Implementation of the CCSD-PCM linear response function for frequency dependent properties in solution: Application to polarizability and specific rotation

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Implementation of the CCSD-PCM linear response function for frequency dependent properties in solution: Application to polarizability and specific rotation

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This work reports the first implementation of the frequency dependent linear response (LR) function for the coupled cluster singles and doubles method (CCSD) combined with the polarizable continuum model of solvation for the calculation of frequency dependent properties in solution. In particular, values of static and dynamic polarizability as well as specific rotation are presented for various test molecules. Model calculations of polarizability show that a common approximation used in the definition of the LR function with solvation models recovers over 70% of the full response while maintaining a computational cost comparable to gas phase LR-CCSD. Calculations of specific rotation for three compounds for which gas phase methods predict the wrong sign of the rotation show that accounting for the electronic response of the solvent may be essential to assign the correct absolute configuration of chiral molecules. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4821087]

I. INTRODUCTION

The inclusion of solvation effects in the calculation of molecular properties is of paramount importance since most chemistry happens in solution. However, the explicit consideration of solvent molecules treated at the same level of theory as the solute is impractical for computational reasons, and some simplification must be introduced. Continuum models replace the atomistic structure of the solvent with a polarizable medium that interacts with the solute through an effective potential. Long range interactions (bulk solvation) are well described with these models while maintaining a low computational cost, albeit at the price of losing the ability to account for specific solute-solvent interactions (for instance, hydrogen bonds). One of the most diffuse members of this family of models is the polarizable continuum model (PCM), initially developed by Tomasi and co-workers.[1–4] PCM describes the solvent as a dielectric characterized by its macroscopic permittivity ε. A cavity of molecular shape (usually, a series of interlocking spheres centered on the solute nuclei) hosts the solute. The dielectric polarization, which depends on the electrostatic potential generated by the nuclei and electron density of the solute, is represented by an apparent surface charge on the cavity surface, and then discretized in finite elements (i.e., the PCM charges). Mutual solute-solvent polarization is obtained by introducing a one-electron PCM operator into the solute Hamiltonian that is used in quantum mechanical (QM) methods.

PCM has been combined with a large variety of methods for the calculation of molecular energy and properties in solution for ground and excited states.[4] In recent years, this effort has been extended to methods belonging to coupled cluster (CC) theory[5,6] by this author and others.[7–11] In particular, Cammi[7] presented the first theoretical development

for the combination of PCM and the CC singles and doubles (CCSD) method. However, previous work done by Christiansen and Mikkelsen on a different solvation model called dielectric continuum (DC) should be mentioned.[12–14] The development of CCSD-PCM (with Hartree-Fock, HF, and Brueckner orbitals)[8,15] includes energy and analytic energy gradients, transition energies, and their analytic gradients in the equilibrium and non-equilibrium regimes in a state-specific (SS) formulation,[10,11] so that both ground and excited states potential energy surfaces can be explored and vertical transition energy computed both in absorption and in emission. Furthermore, a variety of approximate schemes have been proposed that reduce the computational cost to a level comparable to gas phase calculations.[9–11] Christiansen and Mikkelsen used a linear response (LR) formalism for computing the solvent effect on excitation energies and frequency-dependent properties for CCSD with the DC model,[12–14] and the same formalism was re-derived by Cammi for PCM.[16] Recently, I presented the first implementation of the LR-CCSD approach with PCM for excited states, and compared the LR and SS approaches formally and numerically.[17] The SS formalism provides a more complete account of the mutual solute-solvent polarization in the excited state, but is computationally more demanding. On the other hand, the LR formalism lacks some interaction terms but is computationally very efficient (i.e., comparable to the corresponding gas phase method).

The frequency-dependent LR formalism has also been applied in the framework of density functional theory (DFT) with PCM,[18] and in the context of DFT and CC theory with explicit solvent models.[19–22] In this work, I present the first implementation of the frequency-dependent linear response function for the CCSD-PCM method, and applications to the calculation of molecular electric polarizability and specific rotation. The numerical results for the polarizability are used for theoretical comparisons between methods. For the specific

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rotation, on the other hand, a comparison with experimental data in solution is presented.

The paper is organized as follows. The theory of the LR-CCSD-PCM method is reviewed in Sec. II. The results of the numerical tests are presented in Sec. III, and Sec. IV contains a discussion of the results and concluding remarks.

