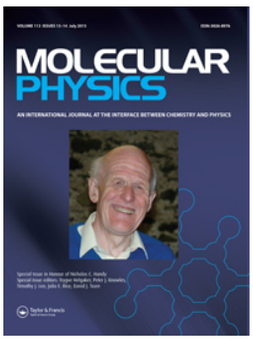

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INVITED ARTICLE

Performance of SOPPA-based methods in the calculation of vertical excitation energies and oscillator strengths

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We present two new modifications of the second-order polarization propagator approximation (SOPPA), SOPPA(SCS-MP2) and SOPPA(SOS-MP2), which employ either spin-component-scaled or scaled opposite-spin MP2 correlation coefficients instead of the regular MP2 coefficients. The performance of these two methods, the original SOPPA method as well as SOPPA(CCSD) and RPA(D) in the calculation of vertical electronic excitation energies and oscillator strengths is investigated for a large benchmark set of 28 medium-sized molecules with 139 singlet and 71 triplet excited states. The results are compared with the corresponding CC3 and CASPT2 results from the literature for both the TZVP set and the larger and more diffuse aug-cc-pVTZ basis set. In addition, the results with the aug-cc-pVTZ basis set are compared with the theoretical best estimates for this benchmark set. We find that the original SOPPA method gives overall the smallest mean deviations from the reference values and the most consistent results.

Keywords: electronically excited states; benchmarks; oscillator strengths; second-order polarization propagator methods; SOPPA; SOPPA(SCS-MP2); SOPPA(SOS-MP2); SOPPA(CCSD); RPA(D); ADC(2)

1. Introduction

Molecular electromagnetic properties describing how electromagnetic radiation affects molecules can elegantly be calculated with propagator or response function methods [1–3]. The central quantity of these methods, that is the propagator or response function, corresponds directly to measurable quantities, such as, e.g. polarisabilities or nuclear magnetic resonance (NMR) spin–spin coupling constants while the poles of the response functions appear at frequencies, which correspond to the measurable differences between the energies of individual states. Approximate expressions for the response functions have been derived starting from many different approaches ranging from density functional theory over Møller–Plesset (MP) perturbation theory to high-level coupled cluster methods.

Among these approximate response function methods are at least three approaches, which treat electron correlation to second-order in MP perturbation theory: the second-order polarization propagator approximation, SOPPA [4–7], the second-order algebraic-diagrammatic construction, ADC(2) [8] and the second-order approximate coupled cluster singles and doubles model CC2 [9]. The performance of these methods in the calculation of vertical electronic excitation energies or even 0–0 transitions is well documented for ADC(2) [10–16] and CC2 [10,11,17–24] but not for SOPPA. Vertical electronic excitation energies have so far been calculated at the SOPPA level mostly for individual molecules (e.g. [5,6,25–32]) apart from a larger set of azo-dyes [33–35]. A more systematic comparison with other methods employing identical basis sets and geometries has, to our knowledge, only be carried out for Ne, BH, CH_2, N_2, C_2, water, benzene, azobenzene and five polycyclic aromatic hydrocarbons [5,6,28,36,37], where it was found that the SOPPA methods predict for these 13 molecules smaller values for the vertical valence excitation energies than CC2, CCSD or CCSDR(3). However, one can question the generality of this conclusion based on only 13 either very similar or very small molecules – in particular, as for the NMR spin–spin coupling constants, systematic comparisons with more accurate methods or experimental data had shown [38–44] that SOPPA and SOPPA(CCSD) are attractive alternatives to CCSD for accurate calculations [38–40]. In the present work, we present therefore the results of a proper benchmarking of five SOPPA-based methods for the calculation of vertical singlet and triplet excitation energies and oscillator strengths. In addition, we investigate for a subset of these SOPPA methods also the influence of including more diffuse and polarization functions in the basis set.

For this purpose, we employ the recently developed benchmark set of 28 organic molecules with a maximum of 139 singlet and 71 triplet states [17–19,45,46], which has

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in the meantime been used in several similar benchmarking studies (e.g. [12,15,16,22,23,47,48]).

The paper is organised as follows: first, the differences in the five SOPPA methods are shortly summarised and computational details are described in the next two sections. The results for the singlet and triplet excitation energies and oscillator strengths obtained with both the TZVP and aug-cc-pVTZ basis sets are presented and compared to CC3, CASPT2 and theoretical best estimates via various statistical evaluations in the following section. The final section offers a summary.

2. Theory of the SOPPA methods

In the polarization propagator methods, vertical electronic excitation energies are obtained as the frequencies ω_n for which the polarization propagator or linear response function exhibits poles [1,2]. This leads to a generalised eigenvalue problem

$$\boldsymbol{E}\boldsymbol{X}_n = \hbar\omega_n \boldsymbol{S}\boldsymbol{X}_n \tag{1}$$

of the molecular Hessian matrix $\boldsymbol{E}$, where $\boldsymbol{S}$ is an overlap matrix and $\boldsymbol{X}_n$ are the eigenvectors, from which the transition dipole moments and thus oscillator strengths are obtained as scalar product with a property gradient vector $\boldsymbol{T}(\hat{\tilde{\mu}})$ of the electric dipole operator $\hat{\tilde{\mu}}$. In the polarization propagator approximation based on MP perturbation theory, all the elements of the Hessian and overlap matrices, $\langle\Psi_0|[\hat{h}_i^\dagger,[\hat{H},\hat{h}_j]]|\Psi_0\rangle$ and $\langle\Psi_0|[\hat{h}_i^\dagger,\hat{h}_j]|\Psi_0\rangle$, and of the property gradient vector, $\langle\Psi_0|[\hat{\tilde{\mu}},\hat{h}_i]|\Psi_0\rangle$, are evaluated through a given order of perturbation theory, where $\hat{H}$ is the field-free electronic Hamiltonian in the Born–Oppenheimer approximation, Ψ_0 is the MP [49] wavefunction of the unperturbed electronic ground state and $\{\hat{h}_i\}$ denote single, double, etc. excitation and de-excitation operators with respect to the Hartree–Fock wavefunction of the unperturbed electronic ground state. The consistent first-order theory is better known as random phase approximation (RPA) or time-dependent Hartree–Fock. The second-order polarization propagator approximation (SOPPA) [4–7] is traditionally defined as the approach, where all the matrix elements involving only single excitation or de-excitation operators are evaluated through second order, all matrix elements involving both single and double (de)-excitation operators through first order and the purely double (de)-excitation terms only through zeroth order as in the related second-order methods CC2 [9] or ADC(2) [13,14]. SOPPA differs from these latter two approaches because it includes in addition to excitation also de-excitation operators in $\{\hat{h}_i\}$, like RPA, leading to a second-order extension of the so-called $\boldsymbol{B}$ matrix of RPA. As a consequence, SOPPA has also an overlap matrix $\boldsymbol{S}$ which is not a unit matrix. Finally, both the SOPPA Hessian matrix $\boldsymbol{E}$ and the $\boldsymbol{M}$ matrix of ADC(2) are Hermitian in contrast to the Jacobian of CC2 and their pure double excitations parts are diagonal and consist of only Hartree–Fock orbital energy differences, i.e. they are treated only at zeroth order. Recently, the SOPPA method for the calculation of vertical excitation energies has been combined with both the polarisable embedding QM/MM model [30] and the polarisable continuum model (PCM) [32].

2.1. RPA(D) and SOPPA(CCSD)

Several modifications of the original SOPPA approach have been presented and tested over the years. In the RPA(D) method [28], RPA with a non-iterative doubles correction, derived by applying perturbation theory to the eigenvalue problem in Equation (1), one adds to the RPA eigenvalues or excitation energies a non-iterative second-order correction consisting essentially of the additional second-order and double excitation terms in the SOPPA Hessian and overlap matrices similarity transformed by the RPA eigenvectors. RPA(D) is thus an approximation to SOPPA, in the same way as the well-known CIS(D) [50] and CCSDR(3) [51] methods are approximations to CC2 and CC3 (as derived by the same perturbation theory approach). The limited previous RPA(D) results [6,28,37] gave the following picture. On the one hand, RPA(D) was found to represent a clear improvement over RPA: for the 25 excited states of six very small molecules [28], the mean error (0.51 eV) was only about half of the value of RPA compared to full configuration interaction (FCI) results, and for the valence states of six aromatic compounds [37], compared to CCSDR(3) reference values, the error was reduced to 2/3 while the spread of errors was reduced by almost a factor of 3. Compared to CIS(D), RPA(D) gave, on average, 0.07 eV lower excitation energies for the six small molecules, while for the aromatic compounds the mean difference amounted to 0.38 eV for valence and 0.12 eV for Rydberg states. On the other hand, when comparing RPA(D) to SOPPA, the deviation from the FCI results was only slightly larger for the six small molecules (0.51 eV versus 0.49 eV), while RPA(D) actually performed significantly better on average than SOPPA for the valence states of the aromatic compounds (mean absolute error 0.31 eV versus 0.55 eV) and equally well for the Rydberg states (0.3 eV) with only a marginally larger spread of errors. For substituted azobenzenes, RPA(D) gave consistently 0.3 eV larger values than SOPPA for the S_1 state and even 0.7 eV for the S_2 state, which for the unsubstituted azobenzene provides a better agreement with recent CCSD or CC2 results [36,52].

In the SOPPA(CCSD) [53] and SOPPA(CC2) [40] denoted approaches, one keeps exactly the form of the SOPPA equations and matrix elements, but replaces in all second-order matrix elements the first-order doubles and second-order singles correlation coefficients of the MP wavefunction by the corresponding CCSD or CC2 doubles and singles amplitudes based on the argument that the MP

correlation coefficients are the solutions of the first iteration of the CCSD amplitudes. Although the resulting wavefunctions are then linearised CCSD or CC2 wavefunctions, the SOPPA(CCSD) or SOPPA(CC2) polarization propagators still differ from the proper CCSD or CC2 linear response functions. For NMR spin–spin coupling constants and polarisabilities, it was found in several studies (see e.g. [40,41,54]) that SOPPA(CCSD) gives results in better agreement with experiment or CCSD reference values than SOPPA, while only in the one previous SOPPA(CCSD) study of electronic excitation energies, SOPPA(CCSD) performed worse compared to the CCSDR(3) reference values for all the studied excited states of the six aromatic molecules [37]. To investigate whether this is a general trend is one of the objectives of the current work.

2.2. *SOPPA(SCS-MP2) and SOPPA(SOS-MP2)*

An alternative way of improving on the results of second-order MP perturbation theory has been proposed by Grimme [55,56] in the form of spin-component-scaled (SCS) perturbation theory, where the contributions to the correlation energy or correlation coefficients from pairs of electrons with parallel- (same) and antiparallel (opposite) spins are scaled differently. Extending on this idea, Head-Gordon and co-workers proposed a simplified approach [57], where the parallel (same) spin terms are completely neglected and the antiparallel (opposite) spin terms are scaled by 1.3. They, thus, named this approach as scaled opposite-spin MP2 (SOS-MP2).

In the meantime, both approaches have also been implemented for the calculation of excitation energies with the CIS(D), CC2 and ADC(2) methods, i.e. SCS-CIS(D) [58,59] and SOS-CIS(D) [59], SCS-CC2 and SOS-CC2 [60] or SOS-ADC(2)[12,60,61]. A comparison between ADC(2) and SOS-ADC(2) for a subset of the benchmark set employed in this study showed significant differences in the mean errors between ADC(2) and two different versions of SOS-ADC(2) [12]. One of them [61] gives on average 0.16 eV larger excitation energies to singlet states than the original ADC(2), while in the intermediate state representation ISR-SOS-ADC(2) [12], where only the MP ground state wavefunction correlation coefficients are scaled, it predicts 0.2 eV lower excitation energies on average.

In this work, we present and investigate for the first time spin-component-scaled and scaled opposite-spin versions of SOPPA, which are obtained by replacing the first-order MP correlation coefficients in the SOPPA expressions by SCS- or SOS-MP2 correlation coefficients. In line with the notation for SOPPA(CCSD) and SOPPA(CC2), these two new models are denoted as SOPPA(SCS-MP2) and SOPPA(SOS-MP2). To investigate whether these low-cost replacements of correlation coefficients will have a similar effect on the results as the replacement by CCSD amplitudes in SOPPA(CCSD) is another objective of the current work. One should note that SOPPA(SOS-MP2) can be considered as an analogue to ISR-SOS-ADC(2).

3. Computational details

All calculations were carried out with the Dalton program package [5,6,62]. For the RPA(D), SOPPA and SOPPA(CCSD) calculations, the official DALTON13 release [63] was employed, while the SOPPA(SOS-MP2) and SOPPA(SCS-MP2) calculations were carried out with a local development version. The employed geometries are the same as in the previous studies [17–19,23,45–48], i.e. they had been optimised at the MP2/6-31G* level.

Both the TZVP [64] and the augmented aug-cc-pVTZ [65,66] basis sets were employed. With the TZVP basis set, vertical singlet excitation energies and associated oscillator strengths in the length representation were computed at the RPA(D), SOPPA, SOPPA(SCS-MP2), SOPPA(SOS-MP2) and SOPPA(CCSD) levels, and in addition to this also vertical triplet excitation energies at the RPA(D), SOPPA and SOPPA(CCSD) levels of theory. In the case of the aug-cc-pVTZ basis set, vertical singlet excitation energies and associated oscillator strengths in the length representation were only calculated with the RPA(D), SOPPA and SOPPA(CCSD) methods. In the latter calculations, i.e. with the aug-cc-pVTZ basis set, the core electrons were kept frozen during the correlated calculations, which had previously been shown to cause negligible deviations (less than 0.01 eV) compared with a fully correlated all-electron treatment [6].

Concerning the RPA(D) calculations, one should note that the excitation energies in RPA(D) are obtained by adding a second-order doubles correction to the RPA eigenvalues. Although these corrections are generally able to correct the wrong ordering of the excited states as often obtained at the RPA level [37], it is nevertheless necessary to calculate significantly more eigenvalues and thus excitation energies in RPA(D) in order to be sure to have found the lowest ones.

