Ion solvation in water: femtosecond spectroscopy of hydrogen-bond dynamics

Kropman, M.F.

Citation for published version (APA):
In this chapter, we present a study of the orientational dynamics of aqueous solvation shells of halogenic anions in bulk water solution with femtosecond two-color mid-infrared spectroscopy. The reorientational motion was studied by simultaneously monitoring the pump–probe signals at parallel and perpendicular pump and probe polarizations. The orientational dynamics has time constants between 2.5 and 12 picoseconds, depending on the type of anion and the temperature. We find that the solvation shell of I\(^-\) shows faster orientational dynamics than the shells of the smaller ions Cl\(^-\) and Br\(^-\).

### 7.1 Introduction

In the previous chapter, it was found that water molecules around the anions Cl\(^-\), Br\(^-\), and I\(^-\) form relatively rigid structures, compared to the more rapidly fluctuating structures that exist in pure liquid water. The relative stiffness of the anionic hydrogen bonds in these shells was revealed by the slow spectral diffusion. The residence time of water molecules in the solvation shell must at least equal the spectral-diffusion time. Therefore, the residence time is at least 10 ps, but possibly much longer. In the present chapter, we aim to study the motion of the entire solvation structure in the solvent. We can measure the orientational-correlation time of an excited O–H group with polarization-resolved pump–probe spectroscopy (see section 2.2.4).

Recently, the reorientational motion of water molecules in pure water (HDO:D\(_2\)O) has been studied with non-linear spectroscopy. In a first study,\(^\text{137}\) two time constants were found in the reorientation of water molecules, 0.7 and 13 ps. In a second study,\(^\text{90}\) in which also the frequency and temperature dependence was studied, a more comprehensive treatment was provided. According to the latter work, a water molecule can reorient only when one of its donated hydrogen-bonds is broken. The spectral-diffusion time was thus found to be important for the orientational dynamics. The results were in general agreement with NMR and dielectric relaxation studies.

The anionic solvation structure, that is assumed to consist of at least six water molecules, can form many hydrogen bonds with the surrounding water, that hinder the reorientational motion. Therefore, long rotational-correlation times should be expected for the solvation shells. For salt solutions, the reorientational motion has been studied with NMR. The results of a large number of studies are summarized in Ref. 96. For the halide ions, the rotational-correlation times found with NMR are of the same order of magnitude as for pure liquid water. One disadvantage of NMR is that the frequency of the applied magnetic pulses is at most 100 MHz,\(^\text{96}\) which limits the time resolution to nanoseconds. Within this time, the water molecules exchange numerous times between...
bulk and solvation shell.\textsuperscript{46,114,105} Therefore, the measured rotation is in fact an average over all molecules in the liquid.

### 7.2 Experiment

The experiments are polarization-resolved two-color femtosecond mid-infrared pump-probe experiments on a dilute (\(<1\) M) solution of HDO dissolved in D\textsubscript{2}O that contains a high concentration (1–3 M) of salt (NaCl, NaBr, or NaI). The generated mid-infrared pulses have a pulse energy up to 30 \(\mu\)J, and a pulse duration of approximately 200 fs. The pump and probe pulses were tuned to 3450 cm\(^{-1}\) and 3200 cm\(^{-1}\), with bandwidths of 80 and 60 cm\(^{-1}\), respectively.

To study the orientational relaxation of the excited HDO molecules, we rotated the polarization of the probe pulse by 45 degrees with respect to the pump polarization using a zero-order \(\lambda/2\) plate. The transmission changes of the probe parallel to the pump \((\ln(T/T_0)_p)\) and perpendicular to the pump \((\ln(T/T_0)_l)\) are measured as a function of the delay \(\tau\) with respect to the pump. These signals are used to calculate the anisotropy parameter \(R\). Details about the setup and the experiment can be found in chapter 2.

To prevent Förster energy transfer between nearby O–H groups, which could influence the anisotropy decay,\textsuperscript{45} the HDO concentration was relatively low: only 0.5 % of the solvent molecules were HDO molecules, the other 99.5 % of the solvent molecules were D\textsubscript{2}O. The ‘safe’ concentration was determined by measuring at different HDO concentrations. Below 0.5 %, there was no measurable dependence of the decay of \(R\) on the HDO concentration.

### 7.3 Results

In figure 7.1, the anisotropy parameter \(R\) is presented as a function of delay for a solution of 3 M NaCl in HDO:D\textsubscript{2}O at different temperatures. Also shown are exponential fits to the data in the delay-time window from 3 to 8 picoseconds in which the observed transients only represent the orientational dynamics of the HDO molecules in the first solvation shell of the Cl\(^-\) ion (it will be shown. At 27 °C, the orientational-relaxation time constant \(\tau_{or}\) of these HDO molecules is 9.6±0.6 ps, which is longer than the value of \(\tau_{or}\) of 2.6 ps of HDO molecules in a solution of HDO in D\textsubscript{2}O.\textsuperscript{95} With increasing temperature, the orientational relaxation becomes much faster: \(\tau_{or}\) decreases to 4.2±0.4 ps at 106 °C.

