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Electronic excitation energies in solution at equation of motion CCSD level within a state specific polarizable continuum model approach

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We present a study of excitation energies in solution at the equation of motion coupled cluster singles and doubles (EOM-CCSD) level of theory. The solvent effect is introduced with a state specific polarizable continuum model (PCM), where the solute-solvent interaction is specific for the state of interest. Three definitions of the excited state one-particle density matrix (1PDM) are tested in order to gain information for the development of an integrated EOM-CCSD/PCM method. The calculations show the accuracy of this approach for the computation of such property in solution. Solvent shifts between nonpolar and polar solvents are in good agreement with experiment for the test cases. The completely unrelaxed 1PDM is shown to be a balanced choice between computational effort and accuracy for vertical excitation energies, whereas the response of the ground state CCSD amplitudes and of the molecular orbitals is important for other properties, as for instance the dipole moment. © *2010 American Institute of Physics*. [doi:10.1063/1.3314221]

I. INTRODUCTION

The study of molecular electronic excited states is fundamental in many areas of modern science. Computational methods capable to accurately reproduce experiments are thus of large interest since they represent effective tools to interpret and often guide experiments. However, the development of such methods is complex especially when the effect of the surrounding environment needs to be taken into account. The modeling of the solvent effect is extremely challenging since many different intermolecular interactions are active and they can couple in a very complex manner. A proper way of including these effects is to consider a large set of solvent molecules together with the chromophore under scrutiny and allowing the whole system to dynamically evolve. This approach is, however, impossible with the present computational capabilities, unless some approximations are introduced.

Fortunately, in many cases, the main solvent effect is electrostatic in nature and it can be reliably approximated with a mean field approach, since the specific and short-range solute-solvent interactions constitute a smaller effect. One of the most successful representations of the solvent mean field effect is obtained through the so-called polarizable continuum model (PCM).[1–4] PCM describes the solvent as a polarizable dielectric medium, characterized by its dielectric constant (ε), in which a cavity of molecular shape is built to host the solute. The presence of the solute charge distribution polarizes the dielectric, and this effect is represented by an apparent surface charge spread on the cavity surface. The solute-solvent interaction is expressed by introducing an interaction potential into the solute Hamiltonian, so that the polarization of the solute density mutually equilibrates with the solvent response.

PCM has been extended to study vertical excitations by introducing the nonequilibrium scheme.[4–6] An electronic transition in the Frank–Condon regime is a fast process, thus the response of the solvent molecules is delayed with respect to the response of the solvent electrons. In the nonequilibrium approximation, the response of the solvent electrons is considered instantaneous, so that they can mutually equilibrate with the new solute charge distribution. This response depends on the optical dielectric constant (ε_∞). The response of the solvent nuclei, on the other hand, is considered frozen in the ground state, and still depends on ε. This approach has been used to successfully study a variety of phenomena and spectroscopies.[4]

The most common strategy to apply PCM to electronic transition calculations is to couple it to linear response methods such as configuration interaction singles (CIS), time-dependent Hartree–Fock (TDHF), and especially time-dependent density functional theory (TDDFT).[4–10] Although TDDFT with PCM represents a valuable tool to study excited states in solution, the large dependence of the results on the choice of the functional often makes the assessment of the quality of the calculations difficult. In this respect, the identification of a benchmark method seems necessary. The equation of motion coupled cluster singles and doubles (EOM-CCSD)[11–13] represents one of the most accurate, and yet affordable, single reference methods to study one-electron transitions in gas phase for small and medium size molecules. Thus it represents the natural choice for the extension to the treatment of the same process in solution.

