

Polarization and solvatochromic shift of *ortho*-betaine in waterTertius L. Fonseca^a, Kaline Coutinho^b, Sylvio Canuto^{b,*}^a Instituto de Física, Universidade Federal de Goiás, CP 131, 74001-970 Goiânia, GO, Brazil^b Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

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Abstract

Betaine dyes are known to show very large transition energy shifts in different solvents. The *ortho*-betaine molecule – a simple two-ring prototype of the $E_T(30)$ Reichardt dye – has been investigated theoretically from a combined statistical and quantum mechanics approach. Using sequential Monte Carlo (MC) simulations and MP2/cc-pVDZ calculations the in-water dipole moment of *ortho*-betaine is obtained as 12.30 ± 0.05 D. This result shows a considerable increase of 75% compared to the *in-vacuum* dipole moment. For comparison, the use of a polarizable continuum model using the same MP2/cc-pVDZ leads to an in-water dipole moment of 11.6 D, in good agreement. This large polarization is incorporated in the classical potential for another MC simulation to generate solute–solvent configurations and to obtain the contribution of the polarization effect in the solvatochromic shift. Using statistically uncorrelated configurations and supermolecular INDO/CIS calculations, including the solute and, explicitly, 230 solvent water molecules, the statistically converged calculated shift is obtained here as 6360 cm^{-1} , in good agreement with the experimental result of 7550 cm^{-1} .

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1. Introduction

Betaine molecules are characterized by charge transfer excitations that show very prominent transition energy shifts in different solvents [1]. The extreme sensitivity of the absorption spectra of betaine molecules in the spectral region of the ultra-violet–visible (UV–Vis) has made it a convenient probe for defining a scale of solvent polarity. In fact the so-called $E_T(30)$ or pyridinium *N*-phenoxide betaine dye (also termed as Reichardt dye) forms the basis of a polarity scale using the large transition energy shift in the different and corresponding solvents [1–3]. Understanding the solvatochromic shift of betaine molecules is thus of essential importance. The theoretical investigation of the solvatochromic and structural changes of the Reichardt dye in different solvents has been very intense in the recent years [4–17]. There is some accumulated and important

knowledge from these previous studies. The large transition energy shift is due to the marked change in the dipole moment upon excitation and there is an important modification in the ground state interring angle with the solvent. The ground state is characterized by a large value of the dipole moment due to a charge separation in the nitrogen (positive) and oxygen (negative) atoms. Upon excitation there is a charge transfer [18,19] and a considerable decrease in the dipole moment. This makes a decreased solvation of the excited state, compared to the ground state, and hence a larger energy separation of these two states, resulting in a large blue shift. In water, the excitation energy compared to low-polarity solvents, shifts [1] by ca. $10,000 \text{ cm}^{-1}$. However, the change in the dipole moment apparently cannot solely answer for such a large shift. It has been confirmed [3–6] that the interring twist is also important and contributes to an increase in the absorption energy shift. An *ortho*-betaine, a variant of the $E_T(30)$, has been synthesized and also shown to present a large transition energy shift [20]. Large shifts of ca. 8000 cm^{-1} have been obtained, in spite of the fact that the X-ray data, in

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crystalline form, indicates that the pyridine and the phenoxy rings are orthogonal, thus supposedly precluding an efficient charge transfer. It is clear that the dipole moment of the ground state is an essential ingredient to understand the solvatochromic shift of betaine in different solvents.

Further theoretical progress for the $E_T(30)$ Reichardt dye is hampered by the large size of the system, composed by seven phenol-type rings. This led Caricato et al. [17] to recently consider semi-empirical methods to systematically analyze the solvent polarity scale based in the $E_T(30)$ dye. In another direction, Rezende and co-workers [21] considered the possibility of decreasing the number of rings without losing the essential aspects of the large shift. They have experimentally considered the solvatochromic behavior of 2- and 4-pyridiniophenoxydes and measured the UV–Vis spectra in different solvents, noting also that they are both subjected to very large shifts. However, as the 4-pyridiniophenoxydes (*para*-betaine) is not soluble in some of the important solvents [21] such as acetone, chloroform and toluene, for instance, the 2-pyridiniophenoxyde (*ortho*-betaine) becomes more relevant, in this context. This *ortho*-betaine (Fig. 1) presents the most important aspects that characterize the betaine solvatochromic behavior. It presents a large shift and the importance of the interring twist has been also verified to exist and be very important in contributing to this solvation energy shift [22]. The shift from toluene to water, for instance, has been measured [21] to be ca. 7550 cm^{-1} .

