

# Combined Monte Carlo and quantum mechanics study of the solvatochromism of phenol in water. The origin of the blue shift of the lowest $\pi$ - $\pi^*$ transition

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A combined and sequential use of Monte Carlo simulations and quantum mechanical calculations is made to analyze the spectral shift of the lowest  $\pi$ - $\pi^*$  transition of phenol in water. The solute polarization is included using electrostatic embedded calculations at the MP2/aug-cc-pVDZ level giving a dipole moment of 2.25 D, corresponding to an increase of 76% compared to the calculated gas-phase value. Using statistically uncorrelated configurations sampled from the MC simulation, first-principle size-extensive calculations are performed to obtain the solvatochromic shift. Analysis is then made of the origin of the blue shift. Results both at the optimized geometry and in room-temperature liquid water show that hydrogen bonds of water with phenol promote a red shift when phenol is the proton-donor and a blue shift when phenol is the proton-acceptor. In the case of the optimized clusters the calculated shifts are in very good agreement with results obtained from mass-selected free jet expansion experiments. In the liquid case the contribution of the solute-solvent hydrogen bonds partially cancels and the total shift obtained is dominated by the contribution of the outer solvent water molecules. Our best result, including both inner and outer water molecules, is  $570 \pm 35 \text{ cm}^{-1}$ , in very good agreement with the small experimental shift of  $460 \text{ cm}^{-1}$  for the absorption maximum.

## 1. Introduction

The ultraviolet-visible (UV-Vis) spectra of phenol in different solvents have attracted experimental interest for decades.<sup>1-13</sup> The long wavelength region of the electronic absorption spectrum of phenol is characterized by a strong and broad transition in the region of 270 nm. The spectral maximum of this absorption shifts on different solvents and this solvatochromism is related to the intermolecular interaction between phenol and the solvent molecules. Among the important types of solute-solvent interaction, the hydrogen bonds between phenol and water have been of particular interest. This is because phenol may be considered a dual molecule<sup>14</sup> having a hydrophobic ring and a hydrophilic OH group. The hydrophilic component, the OH group, is peculiar because it can act simultaneously as a proton-acceptor and a proton-donor of hydrogen bonds. Hence the solvatochromic shift is very dependent on the polarity and the protic properties of the solvent. There has been some theoretical studies of the spectral characteristics of phenol in the gas phase<sup>15-18</sup> but the effect of water in the phenol absorption spectrum still deserves study. Since the early experimental studies it has been discussed that hydrogen bonds where phenol is the proton-acceptor lead to spectral shifts that are opposite to the situation where phenol is the proton-donor. Although this conclusion is naturally more difficult in the liquid situation, experimental studies in

phenol-water clusters obtained in supersonic free jet experiments have given credit to this assumption. In fact, the fluorescence and absorption spectra of phenol-water complexes have been studied experimentally.<sup>7-9</sup>

Fuke and Kaya<sup>8</sup> made an interesting analysis of the spectral position of phenol in water obtained in a supersonic free jet. They have analyzed the  $S_0$ - $S_1$  electronic transition ( $0_0^0$  band) of phenol hydrogen-bonded to water and confirmed that mono-hydrated phenol gives a red shift compared to the free phenol, when phenol is the proton-donor. The mono-hydrated complex where the phenol is the proton-acceptor has not been identified.<sup>8</sup> But considering a dihydrated phenol-water complex—supposedly with the additional water as the proton-acceptor—they obtained a blue shift, compared to the mono-hydrated case, and suggested that when phenol is the proton-acceptor of the hydrogen bond there is a blue shift of the absorption transition compared to free phenol. This information used for the liquid situation suggests that bulk water has a very important role to play in deciding what is the net solvatochromic shift in protic solvents. In fact in the recent experiment<sup>12</sup> the spectral shift of the  $S_0$ - $S_1$  transition (lowest  $\pi$ - $\pi^*$ ) of phenol in water and in ethanol have different signs. The usual rule states that  $\pi$ - $\pi^*$  transitions in polar solvents shift to the red side of the spectrum. In agreement, phenol in liquid ethanol presents a small red shift of  $\sim 370 \text{ cm}^{-1}$ . However, phenol in liquid water shifts to the blue side<sup>12</sup> by nearly the same amount ( $460 \text{ cm}^{-1}$ ). The different sign of these two shifts is unexpected on the basis that water and ethanol normally lead to the same sign for the shift with the magnitude larger for water than for ethanol.

