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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* basis[17]) using the GAUSSIAN program package.[18] The highest

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Unsaturated Aliphatic Hydrocarbons

Ethene   *E*-Butadiene   all-*E*-Hexatriene   all-*E*-Octatetraene   Cyclopropene   Cyclopentadiene   Norbornadiene

Aromatic Hydrocarbons and Heterocycles

Benzene   Naphthalene   Furan   Pyrrole   Imidazole   Pyridine   Pyrazine   Pyrimidine   Pyridazine   *s*-Triazine   *s*-Tetrazine

Aldehydes, Ketones and Amides

Formaldehyde   Acetone   *p*-Benzoquinone   Formamide   Acetamide   Propanamide

Nucleobases

Cytosine   Thymine   Uracil   Adenine

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 set[19] 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
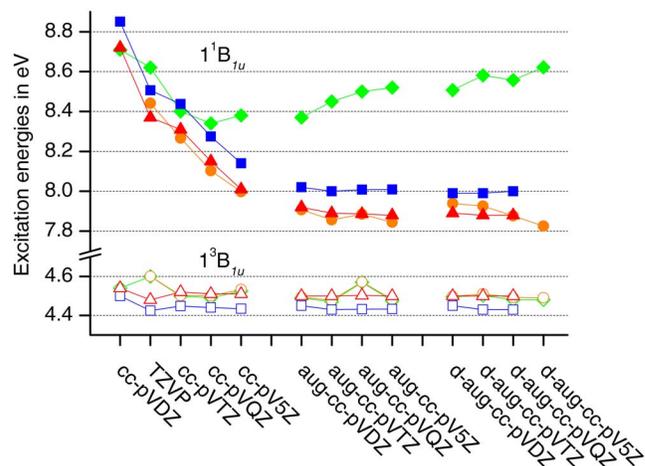
FIG. 2. (Color online) Basis set dependence of the $1\ ^1B_{1u}$ (filled symbols, top) and the $1\ ^3B_{1u}$ (open symbols, bottom) state of ethene with different methods: CCSD (squares, blue), CC3 (triangles, red), CASPT2 with 2,2 (diamonds, green) and 8,20 (circles, orange) active space.