II. THEORY

In this section, I review the theory for the calculation of the linear response function of the CCSD-PCM method. A complete derivation of the formulas can be found elsewhere.[12,16] Also, details about PCM can be found in the literature.[4] The following implementation is limited to symmetric versions of PCM[23,24] either with the integral equation formalism (IEFPCM)[2,3] or the conductor-like (CPCM)[25,26] flavors.

The CC linear response function for an observable X to the Y perturbation oscillating at frequency ω in the presence of a continuum model of solvation can be written as

$$\langle\langle X; Y\rangle\rangle_\omega = \frac{1}{2}C^{\pm\omega}P(XY)\big[\langle\Phi_0|(1+\Lambda)\big[e^{-T}Xe^T, T_\omega^Y\big]|\Phi_0\rangle$$
$$+ \frac{1}{2}\langle\Phi_0|(1+\Lambda)\big[\big[e^{-T}H_N^{PCM}e^T, T_{-\omega}^X\big], T_\omega^Y\big]|\Phi_0\rangle$$
$$+ \frac{1}{2}\langle\Phi_0|(1+\Lambda)\big[\big[e^{-T}\mathbf{V}_Ne^T, T_{-\omega}^X\big], T_\omega^Y\big]|\Phi_0\rangle\cdot\overline{\mathbf{Q}}_N$$
$$+ \frac{1}{2}\langle\Phi_0|(1+\Lambda)\big[e^{-T}\mathbf{V}_Ne^T, T_{-\omega}^X\big]|\Phi_0\rangle$$
$$\cdot\langle\Phi_0|(1+\Lambda)\big[e^{-T}\mathbf{Q}_N^{|\omega|}e^T, T_\omega^Y\big]|\Phi_0\rangle\big], \quad (1)$$

where the permutation operator $C^{\pm\omega}$ changes the sign of the field frequency and takes the complex conjugate of the expression, while the symmetric permutation operator $P(XY)$ switches the X and Y operators at the corresponding frequency $(X, -\omega) \to (Y, \omega)$. Φ_0 is the reference wave function computed in the presence of the reference PCM reaction field, and T and Λ are the CC excitation and de-excitation operators.[5,6] The subscript N indicates the normal-product form of an operator. The effective Hamiltonian H_N^{PCM} includes the PCM operator with the reference charges:

$$H_N^{PCM} = H_N + \mathbf{V}_N \cdot \overline{\mathbf{Q}}_0, \quad (2)$$

where the overbar indicates the expectation value of the charge operator $\mathbf{Q}$, i.e., its trace with a proper one-particle density matrix (1PDM). The operator $\mathbf{V}_N$ is the electrostatic potential on the cavity surface and the bold font is used to indicate the discretization of the apparent surface charge in finite elements. The correlation charges $\overline{\mathbf{Q}}_N$ are obtained from the solution of the ground state CC-PCM equations.[7,8] The reference and correlation charges, $\overline{\mathbf{Q}}_0$ and $\overline{\mathbf{Q}}_N$, are computed with the static dielectric constant ε since they represent the solvent response before the electric field is turned on, and the solute and solvent have had enough time to equilibrate. On the other hand, the perturbed charges in the last term of Eq. (1), indicated with the superscript $|\omega|$ on the charge operator, should be computed with a frequency-dependent permittivity $\varepsilon(\omega)$ where ω is the oscillation frequency of

the impinging light. However, here I introduce the common approximation of using the optical dielectric constant (ε_∞) for frequency-dependent calculations and ε for the static limit:[12,16,27–29]

$$\begin{cases} \varepsilon(\omega) \simeq \varepsilon_\infty & \text{for } \omega \neq 0, \\ \varepsilon(\omega) = \varepsilon & \text{for } \omega = 0, \end{cases} \quad (3)$$

since accurate values of $\varepsilon(\omega)$ are not available in general. The quality of this approximation depends on the solvent response time and on the frequency used, although, it is usually reasonable in the typical range of frequencies studied in experiments. Note, however, that by computing the change in the linear response function with this model at decreasing values of ω one cannot recover the static limit since there is no smooth switching from ε_∞ to ε. A development of PCM in this direction was proposed to study the solvent relaxation after a sudden change in the solute electronic density (e.g., after a vertical electronic excitation),[30,31] but further development for frequency-dependent properties is still ongoing and is beyond the scope of the present work. A further approximation in Eq. (1), introduced in the derivation of the CC linear response function with continuum solvation models in Refs. 12 and 16 and maintained in the present implementation, is that the PCM term quadratic in the perturbed Λ amplitudes is neglected. Such term would couple the equations for the perturbed T and Λ amplitudes, similar to the correlation energy equations. With this assumption, however, the perturbed Λ amplitudes are not necessary to compute the linear response function as in gas phase. This approximation is also used when CC methods are combined with explicit solvent models.[32] Similar to CC response theory in gas phase, orbital relaxation is neglected in the evaluation of the linear response function since it would give rise to second order poles, contrary to the response function for exact states.

