^1A'' (n \rightarrow \pi^*)$	6.38	6.16	5.46	5.47	5.47	5.47	5.47	5.49
	$3^1A'' (n \rightarrow \pi^*)$	6.85		6.08	6.08	6.09	6.10	6.11	6.11
Uracil	$4^1A'' (n \rightarrow \pi^*)$	7.43		6.36	6.36	6.37	6.36	6.36	6.40
	$2^1A' (\pi \rightarrow \pi^*)$	5.23	5.35	4.88	4.88	4.89	4.89	4.89	4.89
	$3^1A' (\pi \rightarrow \pi^*)$	6.15	6.26	5.67	5.68	5.68	5.68	5.68	5.68
	$4^1A' (\pi \rightarrow \pi^*)$	6.74	6.70	5.85	5.85	5.86	5.86	5.86	5.86
	$5^1A' (\pi \rightarrow \pi^*)$	7.42		6.49	6.50	6.51	6.51	6.51	6.51
	$1^1A'' (n \rightarrow \pi^*)$	4.91	4.80	4.45	4.45	4.46	4.46	4.46	4.46
	$2^1A'' (n \rightarrow \pi^*)$	6.28	6.10	5.42	5.43	5.43	5.43	5.43	5.43
	$3^1A'' (n \rightarrow \pi^*)$	6.98	6.56	6.09	6.09	6.10	6.10	6.10	6.10
Adenine	$4^1A'' (n \rightarrow \pi^*)$	7.28		6.34	6.34	6.34	6.34	6.34	6.34
	$2^1A' (\pi \rightarrow \pi^*)$	5.20	5.25	4.22	4.23	4.25	4.25	4.25	4.25
	$3^1A' (\pi \rightarrow \pi^*)$	5.29	5.25	4.78	4.79	4.79	4.79	4.79	4.79
	$4^1A' (\pi \rightarrow \pi^*)$	6.34		6.02	6.03	6.05	6.05	6.05	6.05
	$5^1A' (\pi \rightarrow \pi^*)$	6.64		5.90	5.91	5.94	5.94	5.94	5.94
	$6^1A' (\pi \rightarrow \pi^*)$	6.87		6.49	6.50	6.53	6.53	6.53	6.53
	$7^1A' (\pi \rightarrow \pi^*)$	7.56		6.63	6.64	6.66	6.66	6.66	6.66
	$1^1A'' (n \rightarrow \pi^*)$	5.19	5.12	4.58	4.60	4.68	4.68	4.68	4.68
	$2^1A'' (n \rightarrow \pi^*)$	5.96	5.75	5.03	5.05	5.14	5.14	5.14	5.14

^aSee main paper for notation. SDXX denotes an MR-CISD treatment with a threshold of XX%.

Table S 4: Vertical triplet excitation energies ΔE (eV) of all evaluated molecules for the semiempirical method OM2 using different approaches.^a

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.48	4.50	4.14	4.14	4.14	4.14	4.14	4.14
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	3.34	3.20	3.04	3.04	3.04	3.04	3.04	3.04
	$1^3A_g (\pi \rightarrow \pi^*)$	5.16	5.08	4.56	4.56	4.56	4.56	4.56	4.56
all- <i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	2.71	2.40	2.45	2.46	2.48	2.49	2.49	2.48
	$1^3A_g (\pi \rightarrow \pi^*)$	4.31	4.15	3.79	3.80	3.81	3.81	3.81	3.80
all- <i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	2.33	2.20	2.10	2.12	2.16	2.16	2.21	2.20
	$1^3A_g (\pi \rightarrow \pi^*)$	3.70	3.55	3.21	3.23	3.27	3.29	3.29	3.28
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	4.35	4.34	3.80	3.80	3.80	3.80	3.80	3.80
	$1^3B_1 (\sigma \rightarrow \pi^*)$	6.51	6.62	5.48	5.48	5.48	5.48	5.48	5.48
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.28	3.25	2.87	2.87	2.87	2.87	2.87	2.87
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.11	5.09	4.30	4.30	4.30	4.30	4.30	4.30
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	3.75	3.72	4.27	4.27	4.27	4.27	4.27	4.27
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.22	4.16	4.10	4.10	4.10	4.10	4.10	4.10
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.17	4.15	3.73	3.74	3.74	3.74	3.74	3.74
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	4.90	4.86	4.54	4.54	4.54	4.54	4.54	4.54
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	5.76	5.88	5.80	5.80	5.80	5.80	5.80	5.80
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.38	7.51	6.30	6.30	6.30	6.30	6.30	6.30
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.16	3.11	2.86	2.89	2.93	2.95	2.94	2.94
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	4.25	4.18	3.89	3.91	3.99	4.01	4.00	4.00
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.51	4.47	4.04	4.07	4.09	4.08	4.08	4.10
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.68	4.64	4.25	4.28	4.36	4.36	4.35	4.35
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	4.97	5.11	4.94	4.95	4.96	4.96	4.95	4.95
	$1^3A_g (\pi \rightarrow \pi^*)$	5.53	5.52	4.87	4.90	4.93	4.92	4.91	4.91

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Table S 4 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Furan	$2^3B_{1g} (\pi \rightarrow \pi^*)$	6.21	6.48	6.48	6.49	6.51	6.50	6.51	6.53
	$2^3A_g (\pi \rightarrow \pi^*)$	6.38	6.47	6.50	6.51	6.52	6.51	6.50	6.50
	$3^3A_g (\pi \rightarrow \pi^*)$	6.59	6.79	5.73	5.76	5.81	5.81	5.81	5.81
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	6.64	6.76	5.76	5.79	5.85	5.85	5.89	5.94
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.18	4.17	3.50	3.50	3.50	3.50	3.50	3.49
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.49	5.48	4.54	4.54	4.54	4.54	4.54	4.53
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	4.51	4.48	3.76	3.76	3.77	3.77	3.76	3.76
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.52	5.51	4.59	4.59	4.59	4.59	4.58	4.58
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.65	4.69	3.95	3.95	3.95	3.95	3.95	3.95
	$2^3A' (\pi \rightarrow \pi^*)$	5.74	5.79	4.95	4.95	4.95	4.95	4.94	4.94
	$1^3A'' (n \rightarrow \pi^*)$	6.36	6.37	5.60	5.60	5.60	5.60	5.60	5.60
	$3^3A' (\pi \rightarrow \pi^*)$	6.44	6.55	5.69	5.69	5.69	5.69	5.68	5.68
	$4^3A' (\pi \rightarrow \pi^*)$	7.44		6.20	6.20	6.20	6.20	6.19	6.19
	$2^3A'' (n \rightarrow \pi^*)$	7.51		6.47	6.47	6.47	6.47	6.46	6.46
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	4.27	4.06	3.85	3.86	3.86	3.86	3.85	3.85
	$1^3B_1 (n \rightarrow \pi^*)$	4.57	4.25	4.48	4.48	4.52	4.52	4.51	4.51
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.71	4.64	4.66	4.66	4.67	4.67	4.67	4.67
	$2^3A_1 (\pi \rightarrow \pi^*)$	5.03	4.91	4.74	4.74	4.74	4.74	4.75	4.75
	$1^3A_2 (n \rightarrow \pi^*)$	5.52	5.28	4.96	4.96	5.00	5.00	4.99	4.99
	$2^3B_2 (\pi \rightarrow \pi^*)$	6.03	6.08	5.97	5.97	5.97	5.98	5.97	5.97
	$3^3B_2 (\pi \rightarrow \pi^*)$	7.87		6.59	6.59	6.60	6.61	6.61	6.61
	$3^3A_1 (\pi \rightarrow \pi^*)$	7.56		6.66	6.67	6.67	6.67	6.69	6.69
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.61	1.89	2.35	2.35	2.44	2.42	2.42	2.42
	$1^3A_u (n \rightarrow \pi^*)$	3.28	3.52	3.31	3.31	3.41	3.40	3.40	3.39
	$1^3B_{1g} (n \rightarrow \pi^*)$	4.14	4.21	4.84	4.85	4.86	4.86	4.86	4.86

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Table S 4 – Continued

Molecule	State	CASPT2	TBE	OM2					
				FCI	SDTQ	SD90	SD85	SD80	SD75
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.37	4.33	4.06	4.07	4.07	4.06	4.06	4.05
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	4.39	4.54	4.76	4.76	4.79	4.78	4.78	4.77
	$1^3B_{2g} (n \rightarrow \pi^*)$	4.94	4.93	5.04	5.04	5.07	5.10	5.10	5.10
	$2^3A_u (n \rightarrow \pi^*)$	5.04	5.03	4.40	4.40	4.48	4.47	4.47	4.46
	$1^3B_{3g} (n \Rightarrow \pi^*)$	5.57		5.99	6.00	6.08	6.17	6.17	6.16
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.40	5.38	5.07	5.07	5.11	5.10	5.10	5.09
	$2^3B_{2g} (n \rightarrow \pi^*)$	5.97		6.49	6.50	6.54	6.54	6.54	6.53
	$2^3B_{1g} (n \rightarrow \pi^*)$	6.37		6.28	6.29	6.32	6.35	6.41	6.40
	$2^3B_{3u} (n \rightarrow \pi^*)$	6.54		5.08	5.09	5.16	5.15	5.15	5.15
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	7.08		6.73	6.73	6.74	6.73	6.73	6.72
Formaldehyde	$1^3A_2 (\pi \rightarrow \pi^*)$	3.58	3.50	3.23	3.23	3.23	3.23	3.23	3.23
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.84	5.87	5.63	5.63	5.63	5.63	5.63	5.63
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	4.10	4.05	3.74	3.74	3.74	3.74	3.74	3.74
	$1^3A_1 (\pi \rightarrow \pi^*)$	] 6.04	6.03	5.45	5.45	5.45	5.45	5.45	5.45
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	2.62	2.51	2.48	2.50	2.63	2.63	2.63	2.63
	$1^3A_u (n \rightarrow \pi^*)$	2.66	2.62	3.19	3.21	3.26	3.26	3.26	3.26
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	2.99	2.96	2.77	2.79	2.81	2.81	2.81	2.81
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	3.32	3.41	3.31	3.32	3.35	3.34	3.34	3.34
Formamide	$1^3A'' (n \rightarrow \pi^*)$	5.40	5.36	4.34	4.34	4.34	4.34	4.34	4.34
	$1^3A' (\pi \rightarrow \pi^*)$	5.58	5.74	4.77	4.77	4.77	4.77	4.77	4.77
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	5.41	5.42	4.54	4.54	4.54	4.54	4.54	4.54
	$1^3A' (\pi \rightarrow \pi^*)$	5.63	5.88	4.86	4.86	4.86	4.86	4.86	4.86
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.45	5.45	4.61	4.61	4.61	4.61	4.61	4.61
	$1^3A' (\pi \rightarrow \pi^*)$	5.80	5.90	4.87	4.87	4.87	4.87	4.87	4.87

^aSee main paper for notation. SDXX denotes an MR-CISD treatment with a threshold of XX%.

Table S 5: Vertical singlet excitation energies ΔE (eV) of all evaluated molecules for the semiempirical method OM3 using different approaches.^a

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	8.54	7.80	7.85	7.85	7.85	7.85	7.85	7.85
<i>E</i> -Butadiene	$2^1A_g (\pi \rightarrow \pi^*)$	6.62	6.55	5.98	5.98	5.98	5.98	5.98	5.98
	$1^1B_u (\pi \rightarrow \pi^*)$	6.47	6.18	6.26	6.26	6.26	6.26	6.26	6.26
Hexatriene	$2^1A_g (\pi \rightarrow \pi^*)$	5.42	5.09	4.86	4.86	4.86	4.87	4.88	4.89
	$1^1B_u (\pi \rightarrow \pi^*)$	5.31	5.10	5.36	5.36	5.37	5.37	5.36	5.35
all- <i>E</i> -Octatetraene	$2^1A_g (\pi \rightarrow \pi^*)$	4.64	4.47	4.12	4.13	4.13	4.14	4.14	4.15
	$1^1B_u (\pi \rightarrow \pi^*)$	4.70	4.66	4.79	4.79	4.78	4.78	4.78	4.78
Cyclopropene	$1^1B_2 (\pi \rightarrow \pi^*)$	7.06	7.06	6.39	6.39	6.39	6.39	6.39	6.39
	$1^1B_1 (\sigma \rightarrow \pi^*)$	6.76	6.76	5.93	5.93	5.93	5.93	5.93	5.93
Cyclopentadiene	$2^1A_1 (\pi \rightarrow \pi^*)$	6.31	6.31	5.59	5.59	5.60	5.60	5.60	5.60
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.52		7.53	7.53	7.54	7.54	7.54	7.54
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.51	5.55	5.09	5.09	5.10	5.10	5.10	5.10
Norbornadiene	$1^1A_2 (\pi \rightarrow \pi^*)$	5.34	5.34	6.06	6.06	6.06	6.06	6.06	6.06
	$2^1A_2 (\pi \rightarrow \pi^*)$	7.45		6.74	6.74	6.74	6.74	6.74	6.74
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.11	6.11	6.46	6.46	6.46	6.46	6.46	6.46
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.32		7.42	7.42	7.42	7.42	7.42	7.42
Benzene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.42	6.54	6.03	6.03	6.03	6.03	6.03	6.03
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.04	5.08	4.51	4.51	4.51	4.51	4.51	4.51
	$1^1E_{1u} (\pi \rightarrow \pi^*)$	7.13	7.13	7.20	7.20	7.20	7.20	7.20	7.20
	$1^1E_{2g} (\pi \rightarrow \pi^*)$	8.18	8.41	7.22	7.22	7.22	7.23	7.23	7.23
Naphthalene	$2^1A_g (\pi \rightarrow \pi^*)$	5.87	5.87	5.24	5.27	5.29	5.32	5.34	5.34
	$3^1A_g (\pi \rightarrow \pi^*)$	6.67	6.67	6.03	6.05	6.07	6.10	6.13	6.13
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.77	4.77	4.87	4.87	4.86	4.86	4.86	4.86

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Table S 5 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Furan	$2^1B_{2u} (\pi \rightarrow \pi^*)$	6.33	6.33	6.28	6.28	6.28	6.29	6.29	6.30
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	8.17		8.15	8.18	8.19	8.21	8.21	8.22
	$1^1B_{3u} (\pi \rightarrow \pi^*)$	4.24	4.24	3.82	3.84	3.86	3.90	3.90	3.91
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	6.06	6.06	6.17	6.18	6.19	6.21	6.20	6.21
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	7.74		6.79	6.83	6.86	6.91	6.91	6.92
	$1^1B_{1g} (\pi \rightarrow \pi^*)$	5.99	5.99	5.74	5.76	5.80	5.84	5.83	5.88
	$2^1B_{1g} (\pi \rightarrow \pi^*)$	6.47	6.47	6.30	6.31	6.33	6.34	6.33	6.34
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.50	6.57	5.51	5.51	5.51	5.51	5.51	5.50
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.17	8.13	7.62	7.62	7.62	7.62	7.62	7.64
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.39	6.32	5.88	5.88	5.89	5.89	5.89	5.88
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	6.31	6.37	5.29	5.29	5.29	5.29	5.29	5.29
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.17	7.91	7.16	7.16	7.16	7.16	7.19	7.19
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.57	6.57	5.94	5.94	5.94	5.94	5.93	5.94
Imidazole	$2^1A' (\pi \rightarrow \pi^*)$	6.19	6.19	5.85	5.85	5.86	5.85	5.85	5.85
	$3^1A' (\pi \rightarrow \pi^*)$	6.93	6.93	6.16	6.16	6.16	6.16	6.15	6.15
	$4^1A' (\pi \rightarrow \pi^*)$	8.16		7.69	7.69	7.70	7.70	7.72	7.72
	$1^1A'' (n \rightarrow \pi^*)$	6.81	6.81	6.08	6.08	6.09	6.09	6.08	6.08
	$2^1A'' (n \rightarrow \pi^*)$	7.90		6.70	6.70	6.71	6.71	6.70	6.70
Pyridine	$2^1A_1 (\pi \rightarrow \pi^*)$	6.39	6.26	6.25	6.25	6.25	6.25	6.25	6.25
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.46	7.18	7.63	7.63	7.63	7.64	7.64	7.65
	$4^1A_1 (\pi \rightarrow \pi^*)$	8.69		8.09	8.09	8.10	8.11	8.11	8.11
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.02	4.85	4.83	4.83	4.83	4.85	4.85	4.84
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.27	7.27	7.62	7.62	7.62	7.63	7.63	7.62
	$3^1B_2 (\pi \rightarrow \pi^*)$	8.60		7.44	7.44	7.44	7.46	7.46	7.46
	$1^1B_1 (n \rightarrow \pi^*)$	5.17	4.59	4.86	4.86	4.90	4.90	4.90	4.89

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Table S 5 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Pyrazine	$1^1A_2 (n \rightarrow \pi^*)$	5.51	5.11	4.83	4.84	4.87	4.87	4.87	4.87
	$2^1A_g (\pi \rightarrow \pi^*)$	8.61		8.95	8.95	8.95	8.95	8.97	8.98
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.89	6.58	6.35	6.35	6.36	6.36	6.35	6.35
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.79	7.72	8.67	8.68	8.71	8.71	8.71	8.71
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.85	4.64	5.20	5.20	5.22	5.24	5.23	5.23
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	7.66	7.60	8.11	8.12	8.13	8.14	8.14	8.14
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	8.47		7.68	7.68	7.69	7.71	7.73	7.73
	$1^1A_u (n \rightarrow \pi^*)$	4.70	4.81	3.89	3.89	3.96	3.96	3.96	3.96
	$1^1B_{1g} (n \rightarrow \pi^*)$	6.41	6.60	6.31	6.32	6.35	6.40	6.47	6.47
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.68	5.56	5.85	5.86	5.91	5.91	5.91	5.91
Pyrimidine	$1^1B_{3u} (n \rightarrow \pi^*)$	4.21	3.95	4.03	4.04	4.12	4.12	4.12	4.12
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.63	6.95	6.62	6.62	6.62	6.62	6.61	6.61
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.21		8.25	8.25	8.26	8.26	8.27	8.28
	$4^1A_1 (\pi \rightarrow \pi^*)$	9.19		8.00	8.00	8.02	8.02	8.02	8.03
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.24	5.44	5.22	5.22	5.22	5.23	5.23	5.23
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.64		8.00	8.00	8.00	8.00	8.01	8.01
	$3^1B_2 (\pi \rightarrow \pi^*)$	8.73		8.77	8.77	8.77	8.77	8.79	8.79
	$1^1B_1 (n \rightarrow \pi^*)$	4.44	4.55	4.38	4.38	4.43	4.43	4.42	4.42
	$1^1A_2 (n \rightarrow \pi^*)$	4.80	4.91	4.40	4.40	4.45	4.45	4.44	4.44
	$2^1A_1 (\pi \rightarrow \pi^*)$	5.18	5.18	5.08	5.08	5.08	5.10	5.10	5.10
Pyridazine	$3^1A_1 (\pi \rightarrow \pi^*)$	7.62		7.81	7.81	7.82	7.83	7.83	7.83
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.13		6.60	6.60	6.59	6.58	6.58	6.58
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.29		7.76	7.76	7.76	7.77	7.77	7.77
	$1^1A_2 (n \rightarrow \pi^*)$	4.31	4.31	4.21	4.21	4.24	4.23	4.23	4.23
	$2^1A_2 (n \rightarrow \pi^*)$	5.77	5.77	5.57	5.57	5.60	5.59	5.59	5.59
	$1^1B_1 (n \rightarrow \pi^*)$	3.78	3.78	4.14	4.14	4.16	4.16	4.16	4.16

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Table S 5 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
<i>s</i> -Triazine	$2^1B_1 (n \rightarrow \pi^*)$	6.52		5.51	5.51	5.53	5.52	5.52	5.52
	$2^1A'_1 (\pi \rightarrow \pi^*)$	7.25		7.33	7.33	7.34	7.34	7.34	7.34
	$1^1A'_2 (\pi \rightarrow \pi^*)$	5.79	5.79	5.69	5.69	5.69	5.69	5.70	5.70
	$1^1E' (\pi \rightarrow \pi^*)$	7.50		8.47	8.47	8.48	8.48	8.48	8.49
	$2^1E' (\pi \rightarrow \pi^*)$	8.99		9.03	9.03	9.08	9.08	9.10	9.10
	$1^1A''_1 (n \rightarrow \pi^*)$	4.60	4.60	4.56	4.57	4.59	4.59	4.59	4.57
	$1^1A''_2 (n \rightarrow \pi^*)$	4.66	4.66	4.28	4.28	4.44	4.45	4.44	4.45
	$1^1E'' (n \rightarrow \pi^*)$	4.70	4.70	4.45	4.45	4.56	4.56	4.56	4.57
	$2^1E'' (n \rightarrow \pi^*)$	7.71		7.16	7.17	7.32	7.33	7.32	7.37
<i>s</i> -Tetrazine	$1^1A_u (n \rightarrow \pi^*)$	3.51	3.51	3.08	3.08	3.12	3.11	3.11	3.11
	$2^1A_u (n \rightarrow \pi^*)$	5.50	5.50	5.06	5.06	5.10	5.10	5.10	5.10
	$1^1B_{1g} (n \rightarrow \pi^*)$	4.73	4.73	6.49	6.49	6.50	6.55	6.55	6.55
	$2^1B_{1g} (n \rightarrow \pi^*)$	6.45		5.59	5.60	5.59	5.60	5.60	5.60
	$3^1B_{1g} (n \rightarrow \pi^*)$	6.73		6.71	6.72	6.75	6.77	6.77	6.77
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.20	5.20	6.11	6.11	6.13	6.14	6.14	6.25
	$2^1B_{2g} (n \rightarrow \pi^*)$	6.06		6.64	6.64	6.65	6.65	6.65	6.81
	$1^1B_{3g} (n \Rightarrow \pi^*)$	5.86		5.87	5.88	5.99	6.00	6.02	6.02
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	8.34		9.62	9.62	9.59	9.59	9.61	9.61
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.94		7.23	7.23	7.21	7.21	7.21	7.21
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.42		9.03	9.03	9.02	9.03	9.04	9.04
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.93	4.93	5.74	5.74	5.73	5.74	5.74	5.74
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.14		9.03	9.04	9.03	9.03	9.03	9.03
	$1^1B_{3u} (n \rightarrow \pi^*)$	2.29	2.29	2.88	2.88	2.92	2.92	2.92	2.92
	$2^1B_{3u} (n \rightarrow \pi^*)$	6.77		5.07	5.08	5.10	5.10	5.10	5.10
Formaldehyde	$1^1A_2 (n \rightarrow \pi^*)$	3.99	3.88	3.59	3.59	3.59	3.59	3.59	3.59
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.14	9.10	9.01	9.01	9.01	9.01	9.01	9.01

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Table S 5 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Acetone	$2^1A_1 (\pi \rightarrow \pi^*)$	9.32	9.30	9.89	9.89	9.89	9.89	9.89	9.89
	$1^1A_2 (n \rightarrow \pi^*)$	4.44	4.40	4.05	4.05	4.05	4.05	4.05	4.05
	$2^1A_1 (\pi \rightarrow \pi^*)$	9.31	9.40	8.51	8.51	8.51	8.51	8.51	8.51
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.27	9.10	8.34	8.34	8.34	8.34	8.34	8.34
<i>p</i> -Benzoquinone	$1^1A_u (n \rightarrow \pi^*)$	2.77	2.77	3.36	3.37	3.38	3.38	3.38	3.38
	$1^1B_{1g} (n \rightarrow \pi^*)$	2.76	2.76	2.56	2.58	2.57	2.57	2.57	2.57
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.28	5.28	5.71	5.71	5.71	5.71	5.72	5.72
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.92		7.84	7.87	7.87	7.87	7.88	7.88
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.26	4.26	4.68	4.68	4.70	4.69	4.69	4.69
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	6.96	6.96	6.92	6.93	6.95	6.95	6.95	6.95
	$1^1B_{3u} (n \rightarrow \pi^*)$	5.64	5.64	5.30	5.31	5.38	5.37	5.37	5.37
	$1^1A'' (n \rightarrow \pi^*)$	5.63	5.63	4.82	4.82	4.82	4.82	4.82	4.82
Formamide	$2^1A' (\pi \rightarrow \pi^*)$	7.39	7.39	7.07	7.07	7.07	7.07	7.07	7.07
	$3^1A' (\pi \rightarrow \pi^*)$	10.54		10.11	10.11	10.11	10.11	10.11	10.11
	$1^1A'' (n \rightarrow \pi^*)$	5.69	5.69	4.98	4.98	4.98	4.98	4.98	4.98
Acetamide	$2^1A' (\pi \rightarrow \pi^*)$	7.27	7.27	6.95	6.95	6.95	6.95	6.95	6.95
	$3^1A' (\pi \rightarrow \pi^*)$	10.09		9.02	9.02	9.02	9.02	9.02	9.02
	$1^1A'' (n \rightarrow \pi^*)$	5.72	5.72	5.06	5.06	5.06	5.06	5.06	5.06
Propanamide	$2^1A' (\pi \rightarrow \pi^*)$	7.20	7.20	6.94	6.94	6.94	6.94	6.94	6.94
	$3^1A' (\pi \rightarrow \pi^*)$	9.94		8.50	8.50	8.50	8.50	8.50	8.50
	$2^1A' (\pi \rightarrow \pi^*)$	4.67	4.66	4.39	4.39	4.40	4.40	4.40	4.40
Cytosine	$3^1A' (\pi \rightarrow \pi^*)$	5.53	5.62	5.05	5.05	5.06	5.06	5.06	5.06
	$4^1A' (\pi \rightarrow \pi^*)$	6.40		5.83	5.84	5.84	5.84	5.84	5.84
	$5^1A' (\pi \rightarrow \pi^*)$	6.97		5.96	5.96	5.97	5.97	5.97	5.97
	$1^1A'' (n \rightarrow \pi^*)$	5.12	4.87	4.40	4.40	4.43	4.45	4.45	4.49

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Table S 5 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Thymine	$2^1A'' (n \rightarrow \pi^*)$	5.53	5.26	4.95	4.95	4.98	4.99	4.99	5.05
	$2^1A' (\pi \rightarrow \pi^*)$	5.06	5.20	4.81	4.81	4.82	4.83	4.83	4.83
	$3^1A' (\pi \rightarrow \pi^*)$	6.15	6.27	5.65	5.65	5.65	5.66	5.66	5.66
	$4^1A' (\pi \rightarrow \pi^*)$	6.53	6.53	5.90	5.90	5.90	5.91	5.91	5.91
	$5^1A' (\pi \rightarrow \pi^*)$	7.43		6.72	6.73	6.73	6.74	6.74	6.74
	$1^1A'' (n \rightarrow \pi^*)$	4.95	4.82	4.67	4.68	4.68	4.68	4.69	4.69
	$2^1A'' (n \rightarrow \pi^*)$	6.38	6.16	5.69	5.69	5.70	5.70	5.71	5.71
	$3^1A'' (n \rightarrow \pi^*)$	6.85		6.08	6.08	6.09	6.10	6.11	6.11
Uracil	$4^1A'' (n \rightarrow \pi^*)$	7.43		6.45	6.45	6.45	6.45	6.48	6.48
	$2^1A' (\pi \rightarrow \pi^*)$	5.23	5.35	4.90	4.90	4.91	4.91	4.91	4.91
	$3^1A' (\pi \rightarrow \pi^*)$	6.15	6.26	5.86	5.86	5.87	5.87	5.87	5.87
	$4^1A' (\pi \rightarrow \pi^*)$	6.74	6.70	5.97	5.97	5.98	5.98	5.98	5.98
	$5^1A' (\pi \rightarrow \pi^*)$	7.42		6.74	6.75	6.75	6.75	6.75	6.75
	$1^1A'' (n \rightarrow \pi^*)$	4.91	4.80	4.64	4.64	4.66	4.66	4.66	4.66
	$2^1A'' (n \rightarrow \pi^*)$	6.28	6.10	5.64	5.65	5.65	5.65	5.65	5.65
	$3^1A'' (n \rightarrow \pi^*)$	6.98	6.56	6.10	6.10	6.13	6.10	6.13	6.13
Adenine	$4^1A'' (n \rightarrow \pi^*)$	7.28		6.44	6.44	6.44	6.44	6.44	6.44
	$2^1A' (\pi \rightarrow \pi^*)$	5.20	5.25	4.32	4.33	4.34	4.34	4.34	4.34
	$3^1A' (\pi \rightarrow \pi^*)$	5.29	5.25	4.90	4.90	4.91	4.91	4.91	4.91
	$4^1A' (\pi \rightarrow \pi^*)$	6.34		5.79	5.80	5.82	5.82	5.82	5.82
	$5^1A' (\pi \rightarrow \pi^*)$	6.64		6.13	6.14	6.16	6.16	6.16	6.16
	$6^1A' (\pi \rightarrow \pi^*)$	6.87		6.26	6.27	6.29	6.29	6.29	6.29
	$7^1A' (\pi \rightarrow \pi^*)$	7.56		6.73	6.74	6.76	6.76	6.76	6.76
	$1^1A'' (n \rightarrow \pi^*)$	5.19	5.12	4.61	4.62	4.70	4.70	4.70	4.70
	$2^1A'' (n \rightarrow \pi^*)$	5.96	5.75	5.14	5.16	5.26	5.26	5.26	5.26

^aSee main paper for notation. SDXX denotes an MR-CISD treatment with a threshold of XX%.

Table S 6: Vertical triplet excitation energies ΔE (eV) of all evaluated molecules for the semiempirical method OM3 using different approaches.^a

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.48	4.50	4.16	4.16	4.16	4.16	4.16	4.16
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	3.34	3.20	3.04	3.04	3.04	3.04	3.04	3.04
	$1^3A_g (\pi \rightarrow \pi^*)$	5.16	5.08	4.59	4.59	4.59	4.59	4.59	4.59
all- <i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	2.71	2.40	2.44	2.45	2.47	2.48	2.48	2.47
	$1^3A_g (\pi \rightarrow \pi^*)$	4.31	4.15	3.80	3.81	3.82	3.82	3.82	3.81
all- <i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	2.33	2.20	2.09	2.11	2.14	2.15	2.19	2.19
	$1^3A_g (\pi \rightarrow \pi^*)$	3.70	3.55	3.22	3.24	3.28	3.30	3.30	3.29
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	4.35	4.34	3.72	3.72	3.72	3.72	3.72	3.72
	$1^3B_1 (\sigma \rightarrow \pi^*)$	6.51	6.62	5.65	5.65	5.65	5.65	5.65	5.65
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.28	3.25	2.86	2.86	2.86	2.87	2.86	2.86
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.11	5.09	4.31	4.31	4.31	4.31	4.31	4.31
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	3.75	3.72	4.26	4.26	4.26	4.26	4.26	4.26
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.22	4.16	4.07	4.07	4.07	4.07	4.07	4.07
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.17	4.15	3.75	3.76	3.76	3.76	3.76	3.76
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	4.90	4.86	4.57	4.57	4.57	4.57	4.57	4.57
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	5.76	5.88	5.85	5.85	5.85	5.85	5.85	5.85
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.38	7.51	6.34	6.34	6.34	6.34	6.34	6.34
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.16	3.11	2.87	2.90	2.93	2.96	2.95	2.95
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	4.25	4.18	3.92	3.94	4.01	4.04	4.03	4.03
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.51	4.47	4.06	4.09	4.10	4.11	4.10	4.12
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.68	4.64	4.28	4.31	4.39	4.39	4.38	4.38
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	4.97	5.11	4.98	4.99	4.99	5.00	4.99	4.99
	$1^3A_g (\pi \rightarrow \pi^*)$	5.53	5.52	4.90	4.93	4.95	4.95	4.95	4.95

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Table S 6 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
Furan	$2^3B_{1g} (\pi \rightarrow \pi^*)$	6.21	6.48	6.52	6.52	6.54	6.54	6.55	6.57
	$2^3A_g (\pi \rightarrow \pi^*)$	6.38	6.47	6.56	6.58	6.58	6.57	6.56	6.56
	$3^3A_g (\pi \rightarrow \pi^*)$	6.59	6.79	5.76	5.79	5.83	5.83	5.84	5.84
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	6.64	6.76	5.79	5.83	5.88	5.90	5.92	5.97
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.18	4.17	3.53	3.53	3.53	3.53	3.53	3.52
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.49	5.48	4.59	4.59	4.59	4.59	4.59	4.58
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	4.51	4.48	3.89	3.89	3.89	3.89	3.89	3.89
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.52	5.51	4.64	4.64	4.64	4.64	4.63	4.63
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.65	4.69	4.06	4.06	4.06	4.06	4.05	4.05
	$2^3A' (\pi \rightarrow \pi^*)$	5.74	5.79	5.27	5.27	5.27	5.27	5.26	5.26
	$1^3A'' (n \rightarrow \pi^*)$	6.36	6.37	5.70	5.70	5.71	5.71	5.70	5.70
	$3^3A' (\pi \rightarrow \pi^*)$	6.44	6.55	5.99	5.99	5.99	5.99	5.98	5.98
	$4^3A' (\pi \rightarrow \pi^*)$	7.44		6.37	6.37	6.37	6.37	6.36	6.37
	$2^3A'' (n \rightarrow \pi^*)$	7.51		6.33	6.33	6.33	6.33	6.33	6.33
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	4.27	4.06	3.93	3.94	3.94	3.93	3.94	3.93
	$1^3B_1 (n \rightarrow \pi^*)$	4.57	4.25	4.47	4.47	4.52	4.52	4.52	4.51
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.71	4.64	4.83	4.83	4.84	4.85	4.85	4.84
	$2^3A_1 (\pi \rightarrow \pi^*)$	5.03	4.91	4.97	4.97	4.98	4.98	4.99	4.99
	$1^3A_2 (n \rightarrow \pi^*)$	5.52	5.28	4.74	4.75	4.78	4.78	4.78	4.78
	$2^3B_2 (\pi \rightarrow \pi^*)$	6.03	6.08	6.17	6.17	6.17	6.17	6.17	6.16
	$3^3B_2 (\pi \rightarrow \pi^*)$	7.87		6.82	6.83	6.83	6.85	6.85	6.84
	$3^3A_1 (\pi \rightarrow \pi^*)$	7.56		7.08	7.08	7.08	7.08	7.11	7.10
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.61	1.89	2.36	2.36	2.40	2.40	2.40	2.40
	$1^3A_u (n \rightarrow \pi^*)$	3.28	3.52	2.86	2.87	2.90	2.90	2.90	2.90
	$1^3B_{1g} (n \rightarrow \pi^*)$	4.14	4.21	4.77	4.78	4.76	4.76	4.76	4.76

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Table S 6 – Continued

Molecule	State	CASPT2	TBE	OM3					
				FCI	SDTQ	SD90	SD85	SD80	SD75
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.37	4.33	4.74	4.74	4.72	4.72	4.72	4.72
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	4.39	4.54	5.62	5.62	5.61	5.61	5.61	5.61
	$1^3B_{2g} (n \rightarrow \pi^*)$	4.94	4.93	5.65	5.66	5.65	5.69	5.79	5.79
	$2^3A_u (n \rightarrow \pi^*)$	5.04	5.03	4.78	4.79	4.82	4.82	4.82	4.82
	$1^3B_{3g} (n \Rightarrow \pi^*)$	5.57		5.53	5.53	5.66	5.66	5.66	5.66
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.40	5.38	6.00	6.00	6.00	6.00	6.00	6.00
	$2^3B_{2g} (n \rightarrow \pi^*)$	5.97		6.42	6.43	6.43	6.44	6.58	6.58
	$2^3B_{1g} (n \rightarrow \pi^*)$	6.37		6.65	6.65	6.68	6.71	6.71	6.71
	$2^3B_{3u} (n \rightarrow \pi^*)$	6.54		4.95	4.95	4.98	4.97	4.97	4.97
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	7.08		7.43	7.43	7.43	7.43	7.43	7.43
Formaldehyde	$1^3A_2 (\pi \rightarrow \pi^*)$	3.58	3.50	3.24	3.24	3.24	3.24	3.24	3.24
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.84	5.87	6.07	6.07	6.07	6.07	6.07	6.07
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	4.10	4.05	3.79	3.79	3.79	3.79	3.79	3.79
	$1^3A_1 (\pi \rightarrow \pi^*)$	] 6.04	6.03	5.79	5.79	5.79	5.79	5.79	5.79
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	2.62	2.51	2.40	2.42	2.56	2.56	2.56	2.56
	$1^3A_u (n \rightarrow \pi^*)$	2.66	2.62	3.21	3.23	3.28	3.28	3.28	3.28
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	2.99	2.96	2.90	2.91	2.93	2.93	2.93	2.93
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	3.32	3.41	3.33	3.34	3.36	3.36	3.36	3.36
Formamide	$1^3A'' (n \rightarrow \pi^*)$	5.40	5.36	4.58	4.58	4.58	4.58	4.58	4.58
	$1^3A' (\pi \rightarrow \pi^*)$	5.58	5.74	4.98	4.98	4.98	4.98	4.98	4.98
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	5.41	5.42	4.76	4.76	4.76	4.76	4.76	4.76
	$1^3A' (\pi \rightarrow \pi^*)$	5.63	5.88	5.07	5.07	5.07	5.07	5.07	5.07
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.45	5.45	4.81	4.81	4.81	4.81	4.81	4.81
	$1^3A' (\pi \rightarrow \pi^*)$	5.80	5.90	5.07	5.07	5.07	5.07	5.07	5.07

^aSee main paper for notation. SDXX denotes an MR-CISD treatment with a threshold of XX%.

Table S 7: Vertical excitation energies ΔE , oscillator strengths f , and dipole moments μ of the two lowest singlet excited states of pyridine evaluated by AM1 and OM2 at different optimized ground-state geometries.

Geometry	AM1			OM2		
	MP2 ^a	AM1	OM2	MP2 ^a	AM1	OM2
$1^1B_1 (n \rightarrow \pi^*)$						
ΔE (eV)	4.29	4.30	4.21	4.85	4.84	4.81
f	0.002	0.002	0.002	0.001	0.001	0.001
μ (D)	0.31	0.40	0.23	1.05	1.12	0.98
$1^1B_2 (\pi \rightarrow \pi^*)$						
ΔE (eV)	3.38	3.30	3.38	4.65	4.54	4.65
f	0.005	0.005	0.005	0.008	0.008	0.008
μ (D)	1.14	1.15	1.10	1.68	1.68	1.62

^aBasis set 6-31G*.

1.2 Oscillator strengths

Table S 8: Oscillator strengths (in length representation) for optically allowed transitions.

Molecule	State	Lit. ^a	CASPT2 ^b	CASPT2 ^c	CC2 ^d	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^e	INDO/S2 ^f
Ethene	1 ¹ B _{1u}	0.358–0.494	0.360	0.505	0.431	0.298	0.342	0.340	0.453	0.434	0.446	0.652	0.652
<i>E</i> -Butadiene	1 ¹ B _u	0.52–0.803	0.686	0.858	0.809	0.538	0.611	0.606	0.802	0.795	0.807	1.034	1.034
all- <i>E</i> -Hexatriene	1 ¹ B _u	0.655–1.154	0.850	1.045	1.272	0.751	0.850	0.845	1.119	1.124	1.137	1.460	1.460
all- <i>E</i> -Octatetraene	1 ¹ B _u	1.382	1.832	1.298	1.757	0.962	1.087	1.083	1.430	1.445	1.459	1.865	1.865
Cyclopropene	1 ¹ B ₂		0.101	0.234	0.086	0.202	0.177	0.176	0.238	0.206	0.208	0.386	0.386
	1 ¹ B ₁		0.010	0.010	0.001	0.002	0.001	0.002	0.004	0.001	0.001	0.006	0.006
Cyclopentadiene	2 ¹ A ₁	0.001–0.019	0.000	0.001	0.011	0.000	0.000	0.000	0.001	0.005	0.003	0.037	0.037
	3 ¹ A ₁	0.225–0.538	0.442	0.965	0.658	0.254	0.448	0.553	0.717	0.645	0.691	0.927	0.927
	1 ¹ B ₂	0.099–0.157	0.148	0.164	0.110	0.086	0.101	0.107	0.117	0.109	0.108	0.235	0.235
Norbornadiene	1 ¹ B ₂		0.008	0.090	0.023	0.436	0.322	0.404	0.137	0.120	0.120	0.018	0.018
	2 ¹ B ₂		0.343	0.394	0.185	0.078	0.224	0.164	0.558	0.500	0.534	0.744	0.744
Benzene	1 ¹ E _{1u}	0.323–1.33	0.820	0.856	0.694	0.544	0.624	0.624	0.859	0.834	0.854	0.995	0.995
Naphthalene	1 ¹ B _{2u}	0.082	0.050	0.136	0.094	0.030	0.045	0.052	0.107	0.104	0.111	0.173	0.173
	2 ¹ B _{2u}	0.268	0.313	0.401	0.272	0.151	0.269	0.288	0.410	0.405	0.411	0.627	0.627
	3 ¹ B _{2u}	0.840	0.848	0.709	0.548	0.518	0.569	0.547	0.719	0.687	0.705	0.606	0.606
	1 ¹ B _{3u}	0.000	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.003	0.003
	2 ¹ B _{3u}	1.326	1.337	1.542	1.450	0.941	1.099	1.092	1.522	1.499	1.530	1.784	1.784
	3 ¹ B _{3u}	0.067	0.048	0.008	0.010	0.004	0.010	0.019	0.000	0.004	0.002	0.092	0.092
Furan	2 ¹ A ₁	0.000–0.011	0.002	0.007	0.003	0.000	0.001	0.000	0.001	0.000	0.000	0.051	0.080
	3 ¹ A ₁	0.194–0.494	0.416	0.788	0.506	0.383	0.453	0.444	0.650	0.645	0.683	0.658	0.612
	1 ¹ B ₂	0.144–0.185	0.154	0.196	0.172	0.092	0.113	0.121	0.171	0.165	0.175	0.252	0.271
Pyrrole	2 ¹ A ₁	0.000–0.036	0.020	0.031	0.006	0.000	0.000	0.010	0.001	0.006	0.003	0.002	0.002
	3 ¹ A ₁	0.176–0.706	0.326	0.611	0.532	0.364	0.415	0.396	0.616	0.612	0.616	0.734	0.734
	1 ¹ B ₂	0.099–0.99	0.125	0.205	0.182	0.064	0.071	0.048	0.150	0.124	0.110	0.245	0.245
Imidazole	2 ¹ A'	0.080	0.126	0.229	0.088	0.010	0.010	0.014	0.030	0.033	0.040	0.183	0.183
	3 ¹ A'	0.070	0.143	0.062	0.085	0.111	0.111	0.059	0.147	0.122	0.144	0.049	0.049
	4 ¹ A'		0.594	0.556	0.406	0.358	0.406	0.378	0.567	0.577	0.618	0.566	0.566
	1 ¹ A''		0.011	0.010	0.003	0.005	0.004	0.010	0.009	0.005	0.003	0.020	0.020
	2 ¹ A''		0.013	0.020	0.006	0.011	0.012	0.017	0.014	0.009	0.013	0.001	0.001
Pyridine	2 ¹ A ₁	0.006–0.021	0.005	0.004	0.021	0.036	0.040	0.018	0.035	0.030	0.067	0.076	0.076
	3 ¹ A ₁	0.513–0.67	0.820	0.849	0.498	0.469	0.560	0.608	0.812	0.701	0.745	0.748	0.748
	4 ¹ A ₁		0.03	0.000	0.000	0.002	0.000	0.001	0.002	0.087	0.004		
	1 ¹ B ₂	0.023–0.040	0.018	0.046	0.025	0.005	0.005	0.003	0.012	0.008	0.006	0.068	0.068
	2 ¹ B ₂	0.407–0.65	0.640	0.743	0.549	0.518	0.609	0.604	0.652	0.480	0.520	0.843	0.843
	3 ¹ B ₂		0.158	0.094	0.012	0.009	0.007	0.007	0.172	0.330	0.330		
	1 ¹ B ₁	0.005–0.01	0.009	0.010	0.005	0.002	0.002	0.008	0.003	0.001	0.001	0.013	0.013
Pyrazine	1 ¹ B _{1u}	0.060	0.080	0.107	0.096	0.117	0.118	0.059	0.114	0.110	0.185	0.196	0.196
	2 ¹ B _{1u}	0.370	0.760	0.774	0.424	0.482	0.550	0.599	0.762	0.752	0.707	0.578	0.578
	1 ¹ B _{2u}	0.080	0.070	0.124	0.070	0.026	0.023	0.013	0.045	0.032	0.030	0.179	0.179

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Table S 8 – Continued

Molecule	State	Lit. ^a	CASSCF ^b	CASPT2 ^c	CC2 ^d	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^e	INDO/S2 ^f
Pyrimidine	2 ¹ B _{2u}	0.330	0.660	0.622	0.400	0.608	0.649	0.601	0.781	0.787	0.898	0.799	0.799
	1 ¹ B _{3u}	0.010	0.010	0.013	0.007	0.006	0.005	0.014	0.005	0.003	0.003	0.014	0.014
	2 ¹ A ₁	0.017–0.03	0.050	0.165	0.062	0.059	0.061	0.023	0.052	0.052	0.105	0.142	0.142
	3 ¹ A ₁		0.580	0.539	0.446	0.521	0.587	0.588	0.582	0.526	0.723	0.659	0.659
	4 ¹ A ₁		0.14	0.068		0.001	0.004	0.012	0.203	0.246	0.075	0.001	0.001
	1 ¹ B ₂	0.01–0.026	0.049	0.049	0.023	0.010	0.008	0.004	0.012	0.010	0.010	0.076	0.076
	2 ¹ B ₂	0.41–0.499	0.790	0.768	0.476	0.435	0.484	0.577	0.650	0.802	0.821	0.645	0.645
	3 ¹ B ₂		0.06	0.003		0.105	0.135	0.049	0.179	0.004	0.012	0.191	0.191
Pyridazine	1 ¹ B ₁	0.007–0.01	0.020	0.013	0.006	0.005	0.005	0.013	0.006	0.002	0.003	0.019	0.019
	2 ¹ A ₁		0.009	0.027	0.014	0.002	0.002	0.002	0.007	0.004	0.003	0.041	0.041
	3 ¹ A ₁		0.500	0.742	0.444	0.496	0.600	0.630	0.771	0.541	0.802	1.207	1.027
	1 ¹ B ₂		0.003	0.115	0.009	0.002	0.000	0.003	0.000	0.000	0.014	0.001	0.001
	2 ¹ B ₂		0.750	0.603	0.489	0.542	0.608	0.574	0.402	0.543	0.812	1.054	1.054
	1 ¹ B ₁		0.010	0.010	0.006	0.004	0.004	0.010	0.004	0.002	0.001	0.022	0.022
	2 ¹ B ₁		0.008	0.008	0.005	0.006	0.006	0.012	0.006	0.001	0.002	0.009	0.009
	1 ¹ E'	0.920	0.610	0.681	0.441	0.531	0.552	0.544	0.505	0.605	0.815	1.027	1.027
<i>s</i> -Triazine	2 ¹ E'		0.21	0.044		0.117	0.136	0.097	0.343	0.222	0.009	0.092	0.092
	1 ¹ A ₂ '	0.02–0.027	0.015	0.022	0.017	0.018	0.017	0.030	0.021	0.010	0.011	0.035	0.035
	1 ¹ B _{1u}	0.00–0.054	0.001	0.146	0.017	0.021	0.018	0.008	0.018	0.034	0.153	0.035	0.035
	2 ¹ B _{1u}	0.39–0.630	0.687	0.487	0.376	0.556	0.583	0.387	0.712	0.724	0.672	0.956	0.956
<i>s</i> -Tetrazine	1 ¹ B _{2u}	0.052–0.095	0.045	0.109	0.046	0.027	0.022	0.013	0.033	0.024	0.029	0.163	0.163
	2 ¹ B _{2u}	0.45–0.755	0.733	0.554	0.368	0.643	0.630	0.604	0.808	0.483	0.611	1.213	1.213
	1 ¹ B _{3u}	0.007–0.012	0.013	0.013	0.007	0.008	0.006	0.013	0.007	0.004	0.004	0.027	0.027
	2 ¹ B _{3u}	0.01–0.018	0.017	0.020	0.011	0.013	0.014	0.022	0.012	0.004	0.004	0.028	0.028
	1 ¹ B ₁	0.000–0.001	0.010	0.013	0.079	0.002	0.000	0.000	0.004	0.000	0.000	0.028	0.030
	2 ¹ A ₁	0.063–0.100	0.280	0.451	0.368	0.309	0.401	0.373	0.236	0.371	0.444	0.829	0.849
Formaldehyde	2 ¹ A ₁	0.255	0.326	0.359	0.298	0.305	0.507	0.490	0.635	0.633	0.724	0.786	0.770
Acetone	1 ¹ B ₁	0.003	0.010	0.011	0.000	0.023	0.014	0.005	0.049	0.034	0.037	0.003	0.007
<i>p</i> -Benzoquinone	1 ¹ B _{1u}	0.636–0.704	0.616	0.636	0.538	0.534	0.626	0.650	0.850	0.850	0.844	0.639	0.513
	2 ¹ B _{1u}	0.693	0.624	0.660	0.544	0.389	0.425	0.482	0.626	0.575	0.539	0.881	0.903
Formamide	2 ¹ A'	0.149–0.338	0.371	0.469	0.385	0.304	0.317	0.292	0.404	0.411	0.461	0.265	0.240
	3 ¹ A'		0.131	0.163	0.010	0.149	0.170	0.163	0.148	0.131	0.142	0.345	0.222
	1 ¹ A''	0.000–0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.000	0.001	
Acetamide	2 ¹ A'		0.292	0.469	0.199	0.258	0.262	0.244	0.344	0.346	0.372	0.205	0.186
	3 ¹ A'		0.179	0.163	0.279	0.274	0.365	0.289	0.352	0.361	0.414	0.459	0.522
	1 ¹ A''		0.001	0.001	0.001	0.002	0.003	0.002	0.003	0.003	0.004	0.001	0.002
Propanamide	2 ¹ A'		0.346	0.405	0.138	0.240	0.237	0.228	0.310	0.303	0.309	0.216	0.200
	3 ¹ A'		0.205	0.275	0.189	0.254	0.349	0.273	0.382	0.383	0.478	0.286	0.217
	1 ¹ A''		0.001	0.001	0.000	0.002	0.004	0.002	0.004	0.005	0.006	0.001	0.002
Cytosine	2 ¹ A'	0.052–0.080	0.061	0.093	0.049	0.056	0.056	0.032	0.073	0.074	0.063	0.158	0.175
	3 ¹ A'	0.138–0.181	0.108	0.351	0.165	0.018	0.026	0.061	0.061	0.073	0.048	0.185	0.216
	4 ¹ A'		0.863	0.621	0.632	0.075	0.105	0.165	0.935	0.659	0.203	0.873	0.780

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Table S 8 – Continued

Molecule	State	Lit. ^a	CASSCF ^b	CASPT2 ^c	CC2 ^d	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^e	INDO/S2 ^f
Thymine	5 ¹ A'		0.147	0.369	0.168	0.658	0.711	0.553	0.121	0.402	0.978	0.119	0.152
	1 ¹ A''	0.001–0.002	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002
	2 ¹ A''	0.001–0.003	0.001	0.002	0.002	0.000	0.001	0.001	0.001	0.000	0.001	0.003	0.003
	2 ¹ A'	0.180	0.170	0.334	0.197	0.166	0.154	0.084	0.280	0.231	0.250	0.388	0.397
	3 ¹ A'	0.040	0.170	0.067	0.080	0.037	0.045	0.065	0.101	0.194	0.223	0.192	0.189
	4 ¹ A'	0.180	0.150	0.353	0.250	0.090	0.128	0.105	0.187	0.151	0.093	0.116	0.096
	5 ¹ A'		0.850	0.674	0.515	0.613	0.592	0.613	0.716	0.719	0.803	0.375	0.375
	1 ¹ A''		0.000	0.000	0.000	0.001	0.001	0.001	0.002	0.001	0.002	0.001	0.002
	3 ¹ A''		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Uracil	4 ¹ A''		0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.000	0.002
	2 ¹ A'	0.18–0.26	0.190	0.321	0.197	0.145	0.129	0.070	0.252	0.203	0.212	0.387	0.390
	3 ¹ A'	0.04–0.05	0.080	0.047	0.058	0.034	0.058	0.052	0.078	0.118	0.088	0.193	0.191
	4 ¹ A'	0.035–0.17	0.290	0.249	0.188	0.108	0.125	0.124	0.204	0.201	0.215	0.076	0.060
	5 ¹ A'	0.510	0.760	0.804	0.547	0.596	0.616	0.664	0.723	0.728	0.853	0.133	0.010
	1 ¹ A''		0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002
Adenine	2 ¹ A'	0.004–0.03	0.070	0.154	0.037	0.012	0.021	0.033	0.043	0.050	0.098	0.111	0.111
	3 ¹ A'	0.17–0.36	0.370	0.193	0.276	0.146	0.172	0.215	0.259	0.246	0.242	0.342	0.342
	4 ¹ A'	0.510	0.851	0.536	0.496	0.010	0.007	0.020	0.021	0.419	0.029	0.795	0.795
	5 ¹ A'		0.159	0.001	0.085	0.021	0.018	0.012	0.398	0.095	0.176	0.058	0.058
	6 ¹ A'		0.565	0.010	0.320	0.339	0.343	0.131	0.133	0.403	0.386	0.447	0.447
	7 ¹ A'		0.406	0.036	0.177	0.008	0.054	0.041	0.457	0.182	0.493		
	1 ¹ A''	0.001–0.007	0.001	0.001	0.000	0.001	0.000	0.002	0.000	0.000	0.000	0.002	0.002
	2 ¹ A''	0.003–0.005	0.001	0.007	0.000	0.002	0.002	0.003	0.002	0.001	0.000	0.007	0.007

^aRange of literature values collated in Ref. ¹^bData from publications of the Roos group in the 1990s cited in Ref. ¹^cSA-CASSCF/MS-CASPT2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.^eINDO/S results using charge model II as described in Ref. ²^fINDO/S2 results using special parametrization for oxygen and charge model II as described in Ref. ²

1.3 Dipole moments

Table S 9: State dipole moments (in Debye) of all evaluated molecules.

