A sequential Monte Carlo quantum mechanics study of the hydrogen-bond interaction and the solvatochromic shift of the $n-\pi^*$ transition of acrolein in water

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The sequential Monte Carlo (MC) quantum mechanics (QM) methodology, using time-dependent density-functional theory (TD-DFT), is used to study the solvatochromic shift of the $n-\pi^*$ transition of *trans*-acrolein in water. Using structures obtained from the isothermal-isobaric Metropolis MC simulation TD-DFT calculations, within the B3LYP functional, are performed for the absorption spectrum of acrolein in water. In the average acrolein makes one hydrogen bond with water and the hydrogen-bond shell is responsible for 30% of the total solvatochromic shift, considerably less than the shift obtained for the minimum-energy configurations. MC configurations are sampled after analysis of the statistical correlation and 100 configurations are extracted for subsequent QM calculations. All-electron TD-DFT B3LYP calculations of the absorption transition including acrolein and all explicit solvent molecules within the first hydration shell, 26 water molecules, give a solvatochromic shift of 0.18 ± 0.11 eV. Using simple point charges to represent the solvent the shifts are calculated for the first, second, and third solvation shells. The results converge for the calculated shift of 0.20 ± 0.10 eV in very good agreement with the experimentally inferred result of 0.20 ± 0.05 eV. All average results presented are statistically converged. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2033750]

I. INTRODUCTION

The understanding of solvent effects is of crucial importance to rationalize several experiments and phenomena in chemistry, physics, and biology. Solvent effects are everyday present, for instance, in absorption spectroscopy of organic molecules because most UV-visible absorption spectra are taken in solutions. The interaction of a reference molecule with a solvent leads to changes in the absorption spectrum and this can be used as a probe of the intermolecular interaction between the solvent and the reference molecule in the ground and excited states.[1] Typical examples are provided by the $n-\pi^*$ transition of molecules with a carbonyl C=O group. After excitation, there is a decrease of the molecular dipole moment. The ground state then interacts more with the solvent than does the excited state. This differential stabilization increases the energy difference between the ground and the excited state leading to larger transition energy; i.e., a blueshift. There has been an enormous theoretical interest in the description of the solvent effects of $n-\pi^*$ transition of molecules with a carbonyl group.[2–25] A favorite system has been formaldehyde in aqueous solution in spite of the fact that conclusive experimental result for the solvatochromic shift is not available. Another molecular system of great theoretical interest has been acetone where the existence of experimental results for the blueshift in water has been very useful to gauge the quality of different methods and approximations. Indeed, formaldehyde[2–13] and acetone[14–25] have been subjected to intense theoretical studies of the $n-\pi^*$ transition in water, with variable degrees of success. *Trans*-acrolein (Fig. 1) is another carbonyl compound of great interest. Its experimental absorption spectrum has been studied in the past.[26–37] The singlet $n-\pi^*$ transition in water has been determined experimentally to suffer a sizable blueshift. Theoretically, the $n-\pi^*$ absorption transition of acrolein was studied previously by Ten-no *et al.*[38] using the reference interaction site model (RISM). More recently, three theoretical investigations have appeared. Aquilante *et al.*[39] have used the combined discrete/continuum approach based on the polarizable continuum model (PCM).[40,41] Monte *et al.*[42] have employed the conductorlike screening model[43] (COSMO) con-

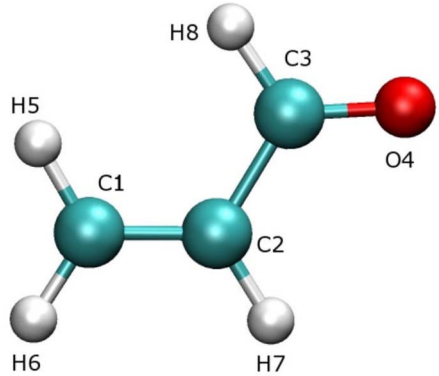

FIG. 1. (Color online) The structure of *s-trans*-acrolein and definition of the atomic indices used in Tables I and II.