The perturbed T amplitudes are computed by solving systems of linear equations of the type:

$$-\langle\Phi_n|e^{-T}Ye^T|\Phi_0\rangle$$
$$= \langle\Phi_n|\big[e^{-T}H_N^{PCM}e^T, T_\omega^Y\big]|\Phi_0\rangle - \omega\langle\Phi_n|T_\omega^Y|\Phi_0\rangle$$
$$+ \langle\Phi_n|\big[e^{-T}\mathbf{V}_Ne^T, T_\omega^Y\big]|\Phi_0\rangle \cdot \overline{\mathbf{Q}}_N$$
$$+ \langle\Phi_n|e^{-T}\mathbf{V}_Ne^T|\Phi_0\rangle$$
$$\cdot \langle\Phi_0|(1+\Lambda)\big[e^{-T}\mathbf{Q}_N^{|\omega|}e^T, T_\omega^Y\big]|\Phi_0\rangle \quad (4)$$

for X and Y, and $\pm\omega$. The expressions in Eqs. (1) and (4) are equivalent to those for gas phase except for the PCM terms. Such terms are similar to those for the calculation of vertical electronic excitation energies, and the reader is referred to Ref. 17 for the explicit expressions and computational considerations.

The linear response function in Eq. (1) can be used to compute molecular electric polarizability when X and Y are replaced by the electric dipole operator. The mixed electric dipole-magnetic dipole polarizability tensor (G' tensor) can be computed when X and Y are the electric and magnetic dipole operators. The G' tensor is related to the specific

rotation $[\alpha]_\omega$ in deg dm^{-1} (g/mL^{-1}) through the formula:[33]

$$[\alpha]_\omega = \frac{(72.0 \times 10^6)\hbar^2 N_A \omega}{c^2 m_e^2 M} \times \left[\frac{1}{3}\text{Tr}(G')\right], \qquad (5)$$

where N_A is Avogadro's number, c is the speed of light in m/s, m_e is the rest mass of the electron in Kg, M is the molecular mass in amu, and G' and ω are in atomic units. The specific rotation can be computed with two choices of gauge for the electric dipole operator: length or velocity gauge (LG or VG, respectively). The former has the correct asymptotic behavior (i.e., $[\alpha]_\omega \rightarrow 0$ for $\omega \rightarrow 0$) but the results are origin dependent for truncated CC expansion and finite basis set. The latter is intrinsically origin independent but has the wrong asymptotic behavior in the same conditions. Pedersen *et al.*[34] proposed a modified VG (MVG) approach where the static limit is subtracted from the VG G' tensor, thus providing the correct asymptotic behavior. MVG is, therefore, more computationally demanding than LG since the static limit linear response function must be computed as well. For a CCSD-PCM calculation of specific rotation in the MVG approach, the perturbed charges in the unphysical static limit are computed with ε_∞ rather than ε since this is an artifact introduced by the truncated cluster expansion and finite basis set. Thus, the unphysical static limit should be computed coherently with the frequency dependent solvent response.

III. NUMERICAL APPLICATIONS

This section reports the calculation of the linear response of molecules in solution at CCSD-PCM level according to Eq. (1). In particular, the properties considered here are isotropic electric polarizability and specific rotation ($[\alpha]_\omega$ in Eq. (5)). The symmetric version of IEFPCM with the continuum surface charge (CSC)[23] scheme is used for all calculations. The cavity is built as a series of interlocking spheres centered on atomic nuclei and using the solvation model D (SMD) radii,[35] unless otherwise specified. Core orbitals are kept frozen when solving the CC equations. All calculations are performed with a development version of the GAUSSIAN suite of programs.[36] The polarizability calculations in Sec. III A are discussed in terms of internal theoretical comparisons since experimental data for this property are difficult to find. On the other hand, calculations of specific rotation in Sec. III B are directly compared to experiment for a sample of molecules where theoretical calculations in gas phase provide the wrong sign of the rotation.

