Solvent effects on the electronic absorption spectrum of camphor using continuum, discrete or explicit approaches

Jacob Kongsted a,*, Benedetta Mennucci b, Kaline Coutinho c, Sylvio Canuto c

a Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark
b Department of Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy
c Instituto de Física, Universidade de São Paulo, C.P. 66318, 05314-970 São Paulo, SP, Brazil

1. Introduction

Understanding solvation phenomena is of great importance in order to rationalize experimental results obtained when a molecule interacts with a liquid environment [1]. This is an every-day need in chemistry laboratory where most molecular spectra are recorded in a specific solvent. In addition, solvation is crucial in most biochemical studies. With the great development achieved in theoretical quantum chemistry for isolated molecules [2] a natural attention is now devoted to solution problems. In recent years this has become a central concern in theoretical physico-chemistry. There are essentially three major theoretical lines of development to include solvent effects in the quantum chemical models: continuum, discrete and explicit approaches. In the continuum model [3,4] the solvent is considered implicitly as a polarizable medium characterized by its dielectric constant. The polarizable continuum model (PCM) [5] has been found to be successful in a large number of applications and is perhaps the most used model at present. Its major difficulty is found when specific interactions such as hydrogen bonds are needed for a proper treatment. The great advantage is that the computational cost is similar to that of the isolated molecule, and since the solvent is described implicitly the results may be rationalized in a manner following the same strategy as for the case of an isolated molecule. In complement, the discrete model (DM) has seen an intense development in the recent years [4]. In this case, discrete solvent molecules are included along with the solute molecule and the calculations are made in such molecular structures composed of the solute and a certain number of discrete solvent molecules treated as point charges. However, in the discrete solvation model the solvent molecules are not treated using quantum mechanics (QM) but rather a classical description of the solvent is imposed. In this spirit the discrete solvation model is also implicit in nature since the explicit solvent electronic degrees of freedom are neglected in the calculations. The spatial distribution of the molecules is generally obtained from computer simulations (Monte Carlo or Molecular Dynamics) and several super-molecular calculations, i.e. calculations including molecular complexes, are performed in order to obtain the statistically converged results. As the simulation is made at a certain temperature, the configurations generated are temperature-dependent and as such represent more realistically the thermodynamic equilibrium conditions. As it can be noted by this simple description, the drawback of the discrete model is that several QM calculations are needed in order to address the explicit averaging. However, the cost of each such QM calculation is roughly the same as the corresponding calculation using the isolated solute molecule. The third class of solvent models describes the solvent as a discrete and explicit medium, i.e. an explicit reference to the solvent electronic structure is kept. In this way all molecular interactions included in the underlying many-body formulation of the specific quantum chemical model are included in the calculation. The main drawback here of course relates to the complexity of performing full QM calculations of such large samples.

In this work, we use the procedures introduced above to analyze the solvent effect on the absorption spectra of the camphor molecule in different solvents. There are three strong motivations for this study. First, in spite of the existence of experimental results [6] on the UV–Vis absorption spectra of camphor there is apparently no systematic theoretical analysis of the...
solvatochromic shifts. Second, the spectral shifts of the absorption band of camphor are a real challenge. These shifts are very small, around 0.05 eV (ca. 500 cm⁻¹) thus making a good target for theoretical methods and an interesting system to probe the performance of different theoretical models. For instance, the lowest and most intense n–π* transition of camphor measured in chloroform shifts by only 0.058 eV (470 cm⁻¹) when measured in methanol. Third, we here present a detailed and systematic comparison of the three solvation schemes and analyze their individual capability to describe solvent effects across the polarity scale. The three conceptually different approaches to introduce the effect of the solvent are analyzed in terms of the electronic transitions of camphor in three very different solvents (cyclohexane, chloroform and methanol).