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In this work we couple the integral equation formalism flavor of PCM (IEF-PCM), which is the most general and widely used formulation,[2,3] with EOM-CCSD and we apply this methodology to two model systems, acrolein and methylencyclopropene (MCP), which are widely studied experimentally and theoretically.[14–23] The coupling is realized through a simple strategy which exploits an external macroiteration PCM procedure,[24,25] which requires the calculation of the excited state charge density. This macroiteration procedure is, in general, not the most efficient strategy to introduce the solvent effect because it requires that the calculation on the solute system is performed many times until self-consistency between the solute charge density and the solvent response is achieved. However, it is relatively easy to implement and provides useful benchmarking data.

Different methodologies have been developed to introduce solvent effects on a coupled cluster wave function, see for example Refs. [26–32], and in particular the recent approach proposed by Cammi[33] for PCM. An investigation of the combination of EOM-CCSD with PCM is however still missing. The scope of this work is therefore twofold. On the one hand, we want to assess the accuracy of EOM-CCSD/PCM in reproducing transition energies in solution. On the other hand, we want to test valuable approximations that will allow the implementation of a really integrated EOM-CCSD/PCM method.

This work is organized as follows. Section II describes the theoretical background and the details of the calculations. The results of the calculations are discussed in Sec. III. Section IV contains a summary of the results and concluding remarks.

II. COMPUTATIONAL DETAILS

We refer the reader to the literature for a detailed description of EOM-CCSD[12,13] and PCM.[4] However, it is worth spending a few words on the external iterative PCM solution.

It has been clearly shown that the extension of PCM (like all other polarizable solvation models) to post-self-consistent-field (SCF) approaches introduces a specificity, which is at the same time the strength of the method and its weakness.[8,9] In particular, the PCM operator, which introduces the polarization effects in the solute Hamiltonian, is a state-specific operator. This means that it depends on the charge density of the solute and, at the same time, modifies it. This dependency is exactly the way a mutual polarization between solute and solvent can be made possible but it also originates a difficulty in the implementation of the method for post-SCF approaches. In fact, to make the response of the solvent (i.e., the PCM charges) mutually equilibrated with the solute charge density, an iterative approach is generally required. At the zero-order level, this iterative scheme can be skipped by accounting for the solvent effects only at the energetic level, that is the post-SCF description of the solute is calculated with a SCF-level solvent response. A possible first-order correction to this description is obtained by recalculating the PCM charges with the gas-phase post-SCF density and correcting the energy for the new solvent contribu-

tion. Finally, a more complete scheme introduces a self-consistent approach. Namely, a first set of charges is calculated from the initial density. Then, a new solute density calculation is performed in the presence of the reaction field represented by such fixed charges (that enter the one-electron Hamiltonian). A new set of charges is calculated with such updated density and so on until self-consistency or, in other words, until mutual polarization between the solute charge distribution and the solvent response. In this approach, any method for which it is possible to compute the one particle density can be directly coupled with PCM.

Thanks to our recent implementation of the EOM-CCSD analytic energy gradients[34–37] in a development version of the GAUSSIAN suite of programs,[38] we can now compute the completely relaxed EOM-CCSD density and use the PCM external iteration algorithm,[24,25] also implemented in GAUSSIAN, to couple the two methods. However, the calculation of the EOM-CCSD relaxed one-particle density matrix (1PDM) is a very expensive task. The 1PDM for the kth excited state can be written as the sum of various terms,

$$\rho_1^k = \rho_1^0 + \langle \Phi_0 | L_k [e^{-T} \{ p^\dagger q \} e^T, R_k] | \Phi_0 \rangle$$
$$+ \langle \Phi_0 | (1 + Z_k) e^{-T} \{ p^\dagger q \} e^T | \Phi_0 \rangle + \text{MO terms}, \quad (1)$$

where ρ_1^0 is the 1PDM of the reference function $| \Phi_0 \rangle$, L_k and R_k are the left and right eigenvectors for the kth state, Z_k is the Z-vector for the kth state, which accounts for the response of the ground state CCSD T amplitudes to a perturbation, and the last term accounts for the response of the molecular orbitals (MOs) to the same perturbation.[34–37,39–42] This last term requires the calculation of the reduced two-particle density matrix (2PDM),