A. Polarizability

The first system under consideration for static polarizability is molecular hydrogen, H_2, in gas and in water. This allows a quantitative assessment of the approximation of neglecting the term quadratic in the perturbed Λ amplitudes in the PCM LR function (see Eq. (1) and related discussion in Sec. II). In fact, CCSD provides the exact wave function for a two-electron system (within the non-relativistic, Born-Oppenheimer, and finite basis set approximations). Therefore, at least in gas phase, the static polarizability tensor

TABLE I. Static isotropic polarizability (a.u.) for H_2 in gas phase and water computed with the analytic LR formula and as numerical differentiation of the electric dipole with various basis sets. The abbreviation (a)pVXZ is used for (aug-)cc-pVXZ.

	pVDZ	apVDZ	pVTZ	apVTZ	pVQZ	apVQZ
Gas	3.62	6.42	4.83	6.57	5.48	6.56
Water						
Numeric	4.62	8.16	6.13	8.35	7.01	8.34
Analytic	4.35	7.67	5.77	7.85	6.58	7.84
Shift						
Numeric	1.00	1.74	1.30	1.78	1.53	1.78
Analytic	0.73	1.25	0.94	1.28	1.10	1.28

computed with the orbital-frozen analytic LR formalism coincides with that computed as numerical differentiation of the electric dipole with respect to an external field. Such correspondence is lost with PCM because of the approximation mentioned above. The data computed with various basis sets of the correlation-consistent family,[37,38] with and without diffuse functions, are reported in Table I. The H_2 bond length is kept at 0.9 Å for all calculations. First, notice that diffuse functions considerably improve basis set convergence, both in gas phase and in solution, since the results with aug-cc-pVDZ are much closer to those with aug-cc-pVQZ than with the quadruple-ζ basis without diffuse functions. When the solvent shift is considered, the analytic result with the approximation on the quadratic Λ term recovers 72% of the full solvent effect consistently across the basis sets. This result is accord with what found for a similar approximation in the calculation of the ground state solvation free energy.[9] This can be considered a good compromise between accuracy and computational effort since these calculations are already very expensive when larger molecules are investigated. Also, other sources of error are likely to be more relevant, starting from the solvation model itself.

The next example is furan, which was studied in Ref. 12 where the CC linear response theory was developed with a related continuum model, DC. This system thus allows for a comparison between different solvation models, and the same geometry is used here. Static and dynamic polarizability (at 632.8 nm) are computed in various solvents using a single sphere cavity as in Ref. 12 (centered in the center of mass of the molecule and with radius 3.3963 Å) and the SMD cavity. The same cavity is used across solvents (for SMD, the radii for water are used). The solvents are water, methanol, acetone, CCl$_4$, and cyclohexane. The corresponding values of ε are 78.54, 32.63, 20.7, 2.228, and 2.209, respectively.[12] The values of ε_∞ are 1.778, 1.758, 1.841, 2.132, and 2.023, respectively. The basis set used for the calculations is aug-cc-pVDZ.

The values of polarizability are reported in Table II. The solvent effect is quite large in the static limit, amounting to 10%–25% for DC, and 7%–18% for PCM with the same cavity (from cyclohexane to water). The larger solvent effect with DC than with PCM is consistent with what found for vertical electronic transition energies.[17] However, both solvation models predict similar trends. The cavity is an important

TABLE II. Static and dynamic (632.8 nm) isotropic polarizability (a.u.) for furan in gas and in solution. The cavities are the same for all of the solvents: the radius of the one-sphere cavity is 3.3963 Å, as in Ref. 12; the SMD cavity uses the radii for water.

	DC-1Sph[12]		PCM-1Sph		PCM-SMD	
	Static	Dynamic	Static	Dynamic	Static	Dynamic
Gas	48.27	49.61	48.27	49.61	48.27	49.61
Water	60.30	53.36	56.85	52.54	63.41	54.21
Methanol	59.89	53.29	56.58	52.49	62.90	54.13
Acetone	59.50	53.58	56.33	52.69	62.41	54.51
CCl$_4$	53.09	54.46	51.87	53.28	54.41	55.85
Cyclohex	53.04	54.15	51.84	53.05	54.35	55.45

factor for this molecule as shown by the comparison between the one-sphere and SMD results with PCM. This is reasonable since one sphere is not a good representation of the solute molecular boundary within the solvent for a planar compound like furan. In fact, the increase in the value of polarizability with the SMD cavity is 13%–31% since the solvent is "closer" to the solute. In general, the large difference between polar and non-polar solvents in the static limit indicates that the electrostatic part of the solvent effect is very important. The differences between solvents in the dynamic case are much smaller, as expected since the the values of ε_∞ are closer to each other. Also, the difference between DC and PCM, and between cavities is much smaller for the dynamic case. Note that the values obtained with CCl$_4$ and cyclohexane are now larger than those with polar solvents since the values of ε_∞ are larger for the former solvents than for the latter.

