Rotational Motion in Liquid Water Is Anisotropic: A Nuclear Magnetic Resonance and Molecular Dynamics Simulation Study

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Abstract: Experimental NMR measurements of the deuterium and ^{17}O T_1 relaxation times in deuterium-enriched liquid water have been performed from 275 to 350 K. These relaxation times can yield rotational correlation times of appropriate molecule-fixed unit vectors if the quadrupole coupling constants and asymmetry parameters are known. We determine the latter from ab initio studies of water clusters and experimental chemical shift measurements. We find that the rotational correlation time for the OD bond vector in $D_2{}^{16}O$ varies from 5.8 ps at 275 K to 0.86 ps at 350 K, and that the rotational correlation time for the out-of-plane vector of dilute $D_2{}^{17}O$ in $D_2{}^{16}O$ varies from 4.4 ps at 275 K to 0.64 ps at 350 K. These results indicate that the rotational motion of water is anisotropic. Molecular dynamics simulations of liquid water are in good agreement with these experiments at the higher temperatures, but the simulation results are considerably faster than experiment at the lower temperatures.

I. Introduction

The molecular structure and dynamics of liquid water have been the subjects of a very large number of experimental[1−12] and theoretical[13−37] studies. One important issue involves the nature of the rotational motion of individual water molecules: Is it isotropic or anisotropic? Several experimental and theoretical works have concluded that the rotational motion is isotropic,[10−12,30] which is perhaps surprising given the very directional nature of hydrogen bonding and the low symmetry of the water molecule. Other simulation studies indicate that the rotational motion is anisotropic.[31,33]

Nuclear magnetic resonance (NMR) T_1 relaxation is due, at least in part, to rotational dynamics. The interpretation of T_1 relaxation studies involving protons can be difficult, since in this case the relaxation comes from both intramolecular and intermolecular dipole−dipole interactions. On the other hand, the T_1 relaxation of a quadrupolar nucleus is dominated by intramolecular interactions. In particular, the relaxation time of a quadrupolar nucleus is related to the rotational correlation time of the principal axis of the electric field gradient tensor at the nucleus. In water the principal axes for deuterium and ^{17}O are orthogonal. Thus T_1 experiments on water enriched with deuterium and ^{17}O can yield the rotational correlation times for two different molecule-fixed unit vectors.

In fact, to determine the rotational correlation time from a T_1 experiment, one also needs the value of the quadrupole constant, χ, and the asymmetry parameter, η. These are known for both deuterium and ^{17}O for an isolated water molecule:[38] $\chi_D = 308$ kHz, $\eta_D = 0.14$; $\chi_O = 10.2$ MHz, $\eta_O = 0.75$. But since hydrogen bonding significantly affects the electronic structure of the water molecule, the quadrupole coupling "constant" and asymmetry parameter depend strongly on a particular molecule's environment. Indeed, the values for ice Ih[4] are quite different from those for an isolated water molecule: $\chi_D = 213$ kHz, $\eta_D = 0.1$; $\chi_O = 6.66$ MHz, $\eta_O = 0.94$. Therefore, to extract rotational correlation times from T_1 measurements one needs accurate temperature-dependent values of the quadrupole coupling constants and asymmetry parameters for liquid water.

An interesting approach to obtaining these parameters was put forth by Huber and co-workers.[28,29] Molecular dynamics simulations were used to generate representative configurations for liquid water. Ab initio calculations on clusters of molecules from these configurations were then performed, and the quadrupole coupling constants and asymmetry parameters were determined for each nucleus in the interior of the cluster. Averages of these numbers gave $\chi_D = 256$ kHz, $\eta_D = 0.164$ and $\chi_O = 8.9$ MHz, $\eta_O = 0.72$ for water at 300 K.

Our approach[39−41] is somewhat similar in spirit to the above, and allows us to obtain more expeditiously the necessary coupling constants and asymmetry parameters as a function of temperature, pressure, and even physical state. Optimized geometries of various water clusters are obtained from ab initio calculations. For each nucleus in the cluster the quadrupole coupling constant, asymmetry parameter, and chemical shift are calculated. T_1 is related theoretically to the rotational correlation time (see below) through the combination $\chi^2(1 + \eta^2/3)$,[42] which is found to be linearly correlated with the chemical shift. The chemical shifts are then measured as a function of temperature, leading to temperature-dependent values for $\chi^2(1 + \eta^2/3)$. From the measured T_1 values we can obtain rotational correlation times as a function of temperature.