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 treatment[22] with a (8,20) active space. This is in line with previous experience[23] 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 $\pi \to \pi^*$, $n \to \pi^*$, and $\sigma \to \pi^*$ 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 approach[22] 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 MOL-CAS code[42] 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 shift[43] 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 approach[22] 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
E-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-E-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-E-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]
	$1\,^1B_{1g}\ (n\rightarrow\pi^*)$	6.13	6.41	6.70	7.13(90.8)	6.75(85.8)	6.60
	$1\,^1B_{1u}\ (\pi\rightarrow\pi^*)$	6.70	6.89	7.10	7.18(95.6)	7.07(93.3)	6.58
	$2\,^1B_{1u}\ (\pi\rightarrow\pi^*)$	7.57	7.79	8.13	8.34(93.9)	8.06(90.9)	7.72
	$2\,^1B_{2u}\ (\pi\rightarrow\pi^*)$	7.70	7.65	8.07	8.29(93.2)	8.05(89.7)	7.60
	$1\,^1B_{3g}\ (\pi\rightarrow\pi^*)$	8.19	8.47	9.42	9.75(83.5)	8.77(61.1)	
	$2\,^1A_g\ (\pi\rightarrow\pi^*)$	8.26	8.61	9.26	9.55(89.1)	8.69(74.2)	
Pyrimidine	$1\,^1B_1\ (n\rightarrow\pi^*)$	3.81	4.44	4.49	4.70(92.7)	4.50(88.4)	4.55
	$1\,^1A_2\ (n\rightarrow\pi^*)$	4.12	4.81	4.84	5.12(92.6)	4.93(88.2)	4.91
	$1\,^1B_2\ (\pi\rightarrow\pi^*)$	4.93	5.24	5.51	5.49(90.5)	5.36(85.7)	5.44
	$2\,^1A_1\ (\pi\rightarrow\pi^*)$	6.72	6.64	7.12	7.17(94.8)	7.06(92.2)	6.95
	$2\,^1B_2\ (\pi\rightarrow\pi^*)$	7.32	7.64	8.08	8.24(93.8)	8.01(90.7)	
	$3\,^1A_1\ (\pi\rightarrow\pi^*)$	7.57	7.21	7.79	7.97(93.5)	7.74(89.7)	
Pyridazine	$1\,^1B_1\ (n\rightarrow\pi^*)$	3.48	3.78	3.90	4.11(93.1)	3.92(89.0)	3.78
	$1\,^1A_2\ (n\rightarrow\pi^*)$	3.66	4.32	4.40	4.76(92.0)	4.49(86.6)	4.32
	$2\,^1A_1\ (\pi\rightarrow\pi^*)$	4.86	5.18	5.37	5.35(90.2)	5.22(85.2)	5.18
	$2\,^1A_2\ (n\rightarrow\pi^*)$	5.09	5.77	5.81	6.00(92.1)	5.74(86.6)	5.77
	$2\,^1B_1\ (n\rightarrow\pi^*)$	5.80	6.52	6.40	6.70(92.0)	6.41(86.6)	
	$1\,^1B_2\ (\pi\rightarrow\pi^*)$	6.61	6.31	7.00	7.09(94.7)	6.93(90.7)	
	$2\,^1B_2\ (\pi\rightarrow\pi^*)$	7.39	7.29	7.57	7.79(93.8)	7.55(90.2)	
	$3\,^1A_1\ (\pi\rightarrow\pi^*)$	7.50	7.62	7.90	8.11(93.8)	7.82(90.5)	
s-Triazine	$1\,^1A_1''\ (n\rightarrow\pi^*)$	3.90	4.60	4.70	4.96(92.3)	4.78(88.0)	4.60
	$1\,^1A_2''\ (n\rightarrow\pi^*)$	4.08	4.68	4.80	4.98(92.5)	4.76(88.0)	4.66
	$1\,^1E''\ (n\rightarrow\pi^*)$	4.36	4.71	4.77	5.01(92.5)	4.81(88.1)	4.71
	$1\,^1A_2'\ (\pi\rightarrow\pi^*)$	5.33	5.79	5.82	5.84(90.2)	5.71(85.1)	5.79
	$2\,^1A_1'\ (\pi\rightarrow\pi^*)$	6.77	7.25	7.52	7.51(93.7)	7.41(90.8)	
	$2\,^1E''\ (n\rightarrow\pi^*)$	7.15	7.72	8.04	8.19(90.9)	7.80(88.1)	
	$1\,^1E'\ (\pi\rightarrow\pi^*)$	8.16	7.49	8.06	8.28(93.7)	8.04(88.8)	
	$2\,^1E'\ (\pi\rightarrow\pi^*)$	8.03	8.99	9.93	10.24(91.2)	9.44(74.3)	
s-Tetrazine	$1\,^1B_{3u}\ (n\rightarrow\pi^*)$	1.96	2.24	2.47	2.71(93.2)	2.53(89.6)	2.24
	$1\,^1A_u\ (\pi\rightarrow\pi^*)$	3.06	3.48	3.67	4.07(92.2)	3.79(87.5)	3.48
	$1\,^1B_{1g}\ (n\rightarrow\pi^*)$	4.51	4.73	5.10	5.32(91.7)	4.97(82.5)	4.73
	$1\,^1B_{2u}\ (\pi\rightarrow\pi^*)$	4.89	4.91	5.20	5.27(90.0)	5.12(84.6)	4.91
	$1\,^1B_{2g}\ (n\rightarrow\pi^*)$	5.05	5.18	5.53	5.70(90.7)	5.34(80.7)	5.18
	$1\,^1B_{3g}\ (n,n\rightarrow\pi^*,\pi^*)$	5.16	5.79				5.79
	$2\,^1A_u\ (n\rightarrow\pi^*)$	5.28	5.47	5.50	5.70(92.5)	5.46(87.4)	5.47
	$2\,^1B_{2g}\ (n\rightarrow\pi^*)$	5.48	6.07	6.32	6.76(90.1)	6.23(79.2)	
	$2\,^1B_{1g}\ (n\rightarrow\pi^*)$	5.99	6.38	6.91	7.25(91.1)	6.87(84.7)	
	$3\,^1B_{1g}\ (n\rightarrow\pi^*)$	6.20	6.74	7.64	8.36(86.9)	7.08(63.2)	
	$2\,^1B_{3u}\ (n\rightarrow\pi^*)$	6.37	6.77	6.70	6.99(93.2)	6.67(86.7)	
