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## INVITED ARTICLE

### Basis set effects on coupled cluster benchmarks of electronically excited states: CC3, CCSDR(3) and CC2

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Vertical electronic excitation energies and one-electron properties of 28 medium-sized molecules from a previously proposed benchmark set are revisited using the augmented correlation-consistent triple-zeta aug-cc-pVTZ basis set in CC2, CCSDR(3), and CC3 calculations. The results are compared to those obtained previously with the smaller TZVP basis set. For each of the three coupled cluster methods, a correlation coefficient greater than 0.994 is found between the vertical excitation energies computed with the two basis sets. The deviations of the CC2 and CCSDR(3) results from the CC3 reference values are very similar for both basis sets, thus confirming previous conclusions on the intrinsic accuracy of CC2 and CCSDR(3). This similarity justifies the use of CC2- or CCSDR(3)-based corrections to account for basis set incompleteness in CC3 studies of vertical excitation energies. For oscillator strengths and excited-state dipole moments, CC2 calculations with the aug-cc-pVTZ and TZVP basis sets give correlation coefficients of 0.966 and 0.833, respectively, implying that basis set convergence is slower for these one-electron properties.

**Keywords:** electronically excited states; benchmarks; coupled cluster methods; CC2; CCSDR(3); CC3

#### 1. Introduction

The importance of an accurate reference data set for excited-state energies and properties is unquestionable. Recently, we introduced a benchmark set [1–3] for vertical electronic excitation energies of 28 medium-sized molecules which represent the most significant organic chromophores. Theoretical best estimates were derived [1] from linear response CC3 and multistate CASPT2 calculations as well as high-level *ab initio* literature values. The main purpose of such a comprehensive reference data set is the validation of existing as well as newly developed methods and the parametrisation of semi-empirical or other adjustable methods. The proposed reference set has already been used in the validation of lower-level coupled cluster methods and approaches based on density functional theory [2–5].

In our previous work we employed a TZVP basis set [6] which was considered sufficiently flexible for the low-lying valence excited states that were of prime interest in our benchmarking. This choice of a medium-size basis set also enabled us to treat the majority of the reference molecules at the CC3 level.

Since the TZVP basis lacks diffuse functions, it is less appropriate for higher-lying valence states and for states which are spatially extended and have (partial) Rydberg character. Therefore, the proper identification of such states may become problematic when using the TZVP basis as in our previous studies [1–3], because the character of these higher-lying states might change upon basis set extension. Rydberg states can often be described effectively by adding a single set of very diffuse functions at the centre of the molecule, as has been done, for example, for benzene or other polycyclic aromatic hydrocarbons (see [7,8] and references therein), but this is not a convenient option for molecules of arbitrary shape. Therefore, we previously studied [1] the basis set dependence of the vertical excitation energy of the high-lying  $1^1B_{1u}$  singlet state in ethene, which is known to be rather diffuse and susceptible to valence-Rydberg mixing, using twelve different correlation consistent basis sets [9,10]. When comparing against the essentially converged excitation energies computed with the most extended aug-cc-pV5Z and d-aug-cc-pVQZ basis sets, we found differences of more than 0.4 eV for the results

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with the TZVP basis, but excellent agreement for those with the aug-cc-pVTZ basis (deviations of less than 0.1 eV).

In this work we use the aug-cc-pVTZ basis set [9,10] in a comprehensive study that includes all 28 original benchmark molecules in CC2 calculations and subsets of 21 and eight molecules at the CCSDR(3) and CC3 levels, respectively. This basis set was chosen because it has been proven to be adequate in coupled cluster calculations of high-lying singlet states not only in the case of ethene [1], but also for a number of other chromophores (see e.g. [11–15]). However, even the aug-cc-pVTZ basis set is not optimal for Rydberg states in general, and hence additional molecule-centred diffuse basis functions may be necessary for an accurate description of states with significant valence–Rydberg mixing.

The paper is organised as follows: computational details are described in the next section. The results for the aug-cc-pVTZ basis are presented and compared to those for the TZVP basis in the following section which also provides various statistical evaluations. The final section offers a summary.

## 2. Computational details

All calculations were performed at the MP2/6-31G\* optimised ground-state geometries [1] using the augmented aug-cc-pVTZ [9,10] basis. The CCSDR(3) [16,17] and CC3 [11,18,19] computations were carried out with the Dalton 2.0 program package [20]. Only singlet states were calculated, with the core electrons being frozen during the coupled cluster calculations which causes negligible deviations (less than 0.01 eV) compared with a fully correlated all-electron treatment [7].

The CC2 [21,22] calculations were done with the parallel version of program RICC2 [23–26] from the TURBOMOLE package (version 5.10) [27], employing the resolution-of-identity approximation [28,29] and the appropriate auxiliary basis set provided by the TURBOMOLE library [30,31]. In the case of CC2, both singlet and triplet excitation energies as well as one-electron properties (dipole moments and oscillator strengths in dipole length representation) were computed. It should be noted that the presence of diffuse functions in the basis set makes the assignment of states more difficult. As in our previous work [1,3], we used the expectation value  $\langle r^2 \rangle$  as one of the criteria to determine the valence character of a given excited state and to identify valence–Rydberg mixings which can be pronounced especially in the high-lying states.

## 3. Results

In Table 1 we present the results for singlet excited states obtained with the CC2, CCSDR(3) and CC3 methods and the aug-cc-pVTZ basis set. Those obtained previously with the TZVP basis set [1,3] are also listed for comparison. Some higher-lying states of the original benchmark set (e.g. in formamide, formaldehyde, and naphthalene) are not included here due to problems in identifying these states when using the aug-cc-pVTZ basis set. Within an acceptable amount of computer time, we could afford to calculate a total of 22 states with the CC3 method and 99 states with the CCSDR(3) method. In both cases, the triples contributions scale formally as  $N^7$  with the number of orbitals  $N$ . But while CC3 has an iterative triples contribution, CCSDR(3) is based on a pseudoperturbation theory expansion of the CC3 eigenvalue problem and thus includes essentially only a non-iterative triples correction which is added to the CCSD excitation energy. The efficient parallel implementation of the RI-CC2 method in the TURBOMOLE program allowed us to compute all the singlet excited states from the original benchmark set at the CC2 level.

In Figure 1 the correlation between the aug-cc-pVTZ and TZVP results is shown graphically for the three coupled cluster methods, while Figure 2 presents histograms for the deviations of the aug-cc-pVTZ from the TZVP results. The corresponding statistical data are given in Table 2.