The sample measured was 99% deuterium-enriched water with natural abundance ^{17}O. We find, from the deuterium relaxation experiments, that the rotational correlation time for the OD bond vector (primarily for $D_2{}^{16}O$) ranges from 5.8 ps at 275 K to 0.86 ps at 350 K. From the ^{17}O relaxation experiments we find that the rotational correlation time for the out-of-plane vector of dilute $D_2{}^{17}O$ in $D_2{}^{16}O$ varies from 4.4 ps at 275 K to 0.64 ps at 350 K. While these correlation times are for D_2O with different isotopes of oxygen, because the oxygen

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atom is very close to the center of mass of the water molecule, changing the isotope of oxygen leads to very small changes in the moments of inertia. Therefore it is quite reasonable to compare the two correlation times. The ratio of the OD bond vector correlation time to the out-of-plane vector correlation time is approximately 1.33 and independent of temperature. This large difference cannot be ascribed to the very small differences in the moments of inertia, leading to the conclusion that the rotational motion of deuterium-enriched water is anisotropic. It is reasonable to assume that the motion of ordinary water is also anisotropic.

To complement these experimental results we have performed molecular dynamics simulations of liquid heavy water from 275 to 350 K, using the SPC/E model,[19] and have calculated the rotational correlation times of the two relevant molecule-fixed unit vectors. Our results are in good agreement with experiment at the higher temperatures, but the theoretical correlation times are considerably shorter than those from experiment at the lower temperatures. The simulations support the assertion that the rotational motion of liquid water is anisotropic.

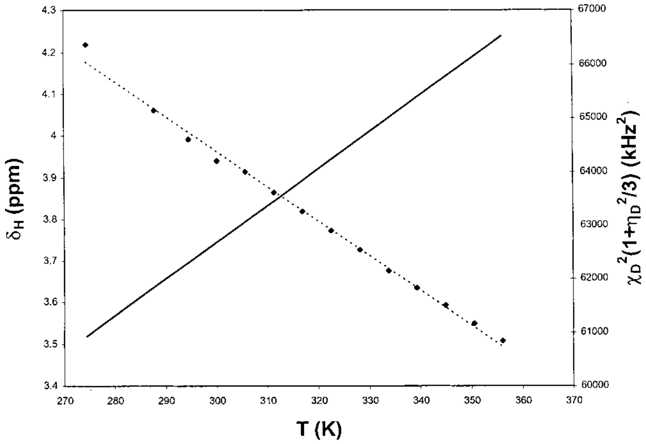

Figure 1. The temperature dependence of δ_H, the experimental isotropic proton chemical shift (diamonds) and fit to it (dashed line), and the deuterium quadrupole coupling factor, $\chi_D^2(1 + \eta_D^2/3)$ (solid line). The proton chemical shift is relative to TMS.

II. Experimental Section

^{2}H (and also ^{1}H—see below) NMR spectra were acquired on a home-built spectrometer operating at 6.93 T using a 6 mm diameter receiver coil; this field corresponds to a proton resonance frequency of 295 MHz. The ^{17}O spectra were taken on a Bruker Avance 300 MHz spectrometer. The temperature was controlled to ±0.1 °C using a home-built temperature controller[43] and the Bruker VT unit, respectively. The temperature was calibrated using the methanol[44] thermometer method. The magnet used with the homemade spectrometer is an eighth-order corrected solenoid manufactured by Cryomagnet Systems. A Bruker magnet was used with the DMX-300 instrument. The magnets and their environments are sufficiently stable that no internal lock is necessary for periods up to several hours. The chemical shift measurements are accurate to ±0.01 ppm. The relaxation times were measured using a standard 180−τ−90 pulse sequence and the data were fit with a standard three-parameter fit program. All relaxation time values are the average of at least three or more separate measurements.

The D_2O was obtained from Cambridge Isotope Lab. All sample tubes were cleaned with nitric acid, rinsed with deionized water, soaked in EDTA, rinsed with deionized water, and then rinsed with dry, reagent acetone. They were then dried for 24 h in a vacuum oven prior to use. The samples were subjected to several freeze−pump−thaw cycles to remove any dissolved oxygen and then sealed under vacuum.

