# Benchmarking Coupled Cluster Methods on Valence Singlet Excited States

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ABSTRACT: In this paper, benchmark results are presented on Coupled Cluster calculation of singlet excitation energies and the corresponding oscillator strength. The test set of Thiel et al. (Schreiber, M.; Silva, M. R. J.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2008**, *128*, 134110) has been used, and the earlier results have been extended by CC3 oscillator strength for the whole set, CC3 excitation energies for larger molecules, and CCSDT results for some small molecules. Accuracy of the members of the hierarchy CC2-CCSD-CC3-CCSDT has been analyzed. The results show that both CC2 and CCSD are quite accurate and the difference to CC3 excitations energies is typically not larger than 0.2−0.3 eV. While the mean deviation of the CC2 results is close to zero, CCSD systematically overshoots the CC3 results by about 0.2 eV. The standard deviation is, however, somewhat

smaller for CCSD, that is, the latter method provides more systematic results. Still, only a few cases could be identified were the absolute value of the error is over 0.3 eV in case of CC2. The results are even better for CCSD, with the exception of uracil, where surprisingly large error of the excitation energies have been found for two of the four lowest $n-\pi^*$ transitions. Both LR (Linear Response) and EOM (Equation of Motion) style oscillator strengths have been calculated. The former is more accurate at both CC2 and CCSD levels, but the difference between them is only 1−2% in case of CCSD. The error of the CC2 oscillator strength are substantially larger than that of CCSD but qualitatively still correct.
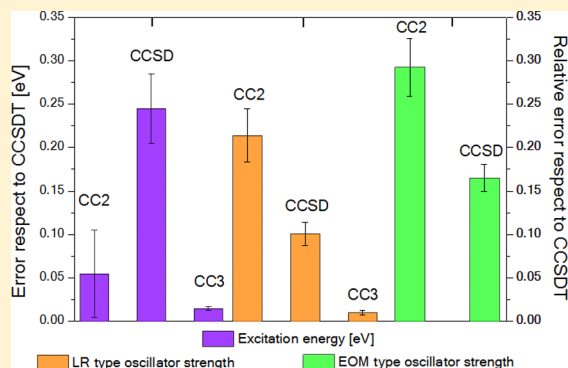
INTRODUCTION

Quantum chemical calculation on the ground state of the molecules became routine and chemical research on characterization of molecular structure, reaction mechanism, etc. is almost always supported by calculations. Methodology is well established: DFT (Density Functional Theory) calculations provide accurate results in most cases and advanced methods are needed for special, more difficult situations only. In these latter cases, methods including explicit treatment of electron correlation, such as MP2 (Møller−Plesset second order), CCSD (Coupled Cluster Singles Doubles), and CCSD(T) (CCSD with approximate triple excitations) can be used, eventually methods with multireference character can be applied in special cases.

Characterization of excited states are more difficult by quantum chemical methods. Still, the help by theoretical calculations is often required since experiments are also not straightforward for excited states. Therefore, the support by theoretical calculations is more or less mandatory in particular for spectroscopy. Since the interest of spectroscopists are also turning toward larger and larger molecules, efficient methods are required for the theoretical treatment.

As of the methods used, in analogy to the ground state, extension of DFT for excited states (Time Dependent DFT, TDDFT) seems to be a cost-effective choice for medium-sized and even for large molecules.[1] The excitation energies calculated by TDDFT methods, in most cases, differ from experimental data only by 0.1−0.5 eV, which is not much worse than the reliability

of accurate ab initio methods.[1] Unfortunately, there are lots of problems related to the special properties of excited states that cannot easily described by TDDFT methods. These problems arise from the fact that the TDDFT method empolys approximate exchange functionals. Without the proper exchange functional, TDDFT fails to properly describe large π-systems, doubly excited, charge transfer and Rydberg states.[1] On the correlated side, CASSCF and CASPT2,[2,3] (see also Pulay[4]) have been the most popular, due to the flexibility of the wave functions. This flexibility has, however, a high price to pay: use of these methods requires considerable experience. Therefore, for accurate calculations, Equation of Motion (EOM)[5] or Linear Response (LR)[6,7] versions of Coupled Cluster (CC) theory[8−10] are of great interest. The advantage here is the hierarchical nature of possible approximation: truncation is possible according to excitation level (singles, doubles, triples)[9] but also perturbational arguments can be used (e.g., EOM-CCSD(2),[11] EOM-CCSDT-3,[12] CC2,[13] CC3,[13] etc.) to obtain cost-effective realization of accurate theory.

Over the years, the applicability of theoretical methods has been extended to larger and larger systems. Recently, even calculations on biological systems became possible, our group has also started investigations on the excited states of the building blocks of DNA.[14−16] Perspective of such research has been summarized in ref 17. One of the conclusion of these studies was

Table 1. Singlet Excitation Energy (ΔE in eV) and Oscillator Strength (f in au) Calculated at Different Levels of CC Theory (TZVP Basis)

