

Probing supercritical water with the $n\text{-}\pi^*$ transition of acetone: A Monte Carlo/quantum mechanics study

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The $n\text{-}\pi^*$ electronic transition of acetone is a convenient and important probe to study supercritical water. The solvatochromic shift of this transition in supercritical water (adopting the experimental condition of $P=340.2$ atm and $T=673$ K) has been studied theoretically using Metropolis *NPT* Monte Carlo (MC) simulation and quantum mechanics (QM) calculations based on INDO/CIS and TDDFT-B3LYP/6-31+G(*d*) methods. MC simulations are used to analyze hydration shells, solute-solvent interaction, and for generating statistically relevant configurations for subsequent QM calculations of the $n\text{-}\pi^*$ transition of acetone. The results show that the average number of hydrogen bonds between acetone and water is essentially 1/3 of that in normal water condition of temperature and pressure. But these hydrogen bonds have an important contribution in the solute stabilization and in the solute-solvent interaction. In addition, they respond for nearly half of the solvatochromic shift. The INDO/CIS calculations explicitly considering all valence electrons of the water molecules, using different solvation shells, up to the third shell (170 water molecules), give a solvatochromic shift of 670 ± 36 cm^{-1} in very good agreement with the experimentally inferred result of $500\text{--}700$ cm^{-1} . It is found that the solvatochromic effect on $n\text{-}\pi^*$ transition of acetone in the supercritical condition is essentially given by the first solvation shell. The time-dependent density-functional theory (TDDFT) calculations are also performed including all solvent molecules up to the third shell, now represented by point charges. This TDDFT-B3LYP/6-31+G(*d*) also gives a good but slightly overestimated result of 825 ± 65 cm^{-1} . For comparison the same study is also made for acetone in water at normal condition. Finally, all average results reported here are statistically converged. © 2007 American Institute of Physics. [DOI: 10.1063/1.2428293]

I. INTRODUCTION

Supercritical (SC) fluids are substances at temperature and pressure conditions above their vapor-liquid critical point. They are important systems of study because of their unusual solvation properties and this leads to increasing theoretical challenges. Fluids at SC conditions may exhibit physical properties that are very different from those under normal conditions of temperature and pressure (NCTP) and can be altered thermodynamically as a result of variations of temperature and/or pressure.¹ These unusual properties have led to a variety of practical applications. For example, in the supercritical region (above 647 K and 220 atm) in which its dielectric constant is considerably decreased, water becomes an excellent solvent for many organic compounds and, as such, it has been used as an effective medium for oxidation of toxic organic compounds.^{2,3} Because of the unique role of water, understanding the properties of supercritical water (SCW) is of particular interest. A direct approach is more difficult and one possibility to obtain information about SCW is to use an organic molecule as a probe. However, the choice has to be made carefully because there are many or-

ganic molecules that are not stable in SCW conditions. Solvatochromic probes are of large use as indicator of solvent polarity⁴ and more recently has also been used in SCW.⁵ Absorption frequency shifts in the ultraviolet-visible region, i.e., solvatochromic shifts, are very sensitive to the intermolecular interaction between a chromophore and the environment. Hence the analysis of the absorption spectrum of a probe molecule gives important clues to the nature of the liquid and this is also the case in the SC conditions of water. It is thus of great interest to analyze solvatochromic shifts in SCW. In this direction, acetone is a simple molecule where the change of the $n\text{-}\pi^*$ transition in normal water (NW) is well characterized and has also been subjected to many theoretical studies. In SCW acetone not only satisfies the crucial condition of being stable but it has also been studied experimentally with a focus on the $n\text{-}\pi^*$ transition.⁵ As in NW the $n\text{-}\pi^*$ transition suffers a blueshift, but this is, of course, reduced in the SCW environment. This present work then addresses to a theoretical description of the $n\text{-}\pi^*$ absorption transition of acetone in SCW. For a better understanding of the solvent effects of SCW it is also important to characterize the hydration structures and solute-solvent interaction. This is then made both in normal and SC conditions so that a direct comparison of these two can be made using the same theoretical methodology. Molecular interactions such as hydrogen bond (HB), which plays an important role on physi-

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cal and chemical properties of water, are dramatically affected in the SC regime of high temperature and high pressure.⁶⁻⁸

In the last decade, there have been many studies on the structural properties of supercritical water⁶⁻¹⁷ motivated by the question of the existence and strength of hydrogen bond in SC conditions.^{18,19} Nevertheless, the presence of the HB in SC conditions has been predicted by different experimental procedures,^{7,9,11,12} although the number of HB, if any, is naturally smaller than those at NCTP. Additionally, these experimental findings have been supported by computer simulation studies using different molecular models for water.^{6,13,15,20} Computer simulation results have shown, for example, that in SC conditions the water properties can be intermediate between liquids and gases and that the tetrahedral ordering of the water molecules present in NCTP is rapidly lost when the temperature is increased or the density is decreased.²⁰ Recently, several studies of solvent effects on organic solutes in SC fluids have been reported.²¹⁻²⁴ In particular, Takebayashi *et al.*²¹ have analyzed structural properties of acetone in SCW with respect to the temperature and water density.

At NCTP, the solvatochromic shift of acetone in aqueous solution has been a subject of intense theoretical studies.²⁵⁻⁴⁴ The $n-\pi^*$ electronic transition involves a reduction of the dipole moment upon excitation and as a consequence the electrostatic solute-solvent interactions lead to major stabilization of the ground state resulting in a larger transition energy, i.e., a blueshift.⁴⁵⁻⁴⁷ This band system is used as a benchmark because there are both theoretical and experimental data available for comparison. Experimental results obtained the solvatochromic shift of the $n-\pi^*$ excitation energy of acetone in water as 1500–1700 cm^{-1} , as compared to gas phase.⁴⁵⁻⁴⁷ In SC water this shift is considerably reduced. Experimental results⁵ for the $n-\pi^*$ electronic transition of acetone in SCW ($P=340.2$ atm and $T=673$ K) obtained the absorption maximum as $\sim 36\,700$ cm^{-1} compared to the same transition in NW seen⁴⁵⁻⁴⁷ at $\sim 37\,700$ cm^{-1} . This corresponds to a redshift close to 1000 cm^{-1} in changing the solvent from normal to SC water. This then indicates a blueshift in SCW compared to isolated acetone of ~ 500 – 700 cm^{-1} . From the theoretical point of view, calculations of solvent effects on the electronic properties of reference molecules have been based on continuum⁴⁸⁻⁵⁴ and discrete^{26,55,56} solvation models. Continuum models may have additional difficulties in handling SCW, because of the remarkable properties, especially the hydrogen bonds between the solute and the solvent and the reduced value of the density and the dielectric constant of water. Explicit solvation models based on a combined quantum mechanics/molecular mechanics (QM/MM) methodology are useful because specific solute-solvent interactions, e.g., hydrogen bond, can be more appropriately treated. A fully QM description of the solute electronic properties in solution solely using *ab initio* methods is computationally very expensive when the solvent molecules are explicitly considered. To circumvent this problem, in QM/MM calculations, in which the solute is treated using an *ab initio* method, the solvent water molecules have been represented by simple point charges.

