Possible Mechanism of OH Frequency Shift Dynamics in Water†

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The results of the recent infrared pump−probe experiment are analyzed, in which the time evolution of the spectrum of the OH-stretching vibration excited by an ultrashort laser pulse in the dilute solution HDO/D_2O was measured. To interpret the results of the experiment, a formalism developed earlier for a different application, optical transitions of the chromophoric molecules in polar solvent, is used. A mechanism of the IR shift dynamics in water is suggested, involving α-relaxation (structural relaxation), which may also be related to the dielectric behavior of water. A suggestion is made for computer simulations as well as for an experimental test of the proposed mechanism.

I. Introduction

The ability of water to form a relatively stable tetrahedral structure in which each molecule couples to four nearest neighbors by four hydrogen bonds is known to be at the origin of many unusual thermal properties of water, such as high melting and boiling temperatures, anomalous density, and heat capacity dependence on temperature. While some hydrogen bonds are broken in liquid water, one can still talk about the extended hydrogen bond network whose rearrangement controls the dynamics of liquid water.[2,3] Breaking and making a hydrogen bond is at the heart of such kinetic properties of water as dielectric relaxation[4] and prototropic mobility.[5]

Recent advances in the development of infrared time-resolved spectroscopy made it possible to observe directly the dynamics of the hydrogen bond in real time. In a pioneering femtosecond pump−probe infrared experiment Gale et al.[6] studied the time evolution of the spectrum of the OH-stretching vibration in the diluted solution HDO/D_2O. An ultrashort pump pulse (150 fs) with the frequency in either the blue or the red wing inside the OH-stretching band was used to excite the OH vibration to its first excited state. An independently tunable probe pulse of the same duration was used to obtain the differential absorption spectrum between 2700 and 3800 cm^{-1} at a fixed pump−probe delay time. A time evolution of the spectral shift, which is characterized by the first moment $\bar{\nu}(t)$ of the spectrum, was observed by varying the delay time. The OH vibration frequency shift relative to the frequency of the nonbonded OH group is directly related to the O−H···O distance and has even served as a synonym for the hydrogen bond strength.[7−10] Thus, on this basis, measuring the time development of the OH frequency allows one to monitor the dynamics of the hydrogen bond. Gale at al.[6] have found that the frequency shift relaxation shows an exponential decay with a good accuracy and that the relaxation time constant is 0.7 ps. A similar experiment has been performed by Woutersen and Bakker,[11] who have used the Brownian oscillator model[12] to interpret their results. We consider a theoretical model to interpret these results and the results for related phenomena.

II. Theory

A theory which describes the transient spectral shift and other nonlinear spectroscopic phenomena was developed earlier in applications to the optical transitions of the chromophoric molecules in polar solvents.[12,13] This theory is analogous to the theory of nonadiabatic transitions[14,15] of a system strongly interacting with the environment, which was also used to describe electron-transfer reactions.[16−18] A similar formalism for vibrational transitions, which also takes into account the finite population and orientation relaxation times, was developed recently.[19,20] For our purposes, however, it is sufficient to use the earlier less sophisticated treatment, which takes into account only the transition frequency fluctuations and neglects the population and orientational relaxation. Originally the theory was developed under the assumption that the role of the environment can be modeled by a collection of harmonic oscillators[16] (the so-called harmonic oscillator model and spin-boson Hamiltonian). It was shown later that the results obtained using this model are valid under rather general conditions.[21−23]

The key quantity which enters into the theory is the correlation function $C_\nu(t)$

$$C_\nu(t) = \langle \delta\nu(t)\, \delta\nu(0)\rangle \tag{1}$$

where in the present case ν is the instantaneous frequency of the main transition of the O−H stretch. In particular, the normalized evolution of the spectral shift can be approximately expressed as[24−27]

$$\frac{\bar{\nu}(t) - \bar{\nu}(\infty)}{\bar{\nu}(0) - \bar{\nu}(\infty)} = \Delta(t) \tag{2}$$

where $\Delta(\boldsymbol{t})$ is $C_\nu(t)$ normalized to unity at its maximum:

$$\Delta(t) = C_\nu(t)/C_\nu(0) \tag{3}$$

Another important quantity which characterizes the contribution of the fluctuations from different spectral regions is the solvent spectral density $J(\omega)$, which is related to $C_\nu(t)$ by a Fourier transform:[28]

$$J(\omega) = 2\int_0^\infty \mathrm{Im}[C_\nu(t)] \sin \omega t\, dt \tag{4}$$

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To relate the spectral dynamics to the statistical and dynamical properties of the solvent, one has to approximate the relationship between the OH-stretching frequency shift and the deviation of the O−H···O hydrogen bond from its most probable configuration. A crucial configurational factor appears to be the bond length *l*,[7−10] as noted earlier. Since we are interested in a relatively small deviation of the OH frequency from its most probable value, this relationship can be approximated as a linear one

$$\delta \nu \propto \delta l \tag{5}$$

As a result, the time evolution of the OH frequency reflects the hydrogen bond dynamics expressed in terms of the correlation function

$$C_l(t) = \langle \delta l(t)\, \delta l(0) \rangle \qquad \Delta(t) = C_l(t)/C_l(0) \tag{6}$$