The proton chemical shift for neat $H_2{}^{16}O$ as a function of temperature from 275 to 350 K is shown in Figure 1, and the ^{17}O chemical shift for dilute $D_2{}^{17}O$ in $D_2{}^{16}O$ is shown in Figure 2. The ^{1}H chemical shift is referenced to TMS, and the ^{17}O chemical shift is referenced to monomer water in an H_2O/CCl_4 mixture (0.03 mol % water) at 273 K. The deuterium T_1 relaxation times for $D_2{}^{16}O$ as a function of temperature are shown in Figure 3, along with a fit of earlier results due to Hindman.[10] The two sets of data were taken almost 30 years apart and with different samples and very different spectrometers; they agree to within ±1%. This provides ample evidence that if the sample temperature is carefully controlled, T_1 measurements can be made to

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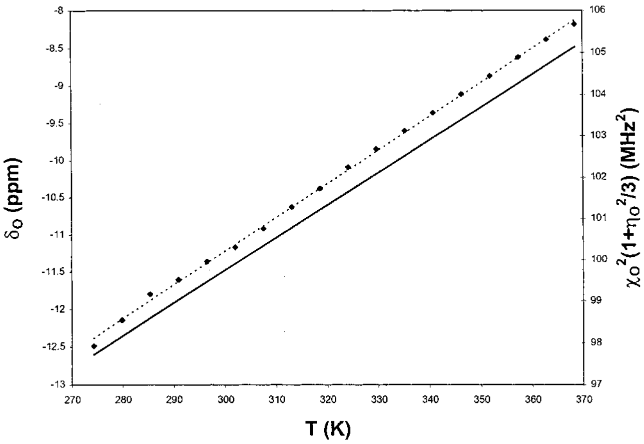

Figure 2. The temperature dependence of δ_O, the experimental isotropic oxygen chemical shift (diamonds) and fit to it (dashed line), and $\chi_O^2(1 + \eta_O^2/3)$ (solid line). The chemical shift is relative to monomer water in CCl_4 at 273 K.

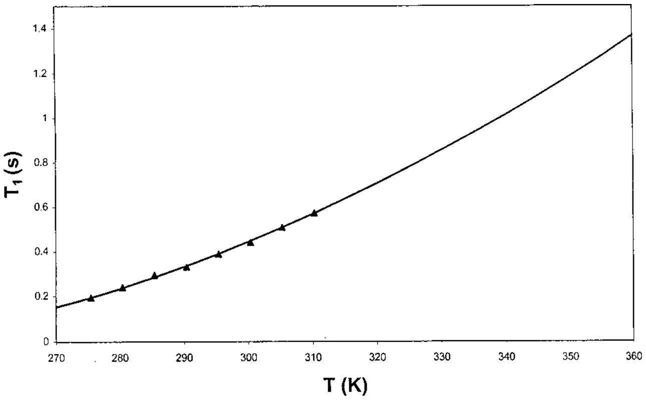

Figure 3. The deuterium relaxation time, T_1, as a function of temperature for neat $D_2{}^{16}O$. The diamonds are our data and the solid line is the best fit from the work of Hindman.[10] The two data sets agree to within ±1%.

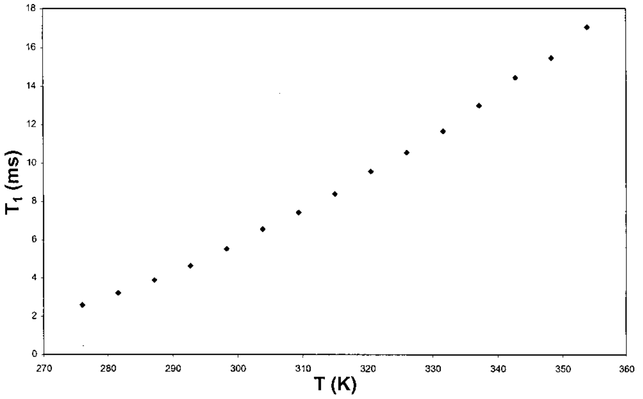

Figure 4. The oxygen relaxation time, T_1, as a function of temperature for dilute $D_2{}^{17}O$ in $D_2{}^{16}O$.

an accuracy of about 1%. ^{17}O T_1 relaxation times for dilute $D_2{}^{17}O$ in $D_2{}^{16}O$ as a function of temperature are shown in Figure 4.

