

Electronic changes due to thermal disorder of hydrogen bonds in liquids: Pyridine in an aqueous environment

Eudes E. Fileti

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

Kaline Coutinho

Universidade de Mogi das Cruzes, CP 411, 08701-970 Mogi das Cruzes, SP, Brazil

Thaciana Malaspina and Sylvio Canuto*

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

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Combined Metropolis Monte Carlo computer simulation and first-principles quantum mechanical calculations of pyridine in water are performed to analyze the role of thermal disorder in the electronic properties of hydrogen bonds in an aqueous environment. The simulation uses the *NVT* ensemble and includes one pyridine and 400 water molecules. Using a very efficient geometric-energetic criterion, the hydrogen bonds between pyridine and water $C_5H_5N \cdots H_2O$ are identified and separated for subsequent quantum mechanical calculations of the electronic and spectroscopic properties. Statistically uncorrelated configurations composed of one pyridine and one water molecule are used to represent the configuration space of the hydrogen bonds in the liquid. The quantum mechanical calculations on these structures are performed at the correlated second-order perturbation theory level and all results are corrected for basis-set superposition error. The results are compared with the equivalent electronic properties of the hydrogen bond in the minimum-energy configuration. Charge transfer, dipole moment, and dipole polarizabilities are calculated for the thermally disordered and minimum-energy structures. In addition, using the mean and anisotropic polarizabilities, the Rayleigh depolarizations are obtained. All properties obtained for the thermally disordered structures are represented by a statistical distribution and a convergence of the average values is obtained. The results indicate that the charge transfer, dipole moment, and average depolarization ratios are systematically decreased in the liquid compared to the optimized cluster. This study quantifies, using *ab initio* quantum mechanics and statistical analysis, the important aspect of the thermal disorder of the hydrogen bond in a liquid system.

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I. INTRODUCTION

Water is the most important liquid and the natural biological solvent [1]. Most of the several anomalous behaviors of water are derived from its great ability to form hydrogen bonds and this is fundamental for the existence of life [2,3]. The study of hydrogen bonds has been a central topic in chemistry and biology [4–6] for quite some time and it is now attracting considerable interest also in physics [7–9]. Hydrogen bond is indeed a fundamental interaction to understand the thermodynamics of protic liquids and a series of biological phenomena that can only occur in water, including proteins, DNA, and enzymatic reactions. Hydrogen bonds between biomolecules are perhaps the most significant process regulating functions in living systems. Most of our understanding of the electronic structure of hydrogen bonds, and the associated properties and spectra, has been derived from studies in clusters where laser vaporization and jet-cooling techniques have produced a large variety of hydrogen-bonded complexes [10–13]. However, the situation found in a cluster is not the same as that in a liquid. Understanding the nature of hydrogen bonds formed between a solute organic molecule and water is crucial for describing

several solvation and biomolecular processes [14]. Whereas in a cluster the hydrogen-bond structure is fixed by a minimum-energy condition, in the aqueous environment there are several configurations governed by the temperature and the related natural disorder of the liquid. Therefore, the proton-acceptor site of a solute molecule in an aqueous environment experiences a great local thermal disorder. The theoretical description of this disorder is a great challenge and it is necessary for the understanding of the important local electronic effects. The hydrogen bonds lead to a local change in the electronic environment and thus also in the atomic charges, dipole moment, and dipole polarizability. Instead of a single value the electronic properties, such as dipole moment and polarizabilities, are more properly described by a statistical distribution of possible values within a certain width. The fluctuation in the electronic anisotropy of a single molecule leads to gas phase depolarization of the light scattered [15]. The dipole anisotropy in the liquid is also responsible for the depolarization of the elastic light scattered [15–17], but the depolarization ratio is now likewise given by a distribution of values. This distribution is a measure of the manifestation of the local electronic change due to the hydrogen bonds formed in the liquid situation, compared to the cluster optimized. The Rayleigh depolarization is one of the important properties that are derived from the polarizabilities, and can serve as an additional useful spectroscopic distinction of hydrogen bonds in clusters and

*Corresponding author. FAX: +55.11.3091-6831; email address: canuto@if.usp.br

in liquids. In this paper, we thus analyze in great detail the local change of the electronic structure calculating charges, dipole moment, and polarizabilities, and from these the Rayleigh light scattering [15–18] in a hydrogen-bonded cluster and in the liquid case. This is used as a quantitative characterization of the influence of the thermal disorder.

