

Real-Time Measurement of the Orientational Dynamics of Aqueous Solvation Shells in Bulk Liquid Water

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We present a study of the orientational dynamics of aqueous solvation shells of halogenic anions in bulk water solution with femtosecond two-color midinfrared spectroscopy. These orientational dynamics have time constants between 2.5 and 12 ps, depending on the type of anion and the temperature. We find that the solvation shell of the larger ion I^- shows faster dynamics than that of the smaller ions Cl^- and Br^- .

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Water possesses many remarkable physical properties of which probably the best known is the decrease in density when liquid water freezes to ice. This behavior, as well as many other anomalous properties of water, results from the fact that water molecules can form extended three-dimensional hydrogen-bonded networks that occupy a relatively large volume.

Raman spectroscopic studies of aqueous salt solutions showed that the addition of cations and anions leads to a breakdown of the three-dimensional networks of water molecules [1]. The water molecules were found to form a directional hydrogen bond with the anions (Cl^- , Br^- , and I^-), with one of the O-H groups of the water molecule pointing toward the center of the dissolved ion. This was also observed in NMR studies [2] and in molecular dynamics simulations [3,4].

The study of aqueous solvation interactions is complicated by the strongly different local environments that water molecules in a liquid solution can have. Because of this inhomogeneity, the normal linear spectroscopic linewidths of the vibrational resonances do not give information on the dynamics of the solvation shell. Recently, it has become possible to investigate the hydrogen-bonded structure and dynamics of liquid water with a nonlinear spectroscopic technique in which the molecules are probed via the response of their O-H stretch vibrations [5–10]. In this technique, the O-H stretch vibration is excited with an intense and ultrashort midinfrared laser pulse and the dynamics of this excitation are probed with a second, ultrashort midinfrared or visible pulse. In this Letter, we report on the study of the orientational dynamics of HDO molecules in the aqueous solvation shells of the halogenic anions Cl^- , Br^- , and I^- in bulk liquid water.

The experiments are two-color femtosecond midinfrared pump-probe experiments on a dilute (0.1 M) solution of HDO dissolved in D_2O that contains a high concentration (1–3 M) of salt (NaCl, NaBr, or NaI). The midinfrared pulses used in these experiments are generated via parametric generation and amplification processes in BBO and KTP crystals from 800 nm pulses of a 1 kHz, 3 mJ, 100 fs Ti:sapphire regenerative/multipass amplifier. The generated midinfrared pulses are tunable between 2.7 and

4 μm , have a pulse energy up to 30 μJ , and a pulse duration of approximately 200 fs. The pump and probe pulses are independently tunable and have bandwidths of 80 and 60 cm^{-1} , respectively.

The pump pulse excites the O-H stretch vibration of approximately 5% of the HDO molecules to the first excited state ($\nu = 1$). This excitation leads to a bleaching of the linear absorption spectrum due to the decrease of the $0 \rightarrow 1$ absorption [$\ln(T/T_0) > 0$, with T the transmission of the probe and T_0 the transmission of the probe in the absence of the pump] and to an induced absorption at lower frequencies due to the $1 \rightarrow 2$ transition [$\ln(T/T_0) < 0$]. The latter absorption is redshifted by approximately 270 cm^{-1} with respect to the $0 \rightarrow 1$ transition, as a result of the anharmonicity of the O-H stretch vibration [5].

To study the orientational relaxation of the excited HDO molecules, we rotated the polarization of the probe pulse by 45° with respect to the pump polarization using a zero-order $\lambda/2$ plate. The transmission changes of the probe parallel to the pump [$\ln(T/T_0)_{\parallel}$] and perpendicular to the pump [$\ln(T/T_0)_{\perp}$] are measured as a function of the delay τ with respect to the pump. These signals are used to calculate the anisotropy parameter,

$$R(\tau) = \frac{\ln[T(\tau)/T_0]_{\parallel} - \ln[(T(\tau)/T_0)_{\perp}]}{\ln[T(\tau)/T_0]_{\parallel} + 2\ln[(T(\tau)/T_0)_{\perp}]}, \quad (1)$$

that reflects the orientational correlation of the O-H vector of an HDO molecule. The numerator of this expression depends on the delay τ due to the presence of orientational relaxation of the excited HDO molecules, vibrational energy relaxation of the excited $\nu = 1$ state, and spectral diffusion effects. The denominator of this expression represents the isotropic signal and is affected by vibrational energy relaxation and spectral diffusion such that the delay dependence of R reflects only the orientational relaxation.