Molecule	State	CASPT2 ^a	CASPT2 ^b	CC2 ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^c	INDO/S2 ^d
Cyclopropene	Ground State	0.48	0.46	0.45	0.43	0.33	0.43	0.38	0.52	0.55	0.42	0.42
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.70	1.02	1.26	1.03	1.85	1.79	1.86	2.13	1.97	1.51	1.51
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	1.92	1.43	1.62	2.23	2.20	2.10	2.52	2.28	2.31	2.69	2.69
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.65	0.02	0.35	0.24	0.64	0.58	0.79	0.82	0.78		
	1 ³ B ₁ ($\sigma \rightarrow \pi^*$)	1.90	1.64	1.77	2.23	2.20	2.10	2.53	2.28	2.31		
Cyclopentadiene	Ground State	0.30	0.31	0.46	0.11	0.38	0.33	0.58	0.50	0.51	0.61	0.61
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.43	0.40	0.68	0.07	0.36	0.31	0.47	0.35	0.36	1.86	1.86
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.87	0.46	1.13	1.70	2.82	2.41	2.00	1.89	1.73	0.26	0.26
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.57	0.32	0.24	0.41	0.08	0.18	0.57	0.76	0.88	0.11	0.11
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	0.17	0.18	0.27	0.28	0.59	0.45	0.63	0.42	0.49		
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.14	0.09	0.05	0.18	0.04	0.10	0.02	0.19	0.21		
Norbornadiene	Ground State	0.12	0.01	0.06	0.10	0.02	0.22	0.30	0.07	0.05	0.07	0.07
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.90	0.10		0.14	0.50	0.18	0.88	1.06	0.90		
	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	1.96	0.32	0.22	0.38	0.33	0.61	0.26	0.38	0.46	0.14	0.14
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	0.55	0.16	0.55	0.65	1.17	0.87	1.81	1.86	1.81	1.59	1.59
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.85	0.93	0.89	0.24	0.63	0.22	0.88	1.00	0.84	0.72	0.72
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.43	0.52	0.07	0.06	0.25	0.08	0.71	0.53	0.55	1.04	1.04
	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	0.16	0.05	0.05	0.07	0.08	0.16	0.30	0.18	0.09		
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.12	0.05	0.18	0.15	0.44	0.15	0.80	0.80	0.71		
Furan	Ground State	0.93	1.01	0.54	0.48	0.07	0.20	0.17	0.63	0.46	0.32	0.23
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.31	1.41	0.83	0.90	0.42	0.12	0.50	0.95	0.68	1.43	1.71
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.37	0.69	0.01	1.16	1.32	1.63	0.79	0.28	0.36	2.00	2.60
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.31	0.22	0.77	0.55	0.80	0.99	0.32	0.22	0.08	1.22	1.20
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.13	1.51	0.74	0.49	0.07	0.20	0.03	0.73	0.31		
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.34	1.28	1.14	1.32	0.96	0.66	1.17	1.61	1.41		
Pyrrole	Ground State	1.77	1.82	2.04	1.64	1.79	2.08	1.94	1.76	1.99	1.60	1.73
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.15	1.10	1.47	1.02	1.25	1.48	1.43	1.17	1.24	2.28	2.40
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.83	3.40	2.60	3.18	3.09	3.21	2.90	2.72	2.83	2.34	2.46
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.12	3.47	1.92	2.90	2.97	3.33	2.57	2.35	2.56	0.72	0.84
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.11	1.25	1.63	1.41	1.58	1.28	1.80	1.15	1.48		
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.97	0.85	1.14	0.47	0.55	0.76	0.67	0.46	0.53		
Imidazole	Ground State	3.70	3.79	3.90	2.95	2.91	3.63	3.38	3.33	3.36	3.51	3.61
	2 ¹ A' ($\pi \rightarrow \pi^*$)	4.61	3.35	4.71	2.75	2.73	3.35	3.61	3.48	3.46	5.19	5.22
	3 ¹ A' ($\pi \rightarrow \pi^*$)	3.00	4.82	3.72	3.97	3.86	4.64	3.83	3.71	3.73	4.55	4.65
	4 ¹ A' ($\pi \rightarrow \pi^*$)	3.85	4.76	4.14	3.50	3.55	4.33	4.03	3.80	3.69	3.02	3.11
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.22	1.11	0.48	0.55	0.60	0.13	0.98	1.39	0.68	1.78	1.77
	2 ¹ A'' ($n \rightarrow \pi^*$)	2.79	2.95	3.34	2.41	2.71	3.05	3.35	3.22	3.23	1.92	2.00
	1 ³ A' ($\pi \rightarrow \pi^*$)	3.17	2.88	3.00	1.81	1.66	2.30	2.13	1.92	1.85		
	2 ³ A' ($\pi \rightarrow \pi^*$)	4.03	3.61	4.56	3.32	3.17	3.17	3.66	3.37	3.52		
	3 ³ A' ($\pi \rightarrow \pi^*$)	4.68	4.90	4.83	4.27	4.69	5.93	5.34	5.59	5.21		

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Table S 9 – Continued

Molecule	State	CASSCF ^a	CASPT2 ^b	CC2 ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^c	INDO/S2 ^d
Pyridine	4 ³ A' ($\pi \rightarrow \pi^*$)	3.32	5.15	4.88	4.63	4.71	5.52	4.91	4.80	4.59		
	1 ³ A'' ($n \rightarrow \pi^*$)	1.38	1.31	1.17	1.60	1.72	0.86	1.69	2.18	2.00		
	2 ³ A'' ($n \rightarrow \pi^*$)	6.19	3.15	3.86	2.63	2.90	3.23	3.53	3.17	3.22		
	Ground State	2.36	2.27	2.30	1.54	1.36	1.76	1.78	1.83	1.78	2.08	2.05
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.28	3.24	2.68	1.71	1.55	1.99	2.03	2.22	1.98	2.39	2.36
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.67	1.22	2.13	2.26	2.20	2.37	2.10	3.39	2.51	2.09	2.07
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.30	3.18		1.47	1.14	1.41	1.71	0.78	1.81		
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	0.93	0.87	1.10	0.21	0.08	1.58	0.39	0.49	0.00	2.21	2.24
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.03	1.99	2.02	1.34	1.14	1.63	1.63	1.68	1.67	1.79	1.77
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.83	2.51	2.69	1.60	1.36	1.65	0.96	0.66	0.82	2.47	2.46
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.57	2.04		1.71	1.50	1.96	2.70	2.94	2.99		
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.40	0.27	1.10	0.20	0.31	0.71	0.23	1.05	0.41	0.63	0.65
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	2.13	2.08	2.15	1.47	1.25	1.69	1.68	1.62	1.67		
	2 ³ A ₁ ($\pi \rightarrow \pi^*$)	2.41	2.28	2.53	1.48	1.28	1.74	1.85	1.99	1.87		
	3 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.73	1.87	1.59	1.56	1.41	1.70	1.59	1.61	1.93		
	1 ³ A ₂ ($n \rightarrow \pi^*$)	0.15	0.65	1.01	0.08	0.05	1.51	0.29	0.55	0.06		
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	2.03	2.03	1.96	1.11	0.96	1.54	1.49	1.64	1.48		
	2 ³ B ₂ ($\pi \rightarrow \pi^*$)	3.79	3.17	3.49	1.20	0.71	0.90	3.73	3.88	3.46		
	3 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.04	1.74	1.16	2.69	2.70	3.02	0.34	0.26	0.82		
	1 ³ B ₁ ($n \rightarrow \pi^*$)	0.51	0.49	1.10	0.33	0.47	0.66	0.30	1.13	0.57		
Pyrimidine	Ground State	2.45	2.40	2.39	1.62	1.44	1.89	1.91	1.98	1.92	2.10	2.08
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	4.01	3.91	3.24	1.96	1.72	2.26	2.42	2.72	2.33	4.19	4.17
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.61	1.56	2.11	2.72	2.20	2.20	1.84	1.93	1.99	0.14	0.11
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.16	3.27		1.98	1.93	2.24	2.78	2.81	2.80	3.23	3.19
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.05	1.26	1.07	0.59	0.52	0.76	1.34	1.72	1.24	2.79	2.76
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.14	2.17	2.26	1.52	1.32	1.82	1.90	1.92	1.93	2.25	2.22
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.26	1.40	1.38	1.93	1.94	2.35	0.65	1.77	1.53	2.05	2.02
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.17	2.28		0.21	0.02	0.78	2.32	1.39	1.74	1.83	1.86
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.60	0.91	0.39	0.56	0.51	0.41	0.86	1.35	1.20	1.18	1.20
	Ground State	4.37	4.26	4.30	3.02	2.77	3.42	3.29	3.48	2.97	4.04	3.99
Pyridazine	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.60	3.64	3.64	2.44	2.25	3.04	2.82	3.09	2.72	2.98	2.94
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	5.09	5.73	4.07	4.39	3.95	4.25	3.47	4.80	3.80	4.36	4.32
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.97	2.15	1.21	2.28	2.39	0.85	1.79	2.85	1.86	0.43	0.38
	2 ¹ A ₂ ($n \rightarrow \pi^*$)	1.74	1.85	1.50	1.19	1.22	1.23	1.78	2.74	1.58	0.96	0.92
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.64	5.12	5.30	4.10	3.45	4.17	3.96	4.42	3.38	4.50	4.47
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	3.93	4.02	3.98	3.03	2.73	3.36	4.43	4.68	3.62	4.37	4.33
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	1.59	1.88	1.10	1.48	1.69	0.79	1.69	2.86	1.62	1.81	1.77
	2 ¹ B ₁ ($n \rightarrow \pi^*$)	1.74	2.12	1.66	1.61	1.51	0.99	1.58	2.57	1.73	0.35	0.39
	Ground State	2.43	2.44	2.20	1.79	1.59	1.67	1.28	2.20	1.70	2.31	2.29
Formaldehyde	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.39	1.46	1.25	1.97	2.03	1.93	1.38	2.47	2.04	1.20	1.70
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	0.50	0.90	0.37	1.37	1.74	1.33	1.05	2.47	2.28	0.11	0.47
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.75	2.69	1.56	2.24	2.09	2.20	0.93	2.58	2.16	0.32	0.78
	1 ³ A ₂ ($n \rightarrow \pi^*$)	1.13	1.35	1.09	1.71	1.79	1.73	1.14	2.25	1.82		

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Table S 9 – Continued

Molecule	State	CASSCF ^a	CASPT2 ^b	CC2 ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^c	INDO/S2 ^d
Acetone	$1^3A_1 (\pi \rightarrow \pi^*)$	0.89	1.05	0.82	0.06	0.20	0.03	0.51	0.37	0.00		
	Ground State	2.92	2.93	2.73	1.98	1.96	1.92	2.02	2.81	2.35	3.24	3.29
	$2^1A_1 (\pi \rightarrow \pi^*)$	3.94	3.18	2.94	2.53	3.43	3.85	2.76	3.55	3.06	3.94	3.64
	$1^1A_2 (n \rightarrow \pi^*)$	2.27	1.48	1.45	2.28	2.32	1.64	1.84	3.01	2.49	1.64	2.26
	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.99	1.31	1.53	2.16	4.80	3.28	3.80	4.83	4.61	5.34	5.81
	$1^3A_1 (\pi \rightarrow \pi^*)$	1.11	1.21	1.17	0.52	0.43	0.39	0.05	0.64	0.36		
Formamide	$1^3A_2 (n \rightarrow \pi^*)$	1.14	1.28	1.24	1.96	2.04	1.40	1.57	2.78	2.25		
	Ground State	4.08	3.79	3.75	3.02	2.92	3.06	2.95	3.68	3.42	3.61	3.72
	$2^1A' (\pi \rightarrow \pi^*)$	6.12	6.10	2.00	6.25	5.94	5.80	5.78	5.92	5.51	1.20	1.80
	$3^1A' (\pi \rightarrow \pi^*)$	5.24	5.10	1.80	4.47	4.08	4.39	4.49	4.79	4.63	7.65	8.43
	$1^1A'' (n \rightarrow \pi^*)$	2.12	1.99	1.98	1.73	1.83	1.76	1.37	2.27	2.13	2.78	1.51
	$1^3A' (\pi \rightarrow \pi^*)$	3.23	3.71	4.21	3.87	4.48	5.13	3.66	4.28	4.28		
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	1.39	1.95	1.80	1.54	1.66	1.58	1.21	2.11	1.98		
	Ground State	4.00	3.77	3.71	2.95	2.88	2.96	2.93	3.62	3.34	3.83	3.94
	$2^1A' (\pi \rightarrow \pi^*)$	6.21	5.87	4.76	6.06	5.81	5.72	5.45	5.57	5.24	7.31	8.25
	$3^1A' (\pi \rightarrow \pi^*)$	5.15	4.53	4.12	4.24	3.95	3.99	3.77	4.31	3.67	4.37	6.24
	$1^1A'' (n \rightarrow \pi^*)$	2.19	1.79	1.69	1.80	1.85	1.45	1.29	2.31	2.00	1.24	1.89
	$1^3A' (\pi \rightarrow \pi^*)$	3.81	3.31	3.82	3.64	4.19	4.93	3.20	3.78	3.85		
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	1.61	1.70	1.51	1.58	1.65	1.26	1.11	2.14	1.83		
	Ground State	4.13	3.60	3.53	2.82	2.69	2.82	2.78	3.45	3.15	3.72	3.83
	$2^1A' (\pi \rightarrow \pi^*)$	5.59	5.78	4.71	5.89	5.58	5.56	5.29	5.38	5.05	6.88	7.86
	$3^1A' (\pi \rightarrow \pi^*)$	4.59	4.21	3.30	4.03	4.21	3.80	3.27	4.33	3.15	5.61	7.19
	$1^1A'' (n \rightarrow \pi^*)$	1.90	1.70	1.56	1.83	2.08	1.51	1.48	2.78	2.32	1.17	1.88
	$1^3A' (\pi \rightarrow \pi^*)$	2.47	3.47	3.82	3.51	3.98	4.77	3.03	3.56	3.65		
Cytosine	$1^3A'' (n \rightarrow \pi^*)$	1.41	1.62	1.40	1.63	1.90	1.33	1.30	2.62	2.15		
	Ground State	7.2	6.34	6.25	4.89	4.66	5.01	5.13	6.08	5.72	6.70	6.74
	$2^1A' (\pi \rightarrow \pi^*)$	4.7	4.58	3.74	4.08	3.98	3.93	2.72	4.19	3.92	5.17	5.84
	$3^1A' (\pi \rightarrow \pi^*)$	7.0	5.73	6.69	4.20	4.55	5.71	4.95	6.01	5.69	6.91	7.21
	$4^1A' (\pi \rightarrow \pi^*)$	6.2	5.92	5.69	6.89	6.62	6.93	4.61	6.39	7.45	5.76	6.02
	$5^1A' (\pi \rightarrow \pi^*)$	9.3	7.02	8.06	5.13	4.62	4.28	7.29	7.18	4.95	7.48	7.47
Thymine	$1^1A'' (n \rightarrow \pi^*)$	4.7	2.56	1.76	2.23	2.60	2.23	1.78	3.59	3.20	1.55	1.74
	$2^1A'' (n \rightarrow \pi^*)$	6.4	2.74	1.03	1.88	2.15	2.28	2.08	3.42	3.18	3.69	4.67
	Ground State	5.0	4.19	4.07	3.30	3.25	3.15	3.15	4.30	3.91	4.16	4.22
	$2^1A' (\pi \rightarrow \pi^*)$	6.5	5.92	5.50	4.97	4.71	4.26	4.89	5.59	5.05	6.65	6.52
	$3^1A' (\pi \rightarrow \pi^*)$	1.5	1.61	2.68	2.05	2.47	2.12	2.25	7.25	6.99	11.23	11.42
	$4^1A' (\pi \rightarrow \pi^*)$	7.8	6.66	6.88	5.18	7.23	3.93	6.14	1.98	2.29	7.40	4.75
Uracil	$5^1A' (\pi \rightarrow \pi^*)$	3.1	3.05	1.40	2.57	2.92	2.10	1.78	2.59	2.34	3.01	3.34
	$1^1A'' (n \rightarrow \pi^*)$	3.2	2.52	1.87	2.36	2.45	2.16	2.34	3.89	3.11	2.67	2.36
	$2^1A'' (n \rightarrow \pi^*)$	4.6	3.92	4.26	3.22	2.62	3.21	3.30	3.81	3.32	3.89	3.56
	$3^1A'' (n \rightarrow \pi^*)$	8.6	6.46	3.92	1.55	1.86	1.55	2.21	3.76	3.00	5.65	4.27
	$4^1A'' (n \rightarrow \pi^*)$	4.1	2.27	2.63	5.79	6.00	6.25	8.24	6.81	6.47	12.28	11.50
	Ground State	4.4	4.31	4.13	3.37	3.27	3.23	3.23	4.38	4.03	4.33	4.41

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Table S 9 – Continued

Molecule	State	CASSCF ^a	CASPT2 ^b	CC2 ^b	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S ^c	INDO/S2 ^d
Adenine	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.3	5.78	5.61	5.15	4.87	4.35	5.00	5.56	4.99	5.98	5.99
	3 ¹ A' ($\pi \rightarrow \pi^*$)	2.4	2.48	3.17	1.91	2.32	2.54	3.58	2.53	2.24	10.49	10.94
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.9	6.52	6.44	5.93	5.79	5.36	6.59	6.70	5.54	5.16	5.43
	5 ¹ A' ($\pi \rightarrow \pi^*$)	3.7	3.16	0.97	2.76	1.89	1.95	1.67	2.66	2.38	5.47	8.48
	1 ¹ A'' ($n \rightarrow \pi^*$)	3.4	2.23	3.33	2.25	2.01	1.91	1.73	3.11	2.42	2.16	1.83
	2 ¹ A'' ($n \rightarrow \pi^*$)	4.8	4.25	4.36	3.31	2.86	3.42	3.71	4.19	3.73	4.38	3.96
	3 ¹ A'' ($n \rightarrow \pi^*$)	8.7	2.17	3.97	1.53	1.42	1.49	2.12	3.34	2.60	4.83	3.62
	4 ¹ A'' ($n \rightarrow \pi^*$)	3.6	6.86	2.01	5.97	6.54	6.58	8.82	7.36	7.02	12.63	11.76
	Ground State	2.50	2.53	2.51	1.95	1.79	2.07	2.15	1.93	1.97	2.44	2.46
	2 ¹ A' ($\pi \rightarrow \pi^*$)	2.37	2.19	2.86	2.12	2.12	2.60	2.60	2.30	2.63	4.28	4.30
	3 ¹ A' ($\pi \rightarrow \pi^*$)	2.30	2.52	2.24	2.84	2.71	2.43	3.01	2.59	2.73	2.68	2.70
	4 ¹ A' ($\pi \rightarrow \pi^*$)	2.13	2.09	2.48	1.49	1.80	2.22	2.18	2.79	2.01	2.52	2.54
	5 ¹ A' ($\pi \rightarrow \pi^*$)	4.60	3.45	3.14	3.74	3.41	2.79	3.37	2.93	3.30	1.16	1.18
	6 ¹ A' ($\pi \rightarrow \pi^*$)	3.42	2.86	4.38	2.50	2.51	3.07	3.02	3.35	2.67	2.86	2.88
	7 ¹ A' ($\pi \rightarrow \pi^*$)	6.41	0.97	1.44	2.22	2.03	1.94	2.64	1.65	3.42		
	1 ¹ A'' ($n \rightarrow \pi^*$)	2.14	1.48	0.59	0.60	0.48	0.63	1.00	0.96	1.02	1.86	1.87
	2 ¹ A'' ($n \rightarrow \pi^*$)	1.93	0.39	1.35	0.29	0.33	0.12	0.47	0.95	0.86	0.61	0.62

^aData from publications of the Roos group in the 1990s cited in Ref. ¹^bSA-CASSCF/MS-CASPT2 as well as RI-CC2 results using MP2/6-31G* ground-state equilibrium geometries (constrained to their highest possible symmetry) and TZVP basis set.^cINDO/S results using charge model II as described in Ref. ²^dINDO/S2 results using special parametrization for oxygen and charge model II as described in Ref. ²

2 Additional correlation and histogram plots: Figures S 1 – S 8

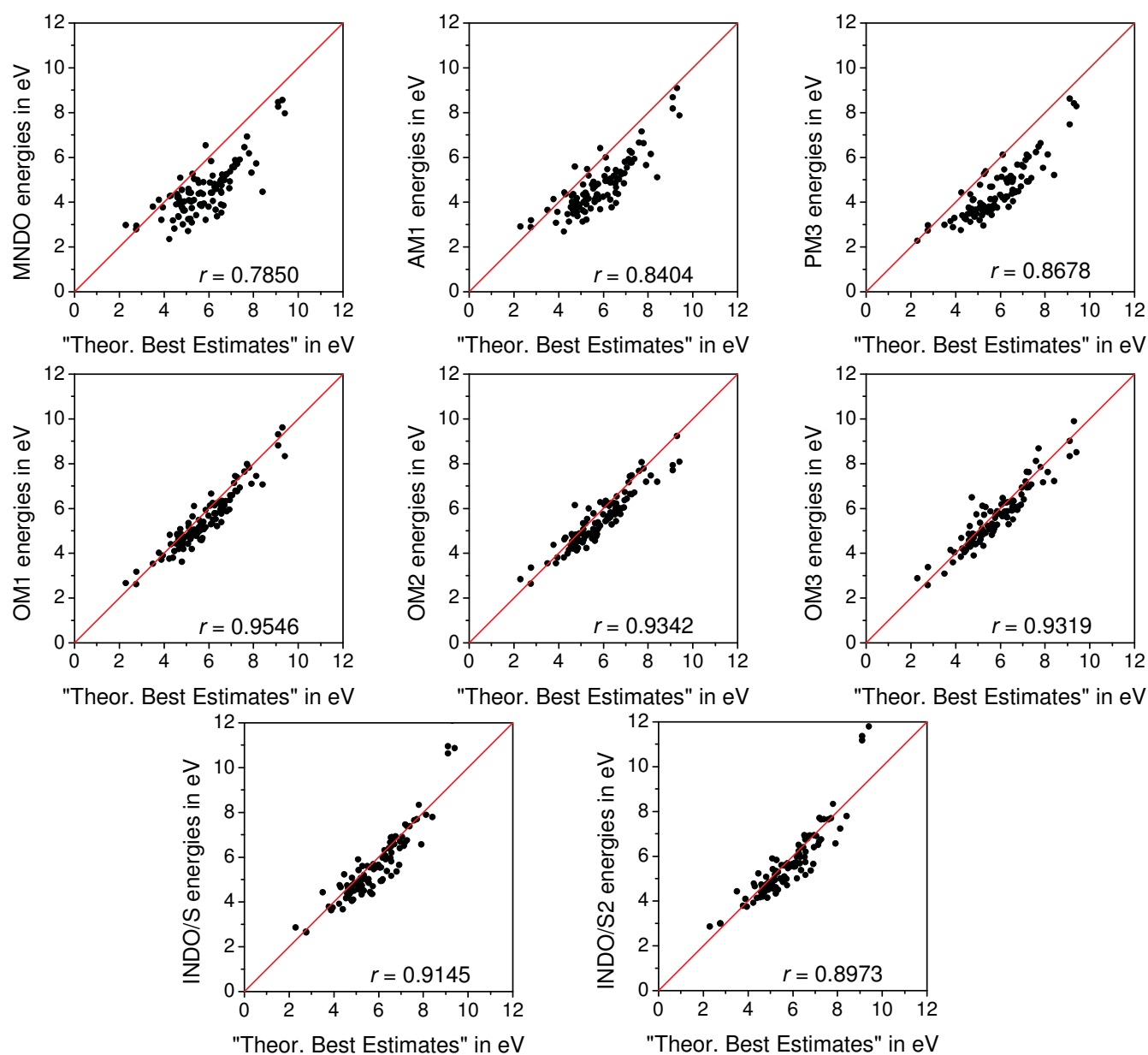


Figure S 1: Correlation plots of vertical excitation energies for all singlet states considered in this study using theoretical best estimates as reference data.

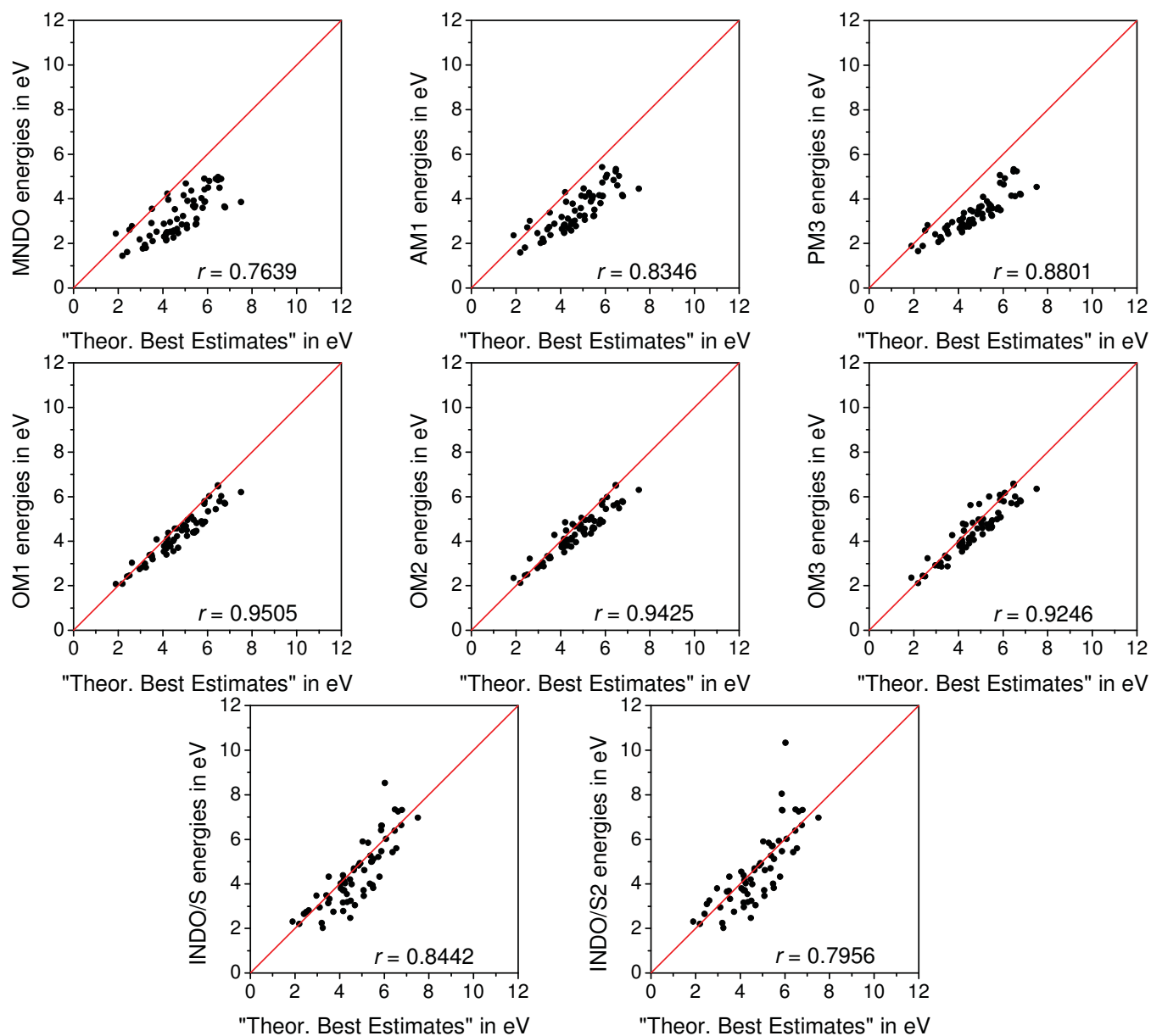


Figure S 2: Correlation plots of vertical excitation energies for all triplet states considered in this study using theoretical best estimates as reference data.

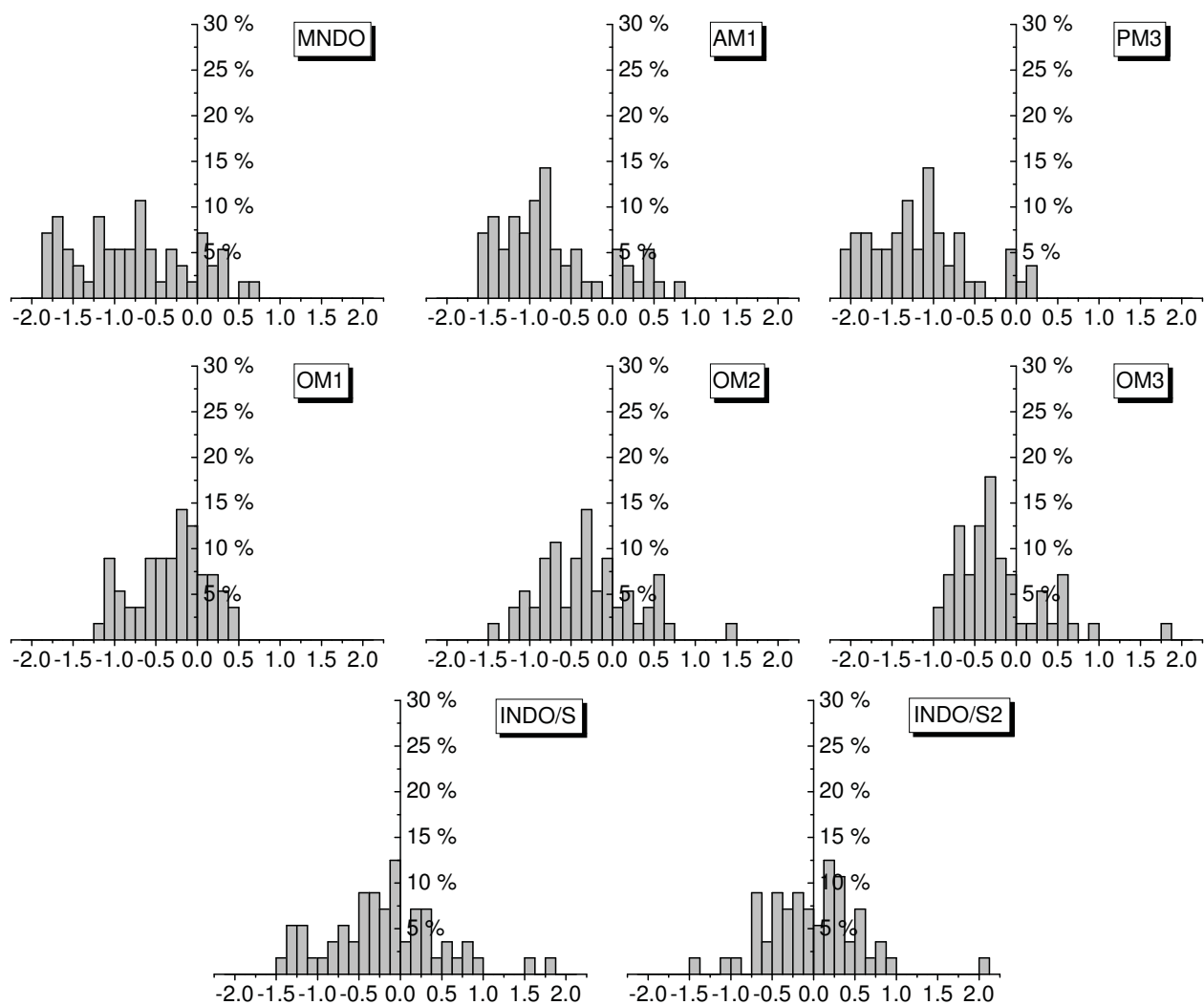


Figure S 3: Histograms of errors in vertical excitation energies for all states of type $n \rightarrow \pi^*$ considered in this study using theoretical best estimates as reference data.

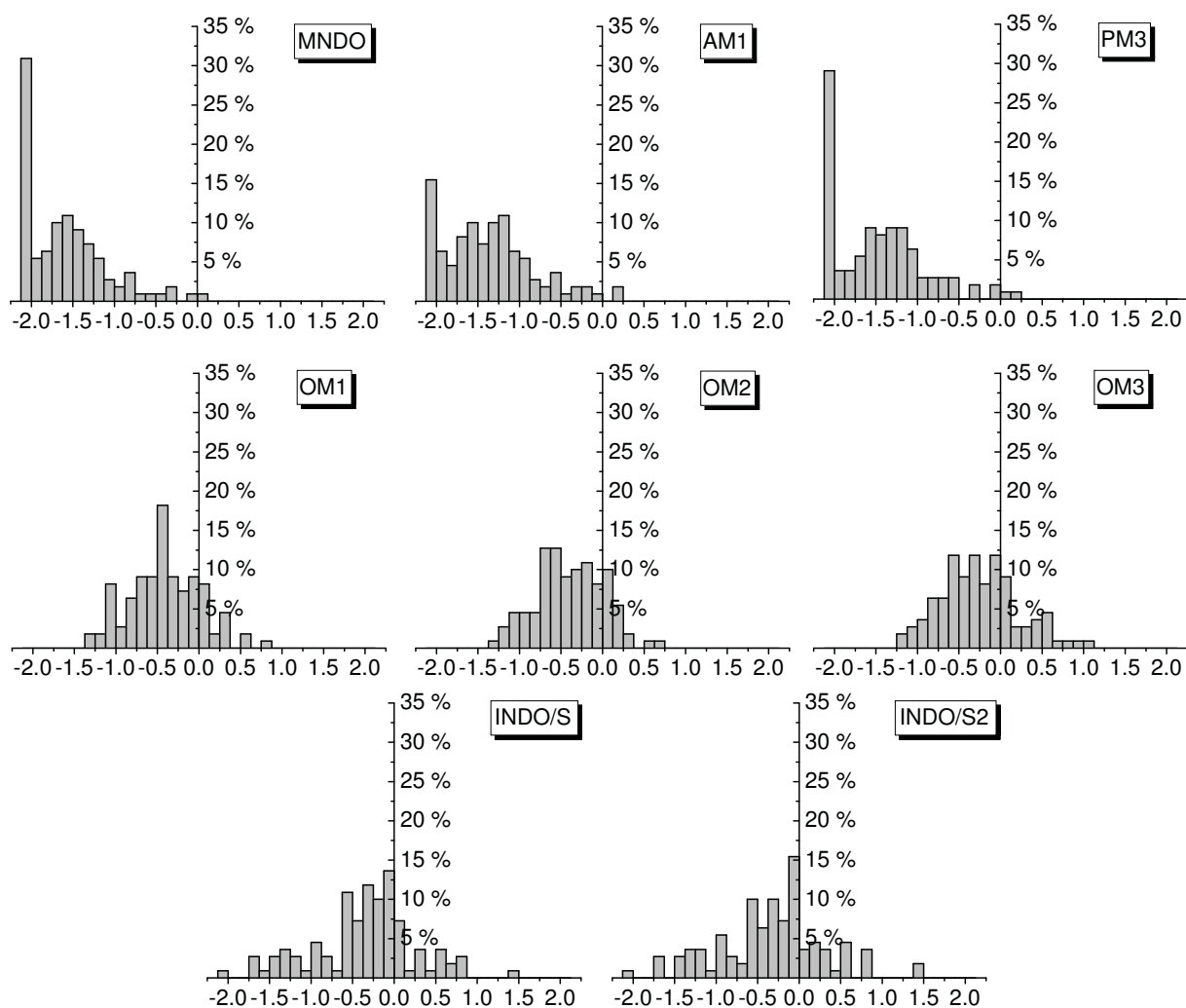


Figure S 4: Histograms of errors in vertical excitation energies for all states of type $\pi \rightarrow \pi^*$ considered in this study using theoretical best estimates as reference data. In the case of MND0, AM1, and PM3, the left-hand column collects all states whose energies are underestimated by more than 2 eV.

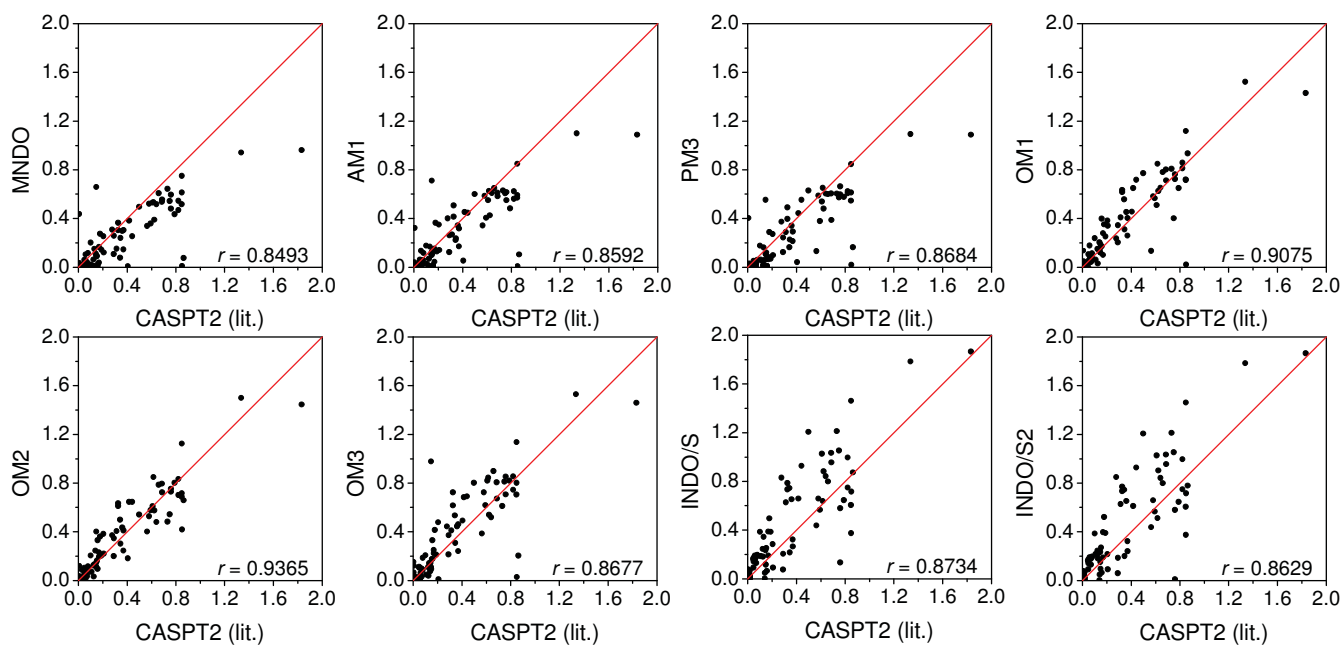


Figure S 5: Correlation plots of oscillator strengths for all dipole-allowed excited states using previous CASPT2 results from the literature as reference data.

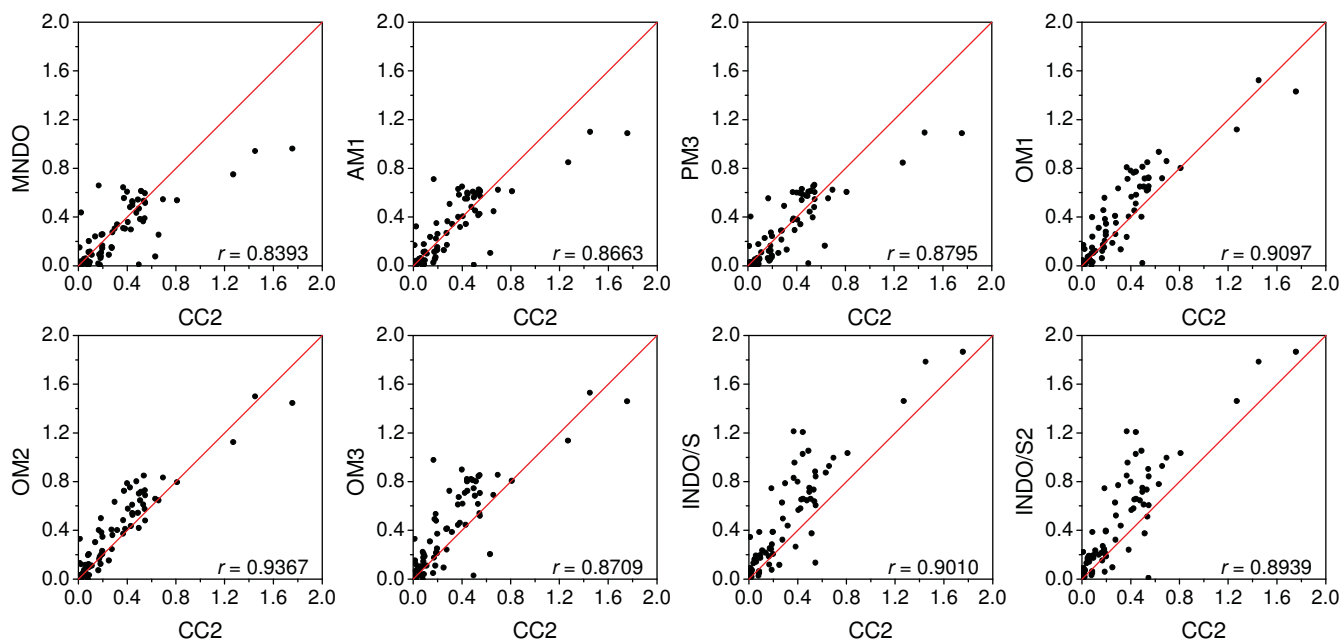


Figure S 6: Correlation plots of oscillator strengths for all dipole-allowed excited states using CC2/TZVP results as reference data.

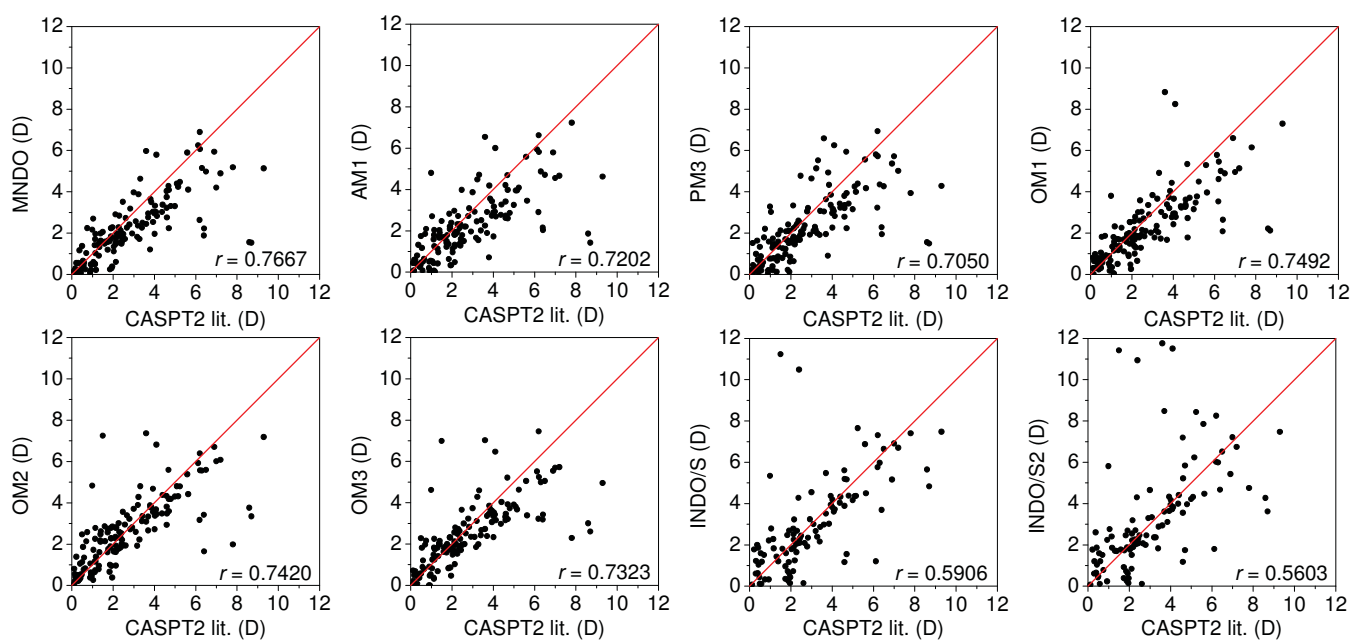


Figure S 7: Correlation plots of state dipole moments (in D) for all states considered using previous CASPT2 results from the literature as reference data.