In this work we use a discrete solvation model, the sequential Monte Carlo/quantum mechanics methodology,^{36,57-60} to study the solvatochromic shift of the $n-\pi^*$ electronic transition of acetone in water in normal and SC conditions. Due to the intrinsic statistical nature of the liquid an appropriate description of solvent effects requires statistical mechanics and some average using a representative number of liquid configurations. Here, isothermal-isobaric Monte Carlo (MC) simulations are performed to generate the structure of the liquid composed by the solute and the solvent molecules in thermodynamic equilibrium. After the MC simulation, the autocorrelation function of the energy is used to sample statistically uncorrelated configurations^{36,57-60} of the acetone and all solvent molecules within a given solvation shell. The use of the autocorrelation function of the energy gives the most efficient sampling procedure and permits to obtain statistically converged results with a relatively small number of configurations.^{36,57-60} These statistically relevant configurations are used in subsequent QM calculations. Explicit solvent molecules are included in a calculation where the wave function is antisymmetric with respect to the entire solute-solvent system. In the largest case a total of 170 water molecules are explicitly considered. We have then used the semiempirical INDO/CIS method with spectroscopic parameterization⁶¹ to systematically calculate the solvatochromic shifts related to the hydrogen bond shell and the additional first, second, and third solvation shells. An important aspect in this methodology is that the solute and the solvent molecules are treated as an all-valence-electron problem. This method has been employed successfully in the determination of spectroscopic shifts of organic solute in solvents.^{36,57-60,62-66} Additionally, we have also used the time-dependent density-functional theory^{67,68} (TDDFT) method including all solvent molecules up to the third solvation shell but considering the solvent water molecules only as simple point charges. The TDDFT has seen increased popularity to calculate electronic transition energies.⁶⁹⁻⁷¹ To the best of our knowledge, this is the first theoretical study of the $n-\pi^*$ transition of acetone in SCW. For comparison, we have also considered acetone in water under NCTP.

II. CALCULATION DETAILS

The experimental study⁵ of acetone in SCW was made with a fixed temperature and pressure. Hence all MC simulations are performed in the isothermic-isobaric, NPT ensemble, where the number of molecules N , the pressure P , and the temperature T are fixed. These MC simulations were performed for 1 acetone molecule plus 703 water molecules. The SC condition was simulated at the thermodynamic condition of the experimental UV-visible absorption spectroscopic study:⁵ $P=340.2$ atm and $T=673$ K. For simplification, in the following when referring to SCW we are considering this specific thermodynamic condition. The molecules interact by the standard Lennard-Jones plus Coulomb potential with three parameters for each interacting site i (ϵ_i , σ_i , and q_i) and geometrical rules of combination $\epsilon_{ij}=(\epsilon_i\epsilon_j)^{1/2}$ and $\sigma_{ij}=(\sigma_i\sigma_j)^{1/2}$. There are several possibilities for the classical potential of water. However, it has been shown that the

extended simple point charge⁷² (SPC/E) model for water leads to good agreement for the critical point of water.^{73,74} Hence this is the potential used here for water. For the acetone we have used the classical parameters ϵ_i and σ_i of the OPLS model and the atomic charges obtained by electrostatic potential fit⁷⁵ (CHELPG) at HF/6-311++G(*d,p*) level of calculation. The geometry and parameters for acetone are the same as that used before.³⁶ For comparison, we also consider the case of acetone in NW ($P=1$ atm and $T=298$ K). In fact, in a previous study³⁶ we have considered acetone in NW, using the same protocol but the SPC (Ref. 76) potential for water and the *NVT* ensemble for the simulation. However, because of the experimental conditions (*NPT*) and, especially the choice of the water potential SPC/E used in the SC case, we find of interest to reconsider the case of acetone in NW with the very same protocol of the SCW. Hence all simulations are repeated for acetone in NW using the *NPT* ensemble and the SPC/E potential. We will refer to the previous study³⁶ as the *NVT(SPC)* model. Of course, we do not expect any sizable changes but it would facilitate a direct comparison of the normal and SC cases avoiding possible calculation artifacts.

All MC simulations were performed with the DICE program⁷⁷ using standard procedures⁷⁸ for the Metropolis sampling technique. We have used the periodic boundary conditions in a cubic box⁷⁸ where each molecule interacts with all other molecules within a center of mass separation that is smaller than the cutoff radius $r_c=18.0$ Å [13.7 Å], in the SCW [NW] condition. Long-range corrections for the Lennard-Jones and Coulomb potentials, for separations larger than r_c , were calculated using the pair radial distribution function and the reaction field method with dipole interactions, respectively. The thermalization stage of the MC simulation used 4.2×10^7 MC steps. After this thermalization, 14.1×10^7 MC steps were performed as the averaging stage of MC simulation. The calculated average density is $\rho=0.46 \pm 0.03$ g/cm³ [$\rho=1.02 \pm 0.01$ g/cm³], for the SCW [NW] condition. The uncertainties are standard deviations of the average value. This large reduction in the density is one of the characteristics of SC water.

As successive configurations generated in the MC are statistically highly correlated, similar to previous works,^{36,57-60} we use the autocorrelation function of the energy to calculate the statistical correlation interval and sample statistically uncorrelated configurations. For the SCW [NW] simulation, configurations separated by 14.1×10^5 [23.9×10^5] MC steps have less than 12% of statistical correlation and were considered as uncorrelated configurations. We have thus sampled 100 uncorrelated configurations to be used in quantum mechanical supermolecular calculations. All average results presented here are verified to be statistically converged similar to previous studies.^{36,57-60} The QM calculations of the $n-\pi^*$ transitions were performed using two theoretical models, the INDO/CIS and TDDFT methods as implemented in the ZINDO (Ref. 61) and the GAUSSIAN-03 (Ref. 79) programs, respectively. TDDFT transition energies were calculated using the B3LYP hybrid functional^{80,81} with the 6-31+G(*d*) basis set. The B3LYP/6-31+G(*d*) model has been recently used to compute the tran-

sition energies of acrolein in water and the solvatochromic shift computed is in very good agreement with the inferred experimental shift.⁸² These two theoretical models are applied in two different conditions. The semiempirical INDO/CIS uses a 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 1384-valence-electron problem, where the wave function delocalizes over the solute-solvent system including exchange and part of the dispersion interaction.⁸³ In the TDDFT all solvent molecules are treated as simple point charges (of the SPC/E model), thus neglecting both exchange and dispersion. Although the INDO/CIS and TDDFT use parameterizations oriented for different purposes, for a consistent result we would expect the TDDFT, using only point charges for the solvent, to give a larger shift. This is because it is known that the mutual solute-solvent polarization, the dispersion interaction, contributes to the solvatochromism with a redshift.⁸⁴