III. Determination of Temperature-Dependent Quadrupole Coupling Constants and Asymmetry Parameters

We consider nine water clusters, including cyclic, linear, cage, and star structures, with varying numbers of hydrogen bonds. For each cluster we perform ab initio calculations at the B3LYP/6-31+G* level of theory.[45] The geometry of each cluster was optimized, and the NMR chemical shielding and electric field gradients were calculated at each hydrogen and oxygen nucleus in each cluster. Theoretical quadrupole coupling constants and asymmetry parameters were calculated from the electric field gradients using a value of 2.860 mb for the deuterium nuclear quadrupole moment and a value of −25.78 mb for the oxygen nuclear quadrupole moment.[46]

As in our previous work,[39−41] it is found that deuterium chemical shifts are linearly correlated with deuterium quadrupole coupling constants, and with the combination $\chi_D^2(1 + \eta_D^2/3)$. The same is true for ^{17}O. One next assumes that in the liquid, the average coupling constants, asymmetry parameters, and chemical shifts are correlated in the same way. Therefore, by measuring the deuterium and ^{17}O chemical shifts in the sample of interest (dilute $D_2{}^{17}O$ in $D_2{}^{16}O$) we can obtain the all-important quantity $\chi^2(1 + \eta^2/3)$ for each nucleus as a function of temperature.

In fact, proton chemical shifts can be measured more easily than deuterium chemical shifts, because the line widths for deuterium are significantly broader. Furthermore, proton chemical shifts are measured with respect to the TMS standard, whereas there is no common standard for deuterium. Except for a small isotope effect, when measured in ppm the proton chemical shift in H_2O should be the same as the deuterium chemical shift in D_2O; indeed, we have verified that the proton chemical shift in ppm of bulk H_2O, with respect to the reference of monomer H_2O in carbon tetrachloride, and the deuterium chemical shift in ppm of bulk D_2O, with respect to the reference of monomer D_2O in carbon tetrachloride, differ by less than 0.050 ppm. Therefore, instead of measuring deuterium chemical shifts in D_2O, we measured proton chemical shifts in H_2O, as a function of temperature. Since the *calculated* proton and deuterium chemical shieldings are the same, we can equally well correlate proton chemical shifts with deuterium quadrupole coupling constants and asymmetry parameters. This, together with our measured proton chemical shifts, leads to $\chi^2(1 + \eta^2/3)$ for deuterium as a function of temperature.

Theoretical proton chemical shieldings were referenced to that for TMS, and theoretical ^{17}O chemical shieldings were referenced to that for (isolated) water monomer, to yield chemical shifts. Recall that the experimental chemical shifts were relative to TMS and to water monomer in CCl_4, respectively. Since the intermolecular interactions between water and carbon tetrachloride are very weak, we consider the comparison for ^{17}O to be reasonable.

The correlations between the calculated deuterium quadrupole coupling constant (open squares) and $\chi_D^2(1 + \eta_D^2/3)$ (diamonds) with the calculated proton isotropic chemical shift are shown in Figure 5. As can be seen, the chemical shift values for the protons in the various water clusters range from about 0 ppm for monomer water to about 7 ppm for the protons that are strongly hydrogen bonded in the larger water clusters. The values for χ_D range from 310 kHz for water monomer and non-hydrogen-bonded protons to 190 kHz for the strongly hydrogen-bonded protons. Both χ_D and $\chi_D^2(1 + \eta_D^2/3)$are approximately linearly correlated with the chemical shift. The linear relation between the isotropic proton chemical shift, δ_H, and the deuterium quadrupole coupling factor, $\chi_D^2(1 + \eta_D^2/3)$, is given by

$$\chi_D^2(1 + \eta_D^2/3) = - 8197.6\delta_H + 95184 \qquad (1)$$

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[45] Frisch, M. J.; et al. *Gaussian98*, Revision A.6; Gaussian: Pittsburgh, PA, 1998.

