

Unveiling Solvents Effect on Excited-State Polarizabilities with the Corrected Linear-Response Model

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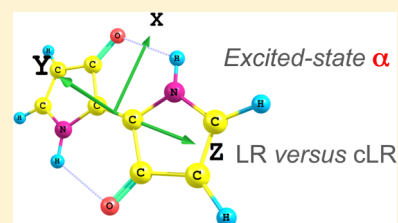
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S Supporting Information

ABSTRACT: Aiming to assess the environmental effects on the dipole moments and polarizabilities of electronically excited-states, we have applied a combined Polarizable Continuum Model/Time-Dependent Density Functional Theory (PCM/TD-DFT) approach on six representative chromophores. For the first time, we compare polarizabilities obtained with gas phase, linear-response and corrected linear response continuum models and we also investigate the relative importance of direct (electronic) and indirect (geometric) environmental contributions for these properties. It is shown that the solvent effects on excited-state polarizabilities tend to be large and can often, but not always, be captured with the computationally efficient linear-response formalism.



INTRODUCTION

The modeling of medium effects remains an important challenge for theoretical chemists, and two families of methods have been designed to tackle this task. On the one hand, explicit approaches, in which the surrounding molecules are explicitly described, present the advantage of accounting for the atomistic nature of solvent–solute interactions (within the selected level of theory), but they require a preliminary sampling study followed by an averaging procedure. On the other hand, implicit methods, in which the environment is treated as a structureless material presenting the macroscopic features of the real bulk, have the advantage to be computationally efficient but are less adequate for treating explicit solute–solvent interactions, e.g., hydrogen bonds. Among the implicit models dedicated to solvation effects, the Polarizable Continuum Model (PCM),¹ is the most widely used in the quantum chemistry community. In PCM, the molecule of interest is placed inside a cavity surrounded by a continuum dielectric medium, whose polarization is represented by induced charges located on the cavity surface which are determined with a self-consistent procedure. Nevertheless, while it could be stated that the use of PCM for most ground-state (GS) properties is well mastered, the investigation of the impact of the solvent on electronically excited-states (ES) remains difficult. This is, among other things, due to the difficulty to determine the variation of the solvent polarization following a change of state of the molecule of interest. Several PCM formulations have been developed for ES, e.g., linear-response (LR),^{2,3} corrected linear-response (cLR),⁴ state-specific (SS),⁵ vertical excitation model (VEM),⁶ and all have been coupled to Time-Dependent Density Functional Theory

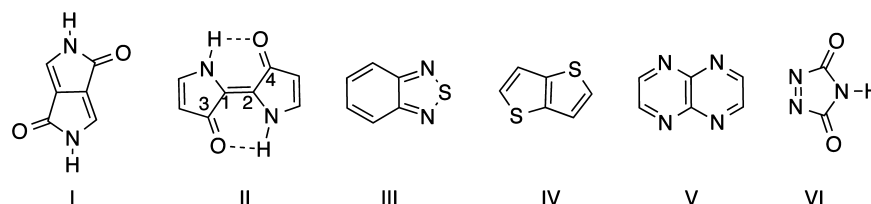
(TD-DFT), a method that is regularly applied to determine ES properties. These formulations differ by the treatment of the change of the solvent polarization from the GS toward the ES, e.g., in the LR scheme, the transition densities are used to determine the change in the PCM charges, whereas in the cLR scheme the one-particle TD-DFT density matrix, that accounts for the orbital relaxation contribution, is used in a perturbation approach. When determining adiabatic properties of ES of solvated molecules, a common procedure is to determine the geometry of these states through LR-PCM-TD-DFT optimizations and next to correct the properties (typically fluorescence wavelengths) by a single-point cLR-PCM-TD-DFT calculation that recovers the relaxation of the PCM charges in the ES. However, recently, we have proposed to perform cLR optimization of the ES structures, therefore paving the way toward fully consistent cLR estimates.⁷ In this previous work, we investigated geometries and emission wavelengths, but there are of course other key ES properties for which solvation might be of importance, and electric dipole moments and polarizabilities clearly belong to that category. The change in molecular dipole moment upon excitation, the so-called excess of dipole moment ($\Delta\mu$), directly influences electrostatic interactions with the solvent leading to experimentally observable shifts in absorption/emission bands. Analogously, the change in the molecular polarizability accompanying the excitation, the so-called excess of polarizability ($\Delta\alpha$), can induce shifts in absorption/emission peaks with a quadratic