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The differential solvation of the  $S_0$  ground and  $S_1$  first excited state may be rationalized in terms of the change in the dipole moment upon excitation. The change in the dipole moment of phenol in water in the  $\pi$ - $\pi^*$  excitation has been measured by the Stark effect.<sup>19</sup> The experiment only detects the absolute value of the change and it indicates that there is a change of  $0.20 \pm 0.20$  D. Further evidence<sup>19</sup> suggests that the dipole moment increases upon excitation. If that is the case, and if it is still valid for phenol in aqueous solution, this would indicate that the solvatochromic shift of this  $\pi$ - $\pi^*$  transition in water would suffer a slight red shift, a situation that is not confirmed. We have then performed calculations at the CIS/aug-cc-pVDZ level and obtained that the vertically excited  $S_1$  state has a dipole moment that is decreased by 0.1 D compared to the  $S_0$  ground state. This would now favor a blue shift. However, given the small change in the dipole moment upon excitation one should not expect a pronounced shift upon solvation. This is compatible with the experimental results. However, the sole consideration of the changes in the gas-phase dipole moment cannot account for the different sign in the solvation shifts of ethanol and water. Early experimental studies<sup>2</sup> were able to show a red shift of *ca.* 1100  $\text{cm}^{-1}$  for the  $S_0$ - $S_2$  band (B-band) at 210 nm but could not distinguish for the  $S_0$ - $S_1$  transition (C-band) at 270 nm. More recently<sup>12</sup> the absorption bands of phenol have been analyzed in different solvents. The vapor spectrum shows the  $S_0$ - $S_1$  band maximum located at 37 130  $\text{cm}^{-1}$  shifting to 37 590  $\text{cm}^{-1}$  in water. This then implies a blue shift of the  $S_0$ - $S_1$  band maximum of 460  $\text{cm}^{-1}$ . Combining the 0-0 transition of free phenol in ref. 8 with the lowest vibration component of phenol in bulk water, the  $\nu_3$  transition of ref. 12, would give a blue shift of 280  $\text{cm}^{-1}$ . Using different vibration components, or the band maximum, gives slightly different results. But in any case a blue shift of  $\sim 250$ -500  $\text{cm}^{-1}$  is obtained. Our study will consider vertical excitations and a comparison with the experimental band maximum is more appropriate. Thus we consider 460  $\text{cm}^{-1}$  as the experimental reference value for the vapor-water blue shift. This is a very small shift (of only 0.06 eV) and a detailed theoretical analysis is necessary.

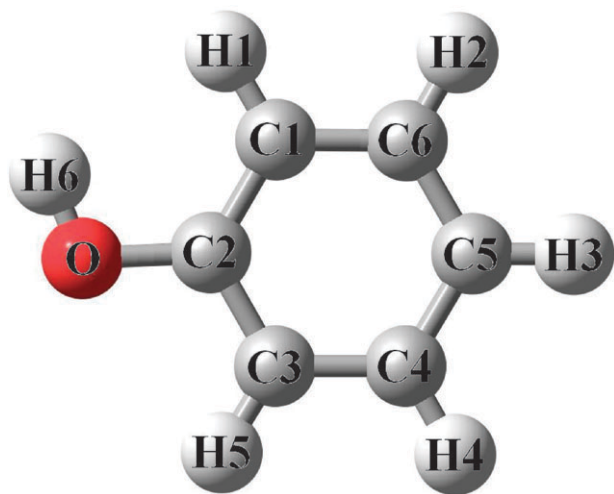
Understanding the origin of the spectral shift of phenol in liquid water is of special experimental and theoretical interest. This is the subject of this paper. In this work we give a detailed analysis of the  $S_0$ - $S_1$  electronic excitation of phenol in water to analyze the different, local *versus* bulk, contributions to the solvatochromic shift of phenol compared to the isolated *in vacuo* situation. We focus on solute-solvent hydrogen bonds and their contribution to the total solvatochromic shift. We consider optimized phenol-water clusters that can be compared with the complexes obtained in free jet expansion experiments and also hydrogen bonds obtained in the liquid situation at room temperature. Next we analyze the influence of the remaining outer water molecules in the liquid. We used the combined and sequential hybrid method of Monte Carlo (MC) simulation and quantum mechanics (QM) calculations (S-MC/QM)<sup>20-23</sup> that has been successfully used in different solvent effects.<sup>20-25</sup> As the spectral shift is very small some attention will be given to the proper inclusion of the solute polarization. MC simulations of phenol in water are made here including the solute polarization by the solvent. After the

simulation, statistically relevant solute-solvent configurations are sampled for QM calculations of the spectrum. Statistical convergence of the results is analyzed and all average values reported here are shown to be converged. As phenol can act both as proton-donor and proton-acceptor of hydrogen bonds with water, these two conditions are analyzed separately. The results obtained here indicate that these two types of hydrogen bonds give an important contribution to the spectral shift of the lowest  $\pi$ - $\pi^*$  transition of phenol in water. It will be shown that in the liquid case their contributions also follow the same sign for spectral shifts as in the free jet experiments, but when combined they essentially cancel out giving only a minor contribution to the total shift. The solvatochromism is thus determined by the bulk water molecules that favor a blue shift in the case of phenol in water.

The main objective of this work is thus to obtain an explanation of the origin of the blue shift of the  $S_0$ - $S_1$ , lowest lying  $\pi$ - $\pi^*$  transition of phenol in water, compared to the gas phase. In the next section we give the computational details of the MC simulation and the QM calculations and describe the iterative procedure for obtaining the solute polarization. In section 3 we discuss all the results. First, we present the solute polarization (subsection 3.1) by the solvent. Then we analyze separately the role of the phenol-water hydrogen bonds in the optimized clusters and compare their structure and spectral shifts with the experimental results from mass-selected free jet expansion measurements (subsection 3.2.1). Next we analyze the total solvatochromism obtained in the liquid environment with the solvent treated as an electrostatic embedding (subsection 3.2.2). Finally we discuss in detail in the subsection 3.2.3 the origin of the  $S_0$ - $S_1$  blue shift considering explicit solvent molecules, the electrostatic contribution and the separate contributions of the proton-donor and proton-acceptor hydrogen bonds. The total spectral shift is then obtained and discussed in terms of the relative contribution of the solute-solvent hydrogen bonds and the outer bulk water molecules. The results demonstrate that the proton-donor and proton-acceptor hydrogen bonds partially cancel and the spectral shift of the lowest  $\pi$ - $\pi^*$  transition of phenol is dominated by the electrostatic contribution of the outer water molecules.

