

Computer Simulation Study on the Reorientational Dynamics of HDO in H₂O

Guocai Tian, Jian Li and Yixin Hua

Abstract—The reorientational dynamics of HOD molecules in liquid water at four different temperatures are studied by computer simulation with SPC/E water model. Reorientational dynamics and correlation times are reported and compared with the recent experiments and those corresponding to pure water at the same conditions. We found that the rotational dynamics speeds up as the temperature is increased since the hydrogen bond interaction between water molecules decreases, the molecules are more freely and rotations are easily and faster.

Index Terms—Reorientational dynamics, HOD, liquid water, computer simulation, time correlation function

I. INTRODUCTION

Liquid water is an important substance in many physical, chemical, and biological processes, such as proton conduction, acid base reactions, and protein folding [1]. It is widely believed that a better understanding of the microscopic properties of water will also increase the understanding of these processes. On the microscopic level liquid water is made up of a network of water molecules that are held together by hydrogen bonds. This network is not static, since molecular rearrangements take place continuously, typically on a picosecond timescale. The reorientation of liquid water involves two distinct processes. One is formed by the ultrafast librational motions of the OH groups that keep the hydrogen bonds intact the other is formed by the complete reorientation of the water molecules involving the breaking and reformation of hydrogen bonds.

Knowledge about the orientational dynamics of water is essential for understanding the (bio)-chemical and physical processes that take place in this liquid, notably chemical reactions and solvation. Therefore, the reorientational motion of molecules in liquid water has been extensively studied for over half a century, in particular by such methods as

dielectric relaxation [2], THz spectroscopy [3], optical and Raman-induced Kerr-effect spectroscopy [4], and nuclear magnetic resonance [5]. However, all of the experimental techniques employed to date probed the orientational motion indirectly or averaged over all molecules in the liquid. In addition, it is often not clear to what kind of molecular motion the relaxation observed with these methods is related. In contrast, polarization resolved pump-probe spectroscopy yields unambiguous information about the dynamics of orientational relaxation of small molecules in the liquid phase [6-7].

Computer simulation is a powerful tool for study the microscopic and dynamics properties of liquids and liquid solutions. It can provide experimentally inaccessible information which may be very useful for a deep understanding of these systems at the molecular level. This information is also very helpful for interpreting experimental data such as those resulting from spectroscopic experiments. Recent years, this method has been used to the rotation dynamics of O-H stretch of HDO molecules in liquid D₂O solvent [8] and pure water [9].

More recently, experimental studies on the have been performed on the reorientational dynamics of O-H stretch of HDO molecules in liquid H₂O at different temperature [10]. But the reorientational mechanism has not been clarified and no theoretical investigation of the problem has been reported up to now. In this work, we report the results of a computer simulation study on the reorientational dynamics of OD-stretch mode of HDO in H₂O at different temperature. The outline of this paper is as follows. Computational details are outlined Section II. Section III gives the structure properties of HOD in H₂O molecules at different temperatures. The reorientations dynamics are analyzed and discussed in Sec.4. Conclusion is given in Sec.5.

II. MODELS AND COMPUTER SIMULATION DETAILS

Molecular dynamics simulations were performed in the microcanonical (NVE) ensemble for two different isotopes of water (H₂¹⁶O and H₂¹⁷O) and HOD in H₂O at four different temperatures (275, 300, 325, and 350 K). In each case, the system consisted of 500 molecules of H₂¹⁶O or H₂¹⁷O for two different isotopes of water, and 1 HOD and 499 H₂O with the DL_POLY package 3.0 [11] using the SPC/E model for water molecules [12]. The particles interactions are simply a simply a pairwise sum of Lennard-Jones (L-J) and Coulomb terms, namely,

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$$V^{\text{inter}} = \sum_{i < j} \left[4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right] \quad (1)$$

Where ϵ and σ are the L-J parameters and r_{ij} denotes the distance between the L-J sites i and j , q_i and q_j are the point charges on site i and j . The L-J parameters and point charges are taken from the original SPC/E model. The L-J parameter ϵ_{ij} and σ_{ij} are obtained using the Lorentz–Berthelot mixing rules $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = (\sigma_i + \sigma_j) / 2$.

The molecules were initially arranged in a cubic box with their centers of mass randomly displaced in face-centered cubic lattice sites. Cubic periodic boundary conditions are used, where the size of the simulation box is chosen to yield an experimental value for H₂O at that temperature [1]. Center-of-mass and angular velocities were assigned randomly from a Boltzmann distribution. The electrostatic forces are treated using the Ewald summation procedure, with the convergence parameter α set to 6.4/L, where L is the edge length of the cubic simulation box in which the particles reside [13]. The rotational degrees of freedom were treated using quaternions. The simulation trajectory is propagated by the leapfrog algorithm with a time step of 1 fs. Each system is equilibrated at that temperature by periodically rescaling the velocities of the molecules until the temperature was kept within ± 2 K for 80 ps without further adjustment, after which a production run of 200 ps is performed to calculate the quantities of interest.