If an anion-bonded water molecule leaves the solvation shell while it is still excited, it will rapidly form a new hydrogen bond with another water molecule, and decay with a time constant of 740 fs. The exchange of water molecules between shell and solvent will therefore not have a great effect on the measurements of the anisotropy. In addition, it was shown in chapter 6 that the residence time of a water molecule in the solvation shells of the studied anions is at least on the order of 20 ps, much longer than \(\tau_{or}\).

The same series of measurements has been performed for solutions of NaBr and NaI. The fitted orientational diffusion time constants \(\tau_{or}\) are shown in figure 7.3 for all three salts and for several temperatures in the range between room temperature and 106 °C. At all temperatures, \(\tau_{or}(I^-) < \tau_{or}(Cl^-) < \tau_{or}(Br^-)\).
7.4 DISCUSSION

The question arises whether the observed reorientation of HDO molecules results from reorientation within the solvation shell of the anion or from reorientation of the complete shell. In the case of reorientation of individual molecules 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 inevitably affects the bond angle or bond length of the O–H⋯X− hydrogen-bond, that are both strongly correlated to the O–H stretch frequency. It was shown in chapter 6 that the dynamics of the spectral diffusion can be measured by probing the induced isotropic bleaching of the 0→1 transition at different probe frequencies. 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.

The time constant $\tau_c$ of this modulation can be obtained by fitting the measurements to a Brownian-oscillator model. In chapter 6, we found that the time constant $\tau_c$ 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. This increase of $\tau_c$ could be well explained within the framework of the Brownian oscillator model, in which the time...
constant $\tau_c$ is related to the frequency $\omega_{HB}$ of the hydrogen-bond stretch vibration via $\tau_c = \gamma/\omega_{HB}^2$\textsuperscript{109} with $\gamma$ the damping of the hydrogen-bond stretch vibration. An increase in temperature leads to a decrease of $\omega_{HB}$, and thus to an increase of $\tau_c$, because the hydrogen-bond vibration is anharmonic\textsuperscript{11} and because the hydrogen-bond interaction decreases with temperature.\textsuperscript{36}

![Figure 7.2](image.png)

**Figure 7.2.** Orientational and spectral-diffusion time constants $\tau_{or}$ and $\tau_c$ of the first solvation shell of Cl$^-$, as a function of temperature. The spectral-diffusion times were obtained in chapter 6. The values of $\tau_{or}$ are the same as in figure 7.3. Comparison of $\tau_{or}$ and $\tau_c$ leads to the conclusion that $\tau_{or}$ represents the reorientation of the entire solvation structure rather than an individual water molecule.

The values of $\tau_{or}$ and $\tau_c$ for a 3 M solution of NaCl in water are displayed in figure 7.2. From the observation that $\tau_c$ is longer than $\tau_{or}$, and from the reversed temperature dependence, 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 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. We would like to stress again that the cation’s solvation shell is expected to be similar to the anion’s shell\textsuperscript{27} and that it likely shows similar dynamics; however, due to the shorter O–H stretch lifetime of the former, we cannot distinguish its reorientational motion from that of the bulk water.

In figure 7.3, the orientational diffusion time constants $\tau_{or}$ of the first solvation shell
Figure 7.3. Orientational diffusion time constants $\tau_{or}$ of the solvation shells of $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ as a function of temperature. The solid curves represent fits of the data using equation (7.4).

of the halogenic anions $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ are presented as a function of temperature.

Surprising is the order of $\tau_{or}$ for the different anions: $\tau_{or}(\text{I}^-) < \tau_{or}(\text{Cl}^-) < \tau_{or}(\text{Br}^-)$ at all temperatures. It seems to be in contradiction with the fact that the bare $\text{I}^-$ ion is larger than $\text{Br}^-$ and $\text{Cl}^-$. In the NMR measurements listed in Ref 96, the order was $\tau_{or}(\text{I}^-) < \tau_{or}(\text{Br}^-) < \tau_{or}(\text{Cl}^-)$. Thus, the NMR results are also in contradiction with the intuitive notion that it should be more difficult to rotate the larger ion than to rotate the smaller. Yet, similar anomalous behavior was observed for the ionic mobility, which is related to translational diffusion.\textsuperscript{3,64} We will come back to this at the end of the Discussion, after modeling the data.

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

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

(7.1)

with $\theta$ the angle with respect to the pump-pulse polarization, $n(\theta, t) d\Omega$ the number of particles in a solid angle $d\Omega$ ($d\Omega = d\phi d\theta \sin \theta$), $\phi$ the azimuth angle, and $D_\theta$ the orientational diffusion constant. Equation (7.1) does not contain any dependence on the azimuth angle $\phi$, because the excitation is symmetric around the pump-pulse polarization axis. The solution of this equation can be written as a sum of exponentially decaying Legendre polynomials $P_l$: 
7.4 ORIENTATIONAL DYNAMICS OF AQUEOUS SOLVATION SHELLS