B. Specific rotation

The calculation of specific rotation is a very useful tool to assist experimentalists in assigning the absolute configuration of a chiral sample. This is usually accomplished by computing the G' tensor as discussed in Sec. II at the minimum equilibrium geometry in gas phase. In this context, accurate theoretical methods such as CCSD become extremely important to properly account for the electronic contributions to this property.[33] However, other effects come into play that influence the value of the specific rotation, and may even change its sign. Such effects include vibrational averaging and, obviously, solvation. The latter is usually ignored, even if the vast majority of measurements is performed in liquid phase. PCM provides a very efficient approach to explore the electronic effect of the solvent, albeit with the limitations discussed in the Introduction.

In this section, three compounds are used as test examples: **1** (1R,3R,5R,7R)-bisnoradamantan-2-one, **2** (1R,5S)-nopinone, and **3** (1S,4R)-norbornanone, shown in Figure 1. These are a subset of the molecules studied by Crawford and Stephens,[39] who compared results at B3LYP[40–44] and CCSD level against experimental data. These molecules are chosen in this work because the calculated CCSD results in gas phase yield the wrong sign compared to measured values of specific rotation in solution. Therefore, they represent a very
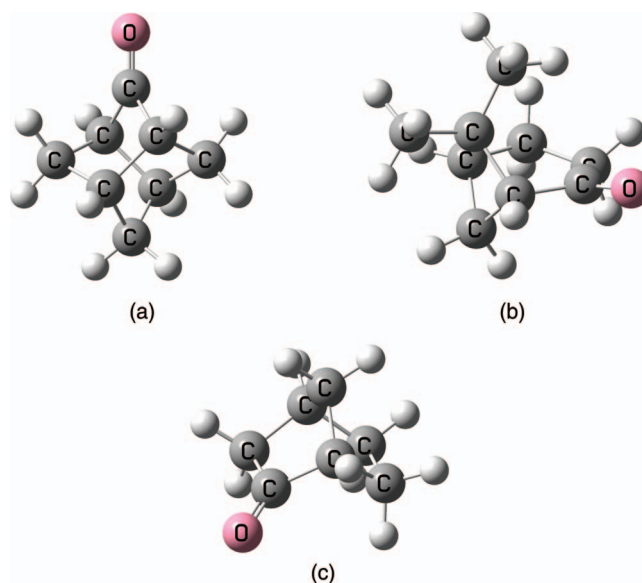

FIG. 1. Structures of the compounds studied in Sec. III B: (a) **1** (1R,3R,5R,7R)-bisnoradamantan-2-one; (b) **2** (1R,5S)-nopinone; and (c) (1S,4R)-norbornanone.

indicative test set to assess the effect of solvation on this property. In particular, measurements were performed in ethanol for **1**, methanol for **2**, and chloroform for **3** at the sodium-D line wavelength (589.3 nm). The measured and calculated data are reported in Table III. The optimized geometries are obtained at B3LYP/6-31G(d) level as in Ref. 39 in gas and in solution (PCM with SMD cavity). In order to differentiate the effect of solvation on the geometry and on the electronic density of the solute, CCSD-PCM calculations are also repeated at the gas phase optimized geometry (reported in the PCM(G) column in Table III). The LR-CCSD calculations are performed using the cc-pVDZ basis set for hydrogen centers and the aug-cc-pVDZ basis set for carbon and oxygen centers as in Ref. 39. LR calculations are reported with both choices of gauge (LG and MVG) discussed in Sec. II.

For compound **1**, the experimental rotation is negative (−78.4 deg dm^{-1} (g/mL)$^{-1}$) while the gas phase results are positive with both approaches (+50.3 deg dm^{-1} (g/mL)$^{-1}$ for MVG and +19.8 deg dm^{-1} (g/mL)$^{-1}$ for LG). The calculated data in solution, however, recover the correct sign (−3.8 deg

TABLE III. Specific Rotation (deg dm^{-1} (g/mL)$^{-1}$) at 589.3 nm. The experimental values are measured in solution (see text for details). The theoretical values are computed at the equilibrium geometry in gas (Gas and PCM(G) columns) and in solution (PCM column).