Motivated by the strong interest involved in six-member nitrogenated aromatic rings, as the building block of proteins and nucleotides [14], the system considered here is the pyridine-water $C_5H_5N \cdots H_2O$ system. In this case, the nitrogen atom of the pyridine molecule is the proton acceptor that makes a hydrogen bond with the hydrogen proton donor of water. We study the local changes in the atomic charges, dipole moment, and dipole polarizabilities of hydrogen-bonded pyridine-water using first-principles quantum mechanical methods in both situations, i.e., the cluster optimized and the disordered liquid. The different results are used for a comparison between the hydrogen bond in the cluster and in the liquid, hence giving a theoretical quantitative information about the influence of the local disorder.

The major difficulties in studying hydrogen bonds in liquids are related to a very large number of possible structures at a given temperature, the nontrivial identification of these bonds in a liquid, and the difficulty in obtaining statistically converged results. All these points are, in fact, related to a correct and realistic representation of the configuration space occupied by the hydrogen-bonded structures. These points are considered and successfully handled here, and we are then able to give an *ab initio* quantitative study of the influence of the local thermally driven disorder in the spectroscopic changes that arise because of hydrogen-bond formation between a molecule and its aqueous environment.

II. THEORETICAL METHODOLOGY

The structure of the liquid is first generated by Metropolis Monte Carlo (MC) computer simulation, using the DICE Monte Carlo statistical mechanics program [19]. The simulations are performed in the canonical (NVT) ensemble with one pyridine molecule plus 400 water molecules using the experimental density of water, which at $T=298.15$ K is 0.9966 g/cm³. The intermolecular interactions are described by the standard Lennard-Jones plus Coulomb potential. For the water molecules we use the SPC potential [20] and for pyridine we use the 11-site OPLS potential [21]. 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 $r_c=11.9$ Å. For separations larger than r_c , we use the long range correction of the potential energy [22]. The simulations consisted of a thermalization stage of 2.0×10^6 MC steps followed by a long averaging stage of 80.0×10^6 MC steps, where the configurations are generated. Successive configurations generated in the MC simulation, which are statistically highly correlated, will not give important additional information. Therefore, we calculate the interval of statistical correlation using the autocorrelation function of the energy [23–25]. For the simulations presented here, after the calculation of the autocorrelation of the energy, we obtain that configurations separated by 320

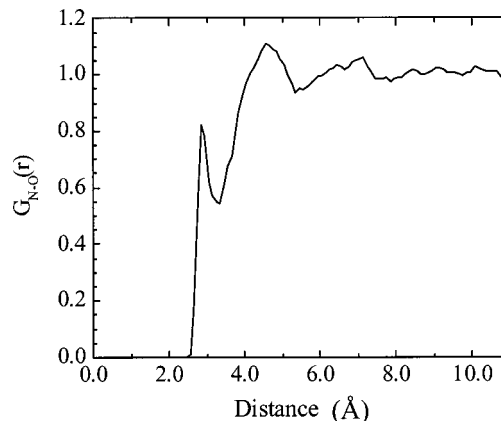


FIG. 1. The radial distribution function between the nitrogen atom of the pyridine and oxygen atom of the water molecules.