Our results will be compared in the following statistical analysis with the results of previous studies carried out for the same benchmark set of molecules, geometries and basis sets. In particular, we compare with CC3 [17,23] and CASPT2 [45] results obtained with the TZVP basis set and with the aug-cc-pVTZ basis set [19,46]. However, some of the CC3/aug-cc-pVTZ results are estimates based on the CC3/TVZP results [17,23] and a TZVP to aug-cc-pVTZ basis set correction obtained at the CCSDR(3) or CC2 level [18,19]. Finally, we will also compare with the set of *theoretical best estimates* (TBE-2) presented in one of the previous studies [46].

4. Results

The present benchmark set consists of 28 molecules with a maximum of 139 singlet states (117 with the aug-cc-pVTZ

Table 1. Vertical excitation energies ΔE (eV) of singlet excited states from calculations with the TZVP basis set.

				SOPPA				
Molecule	State	RPA(D)	SOPPA	(SCS-MP2)	(SOS-MP2)	(CCSD)	CC3[a]	CASPT2[b]
Ethene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.92	7.84	7.78	7.75	7.86	8.37	8.54
E-Butadiene	1^1B_u ($\pi \rightarrow \pi^*$)	6.12	5.88	5.80	5.76	5.86	6.58	6.47
	2^1A_g ($\pi \rightarrow \pi^*$)	7.56	7.29	7.20	7.15	7.31	6.78	6.62
all-*E*-Hexatriene	1^1B_u ($\pi \rightarrow \pi^*$)	5.09	4.80	4.70	4.65	4.74	5.58	5.31
	2^1A_g ($\pi \rightarrow \pi^*$)	6.35	6.30	6.18	6.12	6.29	5.72	5.42
all-*E*-Octatetraene	2^1A_g ($\pi \rightarrow \pi^*$)	5.57	5.49	5.35	5.28	5.46	4.98	4.64
	1^1B_u ($\pi \rightarrow \pi^*$)	4.44	4.12	4.00	3.94	4.01	4.94	4.70
	2^1B_u ($\pi \rightarrow \pi^*$)	6.75	6.55	6.43	6.37	6.53	6.06	5.73
	3^1A_g ($\pi \rightarrow \pi^*$)	6.38	6.13	6.01	5.95	6.05	6.50	6.19
	4^1A_g ($\pi \rightarrow \pi^*$)	7.21	6.68	6.56	6.51	6.66	6.81	6.55
	3^1B_u ($\pi \rightarrow \pi^*$)	7.61	7.43	7.31	7.25	7.38	7.91	8.04
Cyclopropene	1^1B_1 ($\sigma \rightarrow \pi^*$)	6.61	6.57	6.50	6.46	6.61	6.90	6.76
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.88	6.65	6.59	6.57	6.66	7.10	7.06
Cyclopentadiene	1^1B_2 ($\pi \rightarrow \pi^*$)	5.36	5.11	4.98	4.92	5.05	5.73	5.51
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.70	6.63	6.51	6.45	6.61	6.62	6.31
	3^1A_1 ($\pi \rightarrow \pi^*$)	8.46	8.32	8.03	8.14	8.28	8.69	8.52
Norbornadiene	1^1A_2 ($\pi \rightarrow \pi^*$)	5.40	5.05	4.92	4.86	5.01	5.64	5.34
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.51	5.96	5.83	5.77	5.94	6.49	6.11
	2^1B_2 ($\pi \rightarrow \pi^*$)	6.98	7.12	7.01	6.95	7.08	7.64	7.32
	2^1A_2 ($\pi \rightarrow \pi^*$)	7.35	7.22	7.10	7.04	7.21	7.71	7.45
Benzene	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.80	4.69	4.40	4.24	4.52	5.07	5.04
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	6.50	6.15	5.92	5.80	6.05	6.68	6.42
	1^1E_{1u} ($\pi \rightarrow \pi^*$)	7.03	6.96	6.72	6.60	6.77	7.45	7.13
	2^1E_{2g} ($\pi \rightarrow \pi^*$)	9.60	8.60	8.45	8.38	8.56	8.43	8.18
Naphthalene	1^1B_{3u} ($\pi \rightarrow \pi^*$)	3.97	3.86	3.51	3.32	3.61	4.27	4.24
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	5.02	4.41	4.15	4.02	4.24	5.03	4.77
	2^1A_g ($\pi \rightarrow \pi^*$)	5.81	5.68	5.40	5.26	5.51	5.98	5.87
	1^1B_{1g} ($\pi \rightarrow \pi^*$)	5.93	5.77	5.55	5.44	5.67	6.07	5.99
	2^1B_{3u} ($\pi \rightarrow \pi^*$)	5.86	5.74	5.44	5.29	5.47	6.33	6.06
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	6.11	6.08	5.76	5.60	5.85	6.57	6.33
	2^1B_{1g} ($\pi \rightarrow \pi^*$)	6.41	6.26	6.05	5.94	6.13	6.79	6.47
	3^1A_g ($\pi \rightarrow \pi^*$)	7.16	6.90	6.71	6.62	6.82	6.90	6.67
	3^1B_{3u} ($\pi \rightarrow \pi^*$)	9.26	8.41	8.25	8.17	8.34	8.12	7.74
	3^1B_{2u} ($\pi \rightarrow \pi^*$)	7.98	8.04	7.84	7.74	7.93	8.44	8.17
Furan	1^1B_2 ($\pi \rightarrow \pi^*$)	6.46	6.23	6.05	5.97	6.14	6.60	6.39
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.46	6.33	6.14	6.05	6.26	6.62	6.50
	3^1A_1 ($\pi \rightarrow \pi^*$)	8.42	8.21	8.05	7.97	8.14	8.53	8.17
Pyrrole	2^1A_1 ($\pi \rightarrow \pi^*$)	6.28	6.08	5.88	5.78	6.00	6.41	6.31
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.62	6.38	6.19	6.10	6.29	6.71	6.33
	3^1A_1 ($\pi \rightarrow \pi^*$)	8.09	7.96	7.77	7.68	7.87	8.17	8.17
Imidazole	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.77	6.19	5.98	5.88	6.09	6.58	6.19
	$1^1A''$ ($n \rightarrow \pi^*$)	6.86	6.32	6.18	6.10	6.28	6.83	6.81
	$3^1A'$ ($\pi \rightarrow \pi^*$)	6.80	6.73	6.53	6.43	6.63	7.10	6.93
	$2^1A''$ ($n \rightarrow \pi^*$)	7.58	7.54	7.40	7.32	7.51	7.94	7.90
	$4^1A'$ ($\pi \rightarrow \pi^*$)	8.21	8.12	7.93	7.84	8.02	8.45	8.16
Pyridine	1^1B_2 ($\pi \rightarrow \pi^*$)	4.86	4.70	4.39	4.23	4.50	5.15	5.02
	1^1B_1 ($n \rightarrow \pi^*$)	4.94	4.58	4.42	4.34	4.53	5.06	5.17
	1^1A_2 ($n \rightarrow \pi^*$)	5.13	4.91	4.76	4.69	4.87	5.51	5.51
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.72	6.31	6.08	5.96	6.20	6.85	6.39
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.29	7.20	7.71	6.95	6.83	7.70	7.27
	2^1B_2 ($\pi \rightarrow \pi^*$)	7.14	7.09	6.85	6.72	6.88	7.59	7.46
	3^1B_2 ($\pi \rightarrow \pi^*$)	9.79	8.92	8.57	8.53	8.86	8.78	8.60
	4^1A_1 ($\pi \rightarrow \pi^*$)	9.71	8.76	8.60	8.52	8.69	8.68	8.69
Pyrazine	1^1B_{3u} ($n \rightarrow \pi^*$)	4.05	3.72	3.54	3.44	3.64	4.25	4.12
	1^1A_u ($n \rightarrow \pi^*$)	4.68	4.50	4.35	4.28	4.46	5.05	4.70
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.70	4.48	4.16	3.98	4.23	5.02	4.85
	1^1B_{2g} ($n \rightarrow \pi^*$)	5.80	5.34	5.18	5.10	5.27	5.74	5.68

Continue.

Table 1. *continue.*

Molecule	State	RPA(D)	SOPPA	SOPPA (SCS-MP2)	SOPPA (SOS-MP2)	SOPPA (CCSD)	CC3[a]	CASPT2[b]
	1^1B_{1g} ($n \to \pi^*$)	6.73	6.24	6.11	6.05	6.21	6.76	6.41
	1^1B_{1u} ($\pi \to \pi^*$)	7.00	6.52	6.28	6.16	6.39	7.07	6.89
	2^1B_{2u} ($\pi \to \pi^*$)	7.51	7.53	7.26	7.12	7.27	8.05	7.66
	2^1B_{1u} ($\pi \to \pi^*$)	7.66	7.53	7.26	7.13	7.28	8.06	7.79
	1^1B_{3g} ($\pi \to \pi^*$)	9.15	8.93	8.77	8.69	8.86	8.77	8.47
	2^1A_g ($\pi \to \pi^*$)	9.57	8.75	8.51	8.45	8.66	8.70	8.61
Pyrimidine	1^1B_1 ($n \to \pi^*$)	4.30	3.93	3.76	3.67	3.87	4.51	4.44
	1^1A_2 ($n \to \pi^*$)	4.80	4.32	4.16	4.07	4.27	4.93	4.80
	1^1B_2 ($\pi \to \pi^*$)	5.02	4.83	4.52	4.36	4.63	5.37	5.24
	2^1A_1 ($\pi \to \pi^*$)	6.94	6.50	6.26	6.14	6.38	7.06	6.63
	3^1A_1 ($\pi \to \pi^*$)	7.28	7.17	6.92	6.79	6.95	7.74	7.21
	2^1B_2 ($\pi \to \pi^*$)	7.46	7.42	7.17	7.05	7.21	8.01	7.64
Pyridazine	1^1B_1 ($n \to \pi^*$)	3.77	3.31	3.13	3.05	3.22	3.93	3.78
	1^1A_2 ($n \to \pi^*$)	4.73	3.91	3.76	3.69	3.86	4.50	4.31
	2^1A_1 ($\pi \to \pi^*$)	4.88	4.67	4.34	4.17	4.42	5.22	5.18
	2^1A_2 ($n \to \pi^*$)	5.18	5.26	5.09	5.00	5.18	5.75	5.77
	2^1B_1 ($n \to \pi^*$)	6.08	5.91	5.77	5.69	5.86	6.41	6.52
	1^1B_2 ($\pi \to \pi^*$)	6.96	6.38	6.13	6.00	6.22	6.93	6.31
	2^1B_2 ($\pi \to \pi^*$)	7.12	7.01	6.76	6.63	6.77	7.55	7.29
	3^1A_1 ($\pi \to \pi^*$)	7.41	7.35	7.09	6.69	7.11	7.82	7.62
s-Triazine	$1^1A_1''$ ($n \to \pi^*$)	4.33	4.12	3.95	3.87	4.07	4.78	4.60
	$1^1A_2''$ ($n \to \pi^*$)	4.54	4.24	4.07	3.99	4.19	4.76	4.66
	$1^1E''$ ($n \to \pi^*$)	4.56	4.20	4.03	3.95	4.15	4.82	4.70
	$1^1A_2'$ ($\pi \to \pi^*$)	5.18	5.08	4.77	4.60	4.88	5.71	5.79
	$2^1A_1'$ ($\pi \to \pi^*$)	7.24	6.78	6.54	6.41	6.66	7.41	7.25
	$2^1E''$ ($n \to \pi^*$)	8.01	7.47	7.36	7.31	7.46	7.82	7.71
	$1^1E'$ ($\pi \to \pi^*$)	7.52	7.39	7.14	7.02	7.19	8.04	7.50
s-Tetrazine	1^1B_{3u} ($n \to \pi^*$)	2.24	1.80	1.60	1.50	1.66	2.54	2.29
	1^1A_u ($\pi \to \pi^*$)	3.89	3.19	3.02	2.94	3.12	3.80	3.51
	1^1B_{1g} ($n \to \pi^*$)	5.12	4.42	4.27	4.19	4.33	4.98	4.73
	1^1B_{2u} ($\pi \to \pi^*$)	4.65	4.37	3.99	3.79	4.01	5.12	4.93
	1^1B_{2g} ($n \to \pi^*$)	5.52	4.89	4.70	4.61	4.77	5.34	5.20
	2^1A_u ($n \to \pi^*$)	4.98	4.88	4.68	4.59	4.75	5.46	5.50
	2^1B_{2g} ($n \to \pi^*$)	5.86	5.83	5.71	5.65	5.80	6.25	6.06
	2^1B_{1g} ($n \to \pi^*$)	5.90	6.41	6.27	6.19	6.35	6.87	6.45
	3^1B_{1g} ($n \to \pi^*$)	7.71	7.24	7.13	7.08	7.22	7.09	6.73
	2^1B_{3u} ($n \to \pi^*$)	6.40	6.21	6.05	5.97	6.14	6.68	6.77
	1^1B_{1u} ($\pi \to \pi^*$)	7.57	6.84	6.56	6.41	6.57	7.45	6.94
	2^1B_{1u} ($\pi \to \pi^*$)	7.25	7.15	6.86	6.72	6.84	7.79	7.42
	2^1B_{2u} ($\pi \to \pi^*$)	7.98	7.98	7.68	7.53	7.65	8.51	8.14
	2^1B_{3g} ($\pi \to \pi^*$)	9.38	8.35	8.14	8.04	8.19	8.48	8.34
Formaldehyde	1^1A_2 ($n \to \pi^*$)	3.66	3.45	3.38	3.34	3.44	3.95	3.99
	1^1B_1 ($\sigma \to \pi^*$)	9.00	8.70	8.60	8.55	8.67	9.19	9.14
	3^1A_1 ($\sigma \to \pi^*$)	9.47	9.55	9.49	9.45	9.54	10.45	9.32
Acetone	1^1A_2 ($n \to \pi^*$)	4.03	3.82	3.69	3.62	3.79	4.40	4.44
	1^1B_1 ($\sigma \to \pi^*$)	8.95	8.66	8.52	8.46	8.62	9.17	9.27
	2^1A_1 ($\pi \to \pi^*$)	8.98	8.96	8.87	8.82	8.94	9.65	9.31
p-Benzoquinone	1^1B_{1g} ($n \to \pi^*$)	2.55	2.09	1.95	1.88	2.00	2.75	2.76
	1^1A_u ($n \to \pi^*$)	2.68	2.17	2.02	1.94	2.07	2.85	2.77
	1^1B_{3g} ($\pi \to \pi^*$)	4.53	4.21	4.07	4.00	4.15	4.59	4.26
	1^1B_{1u} ($\pi \to \pi^*$)	5.21	4.76	4.61	4.53	4.62	5.62	5.28
	1^1B_{3u} ($n \to \pi^*$)	6.77	5.22	5.13	5.08	5.21	5.83	5.64
	2^1B_{3g} ($\pi \to \pi^*$)	6.91	6.74	6.61	6.54	6.69	7.28	6.96
	2^1B_{1u} ($\pi \to \pi^*$)	7.97	7.74	7.63	7.57	7.71	7.82	7.92
Formamide	$1^1A''$ ($n \to \pi^*$)	5.23	5.00	4.88	4.81	4.97	5.66	5.63
	$2^1A'$ ($\pi \to \pi^*$)	7.25	7.48	7.38	7.34	7.46	7.23	7.39
Acetamide	$1^1A''$ ($n \to \pi^*$)	5.24	5.01	4.86	4.79	4.97	5.70	5.69

Continue.

