

## Benchmarks for Electronically Excited States: A Comparison of Noniterative and Iterative Triples Corrections in Linear Response Coupled Cluster Methods: CCSDR(3) versus CC3

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**Abstract:** CCSDR(3) calculations of vertical excitation energies are reported for a set of 24 molecules and 121 excited valence singlet states from a recently published benchmark of organic molecules. The same geometries (MP2/6–31G\*) and basis set (TZVP) were employed as in our previous linear response CC2, CCSD, and CC3 calculations. The CCSDR(3) results are compared against the CCSD and CC3 results. Statistical evaluation of all CCSDR(3) excitation energies gives mean absolute deviations of 0.09 eV from CC3 and 0.30 eV from CCSD. For excited states, which are dominated by single excitations, the absolute mean deviation from CC3 is reduced to 0.02 eV and the maximum deviation is 0.09 eV. CCSDR(3) is thus a very cost-effective accurate alternative to CC3.

### 1. Introduction

In two recent studies<sup>1,2</sup> we have presented a benchmark set for the calculation of electronically excited states. This set comprises unsaturated aliphatic hydrocarbons (including polyenes and cyclic compounds), aromatic hydrocarbons and heterocycles, carbonyl compounds, and nucleobases. It consists of 28 medium size organic molecules with a total of 223 excited states (152 singlet and 71 triplet states) and is intended to cover the most important chromophores in organic photochemistry.

In the first study<sup>1</sup> calculations were performed with a series of linear response coupled cluster methods (CC2, CCSD, CC3)<sup>3–15</sup> and with multistate complete-active-space second-order perturbation theory (MS-CASPT2).<sup>16–18</sup> Based on these results and other high-level literature data, best theoretical estimates were chosen for the majority of the studied vertical excitation energies. The comparison of coupled cluster and multireference results showed that CC3 and CASPT2 excitation energies are in excellent agreement

for states which are dominated by single excitations and that CC2 performs on average better than CCSD.

In the second study<sup>2</sup> we have investigated the performance of time-dependent density functional theory (TD-DFT) with three functionals (BP86, B3LYP, and BHLYP) and DFT-based multireference configuration interaction (DFT/MRCI) methods.

Møller–Plesset perturbation theory<sup>19–29</sup> and coupled cluster theory-based<sup>3–15,26–30</sup> response theory methods such as CC3<sup>13–15</sup> are suitable for states with low double excitation contributions. However, CC3 formally scales as  $N^7$  with the number of orbitals  $N$ , and the high computational cost in the iterative treatment of the triple excitations in CC3 restricts its application to small systems and/or small basis sets. Looking for a computationally cheaper but comparably accurate approach, Christiansen and co-workers<sup>31,32</sup> have presented the CCSDR(3) method, in which a noniterative triples correction is added to the linear response CCSD excitation energy. In this respect, CCSDR(3) is analogous to the CCSD(T) method<sup>33</sup> which is so successful for ground-state energies. Both methods include fourth-order terms. In CCSDR(3) the reference singles and doubles amplitudes as well as the energies of single excitation dominated states

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**Table 1.** Vertical Singlet Excitation Energies  $\Delta E$  (eV)