$\times 10^3$ MC steps are statistically relevant (less than 10% statistically correlated). Then, the number of configurations is reduced to 250 uncorrelated configurations without loss of statistical information [26–28]. Thus, after the entire simulation, 250 uncorrelated configurations separated by 320×10^3 MC steps were sampled. An important point now is the identification of the hydrogen bonds in the structures generated in the Monte Carlo simulation. Hydrogen bonds are normally extracted from computer simulation using the pairwise radial distribution function. This gives the coordination of water molecules around the solute, but it cannot be assured that all near-neighbor water molecules are indeed hydrogen bonded [28–32]. This point has been the subject of great concern and the definition of a hydrogen bond in a liquid is not unanimously free from ambiguity. Furthermore, lying close to the solute molecule is not a sufficient condition for a hydrogen-bonded structure as this can be a mere consequence of packing. A very efficient procedure can be obtained using in addition to a geometric, also an energetic criterion [24,26,28–31]. We consider here a hydrogen-bonded structure when the distance $R_{N-O} \leq 3.5$ Å, the angle $\theta(N\hat{O}H) \leq 30^\circ$, and the binding energy is larger than 2.0 kcal/mol. These geometric conditions are obtained from the radial and the angular distribution function. For the energetic criterion, it is important to look at the pairwise energy distribution. First, Fig. 1 shows the pairwise radial distribution function between the N atom of pyridine and O atom of water. The first peak in the $G_{N-O}(r)$ distribution function starts at 2.45 Å and ends at 3.5 Å, with a maximum at 2.94 Å. Hydrogen bonds can be located then for the distance $R_{N-O} \leq 3.5$ Å. A similar analysis gives the criterion for the angle $\theta(N\hat{O}H) \leq 30^\circ$. Figure 2 identifies the hydrogen bonds for pairwise pyridine-water interaction energy less than -2.0 kcal/mol. Using these criteria, in the 250 MC configurations we find 269 hydrogen bonds formed in the nitrogen atom of pyridine. More specifically, we find that in 17% of the configurations the pyridine does not form any hydrogen bonds, in 62% it forms one, in 20% it forms two, and in only 1% it forms three hydrogen bonds. This gives an average of 1.1 hydrogen bonds. There is a total of 155 configurations making one hydrogen bond. All these 155 structures composed of

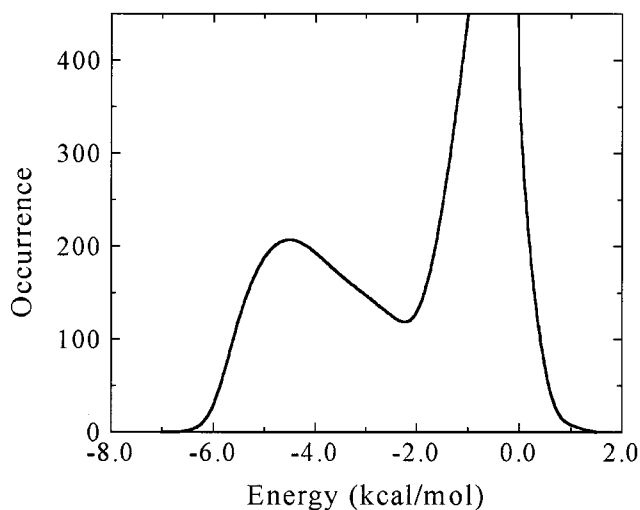


FIG. 2. Histogram of the pairwise energy interaction between pyridine and water.

one pyridine and one water will be submitted to the quantum mechanical calculations. Figure 3 shows, in a single picture, the superposition of all these (1:1) 155 hydrogen-bond structures in the liquid. It clearly shows the efficiency of the identification and the sampling procedure for obtaining hydrogen bonds formed between pyridine and water. Indeed, it can be seen how well the configuration space is filled with all water molecules being indeed hydrogen bonded to the nitrogen site of pyridine. Figure 4 gives the calculated fully optimized structure for the single (1:1) cluster. The calculated hydrogen-bond distance N---H in the cluster is 1.964 Å, corresponding to a distance N-O of 2.947 Å. For comparison, in the liquid case, this average distance is calculated as 2.94 ± 0.16 Å.