Table 1. *continue.*

Molecule	State	RPA(D)	SOPPA	SOPPA (SCS-MP2)	SOPPA (SOS-MP2)	SOPPA (CCSD)	CC3[a]	CASPT2[b]
	$2^1A'$ ($\pi \rightarrow \pi^*$)	7.23	7.02	6.90	6.84	7.00	7.67	7.27
Propanamide	$1^1A''$ ($n \rightarrow \pi^*$)	5.25	5.02	4.87	4.79	4.98	5.72	5.72
	$2^1A'$ ($\pi \rightarrow \pi^*$)	7.17	6.96	6.84	6.77	6.94	7.62	7.20
Cytosine	$2^1A'$ ($\pi \rightarrow \pi^*$)	4.54	4.06	3.87	3.77	4.00	4.72	4.67
	$1^1A''$ ($n \rightarrow \pi^*$)	4.88	4.78	4.63	4.55	4.75	5.16	5.12
	$2^1A''$ ($n \rightarrow \pi^*$)	5.47	4.36	4.20	4.11	4.31	5.52	5.53
	$3^1A'$ ($\pi \rightarrow \pi^*$)	5.31	5.09	4.92	4.84	5.05	5.61	5.53
	$4^1A'$ ($\pi \rightarrow \pi^*$)	6.12	5.92	5.73	5.64	5.83	6.61	6.40
Thymine	$1^1A''$ ($n \rightarrow \pi^*$)	4.61	4.17	4.00	3.91	4.10	4.94	4.95
	$2^1A'$ ($\pi \rightarrow \pi^*$)	5.22	4.74	4.57	4.48	4.68	5.34	5.06
	$3^1A'$ ($\pi \rightarrow \pi^*$)	6.35	5.79	5.63	5.54	5.74	6.34	6.15
	$2^1A''$ ($n \rightarrow \pi^*$)	6.03	5.62	5.45	5.36	5.56	6.59	6.38
	$4^1A'$ ($\pi \rightarrow \pi^*$)	6.29	6.24	6.05	5.96	6.17	6.71	6.53
Uracil	$1^1A''$ ($n \rightarrow \pi^*$)	4.60	4.15	3.98	3.89	4.09	4.90	4.91
	$2^1A'$ ($\pi \rightarrow \pi^*$)	5.33	4.87	4.70	4.61	4.82	5.44	5.23
	$3^1A'$ ($\pi \rightarrow \pi^*$)	6.33	5.78	5.62	5.54	5.73	6.29	6.15
	$2^1A''$ ($n \rightarrow \pi^*$)	5.97	5.55	5.37	5.29	5.49	6.32	6.28
	$4^1A'$ ($\pi \rightarrow \pi^*$)	6.52	6.41	6.23	6.14	6.35	6.84	6.74
	$3^1A''$ ($n \rightarrow \pi^*$)	6.84	6.16	6.01	5.93	6.11	6.87	6.98
	$5^1A''$ ($n \rightarrow \pi^*$)	7.85	6.44	6.28	6.20	6.39	7.12	7.28
Adenine	$2^1A'$ ($\pi \rightarrow \pi^*$)	4.96	4.62	4.32	4.17	4.45	5.18	5.20
	$1^1A''$ ($n \rightarrow \pi^*$)	5.11	4.69	4.51	4.41	4.63	5.34	5.19
	$3^1A'$ ($\pi \rightarrow \pi^*$)	5.30	4.79	4.54	4.41	4.64	5.39	5.29
	$2^1A''$ ($n \rightarrow \pi^*$)	5.79	5.32	5.12	5.02	5.24	5.96	5.96
	$4^1A'$ ($\pi \rightarrow \pi^*$)	6.44	5.99	5.74	5.61	5.81	6.53	6.34

[a]Results with the TZVP basis set from [17] and [23].
[b]Results with the TZVP basis set from [45].

Table 2. Deviations in the vertical excitation energies (eV) of singlet excited states with the TZVP basis set from the CC3/TZVP results.[a]

	RPA(D)	SOPPA	SOPPA(SCS-MP2)	SOPPA(SOS-MP2)	SOPPA(CCSD)
			All		
Count[b]	139	139	139	139	139
Mean	−0.15	−0.46	−0.64	−0.73	−0.56
Abs. mean	0.35	0.51	0.67	0.76	0.60
Std. dev.	0.40	0.29	0.30	0.32	0.31
Maximum (+)	1.17	0.58	0.46	0.40	0.57
Maximum (−)	0.98	1.16	1.32	1.41	1.21
			$\pi \rightarrow \pi^*$		
Count[b]	91	91	91	91	91
Mean	−0.12	−0.40	−0.60	−0.70	−0.51
Abs. mean	0.35	0.47	0.64	0.73	0.58
Std. dev.	0.42	0.31	0.33	0.36	0.35
Maximum (+)	1.17	0.58	0.46	0.40	0.57
Maximum (−)	0.67	0.86	1.13	1.33	1.11
			$n \rightarrow \pi^*$		
Count[b]	44	44	44	44	44
Mean	−0.18	−0.58	−0.74	−0.81	−0.64
Abs. mean	0.32	0.59	0.74	0.81	0.65
Std. dev.	0.34	0.19	0.20	0.21	0.19
Maximum (+)	0.94	0.15	0.04	0.00	0.13
Maximum (−)	0.97	1.16	1.32	1.41	1.21

[a]TZVP results from [17,23].
[b]Total number of considered states.

Table 3. Vertical excitation energies ΔE (eV) of singlet excited states from calculations with the aug-cc-pVTZ (aVTZ) basis set.

Molecule	State	RPA(D)	SOPPA	SOPPA(CCSD)	CC3[a]	CASPT2[b]	TBE-2[c]
Ethene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.50	7.42	7.43	7.89	7.84	7.80
E-Butadiene	1^1B_u ($\pi \rightarrow \pi^*$)	5.78	5.58	5.53	6.21[d]	6.38	6.18
	2^1A_g ($\pi \rightarrow \pi^*$)	7.09	6.79	6.79	6.63	6.43	6.55
all-*E*-Hexatriene	1^1B_u ($\pi \rightarrow \pi^*$)	4.84	4.58	4.48	5.32[d]	5.18	5.10
	2^1A_g ($\pi \rightarrow \pi^*$)	6.52	6.09	6.06	5.77[d]	5.33	5.09
all-*E*-Octatetraene	2^1A_g ($\pi \rightarrow \pi^*$)	5.99	5.36	5.29	4.84[e]	4.52	4.47
	1^1B_u ($\pi \rightarrow \pi^*$)	4.23	3.92	3.79	4.75[e]	4.35	4.66
	2^1B_u ($\pi \rightarrow \pi^*$)	6.31	6.33	6.28	5.51[e]	5.78	
	3^1A_g ($\pi \rightarrow \pi^*$)	6.07	5.81	5.71	5.90[e]	6.42	
	4^1A_g ($\pi \rightarrow \pi^*$)	6.09	5.93	5.87	6.15[e]	7.01	
	3^1B_u ($\pi \rightarrow \pi^*$)	7.43	6.97	6.91		7.69	
Cyclopropene	1^1B_1 ($\sigma \rightarrow \pi^*$)	6.47	6.34	6.37	6.67	6.63	6.67
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.44	6.24	6.23	6.68	6.66	6.68
Cyclopentadiene	1^1B_2 ($\pi \rightarrow \pi^*$)	5.11	4.88	4.79	5.49[d]	5.43	5.55
	2^1A_1 ($\pi \rightarrow \pi^*$)	7.20	6.39	6.35	6.49[d]	6.28	6.28
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.33	7.82	7.77	8.14[d]	8.15	
Norbornadiene	1^1A_2 ($\pi \rightarrow \pi^*$)	5.10	4.79	4.71	5.37[e]	4.98	5.37
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.31	5.68	5.64	6.21[e]	5.94	6.21
	2^1B_2 ($\pi \rightarrow \pi^*$)	6.99	6.45	6.40	7.49[e]	6.62	
	2^1A_2 ($\pi \rightarrow \pi^*$)	6.96	6.84	6.79	7.22[e]	7.20	
Benzene	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.78	4.63	4.43	5.03	4.96	5.08
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	6.25	5.91	5.77	6.42	6.57	6.54
	1^1E_{1u} ($\pi \rightarrow \pi^*$)	6.74	6.67	6.45	7.14	7.36	7.13
	2^1E_{2g} ($\pi \rightarrow \pi^*$)	8.40	8.34	8.24	8.31	8.15	8.15
Naphthalene	1^1B_{3u} ($\pi \rightarrow \pi^*$)	3.92	3.78	3.49	4.25[d]	4.06	4.25
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.79	4.19	3.97	4.82[d]	4.49	4.82
	2^1A_g ($\pi \rightarrow \pi^*$)	5.84	5.52	5.32	5.89[d]	5.83	5.90
	1^1B_{1g} ($\pi \rightarrow \pi^*$)	8.83	5.41	5.26	5.75[d]	5.71	5.75
	2^1B_{3u} ($\pi \rightarrow \pi^*$)	5.64	5.50	5.19	6.11[d]	6.04	6.11
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	5.78	5.85	5.56	6.36[d]	6.05	6.36
	2^1B_{1g} ($\pi \rightarrow \pi^*$)	6.16	5.96	5.79	6.47[d]	6.31	6.46
	3^1A_g ($\pi \rightarrow \pi^*$)	7.13	6.67	6.53	6.86[d]	6.49	6.49
	3^1B_{2u} ($\pi \rightarrow \pi^*$)	7.71	7.58	7.44	7.34[d]	7.92	
	3^1B_{3u} ($\pi \rightarrow \pi^*$)	9.28	8.21	8.13	7.93[e]	6.69	
Furan	1^1B_2 ($\pi \rightarrow \pi^*$)	6.09	5.89	5.77	6.26[d]	6.19	6.32
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.54	6.15	6.05	6.51[d]	6.35	6.57
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.73	7.76	7.65	8.13[d]	7.93	8.13
Pyrrole	2^1A_1 ($\pi \rightarrow \pi^*$)	6.20	5.90	5.79	6.27[d]	6.23	6.37
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.09	5.95	5.83	6.20[d]	6.22	6.57
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.51	7.37	7.25	7.60[d]	7.95	7.91
Imidazole	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.33	5.92	5.79	6.25[e]	6.40	6.25
	$1^1A''$ ($n \rightarrow \pi^*$)	6.77	6.14	6.08	6.65[e]	6.69	6.65
	$3^1A'$ ($\pi \rightarrow \pi^*$)	6.74	6.43	6.29	6.73[e]	6.82	6.73
	$2^1A''$ ($n \rightarrow \pi^*$)	7.36	7.23	7.19	7.58[e]	7.80	
	$4^1A'$ ($\pi \rightarrow \pi^*$)	7.96	8.05	7.93	8.51[e]	8.96	
Pyridine	1^1B_2 ($\pi \rightarrow \pi^*$)	4.82	4.63	4.41	5.12[d]	5.00	4.85
	1^1B_1 ($n \rightarrow \pi^*$)	4.76	4.42	4.34	4.96[d]	5.07	4.59
	1^1A_2 ($n \rightarrow \pi^*$)	4.98	4.77	4.72	5.41[d]	5.49	5.11
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.46	6.06	5.92	6.60[d]	6.59	6.26
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.01	6.96	6.67	7.33[d]	7.72	7.27
	2^1B_2 ($\pi \rightarrow \pi^*$)	7.13	6.83	6.60	7.39[d]	7.49	7.18
	3^1B_2 ($\pi \rightarrow \pi^*$)	8.79	7.85	7.74	7.72[d]	8.06	
	4^1A_1 ($\pi \rightarrow \pi^*$)	9.46	8.55	8.48	8.34[d]	8.28	
Pyrazine	1^1B_{3u} ($n \rightarrow \pi^*$)	3.87	3.55	3.45	4.13[d]	4.02	4.13
	1^1A_u ($n \rightarrow \pi^*$)	4.56	4.40	4.34	4.98[d]	4.75	4.98
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.62	4.40	4.12	4.97[d]	4.80	4.97
	1^1B_{2g} ($n \rightarrow \pi^*$)	5.64	5.18	5.09	5.65[d]	5.56	5.65
	1^1B_{1g} ($n \rightarrow \pi^*$)	6.10	6.14	6.09	6.69[d]	6.47	6.69
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	6.75	6.29	6.11	6.83[d]	6.61	6.83
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	7.66	7.32	7.04	7.81[d]	7.73	7.81

Continue.

Table 3. *continue*.