## 2. Calculation details

Monte Carlo simulations of 1 phenol in 500 water molecules were carried out using the Metropolis sampling in the isothermal-isobaric NPT ( $P = 1$  atm and  $T = 298$  K) ensemble in a cubic box with periodic boundary conditions. The intermolecular interactions are described by the Lennard-Jones (LJ) and the Coulomb potential with 3 parameters for each interacting site  $i$  ( $\epsilon_i$ ,  $\sigma_i$  and  $q_i$ ). For the water molecules, we have used the simple point charge (SPC) model proposed by Berendsen *et al.*<sup>26</sup> For the phenol molecule (see Fig. 1 for atomic labels) we used the LJ potential parameters proposed by Jorgensen and Nguyen.<sup>27</sup> To take into account the polarization by the aqueous environment, the solute atomic charges have been calculated using an iterative procedure based on a series of MC simulations followed by MP2/aug-cc-pVDZ calculations of the dipole moment using



**Fig. 1** The structure of phenol and the atomic labels used in Table 1.

the fit of the atomic charges from the electrostatic potential in a grid (CHELPG).<sup>28</sup> This will be described in more detail below. All QM calculations are made using the GAUSSIAN 03 program.<sup>29</sup> The geometry used for phenol has been obtained by a geometry optimization at the MP2/aug-cc-pVDZ level.

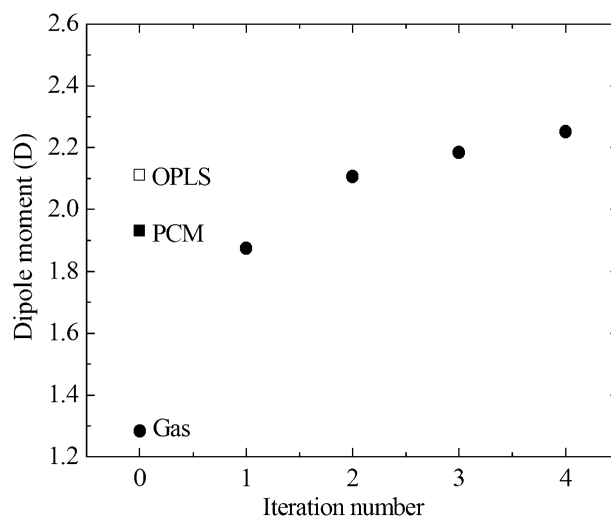
The MC simulations were performed with the DICE program.<sup>30</sup> After thermalization, the simulation was made with  $3.4 \times 10^7$  MC steps.

Using the auto-correlation function of the energy we have calculated the interval of statistical correlation for selecting statistically uncorrelated configurations.<sup>20–23</sup> This sampling selects statistically relevant configurations assuring a fast and systematic convergence with a relatively small number of QM calculations. Here we have used 100 configurations having less than 15% of correlation. As we will show later this is enough to give statistically converged results for the solvatochromic shift. After separating the solute–solvent configurations different QM models are used. The polarization of phenol in water is made using the MP2/aug-cc-pVDZ model. The electronic spectrum is calculated using three methods: time-dependent density functional theory (TD-DFT) within the B3LYP exchange–correlation functional,<sup>31,32</sup> the random-phase approximation within the time-dependent Hartree–Fock method<sup>33–35</sup> and the configuration interaction with perturbed double excitation CIS(D).<sup>36,37</sup> The choice for these methods is based not only on the compromise between simplicity and accuracy but, most of all, the importance of using size-extensive methods, which precludes the regular CISD method. As we will see, the results obtained with the three different methods vary with respect to the calculated excitation energies, but give essentially the same result for the calculated solvatochromic shift.

### 3. Results and discussion

#### 3.1 The polarization of phenol in water

An important aspect considered here is the precise inclusion of the solute polarization effects.<sup>38–43</sup> We have recently developed a procedure to describe the electronic polarization of a



**Fig. 2** Calculated average values of the dipole moments of in-water phenol with respect to the number of iterations.

molecule in solution,<sup>44,45</sup> by iteratively applying the S-QM/MM methodology to calculate the atomic charges of the solute molecule in the presence of the solvent. We first perform MP2/aug-cc-pVDZ calculations for the isolated phenol molecule and obtain the atomic charges using CHELPG electrostatic mapping.<sup>28</sup> These are the charges used in the classical potential of the MC simulation. After this first MC simulation statistically uncorrelated configurations of the liquid are selected to calculate the average atomic charges and dipole moment of the solute embedded in the electrostatic field of the solvent environment using MP2/aug-cc-pVDZ. These average atomic charges of the solute are updated in the Coulomb part of the potential for another MC simulation and subsequently another average atomic charges and dipole moment of the embedded solute are calculated. This process is repeated until convergence in the QM average dipole moment is obtained, when the solute is in electrostatic equilibrium with the solvent. The results are summarized in Fig. 2 and Table 1. As Fig. 2 shows the in-solution dipole moment is obtained in five iterations. Excluding the first point (iteration 0), every entry in this figure corresponds to a statistically converged

**Table 1** Atomic charge distribution and dipole moment of phenol in the gas phase and in aqueous solution (see Fig. 1 for atomic labels)