Using eq 6, one could use the molecular dynamics simulations to estimate the time evolution of the spectral shift.[29]

The statistical theory of nonlinear processes allows one to relate to the observed spectral dynamics the statistical and dynamical properties of the solvent, expressed in terms of the appropriate equilibrium time-correlation function, the bond length autocorrelation function $C_l(t)$, eq 6 in our case. However, it does not provide the correlation function $C_l(t)$ and so does not in itself state the physical mechanism of the observed relaxation. We discuss the physics behind the hydrogen bond dynamics in the context of other physical processes and measurements.

Different physical processes and, therefore, different physical mechanisms may be related to the hydrogen bond dynamics observed with ultrafast vibrational spectroscopy. The water molecule reorientation occurs on a 1−2 ps time scale at room temperature as deduced from the results of the experiments on the Raman-induced Kerr effect,[30] Rayleigh light scattering,[31] and quasi-elastic and inelastic neutron scattering.[32] The OH frequency relaxation does not require, however, the rupture of its hydrogen bond, in contrast to the water molecule reorientation. This physical difference may account for the factor of about 2 difference in the corresponding time scales, the time scale of the former being, as already noted, about 0.7 ps.

Another way of interpreting the results of the *OH* frequency relaxation is to view it as a result of a local structure perturbation.[33] Its mechanism can then be related to the α process, namely, the structural relaxation which is reflected in the density−density correlation function[34]

$$\Phi(\mathbf{r},t) = \langle \rho(\mathbf{r},t)\, \rho(0,0) \rangle \tag{7}$$

and its Fourier transform, the dynamic structure factor $S(\mathbf{q},\omega)$

$$S(\mathbf{q},\omega) = (2\pi)^{-4}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}^3\mathbf{r}\, \mathrm{d}t\, \mathrm{e}^{i\mathbf{qr}-i\omega t}\Phi(\mathbf{r},t) \tag{8}$$

The density fluctuations are differently influenced in the low and high-frequency limits. At low frequencies, when $\omega\tau_\alpha \ll 1$, where τ_α is the α-relaxation time, the α-relaxation appears as a standard viscosity. At high frequencies, when $\omega\tau_\alpha \gg 1$, the liquid shows quasielastic, solidlike behavior. I.e., this τ_α is defined as $1/\omega_\alpha$, where ω_α is the frequency where the transition of the two behaviors occurs. While α-relaxation may have different meanings we mean the slowest relaxation for the property and temperature of interest. The α-relaxation has been observed for water in X-ray measurements[34] and for glycerol−water mixtures in ultrasonic experiments.[35] It was invoked in the Brillouin scattering studies[36] to interpret the observed negative dispersion of the sound velocity. The results of all these studies give a relaxation time $\tau_\alpha = 0.7-0.8$ ps at room temperature, which is in the good agreement with the result of the transient infrared spectroscopy measurement.

It is worth noting so that structural relaxation in water, which is extremely fast, is not well understood. In particular, there is evidence, which is based on the apparent hysteresis in refractive index of water as a function of temperature,[37] that there are different structural relaxation time scales in water depending on the length scale involved.

In principle, one way of testing our assumption that the α-relaxation and IR-relaxation are of similar origin, would be to compare the temperature dependence of the α-relaxation time and the frequency relaxation time over a broad range of temperatures. At temperatures below 0 °C, however, the α-relaxation time becomes larger than the population relaxation time[6,35] of the *OH* vibration and, therefore, the frequency relaxation would become increasingly difficult to observe, because of sensitivity. As an alternative at those low temperatures, molecular dynamic simulations could be used to calculate the dynamic structure factor,[38,39] extract the α-relaxation time from it, and compare it with the numerical result for the frequency relaxation time, using eqs 2, 3, and 6. Accurate ab initio force field calculations with very large basis sets will probably be required for such simulations to reproduce quantitatively the cooperative phenomenon discussed here.

III. Discussion

It is interesting to compare the infrared frequency shift dynamics to the frequency shift dynamics for the electronic transition in the optical region. The physical mechanism of the solvatochromic shift dynamics of an optically excited solute whose dipole moment changes considerably after the excitation is well understood.[41,42] It can be viewed as a result of the dielectric response of the solvent to a sudden change of the solute charge distribution. The solvent spectral density $J(\omega)$, eq 4, and the normalized spectrum shift, eq 2, are expressed in terms of the frequency dependent dielectric permittivity $\epsilon(\omega)$ of the solvent. A particular expression, which contains also the excluded volume effect,[23,43] depends on a specific model of the solute. In the simplest possible case of a spherically symmetric solute with a point charge in its center $J(\omega)$ is given by[42]

$$J(\omega) \propto \mathrm{Im}[\epsilon^{-1}(\omega)] \tag{11}$$

Then the normalized correlation function $\Delta(t)$ is given by $\epsilon(\omega)$ of the solvent:

$$\Delta(t) = \frac{\int_0^{\omega_{\mathrm{op}}} \frac{\mathrm{d}\omega}{\omega} \cos \omega t\, \mathrm{Im}[\epsilon^{-1}(\omega)]}{\int_0^{\omega_{\mathrm{op}}} \frac{\mathrm{d}\omega}{\omega}\, \mathrm{Im}[\epsilon^{-1}(\omega)]} \tag{10}$$

where the frequency ω_{op} corresponds to the transparency region which separates the frequency region of the solvent nuclear motion and the one of the solvent electronic response. A slightly more complicated expression is given for the more realistic model of a point dipole in a sphere.