Light scattering cross section and depolarization are related to the anisotropy of the electronic polarization of a molecular system. As the hydrogen-bond formation leads to

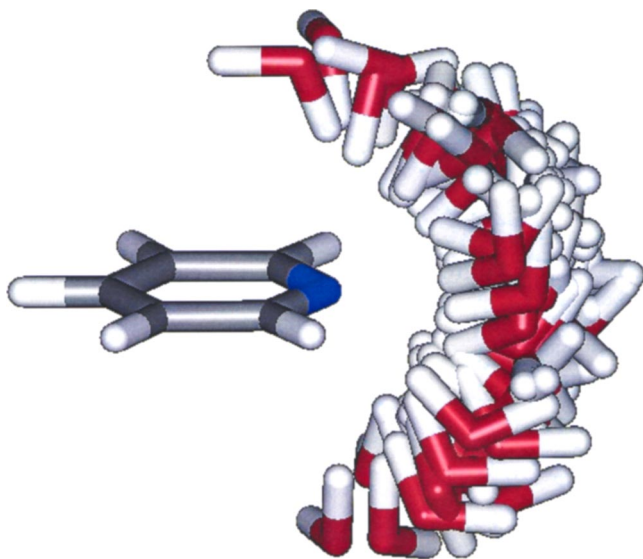


FIG. 3. (Color online) Superposition of configurations of the hydrogen bond formed by pyridine in an aqueous solution.

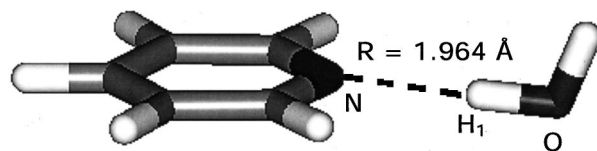


FIG. 4. The structure of the optimized pyridine-water cluster.

a change in the anisotropy, it should lead to a corresponding change in the light depolarization. In the case of the elastic Rayleigh scattering, the degree of depolarization (σ) and intensity of the light scattered (\mathfrak{R}) at right angles to the direction of incidence for natural and plane-polarized light are given by [15,18]

$$\sigma_n = \frac{6(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 7(\Delta\alpha)^2}, \quad \mathfrak{R}_n = 45(\bar{\alpha})^2 + 13(\Delta\alpha)^2, \quad (1)$$

$$\sigma_p = \frac{3(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 4(\Delta\alpha)^2}, \quad \mathfrak{R}_p = 45(\bar{\alpha})^2 + 7(\Delta\alpha)^2. \quad (2)$$

The mean (α) and anisotropic ($\Delta\alpha$) dipole polarizabilities are the invariants of the polarizability tensor and are given by

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

and

$$(\Delta\alpha)^2 = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2] + 3[(\alpha_{xy})^2 + (\alpha_{xz})^2 + (\alpha_{yz})^2]. \quad (4)$$

The maximum values of σ in the Rayleigh scattering corresponds to the most anisotropic case, corresponding to the extreme where $\Delta\alpha = 3\alpha$. In this case, $\sigma_n^{\max} = 1/2$ and $\sigma_p^{\max} = 1/3$. It is also of interest to obtain the depolarization for circularly polarized light. The light circularly polarized scattered backwards may have a component of circular polarization. The degree of reversal is given by [15]

$$\sigma_c = \sigma_n / (1 - \sigma_n). \quad (5)$$

It is easy to see that in this case σ_c^{\max} is 1.

The dipole moment and dipole polarizabilities are calculated individually for each of the 155 (1:1) structures separated from the MC simulation of the liquid and for the optimized (1:1) cluster using the second-order many-body perturbation theory [33] with the Møller-Plesset partitioning [34], using the MP2/6-31+G(d) theoretical model, using GAUSSIAN98 [35].

