Vibrational Spectral Diffusion in Supercritical D_2O from First Principles: An Interplay between the Dynamics of Hydrogen Bonds, Dangling OD Groups, and Inertial Rotation

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We have presented a first principles theoretical study of vibrational spectral diffusion and underlying molecular dynamics in supercritical heavy water at three different densities ranging from 1.1 to 0.39 g cm^{-3}. Our calculations are based on ab initio molecular dynamics simulations for trajectory generation and wavelet analysis for frequency calculations, and no empirical potential parameters are involved in the present study. Calculations of OD frequency−distance (D···O) conditional probabilities reveal that the rate of increase of OD frequency with D···O distance gradually decreases with lowering of density. Also, the maximum probability moves to a higher frequency-larger D···O distance region with decreasing density due to weakening of hydrogen bonds and increased number of dangling OD bonds in these systems. The correlations between the stretch frequencies and the electric fields on D atoms (along OD bonds) are also calculated, and the magnitude of such correlations is found to be similar to those of frequency−distance (D···O) correlations for the present supercritical systems. The vibrational spectral diffusion in supercritical water shows two time scales: one around 100 fs or less and the other in the region of 150−600 fs with the shorter time scale carrying the larger weight. It is found that, unlike ambient water, for supercritical water the slower component of the spectral diffusion does not necessarily capture the hydrogen bond dynamics at all densities. Rather, an interplay between the dynamics of hydrogen bonds, dangling OD groups, and the inertial rotation of OD bonds determines the times scales of spectral diffusion in a rather subtle manner. While the slower component of spectral diffusion at high density is determined by the lifetimes of hydrogen bonds, it is the lifetime of dangling OD groups that decides the slower component at low density, and the reverse holds for the faster components. The fast inertial rotation also shows up as the faster component of spectral diffusion. Dynamical correlations between the relaxation of frequency fluctuations and that of electric field fluctuations are also explored. Our calculations of rotational dynamics show, unlike ambient water, no frequency dependence of the rotational relaxation of OD bonds because of faster interconversion of different hydrogen bonding states and a reduced role of the hydrogen bond strength as a significant determinant of rotational motion caused by higher thermal energy of supercritical states.

1. Introduction

This paper is concerned with vibrational spectral diffusion and underlying molecular dynamics in supercritical water of varying density. The unique solvent properties of liquid water are generally attributed to its fluctuating hydrogen bonds and studies of vibrational spectral diffusion through time-dependent infrared spectroscopy have played a key role in exploring the time scales of these hydrogen bond fluctuations in ambient water.[1−3] The interpretation of the spectral results of these experiments relies on a strong correlation between the stretching frequency of an OH (or OD) bond and the distance or strength of the associated H···O (or D···O) hydrogen bond with its nearest neighbor oxygen. A fluctuation in the strength or distance of the hydrogen bond would lead to a change in the stretching frequency of the covalent bond so that the dynamics of frequency fluctuations, called the spectral diffusion, captures the dynamical fluctuations of the hydrogen bonds in the liquid. For ambient water, such time-dependent infrared spectroscopic studies have been carried out rather extensively in recent years,[1−11] and these studies have also been supported by theoretical calculations at different levels of sophistication.[12−16] Such studies on supercritical water, however, have been very few. On the experimental side of time-dependent vibrational spectroscopy, Vöhringer and co-workers[17] have looked at vibrational energy relaxation vs spectral diffusion in supercritical deuterated water. In these studies, no spectral diffusion was found at time scales greater than 0.3 ps, and it was concluded that, unlike ambient water, the spectral diffusion in supercritical water occurs with a much faster time scale than that of vibrational energy relaxation. On the theoretical side, although there have been a few studies on hydrogen bond dynamics using empirical potential models,[18−20] no study has yet been carried out on vibrational spectral diffusion and its connections to hydrogen bond fluctuations in supercritical water.

The very different chemical and physical properties of supercritical water are thought to be related to the changes in the intermolecular structures and dynamics at elevated temperatures. The unique character of the supercritical water is that its density can be changed from liquidlike to gaslike densities leading to huge changes in its hydration properties, and as a result, chemical reactions occurring in such a medium can also be controlled by changing its temperature, pressure, or density. Thus, a detailed understanding of the molecular interactions, structure, and dynamics of supercritical water is extremely important in studies of chemical and physical processes under

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extreme conditions. In particular, we need to answer some of the key issues of supercritical water such as the (i) nature of hydrogen bonds and their fluctuation dynamics, (ii) changes in fluctuations as one alters the density isothermally in the supercritical phase or as one moves to the supercritical temperature from the ambient state at constant density, (iii) connections of hydrogen bond fluctuations to vibrational spectral diffusions, (iv) other dynamical modes apart from hydrogen bond fluctuations that might be relevant to spectral diffusion in supercritical water, e.g., the dynamics of dangling OD groups, inertial rotation, and electric field fluctuations, and (v) also the primary differences in the spectral diffusion and underlying molecular dynamics of water between supercritical and ambient states.

In the present work, we have addressed the above issues by means of detailed theoretical calculations. In particular, we have employed the methods of ab initio molecular dynamics[21,22] for trajectory generation and wavelet analysis[16,23−25] for frequency calculations. The present calculations are done for three different densities ranging from 1.1 to 0.39 g cm^{-3} at a supercritical temperature of 673 K. In ab initio molecular dynamics simulations, the quantum many-body potentials and forces are obtained directly from on-the-fly quantum electronic structure calculations, and thus no empirical pair potentials are used. We note that the use of ab initio many-body potentials is especially important for supercritical water since all of the commonly used empirical potential models of water are parametrized for ambient water and use of such potentials for supercritical fluids is a questionable issue. From our present ab initio simulations, we first investigated the equilibrium aspects of frequency distributions and frequency−structure correlations in heavy water under supercritical conditions, especially the relations between the fluctuating stretch frequencies of OD modes and associated D···O distance from the nearest neighbor oxygen. Then, the dynamics of spectral diffusion is investigated by means of frequency time correlations. The dynamical results are analyzed in terms of the dynamics of hydrogen bonds, dangling OD groups, and fast inertial rotation of D_2O molecules and also the electric field fluctuations along the OD bonds. The details of the time constants of frequency correlations are found to depend on the density of the supercritical fluid. A first principles calculation of the frequency dependence of rotational relaxation of D_2O molecules is also carried out, and the results of supercritical states are compared with those of ambient water. Connections are also made to the results of recent time dependent infrared spectroscopic studies of supercritical water that are available in the literature.[17]

We have organized the rest of the paper as follows. In section 2, we present the details of ab initio molecular dynamics simulations and calculations of fluctuating frequencies for all the three supercritical systems. The results of frequency distributions and frequency−structure correlations are discussed in section 3. The results of vibrational spectral diffusion and underlying molecular dynamics like that of hydrogen bonds, dangling OD groups, and inertial rotation are presented in section 4. In section 5, we discuss our results of orientational relaxation of OD bonds for different stretching frequencies and our conclusions are briefly summarized in section 6.