Atom	Charge/e			
	Gas phase	OPLS <sup>27</sup>	PCM	Iterative
C1	−0.2661	−0.1150	−0.2929	−0.2794
C2	0.3629	0.1500	0.3957	0.4222
C3	−0.1690	−0.1150	−0.2137	−0.2031
C4	−0.0774	−0.1150	−0.0933	−0.0832
C5	−0.1573	−0.1150	−0.1892	−0.1685
C6	−0.0248	−0.1150	−0.0452	−0.0406
O	−0.5820	−0.5850	−0.6767	−0.7711
H1	0.1174	0.1150	0.1543	0.1484
H2	0.0803	0.1150	0.1018	0.1001
H3	0.1005	0.1150	0.1217	0.1064
H4	0.0870	0.1150	0.1074	0.1017
H5	0.1353	0.1150	0.1539	0.1432
H6	0.3933	0.4350	0.4762	0.5239
$\mu/D$	1.28	2.11	1.93	2.25

average value of the dipole moment of the solute embedded in an average electrostatic configuration of the solvent (ASEC)<sup>46</sup> calculated with MP2/aug-cc-pVDZ. Here, the ASEC was generated with 100 statistically uncorrelated MC configurations of the nearest 200 water molecules represented by point charges (Ph:200PC). This includes all water molecules within the distance of 11.4 Å from phenol.

In the gas phase, the calculated dipole moment of phenol is 1.28 D. This should be compared with the value of 1.22 D for the experimental gas-phase result.<sup>47</sup> In turn, the converged in-water value (Table 1) obtained here is 2.25 D, corresponding to an increase of 76%.

This polarization is consistent with the application of the simpler polarized continuum model (PCM)<sup>48</sup> that gives the value of 1.93 D, for the same theoretical model (MP2/aug-cc-pVDZ) and also with the electrostatic OPLS parameters that gives the value of 2.11 D. We have noted in previous applications<sup>49</sup> that the electronic polarization obtained with the PCM method is slightly smaller compared to the iterative method. The same is true for the OPLS polarization that is usually obtained with HF/6-31G(d) calculations, which gives around 30% of polarization compared with the gas phase. In this particular case of phenol, the OPLS polarization was obtained<sup>27</sup> to describe the free energy of hydration, and leads to an increase of the gas-phase dipole moment of 65% (Table 1). This OPLS polarization is obtained for the aqueous solution and leads to a dipole moment of 2.11 D in good agreement with the iterative method that obtains 2.25 D.

In-solution dipole moments are not easily amenable to experiments and comparison should be made with some care. Indirect results from experiments<sup>12,50</sup> indicate a value for the dipole moment of in-solution phenol of 1.86 D. All the MC results that will be discussed in the following sections have used the polarized in-water phenol with the atomic charges presented in Table 1 for the converged iterative method. In addition, we have also used the PCM polarization in another MC simulation to clarify the role of the solute polarization.

### 3.2 The spectral shift of phenol in water

**3.2.1 Solute–solvent hydrogen bonds in optimized complexes.** In this section we first analyze the hydrogen bonds formed between phenol and water. Although the importance of the hydrogen bonds to the solvatochromic shift of phenol in liquid water is the focus of interest here, we also analyze the phenol–water complexes, as obtained in the minimum-energy configuration, to compare with the results for the supersonic free jet experiments.<sup>8</sup> Four complexes of the hydrogen bonded structures of phenol–water obtained using MP2/aug-cc-pVDZ geometry optimizations are shown in Fig. 3. The first two correspond to the interaction of phenol with a single water molecule. In one case phenol is the proton-acceptor (W:Ph) whereas in the other it is the proton-donor (Ph:W). The hydrogen-bonded complexes of phenol with water have been intensely studied experimentally and theoretically, both the ground and the first  $S_1$  excited state, with the aim of characterizing the structure, the rotation and vibration spectra and the fluorescence emission.<sup>7,10,17,51–65</sup> Although

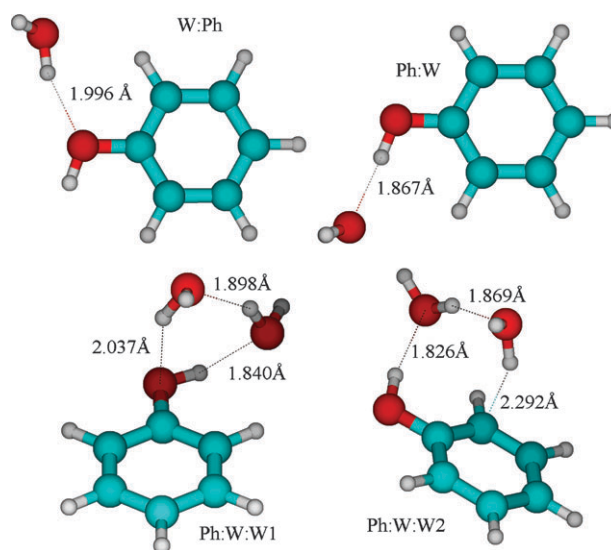


Fig. 3 Optimized hydrogen bonds between phenol and water.

the mono-hydrated Ph:W and W:Ph are of most interest here, in addition, two dihydrated complexes were also considered (Fig. 3).