III. RESULTS AND DISCUSSION

A. Structural aspects and solute-solvent hydrogen bonds

The configuration of water molecules around acetone can be obtained analyzing the radial distribution functions, $G(r)$, between atom pairs of the solute-solvent molecules. Figure 1 shows the radial distribution functions between the oxygen of acetone and the oxygen of water, $G_{O-O}(r)$, and between the oxygen of acetone and the hydrogen of water, $G_{O-H}(r)$, in the supercritical condition with $P=340.2$ atm and $T=673$ K ($\rho=0.46 \pm 0.03$ g/cm³) and in the normal condition of $P=1.0$ atm and $T=298$ K ($\rho=1.02 \pm 0.01$ g/cm³). Comparison between the $G(r)$ of these two thermodynamic states shows significant structural changes of the hydration shell of acetone characterized mainly by substantial changes in their peak heights with slight shift in the peak positions. A similar feature has been previously observed by Takebayashi *et al.*²¹ for acetone in aqueous solution at 673 K as a function of water density. Under SCW [NW] condition, the first peaks in $G_{O-O}(r)$ and in $G_{O-H}(r)$ are, respectively, centered in 2.85 Å [2.75 Å] and 1.85 Å [1.75 Å], starting at 2.45 Å [2.45 Å] and 1.45 Å [1.45 Å] and ending at 3.45 Å [3.15 Å] and 2.55 Å [2.45 Å]. The spherical integration of the first peak in $G_{O-O}(r)$ gives the coordination number, i.e., the average number of nearest water molecules around the oxygen atom of acetone. In the NCTP the coordination number is 2.08 water molecules. This coordination number is sensitively affected by the increase of temperature and pressure. Taking the same distance obtained for NW for the SCW case, there are 1.03 water molecules around acetone, corresponding to a marked decrease of $\sim 50\%$ when compared with the normal condition. These results are consistent with the decrease of the water density in going from NCTP to SC condition. For comparison, the water density at SC condition is reduced by 55%. Equivalent results are obtained for the coordination number and hydrogen bonds, where for each thermodynamic state we used the same criteria. As it cannot be assured that all water molecules within this first coordination shell of the $G_{O-O}(r)$ are indeed hydrogen bonded to acetone

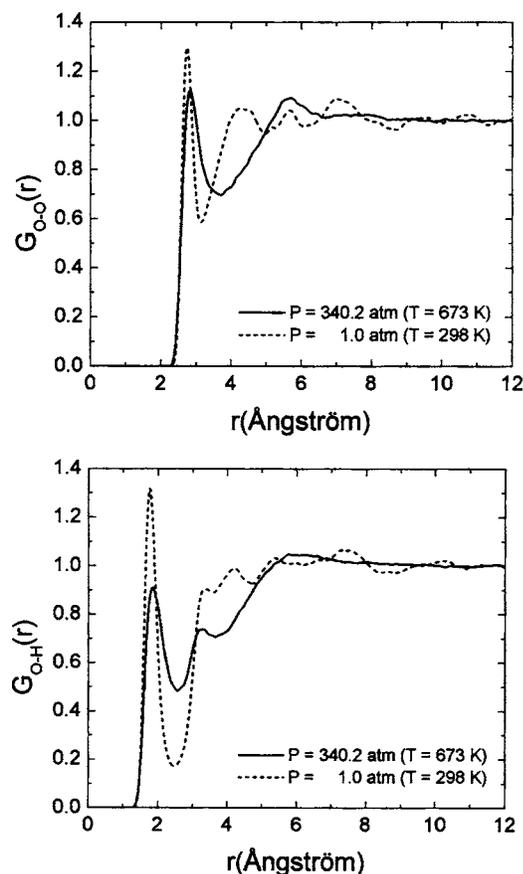


FIG. 1. Radial distribution function between the oxygen atom of acetone and the oxygen atom of water (top) and between the oxygen atom of acetone and the hydrogen atom of water (bottom).

additional criteria are used to identify acetone-water HBs. We use here, in addition, the geometric and energetic criteria to select the hydrogen bonded molecules.^{13,36,85–90} Previous studies have also emphasized that a quantitative analysis of the average number of HB in computer simulation of liquids requires the consideration of their directional and energetic aspects.^{85–90} The energetic criterion of a hydrogen bond is obtained analyzing the distribution of pairwise interaction energy.^{57,85,86} Kalinichev and Bass¹³ have analyzed hydrogen bond in supercritical water from a systematic study of distribution of pairwise energy with increasing temperature at a constant pressure. Their results showed that for most SC states the peak, which describes the HB, becomes so broad that the definition of the energetic criterion is not clear-cut. They have then considered as the energetic threshold the same value defined at ambient conditions independent of the thermodynamic state.

The pairwise energy distribution in the NCTP condition gives for the energetic threshold of hydrogen bond the same value of -2.7 kcal/mol predicted in the previous *NVT(SPC)* simulation.³⁶ As noted by Kalinichev and Bass¹³ and corroborated here, for the SCW state an energetic threshold is not well defined, therefore the NW value was adopted here. To compare the effects of the specific thermodynamic conditions on the average number of HB we have selected the hydrogen bonded molecular pairs considering the same geometric-energetic criteria at SC and normal conditions.

TABLE I. Statistics of the hydrogen bonds formed between acetone and water at supercritical and normal conditions. Also shown are the contributions of the hydrogen bonds to the total solvatochromic shift. The calculated INDO/CIS blueshifts were obtained as average over 600 uncorrelated configurations. Uncertainty is the statistical error.

| Number of HB | $P=1.0$ atm ($T=298$ K) | | $P=340.2$ atm ($T=673$ K) | |
|--------------|--------------------------|----------------------------|----------------------------|----------------------------|
| | Occurrence (%) | Shift (cm^{-1}) | Occurrence (%) | Shift (cm^{-1}) |
| 0 | 1.4 | 0 | 42.0 | 0 |
| 1 | 40.3 | 620 ± 15 | 49.2 | 526 ± 16 |
| 2 | 55.2 | 911 ± 17 | 8.5 | 821 ± 51 |
| 3 | 3.1 | 1048 ± 69 | 0.3 | 1287 ± 244 |
| Average | 1.60 | 785 ± 18 | 0.67 | 332 ± 13 |

Thus, the hydrogen bonds are defined when the separation $R_{O-O} \leq 3.2$ Å (first minimum of the radial distribution function), the angle $\angle O \dots O-H \leq 30^\circ$, and when the interaction energy is at least -2.7 kcal/mol. The statistics of HB for the SCW and NW are given in Table I. From 600 uncorrelated MC configurations the results for the SC state show that 252 (42%) configurations make no hydrogen bonds, 295 (49.2%) form one hydrogen bond, and 51 (8.5%) and 2 (0.3%) configurations have two and three hydrogen bonds, respectively. Hence the most probable value indicates one HB between SCW and acetone, but with an average number of hydrogen bonds of 0.67. This represents a marked reduction of 58% when compared with the average result of 1.60, obtained for the NW. In this condition, a similar value (1.7 hydrogen bonds) has been reported in the *NVT(SPC)* previous study.³⁶ In fact, this is in agreement with the expectation that in SCW, with the present thermodynamic condition, the number of HB with water would be reduced to one-third compared to NW.⁵ At SC condition, our result shows a good overall agreement with that presented by Takebayashi *et al.*²¹ in a systematic study of the average number of HB as a function of temperature and water density.