In Fig. 1, the delay dependence of the induced $1 \rightarrow 2$ absorption is shown for a solution of 3 M NaCl in HDO: D_2O . The signal decays with a fast component with a time constant of 800 ± 100 fs and a slow component with a time constant of approximately 2.3 ± 0.2 ps. Experiments on solutions with different concentrations and different salts revealed that the slow component results

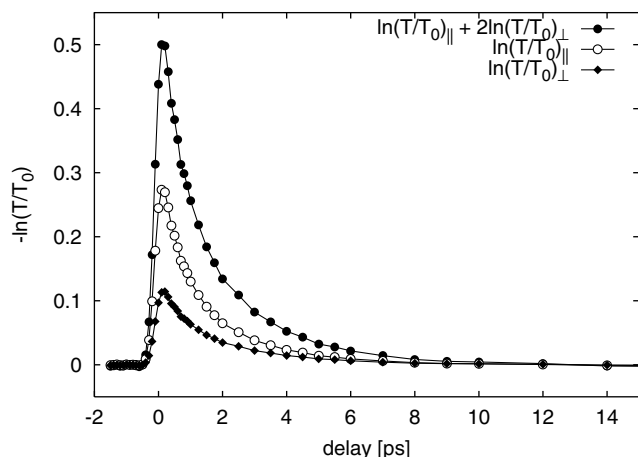


FIG. 1. Pump-probe transients measured for an aqueous solution of 3 M NaCl in HDO:D₂O at 27 °C with a pump frequency of 3450 cm⁻¹ and a probe frequency of 3200 cm⁻¹.

from HDO molecules forming O-H...Cl⁻-type hydrogen bonds with Cl⁻ anions, and the fast component results from HDO molecules forming O-H...O-type hydrogen bonds with D₂O molecules [10]. A great advantage of the large difference in vibrational lifetime is that after a few picoseconds only HDO molecules remain excited that are hydrogen-bonded to the Cl⁻ ion. This enables a very selective measurement of the dynamics of the HDO molecules that form O-H...Cl⁻ hydrogen bonds.

In Fig. 2, the anisotropy parameter R is presented as a function of delay for a solution of 3 M NaCl in HDO:D₂O at different temperatures. Also shown are fits to the data in the delay-time window from 3 to 8 ps in which the observed transients represent only the orientational dynamics of the HDO molecules in the first solvation shell of the Cl⁻ ion. At 27 °C, the orientational relaxation time constant τ_{or} of these HDO molecules is 9.6 ± 0.6 ps, which is quite long in comparison with the value of τ_{or} of 2.6 ps of

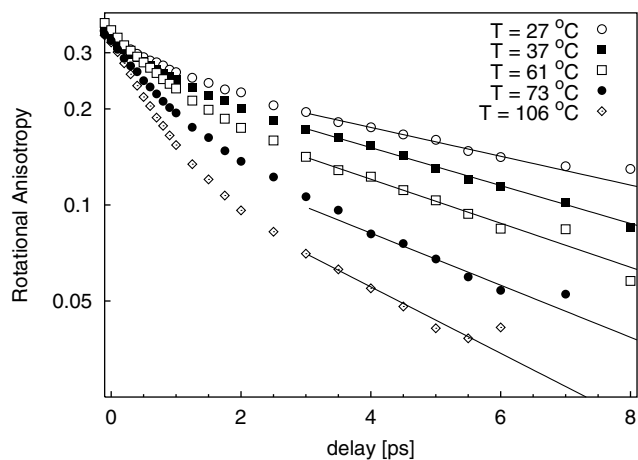


FIG. 2. Anisotropy parameter R as a function of delay τ for a solution of 3 M NaCl in HDO:D₂O at five different temperatures. The pump frequency is 3450 cm⁻¹ and the probe frequency is 3200 cm⁻¹. Also shown are the exponential fits to the transients in the delay-time range from 3 to 8 ps (solid curves).