III. RESULTS AND DISCUSSIONS

We first discuss the local atomic charges as they play a central role in the physical model of the hydrogen bond [4,5,13]. The dominant view adopts the idea that electrostatic interaction is the major contributor toward a realistic model of hydrogen bonds [13,36–39]. There has also been some debate on the charge transfer [39–42] and covalent effects [43–45]. Some recent studies argue that charge transfer cannot be ignored and may give a significant contribution to

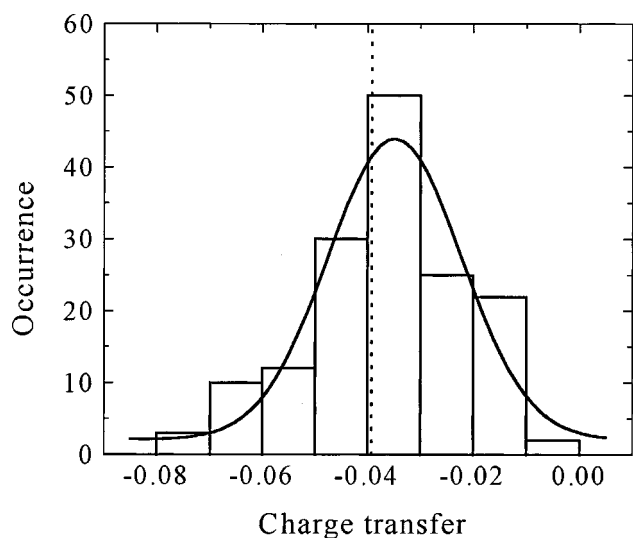


FIG. 5. Charge transfer (in elementary charge unit) from pyridine to water and comparison with the cluster value (vertical dotted line).

stabilize hydrogen bonds [41,42,46–48]. The criticism of computational artifact related to charge transfer has been considered in a recent and detailed theoretical study [49]. Vaart and Merz [49] contend that charge transfer occurs even in the total absence of basis-set superposition error (BSSE). They find that charge is transferred from the hydrogen-bond acceptor to the hydrogen-bond donor by an amount between 0.01 and 0.05 electrons per hydrogen bond. This is a point of great importance, which will be used here to give a possible distinction between the hydrogen-bond interaction between pyridine and water in the minimum-energy and thermally disordered structures. Although atomic charges are not true physical observables and theoretical values are not unique, the calculated trend can still be useful. Here, we use the Mulliken population analysis and the counterpoise correction [50] to BSSE. So all calculations are made with the full basis set of both pyridine and water. We find here that in the minimum-energy configuration, there is a charge transfer from the pyridine to the water molecule of $-0.039e$; i.e., the water is more negative upon hydrogen bonding. This result, corrected for BSSE, is in line with the findings of Vaart and Merz [49]. They also made the observation that this result is not very dependent on the quality of the basis set after correcting for BSSE. However, the Mulliken population results that we obtained here are more systematic. Figure 5 shows

the result of the charge transfer for the configurations of the liquid. In this case, we obtain a statistical distribution of values. As it can be seen, all configurations present a dominant charge transfer (negative results) to the water. In the average, the pyridine transfers to the water molecule -0.036 ± 0.015 elementary charge. Whether this charge transfer plays a significant role in the strength of the hydrogen bond is a subject of debate. However, we find a systematic transfer in both cases, with magnitude comparable to that obtained by Vaart and Merz [49]. Also, as it can be seen, the hydrogen-bond donor (the water molecule) in the minimum-energy configuration of the complex is only slightly more negative. Hence, the role played by charge transfer will be essentially the same in the cluster-optimized and the thermally disordered structures.

The dipole moments of the cluster-optimized structure and the average value for the disordered pyridine-water liquid structure are given in Table I. All these results are again corrected against basis-set superposition error, using the counterpoise correction [50]. The calculated dipole moment for the optimized pyridine-water cluster is 5.07 D, reasonably larger than the calculated average dipole moment for the liquid, 4.71 ± 0.68 D. The conclusion is that the disorder leads to a decrease of the combined dipole moment. In a vector model, the dipole moment of the complex is obtained by a simple vector addition of the dipole moment of the separate parts and this gives the value of 4.73 D (cluster) and 4.54 ± 0.68 D. The disordered structures lead to a smaller dipole moment, reducing its value by 5–10%. Of course, the decrease in the dipole moment leads to a decreased dipole interaction and hence a smaller binding of the hydrogen bond in the liquid compared to the hydrogen bond in the minimum-energy pyridine-water configuration. If now we consider the difference between the vector sum approximation and the explicitly calculated result as an induction effect [5,13,51], we can see that induction contributes to less than 10% both in the cluster and in the thermally disordered structures. Figure 6 shows the distribution of the calculated dipole moment values using the disordered pyridine-water structures and the normal distribution with $\langle \mu \rangle = 4.54$ D and $s = 0.10$ D.