$$\rho_2^k = \langle \Phi_0 | L_k [e^{-T} \{ p^\dagger q^\dagger rs \} e^T, R_k] | \Phi_0 \rangle$$
$$+ \langle \Phi_0 | (1 + Z_k) e^{-T} \{ p^\dagger q^\dagger rs \} e^T | \Phi_0 \rangle, \quad (2)$$

which is the most expensive part of the calculation, since its leading term scales as $o^2 v^4$, with o and v being the number of occupied and virtual orbitals, respectively, and it requires v^4 storage. The 2PDM is then contracted with the two-electron integrals in order to form the right hand side of the coupled perturbed Hartree–Fock equations, which give the response of the orbitals to the perturbation. The perturbation can be an electric field, as in this case, and/or the motion of the nuclei, as in a geometry optimization. In the latter case, the 1PDM and 2PDM are also contracted with the derivatives of the integrals. In the following, we refer to the completely relaxed 1PDM as "1PDM-R."

Since in the self-consistent PCM scheme the density is calculated many times, one can introduce some approximations in Eq. (1) and numerically evaluate the effect on the total energy. The first approximation is to ignore the contribution of the MO response, which avoids the evaluation of the 2PDM. We call this approximation "1PDM-T," where T indicates that the response of the ground state T amplitudes is retained. If the latter is also neglected, the completely unrelaxed density is obtained, "1PDM-U," which is expressed as in Ref. [12].

It is worth noting that the self-consistent PCM scheme is a state specific approach in the sense that the solvent re-

sponse is computed for a specific electronic state of the solute. Therefore the transition energy is calculated as the difference between the total energy of the kth excited state and the total energy of the ground state, both in the field of their own solvent polarization. This is different from the linear response approach, as in TDDFT, where the effect of the solvent on multiple states is obtained simultaneously. For a discussion of the differences between the state specific and linear response PCM approaches, see, for example, Refs. 4, 8–10, 24, and 25.

We test the three definitions of the 1PDM in the computation of vertical transition energies, through the nonequilibrium PCM scheme, in order to gain information about the importance of the various terms, and use it for a future development of an integrated, linear response-like EOM-CCSD/PCM method. The ground state energy in solution is, however, always calculated with the totally relaxed density. Additionally, the first step of the self-consistent PCM cycle is done in gas phase, so we can assess the total effect of the solvent on the energy. We also performed calculations in the equilibrium solvation regime, which is when the solvent molecules have the time to equilibrate with the new solute charge distribution. Although only the nonequilibrium data can be directly compared with the experimental vertical transition energies, the equilibrium solvation is important when excited state properties are of interest, for instance, dipole moments or geometry optimizations. Thus, it is useful to compare the various definitions of the 1PDM also in this case.

We point out that only the electrostatic contribution of the solvent effect is taken into account in our calculations, whereas other contributions such as dispersion, repulsion and cavitation are neglected. Usually, their effect is smaller than the electrostatic one. Furthermore, this approximation should be even less severe in the context of this work, since we mainly focus on the solvatochromic shift in the transition energies between two solvents.

The calculations are performed at the optimized geometry in the corresponding medium, gas phase or solution. The optimizations are carried out at B3LYP[43,44] and B3LYP/PCM levels of theory with the aug-cc-pVTZ basis set. The single point coupled cluster calculations are carried out with the 6-31+G* and aug-cc-pVDZ basis sets. The PCM cavity is built with a new algorithm based on the work of York and Karplus,[45] which uses gaussian functions instead of point charges to avoid discontinuities on the cavity surface. We used van der Waals atomic radii, 1.925 Å for C, 1.750 Å for O, and 1.443 Å for H, scaled for a factor of 1.1. The van der Waals radii are chosen because of their availability for most of the periodic table, whereas the scaling factor of 1.1 provides a cavity with a surface close to the solvent excluded surface. We also set a very tight convergence criterion, since we are not interested here in the efficiency of the method, that is when the root mean square of the change in the value of the PCM charges becomes smaller than 10^{-9}.