In this work we study the solvatochromic shift of 2-phenoxyde (*ortho*-betaine, from now on OB) in water compared to the isolated *in-vacuum* situation. We focus on the importance of the solute polarization using an iterative procedure to obtain the in-water dipole moment of the ground state. As we will see there is indeed a very large polarization with the in-water dipole moment being considerably increased due to the solvent field. Next, we analyze the importance of this polarization in the calculated absorption spectrum in water.

In this study we consider the combined and sequential use of Monte Carlo (MC) simulation and quantum mechanics (QM) calculations (S-MC/QM) [23]. MC simulations of OB in water are made and statistically relevant

configurations are sampled for quantum mechanics (QM) calculations of the spectrum. In these latter we use explicitly a large number of water solvent molecules. In the larger calculation a total of 230 solvent water molecules are used. One hundred QM calculations are used to obtain statistically converged results.

2. Calculation details

Monte Carlo simulations of 1 OB in 900 water molecules were carried out using the Metropolis sampling in the canonical (constant number of molecules, volume and temperature) NVT ensemble in a cubic box with periodic boundary conditions [24]. The intermolecular interaction is described by the Lennard–Jones (LJ) plus Coulomb potential with three parameters for each interacting site i (ϵ_i , σ_i and q_i). For the water molecules, we have used the simple point charge (SPC) model proposed by Berendsen et al. [25]. For the solute, the LJ parameters were obtained combining the potentials of the phenol molecule proposed by Jorgensen and Nguyen [26] and the pyridine molecule proposed by Jorgensen et al. [27]. To take into account the polarization by the solvent molecules, the solute charges have been calculated using an iterative procedure based on separated MC simulations followed by MP2/cc-pVDZ calculations of the dipole moment and the fit of the charges from electrostatic potential in a grid (CHELPG) [28] to obtain the atomic charges. This will be described in more detail below. All QM calculations are made using the GAUSSIAN 03 program [29]. In a previous work [22], the molecular structures of the OB were optimized at the MP2/6-31G level of calculation and this geometry is adopted here. In the water environment Helmholtz free energy calculations [22] show an increase of the torsion angle between the phenoxide and the pyridinium rings (see Fig. 1). The free energy calculation indicates that the most stable interring angle of OB in water is 60° . Hence, in this work all simulations and QM calculation have assumed this angle. Of course, the ideal situation would be to have the solute molecule totally flexible during the simulation. However, it should be noted that different conformation may require different charge polarization [22] making it difficult, at the present stage, to automatically update the potential for different accessible conformations. This would lead to a bias where the conformations accessed by the simulation would be a consequence of the previously selected parameters. Hence, our procedure just makes it sure that the important interring twist is included.

The MC simulations were performed with the DICE program [30]. In all simulations the thermalization stage comprised 2.7×10^7 MC steps and was followed by the average stage of 1.8×10^8 MC steps. The cutoff distance in which each molecule interacts with all other molecules is truncated at half the box length. The experimental value of the water density (0.9966 g/cm^3) was used to determine the size of cubic box ($L = 3.011\text{ nm}$). Long range electrostatic corrections for the LJ and Coulomb potentials, for

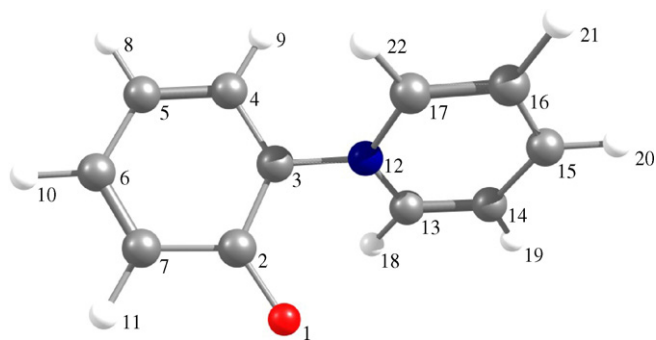


Fig. 1. The 2-pyridiniophenoxyde (*ortho*-betaine) molecule. Atomic indices are used to define (see Table 1) the electrostatic parameters.

separations larger than the cutoff distance, were calculated using the pair radial distribution function and the reaction field method with dipole interactions, respectively.