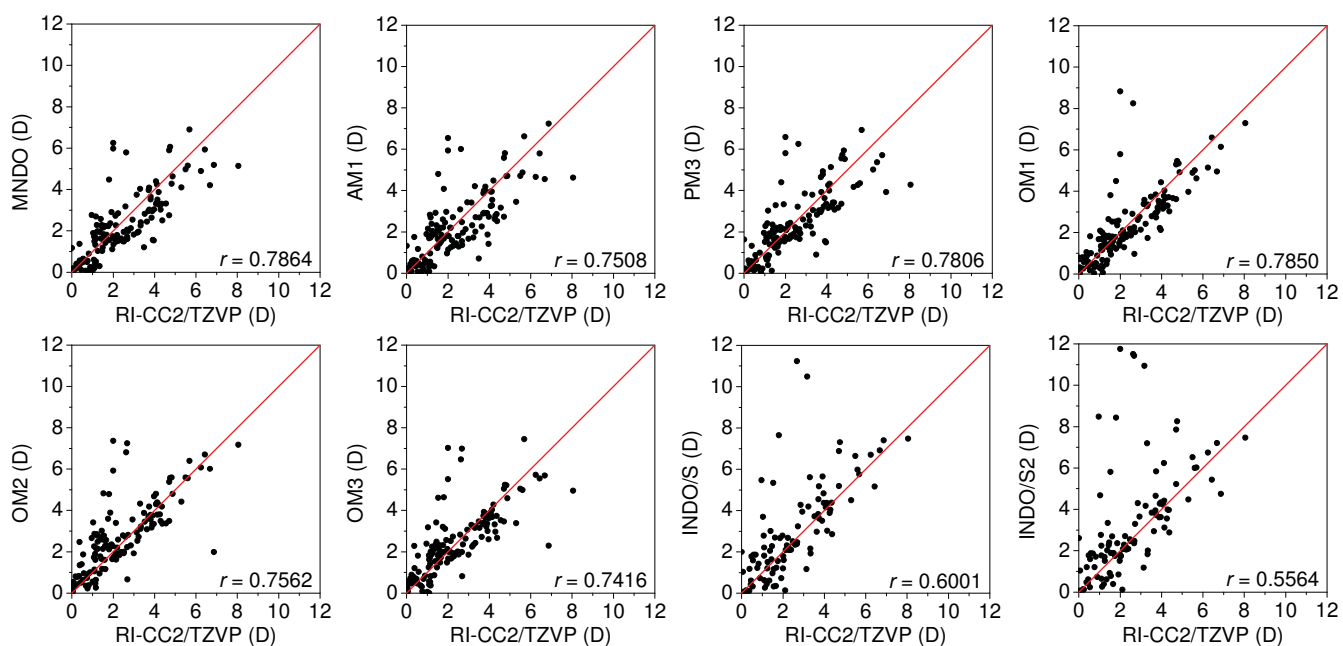


Figure S 8: Correlation plots of state dipole moments (in D) for all states considered using RI-CC2/TZVP results as reference data.

3 Additional statistical results: Tables S 10 – S 22

Table S 10: Deviations of semiempirical vertical excitation energies (in eV) for singlet states with respect to *ab initio* reference data.

	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	150	150	150	150	150	150	146	146
Mean	-1.26	-1.07	-1.40	-0.20	-0.21	-0.03	0.00	0.11
Abs. Mean	1.35	1.17	1.42	0.46	0.50	0.49	0.55	0.60
Std. Dev.	1.55	1.33	1.60	0.57	0.63	0.62	0.74	0.84
Max. (+) dev.	1.38	1.25	0.46	0.94	1.64	1.98	2.32	3.77
Max. (−) dev.	3.44	2.79	2.88	1.77	1.81	1.70	2.17	2.17
MS-CASPT2/TZVP results ^a								
Count ^b	150	150	150	150	150	150	146	146
Mean	-1.52	-1.32	-1.65	-0.45	-0.46	-0.28	-0.25	-0.13
Abs. Mean	1.55	1.36	1.66	0.53	0.58	0.53	0.54	0.55
Std. Dev.	1.75	1.52	1.81	0.65	0.69	0.64	0.71	0.80
Max. (+) dev.	0.69	0.85	0.19	0.76	1.42	1.76	2.77	4.22
Max. (−) dev.	3.86	3.40	3.58	1.82	1.68	1.69	1.71	1.71
CC3/TZVP results ^a								
Count ^b	117	117	117	117	117	117	115	115
Mean	-1.69	-1.48	-1.76	-0.59	-0.60	-0.40	-0.39	-0.30
Abs. Mean	1.70	1.50	1.77	0.62	0.67	0.58	0.63	0.66
Std. Dev.	1.92	1.68	1.92	0.75	0.80	0.71	0.77	0.86
Max. (+) dev.	0.45	0.61	0.11	0.46	1.18	1.52	1.77	3.09
Max. (−) dev.	4.17	3.60	3.49	1.76	1.86	1.61	1.74	1.74
Theoretical best estimates ^a								
Count ^b	104	104	104	104	104	104	103	103
Mean	-1.30	-1.12	-1.40	-0.34	-0.36	-0.22	-0.23	-0.11
Abs. Mean	1.35	1.19	1.41	0.45	0.50	0.45	0.51	0.51
Std. Dev.	1.55	1.34	1.55	0.55	0.59	0.54	0.70	0.77
Max. (+) dev.	0.69	0.85	0.19	0.76	1.42	1.76	2.79	4.24
Max. (−) dev.	3.95	3.30	3.21	1.34	1.39	1.19	1.45	1.45

^aSee Ref. ¹

^bTotal number of states considered.

Table S 11: Deviations of semiempirical vertical excitation energies (in eV) for singlet states of the hydrocarbons in the benchmark set with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	30	30	30	30	30	30	30	30
Mean	-1.46	-1.14	-1.07	-0.03	-0.06	-0.01	0.02	0.02
Abs. Mean	1.46	1.14	1.08	0.40	0.41	0.41	0.36	0.36
Std. Dev.	1.67	1.34	1.28	0.48	0.49	0.49	0.44	0.44
Max. (+) dev.	—	—	0.10	0.94	0.96	1.02	0.85	0.85
Max. (−) dev.	3.44	2.79	2.70	0.86	1.03	1.06	0.78	0.78
MS-CASPT2/TZVP results ^a								
Count ^b	30	30	30	30	30	30	30	30
Mean	-1.79	-1.47	-1.40	-0.35	-0.38	-0.34	-0.30	-0.30
Abs. Mean	1.79	1.47	1.40	0.46	0.46	0.45	0.41	0.41
Std. Dev.	1.98	1.63	1.57	0.56	0.56	0.54	0.45	0.45
Max. (+) dev.	—	—	0.04	0.76	0.66	0.72	0.59	0.59
Max. (−) dev.	3.72	3.07	2.98	1.11	1.05	0.99	0.84	0.84
CC3/TZVP results ^a								
Count ^b	30	30	30	30	30	30	30	30
Mean	-2.01	-1.69	-1.62	-0.58	-0.61	-0.56	-0.53	-0.53
Abs. Mean	2.01	1.69	1.62	0.62	0.63	0.59	0.56	0.56
Std. Dev.	2.19	1.84	1.77	0.72	0.73	0.70	0.64	0.64
Max. (+) dev.	—	—	—	0.46	0.36	0.42	0.26	0.26
Max. (−) dev.	4.17	3.60	3.49	1.76	1.64	1.61	1.14	1.14
Theoretical best estimates ^a								
Count ^b	25	25	25	25	25	25	25	25
Mean	-1.68	-1.36	-1.29	-0.27	-0.29	-0.25	-0.20	-0.20
Abs. Mean	1.68	1.36	1.29	0.42	0.41	0.40	0.42	0.42
Std. Dev.	1.89	1.55	1.48	0.52	0.51	0.49	0.47	0.47
Max. (+) dev.	—	—	0.04	0.76	0.66	0.72	0.81	0.81
Max. (−) dev.	3.95	3.30	3.21	1.34	1.22	1.19	0.84	0.84

^aSee Ref.¹

^bTotal number of states considered.

Table S 12: Deviations of semiempirical vertical excitation energies (in eV) for singlet states in the CHN-containing molecules from the benchmark set with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	73	73	73	73	73	73	69	69
Mean	-1.21	-1.07	-1.52	-0.18	-0.12	0.11	-0.11	-0.11
Abs. Mean	1.37	1.23	1.52	0.47	0.48	0.57	0.61	0.61
Std. Dev.	1.59	1.40	1.69	0.59	0.63	0.71	0.78	0.78
Max. (+) dev.	1.38	1.25	0.31	0.90	1.64	1.98	1.44	1.44
Max. (−) dev.	3.25	2.73	2.88	1.76	1.81	1.70	2.17	2.17
MS-CASPT2/TZVP results ^a								
Count ^b	73	73	73	73	73	73	69	69
Mean	-1.45	-1.30	-1.75	-0.41	-0.35	-0.12	-0.33	-0.33
Abs. Mean	1.51	1.37	1.75	0.49	0.53	0.54	0.53	0.53
Std. Dev.	1.74	1.56	1.89	0.64	0.65	0.68	0.68	0.68
Max. (+) dev.	0.69	0.85	0.02	0.55	1.42	1.76	0.96	0.96
Max. (−) dev.	3.86	3.40	3.58	1.82	1.68	1.69	1.71	1.71
CC3/TZVP results ^a								
Count ^b	62	62	62	62	62	62	60	60
Mean	-1.57	-1.42	-1.87	-0.55	-0.50	-0.25	-0.46	-0.46
Abs. Mean	1.59	1.46	1.87	0.56	0.59	0.54	0.61	0.61
Std. Dev.	1.82	1.63	1.98	0.69	0.70	0.70	0.75	0.75
Max. (+) dev.	0.45	0.61	—	0.13	1.18	1.52	0.83	0.83
Max. (−) dev.	4.01	3.44	3.45	1.68	1.57	1.59	1.74	1.74
Theoretical best estimates ^a								
Count ^b	43	43	43	43	43	43	42	42
Mean	-1.11	-1.01	-1.43	-0.27	-0.21	-0.09	-0.34	-0.34
Abs. Mean	1.22	1.13	1.43	0.38	0.45	0.46	0.48	0.48
Std. Dev.	1.41	1.27	1.53	0.49	0.54	0.57	0.63	0.63
Max. (+) dev.	0.69	0.85	—	0.37	1.42	1.76	0.92	0.92
Max. (−) dev.	3.00	2.60	2.58	1.16	1.09	1.08	1.45	1.45

^aSee Ref.¹

^bTotal number of states considered.

Table S 13: Deviations of semiempirical vertical excitation energies (in eV) for singlet states in the oxygen-containing molecules from the benchmark set with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	47	47	47	47	47	47	47	47
Mean	-1.22	-1.01	-1.43	-0.34	-0.44	-0.24	0.15	0.50
Abs. Mean	1.26	1.08	1.48	0.48	0.58	0.41	0.60	0.73
Std. Dev.	1.39	1.19	1.63	0.60	0.71	0.54	0.83	1.09
Max. (+) dev.	0.45	0.69	0.46	0.73	0.85	0.87	2.32	3.77
Max. (−) dev.	2.63	2.21	2.70	1.77	1.70	1.58	1.80	1.20
MS-CASPT2/TZVP results ^a								
Count ^b	47	47	47	47	47	47	47	47
Mean	-1.45	-1.25	-1.67	-0.57	-0.68	-0.48	-0.09	0.26
Abs. Mean	1.46	1.29	1.69	0.65	0.73	0.57	0.63	0.65
Std. Dev.	1.59	1.39	1.82	0.72	0.81	0.64	0.87	1.08
Max. (+) dev.	0.18	0.42	0.19	0.56	0.58	0.60	2.77	4.22
Max. (−) dev.	2.97	2.54	2.60	1.30	1.60	1.44	1.44	0.97
CC3/TZVP results ^a								
Count ^b	25	25	25	25	25	25	25	25
Mean	-1.59	-1.36	-1.68	-0.71	-0.87	-0.60	-0.04	0.36
Abs. Mean	1.60	1.40	1.69	0.76	0.91	0.66	0.77	0.91
Std. Dev.	1.81	1.58	1.93	0.89	1.06	0.78	0.92	1.26
Max. (+) dev.	0.10	0.34	0.11	0.32	0.50	0.52	1.77	3.09
Max. (−) dev.	3.09	2.66	3.19	1.57	1.86	1.56	1.37	1.30
Theoretical best estimates ^a								
Count ^b	36	36	36	36	36	36	36	36
Mean	-1.27	-1.09	-1.46	-0.47	-0.55	-0.35	-0.12	0.22
Abs. Mean	1.29	1.14	1.48	0.57	0.62	0.47	0.62	0.61
Std. Dev.	1.44	1.25	1.63	0.64	0.69	0.52	0.88	1.04
Max. (+) dev.	0.18	0.42	0.19	0.56	0.58	0.60	2.79	4.24
Max. (−) dev.	3.04	2.61	2.53	1.19	1.39	1.06	1.37	0.90

^aSee Ref.¹

^bTotal number of states considered.

Table S 14: Deviations of semiempirical vertical excitation energies (in eV) for $n \rightarrow \pi^*$ singlet states with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	51	51	51	51	51	51	50	50
Mean	-0.63	-0.58	-1.10	-0.12	-0.13	-0.05	0.02	0.21
Abs. Mean	0.89	0.85	1.14	0.50	0.61	0.54	0.72	0.68
Std. Dev.	1.07	0.99	1.33	0.64	0.77	0.71	0.89	0.86
Max. (+) dev.	1.38	1.25	0.46	0.90	1.64	1.98	1.86	2.27
Max. (-) dev.	2.50	2.54	2.77	1.77	1.81	1.70	2.17	2.17
MS-CASPT2/TZVP results ^a								
Count ^b	51	51	51	51	51	51	50	50
Mean	-0.95	-0.90	-1.42	-0.44	-0.45	-0.37	-0.29	-0.10
Abs. Mean	1.05	1.02	1.43	0.51	0.64	0.57	0.63	0.51
Std. Dev.	1.20	1.12	1.56	0.63	0.75	0.68	0.79	0.70
Max. (+) dev.	0.69	0.85	0.19	0.40	1.42	1.76	1.81	2.22
Max. (-) dev.	2.08	2.07	2.85	1.30	1.56	1.69	1.71	1.71
CC3/TZVP results ^a								
Count ^b	38	38	38	38	38	38	38	38
Mean	-0.90	-0.90	-1.42	-0.41	-0.45	-0.38	-0.22	-0.10
Abs. Mean	0.95	0.99	1.43	0.45	0.62	0.58	0.55	0.51
Std. Dev.	1.11	1.11	1.56	0.57	0.74	0.70	0.74	0.73
Max. (+) dev.	0.45	0.61	0.11	0.32	1.18	1.52	1.77	2.17
Max. (-) dev.	2.11	2.10	2.88	1.24	1.46	1.59	1.74	1.74
Theoretical best estimates ^a								
Count ^b	41	41	41	41	41	41	40	40
Mean	-0.77	-0.71	-1.19	-0.30	-0.30	-0.21	-0.25	-0.05
Abs. Mean	0.89	0.86	1.20	0.41	0.53	0.45	0.57	0.46
Std. Dev.	1.03	0.95	1.32	0.52	0.63	0.55	0.75	0.67
Max. (+) dev.	0.69	0.85	0.19	0.40	1.42	1.76	1.85	2.26
Max. (-) dev.	1.86	1.57	2.33	1.19	1.39	0.92	1.45	1.45

^aSee Ref. ¹

^bTotal number of states considered.

Table S 15: Deviations of semiempirical vertical excitation energies (in eV) for $\pi \rightarrow \pi^*$ singlet states with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	99	99	99	99	99	99	96	96
Mean	-1.59	-1.32	-1.56	-0.24	-0.25	-0.01	-0.01	0.06
Abs. Mean	1.59	1.33	1.56	0.44	0.44	0.46	0.47	0.56
Std. Dev.	1.74	1.47	1.72	0.54	0.55	0.57	0.65	0.83
Max. (+) dev.	0.11	0.32	0.24	0.94	0.96	1.50	2.32	3.77
Max. (−) dev.	3.44	2.79	2.88	1.23	1.61	1.45	1.72	1.72
MS-CASPT2/TZVP results ^a								
Count ^b	99	99	99	99	99	99	96	96
Mean	-1.81	-1.53	-1.77	-0.46	-0.46	-0.23	-0.22	-0.15
Abs. Mean	1.81	1.54	1.78	0.55	0.54	0.51	0.49	0.57
Std. Dev.	1.97	1.69	1.92	0.66	0.66	0.62	0.67	0.84
Max. (+) dev.	0.01	0.19	0.17	0.76	0.66	1.61	2.77	4.22
Max. (−) dev.	3.86	3.40	3.58	1.82	1.68	1.44	1.60	1.60
CC3/TZVP results ^a								
Count ^b	79	79	79	79	79	79	77	77
Mean	-2.06	-1.75	-1.93	-0.68	-0.67	-0.42	-0.47	-0.40
Abs. Mean	2.06	1.75	1.93	0.70	0.69	0.58	0.67	0.74
Std. Dev.	2.21	1.89	2.07	0.82	0.83	0.71	0.78	0.92
Max. (+) dev.	—	—	—	0.46	0.36	1.24	1.64	3.09
Max. (−) dev.	4.17	3.60	3.49	1.76	1.86	1.61	1.60	1.60
Theoretical best estimates ^a								
Count ^b	63	63	63	63	63	63	63	63
Mean	-1.65	-1.38	-1.54	-0.36	-0.38	-0.22	-0.21	-0.15
Abs. Mean	1.65	1.39	1.55	0.48	0.48	0.45	0.47	0.54
Std. Dev.	1.81	1.54	1.69	0.57	0.57	0.53	0.66	0.83
Max. (+) dev.	0.01	0.19	0.17	0.76	0.66	0.96	2.79	4.24
Max. (−) dev.	3.95	3.30	3.21	1.34	1.32	1.19	1.41	1.41

^aSee Ref.¹

^bTotal number of states considered.

Table S 16: Deviations of semiempirical vertical excitation energies (in eV) for triplet states with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	72	72	72	72	72	72	69	69
Mean	-1.28	-1.04	-1.25	-0.22	-0.15	-0.03	0.02	0.17
Abs. Mean	1.38	1.16	1.29	0.43	0.46	0.44	0.69	0.77
Std. Dev.	1.54	1.29	1.43	0.52	0.55	0.55	0.89	1.04
Max. (+) dev.	0.98	0.91	0.55	0.76	1.20	1.33	2.54	4.35
Max. (−) dev.	3.27	2.67	2.60	1.07	1.07	1.19	1.80	1.80
MS-CASPT2/TZVP results ^a								
Count ^b	72	72	72	72	72	72	69	69
Mean	-1.54	-1.30	-1.51	-0.48	-0.41	-0.29	-0.24	-0.09
Abs. Mean	1.58	1.34	1.52	0.54	0.53	0.50	0.67	0.74
Std. Dev.	1.76	1.50	1.66	0.64	0.63	0.59	0.88	1.02
Max. (+) dev.	0.82	0.75	0.27	0.47	0.74	1.23	2.48	4.29
Max. (−) dev.	3.62	3.14	3.19	1.45	1.45	1.59	2.04	2.04
CC3/TZVP results ^a								
Count ^b	71	71	71	71	71	71	69	69
Mean	-1.60	-1.36	-1.56	-0.53	-0.46	-0.34	-0.28	-0.13
Abs. Mean	1.62	1.39	1.57	0.56	0.55	0.50	0.66	0.73
Std. Dev.	1.80	1.54	1.70	0.67	0.65	0.60	0.86	1.00
Max. (+) dev.	0.54	0.47	0.20	0.41	0.64	1.08	2.50	4.30
Max. (−) dev.	3.64	3.10	3.15	1.41	1.44	1.58	2.02	2.02
Theoretical best estimates ^a								
Count ^b	63	63	63	63	63	63	63	63
Mean	-1.52	-1.27	-1.41	-0.45	-0.38	-0.26	-0.31	-0.15
Abs. Mean	1.55	1.30	1.42	0.49	0.47	0.45	0.65	0.72
Std. Dev.	1.72	1.44	1.55	0.61	0.58	0.54	0.86	1.01
Max. (+) dev.	0.54	0.47	0.20	0.41	0.64	1.08	2.49	4.30
Max. (−) dev.	3.66	3.06	2.98	1.31	1.21	1.17	2.01	2.01

^aSee Ref. ¹

^bTotal number of states considered.

Table S 17: Deviations of semiempirical vertical excitation energies (in eV) for triplet states in the hydrocarbons from the benchmark set with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	27	27	27	27	27	27	27	27
Mean	-1.54	-1.21	-1.14	-0.12	-0.07	-0.05	-0.08	-0.08
Abs. Mean	1.54	1.21	1.14	0.34	0.33	0.33	0.58	0.58
Std. Dev.	1.66	1.32	1.26	0.41	0.41	0.41	0.77	0.77
Max. (+) dev.	—	—	—	0.75	0.85	0.84	1.62	1.62
Max. (−) dev.	3.27	2.67	2.59	0.92	0.82	0.78	1.44	1.44
MS-CASPT2/TZVP results ^a								
Count ^b	27	27	27	27	27	27	27	27
Mean	-1.85	-1.51	-1.45	-0.42	-0.38	-0.36	-0.39	-0.39
Abs. Mean	1.85	1.51	1.45	0.48	0.45	0.44	0.59	0.59
Std. Dev.	1.95	1.60	1.54	0.55	0.53	0.51	0.77	0.77
Max. (+) dev.	—	—	—	0.33	0.52	0.51	1.12	1.12
Max. (−) dev.	3.53	2.93	2.85	1.18	1.08	1.04	1.65	1.65
CC3/TZVP results ^a								
Count ^b	27	27	27	27	27	27	27	27
Mean	-1.88	-1.54	-1.48	-0.45	-0.41	-0.39	-0.42	-0.42
Abs. Mean	1.88	1.54	1.48	0.48	0.46	0.44	0.57	0.57
Std. Dev.	1.98	1.64	1.58	0.57	0.56	0.53	0.75	0.75
Max. (+) dev.	—	—	—	0.36	0.55	0.54	0.85	0.85
Max. (−) dev.	3.64	3.04	2.96	1.29	1.19	1.15	1.63	1.63
Theoretical best estimates ^a								
Count ^b	27	27	27	27	27	27	27	27
Mean	-1.84	-1.50	-1.44	-0.42	-0.37	-0.35	-0.38	-0.38
Abs. Mean	1.84	1.50	1.44	0.45	0.42	0.41	0.57	0.57
Std. Dev.	1.96	1.61	1.55	0.55	0.54	0.52	0.74	0.74
Max. (+) dev.	—	—	—	0.36	0.55	0.54	0.85	0.85
Max. (−) dev.	3.66	3.06	2.98	1.31	1.21	1.17	1.63	1.63

^aSee Ref.¹

^bTotal number of states considered.

Table S 18: Deviations of semiempirical vertical excitation energies (in eV) for triplet states in the CHN-containing molecules from the benchmark set with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	29	29	29	29	29	29	26	26
Mean	-1.08	-0.95	-1.37	-0.19	-0.08	0.11	0.07	0.07
Abs. Mean	1.27	1.15	1.40	0.44	0.51	0.55	0.77	0.77
Std. Dev.	1.48	1.31	1.55	0.53	0.61	0.66	0.97	0.97
Max. (+) dev.	0.98	0.91	0.43	0.67	1.20	1.33	1.75	1.75
Max. (−) dev.	3.03	2.55	2.60	0.86	1.05	1.19	1.80	1.80
MS-CASPT2/TZVP results ^a								
Count ^b	29	29	29	29	29	29	26	26
Mean	-1.37	-1.24	-1.66	-0.49	-0.37	-0.18	-0.21	-0.21
Abs. Mean	1.45	1.31	1.68	0.55	0.57	0.57	0.71	0.71
Std. Dev.	1.69	1.52	1.82	0.68	0.69	0.69	0.91	0.91
Max. (+) dev.	0.82	0.75	0.27	0.47	0.74	1.23	1.33	1.33
Max. (−) dev.	3.62	3.14	3.19	1.45	1.45	1.59	2.04	2.04
CC3/TZVP results ^a								
Count ^b	28	28	28	28	28	28	26	26
Mean	-1.48	-1.35	-1.76	-0.58	-0.47	-0.25	-0.28	-0.28
Abs. Mean	1.52	1.39	1.76	0.59	0.60	0.57	0.71	0.71
Std. Dev.	1.76	1.58	1.89	0.71	0.70	0.68	0.89	0.89
Max. (+) dev.	0.54	0.47	—	0.19	0.64	1.08	1.34	1.34
Max. (−) dev.	3.58	3.10	3.15	1.41	1.44	1.58	2.02	2.02
Theoretical best estimates ^a								
Count ^b	20	20	20	20	20	20	20	20
Mean	-1.24	-1.10	-1.44	-0.39	-0.27	-0.05	-0.43	-0.43
Abs. Mean	1.29	1.16	1.44	0.43	0.44	0.49	0.70	0.70
Std. Dev.	1.50	1.32	1.55	0.56	0.52	0.56	0.92	0.92
Max. (+) dev.	0.54	0.47	—	0.19	0.64	1.08	0.86	0.86
Max. (−) dev.	2.63	2.28	2.43	1.05	0.92	0.87	2.01	2.01

^aSee Ref.¹

^bTotal number of states considered.

Table S 19: Deviations of semiempirical vertical excitation energies (in eV) for triplet states in the oxygen-containing molecules from the benchmark set with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	16	16	16	16	16	16	16	16
Mean	-1.20	-0.93	-1.20	-0.43	-0.39	-0.24	0.10	0.74
Abs. Mean	1.32	1.09	1.32	0.58	0.56	0.42	0.74	1.10
Std. Dev.	1.44	1.19	1.46	0.66	0.64	0.51	0.95	1.47
Max. (+) dev.	0.49	0.74	0.55	0.76	0.94	0.96	2.54	4.35
Max. (−) dev.	2.30	1.93	2.44	1.07	1.07	0.87	1.34	1.15
MS-CASPT2/TZVP results ^a								
Count ^b	16	16	16	16	16	16	16	16
Mean	-1.33	-1.06	-1.32	-0.56	-0.52	-0.37	-0.02	0.61
Abs. Mean	1.34	1.11	1.35	0.61	0.58	0.47	0.74	1.04
Std. Dev.	1.51	1.25	1.52	0.70	0.67	0.54	0.98	1.46
Max. (+) dev.	0.10	0.35	0.16	0.37	0.55	0.57	2.48	4.29
Max. (−) dev.	2.64	2.27	2.30	1.05	1.06	0.90	1.55	1.49
CC3/TZVP results ^a								
Count ^b	16	16	16	16	16	16	16	16
Mean	-1.35	-1.07	-1.34	-0.57	-0.53	-0.39	-0.04	0.60
Abs. Mean	1.38	1.15	1.37	0.62	0.60	0.49	0.73	1.02
Std. Dev.	1.54	1.29	1.56	0.73	0.70	0.57	0.97	1.44
Max. (+) dev.	0.14	0.39	0.20	0.41	0.59	0.61	2.50	4.30
Max. (−) dev.	2.63	2.26	2.40	1.04	1.03	0.89	1.55	1.48
Theoretical best estimates ^a								
Count ^b	16	16	16	16	16	16	16	16
Mean	-1.35	-1.07	-1.34	-0.57	-0.53	-0.39	-0.04	0.60
Abs. Mean	1.38	1.15	1.37	0.62	0.60	0.49	0.72	1.02
Std. Dev.	1.54	1.29	1.56	0.73	0.70	0.57	0.96	1.44
Max. (+) dev.	0.14	0.39	0.20	0.41	0.59	0.61	2.49	4.30
Max. (−) dev.	2.63	2.26	2.40	1.04	1.03	0.89	1.54	1.48

^aSee Ref.¹

^bTotal number of states considered.

Table S 20: Deviations of semiempirical state dipole moments (in D) for singlet excited states with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	90	90	90	90	90	90	86	86
Mean	-0.74	-0.72	-0.78	-0.57	-0.16	-0.46	0.18	0.28
Abs. Mean	1.07	1.17	1.20	1.15	1.05	1.12	1.45	1.57
Std. Dev.	1.67	1.75	1.80	1.70	1.65	1.71	2.37	2.49
Max. (+) dev.	2.37	3.81	2.98	5.22	5.75	5.49	9.73	9.92
Max. (−) dev.	7.17	7.28	7.21	6.58	5.82	6.10	4.92	5.08
MS-CASPT2/TZVP results ^a								
Count ^b	90	90	90	90	90	90	86	86
Mean	-0.39	-0.37	-0.43	-0.22	0.19	-0.10	0.50	0.60
Abs. Mean	0.79	0.85	0.84	0.79	0.83	0.86	1.27	1.39
Std. Dev.	1.07	1.18	1.17	1.17	1.29	1.29	2.23	2.31
Max. (+) dev.	3.52	3.73	3.98	5.97	5.64	5.38	10.01	9.81
Max. (−) dev.	4.91	4.60	4.91	4.25	4.68	4.37	4.90	4.30
RI-CC2/TZVP results ^a								
Count ^b	88	88	88	88	88	88	85	85
Mean	-0.02	-0.01	-0.08	0.11	0.53	0.23	0.80	0.90
Abs. Mean	0.96	0.99	0.95	0.86	1.01	1.00	1.36	1.49
Std. Dev.	1.26	1.33	1.33	1.36	1.50	1.46	2.40	2.55
Max. (+) dev.	4.25	4.53	4.57	6.81	5.35	5.01	10.62	9.75
Max. (−) dev.	2.93	3.44	3.78	1.85	4.90	4.59	1.98	2.13

^aReference data listed in Table S9. See Ref.^{1,3}

^bOnly singlet excited states are considered.

Table S 21: Deviations of semiempirical state dipole moments (in D) for ground states and singlet excited states with respect to *ab initio* reference data.

	Method							
	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S	INDO/S2
Published CASPT2 results ^a								
Count ^b	108	108	108	108	108	108	104	104
Mean	-0.78	-0.76	-0.78	-0.61	-0.20	-0.47	0.11	0.20
Abs. Mean	1.04	1.13	1.14	1.10	0.94	1.03	1.25	1.35
Std. Dev.	1.58	1.67	1.69	1.61	1.52	1.59	2.16	2.26
Max. (+) dev.	2.37	3.81	2.98	5.22	5.75	5.49	9.73	9.92
Max. (−) dev.	7.17	7.28	7.21	6.58	5.82	6.10	4.92	5.08
MS-CASPT2/TZVP results ^a								
Count ^b	108	108	108	108	108	108	104	104
Mean	-0.46	-0.44	-0.46	-0.28	0.12	-0.15	0.40	0.49
Abs. Mean	0.74	0.84	0.81	0.77	0.74	0.79	1.08	1.19
Std. Dev.	1.00	1.14	1.11	1.11	1.18	1.20	2.03	2.11
Max. (+) dev.	3.52	3.73	3.98	5.97	5.64	5.38	10.01	9.81
Max. (−) dev.	4.91	4.60	4.91	4.25	4.68	4.37	4.90	4.30
RI-CC2/TZVP results ^a								
Count ^b	106	106	106	106	106	106	103	103
Mean	-0.16	-0.14	-0.17	-0.02	0.40	0.12	0.65	0.73
Abs. Mean	0.91	0.96	0.90	0.83	0.88	0.90	1.16	1.26
Std. Dev.	1.19	1.27	1.25	1.28	1.38	1.35	2.18	2.32
Max. (+) dev.	4.25	4.53	4.57	6.81	5.35	5.01	10.62	9.75
Max. (−) dev.	2.93	3.44	3.78	1.85	4.90	4.59	1.98	2.13

^aReference data listed in Table S9. See Ref. ^{1,3}

^bOnly the ground state and singlet excited states are considered.

Table S 22: Statistical results for the set of 166 vertical excitation energies (in eV) using different CI treatments^a in combination with the OM1, OM2 and OM3 methods. Theoretical best estimates are taken as reference.

	FCI	CISDTQ	MR-CISD			
Threshold (%)			90	85	80	75
OM1 Hamiltonian						
Count ^b	166	166	166	166	166	166
Mean	-0.38	-0.38	-0.36	-0.35	-0.35	-0.35
Abs. Mean	0.47	0.46	0.46	0.45	0.45	0.45
Std. Dev.	0.57	0.57	0.56	0.56	0.56	0.56
Max. (+) dev.	0.76	0.76	0.76	0.76	0.76	0.76
Max. (−) dev.	1.34	1.34	1.34	1.34	1.34	1.34
OM2 Hamiltonian						
Count ^b	166	166	166	166	166	166
Mean	-0.37	-0.36	-0.35	-0.35	-0.34	-0.34
Abs. Mean	0.49	0.49	0.48	0.48	0.48	0.48
Std. Dev.	0.59	0.59	0.58	0.58	0.58	0.58
Max. (+) dev.	1.42	1.42	1.45	1.45	1.51	1.51
Max. (−) dev.	1.39	1.39	1.39	1.39	1.39	1.39
OM3 Hamiltonian						
Count ^b	166	166	166	166	166	166
Mean	-0.24	-0.24	-0.22	-0.22	-0.22	-0.21
Abs. Mean	0.45	0.45	0.44	0.44	0.44	0.44
Std. Dev.	0.54	0.54	0.53	0.53	0.53	0.53
Max. (+) dev.	1.76	1.76	1.77	1.82	1.82	1.82
Max. (−) dev.	1.19	1.19	1.19	1.18	1.18	1.18

^aSee main paper for notation.

^bTotal number of states considered.

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Paper V

*Basis set effects on coupled cluster benchmarks of electronically
excited states: CC3, CCSDR(3) and CC2*

M. R. Silva-Junior, S. P. A. Sauer, M. Schreiber and W. Thiel

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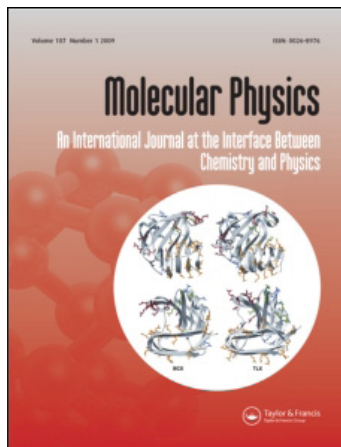
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Basis set effects on coupled cluster benchmarks of electronically excited states: CC3, CCSDR(3) and CC2

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INVITED ARTICLE

Basis set effects on coupled cluster benchmarks of electronically excited states: CC3, CCSDR(3) and CC2

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Vertical electronic excitation energies and one-electron properties of 28 medium-sized molecules from a previously proposed benchmark set are revisited using the augmented correlation-consistent triple-zeta aug-cc-pVTZ basis set in CC2, CCSDR(3), and CC3 calculations. The results are compared to those obtained previously with the smaller TZVP basis set. For each of the three coupled cluster methods, a correlation coefficient greater than 0.994 is found between the vertical excitation energies computed with the two basis sets. The deviations of the CC2 and CCSDR(3) results from the CC3 reference values are very similar for both basis sets, thus confirming previous conclusions on the intrinsic accuracy of CC2 and CCSDR(3). This similarity justifies the use of CC2- or CCSDR(3)-based corrections to account for basis set incompleteness in CC3 studies of vertical excitation energies. For oscillator strengths and excited-state dipole moments, CC2 calculations with the aug-cc-pVTZ and TZVP basis sets give correlation coefficients of 0.966 and 0.833, respectively, implying that basis set convergence is slower for these one-electron properties.

Keywords: electronically excited states; benchmarks; coupled cluster methods; CC2; CCSDR(3); CC3

1. Introduction

The importance of an accurate reference data set for excited-state energies and properties is unquestionable. Recently, we introduced a benchmark set [1–3] for vertical electronic excitation energies of 28 medium-sized molecules which represent the most significant organic chromophores. Theoretical best estimates were derived [1] from linear response CC3 and multistate CASPT2 calculations as well as high-level *ab initio* literature values. The main purpose of such a comprehensive reference data set is the validation of existing as well as newly developed methods and the parametrisation of semi-empirical or other adjustable methods. The proposed reference set has already been used in the validation of lower-level coupled cluster methods and approaches based on density functional theory [2–5].

In our previous work we employed a TZVP basis set [6] which was considered sufficiently flexible for the low-lying valence excited states that were of prime interest in our benchmarking. This choice of a medium-size basis set also enabled us to treat the majority of the reference molecules at the CC3 level.

Since the TZVP basis lacks diffuse functions, it is less appropriate for higher-lying valence states and for states which are spatially extended and have (partial) Rydberg character. Therefore, the proper identification of such states may become problematic when using the TZVP basis as in our previous studies [1–3], because the character of these higher-lying states might change upon basis set extension. Rydberg states can often be described effectively by adding a single set of very diffuse functions at the centre of the molecule, as has been done, for example, for benzene or other polycyclic aromatic hydrocarbons (see [7,8] and references therein), but this is not a convenient option for molecules of arbitrary shape. Therefore, we previously studied [1] the basis set dependence of the vertical excitation energy of the high-lying 1^1B_{1u} singlet state in ethene, which is known to be rather diffuse and susceptible to valence-Rydberg mixing, using twelve different correlation consistent basis sets [9,10]. When comparing against the essentially converged excitation energies computed with the most extended aug-cc-pV5Z and d-aug-cc-pVQZ basis sets, we found differences of more than 0.4 eV for the results

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with the TZVP basis, but excellent agreement for those with the aug-cc-pVTZ basis (deviations of less than 0.1 eV).

In this work we use the aug-cc-pVTZ basis set [9,10] in a comprehensive study that includes all 28 original benchmark molecules in CC2 calculations and subsets of 21 and eight molecules at the CCSDR(3) and CC3 levels, respectively. This basis set was chosen because it has been proven to be adequate in coupled cluster calculations of high-lying singlet states not only in the case of ethene [1], but also for a number of other chromophores (see e.g. [11–15]). However, even the aug-cc-pVTZ basis set is not optimal for Rydberg states in general, and hence additional molecule-centred diffuse basis functions may be necessary for an accurate description of states with significant valence–Rydberg mixing.

The paper is organised as follows: computational details are described in the next section. The results for the aug-cc-pVTZ basis are presented and compared to those for the TZVP basis in the following section which also provides various statistical evaluations. The final section offers a summary.

2. Computational details

All calculations were performed at the MP2/6-31G* optimised ground-state geometries [1] using the augmented aug-cc-pVTZ [9,10] basis. The CCSDR(3) [16,17] and CC3 [11,18,19] computations were carried out with the Dalton 2.0 program package [20]. Only singlet states were calculated, with the core electrons being frozen during the coupled cluster calculations which causes negligible deviations (less than 0.01 eV) compared with a fully correlated all-electron treatment [7].

The CC2 [21,22] calculations were done with the parallel version of program RICC2 [23–26] from the TURBOMOLE package (version 5.10) [27], employing the resolution-of-identity approximation [28,29] and the appropriate auxiliary basis set provided by the TURBOMOLE library [30,31]. In the case of CC2, both singlet and triplet excitation energies as well as one-electron properties (dipole moments and oscillator strengths in dipole length representation) were computed. It should be noted that the presence of diffuse functions in the basis set makes the assignment of states more difficult. As in our previous work [1,3], we used the expectation value $\langle r^2 \rangle$ as one of the criteria to determine the valence character of a given excited state and to identify valence–Rydberg mixings which can be pronounced especially in the high-lying states.

3. Results

In Table 1 we present the results for singlet excited states obtained with the CC2, CCSDR(3) and CC3 methods and the aug-cc-pVTZ basis set. Those obtained previously with the TZVP basis set [1,3] are also listed for comparison. Some higher-lying states of the original benchmark set (e.g. in formamide, formaldehyde, and naphthalene) are not included here due to problems in identifying these states when using the aug-cc-pVTZ basis set. Within an acceptable amount of computer time, we could afford to calculate a total of 22 states with the CC3 method and 99 states with the CCSDR(3) method. In both cases, the triples contributions scale formally as N^7 with the number of orbitals N . But while CC3 has an iterative triples contribution, CCSDR(3) is based on a pseudoperturbation theory expansion of the CC3 eigenvalue problem and thus includes essentially only a non-iterative triples correction which is added to the CCSD excitation energy. The efficient parallel implementation of the RI-CC2 method in the TURBOMOLE program allowed us to compute all the singlet excited states from the original benchmark set at the CC2 level.

In Figure 1 the correlation between the aug-cc-pVTZ and TZVP results is shown graphically for the three coupled cluster methods, while Figure 2 presents histograms for the deviations of the aug-cc-pVTZ from the TZVP results. The corresponding statistical data are given in Table 2.

Upon inspection of the numerical results and the histograms in Figure 2, one immediately sees a systematic lowering of the calculated excitation energies when going from the TZVP to the larger aug-cc-pVTZ basis, for each of the three coupled cluster methods. There are only three states at the CC2 level ($4^1A'$ in imidazole, $2^1A''$ in cytosine, and $3^1A''$ in uracil) and six at the CCSDR(3) level (2^1A_g in all-*E*-hexatriene, 2^1A_g in pyrazine, $1^1A'_2$ in *s*-triazine, 3^1B_{1g} and 2^1B_{3g} in *s*-tetrazine and 1^1A_u in *p*-benzoquinone) which have a higher energy with the aug-cc-pVTZ basis. These are mostly states with rather low single excitation weights, $\%R_1$, in the CC3/TZVP calculations [3]. The correlation (Figure 1) between the results with the two basis sets is almost perfect, with correlation coefficients of 0.9951, 0.9945, and 0.9967 for CC2, CCSDR(3), and CC3, respectively. Only for high-lying states with energies above 8 eV there are a few outliers. The largest one concerns the 3^1B_2 state in pyridine at the CC2 (−1.34 eV) and CCSDR(3) (−1.05 eV) levels, which also has a low single excitation weight, $\%R_1$, in the CC3/TZVP calculations [3]. The second largest outliers are found for the 4^1A_1 state in cyclopentadiene at the

Table 1. Vertical excitation energies ΔE (eV) of singlet excited states from coupled-cluster calculations with the TZVP^a and aug-cc-pVTZ^b basis sets.

Molecule	State	CC2		CCSDR(3)		CC3	
		TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	8.40	7.90	8.37	7.87	8.37	7.89
<i>E</i> -Butadiene	$1^1B_u (\pi \rightarrow \pi^*)$	6.49	6.13	6.56	6.19		
	$2^1A_g (\pi \rightarrow \pi^*)$	7.63	7.06	6.95	6.82	6.77	6.63
all- <i>E</i> -Hexatriene	$1^1B_u (\pi \rightarrow \pi^*)$	5.41	5.18	5.56	5.30		
	$2^1A_g (\pi \rightarrow \pi^*)$	6.67	6.43	6.04	6.09		
all- <i>E</i> -Octatetraene	$2^1A_g (\pi \rightarrow \pi^*)$	5.87	5.74				
	$1^1B_u (\pi \rightarrow \pi^*)$	4.72	4.53				
	$2^1B_u (\pi \rightarrow \pi^*)$	6.91	6.37				
	$3^1A_g (\pi \rightarrow \pi^*)$	6.72	6.12				
	$4^1A_g (\pi \rightarrow \pi^*)$	7.01	6.36				
Cyclopropene	$1^1B_1 (\sigma \rightarrow \pi^*)$	6.96	6.73	6.89	6.67	6.90	6.67
	$1^1B_2 (\pi \rightarrow \pi^*)$	7.17	6.72	7.10	6.68	7.10	6.68
Cyclopentadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	5.69	5.47	5.72	5.48		
	$2^1A_1 (\pi \rightarrow \pi^*)$	7.05	6.80	6.76	6.64		
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.86	8.19	8.72	8.17		
Norbornadiene	$1^1A_2 (\pi \rightarrow \pi^*)$	5.57	5.30				
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.37	6.09				
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.65	7.50				
	$2^1A_2 (\pi \rightarrow \pi^*)$	7.66	7.17				
Benzene	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.27	5.22	5.12	5.09	5.07	5.03
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.68	6.45	6.70	6.44	6.68	6.42
	$1^1E_{1u} (\pi \rightarrow \pi^*)$	7.44	7.12	7.45	7.16	7.45	7.14
	$2^1E_{2g} (\pi \rightarrow \pi^*)$	9.03	8.49	8.71	8.56	8.43	8.31
Naphthalene	$1^1B_{3u} (\pi \rightarrow \pi^*)$	4.45	4.38	4.34	4.32		
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.96	4.75	5.08	4.87		
	$2^1A_g (\pi \rightarrow \pi^*)$	6.22	6.07	6.09	6.01		
	$1^1B_{1g} (\pi \rightarrow \pi^*)$	6.21	5.82	6.26	5.94		
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	6.25	6.02	6.35	6.13		
	$2^1B_{1g} (\pi \rightarrow \pi^*)$	6.82	6.44	6.81	6.48		
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	6.57	6.35	6.60	6.39		
	$3^1A_g (\pi \rightarrow \pi^*)$	7.34	7.10	7.29	7.25		
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	8.46	7.90				
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	8.85	8.66				
Furan	$1^1B_2 (\pi \rightarrow \pi^*)$	6.75	6.37	6.64	6.30		
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.87	6.70	6.71	6.60		
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.78	8.23	8.57	8.17		
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	6.61	6.42	6.47	6.34		
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.88	6.85	6.74	6.23		
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.44	7.81	8.20	7.63		
Imidazole	$1^1A'' (n \rightarrow \pi^*)$	6.86	6.69				
	$2^1A' (\pi \rightarrow \pi^*)$	6.73	6.40				
	$3^1A' (\pi \rightarrow \pi^*)$	7.28	6.91				
	$2^1A'' (n \rightarrow \pi^*)$	8.00	7.64				
	$4^1A' (\pi \rightarrow \pi^*)$	8.62	8.68				
Pyridine	$1^1B_2 (\pi \rightarrow \pi^*)$	5.32	5.26	5.20	5.17		
	$1^1B_1 (n \rightarrow \pi^*)$	5.12	4.97	5.12	5.02		
	$1^1A_2 (n \rightarrow \pi^*)$	5.39	5.27	5.55	5.46		
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.88	6.64	6.88	6.63		
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.72	7.43	7.72	7.41		
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.61	7.32	7.61	7.35		
	$3^1B_2 (\pi \rightarrow \pi^*)$	9.37	8.03	9.09	8.04		
	$4^1A_1 (\pi \rightarrow \pi^*)$	9.00	8.59	9.00	8.65		

(continued)

Table 1. (Continued).

Molecule	State	CC2		CCSDR(3)		CC3	
		TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ
Pyrazine	$1^1B_{3u} (n \rightarrow \pi^*)$	4.26	4.12	4.31	4.20		
	$1^1A_u (n \rightarrow \pi^*)$	4.95	4.86	5.11	5.05		
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.13	5.07	5.07	5.02		
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.92	5.79	5.86	5.77		
	$1^1B_{1g} (n \rightarrow \pi^*)$	6.70	6.61	6.86	6.80		
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	7.10	6.86	7.10	6.86		
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	8.13	7.92	8.09	7.89		
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.07	7.82	8.08	7.84		
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	9.42	9.00	9.16	9.08		
	$2^1A_g (\pi \rightarrow \pi^*)$	9.26	9.08	9.04	9.13		
Pyrimidine	$1^1B_1 (n \rightarrow \pi^*)$	4.49	4.37	4.56	4.48		
	$1^1A_2 (n \rightarrow \pi^*)$	4.84	4.75	4.97	4.90		
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.51	5.46	5.42	5.40		
	$2^1A_1 (\pi \rightarrow \pi^*)$	7.12	6.94	7.10	6.86		
	$2^1B_2 (\pi \rightarrow \pi^*)$	8.08	7.82	8.02	7.83		
Pyridazine	$3^1A_1 (\pi \rightarrow \pi^*)$	7.79	7.53	7.77	7.56		
	$1^1B_1 (n \rightarrow \pi^*)$	3.90	3.79	3.99	3.92		
	$1^1A_2 (n \rightarrow \pi^*)$	4.40	4.30	4.57	4.52		
	$2^1A_1 (\pi \rightarrow \pi^*)$	5.37	5.32	5.28	5.26		
	$2^1A_2 (n \rightarrow \pi^*)$	5.81	5.70	5.84	5.76		
	$2^1B_1 (n \rightarrow \pi^*)$	6.40	6.27	6.49	6.41		
	$1^1B_2 (\pi \rightarrow \pi^*)$	7.00	6.79	6.99	6.74		
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.57	7.33	7.58	7.36		
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.90	7.70	7.86	7.58		
<i>s</i> -Triazine	$1^1A''_1 (n \rightarrow \pi^*)$	4.70	4.60	4.81	4.74		
	$1^1A''_2 (n \rightarrow \pi^*)$	4.80	4.71	4.83	4.79		
	$1^1E'' (n \rightarrow \pi^*)$	4.77	4.68	4.87	4.81		
	$1^1A'_2 (\pi \rightarrow \pi^*)$	5.82	5.80	5.76	5.77		
	$2^1A'_1 (\pi \rightarrow \pi^*)$	7.52	7.26	7.44	7.21		
	$2^1E'' (n \rightarrow \pi^*)$	8.04	7.97	7.95	7.93		
	$1^1E' (\pi \rightarrow \pi^*)$	8.06	7.88	8.07	7.87		
<i>s</i> -Tetrazine	$1^1B_{3u} (n \rightarrow \pi^*)$	2.47	2.39	2.61	2.56	2.53	2.46
	$1^1A_u (n \rightarrow \pi^*)$	3.67	3.61	3.88	3.86		
	$1^1B_{1g} (n \rightarrow \pi^*)$	5.10	5.00	5.15	5.08	4.97	4.87
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.20	5.16	5.20	5.18	5.12	5.08
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.53	5.45	5.51	5.47	5.34	5.28
	$2^1A_u (n \rightarrow \pi^*)$	5.50	5.40	5.56	5.49		
	$2^1B_{2g} (n \rightarrow \pi^*)$	6.32	6.23	6.43	6.40	6.23	6.16
	$2^1B_{1g} (n \rightarrow \pi^*)$	6.91	6.82	6.98	6.94	6.87	6.80
	$3^1B_{1g} (n \rightarrow \pi^*)$	7.64	7.42	7.60	7.64		
	$2^1B_{3u} (n \rightarrow \pi^*)$	6.70	6.61	6.77	6.72	6.67	6.60
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	7.60	7.51	7.54	7.27	7.45	7.18
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.75	7.65	7.83	7.65	7.79	7.59
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.65	8.45	8.58	8.40		
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	8.97	8.85	8.86	8.90		
Formaldehyde	$1^1A_2 (n \rightarrow \pi^*)$	4.09	4.00	3.94	3.89	3.95	3.88
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.35	9.19	9.19	9.06	9.18	9.05
Acetone	$1^1A_2 (n \rightarrow \pi^*)$	4.52	4.45	4.39	4.39	4.40	4.38
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.29	9.11	9.17	9.04		
	$2^1A_1 (\pi \rightarrow \pi^*)$	9.74	9.31	9.66	8.92	9.65	8.90
<i>p</i> -Benzoquinone	$1^1A_u (n \rightarrow \pi^*)$	2.92	2.88	3.01	3.02		
	$1^1B_{1g} (n \rightarrow \pi^*)$	2.81	2.76	2.90	2.89		
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.69	4.53	4.69	4.54		
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.59	5.46	5.65	5.51		

(continued)

Table 1. (Continued).

