

Water Dynamics: Fluctuation, Relaxation, and Chemical Reactions in Hydrogen Bond Network Rearrangement

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I. Introduction

Water is the most ubiquitous substance on Earth and known to have anomalous properties, which arise from the nature of the hydrogen bonds: decrease of viscosity with pressure, large heat capacity and surface tension, density maximum at 4 °C, melting with pressure, and many others.^{1–3} In addition to these well-known anomalies, water also exhibits singular features in extreme conditions. Water becomes, for example, highly reactive at high temperature and high pressure, supercritical water, and can decompose numerous polymers and various hazardous chemicals.⁴ It can thus be a key substance for solving a difficult environmental problem. At low temperature, water forms a so-called clathrate–hydrate structure containing significant amounts of gas molecules (CO₂, CH₄, etc.).⁵ The existence of a great amount of methane in the clathrate–hydrate form on Earth is one of the most arduous future environmental problems, bearing on global warming. Methane in the clathrate–hydrate form is also an important resource for solving the energy problem. The recent important finding is that there exist various novel phases in low-temperature pure water and high-density amorphous, low-density amorphous, and new crystalline ice structures.^{6–8}

In the present Account, we focus on the dynamical aspects of water at the molecular level and its effect on chemical reactions, recently investigated. Water dynamics is strongly controlled by the hydrogen bond network; there exist intermittent collective molecular motions associated with the rearrangement of the hydrogen bond network

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and concomitant fluctuation and relaxation in water.^{9–13} The mechanism of proton transfer in liquid water is then investigated as an example to demonstrate the effects of such water dynamics on chemical reactions.^{14,15} The global nature of the water potential energy surface is analyzed in detail to clarify the molecular mechanism of how water freezes into a crystalline ice.¹⁶

In the present Account, various theoretical methods, such as molecular dynamics, normal mode and reaction coordinate analyses, and quenching and annealing techniques, were used to analyze water dynamics and explore the global nature of the water potential energy surface. The empirical potential TIP4P without including intramolecular degrees of freedom is mostly employed to describe the water–water molecular interaction in the molecular dynamics calculations.

II. Dynamics

The most stable structure of water is a crystalline ice, consisting of six-membered rings of water molecules as basic units, forming an extended three-dimensional hydrogen bond network. Upon melting, water absorbs a latent heat of 80 cal/g (1.4 kcal/mol), which is equivalent to breaking about 10% of its hydrogen bonds, and the system becomes “frustrated”. Water thus has a rugged potential energy surface involving various deep energy minima with different hydrogen bond network structures.¹⁷ Water undergoes sluggish dynamics on this potential energy surface. On a short time scale liquid water is thus amorphous gel-like, while on a much longer time scale it exhibits diffusional motion as an ordinal liquid. Between these time scales, the hydrogen bond network rearrangement occurs intermittently and locally in space, involving the local collective motions of tens of water molecules accompanied by large energy fluctuation.^{9–12}

A. Hydrogen Bond Network Rearrangement and Collective Molecular Motion. To identify the intermittent collective molecular motions associated with the hydrogen bond network rearrangement in water, inherent structure analysis was employed.⁹ Inherent structure analysis is used to identify the local minima (called the inherent structures, which are considered as the fundamental structures) of the potential energy wells, which are sequentially visited by the system along the trajectory.¹⁸ In the trajectory, the system undergoes well to well transitions (inherent structure transitions) after exhibiting vibrational motions in individual wells (see Figure 1). In Figure 2 a, we plot the distance matrix of the system with 64 water molecules. A distance matrix is defined by

$$D(t_m, t_n) = \left(\sum_{i=1}^N |r_i(t_m) - r_i(t_n)|^2 \right)^{1/2} \quad (1)$$

where $r_i(t_n)$ is the position of the center of mass of the i th water molecule in the inherent structure at time t_n , $t_n =$

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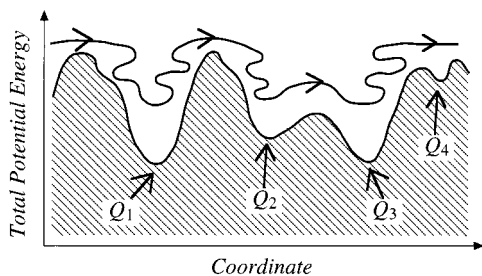


FIGURE 1. One-dimensional picture of liquid dynamics. A system exhibits vibrational motions in individual potential energy wells and then makes the transition to neighbor wells in a trajectory. Minima of potential energy wells (Q_1, Q_2, Q_3, \dots) are called inherent structures, representing fundamental structures of the system.

$n\Delta t$ (Δt is a time interval, 10 fs). A plot almost identical to that in Figure 2a is obtained when the molecular rotations are also accounted for in the distance calculations.¹⁹ We can see that certain sets of sequential inherent structures form island structures (basins); they are mutually separated with small energy barriers and small structure differences. The transitions among inherent structures within a basin (minor inherent structure transitions) occur easily and frequently.