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tinuum solvation model combined with a multireference singles and doubles configuration interaction including quadruple correction to size extensivity (MR-CISD+Q). The most recent study was made by Martin *et al.*[44] using an averaged solvent electrostatic potential (ASEP) obtained from molecular-dynamics simulation. In spite of the relative success of the previous theoretical treatments it is still missing a study with *explicit* inclusion of the solvent water molecules. This requires a larger computational effort. For this reason semiempirical models combined with Monte Carlo simulations have been used in the past.[3,4,20,45] First-principle, all-electron calculations with explicit consideration of the solvent molecules are important steps towards the understanding of solvent effects. Time-dependent density-functional theory combined with computer simulation of the liquid structure is a natural choice at present.

In this work we consider the sequential Monte Carlo/quantum mechanics (S-MC/QM) methodology[3,4,20,45,46] to study in detail the shift of the $n-\pi^*$ transition of acrolein in water compared to gas phase. In the S-MC/QM methodology, MC simulations are performed to generate the structure of the liquid composed by the solute and the solvent molecules. After the simulation statistically relevant configurations are sampled for subsequent QM calculations of the acrolein and all solvent molecules within a given solvation shell. One crucial advantage of the sequential approach is that after the simulation all the statistical information are available thus permitting an efficient protocol for the QM calculations,[4,45] in particular, efficiently sampling configurations for the subsequent QM calculations. For the present study of acrolein in water the QM calculations are made at time-dependent density-functional theory (TD-DFT) level.[47,48]

An important aspect that is attracting interest is the understanding of the contribution of the hydrogen-bond shell. One aspect that is important in this context is the determination of the solute-solvent hydrogen-bond structure. There have been studies attempting to describe the participation of the hydrogen-bond shell by the use of geometry-optimized structures.[49–51] In other cases the use of explicit water molecules in the cavity of continuum models for the representation of the local effects of hydrogen bonds in solute-solvent interaction has been found to be necessary.[52–54] Geometry-optimization minimizes the energy and generally overestimates the interaction between the reference molecule and the solvent and may lead to artificial results with respect to the liquid situation at room temperature. Martin *et al.*[44] used averaged electrostatic potential to estimate that the hydrogen-bond shell is responsible for ca. 35% of the total shift of acrolein in water. This seems to be a relatively small contribution but it is in agreement with our own previous results obtained for other systems.[3,4,20,55,56] In this work we make a detailed analysis of the structure of the hydrogen bonds formed between acrolein and water, in the liquid environment, and next we calculate its contribution to the total solvatochromic shift. Also, we calculate the contribution of the first solvation shell considering the solute and the solvent molecules as an all-electron problem. In addition, representing the solvent water molecules by point charges, we calculate the solvatochromic shifts due to the first, second, and third solvation shells. These results are compared with previous theoretical and experimental values. In this direction, we find necessary a brief analysis (Sec. III A) of the experimental values because as the results in gas phase and in aqueous solution come from very different sources there has been some space for uncertainties.

TABLE I. Potential parameters of acrolein and water used in the MC simulation.

Atom	q (e)	ε (kcal/mol)	σ (Å)
	Acrolein		
C1	−0.2859	0.076	3.550
C2	−0.1261	0.076	3.550
C3	0.4803	0.105	3.750
O4	−0.4318	0.210	2.960
H5	0.1458	0.030	2.420
H6	0.1367	0.030	2.420
H7	0.1122	0.030	2.420
H8	−0.0312	0.015	2.420
	Water		
O	−0.820	0.155	3.165
H	0.410	0.000	0.000

II. CALCULATION DETAILS

The MC simulation is performed using standard procedures[57] for the Metropolis sampling technique in the isothermal-isobaric ensemble, where the number of molecules N, the pressure p, and the temperature T are fixed. We have used the periodic boundary conditions and image method in a cubic box of size L with one acrolein molecule embedded in 500 molecules of water in normal conditions ($T=298$ K and $p=1$ atm). The acrolein and the water molecules interact by the Lennard-Jones plus Coulomb potential with three parameters for each interacting site i (ε_i, σ_i, and q_i).

