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Vibrational Frequency Fluctuation of Ions in Aqueous Solutions Studied by Three-Pulse Infrared Photon Echo Method

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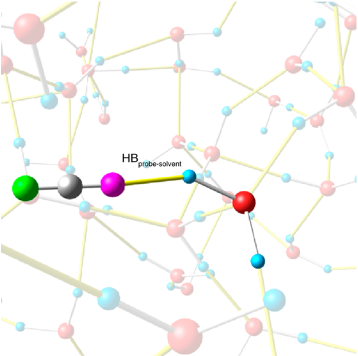

In liquid water, hydrogen bonds form three-dimensional network structures, which have been modeled in various molecular dynamics simulations. Locally, the hydrogen bonds continuously form and break, and the network structure continuously fluctuates. In aqueous solutions, the water molecules perturb the solute molecules, resulting in fluctuations of the electronic and vibrational states. These thermal fluctuations are fundamental to understanding the activation processes in chemical reactions and the function of biopolymers.

In this Account, we review studies of the vibrational frequency fluctuations of solute molecules in aqueous solutions using three-pulse infrared photon echo experiments. For comparison, we also briefly describe dynamic fluorescence Stokes shift experiments for investigating solvation dynamics in water. The Stokes shift technique gives a response function, which describes the energy relaxation in the nonequilibrium state and corresponds to the transition energy fluctuation of the electronic state at thermal equilibrium in linear response theorem. The dielectric response of water in the megahertz to terahertz frequency region is a key physical quantity for understanding both of these frequency fluctuations because of the influence of electrostatic interactions between the solute and solvent. We focus on the temperature dependence of the three experiments to discuss the molecular mechanisms of both the frequency fluctuations in aqueous solutions.

We used a biexponential function with sub-picosecond and picosecond time constants to characterize the time-correlation functions of both the vibrational and electronic frequency fluctuations. We focus on the slower component, with time constants of 1−2 ps for both the frequency fluctuations at room temperature. However, the temperature dependence and isotope effect for the time constants differ for these two types of fluctuations. The dielectric interactions generally describe the solvation dynamics of polar solvents, and hydrodynamic theory can describe the slow component for the electronic states. Compared with the slow component of the solvation dynamics, however, the picosecond component for the vibrational frequency fluctuations is less sensitive to temperature. Therefore, the slow component of the vibrational frequency fluctuation is determined by different underlying dynamics, which are important for the solvation dynamics of the electronic state. The time constant for the picosecond component for the vibrational frequency fluctuation does not significantly depend on the solute. We propose that the vibrational frequency fluctuates because of the constant structural changes in the hydrogen-bonding network of water molecules around the solute.

Introduction

Liquid water forms a three-dimensional hydrogen bonding network, in which hydrogen bonds are continuously broken and formed, and the network structure fluctuates. The fluctuation of the hydrogen bond network accompanies a large fluctuation in the potential energy in the system.[1] These water dynamics cause fluctuations in the intramolecular energy levels of a solute molecule, such as the vibrational and electronic states, and thus affect properties of solute molecules in water. Therefore, chemical reactions in

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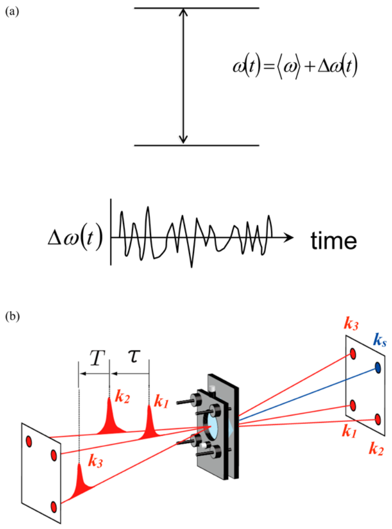

FIGURE 1. (a) Schematic illustration of the frequency fluctuation. (b) Illustration of the pulse geometry for the three-pulse photon echo experiment.

aqueous solutions and the functionality of biological molecules, such as proteins, are influenced by the fluctuations in water. It is crucial to examine the dynamical effect of water on the solute molecule in order to understand these chemical and biological effects.

In this Account we review three-pulse infrared (IR) photon echo studies of the frequency fluctuations of the vibrational states of ionic solute molecules in aqueous solutions. The three-pulse IR photon echo is an optical analogue of the accumulated spin echo in magnetic resonance and is capable of distinguishing homogeneous and inhomogeneous contributions to the transition frequency. Inhomogeneity means that each oscillator exists in a different local environment, giving a distribution of the transition frequencies The frequency fluctuation is characterized by the frequency time-correlation function (FTCF), which is defined as

$$M(t) = \langle \Delta\omega(t)\Delta\omega(0)\rangle \qquad (1)$$

where $\Delta\omega(t)$ is the shift of the vibrational frequency at time t from the average value (Figure 1a).