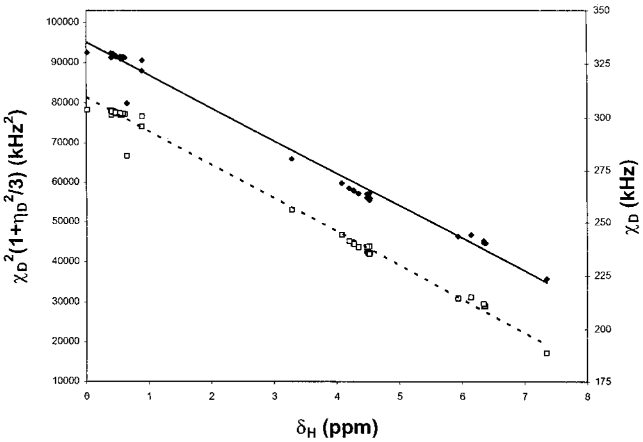

Figure 5. The correlations between the deuterium quadrupole coupling constant (open squares), $\chi_D^2(1 + \eta_D^2/3)$ (diamonds), and the proton isotropic chemical shift, δ_H. The Gaussian98 calculations for both quantities were done at the B3LYP/6-31+G* level of theory. Also shown are linear fits to the data.

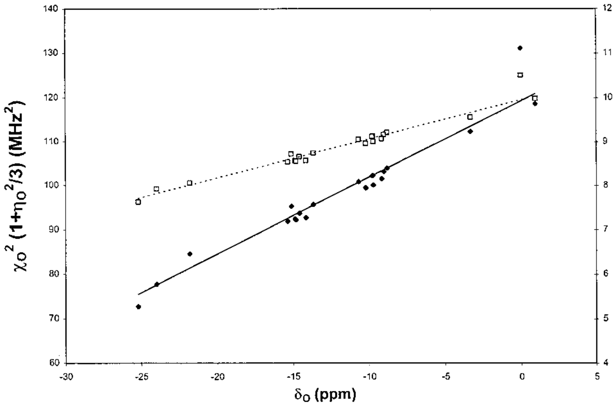

Figure 6. The correlations between the oxygen quadrupole coupling constant (open squares), $\chi_O^2(1 + \eta_O^2/3)$ (diamonds), and the oxygen isotropic chemical shift, δ_O. The Gaussian98 calculations for both quantities were done at the B3LYP/6-31+G* level of theory. Also shown are linear fits to the data.

where δ_H is in ppm and χ_D is in kHz. A similar relation holds for δ_H and χ_D:

$$\chi_D = -15.97\delta_H + 309.88 \tag{2}$$

These are shown graphically in Figure 5; the R^2 values are both 0.99.

Similar results for the correlations between the ^{17}O chemical shift and quadrupole coupling constant and factor are shown in Figure 6. The value of $\chi_O^2(1 + \eta_O^2/3)$ ranges from 131 MHz^2 for monomer water down to 72 MHz^2 for the most strongly hydrogen-bonded oxygen in the larger water clusters. The value for χ_O ranges from about 8 to 10 MHz. The linear relation between the chemical shift and the quadrupole coupling factor is given by

$$\chi_O^2(1 + \eta_O^2/3) = 1.74\delta_O + 119.24 \tag{3}$$

while the linear relation between the chemical shift and the quadrupole coupling constant is

$$\chi_O = 0.0893\delta_O + 9.9573 \tag{4}$$

δ_O is in ppm and χ_O is in MHz. These linear relations are shown in Figure 6; the R^2 values are 0.95 and 0.96, respectively.

To obtain the temperature dependencies of the quadrupole coupling factors we first fit the experimental chemical shifts in Figures 1 and 2 as a function of temperature to get

$$\delta_H = -0.0084T + 6.48 \tag{5}$$

$$\delta_O = 0.0453T - 24.83 \tag{6}$$

where T is in Kelvin and the chemical shifts have units of ppm. These fits are shown in Figures 1 and 2, and the R^2 values for both are 0.99.

These can then be combined with eqs 1−4 to give

$$\chi_D = 0.134T + 206.4 \tag{7}$$

$$\chi_O = 0.00405T + 7.74 \tag{8}$$

$$\chi_D^2(1 + \eta_D^2/3) = 68.86T + 42064 \tag{9}$$

$$\chi_O^2(1 + \eta_O^2/3) = 0.0788T + 76.04 \tag{10}$$

These results for the quadrupole coupling factors are shown in Figures 1 and 2.

