

Solvent effects in emission spectroscopy: A Monte Carlo quantum mechanics study of the $n \leftarrow \pi^*$ shift of formaldehyde in water

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(Received 22 June 2000; accepted 1 September 2000)

Supermolecular calculations that treat both the solute and the solvent quantum-mechanically are performed to analyze the solvatochromism of the first emission transition of formaldehyde in water. The liquid structures are generated by NVT Metropolis Monte Carlo simulation assuming a fully relaxed excited state. The autocorrelation function is calculated to obtain an efficient ensemble average. A detailed analysis of the hydrogen bonds and their contribution to the solvation shift is presented. On average, 0.7 hydrogen bonds are formed in the excited state, about three times less than in the ground state. Quantum-mechanical calculations using the intermediate neglect of differential overlap with singly excited configuration interaction (INDO/CIS) are then performed in the supermolecular clusters corresponding to the hydrogen bond shell and the first, second, and third solvation shells. The third solvation shell extends up to 10 Å from the center of mass of formaldehyde, showing the very long-range effects on the solvation shift of this polar molecule. The largest cluster includes one formaldehyde and 142 water molecules. INDO/CIS calculations are performed on this cluster with a properly antisymmetric reference ground state wave function involving all valence electrons. The estimated limit value for the solvatochromic shift of the $n \leftarrow \pi^*$ emission transition of fully relaxed formaldehyde in water, compared to the gas phase, is $\approx 1650 \text{ cm}^{-1}$. The total Stokes shift of formaldehyde in water is calculated as $\approx 550 \text{ cm}^{-1}$. © 2000 American Institute of Physics. [S0021-9606(00)51544-X]

I. INTRODUCTION

The study of solvent effects in molecular absorption spectroscopy has attracted considerable attention in recent years.¹⁻⁴ For one reason this is related to the simple fact that most experiments are done in solution. For the other, an UV-Vis absorption spectrum is very sensitive to solvent effects and it can thus be used judiciously in modeling intermolecular interaction. Early studies have used classical analysis to relate spectral shifts to the index of refraction and dielectric constant. More recently, the original ideas of Onsager⁵ and Kirkwood⁶ of enclosing the solute in a cavity and interacting with the solvent as a polarizable dielectric continuum has been extended.⁷⁻¹⁶ This self-consistent-reaction field has been used successfully in the study of solvatochromic shifts of polar solutes. An approach that is gaining wide acceptance is the use of a combined quantum mechanics/molecular mechanics method.¹⁷⁻²³ Another somewhat similar approach that has seen increased acceptability is the combined use of quantum mechanics with some sort of computer simulation of liquids.²⁴⁻²⁹ As a liquid has not one but several structures at a given temperature, computer simulation can generate the molecular structures of the liquid for subsequent quantum mechanical calculations.^{25,28,29} This leads naturally to the so-called supermolecular model, where

the solvent molecules around the solute are explicitly included in the quantum mechanical treatment. Several of these calculations are necessary to obtain the ensemble average that indeed characterizes the statistical nature of the liquid. This is an approach that is conceptually sound, in the sense that the solvent molecules are explicitly considered (thus taking into account the microscopic structure of the solvent) and a proper statistical ensemble is used. It includes naturally the solvent contribution to the line-shape broadening of the transition. However, it is clear that such an approach is very demanding computationally. Several quantum mechanical calculations are necessary in the supermolecules composed by the solute and several solvent molecules. One possible simplification has recently been suggested³⁰ that averages the electrostatic potential thus reducing the number of quantum mechanical calculations. Another procedure recently proposed by us is to use the autocorrelation function of the energy of the configuration obtained in the Monte Carlo simulation.³¹ As the Metropolis Monte Carlo is a Markovian³² process, the total number of quantum mechanical calculations can be dramatically reduced if statistically correlated structures are avoided.^{28,29,31} Therefore we make a detailed analysis of the autocorrelation function of the energy. This is the analog of the time-correlation function in molecular dynamics and allows the determination of the correlation-time analog in a Monte Carlo simulation. To reduce further the calculations, the size of the supermolecules to be used can be systematically analyzed using the pairwise