2. Method

In the following, we will very briefly introduce the theoretical concepts related to two of the solvation models. The explicit solvation model will not be described in detail since this scheme mainly relates to the application of a specific quantum chemical model to large samples. Thus, all physical effects included in the formulation of this quantum chemical model will be included in the corresponding predictions of the solvatochromic shifts.

2.1. The solvent models

2.1.1. The polarizable dielectric continuum model (PCM)

In the PCM approach the solvent is represented as a homogeneous dielectric continuum which is polarized by the solute situated in a molecular shaped cavity embedded in the dielectric continuum. The cavity is defined by assigning spheres of a given radius to each atom (or a group of atoms) forming the solute and considering the final envelope of these interlocking spheres [5]. The procedure is then to solve the Poisson equation and thereby derive the potential characterizing the electrostatics. In our context, the formalism used to solve the Poisson equation is the integral equation formalism (IEF) [7–8] version of PCM. In this model, the potential is defined by the sum of the potential produced by the solute charge distribution and the potential due to an apparent surface charge (ASC) distribution that arises due to polarization of the dielectric medium. The latter charge distribution gives rise to the reaction-field perturbing the electronic structure of the solute. In order to solve for the ASC distribution, a partitioning of the cavity surface into N finite elements, called tesserae, is invoked. Each tessera contains a point charge (qk), and the potential due to the polarization of the dielectric medium is then discretized according to

$$\phi(\mathbf{r}) = \sum_{k=1}^{N} \frac{q_k}{|\mathbf{r} - \mathbf{r}_k|}$$

where \(\mathbf{r}_k\) is the position of tessera \(k\) and \(q_k\) the corresponding charge. The point charges entering Eq. (1) may be determined from either a matrix equation or through iterations [5].

The coupling between the solute and the PCM is introduced by adding to the Hamiltonian of the isolated molecule (\(\hat{H}_0\)) the electrostatic potential in Eq. (1), i.e. we define the following effective Hamiltonian

$$\hat{H}_{el} |\Psi\rangle = (\hat{H}_0 + \hat{\phi}) |\Psi\rangle = E |\Psi\rangle,$$

where we have introduced an electronic operator \(\hat{\phi}\) corresponding to the electrostatic potential in Eq. (1). Note that the potential depends on the electronic density which means that Eq. (2) becomes nonlinear in \(\phi\).

2.1.2. The discrete model (DM)

The most significant difference between the PCM and the discrete model (DM) is that the DM keeps the atomistic nature of the solvent molecules. Due to the inherently dynamical nature of a solvent, an explicit averaging needs to be considered. Usually, such a set of solute–solvent structures is obtained from molecular dynamics (MD) or Monte Carlo (MC) simulations. In the majority of discrete solvation models a decoupling between the simulation and the quantum chemistry is invoked. This means that one accounts for thermodynamics effects using methods rooted in classical MD/MC, and then considers the quantum mechanical calculations in a number of snapshots extracted from the classical simulations. This is also the route followed in the present study. The permanent charge distribution of the solvent molecules is represented through multicenter multipole expansions. In the present work we truncate this expansion after the zeroth order (charge) term. These charge posses an increased value, as compared to the corresponding vacuum charges, due to an implicit account of polarization. As in the case of the PCM, the effect of the solvent is introduced by including in the vacuum Hamiltonian the potential due to the solvent partial charges

$$\phi(\mathbf{r}) = \sum_{k=1}^{N} \frac{q_k}{|\mathbf{r} - \mathbf{r}_k|},$$

where \(\mathbf{r}_k\) is the position of site \(k\) and \(q_k\) the corresponding charge. The sum runs over all solvent sites which may be located at the solvent nuclei, bond-midpoints, lone-pair positions or other depending on the specific solvent model. In addition to the electrostatic term, a contribution representing dispersion and repulsion will also contribute to the total energy. However, these terms are usually assumed to be independent of the electronic coordinates and therefore, enter the electronic Hamiltonian as simple constants, i.e. on the same footing as the conventional nuclear–nuclear repulsion energy.