III. STRUCTURE PROPERTIES

The local structure of a solution can be conveniently studied by means of the radial distribution functions. The radial distribution function is a useful physical tool to describe the micro-structure of a system. The radial distribution functions of HOD in water at different temperature obtained from molecular dynamics simulation are given in Fig 1.

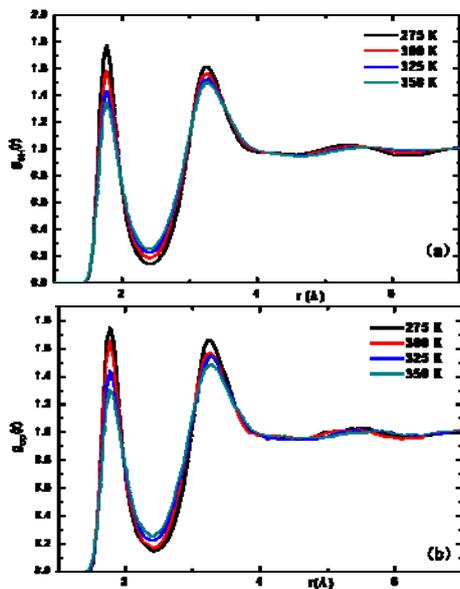


Figure 1 Radial distribution functions for O and H (a) and for O and D (b) of HOD in liquid water at different temperatures.

The $g_{OH}(r)$ shown in Figure 1(a) has peaks at distances of 0.18 nm and 0.33 nm between atom O and atom H. The 0.18 nm peak is at the distance between an oxygen and a hydrogen along a hydrogen bond. 0.33nm is the distance from oxygen to an hydrogen of the neighboring hydrogen-bonded molecule. With the temperature increase, the first peak values (from 1.74 for 275K, 1.64 for 300K, 1.43 for 325 K to 1.29 for 325K) and the second peak values (from 1.62 at 275K, 1.56 at 300K, 1.52 at 325K to 1.49 at 350K) for O and H are decreased while the first minimum values for O and H are increased from 0.142 for 275K, 0.189 for 300K, 0.229 for 325K to 0.256 for 350K. It is shown that the intermolecular interactions of hydrogen bond between water molecules decreases for water molecules with the temperature increases.

Figure 1(b) shows $g_{OD}(r)$ with two peaks at 0.18 and 0.33nm. The 0.178nm peak is at the distance between an oxygen and a hydrogen along a hydrogen bond. 0.33nm is the distance from oxygen to a hydrogen of the neighboring hydrogen-bonded molecule. With the temperature increase, the first peak values (from 1.74 for 275K, 1.64 for 300K, 1.43 for 325 K to 1.29 for 325K) and the second peak values (from 1.62 at 275K, 1.56 at 300K, 1.52 at 325K to 1.49 at 350K) for O and H are decreased while the first minimum values for O and H are increased from 0.142 for 275K, 0.189 for 300K, 0.229 for 325K to 0.256 for 350K. It was shown that the intermolecular interactions of hydrogen bond between water molecules decreases for water molecules with the temperature increases. With the increase of temperature, the average hydrogen bond coordination number of water decreases while the distribution of hydrogen bond angles broadens and the peak value of hydrogen bond angles reduces, i.e., the hydrogen bond interaction between water molecules decreases.

IV. REORIENTATIONAL DYNAMICS

Molecular reorientational motions in liquids are usually analyzed through the time correlation functions:

$$C_l^\alpha(t) = \left\langle P_l(\bar{u}^\alpha(t) \bar{u}^\alpha(0)) \right\rangle. \quad (2)$$

where P_l is the l^{th} Legendre polynomial and \bar{u}^α is a unit vector along a given molecular direction, and the angular brackets denote an ensemble average. $C_l^\alpha(t)$ indicates how a given molecular direction changes its orientation in time and can be related to the dielectric relaxation and NMR experiments, for example, $C_1^\alpha(t)$ is directly related with dielectric relaxation measurements, whereas $C_2^\alpha(t)$ is related with dipolar relaxation NMR experiments, respectively. Rotational correlation times τ_l^α are given by the time integral of the rotational time correlation function:

$$\tau_l^\alpha = \int_0^\infty dt C_l^\alpha(t) = \int_0^\infty dt \left\langle P_l(\bar{u}^\alpha(t) \bar{u}^\alpha(0)) \right\rangle. \quad (3)$$

In present work, we calculated rotation correlation function and ration time of two unit vectors $\bar{u}^{\text{O-H}}$ and

$\bar{u}^{\text{H-H}}$ along with the O-H and H-H directions and $\bar{u}^{\text{out}} = \bar{u}^{\text{OH}} \times \bar{u}^{\text{HH}}$ along with the out-of-plane vector.