molecule	state	CCSD (% $R_1$ ) <sup>a</sup> ref 1	CCSDR(3) ( $\Delta$ ) <sup>b</sup> this work	CC3 (% $R_1$ ) <sup>a</sup> ref 1
ethene	1 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	8.51 (97.2)	8.36 (−0.01)	8.37 (96.9)
<i>E</i> -butadiene	1 <sup>1</sup> B <sub>u</sub> ( $\pi \rightarrow \pi^*$ )	6.72 (95.5)	6.56 (−0.02)	6.58 (93.7)
	2 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	7.42 (85.8)	6.95 (0.18)	6.77 (72.8)
<i>all-E</i> -hexatriene	1 <sup>1</sup> B <sub>u</sub> ( $\pi \rightarrow \pi^*$ )	5.72 (95.0)	5.56 (−0.02)	5.58 (92.6)
	2 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	6.61 (84.7)	6.04 (0.32)	5.72 (65.8)
<i>all-E</i> -octatetraene	2 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	5.99 (85.4)	5.40 (0.43)	4.97 (62.9)
	1 <sup>1</sup> B <sub>u</sub> ( $\pi \rightarrow \pi^*$ )	5.07 (94.7)	4.93 (−0.01)	4.94 (91.9)
	2 <sup>1</sup> B <sub>u</sub> ( $\pi \rightarrow \pi^*$ )	6.89 (81.3)	6.91 (0.30)	6.06 (58.5)
	3 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	6.98 (92.0)	6.72 (0.23)	6.50 (71.6)
	4 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	7.05 (89.9)	7.01 (−0.05)	6.81 (92.1)
	3 <sup>1</sup> B <sub>u</sub> ( $\pi \rightarrow \pi^*$ )	8.15 (94.6)	7.95 (0.03)	7.91 (91.9)
cyclopropene	1 <sup>1</sup> B <sub>1</sub> ( $\sigma \rightarrow \pi^*$ )	6.96 (94.5)	6.89 (−0.01)	6.90 (93.0)
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	7.24 (96.3)	7.10 (0.00)	7.10 (95.5)
cyclopentadiene	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	5.87 (95.7)	5.72 (−0.01)	5.73 (94.3)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	7.05 (89.4)	6.76 (0.14)	6.61 (79.3)
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	8.95 (95.8)	8.72 (0.02)	8.69 (93.1)
norbornadiene	1 <sup>1</sup> A <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	5.80 (95.3)	5.65 (0.01)	5.64 (93.4)
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	6.69 (94.5)	6.51 (0.02)	6.49 (91.9)
	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	7.87 (95.5)	7.65 (0.01)	7.64 (93.8)
	2 <sup>1</sup> A <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	7.87 (95.0)	7.73 (0.02)	7.71 (93.0)
benzene	1 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	5.19 (90.5)	5.12 (0.04)	5.07 (85.8)
	1 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	6.74 (95.6)	6.70 (0.02)	6.68 (93.6)
	1 <sup>1</sup> E <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	7.65 (94.5)	7.45 (0.00)	7.45 (92.2)
	2 <sup>1</sup> E <sub>2g</sub> ( $\pi \rightarrow \pi^*$ )	9.21 (84.9)	8.71 (0.29)	8.43 (65.6)
naphthalene	1 <sup>1</sup> B <sub>3u</sub> ( $\pi \rightarrow \pi^*$ )	4.41 (90.5)	4.34 (0.07)	4.27 (85.2)
	1 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	5.21 (94.3)	5.08 (0.05)	5.03 (90.6)
	2 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	6.23 (90.1)	6.09 (0.11)	5.98 (82.2)
	1 <sup>1</sup> B <sub>1g</sub> ( $\pi \rightarrow \pi^*$ )	6.53 (91.4)	6.26 (0.20)	6.07 (79.6)
	2 <sup>1</sup> B <sub>3u</sub> ( $\pi \rightarrow \pi^*$ )	6.55 (93.9)	6.35 (0.02)	6.33 (90.7)
	2 <sup>1</sup> B <sub>1g</sub> ( $\pi \rightarrow \pi^*$ )	6.97 (93.8)	6.81 (0.02)	6.79 (91.3)
	2 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	6.77 (93.8)	6.60 (0.03)	6.57 (90.5)
	3 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	7.77 (88.4)	7.29 (0.39)	6.90 (70.0)
	3 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	8.77 (93.5)	8.53 (0.08)	8.44 (87.9)
	3 <sup>1</sup> B <sub>3u</sub> ( $\pi \rightarrow \pi^*$ )	9.03 (84.1)	8.50 (0.38)	8.12 (58.7)
furan	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	6.80 (94.9)	6.64 (0.04)	6.60 (92.9)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	6.89 (90.8)	6.71 (0.09)	6.62 (84.9)
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	8.83 (94.2)	8.57 (0.04)	8.53 (90.7)