IR photon echo is a time-domain nonlinear technique based on the third-order nonlinearity of the polarization.[2] The sub-picosecond IR pulse with a pulse duration of 150 fs is split into three beams, which are focused on the sample in the boxcar geometry (Figure 1b). The photon echo signal is detected in the phase-matched $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ direction, where $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ are the wavevectors of the first, second, and third pulses, respectively. The time intervals are defined as τ and T: τ is the time interval between the $\mathbf{k}_1$ and $\mathbf{k}_2$ beams, and the population time, T, is the time interval between the $\mathbf{k}_2$ and $\mathbf{k}_3$ beams for $\tau > 0$ or between the $\mathbf{k}_1$ and $\mathbf{k}_3$ beams for $\tau < 0$.

We also describe the energy fluctuation of the electronic state of the solute to compare it with the vibrational case using the dynamic fluorescence Stokes shift experiment. In this technique, a probe molecule is excited to the electronically excited state, and the charge distribution of a probe molecule is altered instantaneously. The dynamic response of solvents is monitored by measuring the time dependence of the emission frequency, which is called the fluorescence dynamic Stokes shift. The relaxation is characterized by the response function,

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \qquad (2)$$

where $\nu(t)$, $\nu(0)$, and $\nu(\infty)$ are the peak wavenumbers of the time-dependent fluorescence spectra at t, 0, and ∞, respectively. In linear-response theory, the time correlation function (TCF) of the fluctuation in the equilibrium state is proportional to the normalized response function, which characterizes relaxation of the nonequilibrium state.

During these measurements, the solvent environment around the probe is polarized by the change in its charge distribution. On a microscopic level, the dynamics are complex, because in highly polar solvents the response arises not from the behavior of a single particle, but rather from the collective behavior of many molecules acting simultaneously. However, the overall time scale of solvation can be predicted with good accuracy by simply ignoring the molecular nature of the solvent and treating it as a dielectric continuum that possesses a frequency-dependent dielectric constant, $\varepsilon(\omega)$. Therefore, we will briefly explain the dielectric relaxation of liquid water and how it relates to the solvation dynamics. We will focus on the effect of the temperature dependence and the isotope effect on both the frequency fluctuations and compare them in light of the theoretical predictions using the dielectric relaxation of water. We will discuss the important interactions between the solute and solvent and the solvent dynamics, which dominate the vibrational frequency fluctuation.

Three-Pulse IR Photon Echo Experiments in Aqueous Solutions

A photon echo signal is expressed by integrating the third-order nonlinear polarization with respect to t:[3]

$$I(\tau, T) = \int_0^{\infty} \left| P(t, T, \tau) \right|^2 \mathrm{d}t \qquad (3)$$

TABLE 1. Parameters of Absorption Spectra of Probe Molecule and Population and Rotational Relaxation Times at Room Temperature

solute	solvent	ν_{max}/cm^{-1}	$\Delta\nu$/cm^{-1} (fwhm)	population relaxation time T_1/ps	orientational relaxation time T_R/ps	ref
OCN^-	CH_3OH	2161	20	2.9	6.6	5
SCN^-	CH_3OH	2062	45	11.0	8.8	5
SCN^-	D_2O	2063	35	18.3	4.7	7
N_3^-	D_2O	2043	18	2.3	7.1	54
N_3^-	H_2O	2048	25	0.8 ± 0.1	1.3 ± 0.3	55
$[Fe(CN)_6]^{4-}$	D_2O	2036	16	0.70 (17%), 23.0(83%)	2.6	6
$[Fe(CN)_6]^{4-}$	H_2O	2037	16	0.60 (20%), 3.7 (80%)	2.0	6
$[Ru(CN)_6]^{4-}$	D_2O	2045	14	0.8 ± 0.1 (39%), 20.8 ± 1.3 (61%)[b]	3.1 ± 0.4	9
$[Fe(CN)_5(NO)]^{3-}$[a]	D_2O	1935	16	7.3	16	11
$[Fe(CN)_5(NO)]^{3-}$	H_2O	1936	15	22	20	11

[a] The probe vibrational mode is the NO stretching mode. [b] Obtained from the isotropic component of the pump–probe signal for the $v = 2-1$ transition. [c] From Li, M.; Owrutsky, J.; Sarisky, M.; Culver, J. P.; Yodh, A.; Hochstrasser, R. M. *J. Chem. Phys*. **1993**, *98*, 5499–5507.