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Scheme 1. Representation of the Six Molecules under Investigation; for Molecule II, the Central Carbon Atoms Are Numbered



dependence on the amplitude of the applied external electric field. This effect, called the Stark effect or electroabsorption/emission, is the main source of experimental data for ES polarizabilities.⁸ The shifts in absorption/emission can therefore be used for developing solvent polarity scales.⁹ The dipole polarizability of a solute in its GS and ES is also an important descriptor for dispersion interactions between solvent and solute, as demonstrated by Marenich and co-workers.¹⁰ It has been observed in polyenes, as well as in some other organic molecules, that the ES polarizabilities can be significantly larger than their GS counterparts.^{11–14}

While the GS dipole moment and polarizability, at least for closed-shell medium-size molecules, can nowadays be routinely handled, the ES properties are still a challenge for computational methods. Therefore, despite its importance in various areas, the number of calculations devoted to the ES polarizability is still rather small and usually limited to the gas phase.^{12–14} However, according to the work of Caricato,¹⁵ even the isotropic polarizability of a small and nonpolar hydrogen molecule can increase by 30% in the presence of water solvent. As for emission, one can apply two different approaches to calculate the polarizability of ES in the presence of solvent: explicit and implicit models. Gupta et al.¹⁶ used the supramolecular approach for calculating polarizabilities of ES of methanol and contrary to water clusters they found that ES polarizability is not a monotonic function of the cluster size. The need of a large number of solvent molecules for attaining converged solvent effects limits the applications of explicit approaches to small systems, and thus continuum solvent models have been favored in the field. Ferrighi et al. implemented ES polarizability of solvated molecules using cubic response theory and the PCM model for multi-configuration self-consistent field (MCSCF) method.¹⁷ We note that the combination of MCSCF with PCM is state-specific in the sense of solvation treatment. Recently, Caricato¹⁵ implemented linear response PCM model for CCSD calculations of electric properties including polarizabilities. Excited state polarizabilities of solvated molecules have also been calculated using both equilibrium and nonequilibrium solvation models by Ruud et al.¹⁸ While the mentioned wave function-based approaches are undoubtedly useful for benchmark-type calculations, the TD-DFT methodology often serves as a promising alternative for studying larger systems. Nevertheless, the question of a proper treatment of the polarization of the cavity encountered in absorption/emission TD-DFT studies arises even more importantly for polarizabilities. To the best of our knowledge, no previous work comparing the LR and cLR solvation treatments for calculation of ES electric properties has appeared.

Here, we have computed GS and ES polarizabilities of six representative chromophores using different environmental models. The six treated molecules are displayed in Scheme 1. The first four are characterized by $\pi \rightarrow \pi^*$ transitions: I is a

diketopyrrolopyrrole core, II is the H-shaped chromogen of the indigoid family, III is 2,1,3-benzothiadiazole, and IV is thieno[2,3-*b*]thiophene. The latter two aza-compounds are used as examples of $n \rightarrow \pi^*$ chromogens. It is important to state that the data presented in the present work have been obtained on the corresponding geometries (GS/ES polarizabilities on the optimal GS/ES structure); they thus represent adiabatic values.