III. RESULTS

The systems we analyze are acrolein and MCP, see Figs. 1 and 2.[14–23] We consider the first two excitations in a polar
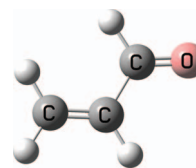

FIG. 1. Acrolein.

and in a nonpolar solvent for both molecules, since the response of the solvent is very different for the two states. In particular, the solvent shift ($\Delta E_{polar} - \Delta E_{nonpolar}$) has a different sign for the two states for both molecules. Experimental data are available in solution and, for acrolein, also in gas phase, thus a direct comparison is possible. We report the results as transition energies, both for nonequilibrium and equilibrium solvation, although total energies would be more appropriate for the latter, because the reference, i.e., the ground state energy, is the same and the comparison is easier.

For acrolein the solvents are water and cyclohexane. The results for the vertical excitations are reported in Tables I and II. The results for the first transition in gas phase show a good agreement with the experiment, which is overestimated by 0.23 and 0.27 eV with the large and small basis sets, respectively. The results in solution are of the same quality, as they show errors of the same magnitude. The experimental solvent shift, 0.23 eV, is thus very well reproduced by the calculations. The results vary very little with the definitions of the 1PDM, with differences of the order of 0.02 eV, thus much smaller than the difference from the experimental values. The second transition shows a larger error in the gas phase, as the experimental value is overestimated by 0.51 and 0.67 eV with the large and small basis sets, respectively.[46] The errors in solution are slightly larger, even with the aug-cc-pVDZ basis, and of the order of 0.65 eV. This is probably due to nonelectrostatic solvent effects, which are neglected in our calculations, but are shown to have a significant contribution for this transition.[23] This is also evident considering the shift in the transition energy passing from gas phase to the nonpolar solvent. However, these effects are similar between the two solvents and the experimental solvent shift, −0.21 eV, is still quite well reproduced, indicating that the electrostatic continuum model is able to describe the basic physics of the phenomenon. The differences due to the 1PDM are again much smaller than the other errors, with differences of at most 0.03 eV. The results for the equilibrium solvation are reported in Tables III and IV. Since there is no comparison to experiment, the only important information is the comparison between the various definitions of the 1PDM. In this case the differences are large for the polar solvent as much as 0.05 eV for the first transition and 0.09 eV for the second one. On the other hand, the
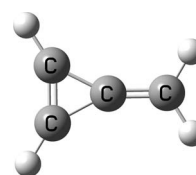

FIG. 2. MCP.

TABLE I. Nonequilibrium (vertical) transition energies and solvent shift (eV) for the first excited state ($n \rightarrow \pi^*$, A″) of acrolein in gas phase, in water (ε=78.4, ε_∞=1.8), and in cyclohexane (ε=2.0, ε_∞=2.0) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Water		Cyclohexane		Solvent shift	
Expt.	3.71[a]		3.94[b]		3.71[c]		+0.23	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
1PDM-U	3.98	3.94	4.20	4.16	3.96	3.92	+0.23	+0.24
1PDM-T			4.19	4.15	3.97	3.93	+0.22	+0.22
1PDM-R			4.18	4.14	3.98	3.93	+0.20	+0.21

[a]Reference 15.
[b]Reference 16.
[c]Reference 18.

TABLE II. Nonequilibrium (vertical) transition energies and solvent shift (eV) for the second excited state ($\pi \rightarrow \pi^*$, A′) of acrolein in gas phase, in water (ε=78.4, ε_∞=1.8), and in cyclohexane (ε=2.0, ε_∞=2.0) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Water		Cyclohexane		Solvent shift	
Expt.	6.41[a]		5.90[b]		6.11[c]		−0.21	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
1PDM-U	7.08	6.89	6.57	6.51	6.83	6.74	−0.26	−0.23
1PDM-T			6.59	6.53	6.84	6.76	−0.25	−0.23
1PDM-R			6.60	6.54	6.85	6.76	−0.25	−0.22

[a]Reference 15.
[b]Reference 16.
[c]Reference 17.