Dipole polarizability is an important electronic property that has been very much used in cluster characterization [52–54], including hydrogen-bonded system [18,55]. The interest here is to analyze the changes in dipole polarizabilities coming from thermal disorder of the solute-water system and the

TABLE I. Calculated dipole moment and polarizabilities of hydrogen-bonded pyridine and water. Results shown for the liquid are average values and the standard deviations are also shown. Vector model assumes a simple vector addition of the dipole moments of the separate molecules.

	Pyridine	Cluster (1:1)	Liquid (1:1)
Dipole moment (D)	2.51	5.07	4.71 ± 0.68
Vector model		4.73	4.54 ± 0.10
Dipole polarizability (a.u.)			
Mean	60.00	68.16	68.37 ± 0.24
Anisotropy	35.11	39.29	37.36 ± 2.07

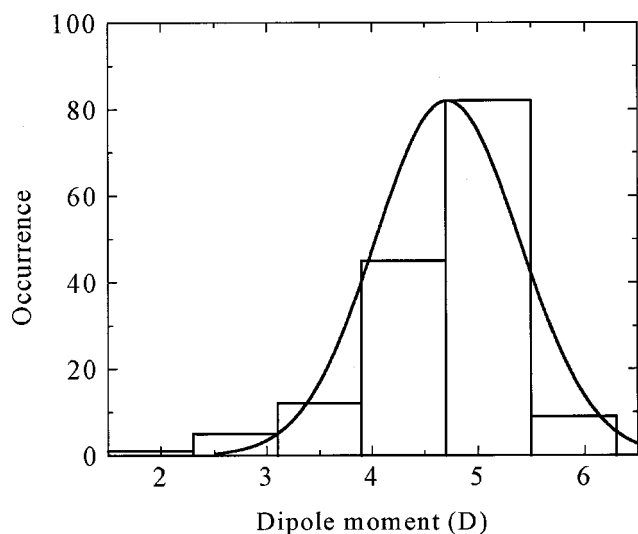


FIG. 6. Distribution of calculated dipole moment values and the normal distribution with $\langle\mu\rangle=4.54$ D and $s=0.10$ D.

consequence of this change in the Rayleigh properties. The calculated polarizabilities for the minimum-energy and thermally disordered systems are summarized in Table II. The mean polarizability of the pyridine-water system is essentially additive, but the anisotropy is more sensitive to the binding. This additivity is not surprising and has been noted before [18,55,56] for geometry-optimized clusters. In the liquid, this additivity is more peculiar because the polarizability becomes a statistical distribution. The mean dipole polarizability is slightly larger due to the distribution of the thermal disorder. The standard deviation s for the liquid reflects the large variation seen in the liquid case. Thus, the final value represented by $\langle\alpha\rangle\pm s$ shows the two information that describe the normal distribution and comprises 68% of the data. Figure 7 shows the convergence of the calculated mean and anisotropic polarizabilities when the number of configurations L increases up to the maximum $L=155$, used here. The results clearly demonstrate that the average value converges after around 100 quantum-mechanical polarizability calculations. The hydrogen bonds sampled from the MC simulation, and shown previously in Fig. 3, are indeed able to represent the configuration space necessary to give statistically converged results.

The inhomogeneity in the electronic distribution leads to depolarization of the light elastically scattered and this Rayleigh depolarization is obtained from the local dipole polarizabilities. Upon hydrogen-bond formation in the aqueous environment, the depolarization ratios become a distribution

TABLE II. Calculated Rayleigh depolarization ratio (10^{-2}) of hydrogen-bonded pyridine and water. The results shown for the liquid are average values and the standard deviation is also given.