molecule	state	CC2			CCSD			CC3			CCSDT	
		ΔE	f_{LR}	f_{EOM}	ΔE	f_{LR}	f_{EOM}	ΔE	f_{LR}	singles^a	ΔE	f_{LR}
ethene	1 $^1B_{2u}$ ($\pi-\pi^*$)	8.40	0.431	0.466	8.51	0.410	0.418	8.37	0.389	96.86	8.38	0.389
E-butadiene	1 ^1B_u ($\pi-\pi^*$)	6.49	0.810	0.883	6.72	0.776	0.801	6.58	0.726	93.74	6.59	0.725
	2 ^1A_g ($\pi-\pi^*$)	7.64	0.000	0.000	7.42	0.000	0.000	6.78	0.000	72.85	6.66	0.000
all-E-hexatriene	1 ^1B_u ($\pi-\pi^*$)	5.41	1.273	1.395	5.72	1.213	1.256	5.58	1.129	92.58		
	2 ^1A_g ($\pi-\pi^*$)	6.67	0.000	0.000	6.61	0.000	0.000	5.72	0.000	65.83		
all-E-octatetraene	1 ^1B_u ($\pi-\pi^*$)	4.72	1.758	1.932	5.07	1.665	1.727	4.94	1.549	91.87		
	2 ^1A_g ($\pi-\pi^*$)	5.88	0.000	0.000	5.98	0.000	0.000	4.98	0.000	62.99		
cyclopropene	1 $^1B_1$ ($\sigma-\pi^*$)	6.96	0.001	0.002	6.96	0.001	0.001	6.90	0.001	92.97	6.89	0.001
	1 $^1B_2$ ($\pi-\pi^*$)	7.17	0.086	0.096	7.24	0.083	0.087	7.10	0.083	95.46	7.11	0.082
cyclopentadiene	1 $^1B_2$ ($\pi-\pi^*$)	5.69	0.110	0.120	5.86	0.097	0.103	5.73	0.093	94.33	5.75	0.092
	2 $^1A_1$ ($\pi-\pi^*$)	7.05	0.011	0.012	7.05	0.008	0.000	6.62	0.005	79.29	6.54	0.004
	3 $^1A_1$ ($\pi-\pi^*$)	8.86	0.658	0.705	8.95	0.648	0.673	8.69	0.596	93.14	8.71	0.563
norbornadiene	1 $^1A_2$ ($\pi-\pi^*$)	5.57	0.000	0.000	5.80	0.000	0.000	5.64	0.000	93.42		
	1 $^1B_2$ ($\pi-\pi^*$)	6.37	0.024	0.026	6.68	0.029	0.031	6.49	0.027	91.86		
	2 $^1B_2$ ($\pi-\pi^*$)	7.65	0.185	0.203	7.87	0.187	0.197	7.64	0.185	93.84		
	2 $^1A_2$ ($\pi-\pi^*$)	7.66	0.000	0.000	7.87	0.000	0.000	7.71	0.000	92.96		
benzene	1 $^1B_{2u}$ ($\pi-\pi^*$)	5.27	0.000	0.000	5.19	0.000	0.000	5.07	0.000	85.83		
	1 $^1B_{1u}$ ($\pi-\pi^*$)	6.68	0.000	0.000	6.74	0.000	0.000	6.68	0.000	93.59		
	1 $^1E_{1u}$ ($\pi-\pi^*$)	7.44	0.695	0.732	7.65	0.686	0.729	7.45	0.630	92.22		
	2 $^1E_{2g}$ ($\pi-\pi^*$)	9.03	0.000	0.000	9.21	0.000	0.000	8.43	0.000	72.33		
naphthalene	1 $^1B_{3u}$ ($\pi-\pi^*$)	4.45	0.000	0.000	4.41	0.000	0.000	4.27	0.000	85.24		
	1 $^1B_{2u}$ ($\pi-\pi^*$)	4.96	0.094	0.105	5.21	0.083	0.092	5.03	0.085	90.61		
	2 ^1A_g ($\pi-\pi^*$)	6.22	0.000	0.000	6.23	0.000	0.000	5.98	0.000	82.26		
	1 $^1B_{1g}$ ($\pi-\pi^*$)	6.21	0.000	0.000	6.53	0.000	0.000	6.07	0.000	79.64		
	2 $^1B_{3u}$ ($\pi-\pi^*$)	6.25	1.452	1.533	6.55	1.461	1.563	6.33	1.325	90.67		
	2 $^1B_{2u}$ ($\pi-\pi^*$)	6.57	0.272	0.284	6.77	0.294	0.325	6.57	0.239	90.49		
	2 $^1B_{1g}$ ($\pi-\pi^*$)	6.82	0.000	0.000	6.97	0.000	0.000	6.79	0.000	91.25		
	3 ^1A_g ($\pi-\pi^*$)	7.34	0.000	0.000	7.76	0.000	0.000	6.90	0.000	70.04		
	3 $^1B_{3u}$ ($\pi-\pi^*$)	8.86	0.010	0.011	9.03	0.014	0.015	8.12	0.005	58.72		
	3 $^1B_{2u}$ ($\pi-\pi^*$)	8.46	0.549	0.576	8.77	0.538	0.570	8.44	0.498	87.93		
furan	1 $^1B_2$ ($\pi-\pi^*$)	6.75	0.172	0.184	6.80	0.159	0.167	6.60	0.155	92.89		
	2 $^1A_1$ ($\pi-\pi^*$)	6.88	0.003	0.003	6.89	0.001	0.002	6.62	0.001	84.92		
	3 $^1A_1$ ($\pi-\pi^*$)	8.79	0.507	0.538	8.83	0.500	0.525	8.53	0.450	90.67		
pyrrole	2 $^1A_1$ ($\pi-\pi^*$)	6.61	0.006	0.006	6.61	0.005	0.006	6.41	0.004	85.97		
	1 $^1B_2$ ($\pi-\pi^*$)	6.88	0.182	0.193	6.87	0.166	0.174	6.71	0.167	91.64		
	3 $^1A_1$ ($\pi-\pi^*$)	8.44	0.533	0.562	8.43	0.527	0.553	8.17	0.478	90.20		
imidazole	2 $^1A'$ ($\pi-\pi^*$)	6.73	0.089	0.094	6.79	0.088	0.092	6.58	0.081	87.24		
	2 $^1A''$ ($n-\pi^*$)	6.86	0.003	0.003	7.01	0.005	0.005	6.83	0.004	87.62		
	3 $^1A'$ ($\pi-\pi^*$)	7.28	0.084	0.090	7.27	0.081	0.085	7.10	0.082	89.76		
	4 $^1A''$ ($n-\pi^*$)	8.01	0.006	0.006	8.15	0.004	0.004	7.94	0.005	89.38		
	5 $^1A'$ ($\pi-\pi^*$)	8.63	0.407	0.425	8.69	0.420	0.441	8.45	0.410	88.79		
pyridine	1 $^1B_1$ ($n-\pi^*$)	5.12	0.005	0.005	5.26	0.006	0.006	5.06	0.005	88.15		
	1 $^1B_2$ ($\pi-\pi^*$)	5.32	0.025	0.027	5.27	0.022	0.024	5.15	0.021	85.90		
	2 $^1A_2$ ($n-\pi^*$)	5.39	0.000	0.000	5.73	0.000	0.000	5.51	0.000	87.70		
	2 $^1A_1$ ($\pi-\pi^*$)	6.88	0.021	0.022	6.94	0.015	0.015	6.85	0.014	92.78		
	2 $^1B_2$ ($\pi-\pi^*$)	7.61	0.550	0.579	7.81	0.548	0.586	7.59	0.482	89.67		
	3 $^1A_1$ ($\pi-\pi^*$)	7.72	0.497	0.526	7.94	0.590	0.629	7.70	0.526	91.54		
	5 $^1A_1$ ($\pi-\pi^*$)	9.00	0.000	0.000	9.44	0.002	0.002	8.68	0.004	74.08		
	3 $^1B_2$ ($\pi-\pi^*$)	9.37	0.012	0.012	9.64	0.014	0.015	8.78	0.030	65.18		
	4 $^1B_2$ ($n-R$)	8.79	0.134	0.138	9.39	0.105	0.106	9.11	0.114	88.69		
pyrazine	1 $^1B_{3u}$ ($n-\pi^*$)	4.27	0.007	0.007	4.42	0.008	0.008	4.25	0.007	89.93		
	1 $^1B_{2u}$ ($\pi-\pi^*$)	5.14	0.071	0.076	5.14	0.067	0.071	5.02	0.062	86.25		
	1 ^1A_u ($n-\pi^*$)	4.95	0.000	0.000	5.30	0.000	0.000	5.05	0.000	88.38		
	1 $^1B_{2g}$ ($n-\pi^*$)	5.93	0.000	0.000	6.03	0.000	0.000	5.74	0.000	84.96		
	1 $^1B_{1g}$ ($n-\pi^*$)	6.71	0.000	0.000	7.14	0.000	0.000	6.76	0.000	83.82		
	1 $^1B_{1u}$ ($\pi-\pi^*$)	7.10	0.096	0.102	7.18	0.074	0.078	7.07	0.070	93.34		
	2 $^1B_{2u}$ ($\pi-\pi^*$)	8.08	0.400	0.421	8.29	0.422	0.455	8.05	0.376	89.72		
	2 $^1B_{1u}$ ($\pi-\pi^*$)	8.14	0.424	0.448	8.34	0.458	0.491	8.06	0.407	90.89		