As detailed above, both the PCM and the DM introduce the effect of a solvent by adding to the electronic Hamiltonian a potential due to a charge distribution. However, in case of the PCM, this charge distribution is directly coupled to the specific quantum mechanical problem and physically describes a polarization of the dielectric medium by the quantum mechanically molecular region. Therefore, the PCM charges are modified within each self-consistent-field iteration. In contrast, the DM charges are in the model employed in this work of fixed magnitude and describe the solute polarization implicitly. Extensions of the DM model to include polarization explicitly leads to a self-consistent-reaction-field like approach but will not be exploited in this presentation. A possible advantage of the DM method as compared to PCM is its potential ability to better mimic local anisotropies in the solvent and the possibility to better describe the effect of hydrogen bonding. We note that both solvent models describe the solvent as a purely classical medium. It is, as detailed later in this work, possible to include some of the solvent molecules directly into the quantum mechanical calculations. In such cases super-molecular (solute–solvent) structures should be extracted from molecular simulations. These structures are temperature-dependent and do not correspond to any geometry optimization that lead to lowest energy conformations, not present in real systems at non-zero temperatures. We note that both the DM and PCM models include in this work only the electrostatic energy component. Thus the focus will be on oriented towards analyzing the limits and potentialities of such electrostatics only descriptions.
3. Computational details

3.1. MC simulations

We have performed a series of NPT (pressure of 1 atm and temperature of 23 °C) MC simulations of camphor (see Fig. 1) in the three solvents cyclohexane (C$_6$H$_{12}$), chloroform (CHCl$_3$) and methanol (CH$_3$OH). These simulations were performed using the Metropolis algorithm with periodic boundary condition [9] for 1 camphor molecule plus $N = 450$ solvent molecules for the three solvents. During the MC simulation the volume of the box is allowed to change in order to keep the pressure constant. Furthermore, the rate of acceptance/rejection is auto-adjusted to 50%. The solute geometries have been optimized in the different solvents using PCM and the density-functional theory within the B3LYP/6-31G(d) model. In the MC simulations all molecules were treated as rigid bodies. This is justified by the fact that camphor is dominated by only one molecular conformation which is fairly rigid. In addition, as will be discussed in great detail later, geometrical changes lead only to mild differences in the excitation energies. The molecules interact by the standard Lennard–Jones (LJ) plus Coulomb potential with three parameters for each interacting site $i$ ($(\varepsilon_i, \sigma_i, q_i)$) and the geometrical rule of combination $\varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \cdot \sigma_j)^{1/2}$.

The interatomic potentials used have been taken from the OPLS-AA force field with parameters for cyclohexane in the chair conformation [10], chloroform [11] and methanol [12]. For the camphor molecule we obtained the parameters also from the OPLS-AA [13] but the charges were obtained in three different ways and will be described below.

The MC simulation consisted of a thermalization stage of $10.8 \times 10^6$ MC steps followed by a production run of $7.20 \times 10^8$. Since statistically correlated configurations do not give important additional information we calculate the auto-correlation function of the energy to select statistically relevant configurations for the QM calculations. Thus, after the simulation, as in several applications before [14,15], we have calculated the auto-correlation function of the energy to separate 100 configurations with less than 10% of statistical correlation. These 100 configurations are used in the QM calculations of the spectrum in the discrete model. If the solvent is to be represented by only the electrostatic embedding (solvent represented by point charges only) an alternative of performing a QM calculation for each of the 100 configurations is to use the average solvent electrostatic configuration (ASEC) [16] to obtain the same statistical average with just one QM calculation. This ASEC procedure is described in more detail elsewhere [17] and follows closely the idea of the average solvent electrostatic potential developed by Sánchez et al. [18–20].