B. The $n-\pi^*$ transition of acetone in supercritical water

The contribution of the hydrogen bonded configurations to the solvatochromic shift of the $n-\pi^*$ transition of acetone in water is analyzed first. Table I gives the statistics of hydrogen bonds formed between the solute acetone and the solvent water in the two thermodynamic conditions considered. It also lists the calculated shifts for this variety, as obtained at the INDO/CIS level. In the SC condition the total contribution of the HB to the $n-\pi^*$ shift is obtained as 332 ± 13 cm^{-1} . Under NCTP, the corresponding shift is calculated to be 785 ± 18 cm^{-1} , this being 14% larger than that obtained in the previous *NVT(SPC)* work³⁶ as a consequence of the different potential models used for water. From these later results, the shift obtained in the SCW case is decreased to nearly half (58%) compared to NW, which is again consistent with the decrease of the water density. It is interesting to note that in the SC condition, considering the statistical aspect, most of the contribution of the HB to the solvatochromic

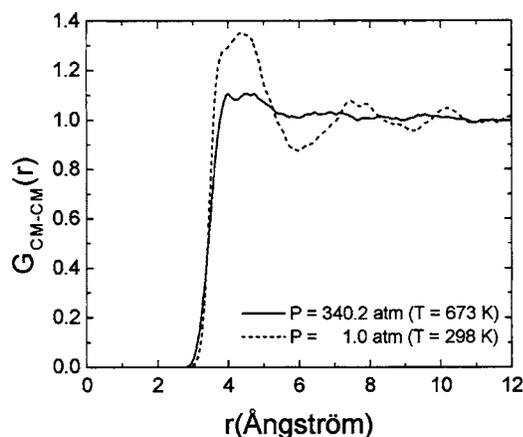


FIG. 2. Radial distribution function between the center of masses of acetone and water.

mic shift is obtained from the most probable value of only one HB configuration. In fact, weighted by the occurrence (49.2%) the shift due to the most probable number of HB is 260 cm^{-1} , accounting for nearly 80% of the total HB contribution. Comparison of the contribution of the HB shell to the solvatochromic shifts obtained for SCW and NW shows that it is responsible, respectively, for 50% and 56% of the total solvatochromic shift. This represents some slight changes regarding our previous study³⁶ for the NCTP of water. We find in the *NVT(SPC)* model³⁶ that the HB shell is responsible for a contribution of 690 cm^{-1} . Using the SPC/E potential we now find the value of 785 cm^{-1} .

To quantify separately the contribution of the different solvation shells we have next analyzed the radial distribution function between the center of mass of acetone and water. Figure 2 shows the $G_{\text{c.m.-c.m.}}(r)$ in the SC and NCTP conditions. In the NCTP three solvation shells of water can be discerned. The first shell starts at 3.0 \AA and ends at 6.1 \AA , whereas the second and the third shells end at 9.1 and 10.8 \AA , respectively. The spherical integration of $G_{\text{c.m.-c.m.}}(r)$ within these values gives 30, 104, and 174 water molecules around the acetone as the number of solvent water molecules up to the first, second, and third solvation shells, respectively. These are the same numbers obtained in the previous *NVT(SPC)* study.³⁶ Again, for the acetone in SCW the structures of the solvation shells are not well defined. Using the same limits for NCTP as above, the corresponding results for the integration of $G_{\text{c.m.-c.m.}}(r)$ for the SC condition are 14, 50, and 81, respectively. This reduced number of solvent molecules in the SCW compared to the NW case reflects the ratio between the densities of water in the two conditions. To have a direct comparison we used in the SC condition the same number of solvent molecules as in the NCTP case. Table II presents the calculated solvatochromic shifts obtained using the different solvation shells, both in the SC and the NCTP, together with the experimental results. These averages are obtained from 100 QM calculations, using statistically uncorrelated configurations, as discussed above. In the SC condition, the INDO/CIS results reveal that the second and third solvation shells give essentially the same results, within the statistical error, suggesting that in this case the first solvation shell is responsible for most of the solvato-

TABLE II. Solvatochromic shift (cm^{-1}) of acetone in water, both in supercritical and normal conditions, using different solvation shells. Calculated INDO/CIS and TDDFT-B3LYP/6-31+G(*d*) blueshift values were obtained as average over 100 uncorrelated configurations. Uncertainty is the statistical error. Standard deviation is ten times larger.

| Method/ solvation shell | Number of solvent molecules | $P=1.0\text{ atm}$ ($T=298\text{ K}$) | $P=340.2\text{ atm}$ ($T=673\text{ K}$) |
|-------------------------------|--------------------------------|--|--|
| INDO/CIS | | | |
| First | 30 | 1196 ± 40 | 627 ± 36 |
| Second | 100 | 1356 ± 37 | 660 ± 36 |
| Third | 170 | 1390 ± 34 | 670 ± 36 |
| TDDFT-B3LYP/631+G(<i>d</i>) | | | |
| Third | 170 | 1640 ± 70 | 825 ± 65 |
| Expt. | | $1500\text{--}1700^{\text{a}}$ | $\sim 500\text{--}700^{\text{b}}$ |

^aReferences 45–47.

^bReference 5.

chromic shift. For the largest case, the third solvation shell, the INDO/CIS result gives a blueshift of $670\pm 36\text{ cm}^{-1}$ for the SCW and $1390\pm 34\text{ cm}^{-1}$ for NW conditions. The latter result is essentially the same (1296 cm^{-1}) but slightly increased by 94 cm^{-1} compared to that previously reported³⁵ in the *NVT(SPC)* model. For the third solvation shell, the corresponding values obtained using the TDDFT-B3LYP/6-31+G(*d*) level of calculation are 825 ± 65 and $1640\pm 70\text{ cm}^{-1}$. At SC condition, the prediction of the solvatochromic shift based on INDO/CIS calculation ($670\pm 36\text{ cm}^{-1}$) is in very good concordance with available experimental result of $500\text{--}700\text{ cm}^{-1}$ but the TDDFT model ($825\pm 65\text{ cm}^{-1}$) gives a slightly overestimated result. Differently, at NCTP, the prediction based on INDO/CIS calculation gives a slightly underestimated result ($1390\pm 34\text{ cm}^{-1}$), while the prediction based on TDDFT calculation ($1640\pm 70\text{ cm}^{-1}$) is in very good agreement with the experimental result of $1500\text{--}1700\text{ cm}^{-1}$. Additionally, this TDDFT shift compares well with the reported calculations based on Car-Parrinello molecular dynamics (CPMD) in combination with TDDFT. Using restricted open-shell Kohn-Sham DFT calculations in CPMD Röhrig *et al.*⁴⁰ obtained the shift as 2016 cm^{-1} . Within the plane-wave pseudopotential framework, Bernasconi *et al.*⁴¹ obtained a CPMD-TDDFT shift of 1532 cm^{-1} . More recently, Crescenzi *et al.*⁴² calculated a CPMD-TDDFT shift of 1694 cm^{-1} , using the 6-311++G(*2d*,*2p*) basis set rather than plane waves. Aidas *et al.*⁴³ presented an account of several previous studies of the solvatochromic shift of the $n\text{-}\pi^*$ transition of acetone in NW. For the SCW, however, we were not able to find any previous theoretical result.

