

Benchmarks of electronically excited states: Basis set effects on CASPT2 results

Mario R. Silva-Junior, Marko Schreiber, Stephan P. A. Sauer, and Walter Thiel

Citation: *The Journal of Chemical Physics* **133**, 174318 (2010); doi: 10.1063/1.3499598

View online: <http://dx.doi.org/10.1063/1.3499598>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/133/17?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Probing ground and low-lying excited states for HIO₂ isomers](#)

J. Chem. Phys. **141**, 234303 (2014); 10.1063/1.4903789

[An experimental and theoretical investigation into the excited electronic states of phenol](#)

J. Chem. Phys. **141**, 074314 (2014); 10.1063/1.4893116

[Benchmarks for electronically excited states: Time-dependent density functional theory and density functional theory based multireference configuration interaction](#)

J. Chem. Phys. **129**, 104103 (2008); 10.1063/1.2973541

[Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3](#)

J. Chem. Phys. **128**, 134110 (2008); 10.1063/1.2889385

[Electronic spectra of heteroatom-containing isoelectronic carbon chains C_{2n}S and C_{2n}Cl + \(n = 1 – 5\)](#)

J. Chem. Phys. **124**, 124319 (2006); 10.1063/1.2179068



Benchmarks of electronically excited states: Basis set effects on CASPT2 results

Mario R. Silva-Junior,¹ Marko Schreiber,¹ Stephan P. A. Sauer,² and Walter Thiel^{1,a)}

¹Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

²Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

(Received 23 August 2010; accepted 20 September 2010; published online 5 November 2010)

Vertical excitation energies and one-electron properties are computed for the valence excited states of 28 medium-sized organic benchmark molecules using multistate multiconfigurational second-order perturbation theory (MS-CASPT2) and the augmented correlation-consistent aug-cc-pVTZ basis set. They are compared with previously reported MS-CASPT2 results obtained with the smaller TZVP basis. The basis set extension from TZVP to aug-cc-pVTZ causes rather minor and systematic shifts in the vertical excitation energies that are normally slightly reduced (on average by 0.11 eV for the singlets and by 0.09 eV for the triplets), whereas the changes in the calculated oscillator strengths and dipole moments are somewhat more pronounced on a relative scale. These basis set effects at the MS-CASPT2 level are qualitatively and quantitatively similar to those found at the coupled cluster level for the same set of benchmark molecules. The previously proposed theoretical best estimates (TBE-1) for the vertical excitation energies for 104 singlet and 63 triplet excited states of the benchmark molecules are upgraded by replacing TZVP with aug-cc-pVTZ data that yields a new reference set (TBE-2). Statistical evaluations of the performance of density functional theory (DFT) and semiempirical methods lead to the same ranking and very similar quantitative results for TBE-1 and TBE-2, with slightly better performance measures with respect to TBE-2. DFT/MRCI is most accurate among the investigated DFT-based approaches, while the OMx methods with orthogonalization corrections perform best at the semiempirical level. © 2010 American Institute of Physics. [doi:10.1063/1.3499598]

I. INTRODUCTION

Theoretical studies of photophysical and photochemical processes demand an accurate description of electronically excited states. The performance of the available theoretical methods in this area can be assessed by suitable benchmarks. Recently we introduced a standard benchmark set for this purpose¹ that consists of 28 medium-sized molecules and covers the most relevant organic chromophores. Theoretical reference data were generated using multistate complete-active-space second-order perturbation theory (MS-CASPT2) and linear response coupled cluster theory (CC2, CCSD, CC3). Based on these data and high-level *ab initio* results from the literature, theoretical best estimates (TBE) were derived for the vertical excitation energies of 104 singlet and 63 triplet states.¹ This benchmark set has been used in evaluations of other *ab initio* approaches,²⁻⁵ density functional theory (DFT) methods,⁶⁻⁹ and semiempirical methods.¹⁰

The proposed benchmark set¹ targets valence excited states. Therefore, our original *ab initio* calculations employed the TZVP basis,¹¹ which was considered flexible enough to describe these states adequately. This choice allowed us to adopt a standard active space in the MS-CASPT2 calculations (including all π and π^* orbitals as

well as any n and σ orbital involved), and it had the additional advantage that coupled cluster CC3 calculations remained feasible for the majority of the molecules. On the other hand, the absence of diffuse functions in the TZVP basis implies that high-lying valence states with rather diffuse character may not be described properly, especially in the case of partial valence-Rydberg mixing. This was one of the reasons why we assigned TBE values on the basis of our own calculations only for transitions up to 7 eV.¹

It is clearly desirable to improve the reference data in our benchmark set by using a basis set larger than TZVP. The augmented correlation consistent triple-zeta basis (aug-cc-pVTZ) (Refs. 12 and 13) would seem to be a natural choice since it has often been used in excited-state work on medium-sized molecules. In our original benchmark study,¹ we analyzed the basis set convergence of the vertical excitation energy for the high-lying ¹B_{1u} singlet state of ethene at the CC and CASPT2 levels using twelve different correlation consistent basis sets,^{12,13} and we found that the essentially converged aug-cc-pV5Z and d-aug-cc-pVQZ results were well reproduced when using the aug-cc-pVTZ basis (within 0.1 eV) whereas the TZVP values were too high (by more than 0.4 eV). These and many other results indicate that the aug-cc-pVTZ basis set is flexible enough to describe rather diffuse valence states. Of course, a proper representation of Rydberg states will require further augmentation, typically

^{a)}Electronic mail: thiel@mpi-muelheim.mpg.de.

by sets of molecule-centered diffuse basis functions (for early examples, see Refs. 14–22). In the present work, we use the aug-cc-pVTZ basis exclusively since we focus on valence excited states and not on Rydberg states (which are not included in our benchmark set).

In a separate study, we have reported coupled cluster results with the aug-cc-pVTZ basis for the valence excited states of all 28 benchmark molecules.²³ The basis set effects upon going from TZVP to aug-cc-pVTZ were quite uniform in the CC2, CCSDR(3), and CC3 calculations. For each of the three coupled cluster variants, a correlation coefficient greater than 0.994 was found between the vertical excitation energies computed with the two basis sets, and the aug-cc-pVTZ values were generally somewhat lower than the TZVP values (typically by 0.2 eV for singlets).²³ We have now carried out a corresponding systematic MS-CASPT2 study using the aug-cc-pVTZ basis throughout, with the objective to explore the basis set effects at the MS-CASPT2 level and to improve the theoretical best estimates for vertical excitation energies.

This article is organized as follows: Computational details are outlined in Sec. II. The MS-CASPT2/aug-cc-pVTZ results are presented in the following section and compared with the results from MS-CASPT2/TZVP and CC/aug-cc-pVTZ calculations.^{1,23} Some of the theoretical best estimates are also upgraded in this section. Statistical evaluations of several approximate methods are then provided with respect to the updated theoretical best estimates. Section IV offers a brief summary.

II. COMPUTATIONAL METHODS

All calculations were performed using the MP2/6-31G* optimized ground-state equilibrium geometries¹ and the aug-cc-pVTZ basis set.^{12,13} The active space for the present CASSCF (complete-active-space self-consistent-field) calculations^{24,25} generally differs substantially from the standard active space that was adopted previously (consisting of all π and π^* orbitals as well as any relevant n and σ orbitals).¹ This standard active space is appropriate for the TZVP basis, but not for the larger aug-cc-pVTZ basis, where its use often leads to convergence problems in the CASSCF procedure or to low reference weights. Therefore, the active space was optimized for each individual molecule by adding other orbitals as appropriate. The CASSCF reference functions were then determined using state averaging (SA) with equal weights for all states of a given symmetry. The number of states included in the SA procedure was generally larger in the CASSCF/aug-cc-pVTZ calculations than in the previous CASSCF/TZVP calculations,¹ because many Rydberg states now appear lower in energy than some high-lying valence states that need to be covered. The choice of the active space and of the states included in the SA procedure was guided by the idea to aim at the most compact representation that would still ensure a reasonable and balanced description of all targeted valence excited states. These choices are specified for each individual molecule in the supporting information.²⁶

The CASSCF reference wave function served as starting

point for the subsequent MS-CASPT2 calculations.^{27–29} Since the aug-cc-pVTZ basis is more flexible and more diffuse than the TZVP basis, problems with intruder states appeared more often during the CASPT2 calculations than before.¹ They were identified by checking the weight of the reference function in the perturbation treatment, and the level-shift technique^{30,31} was applied to overcome such problems. If this approach was insufficient, the CASSCF setup was modified by including additional orbitals in the active space. Electronic transition dipole moments were calculated from the perturbatively modified wave functions and combined with the MS-CASPT2 energies to obtain the oscillator strengths.^{32,33}

