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Benchmarking two-photon absorption with CC3 quadratic response theory, and comparison with density-functional response theory

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We present a detailed study of the effects of electron correlation on two-photon absorption calculated by coupled cluster quadratic response theory. The hierarchy of coupled cluster models CCS, CC2, CCSD, and CC3 has been used to investigate the effects of electron correlation on the two-photon absorption cross sections of formaldehyde (CH_2O), diacetylene (C_4H_2), and water (H_2O). In particular, the effects of triple excitations on two-photon transition cross sections are determined for the first time. In addition, we present a detailed comparison of the coupled cluster results with those obtained from Hartree-Fock and density-functional response theories. We have investigated the local-density approximation, the pure Becke-Lee-Yang-Parr (BLYP) functional, the hybrid Becke-3-parameter-Lee-Yang-Parr (B3LYP), and the Coulomb-attenuated B3LYP (CAM-B3LYP) functionals. Our results show that the CAM-B3LYP functional, when used in conjuction with a one-particle basis-set containing diffuse functions, has much promise; however, care must still be exercised for diffuse Rydberg-type states. © *2006 American Institute of Physics.*
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INTRODUCTION

In the computation of multiphoton transitions, response theory has become the *ab initio* method of choice. For two-photon absorption, the transition strength may be calculated from the single residue of the quadratic response function.[1] Coupled cluster singles and doubles (CCSD) response theory has previously been used to determine the two-photon transition probability rate constants of helium, neon, and argon, with good agreement with experimental results.[2] The effect of triple excitations has not previously been investigated for two-photon absorption; indeed only a few other coupled cluster studies of two-photon absorption have been performed.[3,4] On the other hand, a number of calculations of two-photon absorption at the uncorrelated Hartree-Fock (HF),[5–9] multiconfiguration self-consistent-field (MCSCF),[5,10,11] and density-functional theory[12–14] (DFT) levels have appeared. Here we perform some benchmark computations on the two-photon absorption of selected states of formaldehyde (CH_2O), diacetylene (C_4H_2), and water

(H_2O), with large one-particle basis sets, using a recent implementation of CC3 quadratic response theory.[15,16]

Benchmarking two-photon absorption from response theoretical methods is important as multiphoton spectroscopy is becoming an increasingly important spectroscopic technique, enabling the excitation of inaccessible one-photon states, with a much greater resolution power in, for example, photodynamic therapies.[17] However, there are significant problems in assigning absolute values to two-photon absorption cross sections, including vibrational effects, solvent effects, laser factors, and so on. This paper is aimed at obtaining a greater understanding of the effects of correlation and single-particle basis-set errors. We hope that this will be a first step on the road to the accurate computational determination of absolute two-photon absorption cross sections.

The coupled cluster hierarchy of models, as generated by the coupled cluster singles (CCS) model, the CC2 model,[18] the coupled cluster singles-and-doubles (CCSD) model,[19] the CC3 model,[20,21] the coupled cluster singles-doubles-and-triples model CCSDT,[22] etc, has the appealing property that one is able to systematically approach the exact correlated energy in a given one-particle basis set. Similarly one can

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TABLE I. Formaldehyde (CH$_2$O) two-photon absorption calculated from *ab initio* quadratic response theory. Excitation energy E (in eV) and two-photon transition strengths δ^{TP} (in a.u.) for the lowest excited (1 $^1A_2$) $n\pi^*$ state. Resonant absorption of two-photons each with half the excitation energy is assumed.

Basis	HF		CCS		CC2		CCSD		CC3	
	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}
cc-pVDZ	4.370	0.043	4.546	0.100	4.224	0.023	4.083	0.025	4.066	0.020
aug-cc-pVDZ	4.370	0.031	4.542	0.012	4.077	0.415	4.006	0.187	3.989	0.200
d-aug-cc-pVDZ	4.370	0.041	4.539	0.020	4.068	0.540	3.998	0.239	3.981	0.252
t-aug-cc-pVDZ	4.360	0.041	4.539	0.020	4.067	0.543	3.997	0.240	3.980	0.253
cc-pVTZ	4.390	0.023	4.576	0.058	4.136	0.002	4.043	0.007	4.000	0.003
aug-cc-pVTZ	4.380	0.035	4.565	0.015	4.053	0.379	3.995	0.168	3.951	0.193
d-aug-cc-pVTZ	4.380	0.034	4.563	0.015	4.050	0.409	3.993	0.175	3.948	0.201
t-aug-cc-pVTZ	4.380	0.035	4.563	0.015	4.049	0.412	3.993	0.177	3.948	0.202
cc-pVQZ	4.390	0.003	4.575	0.016	4.099	0.009	4.029	0.002	3.978	0.005
aug-cc-pVQZ	4.380	0.036	4.564	0.016	4.052	0.368	4.003	0.161	3.951	0.189
d-aug-cc-pVQZ	4.380	0.035	4.564	0.015	4.051	0.374	4.003	0.161	3.949	0.200
t-aug-cc-pVQZ	4.380	0.035	4.564	0.015	4.051	0.375	4.003	0.161		
cc-pV5Z	4.390	0.000	4.568	0.000	4.072	0.060	4.016	0.022		
aug-cc-pV5Z	4.380	0.034	4.564	0.014	4.053	0.348	4.006	0.151		
6-31G*	4.450	0.174	4.624	0.295	4.255	0.190	4.093	0.150	4.084	0.139
6-31+G*	4.410	0.061	4.577	0.122	4.136	0.011	4.017	0.000	4.016	0.000
6-31++G**	4.380	0.051	4.553	0.105	4.156	0.015	4.052	0.000	4.055	0.000
6-311++G**	4.360	0.049	4.531	0.098	4.107	0.006	4.008	0.001	3.987	0.000

investigate the effects of electron correlation on a particular property (static or dynamic) by comparing the properties derived from the response functions for each coupled cluster model. In particular, coupled cluster response theory has been shown to give highly accurate results for one-photon absorption (i.e., excitation energies and oscillator strengths), with a decrease in error of around a factor of 3 compared to full configuration interaction, at each succeeding coupled cluster model in the hierarchy.[23,24] Similar high quality is found in benchmark calculations of linear-response[25,26] and nonlinear-response functions,[27–31] from which the two-photon absorption derives. Indeed for molecules whose ground-state wave function is dominated by a single determinant, CC3 response theory represents the most accurate, generally applicable model available today for a range of response properties including nonlinear optical properties and excitation energies.