Using the auto-correlation function of the energy we have calculated the interval of statistical correlation for selecting statistically uncorrelated configurations [31–34]. This sampling gives the relevant statistical configurations assuring a fast and systematic convergence with a relatively small number of QM calculations. Here we have used 100 configurations having less than 10% of correlation. Each configuration is composed of one OB surrounded by 150 or 230 water molecules and were separately submitted to quantum mechanical (QM) calculations. Because of the large size of these supermolecular structures the QM calculations of the $n-\pi^*$ transitions were performed using the semi-empirical INDO/CIS [35] method as implemented in the ZINDO program [36]. The INDO/CIS uses a spectroscopic parametrization [35] and a reference wave function that includes all valence electrons both in the solute and in the solvent. In the largest calculation presented here this

corresponds to a 1904 valence-electron problem, where the wave function delocalizes over the solute–solvent system including exchange and part of the dispersion interaction [37].

3. Results and discussion

3.1. The polarization of ortho-betaine in water

An important aspect that is of central concern in theoretical studies of solvent effects is the precise inclusion of the solute polarization effects [38–45]. Traditionally, there are two ways of including this solvent polarization effect. One is the simplest inclusion of an implicit polarization [40], where the dipole moment and charges of the solute are re-scaled by some appropriate factor. In the other, some additional term is added in the classical potential, making the polarizable models [41–45]. We have recently developed a procedure to describe the electronic polarization of a molecule in solution [46,47], by iteratively applying the S-QM/MM methodology to calculate the dipole moment of the solute molecule in the presence of the solvent. Upon convergence, the solute is in electrostatic equilibrium with the solvent.

We first perform MP2/cc-pVDZ calculations for the isolated OB molecule and obtain the atomic charges using CHELPG electrostatic mapping [28]. 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

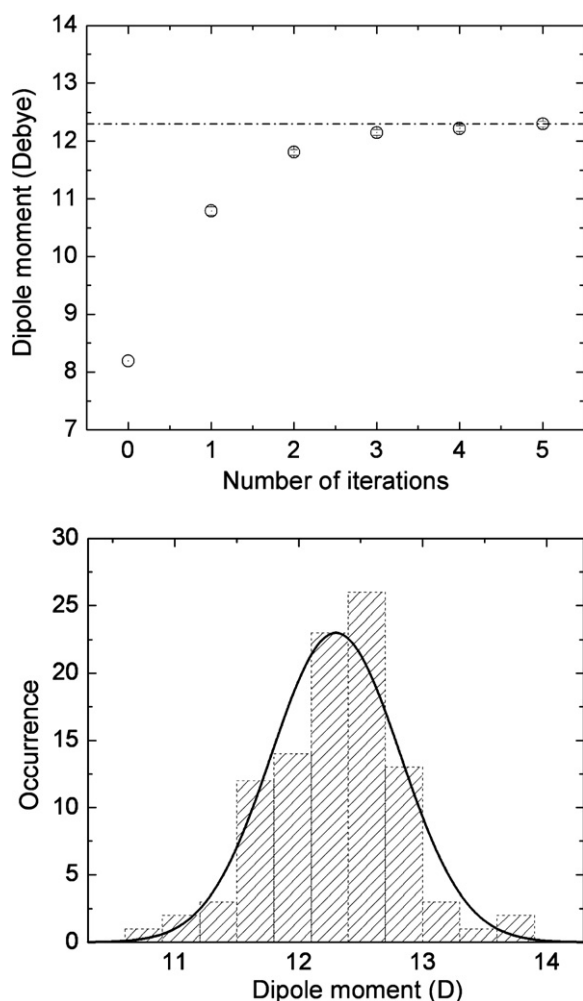


Fig. 2. Calculated average values of the dipole moments with respect to the number of iterations (top). Also shown (bottom) is the gaussian distribution of the 100 MP2/cc-pVDZ calculated dipole moment values of the last iteration.

Table 1
Electrostatic parameters and dipole moment (see Fig. 1)

Atom	Charge (<i>e</i>)		
	Gas phase	PCM	Converged
O ₁	−0.5943	−0.7091	−0.8029
C ₂	0.4221	0.4189	0.4551
C ₃	−0.1962	−0.1878	−0.1880
C ₄	−0.1154	−0.1044	−0.0890
C ₅	−0.1559	−0.1980	−0.1830
C ₆	−0.0703	−0.0821	−0.0794
C ₇	−0.2250	−0.2730	−0.2724
H ₈	0.0904	0.1130	0.1127
H ₉	0.0681	0.1076	0.1116
H ₁₀	0.0789	0.0963	0.0913
H ₁₁	0.0985	0.1044	0.1065
N ₁₂	0.1898	0.1645	0.1764
C ₁₃	−0.0341	−0.0194	−0.0115
C ₁₄	−0.0205	−0.0490	−0.0502
C ₁₅	−0.0820	−0.0470	−0.0276
C ₁₆	−0.0824	−0.0852	−0.0775
C ₁₇	0.0230	0.0286	0.0319
H ₁₈	0.1464	0.1554	0.1423
H ₁₉	0.1146	0.1449	0.1381
H ₂₀	0.1124	0.1370	0.1310
H ₂₁	0.1242	0.1552	0.1546
H ₂₂	0.1077	0.1292	0.1300
μ (D)	8.19	11.55	12.30 ± 0.05