There are islands (basins) of various sizes, distributed randomly in time, and thus the transitions among the islands (called the basin–basin transitions) occur intermittently.^{19,20} The basin–basin transitions comprise large inherent structure changes (for example, see Figure 3) but involve relatively small energy barriers. These transitions were found to take place only when the system finds the phase-dynamics matching (right position and right momentum) to pass through narrow and entangled long pathways, not involving large energy barriers. Until the system finds such a phase-dynamics matching, numerous minor inherent structure transitions take place within a basin. The basin–basin transitions thus might be called “entropy bottlenecked”.^{19,20} The basin–basin transitions may correspond to α -type relaxation while the minor inherent structure transitions correspond to β -type relaxation in the terminology of the glass dynamics.⁸

To see how the intermittent collective motions are associated with the hydrogen bond network rearrangement in water, we have employed a Hamming matrix of the graph theory.¹³ A Hamming matrix can quantify the creation and annihilation of the hydrogen bonds along the trajectory. The hydrogen bond network can be represented by a directed graph (digraph). The rearrangement of the hydrogen bond network then corresponds to the connection and disconnection of the edges of a digraph. The hydrogen bond network of the system consisting of N molecules can be expressed by a $N \times N$ adjacency matrix, whose element a_{ij} is 1 when the hydrogen bond is donated from molecule i to molecule j (one of the hydrogen atoms of molecule i forms the hydrogen bond with the oxygen atom of water molecule j), and 0 otherwise.

The Hamming distance between two inherent structures at times t_m and t_n is defined as

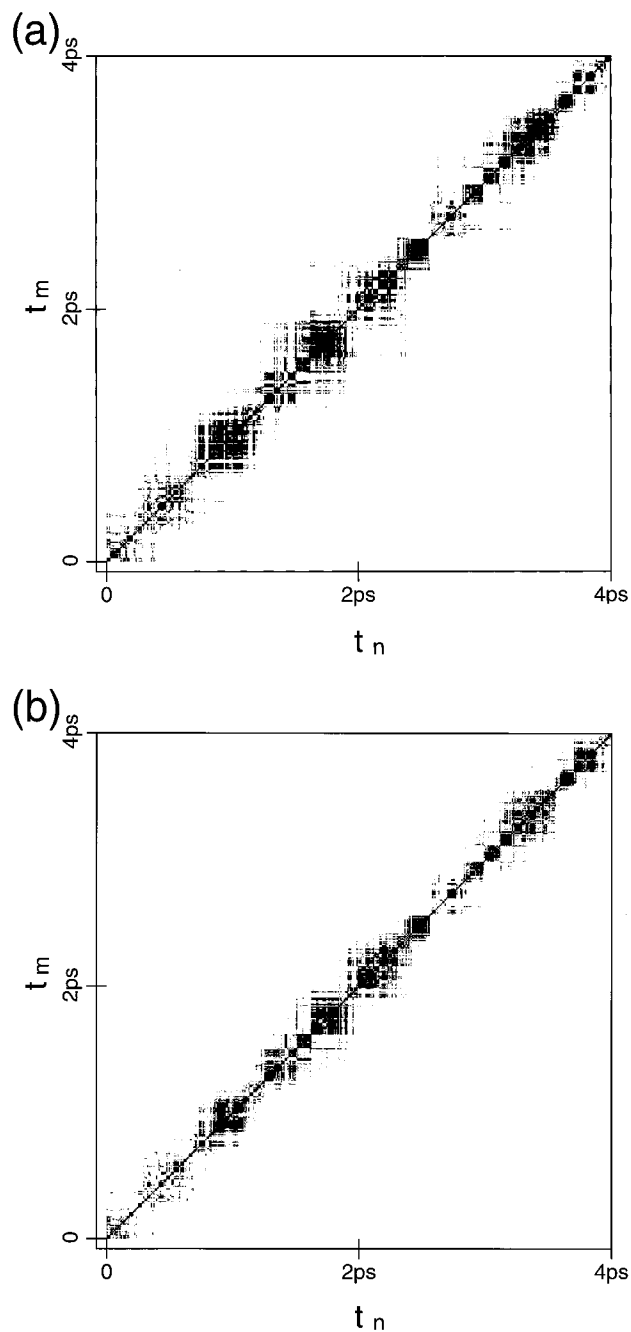


FIGURE 2. (a) Euclidean and (b) Hamming distance matrixes of liquid water. Pixels are shaded according to the value of each element in the distance matrix (eqs 1 and 2). A darker (lighter) shaded pixel indicates the smaller (larger) distance. The system has 64 water molecules. The temperature is 300 K, and the time interval Δt is 10 fs.

$$D_H(t_m, t_n) = \sum_{i \neq j} |a_{ij}(t_m) - a_{ij}(t_n)| \quad (2)$$

where the summation is performed over all different pairs of sites (i, j). In Figure 2b, we plot the Hamming distance matrix of the system with 64 water molecules. The patterns of the island structures and the island–island transitions in the Euclidean distance matrix (Figure 2a) are almost identical to those in the Hamming distance matrix (Figure 2b), meaning that the intermittent collective motions are indeed associated with large hydrogen bond network