The distinction between the calculated solvatochromic shifts obtained by INDO/CIS and TDDFT-B3LYP/6-31+G(*d*) is now briefly discussed. In the INDO/CIS the wave function delocalizes over the solute and the solvent, whereas in the TDDFT case the solvent is treated as simple point charges. In the present MC simulation the atomic charges of the solute were obtained from a HF/6-311++G(*d*,*p*) calculation thus including an *ad hoc* implicit polarization.⁹¹ As it is typical the dipole moment of acetone used in this case (3.59 D) is $\sim 20\%$ larger than the gas phase result of

TABLE III. Calculated in-water dipole moments of acetone (Debye) in two thermodynamic conditions. Uncertainty is the statistical error. Standard deviation is ten times larger.

| | $P=1.0$ atm ($T=298$ K) | $P=340.2$ atm ($T=673$ K) |
|--------------------|----------------------------------|----------------------------|
| B3LYP/6-31+G(d) | 4.65 ± 0.04 | 4.02 ± 0.04 |
| Previous estimates | $4.44^a, 4.52^b, 4.80^c, 4.90^d$ | ... |

^aReference 43.

^bReference 32.

^cReference 93.

^dReference 40.

2.93 D.⁹² The B3LYP/6-31+G(d) model gives, for comparison, a gas phase dipole moment of 3.24 D. An appropriate treatment of the solute polarization including the coupling with the solvent^{32,92} leading to an in-solution charge distribution is expected to increase the dipole moment.⁹³ For SCW the in-water increase of the dipole moment is expected to be smaller than for NW due to the low density of water in this case. Table III shows the calculated in-water dipole moments of acetone. For NW the present theoretical result is in due agreement with previous and recent theoretical estimates^{32,40,43,93} and suggests that the increase in the dipole moment of acetone in changing from the gas phase to the SCW environment (0.78 D) is $\sim 55\%$ of the increase in the NW environment (1.41 D). Again, these results follow the relative water density in the SC and NCTP conditions.

Another important issue is the inclusion of dispersion interaction that is responsible for a redshift contribution.⁸⁴ This is essential for quantitative estimates of spectroscopic shifts. It has been shown that a representative part of the dispersion contribution to solvatochromic shifts can be obtained when the system is treated as an all-electron problem,⁸³ i.e., electrons are appropriately described by an antisymmetric wave function delocalized over the solute and the solvent, even when the transition energies are calculated using a singly excited configuration interaction. Despite its good agreement with experiment, current DFT methods do not appropriately include dispersion interaction and it should be expected that quantum mechanics calculations, using only point charge to represent the solvent, overestimate the total blueshift. In the supercritical condition the reduced density of SCW makes the interaction less significant and TDDFT should only slightly overestimate the solvent shift in comparison with experimental data. Overall, both theoretical models give good results in the SCW and NW conditions.

In Figs. 3 and 4 are displayed the calculated absolute transition energy including all solvent molecules up to the third solvation shell, both at SC and NCTP. For reference, the experimental^{5,45-47} $n-\pi^*$ transitions of acetone in NW and SCW are, respectively, $\sim 37\,700$ and $\sim 36\,700$ cm^{-1} . The energies were individually computed for 100 uncorrelated configurations and are shown in Figs. 3 and 4. For all configurations considered there is no overlap between the numerical values of the energies calculated with different methods and the TDDFT transition energies are higher than the corresponding INDO/CIS counterparts. Transition energy distributions show the typical spectral broadening caused by the thermal motion of the solvent molecules around the solute.

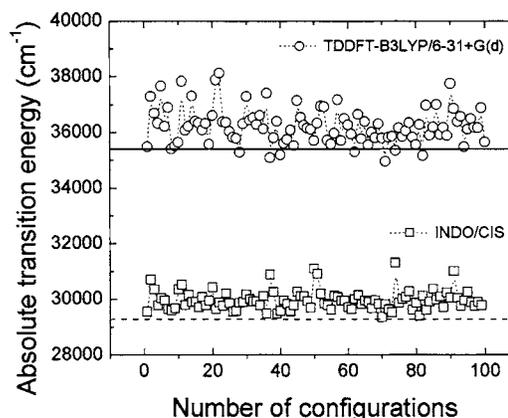


FIG. 3. Distribution of calculated $n-\pi^*$ transition energy of acetone in water at supercritical condition. The solid and dashed lines correspond to the results in gas phase. TDDFT (INDO/CIS) gives a value of $35\,404$ cm^{-1} ($29\,284$ cm^{-1}).

Although both methods predict good results for the solvatochromic shift, the average value of the TDDFT absolute transition energy is in better concordance with experimental results than the INDO/CIS. Also, there is a small redshift for some individual configurations in TDDFT results at SC conditions.

C. Comparative analysis of the normal and supercritical water

The solvatochromic shifts calculated in the previous section are a direct consequence of the interaction of the solute with the solvent environment. Hence, for complementarity a brief description of the solute-solvent interaction energy in the two cases considered, the NW and SCW, is presented. Table IV gives the results obtained from the classical simulation and separates the interaction in the short- and long-range solute-solvent interactions. First, the focus is on the short-range effect as described by the hydrogen bond solvation shells. Interestingly, one notes that the average hydrogen bond interaction is similar in the two cases leading to a value of ~ 5.6 kcal/mol per hydrogen bond in the NW and SCW. However, as acetone makes on average 1.60 HB in the

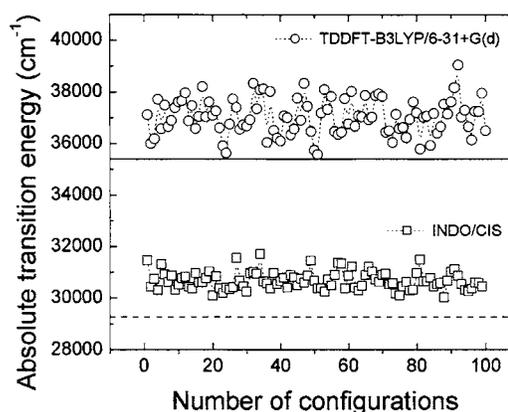


FIG. 4. Distribution of calculated $n-\pi^*$ transition energies of acetone in water at ambient condition. The solid and dashed lines correspond to the results in gas phase. TDDFT (INDO/CIS) gives a value of $35\,404$ cm^{-1} ($29\,284$ cm^{-1}).