Uncertainty is the statistical error. Standard deviation is ten times larger.

dipole moment and atomic charges of the solute in the presence of the solvent (represented by fixed SPC charges) using MP2/cc-pVDZ. These charges are updated in the coulomb part of the potential for another MC simulation and subsequent another dipole moment and atomic charges. The process is repeated until convergence in the QM dipole moment is attained. The results are summarized in Fig. 2 and Table 1. As Fig. 2 (top) shows the convergence in the dipole moment is obtained in five iterations. Each entry in this Fig. 2 corresponds to a statistically converged average value of the dipole moment obtained using MP2/cc-pVDZ. In the gas phase (interring angle of 30°) the calculated dipole moment of OB is 7.07 D. There is apparently no experimental value for the gas phase dipole moment of OB. A previous estimate [22] of 8.6 D obtained at the MP2/6-31G seems too large as expected for the MP2 model with this basis set. This seems to be an interesting result for an intermediate solute polarization. We now estimate the experimental gas phase dipole moment (angle of 30°) to be close to 7.1 D. In turn, the converged in-water

(angle of 60°) value is obtained here as 12.30 ± 0.05 D, corresponding to a very large increase of ca. 75%. Although this polarization may seem to be very large it is consistent with the application of the simpler polarized continuum model (PCM) [48] that gives the value of 11.6 D, for the same theoretical model (MP2/cc-pVDZ). Some recent applications of the PCM method to obtain solvent shifts in organic molecules corroborate the importance of large solute polarity as a condition to calibrate the cavity size [49]. Fig. 2 (bottom) shows the distribution of calculated values of the dipole moment obtained using the statistically uncorrelated configurations extracted from the MC simulation.

3.2. The solvatochromic shift of ortho-betaine in water

We first briefly characterize the electronic transitions involved in the observed large solvent shifts. For the Reichardt betaine the transition involved is the HOMO $\rightarrow$ LUMO transition having a π - π^* character (see, e.g. Ref.