The quadrupole coupling constant for deuterium, from eq 7, ranges from 243 kHz at 275 K to 253 kHz at 350 K, and is 247 kHz at 300 K. This latter value should be compared with the theoretical value of 256 ± 5 kHz obtained by Eggenberger et al.[29] Those workers also found a similar weak temperature dependence. The quadrupole coupling constant for ^{17}O, from eq 8, ranges from 8.85 MHz at 275 K to 9.16 MHz at 350 K, and is 8.96 MHz at 300 K, in excellent agreement with the value of 8.9 ± 0.3 MHz found by Eggenberger et al.[28] Leyte and co-workers have used experimental approaches to obtain these quadrupole coupling constants; they find respectively 253 ± 6 kHz and 8.0 ± 0.2 MHz.[12]

IV. Rotational Correlation Times

For a nucleus with spin quantum number I, it is well-known that the NMR relaxation time, T_1, is related to the quadrupole coupling constant, χ, the quadrupole asymmetry parameter, η, and the rotational correlation time, τ, by[42]

$$\frac{1}{T_1} = \frac{3\pi^2}{10}\frac{2I + 3}{I^2(2I - 1)}\chi^2\left(1 + \frac{\eta^2}{3}\right)\tau \tag{11}$$

τ is given by the time integral of the second-rank rotational time-correlation function:

$$\tau = \int_0^\infty \mathrm{d}t\langle P_2(\hat{u}(t)\cdot\hat{u}(0))\rangle \tag{12}$$

$\hat{u}(t)$ is the unit vector along the principal axis of the molecular coordinate system that diagonalizes the electric field gradient tensor at the nucleus, and $P_2(x)$ is the second Legendre polynomial. The angular brackets denote an ensemble average.

In the water molecule, for deuterium the principal axis is the OD bond vector, while for ^{17}O it is the out-of-plane vector. Thus in this case the deuterium and oxygen rotational correlation times, τ_D and τ_O, respectively, correspond to motion of orthogonal unit vectors.

From the measured T_1 relaxation times in Figures 3 and 4, and eqs 9 and 10 for the temperature-dependent quadrupole coupling factors, we can determine the correlation times from the above. For deuterium and ^{17}O, I is 1 and $^5/_2$, respectively.

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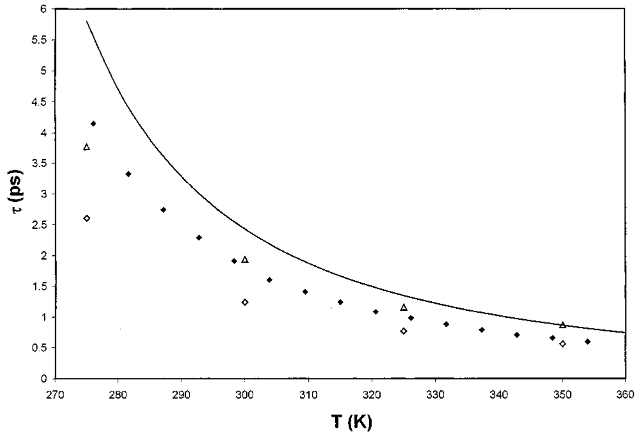

Figure 7. Rotational correlation times vs temperature for deuterium (solid line) and oxygen (diamonds). Also shown are results from molecular dynamics simulations for deuterium (open triangles) and oxygen (open diamonds).

The results are shown in Figure 7. The solid line for deuterium comes from Hindman's fit.[10] We see that both correlation times are quite temperature dependent, ranging from 5.8 ps at 275 K to 0.86 ps at 350 K for deuterium, and from 4.4 ps at 275 K to 0.64 ps at 350 K for oxygen. The more or less constant ratio of these times of about 1.33 unambiguously shows that the rotational motion of water molecules in liquid water is anisotropic, in that the correlation times for two orthogonal unit vectors are not equal.

V. Molecular Dynamics Simulations

Molecular dynamics simulations were performed in the microcanonical (NVE) ensemble using the SPC/E potential[19] for two different isotopes of water ($D_2{}^{16}O$ and $D_2{}^{17}O$) at four different temperatures (275, 300, 325, and 350 K). In each case, the system consisted of 500 molecules of that isotope. We used periodic boundary conditions, and the long-range electrostatic interactions were treated with an approximation to the Ewald summation as discussed by Adams and Dubey.[47] The equations of motion were integrated using the leapfrog algorithm[48,49] with a time step of 1 fs, and the rotational degrees of freedom were treated using quaternions.