pyrrole	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	6.61 (91.2)	6.47 (0.07)	6.40 (86.0)
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	6.87 (94.2)	6.74 (0.03)	6.71 (91.6)
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	8.44 (93.7)	8.20 (0.04)	8.17 (90.2)
imidazole	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	7.01 (92.4)	6.87 (0.05)	6.82 (87.6)
	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	6.80 (92.0)	6.64 (0.06)	6.58 (87.2)
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	7.27 (93.1)	7.15 (0.05)	7.10 (89.8)
	2 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	8.15 (93.3)	7.98 (0.05)	7.93 (89.4)
	4 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	8.70 (92.7)	8.49 (0.04)	8.45 (88.8)
pyridine	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	5.27 (90.6)	5.20 (0.05)	5.15 (85.9)
	1 <sup>1</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	5.25 (92.8)	5.12 (0.07)	5.05 (88.1)
	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	5.73 (92.4)	5.55 (0.05)	5.50 (87.7)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	6.94 (95.3)	6.88 (0.03)	6.85 (92.8)
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	7.94 (94.2)	7.72 (0.01)	7.70 (91.5)
	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	7.81 (93.5)	7.61 (0.02)	7.59 (89.7)
	4 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	9.45 (89.5)	9.00 (0.33)	8.68 (74.1)
	3 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	9.64 (84.4)	9.09 (0.32)	8.77 (65.2)
pyrazine	1 <sup>1</sup> B <sub>3u</sub> ( $n \rightarrow \pi^*$ )	4.42 (93.4)	4.31 (0.06)	4.24 (89.9)
	1 <sup>1</sup> A <sub>u</sub> ( $n \rightarrow \pi^*$ )	5.29 (92.7)	5.11 (0.06)	5.05 (88.4)
	1 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	5.14 (90.8)	5.07 (0.05)	5.02 (86.2)
	1 <sup>1</sup> B <sub>2g</sub> ( $n \rightarrow \pi^*$ )	6.02 (92.1)	5.86 (0.12)	5.74 (85.0)
	1 <sup>1</sup> B <sub>1g</sub> ( $n \rightarrow \pi^*$ )	7.13 (90.8)	6.86 (0.11)	6.75 (83.8)
	1 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	7.18 (95.6)	7.10 (0.03)	7.07 (93.3)
	2 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	8.34 (93.9)	8.09 (0.03)	8.06 (90.9)
	2 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	8.29 (93.2)	8.08 (0.03)	8.05 (89.7)
	1 <sup>1</sup> B <sub>3g</sub> ( $\pi \rightarrow \pi^*$ )	9.75 (83.5)	9.16 (0.39)	8.77 (61.1)
	2 <sup>1</sup> A <sub>g</sub> ( $\pi \rightarrow \pi^*$ )	9.55 (89.1)	9.04 (0.35)	8.69 (74.2)
pyrimidine	1 <sup>1</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	4.70 (92.7)	4.56 (0.06)	4.50 (88.4)
	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	5.12 (92.6)	4.97 (0.05)	4.93 (88.2)
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	5.49 (90.5)	5.42 (0.05)	5.36 (85.7)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	7.17 (94.8)	7.10 (0.04)	7.06 (92.2)
	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	8.24 (93.8)	8.02 (0.02)	8.01 (90.7)
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	7.97 (93.5)	7.77 (0.03)	7.74 (89.7)
pyridazine	1 <sup>1</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	4.11 (93.1)	3.99 (0.07)	3.92 (89.0)
	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	4.76 (92.0)	4.57 (0.08)	4.49 (86.6)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	5.35 (90.2)	5.28 (0.06)	5.22 (85.2)
	2 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	6.00 (92.1)	5.84 (0.10)	5.74 (86.6)
	2 <sup>1</sup> B <sub>1</sub> ( $n \rightarrow \pi^*$ )	6.70 (92.0)	6.49 (0.08)	6.41 (86.6)
	1 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	7.09 (94.7)	6.99 (0.07)	6.93 (90.7)
	2 <sup>1</sup> B <sub>2</sub> ( $\pi \rightarrow \pi^*$ )	7.79 (93.8)	7.58 (0.04)	7.55 (90.2)
	3 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	8.11 (93.8)	7.86 (0.04)	7.82 (90.5)