$$U_{ab}=\sum_{i}^{a}\sum_{j}^{b}4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\frac{q_iq_je^2}{r_{ij}}, \tag{1}$$

where i and j are the sites in systems a and b, respectively, r_{ij} is the interatomic distance between the sites i and j, e is the elementary charge, $\varepsilon_{ij}=(\varepsilon_i\varepsilon_j)^{1/2}$, and $\sigma_{ij}=(\sigma_i\sigma_j)^{1/2}$. For the water molecules we used the simple point-charges[58] (SPC) parameters. For the acrolein we use the all-atom optimized parameters for liquid simulations (OPL/AA).[59] The atomic charges are obtained from an electrostatic fit (CHELPG) (Ref. 60) using a coupled-cluster calculation with a correlation-consistent[61] basis set, CCD/cc-pVDZ. The interatomic potentials for both acrolein and water are given in Table I. The geometry of the acrolein was obtained from a MP2/6-311++G(d,p) optimization. The calculated C=O, C1–C2, and C2–C3 distances are, respectively, 1.219, 1.344, and 1.477 Å, in very good agreement with the corresponding experimental results of 1.219, 1.345, and 1.470 Å.[62] It is known that carbonyl molecules relax the geometry in water with a slight increase of the C=O distance. Hence, in the

simulations this distance has been increased by 0.005 Å. As we shall see, this corresponds basically to the lengthening derived from the hydrogen bond between acrolein and water.

The MC simulation was performed with the DICE program[63] and used procedures described previously.[3,4,20,45] After the thermalization, 50×10^6 MC steps are performed. The average density is calculated as 0.989 ± 0.007 g/cm^3 in agreement with the result for liquid water. After calculating the autocorrelation function of the energy, we have sampled configurations with less than 10% of statistical correlation.[3,4,20,45,64] One hundred configurations are separated that represent the entire simulation.[64] As in previous applications[3,4,20,46] statistically converged results are obtained in all cases. The hydrogen-bonded structures are identified using the energetic and geometric criteria and will be discussed in more detail in Sec. III. The subsequent QM calculations of the $n-\pi^*$ transitions are made using TD-DFT using the 6-31+G(d) basis with the three-parameter hybrid B3LYP exchange potential,[65,66] as implemented in the GAUSSIAN 98.[67]

As a reference for the solvatochromic shift, the $n-\pi^*$ transition of isolated acrolein is calculated to be 3.60 eV. For comparison, recent theoretical results obtained the values of 3.69 eV using CASPT2 and 3.97 eV using CASSCF.[44] The use of the same methods in Ref. 39 obtained 3.63 and 3.93 eV, respectively. Multireference CI calculations obtained 3.85 eV.[42] Experimental values show absorption maximum close to 3.69–3.71 eV.[28,29,35]

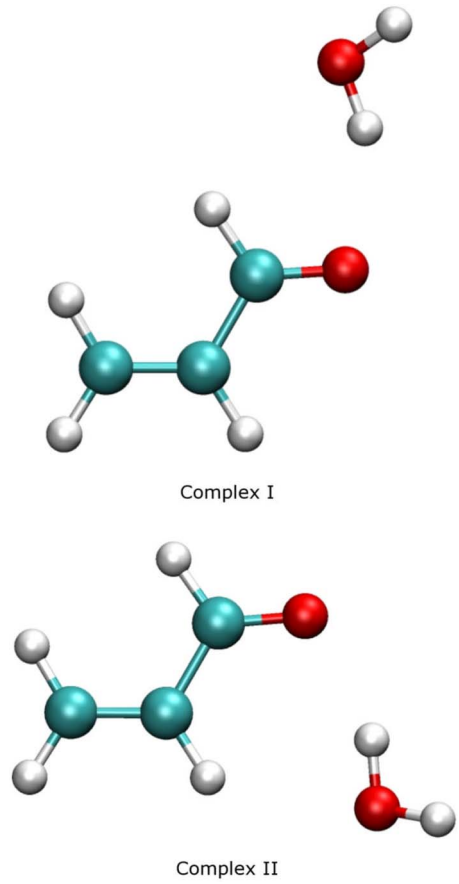

FIG. 2. (Color online) The optimized hydrogen-bonded structures of acrolein-water.

III. RESULTS AND DISCUSSION

In discussing the results for the energy shift of the $n-\pi^*$ transition of acrolein in water we separate the contributions arising from the hydrogen bond and the other hydration shells. However, it is useful to first analyze briefly the experimental and previous theoretical results for the $n-\pi^*$ transition of acrolein because there seems to be some misinterpretations and, also, because this will gauge the accuracy of the different theoretical results.