Molecule	State	RPA(D)	SOPPA	SOPPA(CCSD)	CC3[a]	CASPT2[b]	TBE-2[c]
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	7.35	7.31	6.86	7.86[d]	7.71	7.86
	1^1B_{3g} ($\pi \rightarrow \pi^*$)	9.12	8.65	8.54	8.69[d]	8.33	
	2^1A_g ($\pi \rightarrow \pi^*$)	9.26	8.50	8.39	8.78[d]	8.30	
Pyrimidine	1^1B_1 ($n \rightarrow \pi^*$)	4.13	3.79	3.71	4.43[d]	4.34	4.43
	1^1A_2 ($n \rightarrow \pi^*$)	4.61	4.20	4.13	4.85[d]	4.74	4.85
	1^1B_2 ($\pi \rightarrow \pi^*$)	4.98	4.78	4.55	5.34[d]	5.17	5.34
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.68	6.25	6.10	6.82[d]	6.81	6.82
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.06	6.94	6.66	7.53[d]	7.26	
	2^1B_2 ($\pi \rightarrow \pi^*$)	7.23	7.20	6.97	7.81[d]	7.74	
Pyridazine	1^1B_1 ($n \rightarrow \pi^*$)	3.61	3.17	3.06	3.85[d]	3.71	3.85
	1^1A_2 ($n \rightarrow \pi^*$)	4.60	3.79	3.73	4.44[d]	4.18	4.44
	2^1A_1 ($\pi \rightarrow \pi^*$)	4.85	4.62	4.33	5.20[d]	5.06	5.20
	2^1A_2 ($n \rightarrow \pi^*$)	5.04	5.11	5.01	5.66[d]	5.67	5.66
	2^1B_1 ($n \rightarrow \pi^*$)	6.03	5.77	5.70	6.33[d]	6.13	
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.70	6.12	5.93	6.67[d]	6.34	
	2^1B_2 ($\pi \rightarrow \pi^*$)	6.88	6.78	6.50	7.33[d]	7.45	
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.15	6.96	6.79	7.55[d]	7.17	
s-Triazine	$1^1A_1''$ ($n \rightarrow \pi^*$)	4.21	4.02	3.95	4.70[d]	4.54	4.70
	$1^1A_2''$ ($n \rightarrow \pi^*$)	4.43	4.14	4.07	4.71[d]	4.60	4.71
	$1^1E''$ ($n \rightarrow \pi^*$)	4.18	4.09	4.03	4.75[d]	4.63	4.75
	$1^1A_2'$ ($\pi \rightarrow \pi^*$)	5.17	5.05	4.84	5.71[d]	5.75	5.71
	$2^1A_1'$ ($\pi \rightarrow \pi^*$)	6.98	6.55	6.39	7.18[d]	7.20	
	$2^1E''$ ($n \rightarrow \pi^*$)	7.73	7.36	7.39	7.78[d]	7.55	
	$1^1E'$ ($\pi \rightarrow \pi^*$)	7.29	7.17	6.95	7.85[d]	7.36	
s-Tetrazine	1^1B_{3u} ($n \rightarrow \pi^*$)	2.11	1.69	1.53	2.46	2.27	2.46
	1^1A_u ($\pi \rightarrow \pi^*$)	3.76	3.11	3.02	3.78[d]	3.40	3.78
	1^1B_{1g} ($n \rightarrow \pi^*$)	4.96	4.28	4.17	4.87	4.74	4.87
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.60	4.31	3.93	5.08	4.89	5.08
	1^1B_{2g} ($n \rightarrow \pi^*$)	5.38	4.76	4.63	5.28	5.07	5.28
	2^1A_u ($n \rightarrow \pi^*$)	4.87	4.75	4.60	5.39[d]	5.32	5.39
	2^1B_{2g} ($n \rightarrow \pi^*$)	5.79	5.72	5.67	6.16	5.84	
	2^1B_{1g} ($n \rightarrow \pi^*$)	5.85	6.31	6.23	6.80	6.33	
	3^1B_{1g} ($n \rightarrow \pi^*$)	7.70	7.07	7.03	7.12[d]	6.64	
	2^1B_{3u} ($n \rightarrow \pi^*$)	6.28	6.10	6.01	6.60	6.59	
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.31	6.59	6.31	7.18	6.84	
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	7.05	6.95	6.60	7.59	7.20	
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	7.75	7.79	7.43	8.33[d]	8.00	
	2^1B_{3g} ($\pi \rightarrow \pi^*$)	9.28	8.18	8.00	8.51[d]	8.19	
Formaldehyde	1^1A_2 ($n \rightarrow \pi^*$)	3.58	3.36	3.34	3.88	4.01	3.88
	1^1B_1 ($\sigma \rightarrow \pi^*$)	8.86	8.55	8.51	9.05	9.12	9.04
	3^1A_1 ($\sigma \rightarrow \pi^*$)	9.10	8.85	8.78	9.31	9.47	9.29
Acetone	1^1A_2 ($n \rightarrow \pi^*$)	3.99	3.75	3.70	4.38	4.49	4.38
	1^1B_1 ($\sigma \rightarrow \pi^*$)	8.79	8.48	8.44	9.04[d]	9.25	9.04
	2^1A_1 ($\pi \rightarrow \pi^*$)	7.76	8.31	8.26	8.90	9.19	8.90
p-Benzoquinone	1^1B_{1g} ($n \rightarrow \pi^*$)	2.50	2.04	1.95	2.74[d]	2.81	2.74
	1^1A_u ($n \rightarrow \pi^*$)	2.64	2.12	2.02	2.86[d]	2.83	2.86
	1^1B_{3g} ($\pi \rightarrow \pi^*$)	4.32	4.01	3.92	4.44[d]	4.37	4.44
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	5.06	4.62	4.46	5.47[d]	5.41	5.47
	1^1B_{3u} ($n \rightarrow \pi^*$)	7.11	5.09	5.06	5.71[d]	5.55	5.55
	2^1B_{3g} ($\pi \rightarrow \pi^*$)	6.71	6.58	6.50	7.16[d]	6.99	7.16
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	7.62	7.45	7.40	7.62[d]	7.87	
Formamide	$1^1A''$ ($n \rightarrow \pi^*$)	5.12	4.86	4.82	5.55	5.58	5.55
	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.74	6.84	6.80	7.35	7.45	7.35
Acetamide	$1^1A''$ ($n \rightarrow \pi^*$)	5.15	4.88	4.83	5.62[d]	5.69	5.62
	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.58	6.50	6.46	7.14[d]	7.12	7.14
Propanamide	$1^1A''$ ($n \rightarrow \pi^*$)	5.16	4.89	4.84	5.65[d]	5.74	5.65
	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.52	6.72	6.67	7.09[d]	7.17	7.09

[a]Results with the aug-cc-pVTZ from [19], if not otherwise marked.
[b]Results with the aug-cc-pVTZ from [46].
[c]TBE-2 values from [46].
[d]CC3/TZVP result from [17] with basis set correction from CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/TZVP from [19].
[e]CC3/TZVP result from [17] or [23] with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP from [19].

Table 4. Deviations in the vertical excitation energies (eV) of singlet excited states: aug-cc-pVTZ versus TZVP results.

	RPA(D)	SOPPA	SOPPA(CCSD)
Count[a]	117	117	117
Mean	−0.22	−0.24	−0.26
Abs. mean	0.25	0.24	0.26
Std. dev.	0.27	0.17	0.17
Maximum (−)	1.22	1.07	1.12

[a]Total number of considered states.

Table 5. Deviations in the vertical excitation energies (eV) of singlet excited states with the aug-cc-pVTZ basis set from the CC3/aug-cc-pVTZ results.[a]

	RPA(D)	SOPPA	SOPPA(CCSD)
Count[b]	116	116	116
Mean	−0.16	−0.45	−0.58
Abs. mean	0.38	0.50	0.61
Std. dev.	0.44	0.29	0.31
Maximum (+)	1.40	0.82	0.77
Maximum (−)	1.14	1.04	1.15

[a]Results from [19] and [17,23] with basis set corrections from CCSDR(3)/aug-cc-pVTZ or CC2/aug-cc-pVTZ.
[b]Total number of considered states.

Table 6. Deviations in the vertical excitation energies (eV) of singlet excited states with the aug-cc-pVTZ basis set from the TBE-2 set of results.

	RPA(D)	SOPPA	SOPPA(CCSD)
Count[a]	81	81	81
Mean	−0.18	−0.47	−0.59
Abs. mean	0.37	0.54	0.65
Std. dev.	0.44	0.31	0.33
Maximum (+)	1.56	1.00	0.97
Maximum (−)	1.14	0.85	1.15

[a]Total number of considered states.

basis set) and 71 triplet states. In the following, we compare the results obtained from the different SOPPA methods with the CC3, CASPT2, and TBE-2 reference data in Tables 1, 3, 7 and 9. The performance of the SOPPA methods will be discussed separately for the singlet and triplet states and for the two chosen basis sets. Various statistical analyses are presented in Tables 2, 4, 5, 6, 8, 10 and 11 and in Figures 1–14 with regard to CC3 reference data, and in the tables and figures of the supplemental online material (SI) with regard to CASPT2 reference data.

4.1. *Singlet excitation energies with the TZVP basis set*

In Figure 1, the deviations from the CC3/TZVP results are shown for all five SOPPA methods in form of histograms. It can clearly be seen that, apart from some outliers, all five SOPPA-based methods tend to underestimate the vertical

Table 7. Vertical excitation energies ΔE (eV) of triplet excited states from SOPPA, SOPPA(CCSD) and CC3 calculations with the TZVP basis sets.

Molecule	State	SOPPA	SOPPA (CCSD)	CC3[1]
Ethene	1^3B_{1u} ($\pi \rightarrow \pi^*$)	3.95	4.04	4.48
E-Butadiene	1^3B_u ($\pi \rightarrow \pi^*$)	2.77	2.80	3.32
	1^3A_g ($\pi \rightarrow \pi^*$)	4.68	4.69	5.17
all-*E*-Hexatriene	1^3B_u ($\pi \rightarrow \pi^*$)	2.13	2.10	2.69
	1^3A_g ($\pi \rightarrow \pi^*$)	3.80	3.79	4.32
all-*E*-Octatetraene	1^3B_u ($\pi \rightarrow \pi^*$)	1.73	1.65	2.30
	1^3A_g ($\pi \rightarrow \pi^*$)	3.14	3.11	3.67
Cyclopropene	1^3B_2 ($\pi \rightarrow \pi^*$)	3.89	3.91	4.34
	1^3B_1 ($\sigma \rightarrow \pi^*$)	6.24	6.28	6.62
Cyclopentadiene	1^3B_2 ($\pi \rightarrow \pi^*$)	2.75	2.71	3.25
	1^3A_1 ($\pi \rightarrow \pi^*$)	4.63	4.61	5.09
Norbornadiene	1^3A_2 ($\pi \rightarrow \pi^*$)	3.16	3.12	3.72
	1^3B_2 ($\pi \rightarrow \pi^*$)	3.64	3.60	4.16
Benzene	1^3B_{1u} ($\pi \rightarrow \pi^*$)	3.73	3.56	4.12
	1^3E_{1u} ($\pi \rightarrow \pi^*$)	4.56	4.45	4.90
	1^3B_{2u} ($\pi \rightarrow \pi^*$)	5.66	5.56	6.04
	1^3E_{2g} ($\pi \rightarrow \pi^*$)	7.46	7.42	7.49
Naphthalene	1^3B_{2u} ($\pi \rightarrow \pi^*$)	2.68	2.44	3.11
	1^3B_{3u} ($\pi \rightarrow \pi^*$)	3.78	3.61	4.18
	1^3B_{1g} ($\pi \rightarrow \pi^*$)	4.04	3.90	4.47
	2^3B_{2u} ($\pi \rightarrow \pi^*$)	4.29	4.07	4.64
	2^3B_{3u} ($\pi \rightarrow \pi^*$)	4.66	4.48	5.11
	1^3A_g ($\pi \rightarrow \pi^*$)	5.15	5.03	5.52
	2^3B_{1g} ($\pi \rightarrow \pi^*$)	6.00	5.90	6.48
	2^3A_g ($\pi \rightarrow \pi^*$)	6.37	6.24	6.47
	3^3A_g ($\pi \rightarrow \pi^*$)	6.46	6.34	6.79
	3^3B_{1g} ($\pi \rightarrow \pi^*$)	6.69	6.60	6.76
Furan	1^3B_2 ($\pi \rightarrow \pi^*$)	3.77	3.68	4.17
	1^3A_1 ($\pi \rightarrow \pi^*$)	5.03	4.96	5.48
Pyrrole	1^3B_2 ($\pi \rightarrow \pi^*$)	4.11	4.01	4.48
	1^3A_1 ($\pi \rightarrow \pi^*$)	5.13	5.05	5.51
Imidazole	$1^3A'$ ($\pi \rightarrow \pi^*$)	4.30	4.20	4.69
	$2^3A'$ ($\pi \rightarrow \pi^*$)	5.40	5.30	5.79
	$1^3A''$ ($n \rightarrow \pi^*$)	5.85	5.81	6.37
	$3^3A'$ ($\pi \rightarrow \pi^*$)	6.21	6.11	6.55
	$4^3A'$ ($\pi \rightarrow \pi^*$)	7.41	7.41	7.42
	$2^3A''$ ($n \rightarrow \pi^*$)	7.07	7.05	7.51
Pyridine	1^3A_1 ($\pi \rightarrow \pi^*$)	3.88	3.68	4.25
	1^3B_1 ($n \rightarrow \pi^*$)	3.97	3.91	4.50
	1^3B_2 ($\pi \rightarrow \pi^*$)	4.48	4.35	4.86
	2^3A_1 ($\pi \rightarrow \pi^*$)	4.71	4.57	5.05
	1^3A_2 ($n \rightarrow \pi^*$)	4.87	4.83	5.46
	2^3B_2 ($\pi \rightarrow \pi^*$)	6.03	5.90	6.40
	3^3B_2 ($\pi \rightarrow \pi^*$)	7.83	7.77	7.83
	3^3A_1 ($\pi \rightarrow \pi^*$)	7.59	7.51	7.66
s-Tetrazine	1^3B_{3u} ($n \rightarrow \pi^*$)	1.13	1.00	1.89
	1^3A_u ($n \rightarrow \pi^*$)	2.91	2.84	3.52
	1^3B_{1g} ($n \rightarrow \pi^*$)	3.53	3.45	4.21
	1^3B_{1u} ($\pi \rightarrow \pi^*$)	3.94	3.51	4.33
	1^3B_{2u} ($\pi \rightarrow \pi^*$)	4.10	3.82	4.54
	1^3B_{2g} ($n \rightarrow \pi^*$)	4.32	4.21	4.93
	2^3A_u ($n \rightarrow \pi^*$)	4.40	4.27	5.03
	2^3B_{1u} ($\pi \rightarrow \pi^*$)	4.88	4.67	5.38
	2^3B_{2g} ($n \rightarrow \pi^*$)	5.55	5.51	6.04
	2^3B_{1g} ($n \rightarrow \pi^*$)	6.23	6.18	6.60
	2^3B_{3u} ($n \rightarrow \pi^*$)	6.02	5.96	6.53

Continue.