	$1\,^1B_{1u}\ (\pi\rightarrow\pi^*)$	7.13	6.96	7.60	7.66(94.9)	7.45(91.0)	
	$2\,^1B_{1u}\ (\pi\rightarrow\pi^*)$	7.54	7.43	7.75	8.06(93.4)	7.79(90.2)	
	$2\,^1B_{2u}\ (\pi\rightarrow\pi^*)$	7.94	8.15	8.65	8.88(93.2)	8.51(87.7)	
	$2\,^1B_{3g}\ (\pi\rightarrow\pi^*)$	8.12	8.32	8.97	9.44(84.3)	8.47(63.6)	
Formaldehyde	$1\,^1A_2\ (n\rightarrow\pi^*)$	3.91	3.98	4.09	3.97(93.4)	3.95(91.2)	3.88
	$1\,^1B_1\ (\sigma\rightarrow\pi^*)$	9.09	9.14	9.35	9.26(93.4)	9.18(90.9)	9.1
	$2\,^1A_1\ (\pi\rightarrow\pi^*)$	9.77	9.31	10.34	10.54(94.4)	10.45(91.3)	9.3
Acetone	$1\,^1A_2\ (n\rightarrow\pi^*)$	4.18	4.42	4.52	4.43(93.4)	4.40(90.8)	4.40
	$1\,^1B_1\ (\sigma\rightarrow\pi^*)$	9.10	9.27	9.29	9.26(93.8)	9.17(91.5)	9.1
	$2\,^1A_1\ (\pi\rightarrow\pi^*)$	9.16	9.31	9.74	9.87(93.5)	9.65(90.1)	9.4
p-Benzoquinone	$1\,^1A_u\ (n\rightarrow\pi^*)$	2.50	2.80	2.92	3.19(91.7)	2.85(83.0)	2.80
	$1\,^1B_{1g}\ (n\rightarrow\pi^*)$	2.50	2.78	2.81	3.07(92.0)	2.75(84.1)	2.78
	$1\,^1B_{3g}\ (\pi\rightarrow\pi^*)$	4.19	4.25	4.69	4.93(92.7)	4.59(87.9)	4.25
	$1\,^1B_{1u}\ (\pi\rightarrow\pi^*)$	5.15	5.29	5.59	5.89(92.5)	5.62(88.4)	5.29
	$1\,^1B_{3u}\ (n\rightarrow\pi^*)$	5.15	5.60	5.69	6.55(91.0)	5.82(75.2)	5.60
	$2\,^1B_{3g}\ (\pi\rightarrow\pi^*)$	6.34	6.98	7.36	7.62(91.0)	7.27(88.8)	6.98
	$2\,^1B_{1u}\ (\pi\rightarrow\pi^*)$	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	$1\,^1A''\,(n\to\pi^*)$	5.61	5.63	5.76	5.66(93.6)	5.65(90.7)	5.63
	$2\,^1A'\,(\pi\to\pi^*)$	7.41	7.44	8.15	4.52(92.9)	8.27(87.9)	7.44
	$3\,^1A'\,(\pi\to\pi^*)$	10.50	10.54	11.24	11.34(92.7)	10.93(86.6)	
Acetamide	$1\,^1A''\,(n\to\pi^*)$	5.54	5.80	5.77	5.71(93.5)	5.69(90.6)	5.80
	$2\,^1A'\,(\pi\to\pi^*)$	7.21	7.27	7.66	7.85(92.8)	7.67(89.1)	7.27
	$3\,^1A'\,(\pi\to\pi^*)$	10.08	10.09	10.71	10.77(93.0)	10.50(88.7)	
Propanamide	$1\,^1A''\,(n\to\pi^*)$	5.48	5.72	5.78	5.74(93.6)	5.72(90.6)	5.72
	$2\,^1A''\,(\pi\to\pi^*)$	7.28	7.20	7.56	7.80(93.0)	7.62(89.2)	7.20
	$3\,^1A'\,(\pi\to\pi^*)$	9.95	9.94	10.33	10.34(93.3)	10.06(89.0)	
Cytosine	$2\,^1A'\,(\pi\to\pi^*)$	4.39	4.68	4.80	4.98(91.6)		4.66
	$1\,^1A''\,(n\to\pi^*)$	5.00	5.12	5.13	5.45(92.5)		4.87
	$2\,^1A''\,(n\to\pi^*)$	6.53	5.54	5.01	5.99(92.6)		5.26
	$3\,^1A'\,(\pi\to\pi^*)$	5.36	5.54	5.71	5.95(91.1)		5.62
	$4\,^1A'\,(\pi\to\pi^*)$	6.16	6.40	6.65	6.81(92.3)		
	$5\,^1A'\,(\pi\to\pi^*)$	6.74	6.98	6.94	7.23(91.9)		
	$6\,^1A'\,(\pi\to\pi^*)$	7.61	8.23	8.45	8.69(92.1)		
Thymine	$1\,^1A''\,(n\to\pi^*)$	4.39	4.94	4.94	5.14(92.5)		4.82
	$2\,^1A'\,(\pi\to\pi^*)$	4.88	5.06	5.39	5.60(93.0)		5.20
	$3\,^1A'\,(\pi\to\pi^*)$	5.88	6.15	6.46	6.78(90.9)		6.27
	$2\,^1A''\,(n\to\pi^*)$	5.91	6.38	6.33	6.57(93.3)		6.16
	$4\,^2A'\,(\pi\to\pi^*)$	6.10	6.52	6.80	7.05(92.5)		6.53
	$4\,^1A''\,(n\to\pi^*)$	6.15	6.86	6.73	7.67(91.6)		
	$5\,^1A''\,(n\to\pi^*)$	6.70	7.43	7.18	7.87(91.6)		
	$5\,^1A'\,(\pi\to\pi^*)$	7.13	7.43	7.71	7.90(91.8)		
Uracil	$1\,^1A''\,(n\to\pi^*)$	4.54	4.90	4.91	5.11(92.4)		4.80
	$2\,^1A'\,(\pi\to\pi^*)$	5.00	5.23	5.52	5.70(92.6)		5.35
	$3\,^1A'\,(\pi\to\pi^*)$	5.82	6.15	6.43	6.76(90.6)		6.26
	$2\,^1A''\,(n\to\pi^*)$	6.00	6.27	6.73	7.68(91.5)		6.10
	$3\,^1A''\,(n\to\pi^*)$	6.37	6.97	6.26	6.50(93.3)		6.56
	$4\,^1A'\,(\pi\to\pi^*)$	6.46	6.75	6.96	7.19(92.5)		6.70
	$5\,^1A''\,(n\to\pi^*)$	6.95	7.28	7.12	7.74(91.7)		
	$5\,^1A'\,(\pi\to\pi^*)$	7.00	7.42	7.66	7.81(91.8)		
Adenine	$2\,^1A'\,(\pi\to\pi^*)$	5.13	5.20	5.28	5.37(91.3)		5.25
	$3\,^1A'\,(\pi\to\pi^*)$	5.20	5.30	5.42	5.61(92.9)		5.25
	$1\,^1A''\,(n\to\pi^*)$	6.15	5.21	5.27	5.58(92.6)		5.12
	$2\,^1A''\,(n\to\pi^*)$	6.86	5.97	5.91	6.19(92.9)		5.75
	$4\,^1A'\,(\pi\to\pi^*)$	6.24	6.35	6.58	6.83(92.3)		
	$5\,^1A'\,(\pi\to\pi^*)$	6.72	6.64	6.93	7.17(91.8)		
	$6\,^1A'\,(\pi\to\pi^*)$	6.99	6.88	7.49	7.72(91.9)		
	$7\,^1A'\,(\pi\to\pi^*)$	7.57	7.56	8.04	8.47(91.1)		