As an alternative to *ab initio* many-body response theory, DFT response theory has become increasingly popular for the computation of one-photon excitation energies, and associated oscillator strengths, of medium to large molecules where, for example, a coupled cluster wave-function treatment is presently intractable. In the Kohn-Sham DFT, one uses the density obtained from the one-particle Kohn-Sham determinant, together with an approximate exchange-correlation functional to obtain the ground-state energy. DFT response theory proceeds in a manner similar to Hartree-Fock response theory, typically making the temporal adiabatic approximation to the time-dependent exchange-correlation potential, and one obtains the response of the Kohn-Sham orbitals to an applied perturbation.

It is only recently that higher-order response methods have been generally available for DFT (Refs. 32–35) [for example, in the DALTON (Ref. 36) program (Ref. 35)]. In particular, the choice of exchange-correlation functional and basis-set requirements for two-photon transition strengths is not well understood. Here, in addition to benchmark coupled cluster results, we also report DFT results using the local-density approximation (LDA), the Becke-Lee-Yang-Parr (BLYP) functional,[37,38] the Becke-3-parameter-Lee-Yang-Parr B3LYP functional,[39] and the recently developed Coulomb-attenuated B3LYP (CAM-B3LYP) functional.[40] While there is no systematic improvement possible within DFT, the choice of functionals investigated here allows one to determine the importance of flexibility in the exchange contribution, by keeping the LYP correlation functional[38] fixed and investigating the use of Becke's standard exchange functional,[37] his three-parameter hybrid exchange functional,[39] and the Coulomb-attenuated extension of this functional by Yanai *et al.*, which was designed to give an improved long-range exchange potential by "switching on" and increasing the amount of pure Hartree-Fock exchange as the interelectronic distance increases.[40] As we show below, this increased flexibility in the exchange functional is crucial in getting two-photon transition strengths comparable to highly correlated *ab initio* methods.

In this study we have investigated the two-photon absorption of the following molecules: (a) formaldehyde (CH$_2$O), the $\tilde{X}\ ^1A_1 \rightarrow 1\ ^1A_2(n\pi*)$ transition; (b) diacetylene (C$_4$H$_2$), the $\tilde{X}\ ^1\Sigma_g^+ \rightarrow 1\ ^1\Pi_g$ transition; and (c) water (H$_2$O), the $\tilde{X}\ ^1A_1 \rightarrow 2,3\ ^1A_1$, 1, 2 $^1B_1$, and 1 $^1A_2$ transitions. For water, calculations up to the CCSD level have also been reported by Thomsen *et al.*[3] and Nielsen *et al.*[4] The transitions investigated here represent a reasonably broad range of excited states, i.e., from simple-valence transitions, to quasicharge-transfer transitions, to transitions involving Rydberg character.

054322-3   Two-photon absorption

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TABLE II. Formaldehyde (CH_2O) two-photon absorption calculated from density-functional quadratic response theory. Excitation energy E (in eV) and two-photon transition strengths δ^{TP} (in a.u.) for the lowest excited $(1\ ^1A_2)\ n\pi^*$ state. Resonant absorption of two-photons each with half the excitation energy is assumed.

Basis	LDA		BLYP		B3LYP		CAM-B3LYP	
	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}
cc-pVDZ	3.740	0.008	3.890	0.008	3.950	0.017	3.930	0.025
aug-cc-pVDZ	3.650	0.614	3.780	0.758	3.880	0.348	3.880	0.206
d-aug-cc-pVDZ	3.640	0.767	3.780	0.978	3.880	0.436	3.870	0.259
t-aug-cc-pVDZ	3.640	0.774	3.780	0.984	3.880	0.436	3.870	0.258
cc-pVTZ	3.720	0.001	3.880	0.002	3.950	0.001	3.940	0.004
aug-cc-pVTZ	3.660	0.661	3.800	0.841	3.900	0.387	3.900	0.229
d-aug-cc-pVTZ	3.660	0.724	3.800	0.951	3.900	0.415	3.900	0.239
t-aug-cc-pVTZ	3.660	0.731	3.800	0.957	3.900	0.419	3.900	0.242
cc-pVQZ	3.700	0.041	3.860	0.045	3.940	0.014	3.930	0.004
aug-cc-pVQZ	3.660	0.692	3.800	0.890	3.900	0.404	3.900	0.238
d-aug-cc-pVQZ	3.660	0.723	3.800	0.952	3.900	0.415	3.900	0.239
t-aug-cc-pVQZ	3.660	0.724	3.800	0.951	3.900	0.415	3.900	0.239
cc-pV5Z	3.680	0.147	3.830	0.169	3.920	0.071	3.910	0.034
aug-cc-pV5Z	3.660	0.693	3.800	0.896	3.900	0.398	3.900	0.231
d-aug-cc-pV5Z	3.660	0.723	3.800	0.948	3.900	0.414	3.900	0.238
t-aug-cc-pV5Z	3.660	0.722	3.800	0.949	3.900	0.414	3.900	0.238
6-31G*	3.830	0.137	3.990	0.139	4.050	0.149	4.020	0.156
6-31+G*	3.740	0.050	3.890	0.095	3.970	0.095	3.960	0.000
6-31++G**	3.710	0.070	3.860	0.136	3.860	0.136	3.930	0.000
6-311++G**	3.680	0.031	3.820	0.066	3.820	0.066	3.900	0.000

THEORY AND COMPUTATIONAL DETAILS

The sum-over-states (spectral or Lehman) representation of the two-photon transition moment is[41]

$$M_{f\leftarrow 0}^{\alpha\beta}(\omega_\beta) = \sum_{n\neq 0}\left[\frac{\langle f|(\beta-\langle 0|\beta|0\rangle)|n\rangle\langle n|\alpha|0\rangle}{(\omega_\alpha-\omega_{n0})}\right.$$
$$\left.+\frac{\langle f|(\alpha-\langle 0|\alpha|0\rangle)|n\rangle\langle n|\beta|0\rangle}{(\omega_\beta-\omega_{n0})}\right] \quad (1)$$

$$=\hat{P}^{\alpha\beta}(\omega_\alpha,\omega_\beta)\sum_n\frac{\langle f|\beta|n\rangle\langle n|\alpha|0\rangle}{(\omega_\alpha-\omega_{n0})}, \quad (2)$$