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Table 1. continued

molecule	state	CC2			CCSD			CC3			CCSDT	
		ΔE	f_{LR}	f_{EOM}	ΔE	f_{LR}	f_{EOM}	ΔE	f_{LR}	singles[a]	ΔE	f_{LR}
	$3\ ^1A_g\ (\pi-\pi^*)$	9.26	0.000	0.000	9.55	0.000	0.000	8.70	0.000	74.29		
	$1\ ^1B_{3g}\ (\pi-\pi^*)$	9.31	0.000	0.000	9.74	0.000	0.000	8.77	0.000	61.14		
pyrimidine	$1\ ^1B_1\ (n-\pi^*)$	4.49	0.006	0.006	4.70	0.007	0.007	4.51	0.006	88.37		
	$1\ ^1A_2\ (n-\pi^*)$	4.85	0.000	0.000	5.13	0.000	0.000	4.93	0.000	88.26		
	$1\ ^1B_2\ (\pi-\pi^*)$	5.51	0.023	0.024	5.49	0.022	0.023	5.37	0.021	85.68		
	$2\ ^1A_1\ (\pi-\pi^*)$	7.12	0.062	0.066	7.17	0.038	0.040	7.06	0.043	92.23		
	$3\ ^1A_1\ (\pi-\pi^*)$	7.79	0.446	0.470	7.97	0.460	0.495	7.74	0.391	89.76		
	$2\ ^1B_2\ (\pi-\pi^*)$	8.08	0.479	0.506	8.24	0.467	0.501	8.01	0.415	90.65		
pyridazine	$1\ ^1B_1\ (n-\pi^*)$	3.91	0.006	0.006	4.12	0.007	0.007	3.93	0.006	88.95		
	$1\ ^1A_2\ (n-\pi^*)$	4.41	0.000	0.000	4.76	0.000	0.000	4.50	0.000	86.62		
	$2\ ^1A_1\ (\pi-\pi^*)$	5.37	0.014	0.015	5.35	0.014	0.015	5.22	0.014	85.16		
	$2\ ^1A_2\ (n-\pi^*)$	5.82	0.000	0.000	6.00	0.000	0.000	5.75	0.000	85.66		
	$2\ ^1B_1\ (n-\pi^*)$	6.40	0.005	0.005	6.70	0.005	0.005	6.42	0.005	86.59		
	$1\ ^1B_2\ (\pi-\pi^*)$	7.00	0.009	0.010	7.09	0.006	0.006	6.93	0.012	90.67		
	$2\ ^1B_2\ (\pi-\pi^*)$	7.57	0.489	0.514	7.79	0.458	0.491	7.55	0.340	90.20		
	$3\ ^1A_1\ (\pi-\pi^*)$	7.91	0.445	0.472	8.11	0.493	0.529	7.82	0.433	90.48		
s-triazine	$1\ ^1A_2''\ (n-\pi^*)$	4.80	0.017	0.018	4.99	0.018	0.019	4.76	0.016	88.02		
	$1\ ^1A_1''\ (n-\pi^*)$	4.69	0.000	0.000	4.96	0.000	0.000	4.78	0.000	88.03		
	$1\ ^1E''\ (n-\pi^*)$	4.78	0.000	0.000	5.02	0.000	0.000	4.82	0.000	88.10		
	$1\ ^1A_2'\ (\pi-\pi^*)$	5.83	0.000	0.000	5.84	0.000	0.000	5.71	0.000	85.13		
	$2\ ^1A_1'\ (\pi-\pi^*)$	7.52	0.000	0.000	7.51	0.000	0.000	7.41	0.000	90.83		
	$2\ ^1E''\ (n-\pi^*)$	8.06	0.000	0.000	8.21	0.000	0.000	7.82	0.000	81.49		
	$1\ ^1E'\ (\pi-\pi^*)$	8.06	0.441	0.467	8.28	0.437	0.472	8.04	0.386	88.79		
	$2\ ^1E'\ (\pi-\pi^*)$	9.93	0.011	0.012	10.24	0.058	0.059	9.44	0.005	74.27		
s-tetrazine	$1\ ^1B_{3u}\ (n-\pi^*)$	2.47	0.007	0.008	2.72	0.009	0.009	2.54	0.007	89.57		
	$1\ ^1A_u\ (\pi-\pi^*)$	3.68	0.000	0.000	4.08	0.000	0.000	3.80	0.000	87.51		
	$1\ ^1B_{1g}\ (n-\pi^*)$	5.11	0.000	0.000	5.33	0.000	0.000	4.98	0.000	82.48		
	$1\ ^1B_{2u}\ (\pi-\pi^*)$	5.20	0.046	0.050	5.27	0.047	0.050	5.12	0.044	84.59		
	$1\ ^1B_{2g}\ (\pi-\pi^*)$	5.54	0.000	0.000	5.70	0.000	0.000	5.34	0.000	80.73		
	$2\ ^1A_u\ (n-\pi^*)$	5.50	0.000	0.000	5.70	0.000	0.000	5.46	0.000	87.38		
	$2\ ^1B_{2g}\ (n-\pi^*)$	6.33	0.000	0.000	6.77	0.000	0.000	6.25	0.000	79.17		
	$2\ ^1B_{3u}\ (n-\pi^*)$	6.71	0.011	0.012	7.00	0.012	0.013	6.68	0.011	86.74		
	$2\ ^1B_{1g}\ (n-\pi^*)$	6.91	0.000	0.000	7.25	0.000	0.000	6.87	0.000	84.73		
	$3\ ^1B_{1g}\ (n-\pi^*)$	7.65	0.000	0.000	8.36	0.000	0.000	7.09	0.000	63.21		
	$1\ ^1B_{1u}\ (\pi-\pi^*)$	7.60	0.017	0.018	7.66	0.003	0.003	7.45	0.002	91.05		
	$2\ ^1B_{1u}\ (\pi-\pi^*)$	7.75	0.376	0.394	8.06	0.381	0.413	7.79	0.349	90.16		
	$3\ ^1B_{3g}\ (\pi-\pi^*)$	8.98	0.000	0.000	9.43	0.000	0.000	8.48	0.000	63.57		
	$2\ ^1B_{2u}\ (\pi-\pi^*)$	8.65	0.367	0.390	8.88	0.333	0.362	8.51	0.307	87.73		
formaldehyde	$1\ ^1A_2\ (n-\pi^*)$	4.10	0.000	0.000	3.97	0.000	0.000	3.95	0.000	91.16	3.93	0.000
	$1\ ^1B_1\ (\sigma-\pi^*)$	9.36	0.003	0.003	9.26	0.003	0.003	9.19	0.003	90.94	9.17	0.003
	$3\ ^1A_1\ (\pi-\pi^*)$	10.34	0.368	0.390	10.54	0.373	0.382	10.45	0.348	91.33	10.44	0.347
acetone	$1\ ^1A_2\ (n-\pi^*)$	4.53	0.000	0.000	4.44	0.000	0.000	4.40	0.000	90.85		
	$1\ ^1B_1\ (\sigma-\pi^*)$	9.30	0.000	0.000	9.26	0.000	0.000	9.17	0.000	91.46		
	$3\ ^1A_1\ (\pi-\pi^*)$	9.74	0.297	0.318	9.86	0.257	0.266	9.65	0.245	90.13		
p-benzoquinone	$1\ ^1B_{1g}\ (n-\pi^*)$	2.81	0.000	0.000	3.07	0.000	0.000	2.75	0.000	84.08		
	$1\ ^1A_u\ (n-\pi^*)$	2.92	0.000	0.000	3.19	0.000	0.000	2.85	0.000	83.06		
	$1\ ^1B_{3g}\ (\pi-\pi^*)$	4.69	0.000	0.000	4.93	0.000	0.000	4.59	0.000	87.92		
	$1\ ^1B_{1u}\ (\pi-\pi^*)$	5.59	0.539	0.606	5.89	0.558	0.595	5.62	0.485	88.35		
	$1\ ^1B_{3u}\ (n-\pi^*)$	5.69	0.000	0.000	6.55	0.001	0.001	5.83	0.000	75.25		
	$2\ ^1B_{3g}\ (\pi-\pi^*)$	7.36	0.000	0.000	7.62	0.000	0.000	7.28	0.000	83.86		
	$2\ ^1B_{1u}\ (\pi-\pi^*)$	8.31	0.545	0.614	8.47	0.506	0.531	7.82	0.131	68.70		
formamide	$1\ ^1A''\ (n-\pi^*)$	5.76	0.001	0.001	5.66	0.001	0.001	5.66	0.001	90.75	5.63	0.001
	$2\ ^1A'\ (\pi-\pi^*)^b$	7.20	0.000	0.001	7.51	0.067	0.070	7.24	0.030	87.89	7.24	0.030
	$3\ ^1A'\ (n-R)^b$	8.16	0.389	0.406	8.52	0.373	0.387	8.27	0.386	87.95	8.27	0.388
	$4\ ^1A'\ (n-R)$	8.00	0.229	0.236	8.73	0.132	0.134	8.47	0.125	87.86	8.46	0.122
	$7\ ^1A'\ (\pi-\pi^*)^c$	11.50	0.124	0.127	11.33	0.102	0.105	10.94	0.110	86.64	10.90	0.104
	$8\ ^1A'\ (n-R)^c$	11.24	0.009	0.010	11.98	0.037	0.038	11.77	0.021	89.25	11.75	0.028
acetamide	$1\ ^1A''\ (n-\pi^*)$	5.77	0.001	0.001	5.72	0.001	0.001	5.70	0.001	90.63		
	$3\ ^1A'\ (\pi-\pi^*)$	7.67	0.198	0.209	7.85	0.223	0.231	7.67	0.207	89.08		