TABLE IV. MC simulation results for hydrogen bond and solute-solvent interaction energies E_{SX} (kcal/mol).

| Interaction energy | $P=1.0$ atm ($T=298$ K) | $P=340.2$ atm ($T=673$ K) |
|--|--------------------------|----------------------------|
| E_{SX}^{HB} per HB | -5.60 ± 1.23 | -5.64 ± 1.12 |
| E_{SX}^{HB} | -8.96 ± 1.23 | -3.78 ± 1.12 |
| $E_{SX}^{\text{1st shell}^{\text{a}}}$ | -19.93 ± 1.51 | -9.73 ± 1.12 |
| $E_{SX}^{\text{bulk}^{\text{b}}}$ | -24.13 ± 3.39 | -11.39 ± 4.14 |

^aThe first solvation shell has 14 [30] water molecules at supercritical [normal] condition (within a spherical radius of 6.1 Å [6.1 Å]).

^bThe total solvation shell has 382 [362] water molecules at supercritical [normal] condition (within a spherical radius of 18.2 Å [13.7 Å]).

NCTP, compared to an average of 0.67 in the SC situation, this leads to a total solute-solvent HB interaction of -8.96 ± 1.23 and -3.78 ± 1.12 kcal/mol in the NCTP and SC conditions. This indicates that the stability of acetone in SCW is reduced compared to the normal situation with a sizable contribution from the hydrogen bond solvation shells. In this case, a reduction of ~ 5.2 kcal/mol. Looking also for the long-range contribution one can note that this difference in interaction increases to ~ 10.2 kcal/mol when considering the first solvation shell including all solvent molecules with $R \leq 6.1$ Å. Further extension to the bulk leads to the final differential interaction energy of 13.7 kcal/mol, for the contribution of the solute-solvent energy to the differential enthalpy. Most of this difference could perhaps be traced to the decreasing water density making solute-solvent interaction more attractive in the NW than in SCW. In fact, the reduction in the density closely follows the solute-solvent interaction energy (45%). But it should be admitted that these results for the solute-solvent were obtained from the classical MC simulation and represent an important but only a first estimate of the interaction energies. A quantitative estimate requires a more rigorous quantum treatment with inclusion of electron correlation effects.⁹⁴

D. Analysis of statistical convergence

Finally, a discussion of the statistical convergence of the calculated results is performed. The efficient sampling of configurations^{36,57-60} from the statistical simulation for the

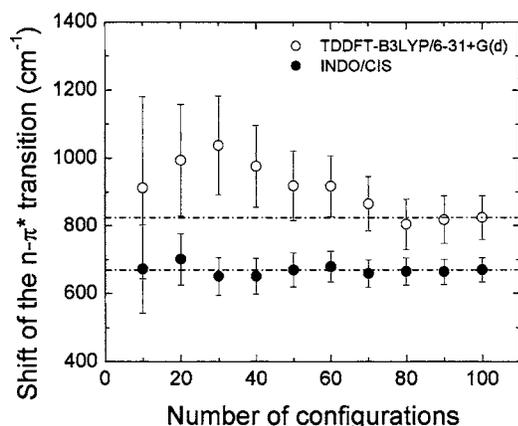


FIG. 5. Statistical convergence of the solvatochromic shift of acetone in water in the supercritical condition. Uncertainty is the statistical error. Standard deviation is ten times larger.

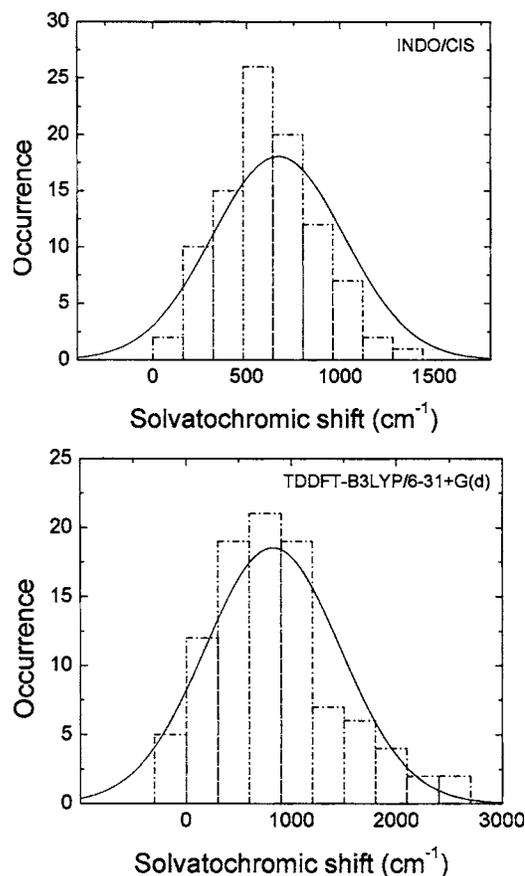


FIG. 6. Histogram of the $n-\pi^*$ electronic transition shifts calculated using the INDO/CIS (top) and the TDDFT (bottom) methods.

subsequent QM calculations plays a crucial role for the average value presenting a fast and systematic convergence pattern independent of the set of configurations selected.⁹⁵ As in previous works,^{36,57-60} the interval of statistical correlation, obtained from the autocorrelation function of the energy, has been used to select the statistically uncorrelated configurations. As Fig. 5 shows the calculated average solvatochromic shift of the $n-\pi^*$ transition of acetone in SCW converges after around 50 configurations in the INDO/CIS case and after around 70 configurations in the TDDFT case. Figure 6 shows the distribution of calculated results for the INDO/CIS and TDDFT solvatochromic shifts of the $n-\pi^*$ transition of acetone in SCW.