[a]Data from publications by the Roos group in the 1990s. See Supporting Information for references.
[b]Calculated using MP2/6-31G^* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.
[c]Calculated using MP2/6-31G^* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.
[d]Weight of the single excitations in the coupled cluster calculations.
[e]Best 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
E-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-E-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-E-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
Norbornadiene	$1\,^3A_2\,(\pi\rightarrow\pi^*)$	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)	
s-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]
	$1\ ^3B_{3g}\ (n,n\to\pi^*,\pi^*)$	5.08	5.50				
	$2\ ^3B_{1u}\ (\pi\to\pi^*)$	5.09	5.40	5.67	5.48(97.5)	5.38(96.5)	5.38
	$2\ ^3B_{2g}\ (n\to\pi^*)$	5.30	5.97	6.05	6.51(96.8)	6.04(93.0)	
	$2\ ^3B_{1g}\ (n\to\pi^*)$	5.68	6.31	6.72	7.11(96.9)	6.60(92.3)	
	$2\ ^3B_{3u}\ (n\to\pi^*)$	6.14	6.54	6.52	6.80(97.5)	6.53(95.8)	
	$2\ ^3B_{2u}\ (\pi\to\pi^*)$	6.81	7.10	7.65	7.46(97.7)	7.36(96.8)	
Formaldehyde	$1\ ^3A_2\ (\pi\to\pi^*)$	3.48	3.58	3.57	3.52(98.6)	3.55(98.1)	3.50
	$1\ ^3A_1\ (\pi\to\pi^*)$	5.99	5.84	6.08	5.78(99.3)	5.83(99.2)	5.87
Acetone	$1\ ^3A_2\ (n\to\pi^*)$	3.90	4.08	4.08	4.03(98.4)	4.05(97.9)	4.05
	$1\ ^3A_1\ (\pi\to\pi^*)$	5.98	6.03	6.27	5.94(99.1)	6.03(98.9)	6.03
p-Benzoquinone	$1\ ^3B_{1g}\ (n\to\pi^*)$	2.17	2.63	2.47	2.71(97.9)	2.51(95.9)	2.51
	$1\ ^3A_u\ (n\to\pi^*)$	2.27	2.68	2.59	2.83(97.8)	2.62(95.7)	2.62
	$1\ ^3B_{1u}\ (\pi\to\pi^*)$	2.91	2.99	3.12	2.89(98.5)	2.96(97.8)	2.96
	$1\ ^3B_{3g}\ (\pi\to\pi^*)$	3.19	3.31	3.50	3.42(98.6)	3.41(98.0)	3.41
Formamide	$1\ ^3A''\ (n\to\pi^*)$	5.34	5.40	5.39	5.32(98.4)	5.36(97.8)	5.36
	$1\ ^3A'\ (\pi\to\pi^*)$	5.69	5.58	5.94	5.67(98.7)	5.74(98.4)	5.74
Acetamide	$1\ ^3A''\ (n\to\pi^*)$	5.24	5.53	5.42	5.39(98.4)	5.42(98.3)	5.42
	$1\ ^3A'\ (n\to\pi^*)$	5.57	5.75	6.06	5.83(98.7)	5.88(98.3)	5.88
Propanamide	$1\ ^3A''\ (n\to\pi^*)$	5.28	5.44	5.44	5.41(98.4)	5.45(97.7)	5.45
	$1\ ^3A'\ (\pi\to\pi^*)$	5.94	5.79	6.07	5.84(98.7)	5.90(98.3)	5.90