Table 1. continued

molecule	state	CC2			CCSD			CC3			CCSDT	
		ΔE	f_{LR}	f_{EOM}	ΔE	f_{LR}	f_{EOM}	ΔE	f_{LR}	singles[a]	ΔE	f_{LR}
	8 ¹A′ (π−π*)	10.71	0.278	0.288	10.77	0.299	0.305	10.51	0.263	88.67		
propanamide	1 ¹A″ (n−π*)	5.79	0.000	0.000	5.74	0.000	0.000	5.72	0.000	90.64		
	3 ¹A′ (π−π*)	7.57	0.136	0.144	7.80	0.180	0.186	7.62	0.170	89.16		
	7 ¹A′ (π−π*)	10.33	0.188	0.195	10.33	0.148	0.152	10.07	0.136	89.04		
cytosine	2 ¹A′ (π−π*)	4.80	0.049	0.053	4.98	0.058	0.062	4.72	0.046	85.92		
	1 ¹A″ (n−π*)	5.02	0.001	0.001	5.45	0.002	0.002	5.16	0.001	85.80		
	2 ¹A″ (n−π*)	5.44	0.002	0.002	6.00	0.000	0.000	5.52	0.001	83.00		
	3 ¹A′ (π−π*)	5.72	0.165	0.176	5.95	0.177	0.186	5.61	0.130	84.52		
	3 ¹A″ (n−π*)	5.98	0.000	0.000	6.37	0.000	0.000	5.97	0.000	81.26		
	4 ¹A′ (π−π*)	6.65	0.631	0.672	6.81	0.607	0.641	6.61	0.520	88.06		
	6 ¹A″ (n−π*)	6.84	0.000	0.000	7.16	0.001	0.001	6.83		89.13		
thymine	1 ¹A″ (n−π*)	4.95	0.000	0.000	5.14	0.000	0.000	4.94	0.000	86.36		
	2 ¹A′ (π−π*)	5.39	0.197	0.218	5.60	0.222	0.235	5.34	0.172	88.96		
	3 ¹A′ (π−π*)	6.47	0.080	0.087	6.78	0.071	0.075	6.34	0.072	82.92		
	2 ¹A″ (n−π*)	6.34	0.000	0.000	6.58	0.000	0.000	6.59	0.000	89.32		
	4 ¹A′ (π−π*)	6.80	0.250	0.262	7.05	0.285	0.297	6.71	0.197	88.41		
uracil	1 ¹A″ (n−π*)	4.92	0.000	0.000	5.12	0.000	0.000	4.90	0.000	86.02		
	2 ¹A′ (π−π*)	5.53	0.198	0.218	5.70	0.224	0.237	5.44	0.174	88.41		
	3 ¹A′ (π−π*)	6.44	0.058	0.063	6.76	0.061	0.064	6.29	0.046	82.70		
	2 ¹A″ (n−π*)	6.26	0.000	0.000	6.50	0.000	0.000	6.32	0.000	87.91		
	4 ¹A′ (π−π*)	6.97	0.188	0.197	7.19	0.209	0.220	6.84	0.152	88.14		
	5 ¹A″ (n−π*)	6.73	0.000	0.000	7.69	0.001	0.001	6.87		86.50		
	6 ¹A″ (n−π*)	7.12	0.000	0.000	7.74	0.000	0.000	7.12		83.49		
adenine	2 ¹A′ (π−π*)	5.29	0.037	0.040	5.37	0.002	0.003	5.18		85.73		
	1 ¹A″ (n−π*)	5.28	0.001	0.001	5.58	0.001	0.001	5.34	0.001	88.27		
	3 ¹A′ (π−π*)	5.42	0.277	0.297	5.61	0.297	0.315	5.39		86.22		
	2 ¹A″ (n−π*)	5.92	0.002	0.002	6.19	0.002	0.002	5.96	0.002	88.88		
	4 ¹A′ (π−π*)	6.59	0.497	0.521	6.83	0.513	0.552	6.53		86.04		