Excitation energies are determined by the energy difference between a given excited state and the ground state. In the case of singlet excited states of the same symmetry as the ground state, the natural procedure is to refer to the MS-CASPT2 ground-state energy since the states of the same symmetry are treated together on the same footing. In other cases, the alternative is to choose the separately computed single-state SS-CASPT2 ground-state energy as reference.¹ We have checked both options for all 28 benchmark molecules and find a mean absolute deviation of 0.06 eV between the two types of ground-state energies with the aug-cc-pVTZ basis (see Table I of the supporting information²⁶) and rather small differences between these two options in the statistical evaluations (see Table II of the supporting information²⁶). For the sake of consistency, we continue to follow the previously adopted protocol, i.e., using the SS-CASPT2 ground-state energy for excited states of different symmetry.¹

The current CASPT2 calculations were carried out with the MOLCAS program (version 6.4).³⁴

III. RESULTS AND DISCUSSION

Detailed numerical results of the CASPT2/TZVP and CASPT2/aug-cc-pVTZ calculations are documented in the supporting information (Tables III-XXX).²⁶ There is one table for each benchmark molecule that contains, for each state considered, the computed vertical excitation energy, oscillator strength, dipole moment, and expectation value of $\langle z^2 \rangle$ as a measure of its spatial extent with respect to a suitable Cartesian coordinate z . Experimental data from the literature are also given with the corresponding references. The footnotes in these tables specify computational details of the CASPT2 calculations, especially the chosen active space and the number of states included in the SA procedure.

A. Basis set effects

The vertical excitation energies for the singlet and triplet states of our benchmark molecules are collected in Tables I and II, respectively. These tables contain our previous CASPT2/TZVP results,¹ the current CASPT2/aug-cc-pVTZ results, our most accurate coupled cluster results, our previous best theoretical estimates (TBE-1), and the current upgrade (TBE-2).

The coupled cluster results are taken or derived from previous studies^{1,23,35} and can be classified as follows: (a)

TABLE I. Vertical excitation energies ΔE (eV) for singlet states: CASPT2 and coupled cluster (CC) results, with the previous set of theoretical best estimates (TBE-1) and its current upgrade (TBE-2).

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Ethene	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	8.54	7.84	7.89 ^f	7.80	7.80
E-Butadiene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	6.47	6.38	6.21 ^g	6.18	6.18
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	6.62	6.43	6.63 ^f	6.55	6.55
E-Hexatriene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	5.31	5.18	5.32 ^g	5.10	5.10
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.42	5.33	5.77 ^g	5.09	5.09
E-Octatetraene	2 ¹ A _g ($\pi \rightarrow \pi^*$)	4.64	4.52	4.75 ^h	4.47	4.47
	1 ¹ B _u ($\pi \rightarrow \pi^*$)	4.70	4.35	4.84 ^h	4.66	4.66
Cyclopropene	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	6.76	6.63	6.67 ^f	6.76	6.67
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.06	6.66	6.68 ^f	7.06	6.68
Cyclopentadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.51	5.43	5.49 ^g	5.55	5.55
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.28	6.49 ^g	6.31	6.28
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.52	8.15	8.14 ^g		
Norbornadiene	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	5.34	4.98	5.37 ^h	5.34	5.37
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.11	5.94	6.21 ^h	6.11	6.21
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.32	6.62	7.49 ^h		
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$)	7.45	7.20	7.22 ^h		
Benzene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.04	4.96	5.03 ^f	5.08	5.08
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.42	6.57	6.42 ^f	6.54	6.54
	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	7.13	7.36	7.14 ^f	7.13	7.13
	1 ¹ E _{2g} ($\pi \rightarrow \pi^*$)	8.18	8.15	8.31 ^f	8.41	8.15
Naphthalene	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	4.24	4.06	4.25 ^g	4.24	4.25
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.77	4.49	4.82 ^g	4.77	4.82
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	5.87	5.83	5.90 ^g	5.87	5.90
	1 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	5.99	5.71	5.75 ^g	5.99	5.75
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	6.06	6.04	6.11 ^g	6.06	6.11
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	6.33	6.05	6.36 ^g	6.33	6.36
	2 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	6.47	6.31	6.46 ^g	6.47	6.46
	3 ¹ A _g ($\pi \rightarrow \pi^*$)	6.67	6.49	6.86 ^g	6.67	6.49
	3 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	7.74	6.69	8.32 ^h		
	3 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	8.17	7.92	7.88 ^h		
Furan	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.39	6.19	6.26 ^g	6.32	6.32
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.50	6.35	6.51 ^g	6.57	6.57
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.17	7.93	8.13 ^g	8.13	8.13
Pyrrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.31	6.23	6.27 ^g	6.37	6.37
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.33	6.22	6.20 ^g	6.57	6.57
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.17	7.95	7.60 ^g	7.91	7.91
Imidazole	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.19	6.40	6.25 ^h	6.19	6.25
	1 ¹ A'' ($n \rightarrow \pi^*$)	6.81	6.69	6.65 ^h	6.81	6.65
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.93	6.82	6.73 ^h	6.93	6.73
	2 ¹ A'' ($n \rightarrow \pi^*$)	7.90	7.80	7.57 ^h		
	4 ¹ A' ($\pi \rightarrow \pi^*$)	8.16	8.96	8.51 ^h		
Pyridine	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.02	5.00	5.12 ^g	4.85	4.85
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	5.17	5.07	4.95 ^g	4.59	4.59
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.51	5.49	5.41 ^g	5.11	5.11
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.39	6.59	6.60 ^g	6.26	6.26
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.27	7.72	7.33 ^g	7.27	7.27
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.46	7.49	7.39 ^g	7.18	7.18
	3 ¹ B ₂ ($\pi \rightarrow \pi^*$)	8.60	8.06	7.72 ^g		
	4 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.69	8.28	8.33 ^g		
Pyrazine	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	4.12	4.02	4.13 ^g	3.95	4.13
	1 ¹ A _u ($n \rightarrow \pi^*$)	4.70	4.75	4.98 ^g	4.81	4.98
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.85	4.80	4.97 ^g	4.64	4.97
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.68	5.56	5.65 ^g	5.56	5.65
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.41	6.47	6.69 ^g	6.60	6.69
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.89	6.61	6.83 ^g	6.58	6.83
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.66	7.73	7.81 ^g	7.60	7.81
	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.79	7.71	7.86 ^g	7.72	7.86
	1 ¹ B _{3g} ($\pi \rightarrow \pi^*$)	8.47	8.33	8.69 ^g		
	2 ¹ A _g ($\pi \rightarrow \pi^*$)	8.61	8.30	8.78 ^g		

TABLE I. (Continued.)