IV. CONCLUSIONS

The spectroscopic analysis of a reference molecule in supercritical solvents is a useful probe both for time-dependent⁹⁶ and stationary solute-solvent interactions.⁵ For SCW an important probe has been the solvation shift of the $n-\pi^*$ transition of acetone.⁵ This solvatochromic shift of acetone in SCW has been studied theoretically using Metropolis *NPT* Monte Carlo simulation and quantum mechanics calculations based on INDO/CIS and TDDFT-B3LYP/6-31+G(*d*) methods. MC simulations are used to analyze hydration shells, solute-solvent interaction, and for generating statistically relevant configurations for subsequent QM calculations of the $n-\pi^*$ transition of acetone. The MC

results show how the increase of temperature and the decrease of water density from NCTP to SC condition affect the hydration distribution of the solvent molecules around the solute. As a consequence there is a substantial reduction of the average number of solute-solvent hydrogen bonds, of the order of 58%, when compared with the result obtained for the NCTP condition. This is consistent with the corresponding decrease in the water density. In the supercritical condition used here the contribution of the hydrogen bond shell to the solvatochromic shift is obtained as $332 \pm 13 \text{ cm}^{-1}$ representing a contribution of nearly 50% of the total calculated shift, obtained here as $670 \pm 36 \text{ cm}^{-1}$,¹ in good concordance with the available experimental results ($500\text{--}700 \text{ cm}^{-1}$). The calculated INDO/CIS solvatochromic shifts present a rapid and systematic convergence with respect to the number of solvation shells. In fact, the first solvation shell nearly responds for the entire effect. Whereas the INDO/CIS calculations explicitly consider the electronic structure of the solvent water molecules, with a wave function that is antisymmetric over the entire solute-solvent region, the TDDFT calculations consider the solvent molecules as simple point charges. The TDDFT-B3LYP/6-31+G(*d*) calculations also give a good but slightly overestimated blue-shift of $825 \pm 65 \text{ cm}^{-1}$ for the $n\text{-}\pi^*$ transition of acetone in supercritical water.

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- ¹ S. C. Tucker, Chem. Rev. (Washington, D.C.) **99**, 391 (1999).
- ² P. E. Savage, Chem. Rev. (Washington, D.C.) **99**, 603 (1999).
- ³ M. Watanabe, T. Sato, H. Inomata, R. L. Smith, Jr., K. Arai, A. Kruse, and E. Dinjus, Chem. Rev. (Washington, D.C.) **104**, 5803 (2004).
- ⁴ C. Reichardt, *Solvent Effects in Organic Chemistry* (Verlag Chemie, Weinheim, New York, 1979).
- ⁵ G. E. Bennett and K. P. Johnston, J. Phys. Chem. **98**, 441 (1994).
- ⁶ A. A. Chialvo and P. T. Cummings, J. Chem. Phys. **101**, 4466 (1994).
- ⁷ Y. E. Gorbaty and A. G. Kalinichev, J. Phys. Chem. **99**, 5336 (1995).
- ⁸ T. I. Mizan, P. E. Savage, and R. M. Ziff, J. Phys. Chem. **100**, 403 (1996).
- ⁹ N. Matubayasi, C. Wakai, and M. Nakahara, Phys. Rev. Lett. **78**, 2573 (1997).
- ¹⁰ N. Matubayasi, C. Wakai, and M. Nakahara, J. Chem. Phys. **107**, 9133 (1997).
- ¹¹ M. M. Hoffmann and M. S. Conradi, J. Am. Chem. Soc. **119**, 3811 (1997).
- ¹² M.-C. Bellissent-Funel, T. Tassaing, H. Zhao, D. Beysens, B. Guillot, and Y. Guissani, J. Chem. Phys. **107**, 2942 (1997).
- ¹³ A. G. Kalinichev and J. D. Bass, Chem. Phys. Lett. **231**, 301 (1994).
- ¹⁴ A. G. Kalinichev and J. D. Bass, J. Phys. Chem. A **101**, 9720 (1997).
- ¹⁵ A. A. Chialvo, P. T. Cummings, J. M. Simonson, R. E. Mesmer, and H. D. Cochran, Ind. Eng. Chem. Res. **37**, 3021 (1998).
- ¹⁶ J. Martí, J. Chem. Phys. **110**, 6876 (1999).
- ¹⁷ N. Matubayasi, C. Wakai, and M. Nakahara, J. Chem. Phys. **110**, 8000 (1999).
- ¹⁸ P. Postorino, R. H. Tromp, M. A. Ricci, A. K. Soper, and G. W. Neilson, Nature (London) **366**, 668 (1993).
- ¹⁹ R. H. Tromp, P. Postorino, G. W. Neilson, M. A. Ricci, and A. K. Soper, J. Chem. Phys. **101**, 6210 (1994).
- ²⁰ R. D. Mountain, J. Chem. Phys. **90**, 1866 (1989).
- ²¹ Y. Takebayashi, S. Yoda, T. Sugeta, K. Otake, T. Sako, and M. Nakahara, J. Chem. Phys. **120**, 6100 (2004).
- ²² C. Nieto-Draghi, J. B. Àvalos, O. Contreras, P. Ungerer, and J. Ridard, J. Chem. Phys. **121**, 10566 (2004).
- ²³ I. M. Svishchev and A. Y. Plugatyr, J. Phys. Chem. B **109**, 4123 (2005).
- ²⁴ A. Plugatyr, I. Nahtigal, and I. M. Svishchev, J. Chem. Phys. **124**, 024507 (2006).
- ²⁵ T. Fox and N. Rösch, Chem. Phys. Lett. **191**, 33 (1992).
- ²⁶ J. Gao, J. Am. Chem. Soc. **116**, 9324 (1994).
- ²⁷ S. Ten-no, F. Hirata, and S. Kato, J. Chem. Phys. **100**, 7443 (1994).
- ²⁸ M. A. Thompson, J. Phys. Chem. **100**, 14492 (1996).
- ²⁹ F. C. Grozema and P. Th. Van Duijnen, J. Phys. Chem. A **102**, 7984 (1998).
- ³⁰ K. Coutinho, N. Saavedra, and S. Canuto, J. Mol. Struct.: THEOCHEM **466**, 69 (1999).
- ³¹ M. Cossi and V. Barone, J. Chem. Phys. **112**, 2427 (2000).
- ³² M. E. Martín, M. L. Sánchez, F. J. Olivares del Valle, and M. A. Aguilar, J. Chem. Phys. **113**, 6308 (2000).
- ³³ A. H. de Vries and P. Th. van Duijnen, Int. J. Quantum Chem. **57**, 1067 (1996).
- ³⁴ L. Serrano-Andrés, M. P. Fülscher, and G. Karlström, Int. J. Quantum Chem. **65**, 167 (1997).
- ³⁵ M. Sulpizi, U. F. Röhrig, J. Hutter, and U. Rothlisberger, Int. J. Quantum Chem. **101**, 671 (2005).
- ³⁶ K. Coutinho and S. Canuto, J. Mol. Struct.: THEOCHEM **632**, 235 (2003).
- ³⁷ Y. J. Shiu, M. Hayashi, A. M. Mebel, Y. T. Chen, and S. H. Lin, J. Chem. Phys. **115**, 4080 (2001).
- ³⁸ D. W. Liao, A. M. Mebel, M. Hayashi, Y. J. Shiu, Y. T. Chen, and S. H. Lin, J. Chem. Phys. **111**, 205 (1999).
- ³⁹ K. Naka, A. Morita, and S. Kato, J. Chem. Phys. **110**, 3484 (1999).
- ⁴⁰ U. F. Röhrig, I. Frank, J. Hutter, A. Laio, J. Vandevondele, and U. Rothlisberger, ChemPhysChem **4**, 1177 (2003).
- ⁴¹ L. Bernasconi, M. Sprik, and J. Hutter, J. Chem. Phys. **119**, 12417 (2003).
- ⁴² O. Crescenzi, M. Pavone, F. Angelis, and V. Barone, J. Phys. Chem. B **109**, 445 (2005).
- ⁴³ K. Aidas, J. Kongsted, A. Osted, K. V. Mikkelsen, and O. Christiansen, J. Phys. Chem. A **109**, 8001 (2005).
- ⁴⁴ C. Angeli, S. Borini, L. Ferrighi, and R. Cimraglia, J. Chem. Phys. **122**, 114304 (2005).
- ⁴⁵ N. S. Bayliss and E. G. McRae, J. Phys. Chem. **58**, 1006 (1954).
- ⁴⁶ W. P. Hayes and C. J. Timmons, Spectrochim. Acta **21**, 529 (1965).
- ⁴⁷ N. S. Bayliss and G. Wills-Johnson, Spectrochim. Acta, Part A **24**, 551 (1968).
- ⁴⁸ O. Tapia and O. Goscinski, Mol. Phys. **29**, 1653 (1975).
- ⁴⁹ J. L. Rivail and D. Rinaldi, Chem. Phys. **18**, 233 (1976).
- ⁵⁰ S. Miertus, E. Scrocco, and J. Tomasi, J. Chem. Phys. **55**, 117 (1981).
- ⁵¹ M. M. Karelson and M. C. Zerner, J. Phys. Chem. **96**, 6949 (1992).
- ⁵² J. Tomasi and M. Persico, Chem. Rev. (Washington, D.C.) **94**, 2027 (1994).
- ⁵³ J. Tomasi, Theor. Chem. Acc. **112**, 184 (2004).
- ⁵⁴ J. Tomasi, B. Mennucci, and R. Cammi, Chem. Rev. (Washington, D.C.) **105**, 2999 (2005).
- ⁵⁵ J. T. Blair, K. Krogh-Jespersen, and R. M. Levy, J. Am. Chem. Soc. **111**, 6948 (1989).
- ⁵⁶ J. Zeng, N. S. Hush, and J. R. Reimers, J. Chem. Phys. **99**, 1496 (1993).
- ⁵⁷ S. Canuto and K. Coutinho, Int. J. Quantum Chem. **77**, 192 (2000).
- ⁵⁸ K. Coutinho and S. Canuto, J. Chem. Phys. **113**, 9132 (2000).
- ⁵⁹ K. Coutinho, S. Canuto, and M. C. Zerner, J. Chem. Phys. **112**, 9874 (2000).
- ⁶⁰ S. Canuto, K. Coutinho, and D. Trzresniak, Adv. Quantum Chem. **41**, 161 (2003).
- ⁶¹ J. Ridley and M. C. Zerner, Theor. Chim. Acta **32**, 111 (1973).
- ⁶² A. Broo, G. Pearl, and M. C. Zerner, J. Phys. Chem. A **101**, 2478 (1997).
- ⁶³ S. Canuto, D. Trzresniak, and K. Coutinho, *Current Developments in Atomic, Molecular and Chemical Physics with Applications*, edited by M. Manmohan (Kluwer Plenum, Dordrecht, 2002), p. 127.
- ⁶⁴ K. J. de Almeida, K. Coutinho, W. B. de Almeida, W. R. Rocha, and S. Canuto, Phys. Chem. Chem. Phys. **3**, 1583 (2001).
- ⁶⁵ W. R. Rocha, K. J. de Almeida, K. Coutinho, and S. Canuto, Chem. Phys. Lett. **345**, 171 (2001).
- ⁶⁶ W. R. Rocha, V. M. Martins, K. Coutinho, and S. Canuto, Theor. Chem. Acc. **108**, 31 (2002).
- ⁶⁷ E. K. U. Gross and W. Kohn, Adv. Quantum Chem. **21**, 255 (1990).
- ⁶⁸ M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem.