A. Survey of previous experimental and theoretical solvatochromic shifts

It is generally believed that the first reliable UV-vis absorption study of acrolein was made by Walsh.[26] But this study does not consider the lowest transitions and hence give no information on the location of the $n-\pi^*$ excitation. However, it quotes previous studies on gas phase[27,28] where this state has been observed *around* 330 nm (3.75 eV). This value has often been considered as the value in gas phase. However, Blacet *et al.*[29] showed that the gas phase $n-\pi^*$ transition is a very broad absorption with a maximum in the region of 3.69–3.71 eV (334–336 nm), in agreement with previous work made by Lüthy[28] and later by Inuzuka.[35] This is the value we use here for the gas phase result. There are some consequences to this. One is that the solvatochromic shift from gas to n-hexane [measured at 3.71 eV (Ref. 30)] would be a small but positive (blue) shift instead of a supposed redshift.[42] It is natural to expect a blueshift in $n-\pi^*$ transitions because of the dipole moment decrease upon excitation. Due to the low polarity of n-hexane this would imply a minor blueshift and that is indeed compatible if the gas phase value is taken between 3.69 and 3.71 eV, as suggested here. The blueshift of $n-\pi^*$ transitions is a characteristic feature used experimentally to characterize electronic transitions. For instance, the shift of 0.05 eV in changing the solvent from carbon tetrachloride to ethanol has been used to characterize the nature of the absorption of acrolein as the $n-\pi^*$ transition in early experimental studies.[35] Forbes and Shilton[31] have measured acrolein in cyclohexane and ethanol but considered only the $\pi-\pi^*$ transition. Becker *et al.*[32] measured the $n-\pi^*$ transition in solution of 2-methyltetrahydrofuran and found a value of 3.74 eV at room temperature. Again, this value indicates a blueshift with respect to the gas phase value of 3.69–3.71 eV. Otherwise, e.g., taking the 3.75 eV value, one would conclude again for a suspicious redshift.

The absorption spectrum of acrolein in water was first reported by Lüthy[28] with an observed maximum at 3.86 eV. Later, Buswell *et al.*[33] in an interesting study of the chemical stability with time of the acrolein-water solution used short-time results (prior to any possible chemical reaction) and obtained a broad absorption with a maximum that can be inferred between 3.86 and 3.91 eV. An additional report by Mackinney and Temmer[34] suggests the absorption of the $n-\pi^*$ transition of acrolein in water at 3.94 eV. These results would suggest a blueshift of the $n-\pi^*$ transition of acrolein in water, compared to gas phase, lying in the broad range of

TABLE II. Optimized geometrical parameters (Å) of the acrolein-water complexes (Fig. 2) and comparison with the optimized geometry of isolated acrolein. See Fig. 1 for definitions. Counterpoise-corrected binding energies (kcal/mol) are also given.

	ΔE^{CP}	C1–C2	C2–C3	C3–O4	O···H
Isolated	···	1.344	1.477	1.219	···
Complex I	4.7	1.345	1.472	1.224	1.976
Complex II	5.2	1.346	1.473	1.224	1.987

0.15–0.25 eV. Hence we consider henceforth that the experimental value for the shift of the $n-\pi^*$ transition of acrolein in water should be represented by 0.20±0.05 eV. This uncertainty is related only to the different sources of experimental results and not the absorption linewidth. The $n-\pi^*$ transition of acrolein is, in fact, very broad both in gas and in solution adding additional uncertainties. For the sake of comparing theoretical results we use the experimentally inferred shift of the absorption maximum of 0.20±0.05 eV, in going from gas to aqueous environment. As a comparison, the corresponding shift in acetone is 0.21 eV.

We now discuss the recent theoretical results. Ten-no *et al.*[38] using the RISM method obtained the shift of 0.19 eV for the $n-\pi^*$ transition of acrolein in water. Aquilante *et al.*[39] combining discrete/continuum approach in the PCM and a TD-DFT within the PBE functional obtained a shift of 0.20 eV, in very good agreement with the experimental result. When the CASPT2 calculation was employed the shift increased to 0.33 eV, a value that seems to be too large. Adding two explicit water molecules, hydrogen bonded to acrolein, the shift increased further in both TD-DFT and CASPT2. Monte *et al.*[42] using the COSMO continuum solvation model combined with MR-CISD+Q obtained the value of 0.21 eV for the blueshift. This value is in good agreement with the experimental value. For *n*-hexane their calculated blueshift[42] is larger than the experimental result but has the correct sign for the gas phase assignment suggested here. The more recent study of Martin *et al.*[44] using the ASEP from molecular-dynamics simulation obtained the result of 0.26 eV using the gas phase geometry of acrolein. The value of 0.19 eV was obtained, after allowing for solute geometry relaxation.[44]