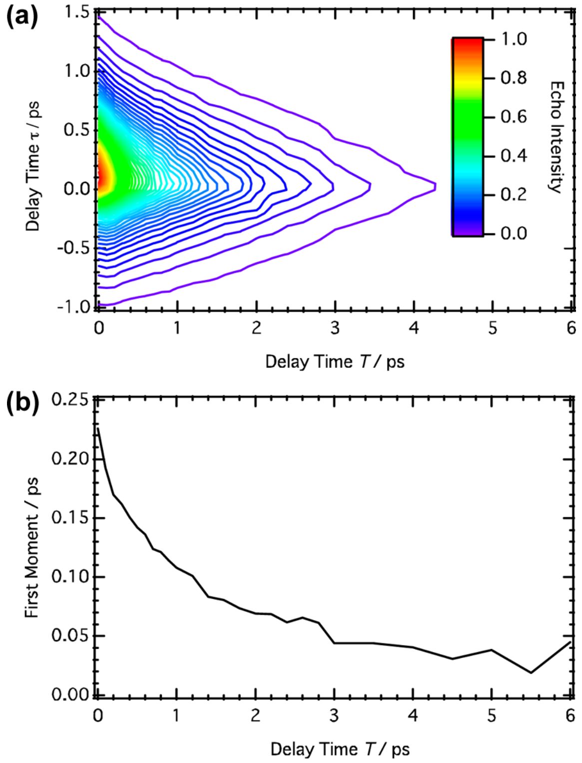

FIGURE 2. (a) Three-pulse photon echo signal plotted against delay times, *t* and *T*, for the antisymmetric stretching mode of azide in D_2O at 303 K. (b) First moment of the photon echo signal from the experimental results.

Third-order polarization is expressed by the convolution of the response function, $R(t_1,t_2,t_3)$, with the electric fields of the laser pulses.[3] The response function can be described by the product of an isotropic vibrational response function and an orientational response function. The orientational response function depends on the polarization of the external electric fields. A detailed description of the isotropic part of the response functions has been published elsewhere.[2−4] The isotropic part is affected by both the population relaxation of the excited vibrational state and the vibrational frequency fluctuations. Thus, information about the FTCF can be extracted from the analysis of the three-pulse photon echo signals.

This means that information about the population relaxation and orientational relaxation of the vibrational state is required in order to analyze the photon echo signal. These dynamical quantities were investigated by the pump−probe or transient grating technique in the IR region, which are also third-order nonlinear techniques. In Table 1, we summarize the results from the FTIR measurements of the probe molecule together with those of the population relaxation and orientational relaxation for methanol and aqueous solutions at room temperature.[5−11] The results for the temperature dependence on N_3^- in aqueous solutions can be found in ref 10.

We have studied the vibrational frequency fluctuation of probes, such as triatomic ions and metal complexes with CN or NO ligands, in various hydrogen-bonding solvents, including water droplets in reverse micelles.[5−14] The concentrations of the solutes were 20−60 mM, which are low enough to ensure that the solvation shells do not overlap. Figure 2a shows the three-pulse IR photon echo signals of N_3^- in D_2O at 303 K under all-parallel polarization conditions. At population times, *T*, before 0.4 ps, the center of mass of the photon echo signal is located at 200−250 fs, indicating an inhomogeneous distribution of the vibrational frequency. The peak of the echo signal shifts toward zero as *T* increases. This behavior shows that the local environment of each oscillator is inhomogeneously distributed and evolves on a time scale of a few picoseconds. The degree of asymmetry of the photon echo signal along the τ-axis is characterized by calculating the first moment of the photon echo signal as a function of *T* (Figure 2b). The first moment is