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radial distribution function. For nonpolar molecules the long range effects are not very important. Indeed, it has been noted previously²⁸ that the calculation of the solvatochromic shifts of benzene in different solvents, both polar and nonpolar, it suffices to consider only the first solvation shell. For benzene in water this amounts to a supermolecule composed of one benzene and 18 solvent water molecules.²⁸ Although this might be a reasonably large supermolecule for *ab initio* calculations it is well within the reach of semiempirical technology. For polar solutes, such as formaldehyde, this extends to a considerable larger distance. For instance, the solvation shift of the first absorption transition of formaldehyde in water requires the inclusion of at least the third solvation shell, extending the effects up to a center-of-mass distance of more than 8 Å away from formaldehyde.²⁹

The solvation of molecular excited electronic states has been studied by several groups,^{33–38} but the specific consideration of fluorescence shift is more sparse.^{33,34,38,39} A fundamental question has to do with the relaxation time of the excited state in the solvent. For the absorption, it is generally assumed that the transition is vertical, obeying the Franck–Condon principle. The ground state is in equilibrium with the solvent and no relaxation time is involved for the ground state. Upon vertical excitation the excited state has no time to equilibrate with the solvent, and both the geometry and electronic structures are unrelaxed. For the emission, instead, the transition initiates in the excited state. If the relaxation time is smaller than the lifetime of the excited state, the system may relax before emitting. If however, the relaxation is slow, the emission will occur in a nonrelaxed state. In fact, the fluorescence spectrum may be a superposition of instantaneous transitions depending on the solvent relaxation.⁴⁰ Formaldehyde is known to be planar in the ground state and out of plane in the $n-\pi^*$ excited state. The relaxation of the excited state has been studied by Levy *et al.*³³ using molecular dynamics simulation. They used the equilibrium geometry of the excited state and found out that the solvent relaxation is very fast. After 100 fs the first solvation shell was fully relaxed. After an additional 500 fs, the relaxation was nearly complete, extending to a region of 7.5 Å. In this paper we study the solvation shift of the $n-\pi^*$ state of formaldehyde in the emission. For this we use our combined Monte Carlo–quantum mechanics approach that was very successful in the absorption study.^{28,29} We assume that the excited state is fully relaxed and perform a Monte Carlo simulation of formaldehyde in the $n-\pi^*$ excited state in water. Both the geometry and the classical potential of formaldehyde corresponds to the $n-\pi^*$ excited state. The situation is illustrated in Fig. 1. The solvatochromic shift in the absorption is given by the difference in the transition energies in the gas phase and in solution; i.e., $\Delta\nu^a = \nu_1 - \nu_0$. In the fully relaxed excited state the solvatochromic shift in the emission is given by $\Delta\nu^e = \nu_3 - \nu_2$.

It is a well-known fact that upon absorption the $n-\pi^*$ transition leads to a decrease of the dipole moment and the solvatochromic shift is to the blue side of the spectrum, increasing the transition energy. In the relaxed out-of-plane geometry the excited state also has a dipole moment that is smaller than the dipole moment of the ground state in the

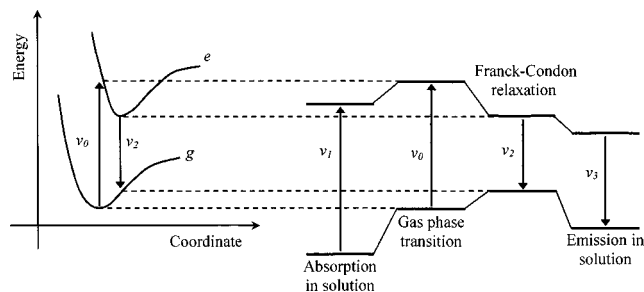


FIG. 1. An illustration of the solvatochromic shift in the absorption ($\Delta\nu^a = \nu_1 - \nu_0$) and the fully relaxed emission ($\Delta\nu^e = \nu_3 - \nu_2$).

geometry of the excited state. In fact, the dipole moment of the ground state is found to be larger in the geometry of the excited state than in its own equilibrium geometry.^{34,38} Thus, in a similar reasoning, the solvation shift in the fluorescence should also increase the transition energy. In neither case, absorption or emission, the solvation shift is determined experimentally. Formaldehyde in water forms oligomers and the experimental shift is not well determined. However, several theoretical investigations were performed in the absorption shift of formaldehyde in water.^{18–25,29,30,41–51} Direct calculations and a comparison with the acetone case, where experimental results are known, indicate that the solvation shift for the absorption of formaldehyde in water is close to 2500 cm^{-1} .

There are several reasons to pursue a theoretical investigation of the fluorescence shift of formaldehyde in water. First, formaldehyde is a prototype of the carbonyl bond that is so important and related to acetaldehyde, acetone, etc. Second, there are indeed very few studies of the solvation effects of excited states as related to electronic spectroscopy. Finally, the solvation shift in fluorescence spectroscopy is a challenging problem where we can test the supermolecular approach involving simulation methods and quantum mechanical calculations with explicit consideration of the solvent.