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Pyrimidine	1 ¹ B ₁ (<i>n</i> → π^*)	4.44	4.34	4.43 ^g	4.55	4.43
	1 ¹ A ₂ (<i>n</i> → π^*)	4.80	4.74	4.85 ^g	4.91	4.85
	1 ¹ B ₂ (π → π^*)	5.24	5.17	5.34 ^g	5.44	5.34
	2 ¹ A ₁ (π → π^*)	6.63	6.81	6.82 ^g	6.95	6.82
	3 ¹ A ₁ (π → π^*)	7.21	7.26	7.53 ^g		
	2 ¹ B ₂ (π → π^*)	7.64	7.74	7.82 ^g		
Pyridazine	1 ¹ B ₁ (<i>n</i> → π^*)	3.78	3.71	3.85 ^g	3.78	3.85
	1 ¹ A ₂ (<i>n</i> → π^*)	4.31	4.18	4.44 ^g	4.31	4.44
	2 ¹ A ₁ (π → π^*)	5.18	5.06	5.20 ^g	5.18	5.20
	2 ¹ A ₂ (<i>n</i> → π^*)	5.77	5.67	5.66 ^g	5.77	5.66
	1 ¹ B ₂ (π → π^*)	6.31	6.34	6.68 ^g		
	2 ¹ B ₁ (<i>n</i> → π^*)	6.52	6.13	6.33 ^g		
	2 ¹ B ₂ (π → π^*)	7.29	7.45	7.33 ^g		
	3 ¹ A ₁ (π → π^*)	7.62	7.17	7.54 ^g		
<i>s</i> -Triazine	1 ¹ A ₁ ^{''} (<i>n</i> → π^*)	4.60	4.54	4.70 ^g	4.60	4.70
	1 ¹ A ₂ ^{''} (<i>n</i> → π^*)	4.66	4.60	4.71 ^g	4.66	4.71
	1 ¹ E ^{''} (<i>n</i> → π^*)	4.70	4.63	4.75 ^g	4.70	4.75
	1 ¹ A ₂ ['] (π → π^*)	5.79	5.75	5.71 ^g	5.79	5.71
	2 ¹ A ₁ ['] (π → π^*)	7.25	7.20	7.18 ^g		
	1 ¹ E ['] (π → π^*)	7.50	7.36	7.84 ^g		
	2 ¹ E ^{''} (<i>n</i> → π^*)	7.71	7.55	7.78 ^g		
	2 ¹ E ['] (π → π^*)	8.99	9.02	9.44 ^g		
<i>s</i> -Tetrazine	1 ¹ B _{3u} (<i>n</i> → π^*)	2.29	2.27	2.46 ^f	2.29	2.46
	1 ¹ A _u (<i>n</i> → π^*)	3.51	3.40	3.78 ^g	3.51	3.78
	1 ¹ B _{1g} (<i>n</i> → π^*)	4.73	4.74	4.87 ^f	4.73	4.87
	1 ¹ B _{2u} (π → π^*)	4.93	4.89	5.08 ^f	4.93	5.08
	1 ¹ B _{2g} (<i>n</i> → π^*)	5.20	5.07	5.28 ^f	5.20	5.28
	2 ¹ A _u (<i>n</i> → π^*)	5.50	5.32	5.39 ^g	5.50	5.39
	1 ¹ B _{3g} (<i>n, n</i> → π^*, π^*)	5.86	5.76		5.79	5.76
	2 ¹ B _{2g} (<i>n</i> → π^*)	6.06	5.84	6.16 ^f		
	2 ¹ B _{1g} (<i>n</i> → π^*)	6.45	6.33	6.80 ^f		
	3 ¹ B _{1g} (<i>n</i> → π^*)	6.73	6.64	7.12 ^g		
	2 ¹ B _{3u} (<i>n</i> → π^*)	6.77	6.59	6.60 ^f		
	1 ¹ B _{1u} (π → π^*)	6.94	6.84	7.18 ^f		
	2 ¹ B _{1u} (π → π^*)	7.42	7.20	7.59 ^f		
	2 ¹ B _{2u} (π → π^*)	8.14	8.00	8.33 ^g		
	2 ¹ B _{3g} (π → π^*)	8.34	8.19	8.51 ^g		
	Formaldehyde	1 ¹ A ₂ (<i>n</i> → π^*)	3.99	4.01	3.88 ^f	3.88
1 ¹ B ₁ (σ → π^*)		9.14	9.12	9.05 ^f	9.1	9.04 ⁱ
2 ¹ A ₁ (π → π^*)		9.32	9.47	9.31 ^f	9.3	9.29 ⁱ
Acetone	1 ¹ A ₂ (<i>n</i> → π^*)	4.44	4.49	4.38 ^f	4.40	4.38
	1 ¹ B ₁ (σ → π^*)	9.27	9.25	9.04 ^g	9.1	9.04
	2 ¹ A ₁ (π → π^*)	9.31	9.19	8.90 ^f	9.4	8.90
<i>p</i> -Benzoquinone	1 ¹ B _{1g} (<i>n</i> → π^*)	2.76	2.81	2.74 ^g	2.76	2.74
	1 ¹ A _u (<i>n</i> → π^*)	2.77	2.83	2.86 ^g	2.77	2.86
	1 ¹ B _{3g} (π → π^*)	4.26	4.37	4.44 ^g	4.26	4.44
	1 ¹ B _{1u} (π → π^*)	5.28	5.41	5.47 ^g	5.28	5.47
	1 ¹ B _{3u} (<i>n</i> → π^*)	5.64	5.55	5.71 ^g	5.64	5.55
	2 ¹ B _{3g} (π → π^*)	6.96	6.99	7.16 ^g	6.96	7.16
	2 ¹ B _{1u} (π → π^*)	7.92	7.87	7.62 ^g		
	2 ¹ B _{3u} (π → π^*)	7.92	7.87	7.62 ^g		
Formamide	1 ¹ A ^{''} (<i>n</i> → π^*)	5.63	5.58	5.55 ^f	5.63	5.55
	2 ¹ A ['] (π → π^*)	7.39	7.45	7.35 ^f	7.39	7.35
	3 ¹ A ['] (π → π^*)	10.54	10.47			
Acetamide	1 ¹ A ^{''} (<i>n</i> → π^*)	5.69	5.69	5.62 ^g	5.69	5.62
	2 ¹ A ['] (π → π^*)	7.27	7.12	7.14 ^g	7.27	7.14
	3 ¹ A ['] (π → π^*)	10.09	10.03	9.66 ^g		
Propanamide	1 ¹ A ^{''} (<i>n</i> → π^*)	5.72	5.74	5.65 ^g	5.72	5.65
	2 ¹ A ['] (π → π^*)	7.20	7.17	7.09 ^g	7.20	7.09
	3 ¹ A ['] (π → π^*)	9.94	9.85	9.44 ^h		
Cytosine	2 ¹ A ['] (π → π^*)	4.67	4.52	4.69 ^j	4.66	4.66

TABLE I. (Continued.)

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Thymine	1 ¹ A'' ($n \rightarrow \pi^*$)	5.12	5.03	4.91 ^f	4.87	4.87
	2 ¹ A'' ($n \rightarrow \pi^*$)	5.53	5.44	5.33 ^f	5.26	5.26
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.53	5.43	5.56 ^f	5.62	5.62
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.40	6.09	6.29 ^f		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.97	6.68	6.62 ^f		
	1 ¹ A'' ($n \rightarrow \pi^*$)	4.95	4.86	4.83 ^f	4.82	4.82
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.06	4.91	5.19 ^f	5.20	5.20
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.15	6.01	6.26 ^f	6.27	6.27
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.38	6.22	6.16 ^f	6.16	6.16
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.53	6.32	6.50 ^f	6.53	6.53
Uracil	3 ¹ A'' ($n \rightarrow \pi^*$)	6.85	6.59	6.55 ^f		
	4 ¹ A'' ($n \rightarrow \pi^*$)	7.43	7.05	7.00 ^f		
	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.43	7.33	7.47 ^f		
	1 ¹ A'' ($n \rightarrow \pi^*$)	4.91	4.80	4.81 ^f	4.80	5.00
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.23	5.06	5.33 ^f	5.35	5.25
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.15	6.00	6.24 ^f	6.26	6.26
	2 ¹ A'' ($n \rightarrow \pi^*$)	6.28	6.15	6.09 ^f	6.10	6.10
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.74	6.47	6.66 ^f	6.70	6.70
	3 ¹ A'' ($n \rightarrow \pi^*$)	6.98	6.73	6.55 ^f	6.56	6.56
	4 ¹ A'' ($n \rightarrow \pi^*$)	7.28	6.93	6.95 ^f		
Adenine	5 ¹ A' ($\pi \rightarrow \pi^*$)	7.42	7.37	7.48 ^f		
	1 ¹ A'' ($n \rightarrow \pi^*$)	5.19	5.04	5.13 ^f	5.12	5.12
	2 ¹ A' ($\pi \rightarrow \pi^*$)	5.20	5.11	5.20 ^f	5.25	5.25
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.29	5.02	5.20 ^f	5.25	5.25
	2 ¹ A'' ($n \rightarrow \pi^*$)	5.96	5.75	5.74 ^f	5.75	5.75
	4 ¹ A' ($\pi \rightarrow \pi^*$)	6.34	6.25			
	5 ¹ A' ($\pi \rightarrow \pi^*$)	6.64	6.65			
6 ¹ A' ($\pi \rightarrow \pi^*$)	6.87	6.96				
7 ¹ A' ($\pi \rightarrow \pi^*$)	7.56	7.55				

^aSA-CASSCF/MS-CASPT2 results using TZVP basis and MP2/6-31G* ground-state equilibrium geometries. See Ref. 1.

^bSA-CASSCF/MS-CASPT2 results using aug-cc-pVTZ basis and MP2/6-31G* ground-state equilibrium geometries.

^cBest own coupled cluster results using MP2/6-31G* ground-state equilibrium geometries.

^dOriginal theoretical best estimates for vertical excitation energies. See Ref. 1 for details.

^eUpdated theoretical best estimates for vertical excitation energies. See text.

^fCC3/aug-cc-pVTZ results.

^gCC3/TZVP results with basis set correction from CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/TZVP.