2. Ab Initio Molecular Dynamics Simulations and Time Series Analysis for Frequency Calculations

The ab initio molecular dynamics simulations are carried out by employing the Car−Parrinello method[21,22] and the CPMD code.[26] We have considered supercritical water of three different densities of 1.1, 0.78, and 0.39 g cm^{-3} at 673 K. Each simulation system contains 32 D_2O molecules in a cubic box, which is periodically replicated in three dimensions, and the length of the box is 9.865, 11.10, and 13.98 Å for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. The electronic structures of the extended simulation systems were represented by the Kohn−Sham (KS) formulation[27] of density functional theory within a plane wave basis. The core electrons were treated via the norm conserving atomic pseudopotentials of Troullier-Martins,[28] and the plane-wave expansion of the KS orbitals was truncated at a kinetic energy of 70 Ry. A fictitious mass of $\mu = 800$ au was assigned to the electronic degrees of freedom, and the coupled equations of motion describing the system dynamics were integrated by using a time step of 3 au. We used the BLYP[29] density functional in the present simulations. We note that the same density functional was also employed in an earlier ab initio molecular dynamics simulation of supercritical water.[30] The focus of this earlier study was, however, on the equilibrium structural aspects rather than on the dynamics. In the present work, initial configurations of water molecules were generated by carrying out classical molecular dynamics simulations using the empirical multisite SPC/E[31] interaction potential. Then, for the ab initio molecular dynamics simulations, we equilibrated all the systems for 8 ps in canonical ensemble at 673 K, and thereafter, we continued the runs in microcanonical ensemble for another 15−25 ps for calculations of various equilibrium and dynamical quantities.

The time-dependent vibrational frequencies of OD bonds are obtained from a time series analysis of the ab initio molecular dynamics trajectories. In particular, we have employed the wavelet analysis method,[24] which is more efficient than the so-called windowed Fourier transform methods because it adjusts the size of the time window automatically according to the frequency of oscillations and thus provides a better localization in time of the spectral information of a trajectory. The basic idea of the wavelet analysis is to express a time dependent function $f(t)$ in terms of basis functions which are constructed as translations and dilations of a mother wavelet[24]

$$\psi_{a,b}(t) = a^{-1/2}\psi\left(\frac{t-b}{a}\right) \tag{1}$$

where the mother wavelet has to have compact support for it to be useful, i.e., it should decay to zero rapidly for $t \rightarrow \pm\infty$. The coefficients of the expansion are given by the wavelet transform of $f(t)$, which is defined as

$$L_{\psi}f(a,b) = a^{-1/2}\int_{-\infty}^{\infty} f(t)\bar{\psi}\left(\frac{t-b}{a}\right)dt \tag{2}$$

for $a > 0$ and b real. Following previous work,[16,24,25] we have taken the mother wavelet to be of Morlet−Grossman form.[32] The wavelet transform of eq 2 produces a complex surface as a function of the variables a and b. The inverse of the scale factor a is proportional to the frequency, and thus the wavelet transform of eq 2 at each b gives the frequency content of $f(t)$ over a time window about b. Since we are interested in the OD stretching frequencies, the time-dependent function $f(t)$ for a given OD bond is constructed to be a complex function with its real and imaginary parts corresponding to the instantaneous OD distance and the corresponding momentum along the OD bond.[16] The stretching frequency at a given time $t = b$ is then determined from the scale a that maximizes the modulus of the corresponding wavelet transform at b, and the process is repeated for the entire trajectories and for all the OD bonds that are there in the present simulation systems.

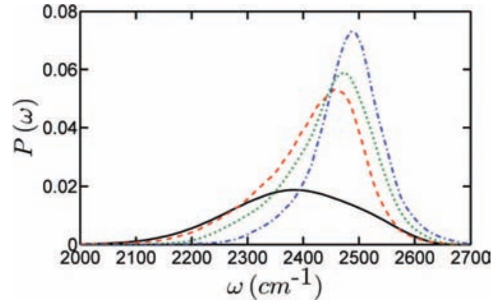

Figure 1. The distribution of OD stretch frequencies of supercritical heavy water at 673 K. The red dashed, green dotted, and blue dashed−dotted curves are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. The corresponding results for liquid D_2O under ambient conditions at 300 K are shown by the black solid curve.

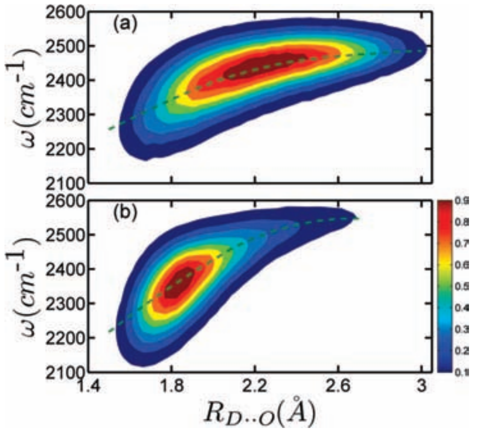

Figure 2. The joint probability distributions of OD frequency and D···O distance at density 1.1 g cm^{-3}. The results of (a) are for T = 673 K. The corresponding results for normal water at room temperature are shown in (b) (ref 16).