We perform a systematic study of the $n-\pi^*$ blue shift of formaldehyde in water, where the solvent molecules are explicitly included in the quantum mechanical calculations. This includes the electrostatic interaction between the solute and the solvent and the corresponding induced polarizations both in the solute and in the solvent. We use Monte Carlo simulations to generate structures of the liquid and supermolecular quantum mechanical calculations, with all-valence electrons, to obtain the separate contributions of the different solvation shells to the spectroscopic shift. Starting from the hydrogen bonded water, we analyze the contribution of the first, second, and third solvation shells. The largest calculation involves the ensemble average of many quantum mechanical results obtained with the formaldehyde solute surrounded by as much as 142 water solvent molecules. This latter starts with a self-consistent-field intermediate neglect of differential overlap (INDO) calculation with a properly antisymmetric wave function with 1148 valence electrons. The transition energies are obtained next using a singly excited configuration interaction (CIS). The final result is estimated after extrapolation to the bulk limit. Thus, we not only

investigate how the solvation shells influence the shift but we also extrapolate our results to obtain our best estimate of the solvatochromic shift of the $n \leftarrow \pi^*$ emission transition of formaldehyde in water, compared to the gas phase. The INDO/CIS method has proven to be a very successful theory for spectroscopy and spectroscopic shifts.^{27–29,52} It can be remarked that the use of *ab initio* theories is prohibitive, not only because of the computational effort involved in these large supermolecules, but also because as we analyze the solvation effects with the size of the supermolecules; the use of size-extensive methods is imperative. CIS is not only a simple theoretical model but it also includes several advantages. It is size extensive and, as most excited states are dominated by single excitations, it is a favorite model for semiempirical theories.⁵² This approach has been successfully used to obtain solvatochromic shifts in an absorption UV-Vis spectrum in both polar and nonpolar solutes and solvents.^{28,29,53}

II. METHODS OF CALCULATION

A. Monte Carlo simulation

The Monte Carlo (MC) simulation is performed using standard procedures for the Metropolis sampling technique⁵⁴ in the canonical ensemble, where the number of molecules N , the volume V , and the temperature T are fixed. As usual, periodic boundary conditions in a cubic box³² are used. In our simulation, we use one formaldehyde molecule plus 343 molecules of water. The volume of the cubic box is determined by the experimental density of the water, $\rho = 0.9966 \text{ g/cm}^3$ at $T = 25^\circ \text{C}$. The molecules interact by the Lennard-Jones plus Coulomb potential with three parameters for each atom i (ϵ_i , σ_i , and q_i):

$$U_{ab} = \sum_i^a \sum_j^b 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j e^2}{r_{ij}},$$

where $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$. For the water molecules, we used the SPC potential developed by van Gunsteren *et al.*⁵⁵ For the excited state of formaldehyde, we used the geometry and classical parameters of Levy *et al.*³³ In the calculation of the pairwise energy, each molecule interacts with all other molecules within a center of mass separation that is smaller than the cutoff radius $r_c = 10.9 \text{ \AA}$. For separations larger than r_c , we use the long range correction of the potential energy.³² The initial configuration is generated randomly, considering the position and the orientation of each molecule. A new configuration is generated after 344 MC steps, i.e., after selecting all molecules sequentially and trying to translate it in all the Cartesian directions and also rotate it around a randomly chosen axis. The maximum allowed displacement of the molecules is auto-adjusted after 17 200 MC steps to give an acceptance rate of new configurations around 50%. The maximum rotation angle is fixed during the simulation in $\delta\theta = \pm 15^\circ$. The full simulation⁵⁶ involves a thermalization stage of about 5.16×10^6 MC steps followed by an averaging stage of 27.52×10^6 MC steps. This is a large simulation by all standards. In terms of computational effort this would correspond in molecular dynamics to a simulation of 400 ps if a time interval of 5 fs is used.