Before submitting these four complexes to QM calculations of the electronic excitation it is interesting to make a brief analysis of these complexes with respect to previous studies. The more stable<sup>60</sup> Ph:W complex has attracted much more interest than the W:Ph complex. For Ph:W, the rotational constants have been assigned experimentally<sup>10,61,62</sup> as 4.292, 1.092 and 0.874 GHz. Theoretically the results<sup>17</sup> obtained at the CAS(8,7)/6-31G(d,p) level are 4.317, 1.077 and 0.866 GHz and obtained<sup>66</sup> at the MP2/6-31G(d) are 4.255, 1.114 and 0.887 GHz. These numbers can now be compared with our MP2/aug-cc-pVDZ values of 4.178, 1.111 and 0.882 MHz. Our results are seen to be in good agreement with both experiment and the previous theoretical results (Table 2). For W:Ph our calculated geometry is in good agreement with a previous CAS(8,7)/6-31G(d,p) result.<sup>60</sup>

For the dihydrated complexes less information is available. In this case the first structure (Ph:W:W1) has been obtained before<sup>63,65–67</sup> whereas the second (Ph:W:W2) is similar to the structure obtained by coupled cluster response theory CC2 model in ref. 65. We find conformer Ph:W:W1 to be more stable than conformer Ph:W:W2 by *ca.* 1.5 kcal mol<sup>-1</sup> at the MP2/aug-cc-pVDZ. All these four structures reported here at the MP2/aug-cc-pVDZ level are verified to correspond to true energy minimum by calculating the second derivatives (vibration frequencies). Some optimized structural parameters are shown in Fig. 3. As it can be seen the results obtained here are in agreement with the MP2 results of ref. 66 and both differ slightly from the results of Fang and Liu<sup>63</sup> of 2.660, 0.730 and 0.64 GHz. Unfortunately structural and rotational parameters are apparently not reported for the Ph:W:W2. Schemmel and Schültz<sup>65</sup> have analyzed several possible structures of the ground and excited states of phenol bound to two water molecules but have focused in the anomalous photophysics of the dihydrated phenol–water complexes.

**Table 2** Experimental values<sup>10,61,62</sup> and calculated dipole moments (Debye) and rotational constants (GHz) for the phenol–water complexes (see Fig. 3), obtained using MP2/aug-cc-pVDZ. In parenthesis are shown the theoretical results obtained in ref. 66 using MP2/6-31G(d)

	Exp.	W:Ph	Ph:W	Ph:W:W1	Ph:W:W2
$\mu$	—	2.82	3.82 (3.89)	1.25 (1.10)	2.06
$A$	4.292	3.951	4.178 (4.225)	2.442 (2.532)	2.152
$B$	1.092	1.151	1.111 (1.114)	0.848 (0.832)	0.993
$C$	0.874	0.893	0.882 (0.887)	0.775 (0.751)	0.859

The four complexes considered in Fig. 3 will now be submitted to QM calculations of the electronic spectrum to obtain the  $S_0$ – $S_1$  spectral shift and compare with experiment. In the jet cooling expansion mass-selected complexes are analyzed by UV light and the electronic spectrum is recorded. The results<sup>8</sup> indicate that when phenol acts as the proton-donor (Ph:W) the absorption spectrum of this complex presents a red shift of the lowest  $\pi$ – $\pi^*$  transition, compared to the case of isolated phenol. The experimental shift<sup>8,65</sup> for the Ph:W complex is  $-350\text{ cm}^{-1}$  compared to the same  $S_0$ – $S_1$  ( $\pi$ – $\pi^*$ ) transition in the gas phase. Our result obtained at the TD-HF/aug-cc-pVDZ is  $-400\text{ cm}^{-1}$ , in very good agreement with experiment both in sign and magnitude. The corresponding results using CIS(D) and TD-B3LYP with the same basis set are, respectively,  $-390$  and  $-540\text{ cm}^{-1}$ . These results are summarized in Table 3. It is thus corroborated that when phenol is the proton-donor a red shift occurs. All theoretical methods agree on this giving similar magnitude in good agreement with the experimental value. The possible blue shift when phenol is the proton-acceptor has not been reported experimentally for the single water situation but rather it has been reported<sup>8,65</sup> that a second water in the monohydrated complex forming a dihydrated phenol leads to a blue shift of  $263\text{ cm}^{-1}$  with respect to the previous described Ph:W monohydrated proton-donor phenol. Thus this leads to a resultant red shift of  $90\text{ cm}^{-1}$  compared to the absorption spectrum of isolated phenol. This is indicative that the second water (where phenol is now the proton-acceptor) induces a blue shift. To analyze the detailed origin of the spectral shift we will now consider the present theoretical results for the monohydrated case W:Ph, where phenol is the proton-acceptor. These results are also shown in Table 3. It is seen that all theoretical methods give a blue shift in this case. The magnitude of the shift is similar to the counterpart magnitude in the case of proton-donor phenol. For instance, TD-HF/aug-cc-pVDZ gives a blue shift of  $380\text{ cm}^{-1}$  and a red shift of  $400\text{ cm}^{-1}$ .

A comparison can also be made now for the two dihydrated complexes as shown in Table 3. Our results indicate a minor shift for the more stable Ph:W:W1 complex (see Fig. 3) and a

**Table 3** Calculated solvatochromic shift ( $\text{cm}^{-1}$ ) of the lowest  $\pi$ – $\pi^*$  transition of phenol in water using optimized hydrogen bond geometries (see Fig. 3)

Method	Ph:W	W:Ph	Ph:W:W	
			1	2
CIS(D)/aug-cc-pVDZ	$-390$	$370$	$20$	$-380$
TD-B3LYP/aug-cc-pVDZ	$-540$	$520$	$-50$	$-790$
TD-HF/aug-cc-pVDZ	$-400$	$380$	$20$	$-350$
Exp. <sup>8</sup>	$-350$	—	$-90$	$-90$

more substantial shift for the Ph:W:W2 complex. The experimental work reports a shift of  $-90\text{ cm}^{-1}$  identifying this as a dihydrate from mass selection. As we find two dihydrated complexes, and there are several other possibilities,<sup>65</sup> it is difficult to make a clear assignment of the experimental result. The theoretical results agree that the shift for the dihydrated complexes are small but only the TD-B3LYP/aug-cc-pVDZ result is in good agreement with the reported experimental value. All methods agree that a more substantial shift is obtained for the other conformer. Given the close proximity of the energy values (within  $1.5\text{ kcal mol}^{-1}$ ) for different conformers it is conceivable that more than one conformer is produced in the free jet expansion.