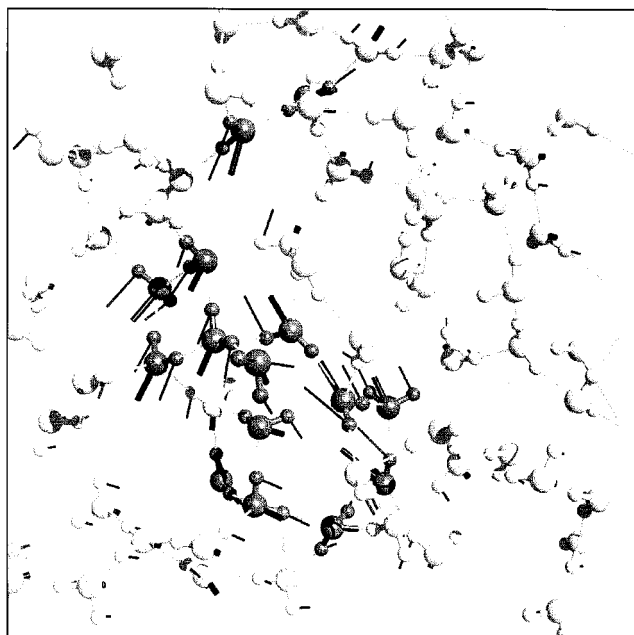


FIGURE 3. Collective molecular motion in liquid water. Solid lines indicate the molecular displacements from an inherent structure (whose water molecular positions and hydrogen bond network are shown) to the next along the trajectory. The dark water molecules move largely. Note that tens of water molecules in local space move together. The system contains 216 water molecules. Only water molecules in one layer are shown.

rearrangement.¹³ In a large system, many intermittent collective motions do occur independently at a time at different places of the system, and their total sum yields a band structure in both the Euclidean and the Hamming distance matrixes, seemingly equivalent to the trace of diffusional motion.¹³ Therefore, to observe the intermittent collective motions, we need to detect the structure changes in a local area of the system, on the order of 10 Å, in a diameter.

B. Short Time Dynamics. In a trajectory, the system yields several vibrational motions in an individual potential energy well and then jumps to the next well.^{9,21} Figure 4 shows the distribution of these vibrational motions (modes) in liquid water, evaluated at water structures (inherent or instantaneous structures) along the trajectory.^{19,22,23} We can see in the figure that there are three distinct broad bands of intermolecular modes, peaked at ~ 60 , ~ 200 , and $500\text{--}600\text{ cm}^{-1}$. Two broad bands peaked at ~ 60 and 200 cm^{-1} consist of the hindered translational (center of mass) motions of water molecules, combined to form $\text{O}\cdots\text{O}\cdots\text{O}$ bending and $\text{O}\cdots\text{O}$ stretching,²⁴ respectively, as shown in Figure 5, where the vector components of normal modes are plotted. The modes above 400 cm^{-1} consist of librational (hindered rotational) motions and are delocalized; i.e., their components are extended over many water molecules. Note that these are collective modes, but must be distinguished from the "intermittent collective motions" associated with the hydrogen bond network rearrangement discussed in the previous subsection. The ~ 60 and 200 cm^{-1} modes are less delocalized but still extended over molecules. The modes located from

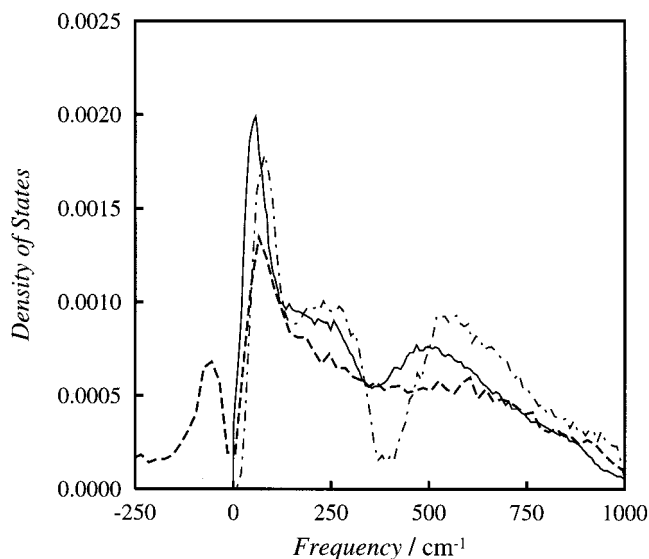


FIGURE 4. Normal mode distribution of liquid water. Normal modes are calculated at the instantaneous structures (INM) and inherent structure (QNM) along the trajectory, and evaluated from the velocity–velocity correlation function (VTCF). Solid, dashed, and dashed–dotted lines are for VTCF, INM, and QNM, respectively. Imaginary modes in INM are plotted in the negative frequency as $-|\omega|$. The system contains 216 water molecules.

300 to 400 cm^{-1} , consisting of the motions of molecules with dangling hydrogen bonds, are found to be very localized (not shown in the figures).^{9,19,20}

Experimentally these vibrational bands are observed by far infrared (far-IR), Raman scattering, and incoherent neutron scattering spectra. Low-frequency, ~ 60 and $\sim 200\text{ cm}^{-1}$, modes are weak in far-IR and Raman spectra. This is because the hindered translational molecular motions, not causing the dipole rotations, do not yield a direct contribution to Raman and far-IR intensities, but only through the collision-induced term.^{21,25} The librational modes, inducing the dipole rotations, yield much stronger far-IR and Raman intensities. The $\sim 200\text{ cm}^{-1}$ peak is found to be sensitive to the hydrogen bond network structure; its intensity increases with decreasing temperature.²⁴ On the contrary, the $\sim 60\text{ cm}^{-1}$ peak, although its motion is more extended over the hydrogen bond network, is somehow less sensitive to temperature.

It has been found that the normal mode description is often very successful in describing experimental spectra of various relaxation processes in liquids.^{22,26} This is because most experiments detect the effects of all individual motions almost evenly (note that vibrations are dominant in number). They are thus not suited for detecting specific motions such as the hydrogen bond network rearrangement dynamics.