The geometry and the atomic charges used for the camphor molecules were obtained in three different ways: (i) with geometry optimized in chloroform with B3LYP/6-31G(d)/PCM and atomic charges calculated with B3LYP/6-31G(d)/CHELPG/PCM in the respective solvent (ii) with geometry and atomic charges obtained with B3LYP/6-31G(d)/CHELPG/PCM in the respective solvent; and (iii) with geometry and atomic charges obtained with B3LYP/6-31G(d)/CHELPG/ASEC of the previous simulations. The CHELPG procedure used to obtain the atomic charges is the electrostatic potential fit of Breneman and Wiberg [21].

Table 1 shows the calculated in-solvent interatomic distances and atomic charges of the C=O group of camphor. The charges obtained with the B3LYP/6-31G(d)/CHELPG/PCM are used next in the corresponding MC simulations. Using the B3LYP/6-31G(d)/CHELPG/ASEC model, including in-solvent geometry optimization the atomic charges can be obtained and are also given in Table 1. We note that atomic charges obtained with the ASEC procedure are slightly larger than those obtained with PCM suggesting an additional polarization and a consequent increase in the electrostatic interaction between the solute and the solvent. It can also be noted that although similar results are obtained for the C=O bond distance the trends are different. The C=O distance in CH$_3$OH is larger with the ASEC than with PCM, but the reverse occurs in CHCl$_3$ and CdH$_{12}$. As will we see these geometry relaxations of the solute in the presence of the solvent give an interesting contribution to the absorption shift.

Table 2 summarizes the results obtained for the average density of the solution and the dipole moments of the solute in the three solvents, using the three different procedures to obtain the geometry and the solute charges. As the simulations are made in the NPT ensemble the density can be obtained and the results shown in Table 2 indicate a good agreement with experiment. Except for the nonpolar CdH$_{12}$ solvent the calculated dipole moments using the ASEC procedure are larger than those obtained using PCM. For instance the dipole moment of camphor in methanol is calculated as 4.03 D using the PCM and 4.56 D using the ASEC procedure generated from the MC simulation. All MC simulations have been performed using the DICE program [22] and all QM calculations were performed using GAUSSIAN-03 [23].

3.2. Electronic structure calculations

The calculations of the lowest electronic excitation energy (of $n \rightarrow \pi^*$ character) of camphor in different environments have been performed using the time-dependent DFT model at the B3LYP/aug-cc-pVDZ level. For the discrete model these QM calculations are made on statistically uncorrelated configurations sampled from the MC simulation, as described above. Each configuration is composed of a limited number of solvent molecules (those closest to the CO chromophoric group) and the remaining solvent molecules are treated as classical point charges (electrostatic embedding). In addition, we have performed calculations where the solvent is described either using only PCM or including a limited number of solvent molecules in the quantum mechanical portion of the system and the rest using PCM. In the latter case explicit averaging is required and we consider the same snapshots as used for the MC description of the solvent. In all the PCM calculations the oxygen radius used was $R_0 = 1.750 \text{ Å}$. For carbon we have used different...
spheres depending on the number of covalent bonds with hydrogen atoms. Thus, \( R_c = 1.925, 2.125, 2.325 \) and 2.525 \( \text{Å} \) for carbon atoms bonded with 0, 1, 2 or 3 hydrogen atoms, respectively. The dielectric constants used are \( \varepsilon = 4 \) and \( \varepsilon_{\text{pol}} \): 2.06 and 2.02 for cyclohexane, 4.90 and 2.09 for chloroform, 32.63 and 1.76 for methanol, where \( \varepsilon_{\text{pol}} \) refers to the optical dielectric constant. In the comparison between computed and experimental data we compare the predicted vertical electronic excitation energy with the experimental peak of maximum absorption.