### 3.2.2 The solvatochromic shift of phenol in liquid water.

Now we analyze the situation in the liquid environment corresponding to phenol in water at room temperature. Using the configurations generated by the MC simulation we selected 100 statistically uncorrelated configurations composed of the central phenol molecule surrounded by 200 water molecules. We consider the solvent molecules only represented by the electrostatic field with the ASEC(Ph:200PC), as described in section 3.1. The solvatochromic shift was calculated, with the three theoretical models and two different electrostatic parameters for the solute calculated with the iterative and PCM polarizations (see section 3.1). All values are blue shifted, in agreement with experiment for the aqueous solution.<sup>12</sup> The results for the calculated spectral shift are shown in Table 4. Again, different theoretical methods give essentially the same blue shift, in the range of  $500$ – $700\text{ cm}^{-1}$ , in good agreement with the experimental result<sup>12</sup> of  $460\text{ cm}^{-1}$ .

### 3.2.3 Role of the hydrogen bonds and the origin of the spectral blue shift.

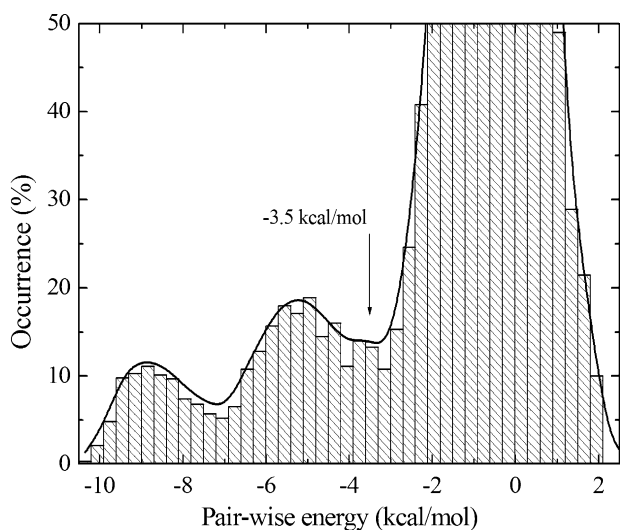
We now analyze in more detail the different contributions of the explicit hydrogen bonds and the remaining bulk water. We first identify the solute–solvent hydrogen bonds in the liquid situation. The nearest solvent molecules can be selected on the basis of a simple geometric criterion derived from the radial distribution function. But in the case of hydrogen bonds an additional criterion is necessary because we cannot be assured that all the nearest water molecules are indeed hydrogen bonded to the solute. We then use both the geometrical and energetic criteria. The geometrical uses the radial and angular distribution function as discussed before.<sup>20,23</sup> Fig. 4 shows the solute–solvent pair-wise energy distribution. As phenol can act both as a proton-donor and a proton-acceptor there are two structures seen below  $-3.5\text{ kcal mol}^{-1}$  corresponding to these two hydrogen bonds.

Using these criteria ( $R_{\text{O-O}} \leq 3.2\text{ \AA}$ ,  $\alpha_{(\text{O-OH})} \leq 40^\circ$  and  $\Delta E \leq -3.5\text{ kcal mol}^{-1}$ ) we find that there is an average of 1.0 hydrogen bonds where phenol is the proton donor



**Table 4** Calculated solvatochromic shift ( $\text{cm}^{-1}$ ) of the lowest  $\pi$ - $\pi^*$  transition of phenol in liquid water at room temperature. Calculations are made for one phenol embedded in the electrostatic field of 200 water molecules treated as simple point charge, ASEC(Ph:200PC). See text for details

Method	Shift (PCM polarization)	Shift (Iterative polarization)
CIS(D)/aug-cc-pVDZ	515	550
TD-B3LYP/aug-cc-pVDZ	530	670
TD-HF/aug-cc-pVDZ	520	565
Exp. <sup>12</sup>	460	460

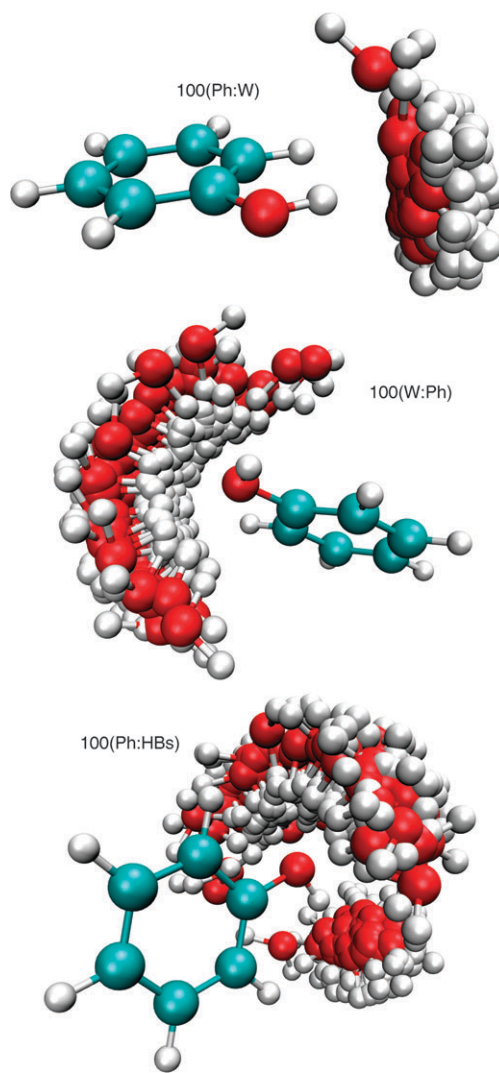


**Fig. 4** Histogram of the pair-wise energy interaction between phenol and water.

(Ph:W) and 1.1 when the phenol is the proton acceptor (W:Ph). This is in agreement with a previous simulation<sup>67</sup> that used another potential for water and phenol. Using the PCM polarization gives similar results.