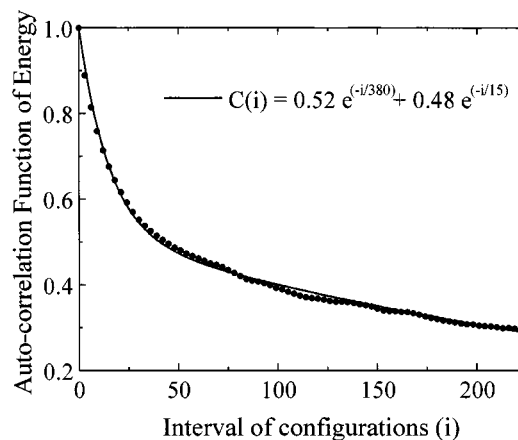


FIG. 2. Calculated autocorrelation function of the energy for the excited state of formaldehyde in water and the best exponential fit.

During the averaging stage some thermodynamical properties, as the internal energy and the heat capacity at constant volume, are calculated, and they are in agreement with that calculated for liquid water. The radial distribution function is also calculated during the averaging stage in the simulation. After completing the cycle over all 344 molecules, a configuration is generated and separated. Thus, the total number of configurations generated by the MC simulation is 80 000.

As quantum mechanical calculations will be performed on the configurations generated by the MC simulation, it is important to optimize the statistics. Structures that are statistically very correlated will not give important additional information. Therefore we calculate the autocorrelation function of the energy.^{28,29,31,57} For Markovian processes this follows an exponentially decaying function,^{31,58,59}

$$C(i) = \sum_j^n c_j e^{-i/\tau_j},$$

where i is the interval between configurations of the Monte Carlo simulation. The correlation step is

$$\tau = \int_0^\infty C(i) di.$$

Figure 2 shows the calculated autocorrelation function of the energy of formaldehyde in the first excited electronic state in water. From this and the equation above it can be seen that the correlation step is ~ 200 . Therefore, in calculating the averages we decided to select structures in an interval of 800 steps. As the total length of the configurations generated is 80 000 (see above), the averages are taken over 100 configurations, with a correlation of only 6%. These 100 configurations will be subjected to quantum mechanical supermolecular calculations.

B. Quantum mechanical calculations

The transition energies are calculated using the ZINDO program⁶⁰ within the INDO/CIS model, in the supermolecules generated by the Monte Carlo simulations. The quantum mechanical calculations are then performed for the supermolecular cluster composed of one formaldehyde and all

solvent molecules within a particular solvation shell. Each water molecule includes eight valence electrons, and the Hartree–Fock wave function is antisymmetric with respect to the entire solute–solvent system. Next, CIS calculations are performed to obtain the transition energies. In the Metropolis sampling technique⁵⁴ the configurations are generated with the appropriate Boltzmann weights. Therefore, the solvatochromic shift can be obtained as a simple average over a chain of L energy values:

$$\langle \Delta E \rangle = \frac{1}{L} \sum_n^L \Delta E_n,$$

where ΔE is the difference between the calculated energy transition of formaldehyde in water, using the Monte Carlo supermolecular structures, and isolated formaldehyde. For the first, second, or third hydration shells the value of L is 100, obtained previously from the autocorrelation function. To check on the stability of the results, calculations were performed also with $L=60$, corresponding to 48 000 MC configurations. $L=100$ corresponds to 80 000 MC configurations. For the hydrogen bonds a specific statistics will be performed, where we analyze the number of hydrogen bonds in each configuration, using both the geometric and energetic criteria.^{29,61,62} In total, nearly 500 quantum mechanical calculations are performed.

III. RESULTS AND DISCUSSIONS

A. Hydrogen bond

We first analyze the influence of the hydrogen bonds that are formed between the solute formaldehyde and the solvent water. This influence is usually studied using a cluster model, with an optimized geometric structure obtained for the hydrogen bonded solute–solvent.^{45,46,50} This more exactly corresponds to the situation found in jet-cooling experiments and very low temperature. It may thus not correspond to the real disordered situation of the liquid in room temperature. We should expect that in a simple dimer composed of one solute and one solvent molecule, the hydrogen bond is stronger than in the situation found in a real liquid, where the water is not only bound to the solute but also to the other surrounding water molecules. In the dimer solute–solvent the influence of the hydrogen bond is exaggerated.⁶³ The precise definition of a hydrogen bond is not easy in the real liquid case and definite criterion are necessary to proceed to an identification in the configurations generated by the Monte Carlo simulation. The most common, but not necessarily the best, way is by the use of the pairwise radial distribution function that defines also the solvation shells.³² Figure 3 shows the radial distribution function between the oxygen of formaldehyde and the hydrogen of water, $G_{O-H}(r)$. As it can be seen, there is a hydrogen bond peak that starts at around 1.8 Å and has a minimum at 2.25 Å. Spherical integration of this peak gives a coordination number of 0.6; i.e., an average of 0.6 hydrogen-bonded water molecules. As expected, this number is smaller than that obtained for the ground state.²⁹ We call this the HB solvation, to separate it from the other solvation shells. If a different geometry of formaldehyde is used, this number changes only