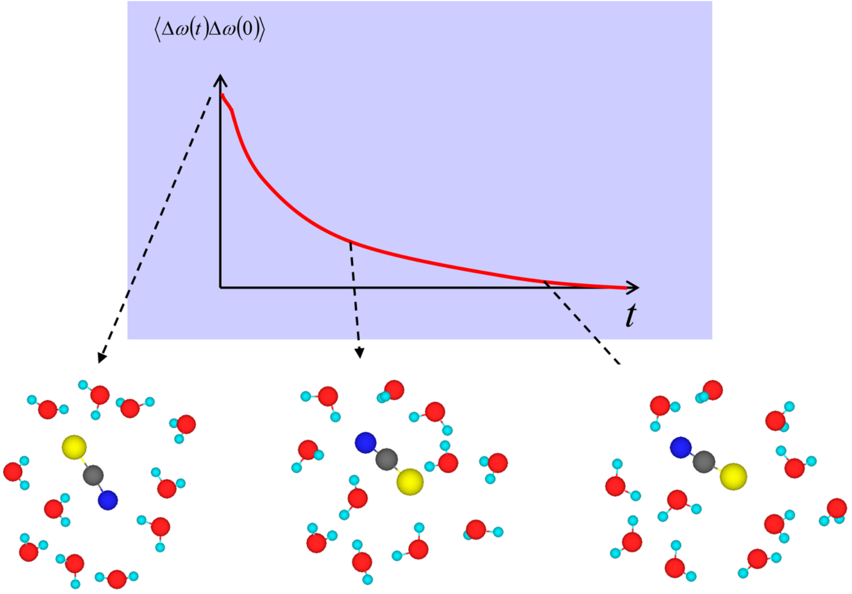

FIGURE 3. Schematic illustration of the microscopic dynamics in solution and the time dependence of the first moment of the photon echo signal. The water molecules around the probe ion evolve with time, which is observed as the decay of the first moment.

defined as

$$FM(T) = \frac{\int_{-\infty}^{\infty} d\tau \tau I(\tau, T)}{\int_{-\infty}^{\infty} d\tau I(\tau, T)} \qquad (4)$$

where $I(\tau, T)$ is the intensity of the experimentally observed photon echo signals. As T increases, the frequencies are sampled throughout the inhomogeneously broadened spectrum (Figure 3). The decay time scale of the first moment is approximately proportional to that of the FTCF of the frequency fluctuation.[15−17] The first moment of the three-pulse IR photon echo signals can be directly obtained from the experimental data without complex numerical simulations. The first moment is a useful quantity for surveying the sample imhomogeneity.

We quantitatively evaluated the parameters for the FTCF of the vibrational transition frequency fluctuation by simulating the temporal profile of the photon echo signals, and considering the pulse duration and IR absorption spectrum simultaneously. The FTCF of the vibrational frequency fluctuation is assumed to be a sum of exponentials plus a quasi-static component that is independent of delay time for the duration of the measurement:

$$M(t) = \sum_{i=1}^{2} \Delta_i^2 \exp\left(-\frac{t}{\tau_i}\right) + \Delta_0^2 \qquad (5)$$

Table 2 summarizes the parameters in eq 5 for various ions in aqueous solutions.[5−11,14] The table also includes the results for the triatomic ions in methanol for comparison. The ultrafast component has a rapid modulation limit ($\tau_1\Delta_1 < 1$); thus, only the dephasing time ($1/\tau_1\Delta_1^2$) can be obtained accurately, and the uncertainty of the amplitude, Δ_1, and the time constant, τ_1, may be ±50%. Pure dephasing time, $T_2^*(= 1/\Delta_1^2\tau_1)$ is used to describe this component in the correlation function (Table 2). This time scale is similar to the ultrafast component observed in the solvation dynamics for the electronic state in water, which is attributed to the inertial motion of the solvent. The slow and quasi-static components of the amplitudes of the FTCF were determined within errors of a few percent; the error was estimated from the fitting to the experimental results. However, the uncertainty of the time constant, τ_2, was estimated to be around ±20%.

The temperature dependence of the FTCF parameters for N_3^- in D_2O are summarized in Figure 4. Investigation of the temperature dependence of the time constants is important to understand molecular mechanisms of the fluctuations. The decay time, τ_E, of the first moment of the photon echo signal, which can be fitted by a single-exponential function for all temperatures, was plotted. τ_E was directly obtained from the experimental results without performing any simulations of the photon echo signals. The results in Table 2 and Figure 4 show that the FTCF is expressed by a biexponential function with a quasi-static term, and the time constant of the fast component is about 0.1 ps and that of the slow component is several picoseconds. Furthermore, the time constant for the slow component did not significantly depend on the solute.

TABLE 2. Parameters for Time-Correlation Function of Frequency Fluctuations

molecule	solvent	Δ_1 (ps^{-1})	τ_1 (ps)	T_2^* (ps)	Δ_2 (ps^{-1})	τ_2 (ps)	Δ_∞ (ps^{-1})	ref
OCN^-	CH_3OH	1.3	0.12	4.9	1.6	4.5	0.55	5
SCN^-	CH_3OH	2.6	0.09	1.6	3.6	4.1	0.1	5
SCN^-	D_2O	4.3	0.08	0.7	2.7	1.3	0.0	7
N_3^-	D_2O	2.6	0.08	1.8	1.4	1.3	0.3	2
N_3^-	H_2O	4.0	0.08	0.8	1.0	1.2	0.2	14
$[Fe(CN)_6]^{4-}$	D_2O	2.8	0.08	1.6	1.15	1.5	0.0	6
$[Fe(CN)_6]^{4-}$	H_2O	2.95	0.08	1.4	1.0	1.4	0.0	6
$[Ru(CN)_6]^{4-}$	D_2O	3.0	0.08	1.4	0.8	1.4	0.1	9
$[Fe(CN)_5(NO)]^{3-}$	D_2O	3.0	0.09	1.2	1.3	1.0	0.2	11
$[Fe(CN)_5(NO)]^{3-}$	H_2O	2.6	0.09	1.6	1.3	1.0	0.2	11