Molecule	State	CC2		CCSDR(3)		CC3	
		TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ
Formamide	$1^1B_{3u} (n \rightarrow \pi^*)$	5.69	5.55	6.09	5.98		
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	7.36	7.17	7.36	7.25		
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	8.31	8.10	8.10	7.90		
	$1^1A'' (n \rightarrow \pi^*)$	5.76	5.59	5.65	5.56	5.65	5.55
	$1^1A'' (n \rightarrow \pi^*)$	5.77	5.61	5.69	5.62		
Acetamide	$2^1A' (\pi \rightarrow \pi^*)$	7.66	7.23	7.69	7.16		
	$3^1A' (\pi \rightarrow \pi^*)$	10.71	10.21	10.56	9.72		
	$1^1A'' (n \rightarrow \pi^*)$	5.78	5.62	5.71	5.64		
	$2^1A' (\pi \rightarrow \pi^*)$	7.56	7.16	7.64	7.12		
Propanamide	$3^1A' (\pi \rightarrow \pi^*)$	10.33	9.71				
	$2^1A' (\pi \rightarrow \pi^*)$	4.80	4.69				
	$1^1A'' (n \rightarrow \pi^*)$	5.43	4.91				
	$2^1A'' (n \rightarrow \pi^*)$	5.01	5.33				
Cytosine	$3^1A' (\pi \rightarrow \pi^*)$	5.71	5.56				
	$4^1A' (\pi \rightarrow \pi^*)$	6.65	6.29				
	$5^1A' (\pi \rightarrow \pi^*)$	6.94	6.62				
	$1^1A'' (n \rightarrow \pi^*)$	4.94	4.83				
	$2^1A' (\pi \rightarrow \pi^*)$	5.39	5.19				
Thymine	$3^1A' (\pi \rightarrow \pi^*)$	6.46	6.26				
	$2^1A'' (n \rightarrow \pi^*)$	6.33	6.16				
	$4^1A' (\pi \rightarrow \pi^*)$	6.80	6.50				
	$4^1A'' (n \rightarrow \pi^*)$	6.73	6.55				
	$5^1A'' (n \rightarrow \pi^*)$	7.18	7.00				
Uracil	$5^1A' (\pi \rightarrow \pi^*)$	7.71	7.47				
	$1^1A'' (n \rightarrow \pi^*)$	4.91	4.81				
	$2^1A' (\pi \rightarrow \pi^*)$	5.52	5.33				
	$3^1A' (\pi \rightarrow \pi^*)$	6.43	6.24				
	$2^1A'' (n \rightarrow \pi^*)$	6.73	6.09				
Adenine	$3^1A'' (n \rightarrow \pi^*)$	6.26	6.55				
	$4^1A' (\pi \rightarrow \pi^*)$	6.96	6.66				
	$5^1A'' (n \rightarrow \pi^*)$	7.12	6.95				
	$5^1A' (\pi \rightarrow \pi^*)$	7.66	7.48				
	$2^1A' (\pi \rightarrow \pi^*)$	5.28	5.20				
	$3^1A' (\pi \rightarrow \pi^*)$	5.42	5.20				
	$1^1A'' (n \rightarrow \pi^*)$	5.27	5.13				
	$2^1A'' (n \rightarrow \pi^*)$	5.91	5.74				

Notes: ^aResults with the TZVP basis set from ref. [1]^bResults with the aug-cc-pVTZ basis set from this work.

CC2 level (−0.67 eV) and for the 2^1A_1 state in acetone at the CCSDR(3) and CC3 levels. For most other states there is close agreement between the aug-cc-pVTZ and TZVP results (see e.g. the 1^1B_{2u} states in benzene and *s*-tetrazine with deviations of less than 0.05 eV for all three methods).

There is another particular outlier in pyrrole that requires some comment. A previous extensive coupled cluster study of pyrrole [32] found significant valence–Rydberg mixing in the three lowest excited $^1B_2$ states showing ‘similar diffuseness and oscillator strengths’. We also see considerable mixing in our coupled cluster calculations: for example, both CC2/aug-cc-pVTZ and

CCSDR(3)/aug-cc-pVTZ yield two strongly mixed $^1B_2$ states at 6.25/6.85 eV and 6.23/6.81 eV, respectively. According to our standard assignment criteria, the more valence-like state occurs at higher energy for CC2 and at lower energy for CCSDR(3), by a small margin in each case, and the corresponding entries in Table 1 are thus 6.85 and 6.23 eV, respectively. At face value, this would seem to indicate a large discrepancy between the CC2 and CCSDR(3) results which are in reality quite similar (see above). We have refrained from imposing correlations between the assignments of separate calculations, to be as unbiased as possible, even though this will artificially deteriorate the

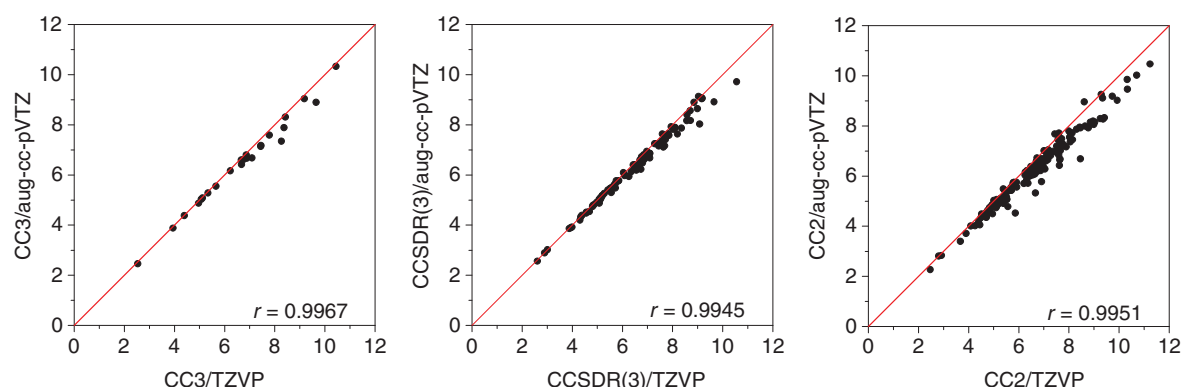


Figure 1. Correlation plots for the vertical excitation energies (eV) of singlet excited states at the CC3, CCSDR(3), and CC2 levels: aug-cc-pVTZ versus TZVP results.

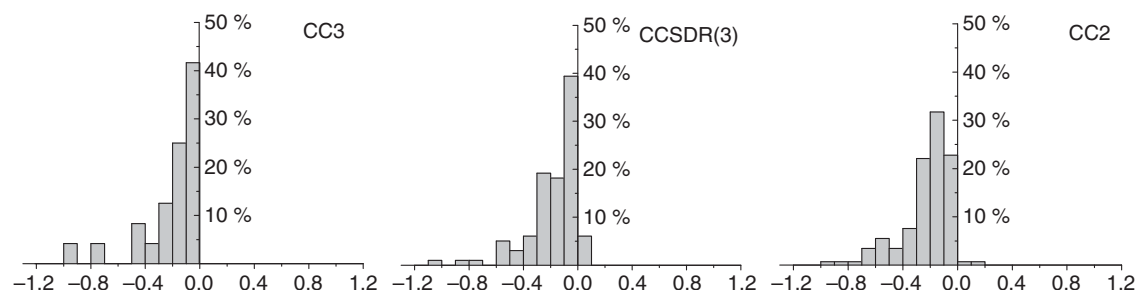


Figure 2. Histograms (in %) of the deviations between aug-cc-pVTZ and TZVP vertical excitation energies (eV) of singlet excited states at the CC3, CCSDR(3), and CC2 levels.

Table 2. Deviations in the vertical excitation energies (eV) of singlet excited states: aug-cc-pVTZ versus TZVP results^a.

	CC2	CC2 ^b	CCSDR(3)	CC3
Count ^c	143	99	99	22
Mean	-0.22	-0.22	-0.18	-0.18
Abs. Mean	0.23	0.22	0.18	0.18
Std. Dev.	0.29	0.28	0.26	0.25
Maximum (-)	1.34	1.34	1.05	0.75

Notes: ^aTZVP results from [1,3].

^bSame subset of states as in CCSDR(3).

^cTotal number of considered states.

statistical results to some extent. Our general conclusions are however not affected by this choice.

The mean and absolute mean deviations in Table 2 are of essentially the same magnitude (about 0.2 eV) for all three coupled cluster methods. This confirms that the basis set effects are very systematic. Looking at the finer details in Table 2, we note that the basis set dependence is slightly more pronounced for CC2 than for CCSDR(3) and CC3, both for the full set of

Table 3. Deviations in the vertical excitation energies (eV) of singlet excited states: CC3/TZVP-based estimates with CC2 and CCSDR(3) basis set corrections versus CC3/aug-cc-pVTZ results. See text.

	CC3 with CC2 correction ^a	CC3 with CCSDR(3) correction ^b
Count ^c	22	22
Mean	-0.02	0.01
Abs. Mean	0.08	0.02
Std. Dev.	0.15	0.02
Maximum (-)	0.42	0.03
Maximum (+)	0.32	0.04

Notes: ^aEstimated $\text{CC3/aug-cc-pVTZ} = \text{CC3/TZVP} + \text{CC2/aug-cc-pVTZ} - \text{CC2/TZVP}$.

^bEstimated $\text{CC3/aug-cc-pVTZ} = \text{CC3/TZVP} + \text{CCSDR(3)/aug-cc-pVTZ} - \text{CCSDR(3)/TZVP}$.

^cTotal number of considered states.

CC2 results as well as for the subset of states that is shared between CC2 and CCSDR(3). Comparing CCSDR(3) and CC3, the statistical data in Table 2 as well as the individual numerical results indicate an

Table 4. Deviation of CC2 and CCSDR(3) excitation energies (eV) of singlet excited states with respect to CC3 results obtained with the same basis set^a.

	Method					
	CC2			CCSDR(3)		
	TZVP ^b	TZVP ^c	aug-cc-pVTZ	TZVP ^d	TZVP ^e	aug-cc-pVTZ
Count ^f	118	22	22	118	22	22
Mean	0.13	0.14	0.11	0.09	0.07	0.08
Abs. Mean	0.16	0.15	0.12	0.09	0.07	0.08
Std. Dev.	0.25	0.25	0.17	0.14	0.11	0.12
Maximum (+)	0.95	0.86	0.43	0.52	0.28	0.25

Notes: ^aColumns labelled with TZVP have CC3/TZVP results [1] as reference data. Columns labelled with aug-cc-pVTZ have the present CC3/aug-cc-pVTZ results as reference data.

^bReference [1].

^cSubset of singlet states from [1], in order to compare directly with the present aug-cc-pVTZ results.

^dReference [3].

^eSubset of singlet states from [3], in order to compare directly with the present aug-cc-pVTZ results.

^fTotal number of considered states. Some data has been discarded whose assignment was considered unreliable.

essentially identical basis set dependence of the computed vertical excitation energies. This suggests an incremental scheme where expensive CC3 calculations that may only be feasible with a smaller basis set (such as TZVP) are augmented with a basis set correction obtained at the cheaper CC2 or CCSDR(3) level.

For the 22 states where CC3/aug-cc-pVTZ results are available, this correction scheme has been tested, with statistical results listed in Table 3. For the estimates obtained from the CC3/TZVP results plus the CCSDR(3) correction, the agreement with the CC3/aug-cc-pVTZ results is almost perfect, with negligible mean and absolute mean deviations of 0.01 and 0.02 eV, respectively, and a maximum deviation of only 0.04 eV. The CC2 correction performs not quite so well: the mean and absolute mean deviations are still quite low (−0.02 and 0.08 eV, respectively), but there are outliers for states with a low CC3/TZVP single excitation weight (maximum deviation of −0.42 eV for 2^1A_g of butadiene and 1^1E_{2g} of benzene, % R_1 below 70%).

In Table 4 we compare the performance of CC2 and CCSDR(3) relative to CC3, both for the TZVP [1,3] and aug-cc-pVTZ basis sets. Table 5 provides an analogous comparison between CC2 and CCSDR(3), again for both basis sets. In each case, the given deviations refer to excitation energies calculated with a lower-level versus a higher-level coupled cluster method (using the same basis). The mean and absolute deviations between the CCSDR(3) and CC3 results are essentially of the same magnitude (0.08 ± 0.01 eV) for both basis sets. In the case of CC2, the mean absolute

Table 5. Deviation of CC2 excitation energies (eV) of singlet excited states with respect to CCSDR(3) results obtained with the same basis set^a.

	TZVP ^b	TZVP ^c	aug-cc-pVTZ
Count ^d	118	99	99
Mean	0.04	0.03	0.00
Abs. Mean	0.11	0.11	0.10
Std. Dev.	0.16	0.15	0.14
Maximum (+)	0.68	0.68	0.62

Notes: ^aColumns labelled with TZVP have CCSDR(3)/TZVP results [3] as reference data. Columns labelled with aug-cc-pVTZ have the present CCSDR(3)/aug-cc-pVTZ results as reference data.

^bCCSDR(3) results from [3] and CC2 results from [1].

^cSubset of singlet states of the CCSDR(3) results from [3] and CC2 results from [1], in order to compare directly with the present aug-cc-pVTZ results.

^dTotal number of considered states.

deviations from the CC3 and CCSDR(3) results are slightly smaller for the aug-cc-pVTZ basis (0.12 and 0.10 eV) than for the TZVP basis (0.16 and 0.11 eV) so that the higher-level results are reproduced slightly better with the larger basis.

Using the CC2 method we have also computed vertical excitation energies for triplet excited states as well as one-electron properties for singlet excited states (oscillator strengths and dipole moments). The correlation between the aug-cc-pVTZ and TZVP results is shown in Figures 3 and 4. The corresponding statistical data for the differences between the aug-cc-pVTZ and TZVP results are given in Table 6. For the vertical

triplet excitation energies, the CC2 results for the two basis sets exhibit very small mean and absolute mean deviations of -0.08 and 0.10 eV, respectively, as well as a very large correlation coefficient of 0.9977 , which confirms the high quality of the previous CC2/TZVP

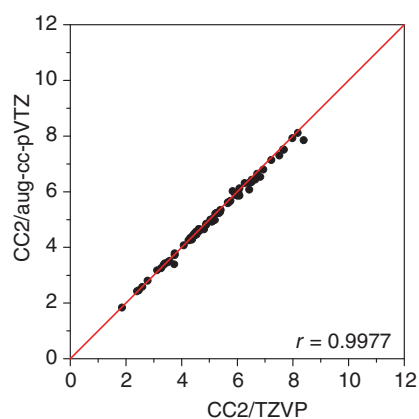


Figure 3. Correlation plot for the vertical excitation energies of triplet excited states: basis set effects for CC2.

results for the triplet states. Obviously the vertical excitation energies for the triplets are even less basis set dependent than those for the singlet excited states.

The situation is less clear-cut for one-electron properties, i.e. for the oscillator strengths and dipole moments of the singlet excited states, which are apparently affected more strongly by the addition of further diffuse and polarisation functions in the basis set. While extension of the basis set leads to a slight systematic lowering in the calculated vertical excitation energies, the one-electron properties change more randomly, although there is also a general overall trend towards lower absolute values (see Figure 4). Stronger variations may be caused by changes in the composition of states when further diffuse and/or polarisation functions are included: two states which are composed of $+/-$ combinations of configuration state functions and thus give rise to bright/dark states could mix differently upon basis set extension and then evolve into two states with moderate intensity. Generally speaking, the oscillator strengths and excited-state dipole moments depend more than the

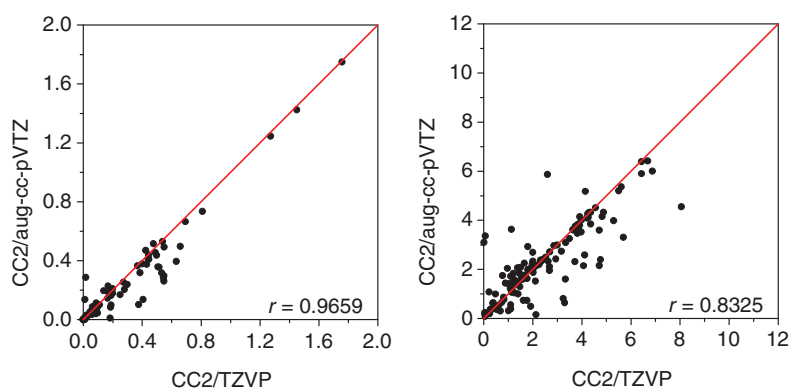


Figure 4. Correlation plots for (left) oscillator strengths and (right) dipole moments of singlet excited states: basis set effects for CC2.

Table 6. Deviations between the CC2/aug-cc-pVTZ and CC2/TZVP results for the vertical excitation energies (eV) of singlet and triplet excited states and for the oscillator strengths and dipole moments (D) of singlet excited states: statistics for all 28 benchmark molecules.

	CC2/aug-cc-pVTZ			
	Singlet states	Triplet states	Osc. strength	Dipole moment
Count ^a	143	71	95	127
Mean	-0.22	-0.08	-0.032	-0.14
Abs. Mean	0.23	0.10	0.047	0.57
Std. Dev.	0.29	0.14	0.088	0.97
Maximum (–)	1.34	0.54	0.287	3.51

Note: ^aTotal number of considered states. Some data has been discarded whose assignment was considered unreliable.

energies on the proper description of the excited-state wavefunctions, and they should thus be more susceptible to basis set effects (especially in the case of diffuse high-lying states). The largest changes in the oscillator strengths indeed occur for the high-lying states of cytosine (4A': -0.238) and uracil (5A': -0.287) where the intensities of these bright states are lowered considerably. For the dipole moments, the largest changes are found for the high-lying states of cytosine (4A': -2.38 D and 5A': -3.51 D). Turning to the statistics again, the correlation coefficients are 0.9659 for the oscillator strengths and 0.8325 for excited-state dipole moments (see Figure 4), which are still reasonably large, but significantly smaller than those for the vertical excitation energies. In summary, the differences between the CC2/aug-cc-pVTZ and CC2/TZVP results for the one-electron properties are still appreciable, and convergence with regard to basis set extension thus appears to be slower for these properties than for the excitation energies.

4. Conclusions

We have revisited a benchmark set of electronically excited states. Vertical excitation energies to singlet excited states were calculated with the CC2, CCSDR(3) and CC3 coupled cluster linear response methods, using the same geometries as in previous studies, but with the augmented correlation-consistent aug-cc-pVTZ basis instead of the TZVP basis. A total of 143 states were covered at the CC2 level. Due to the high computational demands of CCSDR(3) and in particular CC3, a smaller number of states were investigated with these methods, i.e. 99 with CCSDR(3) and 22 with CC3.

Inspection of the individual numerical results and statistical evaluations for the aug-cc-pVTZ and TZVP data show that the basis set effects on the calculated singlet excitation energies are rather uniform, for each of the three coupled cluster methods investigated. There is a systematic lowering of the computed energies upon basis set extension, of typically about 0.2 eV on average. This provides some justification for an incremental scheme where CC3 results obtained with a moderate basis are augmented by applying a basis set correction determined with a less costly coupled cluster method such as CC2 or CCSDR(3).

In the case of triplet excited states, the CC2 vertical excitation energies are even less basis set dependent than in the singlet case, since going from TZVP to aug-cc-pVTZ causes only a very minor lowering of typically 0.1 eV. By contrast, the changes in the CC2 oscillator strengths and dipole moments for singlet excited states are less systematic and sometimes

rather random. Hence, further convergence studies are desirable for these one-electron properties.

To conclude, some of the calculated vertical excitation energies, in particular those to high-lying singlet states, are significantly lowered by the inclusion of additional diffuse and polarisation functions in the aug-cc-pVTZ basis set (compared to TZVP), and further changes may be expected upon addition of molecule-centred diffuse functions for states with significant valence-Rydberg mixing. However, in an overall assessment of the present results, the effects of basis set extension on the vertical excitation energies of the chosen benchmark set are rather minor. Therefore, our previous conclusions on the performance of the coupled cluster methods CC2, CCSDR(3), and CC3 in excited-state studies remain valid [1,3].

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Appendix 1. CC2 results for vertical excitation energies of triplet excited states

The CC2 results for vertical excitation energies of triplet excited states are given in Table 7.

Table 7. Vertical excitation energies (eV) of triplet excited states from CC2 calculations with the TZVP^a and aug-cc-pVTZ^b basis sets.

Molecule	State	CC2	
		TZVP	aug-cc-pVTZ
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.52	4.56
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	3.40	3.43
	$1^3A_g (\pi \rightarrow \pi^*)$	5.25	5.24
all- <i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	2.78	2.80
	$1^3A_g (\pi \rightarrow \pi^*)$	4.40	4.42
all- <i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	2.40	2.42
	$1^3A_g (\pi \rightarrow \pi^*)$	3.76	3.78
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	4.44	4.40
	$1^3B_1 (\sigma \rightarrow \pi^*)$	6.65	6.44
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.36	3.37
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.22	5.22
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	3.76	3.72
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.25	4.25
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.31	4.33
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	5.14	5.05
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	6.08	5.86
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.99	7.92
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.27	3.25
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	4.38	4.28
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.64	4.59
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.88	4.81
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	5.11	4.93
	$1^3A_g (\pi \rightarrow \pi^*)$	5.76	5.67
	$2^3B_{1g} (\pi \rightarrow \pi^*)$	6.44	6.07
	$2^3A_g (\pi \rightarrow \pi^*)$	6.83	6.53
	$3^3A_g (\pi \rightarrow \pi^*)$	6.94	6.80
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	7.23	7.14
Furan	$1^3B_2 (\pi \rightarrow \pi^*)$	4.38	4.33
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.67	5.61
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	4.68	4.64
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.72	5.63
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.89	4.85
	$2^3A' (\pi \rightarrow \pi^*)$	6.01	5.86
	$1^3A'' (n \rightarrow \pi^*)$	6.44	6.32
	$3^3A' (\pi \rightarrow \pi^*)$	6.74	6.57
	$4^3A' (\pi \rightarrow \pi^*)$	7.68	7.51
	$2^3A'' (n \rightarrow \pi^*)$	7.52	7.30
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	4.46	4.48
	$1^3B_1 (n \rightarrow \pi^*)$	4.54	4.46
	$1^3B_2 (\pi \rightarrow \pi^*)$	5.07	4.93
	$2^3A_1 (\pi \rightarrow \pi^*)$	5.33	5.24
	$1^3A_2 (n \rightarrow \pi^*)$	5.35	5.24
	$2^3B_2 (\pi \rightarrow \pi^*)$	6.52	6.34
	$3^3B_2 (\pi \rightarrow \pi^*)$	8.39	7.85
	$3^3A_1 (\pi \rightarrow \pi^*)$	8.18	8.11

(continued)

Table 7. (Continued).

Molecule	State	CC2	
		TZVP	aug-cc-pVTZ
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.86	1.83
	$1^3A_u (n \rightarrow \pi^*)$	3.43	3.39
	$1^3B_{1g} (n \rightarrow \pi^*)$	4.30	4.27
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.62	4.66
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	4.81	4.65
	$1^3B_{2g} (n \rightarrow \pi^*)$	5.03	4.99
	$2^3A_u (n \rightarrow \pi^*)$	5.05	4.98
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.67	5.59
	$2^3B_{2g} (n \rightarrow \pi^*)$	6.05	5.98
	$2^3B_{1g} (n \rightarrow \pi^*)$	6.72	6.65
	$2^3B_{3u} (n \rightarrow \pi^*)$	6.52	6.43
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	7.65	7.52
Formaldehyde	$1^3A_2 (\pi \rightarrow \pi^*)$	3.57	3.52
	$1^3A_1 (\pi \rightarrow \pi^*)$	6.08	6.12
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	4.08	4.07
	$1^3A_1 (\pi \rightarrow \pi^*)$	6.27	6.31
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	2.47	2.46
	$1^3A_u (n \rightarrow \pi^*)$	2.59	2.58
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.12	3.18
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	3.50	3.46
Formamide	$1^3A'' (n \rightarrow \pi^*)$	5.39	5.27
	$1^3A' (\pi \rightarrow \pi^*)$	5.94	5.88
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	5.42	5.33
	$1^3A' (\pi \rightarrow \pi^*)$	6.06	5.88
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.44	5.35
	$1^3A' (\pi \rightarrow \pi^*)$	6.07	6.02

Notes: ^aResults with the TZVP basis set from [1].^bResults with the aug-cc-pVTZ basis set from this work.

Appendix 2. CC2 results for oscillator strengths and dipole moments of singlet excited states

The CC2 results for oscillator strengths and dipole moments of singlet excited states are given in Tables 8 and 9, respectively.

Table 8. Oscillator strengths (in dipole length representation) for optically allowed transitions from CC2 calculations^a.

Molecule	State	CC2	
		TZVP ^b	aug-cc-pVTZ ^c
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.431	0.375
<i>E</i> -Butadiene	$1^1B_u (\pi \rightarrow \pi^*)$	0.809	0.734
all- <i>E</i> -Hexatriene	$1^1B_u (\pi \rightarrow \pi^*)$	1.272	1.246
all- <i>E</i> -Octatetraene	$1^1B_u (\pi \rightarrow \pi^*)$	1.757	1.749

(continued)

Table 8. (Continued).

Molecule	State	CC2	
		TZVP ^b	aug-cc-pVTZ ^c
Cyclopropene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.086	0.072
	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.001	0.000
Cyclopentadiene	$2^1A_1 (\pi \rightarrow \pi^*)$	0.011	0.001
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.658	0.497
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.110	0.100
Norbornadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.023	0.020
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.185	0.083
Benzene	$1^1E_{1u} (\pi \rightarrow \pi^*)$	0.694	0.664
Naphthalene	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.094	0.078
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.272	0.253
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	0.548	0.297
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	1.450	1.424
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	0.010	0.015
Furan	$2^1A_1 (\pi \rightarrow \pi^*)$	0.003	0.000
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.506	0.358
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.172	0.184
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	0.006	0.001
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.532	0.317
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.182	0.011
Imidazole	$2^1A' (\pi \rightarrow \pi^*)$	0.088	0.112
	$3^1A' (\pi \rightarrow \pi^*)$	0.085	0.040
	$4^1A' (\pi \rightarrow \pi^*)$	0.406	0.136
	$1^1A'' (n \rightarrow \pi^*)$	0.003	0.002
	$2^1A'' (n \rightarrow \pi^*)$	0.006	0.002
Pyridine	$2^1A_1 (\pi \rightarrow \pi^*)$	0.021	0.014
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.498	0.436
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.025	0.032
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.549	0.493
	$1^1B_1 (n \rightarrow \pi^*)$	0.005	0.005
Pyrazine	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.096	0.045
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.424	0.470
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.070	0.084
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.400	0.378
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.007	0.001
Pyrimidine	$2^1A_1 (\pi \rightarrow \pi^*)$	0.062	0.086
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.446	0.410
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.023	0.029
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.476	0.515
	$1^1B_1 (n \rightarrow \pi^*)$	0.006	0.005
Pyridazine	$2^1A_1 (\pi \rightarrow \pi^*)$	0.014	0.017
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.444	0.438
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.009	0.003
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.489	0.455
	$1^1B_1 (n \rightarrow \pi^*)$	0.006	0.005
<i>s</i> -Triazine	$2^1B_1 (n \rightarrow \pi^*)$	0.005	0.004
	$1^1E' (\pi \rightarrow \pi^*)$	0.441	0.410
<i>s</i> -Tetrazine	$1^1A''_2 (n \rightarrow \pi^*)$	0.017	0.015
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.017	0.286
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.376	0.102
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.046	0.054
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.368	0.364
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.007	0.006
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.011	0.011

(continued)

Table 8. (Continued).

Molecule	State	CC2	
		TZVP ^b	aug-cc-pVTZ ^c
Formaldehyde	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	0.079	0.001
Acetone	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.298	0.238
<i>p</i> -Benzoquinone	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.538	0.530
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	0.544	0.283
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	0.000	0.001
Formamide	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.001
Acetamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.199	0.210
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.279	0.204
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.000
Propanamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.138	0.196
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.189	0.099
Cytosine	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.049	0.050
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.165	0.144
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.632	0.395
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.168	0.228
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.001	0.001
	2 ¹ A'' ($n \rightarrow \pi^*$)	0.002	0.001
Thymine	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.197	0.179
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.080	0.041
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.250	0.168
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.515	0.356
	3 ¹ A'' ($n \rightarrow \pi^*$)	0.000	0.001
Uracil	2 ¹ A' ($\pi \rightarrow \pi^*$)	0.197	0.178
	3 ¹ A' ($\pi \rightarrow \pi^*$)	0.058	0.034
	4 ¹ A' ($\pi \rightarrow \pi^*$)	0.188	0.163
	5 ¹ A' ($\pi \rightarrow \pi^*$)	0.547	0.260
	3 ¹ A'' ($n \rightarrow \pi^*$)	0.000	0.001

Notes: ^aOnly values above 0.001 are listed.^bResults with the TZVP basis set from [1].^cResults with the aug-cc-pVTZ basis set from this work.

Table 9. Dipole moments (in Debye) of singlet excited states from CC2 calculations.

Molecule	State	CC2	
		TZVP ^a	aug-cc-pVTZ ^b
Cyclopropene	Ground State	0.45	0.44
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.26	1.04
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	1.62	0.73
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.35	0.37
	1 ³ B ₁ ($\sigma \rightarrow \pi^*$)	1.77	1.62
Cyclopentadiene	Ground State	0.46	0.45
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.68	0.30
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.13	3.63
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.24	0.20
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	0.27	0.37
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.05	0.18
Norbornadiene	Ground State	0.06	0.09
	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	0.22	1.08

(continued)

Table 9. (Continued).

Molecule	State	CC2	
		TZVP ^a	aug-cc-pVTZ ^b
Furan	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	0.55	0.36
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.89	1.44
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.07	3.36
	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	0.05	0.24
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	0.18	0.23
	Ground State	0.62	1.87
Pyrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.83	0.77
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	0.01	3.10
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	0.77	1.74
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	0.74	0.65
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.14	1.06
	Ground State	2.02	1.87
Imidazole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	1.47	1.29
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.60	5.87
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.92	4.90
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.63	1.62
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.14	1.09
	Ground State	3.91	3.79
Pyridine	2 ¹ A' ($\pi \rightarrow \pi^*$)	4.71	3.60
	3 ¹ A' ($\pi \rightarrow \pi^*$)	3.72	2.31
	4 ¹ A' ($\pi \rightarrow \pi^*$)	4.14	5.18
	1 ¹ A'' ($n \rightarrow \pi^*$)	0.48	0.99
	2 ¹ A'' ($n \rightarrow \pi^*$)	3.34	3.09
	1 ³ A' ($\pi \rightarrow \pi^*$)	3.00	2.99
	2 ³ A' ($\pi \rightarrow \pi^*$)	4.56	4.51
	3 ³ A' ($\pi \rightarrow \pi^*$)	4.83	4.15
	4 ³ A' ($\pi \rightarrow \pi^*$)	4.88	4.32
	1 ³ A'' ($n \rightarrow \pi^*$)	1.17	1.44
	2 ³ A'' ($n \rightarrow \pi^*$)	3.86	3.67
	Ground State	2.33	2.31
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.68	2.11
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.13	0.15
Pyrimidine	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.10	0.39
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.02	2.01
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.69	2.71
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	1.10	0.40
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	2.15	2.15
	2 ³ A ₁ ($\pi \rightarrow \pi^*$)	2.53	2.49
	3 ³ A ₁ ($\pi \rightarrow \pi^*$)	1.59	1.74
	1 ³ A ₂ ($n \rightarrow \pi^*$)	1.01	0.32
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.96	1.97
	2 ³ B ₂ ($\pi \rightarrow \pi^*$)	3.49	3.25
Pyridazine	3 ³ B ₂ ($\pi \rightarrow \pi^*$)	1.16	1.26
	1 ³ B ₁ ($n \rightarrow \pi^*$)	1.10	0.55
	Ground State	2.43	2.40
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.24	0.81
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	2.11	1.52
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	1.07	1.34
Pyridazine	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	2.26	2.19
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	1.38	2.06
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	0.39	0.64
	Ground State	4.36	4.33
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	3.64	3.61
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	4.07	2.15

(continued)

Table 9. (Continued).

Molecule	State	CC2	
		TZVP ^a	aug-cc-pVTZ ^b
	$1^1A_2 (n \rightarrow \pi^*)$	1.21	1.84
	$2^1A_2 (n \rightarrow \pi^*)$	1.50	2.08
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.30	3.98
	$2^1B_2 (\pi \rightarrow \pi^*)$	3.98	4.01
	$1^1B_1 (n \rightarrow \pi^*)$	1.10	1.72
	$2^1B_1 (n \rightarrow \pi^*)$	1.66	2.25
Formaldehyde	Ground State	2.32	2.38
	$1^1A_2 (n \rightarrow \pi^*)$	1.25	1.38
	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.37	0.62
	$1^3A_2 (n \rightarrow \pi^*)$	1.09	1.21
	$1^3A_1 (\pi \rightarrow \pi^*)$	0.82	0.86
Acetone	Ground State	2.86	2.97
	$2^1A_1 (\pi \rightarrow \pi^*)$	2.94	2.42
	$1^1A_2 (n \rightarrow \pi^*)$	1.45	1.84
	$1^1B_1 (\sigma \rightarrow \pi^*)$	1.53	1.78
	$1^3A_1 (\pi \rightarrow \pi^*)$	1.17	1.33
	$1^3A_2 (n \rightarrow \pi^*)$	1.24	1.59
Formamide	Ground State	3.86	3.84
	$2^1A' (\pi \rightarrow \pi^*)$	2.00	2.69
	$3^1A' (\pi \rightarrow \pi^*)$	1.80	2.93
	$1^1A'' (n \rightarrow \pi^*)$	1.98	2.20
	$1^3A' (\pi \rightarrow \pi^*)$	4.21	4.09
	$1^3A'' (n \rightarrow \pi^*)$	1.80	1.99
Acetamide	Ground State	3.86	3.81
	$2^1A' (\pi \rightarrow \pi^*)$	4.76	2.40
	$3^1A' (\pi \rightarrow \pi^*)$	4.12	2.58
	$1^1A'' (n \rightarrow \pi^*)$	1.69	1.77
	$1^3A' (\pi \rightarrow \pi^*)$	3.82	3.54
	$1^3A'' (n \rightarrow \pi^*)$	1.51	1.58
Propanamide	Ground State	3.65	3.61
	$2^1A' (\pi \rightarrow \pi^*)$	4.71	2.16
	$3^1A' (\pi \rightarrow \pi^*)$	3.30	0.64
	$1^1A'' (n \rightarrow \pi^*)$	1.56	1.59
	$1^3A' (\pi \rightarrow \pi^*)$	3.82	3.46
	$1^3A'' (n \rightarrow \pi^*)$	1.40	1.44
Cytosine	Ground State	6.44	6.39
	$2^1A' (\pi \rightarrow \pi^*)$	3.74	3.76
	$3^1A' (\pi \rightarrow \pi^*)$	6.69	6.42
	$4^1A' (\pi \rightarrow \pi^*)$	5.69	3.31
	$5^1A' (\pi \rightarrow \pi^*)$	8.06	4.55
	$1^1A'' (n \rightarrow \pi^*)$	1.76	0.74
Thymine	$2^1A'' (n \rightarrow \pi^*)$	1.03	1.41
	Ground State	4.24	4.26
	$2^1A' (\pi \rightarrow \pi^*)$	5.50	5.20
	$3^1A' (\pi \rightarrow \pi^*)$	2.68	1.96
	$4^1A' (\pi \rightarrow \pi^*)$	6.88	6.00
	$5^1A' (\pi \rightarrow \pi^*)$	1.40	1.00
Uracil	$1^1A'' (n \rightarrow \pi^*)$	1.87	2.02
	$2^1A'' (n \rightarrow \pi^*)$	4.26	4.12
	$3^1A'' (n \rightarrow \pi^*)$	3.92	4.15
	$4^1A'' (n \rightarrow \pi^*)$	2.63	2.33
	Ground State	4.30	4.32
	$2^1A' (\pi \rightarrow \pi^*)$	5.61	5.36
	$3^1A' (\pi \rightarrow \pi^*)$	3.17	2.74

(continued)

Table 9. (Continued).

Molecule	State	CC2	
		TZVP ^a	aug-cc-pVTZ ^b
	$4^1A' (\pi \rightarrow \pi^*)$	6.44	5.90
	$5^1A' (\pi \rightarrow \pi^*)$	0.97	2.04
	$1^1A'' (n \rightarrow \pi^*)$	3.33	1.60
	$2^1A'' (n \rightarrow \pi^*)$	4.36	3.85
	$3^1A'' (n \rightarrow \pi^*)$	3.97	3.52
	$4^1A'' (n \rightarrow \pi^*)$	2.01	2.33

Notes: ^aResults with the TZVP basis set from [1].^bResults with the aug-cc-pVTZ basis set from this work.

Paper VI

*Benchmarks of electronically excited states: Basis set
effects on CASPT2 results*

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Benchmarks of electronically excited states: Basis set effects on CASPT2 results

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Vertical excitation energies and one-electron properties are computed for the valence excited states of 28 medium-sized organic benchmark molecules using multistate multiconfigurational second-order perturbation theory (MS-CASPT2) and the augmented correlation-consistent aug-cc-pVTZ basis set. They are compared with previously reported MS-CASPT2 results obtained with the smaller TZVP basis. The basis set extension from TZVP to aug-cc-pVTZ causes rather minor and systematic shifts in the vertical excitation energies that are normally slightly reduced (on average by 0.11 eV for the singlets and by 0.09 eV for the triplets), whereas the changes in the calculated oscillator strengths and dipole moments are somewhat more pronounced on a relative scale. These basis set effects at the MS-CASPT2 level are qualitatively and quantitatively similar to those found at the coupled cluster level for the same set of benchmark molecules. The previously proposed theoretical best estimates (TBE-1) for the vertical excitation energies for 104 singlet and 63 triplet excited states of the benchmark molecules are upgraded by replacing TZVP with aug-cc-pVTZ data that yields a new reference set (TBE-2). Statistical evaluations of the performance of density functional theory (DFT) and semiempirical methods lead to the same ranking and very similar quantitative results for TBE-1 and TBE-2, with slightly better performance measures with respect to TBE-2. DFT/MRCI is most accurate among the investigated DFT-based approaches, while the OMx methods with orthogonalization corrections perform best at the semiempirical level. © 2010 American Institute of Physics. [doi:10.1063/1.3499598]

I. INTRODUCTION

Theoretical studies of photophysical and photochemical processes demand an accurate description of electronically excited states. The performance of the available theoretical methods in this area can be assessed by suitable benchmarks. Recently we introduced a standard benchmark set for this purpose¹ that consists of 28 medium-sized molecules and covers the most relevant organic chromophores. Theoretical reference data were generated using multistate complete-active-space second-order perturbation theory (MS-CASPT2) and linear response coupled cluster theory (CC2, CCSD, CC3). Based on these data and high-level *ab initio* results from the literature, theoretical best estimates (TBE) were derived for the vertical excitation energies of 104 singlet and 63 triplet states.¹ This benchmark set has been used in evaluations of other *ab initio* approaches,^{2–5} density functional theory (DFT) methods,^{6–9} and semiempirical methods.¹⁰

The proposed benchmark set¹ targets valence excited states. Therefore, our original *ab initio* calculations employed the TZVP basis,¹¹ which was considered flexible enough to describe these states adequately. This choice allowed us to adopt a standard active space in the MS-CASPT2 calculations (including all π and π^* orbitals as

well as any n and σ orbital involved), and it had the additional advantage that coupled cluster CC3 calculations remained feasible for the majority of the molecules. On the other hand, the absence of diffuse functions in the TZVP basis implies that high-lying valence states with rather diffuse character may not be described properly, especially in the case of partial valence-Rydberg mixing. This was one of the reasons why we assigned TBE values on the basis of our own calculations only for transitions up to 7 eV.¹

It is clearly desirable to improve the reference data in our benchmark set by using a basis set larger than TZVP. The augmented correlation consistent triple-zeta basis (aug-cc-pVTZ) (Refs. 12 and 13) would seem to be a natural choice since it has often been used in excited-state work on medium-sized molecules. In our original benchmark study,¹ we analyzed the basis set convergence of the vertical excitation energy for the high-lying ${}^1B_{1u}$ singlet state of ethene at the CC and CASPT2 levels using twelve different correlation consistent basis sets,^{12,13} and we found that the essentially converged aug-cc-pV5Z and d-aug-cc-pVQZ results were well reproduced when using the aug-cc-pVTZ basis (within 0.1 eV) whereas the TZVP values were too high (by more than 0.4 eV). These and many other results indicate that the aug-cc-pVTZ basis set is flexible enough to describe rather diffuse valence states. Of course, a proper representation of Rydberg states will require further augmentation, typically

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by sets of molecule-centered diffuse basis functions (for early examples, see Refs. 14–22). In the present work, we use the aug-cc-pVTZ basis exclusively since we focus on valence excited states and not on Rydberg states (which are not included in our benchmark set).

In a separate study, we have reported coupled cluster results with the aug-cc-pVTZ basis for the valence excited states of all 28 benchmark molecules.²³ The basis set effects upon going from TZVP to aug-cc-pVTZ were quite uniform in the CC2, CCSDR(3), and CC3 calculations. For each of the three coupled cluster variants, a correlation coefficient greater than 0.994 was found between the vertical excitation energies computed with the two basis sets, and the aug-cc-pVTZ values were generally somewhat lower than the TZVP values (typically by 0.2 eV for singlets).²³ We have now carried out a corresponding systematic MS-CASPT2 study using the aug-cc-pVTZ basis throughout, with the objective to explore the basis set effects at the MS-CASPT2 level and to improve the theoretical best estimates for vertical excitation energies.

This article is organized as follows: Computational details are outlined in Sec. II. The MS-CASPT2/aug-cc-pVTZ results are presented in the following section and compared with the results from MS-CASPT2/TZVP and CC/aug-cc-pVTZ calculations.^{1,23} Some of the theoretical best estimates are also upgraded in this section. Statistical evaluations of several approximate methods are then provided with respect to the updated theoretical best estimates. Section IV offers a brief summary.

II. COMPUTATIONAL METHODS

All calculations were performed using the MP2/6-31G* optimized ground-state equilibrium geometries¹ and the aug-cc-pVTZ basis set.^{12,13} The active space for the present CASSCF (complete-active-space self-consistent-field) calculations^{24,25} generally differs substantially from the standard active space that was adopted previously (consisting of all π and π^* orbitals as well as any relevant n and σ orbitals).¹ This standard active space is appropriate for the TZVP basis, but not for the larger aug-cc-pVTZ basis, where its use often leads to convergence problems in the CASSCF procedure or to low reference weights. Therefore, the active space was optimized for each individual molecule by adding other orbitals as appropriate. The CASSCF reference functions were then determined using state averaging (SA) with equal weights for all states of a given symmetry. The number of states included in the SA procedure was generally larger in the CASSCF/aug-cc-pVTZ calculations than in the previous CASSCF/TZVP calculations,¹ because many Rydberg states now appear lower in energy than some high-lying valence states that need to be covered. The choice of the active space and of the states included in the SA procedure was guided by the idea to aim at the most compact representation that would still ensure a reasonable and balanced description of all targeted valence excited states. These choices are specified for each individual molecule in the supporting information.²⁶

The CASSCF reference wave function served as starting

point for the subsequent MS-CASPT2 calculations.^{27–29} Since the aug-cc-pVTZ basis is more flexible and more diffuse than the TZVP basis, problems with intruder states appeared more often during the CASPT2 calculations than before.¹ They were identified by checking the weight of the reference function in the perturbation treatment, and the level-shift technique^{30,31} was applied to overcome such problems. If this approach was insufficient, the CASSCF setup was modified by including additional orbitals in the active space. Electronic transition dipole moments were calculated from the perturbatively modified wave functions and combined with the MS-CASPT2 energies to obtain the oscillator strengths.^{32,33}

Excitation energies are determined by the energy difference between a given excited state and the ground state. In the case of singlet excited states of the same symmetry as the ground state, the natural procedure is to refer to the MS-CASPT2 ground-state energy since the states of the same symmetry are treated together on the same footing. In other cases, the alternative is to choose the separately computed single-state SS-CASPT2 ground-state energy as reference.¹ We have checked both options for all 28 benchmark molecules and find a mean absolute deviation of 0.06 eV between the two types of ground-state energies with the aug-cc-pVTZ basis (see Table I of the supporting information²⁶) and rather small differences between these two options in the statistical evaluations (see Table II of the supporting information²⁶). For the sake of consistency, we continue to follow the previously adopted protocol, i.e., using the SS-CASPT2 ground-state energy for excited states of different symmetry.¹

The current CASPT2 calculations were carried out with the MOLCAS program (version 6.4).³⁴

III. RESULTS AND DISCUSSION

Detailed numerical results of the CASPT2/TZVP and CASPT2/aug-cc-pVTZ calculations are documented in the supporting information (Tables III–XXX).²⁶ There is one table for each benchmark molecule that contains, for each state considered, the computed vertical excitation energy, oscillator strength, dipole moment, and expectation value of $\langle z^2 \rangle$ as a measure of its spatial extent with respect to a suitable Cartesian coordinate z . Experimental data from the literature are also given with the corresponding references. The footnotes in these tables specify computational details of the CASPT2 calculations, especially the chosen active space and the number of states included in the SA procedure.

A. Basis set effects

The vertical excitation energies for the singlet and triplet states of our benchmark molecules are collected in Tables I and II, respectively. These tables contain our previous CASPT2/TZVP results,¹ the current CASPT2/aug-cc-pVTZ results, our most accurate coupled cluster results, our previous best theoretical estimates (TBE-1), and the current upgrade (TBE-2).

The coupled cluster results are taken or derived from previous studies^{1,23,35} and can be classified as follows: (a)

TABLE I. Vertical excitation energies ΔE (eV) for singlet states: CASPT2 and coupled cluster (CC) results, with the previous set of theoretical best estimates (TBE-1) and its current upgrade (TBE-2).

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Ethene	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.54	7.84	7.89 ^f	7.80	7.80
E-Butadiene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	6.47	6.38	6.21 ^g	6.18	6.18
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	6.62	6.43	6.63 ^f	6.55	6.55
E-Hexatriene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	5.31	5.18	5.32 ^g	5.10	5.10
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.42	5.33	5.77 ^g	5.09	5.09
E-Octatetraene	2 ¹ A _g ($\pi \rightarrow \pi^*$)	4.64	4.52	4.75 ^h	4.47	4.47
	1 ¹ B _u ($\pi \rightarrow \pi^*$)	4.70	4.35	4.84 ^h	4.66	4.66
Cyclopropene	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	6.76	6.63	6.67 ^f	6.76	6.67
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.06	6.66	6.68 ^f	7.06	6.68
Cyclopentadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.51	5.43	5.49 ^g	5.55	5.55
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.28	6.49 ^g	6.31	6.28
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.52	8.15	8.14 ^g		
Norbornadiene	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	5.34	4.98	5.37 ^h	5.34	5.37
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.11	5.94	6.21 ^h	6.11	6.21
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.32	6.62	7.49 ^h		
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	7.45	7.20	7.22 ^h		
Benzene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.04	4.96	5.03 ^f	5.08	5.08
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.42	6.57	6.42 ^f	6.54	6.54
	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	7.13	7.36	7.14 ^f	7.13	7.13
	1 ¹ E _{2g} ($\pi \rightarrow \pi^*$)	8.18	8.15	8.31 ^f	8.41	8.15
Naphthalene	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	4.24	4.06	4.25 ^g	4.24	4.25
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.77	4.49	4.82 ^g	4.77	4.82
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.87	5.83	5.90 ^g	5.87	5.90
	1 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	5.99	5.71	5.75 ^g	5.99	5.75
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	6.06	6.04	6.11 ^g	6.06	6.11
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	6.33	6.05	6.36 ^g	6.33	6.36
	2 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	6.47	6.31	6.46 ^g	6.47	6.46
	3 ¹ A _g ($\pi \rightarrow \pi^*$)	6.67	6.49	6.86 ^g	6.67	6.49
	3 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	7.74	6.69	8.32 ^h		
	3 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.17	7.92	7.88 ^h		
Furan	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.39	6.19	6.26 ^g	6.32	6.32
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.50	6.35	6.51 ^g	6.57	6.57
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.17	7.93	8.13 ^g	8.13	8.13
Pyrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.23	6.27 ^g	6.37	6.37
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.33	6.22	6.20 ^g	6.57	6.57
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.17	7.95	7.60 ^g	7.91	7.91
Imidazole	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.19	6.40	6.25 ^h	6.19	6.25
	1 ¹ A'' ($n \rightarrow \pi^*$)	6.81	6.69	6.65 ^h	6.81	6.65
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.93	6.82	6.73 ^h	6.93	6.73
	2 ¹ A'' ($n \rightarrow \pi^*$)	7.90	7.80	7.57 ^h		
	4 ¹ A' ($\pi \rightarrow \pi^*$)	8.16	8.96	8.51 ^h		
Pyridine	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.02	5.00	5.12 ^g	4.85	4.85
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	5.17	5.07	4.95 ^g	4.59	4.59
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.51	5.49	5.41 ^g	5.11	5.11
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.39	6.59	6.60 ^g	6.26	6.26
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.27	7.72	7.33 ^g	7.27	7.27
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.46	7.49	7.39 ^g	7.18	7.18
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	8.60	8.06	7.72 ^g		
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.69	8.28	8.33 ^g		
Pyrazine	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	4.12	4.02	4.13 ^g	3.95	4.13
	1 ¹ A _u ($n \rightarrow \pi^*$)	4.70	4.75	4.98 ^g	4.81	4.98
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.85	4.80	4.97 ^g	4.64	4.97
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.68	5.56	5.65 ^g	5.56	5.65
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.41	6.47	6.69 ^g	6.60	6.69
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.89	6.61	6.83 ^g	6.58	6.83
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.66	7.73	7.81 ^g	7.60	7.81
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.79	7.71	7.86 ^g	7.72	7.86
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	8.47	8.33	8.69 ^g		
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	8.61	8.30	8.78 ^g		

TABLE I. (Continued.)