[a]Data from publications by the Roos group in the 1990s. See Supporting Information for references.

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

[c]Calculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.

[d]Weight of the single excitations in the coupled cluster calculations.

[e]Best 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 $\pi\to\pi^*$ and $\pi\to3d\pi$ 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→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 mixing[23] 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→LUMO and HOMO→LUMO+1), but also from the HOMO→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 survey[284] 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 extrapolation[211]) 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 calculations[248] 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 calculations[23] place the $1\,^1B_u$ and $2\,^1A_g$ states at 5.01 and 5.20 eV, respectively, while more recent multireference perturbation (MRMP) calculations with a large active space and basis-set corrections[243] 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 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 past[159] 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 spectrum[127]). 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 calculations[160] 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 $^1A_1$ 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 $^1A_1$ 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 set[32] 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 framework[286] indicate that the actual absorption maximum lies 0.13 eV below the vertical excitation energy[32] 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 $^1A_1$ valence state is found at 7.9 eV.[140] For the $2\,^1A_1$ state, the previous[161] 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 $^1A_1$ 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 $^1B_2$ states at 6.11 and 7.32 eV, and a second $^1A_2$ state at 7.44 eV. The MS-CASPT2 solutions for the two $^1B_2$ states are dominated by single $\pi \rightarrow \pi^*$ excitations ($^1B_2$: 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 $^1A_2$ states occur at similar energies as presently (5.28 and 7.36 eV), but the two $^1B_2$ 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 $^1B_2$ 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 $^1B_2$ 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 energies[163] 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 triplets[27] 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 (^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 previous[164] 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 study[161] 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 data[241] ($1\,^1B_2$: 6.44 eV, $2\,^1A_1$: 6.53 eV) and CC3/ANO data[194] ($1\,^1B_2$: 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[30] ($1\,^1B_2$: 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 estimates[31] ($1\,^1A_1$: 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 study[193] 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 states[165] 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/$(\widetilde{T})$ 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/$(\widetilde{T})$ 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 calculations[275] 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 results[167] 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 values[167] (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($\widetilde{T}$) study[213] 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 corrections[33] 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 results[167] 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($\widetilde{T}$) 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($\widetilde{T}$) 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 $^1E''$ states. For the latter two $n\rightarrow\pi^*$ transitions, the reported experimental values[122] 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 cluster[29] 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-AQCC[261] 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 CASPT2[169] 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 $n \to \pi^*$ singlet excitation and the two lowest triplet excitations, whereas CC3 gives a considerably higher energy (by 0.4 eV) than CASPT2 for the lowest $\pi \to \pi^*$ 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 molecules[257] 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 $\to$ LUMO excitation (78% weight in CASSCF). The wave functions of the next two $\pi \to \pi^*$ singlet states also contain large contributions from a single excitation (74% HOMO $-1 \to$ LUMO in 3 $^1A'$ and 62% HOMO $\to$ 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 $\pi \to \pi^*$ singlet lies below the first $n \to \pi^*$ 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 $n \to \pi^*$ singlet was found in an early CASPT2 study[173] 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 $\pi \to \pi^*$ 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 $\pi \to \pi^*$ ($^1A'$) states and by 0.5–0.7 eV for the $n \to \pi^*$ ($^1A''$) 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 $n \to \pi^*$ states). Both CASPT2/TZVP and CC2/TZVP predict the 1 $^1A''$ somewhat below the 2 $^1A'$ state, in line with CC2/aug-cc-pVTZ[257] 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 $n \to \pi^*$ states).

All theoretical calculations place the lowest $\pi \to \pi^*$ state (2 $^1A'$) above the lowest $n \to \pi^*$ 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 study[175] gave excitation energies of more than 6 eV for the $n \to \pi^*$ states, about 1 eV higher than all more recent studies which place both the lowest $n \to \pi^*$ and $\pi \to \pi^*$ 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 $\pi \to \pi^*$ 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

[a]From the literature, see Table I and Supporting Information.
[b]Total 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.

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 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

[a]From the literature, see Table I and Supporting Information.
[b]Total number of considered states.

TABLE V. Deviations in excitation energies of singlet excited $n \to \pi^*$ 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

[a]From the literature, see Table I and Supporting Information.
[b]Total number of considered states.
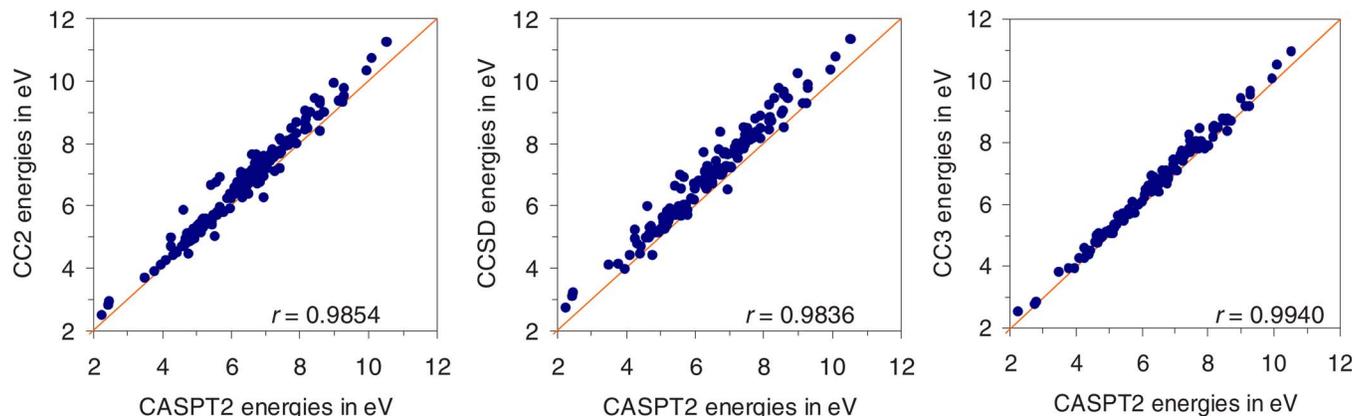
FIG. 3. (Color online) Correlation plots for all calculated singlet excited states: CC/TZVP vs CASPT2/TZVP vertical excitation energies.