Upon inspection of the numerical results and the histograms in Figure 2, one immediately sees a systematic lowering of the calculated excitation energies when going from the TZVP to the larger aug-cc-pVTZ basis, for each of the three coupled cluster methods. There are only three states at the CC2 level ( $4^1A'$  in imidazole,  $2^1A''$  in cytosine, and  $3^1A''$  in uracil) and six at the CCSDR(3) level ( $2^1A_g$  in all-*E*-hexatriene,  $2^1A_g$  in pyrazine,  $1^1A_2$  in *s*-triazine,  $3^1B_{1g}$  and  $2^1B_{3g}$  in *s*-tetrazine and  $1^1A_u$  in *p*-benzoquinone) which have a higher energy with the aug-cc-pVTZ basis. These are mostly states with rather low single excitation weights,  $\%R_1$ , in the CC3/TZVP calculations [3]. The correlation (Figure 1) between the results with the two basis sets is almost perfect, with correlation coefficients of 0.9951, 0.9945, and 0.9967 for CC2, CCSDR(3), and CC3, respectively. Only for high-lying states with energies above 8 eV there are a few outliers. The largest one concerns the  $3^1B_2$  state in pyridine at the CC2 (−1.34 eV) and CCSDR(3) (−1.05 eV) levels, which also has a low single excitation weight,  $\%R_1$ , in the CC3/TZVP calculations [3]. The second largest outliers are found for the  $4^1A_1$  state in cyclopentadiene at the

Table 1. Vertical excitation energies  $\Delta E$  (eV) of singlet excited states from coupled-cluster calculations with the TZVP<sup>a</sup> and aug-cc-pVTZ<sup>b</sup> basis sets.

Molecule	State	CC2		CCSDR(3)		CC3	
		TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	8.40	7.90	8.37	7.87	8.37	7.89
<i>E</i> -Butadiene	$1^1B_u (\pi \rightarrow \pi^*)$	6.49	6.13	6.56	6.19		
	$2^1A_g (\pi \rightarrow \pi^*)$	7.63	7.06	6.95	6.82	6.77	6.63
all- <i>E</i> -Hexatriene	$1^1B_u (\pi \rightarrow \pi^*)$	5.41	5.18	5.56	5.30		
	$2^1A_g (\pi \rightarrow \pi^*)$	6.67	6.43	6.04	6.09		
all- <i>E</i> -Octatetraene	$2^1A_g (\pi \rightarrow \pi^*)$	5.87	5.74				
	$1^1B_u (\pi \rightarrow \pi^*)$	4.72	4.53				
	$2^1B_u (\pi \rightarrow \pi^*)$	6.91	6.37				
	$3^1A_g (\pi \rightarrow \pi^*)$	6.72	6.12				
Cyclopropene	$4^1A_g (\pi \rightarrow \pi^*)$	7.01	6.36				
	$1^1B_1 (\sigma \rightarrow \pi^*)$	6.96	6.73	6.89	6.67	6.90	6.67
Cyclopentadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	7.17	6.72	7.10	6.68	7.10	6.68
	$2^1A_1 (\pi \rightarrow \pi^*)$	5.69	5.47	5.72	5.48		
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.05	6.80	6.76	6.64		
Norbornadiene	$3^1A_1 (\pi \rightarrow \pi^*)$	8.86	8.19	8.72	8.17		
	$1^1A_2 (\pi \rightarrow \pi^*)$	5.57	5.30				
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.37	6.09				
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.65	7.50				
Benzene	$2^1A_2 (\pi \rightarrow \pi^*)$	7.66	7.17				
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.27	5.22	5.12	5.09	5.07	5.03
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	6.68	6.45	6.70	6.44	6.68	6.42
	$1^1E_{1u} (\pi \rightarrow \pi^*)$	7.44	7.12	7.45	7.16	7.45	7.14
Naphthalene	$2^1E_{2g} (\pi \rightarrow \pi^*)$	9.03	8.49	8.71	8.56	8.43	8.31
	$1^1B_{3u} (\pi \rightarrow \pi^*)$	4.45	4.38	4.34	4.32		
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	4.96	4.75	5.08	4.87		
	$2^1A_g (\pi \rightarrow \pi^*)$	6.22	6.07	6.09	6.01		
	$1^1B_{1g} (\pi \rightarrow \pi^*)$	6.21	5.82	6.26	5.94		
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	6.25	6.02	6.35	6.13		
	$2^1B_{1g} (\pi \rightarrow \pi^*)$	6.82	6.44	6.81	6.48		
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	6.57	6.35	6.60	6.39		
	$3^1A_g (\pi \rightarrow \pi^*)$	7.34	7.10	7.29	7.25		
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	8.46	7.90				
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	8.85	8.66				
Furan	$1^1B_2 (\pi \rightarrow \pi^*)$	6.75	6.37	6.64	6.30		
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.87	6.70	6.71	6.60		
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.78	8.23	8.57	8.17		
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	6.61	6.42	6.47	6.34		
	$1^1B_2 (\pi \rightarrow \pi^*)$	6.88	6.85	6.74	6.23		
	$3^1A_1 (\pi \rightarrow \pi^*)$	8.44	7.81	8.20	7.63		
Imidazole	$1^1A'' (n \rightarrow \pi^*)$	6.86	6.69				
	$2^1A' (\pi \rightarrow \pi^*)$	6.73	6.40				
	$3^1A' (\pi \rightarrow \pi^*)$	7.28	6.91				
	$2^1A'' (n \rightarrow \pi^*)$	8.00	7.64				
	$4^1A' (\pi \rightarrow \pi^*)$	8.62	8.68				
Pyridine	$1^1B_2 (\pi \rightarrow \pi^*)$	5.32	5.26	5.20	5.17		
	$1^1B_1 (n \rightarrow \pi^*)$	5.12	4.97	5.12	5.02		
	$1^1A_2 (n \rightarrow \pi^*)$	5.39	5.27	5.55	5.46		
	$2^1A_1 (\pi \rightarrow \pi^*)$	6.88	6.64	6.88	6.63		
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.72	7.43	7.72	7.41		
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.61	7.32	7.61	7.35		
	$3^1B_2 (\pi \rightarrow \pi^*)$	9.37	8.03	9.09	8.04		
	$4^1A_1 (\pi \rightarrow \pi^*)$	9.00	8.59	9.00	8.65		

(continued)

Table 1. (Continued).