HDO molecules in a solution of HDO in D₂O [9]. With increasing temperature, the orientational relaxation becomes much faster: τ_{or} decreases to 4.2 ± 0.4 ps at 106 °C.

The question now arises whether the observed reorientation of HDO molecules results from the reorientation of these molecules within the solvation shell of Cl⁻ or from the orientational diffusion of the complete shell. If the reorientation would take place within the shell, the O-H stretch frequency should be subject to a spectral diffusion process that is at least as fast as the reorientation, because such a reorientation would inevitably affect the O-H...Cl⁻ hydrogen-bond length, which is strongly correlated to the O-H stretch frequency [11]. The dynamics of the spectral diffusion can be measured by probing the induced isotropic bleaching of the 0 → 1 transition at different probe frequencies [10,12]. As the hydrogen-bond length of a molecule changes, the molecule spectrally diffuses away from the frequency at which it was excited, resulting in a faster decay if pump and probe have the same frequency and in a slower decay if the probe frequency differs from that of the pump.

In Fig. 3, it is shown that the isotropic bleaching signal decays faster at a probe frequency of 3600 cm⁻¹ (close to the pump frequency of 3575 cm⁻¹) than at a probe frequency of 3450 cm⁻¹. This observation implies that the hydrogen-bond length indeed changes. The time constant τ_c of this modulation can be obtained by fitting the measurements to a Brownian oscillator model [10,12,13]. In this model, the spectral dynamics of a high-frequency mode (O-H stretch vibration) results from the coupling to a low-frequency mode (hydrogen-bond stretching mode),

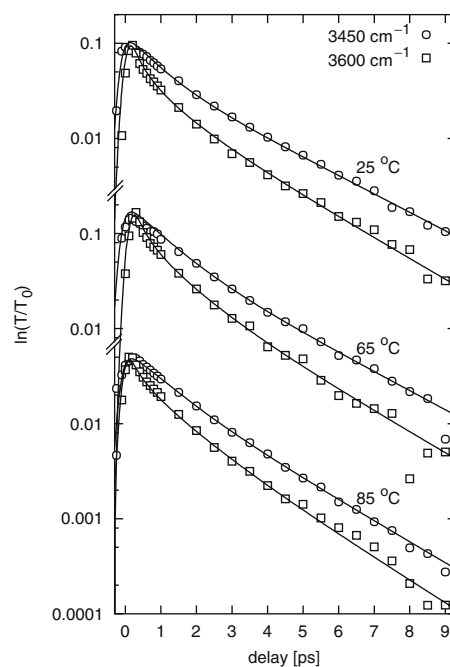


FIG. 3. Pump-probe transients measured for a solution of 3 M NaCl in HDO:D₂O at three different temperatures. The transients are measured with a pump frequency of 3575 cm⁻¹ and two different probe frequencies.

of which the coordinate is stochastically modulated due to interactions with a bath. We describe the observed transients with two Brownian oscillators, one representing the O-H...O system and one representing the O-H...Cl⁻ system. From the fit to the transients shown in Fig. 3, and to measurements at other probe frequencies (not shown here), we find that the time constant τ_c of the modulation of the O-H...Cl⁻ hydrogen-bond length increases from 14 ± 2 ps at 25 °C, to 24 ± 5 ps at 65 °C, to 30 ± 6 ps at 85 °C [12]. This increase of τ_c can be well explained within the framework of the Brownian oscillator model. The time constant τ_c is related to the frequency ω_{HB} of the hydrogen-bond stretch vibration via $\tau_c = \gamma/\omega_{\text{HB}}^2$ [14], with γ being the damping of the hydrogen-bond stretch vibration. An increase in temperature leads to a decrease of ω_{HB} , and thus to an increase of τ_c , because the hydrogen-bond vibration is anharmonic [15] and because the hydrogen-bond interaction decreases with temperature [16].