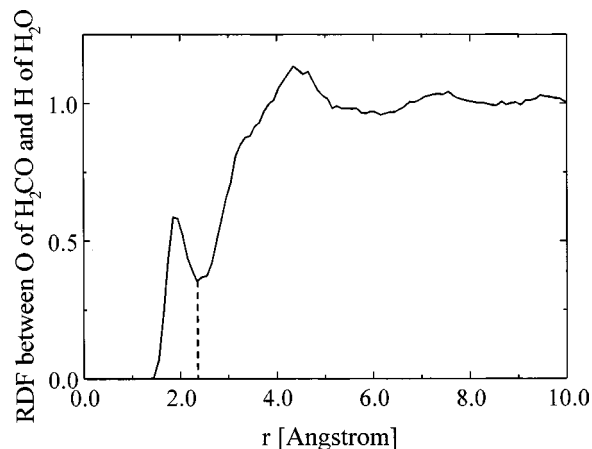


FIG. 3. The pairwise radial distribution function between the oxygen atom of formaldehyde and the hydrogen atom of water.

slightly. For an excited state geometry obtained with an *ab initio* optimization at the CIS/6-31++G(*d,p*) level and an equivalent Monte Carlo simulation, we obtain 0.52 hydrogen bonds from the integration of the $G_{O-H}(r)$ radial distribution function.

Hydrogen bonds are better obtained using geometric and energetic criteria, as suggested by Jorgensen.^{29,61,62} Our criteria are that a hydrogen bond is obtained whenever formaldehyde and any nearby water molecule satisfy $R_{O-O} \leq 3.35$ Å, $\alpha_{O-OH} \leq 34^\circ$, and $E \leq -2.0$ kcal/mol. Thus the distance between the oxygen atoms of formaldehyde and water is less than 3.36 Å, the angle formed between the oxygen atom of formaldehyde and the OH bond of water is less than 35° , and the binding energy is at least 2.0 kcal/mol. This turns out to be a very good way of obtaining hydrogen bonds in the liquid.^{29,61,62} With this, in the 100 MC configurations we find 73 hydrogen bonds formed between water and excited-state formaldehyde. This gives an average of 0.73 bonds, slightly larger than the result obtained upon integration of the first peak of the $G_{O-H}(r)$ radial distribution function. In comparison with the ground state of formaldehyde²⁰ we find an average of 1.9 hydrogen bonds using the same geometric and energetic criterium. Thus in the excited state the average number of hydrogen bonds is considerably reduced, by a factor of nearly 3. However, small, there is still some hydrogen bonds formed in the $n-\pi^*$ excited state of formaldehyde. The influence of the hydrogen bond shell can now be analyzed in a very detailed form. Table I gives the statistics obtained for the hydrogen bonds formed. We find that 30% of the configurations make no hydrogen bonds, but 58% of the configurations have one hydrogen bond, 11% forms two hydrogen bonds, and 1% form three hydrogen bonds. In the subsequent quantum mechanical calculations these structures can be analyzed separately (Table I). As shown, the total blue shift contribution of the HB solvation is 189 ± 46 cm⁻¹. But those structures with one and two hydrogen bonds contribute, respectively, to 270 and 273 cm⁻¹.

B. Solvation shells

We can now analyze the outer shells. Figure 4 shows the radial distribution function between the center of mass of

TABLE I. Statistics of the hydrogen bonds formed between formaldehyde in the first excited state and water and their contribution to the blue shift of the emission transition. Geometric and energetic criteria are used to sort out a hydrogen bond (Refs. 29, 61, and 62). The first set uses an average of over 60 configurations; the second set uses an average over 100 configurations obtained from the Monte Carlo. See the text.