where $|0\rangle$, $|n\rangle$, and $|f\rangle$ are the initial, intermediate, and final electronic states, α and β are the components of the dipole operator $(\alpha,\beta=x,y,z)$, ω_{n0} is the transition frequency to the intermediate (virtual) state, and ω_α and ω_β are the photon energies which satisfy the matching condition that $\omega_\alpha+\omega_\beta=\omega_{f0}$. The operator $\hat{P}^{\alpha\beta}$ symmetrizes with respect to permutation of α and β together with their associated frequencies. In response theory of exact states, the two-photon transition moments are also symmetric with respect to complex conjugation and sign inversion of the frequencies. By contrast, in coupled cluster response theory, which uses a biorthonormal parametrization for bra and ket states, $M_{f\leftarrow 0}^{\alpha\beta}(\omega_\beta)$ and $M_{0\leftarrow f}^{\alpha\beta}(-\omega_\beta)$ are not related by complex conjugation. Instead, one works with transition strengths, which are obtained as a symmetrized product of "left" and "right" transition moments,[2,41,42]

$$S_{\alpha\beta,\gamma\delta}^{0f}(\omega) = \tfrac{1}{2}\{M_{0\leftarrow f}^{\alpha\beta}(-\omega)M_{f\leftarrow 0}^{\gamma\delta}(\omega)$$
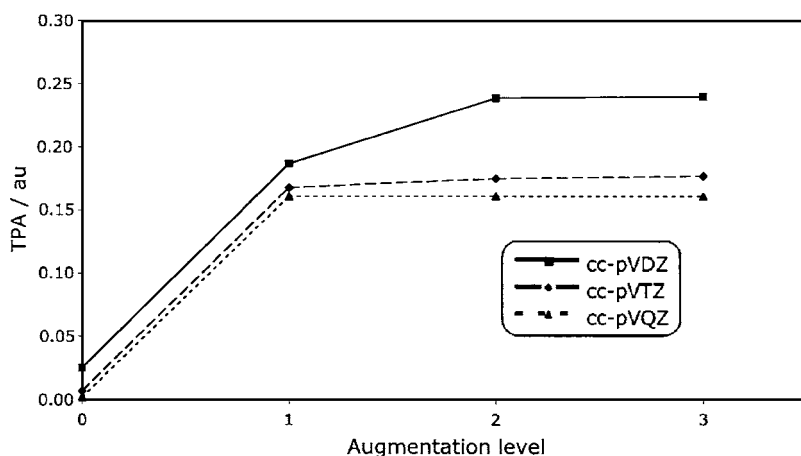$$+M_{0\leftarrow f}^{\gamma\delta}(-\omega)^*M_{f\leftarrow 0}^{\alpha\beta}(\omega)^*\}. \quad (3)$$

FIG. 1. Effect of cc-pVXZ $(X=D,T,Q)$ basis-set augmentation level in the computation of two-photon transition strengths to the lowest excited $(1\ ^1A_2)n\pi^*$ state of formaldehyde at the CCSD level.

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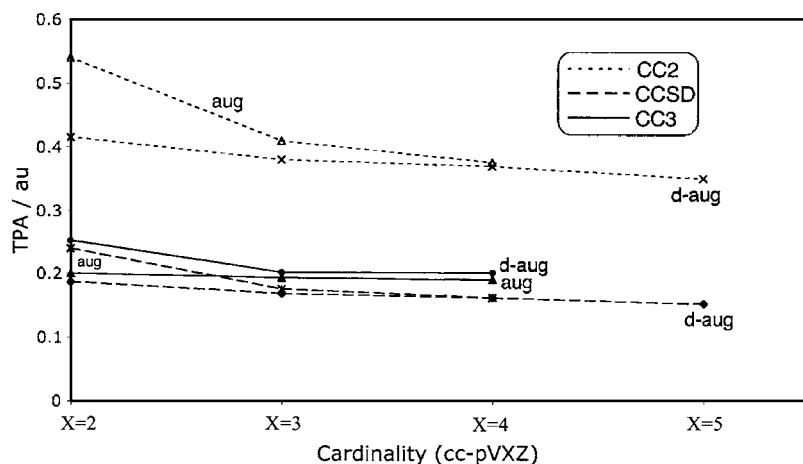
FIG. 2. Effect of cc-pVXZ ($X=D,T,Q$) basis-set cardinality in the computation of two-photon transition strengths to the ($1\,^1A_2$) $n\pi^*$ state of formaldehyde for the CC2, CCSD, and CC3 coupled cluster models, in both singly and doubly augmented basis sets.

Finally, the rotationally averaged two-photon transition strength is given by

$$\delta^{TP} = F\delta_F + G\delta_G + H\delta_H, \qquad (4)$$

$$\delta_F = \frac{1}{30} \sum_{\alpha,\beta} S_{\alpha\alpha\beta\beta}, \qquad (5)$$

$$\delta_G = \frac{1}{30} \sum_{\alpha,\beta} S_{\alpha\beta\alpha\beta}, \qquad (6)$$

$$\delta_H = \frac{1}{30} \sum_{\alpha,\beta} S_{\alpha\beta\beta\alpha}, \qquad (7)$$

where the F, G, and H coefficients depend on the polarization of the incident laser beams. For parallel linearly polarized light: $F=G=H=2$; for perpendicular linearly polarized light: $F=-1$, $G=4$, $H=1$; and for circularly polarized light: $F=-1$, $G=H=3$. The summations in Eqs. (5)–(7) are over dipole operator components, see Ref. 42 for further details. The results quoted in Tables I–VI refer to parallel linearly polarized light. The values of δ^{TP} for all light beam polarizations, and transition probability rate constants, are tabulated and given as supplementary material [see EPAPS supporting information (Ref. 43)].

Modern response theoretical methods do not use the sum-over-states expression [Eq. (2)] for the transition moments, rather much simpler sets of linear eigenvalue equa-

tions are solved.[41,44] In particular, see Ref. 45 for a discussion of direct iterative solutions of the random-phase approximation (RPA) equations, used in modern implemenations of DFT response theory.

The sum-over-states expression is nevertheless useful in an interpretative context, and as such shows that sufficent flexibility in the wave function is required in order to describe all the intermediate states appropriately. As we shall show this boils down to diffuse basis functions being an absolute necessity, even for simple low-lying valence excitations.

All computations were performed using a local version of the DALTON program[36] on an SGI Altix 3700/Itanium 2 machine. All electrons were correlated in the coupled cluster computations, i.e., the core orbitals were not kept frozen. In addition, the orbitals were not allowed to relax to the external fields in the coupled cluster calculations. In all calculations of two-photon transition strengths the resonant absorption of two photons each with half the excitation energy is assumed.