Table 1. Continued

molecule	state	CCSD (% $R_1$ ) <sup>a</sup> ref 1	CCSDR(3) ( $\Delta$ ) <sup>b</sup> this work	CC3 (% $R_1$ ) <sup>a</sup> ref 1
s-triazine	1 <sup>1</sup> A <sub>1</sub> ' ( $n \rightarrow \pi^*$ )	4.96 (92.3)	4.81 (0.04)	4.78 (88.0)
	1 <sup>1</sup> A <sub>2</sub> ' ( $n \rightarrow \pi^*$ )	4.98 (92.5)	4.83 (0.07)	4.76 (88.0)
	1 <sup>1</sup> E'' ( $n \rightarrow \pi^*$ )	5.01 (92.5)	4.87 (0.05)	4.81 (88.1)
	1 <sup>1</sup> A <sub>2</sub> ' ( $\pi \rightarrow \pi^*$ )	5.84 (90.2)	5.76 (0.06)	5.71 (85.1)
	2 <sup>1</sup> A <sub>1</sub> ' ( $\pi \rightarrow \pi^*$ )	7.51 (93.7)	7.44 (0.03)	7.41 (90.8)
	2 <sup>1</sup> E'' ( $n \rightarrow \pi^*$ )	8.19 (90.9)	7.95 (0.15)	7.80 (88.1)
	1 <sup>1</sup> E' ( $\pi \rightarrow \pi^*$ )	8.28 (93.7)	8.07 (0.02)	8.04 (88.8)
	2 <sup>1</sup> E' ( $\pi \rightarrow \pi^*$ )	10.24 (91.2)	9.89 (0.46)	9.44 (74.3)
s-tetrazine	1 <sup>1</sup> B <sub>3u</sub> ( $n \rightarrow \pi^*$ )	2.71 (93.2)	2.61 (0.08)	2.53 (89.6)
	1 <sup>1</sup> A <sub>u</sub> ( $\pi \rightarrow \pi^*$ )	4.07 (92.2)	3.88 (0.08)	3.79 (87.5)
	1 <sup>1</sup> B <sub>1g</sub> ( $n \rightarrow \pi^*$ )	5.32 (91.7)	5.15 (0.18)	4.97 (82.5)
	1 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	5.27 (90.0)	5.20 (0.08)	5.12 (84.6)
	1 <sup>1</sup> B <sub>2g</sub> ( $n \rightarrow \pi^*$ )	5.70 (90.7)	5.51 (0.17)	5.34 (80.7)
	2 <sup>1</sup> A <sub>u</sub> ( $n \rightarrow \pi^*$ )	5.70 (92.5)	5.56 (0.10)	5.46 (87.4)
	2 <sup>1</sup> B <sub>2g</sub> ( $n \rightarrow \pi^*$ )	6.76 (90.1)	6.43 (0.20)	6.23 (79.2)
	2 <sup>1</sup> B <sub>1g</sub> ( $n \rightarrow \pi^*$ )	7.25 (91.1)	6.98 (0.11)	6.87 (84.7)
	3 <sup>1</sup> B <sub>1g</sub> ( $n \rightarrow \pi^*$ )	8.36 (86.9)	7.60 (0.52)	7.08 (63.2)
	2 <sup>1</sup> B <sub>3u</sub> ( $n \rightarrow \pi^*$ )	6.99 (93.2)	6.77 (0.10)	6.67 (86.7)
	1 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	7.66 (94.9)	7.54 (0.09)	7.45 (91.0)
	2 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	8.06 (93.4)	7.83 (0.04)	7.79 (90.2)
	2 <sup>1</sup> B <sub>2u</sub> ( $\pi \rightarrow \pi^*$ )	8.88 (93.2)	8.58 (0.07)	8.51 (87.7)
	2 <sup>1</sup> B <sub>3g</sub> ( $\pi \rightarrow \pi^*$ )	9.44 (84.3)	8.86 (0.39)	8.47 (63.6)
formaldehyde	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	3.97 (93.4)	3.94 (0.00)	3.95 (91.2)
	1 <sup>1</sup> B <sub>1</sub> ( $\sigma \rightarrow \pi^*$ )	9.26 (93.4)	9.19 (0.00)	9.18 (90.9)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	10.54 (94.4)	10.43 (−0.02)	10.45 (91.3)
acetone	1 <sup>1</sup> A <sub>2</sub> ( $n \rightarrow \pi^*$ )	4.43 (93.4)	4.39 (0.00)	4.40 (90.8)
	1 <sup>1</sup> B <sub>1</sub> ( $\sigma \rightarrow \pi^*$ )	9.26 (93.8)	9.17 (0.01)	9.17 (91.5)
	2 <sup>1</sup> A <sub>1</sub> ( $\pi \rightarrow \pi^*$ )	9.87 (93.5)	9.66 (0.01)	9.65 (90.1)
<i>p</i> -benzoquinone	1 <sup>1</sup> A <sub>u</sub> ( $n \rightarrow \pi^*$ )	3.19 (91.7)	3.01 (0.16)	2.85 (83.0)
	1 <sup>1</sup> B <sub>1g</sub> ( $n \rightarrow \pi^*$ )	3.07 (92.0)	2.90 (0.15)	2.75 (84.1)
	1 <sup>1</sup> B <sub>3g</sub> ( $\pi \rightarrow \pi^*$ )	4.93 (92.7)	4.69 (0.11)	4.59 (87.9)
	1 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	5.89 (92.5)	5.65 (0.03)	5.62 (88.4)
	1 <sup>1</sup> B <sub>3u</sub> ( $n \rightarrow \pi^*$ )	6.55 (91.0)	6.09 (0.27)	5.82 (75.2)
	2 <sup>1</sup> B <sub>3g</sub> ( $\pi \rightarrow \pi^*$ )	7.62 (91.0)	7.36 (0.08)	7.27 (83.8)
	2 <sup>1</sup> B <sub>1u</sub> ( $\pi \rightarrow \pi^*$ )	8.47 (91.7)	8.10 (0.28)	7.82 (68.6)
formamide	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	5.66 (93.6)	5.65 (−0.01)	5.65 (90.7)
	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	8.52 (92.9)	8.30 (0.03)	8.27 (87.9)
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	11.34 (92.7)	11.06 (0.13)	10.93 (86.6)
acetamide	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	5.71 (93.5)	5.69 (−0.01)	5.69 (90.6)
	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	7.85 (92.8)	7.69 (0.02)	7.67 (89.1)
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	10.77 (93.0)	10.56 (0.06)	10.50 (88.7)
propanamide	1 <sup>1</sup> A'' ( $n \rightarrow \pi^*$ )	5.74 (93.6)	5.71 (−0.01)	5.72 (90.6)
	2 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	7.80 (93.0)	7.64 (0.02)	7.62 (89.2)
	3 <sup>1</sup> A' ( $\pi \rightarrow \pi^*$ )	10.34 (93.3)	10.13 (0.06)	10.06 (89.0)

<sup>a</sup> Weight of the single excitations in the coupled cluster calculations. <sup>b</sup> Difference between CCSDR(3) and CC3 results (in parenthesis).