TABLE III. Equilibrium transition energies and solvent shift (eV) for the first excited state ($n \rightarrow \pi^*$, A″) of acrolein in gas phase, in water (ε=78.4), and in cyclohexane (ε=2.0) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Water		Cyclohexane		Solvent shift	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
1PDM-U	3.98	3.94	3.92	3.86	3.96	3.92	−0.04	−0.06
1PDM-T			3.95	3.89	3.97	3.93	−0.02	−0.04
1PDM-R			3.96	3.91	3.98	3.93	−0.02	−0.03

TABLE IV. Equilibrium transition energies and solvent shift (eV) for the second excited state ($\pi \rightarrow \pi^*$, A′) of acrolein in gas phase, in water (ε=78.4), and in cyclohexane (ε=2.0) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Water		Cyclohexane		Solvent shift	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
1PDM-U	7.08	6.89	6.11	6.11	6.83	6.75	−0.72	−0.64
1PDM-T			6.17	6.17	6.83	6.76	−0.67	−0.59
1PDM-R			6.20	6.20	6.85	6.76	−0.65	−0.56

TABLE V. Nonequilibrium (vertical) transition energies and solvent shift (eV) for the first excited state ($\pi \rightarrow \pi^*$, B_2) of MCP in gas phase, in methanol ($\varepsilon=32.6$, $\varepsilon_\infty=1.8$), and in n-pentane ($\varepsilon=1.8$, $\varepsilon_\infty=1.8$) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Methanol		N-pentane		Solvent shift	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
Expt.			4.49[a]		4.01[a]		+0.48	
1PDM-U	4.68	4.61	4.81	4.76	4.48	4.41	+0.33	+0.35
1PDM-T			4.82	4.78	4.50	4.43	+0.32	+0.35
1PDM-R			4.84	4.79	4.53	4.46	+0.31	+0.33

[a]Reference 20.

TABLE VI. Nonequilibrium (vertical) transition energies and solvent shift (eV) for the second excited state ($\pi \rightarrow \pi^*$, A_1) of MCP in gas phase, in methanol ($\varepsilon=32.6$, $\varepsilon_\infty=1.8$), and in n-pentane ($\varepsilon=1.8$, $\varepsilon_\infty=1.8$) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Methanol		N-pentane		Solvent shift	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
Expt.			5.90[a]		6.02[a]		−0.12	
1PDM-U	6.25	6.19	6.15	6.10	6.17	6.11	−0.02	−0.01
1PDM-T			6.15	6.10	6.17	6.11	−0.02	−0.01
1PDM-R			6.13	6.09	6.17	6.11	−0.04	−0.02

[a]Reference 20.

TABLE VII. Equilibrium transition energies and solvent shift (eV) for the first excited state ($\pi \rightarrow \pi^*$, B_2) of MCP in gas phase, in methanol ($\varepsilon=32.6$), and in n-pentane ($\varepsilon=1.8$) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Methanol		N-pentane		Solvent shift	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
1PDM-U	4.68	4.61	4.14	4.06	4.48	4.41	−0.34	−0.35
1PDM-T			4.21	4.13	4.50	4.43	−0.29	−0.30
1PDM-R			4.29	4.21	4.53	4.46	−0.24	−0.25

TABLE VIII. Equilibrium transition energies and solvent shift (eV) for the second excited state ($\pi \rightarrow \pi^*$, A_1) of MCP in gas phase, in methanol ($\varepsilon=32.6$), and in n-pentane ($\varepsilon=1.8$) with the different choices of the 1PDM, defined in Sec. II, and two basis sets (VDZ is short for aug-cc-pVDZ). The transition energy calculations are performed at the optimized geometry in the corresponding medium.