Table 7. *continue*.

Molecule	State	SOPPA	SOPPA (CCSD)	CC3[1]
	2^3B_{2u} ($\pi \rightarrow \pi^*$)	7.02	6.80	7.36
Formaldehyde	1^3A_2 ($\pi \rightarrow \pi^*$)	2.93	2.92	3.55
	1^3A_1 ($\pi \rightarrow \pi^*$)	5.42	5.36	5.83
Acetone	1^3A_2 ($n \rightarrow \pi^*$)	3.39	3.35	4.05
	1^3A_1 ($\pi \rightarrow \pi^*$)	5.60	5.53	6.03
p-Benzoquinone	1^3B_{1g} ($n \rightarrow \pi^*$)	1.74	1.65	2.51
	1^3A_u ($n \rightarrow \pi^*$)	1.83	1.73	2.62
	1^3B_{1u} ($\pi \rightarrow \pi^*$)	2.44	2.29	2.96
	1^3B_{3g} ($\pi \rightarrow \pi^*$)	2.89	2.83	3.41
Formamide	$1^3A''$ ($n \rightarrow \pi^*$)	4.66	4.62	5.36
	$1^3A'$ ($\pi \rightarrow \pi^*$)	5.35	5.30	5.74
Acetamide	$1^3A''$ ($n \rightarrow \pi^*$)	4.69	4.65	5.42
	$1^3A'$ ($\pi \rightarrow \pi^*$)	5.45	5.40	5.88
Propanamide	$1^3A''$ ($n \rightarrow \pi^*$)	4.70	4.66	5.45
	$1^3A'$ ($\pi \rightarrow \pi^*$)	5.46	5.41	5.90

[a]Results from [17].

singlet excitation energies compared to CC3 (albeit to a different extent).

The four SOPPA methods can directly be compared as they have almost the same standard deviations of 0.3 eV.

Table 8. Deviations in the vertical excitation energies (eV) of triplet excited states with the TZVP basis set from the CC3/TZVP results.[a]

	SOPPA	SOPPA(CCSD)
Count[b]	71	71
Mean	−0.45	−0.54
Abs. mean	0.45	0.54
Std. dev.	0.17	0.18
Maximum (−)	0.79	0.89

[a]TZVP results from [17].
[b]Total number of considered states.

Both the histograms in Figure 1 and the mean (absolute) deviations and maximum positive and negative deviations in Table 2 show that the amount to which the SOPPA methods underestimate the CC3 singlet excitation energies increases in the series SOPPA < SOPPA(CCSD) < SOPPA(SCS-MP2) < SOPPA(SOS-MP2), which implies that the original SOPPA method actually performs best compared to CC3, confirming the findings of the previous study on the much smaller test set of six aromatic molecules [37]. Furthermore, replacing the MP correlation coefficients by scaled coefficients in the SOPPA(SCS-MP2) and

Table 9. Oscillator strengths (in dipole length representation) for optically allowed transitions calculated with the TZVP and aug-cc-pVTZ (aVTZ) basis sets.[a]

						SOPPA				
		RPA(D)		SOPPA		(SCS-MP2)	(SOS-MP2)	(CCSD)		CC3[b]
Molecule	State	TZVP	aVTZ	TZVP	aVTZ	TZVP	TZVP	TZVP	aVTZ	TZVP
Ethene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	0.452	0.401	0.379	0.346	0.376	0.375	0.355	0.326	0.389
E-Butadiene	1^1B_u ($\pi \rightarrow \pi^*$)	0.870	0.780	0.677	0.639	0.468	0.462	0.604	0.575	0.726
all-*E*-Hexatriene	1^1B_u ($\pi \rightarrow \pi^*$)	1.317	1.251	1.009	0.984	0.868	0.849	0.862	0.846	1.129
all-*E*-Octatetraene	1^1B_u ($\pi \rightarrow \pi^*$)	1.776	1.709	1.332	1.304	0.936	0.906	1.095	1.078	1.549
Cyclopropene	1^1B_1 ($\sigma \rightarrow \pi^*$)	0.001	0.010	0.001	0.001	0.001	0.001	0.001	0.001	0.001
	1^1B_2 ($\pi \rightarrow \pi^*$)	0.125	0.099	0.082	0.070	0.083	0.083	0.079	0.068	0.083
Cyclopentadiene	1^1B_2 ($\pi \rightarrow \pi^*$)	0.096	0.084	0.089	0.080	0.084	0.082	0.078	0.072	0.093
	2^1A_1 ($\pi \rightarrow \pi^*$)	0.029	0.034	0.011	0.002	0.009	0.008	0.009	0.001	0.005
	3^1A_1 ($\pi \rightarrow \pi^*$)	0.675	0.304	0.593	0.409	0.583	0.579	0.564	0.378	0.596
Norbornadiene	1^1B_2 ($\pi \rightarrow \pi^*$)	0.195	0.221	0.027	0.027	0.026	0.025	0.027	0.026	0.027
	2^1B_2 ($\pi \rightarrow \pi^*$)	0.116	0.059	0.177	0.104	0.174	0.173	0.168	0.101	0.185
Benzene	1^1E_{1u} ($\pi \rightarrow \pi^*$)	0.668	0.646	0.611	0.594	0.587	0.575	0.555	0.541	0.630
Naphthalene	1^1B_{2u} ($\pi \rightarrow \pi^*$)	0.077	0.060	0.075	0.061	0.068	0.065	0.070	0.057	0.085
	2^1B_{3u} ($\pi \rightarrow \pi^*$)	1.408	1.333	1.239	1.220	1.149	1.105	1.073	1.052	1.325
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	0.385	0.346	0.236	0.215	0.227	0.223	0.221	0.202	0.239
	3^1B_{3u} ($\pi \rightarrow \pi^*$)	0.023	0.009	0.008	0.008	0.014	0.014	0.008	0.008	0.005
	3^1B_{2u} ($\pi \rightarrow \pi^*$)	0.380	0.259	0.492	0.393	0.471	0.460	0.437	0.353	0.498
Furan	1^1B_2 ($\pi \rightarrow \pi^*$)	0.148	0.158	0.138	0.148	0.132	0.129	0.132	0.140	0.155
	2^1A_1 ($\pi \rightarrow \pi^*$)	0.000	0.024	0.007	0.003	0.008	0.008	0.008	0.004	0.001
	3^1A_1 ($\pi \rightarrow \pi^*$)	0.556	0.385	0.450	0.401	0.442	0.437	0.429	0.386	0.450
Pyrrole	2^1A_1 ($\pi \rightarrow \pi^*$)	0.004	0.005	0.008	0.003	0.009	0.009	0.008	0.004	0.004
	1^1B_2 ($\pi \rightarrow \pi^*$)	0.163	0.176	0.147	0.169	0.142	0.140	0.145	0.165	0.167
	3^1A_1 ($\pi \rightarrow \pi^*$)	0.549	0.280	0.481	0.345	0.472	0.468	0.463	0.355	0.478
Imidazole	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.182		0.068		0.063	0.060	0.066		0.081
	$1^1A''$ ($n \rightarrow \pi^*$)	0.005	0.001	0.003	0.002	0.003	0.003	0.003	0.002	0.004
	$3^1A'$ ($\pi \rightarrow \pi^*$)	0.036		0.080		0.079	0.079	0.079		0.082

Continue.

Table 9. *continue*.

						SOPPA				
		RPA(D)		SOPPA		(SCS-MP2)	(SOS-MP2)	(CCSD)		CC3[b]
Molecule	State	TZVP	aVTZ	TZVP	aVTZ	TZVP	TZVP	TZVP	aVTZ	TZVP
	$2^1A''$ ($n \rightarrow \pi^*$)	0.000	0.008	0.002	0.003	0.000	0.000	0.006	0.002	0.005
	$4^1A'$ ($\pi \rightarrow \pi^*$)	0.390		0.381		0.326	0.323	0.364		0.410
Pyridine	1^1B_1 ($n \rightarrow \pi^*$)	0.005	0.004	0.005	0.004	0.004	0.004	0.004	0.004	0.005
	1^1B_2 ($\pi \rightarrow \pi^*$)	0.054	0.062	0.018	0.023	0.017	0.016	0.017	0.022	0.021
	2^1A_1 ($\pi \rightarrow \pi^*$)	0.010	0.009	0.012	0.007	0.010	0.009	0.011	0.008	0.014
	2^1B_2 ($\pi \rightarrow \pi^*$)	0.509	0.355	0.497	0.491	0.479	0.470	0.454	0.429	0.482
	3^1A_1 ($\pi \rightarrow \pi^*$)	0.603	0.595	0.524	0.491	0.513	0.506	0.485	0.458	0.526
	5^1A_1 ($\pi \rightarrow \pi^*$)	0.000	0.004	0.001	0.004	0.000	0.000	0.000	0.014	0.004
	3^1B_2 ($\pi \rightarrow \pi^*$)	0.000	0.009	0.009	0.000	0.106	0.104	0.005	0.000	0.030
Pyrazine	1^1B_{3u} ($n \rightarrow \pi^*$)	0.006	0.005	0.006	0.005	0.005	0.005	0.005	0.004	0.007
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	0.120	0.133	0.051	0.062	0.049	0.048	0.049	0.059	0.062
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	0.036	0.033	0.062	0.051	0.056	0.053	0.057	0.049	0.070
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	0.369	0.297	0.395	0.380	0.383	0.377	0.359	0.347	0.376
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	0.524	0.523	0.414	0.299	0.408	0.405	0.379	0.255	0.407
Pyrimidine	1^1B_1 ($n \rightarrow \pi^*$)	0.007	0.005	0.005	0.004	0.005	0.005	0.005	0.004	0.006
	1^1B_2 ($\pi \rightarrow \pi^*$)	0.056	0.064	0.016	0.021	0.015	0.015	0.015	0.020	0.021
	2^1A_1 ($\pi \rightarrow \pi^*$)	0.019	0.019	0.032	0.026	0.029	0.027	0.033	0.028	0.043
	3^1A_1 ($\pi \rightarrow \pi^*$)	0.498	0.488	0.424	0.346	0.411	0.404	0.386	0.374	0.391
	2^1B_2 ($\pi \rightarrow \pi^*$)	0.457	0.449	0.449	0.432	0.447	0.442	0.425	0.365	0.415
Pyridazine	1^1B_1 ($n \rightarrow \pi^*$)	0.003	0.005	0.005	0.004	0.005	0.004	0.005	0.003	0.006
	2^1A_1 ($\pi \rightarrow \pi^*$)	0.038	0.042	0.011	0.014	0.010	0.010	0.011	0.014	0.014
	2^1B_1 ($n \rightarrow \pi^*$)	0.014	0.011	0.005	0.004	0.004	0.004	0.004	0.004	0.005
	1^1B_2 ($\pi \rightarrow \pi^*$)	0.002	0.002	0.011	0.012	0.012	0.013	0.018	0.016	0.012
	2^1B_2 ($\pi \rightarrow \pi^*$)	0.509	0.506	0.338	0.409	0.392	0.391	0.367	0.374	0.340
	3^1A_1 ($\pi \rightarrow \pi^*$)	0.478	0.479	0.437	0.138	0.429	0.424	0.405	0.353	0.433
s-Triazine	$1^1A_2''$ ($n \rightarrow \pi^*$)	0.015	0.012	0.014	0.012	0.013	0.013	0.013	0.011	0.016
	$1^1E'$ ($\pi \rightarrow \pi^*$)	0.456	0.460	0.418	0.451	0.404	0.397	0.387	0.411	0.386
s-Tetrazine	1^1B_{3u} ($n \rightarrow \pi^*$)	0.007	0.005	0.005	0.004	0.004	0.004	0.004	0.003	0.007
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	0.090	0.097	0.034	0.040	0.033	0.032	0.032	0.038	0.044
	2^1B_{3u} ($n \rightarrow \pi^*$)	0.009	0.019	0.010	0.009	0.009	0.009	0.009	0.008	0.011
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	0.000	0.000	0.011	0.009	0.020	0.025	0.063	0.040	0.002
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	0.393	0.393	0.335	0.335	0.312	0.300	0.241	0.256	0.349
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	0.287	0.300	0.315	0.310	0.311	0.308	0.288	0.273	0.307
Formaldehyde	3^1A_1 ($\pi \rightarrow \pi^*$)	0.193	0.201	0.395	0.153	0.382	0.375	0.366	0.150	0.348
	1^1B_1 ($\sigma \rightarrow \pi^*$)	0.001	0.000	0.004	0.001	0.004	0.004	0.003	0.001	0.003
Acetone	2^1A_1 ($\pi \rightarrow \pi^*$)	0.274	0.173	0.316	0.245	0.303	0.296	0.294	0.235	0.245
p-Benzoquinone	1^1B_{1u} ($\pi \rightarrow \pi^*$)	0.769	0.740	0.487	0.470	0.460	0.447	0.420	0.407	0.485
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	0.263	0.250	0.377	0.395	0.364	0.357	0.317	0.347	0.131
Formamide	$1^1A''$ ($n \rightarrow \pi^*$)	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.000	0.001
	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.193	0.140	0.360	0.250	0.307	0.298	0.335	0.232	0.386
Acetamide	$1^1A''$ ($n \rightarrow \pi^*$)	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.197	0.152	0.225	0.099	0.166	0.165	0.216	0.097	0.207
Propanamide	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.169	0.126	0.188	0.134	0.135	0.135	0.181	0.127	0.170
Cytosine	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.104		0.035		0.034	0.034	0.035		0.046
	$1^1A''$ ($n \rightarrow \pi^*$)	0.002		0.002		0.000	0.000	0.002		0.001
	$2^1A''$ ($n \rightarrow \pi^*$)	0.000		0.000		0.002	0.002	0.000		0.001
	$3^1A'$ ($\pi \rightarrow \pi^*$)	0.267		0.170		0.147	0.143	0.161		0.130
	$4^1A'$ ($\pi \rightarrow \pi^*$)	0.406		0.579		0.537	0.533	0.541		0.520
Thymine	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.313		0.185		0.174	0.169	0.172		0.172
	$3^1A'$ ($\pi \rightarrow \pi^*$)	0.304		0.073		0.071	0.072	0.070		0.072
	$4^1A'$ ($\pi \rightarrow \pi^*$)	0.116		0.251		0.237	0.231	0.238		0.197
Uracil	$2^1A'$ ($\pi \rightarrow \pi^*$)	0.318		0.190		0.180	0.181	0.179		0.174
	$3^1A'$ ($\pi \rightarrow \pi^*$)	0.095		0.054		0.051	0.052	0.053		0.046
	$4^1A'$ ($\pi \rightarrow \pi^*$)	0.294		0.190		0.158	0.154	0.183		0.152
Adenine	$1^1A''$ ($n \rightarrow \pi^*$)	0.000		0.001		0.001	0.001	0.001		0.001
	$2^1A''$ ($n \rightarrow \pi^*$)	0.001		0.002		0.001	0.001	0.001		0.002

[a]Only values above 0.001 are listed.
[b]Results from [23].