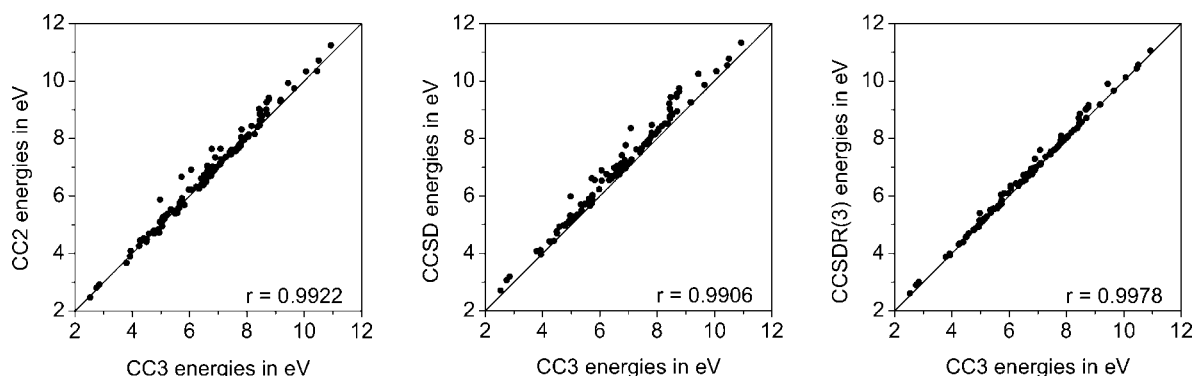
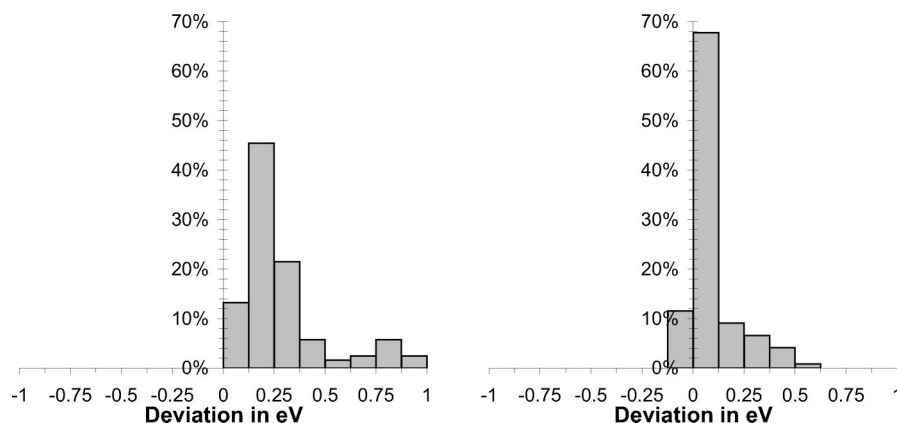


Figure 1. Correlation plots for all calculated singlet excited states: Coupled cluster vertical excitation energies.

are correct to third order whereas the reference triples amplitudes and the energies of double excitation dominated states are correct to second order exactly as in CC3.<sup>31,32</sup> While the computational scaling of CCSDR(3) is of the same order as in CC3, the  $N^7$  step is noniterative in CCSDR(3),

which implies a much smaller prefactor and therefore significant computational savings. Formally CCSDR(3) is based on a pseudoperturbation theory expansion of the CC3 eigenvalue problem and therefore bears some similarity to the CIS(D)<sup>34</sup> and RPA(D)<sup>21,23</sup> methods, which are based on



**Figure 2.** Histogram of the frequency of deviation (from CC3/TZVP in %) of all calculated CCSD/TZVP (left) and CCSDR(3)/TZVP (right) singlet excited states.

**Table 2.** Deviations in Excitation Energies of 121 Singlet Excited States with Respect to CC3/TZVP

	method		
	CC2 <sup>a</sup>	CCSD <sup>a</sup>	CCSDR(3)
mean	0.13	0.30	0.09
abs mean	0.17	0.30	0.09
std dev	0.26	0.38	0.14
maximum	0.95	1.28	0.52

<sup>a</sup> CC2/TZVP and CCSD/TZVP results from ref 1.

the corresponding expansion of the CC2<sup>3,4</sup> or second-order polarization propagator approximation (SOPPA)<sup>19,20,22,24,25</sup> eigenvalue problem.

CCSDR(3) calculations have previously been carried out for a number of small<sup>31,32,35–37</sup> and medium size<sup>36,38–45</sup> molecules; however, a systematic comparison with CC3 and CCSD has not yet been published. In this article we present such a study for singlet excitation energies using our recently published benchmark set.<sup>1</sup> We have calculated CCSDR(3) excitation energies for 121 excited valence singlet states in 24 molecules, i.e. all the singlet states from the benchmark set for which CC3 results are available.<sup>1</sup> The new CCSDR(3) results are compared with the previously published CCSD and CC3 data. On the basis of a statistical evaluation of our results, we derive rules of thumb for the accuracy of the noniterative triples correction of CCSDR(3) relative to the iterative correction in CC3.

Although this study is only concerned with the question of how well CCSDR(3) with its noniterative triples correction is able to reproduce the results of CC3 calculations, we emphasize that CCSDR(3) is by no means the only method which includes noniterative triples corrections in the calculation of excitation energies. Several methods, EOM-CCSD(T), EOM-CCSD(T'), and EOM-CCSD(T̄), have been proposed<sup>46–49</sup> that are based on the equation-of-motion coupled cluster approach (EOM-CC) developed by Bartlett and others.<sup>50–63</sup> Piecuch and co-workers have extended the completely renormalized coupled-cluster theory<sup>64–66</sup> to the calculation of excitation energies, by adding noniterative triples corrections to the EOM-CCSD energies in their CR-EOMCCSD(T), CR-EOMCCSD(T)<sub>L</sub>, and r-CR-EOMCCSD(T) treatments<sup>65,67–71</sup> which are based on the methods of moments of coupled cluster equations.<sup>67,68,72–75</sup> Finally one

should also note in this context a recent approach<sup>76</sup> based on the EOM-CC(m)PT(n) methods,<sup>77,78</sup> the similarity transformed EOM-CC method (STEOM)<sup>79–82</sup> that implicitly includes triples excitations, the Fock space coupled cluster theory,<sup>83</sup> the SAC-CI approach of Nakatsuji,<sup>84,85</sup> and the spin-flip equation-of-motion coupled cluster method by Krylov and co-workers.<sup>86–90</sup>

The remaining parts of the paper are structured as follows. In Section 2 the details of the calculations are specified. In Section 3 the CCSDR(3) results are discussed in comparison with the previously published CCSD and CC3 results. Conclusions are drawn in section 4.