METHODS

Most calculations have been performed with the latest version of Gaussian09 program (modified for cLR optimization, see ref 7.).¹⁹ We have systematically applied an improved energy convergence threshold (at least 10^{-10} au), a tight geometry optimization criterion (10^{-5} au on the residual root-mean-square force), and a high-level DFT integration grid (so-called *ultrafine* grid) in order to ensure the numerical stability of the presented data. The ground and excited-states geometry optimizations have been performed with the M06-2X/6-31G(d) approach,²⁰ and these geometries have been extensively described elsewhere.⁷ For both gas and LR-PCM calculations, we have checked that these geometries correspond to true minima of the potential energy surface by performing frequency calculations. As stated in the Introduction, both LR and cLR PCM models have been used, and default parameters have been used for the PCM cavity. Dichloromethane was used as a solvent, and the equilibrium PCM limit was systematically considered.

The excited-state polarizabilities and dipole moments have been obtained by the Finite Field (FF) procedure based on the TD-DFT energies computed with the M06-2X exchange-correlation functional and Sadlej's POL²¹ atomic basis set especially designed to reproduce linear and nonlinear optical properties. Since our interest in the ES is limited to the first valence ES there is no need to enlarge the basis set or to augment it with functions designed for the characterization of the Rydberg transitions. The problem of higher-order terms in the FF procedure for electric properties was overcome by using the Romberg procedure.^{22,23} The minimum external electric field F_L was set to 4×10^{-4} au ($1 \text{ au} = 5.1422 \times 10^{11} \text{ V m}^{-1}$), and the other field amplitudes were given by $\pm 2^k F_L$ with $k = 1, 2, \dots, 5$. For one molecule a more demanding cubic response CC2²⁴ calculation of the ES polarizability was done using the Dalton code²⁵ in order to assess the quality of the M06-2X predictions.

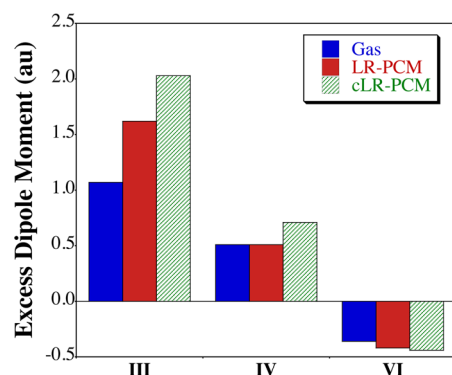
RESULTS AND DISCUSSION

Table 1 collects the dipole moments computed for both GS and ES for III, IV and V, whereas Figure 1 gives the corresponding $\Delta\mu$. All other molecules present null permanent dipole moments in both electronic states due to the presence of an inversion center. We also underline that V is planar in its

Table 1. Ground and Excited-State Dipole Moments Obtained for the Non-centrosymmetric Molecules of Figure 1 Using Different Environmental Models^a

	ground state		excited state		
	gas	solvent	gas	solvent (LR)	solvent (cLR)
III	0.77	0.92 (+27%)	1.84	2.54 (+37%)	2.95 (+60%)
IV	0.00	0.00	0.51	0.51 (+0%)	0.71 (+39%)
VI	1.02	1.26 (+24%)	0.66	0.84 (+27%)	0.82 (+24%)

^aThe solvent considered is dichloromethane, and all calculations are made using a consistent approach for geometry optimization and property calculation (see Methods). The data in parentheses indicate the percentage of increase compared to gas phase. All results are in au.

**Figure 1.** Computed $\Delta\mu$ for the three nonsymmetric molecules using different environmental models.

ground state but undergoes puckering in the ES,⁷ which explains the appearance of a dipole moment only in the latter.