Molecule	State	CC2		CCSDR(3)		CC3	
		TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ
Pyrazine	$1^1B_{3u} (n \rightarrow \pi^*)$	4.26	4.12	4.31	4.20		
	$1^1A_u (n \rightarrow \pi^*)$	4.95	4.86	5.11	5.05		
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.13	5.07	5.07	5.02		
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.92	5.79	5.86	5.77		
	$1^1B_{1g} (n \rightarrow \pi^*)$	6.70	6.61	6.86	6.80		
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	7.10	6.86	7.10	6.86		
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	8.13	7.92	8.09	7.89		
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.07	7.82	8.08	7.84		
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	9.42	9.00	9.16	9.08		
	$2^1A_g (\pi \rightarrow \pi^*)$	9.26	9.08	9.04	9.13		
Pyrimidine	$1^1B_1 (n \rightarrow \pi^*)$	4.49	4.37	4.56	4.48		
	$1^1A_2 (n \rightarrow \pi^*)$	4.84	4.75	4.97	4.90		
	$1^1B_2 (\pi \rightarrow \pi^*)$	5.51	5.46	5.42	5.40		
	$2^1A_1 (\pi \rightarrow \pi^*)$	7.12	6.94	7.10	6.86		
	$2^1B_2 (\pi \rightarrow \pi^*)$	8.08	7.82	8.02	7.83		
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.79	7.53	7.77	7.56		
Pyridazine	$1^1B_1 (n \rightarrow \pi^*)$	3.90	3.79	3.99	3.92		
	$1^1A_2 (n \rightarrow \pi^*)$	4.40	4.30	4.57	4.52		
	$2^1A_1 (\pi \rightarrow \pi^*)$	5.37	5.32	5.28	5.26		
	$2^1A_2 (n \rightarrow \pi^*)$	5.81	5.70	5.84	5.76		
	$2^1B_1 (n \rightarrow \pi^*)$	6.40	6.27	6.49	6.41		
	$1^1B_2 (\pi \rightarrow \pi^*)$	7.00	6.79	6.99	6.74		
	$2^1B_2 (\pi \rightarrow \pi^*)$	7.57	7.33	7.58	7.36		
	$3^1A_1 (\pi \rightarrow \pi^*)$	7.90	7.70	7.86	7.58		
<i>s</i> -Triazine	$1^1A''_1 (n \rightarrow \pi^*)$	4.70	4.60	4.81	4.74		
	$1^1A''_2 (n \rightarrow \pi^*)$	4.80	4.71	4.83	4.79		
	$1^1E'' (n \rightarrow \pi^*)$	4.77	4.68	4.87	4.81		
	$1^1A'_2 (\pi \rightarrow \pi^*)$	5.82	5.80	5.76	5.77		
	$2^1A'_1 (\pi \rightarrow \pi^*)$	7.52	7.26	7.44	7.21		
	$2^1E'' (n \rightarrow \pi^*)$	8.04	7.97	7.95	7.93		
	$1^1E' (\pi \rightarrow \pi^*)$	8.06	7.88	8.07	7.87		
<i>s</i> -Tetrazine	$1^1B_{3u} (n \rightarrow \pi^*)$	2.47	2.39	2.61	2.56	2.53	2.46
	$1^1A_u (n \rightarrow \pi^*)$	3.67	3.61	3.88	3.86		
	$1^1B_{1g} (n \rightarrow \pi^*)$	5.10	5.00	5.15	5.08	4.97	4.87
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.20	5.16	5.20	5.18	5.12	5.08
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.53	5.45	5.51	5.47	5.34	5.28
	$2^1A_u (n \rightarrow \pi^*)$	5.50	5.40	5.56	5.49		
	$2^1B_{2g} (n \rightarrow \pi^*)$	6.32	6.23	6.43	6.40	6.23	6.16
	$2^1B_{1g} (n \rightarrow \pi^*)$	6.91	6.82	6.98	6.94	6.87	6.80
	$3^1B_{1g} (n \rightarrow \pi^*)$	7.64	7.42	7.60	7.64		
	$2^1B_{3u} (n \rightarrow \pi^*)$	6.70	6.61	6.77	6.72	6.67	6.60
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	7.60	7.51	7.54	7.27	7.45	7.18
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	7.75	7.65	7.83	7.65	7.79	7.59
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	8.65	8.45	8.58	8.40		
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	8.97	8.85	8.86	8.90		
	Formaldehyde	$1^1A_2 (n \rightarrow \pi^*)$	4.09	4.00	3.94	3.89	3.95
$1^1B_1 (\sigma \rightarrow \pi^*)$		9.35	9.19	9.19	9.06	9.18	9.05
Acetone	$1^1A_2 (n \rightarrow \pi^*)$	4.52	4.45	4.39	4.39	4.40	4.38
	$1^1B_1 (\sigma \rightarrow \pi^*)$	9.29	9.11	9.17	9.04		
	$2^1A_1 (\pi \rightarrow \pi^*)$	9.74	9.31	9.66	8.92	9.65	8.90
<i>p</i> -Benzoquinone	$1^1A_u (n \rightarrow \pi^*)$	2.92	2.88	3.01	3.02		
	$1^1B_{1g} (n \rightarrow \pi^*)$	2.81	2.76	2.90	2.89		
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	4.69	4.53	4.69	4.54		
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	5.59	5.46	5.65	5.51		

(continued)

Table 1. (Continued).

Molecule	State	CC2		CCSDR(3)		CC3	
		TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ	TZVP	aug-cc-pVTZ
	$1^1B_{3u} (n \rightarrow \pi^*)$	5.69	5.55	6.09	5.98		
	$2^1B_{3g} (\pi \rightarrow \pi^*)$	7.36	7.17	7.36	7.25		
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	8.31	8.10	8.10	7.90		
Formamide	$1^1A'' (n \rightarrow \pi^*)$	5.76	5.59	5.65	5.56	5.65	5.55
Acetamide	$1^1A'' (n \rightarrow \pi^*)$	5.77	5.61	5.69	5.62		
	$2^1A' (\pi \rightarrow \pi^*)$	7.66	7.23	7.69	7.16		
Propanamide	$3^1A' (\pi \rightarrow \pi^*)$	10.71	10.21	10.56	9.72		
	$1^1A'' (n \rightarrow \pi^*)$	5.78	5.62	5.71	5.64		
	$2^1A' (\pi \rightarrow \pi^*)$	7.56	7.16	7.64	7.12		
Cytosine	$3^1A' (\pi \rightarrow \pi^*)$	10.33	9.71				
	$2^1A' (\pi \rightarrow \pi^*)$	4.80	4.69				
	$1^1A'' (n \rightarrow \pi^*)$	5.43	4.91				
Thymine	$2^1A'' (n \rightarrow \pi^*)$	5.01	5.33				
	$3^1A' (\pi \rightarrow \pi^*)$	5.71	5.56				
	$4^1A' (\pi \rightarrow \pi^*)$	6.65	6.29				
	$5^1A' (\pi \rightarrow \pi^*)$	6.94	6.62				
	$1^1A'' (n \rightarrow \pi^*)$	4.94	4.83				
	$2^1A' (\pi \rightarrow \pi^*)$	5.39	5.19				
	$3^1A' (\pi \rightarrow \pi^*)$	6.46	6.26				
Uracil	$2^1A'' (n \rightarrow \pi^*)$	6.33	6.16				
	$4^1A' (\pi \rightarrow \pi^*)$	6.80	6.50				
	$4^1A'' (n \rightarrow \pi^*)$	6.73	6.55				
	$5^1A'' (n \rightarrow \pi^*)$	7.18	7.00				
	$5^1A' (\pi \rightarrow \pi^*)$	7.71	7.47				
	$1^1A'' (n \rightarrow \pi^*)$	4.91	4.81				
	$2^1A' (\pi \rightarrow \pi^*)$	5.52	5.33				
	$3^1A' (\pi \rightarrow \pi^*)$	6.43	6.24				
Adenine	$2^1A'' (n \rightarrow \pi^*)$	6.73	6.09				
	$3^1A'' (n \rightarrow \pi^*)$	6.26	6.55				
	$4^1A' (\pi \rightarrow \pi^*)$	6.96	6.66				
	$5^1A'' (n \rightarrow \pi^*)$	7.12	6.95				
	$5^1A' (\pi \rightarrow \pi^*)$	7.66	7.48				
	$2^1A' (\pi \rightarrow \pi^*)$	5.28	5.20				
	$3^1A' (\pi \rightarrow \pi^*)$	5.42	5.20				
	$1^1A'' (n \rightarrow \pi^*)$	5.27	5.13				
	$2^1A'' (n \rightarrow \pi^*)$	5.91	5.74				

Notes: <sup>a</sup>Results with the TZVP basis set from ref. [1]

<sup>b</sup>Results with the aug-cc-pVTZ basis set from this work.