III. Experimental Observations of Intermittent Collective Motions

It is then of interest to determine how we can experimentally observe the intermittent collective motions associated with the hydrogen bond network rearrangement, which are buried under vibrations.

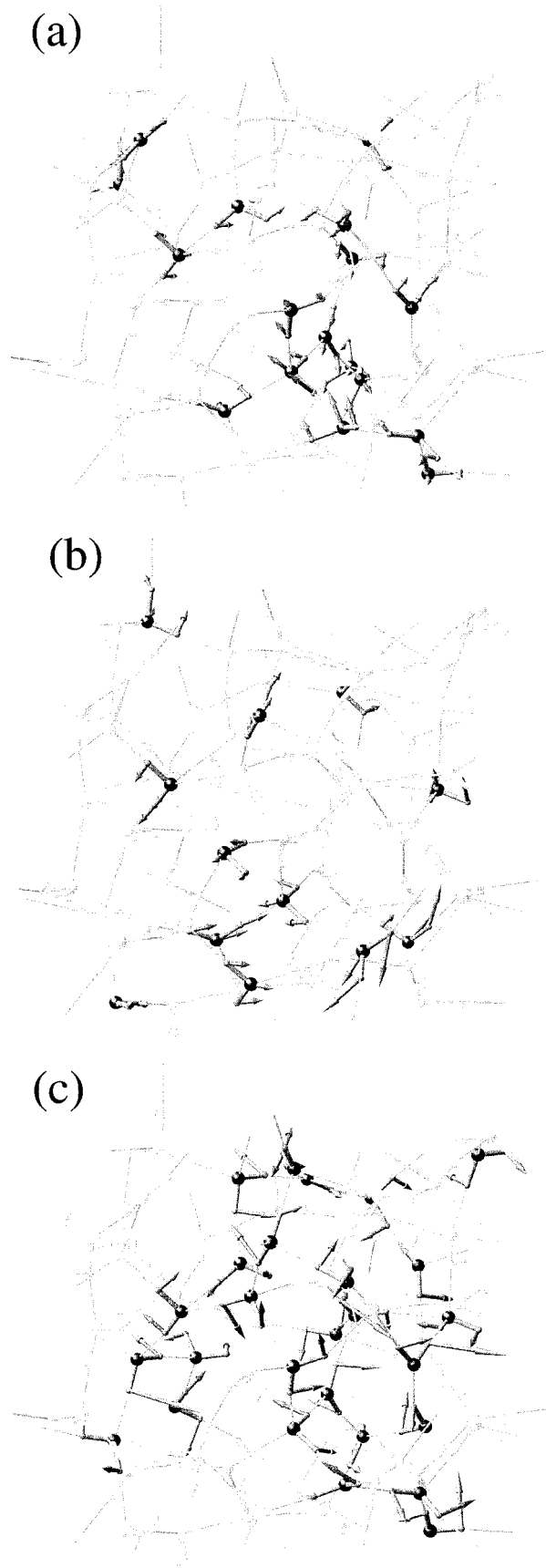


FIGURE 5. Normal mode displacement vectors at (a) 66 cm^{-1} , (b) 227 cm^{-1} , and (c) 581 cm^{-1} at a configuration of liquid water. Lines with arrows indicate the atomic displacements. The dark water molecules move largely. The system contains 64 water molecules.

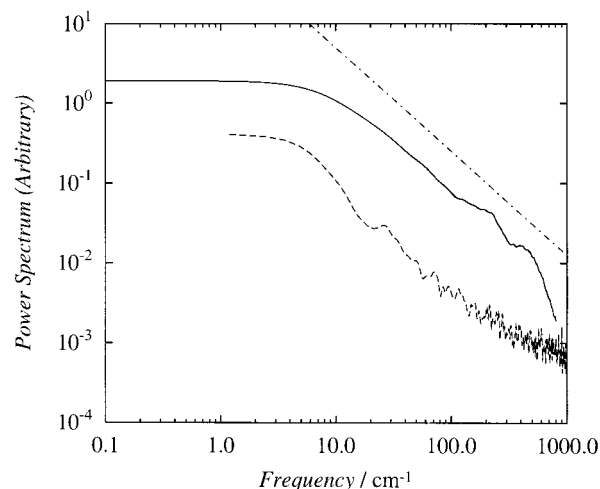


FIGURE 6. Power spectrum of the Raman scattering intensity of liquid water. The solid line is for the instantaneous structures and the dashed line is for the inherent structures along a trajectory. The dashed-dotted straight line indicates $1/f^\alpha$ with $\alpha = 1.3$ (f is frequency). The system contains 216 water molecules.

A. Depolarized Raman Scattering Profile. There is an indirect way to detect intermittent local collective motions. The intermittent character of the dynamics is known to appear as a so-called $1/f$ spectrum.¹⁰ Namely, a power spectrum is proportional to the inverse of the frequency, f , as $f^{-\alpha}$ ($\alpha < 2$). A $1/f$ spectrum is an indicator of the existence of multiscale relaxations in dynamics.²⁷ For example, Fourier transform of a series of intermittent pulses, the simplest example of it, is easily shown to be a type of $1/f$ spectrum.