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Pyrimidine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.44	4.34	4.43 ^g	4.55	4.43
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.80	4.74	4.85 ^g	4.91	4.85
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.24	5.17	5.34 ^g	5.44	5.34
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.63	6.81	6.82 ^g	6.95	6.82
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.21	7.26	7.53 ^g		
Pyridazine	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.64	7.74	7.82 ^g		
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	3.78	3.71	3.85 ^g	3.78	3.85
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.31	4.18	4.44 ^g	4.31	4.44
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	5.18	5.06	5.20 ^g	5.18	5.20
	2 ¹ A ₂ ($n \rightarrow \pi^*$)	5.77	5.67	5.66 ^g	5.77	5.66
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.31	6.34	6.68 ^g		
	2 ¹ B ₁ ($n \rightarrow \pi^*$)	6.52	6.13	6.33 ^g		
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.29	7.45	7.33 ^g		
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.62	7.17	7.54 ^g		
	1 ¹ A ₁ ' ($n \rightarrow \pi^*$)	4.60	4.54	4.70 ^g	4.60	4.70
<i>s</i> -Triazine	1 ¹ A ₂ ' ($n \rightarrow \pi^*$)	4.66	4.60	4.71 ^g	4.66	4.71
	1 ¹ E'' ($n \rightarrow \pi^*$)	4.70	4.63	4.75 ^g	4.70	4.75
	1 ¹ A ₂ ' ($\pi \rightarrow \pi^*$)	5.79	5.75	5.71 ^g	5.79	5.71
	2 ¹ A ₁ ' ($\pi \rightarrow \pi^*$)	7.25	7.20	7.18 ^g		
	1 ¹ E' ($\pi \rightarrow \pi^*$)	7.50	7.36	7.84 ^g		
	2 ¹ E'' ($n \rightarrow \pi^*$)	7.71	7.55	7.78 ^g		
	2 ¹ E' ($\pi \rightarrow \pi^*$)	8.99	9.02	9.44 ^g		
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	2.29	2.27	2.46 ^f	2.29	2.46
	1 ¹ A _u ($n \rightarrow \pi^*$)	3.51	3.40	3.78 ^g	3.51	3.78
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	4.73	4.74	4.87 ^f	4.73	4.87
<i>s</i> -Tetrazine	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.93	4.89	5.08 ^f	4.93	5.08
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.20	5.07	5.28 ^f	5.20	5.28
	2 ¹ A _u ($n \rightarrow \pi^*$)	5.50	5.32	5.39 ^g	5.50	5.39
	1 ¹ B _{3g} ($n, n \rightarrow \pi^*, \pi^*$)	5.86	5.76		5.79	5.76
	2 ¹ B _{2g} ($n \rightarrow \pi^*$)	6.06	5.84	6.16 ^f		
	2 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.45	6.33	6.80 ^f		
	3 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.73	6.64	7.12 ^g		
	2 ¹ B _{3u} ($n \rightarrow \pi^*$)	6.77	6.59	6.60 ^f		
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.94	6.84	7.18 ^f		
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.42	7.20	7.59 ^f		
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.14	8.00	8.33 ^g		
	2 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	8.34	8.19	8.51 ^g		
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	3.99	4.01	3.88 ^f	3.88	3.88
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	9.14	9.12	9.05 ^f	9.1	9.04 ⁱ
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	9.32	9.47	9.31 ^f	9.3	9.29 ^j
Formaldehyde	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.44	4.49	4.38 ^f	4.40	4.38
	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	9.27	9.25	9.04 ^g	9.1	9.04
Acetone	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	9.31	9.19	8.90 ^f	9.4	8.90
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	2.76	2.81	2.74 ^g	2.76	2.74
<i>p</i> -Benzoquinone	1 ¹ A _u ($n \rightarrow \pi^*$)	2.77	2.83	2.86 ^g	2.77	2.86
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	4.26	4.37	4.44 ^g	4.26	4.44
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	5.28	5.41	5.47 ^g	5.28	5.47
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	5.64	5.55	5.71 ^g	5.64	5.55
	2 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	6.96	6.99	7.16 ^g	6.96	7.16
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.92	7.87	7.62 ^g		
	1 ¹ A'' ($n \rightarrow \pi^*$)	5.63	5.58	5.55 ^f	5.63	5.55
Formamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	7.39	7.45	7.35 ^f	7.39	7.35
	3 ¹ A' ($\pi \rightarrow \pi^*$)	10.54	10.47			
Acetamide	1 ¹ A'' ($n \rightarrow \pi^*$)	5.69	5.69	5.62 ^g	5.69	5.62
	2 ¹ A' ($\pi \rightarrow \pi^*$)	7.27	7.12	7.14 ^g	7.27	7.14
	3 ¹ A' ($\pi \rightarrow \pi^*$)	10.09	10.03	9.66 ^g		
	1 ¹ A'' ($n \rightarrow \pi^*$)	5.72	5.74	5.65 ^g	5.72	5.65
Propanamide	2 ¹ A' ($\pi \rightarrow \pi^*$)	7.20	7.17	7.09 ^g	7.20	7.09
	3 ¹ A' ($\pi \rightarrow \pi^*$)	9.94	9.85	9.44 ^h		
Cytosine	2 ¹ A' ($\pi \rightarrow \pi^*$)	4.67	4.52	4.69 ^j	4.66	4.66

TABLE I. (Continued.)

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Thymine	1 ¹ A'' ($n \rightarrow \pi^*$)	5.12	5.03	4.91 ^j	4.87	4.87
	2 ¹ A'' ($n \rightarrow \pi^*$)	5.53	5.44	5.33 ^j	5.26	5.26
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.53	5.43	5.56 ^j	5.62	5.62
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.40	6.09	6.29 ^j		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.97	6.68	6.62 ^j		
	1 ¹ A'' ($n \rightarrow \pi^*$)	4.95	4.86	4.83 ^j	4.82	4.82
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.06	4.91	5.19 ^j	5.20	5.20
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.15	6.01	6.26 ^j	6.27	6.27
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.38	6.22	6.16 ^j	6.16	6.16
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.53	6.32	6.50 ^j	6.53	6.53
Uracil	3 ¹ A'' ($n \rightarrow \pi^*$)	6.85	6.59	6.55 ^j		
	4 ¹ A'' ($n \rightarrow \pi^*$)	7.43	7.05	7.00 ^j		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.43	7.33	7.47 ^j		
	1 ¹ A'' ($n \rightarrow \pi^*$)	4.91	4.80	4.81 ^j	4.80	5.00
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.23	5.06	5.33 ^j	5.35	5.25
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.15	6.00	6.24 ^j	6.26	6.26
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.28	6.15	6.09 ^j	6.10	6.10
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.74	6.47	6.66 ^j	6.70	6.70
	3 ¹ A'' ($n \rightarrow \pi^*$)	6.98	6.73	6.55 ^j	6.56	6.56
	4 ¹ A'' ($n \rightarrow \pi^*$)	7.28	6.93	6.95 ^j		
Adenine	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.42	7.37	7.48 ^j		
	1 ¹ A'' ($n \rightarrow \pi^*$)	5.19	5.04	5.13 ^j	5.12	5.12
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.20	5.11	5.20 ^j	5.25	5.25
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.29	5.02	5.20 ^j	5.25	5.25
	2 ¹ A'' ($n \rightarrow \pi^*$)	5.96	5.75	5.74 ^j	5.75	5.75
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.34	6.25			
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.64	6.65			
	6 ¹ A' ($\pi \rightarrow \pi^*$)	6.87	6.96			
	7 ¹ A' ($\pi \rightarrow \pi^*$)	7.56	7.55			

^aSA-CASSCF/MS-CASPT2 results using TZVP basis and MP2/6-31G* ground-state equilibrium geometries. See Ref. 1.^bSA-CASSCF/MS-CASPT2 results using aug-cc-pVTZ basis and MP2/6-31G* ground-state equilibrium geometries.^cBest own coupled cluster results using MP2/6-31G* ground-state equilibrium geometries.^dOriginal theoretical best estimates for vertical excitation energies. See Ref. 1 for details.^eUpdated theoretical best estimates for vertical excitation energies. See text.^fCC3/aug-cc-pVTZ results.^gCC3/TZVP results with basis set correction from CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/TZVP.^hCC3/TZVP results with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP.ⁱCC3/aug-cc-pVQZ results as theoretical best estimates. From Supporting Information of Ref. 1.^jCC2/aug-cc-pVTZ results. Reference 23.

CC3/aug-cc-pVTZ; (b) CC3/TZVP with basis set correction from CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/TZVP; (c) CC3/TZVP with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP; and (d) CC2/aug-cc-pVTZ. Hence, all coupled cluster data refer to the aug-cc-pVTZ basis set, but there are differences in the quality of the coupled cluster treatment. The CC3/aug-cc-pVTZ results (a) are most accurate. The composite results (b) and (c) and the CC2 data (d) reproduce (a) quite well: for the 22 singlet excited states where CC3/aug-cc-pVTZ results are available, the mean absolute deviations are 0.02, 0.08, and 0.12 eV, respectively.²³ For the larger set of 121 singlet excited states with TZVP results, the mean absolute deviation between CC3/TZVP and CC2/TZVP amounts to 0.07 eV.¹ Hence, the coupled cluster results in Table I are of CC3/aug-cc-pVTZ quality for (a) and (b) and close to it for (c) and (d) (normally within 0.1 eV). In the case of triplet excited states, most of the entries in Table II are of type (c), but they are still expected to be close to CC3/aug-cc-pVTZ quality since the basis set corrections are generally quite small for the triplet states.

We now address basis set effects on the vertical excitation energies at the MS-CASPT2 level. The inspection of the first two data columns of Tables I and II shows that the computed energies normally decrease slightly upon enlarging the basis from TZVP to aug-cc-pVTZ. The changes are generally quite moderate, and there is an excellent correlation between the two sets of computed energies, with a correlation coefficient of 0.9899 both for the singlet and triplet states (see Fig. 1). Histograms of the corresponding deviations are depicted in Fig. 2. The shifts due to basis set extension remain within 0.1 (0.2) eV for 43% (73%) of the singlet excited states, and for 53% (87%) of the triplet excited states. The statistical evaluation in Table III yields a mean absolute deviation between the two sets of calculated energies of 0.16 eV for the singlets and 0.12 eV for the triplets. The vertical excitation energies from MS-CASPT2/aug-cc-pVTZ are lower than those from MS-CASPT2/TZVP on average, by 0.11 eV for the singlets and 0.09 eV for the triplets. The basis set effects on the coupled cluster results show the same over-

TABLE II. Vertical excitation energies ΔE (eV) for triplet states: CASPT2 and coupled cluster (CC) results, with the previous set of theoretical best estimates (TBE-1) and its current upgrade (TBE-2).

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Ethene	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.48	4.48	4.50 ^f	4.50	4.50
E-Butadiene	1 ³ B _u ($\pi \rightarrow \pi^*$)	3.34	3.30	3.34 ^g	3.20	3.20
	1 ³ A _g ($\pi \rightarrow \pi^*$)	5.16	5.08	5.15 ^f	5.08	5.08
E-Hexatriene	1 ³ B _u ($\pi \rightarrow \pi^*$)	2.71	2.67	2.71 ^g	2.40	2.40
	1 ³ A _g ($\pi \rightarrow \pi^*$)	4.31	4.22	4.33 ^g	4.15	4.15
E-Octatetraene	1 ³ B _u ($\pi \rightarrow \pi^*$)	2.33	2.27	2.32 ^g	2.20	2.20
	1 ³ A _g ($\pi \rightarrow \pi^*$)	3.70	3.61	3.69 ^g	3.55	3.55
Cyclopropene	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.35	4.26	4.28 ^f	4.34	4.28
	1 ³ B ₁ ($\sigma \rightarrow \pi^*$)	6.51	6.36	6.40 ^f	6.62	6.40
Cyclopentadiene	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	3.28	3.21	3.26 ^g	3.25	3.26
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.11	5.02	5.09 ^g	5.09	5.09
Norbornadiene	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	3.75	3.65	3.68 ^g	3.72	3.68
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.22	4.16	4.16 ^g	4.16	4.16
Benzene	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.17	4.13	4.12 ^f	4.15	4.15
	1 ³ E _{1u} ($\pi \rightarrow \pi^*$)	4.90	4.76	4.81 ^f	4.86	4.86
	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	5.76	5.72	5.78 ^f	5.88	5.88
	1 ³ E _{2g} ($\pi \rightarrow \pi^*$)	7.38	7.32	7.45 ^f	7.51	7.51
Naphthalene	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	3.16	3.04	3.09 ^g	3.11	3.09
	1 ³ B _{3u} ($\pi \rightarrow \pi^*$)	4.25	4.03	4.09 ^g	4.18	4.09
	1 ³ B _{1g} ($\pi \rightarrow \pi^*$)	4.51	4.33	4.42 ^g	4.47	4.42
	2 ³ B _{2u} ($\pi \rightarrow \pi^*$)	4.68	4.54	4.56 ^g	4.64	4.56
	2 ³ B _{3u} ($\pi \rightarrow \pi^*$)	4.97	4.72	4.92 ^g	5.11	4.92
	1 ³ A _g ($\pi \rightarrow \pi^*$)	5.53	5.35	5.42 ^g	5.52	5.42
	2 ³ B _{1g} ($\pi \rightarrow \pi^*$)	6.21	6.12	6.12 ^g	6.48	6.12
	2 ³ A _g ($\pi \rightarrow \pi^*$)	6.38	6.12	6.17 ^g	6.47	6.17
	3 ³ A _g ($\pi \rightarrow \pi^*$)	6.59	6.55	6.65 ^g	6.79	6.65
	3 ³ B _{1g} ($\pi \rightarrow \pi^*$)	6.64	6.49	6.67 ^g	6.76	6.67
Furan	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.18	4.06	4.11 ^g	4.17	4.11
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.49	5.34	5.43 ^g	5.48	5.43
Pyrrole	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.51	4.39	4.44 ^g	4.48	4.44
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.52	5.35	5.42 ^g	5.51	5.42
Imidazole	1 ³ A' ($\pi \rightarrow \pi^*$)	4.65	4.57	4.65 ^g	4.69	4.65
	2 ³ A' ($\pi \rightarrow \pi^*$)	5.74	5.56	5.64 ^g	5.79	5.64
	1 ³ A'' ($n \rightarrow \pi^*$)	6.36	6.29	6.25 ^g	6.37	6.25
	3 ³ A' ($\pi \rightarrow \pi^*$)	6.44	6.47	6.38 ^g	6.55	6.38
	4 ³ A' ($\pi \rightarrow \pi^*$)	7.44		7.25 ^g		
	2 ³ A'' ($n \rightarrow \pi^*$)	7.51	7.40	7.29 ^g		
Pyridine	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	4.27	4.23	4.28 ^g	4.06	4.06
	1 ³ B ₁ ($n \rightarrow \pi^*$)	4.57	4.54	4.42 ^g	4.25	4.25
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.71	4.66	4.72 ^g	4.64	4.64
	2 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.03	4.92	4.96 ^g	4.91	4.91
	1 ³ A ₂ ($n \rightarrow \pi^*$)	5.52	5.47	5.35 ^g	5.28	5.28
	2 ³ B ₂ ($\pi \rightarrow \pi^*$)	6.03	6.09	6.22 ^g	6.08	6.08
	3 ³ A ₁ ($\pi \rightarrow \pi^*$)	7.56	6.11	7.59 ^g		
	3 ³ B ₂ ($\pi \rightarrow \pi^*$)	7.87	7.61	7.29 ^g		
s-Tetrazine	1 ³ B _{3u} ($n \rightarrow \pi^*$)	1.61	1.63	1.87 ^f	1.89	1.87
	1 ³ A _u ($n \rightarrow \pi^*$)	3.28	3.23	3.49 ^f	3.52	3.49
	1 ³ B _{1g} ($n \rightarrow \pi^*$)	4.14	4.04	4.18 ^f	4.21	4.18
	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.37	4.36	4.36 ^f	4.33	4.36
	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	4.39	4.25	4.39 ^f	4.54	4.39
	1 ³ B _{2g} ($n \rightarrow \pi^*$)	4.94	4.82	4.89 ^f	4.93	4.89
	2 ³ A _u ($n \rightarrow \pi^*$)	5.04	4.91	4.96 ^f	5.03	4.96
	2 ³ B _{1u} ($\pi \rightarrow \pi^*$)	5.40	5.26	5.32 ^f	5.38	5.32
	2 ³ B _{2g} ($n \rightarrow \pi^*$)	5.97	5.78	5.97 ^f		
	2 ³ B _{1g} ($n \rightarrow \pi^*$)	6.37	6.02	6.54 ^f		
	2 ³ B _{3u} ($n \rightarrow \pi^*$)	6.54	6.39	6.45 ^f		
	2 ³ B _{2u} ($\pi \rightarrow \pi^*$)	7.08	7.01	7.21 ^f		
Formaldehyde	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	3.58	3.62	3.49 ^f	3.50	3.50 ^h
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.84	5.85	5.86 ^f	5.87	5.87 ^h

TABLE II. (Continued.)

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Acetone	1 ³ A ₂ ($n \rightarrow \pi^*$)	4.10	4.17	4.05 ^f	4.05	4.05
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	6.04	6.09	6.07 ^f	6.03	6.07
<i>p</i> -Benzoquinone	1 ³ B _{1g} ($n \rightarrow \pi^*$)	2.62	2.63	2.50 ^g	2.51	2.50
	1 ³ A _u ($n \rightarrow \pi^*$)	2.66	2.66	2.61 ^g	2.62	2.61
	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	2.99	3.00	3.02 ^g	2.96	3.02
	1 ³ B _{3g} ($\pi \rightarrow \pi^*$)	3.32	3.30	3.37 ^g	3.41	3.37
	1 ³ A'' ($n \rightarrow \pi^*$)	5.40	5.32	5.28 ^f	5.36	5.28
Formamide	1 ³ A' ($\pi \rightarrow \pi^*$)	5.58	5.68	5.69 ^f	5.74	5.69
	1 ³ A'' ($n \rightarrow \pi^*$)	5.41	5.40	5.35 ^g	5.42	5.35
Acetamide	1 ³ A' ($\pi \rightarrow \pi^*$)	5.63	5.86	5.71 ^g	5.88	5.71
	1 ³ A'' ($n \rightarrow \pi^*$)	5.45	5.56	5.38 ^g	5.45	5.38
Propanamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.80	6.03	6.08 ^g	5.90	6.08
	1 ³ A' ($\pi \rightarrow \pi^*$)					

^aSA-CASSCF/MS-CASPT2 results using TZVP basis and MP2/6-31G* ground-state equilibrium geometries. See Ref. 1.^bSA-CASSCF/MS-CASPT2 results using aug-cc-pVTZ basis and MP2/6-31G* ground-state equilibrium geometries.^cBest own coupled cluster results using MP2/6-31G* ground-state equilibrium geometries.^dOriginal theoretical best estimates for vertical excitation energies. See Ref. 1 for details.^eUpdated theoretical best estimates for vertical excitation energies. See text.^fCC3/aug-cc-pVTZ results.^gCC3/TZVP results with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP. See Ref. 23.^hCC3/aug-cc-pVQZ results as theoretical best estimates. From Supporting Information of Ref. 1.

all trends and are of comparable magnitude (somewhat more pronounced in the case of the singlets, see Table III).²³

There are a few cases where basis set enlargement from TZVP to aug-cc-pVTZ leads to drastic shifts in the MS-CASPT2 excitation energies. Changes of more than 0.4 eV occur for nine singlet states. One of these corresponds to a double excitation in *p*-benzoquinone, while the other eight of these states lie above 7 eV; the appearance of large basis set effects does not seem surprising for such high-lying valence states that are rather diffuse. In the triplet manifold, there is only one high-lying state with a huge shift (pyridine, 3 ³A₁). It should be noted that these problematic cases are not included among the states for which we derive theoretical best estimates, except for the 1 ¹B_{1u} state in ethene where reliable reference data are available from other calculations.¹

The theoretical results for the individual benchmark molecules and their relation to the available experimental data have been discussed in detail in our previous work.¹ To avoid repetition, we only make very few remarks on some individual excited states here, in order to point out specific features in the MS-CASPT2/aug-cc-pVTZ results. In norbornadiene, the first two excited singlet states (1 ¹A₂ and 1 ¹B₂) appear to be too low in energy compared with all previously published CASPT2 and coupled cluster results, and the experimental value for the first transition seems to be

underestimated.¹ A number of singlet excited states become significantly more diffuse when the basis is enlarged from TZVP to aug-cc-pVTZ, including 1 ¹B_u in butadiene and hexatriene, 3 ¹A₁ in cyclopentadiene, 1 ¹E_{1u} in benzene, 3 ¹A₁ in furan, 1 ¹B₂ and 3 ¹A₁ in pyrrole, 2 ¹B₂ in pyridine and pyridazine, and 2 ¹A' as well as 3 ¹A' in formamide and acetamide. Two valence excited states (4 ³A' in imidazole and 6 ¹A' in cytosine) could not be safely identified in the MS-CASPT2/aug-cc-pVTZ calculations because of assignment problems (valence-Rydberg mixing).

Basis set effects on oscillator strengths and dipole moments are presented in Fig. 3 and Table IV. The correlations between the results from MS-CASPT2/TZVP and MS-CASPT2/aug-cc-pVTZ still seem reasonable, with correlation coefficients of 0.9469 for the oscillator strengths and 0.8871 for the dipole moments, which are of the same order as the corresponding CC2 values of 0.9659 and 0.8325.²³ The relatively low values for the dipole moment reflect changes in the electronic character especially of high-lying (diffuse) excited states upon basis set extension. For example, the dipole moment of the 3 ¹A₁ state of cyclopentadiene increases from 0.46 to 4.43 D with MS-CASPT2, and from 1.13 to 3.63 D with CC2; by contrast, the corresponding changes are 0.01 D for the ground state and less than 0.15 D for the first excited singlet state of cyclopentadiene.

TABLE III. Deviations in the vertical excitation energies (eV): aug-cc-pVTZ vs TZVP results.

	CASPT2 singlets	CASPT2 triplets	CC2 ^a singlets	CC2 ^a triplets	CC3 ^a singlets
Count ^b	151	70	143	71	22
Mean	-0.11	-0.09	-0.22	-0.08	-0.18
Abs. mean	0.16	0.12	0.23	0.10	0.18
Std. dev.	0.22	0.21	0.29	0.14	0.25
Maximum (+)	0.80	0.23	0.20	0.06	...
Maximum (-)	1.05	1.45	1.34	0.54	0.75

^aResults from Ref. 23.^bTotal number of considered states.

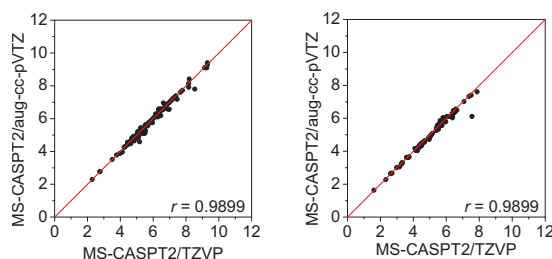


FIG. 1. Correlation plots for the vertical excitation energies (eV) at the CASPT2 level: aug-cc-pVTZ vs TZVP results for singlets (left) and triplets (right).

According to the statistical evaluation (Table IV) basis set extension from TZVP to aug-cc-pVTZ leads to similar changes in MS-CASPT2 and CC2: the oscillator strengths are reduced by similar amounts on average (by 0.039 and 0.032, respectively), and the mean absolute deviations are of comparable magnitude both for the oscillator strengths (0.063 versus 0.047) and the dipole moments (0.52 versus 0.57 D).

B. Theoretical best estimates

In our first benchmark study, we had selected best estimates for the vertical excitation energies of 104 singlet excited states and 63 triplet excited states in our set of 28 benchmark molecules.¹ They were adopted from published highly correlated *ab initio* studies with large basis sets, for example, using multireference configuration interaction (MRCI), multireference perturbation theory (MRMP), or coupled cluster methods. In the absence of such literature data, these estimates were derived from our own calculations using the following guidelines: CC3/TZVP values were taken for the triplet states (all with single excitation weights of more than 93%). CASPT2/TZVP values were favored for the singlet excited states because there is normally at least one singlet state in each benchmark molecule with a CC3/TZVP single excitation weight of less than 90%. Given the limitations of the TZVP basis, CC3/TZVP or CASPT2/TZVP energies were usually not accepted as best estimates if they exceeded 7 eV or if there was reason to assume that diffuse basis functions are essential for a given state.

Following these guidelines, the previously chosen theoretical best estimates (TBE-1) for the valence excited singlet states were taken from published MRCI (9), MRMP (4), and coupled cluster (45) calculations with large basis sets as well as from own CASPT2/TZVP (43) and CC3/TZVP (3) values.

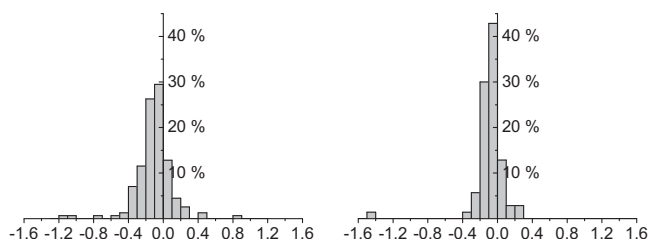


FIG. 2. Histograms (%) of the deviations between CASPT2/aug-cc-pVTZ and CASPT2/TZVP vertical excitation energies of singlet (left) and triplet (right) excited states.

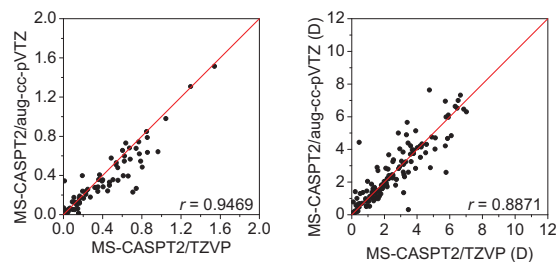


FIG. 3. Correlation plots for the oscillator strengths (left) and dipole moments (right, in D) of singlet excited states: aug-cc-pVTZ vs TZVP results.

In the case of the triplets, the TBE-1 values came from MRCI (9), MRMP (4), and coupled cluster (6) literature data as well as from own CC3/TZVP (44) calculations.

An obvious question is whether these theoretical best estimates should be upgraded in view of our new results with the larger aug-cc-pVTZ basis, in order to derive an improved set of reference data (called TBE-2). We have checked the previously adopted¹ *ab initio* values from the literature and found that they can generally be retained. In several cases, the present results with the aug-cc-pVTZ basis are of similar quality and numerically close to the literature values, but in the absence of significant improvements, it seems better to keep the TBE-1 values of these states, for the sake of consistency.

On the other hand, the TBE-1 values taken from our previous CASPT2/TZVP and CC3/TZVP calculations should be replaced by our new results with the aug-cc-pVTZ basis. We have adopted the general guideline to use the coupled cluster results (CC/aug-cc-pVTZ) from Tables I and II as TBE-2 values, except for states with CC3/TZVP single excitation weights¹ of less than 80%, where we use the MS-CASPT2/aug-cc-pVTZ results. In the case of the triplet states, this convention is consistent with our previous benchmarking (see above).¹ In the case of the singlet states, we have now shifted from MS-CASPT2 to coupled cluster results in the selection of the TBE-2 values. This is motivated by two observations. First, the MS-CASPT2 calculations with the aug-cc-pVTZ basis are less standardized than those with the TZVP basis due to the need to choose individually optimized active spaces and state averaging procedures, and second, it seems difficult to avoid occasional outliers in the MS-CASPT2/aug-cc-pVTZ results when using such molecule-specific procedures. The CC/aug-cc-pVTZ results appear to be more robust in general.

We have nevertheless also checked the alternative option of adopting the MS-CASPT2/aug-cc-pVTZ results as theoretical best estimates (when replacing TZVP-based data). The mean absolute deviation between the chosen CC/aug-cc-pVTZ and the MS-CASPT2/aug-cc-pVTZ values is 0.08 eV for the 44 relevant triplet states, and 0.15 eV for the 43 relevant singlet states. We have confirmed that this alternative choice would lead only to minor changes in the quantitative statistical evaluations and to no changes in the corresponding qualitative conclusions (see below). We will therefore not discuss this alternative any more.

In the following, we comment on some of the individual TBE-2 choices. As explained above, CC/aug-cc-pVTZ val-

TABLE IV. Deviations in the oscillator strengths and dipole moments (D) of singlet excited states: aug-cc-pVTZ vs TZVP results.

	CASPT2		CC2 ^a	
	Osc. strength	Dipole moment	Osc. strength	Dipole moment
Count ^b	106	138	95	127
Mean	−0.039	−0.01	−0.032	−0.14
Abs. mean	0.063	0.52	0.047	0.57
Std. dev.	0.115	0.85	0.088	0.97
Maximum (+)	0.334	3.97	0.269	3.29
Maximum (−)	0.479	3.19	0.287	3.51

^aResults from Ref. 23.^bTotal number of considered states.

ues were favored among our own results unless the CC3/TZVP single excitation weight was below 80%. This was the case for the 2^1A_1 state of cyclopentadiene, the 1^1E_{1g} state of benzene, the 3^1A_g state of naphthalene, and the 1^1B_{3u} state of *p*-benzoquinone, where the TBE-2 values were taken from MS-CASPT2 calculations. Likewise, the MS-CASPT2/aug-cc-pVTZ result was adopted for the doubly excited 1^1B_{3g} state of *s*-tetrazine that is not well described at the CC level. The TBE-1 and TBE-2 values are normally quite close to each other (see above), but there are exceptions with deviations of more than 0.3 eV, i.e., 1^1B_2 in cyclopropene, 1^1B_{2u} in pyrazine, 2^1A_1 in acetone, and 2^3B_{1g} in naphthalene. In two of these cases, the revision is supported by the close agreement between the MS-CASPT2/aug-cc-pVTZ and CC/aug-cc-pVTZ results (cyclopropene, naphthalene), while in acetone the directly computed CC3/aug-cc-pVTZ value for the 2^1A_1 state is now preferred over the indirectly deduced TBE-1 value.¹ In a similar vein, we adopt the directly computed CC3/aug-cc-pVQZ energies¹ as TBE-2 values for the high-lying 1^1B_1 and 2^1A_1 states in formaldehyde.

For pyrazine, literature data from EOM-CCSD($\tilde{T}$) calculations using a DZ2P basis with one set of diffuse functions were selected for TBE-1.¹ It has been pointed out³⁶ that the resulting TBE-1 value for the 1^1B_{2u} state (4.64 eV) cannot be reliable since it is lower than the experimental vertical excitation energy (4.81 eV), and even below the adiabatic excitation energy (4.69 eV). We have now adopted the CC/aug-cc-pVTZ energies for all states of pyrazine (1^1B_{2u} at 4.97 eV).

In the case of *s*-tetrazine, it has been argued that the CASPT2 excitation energies tend to be too low in general.³⁷ The TBE-2 values taken from CC/aug-cc-pVTZ calculations are indeed mostly higher than both the corresponding MS-CASPT2/aug-cc-pVTZ data and the previous TBE-1 values from MS-CASPT2/TZVP calculations.

For uracil, completely renormalized EOM-CCSD(T)/aug-cc-pVTZ energies are available for the first two excited singlet states (5.00 and 5.25 eV) (Ref. 38) that are adopted for TBE-2. They are reasonably close to the published CC2/aug-cc-pVQZ values (4.80 and 5.35 eV) (Ref. 35) and to our present CC2/aug-cc-pVTZ results (4.81 and 5.33 eV). For the remaining singlet excited states in uracil and the other nucleobases, the TBE-2 values are again (as in TBE-1) taken from the published CC2/aug-cc-pVXZ energies (X=T for

cytosine, thymine, and adenine; X=Q for uracil).³⁵ Our own CC2/aug-cc-pVTZ energies are of course very close to these values (being computed at slightly different optimized ground state geometries, MP2 versus CC2).

In summary, the TBE-2 set for the valence excited singlet states is comprised of published MRCI (9), MRMP (4) and coupled cluster (29) calculations with large basis sets as well as of own MS-CASPT2 (5) and coupled cluster (57) calculations, mostly with the aug-cc-pVTZ basis. In the case of the triplets, the TBE-2 values are taken from MRCI (9), MRMP (4), and coupled cluster (4) literature data as well from own coupled cluster (46) calculations that aim at CC3/aug-cc-pVTZ accuracy.

C. Statistical evaluations

The TBE-1 values have previously been used in statistical evaluations of the performance of DFT-based and semiempirical methods for electronically excited states.^{6,23} These evaluations covered time-dependent density functional theory (TD-DFT) with three standard functionals (BP86, B3LYP, and BHLYP), a parametrized DFT-based multireference configuration interaction method (DFT/MRCI), standard semiempirical methods (MNDO, AM1, PM3, INDO/S), and semiempirical methods with orthogonalization corrections (OM1, OM2, and OM3). An obvious question is to what extent the statistical performance measures change when using the upgraded TBE-2 values as reference data. The results of such an analysis are given in Table V for the singlet excited states and in Table VI for the triplet excited states, while the corresponding correlation plots are shown in Figs. 4 and 5, respectively.

It is evident from these results that there is very little change in the statistical performance data by the upgrade from TBE-1 to TBE-2. Focusing on the mean absolute deviations (MAD) for the best DFT-based and semiempirical methods, there are mostly slight improvements when going to TBE-2. In the case of the singlets, the MAD values drop from 0.22 to 0.20 eV for DFT/MRCI and from 0.45–0.50 to 0.41–0.47 eV for the OMx methods, while there is no change for TD-B3LYP (0.27 eV). In the case of the triplets, the corresponding lowerings are from 0.45 to 0.40 eV for TD-B3LYP, from 0.25 to 0.20 eV for DFT/MRCI, and from 0.45–0.49 to 0.44–0.47 eV for the OMx methods. The correlation plots for the TBE-2 reference data look very similar

TABLE V. Deviations of vertical excitation energies (eV) for singlet excited states from DFT and semiempirical methods with respect to theoretical best estimates.

	TD-BP86	TD-B3LYP	TD-BHLYP	DFT/MRCI	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S
TBE-1 reference ^a											
Count ^b	104	104	104	104	104	104	104	104	104	104	103
Mean	−0.44	−0.07	0.43	−0.13	−1.30	−1.12	−1.40	−0.34	−0.36	−0.22	−0.23
Abs. mean	0.52	0.27	0.50	0.22	1.35	1.19	1.41	0.45	0.50	0.45	0.51
Std. dev.	0.62	0.33	0.62	0.29	1.55	1.34	1.55	0.55	0.59	0.54	0.70
Max. (+) dev.	0.65	1.02	1.73	0.75	0.69	0.85	0.19	0.76	1.42	1.76	2.79
Max. (−) dev.	1.37	0.75	0.56	0.90	3.95	3.30	3.21	1.34	1.39	1.19	1.45
Correl. coef.	0.9566	0.9716	0.9444	0.9823	0.7850	0.8404	0.8678	0.9456	0.9342	0.9319	0.9145
TBE-2 reference											
Count ^b	104	104	104	104	104	104	104	104	104	104	103
Mean	−0.45	−0.08	0.41	−0.13	−1.31	−1.12	−1.41	−0.34	−0.35	−0.22	−0.23
Abs. mean	0.53	0.27	0.48	0.20	1.34	1.17	1.41	0.43	0.47	0.41	0.52
Std. dev.	0.63	0.33	0.60	0.26	1.53	1.32	1.54	0.52	0.55	0.49	0.70
Max. (+) dev.	0.64	0.78	1.57	0.79	0.78	0.71	0.10	0.73	1.28	1.62	2.78
Max. (−) dev.	1.37	0.71	0.40	0.64	3.69	3.04	2.95	1.19	1.33	1.09	1.41
Correl. coef.	0.9583	0.9740	0.9476	0.9862	0.7942	0.8503	0.8748	0.9525	0.9431	0.9420	0.9157

^aStatistical evaluations for DFT-based and semiempirical methods taken from Refs. 6 and 10, respectively.^bTotal number of states considered.

to those published previously for TBE-1.^{6,23} This is as expected, of course, since the changes in the reference data between TBE-1 and TBE-2 are rather minor overall (see Fig. 6 and Table VII).

IV. CONCLUSIONS

In this article, we have studied basis set effects in MS-CASPT2 calculations of valence excited states in a recently defined benchmark set. Vertical excitation energies and one-electron properties were computed for all 28 benchmark molecules covering 151 singlet and 70 triplet excited states. The previous results with the TZVP basis were compared against the current results with the larger aug-cc-pVTZ basis

that is more flexible and thus more suitable for also properly describing rather diffuse valence states. This basis set extension leads to a slight but systematic lowering of the vertical excitation energies on average by 0.11 eV for the singlets and 0.09 eV for the triplets, in each case with a correlation coefficient of 0.9899. For one-electron properties such as oscillator strengths and dipole moments, the basis set effects are less systematic, as indicated by lower correlation coefficients between the aug-cc-pVTZ and TZVP results (0.9469 and 0.8871, respectively). Judging from the changes between the aug-cc-pVTZ and TZVP results on a relative scale, basis set convergence seems to be more difficult to achieve for these one-electron properties than for the excitation energies.

TABLE VI. Deviations of vertical excitation energies (eV) for triplet excited states from DFT and semiempirical methods with respect to theoretical best estimates.

	TD-BP86	TD-B3LYP	TD-BHLYP	DFT/MRCI	MNDO	AM1	PM3	OM1	OM2	OM3	INDO/S
TBE-1 reference ^a											
Count ^b	63	63	63	63	63	63	63	63	63	63	63
Mean	−0.53	−0.45	−0.55	−0.24	−1.50	−1.27	−1.41	−0.45	−0.38	−0.26	−0.31
Abs. Mean	0.53	0.45	0.60	0.25	1.55	1.30	1.42	0.49	0.47	0.45	0.65
Std. Dev.	0.61	0.49	0.76	0.28	1.72	1.44	1.55	0.61	0.58	0.54	0.86
Max. (+) dev.	...	...	0.58	0.19	0.55	0.47	0.20	0.41	0.64	1.08	2.49
Max. (−) dev.	1.48	0.93	1.82	0.49	3.66	3.06	2.98	1.31	1.21	1.17	2.01
Correl. coef.	0.9697	0.9880	0.9394	0.9942	0.7639	0.8346	0.8801	0.9505	0.9425	0.9246	0.8442
TBE-2 reference											
Count ^b	63	63	63	63	63	63	63	63	63	63	63
Mean	−0.48	−0.40	−0.50	−0.19	−1.47	−1.22	−1.37	−0.40	−0.33	−0.22	−0.26
Abs. Mean	0.48	0.40	0.57	0.20	1.50	1.26	1.38	0.47	0.46	0.44	0.64
Std. Dev.	0.55	0.44	0.74	0.23	1.67	1.40	1.50	0.57	0.55	0.52	0.84
Max. (+) dev.	...	...	0.59	0.19	0.56	0.49	0.21	0.42	0.67	1.23	2.45
Max. (−) dev.	1.12	0.83	1.85	0.57	3.66	3.06	2.98	1.31	1.21	1.17	1.97
Correl. coef.	0.9738	0.9888	0.9341	0.9945	0.7563	0.8283	0.8709	0.9438	0.9365	0.9193	0.8440

^aStatistical evaluations for DFT-based and semiempirical methods taken from Refs. 6 and 10, respectively.^bTotal number of states considered.

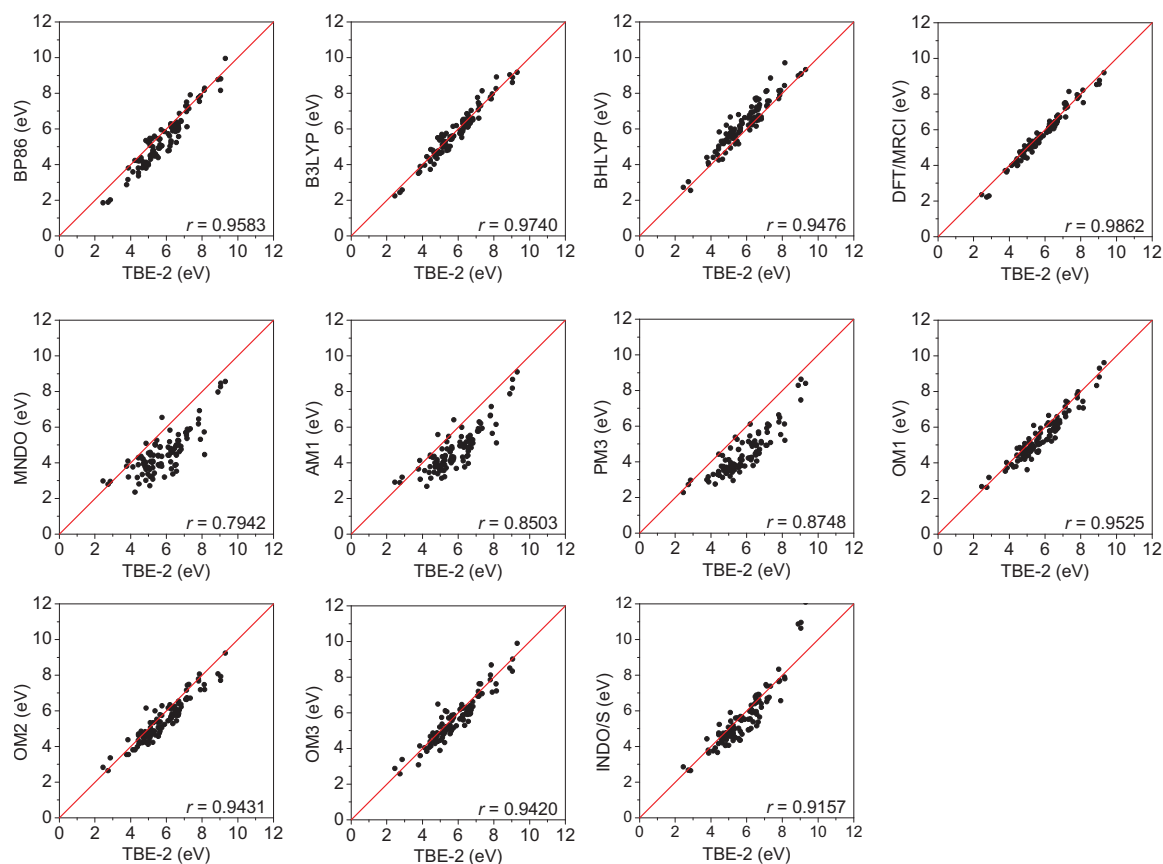


FIG. 4. Correlation plots for the singlet excited states from DFT and semiempirical methods with respect to the TBE-2 reference set of vertical excitation energies (eV).

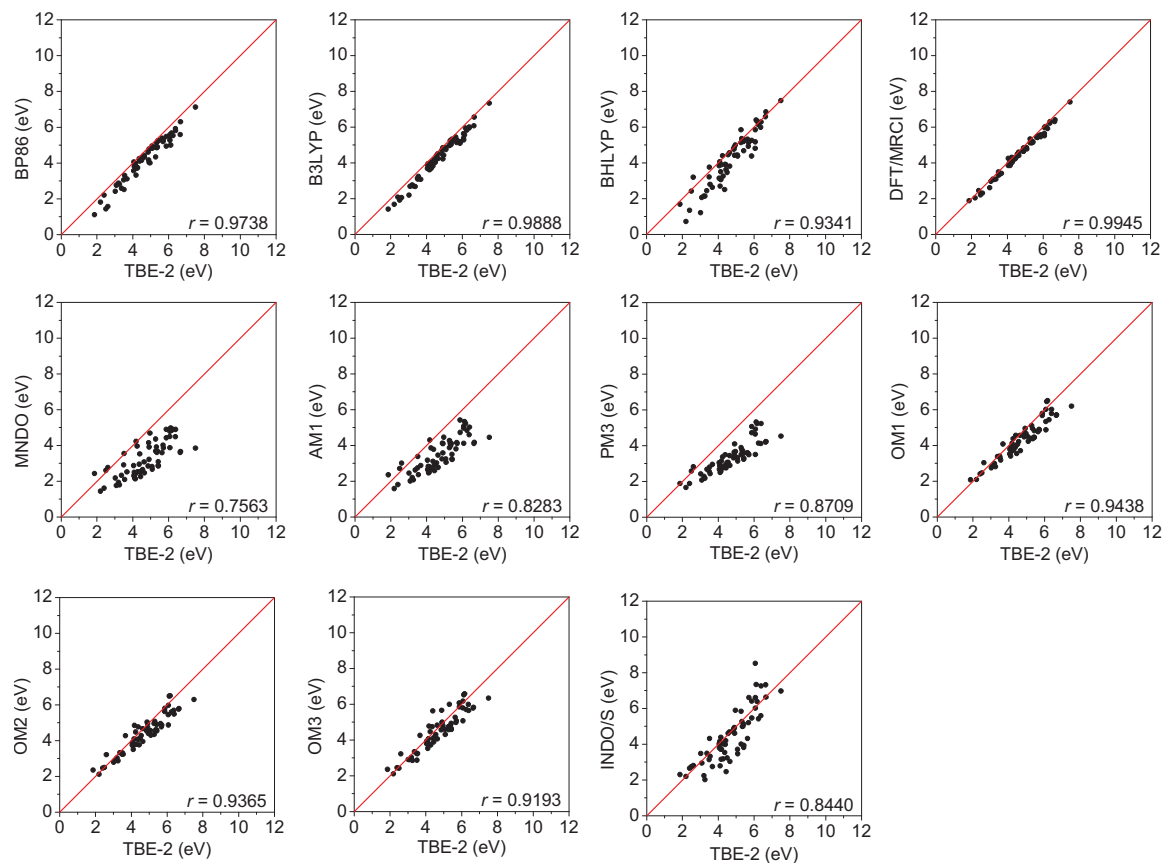


FIG. 5. Correlation plots for the triplet excited states from DFT and semiempirical methods with respect to the TBE-2 reference set of vertical excitation energies (eV).

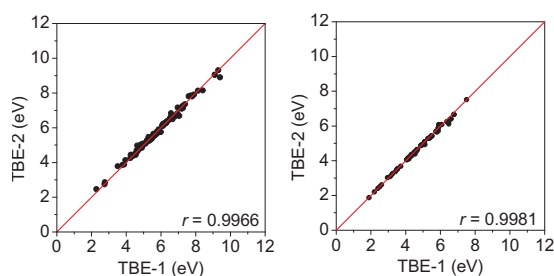


FIG. 6. Correlation plots for the singlet (left) and triplet (right) theoretical best estimates of vertical excitation energies (eV).

The basis set effects observed at the MS-CASPT2 level are generally rather similar to those found in coupled cluster calculations,²³ both qualitatively and quantitatively.

The previously proposed theoretical best estimates (TBE-1) for the vertical excitation energies of 104 singlets and 63 triplets have been revisited, and an upgrade version was derived (TBE-2). Most of the previously chosen *ab initio* results from the literature were retained, while the TZVP-based values from own calculations were mostly replaced by the present results with the larger aug-cc-pVTZ basis. Since the MS-CASPT2/aug-cc-pVTZ and CC/aug-cc-pVTZ excitation energies are normally of similar quality and numerically close to each other, it was difficult to make a choice, and TBE sets derived from these two approaches have correlation coefficients above 0.996 both for the singlet and triplet states. In view of the greater uniformity of the coupled cluster procedures, we finally decided to adopt the CC/aug-cc-pVTZ results unless the CC3/TZVP single excitation weight is lower than 80% for a given state in which case the MS-CASPT2/aug-cc-pVTZ result is preferred for TBE-2. The upgrade from TBE-1 to TBE-2 leads to rather minor changes, as can be seen from the low mean absolute deviations between the two sets that amount to 0.08 and 0.06 eV for the singlet and triplet states, respectively. It is therefore not surprising that the performance measures of DFT-based and semiempirical methods do not change much when being reevaluated using the upgraded TBE-2 values as reference data. The ranking of the methods remains the same, and the previously reported qualitative conclusions remain valid, with DFT/MRCI performing best among the studied DFT-based approaches and the OMx methods performing best at the semiempirical level.

TABLE VII. Deviations in the theoretical best estimates of vertical excitation energies (eV): TBE-1 vs TBE-2. (For the definition of TBE-1 and TBE-2 reference sets, see text.)