B. Solute-solvent hydrogen-bond shell

We now consider our results for the contribution of the hydrogen-bond shell to the solvatochromic shift. In this context it is appropriate to first analyze the difference between the minimum-energy structure, obtained using geometry optimization, and the structures that are obtained in the liquid case at room temperature. Hence, we made a geometry optimization of the acrolein-water complex using the second-order MP(2)/6-311++G(d,p) level of calculation. Two nearly equivalent structures are obtained, as shown in Fig. 2. These are similar to the optimized structure of acrolein-water obtained in Ref. 39. The complex II, where the water molecule is closer to the C═C bond, is found to be slightly more stable. The calculated binding energies after correcting for basis set superposition error using the counterpoise procedure[68] are 4.68 and 5.18 kcal/mol for complexes I and II, respectively. Table II gives the most important geometry parameters of the two complexes and compares with the isolated case. As expected there is a lengthening of the C═O distance and this is found to be very similar for the two complexes. The calculated $n-\pi^*$ transition using these two optimized clusters gives a transition shift compared to the isolated molecule of 0.16 and 0.18 eV for the complexes I and II, respectively. It is interesting to note how these are in close numerical agreement with the observed shift of 0.20±0.05 eV. This agreement has been noted before in the case of acetone[19] but cannot be taken in general. A more realistic representation should consider the character of a liquid system. As a liquid cannot be represented by minimum-energy structures it is of interest to compare this picture with that obtained from the MC simulation.

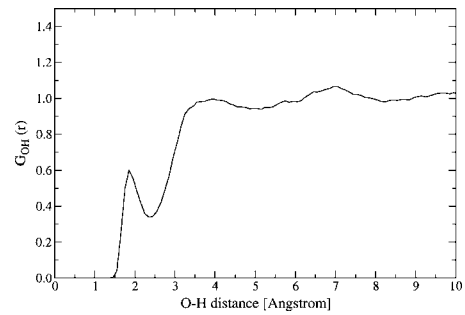

FIG. 3. Radial distribution function between the oxygen atom of acrolein and the hydrogen atom of water.

The identification of hydrogen bonds in liquid structures is made using the geometric-energetic criteria, which have been discussed before.[69–72] The radial distribution function (RDF) between the oxygen atom of acrolein and the hydrogen atom of water is shown in Fig. 3. A clear peak is seen between 1.5 and 2.35 Å that is normally attributed to hydrogen bonding. It cannot be assured, however, that all water molecules that are in this coordination are indeed hydrogen bonded to acrolein. Therefore, we have in addition analyzed the angle and energy distributions and we have then chosen the following criteria for identifying the hydrogen bonds in the liquid: $R_{OH} \leqslant 2.35$ Å, $\Theta_{OOH} \leqslant 41°$, and $E_{bond} \geqslant 2$ kcal/mol. Table III shows the detailed statistics of the hydrogen bonds. Nearly 60% of the configurations present one hydrogen bond, about 20% present two hydrogen bonds, and a very small number of 1% even presented three hydrogen bonds. In the average, the oxygen site of acrolein makes 1.0 hydrogen bond with water and this is also the most probable value obtained from 60% of the configurations. Hence,

TABLE III. Statistics of hydrogen bonds (HBs) between acrolein and water. See text.

Number of HB	% of configurations
0	19
1	60
2	20
3	1
Average	1.02

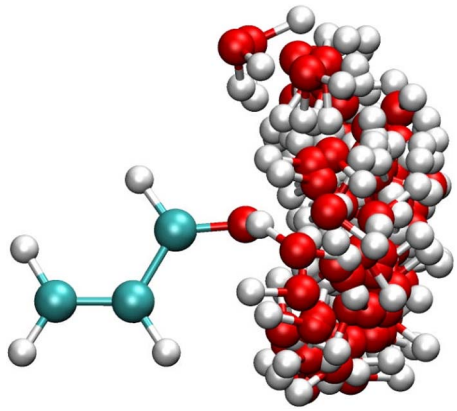

FIG. 4. (Color online) The superposition of the hydrogen-bond structures obtained from the MC simulation of the liquid. Note the configuration space spanned by the water molecules.