Raman scattering detects the polarization fluctuation. The spectrum of the depolarized Raman scattering calculated from the trajectory is plotted in Figure 6.²¹ We can see that liquid water has a very wide Raman scattering spectrum, which can be divided into three parts, a power law region above $5\text{--}20\text{ cm}^{-1}$, a near white noise region below 3 cm^{-1} , and the in between transition region.²⁸ Such a baseline profile of Raman scattering of liquid water is quite different from those of unassociated liquids, which yield Lorentzian dependence in the low-frequency region. The power law part indeed corresponds to the structural rearrangement dynamics of the hydrogen bond network structure.²¹ We can see that this power law part yields the $1/f^\alpha$ frequency dependence with an exponent of $\alpha = 1.3$, which is in good agreement with Walrafen's experimental results.^{21,28} The signals of inter- and intramolecular vibrational motions, discussed in the previous section, are seen as two shoulders at ~ 200 and 500 cm^{-1} , superimposed on this power law profile.

It is, however, a very difficult task to determine exactly the low-frequency profile by subtracting the vibrational elements experimentally. Various functions other than a power law curve might also fit the spectrum profile well.²⁹ More experiments must be done to extend the spectrum to the very low-frequency region for its final determination.

B. Neutron Scattering and Inelastic X-ray Scattering. We can obtain both the spatial (in k space) and the

temporal (in ω space) information of the density fluctuation in a system by using neutron scattering.³⁰ It is therefore expected that this method is useful for analyzing the spatial–temporal nature of intermittent collective motions associated with the hydrogen bond network rearrangement in water. Teixeira et al.³⁰ used coherent inelastic neutron scattering on D₂O, which provides mainly information on the longitudinal oxygen density fluctuation in water, at room temperature for the large wave vector k and found a collective sound wave with a velocity of 3310 m/s, about 2 times faster than the normal sound velocity. A sound wave with a velocity of ~ 1400 m/s (normal velocity wave) was observed at small k in the Brillouin light scattering experiment.³¹

There had been no experiment to illustrate the dispersion relation of the longitudinal sound wave (L-wave) in the region of intermediate k . Recently, Sette et al.³² have performed a precise inelastic X-ray scattering experiment and showed that the velocity of this wave smoothly changes from the low value (normal velocity) to the high value (fast velocity) around $k = 2 \text{ nm}^{-1}$. They also found that the “dominantly transverse character” sound wave (T-wave) appears by branching out from the normal speed wave from this region; there exist two sound waves, L- and T-waves, for $k > 4 \text{ nm}^{-1}$. At very large k , the frequency of the T-wave converges to the O \cdots O \cdots O bending frequency ($\sim 60 \text{ cm}^{-1}$) and that of the L-wave to the O \cdots O stretching frequency ($\sim 200 \text{ cm}^{-1}$). In a polycrystalline ice *Ih*, T- and L-waves have velocities of ~ 2000 and ~ 4000 m/s, respectively.

The existence of two sound waves in liquid water was predicted by MD calculation before the experiments.^{21,33} It was shown theoretically that the velocity of L-wave reduces to the normal speed when the three-dimensional nature of the hydrogen bond network is decreased.²¹ The physical origin of the fast-velocity wave is thus a longitudinal wave traveling in a temporal hydrogen bond network region (“cluster”) formed along the hydrogen bond network rearrangement.^{21,30,34} The velocity of the L-wave transforms from the normal speed (predicted by hydrodynamics theory for liquids) to the fast speed (that of a wave propagating in the “solid” phase), called a positive dispersion, when the experimental measurement begins detecting the dynamics of this temporal hydrogen bond network cluster.^{21,30,34} It should be mentioned here that both L- and T-waves are more distinct in a midsize water molecular cluster (e.g., (H₂O)₁₀₈) than in liquid water.²¹

The cluster corresponding to $k \approx 2 \text{ nm}^{-1}$ where the positive dispersion begins to take place is about 30 Å in length.³² It is much larger than the size of the “intermittent collective motions”, which we have been discussing; these sound waves are not directly related to the intermittent collective motions. To identify the intermittent collective motions in this experiment, we need to analyze a relaxation process with smaller ω and larger k values (the lower energy and smaller spatial region) in more detail.

C. Time Domain Higher Order Nonlinear Spectroscopies. The effects of intermittent collective motions

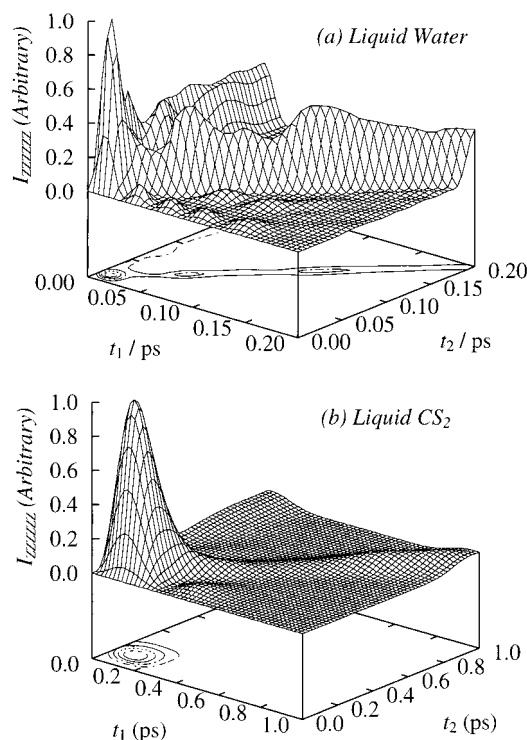


FIGURE 7. Square of the fifth-order response functions of (a) water and (b) CS₂.