^hCC3/TZVP results with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP.

ⁱCC3/aug-cc-pVQZ results as theoretical best estimates. From Supporting Information of Ref. 1.

^jCC2/aug-cc-pVTZ results. Reference 23.

CC3/aug-cc-pVTZ; (b) CC3/TZVP with basis set correction from CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/TZVP; (c) CC3/TZVP with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP; and (d) CC2/aug-cc-pVTZ. Hence, all coupled cluster data refer to the aug-cc-pVTZ basis set, but there are differences in the quality of the coupled cluster treatment. The CC3/aug-cc-pVTZ results (a) are most accurate. The composite results (b) and (c) and the CC2 data (d) reproduce (a) quite well: for the 22 singlet excited states where CC3/aug-cc-pVTZ results are available, the mean absolute deviations are 0.02, 0.08, and 0.12 eV, respectively.²³ For the larger set of 121 singlet excited states with TZVP results, the mean absolute deviation between CC3/TZVP and CC2/TZVP amounts to 0.07 eV.¹ Hence, the coupled cluster results in Table I are of CC3/aug-cc-pVTZ quality for (a) and (b) and close to it for (c) and (d) (normally within 0.1 eV). In the case of triplet excited states, most of the entries in Table II are of type (c), but they are still expected to be close to CC3/aug-cc-pVTZ quality since the basis set corrections are generally quite small for the triplet states.

We now address basis set effects on the vertical excitation energies at the MS-CASPT2 level. The inspection of the first two data columns of Tables I and II shows that the computed energies normally decrease slightly upon enlarging the basis from TZVP to aug-cc-pVTZ. The changes are generally quite moderate, and there is an excellent correlation between the two sets of computed energies, with a correlation coefficient of 0.9899 both for the singlet and triplet states (see Fig. 1). Histograms of the corresponding deviations are depicted in Fig. 2. The shifts due to basis set extension remain within 0.1 (0.2) eV for 43% (73%) of the singlet excited states, and for 53% (87%) of the triplet excited states. The statistical evaluation in Table III yields a mean absolute deviation between the two sets of calculated energies of 0.16 eV for the singlets and 0.12 eV for the triplets. The vertical excitation energies from MS-CASPT2/aug-cc-pVTZ are lower than those from MS-CASPT2/TZVP on average, by 0.11 eV for the singlets and 0.09 eV for the triplets. The basis set effects on the coupled cluster results show the same over-

TABLE II. Vertical excitation energies ΔE (eV) for triplet states: CASPT2 and coupled cluster (CC) results, with the previous set of theoretical best estimates (TBE-1) and its current upgrade (TBE-2).

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Ethene	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.48	4.48	4.50 ^f	4.50	4.50
E-Butadiene	1 ³ B _u ($\pi \rightarrow \pi^*$)	3.34	3.30	3.34 ^g	3.20	3.20
	1 ³ A _g ($\pi \rightarrow \pi^*$)	5.16	5.08	5.15 ^f	5.08	5.08
E-Hexatriene	1 ³ B _u ($\pi \rightarrow \pi^*$)	2.71	2.67	2.71 ^g	2.40	2.40
	1 ³ A _g ($\pi \rightarrow \pi^*$)	4.31	4.22	4.33 ^g	4.15	4.15
E-Octatetraene	1 ³ B _u ($\pi \rightarrow \pi^*$)	2.33	2.27	2.32 ^g	2.20	2.20
	1 ³ A _g ($\pi \rightarrow \pi^*$)	3.70	3.61	3.69 ^g	3.55	3.55
Cyclopropene	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.35	4.26	4.28 ^f	4.34	4.28
	1 ³ B ₁ ($\sigma \rightarrow \pi^*$)	6.51	6.36	6.40 ^f	6.62	6.40
Cyclopentadiene	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	3.28	3.21	3.26 ^g	3.25	3.26
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.11	5.02	5.09 ^g	5.09	5.09
Norbornadiene	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	3.75	3.65	3.68 ^g	3.72	3.68
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.22	4.16	4.16 ^g	4.16	4.16
Benzene	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.17	4.13	4.12 ^f	4.15	4.15
	1 ³ E _{1u} ($\pi \rightarrow \pi^*$)	4.90	4.76	4.81 ^f	4.86	4.86
	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	5.76	5.72	5.78 ^f	5.88	5.88
	1 ³ E _{2g} ($\pi \rightarrow \pi^*$)	7.38	7.32	7.45 ^f	7.51	7.51
Naphthalene	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	3.16	3.04	3.09 ^g	3.11	3.09
	1 ³ B _{3u} ($\pi \rightarrow \pi^*$)	4.25	4.03	4.09 ^g	4.18	4.09
	1 ³ B _{1g} ($\pi \rightarrow \pi^*$)	4.51	4.33	4.42 ^g	4.47	4.42
	2 ³ B _{2u} ($\pi \rightarrow \pi^*$)	4.68	4.54	4.56 ^g	4.64	4.56
	2 ³ B _{3u} ($\pi \rightarrow \pi^*$)	4.97	4.72	4.92 ^g	5.11	4.92
	1 ³ A _g ($\pi \rightarrow \pi^*$)	5.53	5.35	5.42 ^g	5.52	5.42
	2 ³ B _{1g} ($\pi \rightarrow \pi^*$)	6.21	6.12	6.12 ^g	6.48	6.12
	2 ³ A _g ($\pi \rightarrow \pi^*$)	6.38	6.12	6.17 ^g	6.47	6.17
	3 ³ A _g ($\pi \rightarrow \pi^*$)	6.59	6.55	6.65 ^g	6.79	6.65
	3 ³ B _{1g} ($\pi \rightarrow \pi^*$)	6.64	6.49	6.67 ^g	6.76	6.67
Furan	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.18	4.06	4.11 ^g	4.17	4.11
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.49	5.34	5.43 ^g	5.48	5.43
Pyrrrole	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.51	4.39	4.44 ^g	4.48	4.44
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.52	5.35	5.42 ^g	5.51	5.42
Imidazole	1 ³ A' ($\pi \rightarrow \pi^*$)	4.65	4.57	4.65 ^g	4.69	4.65
	2 ³ A' ($\pi \rightarrow \pi^*$)	5.74	5.56	5.64 ^g	5.79	5.64
	1 ³ A'' ($n \rightarrow \pi^*$)	6.36	6.29	6.25 ^g	6.37	6.25
	3 ³ A' ($\pi \rightarrow \pi^*$)	6.44	6.47	6.38 ^g	6.55	6.38
	4 ³ A' ($\pi \rightarrow \pi^*$)	7.44		7.25 ^g		
	2 ³ A'' ($n \rightarrow \pi^*$)	7.51	7.40	7.29 ^g		
Pyridine	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	4.27	4.23	4.28 ^g	4.06	4.06
	1 ³ B ₁ ($n \rightarrow \pi^*$)	4.57	4.54	4.42 ^g	4.25	4.25
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.71	4.66	4.72 ^g	4.64	4.64
	2 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.03	4.92	4.96 ^g	4.91	4.91
	1 ³ A ₂ ($n \rightarrow \pi^*$)	5.52	5.47	5.35 ^g	5.28	5.28
	2 ³ B ₂ ($\pi \rightarrow \pi^*$)	6.03	6.09	6.22 ^g	6.08	6.08
	3 ³ A ₁ ($\pi \rightarrow \pi^*$)	7.56	6.11	7.59 ^g		
	3 ³ B ₂ ($\pi \rightarrow \pi^*$)	7.87	7.61	7.29 ^g		
s-Tetrazine	1 ³ B _{3u} ($n \rightarrow \pi^*$)	1.61	1.63	1.87 ^f	1.89	1.87
	1 ³ A _u ($n \rightarrow \pi^*$)	3.28	3.23	3.49 ^f	3.52	3.49
	1 ³ B _{1g} ($n \rightarrow \pi^*$)	4.14	4.04	4.18 ^f	4.21	4.18
	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.37	4.36	4.36 ^f	4.33	4.36
	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	4.39	4.25	4.39 ^f	4.54	4.39
	1 ³ B _{2g} ($n \rightarrow \pi^*$)	4.94	4.82	4.89 ^f	4.93	4.89
	2 ³ A _u ($n \rightarrow \pi^*$)	5.04	4.91	4.96 ^f	5.03	4.96
	2 ³ B _{1u} ($\pi \rightarrow \pi^*$)	5.40	5.26	5.32 ^f	5.38	5.32
	2 ³ B _{2g} ($n \rightarrow \pi^*$)	5.97	5.78	5.97 ^f		
	2 ³ B _{1g} ($n \rightarrow \pi^*$)	6.37	6.02	6.54 ^f		
	2 ³ B _{3u} ($n \rightarrow \pi^*$)	6.54	6.39	6.45 ^f		
	2 ³ B _{2u} ($\pi \rightarrow \pi^*$)	7.08	7.01	7.21 ^f		
Formaldehyde	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	3.58	3.62	3.49 ^f	3.50	3.50 ^h
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.84	5.85	5.86 ^f	5.87	5.87 ^h

TABLE II. (Continued.)