the approximation of using one hydrogen bond to represent the hydrogen-bonded acrolein-water complex represents the most probable statistical situation. The statistics are obtained for a fixed C═O distance and might slightly alter if it is allowed to change. As the hydrogen-bond structures are obtained from a classical simulation it is important to discuss the difference regarding a quantum situation. The hydrogen-bond interaction between acrolein and one water molecule is obtained from the MC simulation as -3.40 ± 0.71 kcal/mol. This compares very favorably with the result of -3.41 ± 0.89 kcal/mol obtained using the same configurations in the quantum-mechanical B3LYP/6-31+G(d) model. Hence, it seems that the hydrogen-bond interaction is reasonably well described. Figure 4 shows a superposition of the hydrogen-bonded structures between acrolein and water obtained in the classical liquid simulation. This picture gives a very good illustration of the configuration space that is spanned by the water molecules that are hydrogen bonded to acrolein. As it should be noted these structures obtained in the liquid case are, in fact, distinct from the minimum-energy structures (cf. Fig. 2). They give a distribution of the accessible structures at room temperature. Using the 60 configurations that make one hydrogen bond in the liquid case, we have calculated the solvatochromic shift of the $n-\pi^*$ transition of acrolein. The corresponding result of 0.06 eV is considerably smaller than that obtained using optimized complexes. This result is in agreement with the result of 0.07 eV obtained by Martin *et al.*[44] and gives the same picture that emerged in our previous studies of formaldehyde,[3,4] acetone,[19] formamide,[55] and *N*-methyl acetamide.[56] Table IV summarizes the calculated $n-\pi^*$ transition obtained using the two optimized complexes and compares with the average value obtained for the liquid situation. It is clear that the minimum-energy, geometry-optimized structure cannot represent the distribution of the liquid situation. Similar conclusion has been obtained recently by Mennucci and Martinez[73] in their study of the solvatochromic shift of *N*-methyl acetamide. Dipole moments of optimized complexes are different from the average dipole moment in the liquid case and their use may lead to erroneous conclusions also on solvation problems.[74]

TABLE IV. Excitation energy and solvatochromic shift (eV) obtained from TD-DFT calculations of the hydrogen-bonded acrolein-water systems. Complexes I and II are geometry optimized. See Figs. 2 and 3. Theoretical uncertainty is the standard deviation.

	ΔE ($n-\pi^*$)	Shift
Complex I	3.76	0.16
Complex II	3.78	0.18
Liquid	3.66±0.04	0.06
Expt.[a]	···	0.20±0.05

[a]See Sec. III A.

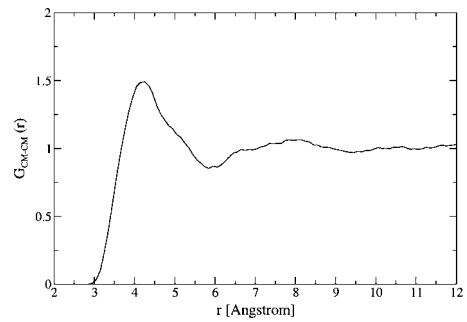

FIG. 5. Radial distribution function between the centers of mass of acrolein and water.

C. All-electron treatment of the first solvation shell

The combined and sequential use of the Monte Carlo simulation and the time-dependent DFT level[75,76] of calculation is an important step toward the first-principle calculation of solvent effects with the explicit consideration of the (electronic structure of the) solvent molecules. Hence, we now discuss the contribution of the first solvation shell to the solvatochromic shift of acrolein in water considering the acrolein and the solvent molecules as an all-electron problem. Figure 5 shows the RDF between the centers of mass of acrolein and water. The first solvation shell is easily discernible. A clear structure is seen to start at 3.0 Å and to end at 5.85 Å with a pronounced maximum at 4.25 Å. Integration of this peak gives the coordination number or the number of water molecules in the first solvation shell as 26 water molecules. A second structure can be seen that has a maximum

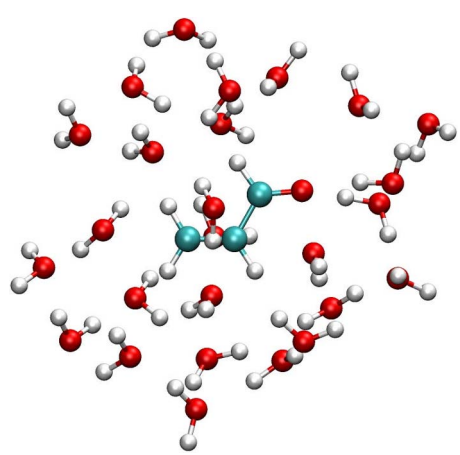

FIG. 6. (Color online) One configuration showing the acrolein molecule surrounded by 26 water molecules, composing the first hydration shell.