### 4. Results

#### 4.1. Structural insight from the MC simulations

The radial distribution functions (RDFs) for the center-of-mass (CM) of camphor and the CM of either cyclohexane, chloroform or methanol are shown in Fig. 2a, b or c, respectively. The solvation shells are easily discernible and a first solvation shell is seen close to 8 \( \text{Å} \) for the three solvents. Based on these a set of solvation shells around camphor are defined by spherical integration of the RDFs. For example, in the case of methanol a first solvation shell starts at 4.14 \( \text{Å} \), reaches a maximum at 5.55 \( \text{Å} \) and ends at 7.55 \( \text{Å} \). Spherical integration of this first peak (from 4.14 till 7.55 \( \text{Å} \)) leads to a coordination of 22 methanol molecules. Then a second solvation shell extends till 12.0 \( \text{Å} \). Integration up to this points (from 4.14 till 12.0 \( \text{Å} \)) gives a total of 100 methanol molecules up to this second shell. Additional integration until the end of the third solvation shell gives 186 methanol molecules. This is clearly shown in Fig. 2c. For camphor in cyclohexane, we obtain 15 solvent molecules in the first solvation shell, 51 up to the second solvation shell and 102 up to the third solvent shell. These numbers are indicated in Fig. 2a. Similar analysis for chloroform is shown in Fig 2b. From this figure it is evident that the spatial extension as well as the number of solvent molecules in the first solvation shells are related to the polarity of the solvent, i.e. to the magnitude of the static dielectric constant of the solvent: increasing the polarity leads to the presence of more solvent molecules in the first solvation shell as well as to a more compact solvent shells. In addition, the width of the RDFs associated with the first solvation shells also increase as a function of the solvent polarity. This is due to the fact that the repulsive part of the LJ potential becomes more dominant for the less polar solvents leading to a decreased anisotropic character of the solvent molecules. Another important aspect related to the solvation shells extension is the size of the solvent molecule. Here, the solvent with lower polarity is the largest one and the solvent with higher polarity is the smallest one. Therefore, this fact also influences the number of molecules in the solvation shell and its width. Table 3 summarizes the coordination numbers of camphor in the different solvents.

The QM calculations will take these into consideration on defining the number of explicit solvent molecules to be considered and the remaining molecules in the electrostatic embedding. The largest number of solvent molecules considered will be made using the semi-empirical ZINDO [24,25] model, where the first and the second solvation shells will be explicit with the remaining treated as classical point charges. For instance, in the case of methanol we will consider 100 explicit solvent molecules electrostatically embedded in the field of the remaining 86 outer solvent molecules.

#### 4.2. The \( n \rightarrow \pi^* \) transition of camphor in different solvents

In the \( n \rightarrow \pi^* \) electronic transition of camphor an electron is promoted from the oxygen non-bonding lone pair to the anti-bonding \( \pi^* \) orbital leading to a reduction of the excited state dipole moment as compared to that of the ground state. Therefore, the solute–solvent interaction in polar solvents is relatively larger with the solute in its ground state compared to the excited state. This results in a blue shift of the excitation energy. However, in the case of nonpolar solvents (as cyclohexane) the effects of dispersion might become significant and should be properly considered [26] although this effect is more likely to be dominant for solvents possessing highly conjugated structures. In Table 4, we present the results for the excitation energy in the three solvents. Here, we have used the solvent of intermediate polarity (chloroform) as

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### Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>( R_C ) (( \text{Å} ))</th>
<th>( Q_c )</th>
<th>( Q_c^* )</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase</td>
<td>1.2120</td>
<td>0.4833</td>
<td>-0.4885</td>
<td>-</td>
</tr>
<tr>
<td>PCM</td>
<td>1.2142</td>
<td>0.4980</td>
<td>-0.5179</td>
<td>( \text{CH}_3 \text{H}_2 )</td>
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<tr>
<td></td>
<td>1.2166</td>
<td>0.5063</td>
<td>-0.5384</td>
<td>( \text{CHCl}_3 )</td>
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<tr>
<td></td>
<td>1.2185</td>
<td>0.5217</td>
<td>-0.5622</td>
<td>( \text{CH}_2\text{OH} )</td>
</tr>
<tr>
<td>ASEC</td>
<td>1.2121</td>
<td>0.5372</td>
<td>-0.5470</td>
<td>( \text{CH}_3 \text{H}_2 )</td>
</tr>
<tr>
<td></td>
<td>1.2155</td>
<td>0.5610</td>
<td>-0.5913</td>
<td>( \text{CHCl}_3 )</td>
</tr>
<tr>
<td></td>
<td>1.2202</td>
<td>0.6340</td>
<td>-0.6695</td>
<td>( \text{CH}_2\text{OH} )</td>
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### Table 2