3. Frequency−Structure Correlations

The vibrational frequency of an OD bond in water fluctuates due to fluctuations in its interactions with the surrounding molecules caused by their continual motion. Since the connection between an OD frequency and the length (or strength) of the hydrogen bond between the D atom and the nearest oxygen of a neighboring water has played a key role in the interpretations of time-dependent vibrational spectral shifts in ambient water,[1−11] it is important to critically analyze from first principles the presence of any such frequency−structure correlations in the supercritical state and also changes of such correlations with variation of density and temperature. In Figure 1, we have shown the distributions of OD vibrational frequencies for the three different densities considered here. For this figure, and also for Figures 2 and 3 shown later, we have used the MATLAB package to smooth the raw simulation data using the loess method with a span of about 6−8%.[33] In Figure 1, we have also shown the frequency distributions of OD bonds of ambient water at 300 K as obtained in our earlier study.[16] In general, the frequency distributions of supercritical water are narrower and blue-shifted compared to that of ambient water. Also, at the supercritical temperature, a decrease of width and an increase of average frequency is found with decrease of density which are in general agreement with experimental findings of supercritical water.[17]

In Figures 2 and 3, we have shown our results of frequency−structure correlations through the contour plots of the conditional probability of observing a particular frequency for a given D···O distance. The results of Figure 2 are for density 1.1 g cm^{-3}, and those of Figure 3 are for the two lower densities. The corresponding results for ambient water at 300 K[16] are also shown in Figure 2 for comparison. In all cases, substantial dispersions are found in the probability distributions which rule out the possibility of assigning a single instantaneous frequency to a given D ·· O distance. On average, however, the frequency is seen to increase with the D···O distance. However, the rate of increase gradually decreases with lowering of density. Also, the maximum probability moves to a larger distance−higher frequency value with decreasing density. A clear change in the shape is observed in the distributions for ambient and supercritical water at the same density (Figure 2). In the supercritical state, the distribution is more horizontal and extended to larger D···O distances, which can be linked to the weaker and less number of hydrogen bonds at the elevated temperature. The dividing surface between the hydrogen-bonded and non-hydrogen-bonded states as given by the present geometric criterion is shown by the vertical dashed line in these figures. It is seen clearly that while a major part of the probability distribution falls on the left side of the dividing line for the ambient water or the supercritical water at higher density (1.1 g cm^{-3}), it is the other way around for the lowest density system considered here (0.39 g cm^{-3}). For the lowest density system, the major part of the frequency−distance probability distribution falls in the non-hydrogen-bonded region, which means, unlike the higher density systems, the dynamics of frequency fluctuations in the lowest density system may not capture much of the hydrogen bond dynamics. A decrease in the number of hydrogen bonds enhances the number of dangling OD groups, which is responsible for almost horizontal stretching of the distributions toward higher D···O distances for low density systems. For the system of intermediate density (0.78 g cm^{-3}), significant parts of the probability distribution are found to fall on both sides of the dividing line which means the dynamics of both hydrogen bonds, and dangling OD modes are likely to influence the relaxation of frequency fluctuations in this system. This is indeed supported by our dynamical results of section 4.

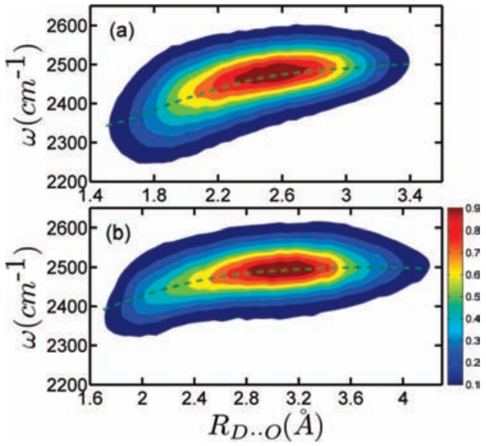

Figure 3. The joint probability distributions of OD frequency and D···O distance at the supercritical temperature of 673 K. The results of (a) and (b) are for densities 0.78 and 0.39 g cm^{-3}, respectively.

The frequency−distance statistical correlations discussed above can also be quantified in terms of the correlation coefficient defined by

$$\chi_x = \frac{\langle (x - \langle x \rangle)(\omega_{\mathrm{OD}} - \langle \omega_{\mathrm{OD}} \rangle)\rangle}{\sqrt{\langle (x - \langle x \rangle)^2 > \langle (\omega_{\mathrm{OD}} - \langle \omega_{\mathrm{OD}} \rangle)^2 \rangle}} \qquad (3)$$

where x is the D···O distance denoted by R. Clearly, $\chi_R = 1.0$ for a perfect linear correlation, and it is −1 if the correlation is perfect but in the reverse direction, i.e., anticorrelated. A zero value of the correlation coefficient χ_R means there is no statistical correlation between the OD frequency and the D···O distance. For the present supercritical systems, the values of χ_R are found to be 0.58, 0.50, and 0.33 for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. A similar calculation for ambient water gives a value of 0.70 for the above correlation coefficient. Clearly, for ambient water, the correlation between the stretch frequency and the hydrogen bond distance is reasonably strong which is in agreement with previous findings[12,13,34] where a different methodology was employed to calculate these correlations. It is interesting to note that the correlation remains significant for the supercritical water at higher density as well. Even for the lowest density supercritical water studied here, the correlation coefficient is still far above zero which means a statistical correlation between the stretch frequency and the nearest D···O distance continues to exist, although to a lesser extent, even at elevated temperatures of supercritical states. This holds even when the nearest D···O distance exceeds the typical hydrogen bond distance so that the nearest water is no longer hydrogen bonded to the OD group of interest.

Our calculated average stretch frequencies of supercritical D_2O are 2415, 2450, and 2480 cm^{-1} for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively, which are somewhat red-shifted compared to the corresponding experimental values.[17] This difference is likely due to the systematic errors introduced by the density functional, electronic fictitious mass, and the finite basis set cutoff.[35,36] Use of pseudopotentials and finite system size might also influence the calculated frequencies. Such systematic errors could have been accounted for by using constant scaling factors,[14,15] but we preferred to deal with the frequencies as obtained from our calculations because the normalized dynamics of spectral diffusion, which is the primary focus of this work, will remain unchanged by the use of any such scaling factors. Also, we note that even for the lowest density of 0.35 g cm^{-3} that we have considered here the OD stretch frequency (2480 cm^{-1}) is less than that of an isolated water (2560 cm^{-1}) found from the same level of calculations. Thus, there are still some net attractive interactions in supercritical water at densities as low as 0.35 g cm^{-3}, which is consistent with the finite nonzero value of the frequency−distance correlation coefficient of this system discussed in the previous paragraph. Recent experiments[17] have also reported similar findings on stretch frequencies with variation of density but such results from first principles theoretical calculations are reported here for the first time for supercritical water.