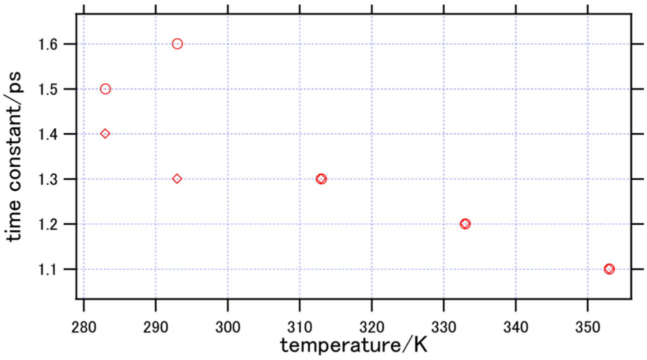

FIGURE 4. Temperature dependence of the FTCF parameters for the vibrational frequency fluctuation of the antisymmetric stretching mode of azide in D_2O.[10] The decay times of the first moment τ_E (circles) and the slow time constants of FTCF τ_2 (diamonds).

Dielectric Relaxation of Water

The frequency-dependent dielectric constant $\varepsilon(\omega)$ is calculated from the TCF of the total dipole moment of the system, $\mathbf{M}(t)$:[18]

$$\Phi(t) = \langle \mathbf{M}(t)\cdot\mathbf{M}(0)\rangle/\langle \mathbf{M}(0)^2\rangle \tag{6}$$

$$\frac{\varepsilon(\omega) - 1}{\varepsilon_0 - 1} = 1 - i\omega\int_0^\infty \mathrm{d}t e^{-i\omega t}\Phi(t) \tag{7}$$

where ε_0 is the dielectric constant at zero frequency. Because $\mathbf{M}(t)$ is a sum of the individual dipole moment $\boldsymbol{\mu}_i(t)$, that is, $\mathbf{M}(t) = \Sigma_i\boldsymbol{\mu}_i(t)$, $\Phi(t)$ carries information about the correlation of the different dipoles, $\langle\mu_i(t)\mu_j(0)\rangle$. Therefore, the dielectric response involves the collective behavior of many molecules. Local structures in water are well developed because of hydrogen bonding, which makes the dielectric constant of the liquid quite large.[19]

The dielectric response of water has been studied for many years. The frequency-dependent dielectric constant is represented by a double Debye model with sub-picosecond τ_{D1} and picosecond τ_{D2} time constants:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_1}{1 + i\omega\tau_{D1}} + \frac{\varepsilon_2}{1 + i\omega\tau_{D2}} \tag{8}$$

where ε_∞ is the infinite frequency dielectric constant. The slow Debye component, τ_{D2}, has been extensively investigated by dielectric loss measurements in the megahertz and gigahertz regions, and recent progress in terahertz time-domain spectroscopy (THz-TDS) has allowed the fast Debye component, τ_{D1}, to be studied in detail. Equation 7 shows that $\varepsilon(\omega)$ becomes a single Debye relaxation form if the TCF is expressed by an exponential function. The temperature dependence of τ_{D2} is almost proportional to η/T, where η is the viscosity of water and T is the temperature, indicating that this component can be described by a hydrodynamic model.

Recently, Yada et al. determined the temperature dependence of the dielectric response of H_2O and D_2O from 270 to 362 K by THz-TDS, by using an attenuated total reflection method.[20] They investigated the fast Debye component in detail and found that it has a sub-picosecond time scale and shows weaker temperature dependence than the slow component. The temperature dependence of τ_{D2} and τ_{D1} is plotted in Figure 5. Furthermore, the difference between the fast component time constant for D_2O and H_2O is negligible, which is also in sharp contrast to the slow Debye component.

Several theoretical calculations have demonstrated the molecular origin of the high-frequency response of the dielectric relaxation in water. Cho et al. performed normal-mode analysis of liquid water; the stable instantaneous normal modes below 100 cm^{-1} that are largely translational are also delocalized.[21] Their results provide quantitative evidence that the low-frequency modes may be associated with large-scale, collective motions. Further analysis, numerical simulation, and detailed discussions are required in future studies.