Number of HB	Set 1		Set 2	
	Occurrence	Shift (cm^{-1})	Occurrence	Shift (cm^{-1})
0	31.7%	0	30.0%	0
1	61.7%	248 ± 32	58.0%	270 ± 34
2	5.0%	305 ± 67	11.0%	273 ± 46
3	1.6%	234	1.0%	234
Total	100% (50)	172 ± 67	100% (73)	189 ± 46

formaldehyde and water. Three solvation shells are discerned. The first shell starts at 2.8 Å, ending at 5.15 Å. The second ends at 7.15 Å and a third solvation extends at around 10.0 Å, close to the cutoff radius. Integration of the radial distribution function gives a total of 19 and 50 and 142 water molecules from the solute center of mass up to the limit of these three shells, respectively. Again, we can obtain separately the contribution of each solvation shell. This is of importance because it exposes the long-range effects of a polar molecule. Table II thus gives the calculated solvatochromic shift and summarizes the results. The largest calculation is composed of the formaldehyde and 142 water molecules and gives a calculated blue shift of $1451 \pm 63 \text{ cm}^{-1}$. For comparison, Table II also shows the results obtained for a simulation that is 40% shorter. As it can be seen that results are stable with respect to the average and the two simulations give essentially the same result, within the theoretical error bar (the statistical deviation). It is remarkable that molecules within a distance of 10 Å can still influence the solvation shift. A similar observation^{29,34} has been made in the case of the solvation shift in the absorption $n-\pi^*$ transition of formaldehyde in water. This shows that the treatment of polar molecules require the consideration of long-range effects extending beyond the third solvation shell, in a distance that is very large. Thus, the results obtained so far can serve as a lower bound to our best estimate. The analysis of the variation of the shift with the solvation shells (Fig. 5) shows that

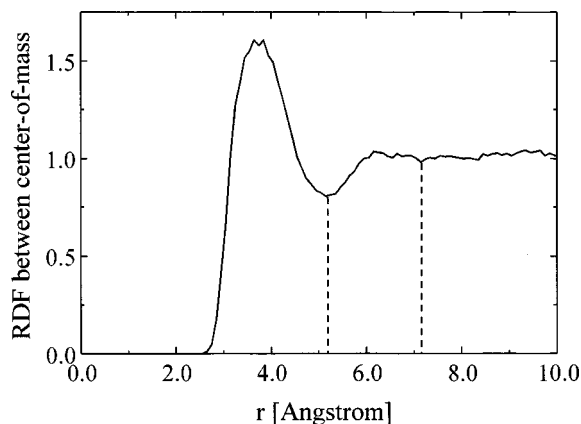


FIG. 4. The pairwise radial distribution function between the center of mass of formaldehyde and water.

TABLE II. The variation of the calculated (INDO/CIS) shift (in cm^{-1}) of the $n-\pi^*$ emission transition of formaldehyde in water with the solvation shells. N is the number of water molecules included. M is the total number of valence electrons. L is the number of MC structures used for an ensemble average.

Solvation shell	N	M	L	Distance (Å)	Blue shift
First	19	164	60	5.15	822 ± 70
	19	164	100	5.15	854 ± 51
Second	50	412	60	7.15	1167 ± 73
	50	412	100	7.15	1213 ± 59
Third	142	1148	60	10.0	1427 ± 72
	142	1148	100	10.0	1451 ± 63
Limit	Bulk				~ 1650

indeed this is not a limit value with respect to the number of solvent molecules included. It is important for the future consideration of solvent effects to realize that polar molecules, especially in protic solvents, extends the microscopic behavior of the solvent distribution to considerably larger distances. It has been noted before that a small number of solvent molecules cannot adequately describe the solvatochromic shift of the absorption spectrum of formaldehyde in water.^{24,29,41,43-45,51} It is interesting to mention that the dipole moment of the formaldehyde-water hydrogen bonded complex increases by 60%–70%, as compared with formaldehyde alone.⁶⁴ This local increase in the dipole moment leads to a larger effect on the solvent distribution of the outer solvation shells.⁶⁴ The results of Table II are summarized in Fig. 5 and suggests that the monotonic behavior of the calculated energy shift permits an extrapolation of the results to the bulk limit. In doing so we obtain a limiting value of $\sim 1650 \text{ cm}^{-1}$. This would be our best estimate of the blue shift of the emission of the $n-\pi^*$ state of formaldehyde in water.