4. Spectral Diffusion and Underlying Molecular Dynamics

4.1. Frequency Time Correlation Function. The central dynamical object of interest in the context of vibrational spectral diffusion is the frequency time correlation function defined by

$$C_\omega(t) = \langle \delta\omega(t)\delta\omega(0) \rangle / \langle \delta\omega(0)^2 \rangle \qquad (4)$$

where $\delta\omega(t)$ is the fluctuation from the average frequency at time t. The average of eq 4 is over the initial time and over all the OD groups of the system. The results of the frequency time correlation are shown in Figure 4 for the three systems studied here. A fast decay is found in the short time part of the dynamics, which is then followed by a relatively slower decay. In general, the decay of the frequency correlation in supercritical systems is found to be much faster than that in ambient water.[16] Also, at the supercritical states, the rate of spectral diffusion is found to slow down with decrease of density. A biexponential fit of the type yields two time scales: one around 100 fs or less and the other one in the region of 150−600 fs with the shorter time scale carrying the larger weight for all the systems. The corresponding time scales for the ambient water are about 100 fs and 2 ps,[16] respectively. The details of these time scales and their weights are given in Table 1. We note that the decay of the frequency correlation at the lowest density show a bump at around 300 fs, which could not be reproduced by the above biexponential fit and a fit including a damped oscillatory function[13,16] should reproduce better the simulation results for this system. Indeed, such a fit was carried out which reproduced the bump quite well but without any significant changes of the relaxation times that are reported in Table 1.

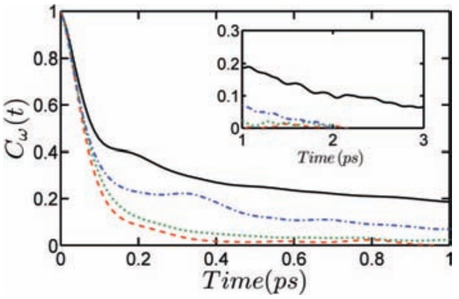

Figure 4. Time correlation functions of OD fluctuating frequencies of supercritical heavy water. The red dashed, green dotted, and blue dashed−dotted curves are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. The corresponding results for liquid D_2O under ambient condition are shown by the black solid curve (ref [16]). The inset shows the long-time behavior of the frequency correlations.

TABLE 1: Time Constants (ps) and Weights of Frequency Time Correlation Function of Heavy Water under Supercritical and Ambient Conditions

density (gm cm^{-3})	temperature (K)	τ_1	τ_2	a_1
1.1	673	0.1	0.15	0.88
0.78	673	0.08	0.19	0.78
0.39	673	0.06	0.56	0.70
1.1	300	0.1	1.85	0.68

4.2. Dynamics of Hydrogen Bonds and Dangling OD Groups. In an attempt to understand the origin of the two relaxation components of the frequency time correlation and their density dependence, we have calculated the lifetimes of hydrogen bonds in these systems by using the so-called population correlation function approach.[36−42] In this approach, we define two hydrogen bond population variables, $h(t)$ and $H(t)$, where $h(t)$ is unity when a particular water−water pair is hydrogen bonded at time t according to an adopted definition and zero otherwise and $H(t) = 1$ if the water−water pair remains continuously hydrogen bonded from $t = 0$ to time t, and it is zero otherwise. To calculate the lifetimes of the hydrogen bonds, we calculate the continuous hydrogen bond time correlation function,[37−40] $S_{HB}(t) = \langle h(0)H(t)\rangle / \langle h(0)^2\rangle$, where ⟨...⟩ denotes an average over all water−water pairs. Clearly, $S_{HB}(t)$ describes the probability that an initially hydrogen bonded water−water pair remains bonded at all times up to t. The associated integrated relaxation time τ_{HB} can be interpreted as the average lifetime of a hydrogen bond between two water molecules. The existence of a hydrogen bond between the D (of OD) and the O of a neighboring water is determined by using a simple geometric criterion that the D···O distance should be less than 2.35 Å. Note that this distance corresponds to the first minimum of the intermolecular D···O radial distribution function (results not shown here). The results of the continuous correlation

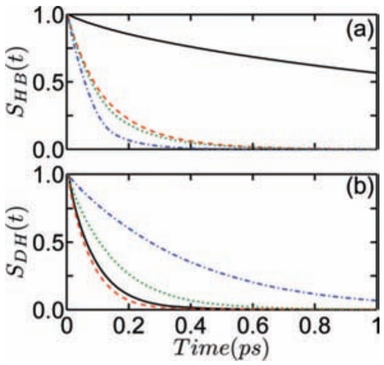

Figure 5. The time dependence of (a) continuous hydrogen bond and (b) dangling OD probability functions for supercritical heavy water. The red dashed, green dotted, and blue dashed−dotted curves are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. The corresponding results for liquid D_2O under ambient condition are shown by the black solid curve.

TABLE 2: Lifetimes (ps) of Hydrogen Bonds and Dangling OD Groups in Heavy Water under Supercritical and Ambient Conditions

density (gm cm^{-3})	temperature (K)	τ_{HB}	τ_{DH}
1.1	673	0.14	0.08
0.78	673	0.12	0.15
0.39	673	0.07	0.40
1.1	300	2.30	0.1

functions are shown in Figure 5 for all the systems studied here, and the calculated lifetimes of the hydrogen bonds are included in Table 2. It is seen that for the high density system (1.1 g cm^{-3}) the hydrogen bond lifetime matches with the slower component of spectral diffusion, whereas for the low density one (0.39 g cm^{-3}), the hydrogen bond lifetime matches with the faster component of the spectral diffusion. Thus, unlike ambient water, for supercritical water the slower component of spectral diffusion does not always capture the dynamics of hydrogen bonds; it depends on the density of the medium.