<table>
<thead>
<tr>
<th>Ion</th>
<th>$r_{h,\text{solv}}$</th>
<th>$r_{\text{HB}}$</th>
<th>$r_h$</th>
<th>$r_{\text{ion}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>2.13 Å</td>
<td>3.23 Å</td>
<td>1.20 Å</td>
<td>1.81 Å</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>2.37 Å</td>
<td>3.40 Å</td>
<td>1.18 Å</td>
<td>1.96 Å</td>
</tr>
<tr>
<td>I$^-$</td>
<td>2.05 Å</td>
<td>3.60 Å</td>
<td>1.20 Å</td>
<td>2.20 Å</td>
</tr>
</tbody>
</table>

**Table 7.1.** Values of $r_{h,\text{solv}}$ obtained from our fit and the hydrogen-bond length, and of $r_h$ from the ionic mobility using the Stokes-Einstein relation for translational diffusion, the ionic radius.

\[ n(\theta, t) = \sum_{i \geq 0} a_i P_i(\cos \theta) e^{-D_{\theta}(i+1)t}, \]  

(7.2)

with $a_i$ 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 $\tau_{\text{or}}$ of the decay of $R(\tau)$ is related to $D_{\theta}$ by $\tau_{\text{or}} = 1/(6D_{\theta})$. The orientational diffusion constant $D_{\theta}$ can be related to the viscosity of the liquid using the Stokes-Einstein relation for orientational diffusion of a sphere:

\[ D_{\theta} = \frac{kT}{8\pi\eta(T) r_{h,\text{solv}}} , \]  

(7.3)

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

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

(7.4)

In figure 7.3, fits of equation (7.4) to the data are shown (solid curves). The only fit parameter is the radius $r_{h,\text{solv}}$. The temperature-dependent viscosities were obtained from temperature-dependent Jones-Dole $A^{18}$ and $B^{97}$ coefficients. The Jones-Dole calculation of the viscosity is valid for low concentrations; however, we verified for NaCl$^{99}$ and for NaBr$^{10}$ that the difference between the calculated curve and experimental data was less than 10% over the whole temperature range, which gives a deviation of $r_{h,\text{solv}}$ of only 3%. The temperature dependence of the orientational diffusion is well described by $\eta(T)/T$. For the hydrodynamic radii we find $r_{h,\text{solv}}(\text{Cl}^-) = 2.1$ Å, $r_{h,\text{solv}}(\text{Br}^-) = 2.4$ Å, and $r_{h,\text{solv}}(\text{I}^-) = 2.1$ Å (precise values are in table 7.1, together with other radii that will appear in the text). These radii can be compared to the hydrodynamic radii $r_h$ obtained from the Stokes-Einstein relation for translational diffusion. From the ionic mobility, related to translational diffusion, we find $r_i = 1.2$ Å for all anions. $r_h$ is significantly smaller than $r_{h,\text{solv}}$ for all anions. If $r_{h,\text{solv}}$ would have been equal to $r_h$, the reorientation would be about 8 times as fast, $\tau_{\text{or}}$ 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 $r_{\text{h,solv}}$ of $I^-$ is even smaller than that of $\text{Br}^-$ and $\text{Cl}^-$. 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 $\text{Cl}^-$ and $\text{Br}^-$. Since $I^-$ is a bigger ion, the electrostatic field felt by the molecules in the solvation shell is weaker, and the anionic hydrogen bonds are weaker. Possibly, the water molecules in the solvation shell have more freedom to go in and out of the shell, creating moments in which the ion is able to displace with a smaller number of molecules attached. Another possible explanation is that the dielectric friction between the ion and its surroundings could be smaller for the larger ions, or that the $\text{Cl}^-$ ion, more than $I^-$, forms short-living clusters of two or more ions, that hinder the diffusive motion.

Both radii obtained, $r_h$ from the ionic mobilities and $r_{\text{h,solv}}$ 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: $r_{\text{ion}}(\text{Cl}^-) = 1.8\ \text{Å}$, $r_{\text{ion}}(\text{Br}^-) = 2.0\ \text{Å}$, and $r_{\text{ion}}(I^-) = 2.2\ \text{Å}$. For $r_{h,\text{solv}}$ one should expect values of at least the anion–water hydrogen-bond length: $r_{\text{HB}}(\text{Cl}^-) = 3.2\ \text{Å}$, $r_{\text{HB}}(\text{Br}^-) = 3.4\ \text{Å}$, and $r_{\text{HB}}(I^-) = 3.6\ \text{Å}$. This deviation is probably caused by the fact 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.

### 7.5 Conclusions

In this chapter, direct time-resolved measurements of the orientational dynamics of HDO molecules in the first solvation shell of $\text{Cl}^-$, $\text{Br}^-$, and $I^-$ in bulk aqueous solution are presented. The selective study of anion-bound water molecules is enabled by their exceptionally long vibrational lifetime. We find that the orientational diffusion is about twice as fast for $I^-$ as for $\text{Br}^-$; for $\text{Cl}^-$ it is in between. 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. The $\text{O–H}$ group of the HDO molecule in the solvation shell thus acts as a label that enables the direct measurement of the orientational diffusion of the solvation structure in the time domain.