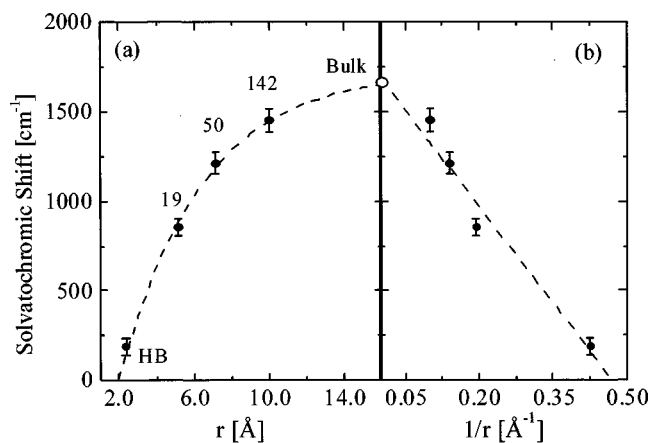


FIG. 5. (a) Calculated blue shift of the $n-\pi^*$ emission of formaldehyde in water, as a function of the solvation shell. Also shown are the number of molecules included in the quantum mechanical calculations. HB is the hydrogen bond shell. The others are the first, second, and third solvation shells. See Figs. 3 and 4. (b) Linear fitting using an inverse function. Note that both (a) and (b) converge to the same extrapolated value.

TABLE III. Summary of the calculated shifts of the $n-\pi^*$ transition of formaldehyde in water. Refer to Fig. 1 for definitions.

	Calculated shift (cm^{-1})
$\nu_1 - \nu_0$	2200
$\nu_3 - \nu_2$	1650
$\nu_2 - \nu_0$	-1270
$\nu_3 - \nu_0$	380
$\nu_1 - \nu_3$	550

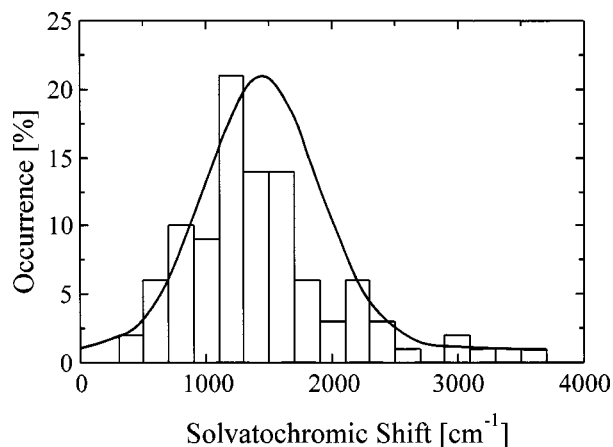
C. Solvatochromic shifts

It is of interest to analyze the total solvatochromic shifts of formaldehyde in water, in the case of absorption and emission. The total shifts are shown in Table III. $\nu_2 - \nu_0$ is the separate contribution of the relaxation of the excited state geometry. $\nu_1 - \nu_0$ is the solvation shift in the absorption and $\nu_1 - \nu_3$ is the Stokes shift (i.e., the difference between the absorption and the emission) in water.

The inclusion of a dispersion contribution to solvatochromic shifts in the CIS model has been analyzed recently.⁵³ We have shown that CIS on a supermolecule that contains only single excitations includes dispersion interactions between the two subsystems when energy differences are taken.⁵³ Our theoretical model presented here includes dispersion interaction, geometry relaxation, and solvent polarization. Sánchez *et al.*³⁸ have also considered the emission of formaldehyde in water using a continuum model. In their study they have considered both the C_{2v} geometry of the ground state and the relaxed geometry of the excited state. They conclude that the geometry relaxation contributes to the shift as much as the solvent polarization. They also find that in the emission process the contribution of dispersion interaction is an appreciable fraction of the total shift. In continuum models dispersion interaction may be considered separately.⁶⁵ Their final result is $\approx 350 \text{ cm}^{-1}$ for the emission shift. Ten-no, Hirata, and Kato, have studied the aqueous formation of formaldehyde in the first excited state using the reference interaction site model³⁴ and obtained the shift of 600 cm^{-1} . They concluded that geometrical relaxation rather than the solvent reorganization plays a crucial role for the fluorescence shift relative to the absorption band. Our result of $\nu_3 - \nu_0 = 380 \text{ cm}^{-1}$ is obtained by subtracting the geometry relaxation of 1270 cm^{-1} from the solvation shift of the relaxed state. The classical analysis made by Levy *et al.*³³ of the fluorescence shift of formaldehyde gives an energy shift of $\approx 1700 \text{ cm}^{-1}$ after relaxation of 1.0 ps and using all water molecules within 7.5 \AA . This classical result is in very good agreement with our Monte Carlo-quantum mechanics result of 1650 cm^{-1} .