We next calculated the dangling OD correlation function $S_{DH}(t)$, which gives the probability that an initially dangling, i.e., non-hydrogen-bonded, OD group remains dangling at all times up to *t*. The associated integrated relaxation time τ_{DH} can be interpreted as the average lifetime of a dangling OD group of a D_2O molecule. The decay of $S_{DH}(t)$ is also shown in Figure 5, and the associated lifetimes are included in Table 2. It is interesting to note that while the decay of the hydrogen bond correlation becomes faster that of the dangling OD correlation becomes slower with decreasing density at the supercritical state. Also, at high density (1.1 g cm^{-3}), the decay of $S_{DH}(t)$ is very similar at the ambient and supercritical temperatures (Figure 5b), while the corresponding dynamics of the hydrogen bond correlation is very different (Figure 5a). It is seen that the slower component of the spectral diffusion at the low density (0.39 g cm^{-3}) and the faster component at the high density (1.1 g cm^{-3}) do roughly correspond to the lifetimes of dangling OD groups at these two densities, respectively, for the supercritical systems. Clearly, there is an interplay between the dynamics of hydrogen bonds and dangling OD groups in determining the rates of spectral diffusion: while the slower component is determined by the hydrogen bond and dangling OD lifetimes at high and low densities, respectively; the reverse is true for the faster component.

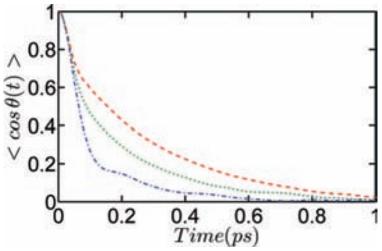

Figure 6. The rotational dynamics of OD bond vectors of supercritical heavy water. The red dashed, green dotted, and blue dashed−dotted curves are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively.

TABLE 3: Time Constants (ps) and Weights of the Relaxation of Rotational Function $\langle\cos\theta(t)\rangle$ of OD Bonds in Supercritical and Ambient Heavy Water

density (gm cm^{-3})	temperature (K)	τ_{rot}^{fast}	τ_{rot}^{slow}	a_{rot}^{fast}
1.1	673	0.09	0.28	0.15
0.78	673	0.08	0.25	0.45
0.39	673	0.06	0.15	0.60
1.1	300	0.1	10.0	0.1

4.3. Inertial Rotation. It is also instructive to look at the density dependence of the dynamics of OD rotational motion at supercritical states. In particular, the fast inertial component of the rotational relaxation is expected to be more significant at low densities, and such rotations can also alter the neighboring environment of an OD group and hence modulate its frequency. Also, since rotational motion plays a primary role in the breaking of hydrogen bonds, it would be interesting to see to what extent the fast inertial rotation contributes to the breaking of hydrogen bonds and hence to the spectral diffusion. In Figure 6, we have shown the decay of the orientational function $\langle\cos\theta(t)\rangle$, where $\theta(t)$ is the angle between the orientations of an OD vector at times 0 and *t* and the average is carried out over all the OD bonds of a system. A biphasic decay is clearly seen in the figure. There is a fast decay due to inertial rotation of the molecules, which is followed by a relatively slower decay. The time scales of a biexponential fit (τ_{rot}^{fast} and τ_{rot}^{slow}) and the associated weights are given in Table 3. For the low density (0.39 g cm^{-3}), which has the maximum weight for the inertial component, the inertial rotational time is found to be very close to the hydrogen bond lifetime signifying the fact that, in this system, hydrogen bonds break mainly through fast inertial rotation of water molecules. This is also reflected in the fact that the faster component of spectral diffusion at low density is very close to both the hydrogen bond lifetime and inertial rotational time. At high density (1.1 g cm^{-3}), on the other hand, the hydrogen bond lifetime is found to be longer than the inertial rotational time. This is due to the fact that at this higher density, the weight of the inertial component is minimum and hence slower diffusional rotation is also necessary for hydrogen bond breaking, which, in turn, decides the slower component of spectral diffusion. In this case, the inertial rotation rather helps a dangling OD to get hydrogen bonded. Hence, the inertial rotational time and dangling OD lifetime are close to each other, and they are also essentially identical with the faster component of the spectral diffusion at this density. The density of 0.78 g cm^{-3} is of intermediate nature. Here the inertial component of rotation has a higher weight compared to that of the higher density system, but still the weight is less than fifty percent, which means slower diffusional motion does make some contribution to the hydrogen bond breaking. Also, at this intermediate density, since the number of hydrogen bonds is significantly reduced, fast inertial rotation alone can not take a dangling OD group to the right kind of environment so as to form a hydrogen bond. Because of these subtleties, the lifetimes of both hydrogen bonds and dangling OD groups are found to be longer than the inertial rotational time with the former times contributing to the slower component of the spectral diffusion. Since the fast inertial rotation can also modulate the OD frequencies due to associated changes in interactions with the surroundings, this fast time scale shows up as the faster component of spectral diffusion at this density although it neither corresponds to hydrogen bond lifetime nor it stands for the lifetimes of dangling OD groups. To the best of our knowledge, such roles of an interplay between the dynamics of hydrogen bonds, dangling OD groups, and inertial rotation in vibrational spectral diffusion in aqueous systems is reported here for the first time.

4.4. Dipole Distributions and Electric Field Fluctuations. An advantage of the ab initio molecular dynamics method is that the changes in molecular polarity with changes of temperature and density can be calculated directly from the simulations. This is an important aspect of the studies of supercritical water since it is known that the solvation properties of supercritical water is different from that of ambient water and a reduction of the polarity of the molecules, in addition to their reduced hydrogen bonding properties, is believed to be a primary factor behind such different solvent characteristics of supercritical water. An altered polarity also changes the electric fields that act on different molecules, both in terms of their magnitude and fluctuation dynamics. Earlier, it has been shown that the electric field along an OD bond can be viewed as a good order parameter that correlates well with the stretch frequency of the OD bond.[34,43] In view of this, we calculated the distributions of dipole moments of the water molecules to see the changes in fluctuations and average dipole moments as we move to the supercritical state from the ambient state and also as we tune the density isothermally at the supercritical state and then we look at the equilibrium and dynamical characteristics of electric fields that are generated by the same charge distributions of the water molecules that give rise to their dipole moments.