These phenol–water hydrogen-bonded structures will now be submitted to QM calculations of the UV-Vis spectrum to determine the corresponding solvatochromic shift. Fig. 5 shows the superposition of 100 structures obtained with phenol as the proton-donor 100(Ph:W), the proton-acceptor 100(W:Ph) and the structures with these two combined hydrogen bonds 100(Ph:HBs) in the bottom. The corresponding results are shown on Table 5. It is interesting to see that the shifts using solute–solvent configurations extracted from the liquid situation follow the same trends of the free jet expansion experiments.<sup>8</sup> The situation will change when including the solvent molecules (see below). When water is the proton donor we obtain a red shift of  $435 \pm 15 \text{ cm}^{-1}$  for the lowest  $\pi$ - $\pi^*$  transition (first line in Table 5). When phenol is the proton acceptor (second line) we obtain a blue shift of  $480 \pm 20 \text{ cm}^{-1}$ . Combining the two types of hydrogen bonded structures (third line) gives a partial cancellation and a net blue shift that is only  $135 \pm 25 \text{ cm}^{-1}$ .

We now include the effects of the bulk water. Using the information derived from the radial distribution function we separate the same 100 configurations, but now we consider the nearest 20 water molecules explicitly embedded in the electrostatic field of the 180 remaining water molecules. This model is called 100(Ph:20W:180PC). Therefore, QM calculations are performed 100 times to obtain the statistical



**Fig. 5** Superposition of 100 configurations of the hydrogen bonds formed by phenol in liquid water. This Figure illustrates the configuration space spanned by the hydrogen bond configurations where phenol is the proton donor (top), proton acceptor (middle) and superposition of the two cases (bottom).

distribution. Using explicit water molecules require some computational compromise and we thus use a simple, locally-dense approximation.<sup>68</sup> We use the aug-cc-pVDZ basis set for the central phenol molecule but the 6-31G basis for the 20 explicit molecules and for all the remaining 180 water molecules we use the electrostatic embedding. This gives a total of 390 contracted Cartesian Gaussian basis functions for each of the 100 QM calculation. And each QM calculation is

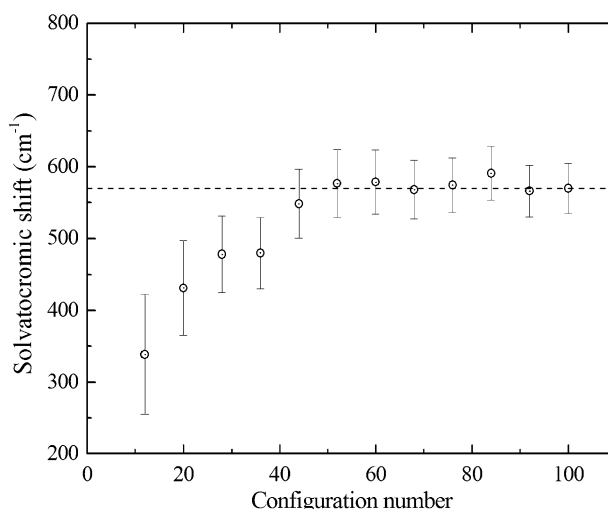
**Table 5** Calculated solvatochromic shift ( $\text{cm}^{-1}$ ) of the lowest  $\pi$ - $\pi^*$  transition of phenol in liquid water at room temperature using different partition of the solute-solvent hydrogen bond contributions using the TD-HF level of calculation (in parenthesis TD-B3LYP with PCM polarization)

Partition	Average solvatochromic shift
100(Ph:W)	$-435 \pm 15$ ( $-630$ )
100(W:Ph)	$480 \pm 20$ (590)
100(Ph:HBs)	$135 \pm 25$ (90)
100(Ph:W:200PC)	$155 \pm 30$ (60)
100(W:Ph:200PC)	$500 \pm 35$ (560)
100(Ph:HBs:200PC)	$310 \pm 40$ (235)
100(Ph:20W:180PC)	$570 \pm 35$
100(Ph:20W-HBs:180PC)	$415 \pm 35$
Exp. <sup>12</sup>	460

made on the system composed of 250 electrons (one phenol and 20 water molecules). The wave function is antisymmetric with respect to the interchange of any two of these electrons. The corresponding results for the solvatochromism are also included in Table 5 and shown to give a solvatochromic shift of  $570 \pm 35 \text{ cm}^{-1}$ , in good agreement with the experimental result of  $460 \text{ cm}^{-1}$ . This is our best result including the inner and the outer solvent water molecules and leading to a good agreement with the experimental result.