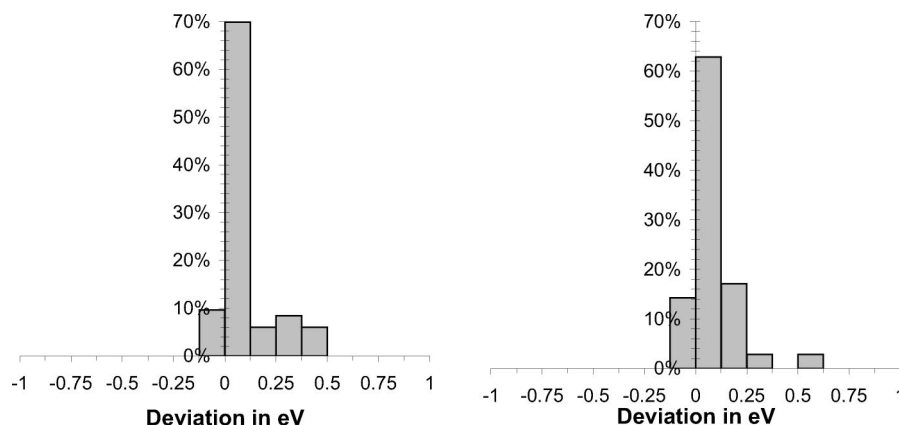
## 2. Computational Details

All calculations were carried out with the Dalton 2.0 program package.<sup>91</sup> The same MP2/6–31G\* optimized geometries<sup>92–95</sup> and TZVP basis set<sup>96</sup> as in our previous studies were employed.<sup>1,2</sup>

As discussed before,<sup>1,2</sup> the TZVP basis set does not contain diffuse functions and might not be able to give a balanced description of excited states that are spatially extended and have (partial) Rydberg character. For the present study this is less important, since we are interested in a direct comparison of correlated ab initio methods in the calculation of valence excited states, which should be much less sensitive to the basis set than the absolute excitation energies. For example, the differences between the linear response CC3 and CCSD results deviate by only a few hundredths of 1 eV from the corresponding literature values<sup>11,13,36,38–42,44,82,97–100</sup> obtained with mostly larger basis sets. Our absolute CC3 excitation energies, on the other hand, tend to be slightly too large, normally by 0.02–0.15 eV and sometimes by up to 0.3 eV.

## 3. Results and Discussion

The CCSDR(3)/TZVP results for the 121 singlet valence states are given in Table 1 together with the previously published<sup>1</sup> CCSD and CC3 results. 83 of these states are of  $\pi \rightarrow \pi^*$  type, 35 are of  $n \rightarrow \pi^*$  type and three are of  $\sigma \rightarrow \pi^*$  type. Figure 1 shows correlation plots between the CC2, CCSD, and CCSDR(3) results on one side and the CC3 results on the other side for all calculated states. Figure 2



**Figure 3.** Histogram of the frequency of deviation (CCSDR(3)/TZVP vs CC3/TZVP, in %) of all calculated singlet  $\pi \rightarrow \pi^*$  (left) and  $n \rightarrow \pi^*$  (right) excited states.

**Table 3.** Deviations in Excitation Energies of 35 Singlet Excited  $n \rightarrow \pi^*$  States with Respect to CC3/TZVP

	method		
	CC2 <sup>a</sup>	CCSD <sup>a</sup>	CCSDR(3)
mean	0.04	0.28	0.10
abs mean	0.10	0.28	0.10
std dev	0.13	0.36	0.14
maximum	0.56	1.28	0.52

<sup>a</sup> CC2/TZVP and CCSD/TZVP results from ref 1.

**Table 4.** Deviations in Excitation Energies of 45 Singlet Excited States of the Benchmark Set with Respect to CC3/TZVP, for States Where the  $R_1$  (CC3) Percentage Exceeds 90%

	method		
	CC2 <sup>a</sup>	CCSD <sup>a</sup>	CCSDR(3)
mean	0.04	0.16	0.02
abs mean	0.09	0.16	0.02
std dev	0.11	0.18	0.03
maximum	0.27	0.30	0.09

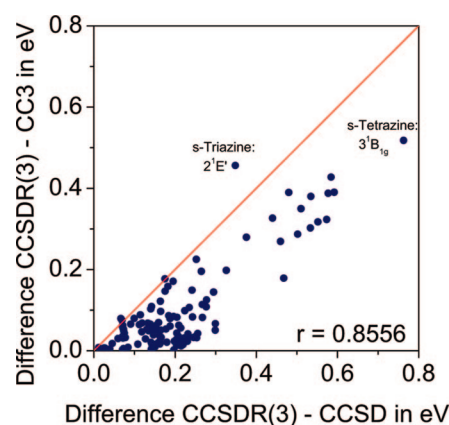
<sup>a</sup> CC2/TZVP and CCSD/TZVP results from ref 1.