As expected the presence of a solvent has a tendency to increase the dipole moments, but the magnitude of this effect depends on the considered state as well as on the choice of the PCM model. For the GS of both **III** and **VI**, we observed a \sim +25% change when solvent effects are accounted for. For the ES of the three molecules, the solvation effects tend to be larger and more system-dependent, with increases up to +60% compared to the gas-phase for **III**, a molecule characterized by a strong photoinduced charge-transfer between the two rings, a situation for which cLR is clearly more suited than LR. For the $n \rightarrow \pi^*$ transition in **VI**, LR and cLR approaches provide very similar ES structural parameters⁷ and emission energies (within 0.01–0.02 eV), and the same holds for the ES dipole moments. A more challenging case is **IV**: LR yields the same ES dipole as in the gas-phase, whereas cLR foresees a strong increase (+39%) of this property. To understand the reasons for this different behaviors, we have computed the cLR ES dipole on the LR geometry (0.52 au) as well as the LR ES dipole on the cLR geometry (0.69 au). These results clearly indicate that the significant cLR correction for **IV** can be mostly ascribed to a geometric rather than to an electronic effect. This is again consistent with the significant differences of puckering angle obtained for cLR and LR optimal ES geometries (see Discussion in ref 7).

For $\Delta\mu$, Figure 1 clearly shows that all environmental models provide the same qualitative conclusions: (i) a negative change for **VI** and (ii) a larger positive variation for **III** than for **IV**. The absolute $\Delta\mu$ values follow a cLR > LR > gas ranking, but it is difficult to know if this trend is general as only three molecules have been tested. For **III** the dipole moment excess computed with cLR (+2.03 au) is about twice its gas-phase counterpart

Table 2. Ground and Excited-State Isotropic Polarizabilities Results Obtained for the Six Molecules of Figure 1 Using Different Environmental Models; See of Table 1 Title for More Details^a

	ground state		excited state		
	gas	solvent	gas	solvent (LR)	solvent (cLR)
I	96	129 (+34%)	124	161 (+30%)	181 (+46%)
II	128	174 (+36%)	209	269 (+29%)	459 (+120%)
III	102	138 (+35%)	122	173 (+42%)	170 (+39%)
IV	105	143 (+36%)	143	190 (+33%)	185 (+29%)
V	97	130 (+34%)	116	163 (+41%)	166 (+43%)
VI	50	63 (+26%)	57	73 (+28%)	74 (+30%)

^aAll results are in au.

(+1.07 au), highlighting that this property is very sensitive to solvation.

The results for the GS and ES isotropic polarizabilities for the six molecules of Figure 1 are presented in Table 2, whereas the components of the tensor are reported in the Supporting Information [SI]. For **II**, we have also performed CC2 calculations of the gas-phase ES α and obtained a value of 228 au, which nicely matches the M06-2X estimate (209 au, 8% discrepancy). Test calculations performed with CAM-B3LYP revealed that M06-2X and CAM-B3LYP excited-state polarizabilities also nicely agree (only 2% difference with the 6-31G(d) atomic basis set), whereas PBE0 yields significantly larger polarizabilities as expected for an exchange-correlation functional including a rather small amount of exact exchange.^{26,27}

As for the dipole moments, solvent effects tend to increase the GS polarizability for all molecules. For the tested compounds, the relative effect is rather uniform (\sim +35%), but for **VI** that is less affected by the medium (+26%). For the ES polarizabilities, both LR and cLR models foresee increases of the gas-phase polarizabilities. For compounds **III**–**VI**, the two PCM models provide excited-state polarizabilities within 5 au of each other that significantly differ from gas-phase results. In other words, for these four compounds, considering solvent effects is essential, but the choice of LR or cLR to perform this task has no significant impact. In the previous analysis on dipoles, for both **III** and **IV**, the cLR and LR ES dipoles differed significantly, but we notice that the ES polarizabilities are very comparable: this seems to show that each PCM model describes a different electron flow upon excitation but they both lead to the same electronic "mobility" in the ES. For **I**, the cLR ES α (181 au) is larger than its LR counterparts (161 au). To better understand this difference we have decomposed the total effect into electronic and geometric contributions by performing mixed calculations: the obtained results are 180 au for the cLR ES α determined on the LR geometry and 162 au for the LR α computed on the cLR structure. This analysis clearly hints that the cLR effect is mostly electronic (and not geometric), contrasting with what was noted above for the dipole moments of **IV**. This small impact of the cLR optimization (compared to its LR counterpart) is unsurprising since we have shown little impact of the solvent model on the geometry for **I**.⁷ For **II** a very large difference between the cLR and LR ES polarizabilities can be observed, the cLR value being nearly twice its LR counterpart. First we have carefully checked that this outcome was not the result of a numerical instability by performing additional calculations with improved energy convergence thresholds (both GS and ES), and it confirmed the