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 significantly (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 $\pi \to \pi^*$ (left) and $n \to \pi^*$ (right) excited states. It is evident that there is closer agreement for the $n \to \pi^*$ states. This is confirmed and quantified by the statistical analysis in Table
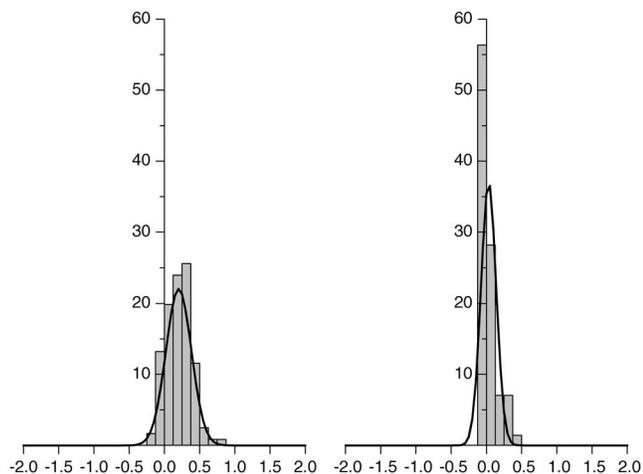
FIG. 4. Histogram for the frequency of deviation (CC3/TZVP vs CASPT2/TZVP, in%) of all calculated singlet (left) and triplet (right) excited states. The normal distribution of the deviation is also shown.
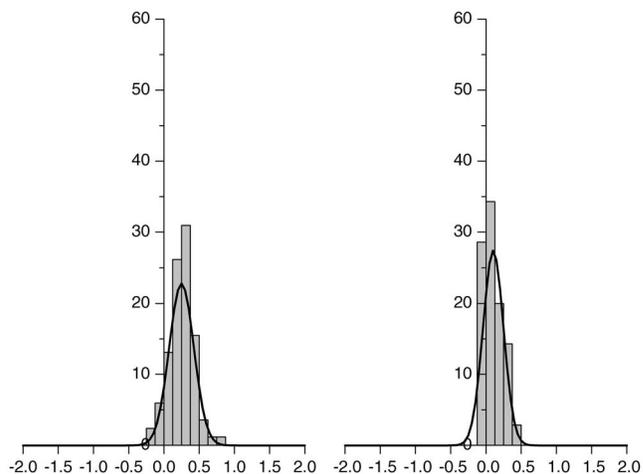
FIG. 5. Histogram of the frequency of deviation (CC3/TZVP vs CASPT2/TZVP, in%) of all calculated singlet $\pi \to \pi^*$ (left) and $n \to \pi^*$ (right) excited states. The normal distribution of the deviation is also shown.
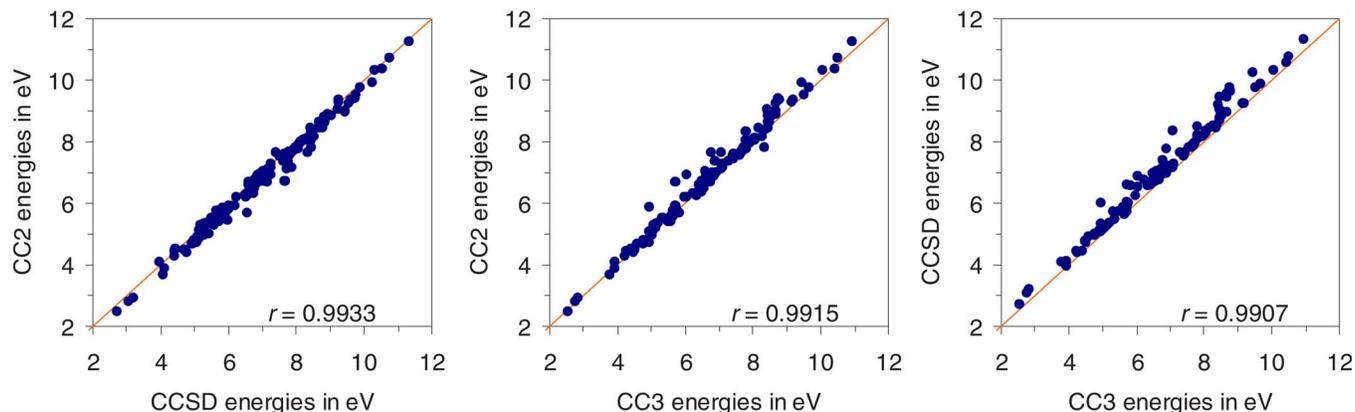
FIG. 6. (Color online) Correlation plots for all calculated singlet excited states: Coupled cluster vertical excitation energies.

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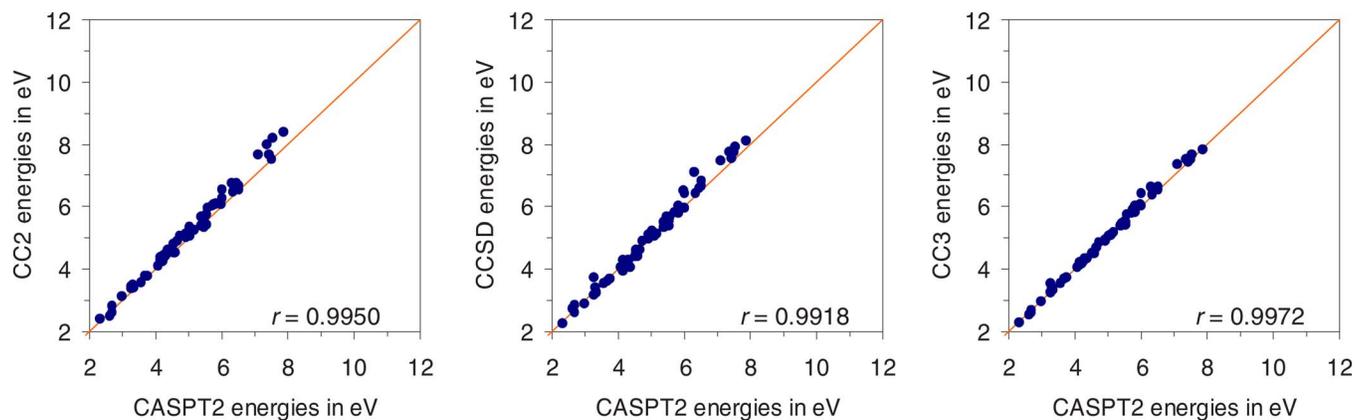
FIG. 7. (Color online) Correlation plots for all calculated triplet excited states: CC/TZVP vs CASPT2/TZVP vertical excitation energies.