TABLE V. Excitation energy (eV) obtained from TD-DFT calculations of the hydrogen bond and different hydration shells. N is the number of water molecules included, R is the radial distance of the shell, and M is the total number of electrons. Theoretical uncertainty is the standard deviation.

	N	R	M	ΔE $(n-\pi^*)$ shift
All-electron				
Hydrogen-bond shell	1	3.35	40	0.06±0.04
First shell	26	5.85	290	0.18±0.11
Simple point charge				
First shell	26	5.85	30	0.19±0.11
Second shell	124	9.65	30	0.20±0.10
Third shell	290	12.35	30	0.20±0.10
Expt.[a]				0.20±0.05

[a]See Sec. III A.

around 8.05 Å ending at 9.65 Å. The integration up to this second minimum gives the total number of water molecules up to this second solvation shell as 124. Including all these molecules explicitly represents a major computational effort in all-electron first-principle calculations. Hence the calculations are made here for the first solvation shell. Figure 6 illustrates one of the structures of this first shell with 1 acrolein and the 26 nearest water molecules.

Calculations are now made on this entire system to obtain the absorption transition corresponding to the $n-\pi^*$ transition of acrolein in water. TD-DFT B3LYP calculation is performed on this system composed of 86 atoms and 290 electrons. One hundred QM calculations of this type are performed to obtain the statistical average, as discussed above. To compromise on the computational effort, the solvent shell is split into two parts. The first part, composed of the nearest 14 water molecules, uses the same 6-31+G(d) basis function as before but for the remaining 12 water molecules we use the smaller 3-21G basis set. Hence, for the water molecules lying beyond the distance of 4.85 Å we use a more modest basis set. In total these TD-DFT quantum-mechanical calculations use 544 contracted Gaussian-type functions. Test calculations indicated that improvements in the basis set change the absorption transition but have much less influence in the spectral shift in solution. The $n-\pi^*$ transition is identified by finding the maximum overlap with the orbitals involved in the $n-\pi^*$ transition of the gas phase. The orbital energy diagram changes with the liquid dynamics so that every configuration must be inspected.

The solvatochromic shift obtained here, using an all-electron approach for the acrolein and the water molecules within the first hydration shell, is 0.18±0.11 eV, in good accord with the experimental value of 0.20±0.05 eV. It is difficult to discern the precise effect of using a smaller basis for the water molecules beyond 4.85 Å. A better basis would probably slightly change the shift. The solute relaxation in water has an increased C═O bond distance and this contributes to a small redshift.[2,19,33,75] In the present case the solute relaxation in the C═O distance contributes to a redshift of 0.03 eV.

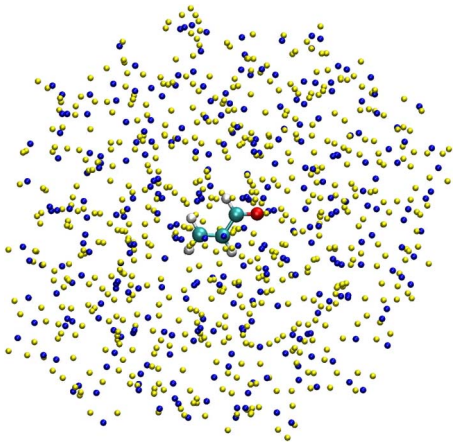

FIG. 7. (Color online) One configuration showing the acrolein molecule surrounded by 290 SPC water molecules.