Molecule	State	CASPT2/TZVP ^a	CASPT2/AVTZ ^b	CC/AVTZ ^c	TBE-1 ^d	TBE-2 ^e
Acetone	1 ³ A ₂ (<i>n</i> → <i>π</i> [*])	4.10	4.17	4.05 ^f	4.05	4.05
	1 ³ A ₁ (<i>π</i> → <i>π</i> [*])	6.04	6.09	6.07 ^f	6.03	6.07
<i>p</i> -Benzoquinone	1 ³ B _{1g} (<i>n</i> → <i>π</i> [*])	2.62	2.63	2.50 ^g	2.51	2.50
	1 ³ A _u (<i>n</i> → <i>π</i> [*])	2.66	2.66	2.61 ^g	2.62	2.61
	1 ³ B _{1u} (<i>π</i> → <i>π</i> [*])	2.99	3.00	3.02 ^g	2.96	3.02
	1 ³ B _{3g} (<i>π</i> → <i>π</i> [*])	3.32	3.30	3.37 ^g	3.41	3.37
	1 ³ A _u (<i>n</i> → <i>π</i> [*])	5.40	5.32	5.28 ^f	5.36	5.28
Formamide	1 ³ A' (<i>π</i> → <i>π</i> [*])	5.58	5.68	5.69 ^f	5.74	5.69
	1 ³ A'' (<i>n</i> → <i>π</i> [*])	5.41	5.40	5.35 ^g	5.42	5.35
Acetamide	1 ³ A' (<i>π</i> → <i>π</i> [*])	5.63	5.86	5.71 ^g	5.88	5.71
	1 ³ A'' (<i>n</i> → <i>π</i> [*])	5.45	5.56	5.38 ^g	5.45	5.38
Propanamide	1 ³ A' (<i>π</i> → <i>π</i> [*])	5.80	6.03	6.08 ^g	5.90	6.08

^aSA-CASSCF/MS-CASPT2 results using TZVP basis and MP2/6-31G* ground-state equilibrium geometries. See Ref. 1.

^bSA-CASSCF/MS-CASPT2 results using aug-cc-pVTZ basis and MP2/6-31G* ground-state equilibrium geometries.

^cBest own coupled cluster results using MP2/6-31G* ground-state equilibrium geometries.

^dOriginal theoretical best estimates for vertical excitation energies. See Ref. 1 for details.

^eUpdated theoretical best estimates for vertical excitation energies. See text.

^fCC3/aug-cc-pVTZ results.

^gCC3/TZVP results with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP. See Ref. 23.

^hCC3/aug-cc-pVQZ results as theoretical best estimates. From Supporting Information of Ref. 1.

all trends and are of comparable magnitude (somewhat more pronounced in the case of the singlets, see Table III).²³

There are a few cases where basis set enlargement from TZVP to aug-cc-pVTZ leads to drastic shifts in the MS-CASPT2 excitation energies. Changes of more than 0.4 eV occur for nine singlet states. One of these corresponds to a double excitation in *p*-benzoquinone, while the other eight of these states lie above 7 eV; the appearance of large basis set effects does not seem surprising for such high-lying valence states that are rather diffuse. In the triplet manifold, there is only one high-lying state with a huge shift (pyridine, 3 ³A₁). It should be noted that these problematic cases are not included among the states for which we derive theoretical best estimates, except for the 1 ¹B_{1u} state in ethene where reliable reference data are available from other calculations.¹

The theoretical results for the individual benchmark molecules and their relation to the available experimental data have been discussed in detail in our previous work.¹ To avoid repetition, we only make very few remarks on some individual excited states here, in order to point out specific features in the MS-CASPT2/aug-cc-pVTZ results. In norbornadiene, the first two excited singlet states (1 ¹A₂ and 1 ¹B₂) appear to be too low in energy compared with all previously published CASPT2 and coupled cluster results, and the experimental value for the first transition seems to be

underestimated.¹ A number of singlet excited states become significantly more diffuse when the basis is enlarged from TZVP to aug-cc-pVTZ, including 1 ¹B_u in butadiene and hexatriene, 3 ¹A₁ in cyclopentadiene, 1 ¹E_{1u} in benzene, 3 ¹A₁ in furan, 1 ¹B₂ and 3 ¹A₁ in pyrrole, 2 ¹B₂ in pyridine and pyridazine, and 2 ¹A' as well as 3 ¹A' in formamide and acetamide. Two valence excited states (4 ³A' in imidazole and 6 ¹A' in cytosine) could not be safely identified in the MS-CASPT2/aug-cc-pVTZ calculations because of assignment problems (valence-Rydberg mixing).

Basis set effects on oscillator strengths and dipole moments are presented in Fig. 3 and Table IV. The correlations between the results from MS-CASPT2/TZVP and MS-CASPT2/aug-cc-pVTZ still seem reasonable, with correlation coefficients of 0.9469 for the oscillator strengths and 0.8871 for the dipole moments, which are of the same order as the corresponding CC2 values of 0.9659 and 0.8325.²³ The relatively low values for the dipole moment reflect changes in the electronic character especially of high-lying (diffuse) excited states upon basis set extension. For example, the dipole moment of the 3 ¹A₁ state of cyclopentadiene increases from 0.46 to 4.43 D with MS-CASPT2, and from 1.13 to 3.63 D with CC2; by contrast, the corresponding changes are 0.01 D for the ground state and less than 0.15 D for the first excited singlet state of cyclopentadiene.

TABLE III. Deviations in the vertical excitation energies (eV): aug-cc-pVTZ vs TZVP results.

	CASPT2 singlets	CASPT2 triplets	CC2 ^a singlets	CC2 ^a triplets	CC3 ^a singlets
Count ^b	151	70	143	71	22
Mean	-0.11	-0.09	-0.22	-0.08	-0.18
Abs. mean	0.16	0.12	0.23	0.10	0.18
Std. dev.	0.22	0.21	0.29	0.14	0.25
Maximum (+)	0.80	0.23	0.20	0.06	...
Maximum (-)	1.05	1.45	1.34	0.54	0.75

^aResults from Ref. 23.

^bTotal number of considered states.

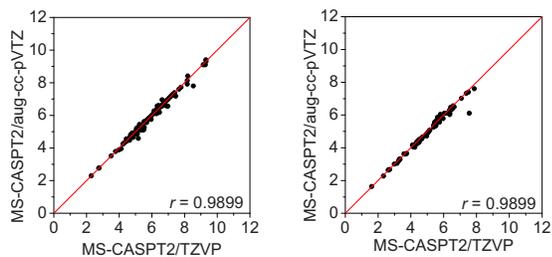


FIG. 1. Correlation plots for the vertical excitation energies (eV) at the CASPT2 level: aug-cc-pVTZ vs TZVP results for singlets (left) and triplets (right).

According to the statistical evaluation (Table IV) basis set extension from TZVP to aug-cc-pVTZ leads to similar changes in MS-CASPT2 and CC2: the oscillator strengths are reduced by similar amounts on average (by 0.039 and 0.032, respectively), and the mean absolute deviations are of comparable magnitude both for the oscillator strengths (0.063 versus 0.047) and the dipole moments (0.52 versus 0.57 D).

B. Theoretical best estimates

In our first benchmark study, we had selected best estimates for the vertical excitation energies of 104 singlet excited states and 63 triplet excited states in our set of 28 benchmark molecules.¹ They were adopted from published highly correlated *ab initio* studies with large basis sets, for example, using multireference configuration interaction (MRCI), multireference perturbation theory (MRMP), or coupled cluster methods. In the absence of such literature data, these estimates were derived from our own calculations using the following guidelines: CC3/TZVP values were taken for the triplet states (all with single excitation weights of more than 93%). CASPT2/TZVP values were favored for the singlet excited states because there is normally at least one singlet state in each benchmark molecule with a CC3/TZVP single excitation weight of less than 90%. Given the limitations of the TZVP basis, CC3/TZVP or CASPT2/TZVP energies were usually not accepted as best estimates if they exceeded 7 eV or if there was reason to assume that diffuse basis functions are essential for a given state.