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

[a]From the literature, see Table II and Supporting Information.
[b]Total 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 strenths, 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,
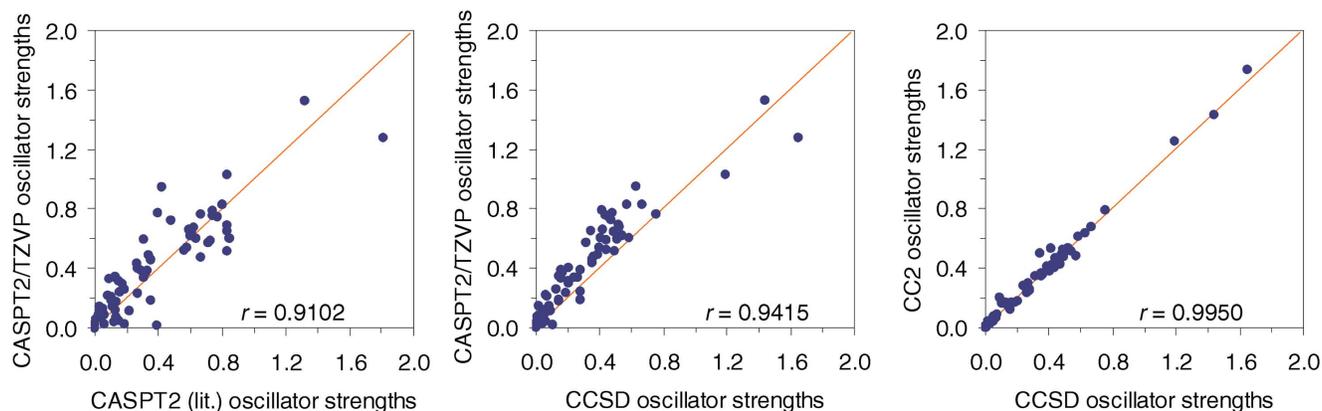
FIG. 8. (Color online) Correlation plots for all dipole-allowed oscillator strengths: CASPT2 (literature) vs CASPT2/TZVP, CCSD/TZVP vs CASPT2/TZVP and CCSD/TZVP vs CC2.