	Singlets	Triplets
Count ^a	104	63
Mean	0.00	-0.05
Abs. mean	0.08	0.06
Std. dev.	0.12	0.10
Maximum (+)	0.33	0.18
Maximum (-)	0.50	0.36

^aTotal number of considered states.

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Benchmarks of electronically excited states: Basis set effects on CASPT2 results

– Supporting Information –

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Appendix A: Additional results including corrections to the multistate CASPT2 ground state energy

TABLE I: Ground-state total energies (a.u.) from MS-CASPT2 and SS-CASPT2 calculations and the corresponding differences (a.u. and eV), TZVP versus aug-cc-pVTZ basis.

	TZVP Basis set				aug-cc-pVTZ Basis set			
	MS-CASPT2	SS-CASPT2	Diff. (au)	Diff. (eV)	MS-CASPT2	SS-CASPT2	Diff. (au)	Diff. (eV)
Ethene								
E-Butadiene	-155.5396737	-155.5379291	0.00174465	0.05	-155.6407926	-155.6401873	0.00060527	0.02
Hexatriene	-232.725112	-232.7239769	0.00113504	0.03	-232.8766319	-232.8745674	0.00206452	0.06
Octatetraene	-309.9073157	-309.9059341	0.00138159	0.04	-310.1084067	-310.1071083	0.00129844	0.04
Cyclopropene								
Cyclopentadiene	-193.5547761	-193.5491172	0.00565894	0.15	-193.6783531	-193.6759595	0.00239356	0.07
Norbornadiene	-270.7309202	-270.7228071	0.00811311	0.22	-270.889313	-270.8898499	-0.00053689	-0.01
Benzene								
Naphthalene	-384.8046758	-384.803527	-0.0011488	0.03	-385.0441751	-385.0418555	0.00231965	0.06
Furan	-229.4509774	-229.4443748	-0.00660259	0.18	-229.5873593	-229.5841473	0.00321198	0.09
Pyrrole	-209.6071271	-209.6045864	-0.00254073	0.07	-209.7423536	-209.7384121	0.0039415	0.11
Imidazole	-225.6437447	-225.6413246	-0.00242004	0.07	-225.7845111	-225.7807651	0.00374602	0.10
Pyridine	-247.6127979	-247.6114702	0.00132768	0.04	-247.7647825	-247.7648474	-0.00000648	0.00
Pyrazine	-263.6323599	-263.631358	0.00100197	0.03	-263.7979211	-263.7961287	0.00179238	0.05
Pyrimidine	-263.6408733	-263.6381206	0.00275265	0.07	-263.8007284	-263.7999485	0.00077996	0.02
Pyridazine	-263.6032259	-263.5999624	0.00326356	0.09	-263.7671842	-263.7656329	0.00155131	0.04
S-Triazine	-279.6737637	-279.6683994	0.00536428	0.15	-279.8455171	-279.839924	0.00559309	0.15
S-Tetrazine	-295.6075775	-295.6072853	0.00029219	0.01	-295.7900451	-295.7917901	-0.00174506	-0.05
Formaldehyde	-114.2430089	-114.2427139	0.00029495	0.01	-114.3093089	-114.3105788	-0.00126992	-0.03
Acetone	-192.6579845	-192.6576057	0.00037883	0.01	-192.7837394	-192.7833558	0.00038356	0.01
p-Benzoquinone	-380.5195349	-380.5221149	-0.00258001	-0.07	-380.746515	-380.7483547	-0.00183971	-0.05
Formamide	-169.5106032	-169.5057736	0.00482961	0.13	-169.608696	-169.6078453	0.00085063	0.02
Acetamide	-208.714964	-208.7104848	0.00447923	0.12	-208.8385464	-208.8376831	0.00086324	0.02
Propanamide	-247.9121751	-247.9077669	0.00440822	0.12	-248.0619863	-248.0613164	0.00066988	0.02
Cytosine	-393.9891334	-393.9799729	0.00916053	0.25	-394.231635	-394.2279902	0.00364481	0.10
Thymine	-453.0667154	-453.0571455	0.00956992	0.26	-453.341796	-453.3373812	0.00441476	0.12
Uracil	-413.8645057	-413.8546676	0.0098381	0.27	-414.1143885	-414.1068853	0.0075032	0.20
Adenine	-466.175432	-466.1701801	0.00525192	0.14	-466.4592127	-466.4562873	0.00292535	0.08

TABLE II: Deviations in excitation energies of singlet excited states of all 28 benchmark molecules with respect to CASPT2/TZVP using two different approaches to compute the ground-state reference energy.

	Method		
	CC2	CC3	CASPT2 ^a
Approach 1 ^b			
Count ^c	152	121	152
Mean	0.29	0.20	-0.23
Abs. Mean	0.32	0.22	0.35
Std. Dev.	0.41	0.27	0.42
Maximum	1.25	0.83	1.02
Approach 2 ^d			
Count ^c	152	121	152
Mean	0.25	0.17	-0.28
Abs. Mean	0.32	0.21	0.37
Std. Dev.	0.41	0.28	0.45
Maximum	1.25	1.13	0.82
Approach 2 ^d			
Count ^c	145	118	145
Mean	0.27	0.17	-0.26
Abs. Mean	0.33	0.22	0.36
Std. Dev.	0.42	0.28	0.44
Maximum	1.25	1.13	0.82

^aCASPT2 results collated from the literature. See Ref. 1 for more details.

^bUsing the multistate CASPT2 ground-state energy for all excited states.

^cTotal number of considered states.

^dUsing the multistate CASPT2 ground-state energy for states of same irreducible representation as the ground state, otherwise using a single-state CASPT2 ground-state energy.

^eTotal number of considered states, where the multistate and single-state procedures make use of the same active space.

Appendix B: Numerical results discussed in the paper: Tables III to XXX

Tables III—XXX document the CASPT2 results for individual molecules. The CASPT2/TZVP data are taken from Refs. 1 and 2. Technical details of the CASPT2/TZVP calculations and associate comments are given in the Supporting Information of Refs. 1 and 2. The footnotes in Tables III—XXX on computational aspects refer to the present CASPT2/aug-cc-pVTZ results.

1. Unsaturated aliphatic hydrocarbons

TABLE III: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of ethene, obtained at the ground state MP2/6-31G* equilibrium geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	f	$\langle x^2 \rangle^b$	ΔE	f	$\langle x^2 \rangle$
Ground state (1^1A_g)				11.6			11.7
Singlet states							
1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.66 ^c , 7.8 ^d , 8.0 ^e	8.54	0.505	14.2	7.84	0.356	15.8
Triplet states							
1^3B_{1u} ($\pi \rightarrow \pi^*$)	4.36 ^f , 4.6 ^g	4.48		11.7	4.48		11.8

^aThe active space is (25020425)8. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Highest root included: 1^1A_g , 3^1B_{1u} , 1^3B_{1u} .

^bExpectation value of x^2 in a.u.

^cFrom Ref. 3, band maximum in optical spectrum.

^dFrom Ref. 4, with correction for zero-point effects.

^eFrom Ref. 5–7, with correction for non-adiabatic effects.

^fFrom Ref. 8, band maximum in electron impact spectrum.

^gFrom Ref. 9, Figure 14.

TABLE IV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of *E*-butadiene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	$\langle z^2 \rangle$
Ground state (1^1A_g)				21.8			21.7
Singlet states							
1^1B_u (V)	5.73 ^c , 5.92 ^d	6.47 ^f	0.858	22.6	6.38	0.635	29.7
2^1A_g (V)		6.62		22.5	6.43		25.4
Triplet states							
1^3B_u	3.22 ^e	3.34		21.5	3.30		21.7
1^3A_g	4.91 ^e	5.16		21.4	5.08		21.9

^aThe active space is (0440)4. In parenthesis: number of active orbitals of symmetry $a_g b_g a_u b_u$, and number of active electrons. Highest root included: 3^1A_g , 3^1B_u , 1^3A_g , 1^3B_{1u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref. 10, 0-0 transition.

^dFrom Ref. 11–15, band maximum.

^eFrom Ref. 11,12, band maximum in electron impact spectrum.

^fDecreases to 6.25 eV when using a larger active space (0330)4 and averaging over three 1^1B_u states. Analogous calculation with IPEA=0: 5.94 eV. See Supporting Information of Ref. 1.

TABLE V: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of all-*E*-hexatriene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	$\langle z^2 \rangle$
Ground state (1^1A_g)				31.5			31.6
Singlet states							
1^1B_u (V)	4.93 ^c	5.31 ^f	1.045	32.1	5.18	0.981	37.0
2^1A_g (V)	5.21 ^d	5.42		31.4	5.33		32.4
Triplet states							
1^3B_u	2.61 ^e	2.71		31.4	2.67		31.8
1^3A_g	4.11 ^e	4.31		31.3	4.22		31.6

^aThe active space is (0 5 6 0) 6. In parenthesis: number of active orbitals of symmetry a_g b_g a_u b_u , and number of active electrons. Level shift 0.1 a.u. Highest root included: 4^1A_g , 3^1B_u , 3^3A_g , 1^3B_{1u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref. 10, 0-0 transition and band maximum in optical spectrum.

^dFrom Ref. 16, band maximum in electron impact spectrum.

^eFrom Ref. 17, two-photon absorption maximum in the liquid.

^fWith one single 1^1B_u root the CASSCF wave function has no *HOMO* $\rightarrow$ *LUMO* CSF contribution. See Ref. 1.

TABLE VI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of all-*E*-octatetraene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	$\langle z^2 \rangle$
Ground state (1^1A_g)				41.4			41.6
Singlet states							
2^1A_g (V)	3.59 ^c	4.64		41.5	4.52		41.8
1^1B_u (V)	4.41 ^d	4.70	1.298	41.7	4.35	1.307	43.9
2^1B_u (V)	5.88 ^e	5.73	0.004	41.5	5.78	0.011	43.6
3^1A_g (V)		6.19		41.3	6.42		42.5
4^1A_g (V)		6.55		41.5	7.01		47.0
3^1B_u (V)		8.04		41.4	7.69		49.5
Triplet states							
1^3B_u	2.10 ^f	2.33		41.3	2.27		41.6
1^3A_g	3.55 ^e	3.70		41.2	3.61		41.5

^aThe active space is (0 8 9 0) 8. In parenthesis: number of active orbitals of symmetry a_g b_g a_u b_u , and number of active electrons. Level shift 0.2 a.u. Highest root included: 6^1A_g , 6^1B_u , 3^3A_g , 1^3B_{1u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref. 18, derived from solution spectra.

^dFrom Ref. 10,19–25.

^eFrom Ref. 19,22.

^fFrom Ref. 22.

TABLE VII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of cyclopropene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle x^2 \rangle^c$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			0.46		14.5		0.46		14.6
Singlet-states									
1^1B_1 ($\sigma \rightarrow \pi^*$)	6.45 ^d	6.76	1.43	0.010	16.6	6.63	1.44	0.009	17.3
1^1B_2 ($\pi \rightarrow \pi^*$)	7.19 ^d , 7.0 ^e	7.06	1.02	0.234	16.5	6.66	0.87	0.241	17.4
Triplet-states									
1^3B_2 ($\pi \rightarrow \pi^*$)	4.16 ^e	4.35	0.02		16.5	4.26	0.02		14.8
1^3B_1 ($\sigma \rightarrow \pi^*$)	^f	6.51	1.64		14.6	6.36	1.50		17.0

^aThe active space is (0 1 5 6) 4. In parenthesis: number of active orbitals of symmetry a_1 b_2 a_2 b_1 , and number of active electrons. Highest root included: 1^1A_1 , 1^1B_1 , 3^1B_2 , 1^3B_1 , 1^3B_2 .

^bDipole moment in Debye (experimental value for the ground state is 0.46 D 26).

^cExpectation value of x^2 in a.u.

^dFrom Ref. 27, broad maxima in optical spectrum around 52000 and 58000 cm^{-1} .

^eFrom Ref. 28, from ion-impact energy-loss spectra.

^fIn Ref. 28, a shoulder at 6.1 eV in the ion-impact energy-loss spectra has been associated with a Rydberg transition. This feature has later been attributed to a transition to the 1^3B_1 valence state in Ref. 29.

TABLE VIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of cyclopentadiene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle x^2 \rangle^c$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			0.31		24.7		0.30		24.8
Singlet states									
1^1B_2	5.30 ^d	5.51	0.32	0.164	25.7	5.43	0.18	0.117	26.4
2^1A_1	6.2 ^e	6.31	0.40	0.001	25.6	6.28	0.65	0.000	25.9
3^1A_1	7.9 ^f	8.52	0.46	0.965	25.5	8.15	4.43	0.642	34.9
Triplet states									
1^3B_2	3.1 ^g	3.28	0.09		24.7	3.21	0.13		24.8
1^3A_1		5.11	0.18		24.5	5.02	0.21		24.7

^aThe active space is (0 8 6 0) 4. In parenthesis: number of active orbitals of symmetry a_1 b_1 a_2 b_2 , and number of active electrons. Highest root included: 8^1A_1 , 6^1B_2 , 1^3A_1 , 1^3B_2 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref. 30.

^eEstimated from experimental data in Ref. 31.

^fFrom Ref. 31.

^gFrom Ref. 32.

TABLE IX: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of norbornadiene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle z^2 \rangle^c$	ΔE	μ	f	$\langle z^2 \rangle$
Ground state (1^1A_1)			0.01		32.3				32.3
Singlet-states ($\pi \rightarrow \pi^*$)									
1^1A_2	5.23 ^d , 5.25 ^f	5.34	0.31		34.2	4.98	1.00		32.7
1^1B_2	6.0 ^g , 5.95 ^{df} , 5.92 ^e	6.11	0.93	0.090	33.2	5.94	1.45	0.131	32.1
2^1B_2	6.7 ^g , 6.65 ^{ef}	7.32	0.52	0.394	32.7	6.62	1.29	0.342	33.2
2^1A_2	7.50 ^f	7.45	0.16		31.7	7.20	0.06		37.5
2^1A_1		7.97	0.10		33.5	7.81	0.78		32.2
Triplet-states ($\pi \rightarrow \pi^*$)									
1^3A_2	3.4 ^d , 3.47 ^e	3.75	0.05		32.7	3.65	0.09		32.9
1^3B_2	3.9 ^{de}	4.22	0.05		32.1	4.16			32.2

^aThe active space is (1432)4. In parenthesis: number of active orbitals of symmetry $a_1 b_2 a_2 b_1$, and number of active electrons. Level shift 0.3 a.u. Highest root included: 5^1A_1 , 10^1A_2 , 12^1B_2 , 4^3A_2 , 4^3B_2 .

^bDipole moment in Debye.

^cExpectation value of z^2 in a.u.

^dFrom Ref. 33,34.

^eFrom Ref. 35.

^fFrom Ref. 36.

^gFrom Ref. 37.

2. Aromatic hydrocarbons and heterocycles

TABLE X: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of benzene, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	$\langle z^2 \rangle$
Ground state (1^1E_{2g})							29.9
Singlet states							
1^1B_{2u}	4.90 ^c	5.04		30.2	4.96		30.7
1^1B_{1u}	6.20 ^c	6.42	0.001	30.2	6.57		34.6
1^1E_{1u}	6.94 ^d	7.13	0.856	30.2	7.36	0.787	38.0
2^1E_{2g}	7.8 ^e	8.18		30.1	8.15		31.3
Triplet states							
1^3B_{1u}	3.94 ^f	4.17		29.8	4.13		29.8
1^3E_{1u}	4.76 ^f	4.90		29.8	4.76		30.2
1^3B_{2u}	5.60 ^f	5.76		29.8	5.72		31.2
1^3E_{2g}	7.24-7.74 ^g	7.38		29.7	7.32		30.1

^aThe active space is (02042050)6. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Level shift 0.1 a.u. Highest root included: 3^1A_g , 3^1B_{1g} , 3^1B_{2u} , 3^1B_{3u} , 2^3A_g , 2^3B_{1g} , 2^3B_{2u} , 2^3B_{3u} .

^bExpectation value of z^2 in a.u.

^cFrom Ref. 38.

^dFrom Ref. 39.

^eFrom Ref. 40.

^fFrom Ref. 41.

^gFrom Ref. 42.

TABLE XI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of naphthalene, obtained at the ground state MP2/6-31G* geometry.

		CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
State	Exp.	ΔE	f	$\langle z^2 \rangle^b$	ΔE	f	$\langle z^2 \rangle$
Singlet states							
Ground state (1^1A_g)				48.1			48.2
1^1B_{3u}	3.97 ^c , 4.0 ^d	4.24		48.1	4.06	0.001	47.8
1^1B_{2u}	4.45 ^c , 4.7 ^d	4.77	0.136	48.5	4.49	0.099	49.0
2^1A_g	5.50 ^e , 5.52 ^f	5.87		48.0	5.83		48.2
1^1B_{1g}	5.28 ^e , 5.22 ^f	5.99		48.5	5.71		54.4
2^1B_{3u}	5.63 ^g , 5.55 ^h , 5.89 ^c	6.06	1.542	48.1	6.04	1.514	50.6
2^1B_{1g}		6.47		48.4	6.31		52.8
2^1B_{2u}	6.14 ^c , 6.0 ^d	6.33	0.401	48.5	6.05	0.354	48.6
3^1A_g	6.01 ^e , 6.05 ^f	6.67		48.0	6.49		48.0
3^1B_{2u}	7.7 ⁱ , 7.6 ^d , 7.4 ^g	8.17	0.709	48.6	7.92	0.230	66.0
3^1B_{3u}		7.74	0.008	47.9	6.69	0.046	49.2
Triplet states							
Ground state (1^3B_{2u}) ^j				47.9	3.04		47.9
1^3B_{3u}		1.09		48.3	0.99		48.2
1^3B_{1g}		1.35		48.2	1.29		48.2
2^3B_{2u}		1.52		47.9	1.50		48.0
2^3B_{3u}		1.81		48.4	1.67		48.7
1^3A_g	2.25 ^k	2.37	0.001	48.1	2.30	0.001	49.0
2^3B_{1g}	3.12 ^l , 3.0 ^m	3.05	0.123	48.3	3.07	0.110	51.8
2^3A_g	2.93 ⁿ	3.22	0.001	48.1	3.07	0.003	50.0
3^3A_g		3.43		48.2	3.51	0.002	49.0
3^3B_{1g}		3.48		47.9	3.45	0.007	48.7

^aThe active space is (0 3 0 4 3 0 5 0) 10. In parenthesis: number of active orbitals of symmetry a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u} , and number of active electrons. Level shift 0.3 a.u. Highest root included: 4^1A_g , 6^1B_{1g} , 10^1B_{2u} , 6^1B_{3u} , 6^3A_g , 6^3B_{1g} , 4^3B_{2u} , 2^3B_{3u} . The covalent 3^1B_{2u} state corresponds to a $1b_{3g}^1 \rightarrow 3b_{1u}^1$ excitation which appears at 10.23 eV 43 and 10.38 eV, current, with CASSCF.

^bExpectation value of z^2 in a.u.

^cFrom Ref. 44.

^dFrom Ref. 45.

^eFrom Ref. 46.

^fFrom Ref. 47.

^gFrom Ref. 48.

^hFrom Ref. 49.

ⁱFrom Ref. 50.

^jThe energy of the 1^3B_{2u} state relative to the singlet ground state 1^1A_g is given in this line. The energies of the other triplet states in the following lines are given relative to the 1^3B_{2u} state.

^kFrom Ref. 51.

^lFrom Ref. 52.

^mFrom Ref. 53.

ⁿFrom Ref. 51, assigned on the basis of transition dipole moments.

TABLE XII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of furan, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ ^b	f	$\langle x^2 \rangle$ ^c	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			1.01		23.9		0.81		24.0
Singlet states									
1^1B_2	6.06 ^d	6.39	0.22	0.196	25.0	6.19	1.41	0.239	28.6
2^1A_1		6.50	1.41	0.007	24.4	6.35	1.53	0.006	25.1
3^1A_1	7.82 ^d	8.17	0.69	0.788	24.4	7.93	1.36	0.546	30.8
Triplet states									
1^3B_2	4.02 ^{de}	4.18	1.51		23.7	4.06	1.27		24.2
1^3A_1	5.22 ^e	5.49	1.28		23.7	5.34	1.02		24.0

^aThe active space is (0 7 5 0) 6. In parenthesis: number of active orbitals of symmetry $a_1 b_1 a_2 b_2$, and number of active electrons. Level shift 0.1 a.u. Highest root included: 8^1A_1 , 3^1B_2 , 1^3A_1 , 1^3B_2 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref. 54.

^eFrom Ref. 55.

TABLE XIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of pyrrole, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ ^b	f	$\langle x^2 \rangle$ ^c	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			1.82		25.5		1.80		25.7
Singlet states									
2^1A_1		6.31	1.10	0.031	25.6	6.23	0.52	0.002	28.0
1^1B_2	5.98 ^{de}	6.33	3.47	0.205	26.5	6.22	0.13	0.167	44.2
3^1A_1	7.54 ^d	8.17	3.40	0.611	25.7	7.95	5.66	0.396	39.6
Triplet states									
1^3B_2	4.21 ^{df}	4.51	0.85		25.3	4.39	0.98		25.7
1^3A_1	5.10 ^f	5.52	1.25		25.4	5.35	1.37		26.2

^aThe active space is (0 7 5 0) 6. In parenthesis: number of active orbitals of symmetry $a_1 b_1 a_2 b_2$, and number of active electrons. Level shift 0.1 a.u. Highest root included: 7^1A_1 , 3^1B_2 , 1^3A_1 , 1^3B_2 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref. 54.

^eFrom Ref. 56.

^fFrom Ref. 55.

TABLE XIV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of imidazole, obtained at the ground state MP2/6-31G* geometry.

State	Exp. ^b	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^c	f	$\langle x^2 \rangle^d$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state ($1^1A'$)			3.70		24.1		3.75		24.1
Singlet-states									
$1^1A''(n \rightarrow \pi^*)$		6.81	1.11	0.010	25.3	6.69	1.11	0.009	26.4
$2^1A'(\pi \rightarrow \pi^*)$	6.00	6.19	3.35	0.229	24.5	6.40	4.88	0.207	29.8
$3^1A'(\pi \rightarrow \pi^*)$	6.53	6.93	4.82	0.062	24.5	6.82	2.87	0.052	30.5
$2^1A''(n \rightarrow \pi^*)$		7.90	2.95	0.020	25.5	7.80	4.03	0.006	29.9
$4^1A'(\pi \rightarrow \pi^*)$		8.16	4.76	0.556	24.6	8.96	7.63	0.350	34.9
Triplet-states									
$1^3A'(\pi \rightarrow \pi^*)$		4.65	2.88		24.0	4.57	2.82		24.1
$2^3A'(\pi \rightarrow \pi^*)$		5.74	3.61		24.0	5.56	4.22		24.9
$1^3A''(n \rightarrow \pi^*)$		6.36	1.31		25.3	6.29	1.59		25.9
$3^3A'(\pi \rightarrow \pi^*)$		6.44	4.90		24.3	6.47	4.76		26.9
$4^3A'(\pi \rightarrow \pi^*)$		7.44	5.15		24.4				
$2^3A''(n \rightarrow \pi^*)$		7.51	3.15		25.6	7.40	3.84		26.9

^aThe active space is (113)8. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.2 a.u. Highest root included: $14^1A'$, $4^1A''$, $4^3A'$, $2^3A''$.

^bFrom Ref. 57.

^cDipole moment in Debye.

^dExpectation value of x^2 in a.u.

TABLE XV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of pyridine, obtained at the ground state MP2/6-31G* geometry.

State	Exp. ^b	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^c	f	$\langle x^2 \rangle^d$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			2.27		28.4		2.20		28.5
Singlet states, $\pi \rightarrow \pi^*$									
1^1B_2 (1^1B_{2u})	4.99	5.02	1.99	0.046	28.6	5.00	2.03	0.025	28.8
2^1A_1 (1^1B_{1u})	6.38	6.39	3.24	0.004	28.7	6.59	2.34	0.004	31.3
3^1A_1 (1^1E_{1u})	7.22	7.46	1.22	0.849	28.7	7.49	1.87	0.848	32.2
2^1B_2 (1^1E_{1u})		7.27 ^e	2.51	0.743	29.8	7.72	2.25	0.267	43.3
4^1A_1 (1^1E_{2g})		8.69	3.18		29.8	8.28	1.35		32.2
3^1B_2 (1^1E_{2g})		8.60 ^e	2.04	0.094	28.4	8.06	1.22	0.009	39.4
Singlet states, $n \rightarrow \pi^*$									
1^1B_1	4.59	5.17 ^f	0.27	0.010	29.6	5.07	0.57	0.007	29.9
1^1A_2	5.43	5.51 ^f	0.87		30.0	5.49	0.86		30.2
Triplet states, $\pi \rightarrow \pi^*$									
1^3A_1	4.10	4.27	2.08		28.2	4.23	2.05		28.3
1^3B_2	4.84	4.71	2.03		28.4	4.66	1.87		28.8
2^3A_1		5.03	2.28		28.2	4.92	2.40		28.6
2^3B_2		6.03	3.17		28.6	6.09	3.07		29.4
3^3A_1		7.56	1.87		28.1	6.11	1.60		28.2
3^3B_2		7.87	1.74		28.4	7.61	1.54		28.1
Triplet states, $n \rightarrow \pi^*$									
1^3B_1		4.57 ^f	0.49		29.7	4.54	0.68		29.9
1^3A_2		5.52 ^f	0.65		29.9	5.47	0.69		30.2

^aThe active space is (1950)8. In parenthesis: number of active orbitals of symmetry a_1 b_1 a_2 b_2 , and number of active electrons. Level Shift: 0.2 a.u. Highest root included: 5^1A_1 , 3^1B_2 , 1^1A_2 , 1^1B_1 , 3^3A_1 , 3^3B_2 , 1^3A_2 , 1^3B_1 .

^bFrom Ref. 58.

^cDipole moment in Debye.

^dExpectation value of x^2 in a.u.

^eThe active space is (1840)8. The 2^1B_2 and 3^1B_2 excitation energies refer to this large active space to overcome an intruder state problem for the 2^1B_2 state (which has very little effect on the computed energies). From Ref. 1

^fThe active space is (1420)8. From Ref. 1

TABLE XVI: Vertical excitation energies ΔE (eV) and other properties of the singlet states of pyrazine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2/TZVP ^{1,2}			CASPT2/AVTZ ^a		
			ΔE	f	$\langle x^2 \rangle^c$	ΔE	f	$\langle x^2 \rangle$
Ground state (1^1A_g)					26.9			27.1
$\pi \rightarrow \pi^*$ -states								
1^1B_{2u} (1^1B_{2u})	4.81	0.062	4.85	0.124	27.3	4.80	0.127	27.4
1^1B_{1u} (1^1B_{1u})	6.51	0.10	6.89	0.107	27.8	6.61	0.176	28.3
2^1B_{1u} (1^1E_{1u})	7.67	0.72	7.79	0.774	27.7	7.71	0.620	30.1
2^1B_{2u} (1^1E_{1u})	7.67	0.72	7.66	0.622	27.4	7.73	0.598	29.6
1^1B_{3g} (1^1E_{2g})			8.47		26.6	8.33		27.6
2^1A_g (1^1E_{2g})			8.61		26.8	8.30		27.0
$n \rightarrow \pi^*$ -states								
1^1B_{3u}	3.83 ^d	0.006	4.12	0.013	28.2	4.02	0.009	28.3
1^1A_u			4.70		28.4	4.75		28.3
1^1B_{2g}	5.46 ^e		5.68		28.1	5.56		28.2
1^1B_{1g}	6.10 ^f		6.41		28.4	6.47		28.6

^aThe active space is (1 5 2 0 2 0 1 5) 10. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Level shift: 0.1 a.u. Highest root included: 5^1A_g , 2^1A_u , 2^1B_{1g} , 1^1B_{2g} , 1^1B_{3g} , 3^1B_{1u} , 4^1B_{2u} , 1^1B_{3u} .

^bFrom Ref. 58.

^cExpectation value of x^2 in a.u.

^d0 – 0 transition.

^eFrom Ref. 59, estimate from solution spectrum.

^fUncertain assignment.

TABLE XVII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of pyrimidine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
			ΔE	μ^c	f	$\langle x^2 \rangle^d$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			2.40			26.9	2.34			27.1
$\pi \rightarrow \pi^*$ -states										
1^1B_2 (1^1B_{2u})	5.12	0.028	5.24	2.17	0.049	27.1	5.17	2.19	0.054	27.0
2^1A_1 (1^1B_{1u})	6.7	0.094	6.63	3.91	0.165	27.2	6.81	2.84	0.189	29.0
3^1A_1 (1^1E_{1u})	7.57	0.72	7.21	1.56	0.539	27.0	7.26	2.90	0.530	27.7
2^1B_2 (1^1E_{1u})	7.57	0.72	7.64	1.40	0.768	27.1	7.74	1.68	0.742	29.7
3^1B_2 (1^1E_{2g})			8.73	2.28	0.003	27.2	8.71	1.50		29.1
4^1A_1 (1^1E_{2g})			9.19	3.27	0.068	27.2	8.75	2.43	0.060	29.5
$n \rightarrow \pi^*$ -states										
1^1B_1	4.16 ^e	0.005	4.44	0.91	0.013	28.0	4.34	0.56	0.010	28.2
1^1A_2	4.62		4.80	1.26		28.2	4.74	1.34		28.5

^aThe active space is (1 1 5 9) 10. In parenthesis: number of active orbitals of symmetry $a_1 b_2 a_2 b_1$, and number of active electrons. Level shift 0.2 a.u. Highest root included: 6^1A_1 , 6^1B_2 , 1^1A_2 , 1^1B_1 .

^bFrom Ref. 58.

^cDipole moment in Debye (experimental value for the ground state is 2.33 D 60).

^dExpectation value of x^2 in a.u.

^e0-0 transition.

TABLE XVIII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of pyridazine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
			ΔE	μ^c	f	$\langle x^2 \rangle^d$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)				4.26		27.1	4.14			27.1
$\pi \rightarrow \pi^*$ -states										
2^1A_1 (1^1B_{2u})	4.9 ^b , 5.0 ^e	0.02	5.18	3.64	0.027	27.1	5.06	3.25	0.041	27.4
1^1B_2 (1^1B_{1u})	6.2 ^b , 6.5 ^e	0.10	6.31	5.12	0.115	27.4	6.34	4.70	0.051	29.5
2^1B_2 (1^1E_{1u})	7.1 ^b , 7.3 ^e		7.29	4.02	0.603	27.7	7.45	4.10	0.655	33.5
3^1A_1 (1^1E_{1u})	7.1 ^b , 7.3 ^e		7.62	5.73	0.742	27.0	7.17	4.21	0.676	29.4
$n \rightarrow \pi^*$ -states										
1^1B_1	3.3 ^f	0.006	3.78	1.88	0.010	28.2	3.71	1.60	0.008	28.4
1^1A_2			4.31	2.15		28.3	4.18	1.78		28.4
2^1A_2	5.3 ^e		5.77	1.85		28.1	5.67	1.83		28.4
2^1B_1	5.5-6.0 ^e		6.52	2.12	0.008	28.2	6.13	1.93	0.006	28.4

^aThe active space is (11 77) 10. In parenthesis: number of active orbitals of symmetry a_1 b_2 a_2 b_1 , and number of active electrons. Level shift 0.1 a.u. Highest root included: 6^1A_1 , 4^1B_2 , 2^1A_2 , 2^1B_1 .

^bFrom Ref. 59.

^cDipole moment in Debye (experimental value for the ground state is 4.22 D 61).

^dExpectation value of x^2 in a.u.

^eFrom Ref. 62.

^f0-0 transition from Ref. 59.

TABLE XIX: Vertical excitation energies ΔE (eV) and other properties of the singlet states of *s*-triazine, obtained at the ground state MP2/6-31G* equilibrium geometry (benzene-like state symmetries in parentheses).

State	Exp. ^b	f^b	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
			ΔE	f	$\langle x^2 \rangle^c$	ΔE	f	$\langle x^2 \rangle$
Ground state ($1^1A'_1$)					25.3			25.6
$\pi \rightarrow \pi^*$ -states								
$1^1A'_2$ (1^1B_{2u})	5.70		5.79		25.5	5.75		25.6
$2^1A'_1$ (1^1B_{1u})	6.86		7.25	0.008	25.4	7.20	0.265	26.2
$1^1E'$ (1^1E_{1u})	7.76	0.73	7.50	0.681	25.4	7.36	0.566	26.1
$2^1E'$ (1^1E_{2g})			8.99	0.044	25.4	9.02	0.097	25.6
$n \rightarrow \pi^*$ -states								
$1^1A''_1$			4.60		26.5	4.54		26.6
$1^1A''_2$	4.59	0.013	4.66	0.022	26.5	4.60	0.024	26.6
$1^1E''$	3.97		4.70		26.5	4.63		26.6
$2^1E''$	6.15		7.71		26.5	7.55		26.5

^aThe active space is (3 10) 12. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.2 a.u. Highest root included: $8^1A'$, $6^1A''$.

^bFrom Ref. 58.

^cExpectation value of x^2 in a.u.

TABLE XX: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of *s*-tetrazine, obtained at the ground state MP2/6-31G* equilibrium geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	f	$\langle x^2 \rangle^b$	ΔE	f	$\langle x^2 \rangle$
Ground state (1^1A_g)				24.4			24.7
$\pi \rightarrow \pi^*$ -singlet states							
1^1B_{2u}	$5.0^c, 4.97^d$	4.93	0.109	24.2	4.89	0.123	24.5
1^1B_{1u}	7.1^{cd}	6.94	0.146	24.7	6.84	0.061	25.1
2^1B_{1u}	7.6^{cd}	7.42	0.487	25.1	7.20	0.577	25.8
2^1B_{2u}	8.3^{cd}	8.14	0.554	26.1	8.00	0.479	25.3
2^1B_{3g}		8.34		24.1	8.19		24.2
3^1A_g		8.97		24.2	8.72		24.4
$n \rightarrow \pi^*$ - and $n, n \rightarrow \pi^*, \pi^*$ -singlet states							
$1^1B_{3u} (n \rightarrow \pi^*)$	$2.25^e, 2.34^c$	2.29	0.013	25.2	2.27	0.010	25.6
$1^1A_u (n \rightarrow \pi^*)$	$\approx 3.4^f$	3.51		25.5	3.40		25.6
$2^1A_g (n, n \rightarrow \pi^*, \pi^*)$		4.66		26.2	4.55		26.5
$1^1B_{1g} (n \rightarrow \pi^*)$		4.73		25.2	4.74		25.4
$1^1B_{2g} (n \rightarrow \pi^*)$		5.20		25.2	5.07		25.4
$1^1B_{3g} (n, n \rightarrow \pi^*, \pi^*)$		5.86		26.3	5.76		26.5
$2^1A_u (n \rightarrow \pi^*)$		5.50		25.3	5.32		25.4
$2^1B_{2g} (n \rightarrow \pi^*)$	$\approx 5.5^d$	6.06		25.3	5.84		25.3
$2^1B_{1g} (n \rightarrow \pi^*)$	5.9^d	6.45		25.2	6.33		25.6
$2^1B_{3u} (n \rightarrow \pi^*)$	$6.6^c, 6.34^d$	6.77	0.020	25.4	6.59	0.018	25.6
$3^1B_{1g} (n \rightarrow \pi^*)$		6.73		25.5	6.64		25.4
Triplet states							
$1^3B_{3u} (n \rightarrow \pi^*)$	1.69^{dg}	1.61		25.3	1.63		25.5
$1^3A_u (n \rightarrow \pi^*)$	2.9^d	3.28		25.6	3.23		25.7
$1^3B_{1g} (n \rightarrow \pi^*)$	3.6^d	4.14		25.3	4.04		25.5
$1^3B_{1u} (\pi \rightarrow \pi^*)$		4.37		24.2	4.36		24.4
$1^3B_{2u} (\pi \rightarrow \pi^*)$		4.39		24.2	4.25		24.7
$1^3B_{2g} (n \rightarrow \pi^*)$		4.94		25.2	4.82		25.5
$2^3A_u (n \rightarrow \pi^*)$		5.04		25.3	4.91		25.6
$1^3B_{3g} (n, n \rightarrow \pi^*, \pi^*)$		5.57		26.5			
$2^3B_{1u} (\pi \rightarrow \pi^*)$		5.40		24.2	5.26		24.4
$2^3B_{2g} (n \rightarrow \pi^*)$		5.97		25.3	5.78		25.5
$2^3B_{1g} (n \rightarrow \pi^*)$		6.37		25.1	6.02		25.3
$2^3B_{3u} (n \rightarrow \pi^*)$		6.54		25.5	6.39		25.6
$2^3B_{2u} (\pi \rightarrow \pi^*)$		7.08		24.8	7.01		25.0

^aThe active space is (14212113)14. In parenthesis: number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Level shift 0.2 a.u. Highest root included: $6^1A_g, 3^1A_u, 4^1B_{1g}, 3^1B_{2g}, 3^1B_{3g}, 3^1B_{1u}, 5^1B_{2u}, 3^1B_{3u}, 2^3A_u, 2^3B_{1g}, 2^3B_{2g}, 1^3B_{3g}, 1^3B_{1u}, 3^3B_{2u}, 2^3B_{3u}$.

^bExpectation value of x^2 in a.u.

^cFrom Ref. 63.

^dFrom Ref. 64.

^eFrom Ref. 65.

^fFrom Ref. 59.

^gFrom Ref. 66.

3. Aldehydes, ketones and amides

TABLE XXI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of formaldehyde, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle x^2 \rangle^c$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			2.44		8.7		2.41		8.7
Singlet states									
1^1A_2 ($n \rightarrow \pi^*$)	3.79 ^d , 4.07 ^e	3.99	1.46		10.0	4.01	1.00		10.2
1^1B_1 ($\sigma \rightarrow \pi^*$)		9.14 ^f	0.90	0.013	8.7	9.12	0.50	0.012	10.2
2^1A_1 ($\pi \rightarrow \pi^*$)		9.32	2.69	0.451	9.41	9.47	1.81	0.242	9.9
Triplet states									
1^3A_2 ($n \rightarrow \pi^*$)	3.50 ^d	3.58	1.35		10.1	3.62	0.85		10.3
1^3A_1 ($\pi \rightarrow \pi^*$)	5.82 ^d	5.84	1.05		8.9	5.85	0.82		9.0

^aThe active space is (2 5 0 2) 6. In parenthesis: number of active orbitals of symmetry a_1 b_1 a_2 b_2 , and number of active electrons. Highest root included: 4^1A_1 , 1^1A_2 , 1^1B_1 , 1^3A_1 , 1^3A_2 .

^bDipole moment in Debye.

^cExpectation value of x^2 in a.u.

^dFrom Ref. 67.

^eFrom Ref. 68.

^fCalculated with active space: (1 2 0 0) 4. See 1,2.

TABLE XXII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of acetone, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle x^2 \rangle^c$	ΔE	μ	f	$\langle x^2 \rangle$
Ground state (1^1A_1)			2.93		18.1		2.93		18.1
Singlet-states									
1^1A_2 ($n \rightarrow \pi^*$)	4.38 ^d	4.44	1.48		19.1	4.49	1.27		19.2
1^1B_1 ($\sigma \rightarrow \pi^*$)		9.27	1.31	0.011	19.0	9.25	0.98	0.009	19.2
2^1A_1 ($\pi \rightarrow \pi^*$)		9.31	3.18	0.359	18.1	9.19	2.45	0.357	19.9
Triplet-states									
1^3A_2 ($n \rightarrow \pi^*$)	4.16 ^{d,e}	4.10	1.28		19.2	4.17	1.07		19.2
1^3A_1 ($\pi \rightarrow \pi^*$)	5.88 ^{d,e}	6.04	1.21		18.2	6.09	1.07		18.3

^aThe active space is (2 2 0 6) 6. In parenthesis: number of active orbitals of symmetry a_1 b_2 a_2 b_1 , and number of active electrons. Highest root included: 4^1A_1 , 1^1A_2 , 1^1B_1 , 1^3A_1 , 1^3A_2 .

^bDipole moment in Debye (experimental value for the ground state is 2.90 D 69).

^cExpectation value of x^2 in a.u.

^dFrom Ref. 67.

^eFrom Ref. 70.

TABLE XXIII: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of *p*-benzoquinone, obtained at the ground state MP2/6-31G* equilibrium geometry.

State	Exp.	f	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
			ΔE	f	$\langle x^2 \rangle^b$	ΔE	f	$\langle x^2 \rangle$
Ground state (1^1A_g)					34.3			34.1
Singlet states								
$1^1B_{1g} (n \rightarrow \pi^*)$	2.7 ^c , 2.49 ^d		2.76		35.5	2.81		35.2
$1^1A_u (n \rightarrow \pi^*)$	2.7 ^c , 2.48 ^d		2.77		35.5	2.83		35.2
$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.4 ^c , 4.07 ^e , 4.4 ^f	0.005 ^f	4.26		34.5	4.37		34.7
$2^1A_g (n \rightarrow \pi^*)$			4.45		36.5	4.52		36.5
$1^1B_{2g} (n \rightarrow \pi^*)$			5.65		35.7	5.59		35.4
$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.4 ^c , 5.12 ^e , 5.4 ^f	0.44 ^f	5.28	0.636	34.6	5.41	0.731	34.7
$1^1B_{3u} (n \rightarrow \pi^*)$			5.64		35.8	5.55		35.8
$2^1B_{2g} (n \rightarrow \pi^*)$			6.59		35.8	6.43		35.9
$2^1B_{1g} (n \rightarrow \pi^*)$			6.13		35.5	5.63		35.4
$2^1A_u (n \rightarrow \pi^*)$			6.04		35.5	6.11		35.1
$3^1A_g (\pi \rightarrow \pi^*)$			6.06		34.5	6.04		34.3
$2^1B_{3g} (\pi \rightarrow \pi^*)$			6.96		35.3	6.99		34.9
$1^1B_{2u} (\pi \rightarrow \pi^*)$			7.32	0.016	34.5	7.17	0.036	34.4
$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.3 ^f	0.81 ^f	7.92	0.660	35.1	7.87	0.393	34.7
$3^1B_{1u} (\pi \rightarrow \pi^*)$			7.34	0.079	34.8	7.46	0.353	34.4
$3^1B_{1g} (n \rightarrow \pi^*)$			7.88		35.3	7.90		36.5
$3^1A_u (n \rightarrow \pi^*)$			7.89		35.3	7.57		34.9
$4^1A_g (\pi \rightarrow \pi^*)$			8.00		34.1	8.01		33.7
$5^1A_g (n \rightarrow \pi^*)$			8.23		36.2	7.98		36.4
Triplet states								
$1^3B_{1g} (n \rightarrow \pi^*)$	2.28 ^g , 2.31 ^h		2.62		35.4	2.63		35.3
$1^3A_u (n \rightarrow \pi^*)$	2.32 ^g , 2.35 ^h		2.66		35.5	2.66		35.3
$1^3B_{1u} (\pi \rightarrow \pi^*)$			2.99		34.4	3.00		34.2
$1^3B_{3g} (\pi \rightarrow \pi^*)$			3.32		34.4	3.30		34.3

^aThe active space is (05111106) 12. In parenthesis number of active orbitals of symmetry $a_g b_{2g} b_{1g} b_{3g} a_u b_{2u} b_{1u} b_{3u}$, and number of active electrons. Level shift 0.3 a.u. Highest root included: 8^1A_g , 3^1A_u , 4^1B_{1g} , 3^1B_{2g} , 2^1B_{3g} , 4^1B_{1u} , 2^1B_{2u} , 2^1B_{3u} , 2^3A_u , 2^3B_{1g} , 2^3B_{3g} , 2^3B_{1u} .

^bExpectation value of x^2 in a.u.

^cBand maxima from Ref. 71.

^d0-0 transitions from Ref. 72.

^e0-0 transitions from Ref. 73.

^fBand maxima from Ref. 74.

^g0-0 transitions from Ref. 75.

^h0-0 transitions from Ref. 76.

TABLE XXIV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of formamide, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle z^2 \rangle^c$	ΔE	μ	f	$\langle z^2 \rangle$
Ground state ($1^1A'$)			4.08		14.1		3.96		13.9
Singlet states									
$1^1A''$ ($n \rightarrow \pi^*$)	5.5 ^d	5.63	1.99	0.001	15.3	5.58	1.93	0.000	15.8
$2^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^e	7.39	6.10	0.469	14.8	7.45	4.84	0.331	19.5
$3^1A'$ ($\pi \rightarrow \pi^*$)		10.54	5.10	0.163	15.2	10.47	4.02	0.129	20.1
Triplet states									
$1^3A''$ ($n \rightarrow \pi^*$)	5.30 ^f	5.40	1.95		15.7	5.32	1.75		15.8
$1^3A'$ ($\pi \rightarrow \pi^*$)		5.58	3.71		14.6	5.68	3.97		15.0

^aThe active space is (89)6. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.2 a.u. Highest root included: $12^1A'$, $3^1A''$, $2^3A'$, $2^3A''$.

^bDipole moment in Debye.

^cExpectation value of z^2 in a.u.

^dFrom Ref. 77,78.

^eFrom Ref. 79,80.

^fFrom Ref. 81.

TABLE XXV: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of acetamide, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle z^2 \rangle^c$	ΔE	μ	f	$\langle z^2 \rangle$
Ground state ($1^1A'$)			4.00		18.8		3.89		18.8
Singlet states									
$1^1A''$ ($n \rightarrow \pi^*$)	5.44 ^d	5.69	1.79	0.001	19.8	5.69	1.27	0.002	20.7
$2^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^e	7.27	5.87	0.469	19.2	7.12	4.67	0.299	26.8
$3^1A'$ ($\pi \rightarrow \pi^*$)	9.9 ^f	10.09	4.53	0.163	19.3	10.03	3.79	0.164	24.9
Triplet states									
$1^3A''$ ($n \rightarrow \pi^*$)		5.41	1.70		20.1	5.40	1.38		20.3
$1^3A'$ ($\pi \rightarrow \pi^*$)		5.63	3.31		19.2	5.86	3.23		19.2

^aThe active space is (89)6. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.3 a.u. Highest root included: $12^1A'$, $3^1A''$, $2^3A'$, $2^3A''$.

^bDipole moment in Debye.

^cExpectation value of z^2 in a.u.

^dFrom Ref. 78.

^eFrom Ref. 80.

^fFrom Ref. 77.

TABLE XXVI: Vertical excitation energies ΔE (eV) and other properties of the singlet and triplet states of propanamide, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}				CASPT2/aug-cc-pVTZ ^a			
		ΔE	μ^b	f	$\langle z^2 \rangle^c$	ΔE	μ	f	$\langle z^2 \rangle$
Ground state ($1^1A'$)			4.13		23.6		3.70		23.6
Singlet states									
$1^1A''$ ($n \rightarrow \pi^*$)	5.44 ^d	5.72	1.70	0.001	24.6	5.74	1.13		25.6
$2^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^e	7.20	5.78	0.405	24.1	7.17	7.40	0.284	32.1
$3^1A'$ ($\pi \rightarrow \pi^*$)	9.9 ^f	9.94	4.21	0.275	24.1	9.85	3.52	0.179	26.3
Triplet states									
$1^3A''$ ($n \rightarrow \pi^*$)		5.45	1.62		24.9	5.56	0.98		25.3
$1^3A'$ ($\pi \rightarrow \pi^*$)		5.80	3.47		23.9	6.03	2.60		23.9

^aThe active space is (89)6. In parenthesis: number of active orbitals of symmetry $a' a''$, and number of active electrons. Level shift: 0.3 a.u. Highest root included: $12^1A'$, $3^1A''$, $4^3A'$, $4^3A''$.

^bDipole moment in Debye.

^cExpectation value of z^2 in a.u.

^dFrom Ref. 77,78.

^eFrom Ref. 80.

^fFrom Ref. 77.

4. Nucleobases

TABLE XXVII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of cytosine, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	μ^b	f	ΔE	μ	f
Ground state ($1^1A'$)			6.34			6.63	
$2^1A'$ ($\pi \rightarrow \pi^*$)	4.6 ^{cde}	4.67	4.58	0.093	4.52	4.31	0.053
$1^1A''$ ($n \rightarrow \pi^*$)	5.0 ^d , 5.3 ^e	5.12	2.56	0.003	5.03	3.36	0.003
$3^1A'$ ($\pi \rightarrow \pi^*$)	5.4 ^c , 5.6 ^d , 5.8 ^e	5.53	5.73	0.351	5.43	6.95	0.238
$4^1A'$ ($\pi \rightarrow \pi^*$)	6.1 ^c , 6.2 ^e , 6.4 ^d	6.40	5.92	0.621	6.09	6.10	0.546
$2^1A''$ ($n \rightarrow \pi^*$)		5.53	2.74	0.002	5.44	2.16	0.001
$5^1A'$ ($\pi \rightarrow \pi^*$)	6.7 ^c , 7.1 ^e	6.97	7.02	0.369	6.68	6.30	0.406
$6^1A'$ ($\pi \rightarrow \pi^*$)		8.22	4.66	0.132			

^aThe active space is (2 12) 14. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.2 a.u. Highest root included: $7^1A'$, $2^1A''$.

^bDipole moment in Debye.

^cFrom Ref. 82.

^dFrom Ref. 83.

^eFrom Ref. 84.