<table>
<thead>
<tr>
<th>Dipole of the solvent</th>
<th>Density of the solution ( (\text{g/cm}^3) )</th>
<th>( \varepsilon )</th>
<th>( \varepsilon_{\text{pol}} )</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3 \text{H}_2 )</td>
<td>0.00 (0.766 ± 0.005)\textsuperscript{a}</td>
<td>1.53 (1.435 ± 0.005)\textsuperscript{b}</td>
<td>2.27 (0.775 ± 0.008)\textsuperscript{c}</td>
<td>( \text{CH}_3 \text{OH} )</td>
</tr>
<tr>
<td>( \text{CHCl}_3 )</td>
<td>0.00 (0.5913)</td>
<td>1.53 (1.435 ± 0.005)</td>
<td>2.27 (0.775 ± 0.008)</td>
<td>( \text{CH}_3 \text{OH} )</td>
</tr>
<tr>
<td>( \text{CH}_2\text{OH} )</td>
<td>0.00 (0.5384)</td>
<td>1.53 (1.435 ± 0.005)</td>
<td>2.27 (0.775 ± 0.008)</td>
<td>( \text{CH}_3 \text{OH} )</td>
</tr>
</tbody>
</table>

\( \textsuperscript{a} \) Experimental density of \( \text{CH}_3 \text{H}_2 \) is 0.774 g/cm\(^3\).

\( \textsuperscript{b} \) Experimental density of \( \text{CHCl}_3 \) is 1.400 g/cm\(^3\).

\( \textsuperscript{c} \) Experimental density of \( \text{CH}_2\text{OH} \) is 0.786 g/cm\(^3\).
Concerning the excitation energy in vacuum we obtain 4.193 eV, which is in very good agreement with the analysis presented in Ref. [27] where a consistent result of 4.20 eV was obtained using a series of quantum chemical methods ranging from time-dependent Hartree–Fock to Coupled Cluster. In addition, this result compares fairly well with Pecul et al. [28] that obtained 4.219 eV using TDDFT. Moving to the condensed phase, we present in Table 4 four sets of calculations taking chloroform as the reference for the solvatochromic shifts.

First, we analyze the influence of the geometry relaxation using both PCM and ASEC. It is seen that in both models the geometry relaxation induced by the solvent leads to a shift that is opposed to the experimental shift. For instance, the geometry relaxation using the PCM results leads to a contribution of +0.010 eV to the shift whereas the experiment indicates a negative shift. The electrostatic contribution has now to overcome this contribution.