Following previous work,[30,44] we have calculated the dipole moments of individual molecules in the supercritical fluid within the maximally localized Wannier functions and Wannier Function Centers method. In this approach, the Kohn−Sham orbitals at each time step is first transformed into maximally localized Wannier functions which allow the total electronic charge to be partitioned into individual molecular contributions[45,46] and provides a very convenient tool to quantitatively analyze the modifications of electronic properties of water in different environments and thermodynamic conditions. For analysis of large systems, like the ones of the present study, the information contained in Wannier functions is contracted by defining a Wannier Function Center (WFC) for each of the Wannier functions and assuming that the electronic charges of different Wannier orbitals are concentrated as point charges in their respective WFCs.[44,45] Clearly, WFCs provide very useful tools to study electronic properties and charge distributions of large systems in condensed phases. In the present work, we have made use of this method to calculate the dipole moments of water molecules, i.e., the dipole moments are calculated from the ion and WFCs positions along with their respective charges. The same ion and WFC charge distributions are also used to calculate the electric field on a D atom along the OD bond due to all other molecules in the system. A great advantage of this method is that, in the spirit of ref 34, we can calculate the collective electric field on a D atom that arises from all other molecules[47] and their periodic images and also a local electric field[47] on the same D atom that arises from the water molecule having the oxygen that is nearest to the D atom.

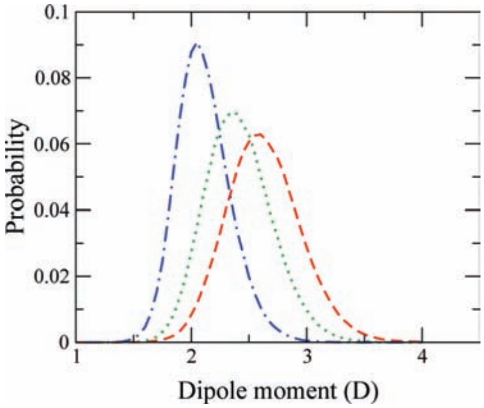

Figure 7. The distributions of molecular dipole moments in supercritical heavy water. The red dashed, green dotted, and blue dashed−dotted curves are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively.

In Figure 7, we have shown the dipole distributions of the three supercritical water systems studied here. As expected, the distributions move toward lower values upon decreasing the density. The average dipole moments are found to be 2.65, 2.43, and 2.1 D for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively, at 673 K. The average dipole moment of ambient water at 300 K is found to be 3.0 D by using the same method. These present dipole moment values are in general agreement with those of ref 30; the small differences could be attributed to slight differences in the density, temperature, and also in the simulation run length. Our calculated dipole moments of supercritical water clearly show a reduction of the polarity due to diminished polarization effects upon increasing the temperature and decreasing the density. At higher densities, hydrogen bonds still exist to a significant extent as confirmed by our hydrogen bond calculations (the number of hydrogen bonds per water is 2.8, 2.3, and 1.4 for the densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively, at 673 K), and hence the electric field induced by surrounding molecules through these hydrogen bonds polarizes the electronic charge distributions and enhances the molecular dipole moments in these systems.

In Figure 8, we have shown the decay of the correlations of electric field fluctuations for the three supercritical water systems. Results are presented for the time dependence of fluctuation correlations for both local and collective electric fields on a D atom (projected along the OD bond), and the results are averaged over electric fields on all the D atoms in a system. The results of the frequency correlations are also included for comparison. To smooth out the electric field fluctuations originating from intramolecular vibrations of covalent OD bonds, the instantaneous electric fields are smoothened over running time windows of 75 fs, which is roughly about five vibrational periods of intramolecular OD stretch vibration. The dynamics of the local and collective electric field correlations are found be rather close to each other at all densities, and both of them are found to follow closely the decay of the frequency correlation for the higher and intermediate density systems. For the lowest density of 0.39 g cm^{-3}; however, the beat or the weak oscillation in the frequency correlation at intermediate times, at around ∼300 fs, is not seen in the electric field correlations. The short and long-time decays of the electric field correlations, however, agree well with those of the frequency correlation for this system. A fit of the frequency correlation by a biexponential function including a damped

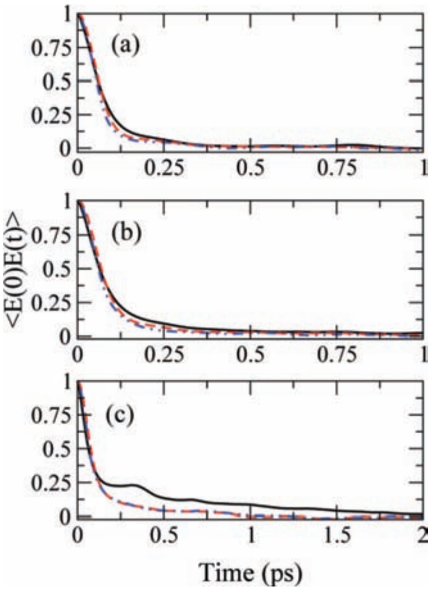

Figure 8. The time correlation functions of local (red dashed) and collective (blue dashed−dotted) electric field fluctuations on D atoms (projected along OD bonds). The black solid curve represents the time correlations of fluctuating stretch frequencies of OD bonds. (a), (b), and (c) are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively.