From the observation that τ_c is longer than τ_{or} it follows that the orientational dynamics of the HDO molecules in the first solvation shell of the Cl⁻ ion must result from motions that do not contribute to the spectral diffusion, i.e., that do not affect the length of the O-H...Cl⁻ hydrogen bond. Hence, the observed reorientation represents the orientational diffusion of the complete solvation structure. The long-living excitation of the anion-bound HDO molecule thus forms a label that, like a flag on a sphere, enables one to follow the orientational motion of the complete anionic solvation structure in the time domain. The cation's solvation shell is expected to be similar to the anion's shell [17] and likely shows similar dynamics; however, due to the shorter O-H stretch lifetime we cannot observe its reorientational motion after 3 ps.

In Fig. 4, the orientational diffusion time constants τ_{or} of the first solvation shell of the halogenic anions Cl⁻, Br⁻, and I⁻ are presented as a function of temperature. These time constants are all obtained from femtosecond two-color pump-probe measurements.

For I⁻, τ_{or} is significantly shorter than for Cl⁻ and Br⁻, which seems to be in contradiction with the fact that the bare I⁻ ion is larger than Cl⁻ and Br⁻. Yet, similar anomalous behavior was observed for the ionic mobility, which is related to translational diffusion [18,19].

The orientational diffusion of the ensemble of aqueous solvation shells that are excited by the pump pulse is described by the equation

$$\frac{\partial n(\theta, t)}{\partial t} = \frac{D_\theta}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial n(\theta, t)}{\partial \theta} \right), \quad (2)$$

with θ the angle with respect to the pump-pulse polarization, $n(\theta, t)d\Omega$ the number of particles in a solid angle $d\Omega$ ($d\Omega = d\phi d\theta \sin\theta$), ϕ the azimuth angle, and D_θ the orientational diffusion constant. Equation (1) does not contain any dependence on the azimuth angle ϕ , because the excitation is symmetric around the pump-pulse polarization axis. The solution of this equation can be written

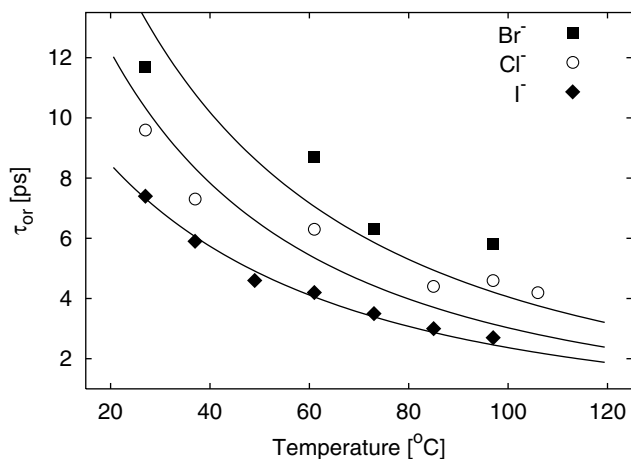


FIG. 4. Orientational diffusion time constants τ_{or} of the solvation shells of Cl⁻, Br⁻, and I⁻ as a function of temperature, measured with femtosecond midinfrared pump-probe experiments. The solid curves represent fits of the data using Eq. (5).

as a sum of exponentially decaying Legendre polynomials P_l :

$$n(\theta, t) = \sum_{l \geq 0} a_l P_l(\cos\theta) e^{-D_\theta l(l+1)t}, \quad (3)$$

with a_l the coefficients that are determined by the distribution of $n(\theta, t)$ at $t = 0$. Because the measured anisotropy $R(\tau)$ equals $\langle P_2(\cos\theta) \rangle$, the time constant τ_{or} of the decay of $R(\tau)$ is related to D_θ by $\tau_{\text{or}} = 1/6D_\theta$. The orientational diffusion constant D_θ can be related to the viscosity of the liquid using the Stokes-Einstein relation for orientational diffusion of a sphere [20]:

$$D_\theta = \frac{kT}{8\pi\eta(T)r_{\text{h,solv}}^3}, \quad (4)$$

with k Boltzmann's constant, T the temperature in Kelvin, $\eta(T)$ the temperature-dependent viscosity, and $r_{\text{h,solv}}$ the hydrodynamic radius of the solvation structure. Combining this equation with $\tau_{\text{or}} = 1/6D_\theta$ gives