RESULTS AND DISCUSSION

Formaldehyde (CH_2O)

We begin by investigating the two-photon absorption in formaldehyde (CH_2O), which has a long history as a test molecule in response theory. The geometry was obtained from a B3LYP/cc-pVTZ optimization. The optimized geo-

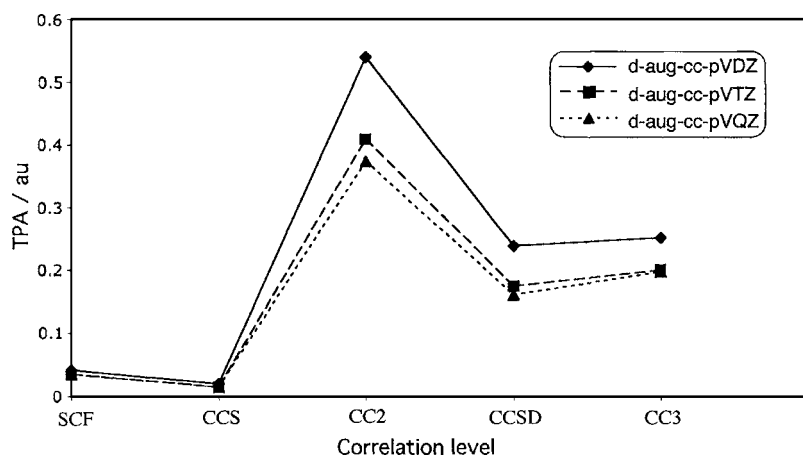
FIG. 3. Effect of electron correlation in the computation of two-photon transition strengths to the ($1\,^1A_2$) $n\pi^*$ state of formaldehyde as obtained from the coupled cluster hierarchy of models in the d-aug-cc-pVXZ ($X=D,T,Q$) basis sets.
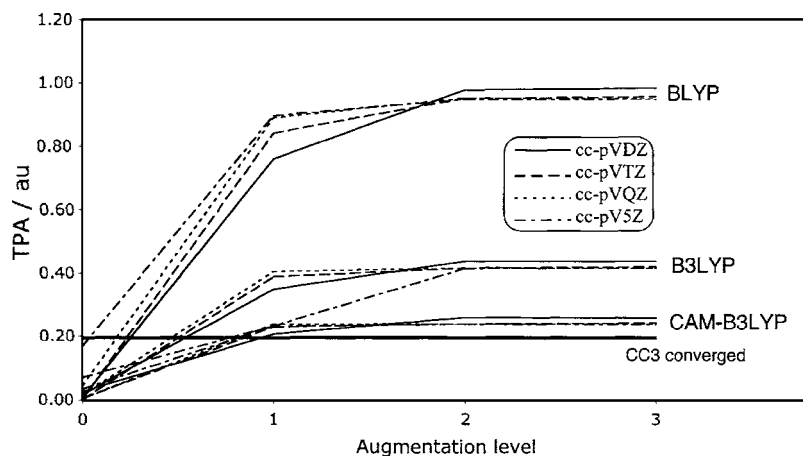
FIG. 4. Two-photon absorption transition strengths to the $(1\ ^1A_2)\ n\pi^*$ state of formaldehyde computed by density-functional response theory for the BLYP, B3LYP, and CAM-B3LYP functionals. The converged CC3 limit is also shown.

metrical parameters (in C_{2v} symmetry) are CO bond length $=1.211$ Å, CH bond length$=1.101$ Å, and the HCH angle $=116.168°$.

The *ab initio* results are listed in Table I and the DFT results in Table II. In Fig. 1 the convergence of the two-photon transition strength (δ^{TP}) with respect to augmentation level is shown for CCSD. Clearly, at least one set of diffuse basis functions is necessary. In the unaugmented cc-pVDZ basis, δ^{TP} is one order of magnitude smaller than the converged CC3 value of 0.200 a.u. Addition of one set of diffuse functions to the cc-pVDZ basis essentially gets the value correct, whereas the addition of more diffuse functions in an even-tempered manner, such that the ratio of the diffuse exponents between each set is constant, causes the value to converge about 25% too high. In the unaugmented cc-pVTZ and cc-pVQZ basis sets, δ^{TP} is two orders of magnitude smaller than the converged value but convergence is reached with a single set of diffuse functions. Figure 2 shows the convergence of δ^{TP} with respect to the cardinal number X of Dunning's cc-pVXZ basis sets. Monotonic convergence of δ^{TP} is observed for all coupled cluster models, which essentially reach their basis-set limit in the augmented triple-zeta basis. The difference between the singly and doubly augmented sets is negligible beyond the triple-zeta level.

Returning to diffuse basis functions, one may wonder why such functions are important for the $n\pi^*$ state of formaldehyde, which is a compact-localized valence state; indeed, the CC3 excitation energy is already correct in the cc-pVDZ basis, see Table I. To explain this, we need to examine the expression for the two-photon transition moment [Eq. (2)]. Although the final state may not need diffuse functions for an accurate representation, the intermediate states $|n\rangle$ contribute to the residue and the flexibility to describe these states is therefore important. It seems that, for a simple low-lying valence state such as the $n\pi^*$ state of formaldehyde, the aug-cc-pVTZ basis is the smallest basis required for a quantitative value of δ^{TP}.

For completeness, we have also tested the Pople-type basis sets in two-photon absorption calculations. As seen from Table I, the coupled cluster values in these basis sets are very poor. The CCSD and CC3 values of δ^{TP}, in particular, are four orders of magnitude too small for the basis sets with diffuse functions. These basis sets should therefore be avoided in two-photon coupled cluster calculations, giving erratic values that may or may not coincide with the converged values (e.g., in the 6-31G* basis).

Now let us examine the effect of electron correlation on δ^{TP} in coupled cluster theory, as illustrated in Fig. 3. Inter-

TABLE III. Diacetylene (C$_4$H$_2$) two-photon absorption calculated from *ab initio* quadratic response theory. Excitation energy E (in eV) and two-photon transition strengths δ^{TP} (in a.u.) for the lowest excited $(1\ ^1\Pi_g)\ \pi\pi^*$ state. Resonant absorption of two-photons each with half the excitation energy is assumed.