The optical solvatochromic shift dynamics in water is bimodal.[40] Initial fast nonexponential relaxation, which occurs on a 50−100 fs time scale, is followed by a slower exponential relaxation with a time constant $\tau_{\mathrm{ss}} = 880$ fs. The results of the calculation using the dielectric permittivity of water in a broad frequency range reproduce the normalized solvatochromic shift evolution well,[44] with no adjustable parameters.

The results of the above consideration, which refers to an electronically excited solute, cannot be directly applied to the infrared frequency shift dynamics, where the solute is excited vibrationally. First, the change of the dipole moment of the water molecule at the vibrational excitation is so small that it can be disregarded in a good approximation. Second, the relaxation observed by Gale et al.[6] is described well by a single exponential and seems to not contain the fast component which is very strong in the optical solvatochromic shift experiment[40] (ca. 50%).

On the other hand, we note that the relaxation time $T_{\mathrm{IR}} = 0.7$ ps measured in the infrared experiment of Gale et al.[6] is close to the slow relaxation time $T_{\mathrm{ss}} = 880$ fs of the solvatochromic shift in water of an optically excited dye molecule, whose dipole moments are different in the ground and excited electronic states.[40] This observation suggests that the relaxation mechanism in both experiments may be related.

To relate the OH frequency shift dynamics[6] to the dielectric property of water we accept a common view of water as a mixture of geometrically different species which are limited to a small set and which are in the dynamical equilibrium with each other.[45,46] For the sake of argument we will assume that there are just two such species, which have a different average OH bond length, even though there may be a broad range of such structures, just as a broad array of relaxation times can be represented approximately by a bimodal distribution. A vibrational excitation of the OH group at a particular frequency will create a subensemble of excited OHD molecules which may considerably deviate from an equilibrium ensemble in terms of the structures described above. As a result, this subensemble will evolve to its equilibrium distribution by interconversion between different species. At the same time, it is not unreasonable to assume that the dipole moments of such structures may change considerably by the transition between different species. Thus, the dielectric relaxation becomes coupled to the structural one.

If the interconversion between different structures is associated with a change in dielectric polarization the structural relaxation may then have a time constant similar to the longitudinal dielectric relaxation time of the solvent. On the other hand, the inertial (fast) component of the dielectric relaxation is expected to be faster than the structural relaxation and so to be in equilibrium with the interconverting structures. Because it does not interact directly with the OH vibration, but only through local structural changes, the inertial component of the dielectric relaxation will not appear as a separate component in the OH frequency shift dynamics. The latter is associated, in the view of the present paper, with the structural relaxation (α-relaxation).

It is worthwhile mentioning that even so the longitudinal dielectric relaxation time, which is observed in optical solvatochromic shift dynamics experiments, should be similar from our point of view to the α-relaxation time, they must not be the same. The difference comes from the uncertainty in geometrical shapes which should be prescribed to the interconverting local structures, as well as from the well-known fact of the dependence of the solvent relaxation time on such a shape.[23,43]

It is useful to summarize our comments on these two probes of water relaxation, namely the infrared OH shift and the optical shift due to change of dipole (and of other charge distribution) of the solute. The dynamical Stokes shift, namely the second of these probes, describes the relaxation of the solvent dielectric polarization by reflecting the changing interaction of new solute dipole with the solvent dielectric polarization. It contains, as already noted, both a fast (vibrational) dielectric polarization component of less than 100 fs, and a slow structural dielectric polarization component of 880 fs.[40] In the case of the IR shift, again as noted above, there is little change of solute dipole and so the primary effect experienced by the solute is the structural (α-relaxation) one, with an observed 700 fs relaxation time. This mechanism offers an interpretation of both why the fast component is missing in the IR shift experiment and why the time-scale of the slow component is approximately the same in both. Analysis of carefully selected correlations in a detailed computer simulation on an accurately calculated potential energy surface can illuminate the mechanism, and in particular the detatiled nature of the alpha-relaxation, further.

The temperature dependence of the solvatochromic shift relaxation time in an infrared experiment compared to the well-known temperature dependence of the Debye relaxation time would help to answer the question about the validity of the suggested mechanism. It would be interesting to try numerically to identify different geometrical configurational species and the shift in their dynamical equilibrium caused by the OH excitation, perhaps by calculating the appropriate structural time-correlation functions from molecular dynamics simulations.[47]

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