CC2 level ( $-0.67$  eV) and for the  $2^1A_1$  state in acetone at the CCSDR(3) and CC3 levels. For most other states there is close agreement between the aug-cc-pVTZ and TZVP results (see e.g. the  $1^1B_{2u}$  states in benzene and *s*-tetrazine with deviations of less than  $0.05$  eV for all three methods).

There is another particular outlier in pyrrole that requires some comment. A previous extensive coupled cluster study of pyrrole [32] found significant valence–Rydberg mixing in the three lowest excited  $1^1B_2$  states showing ‘similar diffuseness and oscillator strengths’. We also see considerable mixing in our coupled cluster calculations: for example, both CC2/aug-cc-pVTZ and

CCSDR(3)/aug-cc-pVTZ yield two strongly mixed  $1^1B_2$  states at  $6.25/6.85$  eV and  $6.23/6.81$  eV, respectively. According to our standard assignment criteria, the more valence-like state occurs at higher energy for CC2 and at lower energy for CCSDR(3), by a small margin in each case, and the corresponding entries in Table 1 are thus  $6.85$  and  $6.23$  eV, respectively. At face value, this would seem to indicate a large discrepancy between the CC2 and CCSDR(3) results which are in reality quite similar (see above). We have refrained from imposing correlations between the assignments of separate calculations, to be as unbiased as possible, even though this will artificially deteriorate the

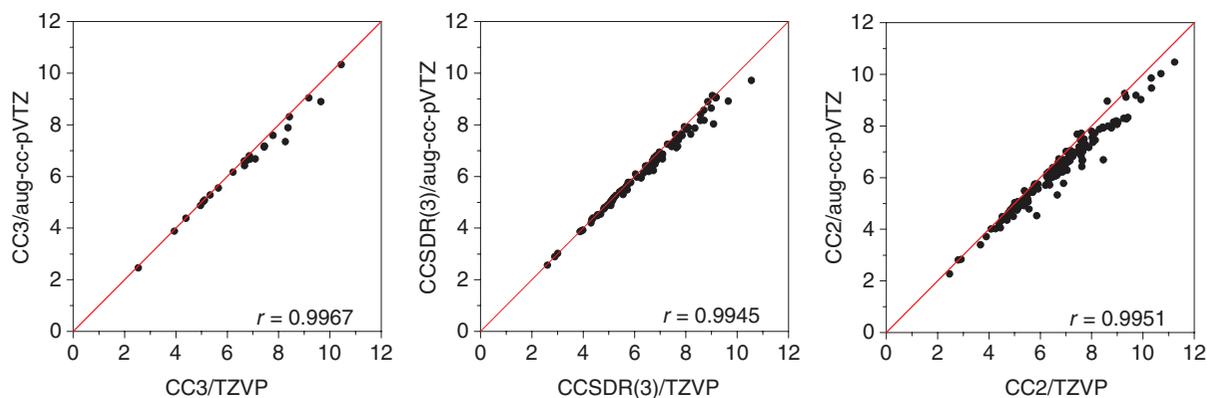


Figure 1. Correlation plots for the vertical excitation energies (eV) of singlet excited states at the CC3, CCSDR(3), and CC2 levels: aug-cc-pVTZ versus TZVP results.

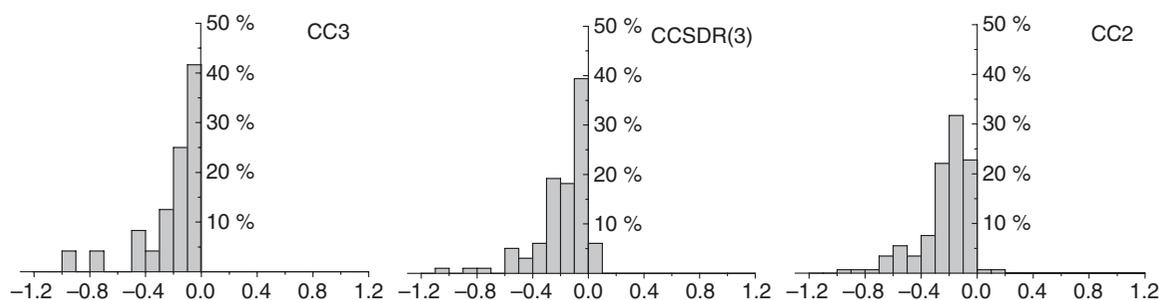


Figure 2. Histograms (in %) of the deviations between aug-cc-pVTZ and TZVP vertical excitation energies (eV) of singlet excited states at the CC3, CCSDR(3), and CC2 levels.

Table 2. Deviations in the vertical excitation energies (eV) of singlet excited states: aug-cc-pVTZ versus TZVP results<sup>a</sup>.

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

Notes: <sup>a</sup>TZVP results from [1,3].

<sup>b</sup>Same subset of states as in CCSDR(3).

<sup>c</sup>Total number of considered states.

statistical results to some extent. Our general conclusions are however not affected by this choice.

The mean and absolute mean deviations in Table 2 are of essentially the same magnitude (about 0.2 eV) for all three coupled cluster methods. This confirms that the basis set effects are very systematic. Looking at the finer details in Table 2, we note that the basis set dependence is slightly more pronounced for CC2 than for CCSDR(3) and CC3, both for the full set of

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

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

Notes: <sup>a</sup>Estimated  $CC3/aug-cc-pVTZ = CC3/TZVP + CC2/aug-cc-pVTZ - CC2/TZVP$ .

<sup>b</sup>Estimated  $CC3/aug-cc-pVTZ = CC3/TZVP + CCSDR(3)/aug-cc-pVTZ - CCSDR(3)/TZVP$ .

<sup>c</sup>Total number of considered states.

CC2 results as well as for the subset of states that is shared between CC2 and CCSDR(3). Comparing CCSDR(3) and CC3, the statistical data in Table 2 as well as the individual numerical results indicate an

Table 4. Deviation of CC2 and CCSDR(3) excitation energies (eV) of singlet excited states with respect to CC3 results obtained with the same basis set<sup>a</sup>.