	Expt.[39]	Gas	PCM(G)	PCM
Modified velocity gauge				
1	− 78.4	50.3	5.3	− 3.8
2	39.9	− 8.4	36.0	44.4
3	29.8	5.0	− 8.0	− 5.9
Length gauge				
1	− 78.4	19.8	− 13.8	− 23.6
2	39.9	− 8.0	30.4	38.7
3	29.8	− 7.9	− 7.6	− 4.9

dm^{-1} (g/mL)$^{-1}$ for MVG and -23.6 deg dm^{-1} (g/mL)$^{-1}$ for LG). The agreement is not quantitative, indicating that other effects are missing (for instance, hydrogen bonds with the carbonyl group or vibrational effects). Nevertheless, the solvent effect is crucial to obtain the correct sign of the rotation. Additionally, the effect of solvation on the geometry is important to obtain the correct sign with the MVG approach (see the PCM(G) column in Table III). The gas phase calculations for compound **2** provide negative values of $[\alpha]_D$, albeit in better agreement between the two gauges (-8.4 and -8.0 deg dm^{-1} (g/mL)$^{-1}$ for MVG and LG, respectively), while the experimental value has a positive sign ($+39.9$ deg dm^{-1} (g/mL)$^{-1}$). The effect of solvation through PCM changes the sign of the calculated value, bringing it to an almost quantitative agreement with experiment (11% and -3% deviations from experiment for MVG and LG, respectively). This seems to indicate that the solvent electronic response has a major contribution for this system. The geometry effect is less important in this case, although it accounts for a change of 23% in the MVG and 27% in the LG results (compare the PCM(G) and PCM columns in Table III), and makes the LG agreement with experiment considerably better when the geometry optimized in solution is used. For the last case, compound **3**, the gas phase MVG approach provides the correct (positive) sign, while the LG result has the wrong (negative) sign. This difference is an indication that CCSD with this basis set is not at convergence with respect to the exact wave function (for which the two choices of gauge are equivalent). The effect of the solvent is to provide a negative sign for the specific rotation with both approaches (and for both geometries). This may be an indication that the electronic response of the solvent is not the cause of the disagreement with experiment, and other effects should be considered (as vibrational averaging).

IV. DISCUSSION AND CONCLUSIONS

This work reports the first implementation of the frequency dependent linear response function at coupled cluster level with the polarizable continuum model of solvation. The method is applied to the calculation of static and dynamic polarizability, and specific rotation. Details of the approximations introduced in the definition of the response function for frequency-dependent properties are discussed in Sec. II.

Calculations of static polarizability for the H$_2$ molecule in solution, reported in Sec. III A, show that neglecting the solvent term quadratic in the perturbed Λ amplitudes allows to recover more than 70% of the total solvent effect. This is a good compromise between accuracy and computational cost since the expression of the LR function takes a form similar to gas phase with this approximation, and the computational effort becomes almost equivalent to that for an isolated molecule.

A comparison with the DC model is shown in Table II for static and dynamic polarizability of furan in gas and various solvents. PCM calculations are repeated using the same one-sphere cavity as DC and a more realistic molecular-shaped cavity. The one-sphere results show the same trends between the two solvation models, although the solvent effect obtained

with DC is considerably larger than with PCM, at least for the static values. Differences are smaller for the dynamic polarizability since the values of ε_∞ are small. A large cavity effect is found when a standard PCM cavity is used, which shows the importance of a realistic cavity shape.

The calculations on specific rotation, reported in Sec. III B, are possibly more interesting since a direct comparison with experimental data is available. Calculations in gas phase for the three compounds chosen, see Figure 1, predict the wrong sign of the rotation compared to experimental data in solution. The results reported in Table III with CCSD-PCM recover the correct sign for two of these compounds, indicating the importance of solvation on this property. The agreement is quantitative for compound **2** while it is only qualitative for compound **1**, which suggests that effects other than the solvent electronic response are missing for the latter (for instance, vibrational effects). For compound **3**, the calculations in solution do not provide the correct sign of the rotation, indicating that other effects are missing.

In conclusion, these results show that the coupling of CCSD and PCM for the calculation of frequency-dependent linear response properties is a promising tool that allows the efficient extension of high level calculations of molecular properties to the condensed phase. The natural development is now the coupling of this approach to an explicit polarizable solvent model[45] that allows the description of specific solute-solvent interactions while PCM can be employed to account for bulk solvent effects.

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