Solvation Dynamics in Aqueous Solutions

The response function of the solvation dynamics, $C(t)$, is profoundly related to the dielectric properties of the solvent.

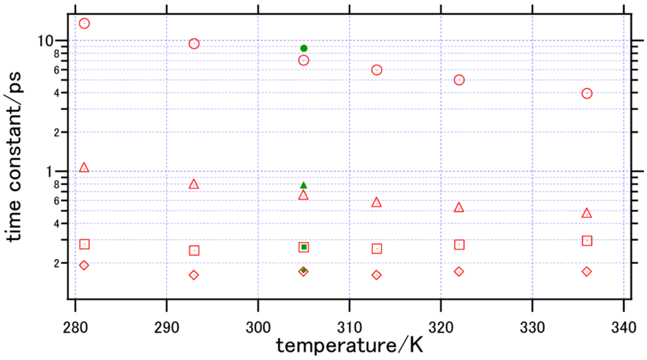

FIGURE 5. Temperature dependence of dielectric properties (τ_{D1}, squares; τ_{D2}, circles) and solvation dynamics (τ_{S1}, diamonds; τ_{S2}, triangles) of H_2O. The Debye time constants are from ref 20. The time constants of the solvation dynamics are calculated from ref 22 and the reported values for the dielectric parameters. The corresponding values for D_2O at 305 K are indicated by the green symbols.

Experimentally, the response functions were monitored mostly by fluorescence up-conversion with fluorescent dyes. It has been theoretically shown that, in dielectric continuum theory, the solvation time, which is the decay time of *C*(*t*), is approximately expressed as

$$\tau_S \approx \frac{\varepsilon_\infty}{\varepsilon_0}\tau_D \tag{9}$$

where τ_D is the Debye relaxation time.[22-24] However, for many liquids, the dielectric response is not described by a single Debye relaxation form. Bagchi et al. derived an analytical expression for *C*(*t*) within dielectric continuum theory for when the dielectric relaxation is expressed by a double Debye model with time constants of τ_{D1} and τ_{D1}, as it is for water. The expression is a biexponential function with time constants τ_{S1} and τ_{S2}.[22] We estimated the temperature dependence of τ_{S1} and τ_{S2} using the reported values of τ_{D1} and τ_{D2} of water, and ignoring the rotational diffusion of the solute molecule (Figure 5). The time constant of the slow solvation component, τ_{S2}, shows a large temperature dependence, which is mainly caused by the temperature change of the slow Debye component, τ_{D2}. This change can be rationalized by a hydrodynamic theory, such as the Stokes–Einstein–Debye model. In contrast, the fast solvation component, τ_{S1}, which is dominated by the contribution from τ_{D1}, is almost independent of temperature.

The solvation dynamics of water have been studied by several groups. Barbara and co-workers reported that *C*(*t*) of water is characterized by a biexponential function with time constants of 0.16 and 1.2 ps.[25] They used an ionic coumarin dye molecule, 7-(dimethylamino)couramin-4-acetate. They also used coumarin 343 as a probe to investigate the temperature dependence of solvation dynamics in water.[26] Fleming and co-workers observed a sub-100-fs component, which was assigned to the inertial motion of the solvent, when the time resolution was improved.[27] Strikingly, the fastest component was the main contribution to the total Stokes shift. They also used the three-pulse photon echo peak shift method, which is based on the third-order nonlinear effect, to investigate solvation dynamics in water.[28]

The picosecond component of the FTCF vibrational frequency fluctuation, τ_2, and that of the solvation dynamics, τ_{S2}, are both around 1 ps at room temperature. However, for the solvation dynamics in D_2O, τ_{S2} is about 20% longer than that in H_2O, mainly because of the different solvent viscosity; the solvent isotope effect on τ_2 is smaller than the effect on τ_{S2}. Furthermore, τ_2 is less sensitive to temperature than τ_{S2}, although both have similar time scales.

These results clearly indicate that the slow component of the vibrational frequency fluctuation is determined by different liquid dynamics which are important for the solvation dynamics of the electronic state. A similar comparison between the vibrational frequency fluctuation and solvation dynamics was made by Fayer and co-workers.[29] They investigated spectral diffusion in the hydroxyl stretch of methanol-*d* dissolved in a solution of methanol-*h* and CCl_4 by vibrational transient hole burning. The dynamics were compared with the dielectric continuum theory predictions, which were used to interpret the solvation dynamics of the electronic state in dipolar solvents. They found that simple continuum theory could not explain the experimental results, suggesting that the dynamics do not result from the long-wavelength collective orientational relaxation of the solvent but arise from fluctuations in the local hydrogen-bonding network.