[a]Singles contribution of the excited state CC3 wave function is also listed, as calculated by Dalton.[39] [b]Strong mixing between these two states. [c]Strong mixing between these two states.

that for larger systems the approximate methods show somewhat different accuracy pattern than for small molecules. It seems to be time for a systematic investigation.

Starting point is the excellent series of benchmark studies by Thiel and co-workers,[18−23] where a test set of 28 molecules and about 150 singlet excited states have been studied. DFT methods (TDDFT with various functionals and DFT/MRCI[24]) have been compared in ref 19, with the conclusion that—at least with the TZVP basis—the TDDFT with B3LYP and DFT/MRCI seem to be the most reliable. Ab initio methods (CASPT2, CC2, CCSD, CC3) have been tested in ref 18. It was concluded that the CC2 method seems to perform better than CCSD,[18] while CCSD systematically overestimates the excitation energy, CC2 gives smaller error with respect to a "best estimate" set.[18] A noniterative Coupled Cluster method CCSDR(3)[25] has been tested in ref 20, while semiempirical methods were investigated in ref 23. Effect of extended basis was finally tested in refs 21 and 22; it was found that applying the aug-cc-pVTZ basis set instead of the TZVP one, the excitation energy is systematicly lowered by about 0.2 eV in average. These studies have been recently augmented with a systematic comparison of various coupled cluster triples methods by Watson et al.[26]

Concerning the Coupled Cluster methods, the conclusions of Thiel and co-workers contradict somewhat to ours obtained by systematic calculations on the fragments of DNA.[14−16] In particular, the accuracy of CC2 in some cases seemed to be less reliable than predicted by Thiel's work. Therefore, we decided to extend these benchmarks by making it even more systematic by

performing additional calculations for singlet excited states. First, we augmented the CC3 data by calculations on the larger systems, in particular nucleobases. Second, to check the reliability of CC3, which, beside the CASPT2, was used as the reference by Thiel et al., we performed EOM-CCSDT calculations for some of the smaller systems. Finally, we have also calculated the oscillator strength by CC3 method for the whole set to provide high level benchmark also for this quantity.

■ METHODS OF CALCULATIONS

There are two, seemingly very different ways to extend Coupled Cluster (CC) theory for excited states. The one is Linear Response (LR) theory,[6,7,27] the other is Equation of Motion (EOM)[5,28,29] extension of CC theory. These methods have been reviewed recently;[10,30] therefore, for details we refer to these articles. For the discussion below, it seems enough to mention that the two strategies result in methods that are equivalent if excitation energy is of interest:[30,31] for example, CCSD-LR[27] and EOM-CCSD[28] will give the same excitation energy. There are, however, also two important differences between the formalisms: one concerns the calculation of transition moment,[31] the other the derivation of approximate versions.

As of the former, EOM methods simply calculate the matrix element of the dipole operator between the excited and ground state wave functions,[28] while LR uses response arguments.[31] The latter requires the solution of a response equation; therefore, it is more expensive. On the other hand, one can argue that the EOM way does not provide an intensive quantity, while LR theory

does.[31] Since for nontruncated (full-CC) case the two methods give the same results,[31] one can hope that by using accurate wave function, the discrepancy between the definitions will not be large.

LR and EOM treatments lead to different methods even for the energy, if perturbation theory is used to truncate the equations. In case of LR theory, CC2-LR[32] has been derived as approximation to CCSD-LR, while CC3-LR[13] was worked out to approximate CCSDT-LR. In case of EOM, the corresponding methods are EOM-CCSD(2)[11] and Partitioned EOM-MBPT(2)[33] to approximate EOM-CCSD, as well as EOM-CCSDT-1[34] and EOM-CCSDT-3[12] to approximate EOM-CCSDT.[35] In what follows, if not misleading, the LR and EOM designations will be omitted, for example CC2 means CC2-LR and CCSDT means EOM-CCSDT if excitations energies are reported.

Triples methods have been benchmarked recently,[26] while second order methods are under investigation in our laboratory. In this paper, we investigate very carefully the CC2−CCSD−CC3−CCSDT series, calculating excitation energies and oscillator strength for singlet valence states both in LR and EOM framework.

The calculations have been performed with different programs. CFOUR[36] has been used for CC2, CCSD, and CC3 excitation energy calculations and for the evaluation of the EOM style oscillator strength. MRCC[37] has been used for the CCSDT calculations and to evaluate the LR style oscillator strength for CCSDT.[38] Dalton2013[39,40] was used for LR type CC2, CCSD, and CC3 excitation energies and oscillator strength.

In order to compare with the results of Thiel and co-workers, the same TZVP basis set[41] was used. We are aware that such basis can not describe Rydberg states and the missing diffuse functions produce some artifacts due to unphyiscal mixing of states. If relevant, we will mention these complications in the discussion below. However, comparison between different methods can be done even for such cases.

To be able to perform also the calculations including triple excitations, the core electrons have been frozen in all calculations presented here. This is in contrast to the calculations of Schreiber et al.,[18] who published all electron calculations. This difference of the ansatz does not introduce discrepancy larger than 0.01 eV.

Geometries have also be taken from ref 18, which are optimized structures at the MP2/6-31G* level.

For the representation of the character of excited states, the natural orbitals of the difference density of the ground and excited states were applied. These natural orbitals along with the corresponding occupation numbers allow an unbiased characterization of $\pi-\pi*$, $n-\pi*$ and also Rydberg states. The single excitation contribution of an excited state is measured as in Dalton,[39] the values used are obtained from the CC3 calculations.