To offer a comparison between these experimental values and simulation, the rotational correlation function $C(t) = P_2(\bar{u}^\alpha(t)\bar{u}^\alpha(0))$ is calculated for neat H_2^{16}O and H_2^{17}O as well as HOD in H_2O and are shown in Figures 2, 3 and 4, respectively. One clearly sees that overall the decay is not at all exponential, and that the initial decay of rotational correlation function $C(t)$ is very fast on the time scale of 30 fs, followed by a pronounced beat with a period of 80 fs, and a slower decay tail. According to our previous study, the initial fast decay and oscillation are due to the libration and hindered translations, where the libration and translations motions are hindered by the relative static structure of surround solvent molecules. Also, it is clearly shown that the rotational dynamics speeds up as the temperature is increased. With temperature increases, the hydrogen-bond interactions and the inharmonic interactions between the inter- or intro-molecular modes of water molecules are decreased, therefore the molecules are freely and the motions are easily and faster.

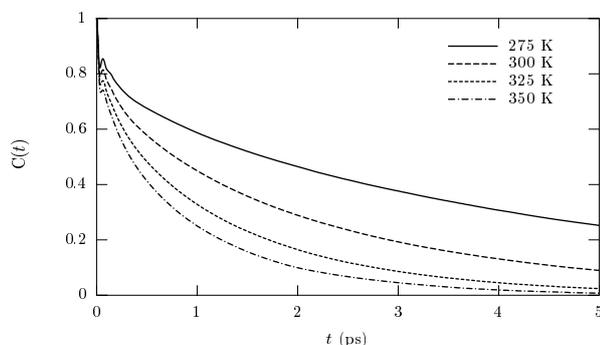


Figure 2 $C(t)$ for H_2^{16}O at four different temperature, \bar{u}^α is the O-H bond vector.

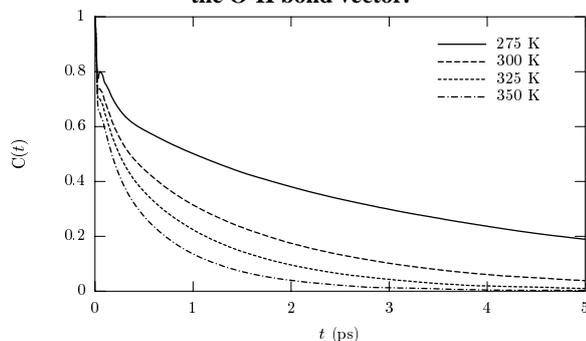


Figure 3 $C(t)$ for H_2^{17}O at four different temperature, \bar{u}^α is the out-of-plane vector.

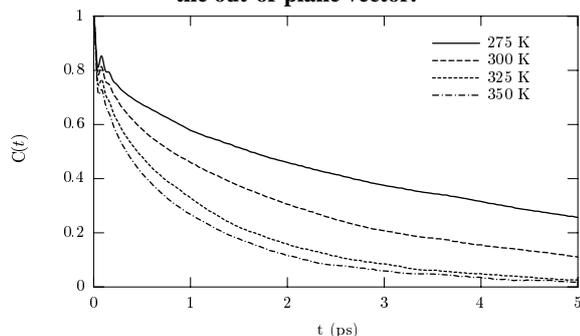


Figure 4 $C(t)$ for HOD in H_2O at four different temperature, \bar{u}^α is the OD bond vector.

The rotation correlation time calculated from Eq. (3) of the $C(t)$ in Figures 2, 3 and 4, respectively, are shown in Table 2. The present result for H_2^{16}O at 300K is in good agreement with the results of the previous molecular simulation studies [14-15] and experiment (1.7-2.6 ps for H_2^{16}O obtain from NMR experiments) [16-17]. It is shown that the correlation time decreases from 3.32 ps at 275K to 0.85ps at 350K as the temperature increases, the same results can be found for H_2^{17}O and for HOD in H_2O . The ratio of the two correlation times $\tau_2^{\text{OH}}/\tau_2^{\text{out}}$ from simulation is roughly and independent of temperature, which is in reasonable agreement with NMR experimental results. The calculated the correlation time of HOD in H_2O is 1.832 ps at 300K, which agrees well with the experiment values 1.5 ps.

Table 2 Rotational correlation time of H_2^{16}O (τ_2^{OH}), H_2^{17}O (τ_2^{out}) and HOD (τ_2^{OD}) in H_2O at different temperatures. The unit of correlation time is ps.

T (K)	τ_2^{OH} (ps)	τ_2^{out} (ps)	τ_2^{OD} (ps)	$\tau_2^{\text{OH}}/\tau_2^{\text{out}}$
275	3.32	2.289	3.500	1.45
300	1.935	1.334	1.832	1.45
325	1.196	0.8345	0.993	1.44
350	0.895	0.618	0.836	1.45

V. CONCLUSION

We have studied the reorientational dynamics of water molecules in aqueous ionic solutions at four different temperatures (275K, 300K, 325K and 350 K) using the molecular dynamics simulation. Reorientational dynamics and correlation times are reported and compared with the recent experiments and those corresponding to pure water at the same conditions. We found that the rotational dynamics speeds up as the temperature is increased since the hydrogen bond interaction between water molecules decreases, the molecules are more freely and rotations are easily and faster. The rotational correlation time obtained for HOD in H_2O at 300K is 1.832 ps which agree well with the experiment results 1.5 ps.

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