The electrostatic part of the shift is analyzed initially considering a fixed geometry. For this purpose we have used the calculated in-solvent geometry corresponding to camphor in chloroform. The results now are more sizable, as expected. Considering the excitation energy obtained with PCM results in a shift of –0.034 eV in good agreement with the experimental value of –0.056 eV for the chloroform–cyclohexane shift. A similar result is obtained representing the solvent by classical point charges. In order to exploit in more detail the role of the first solvation shells, we repeat the calculations including a number of solvent molecules into the region described using quantum mechanics. In this respect, we include explicitly all solvent molecules within a distance of 4 Å from the camphor and treat the remaining as classical point charges or PCM. In the case of chloroform (Fig. 3), this distance is defined as the distance between the oxygen in camphor and the hydrogen in chloroform (the potential hydrogen bond). These calculations are termed ‘extended’ in Table 4. Using such an extended approach part of the solute–solvent non-electrostatic repulsion and dispersion contribution is included in the quantum mechanical portion of the system. Because the dispersion contribution is normally larger than the repulsion it is expected that this will decrease the excitation energy [29,30]. This has a minor effect on the excitation energy in the case of cyclohexane but a more pronounced effect in the case of chloroform, thus leading to a decrease in the solvatochromic shift. This model gives however the best result for the chloroform–methanol shift: the result using this PCM extended model, including explicitly a few solvent molecules within the cavity gives a shift of 0.052 eV, in very good agreement with the experimental value of 0.058 eV. Overall, considering unrelaxed geometry calculations, good results are also obtained by using DM extended model where the use of a limited number of solvent molecules embedded in the point charges of the remaining solvent molecules gives a result for the shift between the two polar solvents (0.050 eV) comparable to the PCM extended result.

Now, we consider the more realistic situation where the geometry is relaxed in each corresponding solvent. This is the third set of calculations shown in Table 4. The results obtained for the PCM and PCM extended cases are essentially a sum of the two effects just described. For instance, in the case of PCM the calculated cyclohexane–chloroform shift of –0.025 eV is basically, the sum
of the geometry effect (0.010 eV) and the pure electrostatic effect (−0.034 eV). This indicates an additive nature of the geometrical relaxation and the solvent electrostatic contribution. It is clear now that PCM gives a reasonably good description for the shift in the polar solvents but fails for the nonpolar solvent leading to an underestimation of the cyclohexane–chloroform shift. Similar results are obtained for the discrete model here limited to the ASEC formulation. However, using the ASEC electrostatic model with the geometry optimized also at the ASEC level gives an overestimated result for the shift in the polar solvents. We attribute this to the larger dipole moment obtained for this model, as discussed in Table 2.

The results from Table 4 clearly show the potential importance of treating some of the nearest solvent molecules at the quantum mechanical level of theory. At this point we may conclude that continuum and discrete solvent models provide results of roughly the same quality in polar solvents provided that the ‘extended’ versions of the DM and PCM are used. However, in the simplest formulations of the DM and PCM, i.e. where all solvent molecules are treated classically or implicitly, respectively, the DM solvation model provides results superior to the PCM. This fact is attributed to a better description of the (anisotropic) electrostatics in the DM model. On the other hand, moving to apolar solvents, where other components than the electrostatics in the solute–solvent interactions may become important, both the DM and the PCM provide less satisfactory results even in their ‘extended’ versions. It would therefore be interesting to analyze the inclusion of a larger number of explicit solvent molecules. This is difficult in an ab initio method but still possible using a semi-empirical model. Therefore we have performed ZINDO calculations explicitly including all solvent molecules up to the second solvation shell and used the remaining solvent molecules as an electrostatic embedding. For instance, in the case of methanol this corresponds to treat explicitly the camphor molecule surrounded by 100 methanol molecules embedded in the electrostatic field of 86 additional solvent molecules treated as simple point charges. These calculations use the corresponding configurations sampled from the MC simulations and the results presented are averages over 100 QM ZINDO calculations of the excitation spectra. These results are shown in Table 4.

As it can be seen the calculated excitation energies are underestimated in the three solvents considered but the calculated shifts, especially the cyclohexane–chloroform shift, are in good agreement with experiments. This clearly suggests that nonpolar solvents are more sensitive to the explicit use of solvent molecules in order to include effects of intermolecular interactions not accounted for by the DM and PCM models.

To analyze the convergence of the average results with respect to the number of solute–solvent configurations used in the QM calculations we show the average results in Fig. 4. We plot this convergence in the case of either all solvent molecules treated as point charges (a) or the ‘extended’ results (b). In addition, we also present the convergence in the case where we include a number of solvent molecules into the region described using quantum mechanics (using the same selections as in (b)), but instead of keeping the additional solvent molecules using a point charge description we describe these solvent molecules using the PCM. In all cases we observe a relatively fast convergence, i.e. including around 70 configurations would represent converged results. No significant differences are observed in the convergence patterns using the three different schemes.