Table 10. Percentage deviations in the oscillator strengths of singlet excited states with the TZVP basis set from the CC3/TZVP results.[a], [b]

	RPA(D)	SOPPA	SOPPA(SCS-MP2)	SOPPA(SOS-MP2)	SOPPA(CCSD)	CC2[c]	B3LYP[d]
Count[e]	72	72	72	72	72	72	70
Mean	43%	1%	0%	−4%	−5%	14%	0%
Abs. mean	68%	19%	26%	28%	21%	23%	30%
Std. dev.	119%	35%	51%	52%	33%	46%	53%
Maximum (+)	622%	188%	254%	246%	142%	315%	328%
Maximum (−)	100%	75%	99%	99%	100%	100%	83%

[a]TZVP results from [23].
[b]Only states for which the CC3 oscillator strengths are larger than 0.002 were included.
[c]TZVP results from [17].
[d]TZVP results from [45].
[e]Total number of considered states.

SOPPA(SOS-MP2) methods has the same qualitative effect as replacing them by CCSD correlation coefficients, but leads to even larger changes. SOPPA exhibits the most narrow (and the most peaked) distribution of deviations from CC3. 30% of the SOPPA results have deviations from CC3 between −0.6 and −0.5 eV, compared with only 25% or 22% with deviations between −0.8 and −0.7 eV in SOPPA(SCS-MP2) or SOPPA(CCSD) and 19% with deviations between −0.9 and −0.8 eV in SOPPA(SOS-MP2). Replacing the MP correlation coefficients, and in particular neglecting the same spin coefficients, thus increases the spread in the errors. From the correlation plots in Figure 2, it can be seen that these shifts from SOPPA to SOPPA(CCSD), SOPPA(SCS-MP2) and SOPPA(SOS-MP2) hold not only for the average deviations but are consistent for each individual state. The correlation plots between the SOPPA methods and the CC3 results, in Figure 3, show that there is no significant bias in the correlation for neither smaller nor larger excitation energies.

However, one can see that the few outliers, where the SOPPA methods predict larger excitation energies than CC3 are all above 5 eV. For all five methods, these are the notorious 2^1A_g states of *E*-butadiene, all-*E*-hexatriene and all-*E*-octatetraene as well as the 2^1B_u state of all-*E*-octatetraene, which have large double excitation character [17], as seen by R_1 values below 70% in the CC3 calculations [18] and for which none of the single reference-based methods can thus be expected to perform well [23]. SOPPA predicts for these states excitation energies ∼0.5 eV larger than CC3. The same holds also for the 3^1B_{3u} state of naphthalene ($R_1 = 59\%$) and for the $2^1A'$ state of formamide ($R_1 = 88\%$), although here SOPPA overestimates CC3 by only 0.29 and 0.25 eV. For a third class of states, SOPPA and SOPPA(CCSD) still predict larger excitation energies than CC3 but now the differences are less than 0.2 eV. Due to the systematic differences between SOPPA and the two new methods SOPPA(SCS-MP2) and SOPPA(SOS-MP2), the latter two methods exhibit deviations less than 0.1 eV from the CC3 results. The SOPPA(SCS-MP2) and SOPPA(SOS-MP2) results are above and below the corresponding CC3 results, respectively. This holds for the 2^1E_{2g} state of benzene, the 1^1B_{3g} state of pyrazine and the 3^1B_{1g} state of s-tetrazine, which also have significant double excitation characters as indicated by a R_1 value smaller than 65% in the CC3 calculations [18]. Also deviating from the general trend are the 2^1A_1 state in cyclopentadiene ($R_1 = 79\%$), the 3^1A_g state of naphthalene ($R_1 = 79\%$), the 3^1B_2 ($R_1 = 65\%$) and 4^1A_1 ($R_1 = 74\%$) states in pyridine, the 2^1A_g state of pyrazine ($R_1 = 74\%$) and the 2^1B_{1u} state in *p*-benzoquinone ($R_1 = 69\%$), where SOPPA and SOPPA(CCSD) are in perfect agreement with the CC3 results while SOPPA(SCS-MP2) and SOPPA(SOS-MP2) thus only slightly underestimate the CC3 results. All of these outliers are states with a significant doubles character and can thus easily be identified as states for which the SOPPA methods quite likely deviate from their usual behaviour.

All but one of these transitions (to the 3^1B_{1g} state of s-tetrazine) are $\pi \rightarrow \pi^*$ transitions. In Table 2, the statistics for the comparison with CC3 is also split up into 91 $\pi \rightarrow \pi^*$ and 44 $n \rightarrow \pi^*$ transitions. In line with the discussion of the outliers above, one finds that the $n \rightarrow \pi^*$ transitions exhibit a more uniform behaviour. The mean and absolute mean deviations are virtually the same, indicating that almost all deviations are negative, and the standard deviations are with ∼0.2 eV also smaller than those for the $\pi \rightarrow \pi^*$ transitions and the total set. The mean deviations for the $n \rightarrow \pi^*$ transitions are also closer to the maxima in the deviation histograms in Figure 1.

Table 11. Basis set effect on the oscillator strengths of singlet excited states at the RPA(D), SOPPA and SOPPA(CCSD) levels: aug-cc-pVTZ versus TZVP.

	RPA(D)	SOPPA	SOPPA(CCSD)
Count[a]	50	54	54
Mean	−7%	−13%	−14%
Abs. mean	20%	20%	20%
Std. dev.	29%	26%	25%
Maximum (+)	111%	31%	33%
Maximum (−)	80%	97%	98%

[a]Total number of considered states.

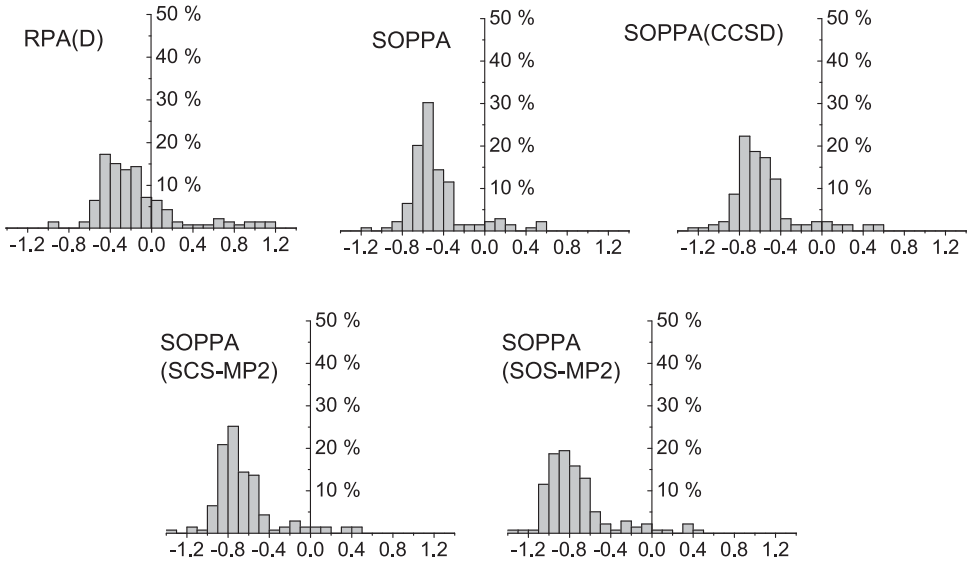

Figure 1. Histograms (in %) of the deviations between RPA(D), SOPPA, SOPPA(CCSD), SOPPA(SCS-MP2), SOPPA(SOS-MP2) and CC3 vertical excitation energies (eV) of singlet excited states calculated with the TZVP basis set.

The RPA(D) results, on the other hand, exhibit a different behaviour. RPA(D) has the smallest mean and even mean absolute deviation of all five methods both for all states and the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions separately (Table 2). For 14% of the states studied here, the RPA(D) excitation energies differ by less than ± 0.1 eV from the CC3 results. However, the difference between the mean and absolute mean deviations and the standard deviations are at the same time significantly larger than for the other methods, indicating that the RPA(D) results are scattered around the CC3 results with a rather large spread, as can be seen in Figures 2 and 3. From the correlation plot, one can also see a slight tendency for larger deviations for the higher lying states. However, one should note in this context, that the assignment of the calculated excitation energies to particular states also becomes significantly less certain for the higher states due to significant mixing. Furthermore, the differences between the RPA(D) and SOPPA result for the states are less systematic (Figure 2), as was observed for the other SOPPA variants. RPA(D) thus leads to smaller deviations but is significantly less consistent than the other methods confirming the findings of the previous study on six aromatic compounds [37].

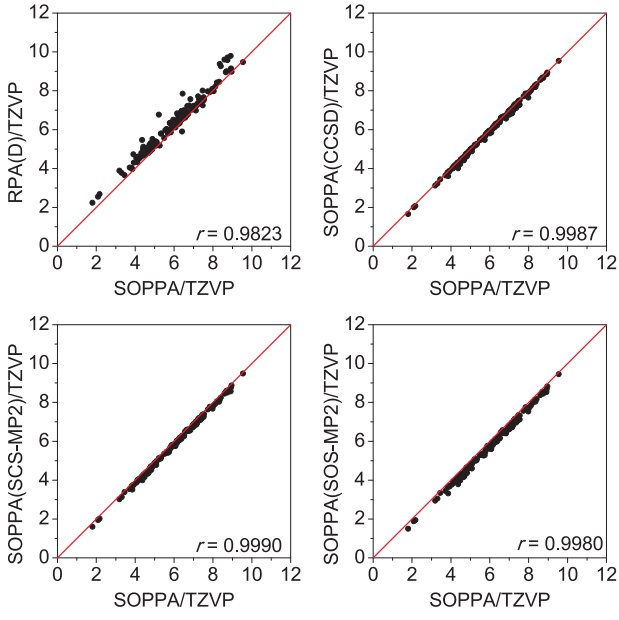

Figure 2. Correlation plots for the vertical excitation energies (eV) of singlet excited states with the TZVP basis set: RPA(D), SOPPA(CCSD) and SOPPA(SCS-MP2), SOPPA(SOS-MP2) vs. SOPPA results.

Compared with the three popular alternatives, B3LYP, CC2 and ADC(2), we can see that the mean deviation for the same benchmark set is -0.46 ± 0.29 eV for SOPPA, -0.29 ± 0.46 eV for B3LYP [45], 0.13 ± 0.26 eV for CC2 [18] and 0.01 ± 0.27 eV [15] or -0.03 ± 0.54 eV [16] for ADC(2) (in the latter case, using two slightly smaller subsets of the standard benchmark set). SOPPA thus underestimates vertical excitation energies more strongly than B3LYP but does so more consistently (as indicated by the standard deviations) and both are outperformed by CC2 and ADC(2). We note in this context that Kánná and Szalay recently reported [23] an even smaller deviation for CC2, 0.04 ± 0.012 eV, but they included only states with more than 80% single excitation character in contrast to our studies. Furthermore, in SOPPA(SOS-MP2), the excitation energies are decreased similarly to ISR-SOS-ADC(2) [12].

In the supplementary online material, the histograms and correlation plots as well as a table with statistical data

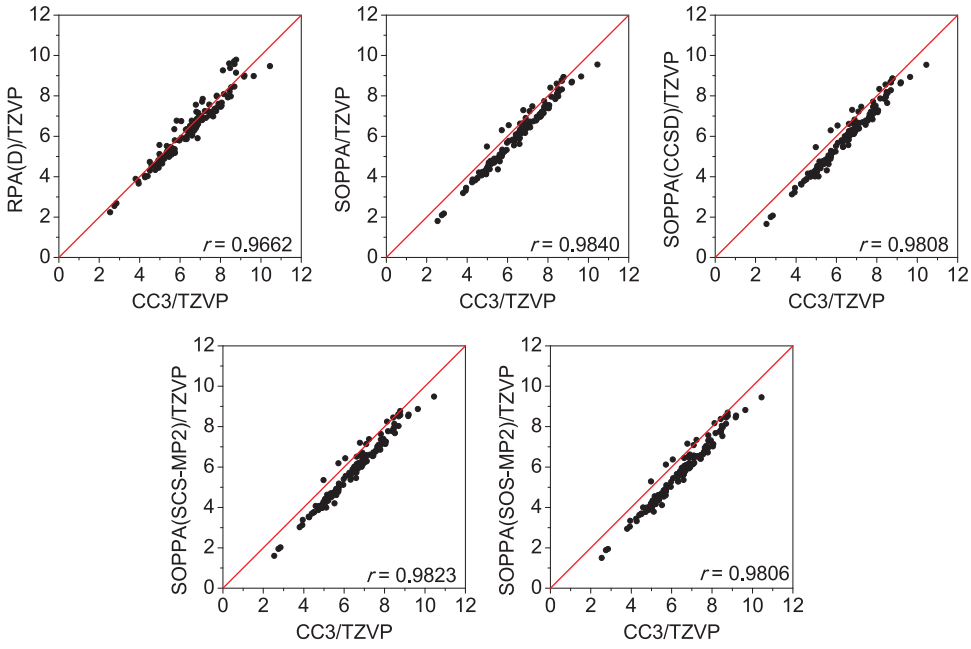

Figure 3. Correlation plots for the vertical excitation energies (eV) of singlet excited states with the TZVP basis set: RPA(D), SOPPA, SOPPA(CCSD) and SOPPA(SCS-MP2), SOPPA(SOS-MP2) vs. CC3 results.

are shown for the comparison with the CASPT2/TZVP results [45]. Although the correlations are slightly less good as with the CC3 reference data leading to more positive outliers and thus a smaller mean deviation but larger standard deviation, 0.03 ± 0.42 eV for RPA(D), −0.28 ± 0.34 eV for SOPPA, −0.37 ± 0.35 eV for SOPPA(CCSD), −0.46 ± 0.35 eV for SOPPA(SCS-MP2) and −0.55 ± 0.36 eV for SOPPA(SOS-MP2), the main conclusions and the ordering of the performance of the methods are the same.