Depolarization	Pyridine	Cluster (1:1)	Liquid (1:1)
σ_p	2.21	2.15	1.94 ± 0.20
σ_n	4.33	4.21	3.81 ± 0.38
σ_c	4.53	4.40	3.96 ± 0.41

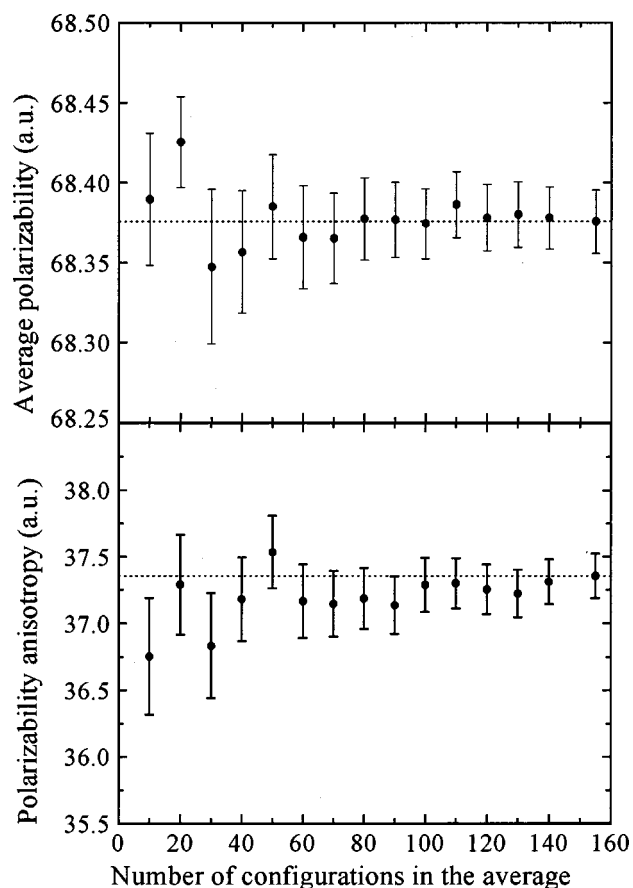


FIG. 7. Convergence of the calculated mean and anisotropic dipole polarizabilities (in atomic units). The statistical error is shown.

with the average value being decreased with respect to the value obtained for the cluster optimized. In the liquid case, these are always smaller than in the cluster-optimized case. A clear distinction between the two cases can be made and it is quite interesting for all polarizations that the reduction in the ratios, going from the optimized to the liquid case, is the same 10%. In general terms, the average result of the depolarization ratios differ by only 10% from the cluster-optimized case. The thermal motion, however, implies a

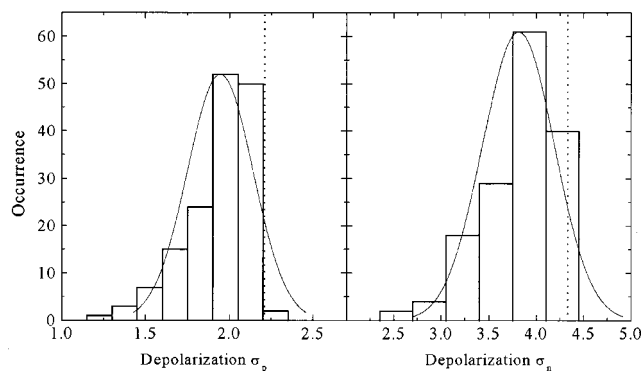


FIG. 8. Histogram showing the distribution of depolarization (dimensionless) in the liquid and comparison with the cluster value (vertical dotted line).