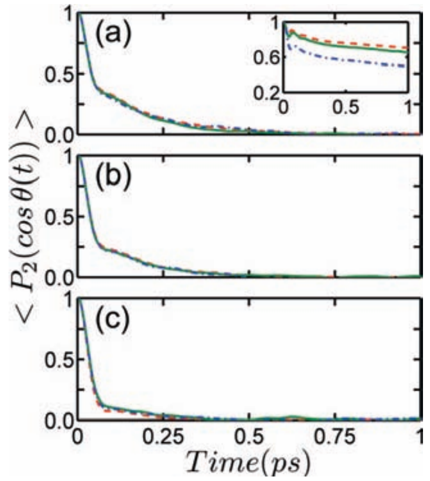

Figure 9. The time dependence of the second-rank orientational correlation function of OD bonds of different initial frequencies. The red dashed, green solid, and blue dashed−dotted curves are for OD frequency $\Delta\omega < -100$ cm^{-1}, $\Delta\omega = \pm 50$ cm^{-1}, and $\Delta\omega > 100$ cm^{-1}, respectively, where $\Delta\omega$ represents the deviation from the average frequency of a given system. The results of (a), (b), and (c) are for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. The inset in part a shows the corresponding results for liquid D_2O at 300 K (ref 52).

oscillatory term gives a frequency of about 85 cm^{-1} for this oscillation. Clearly, this oscillation would not have originated from the broad intermolecular peak reported by Boero et al.,[30] which was located at around 250 cm^{-1} and was attributed to the effects of hydrogen bond network destabilization on the librational and intermolecular stretch modes. It is possible that the oscillation in the present frequency correlation arises from small cluster formation at the lower density and the weak oscillation frequency of 85 cm^{-1} may correspond to a combination of intermolecular bending and weakened stretch modes of such small clusters, perhaps dimers in particular. A biexponential fit to the electric field correlations for this system produces the following relaxation times: 0.09 and 0.48 ps for the local field and 0.08 and 0.45 ps for the collective electric field, and these time constants are to be compared with the time scales of 0.06 and 0.56 ps for the frequency correlation (Table 1). Thus, apart from the beat or weak oscillation at intermediate times, the overall decay of electric field fluctuations seems to correlate well with that of frequency fluctuations. The fact that both local and collective electric fields follow closely the dynamics of frequency fluctuations seems to indicate that, for the present supercritical systems, the electric field of the nearest water plays the major role in determining the OD stretch frequencies and the electric fields from other water molecules play a relatively minor role. This could also be linked to a faster decay of spatial correlations of water molecules at supercritical states. The correlation coefficients (χ_E) between the OD stretch frequencies and local electric fields are found to be −0.63, −0.58, and −0.36 for densities 1.1, 0.78, and 0.39 g cm^{-3}, respectively. Hence, although the frequency fluctuations do correlate with electric field fluctuations which is in general agreement with the results of earlier studies on ambient water,[34,43] the strength of such correlations decreases with decreasing density for supercritical water. Also, for the present supercritical systems, the magnitudes of frequency−electric field correlations are found to be similar to those of frequency−distance (D···O) correlations discussed in section 3.

5. Frequency Dependence of Rotational Motion

An important aspect of water dynamics is the frequency dependence of its rotational motion.[48−51] Under ambient conditions, some of the recent polarization resolved time dependent infrared spectroscopic studies have revealed that the short-time reorientation of water molecules occurs at a faster rate on the blue side of the stretch band than on the red side, and at long times, the relaxation becomes frequency independent.[48,51] Initially, the long-time frequency independent decay was reported to occur after the spectral diffusion time of about 1.5 ps,[48] but more recent studies have shown that the relaxation becomes frequency independent, within the experimental errors, after about 200 fs.[51] Only the inertial component of rotation, which is responsible for the fast initial decay within first 200 fs, was found to be affected by the choice of frequency of the OD oscillators. Such frequency-dependent short-time dynamics was attributed to varying hydrogen bond strengths for different stretch frequencies: OD groups absorbing in the blue are linked to weak hydrogen bonds, and hence they can rotate more freely with a larger amplitude of the inertial motion compared to those at the red side which are linked to stronger hydrogen bonds. After this initial relaxation, the molecules lose their memory of initial hydrogen bonded state and hence they all rotate at the same rate at long times. However, no such polarization and frequency resolved study of rotational motion has yet been carried out for supercritical water.

Since the experimentally measured rotational anisotropy in polarization resolved experiments is directly related to the second-rank rotational function $\langle P_2(\cos\theta(t))\rangle$ (P_2 is the Legendre Polynomial of rank 2), we have calculated this quantity as a function of OD frequency. We first divided the entire OD frequency distribution into three regions: Region I corresponds to frequencies less than $\bar{\omega} - 100$ cm^{-1}, region II contains frequencies in the range $\bar{\omega} \pm 50$ cm^{-1}, and region III corresponds to frequencies higher than $\bar{\omega} + 100$ cm^{-1}, where $\bar{\omega}$ is the average frequency of OD bonds for a given system and the time dependent rotational function is then calculated subject to the constraint that the frequency of the tagged OD bond belongs to a given region at time $t = 0$. The results of these calculations are shown in Figure 9 where the corresponding results for ambient water[52] are also included for comparison. As expected, for all the systems, it is found that there is a fast inertial decay followed by a slower relaxation. Importantly, unlike ambient water, essentially no frequency dependence is observed for the rotational relaxation in supercritical systems which, in part, can be attributed to faster spectral diffusion in these systems. The amplitudes of the inertial rotation are found to be 0.55, 0.72, and 0.9 for densities 1.1, 0.78, and 0.39 g cm^{-3} but remain essentially unchanged with respect to changes of frequencies. For supercritical water, the memory of the initial hydrogen bonding state is lost very fast, and hence all OD groups are found to rotate in essentially the same rate, even during the period of fast inertial motion, irrespective of their initial frequency or hydrogen bonding state. Another contributing factor to this frequency independence is the fact that the role of hydrogen bond strength as a significant determinant of rotational motion is greatly reduced by the higher thermal energy of supercritical water. We note in this context the recent work of Fayer and co-workers[51] where the frequency dependence of reorientational motion in liquid water was studied at varying temperatures from 1 to 65 °C. The amplitude of the initial inertial relaxation was found to depend rather strongly on the OD frequency at higher temperatures due to a correlation between the OD frequency and D···O hydrogen bond strength. However, no such frequency dependence was found at low temperatures which was attributed to increasing collective effects so that the strength of the D···O hydrogen bond was no longer the single determinant of OD rotation. The present study shows that, at very high temperature, the amplitudes of inertial rotation and hence the rates of rotational relaxation again become frequency independent due to fast interconversion of various hydrogen bonding states and a reduced role of hydrogen bond strength as a determinant of rotational motion because of higher thermal energy. Of course, these two aspects are interrelated. For ambient water, however, a clear increase of the amplitude of inertial rotation is observed with increasing frequency (inset of Figure 7a). Thus, the slope of the inertial amplitude versus frequency curve[51] is expected to show a nonmonotonic temperature dependence as one moves from very low to supercritical temperatures.