■ RESULTS AND DISCUSSION

Table 1 shows the results of all calculations. Excitations energies and oscillator strengths are listed, which were obtained at the CC2, CCSD, CC3, and CCSDT levels of theory. Oscillator strengths are given in both the EOM and LR representation (see above). In addition, singles contribution to the excited state CC3 wave function is also listed, as calculated by Dalton.[39]

Some of the results in the table might seem as repetition of those of Schreiber et al.:[18] CC2 as well as CCSD excitation energies and the corresponding LR type oscillator strength were already published in the cited works. Also, for most of the

molecules CC3 excitation energies were available before. The numbers here have been, however, obtained within the frozen core approximation, while Schreiber et al.[18] performed all electron calculations. The differences are quite small not exceeding 0.01 eV, and therefore, recalculation seems not be justified. We have several reasons for doing this, though. First, to be able to perform CC3 calculations for all molecules and CCSDT calculations for some of them, the frozen core approximation is necessary. Then, for a fair comparison of different methods, all the calculations need to be done at the same level. In addition, when checking the results, we have realized some misassignment and inconsistency in the original data. In particular, the neglect of the improperly described Rydberg transitions caused several problems. The table now includes a more consistent set of data which should not contain any of the above problems. For example, to solve the problem caused by the Rydberg transitions, in some cases, we list the excitation energy of these transitions, as well, if the mixing with the valence state does not allow a clear assignment (see for example the discussion on formamide below.)

The most important differences to the results of Schreiber et al.[18] are the following: obvious missprints have been detected for 3 $^1A_1$ state of cyclopentadiene (excitation energy is 8.69 eV instead of 6.69 eV), for 2 $^1A'$ state of formamide (excitation energy is 8.52 instead of 4.52 eV), for 1 $^1A''$ and 2 $^1A''$ states of cytosine (excitation energies are 5.01 and 5.43 eV instead of 5.13 and 5.01 eV), for 3 $^1A'$ state of propanamide (oscillator strength is 0.180 instead of 0.108), modified state numbering (we have chosen to include the not listed Rydberg-like states) was used for imidazole, pyridine, pyrazine, formaldehyde, acetone, formamide, acetamide, propanamide, and uracil.

There are two cases where, on the basis of the natural orbitals of the difference density, we suggest different assignment than Schreiber et al.[18] In case of formamide, we find that 2 $^1A'$ and 3 $^1A'$ as well as 7 $^1A'$ and 8 $^1A'$ pairs of states are strong mixture of $n-R$ and $\pi-\pi*$ components. We see both in the natural orbitals as well as in the expansion coefficients larger $\pi-\pi*$ contribution for states 2 $^1A'$ and 7 $^1A'$, respectively. CC2 mixes up the order of 7 $^1A'$ and 8 $^1A'$ states. Strangely, the large oscillator strength does not go along with this assignment, 3 $^1A'$ shows large oscillator strength. Note, however, that 4 $^1A'$, which is solely a $n-R$ transitions, also bears quite sizable oscillator strength. This is clearly an artifact of the basis we use and therefore not worthy of further discussion. The other case is cytosine: here, we suggest to change the relative order of the 1 $^1A''$ and 2 $^1A''$ states for CC2 and CCSD.

CCSDT excitation energies and oscillator strengths (LR type) could be obtained for the smaller systems (ethene, butadiene, cyclopropene, cyclopentadiene, formaldehyde, and formamide). The agreement between CCSDT and CC3 excitations energies is striking: for single excited states, the largest deviation is 0.04 eV (formamide), but in most cases, it is only 0.01−0.02 eV. (Larger discrepancy is found for the 2 ^1A_g state of butadiene, but this one is clearly a double excited state, which can not be treated properly by any of these CC type methods.) Similar good agreement can be found for the oscillator strength: the discrepancy is very small, even for larger values it is less than 0.01 au for most cases. The largest discrepancy has been found for the 3 $^1A_1$ state of cyclopentadiene. One can therefore conclude that the CC3 results form a very accurate set of benchmark values and comparison to these will give a reliable picture of the accuracy of other methods for both excitation energy and oscillator strength.

The large number of data does not allow a detailed analysis discussing the discrepancies individually, even the molecules cannot be discussed one by one. On the other hand, it allows a detailed statistical analysis. Since it is well-known and theoretically justified that the accuracy of the approximate CC methods diminishes with increasing double excitation character, we define two sets of states for this analysis. The first includes states with a singles contribution larger than 90%, while the second set includes states with this value being larger than 80%. This way there are 43 states in the first set, while there are 126 states in the second, and only 19 states have been completely dropped from the analysis. The latter are either double excited states, such as the $2\ ^1A_g$ state of butadiene, or higher excited states: the approximate methods clearly does not work for these, and the discrepancy often can be as large as 1 eV. Neither of the methods are recommended for these states, and even the accuracy of CC3 is questionable; therefore, their omission from the analysis is justified.

Table 2. Deviation of Excitation Energies for All, for Only $\pi - \pi^*$ and for Only $n-\pi^*$ States with Respect to CC3/TZVP Values above 90% of Single Excitation Contribution

	CC2			CCSD		
	$\Delta E^{(all)}$	$\Delta E^{(\pi-\pi^*)}$	$\Delta E^{(n-\pi^*)}$	$\Delta E^{(all)}$	$\Delta E^{(\pi-\pi^*)}$	$\Delta E^{(n-\pi^*)}$
count	43	35	5	43	35	5
mean	0.04	0.03	0.10	0.16	0.18	0.02
mean abs. dev.	0.08	0.08	0.03	0.07	0.05	0.01
RMS	0.11	0.11	0.11	0.18	0.19	0.02
std. dev.	0.10	0.11	0.03	0.08	0.06	0.01
max.	0.27	0.27	0.15	0.30	0.30	0.04

Table 2 shows the statistics for the first set, while in Figure 1 the error of CC2 and CCSD with respect to CC3 is shown as a function of the singles contribution. Beside the overall statistics, in the table separate columns are devoted to the $\pi-\pi^*$ and $n-\pi^*$ states. For the whole set, CC2 shows significantly smaller mean error, it is only 0.04 eV, while the value for CCSD is 0.16 eV. Since this first set includes mostly $\pi-\pi^*$ transitions, the mean error is similar for this set: 0.03 and 0.18 eV for CC2 and CCSD, respectively. However, for these transitions CCSD seems to be more systematic, since both mean absolute deviations and standard deviations are significantly smaller for CCSD than for CC2. Figure 1 nicely shows this as well: CCSD systematically overestimates the CC3 values by about 0.2 eV with small

deviation, while CC2 values are scattered around the CC3 values but with somewhat larger deviation. The maximum discrepancy is 0.3 eV for CCSD ($3\ ^1A_1$ state of furan) and 0.27 eV for CC2 ($3\ ^1A_1$ state of pyrrole), the former deviating less from the mean value, supporting the conclusion on the systematic nature of the CCSD results. There are only five $n-\pi^*$ states in this set: the lowest excited states of formaldehyde, acetone, fomamide, acetamide, and propanamide. For these, interestingly, the trend seems to be opposite, the mean value is very small for CCSD and 0.1 eV for CC2 (see also in Figure 1).