The molecules were initially arranged in a cubic box with their centers of mass randomly displaced short distances from face-centered cubic lattice sites. The size of the box is chosen so that the molecular density is the same as the experimental value for H_2O at that temperature.[50] Center-of-mass and angular velocities were assigned randomly from a Boltzmann distribution. To facilitate the "melting" of the lattice, an initial temperature of 400 K was used. To maintain this temperature as the lattice melted, the velocities of the molecules were periodically rescaled to 400 K. After running for 20 ps, the system was then cooled to the desired temperature by rescaling the velocities of the molecules. Equilibration continued in this way until the desired temperature was maintained to within ±1 K for 80 ps without adjustment.

A subsequent run of 40 ps followed, during which the correlation functions were evaluated from 0 to 5 ps. Finally, the correlation time was evaluated by numerical integration. As the correlation function had not reached zero within the time it was explicitly calculated, it was assumed to be exponential at long times, and extrapolated accordingly. At lower temperatures, the correlation functions decay rather slowly. In some cases, it was such that the assumption of exponential behavior after 5 ps was questionable. If at 5 ps the function had not decayed to less than 10% of its initial value, the simulation was repeated, running for 80 ps and evaluating the correlation function out to 10 ps.

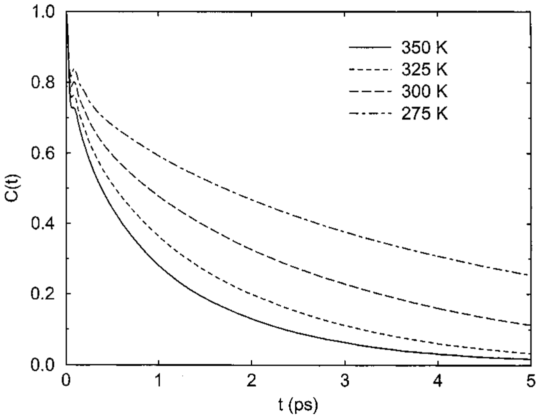

Figure 8. $C(t)$ for $D_2{}^{16}O$ at four different temperatures. $\hat{u}$ is the OD bond vector. The integral from zero to infinity gives τ_D.

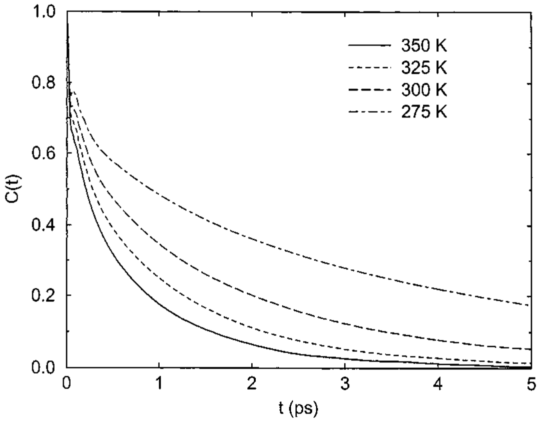

Figure 9. $C(t)$ for $D_2{}^{17}O$ at four different temperatures. $\hat{u}$ is the out-of-plane vector. The integral from zero to infinity gives τ_O.

The rotational correlation function $C(t) = \langle P_2(\hat{u}(t)\cdot\hat{u}(0))\rangle$ for the OD bond vector of $D_2{}^{16}O$ and for the out-of-plane vector of $D_2{}^{17}O$ are shown in Figures 8 and 9, respectively. One clearly sees that overall the decay is not at all exponential, and that there is an extremely fast initial decay on the order of 25 fs. Also, the rotational dynamics clearly speeds up as the temperature is increased. The rotational correlation times, τ_D and τ_O, from the integrals of the $C(t)$ in Figures 8 and 9, respectively, are shown in Figure 7 along with the experimental values. As can be seen, the results are in good agreement with experiment at the highest temperature. However, at lower temperatures, the calculated correlation times are considerably shorter than those from experiment. The ratio of the two correlation times, τ_D/τ_O, from simulation is roughly 1.5 and independent of temperature. This is in reasonable agreement with the ratio of the experimental correlation times, which is about 1.33, and independent of temperature.