TABLE XXVIII: Vertical excitation energies ΔE (eV) and other properties of the singlet states of thymine, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	μ^b	f	ΔE	μ	f
Ground state ($1^1A'$)			4.19			4.20	
$1^1A''$ ($n \rightarrow \pi^*$)	4.9-5.2 ^c	4.95	2.52		4.86 ^e	3.25	
$2^1A'$ ($\pi \rightarrow \pi^*$)	4.95 ^e , 4.8 ^f	5.06	5.92	0.334	4.91	5.97	0.278
$3^1A'$ ($\pi \rightarrow \pi^*$)	6.2 ^e , 5.7 ^f	6.15	1.61	0.067	6.01	2.70	0.067
$2^1A''$ ($n \rightarrow \pi^*$)		6.38	3.92		6.22 ^e	5.14	
$4^1A'$ ($\pi \rightarrow \pi^*$)	6.2 ^f	6.53	6.66	0.353	6.32	7.34	0.283
$3^1A''$ ($n \rightarrow \pi^*$)		6.85	6.46		6.59 ^e	6.53	
$4^1A''$ ($n \rightarrow \pi^*$)		7.43	2.27		7.05 ^e	3.66	
$5^1A'$ ($\pi \rightarrow \pi^*$)	7.4 ^e , >6.7 ^f	7.43	3.05	0.674	7.33	3.28	0.680
$6^1A'$ ($\pi \rightarrow \pi^*$)		8.48	2.83	0.004	8.21	1.94	0.001

^aThe active space is (0 12) 10. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.2 a.u. Highest root included: $8^1A'$, $5^1A''$.

^bDipole moment in Debye.

^cFrom Ref. 85.

^dThe active space is (2 12) 14.

^eFrom Ref. 86.

^fFrom Ref. 87.

TABLE XXIX: Vertical excitation energies ΔE (eV) and other properties of the singlet states of uracil, obtained at the ground state MP2/6-31G* geometry.

State	Exp. ^b	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	μ^c	f	ΔE	μ	f
Ground state ($1^1A'$)			4.31			4.33	
$1^1A''$ ($n \rightarrow \pi^*$)	4.38 ^d 4.9-5.2 ^e	4.91	2.23		4.80	2.79	
$2^1A'$ ($\pi \rightarrow \pi^*$)	5.1	5.23	5.78	0.321	5.06	5.99	0.276
$3^1A'$ ($\pi \rightarrow \pi^*$)	6.0	6.15	2.48	0.047	6.00	2.44	0.045
$2^1A''$ ($n \rightarrow \pi^*$)		6.28	4.25		6.15	4.21	
$3^1A''$ ($n \rightarrow \pi^*$)		6.98	2.17		6.73	1.71	
$4^1A'$ ($\pi \rightarrow \pi^*$)	6.6	6.74	6.52	0.249	6.47	7.00	0.259
$4^1A''$ ($n \rightarrow \pi^*$)		7.28	6.86		6.93	6.46	
$5^1A'$ ($\pi \rightarrow \pi^*$)	6.9-7.0	7.42	3.16	0.804	7.37	1.41	0.212

^aThe active space is (2 12) 14. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.2 a.u. Highest root included: $8^1A'$, $5^1A''$.

^bFrom Ref. 87.

^cDipole moment in Debye.

^dFrom Ref. 88.

^eFrom Ref. 85.

TABLE XXX: Vertical excitation energies ΔE (eV) and other properties of the singlet states of adenine, obtained at the ground state MP2/6-31G* geometry.

State	Exp.	CASPT2/TZVP ^{1,2}			CASPT2/aug-cc-pVTZ ^a		
		ΔE	μ^b	f	ΔE	μ	f
Ground state ($1^1A'$)			2.50			2.43	
$2^1A'$ ($\pi \rightarrow \pi^*$)	4.63 ^c	5.20	2.19	0.154	5.11	2.33	0.398
$3^1A'$ ($\pi \rightarrow \pi^*$)	4.92 ^d	5.29	2.52	0.193	5.02	2.23	0.015
$1^1A''$ ($n \rightarrow \pi^*$)	5.4 ^e	5.19	1.48	0.001	5.04 ^f	1.02	0.002
$4^1A'$ ($\pi \rightarrow \pi^*$)	5.99 ^d	6.34	2.09	0.536	6.25	2.84	0.510
$5^1A'$ ($\pi \rightarrow \pi^*$)	6.33 ^g	6.64	3.45	0.001	6.65	4.39	0.069
$2^1A''$ ($n \rightarrow \pi^*$)		5.96	0.39	0.007	5.75 ^f	0.22	0.007
$6^1A'$ ($\pi \rightarrow \pi^*$)	6.81 ^h	6.87	2.86	0.010	6.96	5.00	0.344
$7^1A'$ ($\pi \rightarrow \pi^*$)	7.75 ^h	7.56	0.97	0.036	7.55	2.04	0.036

^aThe active space is (0 13) 12. In parenthesis: number of active orbitals of symmetry a' a'' , and number of active electrons. Level shift 0.3 a.u. Highest root included: $8^1A'$, $3^1A''$.

^bDipole moment in Debye.

^cFrom Ref.⁸⁹.

^dFrom Ref.⁸⁷.

^eFrom Ref.^{84,90}.

^fThe active space is (3 13) 18.

^gFrom Ref.⁹¹.

^hFrom Ref.⁹².

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Paper VII

*Photophysics of structurally modified flavin derivatives
in the blue light photoreceptor YtvA: A combined experimental
and theoretical study*

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Submitted.

Photophysics of structurally modified flavin derivatives in the blue light photoreceptor YtvA: A combined experimental and theoretical study

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Abstract

The light-induced processes of two derivatives of flavin mononucleotide (1- and 5-deaza flavin mononucleotide, 1DFMN and 5DFMN) incorporated into the LOV domain of YtvA protein from *Bacillus subtilis* have been studied by experimental and computational methods. Quantum mechanics/molecular mechanics (QM/MM) calculations were carried out in which the QM part was treated by density functional theory (DFT) using the B3LYP functional for geometry optimizations and the DFT/MRCI method for spectroscopic properties, while the MM part was described by the CHARMM force field. Experimentally, the spectrum of 1DFMN-YtvA-LOV is red-shifted ($\lambda_{\text{max}} = 530$ nm) with respect to the parent FMN chromophore in the wild-type protein ($\lambda_{\text{max}} = 445$ nm); 1DFMN is incorporated into the protein binding site, but does not undergo any light-induced reactions such as triplet and photoadduct formation. The QM/MM computations confirm the absence of a channel for triplet formation and locate a radiationless channel (via a S_1/S_0 conical intersection) along a hydrogen transfer path that might allow for fast deactivation. By contrast, 5DFMN-YtvA-LOV has a blue-shifted absorption spectrum ($\lambda_{\text{max}} = 410$ nm) and shows similar behavior as FMN in the wild-type protein, both with regard to the photophysics and the formation of a photoadduct with a flavin-cysteinyl covalent bond. The QM/MM calculations predict a mechanism that involves a hydrogen transfer in the T_1 state followed by intersystem crossing and adduct formation in the S_0 state. Experimentally, dark-state recovery occurs only after absorption of a second photon, again including the triplet state. The QM/MM calculations suggest a photochemical mechanism for dark-state recovery that is accessible only for the adduct with a C4a-S bond, but not for alternative adducts with a C5-S bond.

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Introduction

In recent years several blue light- (BL-) sensing photoreceptors have been identified in molecular terms in plants and unicellular organisms. They have been demonstrated to be involved in many regulatory biological processes such as phototropism or to act as stomatal opening sensors for environmental stress.¹⁻³ BL photoreceptors are grouped into three protein families: Cryptochromes, BLUF (Blue-Light Using Flavin)-proteins, and LOV (Light-Oxygen-Voltage)-proteins, the latter being the family that is most frequently found.

LOV-proteins, labelled in plants as phototropins, carry an oxidized flavin mononucleotide (FMN) chromophore ($\lambda_{\text{max}} = 445 \text{ nm}$), noncovalently incorporated into the protein. Absorption of light initiates a photocycle that generates first the triplet form of the chromophore and then a so-called “photoadduct” with a characteristic flavin-cysteiny l covalent bond. This photoadduct ($\lambda_{\text{max}} = 390 \text{ nm}$) is considered the signalling state, yielding in plant phototropins an autophosphorylation of the kinase domain in the C-terminal part of the photoreceptor.² Despite great similarities in protein sequence, three-dimensional structure of the LOV domain, and photocycle, much less physiological information is available for bacterial than for plant LOV-proteins. One of the best studied LOV-proteins is YtvA from *Bacillus subtilis*,⁴ which has been demonstrated to be involved in the light-regulated stress response of this bacterium.^{5,6} Due to potential biotechnological applications, structural modifications in biological photoreceptors have recently been the object of intense research.^{3,7} The main strategies for controlling the signalling mechanism are changing the protein via mutations or replacing the native chromophore by artificial molecules.

Attempts to modify the flavin chromophore in LOV-proteins are impeded by the fact that flavins are ubiquitous in all cells, yielding recombinant proteins always loaded with FMN. Several exchange protocols have been reported, either as in vitro methods⁸ or as in vivo approaches,⁹ and one of the currently studied flavin derivatives has previously been inserted into the LOV2 domain of phototropin from *Avena sativa*.¹⁰ Recently, a novel and successful approach has been presented for exchanging the FMN chromophore by structurally modified flavin derivatives in the binding pocket of YtvA.¹¹ This protocol was applied to incorporate two structurally modified flavins into the LOV-domain, namely 1-carba-1- and 5-carba-5-deazaflavin mononucleotide (1DFMN and 5DFMN, see Figure 1). These chemically synthesized flavins were selected because of their peculiar photophysical behavior. In aqueous solution, the spectral properties of the riboflavin (RF) form of these compounds are very different from each other and from that of the parent RF chromophore: The 1-deaza derivative (1DRF) derivative shows a strong bathochromic shift of its absorption maximum ($\lambda_{\text{max}} = 530 \text{ nm}$). No triplet formation is detected for this compound, and fluorescence can only be observed in the short picosecond time domain.¹² By contrast, the 5-deaza derivative (5DRF) has a significant hypsochromic shift ($\lambda_{\text{max}} = 410 \text{ nm}$), and, compared with the parent FMN chromophore, it exhibits triplet formation to a similar extent and an even larger quantum fluorescence yield ($\Phi_F = 0.5$ vs. $\Phi_F = 0.27$ for RF).^{13,14} It is thus of interest to investigate the effects of the protein binding site on the photophysical and photochemical properties of these deazaflavins.

In this article we address the spectroscopy and reactivity of 1DFMN and 5DFMN chromophores in the LOV domain of YtvA from *Bacillus subtilis*. We have performed a

combined experimental and theoretical study, employing time-resolved absorption and fluorescence spectroscopy as well as quantum-chemical QM/MM calculations, to unravel the photoinduced processes in these systems.

Material and methods

Incorporation of both 1DFMN and 5DFMN as chromophores in the YtvA protein was achieved following a recently developed protocol that is based on the unfolding/refolding of the protein on a His-Trap column.¹¹ The yield of chromophore incorporation was controlled by determining the absorption ratios A_{280}/A_{400} for 5DFMN and A_{280}/A_{500} for 1DFMN, giving values of 3:1 for 5DFMN (WT YtvA: 4:1) and 4.8:1 for 1DFMN (note that the latter compound has a lower extinction coefficient than FMN, $\epsilon_{\text{max}} = 6\,800\text{ cm}^{-1}\text{M}^{-1}$ compared to $\epsilon_{\text{max}} = 12\,500\text{ cm}^{-1}\text{M}^{-1}$). The isolation of recombinant YtvA has been described elsewhere.^{4,15} Absorption spectra and thermal recovery kinetics traces were recorded at a UV2401-PC spectrophotometer (Shimadzu, Duisburg, Germany). Steady-state fluorescence was measured at a Varian Eclipse Fluorimeter by using a 5 nm emission slit width and a scanning speed of 300 nm/min. Fluorescence quantum yields were determined with wild type YtvA as reference ($\Phi_{\text{F}} = 0.22$ in phosphate buffer).² Time-resolved fluorescence was measured on a single photon-counting apparatus (model FL900, Edinburgh Analytical Instruments, Livingston, UK). Transient absorbance changes after nanosecond-laser flash excitation were recorded with the LFP111 detection system (Luzchem, Ontario, Canada). Molecules were excited by a Nd:YAG-driven, tunable OPO laser (Nd:YAG, Innolas, Garching, Germany; OPO, GWU Lasertechnik, Erftstadt, Germany). The experiments (at 20°C with 1 cm light-path quartz cuvettes) were performed in the linear range of laser energy vs. transient absorbance changes with $\lambda_{\text{exc}} =$

450 nm for YtvA WT, 410 nm for 5DFMN-LOV, and 530 nm for 1DFMN-LOV. Data analysis employed the Origin software. A blue light-emitting Led-Lenser V8 lamp was used for steady-state irradiation (Zweibrüder Optoelectronics, Solingen, Germany).

Computational details

Molecular dynamics

Preparatory molecular dynamics (MD) simulations with stochastic boundary conditions and explicit solvent were carried out using the CHARMM (version 31b1)^{16,17} program. The X-ray structure of the YtvA LOV-domain¹⁸ (PDB:2PR5, chain A) was used as starting geometry. The protein atoms and the water molecules were described with the CHARMM22 all-atom force-field¹⁹ and the TIP3P²⁰ model, respectively. Rotamers for asparagine, glutamine, and histidine residues were analyzed with the NQ-FLIPPER (Version 2.7) program.²¹ The protonation states of these residues were defined on the basis of empirical pKa values obtained with the web interface of PROPKA software^{22,23} and thereafter verified by visual inspection. For the remaining residues, the protonation states were determined from the force-field topology using the HBUILD facility in the CHARMM program.²⁴ The initial X-ray coordinates of FMN¹⁸ served as template for building the artificial chromophores in the protein. To avoid the derivation of force-field parameters for the isoalloxazine moiety of 1DFMN and 5DFMN, the MD runs were done with a combined quantum mechanics / molecular mechanics (QM/MM) approach using the self-consistent-charge density functional tight-binding (SCC-DFTB) method as QM component.^{25,26} For the ribityl chain of the deazaflavins, force-field parameters were taken from FAD.²⁷ The QM region was connected to the MM region at the atom CS1 of the deazaflavin (see Figure 1) using the generalized hybrid orbital (GHO) treatment.^{28,29}

This choice of QM/MM boundary seems justified since the ribityl side chain has only a minimal effect on the absorption spectra, while it helps stabilizing the chromophore inside the protein.³⁰ No cutoff was imposed for the QM/MM electrostatic interactions. Within the MM region, a group-based extended electrostatic approach³¹ was used, i.e., the electrostatic interactions were evaluated from Coulomb's law for particles closer than 12 Å, and from group multipole interactions above this distance.

The system was neutralized by placing sodium ions on the protein surface near negatively charged residues. The system was solvated in an equilibrated water ball with a radius of 35 Å, with origin at the center of mass of the isoalloxazine ring of the flavin. A spherical quartic boundary potential was applied on the water molecules, in order to prevent them from diffusing away and to simulate the interface to the bulk. All bonds involving hydrogen were constrained using the SHAKE algorithm, with a relative geometric tolerance of 10^{-10} . The solvated system was relaxed by performing energy minimizations (250 steps of steepest descents; 250 steps of ABNR), with all non-water residues kept frozen. Thereafter, successive MD simulations of 15 ps were run, applying decreasing harmonic restraints (force constants reduced from 90 to 20 kcal/mol*Å²) to the protein and heating the system gradually to 300 K. Finally, all restraints were removed and a production MD of 2 ns was carried out using a NVT ensemble and a time step of 1 fs. The trajectory was visualized with help of the VMD (version 1.8.7) program.³²

QM/MM geometry optimizations

QM/MM optimizations were done for selected snapshots taken randomly from the MD production run. They were carried out in hybrid delocalized internal coordinates (HDLC) using the ChemShell³³ package with the HDLC optimizer.³⁴ The MM part was always

represented by the CHARMM22 force field using the DL_POLY driver as implemented in ChemShell. In the ground-state optimizations with the TURBOMOLE (version 5.9.1) program,^{35,36} the QM region was described by the B3LYP³⁷⁻³⁹ functional and the TZVP basis set.⁴⁰ In the excited-state optimizations of singlet (S_1) states, time-dependent density functional theory (TD-DFT)⁴¹⁻⁴⁵ was applied at the same level (B3LYP/TZVP) making use of the analytical gradient code in TURBOMOLE. For the T_1 state, TD-DFT sometimes failed due to triplet instabilities (i.e., the T_1 state was at some points of the optimization run lower in energy than the singlet ground state), and therefore, unrestricted DFT (UB3LYP/TZVP) was used. An electrostatic embedding scheme⁴⁶ was adopted: the fixed MM charges were incorporated into the one-electron part of the QM Hamiltonian, and QM/MM electrostatic interactions were evaluated from the QM electrostatic potential and the MM atomic charges. No cutoffs were imposed for the nonbonding QM/MM interactions. Hydrogen link atoms were used at the QM/MM boundary with the charge shift model.^{47,48}

After visual inspection of the binding pocket of the YtvA LOV protein with the incorporated artificial chromophore (see left side of Figure 2), we defined a small QM region (QM-1, 38 atoms) and a larger one (QM-2, 100 atoms). QM-1 consists of the isoalloxazine ring (cut by the ribityl chain) and the side chain of CYS62, while QM-2 also includes the vicinal residues of CYS62, the side chain of the surrounding residues, and some water molecules. Both QM regions were used to compute the relative energies of optimized structures (see below and Supporting Information). Spectroscopic calculations with QM-2 were too cumbersome and were thus only done with QM-1 (see below).

The stationary points on the ground-state potential energy surface (PES) of the dark and adduct states were verified by performing QM/MM frequency calculations for the QM-1 region.

To obtain detailed information on the mechanism of adduct formation, reaction paths on the excited-state PES were investigated through QM/MM restrained geometry optimizations along suitably defined reaction coordinates.

Energy evaluations and electronic absorption spectra.

The density functional theory / multireference configuration interaction (DFT/MRCI) method⁴⁹ was used as QM component for more accurate energy evaluations and for calculating electronic absorption and fluorescence spectra at optimized QM/MM geometries (QM region QM-1). This method has been applied successfully to study photophysical processes for diverse chromophores.⁵⁰⁻⁵³ According to recent benchmarks it generally provides reasonably accurate excited-state energies, with typical deviations of around 0.2 eV from a reference set of theoretical best estimates.^{54,55} The underlying idea behind this method is to incorporate dynamical electron correlation at the DFT level while treating strong nondynamical effects by MRCI. Geometry optimizations with DFT/MRCI are currently not yet practical since analytic gradients are not available and numerical gradients are too costly computationally.

Spin-orbit matrix elements (SOME) between correlated DFT/MRCI wave functions were computed with the spin-orbit coupling kit (SPOCK)^{56,57} using the one-center mean-field approximation to the Breit-Pauli Hamiltonian. This non-empirical approach with an effective one-electron operator treats the demanding two-electron terms of the full

Hamiltonian in a Fock-like manner^{58,59} and thus substantially reduces the computational effort without significant loss of accuracy.

Results

YtvA-LOV-1DFMN

Spectroscopy: The absorption spectrum of 1DFMN in YtvA shows two maxima centered at 530 and 360 nm (Figure 3). Compared with FMN in YtvA ($\lambda_{\text{max}} = 445$ nm), there is a strong bathochromic shift of the first band which is even slightly larger for 1DFMN in water ($\lambda_{\text{max}} = 537$ nm).¹² The fine-structured, three-peaked absorption band is indicative of the incorporation of the chromophore into the protein binding site.

Interestingly, light absorption by 1DFMN does not lead to photoinduced processes such as singlet-triplet conversion that are typical for flavins. Likewise, in aqueous solution, 1DFMN lacks photochemical activity,¹⁴ no fluorescence can be detected under steady state-conditions, and only ps detection yields a very weak fluorescence (Φ_F 0.002) with lifetimes of 1.8 and 12.5 ps.¹² In the protein-incorporated form, a small increase of the fluorescence quantum yield is observed in the present work for 1DFMN (Φ_F 0.008), with lifetimes in the low nanosecond range (the low quantum yield and the experimental conditions impaired a more precise measurement of the lifetime).

Molecular dynamics: The initial equilibration of the LOV domain in the MD simulations helps identifying residues that stabilize the chromophore in the binding site. The pterin

moiety of the chromophore is surrounding by polar residues (GLN66, ASN94, ASN104 and GLN123, see Figure 2 left), interacting through hydrogen bonding. The substitution of the nitrogen atom N1 by a non-polar CH group in 1DFMN causes a rotation of the side chain of GLN66 such that it points towards the protein during most of the simulation. On the other hand, the intermolecular distances around the N5 atom and the surrounding residues (CYS62 and GLN123) resemble the situation in the parent chromophore,³⁰ i.e., the thiol group of CYS62 adopts two conformations, being engaged in a hydrogen bond with a water molecule or with the N5 atom of 1DFMN. The variations of selected bond distances along the MD trajectory are plotted in Figure S1 of the Supporting Information.

Theoretical vertical absorption spectra: Vertical excitation energies and oscillator strengths of 1DFMN in YtvA have been computed at the QM/MM optimized geometries of four MD snapshots. Table 1 lists the individual QM(DFT/MRCI)/MM results for the lowest singlet and triplet excited states as well as the corresponding averages and compares them with the DFT/MRCI results for isolated and microsolvated 1DFMN and with the available experimental data for 1DFMN in YtvA. The first band is dominated by a $\pi_H \rightarrow \pi_L$ HOMO-LUMO transition and is computed to occur around 475 nm (2.61 eV) with an oscillator strength of 0.296 (average values); experimentally we observe an absorption maximum at 531 nm (2.34 eV). The transitions at higher energy with mean excitation wavelengths of 369 and 337 nm are of $n \rightarrow \pi_L$ character and thus very weak (not seen experimentally). The second peak in the experimental spectrum (Figure 3) at 368 nm (3.37 eV) corresponds to transition at 348 nm (3.56 eV) which is computed to be

moderately intense (average oscillator strength of 0.097) and associated with partial charge transfer from the thiol group of CYS62 to the isoalloxazine ring.

In the triplet manifold, the lowest state is again of $\pi_H \rightarrow \pi_L$ character, with a mean excitation wavelength of 650 nm (1.91 eV). This is the only triplet state that lies energetically below the intense S_1 state, which has drastic consequences for the photophysics of this system (see below). The second triplet state ($n \rightarrow \pi_L$, 432 nm, 2.87 eV) already lies 0.28 eV above the S_1 state (on average). Finally, the charge-transfer triplet state has an average excitation wavelength of 405 nm (3.06 eV).

1DFMN-LOV photophysics: Geometry optimizations of the S_1 state were carried out at the TD-B3LYP/CHARMM level. The main differences from the optimized ground-state geometry are larger bond distances in the isoalloxazine rings II and III, which can be understood from the nodal pattern of the frontier molecular orbitals (MOs) in these rings (Figure S2, Supporting Information). Geometry relaxation after HOMO-LUMO excitation stabilizes the system by 10.0 kcal/mol at the QM(DFT/MRCI)/MM level. At the optimized S_1 geometry, we compute an emission wavelength of 630 nm (1.97 eV) that matches well with our experimental value of 610 nm (2.03 eV). The calculated oscillator strength (0.16) translates into an estimated fluorescence lifetime of 262 ns, contrary to the experimental observation of a much shorter lifetime. This suggests the presence of other deactivation channels in this system.

Previous experimental results, supported by theoretical calculations,^{12,14} revealed that no triplet state of 1DFMN is formed in water or acetonitrile solution. This also holds for 1DFMN bound to the YtvA-LOV domain. Triplet formation is not seen experimentally,

and according to our calculations, intersystem singlet-triplet crossing is unlikely because of large energy gaps: at its minimum geometry, the S_1 state lies 0.74 eV above the T_1 state and 0.49 eV below the T_2 state (see Table 2).

In addition, the experimental data do not show any evidence of adduct formation for 1DFMN in YvtA-LOV. Excited-state kinetics data in solvent point to a radiationless deactivation of the S_1 state through internal conversion, presumably through a S_1/S_0 conical intersection (CIn). We have used two strategies to search for such conical intersections. The first one is based on the Bearpark algorithm that is implemented in ChemShell at the QM/MM level,^{60,61} making use of the semiempirical OM2/MRCI method as QM component.⁶²⁻⁶⁴ The resulting optimized CIn structure was taken as initial guess for a QM/MM excited-state geometry optimization at the TD-B3LYP/CHARMM level. Close to a S_1/S_0 conical intersection, TD-DFT must fail, and the corresponding geometry is a rough approximation to the conical intersection so that a single-point DFT/MRCI calculation at this geometry will provide a rough estimate of the associate energies. The second and more time-consuming strategy employs restrained excited-state geometry optimizations along suitable reaction coordinates, followed by single-point DFT/MRCI energy evaluations.

Two conical intersections were obtained through these strategies for one snapshot (number 1), with structures illustrated in Figure 4. The first one (left) is characterized by a strong puckering of the CH group at position 1, with an out-of-plane deformation of the hydrogen atom at C1. This bent structure is called E_1 according to the Cremer-Pople-Boeyens classification scheme^{65,66} and resembles the main deactivation channel found in pyrimidine molecules like uracil.⁶⁷⁻⁶⁹ Other major changes relative to the ground-state

geometry are found for the bond lengths in ring III: C1-C10a (+0.12 Å), C4a-C10a (-0.05 Å), and C4-C4a (-0.04 Å); for further data see Table S1 in the Supporting Information. Energetically, however, conical intersections of this type are not accessible, as they are found more than 100 kcal/mol above the ground-state and about 53 kcal/mol (2.3 eV) above the minimum of the S_1 state. This channel should thus play no role in the deactivation process.

By contrast, the second conical intersection (Figure 4, right, found by scans of putative reaction paths) is characterized by a hydrogen transfer from the SH group of the CYS62 residue to the N5 atom of the flavin. This hydrogen transfer is facilitated by the increased proton affinity of N5 in the excited state.⁷⁰ Geometry parameters of the conical intersection (such as the bond lengths in the isoalloxazine core) are close to those of the S_1 minimum, with major differences only in the intermolecular distances between the thiol group and the flavin ring. The migrating hydrogen atom already lies roughly in the flavin plane and is almost bound to N5 (distance of 1.12 Å). Energetically, this conical intersection lies 18.0 kcal/mol below the S_1 minimum and, as expected, ground-state QM/MM geometry optimization of this structure leads to dark-state recovery.

From restrained geometry optimizations along the reaction path for the hydrogen transfer, we can estimate the energy barrier for the transition state relative to the S_1 minimum as 10.9 kcal/mol. This QM(DFT/MRCI)/MM value for the barrier is close to the value of 10.1 kcal/mol obtained from single-point coupled cluster QM(CC2/TZVP)/MM calculations, but about twice as high as the barrier of 5.4 kcal/mol obtained directly from the restrained QM(TD-B3LYP/TZVP)/MM geometry optimizations; however, the latter result is considered less reliable because of the increasing charge-transfer character along

the path. In the transition state, the migrating hydrogen atom is equidistant to the atoms N5 of flavin and sulfur of CYS62 (1.50 Å). Electronically, the transition state is a biradical with one electron localized at the sulfur atom of CYS62 and a second one mainly localized at the flavin atoms N5 and C4a. A linearly interpolated path between the Franck-Condon point and this transition state (Figure S3, Supporting Information) yields an energy barrier in the S_1 state of 11.0 kcal/mol.

Based on these results we now address the deactivation mechanism for the 1DFMN chromophore inside the binding pocket of YtvA-LOV (see Figure 5). After blue-light absorption and population of the S_1 state, geometric relaxation of the chromophore leads to some expansion of flavin rings II and III. Two main deactivation channels are accessible from the S_1 minimum: The chromophore can either decay to the ground-state by fluorescence, with a calculated lifetime in the 250-260 ns range, or it can overcome an energy barrier of ca. 11 kcal/mol in the S_1 state to reach a S_1/S_0 conical intersection, with return to the ground-state PES and recovery of the dark state. In the latter mechanism, one should note that the transition state on the S_1 PES has a similar energy as structures in the Franck-Condon region that are initially populated upon photoexcitation (Table 2). In the absence of dynamics simulations, it is difficult to judge whether the system can overcome or even bypass the S_1 barrier and reach the intersection seam, which lies 29 kcal/mol below the Franck-Condon region and 18 kcal/mol below the S_1 minimum. In the literature, there is at least one report on a non-fluorescent chromophore that is capable of overcoming a similar barrier in excited-state dynamics.⁷¹ At present, the internal conversion mechanism can thus only be regarded as a tentative explanation for the very short fluorescence lifetime of 1DFMN in YtvA-LOV.

YtvA-LOV-5DFMN

Spectroscopy: The absorption maxima of 5DFMN-LOV are found at 400 and 340 nm, significantly blue-shifted relative to the YtvA wild type (WT) protein ($\lambda_{\text{max}} = 445$ nm). Similar to YtvA WT, illumination with blue light leads to the formation a photoproduct with an absorption maximum around 340 nm (Figure 6, A) that overlaps with the second absorption band of the parent state. Under steady-state irradiation, photoproduct formation is complete within 45 min (no further change in absorbance) and thus takes significantly longer than in the case of YtvA WT (7 min). The main difference from YtvA WT is the remarkable stability of the lit state, as incubation for more than one day does not yield any thermal recovery of the initial dark state. In contrast to LOV domains in general, the photoproduct shows an unexpected photochemical activity: Laser flash photolysis ($\lambda_{\text{exc}} = 353$ nm) restores the dark form, but also leads to partial decomposition (Figure 6, B), preventing exhaustive irradiation. One complicating factor in the experimental work is the almost complete overlap between the S_1 absorption band of the lit (“photoadduct”) form and the S_2 absorption band of the parent (“dark”) state.

Incorporation of 5DFMN into the protein reduces the fluorescence life time compared to that in aqueous solution, 3.2 vs. 5 ns, and also causes a slight decrease in Φ_F (from 0.52 in H_2O to 0.45 in LOV, Figure 7). A fluorescence signal can also be detected for the photoproduct of 5DFMN-LOV (around 400 nm), but this fluorescence is very weak and always overlaid by the signal of the not completely converted dark state. A thorough inspection of the emission around 400 nm excludes impurities or detection errors and unambiguously assigns this signal to fluorescence of the photoproduct. The fluorescence

properties of both deazaflavins (in free form and after protein incorporation) are summarized in Table 3.

Nanosecond laser flash excitation of 5DFMN-YtvA at 400 nm gives rise to a broad absorption band centered at 500 nm that decays with a lifetime of 59 μ s (Figure 8), significantly longer than that of the WT protein (1.7 μ s). In order to avoid contributions of the photoproduct (that would cause, due to the spectral overlap of both forms, additional photochemistry during signal accumulation), only single-shot experiments are shown in Figure 8. Interestingly, the triplet lifetime of 5DFMN in aqueous solution ($\tau_T = 14 \mu$ s) is shorter than that of FMN ($\tau_T = 29 \mu$ s).¹⁴ Extended triplet decay times have recently also been reported for a point mutation, N94A ($\tau_T = 129 \mu$ s).⁷² The asparagine residue in the WT protein is known to interact with C(2)=O and N(3)H,¹⁸ stabilizing the conjugative network of the isoalloxazine ring. Exchange of asparagine by alanine at this position thus destabilizes the uracil moiety, and a similar effect may also operate when replacing the N5 atom by a CH group.

Molecular dynamics: The MD simulations show that the substitution of the N5 atom by a CH group directly affects the structure of the binding pocket. In contrast to the case of the 1DFMN chromophore, the side chain of GLN123 adopts a different orientation during the dynamics: The carbonyl group points towards either the flavin ring or the water molecules W642 and W643 (see Figure 2, right), with the first orientation predominant during the simulation. Moreover, since a possible hydrogen acceptor is missing in the flavin (N5 atom), the thiol group of CYS62 interacts via hydrogen bonding with water W622 for most of the MD run.

Theoretical vertical excitation spectra: Table 5 lists the vertical excitation wavelengths and oscillator strengths for the five optimized snapshots and their average values, and compares them with TD-DFT results for the isolated chromophore, with DFT/MRCI results for microsolvated 5DFMN, and with the present experimental values for 5DFMN in YvtA. Plots of the relevant frontier molecular orbitals are shown in Figure S5 (Supporting Information). In the singlet manifold, the calculated excitation wavelengths of the first two intense UV bands (average values of 396 and 329 nm) agree very well with the experimental peak maxima (400 and 335 nm). These excitations correspond to $\pi \rightarrow \pi^*$ transitions (L_a and L_b , respectively) that are localized at the isoalloxazine ring. The next transition with an average wavelength of 301 nm is of $n \rightarrow \pi^*$ type and involves the oxygen lone pair of the C(2)=O group; its computed intensity is about 1000 times smaller than those of the first two transitions. In the triplet manifold, the T_1 state (473 nm, 2.62 eV) and the T_2 state (422 nm, 2.94 eV) are both computed to be energetically lower than the S_1 state (396 nm, 3.13 eV). Both are characterized by $\pi \rightarrow \pi^*$ single excitations (L_a and L_b). The T_3 state (325 nm, 3.82 eV) is of $n \rightarrow \pi^*$ type and lies close to the T_2 state (327 nm, 3.79 eV), which has direct bearing on the photophysics (see below). The calculated order of excited states is thus analogous in the singlet and triplet manifolds.

Overall, the present QM(DFT/MRCI)/MM results for the protein-embedded 5DFMN chromophore are quite close to the TD-DFT results for isolated 5DFMN¹³ and to the DFT/MRCI results for microsolvated 5DFMN in a COSMO continuum solvent.¹⁴

5DFMN-YtvA photophysics and photochemistry: In aqueous solution, 5DFMN undergoes efficient triplet formation via intersystem crossing.¹⁴ Here we investigate the relaxation pathways of 5DFMN in YtvA after photoexcitation. The two lowest bright states, S_1 and S_2 , are accessible experimentally. In the theoretical work, we address the S_1 state and focus on three snapshots (numbers 3-5) to limit the computational effort.

Starting from the Franck-Condon point, geometry optimization of the S_1 state leads to an expansion of rings II and III of the isoalloxazine moiety, whereas the distance between cysteine (SH) hydrogen atom and the C5 atom of flavin remains nearly constant (average value of 4.43 Å in S_1 versus 4.40 Å in S_0), consistent with the local character of this electronic transition. Fluorescence from the S_1 minima of the three snapshots yields emission energies in the range of 2.66-2.88 eV, and the calculated oscillator strengths of 0.1-0.2 translate into lifetimes in the range of 10-90 ns. Fluorescence in 5DFMN-LOV is thus calculated to be one order of magnitude faster than in 1DFMN-LOV. A conical intersection search using the Bearpark method yields an E_1 structure similar to the one shown on the left side of (with puckering of the carba group at position 5). However, this structure lies energetically too high (more than 50 kcal/mol above the S_1 minimum, QM/MM) to play a role in the photocycle. An energetically accessible crossing between the S_1 and T_2 surfaces is found along the S_1 geometry relaxation pathway. At the S_1 minimum geometry, the energy gap between these two states is only 0.05 eV, which readily allows for an intersystem crossing to the T_2 state. According to Kasha's rule, there will then be a very fast internal conversion $T_2 \rightarrow T_1$. Geometry optimization of the T_1 state yields a structure similar to the S_1 state, as expected since the wave function of both states is dominated by a singly excited $\pi \rightarrow \pi^*$ (HOMO-LUMO) configuration.

At the optimized T_1 geometries of the three snapshots, the vertical $T_1 \rightarrow T_n$ excitations have been computed at the DFT/MRCI level to compare with the transient spectra. We find UV/Vis transitions with moderate intensity in the range between 450-525 nm, in good agreement with experiment (see data in Figure 8, B).

The T_1 species is taken as starting point for studying the reaction mechanism. In view of the compact binding pocket and the proximity of the thiol group to the flavin, we have considered hydrogen transfers from the SH group of CYS62 to the flavin molecule. Since the computed barriers for the transfer to the C5a atom are very high (data not shown), we have focused on the transfers to the C5 and C4a atoms (see Figure 1) and performed restrained QM/MM geometry optimizations on the T_1 surface, using the difference of distances $d(S-H) - d(H \cdots C)$ as reaction coordinate (with $C = C5$ or $C4a$). The energies along these pathways are obtained from QM(DFT/MRCI)/CHARMM single-point calculations at optimized QM(UB3LYP)/CHARMM geometries. Because of the high computational effort, these scans have been done only for one snapshot (number 5), which has the thiol group in an optimal position for hydrogen transfer.

Figure 9 shows the calculated QM/MM energy profiles for the T_1 state along with the corresponding S_0 ground-state energies for both reactions. In the initial stage of both reactions, a MM water molecule moves away from CYS62 into hydrogen bonding distance of the flavin O4 atom which causes the early small dip in the energy profiles (Figure 9). Apart from this, there are no other energetically relevant changes in the MM part during the reactions.

The hydrogen transfer to C5 (mechanism 1, black curves in Figure 9) has to overcome an energy barrier of 16.3 kcal/mol in the T_1 state. In the transition state, the H-C5 bond is

already partially formed (1.33 Å) and the C5 atom is slightly pyramidal. Electronically, the excitation is at this point still localized in the flavin moiety. However, the next point along the reaction coordinate already shows 15% charge-transfer character (from CYS62 to flavin), and this contribution increases until the T_1 - S_0 intersystem crossing point (ISC1) is reached. ISC1 is computed as 46.8 kcal/mol above the dark state and contains a covalent H-C5 bond (1.10 Å). Electronically, it is a neutral biradical with spin density distributed over the CYS62 and flavin moieties. The high value of the spin-orbit matrix element at ISC1 (240.0 cm^{-1}) indicates a high probability for T_1/S_0 intersystem crossing. Ground-state geometry optimization starting from ISC1 leads to the formation of a species (called adduct 1) with a covalent S-C4a bond and a sp^3 carbon atom C5 that carries two hydrogen atoms. This adduct resembles the product obtained from the parent FMN chromophore in YvtA-LOV upon blue-light irradiation.¹⁸

A potentially possible hydrogen transfer to C4a, and a bond formation between sulphur and C5, as was suggested in a former study of this system,¹⁰ (mechanism 2, red curves in Figure 9) requires more activation (27.7 kcal/mol) in the T_1 state, the barrier is 11.4 kcal/mol higher than in the case of C5. In the transition state, the C4a atom is pyramidalized, and the migrating hydrogen atom is roughly midway between the thiol sulfur atom (1.61 Å) and C4a (1.51 Å). The charge-transfer character of the T_1 state again increases significantly after passing the transition state. The intersystem crossing point for this reaction (ISC2) lies 51.8 kcal/mol above the ground-state minimum and has a large T_1/S_0 spin-orbit matrix element of 224.6 cm^{-1} . Ground-state geometry optimization from ISC2 leads to an adduct with a covalent S-C5 bond and a quaternary C4a atom (adduct 2).

Using the optimized structures obtained for snapshot 5 (see above) to guide the definition of suitable starting geometries, we have also optimized the possible adducts for snapshots 3 and 4. The resulting relative energies are summarized in Table 5. Both adducts 1 and 2 are higher in energy than the dark state for all snapshots. The two adducts lie within 1 (2) kcal/mol for snapshot 5 (4), whereas adduct 1 is more stable than adduct 2 by 14 kcal/mol for snapshot 3. Although the energy difference of 11.4 kcal/mol in the computed T_1 barriers should favor the formation of adduct 1, we do not yet rule out a possible involvement of adduct 2 at this point. Experimentally, it will be difficult to distinguish between the two adducts by their absorption spectra which are predicted to be very similar (see Tables S4 and S5, Supporting Information).

YtvA-LOV-5DFMN: Dark-state recovery

Spectroscopy: We have investigated the photochemical activity of the photoadduct form of 5DFMN-LOV in more detail, motivated by its unique behavior in LOV domains. Preliminary studies had addressed this photochemistry, but without a thorough time-resolved analysis.¹⁰ Laser flash excitation of the photoadduct form of the 5-deaza protein ($\lambda_{\text{exc}} = 355$ nm) generated a transient species with maximal absorbance around 410 nm and a life time $\tau_T = 46$ μ s (Figure 10). A detailed analysis of the triplet kinetics was performed at detection wavelengths between 375 and 600 nm. This turned out to be difficult as (i) the excitation wavelength used for the photoadduct ($\lambda_{\text{exc}} = 355$ nm) also excited the S_2 state of residual amounts of the photochemically formed parent state, and (ii) the triplet decay from the photoadduct was partly overlaid with the formation kinetics of the parent state, resulting in very low intensity changes. Again, in order to avoid

accumulation of the reaction product (parent state), single-shot experiments were performed. When these μs decay kinetics were followed in the wavelength range between 390 and 430 nm, they yielded widely varying lifetimes; an example for this composed kinetics is given in Figure 11A, showing a low-intensity rise kinetics. Shifting the observation wavelength to 450-600 nm resulted in the detection of the triplet decay with $\tau_{\text{T}} = 46 \mu\text{s}$ (Figure 11, B), identical to the decay time observed at 370-385 nm.

The simultaneous presence of both photoactive forms rendered the spectral analysis difficult. This turned out to be the case also in the fluorescence analysis, in which both photoactive forms were detected. However, the fluorescence spectrum of the photoadduct exhibited a fluorescence band centered around 420 nm, for which an excitation spectrum was recorded, yielding a maximum at 325 nm (coinciding with the absorption maximum of the photoadduct). These findings together with the shorter lifetime of the triplet state clearly ascribe these photochemical properties to the photoadduct.

Theoretical calculations: Experimentally, the 5DFMN-LOV adduct is thermally quite stable. This implies large barriers on the ground state PES to dark-state recovery, which would require hydrogen abstraction from C5 (or C4a) by a strong base in the binding pocket, followed by thiolate elimination. We have not studied these ground-state reactions, but focused on the photophysics and photochemistry of the adducts to model the observed photochemical recovery of the parent state.

In the calculated vertical excitation spectra of adduct 1 (with a covalent S-C4a bond), the first absorption band has an average excitation wavelength of 344 nm (3.60 eV) and a high oscillator strength of 0.367. It is dominated by a single HOMO $\rightarrow$ LUMO transition;

the HOMO contributes to the bonding along the S-C4a bond, contrary to the LUMO which is mainly localized in the flavin rings. The second band at 306 nm (4.05 eV) involves a charge-transfer transition (from the CYS62 sulfur lone pair to the flavin) and is much less intense than the first band (by about one order of magnitude). The other singlet absorption bands are found at shorter wavelengths, with very low intensity. In the triplet manifold, the T_1 state at 404 nm (3.07 eV) also corresponds to a single HOMO→LUMO excitation. The T_2 state at 339 nm (3.66 eV) again has charge-transfer character and is energetically close to the S_1 state (3.60 eV, see above).

On the basis of these spectroscopic results, one might expect that S-C4a bond cleavage could be feasible in the S_1 state. Indeed, excited-state geometry optimization for this state yields a biradical formation already in the S_1 excited state with the S-C4a distance increasing from 1.9 Å in the S_0 ground state to 2.4 Å. Other major changes occur for the bond distances in the flavin ring III (Table S2, Supporting Information). This S_1 minimum of adduct 1 lies only 57 kcal/mol above its ground-state minimum and 85 kcal/mol above the minimum of the dark state. The corresponding fluorescence peak is found at 738 nm (averaged value) and has very low oscillator strength (about 0.01). From the S_1 minimum, one may expect that either the dark state is recovered through hydrogen abstraction or the triplet state is populated via intersystem crossing. Optimization of the T_1 state also yields a biradical structure, but in this case the thiol radical is far apart from the C4a atom of the deazaflavin (3.57 Å, averaged over three snapshots), and the isoalloxazine moiety has an almost planar structure (with two C5-H bonds). Energetically, this T_1 minimum lies 28 kcal/mol above the S_0 ground state of adduct 1.

Dark state recovery can be achieved by hydrogen abstraction on the T_1 surface, through the same transition state as found for the forward reaction (see Figure 12).

We now turn to adduct 2 carrying a covalent S-C5 bond, assuming that it may have been formed in small amounts by the alternative reaction mechanism 2 considered for the T_1 state (see Figure 9). The computed excitation wavelengths of this adduct are given in the Supporting Information (Table S4). Geometry optimization of the S_1 state causes a bond expansion of flavin rings I and II and a slight elongation of S-C5 by 0.02 Å (relative to the ground state), but no bond is broken in this case. Similar results are found for the T_1 state. Hence, the flavin remains covalently bound to the protein in each case so that there is no evidence for photochemical dark-state recovery via adduct 2. Hence, there should be fluorescence from the S_1 minimum (average emission wavelength of 443 nm and oscillator strength of 0.213). The computed triplet-triplet spectrum of adduct 2 exhibits a strong absorption band at 520 nm, with high oscillator strength (0.186).

Rearrangement of adduct 2 on the ground-state surface could yield another adduct 3, by hydrogen transfer to the N1 atom (see Figure 13). It has been suggested on the basis of circular dichroism and ^{13}C NMR measurements that this adduct 3 with a covalent S-C5 bond and a N1-H bond could be the main photoproduct when 5DFMN is incorporated into the LOV2 domain of a phototropin from *Avena Sativa*.¹⁰ We have therefore computed its excitation wavelengths and the associated oscillator strengths (see Table S5, Supporting Information). Again, geometry optimization of the S_1 state does not lead to a minimum, but reaches a S_1/S_0 conical intersection in all snapshots (see Table 4) that is similar to the low-energy conical intersection in 1DFMN-LOV. Hence, there will be fast internal conversion back to the ground state of this adduct, and consequently the dark

state of the chromophore will not be recovered easily by photoexcitation of adduct 3. These results argue against a mechanism for the photoreaction that involves adduct 3.¹⁰

Conclusions

The photophysical and photochemical properties of the chromophores 1-deaza and 5-deaza flavin mononucleotide, 1DFMN and 5DFMN, incorporated into the LOV-domain of the blue light photoreceptor YtvA from *Bacillus subtilis* were characterized spectroscopically and through theoretical calculations.

The QM/MM calculations offer a tentative explanation for the observed lack of any photochemical activity of the protein-incorporated 1-deaza derivative. Photoexcitation of 1DFMN-YtvA populates the bright S_1 state, which after geometry relaxation decays to the ground state either via fluorescence or via internal conversion through a biradicaloid S_1/S_0 conical intersection. The computed fluorescence lifetime is in the 250-260 ns range, much longer than inferred experimentally. The radiationless deactivation pathway from the Franck-Condon region to the conical intersection is downhill overall (by 29 kcal/mol), but there is a barrier of 11 kcal/mol between the S_1 minimum and the conical intersection. If this barrier does not generate a dynamical impediment, there would be a path for fast internal conversion that might rationalize the very short-lived fluorescence of 1DFMN-YtvA (in the low nanosecond regime). This could be checked by excited-state dynamics calculations which are, however, beyond the scope of this work.

The behavior of 5DFMN-YtvA-LOV is less straightforward. This flavin derivative has an absorption with main peaks at 400 and 340 nm (blue-shifted from the WT protein) and a high fluorescence yield ($\Phi_F = 0.52$, compared to 0.27 for the WT protein). It is the first

compound identified so far that generates a thermally stable, photochemically reversible photoadduct in a LOV domain. Blue-light excitation generates the triplet state (supported by the proximity effect) that converts into a photoadduct with an experimentally observed lifetime of 59 μ s. The QM/MM calculations suggest the following mechanism for 5DFMN-YtvA-LOV. After photoexcitation to the S_1 state, there is an efficient intersystem crossing near the S_1 minimum to the T_2 state, which quickly relaxes to the T_1 state. On the T_1 surface, a hydrogen atom can be transferred from the CYS62 thiol group to the C5 atom of the flavin, via a biradicaloid transition state with a barrier of 16 kcal/mol, and the thus formed biradical can undergo another intersystem crossing to the S_0 ground state which triggers the barrierless formation of a photoadduct with a covalent S-C4a bond. In a qualitatively analogous manner, another photoadduct (with a covalent S-C5 bond and hydrogen addition to C4a) could be generated, but the computed barrier on the T_1 surface is quite high (27 kcal/mol). Concerning the photochemical dark-state recovery, photoexcitation of the adduct with the S-C4a bond causes immediate formation of a S_1 biradical already in the excited state with an essentially broken S-C4a bond, followed by intersystem crossing to the triplet state, from which the dark state can be regenerated. According to the QM/MM calculations, this photochemical back reaction is not feasible for other adducts with a S-C5 bond. The mechanistic scenario derived from the theoretical calculations on 5DFMN-YtvA is thus consistent with the experimental findings provided that the reactions involve a photoadduct with a covalent S-C4a bond.

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Supporting Information Available: The supporting information contains 1DFMN MD calculations and energetics, and 5DFMN structural details, energetics using a larger QM region, and Theoretical results for UV spectra of side products in the 5DFMN-LOV photocycle. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for four snapshots of 1DFMN-YtvA. The average values are also listed as well as DFT/MRCI literature values and experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.

State	excitation	snap 1	snap 2	snap 3	snap 4	average	DFT/ MRCI ^a	DFT/ MRCI ^b	exp. ^c
S ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	469 (0.319)	469 (0.308)	480 (0.269)	482 (0.261)	475 (0.289)	473 (0.276)	515	505, 531, 569
S ₂	$n_{\text{O}} \rightarrow \pi_{\text{L}}$	359 (0.073)	359 (0.079)	401 (0.001)	360 (0.001)	369 (0.039)	374 (0.001)	320	
S ₃	$n_{\text{ON2}} \rightarrow \pi_{\text{L}}$ $n_{\text{ON1}} \rightarrow \pi_{\text{L}}$	334	330 (0.001)	348 (0.014)	338 (0.012)	337 (0.009)	346 (0.003)	329	
S ₄	$P_{\text{S}} \rightarrow \pi_{\text{L}}$	356 (0.096)	351 (0.092)	340 (0.069)	347 (0.131)	348 (0.097)	326 (0.060)	362	368
T ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	636	636	676	654	650	660	693	
T ₂	$n_{\text{O}} \rightarrow \pi_{\text{L}}$ $n_{\text{ON2}} \rightarrow \pi_{\text{L}}$	443	442	419	425	432	399	368	
T ₃	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}$	406	403	410	399	405	399	447	
	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}$								

^a DFT/MRCI results in vacuum. From ref. ¹⁴.