Table 4 Calculated excitation energies (in eV) and solvatochromic shifts of camphor in three solvents obtained with B3LYP/aug-cc-pVDZ and ZINDO using different solvation models (PCM, the discrete model using point charges and the explicit). Calculated transition energy in vacuum is 4.193 eV.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Excitation</th>
<th>E(CH$_3$)$_2$</th>
<th>ΔE</th>
<th>E(CH$_3$)</th>
<th>ΔE</th>
<th>E(CH$_3$OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCM</td>
<td>Vacuum</td>
<td>4.184</td>
<td>0.010</td>
<td>4.174</td>
<td>−0.008</td>
<td>4.166</td>
</tr>
<tr>
<td>DM (ASEC)</td>
<td>Vacuum</td>
<td>4.191</td>
<td>0.016</td>
<td>4.175</td>
<td>−0.016</td>
<td>4.159</td>
</tr>
<tr>
<td>PCM (CH$_3$)$_3$</td>
<td>PCM</td>
<td>4.207</td>
<td>−0.034</td>
<td>4.241</td>
<td>0.027</td>
<td>4.268</td>
</tr>
<tr>
<td>PCM (CH$_3$)$_3$</td>
<td>DM</td>
<td>4.175</td>
<td>−0.033</td>
<td>4.208</td>
<td>0.043</td>
<td>4.251</td>
</tr>
<tr>
<td>PCM (CH$_3$)$_3$</td>
<td>DM extended</td>
<td>4.205</td>
<td>−0.012</td>
<td>4.217</td>
<td>0.052</td>
<td>4.269</td>
</tr>
<tr>
<td>PCM (CH$_3$)$_3$</td>
<td>DM extended</td>
<td>4.175</td>
<td>−0.022</td>
<td>4.197</td>
<td>0.050</td>
<td>4.247</td>
</tr>
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<td>PCM</td>
<td>PCM</td>
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<td>−0.025</td>
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<td>DM (ASEC)</td>
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<td>−0.024</td>
<td>4.209</td>
<td>0.049</td>
<td>4.258</td>
</tr>
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<tr>
<td>Experiment [6]</td>
<td>Explicit (1st + 2nd) + 3rdPC</td>
<td>4.147</td>
<td>−0.056</td>
<td>4.203</td>
<td>0.058</td>
<td>4.261</td>
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</table>

Fig. 3. Illustration of one configuration composed of the camphor molecule surrounded by explicit solvent molecules (in this case CH$_3$)$_3$ and embedded in the electrostatic field of the remaining solvent molecules. This is termed as PCM extended on Table 4. Averages are obtained after 100 PCM calculations on these structures obtained after MC simulation.
5. Summary and discussion

In this work we have considered the effect of solvation on the lowest \( \pi \rightarrow \pi^* \) electronic transition of camphor. The solvents considered are cyclohexane, chloroform and methanol representing a large variation in solvent polarity as well as the optical dielectric constant. We have compared the performance of three conceptually different solvent models, i.e. considered solvent effects described by either implicit (PCM), discrete (DM) or explicit (ZINDO) approaches. The implicit and discrete approaches, however, are found to be less successful in predicting solvatochromic effects for solvents of low polarity where an explicit account of a significant number of solvent molecules is mandatory.

Acknowledgments

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References

[6] Excitation energies were extracted from ECD spectra courtesy provided by Prof. C. Rosini at the Dept. of Chemistry of the University of Basilicata, Italy. The spectra were recorded on a JASCO J600 spectropolarimeter at room temperature, using a 0.1 mm cell and concentrations of the order 3 \( \times \) 10\(^{-3} \) M.