D. Solvatochromic shift from inner to outer solvation shells

Using the same configurations of the MC simulation we now calculate the solvatochromic shift of the $n-\pi^*$ transition of acrolein in water representing the solvent as simple point charges. The first shell ends at a distance of 5.85 Å from the center of mass of acrolein (Fig. 5) and includes 26 water molecules. The second shell ends at 9.65 Å and includes 124 water molecules. A third solvation is not easily discernible. We have thus used all water molecules up to the cut-off radius of 12.35 Å. This includes as much as 290 water molecules. For the sake of nomenclature we refer to this as the third solvation shell. Again, for each case, 100 TD-DFT B3LYP calculations are performed for each shell. The results are summarized in Table V that also includes, for comparison, the results obtained in Secs. III B and III C; namely, the all-electron calculations of the hydrogen bond and first solvation shells. As it can be seen the first solvation shell is responsible for most of the shift and gives a result that is equivalent to that obtained by the all-electron treatment of Sec. III C. As current DFT methods do not appropriately include dispersion interaction it is not straightforward to conclude for the reason behind the similarity of the results in terms of solvent polarization. It is known that dispersion interaction contributes to a redshift.[77] The contributions of the outer solvation shells are also shown (Table V) and the results converge with the third solvation shell to the value of 0.20±0.10 eV. For illustration Fig. 7 shows one configura-

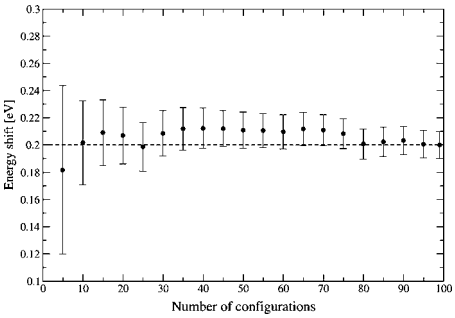

FIG. 8. Statistical convergence of the solvatochromic shift of acrolein in water. Uncertainty is the statistical error.

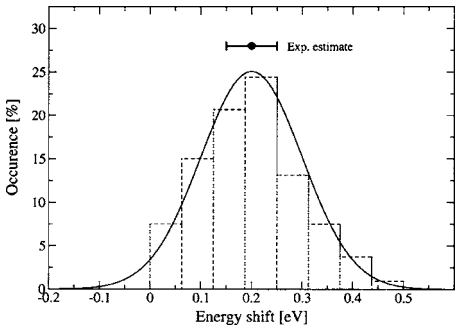

FIG. 9. Histogram of calculated solvatochromic shifts of acrolein in water and comparison with experiment.

tion with the solute and all solvent molecules that compose this third shell.

Having analyzed the convergence of the results with respect to the number of solvent water molecules an important aspect now is the demonstration of the statistical convergence. Figure 8 shows the calculated average value of the solvatochromic shift with increasing number of configurations used. This is shown for the third solvation shell. As it can be seen the average shift converges after around 80 QM calculations. This relatively fast convergence is a consequence of sampling configurations according to statistical correlation as obtained from the autocorrelation function of the energy, discussed before. Here we sampled configurations with less than 10% of statistical correlation.

The statistical distribution of the calculated values is shown in Fig. 9 considering again the case of acrolein and the third solvent shell of water. As one can note there is generally very good agreement between theory and experiment and also among the different theoretical approaches.

IV. SUMMARY AND CONCLUSIONS

A combined Monte Carlo simulation and time-dependent density-functional theory calculations are suggested to study the solvent effects on the $n-\pi^*$ transition of acrolein in water. After generating the liquid structure using Metropolis *NPT* Monte Carlo simulation time-dependent density-functional theory calculations are performed to obtain the excitation energies. This sequential Monte Carlo/quantum mechanics procedure allows an efficient protocol that ensures statistical convergence and the systematic use of different solvation shells. The hydrogen-bond shell is calculated to be responsible for 30% of the total solvatochromic shift, considerably less than the shift obtained for the minimum-energy complexes that ignore the statistical distribution of the liquid situation.

An all-electron calculation of the absorption transition including acrolein and all water molecules within the first hydration shell, composed of 26 water molecules, gives a solvatochromic shift of 0.18±0.11 eV, in good agreement with the experimental shift, inferred to be 0.20±0.05 eV. Systematic calculations are made for the first, second, and third solvation shells using the solvent water molecules as simple point charges. Convergence with respect to the number of solvent molecules is analyzed and the largest case of the third shell, composed of 290 water molecules, gives a size-converged value of 0.20±0.10 eV. It is demonstrated that all average results are statistically converged. Overall, good agreement between theory and experiment is found and also between the previous theoretical approaches.

Finally, perusal of the existing experimental results indicates a variety of data leading to a broad range of acceptable solvatochromic shift. For refinement of the theoretical models, it would be particularly useful to narrow this range, perhaps with reliable single-source experimental results for the solvatochromic shift of acrolein in water.

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