might appear in spectra of higher order nonlinear spectroscopies, since these methods deal with the phase space dynamics of a system.^{26,35} There have been intensive theoretical investigations proposing to apply an echo-type experiment, i.e., off-resonant fifth-order (two-dimensional (2D) Raman) spectroscopy, to distinguish the homogeneous and inhomogeneous elements in liquid dynamics.^{26,36–38} This technique is analogous to the spin–echo experiment, but uses photons. The inhomogeneous elements yield an echo by the “rephasing” of polarization fluctuation caused by molecular motions. Several experimental groups have tried to obtain the fifth-order spectra for intermolecular motions in liquids such as CS₂, CCl₄, and CHCl₃.^{39,40} No clear echo signal has been found for these liquids. It has been, however, pointed out very recently that the experimental spectra obtained may be attributed to other than the fifth-order process, that is, the sequential third-order processes.⁴⁰

We have estimated the spectrum of the fifth-order signal for liquid water and CS₂ by using the normal mode description of intermolecular motions. We can see in Figure 7 that there is a clear distinction in the signal between a structure-forming liquid (water) and a simple liquid (CS₂); water yields a strong echo (Figure 7a), while there is no echo in CS₂ (Figure 7b). There has been no observation of water by this experimental technique yet, since the signal is extremely weak due to the small polarizability of water molecules.

It was found for intermolecular motions of simple liquids that “mode-mixing” reduces the echo signal to a great extent.²⁶ In the fifth-order 2D Raman experiment, a two-quanta transition is involved, and thus two modes with different frequencies are excited in general. The

phases of these different frequency modes (with ω_1 and ω_2) cannot coincide with each other (i.e., cannot “rephase”) to yield an echo. The echo is thus generally very weak for intermolecular motions in simple liquids (Figure 7b).²⁶

Unlikely in simple liquids, many intermolecular modes in water involve rather localized motions, due to the heterogeneity of the molecular environment, that is, caused by the hydrogen bond network rearrangement dynamics (see subsection II.B). This means that the mixing of different frequency modes in the polarization is weak. Large contributions to the echo signal are indeed found to arise from the localized and the higher frequency librational modes in liquid water. It was, however, shown that the anharmonicity of the potential energy surface reduces the echo.³⁷ If a more accurate correlation function is calculated by using MD, instead of using the normal mode description, the intensity of the echo may be further reduced due to the frequency modulation.²⁶ The more detailed theoretical analysis is needed to directly relate that echo signal profile to the intermittent collective dynamics in water.

Other higher order nonlinear spectroscopies, such as the seventh-order response and 2D-IR, could also be applied to deal with the intermolecular motions of liquids, since their dominant terms do not involve the two-quanta transition, which may suppress the echo.²⁶

IV. Global Potential Energy Surfaces

The potential energy surface along liquid water dynamics is very rugged with various deep energy minima.¹⁷ Upon cooling, water might be trapped into one of such local minima and form an amorphous structure. Nevertheless, liquid water always freezes into crystalline ice in ambient conditions.¹

Detailed knowledge of the global nature of the water potential energy surface is required to understand how the hydrogen bond network structure alters upon cooling to form a crystal structure. As the first step to obtain such knowledge, we examine the global potential energy surfaces of water molecular clusters.^{16,41} There are various theoretical methods to manifest the global potential energy surface. We used a so-called eigenvector-following method, which follows the direction of a normal mode at a minimum and determines a reaction coordinate (RC) connecting to the next minimum.^{42,43} We applied it to a $(\text{H}_2\text{O})_{64}$ cluster and determined sequential “lowest” barrier RCs until we reached a deep minimum.¹⁶

Figure 8 shows a plot of the overall potential energy surface of the $(\text{H}_2\text{O})_{64}$ cluster. We can see that the overall potential energy surface, starting from a liquid-state inherent structure, decreases slowly toward lower energy states but has a very rugged structure; the global potential energy surface of this cluster is the mixture of the ladder and rugged types.¹⁶ To reach a global minimum of the water molecular cluster, slow cooling is thus required. Two distinct characteristics are observed: (1) RCs from global minima involve distinct high-energy barriers; definite hydrogen bond breaking is involved (Figure 8b). (2) The