	Gas		Methanol		N-pentane		Solvent shift	
	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ	6-31+G*	VDZ
1PDM-U	6.25	6.19	6.04	5.98	6.17	6.11	−0.13	−0.13
1PDM-T			6.04	5.98	6.17	6.11	−0.13	−0.13
1PDM-R			6.02	5.97	6.17	6.11	−0.15	−0.14

nonpolar solvent still shows a small difference, not surprisingly since in this case there is not much difference between the equilibrium and the nonequilibrium case (as $\varepsilon \simeq \varepsilon_\infty$). The solvent shifts are reported to emphasize the importance of the nonequilibrium model to describe vertical excitations in solution.

In the case of MCP the solvents are methanol and n-pentane. The vertical excitation energies are reported in Tables V and VI. For this molecule there are no experimental data in the gas phase. However, the calculated data in gas phase are reported in order to show the solvent effect on the transition energy. The first transition shows a large shift because the dipole of the excited state points in the opposite direction than in the ground state. Thus the polar solvent stabilizes the ground state better than the excited state (note that in a vertical excitation the solvent molecules are assumed to be frozen in the ground state configuration). The solvent shift is slightly underestimated, 0.31–0.35 eV with respect to 0.48 eV, see Table V. However, this estimate is better than the previously published results: 0.20 eV with CIS/PCM (Ref. 9) and 0.18 eV with CASSCF/PCM.[47] The differences between the definitions of the 1PDM are small also in this case, of the order of 0.03 eV. The solvent effect is much smaller on the second transition, as the solute density does not change a lot. The solvent shift is much smaller, but still opposite in sign, as for acrolein. The calculated data show the correct sign, but the absolute value is again underestimated of about 0.1 eV. The differences between the values calculated with the different 1PDMs are even smaller than for the first transition. In both cases these differences are smaller than the basis set and the solvent effects. The results for the equilibrium solvation are reported in Tables VII and VIII. We note that when the solvent molecules are allowed to relax around the new solute electronic density, the solvent effect on the first transition in methanol becomes much larger than for the nonequilibrium case. The excited state is more stabilized than the ground state, as in the former there is a partial charge separation that polarizes the solvent more than in the ground state. This corresponds to larger differences depending on the choice of the 1PDM, indicating that the effects of the T amplitudes and MO responses are not negligible. The difference in energies is as large as 0.15 eV, see Table VII. This corresponds to large differences in excited state properties, for instance, the dipole moment, reported in Table IX (the geometry is the one of the ground state). The effect of the choice of the 1PDM is even evident on the nonpolar solvent, with differences in the energy of 0.05 eV between 1PDM-U and 1PDM-R. For the second transition, on the other hand, the differences are still small, as the solvent effect is small overall. However, the general trends are correctly reproduced by all choices of the 1PDM.

Finally, Figs. 3 and 4 show the rate of convergence of the transition energy with the PCM macroiterations for the two transitions of acrolein in water, the nonequilibrium and the equilibrium solvation schemes, the two basis sets, and the completely unrelaxed density. Point 0 corresponds to the transition energy in gas phase (at the equilibrium geometry in solution) and point 1 corresponds to the first solvent correction calculated with the gas phase density. The two figures

TABLE IX. Dipole moments (D) of the ground and the first excited states of MCP in methanol. The excited state dipoles are calculated with the various definitions of the 1PDM at the geometry of the ground state.

	6-31+G*	aug-cc-pVDZ
Ground state	-2.65	-2.76
1PDM-U	3.85	3.91
1PDM-T	3.37	3.39
1PDM-R	2.79	2.77

show a very fast convergence of the energy, within 3–7 iterations, in all cases (numerous iterations are reported because of the very tight convergence criteria set for this study). Except for the first transition in the equilibrium regime, where the blueshift is compensated by the solvent reorganization, the solvent effect is not negligible.