Two other aspects will be further considered. First, comparing this theoretical value of  $570 \pm 35 \text{ cm}^{-1}$  with  $565 \text{ cm}^{-1}$  obtained using only the electrostatic embedding of (Table 4) shows that the solvatochromic shift is dominated by the electrostatic interaction with the solvent. Next, to further check on the mild importance of the hydrogen-bond shell we also performed the QM analysis of the role of the bulk water molecules using the same configurations but removing the water molecules that make solute-solvent hydrogen bonds, termed as 100(Ph:20W-HBs:180PC). This corresponds to a “hole” in the hydrogen bond shell, leading to configurations containing only phenol surrounded by the outer water molecules. The corresponding result is now  $415 \pm 35 \text{ cm}^{-1}$ , that compared with the result of  $570 \pm 35 \text{ cm}^{-1}$  (line 100(Ph:20W:180PC) of Table 5) shows the unimportance of the hydrogen bond shell in this case. These results confirm that the participation of the solute-solvent hydrogen bonds in the solvatochromic shift of the lowest  $\pi$ - $\pi^*$  transition essentially cancels giving only a very mild contribution. As a consequence, although water is an important protic solvent, the spectral shift of the lowest  $\pi$ - $\pi^*$  transition of phenol is determined by bulk water.

It is now clear that bare hydrogen bonds, even using the liquid configurations, follow the same trend. It leads to a red shift when phenol is the proton donor and a blue shift when phenol is the proton acceptor. It is now interesting to make a separate analysis using the liquid configurations but now embedded these hydrogen bonds in the electrostatic field of the outer water molecules. Interestingly, we obtain that the red shift turns into a small blue shift as shown in lines 100(Ph:W) and 100(Ph:W:200PC) of Table 5, respectively. As a specific numerical example, using the TD-HF/aug-cc-pVDZ level with iterative polarization the average red shift of the bare proton donor hydrogen bonds change from a red shift of  $435 \text{ cm}^{-1}$  into a small blue shift of  $155 \text{ cm}^{-1}$ , when embedded in the field



**Fig. 6** Calculated solvatochromic shift of the lowest  $\pi$ - $\pi^*$  transition of phenol in water as a function of the number of MC configurations used in the TD-HF QM calculations of phenol surrounded by 20 explicit water molecules embedded in the electrostatic field of 180 water molecules treated as simple point charges, model so-called 100(Ph:20W:180PC).

of the outer solvent molecules. The same behavior is observed with TD-B3LYP/aug-cc-pVDZ with PCM polarization. The average red shift of  $630 \text{ cm}^{-1}$  changes into a small blue shift of  $60 \text{ cm}^{-1}$ , when embedded in the field of the outer solvent molecules.

The net blue shift is now corroborated as being an electrostatic effect of the bulk solvent molecules. Including all hydrogen-bonded structures embedded in the electrostatic field of all water bulk molecules (see line 100(Ph:HBs:200PC) of Table 5), using the TD-HF/aug-cc-pVDZ give a total average blue shift of  $310 \text{ cm}^{-1}$  and using TD-B3LYP/aug-cc-pVDZ with PCM polarization it is  $235 \text{ cm}^{-1}$ .

Before concluding we briefly analyze the statistical convergence of the calculated results. Fig. 6 confirms the convergence of the total calculated shift indicating that statistical convergence is obtained already for 50 QM calculations. This is a consequence of the efficient sampling of MC configurations obtained from the use of the statistical correlation analysis.<sup>20–23</sup>

#### 4. Summary and conclusions

A combined and sequential use of Monte Carlo simulation and quantum mechanical calculations was made to analyze in detail the solvatochromic shift of the lowest  $\pi$ - $\pi^*$  transition of phenol in water. The solute polarization is included using an iterative procedure that brings the solute into an electrostatic equilibrium with the solvent. Calculations at the MP2/aug-cc-pVDZ level obtained an in-water dipole moment of 2.25 D, corresponding to an increase of 76% compared to the calculated gas-phase value. For comparison, a polarization obtained with the continuum PCM method using the same MP2 level gives the value of 1.93 D.

Using statistically uncorrelated configurations sampled from the MC simulation, first-principle size-extensive calculations

were performed to obtain the solvatochromic shift. Different quantum mechanical models are used and they all agree that the  $\pi-\pi^*$  transition of phenol in liquid water shifts to the blue side by *ca.* 500–600  $\text{cm}^{-1}$ , in good agreement with the experimental shift of the absorption band maximum. Analysis was made of the origin of the blue shift. Studies both at the optimized geometry and in room-temperature water clearly indicate that hydrogen bonds of water with phenol give a red shift when phenol is the proton-donor and a blue shift when phenol is the proton-acceptor. In the case of the optimized clusters the calculated shifts are in very good agreement with results obtained from mass-selected free jet expansion experiments. In the liquid case the contribution of the solute–solvent hydrogen bonds partially cancels and the total shift obtained is a consequence of the contribution of the outer water molecules. The iterative polarization leads to larger values than the PCM polarization. The difference is, however, small. Our best result, including both inner and outer water molecules, is  $570 \pm 35 \text{ cm}^{-1}$  using the iterative polarization and  $520 \pm 35 \text{ cm}^{-1}$  using the PCM solute polarization. These should be compared with the experimental shift of  $460 \text{ cm}^{-1}$  for the absorption maximum. Considering the very small magnitude of the shift (corresponding to only 0.06 eV or 3 nm) this should be considered an excellent qualitative and quantitative result and explains the origin of the blue shift of the  $S_0-S_1$  transition of phenol in water. Hence, although water is an important protic solvent, the spectral shift of the lowest  $\pi-\pi^*$  transition of phenol in water, is less influenced by the solute–solvent hydrogen bond shell. We also find from explicit calculations that this solvatochromic shift is dominated by the electrostatic interaction with the solvent. Finally, all average results reported here are statistically converged.

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