^b DFT/MRCI results obtained for a microsolvated structure (four water molecules included) together with COSMO. From ref. ¹⁴.

^c Maxima of experimental spectra. This work.

Table 2: QM and QM/MM energies for snapshot 1 relative to the ground-state minimum, in kcal/mol. The region QM-1 was chosen, and DFT/MRCI used as QM method (see text).						
	S ₀ minimum	S ₁ vertical (minimum)	T ₁ vertical (minimum)	T ₂ vertical (minimum)	S ₁ /S ₀ CIn “E ₁ ” ^a	S ₁ /S ₀ CIn planar ^b
QM	0.0	61.0 (50.9)	45.0 (30.9)	64.5 (62.1)	94.9	28.3
QM/MM	0.0	61.0 (50.3)	45.0 (33.2)	64.5 (61.5)	102.9	32.1
^a Conical intersection illustrated on the left side of Figure 4. The energy gap between S ₁ and S ₀ states is 0.14 eV.						
^b Conical intersection illustrated on the right side of Figure 4. The energy gap between S ₁ and S ₀ states is 0.07 eV.						
Values in parentheses are calculated at the S ₁ minimum geometry.						

Table 3: Fluorescence properties of free flavins in H ₂ O and in protein-bound form.					
	Fluorescence max $\lambda_{\text{max}}/\text{nm}$	Fluorescence life time		Fluorescence quantum yield	
		in H ₂ O, τ_F/ns	in LOV, τ_F/ns	in H ₂ O, Φ_F	in LOV, Φ_F
YtvA WT	520	4.8 ^a	2.2 ^b	0.27 ^a	0.22 ^b
1-deaza LOV	600-645	ps ^c	ns	0.002 ^c	0.008
5-deaza LOV	445	5	3.2	0.52	0.45
^a From ref. ⁷³ . ^a From ref. ² . ^b From ref. ¹² .					

Table 4: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for five snapshots of 5DFMN-YtvA. The average values are also listed as well as TD-DFT and DFT/MRCI literature values and experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.

State	Excitation	snap 1	snap 2	snap 3	snap 4	snap 5	average	TD-DFT ^a	DFT/MRCI ^b	exp. ^c
S ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	397 (0.278)	395 (0.263)	389 (0.322)	392 (0.317)	402 (0.272)	396 (0.290)	373 (0.169)	385 (0.324)	400
S ₂	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}} +$ $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}$	330 (0.258)	339 (0.287)	322 (0.221)	325 (0.212)	327 (0.265)	329 (0.249)	313 (0.135)	325 (0.151)	335
S ₃	$n_{\text{O}} \rightarrow \pi_{\text{L}}$	302 (0.0009)	290 (0.0003)	314 (0.0085)	308 (0.0027)	293 (0.0001)	301 (0.025)	292 (<0.001)	278 (0.000)	
T ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	475	471	472	469	479	473	498	454	500
T ₂	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}} +$ $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}$	426	435	416	415	420	422		414	
T ₃	$n_{\text{O}} \rightarrow \pi_{\text{L}}$	327	327	325	324	325	325		320	

^a TD-B3LYP/6-31G(d) results in vacuum. From ref. ¹³.

^b DFT/MRCI results obtained for a microsolvated structure (four water molecules included) together with COSMO. Oscillator strengths from calculations in vacuum. From ref. ¹⁴.

^c Maxima of experimental spectra. This work.

Table 5: Relative energies of 5DFMN-YtvA species calculated at the QM(DFT/MRCI) / CHARMM level of theory for selected snapshots (see text). Values in kcal/mol.				
	snap 3	snap 4	snap 5	Average
Dark state				
S ₀	0.0	0.0	0.0	0.0
S ₁ vertical	73.5	73.0	71.1	72.5
S ₁ minimum	66.1	65.1	59.3	63.5
T ₁ minimum	54.3	54.7	49.2	52.7
T ₁ transition state 1 / ISC1			65.5 / 46.8	
T ₁ transition state 2 / ISC2			78.5 / 51.8	
Adduct 1				
S ₀	32.2	31.2	21.1	28.2
S ₁ vertical	115.0	113.4	104.8	111.1
S ₁ minimum	90.0	87.3	78.1	85.1
T ₁ minimum	60.9	58.6	48.9	56.1
Transition state			65.5	
Adduct 2				
S ₀	46.2	29.1	21.6	32.3
S ₁ vertical	134.8	118.0	108.3	119.9
S ₁ minimum	121.6	107.0	98.4	107.4
T ₁ minimum	106.9	90.5	79.5	89.5
Adduct 3				
S ₀	21.5	18.5	8.4	16.1
S ₁ /S ₀ CIn	74.3	58.5	49.5	59.9

Table 6: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for three snapshots of adduct 1 of 5DFMN-YtvA. The average values are also listed together with the available experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.						
State	excitation	snap 3	snap 4	snap 5	average	exp. ^a
S ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	345 (0.363)	348 (0.368)	342 (0.348)	344 (0.350)	340
S ₂	$\text{P}_{\text{S}} \rightarrow \pi_{\text{L}}$	300 (0.043)	301 (0.041)	316 (0.064)	306 (0.049)	
S ₃	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}} +$ $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}$	289 (0.008)	290 (0.008)	291 (0.022)	291 (0.013)	
S ₄	$\text{n}_{\text{O}} \rightarrow \pi_{\text{L}}$	285 (0.003)	284 (0.002)	276 (0.002)	280 (0.002)	
T ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	423	426	418	422	410
T ₂	$\text{P}_{\text{S}} \rightarrow \pi_{\text{L}}$	332	334	353	339	
T ₃	many $\pi \rightarrow \pi^*$ contributions	321	321	320	321	
T ₄	many $\pi \rightarrow \pi^*$ contributions	303	304	303	304	

^a Maxima of experimental spectra. This work.

Figure Captions

Figure 1: Flavin mononucleotide (FMN, left) and its 1-deaza, 1DFMN (center) and 5-deaza, 5DFMN (right) derivatives. The ribityl-5'-phosphate chain is shown for all compounds.
Figure 2: Left. QM region QM-2 comprising the binding pocket of YtvA-LOV, with the 5DFMN chromophore and the side chains of the surrounding polar residues. Right. QM region QM-1 containing the 5DFMN chromophore and the side chain of CYS62. The chromophore is represented by the isoalloxazine ring system, with a methyl group replacing the ribityl chain. The atoms colored in purple are replaced by link atoms.
Figure 3: UV-Vis absorption spectra of 1DFMN-LOV (red line) and YtvA WT (black line). The inset shows the fluorescence spectrum of 1DFMN-LOV.
Figure 4: Two S_1/S_0 conical intersections of 1DFMN-LOV: The left one (E_1) is inherent to the isoalloxazine core; the right one (with essentially planar flavin) involves a biradical generated by hydrogen migration from the thiol group toward the flavin ring. Only atoms in the QM region are shown.
Figure 5: Schematic diagram of 1DFMN-LOV photophysics.
Figure 6: A. Steady-state blue-light irradiation of 5DFMN-LOV. B. Laser-induced dark-state recovery.
Figure 7: Fluorescence lifetime decay curves of 5DFMN-LOV ($\lambda_{\text{exc}}=380$ nm, $\lambda_{\text{em}}=445$ nm) in the dark state. The black curve represents the measured fluorescence signal, and the exponential fit is shown in red. The blue curve is the instrumental response function. The residual difference between decay and fit is shown in green.
Figure 8: A. Kinetic decay curves of 5DFMN-LOV upon laser flash excitation ($\lambda_{\text{exc}} = 410$ nm, $\lambda_{\text{obs}} = 500$ nm). These are single-shot experiments (yielding the low signal-to-noise ratio) as the laser excitation causes formation of the photoadduct, and thereby mixed kinetics. Vertical bars indicate the time points, at which the triplet spectra were generated (multiple wavelength detection). B. Transient absorption spectra of 5DFMN-LOV for different time domains. The color coding refers to the colors of the vertical bars from A . Calculated triplet-triplet $T_1 \rightarrow T_n$ excitations for some snapshots (with intensity above 0.05) are shown as vertical lines.
Figure 9: QM(DFT/MRCI)/CHARMM relative energies for restrained optimizations on the T_1 surface along the reaction coordinate $d(\text{S-H}) - d(\text{H}\cdots\text{C})$ for snapshot 5. Two possible hydrogen transfers are considered, from the CYS62 thiol group toward either the C4a atom (red) or the C5 atom (black) of the isoalloxazine moiety.
Figure 10: A. Kinetic decay curves of the photoadduct of 5DFMN-LOV upon laser flash excitation ($\lambda_{\text{exc}} = 355$ nm, $\lambda_{\text{obs}} = 375$ nm). As in Figure 8, single-shot experiments were

performed to avoid the accumulation of the dark state. Vertical bars indicate the time points, at which the full triplet spectrum was recorded. **B.** Transient absorption spectra of the intermediates of the photoadduct of 5DFMN-LOV for different time domains. The color coding refers to the time points (vertical bars) in **A**.

Figure 11: Transient kinetics of the photoadduct state of 5DFMN-LOV: **A.** $\lambda_{\text{exc}} = 355 \text{ nm}$, $\lambda_{\text{obs}} = 430 \text{ nm}$, **B.** $\lambda_{\text{exc}} = 355 \text{ nm}$, $\lambda_{\text{obs}} = 600 \text{ nm}$.

Figure 12: Proposed photocycle of 5DFMN-LOV. From the reactive triplet species, two adducts can be formed via hydrogen transfer and intersystem crossing. The route via ISC1 is favored. Dark-state recovery occurs photochemically. See text for details.

Figure 13: Alternative pathways involving photoadducts 2 and 3 as possible side products of blue-light irradiation. Photoexcitation of these adducts does not lead to dark-state recovery. See text for details.

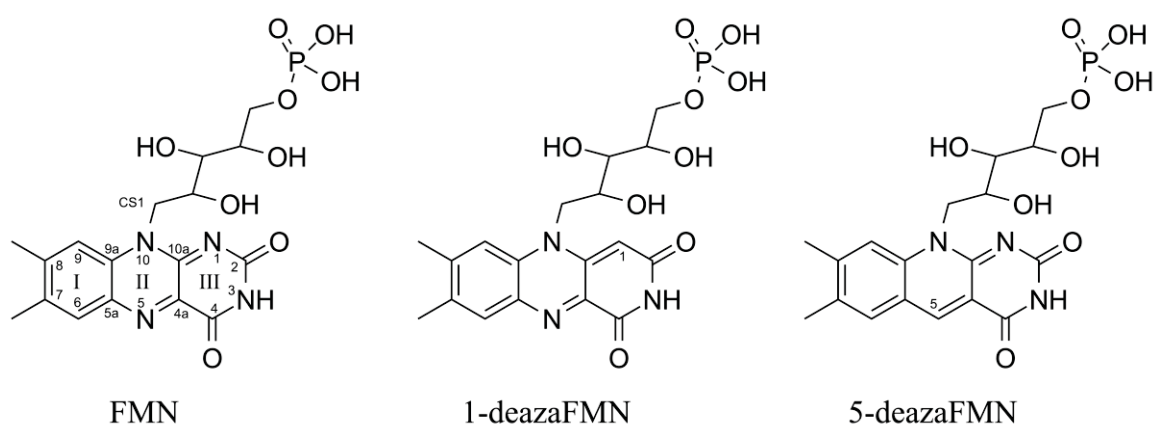


Fig. 1

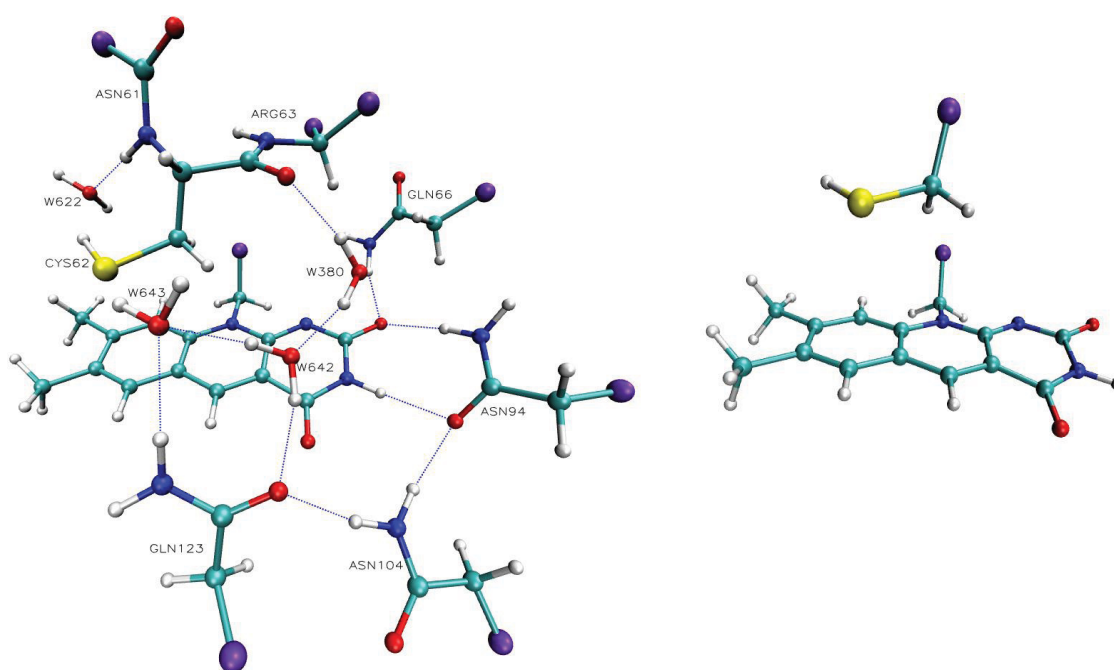


Fig. 2

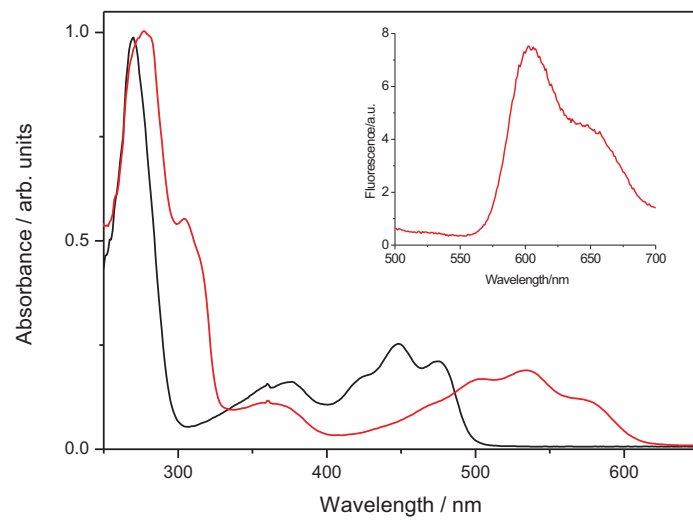


Fig. 3

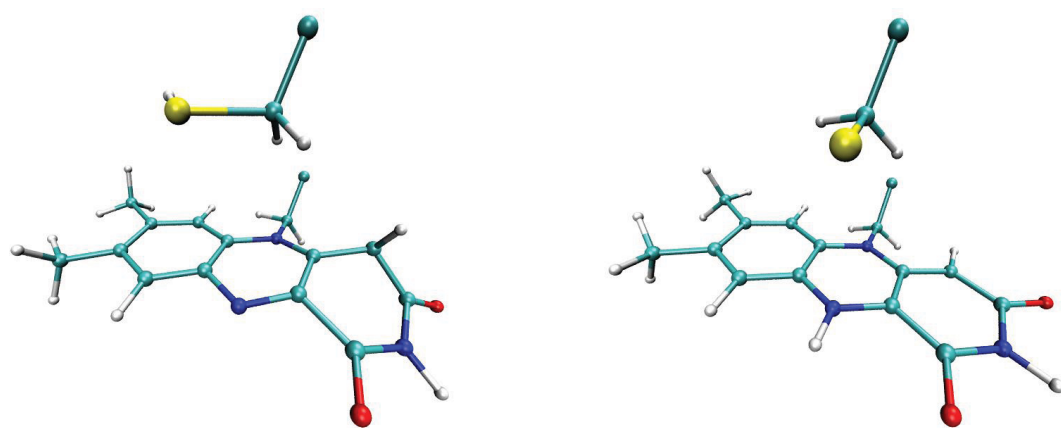


Fig. 4

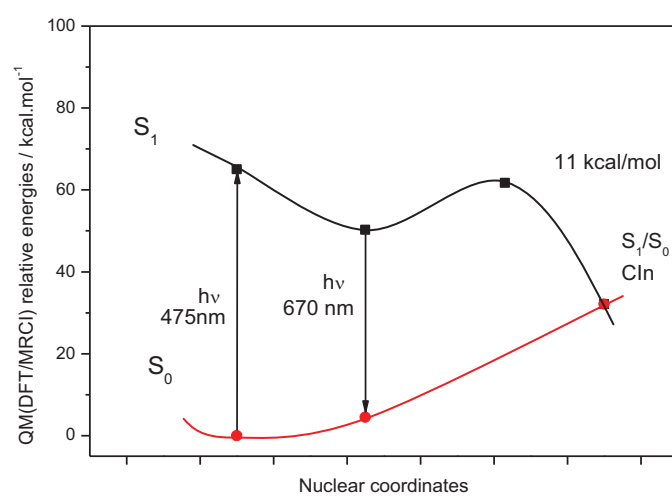


Fig. 5

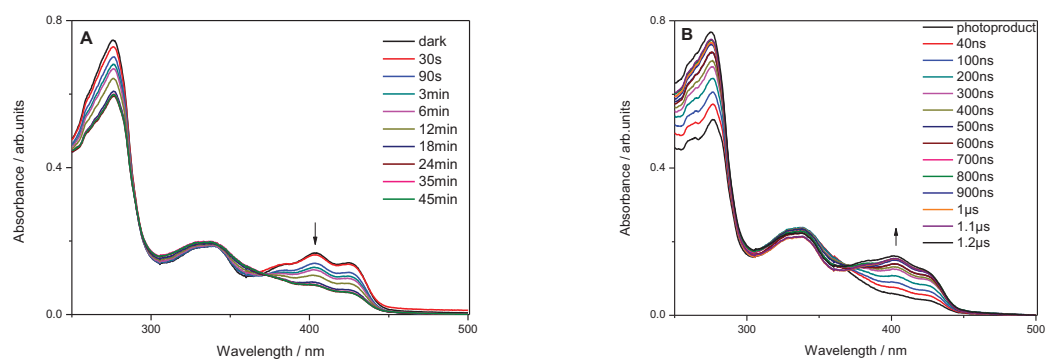


Fig. 6

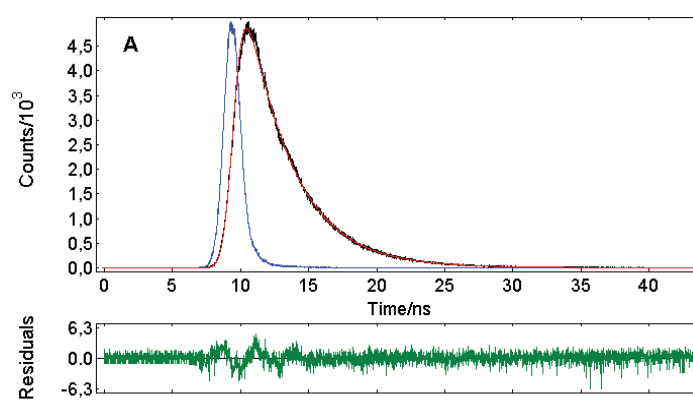


Fig. 7

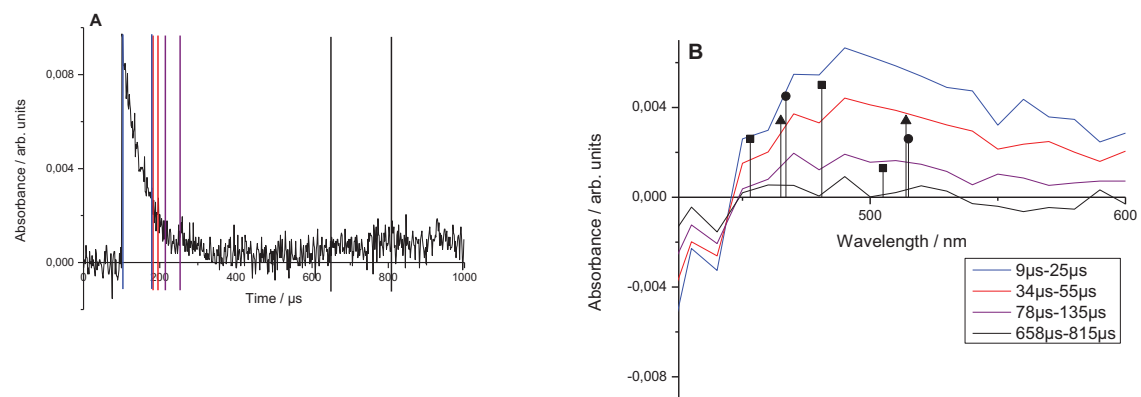


Fig. 8

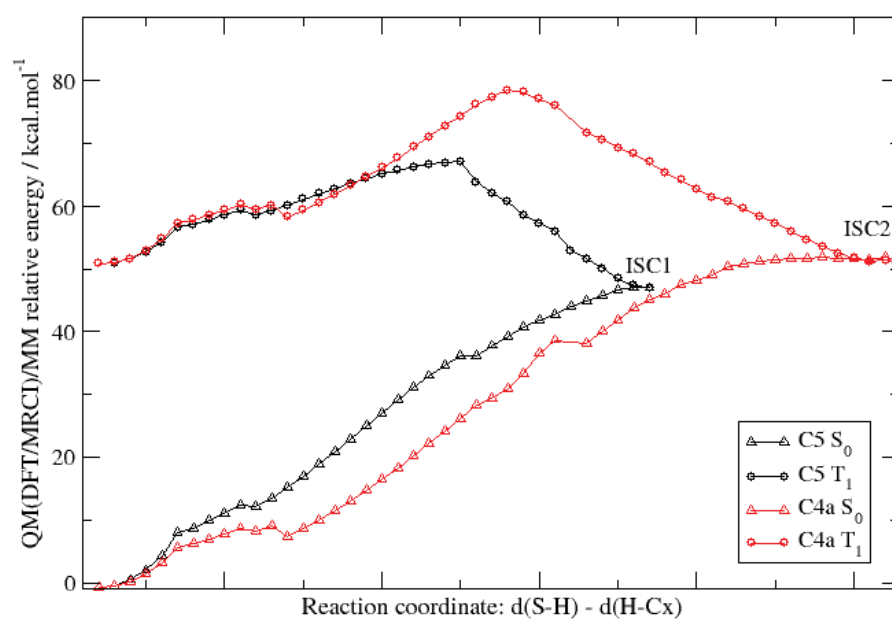


Fig. 9

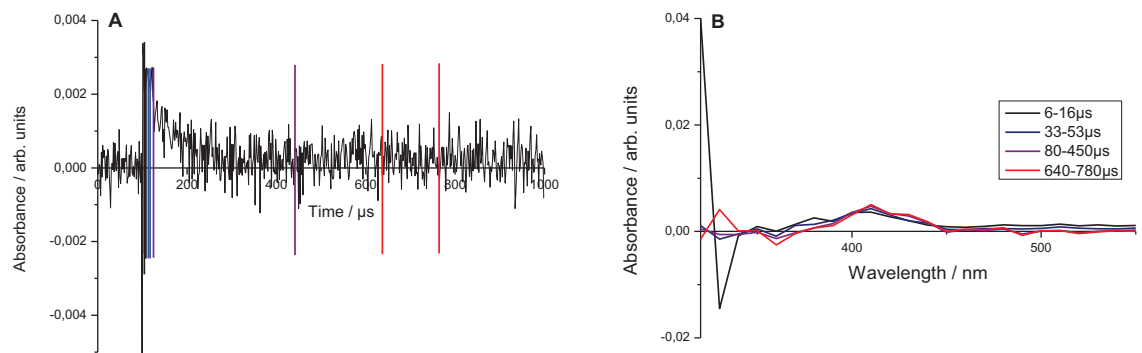


Fig 10

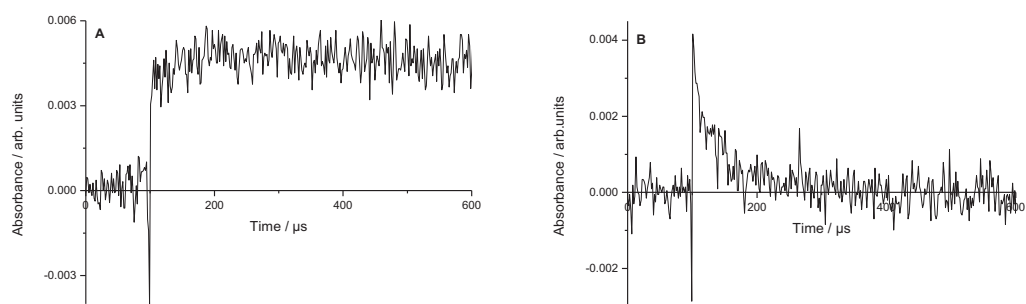


Fig 11

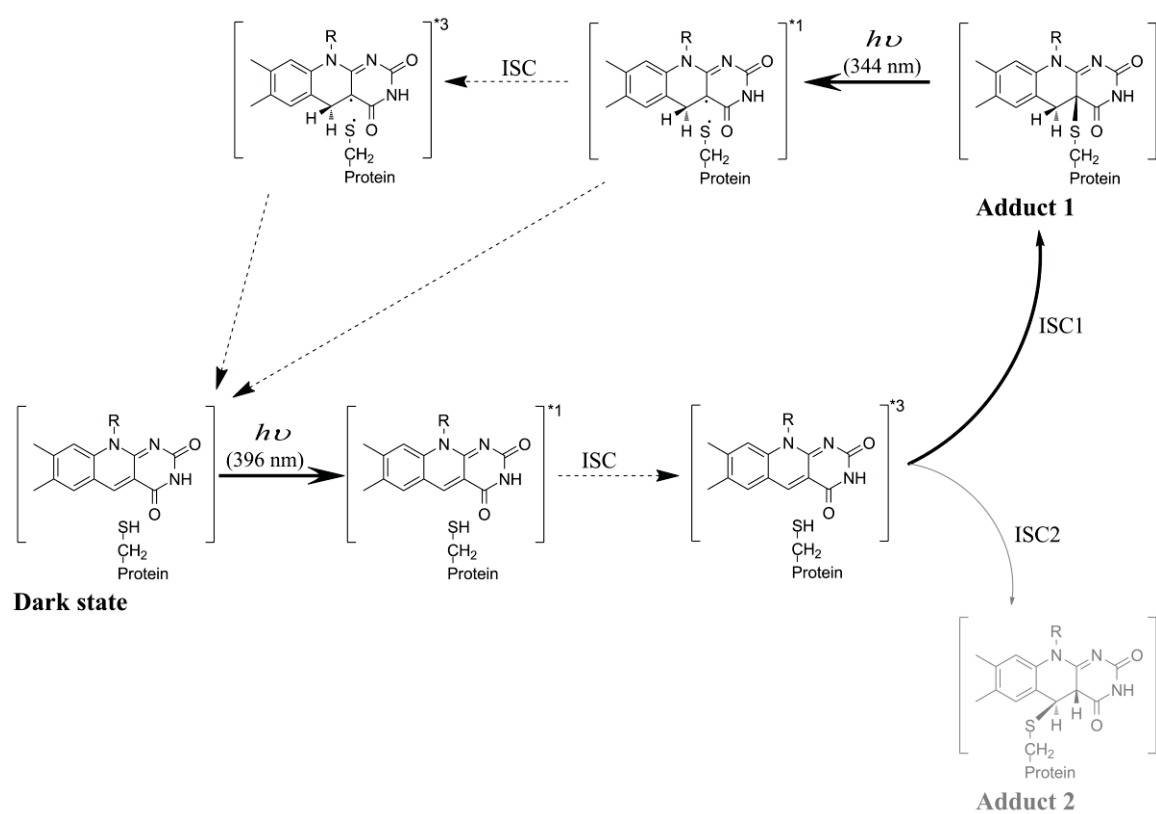


Fig 12

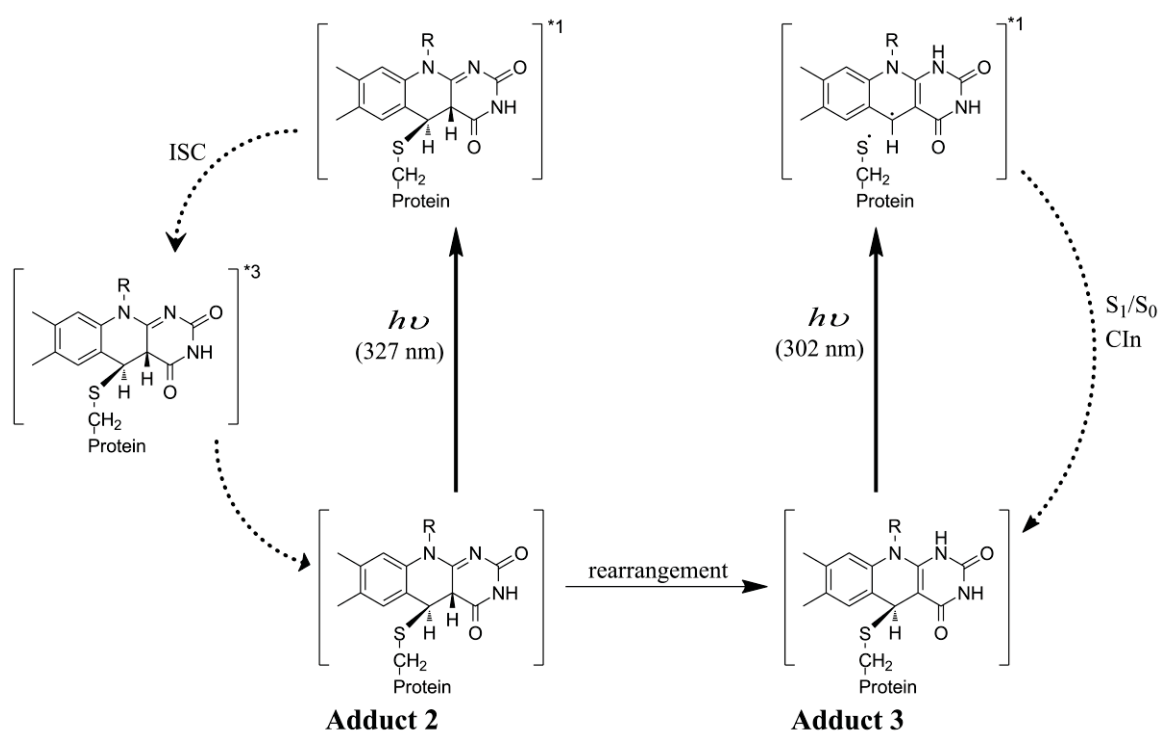
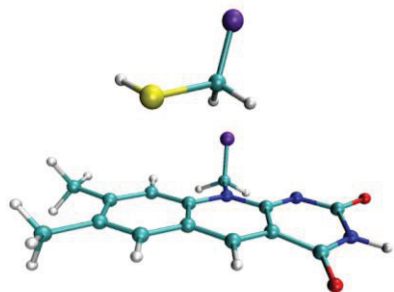


Fig 13

Table of contents graphics (TOC)



Photophysics of structurally modified flavin derivatives in the Ytva-LOV domain: A combined experimental and theoretical study

- Supporting Information -

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1. 1DFMN MD analysis and structural details (Figures S1-S2, Table S1)	S2
2. 1DFMN energetics (Figure S3)	S3
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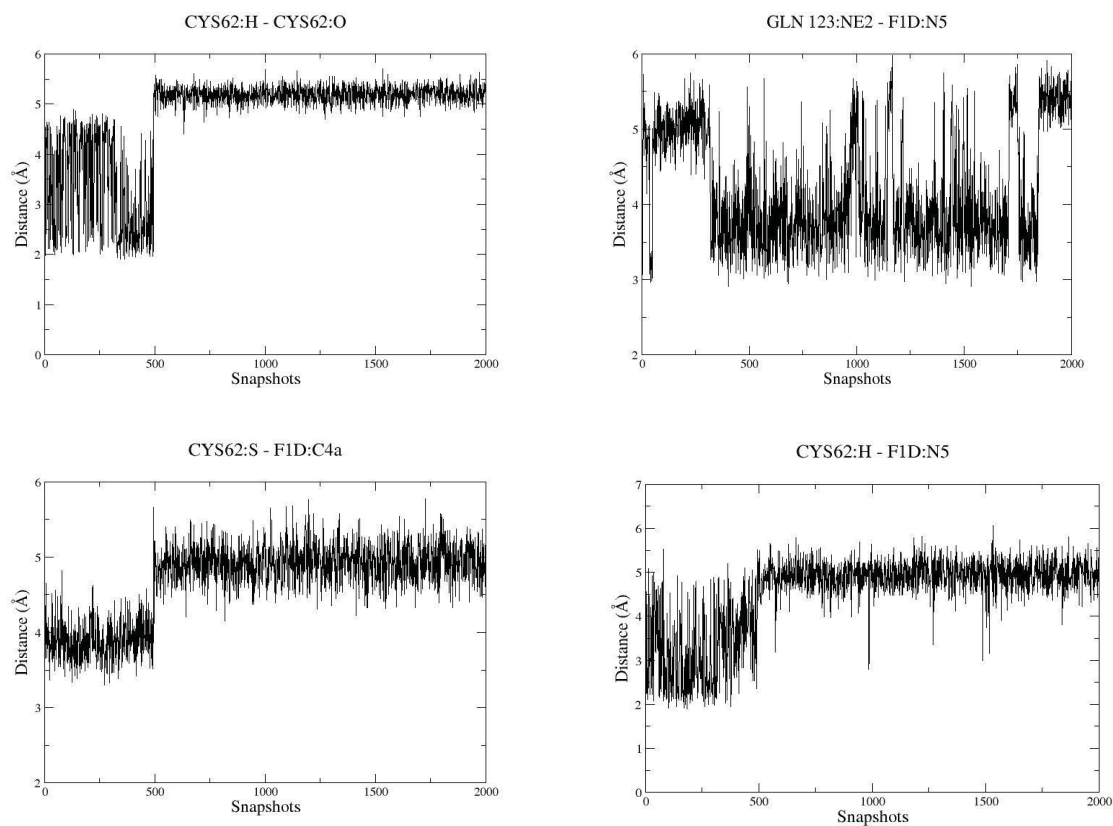


Figure S1: Selected distances from the production MD run for the 1DFMN-YtvA.

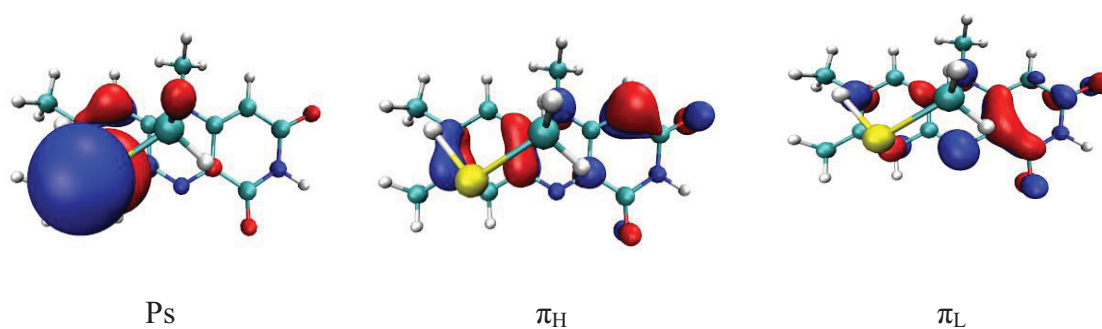


Figure S2: Frontier orbitals for QM region 1 of the 1DFMN chromophore.

Table S1: Selected bond distances (Å) of snapshot 1 for the dark state (S_0), the lowest singlet excited state (S_1) as well as two S_1/S_0 conical intersections of 1DFMN-Ytva, optimized at the (TD)-B3LYP / CHARMM level. The QM region 1 was used.				
	S_0	S_1	CIn E_1^a	CIn planar
N5C5a	1.364	1.335	1.365	1.365
N5C4a	1.294	1.360	1.321	1.345
C4aC10a	1.455	1.426	1.400	1.429
C10aN10	1.376	1.357	1.391	1.390
N10C9a	1.393	1.406	1.424	1.408
C4aC4	1.499	1.444	1.536	1.472
C4O	1.214	1.224	1.207	1.225
C4N3	1.382	1.426	1.416	1.392
N3H	1.013	1.013	1.018	1.013
N3C2	1.391	1.357	1.413	1.403
C2O	1.242	1.246	1.220	1.238
C2C1	1.427	1.445	1.474	1.426
C1C10a	1.374	1.413	1.488	1.383
N5S _{cys}	4.218	4.102	4.044	2.995
N5H _{cys}	4.959	4.874	4.799	1.123
C5aC6	1.409	1.414	1.393	1.401
C6C7	1.381	1.384	1.400	1.385
C7C8	1.419	1.424	1.411	1.419
C8C9	1.385	1.385	1.402	1.390
C9C9a	1.396	1.397	1.397	1.392

^aConical intersection illustrated on the left side of Figure 4 of the manuscript. The energy gap between S_1 and S_0 states is 0.14 eV.

^bConical intersection illustrated on the right side of Figure 4 of the manuscript. The energy gap between S_1 and S_0 states is 0.07 eV.

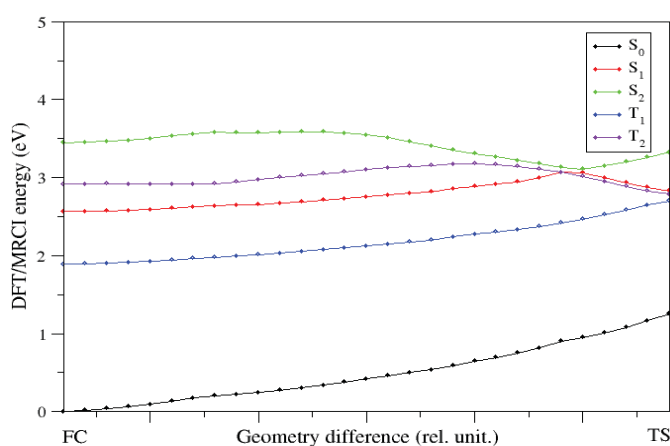


Figure S3: DFT/MRCI energy profiles for several excited states along a linearly interpolated path between the Frank-Condon point (FC) and the transition state for hydrogen transfer on the S_1 surface. Shown are the results for snapshot 1.

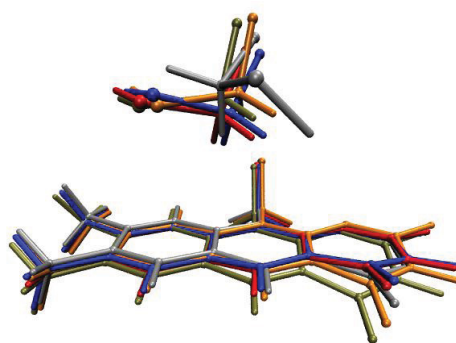


Figure S4: Overlay of QM/MM optimized geometries of the five snapshots of 5DFMN-LOV complex. For clarity, only atoms from the QM region are shown.

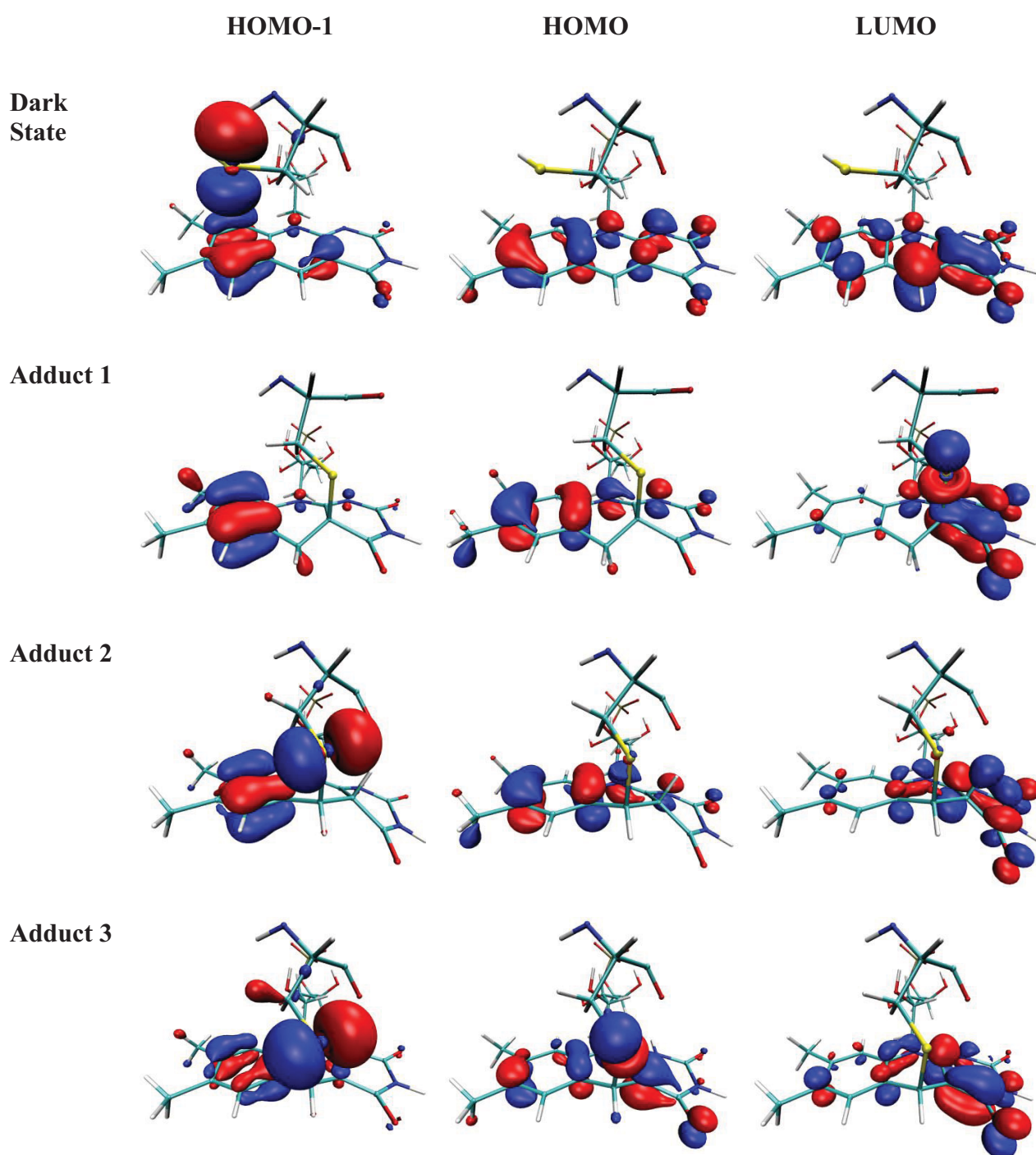


Figure S5: Frontier orbitals for QM region 1 of species involved in the photocycle of 5DFMN.

Table S2: Selected distances (Å) in 5DFMN-LOV (snapshot 5) for stationary points of the reaction mechanism (see manuscript):. Data are given for the dark state (S_0 , S_1 and T_1), adducts 1 and 2 (S_0 , S_1 and T_1), and adduct 3 (S_0 , S_1/S_0). Ground states were optimized at the B3LYP/CHARMM level, S_1 states at the TD-B3LYP/CHARMM level, and T_1 states at the UB3IYP/CHARMM level. The QM region 1 was used.

	Dark state			Adduct 1			Adduct 2			Adduct 3	
	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1/S_0
C4aC5	1.369	1.407	1.406	1.520	1.504	1.467	1.369	1.407	1.406	1.520	1.504
C5C5a	1.408	1.414	1.409	1.493	1.499	1.487	1.408	1.414	1.409	1.493	1.499
C4aC10a	1.438	1.423	1.412	1.515	1.463	1.422	1.438	1.423	1.412	1.515	1.463
C10a N10	1.378	1.392	1.423	1.354	1.395	1.384	1.378	1.392	1.423	1.354	1.395
N10C9a	1.396	1.395	1.384	1.441	1.406	1.420	1.396	1.395	1.384	1.441	1.406
C4C4a	1.459	1.424	1.435	1.532	1.446	1.454	1.459	1.424	1.435	1.532	1.446
C4O	1.240	1.251	1.247	1.220	1.233	1.230	1.240	1.251	1.247	1.220	1.233
C4 N3	1.356	1.393	1.380	1.358	1.392	1.370	1.356	1.393	1.380	1.358	1.392
N3 C2	1.417	1.376	1.383	1.411	1.374	1.404	1.417	1.376	1.383	1.411	1.374
C2O	1.225	1.227	1.229	1.222	1.221	1.229	1.225	1.227	1.229	1.222	1.221
C2 N1	1.359	1.390	1.382	1.365	1.403	1.362	1.359	1.390	1.382	1.365	1.403
N1C10a	1.319	1.324	1.316	1.311	1.296	1.326	1.319	1.324	1.316	1.311	1.296
C4aS _{cys}	4.765	4.782	4.795	1.898	2.395	4.231	4.765	4.782	4.795	1.898	2.395
C5H _{cys}	3.393	3.326	3.334	1.095	1.095	1.100	3.393	3.326	3.334	1.095	1.095
C5aC6	1.415	1.396	1.398	1.389	1.376	1.395	1.415	1.396	1.398	1.389	1.376
C6C7	1.376	1.410	1.402	1.393	1.407	1.391	1.376	1.410	1.402	1.393	1.407
C7C8	1.423	1.409	1.423	1.405	1.420	1.410	1.423	1.409	1.423	1.405	1.420
C8C9	1.384	1.392	1.384	1.393	1.382	1.389	1.384	1.392	1.384	1.393	1.382
C9C9a	1.402	1.409	1.408	1.394	1.411	1.402	1.402	1.409	1.408	1.394	1.411
C9aC5a	1.421	1.432	1.453	1.398	1.421	1.406	1.421	1.432	1.453	1.398	1.421

Table S3: Relative energies of 5DFMN-YtvA for QM region 2 calculated at the B3LYP/CHARMM level for some selected snapshots. Values in kcal mol ⁻¹ .					
		snap 3	snap 4	snap 5	average
Dark state (S ₀) ^a	QM	0.0	0.0	0.0	0.0
	QM/MM	0.0	0.0	0.0	0.0
Adduct 1 (S ₀)	QM	26.8	25.4	5.1	19.1
	QM/MM	32.2	35.7	23.4	30.4
Adduct 2 (S ₀)	QM	25.0	19.9	6.9	17.3
	QM/MM	43.6	31.6	21.1	32.1
Adduct 3 (S ₀)	QM	19.8	26.9	-2.6	14.7
	QM/MM	38.1	29.5	0.0	22.5
^a Absolute QM (QM/MM) energies in a.u.: Snap 3, -2853.212279 (-2966.954472); snap 4: -2853.209447 (-2966.965865); snap 5: -2853.138276 (-2967.068763).					

Table S4: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for three snapshots of adduct 2 of 5DFMN-YtvA. The average values are also listed together with the available experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.

State	excitation	snap 3	snap 4	snap 5	average	exp. ^a
S ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	323 (0.348)	322 (0.374)	330 (0.364)	327 (0.362)	340
S ₂	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}$	297 (0.012)	295 (0.016)	310 (0.013)	301 (0.014)	
S ₃	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}} +$ $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}$	278 (0.029)	275 (0.039)	284 (0.026)	279 (0.031)	
S ₄	$n_{\text{O}} \rightarrow \pi_{\text{L}}$	270 (0.066)	267 (0.039)	268 (0.005)	266 (0.037)	
T ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	399	399	411	404	
T ₂	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}} +$ $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}} +$ $\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}$	337	335	345	340	
T ₃	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}} +$ $\pi_{\text{H-2}} \rightarrow \pi_{\text{L+1}}$	310	309	314	312	
T ₄	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}$	301	299	307	303	

^a Maxima of UV/Vis experimental absorption spectra of photoproduct. This work.

Table S5: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for three snapshots of adduct 3 of 5DFMN-YtvA. The average values are also listed together with the available experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.

State	excitation	snap 3	snap 4	snap 5	average	exp. ^a
S ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	293 (0.143)	298 (0.227)	311 (0.274)	301 (0.215)	340
S ₂	mixed $\pi \rightarrow \pi^*$ contributions	290 (0.132)	291 (0.048)	297 (0.006)	293 (0.062)	
S ₃	mixed $\pi \rightarrow \pi^*$ contributions	263 (0.083)	267 (0.081)	275 (0.048)	268 (0.071)	
S ₄	$n_{\text{O}} \rightarrow \pi_{\text{L}}$	257 (0.005)	254 (0.001)	271 (0.026)	260 (0.011)	
T ₁	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}$	370	376	385	377	
T ₂	mixed $\pi \rightarrow \pi^*$ contributions	338	340	343	340	
T ₃	mixed $\pi \rightarrow \pi^*$ contributions	316	316	313	315	
T ₄	$n_{\text{O}} \rightarrow \pi_{\text{L}}$	302	304	310	305	

^a Maxima of UV/Vis experimental absorption spectra of photoproduct. This work.