Microscopic Dynamics of the Fluctuation

The dynamics of the hydrogen-bonding networks in water have been investigated by ultrafast IR spectroscopy in conjunction with molecular dynamics (MD) simulation.[30-44] In these experiments and MD simulations, the fluctuation of the OH (OD) stretching frequency was monitored for a solution of HOD in D_2O (H_2O). Tokmakoff and co-workers analyzed the 2D line shape of the OH stretching mode of HOD in D_2O. The dynamics showed a short 60 fs decay, an underdamped oscillation on a 130 fs time scale induced by hydrogen bond stretching, and a long time decay constant of 1.4 ps.[41] The MD simulation elucidated the relationship between the FTCF and the time evolution of the liquid structure. Comparison of the experimental and computational results showed that the slow component of the correlation function is due to complete structural reorganization, including the collective rearrangement of the hydrogen-bonding network. Moreover, 2D IR experiments on the OD stretching mode of HOD in H_2O by Fayer and co-workers extracted the FTCF with decay components of 48 fs, 400 fs, and 1.4 ps.[45] The MD simulation, which employed a polarizable water model, predicted a value of the FTCF which was very close to the experimental results. The corresponding spectral diffusion of the HOD in D_2O and H_2O systems shows that the hydrogen bond dynamics of D_2O and H_2O are very similar.[46]

We also observed a small isotope effect on the time scale of the slow component in the FTCF for the ionic solutes in water. Furthermore, the time scales of the longest component in the spectral diffusion of the HOD in the D_2O and H_2O systems were similar to those for the aqueous solution systems. Because of these similarities between pure water and the aqueous solutions, the slow component in the frequency FTCF for the aqueous solutions must originate from the same mechanism as that for the OH or OD stretching mode in the pure water system.

Theoretical studies of the vibrational frequency fluctuations have been conducted for aqueous solution systems using MD simulations. The results for CN^- and N_3^- in water and methanol indicated that the time scale of the hydrogen bond dynamics in methanol is about three times longer than that in water.[47] This was consistent with our experimental observations. However, the MD simulation study also showed that the hydrogen bonding dynamics are very sensitive to the charge distribution of the ion. Because the hydrogen bond dynamics involve short-range electrostatic interactions between the ion and solvent, it is logical that a small change in the charge of the solute affects the time scale on which the hydrogen bonds are formed and broken. Although the charge distributions of the ions and their different effects on the hydrogen bond dynamics are not known quantitatively, the experimental results show that the dynamics of the correlation function are mainly affected by properties that are characteristic of the solvent.

Skinner and co-workers investigated the vibrational frequency fluctuations of N_3^- in D_2O using an MD simulation.[48] They calculated the FTCF of the electric field from the surrounding solvent along the antisymmetric stretching mode of N_3^-, the vibrational frequency fluctuation of the mode, and the solute−solvent hydrogen bond number fluctuation. They also calculated the TCF of the hydrogen bond number fluctuation, $\langle \Delta n(t)\, \Delta n(0) \rangle$, where $\Delta n(t) = n(t) - \langle n \rangle$ is the fluctuation of the number of hydrogen bonds from equilibrium. They found that the hydrogen bond TCF decays slightly faster for longer times ($t > 0.5$ ps) than the FTCF. They also calculated the projection of the electric field along the molecular axis of N_3^- caused by the surrounding water molecules. They showed that the decay of the TCF of the electric field fluctuation is very similar to that of the FTFC of the vibrational transition. This is consistent with the findings reported by Tokmakoff and co-workers for the HOD/D_2O system. They concluded that for longer times ($t > 200$ fs) the relaxation originates from large scale cooperative reorganization and not from specific molecular motions, such as the forming and breaking of hydrogen bonds.[49] Skinner and co-workers also showed that hydrogen bond and electric field fluctuations are not mutually exclusive explanations, because the field is dominated by the nearest neighbors, which are the ones involved in forming and hydrogen bonds.[48] The importance of the electric field fluctuations in the simulated vibrational frequency fluctuations for both the N_3^-/D_2O and the HOD/D_2O systems is consistent with our observation that the long FTCF decay for solutes in aqueous solutions is similar to that of HOD/D_2O system.