The same quantities for the larger set (single excitation contribution above 80%) are given in Table 3. This set includes

Table 3. Deviation of Excitation Energies for All, Only for $\pi-\pi^*$ and for $n-\pi^*$ States with Respect to CC3/TZVP Values above 80% of Single Excitation Contribution

	CC2			CCSD		
	$\Delta E^{(all)}$	$\Delta E^{(\pi-\pi^*)}$	$\Delta E^{(n-\pi^*)}$	$\Delta E^{(all)}$	$\Delta E^{(\pi-\pi^*)}$	$\Delta E^{(n-\pi^*)}$
count	126	77	43	126	77	43
mean	0.04	0.07	0.01	0.23	0.22	0.25
mean abs. dev.	0.09	0.09	0.08	0.08	0.06	0.11
RMS	0.13	0.14	0.09	0.25	0.23	0.30
std. dev.	0.12	0.12	0.09	0.11	0.08	0.15
max.	0.56	0.56	0.22	0.83	0.47	0.83

those molecules which are of particular importance for our projects, most states of larger molecules, heterocycles, nucleobases, keto and amino groups, etc. The picture is very similar to the 90% case: CC2 shows very small mean deviation, the corresponding excitation energies are scattered around the CC3 values, while CCSD has a systematic error slightly above 0.2 eV. Again, the mean absolute deviation and standard deviation is smaller for CCSD. The figure also shows these trends. The behavior of the results is the same now also for $n-\pi^*$ states although some exceptionally large errors also occur.

Not considering the Rydberg states (for which the basis set is not adequate anyway), there is only the $7\ ^1A'$ ($\pi-\pi^*$) transition of formamide with outlier discrepancy (0.56 eV). The relevance of this failure is most probably not high: the artificial valence−Rydberg mixing have been discussed already for these states above. Note also that by changing the order of $7\ ^1A'$ and $8\ ^1A'$ the error would be within the error bar; however, there would be large discrepancy for the oscillator strength.

In case of CCSD, the largest discrepancy (0.47 eV) was found for the $3\ ^1A'$ ($\pi-\pi^*$) transition of uracil; as Figure 1 shows, this is not an outlier, as the decrease of single excitation contribution
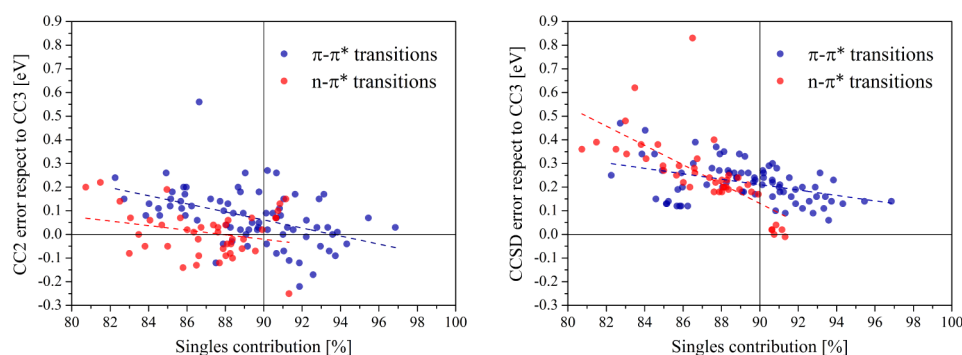

Figure 1. Discrepancy of CC2 (left panel) and CCSD (right panel) excitation energies with respect to CC3 as a function of the singles contribution. The vertical line separates transitions with higher than 90% singles contribution (first set).
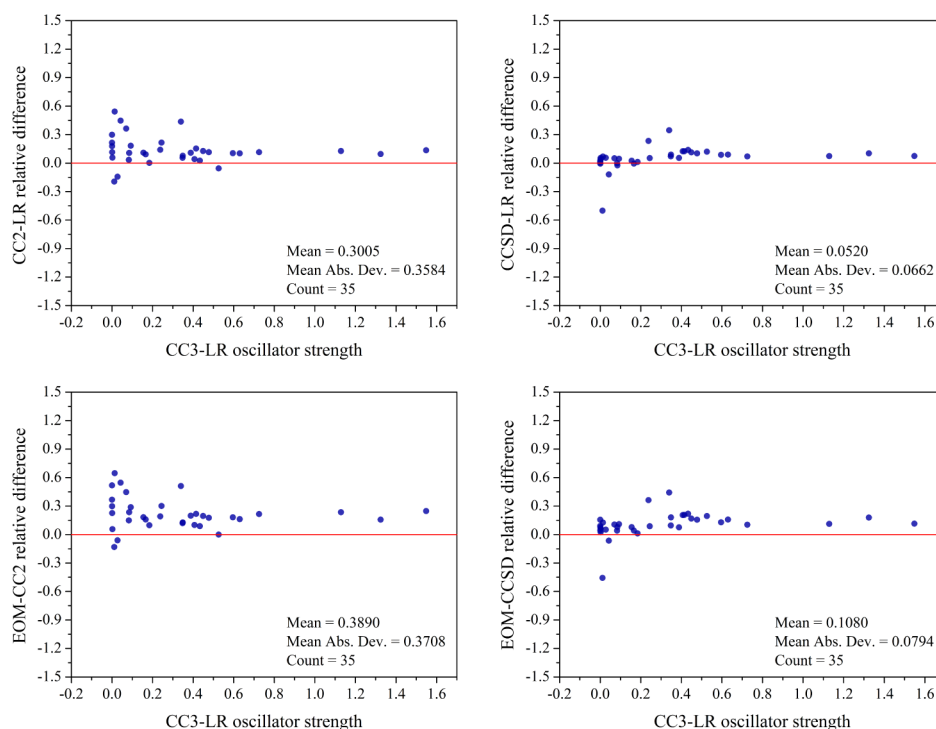
Figure 2. Relative error of the calculated oscillator strength as the function of the CC3 (LR) value. Left panels, CC2; right panels, CCSD; top panels, LR values; bottom panels, EOM values. Only states with single excitation contribution of 90% or higher are included. See text for more detail. The CC2 value of tetrazine have been omitted because near degeneracy of two states produces very large relative error for the small value.
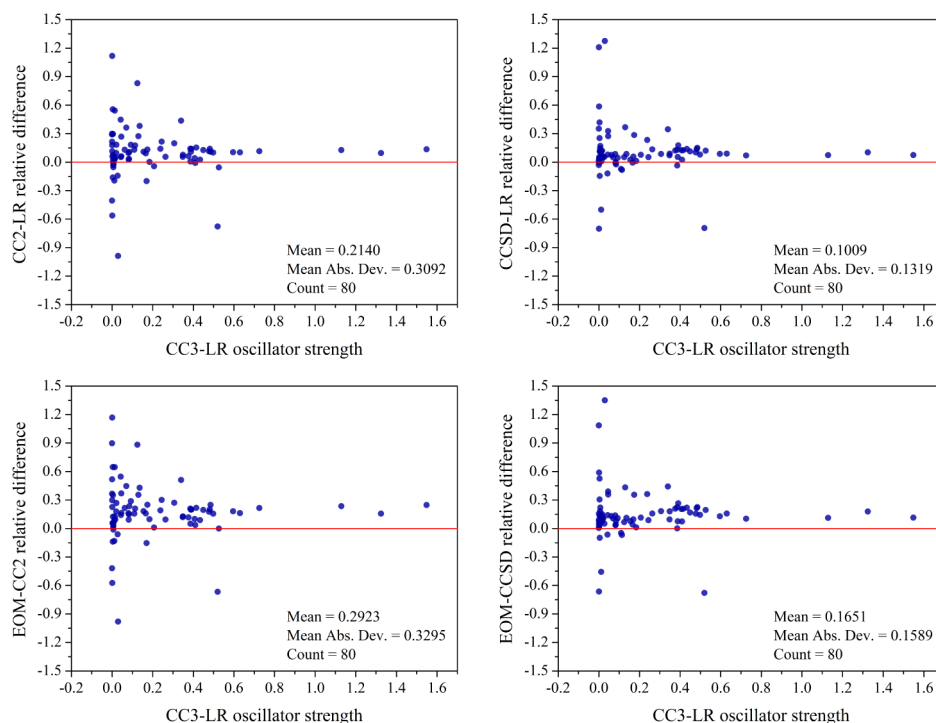

