Ion solvation in water: femtosecond spectroscopy of hydrogen-bond dynamics
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6 Hydrogen-bond dynamics of aqueous solvation shells

In the previous chapters, it was demonstrated that the lifetime of the O–H stretch vibration differs between those hydrogen bonded to an anion and those hydrogen bonded to another water molecule. This difference in vibrational lifetime allows for a clear separation of the response of the anion’s solvation shell from that of the bulk liquid as well as from the cation’s shell. In this chapter, we will use this property to specifically study the hydrogen-bond dynamics of the anion solvation shells. The hydrogen-bond dynamics is strongly related to the spectral dynamics, that can be studied by tuning the pump and probe frequencies through the absorption band. The results are interpreted using the Brownian-oscillator model. The spectral diffusion times thus obtained reveal that the hydrogen-bond dynamics of solvating molecules is much slower than the hydrogen-bond dynamics of bulk liquid water.

6.1 Introduction

The dynamics of chemical reactions in aqueous media are strongly dependent on the interactions between the reacting molecules and the solvating water molecules. In many cases, a chemical reaction can take place only after a water molecule has been removed from the solvation shell, opening the way for the molecules to approach each other and react.

The absorption band of the O–H stretch vibration is inhomogeneously broadened due to the variation in hydrogen-bond length. The hydrogen-bond lengths are not static, but vary in time. Averaged over a sufficiently long period of time, the absorption band of each individual molecule equals the total absorption band. These spectral dynamics cannot be measured with linear spectroscopy. With pump–probe saturation spectroscopy, however, this is possible: one can excite a specific set of molecules, characterized by their hydrogen-bond length, and follow the spectral evolution of this ensemble. Spectral diffusion has been studied for liquid water,\textsuperscript{134,40,41,13} the correlation time of the absorption frequency of one HDO molecule in a solution of HDO:D\textsubscript{2}O was measured to be 500 fs or 700 fs. To date, the experimental study of the hydrogen-bond dynamics in ionic solvation shells has been hindered by the fact that it is quite difficult to distinguish the response of the solvating water molecules from that of the other (bulk) water molecules.

The contribution of bulk water to the response of an aqueous solution can be eliminated by studying small clusters of an ion surrounded by a few water molecules in the gas phase.\textsuperscript{4,6,5,7,15,19,110,128} Since the number of O–H groups is limited, the measured predissociation spectrum can be decomposed into separate absorption components, and a detailed picture of the structure of such a cluster can be obtained. However, no hydrogen-bond dynamics has been studied with this technique, and even if such a study were performed, the results cannot easily be applied to bulk solutions,\textsuperscript{21} where collective modes largely drive the hydrogen-bond dynamics. Techniques like NMR, infrared absorption and Raman
scattering cannot be used either, because the time scales involved in these techniques are much longer than the time scale of the solvation dynamics. Hence, the information on the hydrogen-bond dynamics in aqueous salt solutions is mainly theoretical in nature and originates from molecular-dynamics simulations. In these studies strongly different time constants for the exchange of water molecules between the solvation shell and the bulk were reported, ranging from one picosecond up to hundreds of picoseconds. Very recently an ab-initio molecular-dynamics study was performed on the solvation of \( \text{Br}^- \). For the average residence time of water in the solvation shell of \( \text{Br}^- \) a value of \( 19 \pm 5 \) ps was found.

In the previous chapters it has been shown that the lifetime of the anion-bonded O–H groups is significantly longer than that of the other water molecules. This makes femtosecond mid-infrared saturation spectroscopy an ideal technique to study the spectral diffusion in solvation shells, since it allows for a distinction between the different O–H groups: after a few picoseconds, the only O–H groups that are still excited are those in the anionic solvation shells. In this chapter, we study the hydrogen-bond dynamics of water molecules in anionic solvation shells, in solutions of different salts, concentrations and temperatures.

6.2 Experiment

We performed femtosecond mid-infrared pump–probe experiments on the O–H stretch vibration of HDO molecules in an aqueous solution consisting of a low concentration of HDO (0.1 M) in D\(_2\)O and different concentrations (1 M, 2 M, 3 M, 6 M) of KF, NaCl, NaBr, NaI, and MgCl\(_2\). The pump and probe pulses have a typical energy of 20 and 2 \( \mu \)J, respectively, and a duration of approximately 200 femtoseconds. The spectral bandwidths of the pump and probe pulses are 80 and 60 cm\(^{-1}\). The polarization of the probe pulse is at the magic angle (54.7°) with respect to the polarization of the pumping pulse in order to avoid the measurements to be affected by reorientation of the HDO molecules. In the experiments, both the pump and probe frequencies are tuned through the absorption band of the O–H stretching mode of the HDO molecules.