D. Spectral broadening

Transition line shapes are broadened by solvent effects. This broadening results from the statistical motion of the liquid around the solute. One of the advantages of the present treatment of solvent effects is the possibility of calculating the spectral broadening due to the liquid environment. Figure 6 shows the calculated bandwidth for the largest supermolecular calculations, namely the third solvation shell. One-

FIG. 6. Histogram and Gaussian convolution of the spectral broadening of the calculated blue shift of the $n-\pi^*$ emission of formaldehyde in water.

hundred quantum mechanical calculations of formaldehyde surrounded by 144 water molecules is used to obtain this histogram. It is then convoluted by a Gaussian function and shows a width at half-maximum of $\approx 1200 \text{ cm}^{-1}$. Although for convenience we have convoluted the histogram using a symmetric Gaussian function the spectral broadening due to solvent effects is, in fact, an inhomogeneous broadening.

IV. SUMMARY AND CONCLUSIONS

Fluorescence spectroscopy is largely used in biology and medicine. Although the fluorescence of gases have been measured, by far the large majority of fluorescence spectra are measured in solution. The study of solvent effects in the spectroscopic properties of biomolecules thus require an understanding of the solvent effects in fluorescence spectroscopy, in particular, using water as the natural biological solvent. There has been a large number of theoretical investigations of solvent effects in the absorption spectroscopy, but very few theoretical studies are dedicated to the emission process. It is known that $n-\pi^*$ transitions usually do not fluoresce, in particular, formaldehyde does not fluoresce. The interest in our study is related to the solvent effects in emission and the selection of formaldehyde for that purpose is related to the extensive theoretical literature^{18-26,29,30,41-51} on the solvent effects in the absorption and the interesting theoretical analysis³³ of the excited state dynamics of formaldehyde.

In fact, formaldehyde in water forms oligomers, and even the solvent shift in the absorption is not well known, but this has not precluded theoretical studies of solvent effects in formaldehyde.

The study of solvent shifts in emission spectroscopy requires the consideration of both the relaxation of the excited state and the polarization of the solvent that is now equilibrated with the excited state of the solute. In this study we use the geometry and classical potential of the excited state of formaldehyde to perform a Monte Carlo simulation of formaldehyde in water. The structures generated by the classical simulation are used in subsequent quantum mechanics calculations. A Monte Carlo-quantum mechanics study of

the influence of the hydration shells in the emission of the $n-\pi^*$ state of formaldehyde in water is made. The liquid structures are generated by NVT Metropolis Monte Carlo simulation, assuming a fully relaxed excited state. Both the geometry and the classical potential of formaldehyde corresponds to the $n-\pi^*$ excited state. The solvatochromic shift was analyzed as a function of the solvation shells, starting from the hydrogen bonds. All the solvent molecules are treated quantum-mechanically. The INDO self-consistent field equations are first solved for the entire solute-solvent supermolecule. Then INDO/CIS calculations are performed to obtain the transition energies. To obtain the average, calculations are made on 100 structures generated by the Monte Carlo simulation. These structures are statistically nearly uncorrelated. Indeed, the autocorrelation function is used to obtain structures that are less than 6% correlated. A detailed analysis is made of the contribution of the hydrogen bonds. Next, 100 quantum mechanical calculations were made for each of the solvation shells. In the largest calculation we used 100 supermolecules composed of one formaldehyde surrounded by 142 water molecules, corresponding to the third solvation shell, extending to 10 Å from the center of mass of formaldehyde. The calculated, ensemble average, blue shifts are 180 ± 46 , 854 ± 51 , 1213 ± 59 , and $1451 \pm 63 \text{ cm}^{-1}$, respectively, for the hydrogen bond shell, the first, second, and third solvation shells. It is worth noting that the inclusion of the third solvation shell means that water molecules as far as 10.0 Å from the solute molecule still influences the solvation shifts. This is also found in the absorption case.^{29,34} In the case of nonpolar solutes such as benzene, however, it was found²⁸ that the first solvation shell is enough to give the solvent shift in the absorption transition of the first $\pi-\pi^*$, in both polar and nonpolar solvents. Extrapolating to the bulk limit, using the theoretical results obtained here for the hydrogen bond shell, the first, second, and third solvation shells, gives our best estimate of 1650 cm^{-1} for the solvatochromic shift of the $n-\pi^*$ emission of formaldehyde in water. The geometry relaxation of the excited state of formaldehyde is calculated as 1270 cm^{-1} , giving a solvent shift from the gas phase absorption of 380 cm^{-1} . The total Stokes shift in water is calculated as 550 cm^{-1} .

ACKNOWLEDGMENTS

This work has been partially supported by CNPq, CAPES, and FAPESP (Brazil).

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