Basis	HF		CCS		CC2		CCSD		CC3	
	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}
cc-pVDZ	10.050	2.628	10.077	1.940	9.782	2.615	9.794	2.484	9.608	2.702
aug-cc-pVDZ	7.310	95.408	7.320	95.362	7.258	105.722	7.359	88.992	7.192	98.305
d-aug-cc-pVDZ	7.510	102.570	7.240	85.776	7.132	98.938	7.245	83.066	7.075	92.143
cc-pVTZ	9.380	16.002	9.394	14.675	9.227	14.198	9.283	12.882	9.077	14.089
aug-cc-pVTZ	7.270	91.433	7.273	91.233	7.320	97.768	7.408	82.870	7.214	92.614
d-aug-cc-pVTZ	7.230	86.317	7.237	85.739	7.286	92.272	7.380	78.411		
cc-pVQZ	8.760	30.979	8.769	29.248	8.826	33.314	8.861	29.090		
aug-cc-pVQZ	7.250	88.145	7.258	87.821	7.376	91.730	7.453	78.442		
d-aug-cc-pVQZ	7.230	86.263	7.240	85.669	7.359	89.613	7.439	76.979		
6-31G*	10.890	3.588	10.928	4.808	10.652	2.357	10.571	1.918	10.342	1.868
6-31+G*	7.730	95.751	7.736	94.220	7.644	112.527	7.695	93.782	7.480	105.624
6-31++G**	7.410	126.451	7.418	124.791	7.310	137.489	7.396	117.568	7.187	131.284
6-311++G**	7.470	105.936	7.473	104.967	7.389	112.116	7.473	96.417	7.269	107.466

TABLE IV. Diacetylene (C_4H_2) two-photon absorption calculated from density-functional quadratic response theory. Excitation energy E (in eV) and two-photon transition strengths δ^{TP} (in a.u.) for the lowest excited ($^1\Pi_g$) $\pi\pi^*$ state. Resonant absorption of two-photons each with half the excitation energy is assumed.

Basis	LDA		BLYP		B3LYP		CAM-B3LYP	
	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}
cc-pVDZ	8.450	2.510	7.980	2.471	8.570	2.792	9.150	2.759
aug-cc-pVDZ	6.580	186.163	6.120	215.506	6.560	175.331	6.920	129.286
d-aug-cc-pVDZ	6.470	163.581	6.010	188.470	6.470	156.005	6.850	115.506
cc-pVTZ	8.070	15.513	7.580	15.175	8.110	16.013	8.660	16.183
aug-cc-pVTZ	6.580	176.344	6.100	203.238	6.540	165.477	6.900	119.907
d-aug-cc-pVTZ	6.510	157.919	6.040	183.282	6.490	153.864	6.870	114.084
cc-pVQZ	7.800	45.608	7.320	43.764	7.820	44.438	8.260	40.582
aug-cc-pVQZ	6.570	172.253	6.090	197.915	6.520	160.880	6.890	116.570
d-aug-cc-pVQZ	6.520	159.045	6.040	184.042	6.490	153.968	6.880	113.366
cc-pV5Z	7.350	109.298	6.900	113.322	7.340	102.845	7.700	77.709
aug-cc-pV5Z	6.550	170.031	6.070	196.275	6.510	158.980	6.880	114.971
d-aug-cc-pV5Z	6.520	157.549	6.040	179.697	6.490	153.390	6.880	113.670
6-31G*	9.060	1.656	8.660	1.614	9.280	2.051	9.890	2.620
6-31+G*	6.910	191.009	6.480	203.663	6.930	179.270	7.280	134.930
6-31++G**	6.560	235.364	6.130	268.789	6.580	222.588	6.970	172.254
6-311++G**	6.720	178.263	6.230	207.330	6.680	174.825	7.070	137.282

estingly, we observe oscillations similar to those of the correlation energy itself: HF and CCS underestimate δ^{TP} by several orders of magnitude; CC2 overshoots, giving a value twice as high as the converged value; CCSD reduces it again, slightly underestimating δ^{TP} compared to CC3. In the largest basis sets, the effect of triple excitations is an increase of between 15% and 20% from the CCSD level.

Finally, we discuss the DFT quadratic response computations in Table II. The convergence of δ^{TP} for the BLYP, B3LYP, and CAM-B3LYP functionals with respect to the cardinal number is shown in Fig. 4. Clearly, all functionals converge to a different (too high) value of δ^{TP}. As in coupled cluster theory, all functionals give a value at least an order of magnitude too low without diffuse functions, although only one set of diffuse functions is needed for convergence. Interestingly, the BLYP value converges to a value about five times higher than CC3. The hybrid B3LYP functional (containing exact Hartree-Fock exchange) reduces the error significantly, but it is still twice as large as the converged coupled cluster value. The CAM-B3LYP functional is clearly

the most accurate, converging to within 15% of the coupled cluster value. Again, the results in the Pople-type basis sets are very poor in comparison with the Dunning basis-set family. The 6-31G* result is of the correct order of magnitude but this is fortuitous as augmentation leads to values of δ^{TP} at least four orders of magnitude too small.

Although a systematic improvement is not possible in DFT, it is clear from Fig. 4 that an increase in the proportion of the long-range Hartree-Fock exchange (interaction) dramatically improves the results. Again, we can invoke the sum-over-states expression for the quadratic response function [Eq. (2)] to explain this behavior in terms of an improved description of the intermediate (virtual) states. The CAM-B3LYP functional was designed to predict charge-transfer excitations more accurately by improving the long-range behavior of the exchange potential. For formaldehyde, the $n\pi^*$ state has no charge-transfer character and there is little difference between the B3LYP and CAM-B3LYP excitation energies. Thus, the much improved two-photon absorption strength for CAM-B3LYP must arise from a better
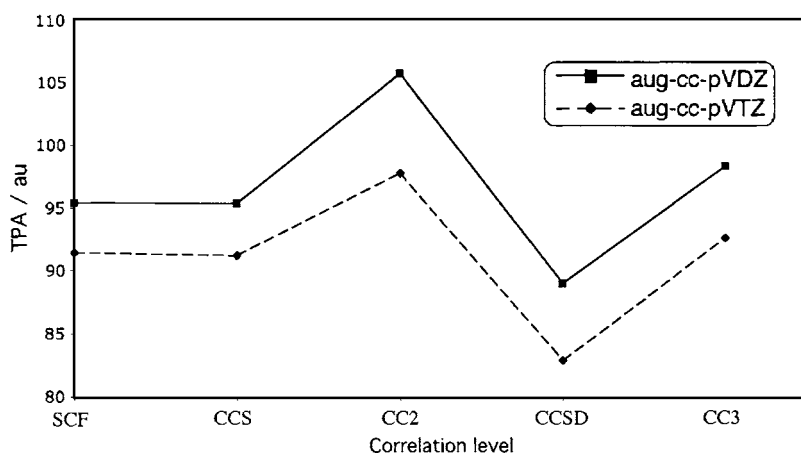