**Table 5.** Comparison of Relative CPU Times between CCSD, CCSDR(3), and CC3 Calculations

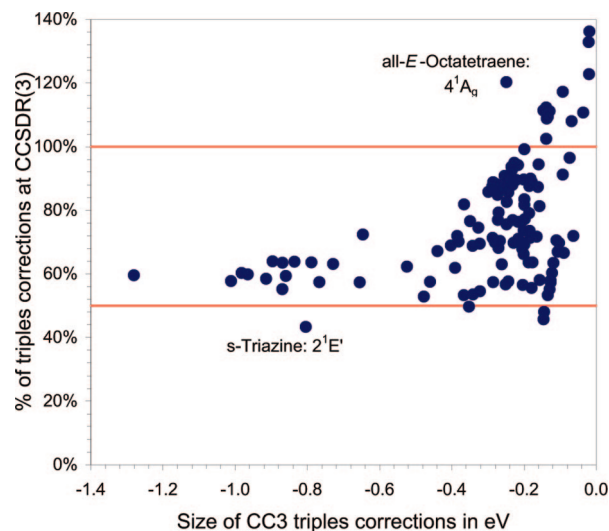
	molecule	
	benzene	naphthalene
basis functions	150	238
states	6 <sup>a</sup>	3
S+D amplitudes	≈ 515 000 <sup>a</sup>	3 353 467
relative CPU time		
CCSD	1	6
CCSDR(3)	22	132
CC3	1012	2706

<sup>a</sup> Six states in four different irreducible representations were calculated in the same run: one  $1A_g$  state with 517029 S+D amplitudes, two  $1B_{3u}$  states with 514210 S+D amplitudes, two  $1B_{2u}$  states with 515667 S+D amplitudes and one  $1B_{1g}$  state with 514202 S+D amplitudes.

presents histograms with the frequency of deviation from CC3 for the CCSD and CCSDR(3) results. It is obvious that compared with CCSD and CC2 the noniterative triples correction in CCSDR(3) leads to a much better agreement with the CC3 results over the whole range of energies. The mean deviation from CC3 (Table 2) drops from 0.30 eV in



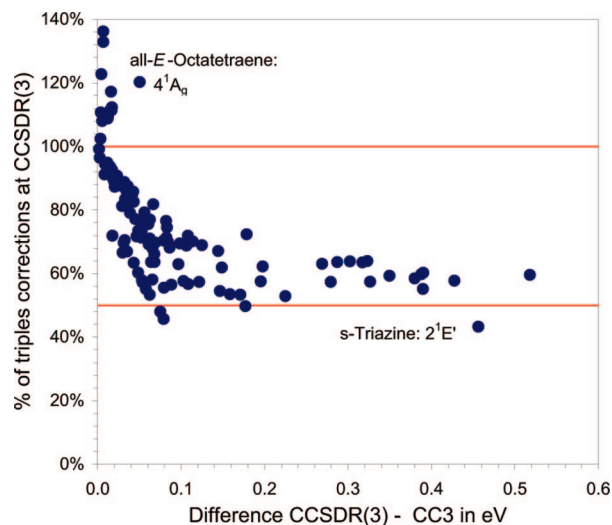
**Figure 4.** Correlation plot for all calculated singlet excited states: energy difference between CCSDR(3) and CC3 versus energy difference between CCSDR(3) and CCSD.



**Figure 5.** Correlation plot for all calculated singlet excited states: percentage of the triples correction obtained in the CCSDR(3) calculations versus the total CC3 triples correction.

CCSD to 0.09 eV in CCSDR(3). The largest deviations from CC3 are found for the  $3^1B_{1g}$  state of *s*-tetrazine (0.52 eV), the  $2^1E'$  state of *s*-triazine (0.46 eV), and the  $2^1A_g$  state of *all-E*-octatetraene (0.43 eV), which is in each case about half





**Figure 6.** Correlation plot for all calculated singlet excited states: percentage of the triples correction obtained in the CCSDR(3) calculations versus the difference between CCSDR(3) and CC3.

the deviation found for CCSD. Correspondingly the standard deviation is also much smaller for CCSDR(3) than for CCSD as can be seen from Figure 2 and Table 2.

The significantly improved performance of CCSDR(3) is not restricted to a particular range of excited-state energies but holds for the whole benchmark set as illustrated in the correlation plots in Figure 1. For less than 10% of the states, CCSDR(3) predicts slightly smaller excitation energies than CC3, whereas the CCSD excitation energies in our benchmark set are always larger than the CC3 energies. We had previously found that CC2 gives excitation energies both larger and smaller than CC3 and consequently performs on average better than CCSD for our benchmark set.<sup>1</sup> However, compared with CCSDR(3), the spread of results is significantly larger in CC2 than in CCSDR(3). This can be seen in the correlation plots (Figure 1) and is also indicated by the standard deviations and maximum deviations in Table 2 which are about twice as large for CC2 than for CCSDR(3).