Following these guidelines, the previously chosen theoretical best estimates (TBE-1) for the valence excited singlet states were taken from published MRCI (9), MRMP (4), and coupled cluster (45) calculations with large basis sets as well as from own CASPT2/TZVP (43) and CC3/TZVP (3) values.

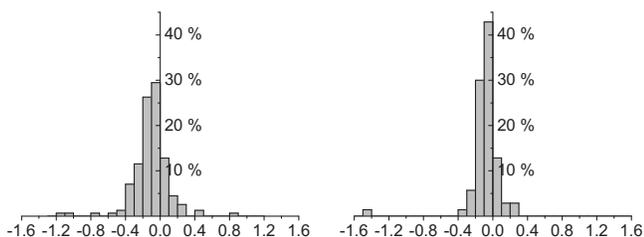


FIG. 2. Histograms (%) of the deviations between CASPT2/aug-cc-pVTZ and CASPT2/TZVP vertical excitation energies of singlet (left) and triplet (right) excited states.

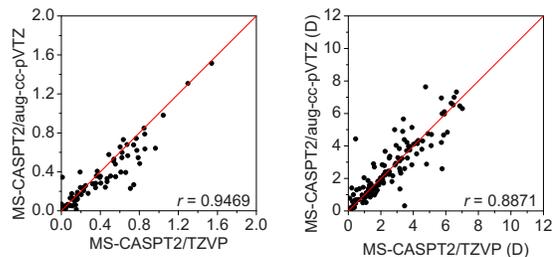


FIG. 3. Correlation plots for the oscillator strengths (left) and dipole moments (right, in D) of singlet excited states: aug-cc-pVTZ vs TZVP results.

In the case of the triplets, the TBE-1 values came from MRCI (9), MRMP (4), and coupled cluster (6) literature data as well as from own CC3/TZVP (44) calculations.

An obvious question is whether these theoretical best estimates should be upgraded in view of our new results with the larger aug-cc-pVTZ basis, in order to derive an improved set of reference data (called TBE-2). We have checked the previously adopted¹ *ab initio* values from the literature and found that they can generally be retained. In several cases, the present results with the aug-cc-pVTZ basis are of similar quality and numerically close to the literature values, but in the absence of significant improvements, it seems better to keep the TBE-1 values of these states, for the sake of consistency.

On the other hand, the TBE-1 values taken from our previous CASPT2/TZVP and CC3/TZVP calculations should be replaced by our new results with the aug-cc-pVTZ basis. We have adopted the general guideline to use the coupled cluster results (CC/aug-cc-pVTZ) from Tables I and II as TBE-2 values, except for states with CC3/TZVP single excitation weights¹ of less than 80%, where we use the MS-CASPT2/aug-cc-pVTZ results. In the case of the triplet states, this convention is consistent with our previous benchmarking (see above).¹ In the case of the singlet states, we have now shifted from MS-CASPT2 to coupled cluster results in the selection of the TBE-2 values. This is motivated by two observations. First, the MS-CASPT2 calculations with the aug-cc-pVTZ basis are less standardized than those with the TZVP basis due to the need to choose individually optimized active spaces and state averaging procedures, and second, it seems difficult to avoid occasional outliers in the MS-CASPT2/aug-cc-pVTZ results when using such molecule-specific procedures. The CC/aug-cc-pVTZ results appear to be more robust in general.

We have nevertheless also checked the alternative option of adopting the MS-CASPT2/aug-cc-pVTZ results as theoretical best estimates (when replacing TZVP-based data). The mean absolute deviation between the chosen CC/aug-cc-pVTZ and the MS-CASPT2/aug-cc-pVTZ values is 0.08 eV for the 44 relevant triplet states, and 0.15 eV for the 43 relevant singlet states. We have confirmed that this alternative choice would lead only to minor changes in the quantitative statistical evaluations and to no changes in the corresponding qualitative conclusions (see below). We will therefore not discuss this alternative any more.

In the following, we comment on some of the individual TBE-2 choices. As explained above, CC/aug-cc-pVTZ val-

TABLE IV. Deviations in the oscillator strengths and dipole moments (D) of singlet excited states: aug-cc-pVTZ vs TZVP results.

	CASPT2		CC2 ^a	
	Osc. strength	Dipole moment	Osc. strength	Dipole moment
Count ^b	106	138	95	127
Mean	-0.039	-0.01	-0.032	-0.14
Abs. mean	0.063	0.52	0.047	0.57
Std. dev.	0.115	0.85	0.088	0.97
Maximum (+)	0.334	3.97	0.269	3.29
Maximum (-)	0.479	3.19	0.287	3.51

^aResults from Ref. 23.^bTotal number of considered states.

ues were favored among our own results unless the CC3/TZVP single excitation weight was below 80%. This was the case for the 2^1A_1 state of cyclopentadiene, the 1^1E_{1g} state of benzene, the 3^1A_g state of naphthalene, and the 1^1B_{3u} state of *p*-benzoquinone, where the TBE-2 values were taken from MS-CASPT2 calculations. Likewise, the MS-CASPT2/aug-cc-pVTZ result was adopted for the doubly excited 1^1B_{3g} state of *s*-tetrazine that is not well described at the CC level. The TBE-1 and TBE-2 values are normally quite close to each other (see above), but there are exceptions with deviations of more than 0.3 eV, i.e., 1^1B_2 in cyclopropene, 1^1B_{2u} in pyrazine, 2^1A_1 in acetone, and 2^3B_{1g} in naphthalene. In two of these cases, the revision is supported by the close agreement between the MS-CASPT2/aug-cc-pVTZ and CC/aug-cc-pVTZ results (cyclopropene, naphthalene), while in acetone the directly computed CC3/aug-cc-pVTZ value for the 2^1A_1 state is now preferred over the indirectly deduced TBE-1 value.¹ In a similar vein, we adopt the directly computed CC3/aug-cc-pVQZ energies¹ as TBE-2 values for the high-lying 1^1B_1 and 2^1A_1 states in formaldehyde.

For pyrazine, literature data from EOM-CCSD (\tilde{T}) calculations using a DZ2P basis with one set of diffuse functions were selected for TBE-1.¹ It has been pointed out³⁶ that the resulting TBE-1 value for the 1^1B_{2u} state (4.64 eV) cannot be reliable since it is lower than the experimental vertical excitation energy (4.81 eV), and even below the adiabatic excitation energy (4.69 eV). We have now adopted the CC/aug-cc-pVTZ energies for all states of pyrazine (1^1B_{2u} at 4.97 eV).

In the case of *s*-tetrazine, it has been argued that the CASPT2 excitation energies tend to be too low in general.³⁷ The TBE-2 values taken from CC/aug-cc-pVTZ calculations are indeed mostly higher than both the corresponding MS-CASPT2/aug-cc-pVTZ data and the previous TBE-1 values from MS-CASPT2/TZVP calculations.

For uracil, completely renormalized EOM-CCSD(T)/aug-cc-pVTZ energies are available for the first two excited singlet states (5.00 and 5.25 eV) (Ref. 38) that are adopted for TBE-2. They are reasonably close to the published CC2/aug-cc-pVQZ values (4.80 and 5.35 eV) (Ref. 35) and to our present CC2/aug-cc-pVTZ results (4.81 and 5.33 eV). For the remaining singlet excited states in uracil and the other nucleobases, the TBE-2 values are again (as in TBE-1) taken from the published CC2/aug-cc-pVXZ energies (X=T for

cytosine, thymine, and adenine; X=Q for uracil).³⁵ Our own CC2/aug-cc-pVTZ energies are of course very close to these values (being computed at slightly different optimized ground state geometries, MP2 versus CC2).

In summary, the TBE-2 set for the valence excited singlet states is comprised of published MRCI (9), MRMP (4) and coupled cluster (29) calculations with large basis sets as well as of own MS-CASPT2 (5) and coupled cluster (57) calculations, mostly with the aug-cc-pVTZ basis. In the case of the triplets, the TBE-2 values are taken from MRCI (9), MRMP (4), and coupled cluster (4) literature data as well from own coupled cluster (46) calculations that aim at CC3/aug-cc-pVTZ accuracy.