6.3 Results

In figure 6.1, delay scans are presented measured at a pump frequency of 3400 cm\(^{-1}\) and six different probe frequencies for a solution of 6 M NaI in HDO:D\(_2\)O. At frequencies \( \geq 3350 \) cm\(^{-1}\), a bleaching (\( \ln(T/T_0) > 0 \), with \( T \) the transmission of the probe and \( T_0 \) the transmission of the probe in absence of the pump) of the \( v = 0 \rightarrow 1 \) transition is observed. At frequencies \( \leq 3300 \) cm\(^{-1}\), an induced absorption (\( \ln(T/T_0) < 0 \)) is observed, which can be assigned to the induced \( v = 1 \rightarrow 2 \) transition. With increasing delay, the bleaching and induced absorption decay due to the energy relaxation of the \( v = 1 \) state of the O–H stretch vibration of the excited HDO molecules.

In figures 6.2–6.4, transients measured for three different salts are presented. The transients are shown on a vertical logarithmic scale to illustrate that at all frequencies the decay is non-exponential and consists of a rapid decay followed by a much slower decay. The curves are scaled with respect to each other for clarity. The amplitude of
the signals depends on both the pump and probe frequencies. For a solution of NaCl, the largest amplitude is observed for pump and probe frequencies of approximately 3450 cm\(^{-1}\), whereas for solutions of NaBr and NaI, the largest amplitude is observed for pump and probe frequencies of approximately 3500 cm\(^{-1}\). All transients can be described as a sum of two exponentials, one with a time constant of 800 femtoseconds and one with a longer time constant that depends on salt and probe frequency. The amplitude of the slow component depends linearly on the concentration of dissolved salt.

The time constant of the slow component shows a small but significant dependence on the probe frequency. To illustrate this more clearly, figures 6.2–6.4 contain calculated dashed curves that run parallel at large delay times (> 3 ps). The time constant of the slow component is observed to increase with increasing frequency difference between pump and probe. If the pump is at 3575 cm\(^{-1}\) (figures 6.2 and 6.3), the fastest decay is observed at 3600 cm\(^{-1}\) and the slowest decay at 3500 cm\(^{-1}\). If the pump is at 3525 cm\(^{-1}\) (figure 6.4), the fastest decay is observed at 3500 cm\(^{-1}\) and the slowest decay at 3600 cm\(^{-1}\). These observations show that the decay time constant of the slow component is affected by a slow spectral-diffusion process with a time constant of approximately 10 picoseconds. Due to this spectral-diffusion process, excited molecules (spectrally) diffuse away from the
excitation frequency, which leads to a faster decay at probe frequencies close to the pump frequency and a slower decay at probe frequencies that significantly differ from the pump frequency.

In figure 6.5, transients are presented that are measured for a solution of 3 M NaCl in HDO:D$_2$O at three different temperatures. At all three temperatures, the transient measured at 3600 cm$^{-1}$ is observed to decay faster than the transient at 3450 cm$^{-1}$, as a result of the above mentioned spectral diffusion. An interesting observation is that the difference in decay rate of the two transients decreases with temperature: at a temperature of 85 °C the two transients show a more similar decay than at room temperature. This observation indicates that the spectral diffusion becomes slower when the temperature increases.
Figure 6.3. As figure 6.2, but for a solution of 1 M NaI in HDO:D$_2$O. The solid curves are calculated using a $\tau_c$ of the modulation of the O-H$\cdots$I$^-$ hydrogen bond of 18 picoseconds. The dashed curves are calculated with $\tau_c = \infty$.

6.4 Spectral diffusion and the Brownian-oscillator model

In an aqueous solution of a salt in HDO:D$_2$O, three different types of HDO molecules can be distinguished: HDO molecules in the first solvation shell of the anion, HDO molecules in the first solvation shell of the cation and HDO molecules that are only surrounded by D$_2$O molecules. In the following, these latter molecules will be denoted as bulk HDO molecules. The three different types of HDO molecules give rise to the fast and the slow component observed in the transient spectral data of figures 6.1–6.5.

The pump- and probe-frequency dependence of the dynamics of the slow component (figures 6.1–6.5) shows that the response of this component is affected by a slow spectral-diffusion process with a time constant of approximately 10 picoseconds. This spectral diffusion reflects the (stochastic) modulation of the hydrogen-bond length because the transition frequency of the O–H stretch vibration and the length of the hydrogen bond are strongly correlated for directional hydrogen bonds.$^{94,82,85}$

For a bulk solution of HDO in D$_2$O, the spectral diffusion of the O–H stretch ab-
Figure 6.4. As figure 6.2, but for a solution of 6 M NaCl in HDO:D$_2$O. The solid curves are calculated using a $\tau_c$ of the modulation of the O-H-Cl$^-$ hydrogen bond of 12 picoseconds. The dashed curves are calculated with $\tau_c = \infty$.