It is obvious from the histograms in Figure 3 and from the comparison of the statistical data for the  $n \rightarrow \pi^*$  transitions alone (Table 3) against the data for all excited states (Table 2) that there is not much difference between the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The largest outlier with respect to CC3, i.e., the  $3^1B_{1g}$  state of *s*-tetrazine, is a  $n \rightarrow \pi^*$  transition, whereas the two next largest outliers, the  $2^1E'$  state of *s*-triazine and the  $2^1A_g$  state of *all-E*-octatetraene, are  $\pi \rightarrow \pi^*$  transitions.

When restricting the statistics to states with a CC3 single excitation weight larger than 90% (called %  $R_1$  in Table 1), the agreement between CCSDR(3) and CC3 becomes almost perfect. The mean deviation is reduced to 0.02 eV, and the maximum deviation is also less than 0.1 eV (see Table 4).

Relative CPU times for two representative calculations of excited states in benzene and naphthalene are collected in Table 5. It is gratifying to see that the necessary CPU time is dramatically reduced in CCSDR(3) compared to CC3. Nevertheless, due to the formal  $N^7$  scaling of CCSDR(3)

these calculations are still considerably more expensive than the simpler CCSD calculations.

It would clearly be desirable to be able to estimate the remaining error of CCSDR(3) relative to CC3 based on the results of the CCSD and CCSDR(3) calculations alone. A correlation plot for the relevant energy differences (Figure 4) shows that the remaining errors in the CCSDR(3) results compared to CC3 are almost always smaller than the changes on going from CCSD to CCSDR(3) (prominent exception: the  $2^1E'$  state of *s*-triazine).

Analyzing the performance of CCSDR(3) as a function of the single excitation weight in the CCSD calculations, one finds that for all states in our benchmark set with a CCSD single excitation weight smaller than 90% the difference between the CCSDR(3) and CC3 results is larger than 0.1 eV. This implies that the data from CCSD calculations allow us to pinpoint states, for which one very likely will encounter larger differences between CCSDR(3) and CC3. However, the opposite is not always true. There is one state in our benchmark set ( $2^1E'$  in *s*-triazine), where the difference is 0.46 eV despite a single excitation weight of 91.2%, while there are two states in *p*-benzoquinone ( $1^1B_{3u}$  and  $2^1B_{1u}$ ) with a single excitation weight of 91–92% which differ by  $\approx 0.27$  eV and in total 15 states with single excitation weights of 91–93% and differences between CCSDR(3) and CC3 in the range between 0.1 and 0.2 eV.

Finally, it is important to know which fraction of the CC3 triples correction can be recovered in an CCSDR(3) calculation. This percentage is shown as a function of the size of the total CC3 triples correction in Figure 5 and as function of the remaining deviation from the CC3 results in Figure 6. It is obvious that with three exceptions (most prominent again the  $2^1E'$  state of *s*-triazine) the CCSDR(3) triples correction gives at least 50% of the iterative CC3 triples correction, and on average it amounts to 78%. Even for the cases with large CC3 triple corrections (0.4 eV or more), CCSDR(3) yields about 60%. On the other hand, there are also some systems where CCSDR(3) overestimates the CC3 triples correction. However, with the exception of the  $4^1A_g$  state of *all-E*-octatetraene, this happens only for states where the remaining difference between CCSDR(3) and CC3 is less than 0.02 eV and the total triples correction is less than 0.16 eV.

## 4. Conclusions

We have carried out CCSDR(3)/TZVP calculations of vertical excitation energies for 24 molecules and a total of 121 valence excited singlet states from a recently published benchmark set of organic molecules.<sup>1</sup> Statistical comparison of these data with the previously published linear response CC2, CCSD, and CC3 results shows that adding the noniterative triples corrections to the CCSD results leads to a substantial improvement over CC2 and CCSD for all states in this benchmark set.

Inclusion of the noniterative triples correction in CCSDR(3) often reproduces the iterative CC3 triples correction almost quantitatively, at dramatically reduced CPU times. For all states, which are dominated by single excitations (CC3 single excitation weight larger than 90%), the

CCSDR(3) results differ by at most 0.1 eV from the CC3 results. More important is that one can obtain a reasonable estimate of the accuracy of the CCSDR(3) results from the size of the triples correction in CCSDR(3) and the single excitation weight in the CCSD calculations. The remaining difference between CCSDR(3) and CC3 is in almost all cases smaller than the noniterative triples correction from CCSDR(3). CCSDR(3) normally gives at least 60% of the CC3 triples correction even if the latter is large ( $>0.4$  eV). Furthermore one can easily identify states for which differences of more than 0.1 eV between CCSDR(3) and CC3 should be expected: for all states in our benchmark with a CCSD single excitation weight smaller than 90%, the CCSDR(3) results deviate from the CC3 results by 0.1 eV or more.

We conclude that CCSDR(3) may play a similar role for excited states as CCSD(T) does for ground states, and that an appropriate sequence of linear response-coupled cluster methods for the calculation of vertical excitation energies is CC2, CCSDR(3), CC3. However, since transition moments are not defined in CCSDR(3), the corresponding sequence for the calculation of oscillator strengths remains CC2, CCSD, CC3.

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