4.2. Singlet excitation energies with the aug-cc-pVTZ basis set

In Table 3, the RPA(D), SOPPA and SOPPA(CCSD) results obtained with the aug-cc-pVTZ basis are shown together with the CC3, CASPT2 and TBE-2 reference data [19,45,46]. Not all CC3 results are authentic CC3/aug-cc-pVTZ results, because some were obtained by adding to the CC3/TZVP results [17,23] a basis set correction obtained as difference between the corresponding CCSDR(3)/TZVP and CCSDR(3)/aug-cc-pVTZ or CC2/TZVP and CC2/aug-cc-pVTZ calculations [19]. The benchmark set studied here is with 24 molecules and 116 excited singlet states slightly smaller than in the TZVP case as we have not included the four nucleobases.

The first question to address is whether adding the extra diffuse functions in the aug-cc-pVTZ basis set has the same effect on the SOPPA, SOPPA(CCSD) and RPA(D) excitation energies, as previously observed for the coupled cluster methods and CASPT2 [19,46], where it was found to be on average −0.22 ± 0.29 eV for CC2 and −0.18 ± 0.25 eV for CC3, while the effect on the CASPT2 results was with −0.11 ± 0.22 eV on average, which is significantly smaller. In Figure 4 and Table 4, one can see that, the additional diffuse functions reduce all excitation energies on average by −0.24 ± 0.17 eV for SOPPA and −0.26 ± 0.17 eV for SOPPA(CCSD), while there are a few states for which the RPA(D) excitation energies increase. These are again the 2^1A_g states of all-*E*-hexatriene and all-*E*-octatetraene and the 2^1A_1 state in cyclopentadiene, which have a large doubles character and in addition the 2^1B_2 state of norbornadien, the 2^1A_g state of naphthalene, the 2^1A_1 state of furan, the 2^1B_{2u} state of pyrazine and the 1^1B_{3u} state in *p*-benzoquinone. As a consequence, the mean shift is slightly smaller (−0.22 eV), but the standard deviation of the shifts is 0.27 eV, which is significantly larger. From the correlation plots in Figure 5, one can see that there is a slight bias to larger basis set effects for larger excitation energies leading to the tail of larger deviations in the histogram in Figure 4.

As a consequence of this almost constant basis set shift, the differences between the SOPPA, SOPPA(CCSD) and RPA(D) excitation energies calculated with the aug-cc-pVTZ basis set, on the one hand, and the CC3/aug-cc-pVTZ excitation energies in Table 3, on the other hand, are almost identical. The mean deviations and standard deviations from the mean deviations in Table 5 are statistically indistinguishable from the corresponding values for the TZVP basis set in Table 2. Only the maximum positive deviations are somewhat larger in the aug-cc-pVTZ basis set than in the TZVP basis set. Also the correlation plots and the histograms of deviations in Figures 7 and 6 show

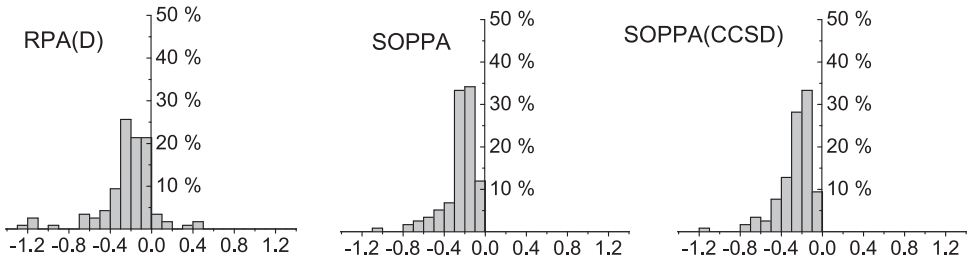

Figure 4. Histograms (in %) of the deviations between aug-cc-pVTZ and TZVP vertical excitation energies (eV) of singlet excited states at the RPA(D), SOPPA and SOPPA(CCSD) levels.

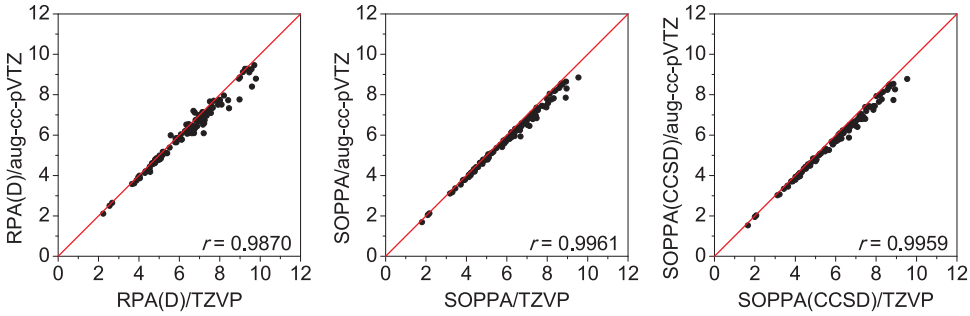

Figure 5. Correlation plots for the vertical excitation energies (eV) of singlet excited states at the RPA(D), SOPPA and SOPPA(CCSD) levels: aug-cc-pVTZ vs. TZVP results.

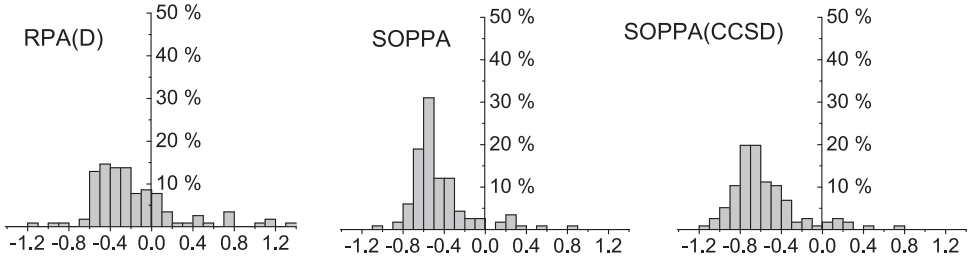

Figure 6. Histograms (in %) of the deviations between RPA(D), SOPPA, SOPPA(CCSD) and CC3 vertical excitation energies (eV) of singlet excited states calculated with the aug-cc-pVTZ basis set.

that there are fewer larger outliers than for the TZVP basis set. For SOPPA and SOPPA(CCSD), the states whose energies are against the general trend overestimated compared to CC3 are again the 2^1A_g states of *E*-butadiene, all-*E*-hexatriene and all-*E*-octatetraene, the 2^1B_u state of all-*E*-octatetraene, the 2^1E_{2g} state of benzene, the 3^1B_{3u} state of naphthalene and the 4^1A_1 state of pyridine, and, now, also the 3^1B_{2u} state of naphthalene and the 3^1B_2 state of pyridine. RPA(D) predicts, in addition, also by 0.1 eV or more larger excitation energies than CC3 for the 3^1A_g state

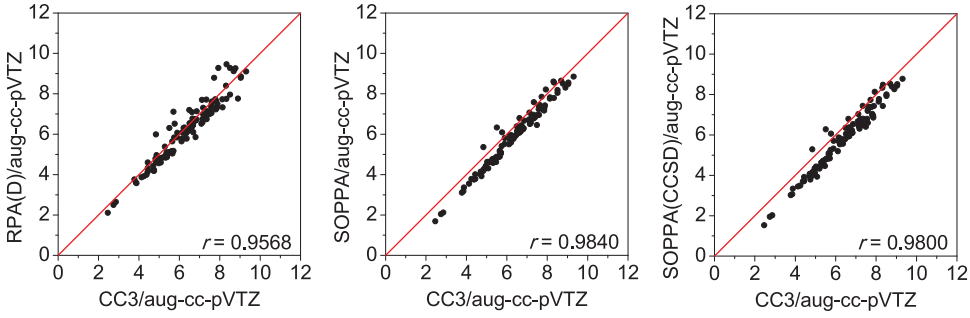

Figure 7. Correlation plots for the vertical excitation energies (eV) of singlet excited states with the aug-cc-pVTZ basis set: RPA(D), SOPPA and SOPPA(CCSD) vs. CC3 results.

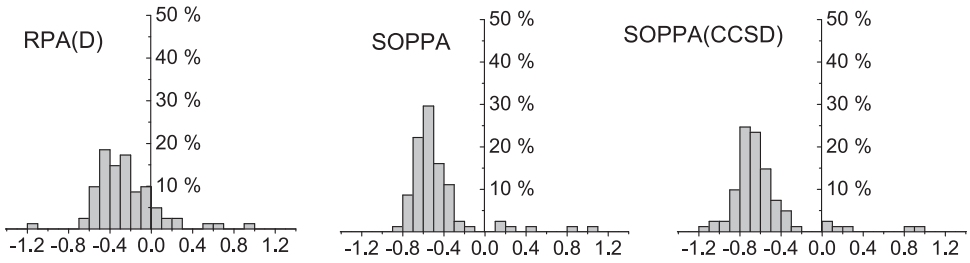

Figure 8. Histograms (in %) of the deviations between RPA(D), SOPPA, SOPPA(CCSD) and TBE-2 vertical excitation energies (eV) of singlet excited states calculated with the aug-cc-pVTZ basis set.

in all-*E*-octatetraene, the 2^1A_1 state in cyclopentadiene, the 3^1A_g state in naphthalene, the 2^1A_g state in pyrazine, the 1^1A_2 state in pyridazine, the 1^1B_{1u} state in s-tetrazine and the 1^1B_{3u} state in p-benzoquinone. Interestingly, RPA shows, on the other hand, only very small deviations ($\leq$0.1 eV) from the CC3 results for the 1^1B_2 state in norbornadiene, the 2^1E_{2g} state of benzene, the 1^1B_{2u}, 2^1A_{1g} and 1^1B_{1g} states of naphthalene, the 2^1A_1 state of furan, the three lowest states of pyrrol and imidazole, the 1^1B_{2g} and 1^1B_{1u} states of pyrazine, the 1^1B_2 state of pyridazine, the $2^1E''$ state of s-triazine, the 1^1A_u, 1^1B_{1g} and 1^1B_{2g} states of s-tetrazine and the 2^1B_{1u} state of *p*-benzoquinone. Overall, RPA(D) deviations are thus more spread out with the most frequent (in total ~55%) deviations being between −0.2 and −0.6 eV as can be seen from Figure 6, which explains the smaller mean deviation, while the most frequent deviation in SOPPA is with 31% between −0.5 and −0.6 eV as for the TZVP basis set and for SOPPA(CCSD) 40% with deviations between −0.6 and −0.8 eV.

In the supplementary online material, we present a comparison with the CASPT2/aug-cc-pVTZ results [46] in the form of histograms, correlation plots and a table with statistical data. In line with the results for the TZVP basis set, the mean deviations are somewhat smaller than for the comparison with the CC3 results, while the standard deviations from these mean values are slightly larger, reflecting mostly the differences between the CASPT2 and CC3 results. The conclusions about the performance of the three methods are, however, unchanged.

Finally, in Table 6 and Figures 8 and 9, we compare the aug-cc-pVTZ results with the theoretical best estimates TBE-2 [46]. Although the number of states in the TBE-2 set is smaller than the number of CC3 states in Table 5 and Figures 6 and 7, the statistics and thus the conclusions are very much the same: SOPPA(CCSD), which on average underestimates the TBE-2 excitation energies by 0.59 ± 0.33 eV, represents no improvement over SOPPA (average underestimation of TBE-2: 0.48 ± 0.31 eV) for excited singlet states, while RPA(D) exhibits a significantly smaller average deviation from TBE-2, −0.18 ± 0.44 eV, although at the price of a larger standard deviation, i.e. a larger number of outliers. All SOPPA methods perform worse than ADC(2), for which a mean error of 0.01 ± 0.08 eV was reported for a slightly smaller subset of the benchmark set [12].

4.3. *Triplet excitation energies with the TZVP basis set*

In Table 7, SOPPA/TZVP and SOPPA(CCSD)/TZVP results for 71 excited triplet states of 20 molecules are presented together with the corresponding CC3/TZVP results [17]. This is for the first time that SOPPA(CCSD) excitation energies for triplet states are reported and the first systematic comparison of SOPPA triplet excitation energies for a larger test set.

The statistical analysis in Table 8 shows a somewhat different behaviour than in the case of the excited singlet

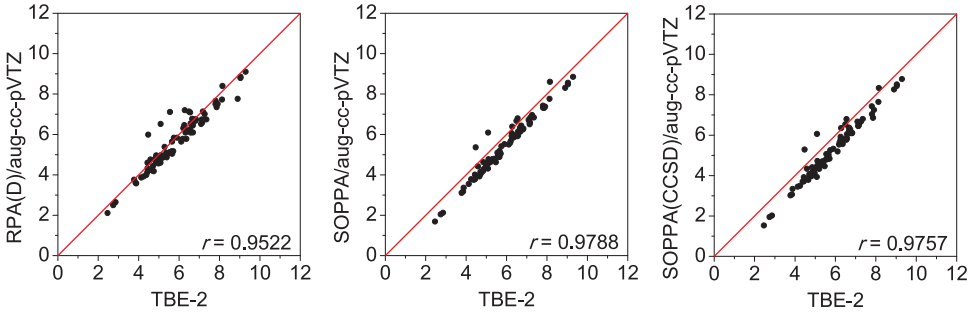

Figure 9. Correlation plots for the vertical excitation energies (eV) of singlet excited states with the aug-cc-pVTZ basis set: RPA(D), SOPPA and SOPPA(CCSD) vs. TBE-2 results.