IV. CONCLUSIONS

In this work we presented the calculations of excitation energies in solution by applying a self-consistent PCM approach at the EOM-CCSD level of theory. Our results show a very good agreement with experimental data, further confirming the accuracy of EOM-CCSD and the ability of PCM to capture the important polarization effects of the solvent on the solute wave function.

We also tested various definitions of the solute 1PDM, namely, the totally relaxed density, which includes the response of the ground state T amplitudes and of the MOs, a partially relaxed density, which neglects the response of the MOs, and a totally unrelaxed density, which neglects both. Our results suggest that for single point vertical excitations, the 1PDM-U is a good approximation, as the deviation from the 1PDM-R results is at most 0.03 eV, and much smaller than other sources of error (like the basis set or the intrinsic EOM-CCSD deviation from the experiment). 1PDM-U is much less expensive to compute, and thus seems to represent the preferred choice to define an integrated, computationally efficient EOM-CCSD/PCM method. This result is consistent with our recent comparison of oscillator and dipole strengths
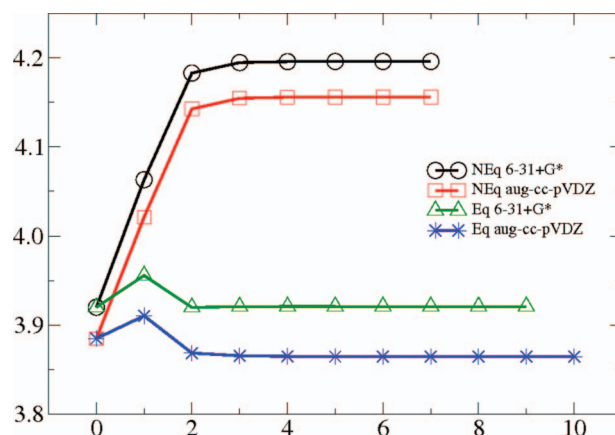

FIG. 3. Convergence of the transition energy (eV) for the PCM macroiterations with the equilibrium (Eq) and nonequilibrium (NEq) schemes for the first transition of acrolein in water with the 1PDM-U. The X axis reports the number of iterations.
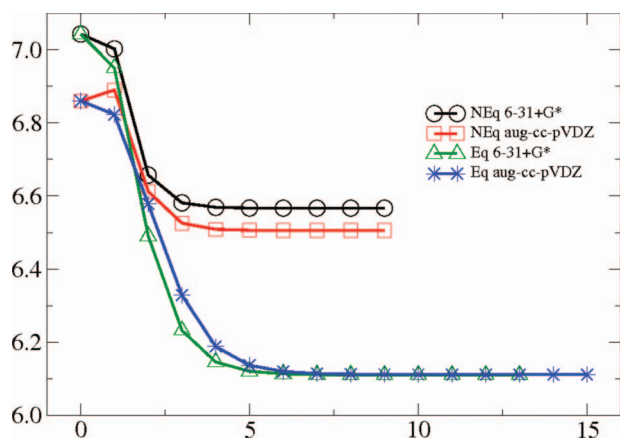
FIG. 4. Convergence of the transition energy (eV) for the PCM macroiterations with the equilibrium (Eq) and nonequilibrium (NEq) schemes for the second transition of acrolein in water with the 1PDM-U. The X axis reports the number of iterations.

calculated in gas phase with the linear response and equation of motion CCSD.[48] However, for excited state properties and geometry optimizations, the contributions of the MO and T responses cannot be neglected, especially for polar solvents, with differences in energy up to 0.15 eV, and 1 D for the dipole moment, between 1PDM-U and 1PDM-R.

These results, even if limited to two systems and few excitations, are a clear indication of the potentialities of the integration between accurate quantum mechanical approaches such as EOM-CCSD and PCMs. As stated in Sec. I, the strategy used here is a simple numerical approach. More refined and more efficient approaches are surely possible; indeed, developments in this direction are already in progress on the guidelines proposed by Cammi.[33]

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