Figure 3. Relative error of the calculated oscillator strength as the function of the CC3 (LR) value. Left panels, CC2; right panels, CCSD; top panels, LR values; bottom panels, EOM values. Only states with single excitation contribution of 80% or higher are included. See text for more detail. CC2 value for tetrazine and furan have been omitted due very large relative error of very small values.

causes the error of the excitation energy to grow. In case of $n-\pi*$ transitions, there are, however, two real outliers: the 3 ^{1}A″ ($n-\pi*$) (0.83 eV) and 5 ^{1}A″ ($n-\pi*$) (0.63 eV) states of uracil. In these cases, there are two lone pair sites (carbonyl oxygen atoms), which, together with the corresponding $\pi*$ orbitals,

allows for four low lying $n-\pi*$ states. CCSD fails badly for the third and fourth $n-\pi*$ states, the discrepancy between CC3 and CCSD excitation energies are as large as 0.6−0.8 eV. On the other hand, CC2 results are very close to the CC3 values. We can not give any explanation for this peculiar failure, the only thing

we could observe is that the natural orbitals of the difference density show a bit stronger mixing of the individual components in case of CCSD. In a subsequent paper, we plan to investigate this problem in more detail. No other state exists where the discrepancy between CCSD and CC3 results are larger than 0.4 eV: considering that CCSD has a systematic error of about 0.2 eV, one can state that, in this repsect, too, CCSD is somewhat more reliable than CC2 where 0.3 eV discrepancies appear dispite of the mean error around 0 eV. Uracil is, however, a worrisome example in case of CCSD.

As the novelty of this paper, the oscillator strengths will be benchmarked and discussed now. In Figures 2 and 3 the relative error of the oscillator strength as a function of the CC3 value is depicted for states with over 90% and 80% single excitation contribution, respectively. The relative error has been chosen for this analysis to allow the comparison of the error of quantities which are very different in magnitude; oscillator strengths change several orders of magnitude in the present set.

It was shown above that CC3 oscillator strength values are quite accurate compared to CCSDT ones; therefore, we safely can use these for testing the CCSD and CC2 values. First compare EOM and LR style values. In all cases (CC2, CCSD, large or small set), the EOM values always show larger error than the LR ones. However, CCSD is always more accurate than CC2, the former having an error somewhat below and above 10% for the LR and EOM quantities, respectively, while CC2 values are clearly more scattered than the respective CCSD values. CCSD-LR values are clearly superior to EOM-CCSD ones, the difference between them is, however, small. Therefore, for applications where this small percentage of error is not relevant, it is enough to calculate this quantity by the substantially cheaper EOM-CCSD method.

In case of CC3 and CCSDT, only LR style oscillator strength is available in programs. Since wave functions including triple excitations are more accurate (closer to full-CI limit), one can assume that the difference between the two types of quantities is even smaller than at the SD level and eventually one can save some resources by not solving the response equation. A quantitative check of this hypotesis will be tested soon.

CONCLUSIONS

In this paper, we have benchmarked Coupled Cluster methods for calculation of excitation energies and oscillator strength. The test set of Thiel et al.[18−23] has been used, and their earlier calculations have been extended by CC3 oscillator strength, CC3 excitation energies for larger molecules, and CCSDT results for some small molecules.

In contrary to the studies by Thiel et al.,[18,21] we do not use "best estimate" to judge the accuracy of the methods; instead, we use the highest possible level to set benchmark for the given one-electron basis (TZVP in this case). In comparison to CCSDT results, it has been observed that CC3 excitation energies and oscillator strength are very accurate for single excited states. (For ethene, CCSDTQ calculation was also performed, resulting vertical excitation energy of 8.358 eV and the oscillator strength of 0.386 which should be compared with the CCSDT values of 8.383 eV and 0.389, respectively.) Therefore, CC3 is recommended and used as benchmark in this study.

Analysis of the results obtained for about 150 singlet excited states of 28 molecules showed that both CC2 and CCSD give quite accurate results, difference to CC3 excitations energies is typically not larger than 0.2−0.3 eV. While the mean deviation of the CC2 excitation energies is close to zero, that is, CC2 values

are scattered around the CC3 values, the CCSD systematically overshoots the CC3 results by about 0.2 eV except a few $n−\pi^*$ transition with large singles contribution. The standard deviation is somewhat smaller for CCSD, which means that these are usually closer to the mean value. However, while in the case of CC2 the error is always smaller than 0.3 eV for clean valence states, CCSD has surprisingly large error for two of the four lowest $n−\pi^*$ transitions of uracil.

LR and EOM style oscillator strength have also been compared. At both CC2 and CCSD level the LR style oscillator strength are more accurate, but in case of CCSD, the difference between LR and EOM style values are not very large (1−2%). This means that the extra computational effort of calculating LR style values can probably saved already at the CCSD level, and even more so on levels including triple excitations.

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Notes
The authors declare no competing financial interest.

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