	Method					
	CC2			CCSDR(3)		
	TZVP <sup>b</sup>	TZVP <sup>c</sup>	aug-cc-pVTZ	TZVP <sup>d</sup>	TZVP <sup>e</sup>	aug-cc-pVTZ
Count <sup>f</sup>	118	22	22	118	22	22
Mean	0.13	0.14	0.11	0.09	0.07	0.08
Abs. Mean	0.16	0.15	0.12	0.09	0.07	0.08
Std. Dev.	0.25	0.25	0.17	0.14	0.11	0.12
Maximum (+)	0.95	0.86	0.43	0.52	0.28	0.25

Notes: <sup>a</sup>Columns labelled with TZVP have CC3/TZVP results [1] as reference data. Columns labelled with aug-cc-pVTZ have the present CC3/aug-cc-pVTZ results as reference data.

<sup>b</sup>Reference [1].

<sup>c</sup>Subset of singlet states from [1], in order to compare directly with the present aug-cc-pVTZ results.

<sup>d</sup>Reference [3].

<sup>e</sup>Subset of singlet states from [3], in order to compare directly with the present aug-cc-pVTZ results.

<sup>f</sup>Total number of considered states. Some data has been discarded whose assignment was considered unreliable.

essentially identical basis set dependence of the computed vertical excitation energies. This suggests an incremental scheme where expensive CC3 calculations that may only be feasible with a smaller basis set (such as TZVP) are augmented with a basis set correction obtained at the cheaper CC2 or CCSDR(3) level.

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

In Table 4 we compare the performance of CC2 and CCSDR(3) relative to CC3, both for the TZVP [1,3] and aug-cc-pVTZ basis sets. Table 5 provides an analogous comparison between CC2 and CCSDR(3), again for both basis sets. In each case, the given deviations refer to excitation energies calculated with a lower-level versus a higher-level coupled cluster method (using the same basis). The mean and absolute deviations between the CCSDR(3) and CC3 results are essentially of the same magnitude (0.08±0.01 eV) for both basis sets. In the case of CC2, the mean absolute

Table 5. Deviation of CC2 excitation energies (eV) of singlet excited states with respect to CCSDR(3) results obtained with the same basis set<sup>a</sup>.

	TZVP <sup>b</sup>	TZVP <sup>c</sup>	aug-cc-pVTZ
Count <sup>d</sup>	118	99	99
Mean	0.04	0.03	0.00
Abs. Mean	0.11	0.11	0.10
Std. Dev.	0.16	0.15	0.14
Maximum (+)	0.68	0.68	0.62

Notes: <sup>a</sup>Columns labelled with TZVP have CCSDR(3)/TZVP results [3] as reference data. Columns labelled with aug-cc-pVTZ have the present CCSDR(3)/aug-cc-pVTZ results as reference data.

<sup>b</sup>CCSDR(3) results from [3] and CC2 results from [1].

<sup>c</sup>Subset of singlet states of the CCSDR(3) results from [3] and CC2 results from [1], in order to compare directly with the present aug-cc-pVTZ results.

<sup>d</sup>Total number of considered states.

deviations from the CC3 and CCSDR(3) results are slightly smaller for the aug-cc-pVTZ basis (0.12 and 0.10 eV) than for the TZVP basis (0.16 and 0.11 eV) so that the higher-level results are reproduced slightly better with the larger basis.

Using the CC2 method we have also computed vertical excitation energies for triplet excited states as well as one-electron properties for singlet excited states (oscillator strengths and dipole moments). The correlation between the aug-cc-pVTZ and TZVP results is shown in Figures 3 and 4. The corresponding statistical data for the differences between the aug-cc-pVTZ and TZVP results are given in Table 6. For the vertical

triplet excitation energies, the CC2 results for the two basis sets exhibit very small mean and absolute mean deviations of  $-0.08$  and  $0.10$  eV, respectively, as well as a very large correlation coefficient of  $0.9977$ , which confirms the high quality of the previous CC2/TZVP

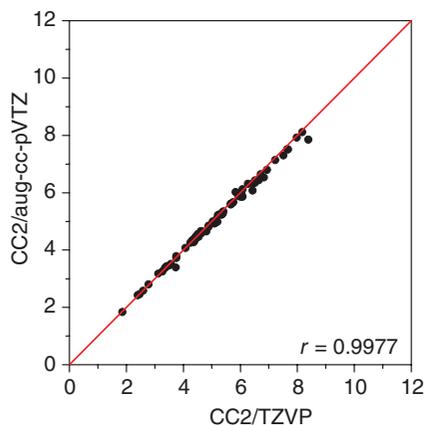


Figure 3. Correlation plot for the vertical excitation energies of triplet excited states: basis set effects for CC2.

results for the triplet states. Obviously the vertical excitation energies for the triplets are even less basis set dependent than those for the singlet excited states.

The situation is less clear-cut for one-electron properties, i.e. for the oscillator strengths and dipole moments of the singlet excited states, which are apparently affected more strongly by the addition of further diffuse and polarisation functions in the basis set. While extension of the basis set leads to a slight systematic lowering in the calculated vertical excitation energies, the one-electron properties change more randomly, although there is also a general overall trend towards lower absolute values (see Figure 4). Stronger variations may be caused by changes in the composition of states when further diffuse and/or polarisation functions are included: two states which are composed of  $+/-$  combinations of configuration state functions and thus give rise to bright/dark states could mix differently upon basis set extension and then evolve into two states with moderate intensity. Generally speaking, the oscillator strengths and excited-state dipole moments depend more than the

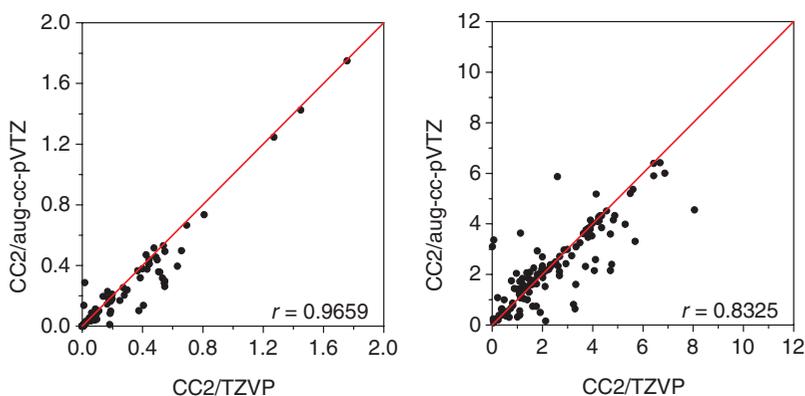


Figure 4. Correlation plots for (left) oscillator strengths and (right) dipole moments of singlet excited states: basis set effects for CC2.

Table 6. Deviations between the CC2/aug-cc-pVTZ and CC2/TZVP results for the vertical excitation energies (eV) of singlet and triplet excited states and for the oscillator strengths and dipole moments (D) of singlet excited states: statistics for all 28 benchmark molecules.