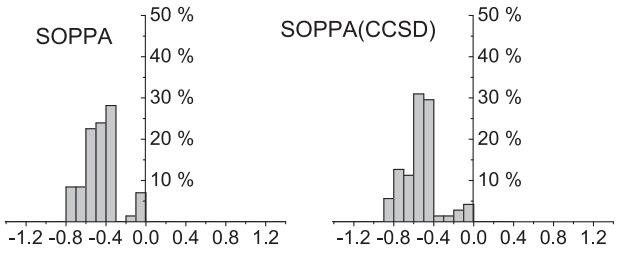

Figure 10. Histograms (in %) of the deviations between SOPPA, SOPPA(CCSD) and CC3 vertical excitation energies (eV) of triplet excited states calculated with the TZVP basis set.

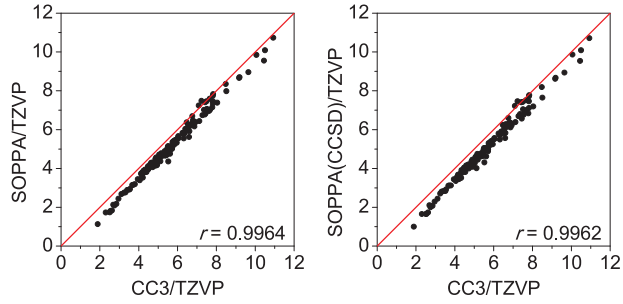

Figure 11. Correlation plots for the vertical excitation energies (eV) of triplet excited states with the TZVP basis set: SOPPA and SOPPA(CCSD) vs. CC3 results.

states in Table 2. As one can see from the histograms of deviations (Figure 10) and the correlation plots (Figure 11), the SOPPA and SOPPA(CCSD) results consistently underestimate all CC3 triplet excitation energies on average by 0.45 ± 0.17 eV and 0.54 ± 0.18 eV, respectively, contrary to the excited singlet states. Although their mean deviations from the CC3 results are thus virtually identical to those for the singlet excited states, the spread of their deviations from CC3 is significantly smaller as seen in Figure 10 and is indicated by the standard deviation from the mean. Furthermore, the peak of the deviations (24%) is for SOPPA between −0.3 and −0.4 eV (74% between −0.3 and −0.6 eV) and for SOPPA(CCSD) with 60% between −0.4 and −0.6 eV and shifted to smaller deviations than for the excited singlet states. Thus, SOPPA and SOPPA(CCSD) perform better for excited triplet states than for excited singlet valence states. A similar behaviour was also observed for the polycyclic hydrocarbons [37], where SOPPA and SOPPA(CCSD) gave significantly better results and were in more consistent agreement with CCSDR(3) results for singlet Rydberg states than for singlet valence states.

The largest outliers above the mean are found for the 1^3E_{2g} state in benzene, the 2^3A_g state in naphthalene, the 3^3B_2 and 3^3A_1 states in pyridine (like for the corresponding singlet states) and in addition the 3^3B_{1g} state in naphthalene and the $4^3A'$ state in imidazole. For all these states, SOPPA and SOPPA(CCSD) gave excitation energies in almost perfect agreement (absolute deviations ≤0.1 eV) with the CC3 results. On the other side, i.e. larger deviations (≤−0.7 eV) than the mean are found for all the $n \rightarrow \pi$ states in *p*-benzoquinone and in the three amides as well as (only for SOPPA(CCSD)) for the $n \rightarrow \pi$ state in acetone and the majority of the states in *s*-tetrazine.

Comparing again with CC2 and B3LYP for the same benchmark set, we can see that SOPPA gives a mean deviation of −0.45 ± 0.17 eV, which is somewhat better

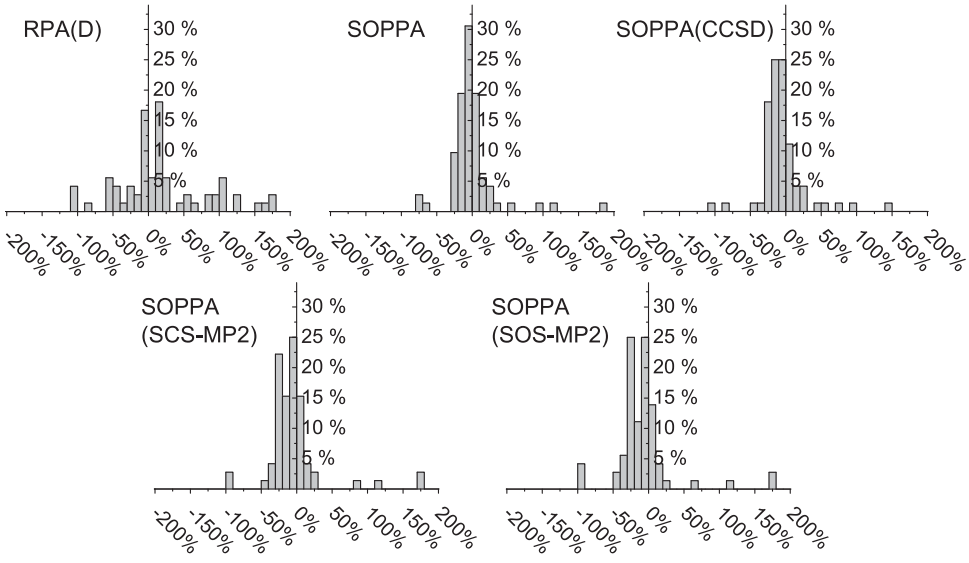

Figure 12. Histograms (in %) of the percentage deviations between RPA(D), SOPPA, SOPPA(CCSD), SOPPA(SCS-MP2), SOPPA(SOS-MP2) and CC3 oscillator strengths for singlet excited states calculated with the TZVP basis set.

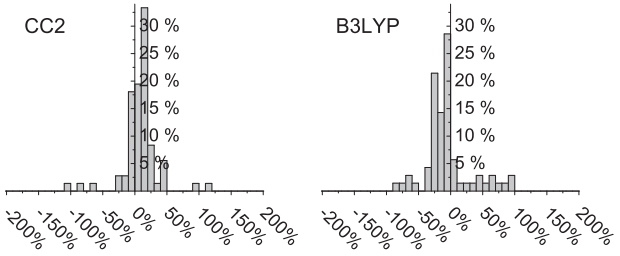

Figure 13. Histograms (in %) of the percentage deviations between CC2, B3LYP and CC3 oscillator strengths for singlet excited states calculated with the TZVP basis set.

than B3LYP with -0.48 ± 0.51 eV [45] in particular with respect to the consistency in the results as indicated by the standard deviation. However, SOPPA performs still not as well as the computationally more expensive CC2 method [17], for which the mean deviation is 0.14 ± 0.14 eV.

4.4. Oscillator strengths with the TZVP and aug-cc-pVTZ basis sets

Finally, the dipole oscillator strengths obtained from all five methods with the TZVP basis set and from RPA(D), SOPPA and SOPPA(CCSD) with the aug-cc-pVTZ basis set are presented in Table 9. Oscillator strengths have previously been discussed only qualitatively [17,19,45,46] due to the lack of appropriate reference data. However, in their recent study [23], Kánná and Szalay reported for the first time CC3/TZVP oscillator strengths for the present benchmark set and even showed with a few examples that they are quite accurate compared to full CCSDT oscillator strengths. We will, therefore, employ them here as reference data and have included them in Table 9.

With these reference values, we have carried out a statistical analysis of the results of the five SOPPA methods using the TZVP basis set and in addition also for the first time for the CC2/TZVP and B3LYP/TZVP results of the earlier studies [17,45]. As already commented on by Kánná and Szalay [23], the oscillator strengths vary by three orders of magnitude and it is, therefore, more meaningful to look at the relative deviations in percent from the CC3 results. However, doing this, we had to exclude all oscillator strengths ≤ 0.002 from the statistics, as small errors in those would otherwise completely dominate the statistics. The resulting statistical data and histograms of relative deviations in percent are shown in Table 10 and Figures 12 and 13. One can see that apart from RPA(D), all the other SOPPA methods including B3LYP perform roughly comparably with mean deviations below 5% (but CC2 14%) and mean absolute deviations between 20% and 30%. Also, the most frequent deviations are for these methods between 0% and −5% (but for CC2 between 15% and 20%). Only in the spread of deviations, the methods differ significantly: SOPPA and SOPPA(CCSD) have a standard deviation of ∼35%, while the other methods, SOPPA(SCS-MP2), SOPPA(SOS-MP2), CC2 and B3LYP have ∼50%. RPA(D), on the other hand, again exhibits a less systematic behaviour with a mean (absolute) deviation of 46% (68%) and a standard deviation of more than 100%. Overall, the original SOPPA method appears to reproduce the CC3 oscillator strengths most closely and even better than CC2 or B3LYP, which is quite contrary to the excitation energies but might be an explanation for the fact that SOPPA performs often as well as CC2 in the calculation of linear response properties [40,54].

In addition to the TZVP basis set, we have also calculated oscillator strengths with the larger aug-cc-pVTZ basis set and the SOPPA, SOPPA(CCSD) and RPA(D) methods. The results are also included in Table 9 and the change in the oscillator strengths due to the change of basis is analyzed statistically in Table 11 and Figure 14. It is quite clear that the additional diffuse functions reduce the oscillator strengths in the majority of cases and on average by 7%–14% with a standard deviation ∼27% as was previously found for the oscillator strengths calculated for the same benchmark set but at the CC2 and CASPT2 level of theory [19,46]. But the spread of outliers is rather large, which is probably not surprising considering the varying size of the oscillator strengths.

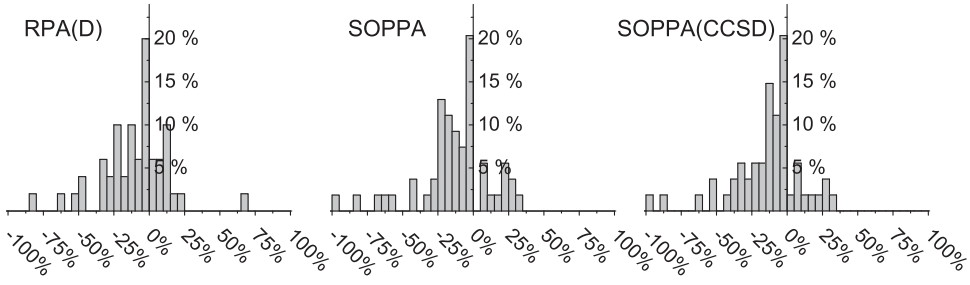

Figure 14. Histograms (in %) of the percentage deviations between aug-cc-pVTZ and TZVP oscillator strengths of singlet excited states at the RPA(D), SOPPA and SOPPA(CCSD) levels.

5. Conclusions

We have presented the so far largest systematic comparison of the performance of SOPPA-based methods for the calculation of singlet and triplet vertical electronic excitation energies and oscillator strengths. Two new modifications of the SOPPA method, a spin-component-scaled and a scaled opposite-spin version, were investigated for the first time. For the 139 singlet and 71 triplet excited states from a previously proposed benchmark set of 28 medium-sized molecules, calculations were performed at the RPA(D), SOPPA, SOPPA(CCSD), SOPPA(SCS-MP2) and SOPPA(SOS-MP2) levels with the TZVP basis set, and for the first three of these approaches also with the larger aug-cc-pVTZ basis set. The results were compared with the corresponding CC3 and CASPT2 results and with the theoretical best estimates for the benchmark set.

We find that all the four SOPPA methods perform worse than both CC2 and ADC(2). They underestimate strongly – with a few exceptions – the CC3 singlet excitation energies (on average by 0.4–0.7 eV, with a standard deviation of 0.3 eV). Among the SOPPA-based methods, SOPPA has the smallest deviations followed by SOPPA(CCSD), SOPPA(SCS-MP2), and finally SOPPA(SOS-MP2), with respect to the CC3 and CASPT2 reference results and the theoretical best estimates, TBE-2, from the literature; hence, the performance deteriorates in the sequence SOPPA $\rightarrow$ SOPPA(CCSD) $\rightarrow$ SOPPA(SCS-MP2) $\rightarrow$ SOPPA(SOS-MP2). Neither replacing the MP correlation coefficients with CCSD amplitudes nor replacing them with scaled MP correlation coefficients seems to improve SOPPA calculations of excitation energies. However, one should note that the scaling factors have not been optimised in the SOPPA(SCS-MP2) and SOPPA(SOS-MP2) methods and are thus optimal for MP2 energies but not necessarily for SOPPA excitation energies. The RPA(D) results, on the other hand, are more spread around the CC3 results, leading to a smaller mean deviation of 0.2 eV but a larger standard deviation of 0.4–0.5 eV depending on the basis set.

For the triplet excitation energies, we find an even more systematic behaviour. All SOPPA and SOPPA(CCSD) excitation energies are below the CC3 values, differing on average by 0.45 ± 0.17 eV for SOPPA and 0.54 ± 0.18 eV for SOPPA(CCSD). The effect of adding more diffuse basis functions in the aug-cc-pVTZ basis set leads in all cases to lower excitation energies for SOPPA and SOPPA(CCSD) with an average shift of 0.25 ± 0.17 eV, while some of the RPA(D) results increase also in energy.

Comparing the oscillator strengths with the recently published CC3 reference values, we find that all SOPPA methods have mean percentage deviations of less than 10% but that SOPPA and SOPPA(CCSD) are more consistent with a standard deviation from the mean of $\sim$30% while SOPPA(SCS-MP2) and SOPPA(SOS-MP2) have standard deviations around 50%. SOPPA oscillator strengths are found to be on average in better agreement with CC3 reference values than even CC2 and B3LYP oscillator strengths. The use of the more diffuse aug-cc-pVTZ basis set leads to changes in the computed oscillator strengths of about 10%, as also previously found for CC2 and CASPT2, but again with similarly large variations.

Summarising, we have to conclude that none of the SOPPA methods can compete with CC2 or ADC(2) in the calculation of vertical excitation energies, while SOPPA predicts oscillator strengths in better agreement with CC3 reference values than CC2. Whether this is the reason for the good performance of SOPPA methods in the calculation of NMR spin–spin coupling constants, despite the errors in the excitation energies, remains to be investigated.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

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