$$\tau_{\text{or}}(T) = \frac{4\pi\eta(T)r_{\text{h,solv}}^3}{3kT}. \quad (5)$$

In Fig. 4, fits of Eq. (5) to the data are shown (solid curves). The only fit parameter is the radius $r_{\text{h,solv}}$. The temperature-dependent viscosities were obtained from temperature-dependent Jones-Dole A [21] and B [22] coefficients. The Jones-Dole calculation of the viscosity is valid for low concentrations; however, we verified for NaCl [23] and for NaBr [24] that the difference between the calculated curve and experimental data was less than 10% over the whole temperature range, which gives a deviation of $r_{\text{h,solv}}$ of only 3%.

The temperature dependence of the orientational diffusion is well described by $\eta(T)/T$. For the hydrodynamic radii we find $r_{\text{h,solv}}(\text{Cl}^-) = 213$ pm, $r_{\text{h,solv}}(\text{Br}^-) = 237$ pm, and $r_{\text{h,solv}}(\text{I}^-) = 205$ pm. These radii can be

compared to the hydrodynamic radii r_h obtained from the Stokes-Einstein relation for translational diffusion. From the ionic mobility [18], related to translational diffusion, we find $r_h(\text{Cl}^-) = 120$ pm, $r_h(\text{Br}^-) = 118$ pm, and $r_h(\text{I}^-) = 120$ pm. For all halogenic ions, r_h is significantly smaller than $r_{h,\text{solv}}$. If $r_{h,\text{solv}}$ would equal r_h , the reorientation would be about 8 times as fast, τ_{or} being on the order of 1 ps. This suggests that the (translational) diffusion steps take place for a significant part without the solvation shell, thus reducing its effective size.

It seems surprising that we find similar values for the hydrodynamic radii r_h of the different ions. From the orientational diffusion times, it follows that the hydrodynamic radius $r_{h,\text{solv}}$ of I^- is even smaller than Br^- and Cl^- . These observations may lead to the straightforward interpretation that the size of the diffusing structure, i.e., the ion with its solvation shell, is smaller for I^- than for Cl^- and Br^- . Another possible explanation is that the dielectric friction between the ion and its surroundings could be smaller for the larger ions [19], or that the Cl^- ion, more than I^- , forms short-living clusters of two or more ions [25] that hinder the diffusive motion.

Both radii obtained, r_h from the ionic mobilities and $r_{h,\text{solv}}$ from the rotational-anisotropy data, are much smaller than expected. The values of r_h should be at least as large as the ionic radii: $r_{\text{ion}}(\text{Cl}^-) = 181$ pm, $r_{\text{ion}}(\text{Br}^-) = 196$ pm, and $r_{\text{ion}}(\text{I}^-) = 220$ pm [18]. For $r_{h,\text{solv}}$ one should expect values of at least the anion-water hydrogen-bond length: $r_{\text{HB}}(\text{Cl}^-) = 323$ pm, $r_{\text{HB}}(\text{Br}^-) = 340$ pm, and $r_{\text{HB}}(\text{I}^-) = 360$ pm [11]. This deviation can be understood by realizing that the Stokes-Einstein relation, in particular the viscosity, is defined for macroscopic objects. In the present case, however, the moving objects are of the same length scale as the molecules of the viscous liquid. In this regime, the concept of viscosity loses its meaning, and the orientational mobility becomes closely connected to the specific interactions between the solvation shell and its surroundings, mainly electrostatic interactions with other ions and hydrogen bonding.

In conclusion, we present direct time-resolved measurements of the orientational dynamics of HDO molecules in the first solvation shell of Cl^- , Br^- , and I^- in bulk aqueous solution. The selective study of anion-bound water molecules is enabled by their exceptionally long vibrational lifetime. From the temperature dependence of the reorientation rate and the comparison with spectral-diffusion data, we conclude that the observed reorientation of the HDO molecules results from the orientational diffusion of the complete solvation structure. This means that the O-H group of the HDO molecule in the solvation shell acts as a label that enables the direct measurement of the orientational diffusion of the solvation structure in the time domain. We find that the orientational diffusion is about twice as fast for I^- as for Br^- ; for Cl^- it is in between.

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