6. Summary and Conclusions

We have presented a first principles theoretical study of vibrational spectral diffusion in supercritical heavy water at three different densities ranging from 1.1 to 0.39 g cm^{-3}. Our calculations are based on ab initio molecular dynamics simulations for trajectory generation and time series analysis based on wavelet method for frequency calculations. No empirical potential parameters are involved in the present study. We first looked at the frequency distributions and frequency−structure correlations of D_2O molecules as functions of solvent density and the results of supercritical water are compared with those of ambient water.[16] It is found that the frequency distributions of supercritical water are narrower and blue-shifted compared to those of ambient water. Also, at the supercritical temperature, a decrease of width and an increase of average frequency is found with decrease of density which are in general agreement with experimental findings.[17] Our calculations of OD frequency−distance (D···O) conditional probabilities reveal that the rate of increase of OD frequency with D···O distance gradually decreases with lowering of density. Also, the maximum probability moves to a larger D···O distance-higher frequency value with decreasing density. At the same density of 1.1 g cm^{-3}, the shape of the contour plots of probability distribution of supercritical water is found to be more horizontal and extended to larger D···O distances than those of ambient water, which can be linked to weaker and less number of hydrogen bonds in the supercritical state. The frequency−distance distributions for the lower densities are even more horizontal and stretched toward higher distances due to the presence of increased number of dangling OD bonds in these systems. The statistical correlations between the stretch frequency and D···O distance are quantified by calculating the so-called correlation coefficients between these two quantities. It is found that the correlation remains significant for the supercritical water at higher density. Even for the lowest density supercritical water studied here, the correlation coefficient is still far above zero which means a statistical correlation between the stretch frequency and the nearest D···O distance continues to exist, although to a lesser extent, even at elevated temperatures of supercritical states. Calculations are also made for the correlations between the electric fields on D atoms (along OD bonds), and the stretch frequencies and the magnitudes of such frequency−electric field correlations are found to be similar to those of frequency−distance (D···O) correlations discussed above. Between the local and collective electric fields, the local electric field is found to correlate somewhat better with the OD stretch frequencies which seems suggest the primary importance of the nearest water, i.e., the one having the oxygen nearest to the D atom of the OD bond, in influencing the vibrational stretch frequency of an OD bond.

The vibrational spectral diffusion in supercritical water is found to occur with a much shorter time scale compared to that in ambient water. In the supercritical phase, the frequency time correlation function decays with two time scales: one around 100 fs or less and the other in the region of 150−600 fs with the short time scale having the larger weight. More importantly, it is found that, unlike ambient water, for supercritical water the slower component of the spectral diffusion does not necessarily correspond to the dynamics of hydrogen bonds at all densities. Rather, an interplay between the dynamics of hydrogen bonds, dangling OD groups, and inertial rotation of OD bonds determines the times scales of spectral diffusion in a rather subtle manner. While the slower component of spectral diffusion at high density is determined by the lifetimes of hydrogen bonds, it is the lifetime of dangling OD groups that decides the slower component at the low density and the reverse is true for the faster components. The fast inertial rotation can also modulate the OD frequencies due to associated changes in interactions with the surroundings, and in fact, this fast inertial rotational time scale also shows up as the faster component of spectral diffusion. We have also calculated the decay of the time correlations of electric fields (both local and collective) on D atoms along an OD bond and compared its dynamics with that of the frequency correlations. Apart from a beat or weak oscillation at intermediate times for the lowest density system, the overall decay of both electric field fluctuations seems to correlate well with that of frequency fluctuations. The fact that both local and collective electric fields follow closely the dynamics of frequency fluctuations seems to suggest again that, for the present supercritical systems, the electric field of the nearest water plays the major role in determining the OD stretch frequencies and the electric fields from other water molecules play a relatively minor role. Also, unlike ambient water, no frequency dependence is observed for the rotational relaxation which can be attributed, in part, to a faster interconversion of different hydrogen bonding states in these supercritical systems. Also, the much higher thermal energy of supercritical states reduces the role of hydrogen bond strength as a significant determinant of rotational motion.

We note that the present study is based on a time dependent frequency analysis of all OD modes of supercritical heavy water of varying density. The time-dependent infrared spectroscopic experiments on liquid or supercritical water, however, consider dilute mixtures of HOD in H_2O or D_2O. We have chosen D_2O purely from a computational efficiency point of view considering the fact that the present calculations are done at the level of first principles without using any empirical model potentials. For a meaningful mimicking of dilute HOD/H_2O or HOD/D_2O fluids, one necessarily needs to consider a very large system to have sufficient number of HOD molecules for statistically reliable results but simulations of such large systems through ab initio molecular dynamics is a very difficult, if not practically impossible, task at present. Hence, like our previous work on ambient water,[16] we considered supercritical aqueous systems of only D_2O and considered every OD bond as a local vibration for the purpose of frequency calculations. This greatly enhanced the number of OD vibrations of interest compared to that of a dilute HOD/H_2O systems of similar sizes and thus allowed us to obtain statistically meaningful results for spectral diffusion from our finite simulation systems. Since the experimental complications of excited-state vibrational energy relaxation through intermolecular resonant channels are not there in the present simulation systems, we expect that the present results of spectral diffusion are not significantly affected by the above choice of treating every OD bond as a local oscillator of interest. Besides, as discussed in section 2, the instantaneous frequencies are calculated directly from the simulated time dependence of OD oscillations and thus any effects of intermode coupling on the vibration of an OD group are implicitly taken into account in our calculations, and hence, the calculated frequencies can be treated as effective local frequencies of OD oscillators. Although, one could have used normal modes to analyze the spectral diffusion, such an analysis ought to be complicated by the fact that the frequency perturbations of such modes arise from two donor hydrogen bonds as compared to only one when the analysis is made in terms of local modes. We finally note that since the present study is based on ab initio molecular dynamics simulations without involving any empirical potentials, it can be readily extended to investigate vibrational spectral diffusion and associated dynamical properties of supercritical aqueous solutions containing ionic and molecular solutes where model potentials are not readily available.

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