- Phys. **108**, 4439 (1998).
- ⁶⁹N. A. Besley, M. T. Oakley, A. J. Cowan, and J. D. Hirst, *J. Am. Chem. Soc.* **126**, 13502 (2004).
- ⁷⁰V. Ludwig, K. Coutinho, and S. Canuto, *Phys. Rev. B* **70**, 214110 (2004).
- ⁷¹G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi, and V. Barone, *J. Chem. Phys.* **124**, 094107 (2006).
- ⁷²H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).
- ⁷³Y. Guissani and B. Guillot, *J. Chem. Phys.* **98**, 8221 (1993).
- ⁷⁴B. Guillot and Y. Guissani, *J. Chem. Phys.* **99**, 8075 (1993).
- ⁷⁵C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.* **11**, 361 (1990).
- ⁷⁶H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans, in *Intermolecular Forces*, edited by B. Pullman (Reidel, Dordrecht, 1981), p. 331.
- ⁷⁷K. Coutinho and S. Canuto, DICE: A Monte Carlo program for molecular liquid simulation, v. 2.8, University of São Paulo, São Paulo, 2003.
- ⁷⁸M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- ⁷⁹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.
- ⁸⁰C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ⁸¹A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ⁸²H. C. Georg, K. Coutinho, and S. Canuto, *J. Chem. Phys.* **123**, 124307 (2005).
- ⁸³S. Canuto, K. Coutinho, and M. C. Zerner, *J. Chem. Phys.* **112**, 7293 (2000).
- ⁸⁴W. Liptay, in *Modern Quantum Chemistry*, edited by O. Sinanoglu (Academic, NY, 1966), Part II, pp. 173–198.
- ⁸⁵T. Malaspina, K. Coutinho, and S. Canuto, *J. Chem. Phys.* **117**, 1692 (2002).
- ⁸⁶W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
- ⁸⁷A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **55**, 3336 (1971).
- ⁸⁸M. Mezei and D. L. Beveridge, *J. Chem. Phys.* **74**, 622 (1981).
- ⁸⁹F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **57**, 1281 (1972).
- ⁹⁰D. C. Rapaport, *Mol. Phys.* **50**, 1151 (1983).
- ⁹¹N. A. McDonald, H. A. Carlson, and W. L. Jorgensen, *J. Phys. Org. Chem.* **10**, 563 (1997).
- ⁹²R. Peter and H. Dreizler, *Z. Naturforsch. A* **20**, 301 (1965).
- ⁹³H. C. Georg, K. Coutinho, and S. Canuto, *Chem. Phys. Lett.* **429**, 119 (2006).
- ⁹⁴T. L. Fonseca, K. Coutinho, and S. Canuto (unpublished).
- ⁹⁵K. Coutinho, M. J. Oliveira, and S. Canuto, *Int. J. Quantum Chem.* **66**, 249 (1998).
- ⁹⁶F. Ingrosso and B. M. Ladanyi, *J. Phys. Chem. B* **110**, 10120 (2006).