C. Statistical evaluations

The TBE-1 values have previously been used in statistical evaluations of the performance of DFT-based and semiempirical methods for electronically excited states.^{6,23} These evaluations covered time-dependent density functional theory (TD-DFT) with three standard functionals (BP86, B3LYP, and BHLYP), a parametrized DFT-based multireference configuration interaction method (DFT/MRCI), standard semiempirical methods (MNDO, AM1, PM3, INDO/S), and semiempirical methods with orthogonalization corrections (OM1, OM2, and OM3). An obvious question is to what extent the statistical performance measures change when using the upgraded TBE-2 values as reference data. The results of such an analysis are given in Table V for the singlet excited states and in Table VI for the triplet excited states, while the corresponding correlation plots are shown in Figs. 4 and 5, respectively.

It is evident from these results that there is very little change in the statistical performance data by the upgrade from TBE-1 to TBE-2. Focusing on the mean absolute deviations (MAD) for the best DFT-based and semiempirical methods, there are mostly slight improvements when going to TBE-2. In the case of the singlets, the MAD values drop from 0.22 to 0.20 eV for DFT/MRCI and from 0.45–0.50 to 0.41–0.47 eV for the OMx methods, while there is no change for TD-B3LYP (0.27 eV). In the case of the triplets, the corresponding lowerings are from 0.45 to 0.40 eV for TD-B3LYP, from 0.25 to 0.20 eV for DFT/MRCI, and from 0.45–0.49 to 0.44–0.47 eV for the OMx methods. The correlation plots for the TBE-2 reference data look very similar

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

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

^aStatistical evaluations for DFT-based and semiempirical methods taken from Refs. 6 and 10, respectively.

^bTotal number of states considered.

to those published previously for TBE-1.^{6,23} This is as expected, of course, since the changes in the reference data between TBE-1 and TBE-2 are rather minor overall (see Fig. 6 and Table VII).

IV. CONCLUSIONS

In this article, we have studied basis set effects in MS-CASPT2 calculations of valence excited states in a recently defined benchmark set. Vertical excitation energies and one-electron properties were computed for all 28 benchmark molecules covering 151 singlet and 70 triplet excited states. The previous results with the TZVP basis were compared against the current results with the larger aug-cc-pVTZ basis

that is more flexible and thus more suitable for also properly describing rather diffuse valence states. This basis set extension leads to a slight but systematic lowering of the vertical excitation energies on average by 0.11 eV for the singlets and 0.09 eV for the triplets, in each case with a correlation coefficient of 0.9899. For one-electron properties such as oscillator strengths and dipole moments, the basis set effects are less systematic, as indicated by lower correlation coefficients between the aug-cc-pVTZ and TZVP results (0.9469 and 0.8871, respectively). Judging from the changes between the aug-cc-pVTZ and TZVP results on a relative scale, basis set convergence seems to be more difficult to achieve for these one-electron properties than for the excitation energies.

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

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

^aStatistical evaluations for DFT-based and semiempirical methods taken from Refs. 6 and 10, respectively.

^bTotal number of states considered.

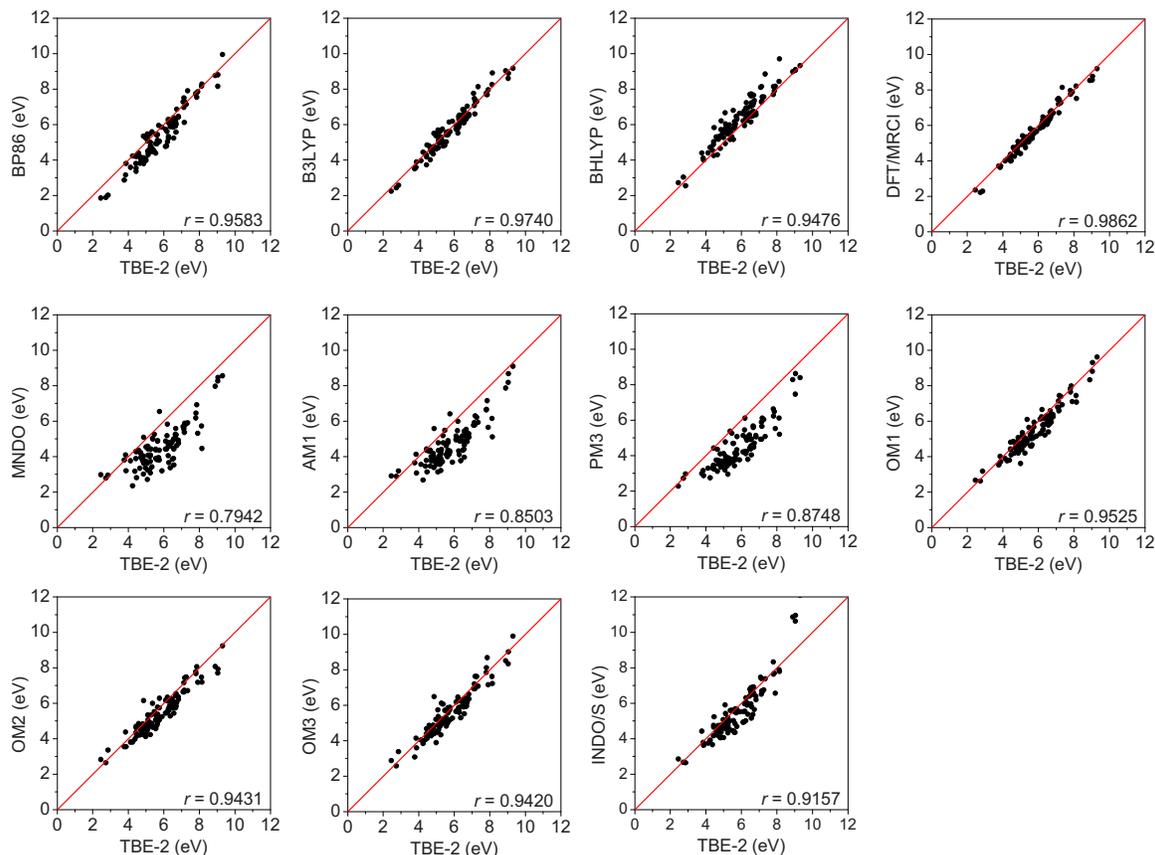


FIG. 4. Correlation plots for the singlet excited states from DFT and semiempirical methods with respect to the TBE-2 reference set of vertical excitation energies (eV).

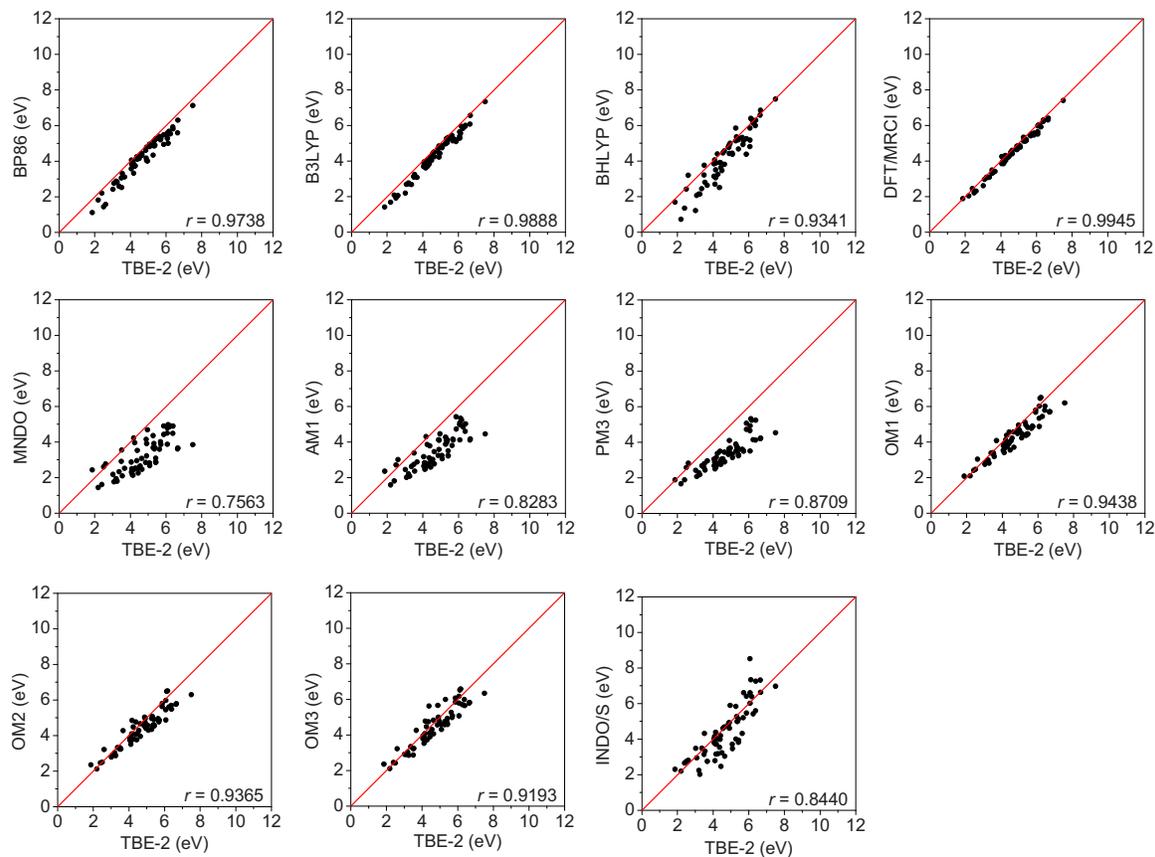


FIG. 5. Correlation plots for the triplet excited states from DFT and semiempirical methods with respect to the TBE-2 reference set of vertical excitation energies (eV).