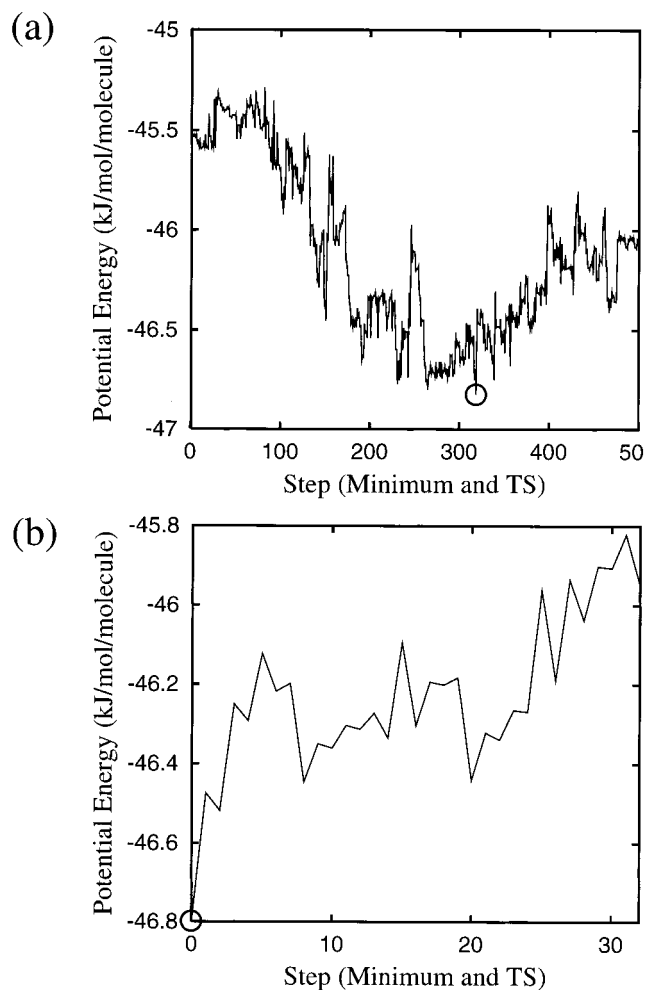


FIGURE 8. Sequential reaction coordinates (SRC) for the water cluster, $(\text{H}_2\text{O})_{64}$. (a) SRC starting from an inherent structure along the “liquid”-state trajectory ($T = 250$ K). A circle indicates the lowest energy minimum in this sequential RC. (b) SRC starting from one of the lowest minima. The step indicates the n th minimum and TS along the SRC.

potential energy surface becomes less sluggish in the intermediate- and high-energy regions. A large-size water molecular cluster, as well as water, thus has both the “strong”-liquid (corresponding to (1)) and the “fragile”-liquid (corresponding to (2)) characteristics, as pointed out by Angell.¹⁷ Recently, Wales and co-workers have clearly shown that a global potential energy surface of a small water molecular cluster, $(\text{H}_2\text{O})_{20}$, has a “banyan tree” structure and is of the strong-liquid type in the middle- and low-energy regions.⁴⁴

The global potential energy surface property of liquid water might be, however, significantly different from that of water molecular clusters found here. A certain “ordered” structure must be created in liquid water as an initial nucleus, which grows into a crystal structure through a nucleation process. It is not known what kind of initial ordered structure is involved. Other (five and seven) membered rings as well as six-membered rings are abundant in liquid water. Therefore, the initial nucleus might be a certain size cluster consisting of six-membered rings, of other-membered rings, or a mixture of six- and

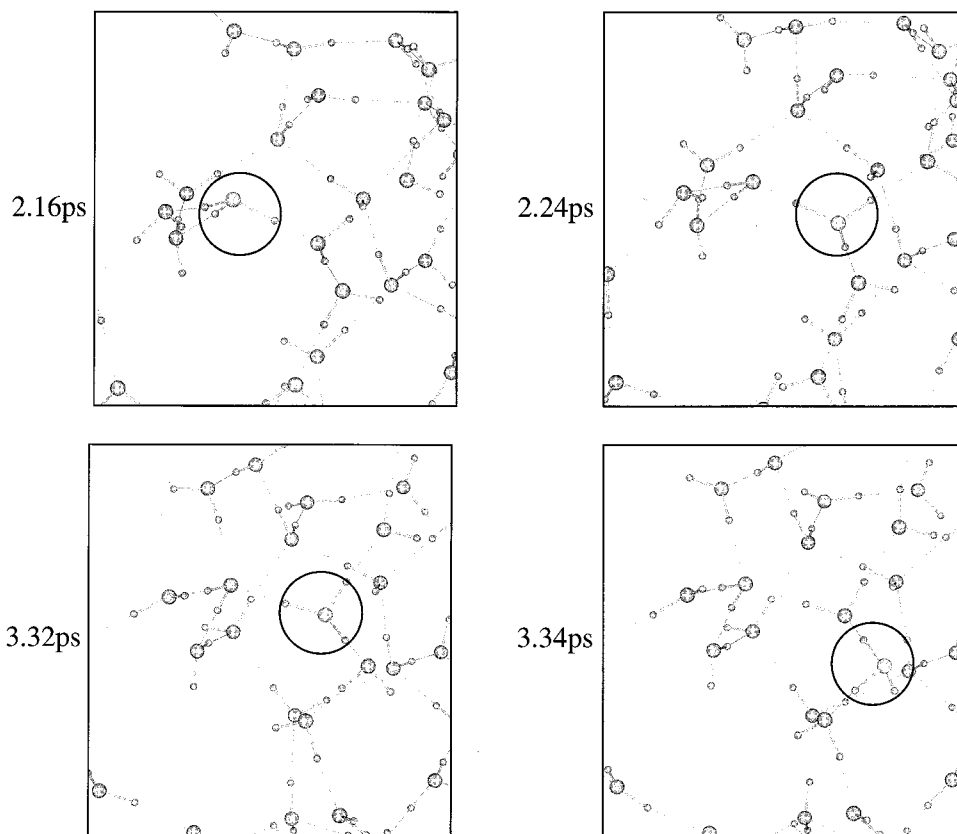


FIGURE 9. Snapshots of water molecules around a proton in liquid water. The circle indicates the location of the proton at time t .

other-membered rings. The initial structure of the latter two cases must be changed to the regular six-membered ring structure at a certain stage of the nucleation process. Spontaneous structure fluctuation creating a well-formed initial nucleus hardly occurs, and thus some “driving” force, such as the funnel character of the potential energy surface discussed here, might be important.^{16,45} Due to the light mass of a hydrogen atom, quantum tunneling might play a significant role in structure rearrangement.⁴⁶

In certain extreme conditions, we can obtain amorphous ices. Two amorphous phases, high-density amorphous and low-density amorphous, have been identified.^{6,8} The first-order transition between these two amorphous phases is considered to terminate at a second critical point which locates around $T = -46$ °C.⁶ The extended dynamical fluctuation in liquid water, discussed above, might be related to the existence of such a second critical point.⁴⁷ Liquid water is then regarded as a mixture of the high-density amorphous and low-density amorphous phases, and fluctuates between these two phases. A correlation length associated with the critical fluctuation must be carefully analyzed in the future to elucidate this point. It is important to analyze how the existence of this second critical point has an effect on the freezing process; the crystallization might start in a low-density-amorphous-like region, which might grow and transform to a crystal structure in some coherent fashion.