FIG. 5. Effect of electron correlation in the computation of two-photon transition strengths to the ($1\,^1\Pi_g$) $\pi\pi^*$ state of diacetylene as obtained from the coupled cluster hierarchy of models in the aug-cc-pVXZ ($X=D,T$) basis sets.
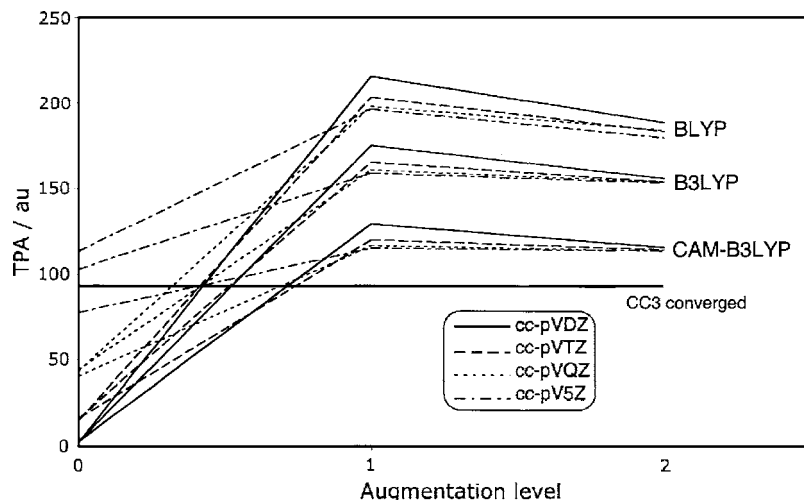
FIG. 6. Two-photon absorption transition strengths to the $(1\,^1\Pi_g)\pi\pi^*$ state of diacetylene computed by density functional response theory for the BLYP, B3LYP, and CAM-B3LYP functionals. The converged CC3 limit is also shown.

description of the intermediate states, as with the inclusion of diffuse functions. Note, however, that the two effects are opposite—that is, a more diffuse basis increases δ^{TP}, while an improved long-range exchange potential decreases δ^{TP}.

Diacetylene (C_4H_2)

We now move on to a more challenging molecule, diacetylene (C_4H_2), concentrating on the two-photon allowed $\tilde{X}\,^1\Sigma_g^+ \rightarrow 1\,^1\Pi_g$ transition. The $D_{\infty h}$ geometry was obtained from a B3LYP/cc-pVTZ optimization, with the optimized values: central CC bond length=1.364 Å, terminal CC bond length=1.204 Å, and CH bond length=1.061 Å.

The *ab initio* results are listed in Table III and the DFT results in Table IV, quoted for the $^1B_{2g}$ component of the degenerate $1\,^1\Pi_g$ electronic state (in the D_{2h} subgroup). In

TABLE V. Water (H_2O) two-photon absorption calculated from *ab initio* quadratic response theory. Excitation energy E (in eV) and two-photon transition strengths δ^{TP} (in a.u.) for the 2, 3 $^1A_1$, 1, 2 $^1B_1$, and 1 $^1A_2$ states. Resonant absorption of two-photons each with half the excitation energy is assumed.

		HF		CCS		CC2		CCSD		CC3	
Basis	State	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}
d-aug-cc-pVDZ	$2\,^1A_1$	10.870	17.071	10.887	18.297	9.220	219.045	9.723	67.453	9.802	54.041
	$3\,^1A_1$	11.410	112.266	11.456	116.402	9.515	127.638	10.044	200.086	10.121	213.343
	$1\,^1B_1$	8.610	2.310	8.653	2.722	7.069	7.510	7.431	4.975	7.495	4.719
	$2\,^1B_1$	11.120	21.980	11.135	22.789	9.235	55.333	9.806	45.405	9.911	45.590
	$1\,^1A_2$	10.280	20.018	10.328	21.520	8.692	61.652	9.179	46.412	9.257	45.570
aug-cc-pVTZ	$2\,^1A_1$	10.920	7.052	10.951	7.517	9.569	12.598	9.948	8.990	9.953	9.071
	$3\,^1A_1$	12.370	118.501	12.440	124.855	10.903	397.132	11.366	275.058	11.373	280.782
	$1\,^1B_1$	8.640	2.351	8.687	2.779	7.244	7.216	7.608	4.832	7.611	4.724
	$2\,^1B_1$	11.760	18.782	11.795	20.114	10.375	41.881	10.815	37.397	10.843	38.512
	$1\,^1A_2$	10.310	20.845	10.359	22.408	8.895	60.592	9.368	44.163	9.384	44.694
d-aug-cc-pVTZ	$2\,^1A_1$	10.860	15.874	10.881	17.127	9.387	181.249	9.866	45.701	9.882	39.280
	$3\,^1A_1$	11.420	117.899	11.466	121.999	9.647	155.895	10.218	210.582	10.231	224.951
	$1\,^1B_1$	8.640	2.383	8.683	2.801	7.236	7.398	7.603	4.827	7.606	4.719
	$2\,^1B_1$	11.140	21.273	11.160	22.015	9.421	48.300	10.005	39.642	10.041	41.108
	$1\,^1A_2$	10.300	20.230	10.349	21.760	8.874	55.877	9.355	41.614	9.370	42.098
aug-cc-pVQZ	$2\,^1A_1$	10.910	7.631	10.938	8.142	9.621	12.911	10.001	9.502	9.983	9.530
	$3\,^1A_1$	12.100	130.434	12.168	137.535	10.593	385.493	11.109	273.071	11.092	282.468
	$1\,^1B_1$	8.640	2.432	8.687	2.863	7.311	7.370	7.679	4.862	7.659	4.808
	$2\,^1B_1$	11.570	20.811	11.599	22.123	10.183	48.538	10.651	40.490	10.656	42.358
	$1\,^1A_2$	10.310	20.819	10.356	22.391	8.962	58.310	9.437	42.106	9.429	43.126
d-aug-cc-pVQZ	$2\,^1A_1$	10.860	15.970	10.883	17.221	9.461	169.032	9.935	40.569	9.927	35.442
	$3\,^1A_1$	11.420	118.597	11.467	122.710	9.713	160.254	10.294	208.177	10.283	223.641
	$1\,^1B_1$	8.640	2.432	8.686	2.858	7.308	7.368	7.678	4.800	7.658	4.738
	$2\,^1B_1$	11.150	21.434	11.160	22.166	9.491	45.540	10.085	37.866	10.095	39.692
	$1\,^1A_2$	10.300	20.127	10.351	21.639	8.951	53.508	9.430	39.673	9.422	40.638

TABLE VI. Water (H_2O) two-photon absorption calculated from density-functional quadratic response theory. Excitation energy E (in eV) and two-photon transition strengths δ^{TP} (in a.u.) for the 2, 3 $^1A_1$, 1, 2 $^1B_1$, and 1 $^1A_2$ states. Resonant absorption of two-photons each with half the excitation energy is assumed.