	CC2/aug-cc-pVTZ			
	Singlet states	Triplet states	Osc. strength	Dipole moment
Count <sup>a</sup>	143	71	95	127
Mean	$-0.22$	$-0.08$	$-0.032$	$-0.14$
Abs. Mean	0.23	0.10	0.047	0.57
Std. Dev.	0.29	0.14	0.088	0.97
Maximum (-)	1.34	0.54	0.287	3.51

Note: <sup>a</sup>Total number of considered states. Some data has been discarded whose assignment was considered unreliable.

energies on the proper description of the excited-state wavefunctions, and they should thus be more susceptible to basis set effects (especially in the case of diffuse high-lying states). The largest changes in the oscillator strengths indeed occur for the high-lying states of cytosine (4A': -0.238) and uracil (5A': -0.287) where the intensities of these bright states are lowered considerably. For the dipole moments, the largest changes are found for the high-lying states of cytosine (4A': -2.38 D and 5A': -3.51 D). Turning to the statistics again, the correlation coefficients are 0.9659 for the oscillator strengths and 0.8325 for excited-state dipole moments (see Figure 4), which are still reasonably large, but significantly smaller than those for the vertical excitation energies. In summary, the differences between the CC2/aug-cc-pVTZ and CC2/TZVP results for the one-electron properties are still appreciable, and convergence with regard to basis set extension thus appears to be slower for these properties than for the excitation energies.

#### 4. Conclusions

We have revisited a benchmark set of electronically excited states. Vertical excitation energies to singlet excited states were calculated with the CC2, CCSDR(3) and CC3 coupled cluster linear response methods, using the same geometries as in previous studies, but with the augmented correlation-consistent aug-cc-pVTZ basis instead of the TZVP basis. A total of 143 states were covered at the CC2 level. Due to the high computational demands of CCSDR(3) and in particular CC3, a smaller number of states were investigated with these methods, i.e. 99 with CCSDR(3) and 22 with CC3.

Inspection of the individual numerical results and statistical evaluations for the aug-cc-pVTZ and TZVP data show that the basis set effects on the calculated singlet excitation energies are rather uniform, for each of the three coupled cluster methods investigated. There is a systematic lowering of the computed energies upon basis set extension, of typically about 0.2 eV on average. This provides some justification for an incremental scheme where CC3 results obtained with a moderate basis are augmented by applying a basis set correction determined with a less costly coupled cluster method such as CC2 or CCSDR(3).

In the case of triplet excited states, the CC2 vertical excitation energies are even less basis set dependent than in the singlet case, since going from TZVP to aug-cc-pVTZ causes only a very minor lowering of typically 0.1 eV. By contrast, the changes in the CC2 oscillator strengths and dipole moments for singlet excited states are less systematic and sometimes

rather random. Hence, further convergence studies are desirable for these one-electron properties.

To conclude, some of the calculated vertical excitation energies, in particular those to high-lying singlet states, are significantly lowered by the inclusion of additional diffuse and polarisation functions in the aug-cc-pVTZ basis set (compared to TZVP), and further changes may be expected upon addition of molecule-centred diffuse functions for states with significant valence-Rydberg mixing. However, in an overall assessment of the present results, the effects of basis set extension on the vertical excitation energies of the chosen benchmark set are rather minor. Therefore, our previous conclusions on the performance of the coupled cluster methods CC2, CCSDR(3), and CC3 in excited-state studies remain valid [1,3].

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### Appendix 1. CC2 results for vertical excitation energies of triplet excited states

The CC2 results for vertical excitation energies of triplet excited states are given in Table 7.

Table 7. Vertical excitation energies (eV) of triplet excited states from CC2 calculations with the TZVP<sup>a</sup> and aug-cc-pVTZ<sup>b</sup> basis sets.

Molecule	State	CC2	
		TZVP	aug-cc-pVTZ
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.52	4.56
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	3.40	3.43
	$1^3A_g (\pi \rightarrow \pi^*)$	5.25	5.24
all- <i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	2.78	2.80
	$1^3A_g (\pi \rightarrow \pi^*)$	4.40	4.42
all- <i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	2.40	2.42
	$1^3A_g (\pi \rightarrow \pi^*)$	3.76	3.78
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	4.44	4.40
	$1^3B_1 (\sigma \rightarrow \pi^*)$	6.65	6.44
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.36	3.37
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.22	5.22
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	3.76	3.72
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.25	4.25
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.31	4.33
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	5.14	5.05
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	6.08	5.86
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.99	7.92
	$1^3A_g (\pi \rightarrow \pi^*)$	5.76	5.67
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.27	3.25
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	4.38	4.28
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.64	4.59
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.88	4.81
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	5.11	4.93
	$2^3A_g (\pi \rightarrow \pi^*)$	6.44	6.07
	$2^3B_{1g} (\pi \rightarrow \pi^*)$	6.83	6.53
	$3^3A_g (\pi \rightarrow \pi^*)$	6.94	6.80
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	7.23	7.14
Furan	$1^3B_2 (\pi \rightarrow \pi^*)$	4.38	4.33
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.67	5.61
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	4.68	4.64
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.72	5.63
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.89	4.85
	$2^3A' (\pi \rightarrow \pi^*)$	6.01	5.86
	$1^3A'' (n \rightarrow \pi^*)$	6.44	6.32
	$3^3A' (\pi \rightarrow \pi^*)$	6.74	6.57
	$4^3A' (\pi \rightarrow \pi^*)$	7.68	7.51
	$2^3A'' (n \rightarrow \pi^*)$	7.52	7.30
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	4.46	4.48
	$1^3B_1 (n \rightarrow \pi^*)$	4.54	4.46
	$1^3B_2 (\pi \rightarrow \pi^*)$	5.07	4.93
	$2^3A_1 (\pi \rightarrow \pi^*)$	5.33	5.24
	$1^3A_2 (n \rightarrow \pi^*)$	5.35	5.24
	$2^3B_2 (\pi \rightarrow \pi^*)$	6.52	6.34
	$3^3B_2 (\pi \rightarrow \pi^*)$	8.39	7.85
$3^3A_1 (\pi \rightarrow \pi^*)$	8.18	8.11	

(continued)

Table 7. (Continued).

Molecule	State	CC2	
		TZVP	aug-cc-pVTZ
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.86	1.83
	$1^3A_u (n \rightarrow \pi^*)$	3.43	3.39
	$1^3B_{1g} (n \rightarrow \pi^*)$	4.30	4.27
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	4.62	4.66
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	4.81	4.65
	$1^3B_{2g} (n \rightarrow \pi^*)$	5.03	4.99
	$2^3A_u (n \rightarrow \pi^*)$	5.05	4.98
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.67	5.59
	$2^3B_{2g} (n \rightarrow \pi^*)$	6.05	5.98
	$2^3B_{1g} (n \rightarrow \pi^*)$	6.72	6.65
	$2^3B_{3u} (n \rightarrow \pi^*)$	6.52	6.43
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	7.65	7.52
Formaldehyde	$1^3A_2 (\pi \rightarrow \pi^*)$	3.57	3.52
	$1^3A_1 (\pi \rightarrow \pi^*)$	6.08	6.12
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	4.08	4.07
	$1^3A_1 (\pi \rightarrow \pi^*)$	6.27	6.31
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	2.47	2.46
	$1^3A_u (n \rightarrow \pi^*)$	2.59	2.58
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.12	3.18
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	3.50	3.46
Formamide	$1^3A'' (n \rightarrow \pi^*)$	5.39	5.27
	$1^3A' (\pi \rightarrow \pi^*)$	5.94	5.88
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	5.42	5.33
	$1^3A' (\pi \rightarrow \pi^*)$	6.06	5.88
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.44	5.35
	$1^3A' (\pi \rightarrow \pi^*)$	6.07	6.02

Notes: <sup>a</sup>Results with the TZVP basis set from [1].<sup>b</sup>Results with the aug-cc-pVTZ basis set from this work.