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
E-Butadiene	$1\,^1B_u\ (\pi\rightarrow\pi^*)$	0.686	0.783	0.809	0.776	0.52–0.803
all-E-Hexatriene	$1\,^1B_u\ (\pi\rightarrow\pi^*)$	0.85	1.045	1.272	1.213	0.655–1.154
all-E-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	$1\,^1B_1\ (n \to \pi^*)$	0.01	0.010	0.006	0.007	
	$2\,^1A_1\ (\pi \to \pi^*)$	0.009	0.027	0.014	0.014	
	$2\,^1B_1\ (n \to \pi^*)$	0.008	0.008	0.005	0.005	
	$1\,^1B_2\ (\pi \to \pi^*)$	0.003	0.115	0.009	0.006	
	$2\,^1B_2\ (\pi \to \pi^*)$	0.75	0.603	0.489	0.459	
	$3\,^1A_1\ (\pi \to \pi^*)$	0.50	0.742	0.444	0.494	
s-Triazine	$1\,^1A_2''\ (n \to \pi^*)$	0.015	0.021	0.017	0.018	0.02–0.027
	$1\,^1E'\ (\pi \to \pi^*)$	0.61	0.680	0.441	0.437	0.92
	$2\,^1E'\ (\pi \to \pi^*)$	0.21	0.044	0.000	0.000	
s-Tetrazine	$1\,^1B_{3u}\ (n \to \pi^*)$	0.013	0.013	0.007	0.009	0.007–0.012
	$1\,^1B_{2u}\ (\pi \to \pi^*)$	0.045	0.110	0.046	0.047	0.052–0.095
	$2\,^1B_{3u}\ (n \to \pi^*)$	0.017	0.021	0.011	0.012	0.01–0.018
	$1\,^1B_{1u}\ (\pi \to \pi^*)$	0.001	0.136	0.017	0.003	0.00–0.054
	$2\,^1B_{1u}\ (\pi \to \pi^*)$	0.687	0.496	0.376	0.381	0.39–0.630
	$2\,^1B_{2u}\ (\pi \to \pi^*)$	0.733	0.588	0.368	0.333	0.45–0.755
Formaldehyde	$1\,^1B_1\ (\sigma \to \pi^*)$	0.01	0.013	0.079	0.074	0.000–0.001
	$2\,^1A_1\ (\pi \to \pi^*)$	0.28	0.451	0.368	0.374	0.063–0.100
Acetone	$1\,^1B_1\ (\sigma \to \pi^*)$	0.010	0.011	0.000	0.000	0.003
	$2\,^1A_1\ (\pi \to \pi^*)$	0.326	0.358	0.298	0.256	0.255
p-Benzoquinone	$1\,^1B_{3g}\ (\pi \to \pi^*)$	0.000	0.000	0.000	0.000	
	$1\,^1B_{1u}\ (\pi \to \pi^*)$	0.616	0.638	0.538	0.558	0.636–0.704
	$1\,^1B_{3u}\ (n \to \pi^*)$	0.000	0.000	0.000	0.001	0.000
	$1\,^1B_{2u}\ (\pi \to \pi^*)$	0.022	0.016	0.000	0.000	
	$2\,^1B_{1u}\ (\pi \to \pi^*)$	0.624	0.660	0.544	0.509	0.693
	$3\,^1B_{1u}\ (\pi \to \pi^*)$	0.030	0.079	0.000	0.000	
Formamide	$1\,^1A''\ (n \to \pi^*)$	0.001	0.001	0.001	0.001	0.000–0.001
	$2\,^1A'\ (\pi \to \pi^*)$	0.371	0.479	0.385	0.371	0.149–0.338
	$3\,^1A'\ (\pi \to \pi^*)$	0.131	0.163	0.010	0.102	
Acetamide	$1\,^1A''\ (n \to \pi^*)$	0.001	0.001	0.001	0.001	
	$2\,^1A'\ (\pi \to \pi^*)$	0.292	0.424	0.199	0.223	
	$3\,^1A'\ (\pi \to \pi^*)$	0.179	0.263	0.279	0.299	
Propanamide	$1\,^1A''\ (n \to \pi^*)$	0.001	0.001	0.000	0.000	
	$2\,^1A'\ (\pi \to \pi^*)$	0.346	0.405	0.138	0.108	
	$3\,^1A'\ (\pi \to \pi^*)$	0.205	0.275	0.189	0.150	
Cytosine	$2\,^1A'\ (\pi \to \pi^*)$	0.061	0.093	0.049	0.058	0.052–0.080
	$1\,^1A''\ (n \to \pi^*)$	0.005	0.003	0.001	0.002	0.001–0.002
	$3\,^1A'\ (\pi \to \pi^*)$	0.108	0.352	0.165	0.178	0.138–0.181
	$4\,^1A'\ (\pi \to \pi^*)$	0.863	0.623	0.632	0.608	
	$2\,^1A''\ (n \to \pi^*)$	0.001	0.002	0.002	0.000	0.001–0.003
	$5\,^1A'\ (\pi \to \pi^*)$	0.147	0.366	0.168	0.159	
	$6\,^1A'\ (\pi \to \pi^*)$	0.239	0.132	0.223	0.112	
Thymine	$1\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$2\,^1A'\ (\pi \to \pi^*)$	0.17	0.334	0.197	0.222	0.18
	$3\,^1A'\ (\pi \to \pi^*)$	0.17	0.067	0.080	0.071	0.04
	$2\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$4\,^1A'\ (\pi \to \pi^*)$	0.15	0.356	0.250	0.285	0.18
	$3\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$4\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$5\,^1A'\ (\pi \to \pi^*)$	0.85	0.672	0.515	0.361	
	$6\,^1A'\ (\pi \to \pi^*)$	0.00	0.004	0.000	0.000	
Uracil	$1\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$2\,^1A'\ (\pi \to \pi^*)$	0.19	0.320	0.197	0.224	0.18–0.26
	$3\,^1A'\ (\pi \to \pi^*)$	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]
	$2\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.001	
	$3\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$4\,^1A'\ (\pi \to \pi^*)$	0.29	0.249	0.188	0.209	0.035–0.17
	$4\,^1A''\ (n \to \pi^*)$	0.00	0.000	0.000	0.000	
	$5\,^1A'\ (\pi \to \pi^*)$	0.76	0.804	0.547	0.430	0.51
Adenine	$2\,^1A'\ (\pi \to \pi^*)$	0.070	0.146	0.037	0.002	0.004–0.03
	$3\,^1A'\ (\pi \to \pi^*)$	0.370	0.201	0.276	0.297	0.17–0.36
	$1\,^1A''\ (n \to \pi^*)$	0.001	0.001	0.000	0.000	0.001–0.007
	$4\,^1A'\ (\pi \to \pi^*)$	0.851	0.538	0.496	0.513	0.51
	$5\,^1A'\ (\pi \to \pi^*)$	0.159	0.001	0.085	0.070	
	$2\,^1A''\ (n \to \pi^*)$	0.001	0.002	0.000	0.000	0.003–0.005
	$6\,^1A'\ (\pi \to \pi^*)$	0.565	0.010	0.320	0.286	
	$7\,^1A'\ (\pi \to \pi^*)$	0.406	0.037	0.177	0.122	

[a]Data from publications by the Roos group in the 1990s. See Supporting Information for references.
[b]Calculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the SA-CASSCF/MS-CASPT2 level using a standard active space.
[c]Calculated using MP2/6-31G* optimized geometries constrained to their highest possible symmetry at the coupled cluster level.
[d]Range 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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