Basis	State	LDA		BLYP		B3LYP		CAM-B3LYP	
		E	δ^{TP}	E	δ^{TP}	E	δ^{TP}	E	δ^{TP}
d-aug-cc-pVDZ	2 $^1A_1$	8.060	241.913	7.710	268.050	8.650	186.824	9.140	84.359
	3 $^1A_1$	8.610	32.095	8.340	29.799	9.050	46.124	9.400	175.308
	1 $^1B_1$	6.510	7.107	6.210	7.082	6.860	5.317	7.090	4.731
	2 $^1B_1$	7.750	3.880	7.480	7.218	8.550	16.314	9.150	47.490
	1 $^1A_2$	7.570	34.483	7.260	47.170	8.190	45.198	8.650	49.857
aug-cc-pVTZ	2 $^1A_1$	8.630	12.300	8.370	12.182	9.040	10.099	9.270	8.402
	3 $^1A_1$	10.150	501.026	9.830	552.318	10.470	341.370	10.740	286.689
	1 $^1B_1$	6.570	7.333	6.260	7.370	6.890	5.513	7.130	4.792
	2 $^1B_1$	9.340	30.583	8.980	36.707	9.710	28.990	10.060	37.049
	1 $^1A_2$	7.890	73.025	7.490	80.808	8.290	56.722	8.690	51.301
d-aug-cc-pVTZ	2 $^1A_1$	8.060	236.610	7.700	264.805	8.660	192.571	9.160	84.125
	3 $^1A_1$	8.610	31.516	8.350	27.490	9.060	43.998	9.420	172.390
	1 $^1B_1$	6.550	8.064	6.240	8.077	6.890	5.771	7.120	4.714
	2 $^1B_1$	7.750	4.046	7.450	6.822	8.550	15.955	9.170	42.042
	1 $^1A_2$	7.600	29.890	7.270	42.106	8.220	45.563	8.680	47.286
aug-cc-pVQZ	2 $^1A_1$	8.620	13.234	8.360	12.734	9.030	10.681	9.260	8.914
	3 $^1A_1$	9.720	491.474	9.390	524.119	10.090	345.958	10.390	295.520
	1 $^1B_1$	6.570	8.007	6.260	7.903	6.900	5.846	7.130	4.976
	2 $^1B_1$	9.040	36.933	8.670	43.540	9.440	34.129	9.820	42.091
	1 $^1A_2$	7.860	74.327	7.470	81.972	8.280	57.244	8.690	51.499
d-aug-cc-pVQZ	2 $^1A_1$	8.050	238.915	7.680	268.968	8.650	195.791	9.160	87.085
	3 $^1A_1$	8.610	28.800	8.350	22.642	9.060	40.782	9.420	173.714
	1 $^1B_1$	6.550	8.487	6.240	8.394	6.890	5.984	7.130	4.838
	2 $^1B_1$	7.790	3.881	7.480	6.608	8.550	20.789	9.170	41.589
	1 $^1A_2$	7.600	27.021	7.270	38.939	8.220	43.927	8.680	46.852

Fig. 5 we show the effect of correlation on δ^{TP}. As for CH_2O, oscillations occur with improvements in the correlation treatment. Again CC2 overestimates the CC3 value but only by 8%, while CCSD underestimates it by about the same amount.

The DFT results in Fig. 6 converge in the same manner as for CH_2O. BLYP gives a δ^{TP} value almost twice the converged coupled cluster value. The error is only slightly reduced with B3LYP, while CAM-B3LYP converges to within 10% of the coupled cluster value. For diacetylene, δ^{TP} is essentially converged with one set of diffuse functions, the effect of a second set being small. We note that the d-aug-cc-pVDZ result is as good as the d-aug-cc-pV5Z result for the DFT methods, which is promising if higher-order DFT response methods are to be applied to large molecules.

Water (H_2O)

As the final molecule benchmarked, water represents much more of a challenge. Its excited states are all quite diffuse, with a significant Rydberg character.[46] Since diffuse functions are important even for one-photon absorption, we have only investigated augmented cc-pVXZ basis sets for this molecule.

The geometry was taken from Ref. 3, in which the two-photon dissociation of water was studied. The C_{2v} geometrical parameters are OH bond length=0.959 Å and HOH angle=104.654°.

The *ab initio* and DFT results are listed in Tables V and VI, respectively. Regarding basis sets, Table V shows that double augmentation is necessary to obtain a quantitative value of δ^{TP}, a singly augmented basis consistently overestimating. In Fig. 7, we have shown coupled cluster convergence of δ^{TP} in the d-aug-cc-pVXZ series, for the lowest excited state (1 $^1B_1$). While CC2 clearly overestimates, CCSD and CC3 converge monotonically to the same result.

The effect of correlation on δ^{TP} for the lowest five excited states of water is shown in Fig. 8. The oscillations are pronounced for the 2 $^1A_1$ state, much less so for the 1, 2 $^1B_1$, and 1 $^1A_2$ states. Surprisingly, the 3 $^1A_1$ value does not oscillate, converging asymptotically from below. Clearly, we should not always expect the same convergence pattern in a molecular property as in the correlation energy.