## Appendix 2. CC2 results for oscillator strengths and dipole moments of singlet excited states

The CC2 results for oscillator strengths and dipole moments of singlet excited states are given in Tables 8 and 9, respectively.

Table 8. Oscillator strengths (in dipole length representation) for optically allowed transitions from CC2 calculations<sup>a</sup>.

Molecule	State	CC2	
		TZVP <sup>b</sup>	aug-cc-pVTZ <sup>c</sup>
Ethene	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.431	0.375
<i>E</i> -Butadiene	$1^1B_u (\pi \rightarrow \pi^*)$	0.809	0.734
all- <i>E</i> -Hexatriene	$1^1B_u (\pi \rightarrow \pi^*)$	1.272	1.246
all- <i>E</i> -Octatetraene	$1^1B_u (\pi \rightarrow \pi^*)$	1.757	1.749

(continued)

Table 8. (Continued).

Molecule	State	CC2	
		TZVP <sup>b</sup>	aug-cc-pVTZ <sup>c</sup>
Cyclopropene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.086	0.072
	$1^1B_1 (\sigma \rightarrow \pi^*)$	0.001	0.000
Cyclopentadiene	$2^1A_1 (\pi \rightarrow \pi^*)$	0.011	0.001
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.658	0.497
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.110	0.100
Norbornadiene	$1^1B_2 (\pi \rightarrow \pi^*)$	0.023	0.020
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.185	0.083
Benzene	$1^1E_{1u} (\pi \rightarrow \pi^*)$	0.694	0.664
Naphthalene	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.094	0.078
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.272	0.253
	$3^1B_{2u} (\pi \rightarrow \pi^*)$	0.548	0.297
	$2^1B_{3u} (\pi \rightarrow \pi^*)$	1.450	1.424
	$3^1B_{3u} (\pi \rightarrow \pi^*)$	0.010	0.015
Furan	$2^1A_1 (\pi \rightarrow \pi^*)$	0.003	0.000
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.506	0.358
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.172	0.184
Pyrrole	$2^1A_1 (\pi \rightarrow \pi^*)$	0.006	0.001
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.532	0.317
	$1^1B_2 (\pi \rightarrow \pi^*)$	0.182	0.011
Imidazole	$2^1A' (\pi \rightarrow \pi^*)$	0.088	0.112
	$3^1A' (\pi \rightarrow \pi^*)$	0.085	0.040
	$4^1A' (\pi \rightarrow \pi^*)$	0.406	0.136
	$1^1A'' (n \rightarrow \pi^*)$	0.003	0.002
Pyridine	$2^1A'' (n \rightarrow \pi^*)$	0.006	0.002
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.021	0.014
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.498	0.436
Pyrazine	$1^1B_2 (\pi \rightarrow \pi^*)$	0.025	0.032
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.549	0.493
	$1^1B_1 (n \rightarrow \pi^*)$	0.005	0.005
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.096	0.045
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.424	0.470
Pyrimidine	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.070	0.084
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.400	0.378
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.007	0.001
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.062	0.086
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.446	0.410
Pyridazine	$1^1B_2 (\pi \rightarrow \pi^*)$	0.023	0.029
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.476	0.515
	$1^1B_1 (n \rightarrow \pi^*)$	0.006	0.005
	$2^1A_1 (\pi \rightarrow \pi^*)$	0.014	0.017
	$3^1A_1 (\pi \rightarrow \pi^*)$	0.444	0.438
<i>s</i> -Triazine	$1^1B_2 (\pi \rightarrow \pi^*)$	0.009	0.003
	$2^1B_2 (\pi \rightarrow \pi^*)$	0.489	0.455
	$1^1B_1 (n \rightarrow \pi^*)$	0.006	0.005
	$2^1B_1 (n \rightarrow \pi^*)$	0.005	0.004
	$1^1E' (\pi \rightarrow \pi^*)$	0.441	0.410
<i>s</i> -Tetrazine	$1^1A''_2 (n \rightarrow \pi^*)$	0.017	0.015
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	0.017	0.286
	$2^1B_{1u} (\pi \rightarrow \pi^*)$	0.376	0.102
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	0.046	0.054
	$2^1B_{2u} (\pi \rightarrow \pi^*)$	0.368	0.364
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.007	0.006
	$1^1B_{3u} (n \rightarrow \pi^*)$	0.011	0.011

(continued)

Table 8. (Continued).

Molecule	State	CC2	
		TZVP <sup>b</sup>	aug-cc-pVTZ <sup>c</sup>
Formaldehyde	1 <sup>1</sup> B <sub>1</sub> ( $\sigma \rightarrow \pi^*$ )	0.079	0.001
Acetone	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	0.298	0.238
<i>p</i> -Benzoquinone	1 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	0.538	0.530
	2 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	0.544	0.283
	1 <sup>1</sup> B <sub>3u</sub> ( $n \rightarrow \pi^*$ )	0.000	0.001
Formamide	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.001	0.001
Acetamide	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.199	0.210
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.279	0.204
	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.001	0.000
Propanamide	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.138	0.196
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.189	0.099
Cytosine	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.049	0.050
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.165	0.144
	4 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.632	0.395
	5 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.168	0.228
	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.001	0.001
	2 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.002	0.001
Thymine	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.197	0.179
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.080	0.041
	4 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.250	0.168
	5 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.515	0.356
	3 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.000	0.001
Uracil	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.197	0.178
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.058	0.034
	4 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.188	0.163
	5 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	0.547	0.260
	3 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.000	0.001

Notes: <sup>a</sup>Only values above 0.001 are listed.<sup>b</sup>Results with the TZVP basis set from [1].<sup>c</sup>Results with the aug-cc-pVTZ basis set from this work.

Table 9. Dipole moments (in Debye) of singlet excited states from CC2 calculations.

Molecule	State	CC2	
		TZVP <sup>a</sup>	aug-cc-pVTZ <sup>b</sup>
Cyclopropene	Ground State	0.45	0.44
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.26	1.04
	1 <sup>1</sup> B <sub>1</sub> ( $\sigma \rightarrow \pi^*$ )	1.62	0.73
	1 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.35	0.37
	1 <sup>3</sup> B <sub>1</sub> ( $\sigma \rightarrow \pi^*$ )	1.77	1.62
Cyclopentadiene	Ground State	0.46	0.45
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	0.68	0.30
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	1.13	3.63
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.24	0.20
	1 <sup>3</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	0.27	0.37
	1 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.05	0.18
Norbornadiene	Ground State	0.06	0.09
	1 <sup>1</sup> A <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.22	1.08

(continued)

Table 9. (Continued).