broadening of the results. Figure 8 shows a comparison between the distribution of depolarization ratios for the disordered liquid structures and the same depolarization for the cluster-optimized case. The calculated values of the depolarization ratios for the minimum-energy case lie outside the half-width of the distribution for the liquid; i.e., they are superior to 85% of the data points of the normal statistical distribution. Although this is a single-case study, it should be mentioned that similar results have been obtained for other systems, with the depolarization calculated for cluster-optimized hydrogen bond giving values that are higher than those obtained by taking into consideration the thermal distribution of structures. Of course, this could also be extended beyond polarization calculations. As dipole polarizabilities are related to intermolecular forces, the results presented here can also be used for rationalizing the interaction of hydrogen-bonded systems with the outer environment. In this case, the solvent effect in the polarizability has to be properly addressed [57,58]. A similar analysis can be made for nuclear-magnetic-resonance chemical shifts [59] and quadrupole coupling constants [60], and, indeed, these can be obtained by using the same theoretical approach. This study is devoted to obtaining quantum mechanical results of liquid systems using statistically converged results.

IV. SUMMARY AND CONCLUSIONS

Hydrogen bonds are becoming a topic of central interest in chemistry, physics, and biology. Several studies have been performed in recent years, which consider different theoretical and experimental aspects. On the theoretical side, most studies have been performed in clusters and this is indeed of great importance to understand gas phase and even solid state properties. For liquids, however, this is not the proper circumstance, since a liquid has several configurations and cannot be treated by a single structure. Especially, it should not be treated by cluster-optimized structures that represent a minimum-energy configuration, which is artificial for a liquid at room temperature. One of the most important structural aspects of the liquid derives from the thermal disorder that gives the statistical essence of a liquid. In this paper, we have focused on the influence of the thermal disorder in the hydrogen-bond structures that are obtained for the pyridine molecule in an aqueous environment. We chose the dipole moment and dipole polarizability as the probe electronic property, including the anisotropic component of the polarizability that is responsible for the light depolarization. The *ab initio* quantum mechanical calculations were performed only on the pyridine and the hydrogen-bonded water and the influence of the outer solvent molecules were not considered. Probe calculations indicated that this has only a small influence that is estimated to be less than 10%. Our results for the

dipole moment, dipole polarizabilities, and depolarization ratios calculated for the hydrogen-bonded pyridine and water are statistically converged values incorporating the inherent disorder nature of the liquid. Since dipole polarizabilities are related to intermolecular forces, the results presented here can also be used for rationalizing the interaction of hydrogen-bonded systems with the outer environment. Similarly, the dipole moment results show that the disorder affects the local dipole moment. In the liquid environment, the thermal disorder leads to an average dipole moment for the complex that is inferior to that for the cluster optimized. However, in the case studied here, the differences are important but not sizable. The charge transfer from the hydrogen-bond acceptor (pyridine) to the hydrogen-bond donor (water) has also been computed. It is found that, on an average, $0.036e$ is transferred to water. This result is only slightly smaller than that obtained for the minimum-energy cluster ($0.039e$). This is indicative that insofar as charge transfer may have a role in the hydrogen bond, in this particular case this role is essentially the same and is not much affected by the thermal disorder. A direct spectroscopic consequence of the dipole polarizability and its anisotropy is the effect of Rayleigh depolarization. Again, the depolarization ratios are given by a distribution, and in the pyridine-water case considered here the standard deviation is about 10% of the average value. Our results indicate that the average depolarization ratios are systematically decreased in the liquid compared to the optimized cluster for all three polarization cases considered here. The calculated Rayleigh intensities are essentially the same. The depolarization ratios are, however, different for the normal, planar, and circular polarized light; but in all these cases we find a reduction of 10% in changing from the optimized to the average thermal distribution of the liquid (1:1) hydrogen bond. Reductions of 20% have been obtained in other systems under studies in our group. The standard deviation in the present case is also calculated as $\sim 10\%$ of the average value. This signifies that in the case considered here, the calculated value for the cluster-optimized structure lies in the boundary (see Fig. 8) of $\langle \sigma \rangle + s$. The values lying below $\langle \sigma \rangle + s$ of the distribution of thermal disordered structures, comprising 85% of the calculated data for the liquid, are smaller than the calculated single value for the cluster-optimized structure. This study quantifies, using *ab initio* quantum mechanics and statistical analysis, the important aspect of the thermal disorder of the hydrogen bond in a liquid system.

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