In an experimental study of the two-photon absorption of water, it was observed that there is an order of magnitude difference between the two-photon cross sections of the 2 $^1A_1$ and 1 $^1B_1$ absorption bands.[3] In sufficiently diffuse ba-
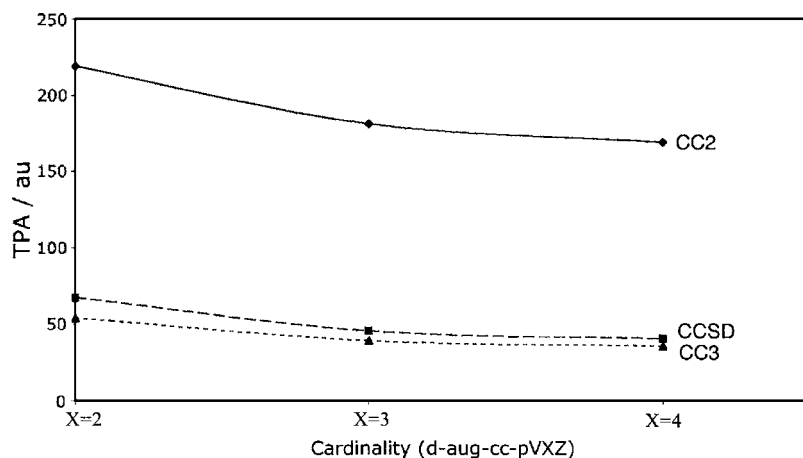
FIG. 7. Effect of basis-set cardinal number in the d-aug-cc-pVXZ ($X=D,T,Q$) series on the computation of two-photon transition strengths to the lowest excited ($1\ ^1B_1$) state of water for the CC2, CCSD, and CC3 coupled cluster models.

sis sets, this feature is also observed in our coupled cluster study (Table V). Thus in a doubly augmented basis set, the $2\ ^1A_1/1\ ^1B_1$ ratio of δ^{TP} is about 10 at the CCSD and CC3 levels; with single augmentation, however, it drops to two, demonstrating the need for at least two sets of diffuse functions. In fact, the d-aug-cc-pVDZ basis outperforms the much larger aug-cc-pVQZ basis in this respect. We have performed calculations of δ^{TP} in a t-aug-cc-pVTZ basis to examine the effect of further augmentation, but we find that the effect is similar to that of increasing the cardinality, i.e., going from d-aug-cc-pVTZ to t-aug-cc-pVTZ produces the results of the same quality as going from d-aug-cc-pVTZ to d-aug-cc-pVQZ. For water this effect is rather small, reducing δ^{TP} by at most 10% of the d-aug-cc-pVTZ value. We are therefore confident that the d-aug-cc-pVQZ values are converged.

Also for the electronic excitations of water the CAM-B3LYP functional performs better than the other functionals (compare the excitation energies in Tables V and VI). However, for this molecule, significant errors persist. While in the previous cases the excitation energies agree with the best coupled cluster predictions within 0.3 eV, the discrepancies are now much larger, the DFT excitation energies being 0.5–1.0 eV too low. Accordingly, the discrepancies between CC3 and CAM-B3LYP two-photon transition strengths are much more significant. This is not entirely unexpected as the excited states of water represent a severe challenge to approximate exchange-correlation functionals in DFT response

theory, where the long-range behavior of the corresponding exchange-correlation potentials is known to be unsatisfactory for such diffuse Rydberg states. We do, however, see that the $2\ ^1A_1/1\ ^1B_1$ ratio of δ^{TP} is qualitatively correct (around 20) with CAM-B3LYP (but not with B3LYP) and that the same issue of double versus single augmentation is important.

CONCLUSIONS

We have perfomed benchmark computations of two-photon absorption using the coupled cluster hierarchy of models, including triple excitation effects via the iterative CC3 model for the first time. Our results show that triple excitations can contribute 15%–20% to the two-photon transition strength, but sometimes the effect is negligible. Furthermore, our results show the importance of diffuse basis functions, even for compact valence excited states. We note, however, that the importance of diffuse basis functions for two-photon absorption may be somewhat special for small molecules. In general, one finds that for excitation energies and (hyper)polarizabilities the effect of diffuse functions decreases rapidly with the size of the molecule/chromophore. Further work is required to determine the importance of diffuse functions for two-photon absorptions of larger molecules.

In general, the HF and CCS results in a large basis differ by an order of magnitude compared to CC3. This is not surprising as excitation energies in error by several eV are
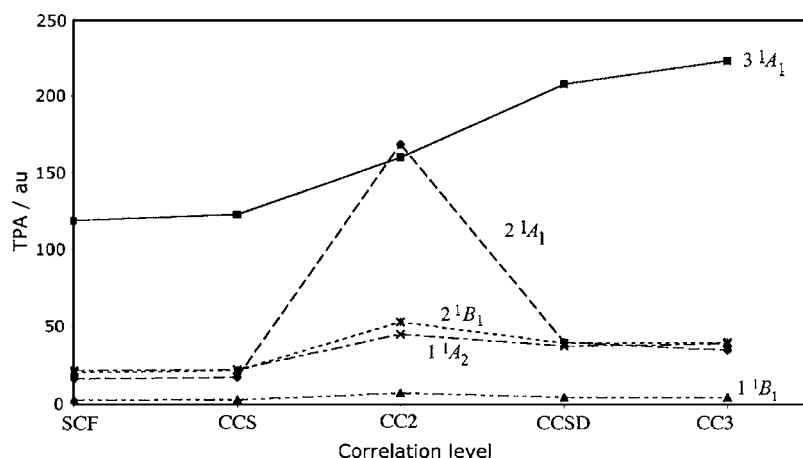

FIG. 8. Effect of electron correlation in the computation of two-photon transition strengths of the first five excited states of water as obtained from the coupled cluster hierarchy of models in the d-aug-cc-pVQZ basis set.

not untypical. Finally, we have compared the benchmark coupled cluster results with those obtained from DFT. For all the molecules, better agreement with the best coupled cluster results in the sequence LDA, BLYP, B3LYP, CAM-B3LYP was obtained. It is noteworthy that CAM-B3LYP with even quite modest sized basis sets gave results in rather good agreement with the best coupled cluster results for the relatively nondiffuse valence states of formaldehyde and diacetylene studied. If this behavior holds more generally there is good potential in using this particular DFT methodology in two-photon calculations for larger molecules. However, the results for water show that diffuse states with significant Rydberg character pose more of a challenge for higher-order DFT response methods (a well-known issue in DFT linear-response theory also). The CAM-B3LYP functional is relatively new and has not seen extensive use in higher-order response methods yet. On the other hand, the deviations of some of the other DFT methods make their use in two-photon calculations somewhat troublesome. Since the two-photon transition strengths are related to the residues of the nonlinear-response functions this may also indicate that care should be exercised in the application of these DFT methods to nonlinear optical properties.

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