Molecule	State	CC2	
		TZVP <sup>a</sup>	aug-cc-pVTZ <sup>b</sup>
Furan	2 <sup>1</sup> A <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.55	0.36
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.89	1.44
	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.07	3.36
	1 <sup>3</sup> A <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.05	0.24
	1 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.18	0.23
	Ground State	0.62	1.87
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	0.83	0.77
Pyrrole	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	0.01	3.10
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	0.77	1.74
	1 <sup>3</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	0.74	0.65
	1 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.14	1.06
	Ground State	2.02	1.87
Imidazole	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	1.47	1.29
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	2.60	5.87
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.92	4.90
	1 <sup>3</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	1.63	1.62
	1 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.14	1.09
	Ground State	3.91	3.79
Pyridine	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	4.71	3.60
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	3.72	2.31
	4 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	4.14	5.18
	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	0.48	0.99
	2 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	3.34	3.09
	1 <sup>3</sup> A' ( $\pi \rightarrow \pi^*$ )	3.00	2.99
	2 <sup>3</sup> A' ( $\pi \rightarrow \pi^*$ )	4.56	4.51
	3 <sup>3</sup> A' ( $\pi \rightarrow \pi^*$ )	4.83	4.15
	4 <sup>3</sup> A' ( $\pi \rightarrow \pi^*$ )	4.88	4.32
	1 <sup>3</sup> A'' ( $n \rightarrow \pi^*$ )	1.17	1.44
2 <sup>3</sup> A'' ( $n \rightarrow \pi^*$ )	3.86	3.67	
Pyrimidine	Ground State	2.33	2.31
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	2.68	2.11
	4 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	2.13	0.15
	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	1.10	0.39
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	2.02	2.01
	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	2.69	2.71
	1 <sup>1</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	1.10	0.40
	1 <sup>3</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	2.15	2.15
	2 <sup>3</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	2.53	2.49
	3 <sup>3</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	1.59	1.74
	1 <sup>3</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	1.01	0.32
	1 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.96	1.97
	2 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	3.49	3.25
	3 <sup>3</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.16	1.26
1 <sup>3</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	1.10	0.55	
Pyrimidine	Ground State	2.43	2.40
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	3.24	0.81
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	2.11	1.52
	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	1.07	1.34
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	2.26	2.19
Pyridazine	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	1.38	2.06
	1 <sup>1</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	0.39	0.64
	Ground State	4.36	4.33
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	3.64	3.61
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	4.07	2.15

(continued)

Table 9. (Continued).

Molecule	State	CC2	
		TZVP <sup>a</sup>	aug-cc-pVTZ <sup>b</sup>
	1 <sup>1</sup> A <sub>2</sub> ( <i>n</i> → $\pi^*$ )	1.21	1.84
	2 <sup>1</sup> A <sub>2</sub> ( <i>n</i> → $\pi^*$ )	1.50	2.08
	1 <sup>1</sup> B <sub>2</sub> ( $\pi$ → $\pi^*$ )	5.30	3.98
	2 <sup>1</sup> B <sub>2</sub> ( $\pi$ → $\pi^*$ )	3.98	4.01
	1 <sup>1</sup> B <sub>1</sub> ( <i>n</i> → $\pi^*$ )	1.10	1.72
	2 <sup>1</sup> B <sub>1</sub> ( <i>n</i> → $\pi^*$ )	1.66	2.25
Formaldehyde	Ground State	2.32	2.38
	1 <sup>1</sup> A <sub>2</sub> ( <i>n</i> → $\pi^*$ )	1.25	1.38
	1 <sup>1</sup> B <sub>1</sub> ( $\sigma$ → $\pi^*$ )	0.37	0.62
	1 <sup>3</sup> A <sub>2</sub> ( <i>n</i> → $\pi^*$ )	1.09	1.21
	1 <sup>3</sup> A <sub>1</sub> ( $\pi$ → $\pi^*$ )	0.82	0.86
Acetone	Ground State	2.86	2.97
	2 <sup>1</sup> A <sub>1</sub> ( $\pi$ → $\pi^*$ )	2.94	2.42
	1 <sup>1</sup> A <sub>2</sub> ( <i>n</i> → $\pi^*$ )	1.45	1.84
	1 <sup>1</sup> B <sub>1</sub> ( $\sigma$ → $\pi^*$ )	1.53	1.78
	1 <sup>3</sup> A <sub>1</sub> ( $\pi$ → $\pi^*$ )	1.17	1.33
	1 <sup>3</sup> A <sub>2</sub> ( <i>n</i> → $\pi^*$ )	1.24	1.59
Formamide	Ground State	3.86	3.84
	2 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	2.00	2.69
	3 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	1.80	2.93
	1 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	1.98	2.20
	1 <sup>3</sup> A' ( $\pi$ → $\pi^*$ )	4.21	4.09
	1 <sup>3</sup> A'' ( <i>n</i> → $\pi^*$ )	1.80	1.99
Acetamide	Ground State	3.86	3.81
	2 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	4.76	2.40
	3 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	4.12	2.58
	1 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	1.69	1.77
	1 <sup>3</sup> A' ( $\pi$ → $\pi^*$ )	3.82	3.54
	1 <sup>3</sup> A'' ( <i>n</i> → $\pi^*$ )	1.51	1.58
Propanamide	Ground State	3.65	3.61
	2 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	4.71	2.16
	3 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	3.30	0.64
	1 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	1.56	1.59
	1 <sup>3</sup> A' ( $\pi$ → $\pi^*$ )	3.82	3.46
	1 <sup>3</sup> A'' ( <i>n</i> → $\pi^*$ )	1.40	1.44
Cytosine	Ground State	6.44	6.39
	2 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	3.74	3.76
	3 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	6.69	6.42
	4 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	5.69	3.31
	5 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	8.06	4.55
	1 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	1.76	0.74
	2 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	1.03	1.41
Thymine	Ground State	4.24	4.26
	2 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	5.50	5.20
	3 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	2.68	1.96
	4 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	6.88	6.00
	5 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	1.40	1.00
	1 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	1.87	2.02
	2 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	4.26	4.12
	3 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	3.92	4.15
	4 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	2.63	2.33
Uracil	Ground State	4.30	4.32
	2 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	5.61	5.36
	3 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	3.17	2.74

(continued)

Table 9. (Continued).

Molecule	State	CC2	
		TZVP <sup>a</sup>	aug-cc-pVTZ <sup>b</sup>
	4 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	6.44	5.90
	5 <sup>1</sup> A' ( $\pi$ → $\pi^*$ )	0.97	2.04
	1 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	3.33	1.60
	2 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	4.36	3.85
	3 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	3.97	3.52
	4 <sup>1</sup> A'' ( <i>n</i> → $\pi^*$ )	2.01	2.33

Notes: <sup>a</sup>Results with the TZVP basis set from [1].<sup>b</sup>Results with the aug-cc-pVTZ basis set from this work.