The fact that the simulation gives correlation times shorter than found experimentally at the lower temperatures is perhaps not so surprising, since the SPC/E potential is known to

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underestimate the number of hydrogen bonds per molecule.[51] With fewer hydrogen bonds the molecules would be able to rotate more freely, and hence the correlation time would be shorter. This effect would be most prevalent at low temperatures where the molecules would form more hydrogen bonds on average.

We might note that for the ^{17}O relaxation the simulated and experimental systems are not identical: the simulation is for neat $D_2{}^{17}O$, while the experimental measurements were performed on a dilute mixture of $D_2{}^{17}O$ in $D_2{}^{16}O$. (We chose a neat system for the simulation since this leads to much better statistical averaging.) We believe this very minor difference is not significant.

Most previous molecular dynamics studies have focused on H_2O, as opposed to the heavier isotopes discussed herein. For example, van der Spoel et al.[31] calculated the second-rank rotational correlation times for the OH and out-of-plane vectors at 300 K, finding 1.6 and 1.1 ps, respectively, for the SPC/E model. These can be compared to our results at 300 K of 1.94 ps for the OD vector in $D_2{}^{16}O$, and 1.24 ps for the out-of-plane vector in $D_2{}^{17}O$. Note that for both vectors our times are somewhat longer because of the heavier masses, but that the ratio of the times for the two different vectors are about the same for our results and for theirs. Svishchev and Kusalik[33] performed simulations of H_2O, D_2O, and T_2O at 300 K with the SPC/E model, and calculated orientational correlation times for the out-of-plane vectors, but not for the bond vectors. For the out-of-plane vector in $D_2{}^{16}O$ they obtain a correlation time of 1.29 ps, quite similar to the value of 1.24 ps calculated herein for $D_2{}^{17}O$. (In this case the isotopic difference between these two molecules should lead to only a very small difference in these correlation times.) By comparing correlation times for different vectors, these authors conclude, as do van der Spoel et al.[31] and we, that the rotational motion of water is anisotropic.

VI. Concluding Remarks

In this paper we have reported deuterium and ^{17}O T_1 relaxation times as a function of temperature for isotopes of liquid water. We have also determined temperature-dependent quadrupolar coupling factors, allowing us to obtain temperature-dependent rotational correlation times for two different, orthogonal, molecule-fixed unit vectors. The significant difference in these times leads to the conclusion that the rotational motion of liquid water is anisotropic. This conclusion is also supported by our molecular dynamics simulations and those of others.[31,33]

Why, then, have other researchers[10−12,30] come to the conclusion, from experiment and simulation, that the rotational motion is isotropic? We believe there are four reasons. First, proton T_1 relaxation time studies are difficult to interpret because the relaxation is due both to intramolecular and intermolecular interactions, and it is hard to disentangle the two. Second, while deuterium and ^{17}O T_1 relaxation times result only from intramolecular interactions, and hence directly yield rotational correlation times, until recently accurate values of quadrupole coupling factors have not been known, leading to uncertainties in the derived correlation times. Third, previous quadrupolar relaxation time studies have compared the rotational correlation time of the OD bond vector for $D_2{}^{16}O$ with the rotational correlation time for the out-of-plane vector of $H_2{}^{17}O$. Since these molecules have quite different moments of inertia, a direct comparison may not be meaningful. (Recall that herein we compared the rotational correlation time of the OD bond vector for $D_2{}^{16}O$ with the rotational correlation time for the out-of-plane vector of $D_2{}^{17}O$, and since these two molecules have much more similar moments of inertia, a direct comparison is more appropriate.) Fourth, the simulation study concluding that the motion is isotropic is based on the ST2 model of liquid water,[16] which is known to overestimate the local tetrahedral structure of water.[30] Perhaps this is responsible for the observed isotropic molecular rotation. Even here, however, a careful look at Table 2 of ref 30 shows that over the range from 275 to 350 K τ_D is consistently longer than τ_O, in agreement with our results and those of others.[31,33]

In summary, our experimental and simulation results indicate strongly that the rotational motion of liquid water is anisotropic. The experimental results will hopefully provide benchmarks for the development of more sophisticated and accurate theoretical models of liquid water.

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