The vibrational frequency fluctuation of the ions in aqueous solutions can be summarized as follows: the hydrogen bond between the ionic probe and the water molecule influences the vibrational transition frequency of the intramolecular mode of the probe. However, the breaking and forming of hydrogen bonds between the solute and solvent is not the main mechanism by which the vibrational mode of the ion is modulated. Instead, the collective dynamics of water around the ion is characteristic of water itself and is important for the vibrational frequency fluctuation. The fluctuation of the local electric field produced by water molecules around the ion may be a source of the vibrational frequency fluctuation, which is the conclusion that Skinner and co-workers also reached in their theoretical work. In this case, the electrostatic interaction between the ionic probe and the adjacent water molecules may make relatively strong hydrogen bonds, and these bonds may be stable and fluctuate without breaking. This is schematically illustrated in Figure 6. There are two possible scenarios for these water molecules coordinated to ions. The first is that the

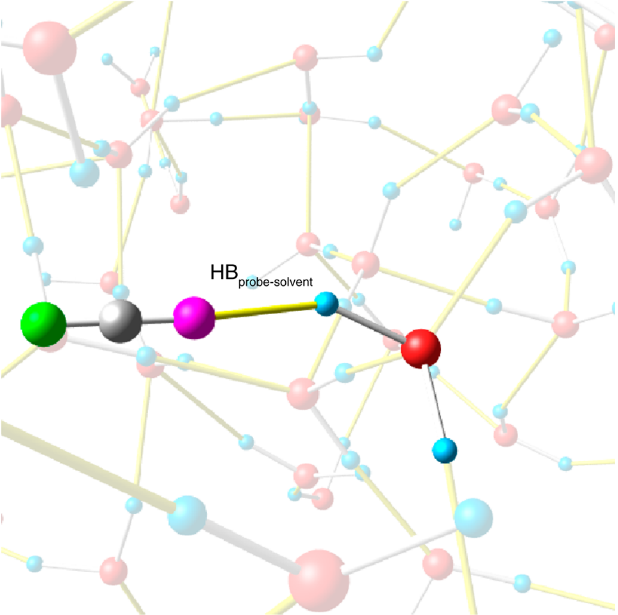

FIGURE 6. Schematic illustration of the vibrational frequency fluctuation of solute molecules in water.

bound water molecules participate in hydrogen bond networks with other water molecules, and the fluctuation of the hydrogen bonds between the ion and water molecules are controlled by the structural rearrangement of the networks. The probe molecule "feels" the fluctuation in the water hydrogen bond network through the ion–water hydrogen bond. The second scenario is that the bound water molecules are not connected to the surrounding network of water molecules, which are not bound to the ion. The latter microscopic picture is consistent with the conclusions drawn by Kuo et al. They used dual frequency 2D IR spectroscopy to investigate the correlation of the vibrations of N_3^- with the OH modes of the bound water molecules. The results showed that the OH bond of water in the solvent shell has frequency fluctuations that are considerably slower than those reported for bulk water, suggesting that the bound water molecules are isolated from the bulk water molecules.

The microscopic picture where the collective dynamics of the surrounding water molecules determine the vibrational frequency fluctuation of the ion also explains several experimental observations, such as the insensitivity of the time constant of the slow component, τ_2, to the solute, and the similarity of τ_2 to the frequency fluctuation time constant for pure water. This picture also suggests that the presence of the ion does not significantly affect the dynamics of the hydrogen-bonding network around the ion probe, at least on the picosecond time scale, because the picosecond component of the TCF nearly depends on the probe ion.

Outlook

We have used ionic probe molecules to study the vibrational dynamics in aqueous solutions. We have chosen these probes because of their high solubility in aqueous solutions. A further challenge would be to investigate the vibrational frequency fluctuations both in hydrophobic and hydrophilic environments, which will give an important insight into the relationship between water and biological functions. Furthermore, the concentrations of the solutions in this work are low enough to avoid the interference of different solvation shells. However, fluctuations in concentrated solutions are also interesting because the environment in living cells is also very congested. Fayer has already studied fluctuations of water in highly concentrated electrolyte solutions and in reverse micelles.[50]

This technique can be also used to probe local fluctuations in heterogeneous systems such as proteins or lipid bilayers. In these experiments, probe molecules, such as azide or its derivatives, are introduced in such biological systems, and the dynamics in the environment around the probe are detected by observing the vibrational frequency fluctuation.[51,52]

Another challenge is to clarify the quasi-static component, Δ_0. Because the chemical system we are studying is in the liquid state, all components should eventually decay to the baseline. We have performed a simulation using a triexponential function without a quasi-static term for the FTCF of the vibrational frequency fluctuation, $\langle\Delta\omega(t)\Delta\omega(0)\rangle = \Sigma_{i=1}^{3}\Delta_i^2 \exp(-t/\tau_i)$.[9] Because of the weak signal intensity in the longer delay time region, it was difficult to determine the Δ_3 and τ_3 values accurately. The slow dynamics in water originate from the collective dynamics in the local structure, which is one of the intrinsic anomalous characteristics of water.[1,53]

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FOOTNOTES

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