data listed in Table 2. Next we computed the cLR ES α on the LR geometry (366 au) and the LR ES α on the cLR geometry (302 au), and this indicated that, in the present case, it is a coupling of geometric and electronic effects that explains the total cLR correction. A detailed explanation of the dramatic increase of polarizability of **II** is not straightforward. First, we note that it is the component of the polarizability tensor along the long axis that is responsible for the change (see the SI). Second, a deeper analysis of structural changes reveals that the two 5-membered rings are mutually less conjugated in the GS compared to the ES. For instance, the bond lengths in the sequence of atoms C3–C1–C2–C4 (see Figure 1) change from 1.500, 1.345, 1.500 Å for the GS to 1.461, 1.380, 1.461 Å for the ES, respectively. Consequently, the response of the charge distribution to an external field due to increased electron mobility can be expected to be larger in the ES. Since the conjugation is sensitive to the surrounding charge density, the polarizability value of the ES is significantly affected by the presence of a polar solvent. For **II** it is also noteworthy that the solvent effects induce significant variations of the ES intramolecular hydrogen bond lengths (see ref 7).

The results are finally summarized in Figure 2 in terms of the change in the molecular polarizability accompanying the

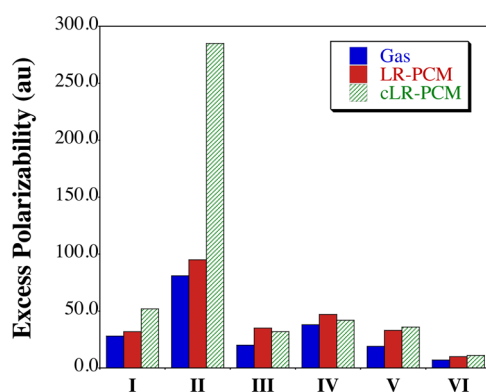


Figure 2. Computed $\Delta\alpha$ for the six compounds using different environmental models.

excitation, the excess of polarizability ($\Delta\alpha$). From this graphical representation it is evident that all methods predict an increase of the polarizability in the excited states. This growth is (i) always larger in condensed phase than in gas-phase, (ii) weaker for the two $n \rightarrow \pi^*$ dyes (**V** and **VI**) compared to the other compounds, (iii) quite similar for all methods except in the case of **II** discussed above, and (iv) not systematically smaller or larger with cLR than with LR.

CONCLUSIONS

We have computed the ground- and excited-state dipole moments and polarizabilities of six compounds using several environmental models. For the first time, adiabatic cLR excited-state polarizabilities have been computed. It turned out that the solvation effects are rather uniform for ground-state properties (slight increase) but are more diverse for excited-state properties. Consequently, including environment in the simulation of ES dipole moments and polarizabilities is crucial even to obtain reasonable chemical rankings. By comparing the present results with our previous work,⁷ it was found that the evolutions of the fluorescence energies when shifting from one PCM model to another do not systematically correlate with the

LR/cLR changes of dipole moments and polarizabilities. In most cases, LR and cLR μ and α differences are small. When instead they are large, the reasons are not univocal as geometric effects (dipole of **IV**), electronic effects (polarizability of **I**) or a combination of them (polarizability of **II**) can explain the variations.

ASSOCIATED CONTENT

Supporting Information

Three dimensional representation of all molecules. Full list of individual Cartesian components of the polarizability tensor for all molecules, in both ground- and excited-states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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