V. Proton Transfer in Hydrogen Bond Network Rearrangement

The hydrogen bond network rearrangement in water has significant effects on chemical reactions. For example, proton transfer in water is strongly controlled by the hydrogen bond network.^{14,15,48} It is found that two geometrical relaxations, (1) hydrogen bond coordination of water molecules and (2) O···O distance shrinkage, are the key elements for fast proton transfer in liquid water. Figure 9 shows the hydrogen bond network configurations along the proton transfer. We can see in the figure that proton transfer takes place almost solely on the three-coordinated water molecules. This is because the water molecule with three protons, $(\text{H}_3\text{O})^+$, has a near planar form due to the Coulombic repulsion among three positively charged hydrogens/protons and a water molecule cannot take a position as the fourth coordinated molecule due to the Coulombic repulsion. The proton is mostly confined between two three-coordinated water molecules, repeating many back and forth motions between these water molecules, and “diffuses” as a $(\text{H}_5\text{O}_2)^+$ unit. Those three-coordinated hydrogen-bonded water molecules are created by structure fluctuation in the hydrogen bond network rearrangement. Fast proton transfer in liquid water is thus a typical example of fluctuation-induced chemical reactions.¹⁵

Proton transfer in ice is also known to be very fast, but its mechanism must be quite different from that in liquid water. All water molecules, including one with the extra

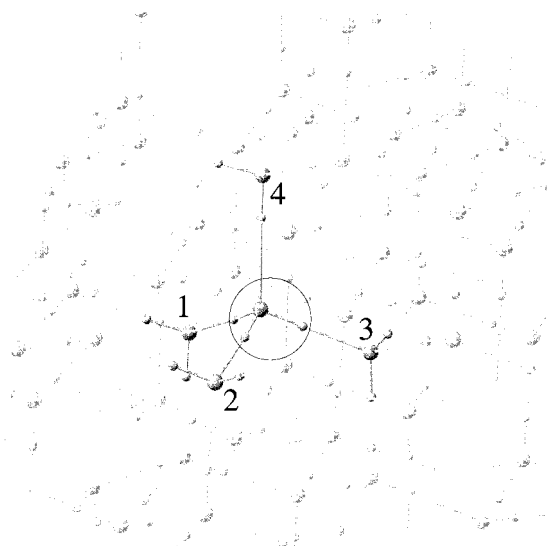


FIGURE 10. Snapshot of water molecules around a proton in ice. The circle indicates the protonated water molecule.

proton, $(\text{H}_3\text{O})^+$, have the four-coordinated tetrahedral structure, due to the structural constraint, in ice (Figure 10), so no significant hydrogen bond network rearrangement takes place. It is found that the $\text{O}\cdots\text{O}$ distance shrinkage due to the Coulombic repulsion between $(\text{H}_3\text{O})^+$ and the fourth coordinated water molecule (see Figure 10) significantly reduces the energy barrier of proton transfer in ice.⁴⁹ Only a very small isotope effect is indeed found experimentally in the proton-transfer rate constant in ice; that is, tunneling is not important, indicating a small barrier involved in proton transfer in ice. It is noted that the experimental data,⁵⁰ showing that proton mobility increases with decreasing temperature, might suggest the importance of a certain coherence of the proton and water molecular motions.

VI. Conclusions

The dynamics of water was investigated. A special emphasis was made to comprehend the nature of intermittent collective motions, associated with the hydrogen bond network rearrangement. The time scale and spatial scale of the hydrogen bond network rearrangement were found to be on the order of 0.1–10 ps and 10 Å, very important ranges where chemical reactions take place. Water thus yields significant solvent dynamical effects on chemical reactions. The effect of the hydrogen bond network rearrangement on chemical reactions was demonstrated in proton transfer in water. Fast proton transfer in water was found to be driven by the hydrogen bond coordination fluctuation caused by the hydrogen bond network rearrangement. The molecular mechanism of freezing in a water system was also investigated by analyzing a global potential energy surface of a water molecular cluster. The global potential energy surface of the water molecular cluster was shown to have a funnel structure, so the system is naturally conveyed to lowest energy minima. This study for water molecular clusters must be extended to liquid water.

Despite intensive investigations, the true origin of long-time dynamical correlation in water, which controls the hydrogen bond network rearrangement, is not clarified yet. We need to find an “order parameter” of the collective dynamics. Such an order parameter must become more distinct upon cooling, and might converge to a parameter characterizing the freezing. An experimental technique for directly detecting the hydrogen bond network rearrangement dynamics and determining such an order parameter must be developed. Such methods will also be very useful in analyzing the formation of amorphous ices and clathrate–hydrates, the high reactivity of supercritical water, and various solvation and relaxation dynamics in water.

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