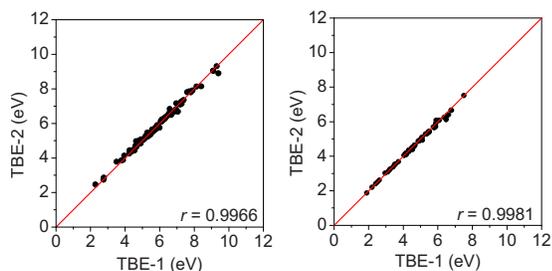


FIG. 6. Correlation plots for the singlet (left) and triplet (right) theoretical best estimates of vertical excitation energies (eV).

The basis set effects observed at the MS-CASPT2 level are generally rather similar to those found in coupled cluster calculations,²³ both qualitatively and quantitatively.

The previously proposed theoretical best estimates (TBE-1) for the vertical excitation energies of 104 singlets and 63 triplets have been revisited, and an upgrade version was derived (TBE-2). Most of the previously chosen *ab initio* results from the literature were retained, while the TZVP-based values from own calculations were mostly replaced by the present results with the larger aug-cc-pVTZ basis. Since the MS-CASPT2/aug-cc-pVTZ and CC/aug-cc-pVTZ excitation energies are normally of similar quality and numerically close to each other, it was difficult to make a choice, and TBE sets derived from these two approaches have correlation coefficients above 0.996 both for the singlet and triplet states. In view of the greater uniformity of the coupled cluster procedures, we finally decided to adopt the CC/aug-cc-pVTZ results unless the CC3/TZVP single excitation weight is lower than 80% for a given state in which case the MS-CASPT2/aug-cc-pVTZ result is preferred for TBE-2. The upgrade from TBE-1 to TBE-2 leads to rather minor changes, as can be seen from the low mean absolute deviations between the two sets that amount to 0.08 and 0.06 eV for the singlet and triplet states, respectively. It is therefore not surprising that the performance measures of DFT-based and semiempirical methods do not change much when being reevaluated using the upgraded TBE-2 values as reference data. The ranking of the methods remains the same, and the previously reported qualitative conclusions remain valid, with DFT/MRCI performing best among the studied DFT-based approaches and the OMx methods performing best at the semiempirical level.

TABLE VII. Deviations in the theoretical best estimates of vertical excitation energies (eV): TBE-1 vs TBE-2. (For the definition of TBE-1 and TBE-2 reference sets, see text.)

	Singlets	Triplets
Count ^a	104	63
Mean	0.00	-0.05
Abs. mean	0.08	0.06
Std. dev.	0.12	0.10
Maximum (+)	0.33	0.18
Maximum (-)	0.50	0.36

^aTotal number of considered states.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (Contract No. SFB 663, project C4). M.R.S.J. gladly acknowledges support by the Deutscher Akademischer Austauschdienst (DAAD).

- M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer, and W. Thiel, *J. Chem. Phys.* **128**, 134110 (2008).
- S. P. A. Sauer, M. Schreiber, M. R. Silva-Junior, and W. Thiel, *J. Chem. Theory Comput.* **5**, 555 (2009).
- J. Shen and S. Li, *J. Chem. Phys.* **131**, 174101 (2009).
- H. H. Falden, K. R. Falster-Hansen, K. L. Bak, S. Rettrup, and S. P. A. Sauer, *J. Phys. Chem. A* **113**, 11995 (2009).
- J. Boström, M. G. Delcey, F. Aquilante, L. Serrano-Andrés, T. B. Pedersen, and R. Lindh, *J. Chem. Theory Comput.* **6**, 747 (2010).
- M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer, and W. Thiel, *J. Chem. Phys.* **129**, 104103 (2008).
- L. Goerigk, J. Moellmann, and S. Grimme, *Phys. Chem. Chem. Phys.* **11**, 4611 (2009).
- D. Jacquemin, V. Wathelet, E. A. Perpète, and C. Adamo, *J. Chem. Theory Comput.* **5**, 2420 (2009).
- D. Jacquemin, E. A. Perpète, I. Ciofini, and C. Adamo, *J. Chem. Theory Comput.* **6**, 1532 (2010).
- M. R. Silva-Junior and W. Thiel, *J. Chem. Theory Comput.* **6**, 1546 (2010).
- A. Schäfer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).
- T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- R. A. Kendall, J. T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh, and B. O. Roos, *J. Chem. Phys.* **98**, 3151 (1993).
- L. Serrano-Andrés, R. Lindh, B. O. Roos, and M. Merchán, *J. Phys. Chem.* **97**, 9360 (1993).
- R. González-Luque, M. Merchán, and B. O. Roos, *Z. Phys. D: At., Mol. Clusters* **36**, 311 (1996).
- L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, B. O. Roos, and M. P. Fülscher, *J. Am. Chem. Soc.* **115**, 6184 (1993).
- B. O. Roos, M. Merchán, R. McDiarmid, and X. Xing, *J. Am. Chem. Soc.* **116**, 5927 (1994).
- J. Lorentzon, P.-Å. Malmqvist, M. P. Fülscher, and B. O. Roos, *Theor. Chim. Acta* **91**, 91 (1995).
- M. Rubio, M. Merchán, E. Ortí, and B. O. Roos, *Chem. Phys.* **179**, 395 (1994).
- J. Lorentzon, M. P. Fülscher, and B. O. Roos, *Theor. Chim. Acta* **92**, 67 (1995).
- M. P. Fülscher and B. O. Roos, *Theor. Chim. Acta* **87**, 403 (1994).
- M. R. Silva-Junior, S. P. A. Sauer, M. Schreiber, and W. Thiel, *Mol. Phys.* **108**, 453 (2010).
- B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, *Chem. Phys.* **48**, 157 (1980).
- B. O. Roos, *Int. J. Quantum Chem.* **S14**, 175 (1980).
- See supplementary material at <http://dx.doi.org/10.1063/1.3499598> for detailed numerical results of the CASPT2/TZVP and own CASPT2/aug-cc-pVTZ calculations and for a literature survey on excitation energies and one-electron properties of the benchmark set.
- K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990).
- K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).
- J. Finley, P.-Å. Malmqvist, B. O. Roos, and L. Serrano-Andrés, *Chem. Phys. Lett.* **288**, 299 (1998).
- B. O. Roos and K. Andersson, *Chem. Phys. Lett.* **245**, 215 (1995).
- B. O. Roos, K. Andersson, M. P. Fülscher, L. Serrano-Andrés, K. Pierloot, M. Merchán, and V. Molina, *J. Mol. Struct.: THEOCHEM* **388**, 257 (1996).
- P. Å. Malmqvist and B. O. Roos, *Chem. Phys. Lett.* **155**, 189 (1989).
- P.-Å. Malmqvist, B. O. Roos, and B. Schimmelpennig, *Chem. Phys. Lett.* **357**, 230 (2002).

- ³⁴G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, and L. Seijo, *Comput. Mater. Sci.* **28**, 222 (2003).
- ³⁵T. Fleig, S. Knecht, and C. Hättig, *J. Phys. Chem. A* **111**, 5482 (2007).
- ³⁶C. Woywod, A. Papp, G. J. Halasz, and A. Vibok, *Theor. Chim. Acta* **125**, 521 (2010).
- ³⁷C. Angeli, R. Cimraglia, and M. Cestari, *Theor. Chim. Acta* **123**, 287 (2009).
- ³⁸E. Epifanovsky, K. Kowalski, P.-D. Fan, M. Valiev, S. Matsika, and A. I. Krylov, *J. Phys. Chem. A* **112**, 9983 (2008).