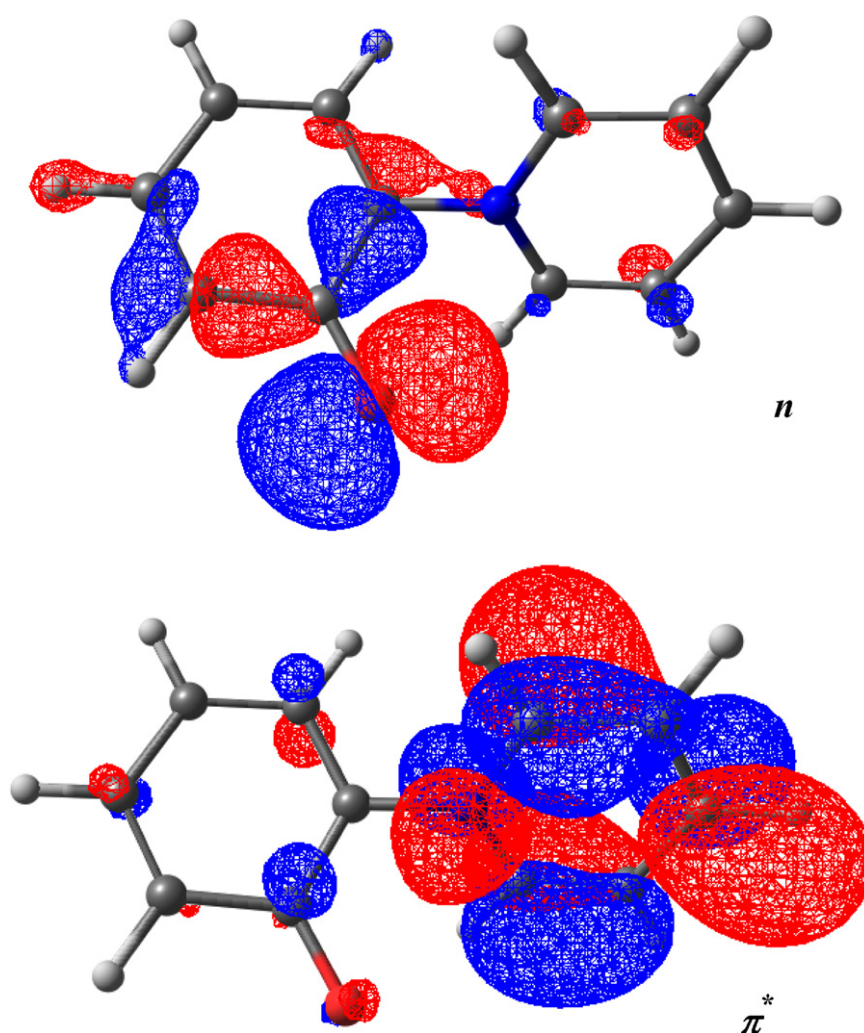


Fig. 3. The molecular orbitals involved in the charge transfer excitation (n - π^* transition).

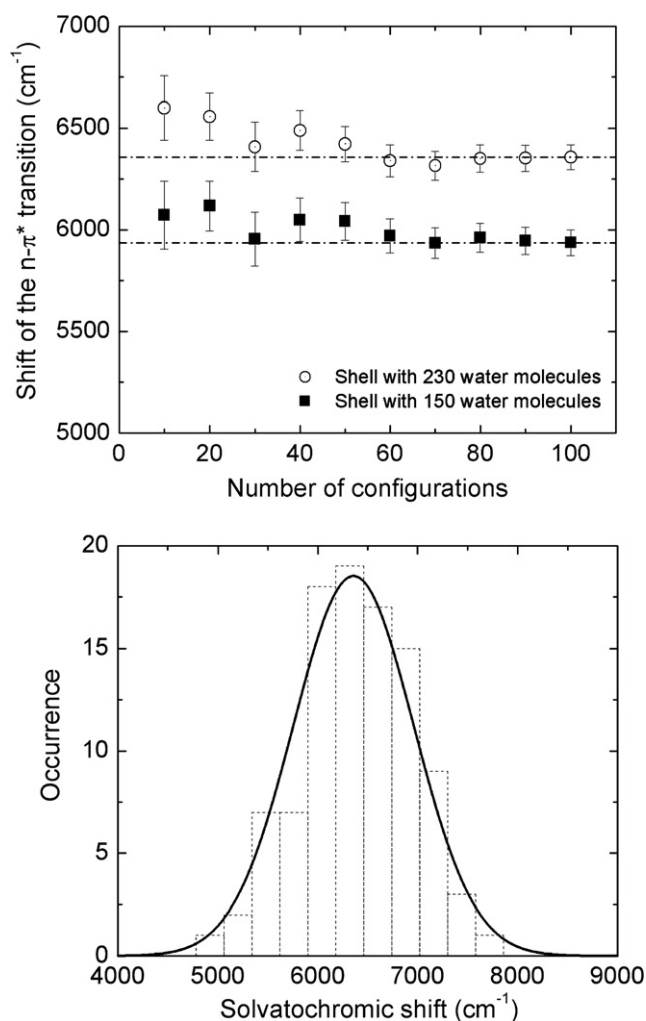


Fig. 4. Statistical convergence of the solvatochromic shift of *ortho*-betaine in water (top). Uncertainty is the statistical error. Standard deviation is ten times larger. The gaussian distribution of the INDO/CIS calculated shifts is shown in the bottom.

[17]). The large shift is rationalized by the charge transfer leading to large variations of the dipole moments in the ground and excited states. In the present OB case there is indeed a low-lying HOMO $\rightarrow$ LUMO π - π^* transition but that is not attributed here as the one involved in the large solvatochromic shift. In gas phase, for instance, this transition is calculated around $15,600\text{ cm}^{-1}$. In fact, the next transition is the HOMO-1 $\rightarrow$ LUMO having n - π^* character. In the gas phase it is calculated around $22,000\text{ cm}^{-1}$, the same region reported by the experiments [21]. This transition also implies a large charge transfer. Fig. 3 shows the n and π^* orbitals involved in the transition clearly showing a pronounced charge transfer. Hence, all results reported here for the solvatochromic shifts of OB are related to this n - π^* transition.

Now we discuss the solvatochromic shift of OB in water, compared to gas phase. Previous results obtained for the solvation shift of OB in water using the interring angle corresponding to the gas phase geometry (30°) gives a shift of only 1530 cm^{-1} . Correcting for the solution angle of 60°

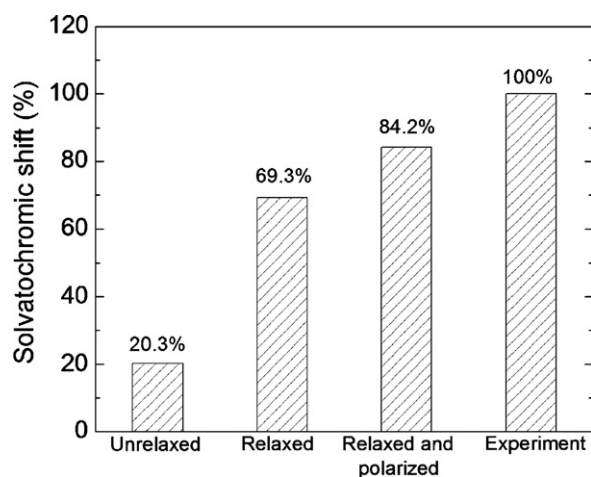


Fig. 5. Separate percentual contributions to the total solvatochromic shift of the n - π^* transition of *ortho*-betaine in water. See text.

gives a better result of 5230 cm^{-1} , but still only ca. 2/3 compared to the experimental shift of 7550 cm^{-1} . Hence, the geometry relaxation of the solute due to the solvent increases the transition energy shift by 3700 cm^{-1} . Now we extend these calculations to include a realistic solute polarization as obtained in the previous section using the iterative procedure in the MC simulations and MP2/cc-pVDZ calculations. Using the converged electrostatic potential ($\mu = 12.30\text{ D}$) a total of 100 configurations, composed of 150 water molecules each, were sampled for the INDO/CIS calculations of the absorption spectrum of OB in water. Next, to check on the possible convergence of the calculated result with the total number of water molecules included we extended the number of solvent molecules to 230 water molecules. This is the largest calculation performed here including a total of 1904 valence electrons. The calculated results are shown in Fig. 4 that shows that statistically converged results are obtained after 60 QM calculations. Using explicitly 150 water molecules the solvatochromic shift converges to an improved value of 5940 cm^{-1} . Extending this to include as much as 230 water molecules the solvatochromic shift converges to the value of 6360 cm^{-1} , which is the best result obtained in this present studies. This indicates that solvent water molecules located in the outer solvation shells can still influence the calculated solvatochromic shift. Fig. 5 summarizes these calculated results giving approximate contributions to the different components of relaxation and polarization contributions.

4. Summary and conclusion

Betaine molecules are characterized by very large solvatochromic shifts. They normally present a high sensitivity to the different solvents and as such have been used in the definition of a solvent polarity scale. The most important system in this direction is the so-called Reichardt dye, $E_T(30)$, that presents a total of seven phenol rings,

thus precluding accurate theoretical investigations with explicit solvent molecules and solute polarization. However, most of the essential characteristics can also be found in smaller betainic systems. To obtain insight into the different possible contributions of solute polarization and the role of using explicitly solvent molecules we have chosen to study the two-ring 2-phenoxyde (*ortho*-betaine) that present a solvatochromic shift in water of ca. 7550 cm^{-1} compared to the gas phase situation. Solute polarization has been included using an iterative procedure that brings the electrostatic equilibrium between the solute and the solvent. Using Monte Carlo simulation and MP2/cc-pVDZ calculations we obtain the dipole moment of *ortho*-betaine as $12.30 \pm 0.05\text{ D}$, corresponding to a very large increase of ca. 75% compared to the gas phase situation. For this particular aspect the polarizable continuum model gives a good approximation leading to an in-water dipole moment value of 11.55 D . Using the converged solute polarization another MC simulation was performed to sample 100 statistically uncorrelated configurations composed of a total of 230 water molecules. Using explicitly 230 water solvent molecules, corresponding to a 1904 valence-electron problem, INDO calculations with spectroscopic parametrization, INDO/CIS, were performed to obtain the best solvatochromic shift of the $n\text{--}\pi^*$ transition as 6360 cm^{-1} , in good agreement with the available experimental result of 7550 cm^{-1} . Finally, considering previous theoretical results we attempt to give an approximate picture of the different contributions related to solute relaxation and solute polarization, to the total calculated solvatochromic shift.

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