In order to determine the precise value of the correlation time constant $\tau_c$ of the stochastic modulation of the O-H-Cl$^-$ hydrogen bond, we modeled the data of figures 6.1–6.5 with the Brownian-oscillator model. Recently, it was shown that this model works well in describing the spectral dynamics of the O-H stretching mode of HDO dissolved in D$_2$O induced by the interactions with the O-H-O hydrogen bond. The determination of $\tau_c$ of the O-H-Cl$^-$ hydrogen bond is greatly facilitated by the large difference in vibrational lifetime between the O-H-O and the O-H-Cl$^-$ component ($X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$).
Figure 6.5. Pump-probe transients measured for a solution of 3 M NaCl in HDO:D$_2$O at three different temperatures. The difference in final decay time of the slow component decreases with increasing temperature which means that the value of $\tau_c$ of the modulation of the O–H⋯Cl$^-$ hydrogen bond increases. The solid curves are calculated using $\tau_c = 14$ ps (25 °C), $\tau_c = 24$ ps (65 °C) and $\tau_c = 30$ ps (85 °C).
The Brownian-oscillator model assumes harmonic potential energy functions for the low-frequency mode (hydrogen bond) that are displaced with respect to each other in the ground and excited state of the O–H stretch oscillator (see figure 6.6). In case the hydrogen bond is a strongly overdamped mode, this results in a Gaussian absorption spectrum for the O–H stretch vibration, in quite good agreement with the experimental observations. Within the Brownian-oscillator model, the spectral dynamics of the transition of the O–H stretch vibrational transition is described with two parameters: the correlation time constant \( \tau_c \), representing the time scale at which the hydrogen-bond length is stochastically modulated, and the width \( \Delta \) of the Gaussian absorption line shape \( e^{-\omega^2/2\Delta^2} \) of the O–H stretch vibration. This width increases with increasing displacement of the harmonic potential energy functions. An explicit expression for the pump–probe signal \( \ln(T/T_0) \) as a function of delay \( \tau \) and pump and probe frequency can be found in the literature:

\[
\ln(T/T_0)(\omega_1, \omega_2, \tau) = \frac{2\pi e^{-\tau/T}}{\sqrt{(\Delta^2 + \delta_1^2)\alpha^2(\tau)}} e^{(-\omega_1 - \omega_E)^2/2(\Delta^2 + \delta_1^2)} \times \left\{ e^{-[\omega_1 - \omega_E(\tau)]^2/2\alpha^2(\tau)} + e^{-[\omega_1 - \omega_E(\tau)]^2/2\alpha^2(\tau)} \right\},
\]

(6.1)

with

\[
\omega_g(\tau) = \omega_E + e^{-\tau/\tau_c} (\omega_0 - \omega_E) \quad (6.2)
\]

\[
\omega_e(\tau) = \omega_E - 2\lambda + e^{-\tau/\tau_c} (\omega_0 - \omega_E + 2\lambda) \quad (6.3)
\]

\[
\lambda = \hbar \Delta^2 / 2k_BT \quad (6.4)
\]

\[
\omega_o = \omega_1 \frac{\Delta^2}{\Delta^2 + \delta_1^2} + \omega_E \frac{\delta_1^2}{\Delta^2 + \delta_1^2} \quad (6.5)
\]

\[
\alpha^2(\tau) = \Delta^2 \left[ 1 - \frac{\Delta^2}{\Delta^2 + \delta_1^2} e^{-\tau/\tau_c} \right] + \delta_1^2 \quad (6.6)
\]

where \( \omega_1, \delta_1 \) and \( \omega_o, \delta_2 \) are the centre frequencies and the spectral widths of pump and probe, respectively. The frequency \( \omega_E \) is the maximum of the linear absorption spectrum and \( T_1 \) is the vibrational lifetime. The parameter \( \lambda \) represents the Stokes shift (=2\lambda) that results from the fact that the position of the minimum of the hydrogen-bond potential of the excited state of the O–H stretch vibration differs from that of the ground state. Hence, excitation of the O–H stretch vibration results in a shift of the hydrogen-bond length to a new equilibrium position and an associated redshift of 2\lambda of the stimulated emission out of the \( v = 1 \) potential to the \( v = 0 \) potential. For harmonic potentials, the Stokes shift is directly related to the width \( \Delta \) of the absorption band. \( \lambda \) itself does not depend on temperature, since it is only determined by the shape and displacement of the harmonic potentials. Nevertheless, in expression (6.4) the temperature \( T \) enters, because the width \( \Delta \) of the absorption band depends on the thermal occupation of the ground-state potential. The two terms between the braces in equation (6.1) correspond to the bleaching (depletion of the \( v = 0 \)) and to the stimulated emission \( v = 1 \rightarrow 0 \) contribution to the transmission change \( \ln(T/T_0) \), respectively.
Figure 6.6. Harmonic potential energy functions for the O–H stretch vibration (ground state and the first two excited states), as a function of the O–H⋯O distance. $\omega_{eg} + \lambda$ is the ground state absorption centre frequency, $2\lambda$ the Stokes shift, $\delta \omega_{an}$ the anharmonic frequency shift; $d$ is the displacement of the potential minimum between $\nu_{OH} = 0$ and $\nu_{OH} = 1$; $ad$ is the displacement of the minima of $\nu_{OH} = 1$ and $\nu_{OH} = 2$.

For all transients, we find an excellent fit using two Brownian oscillators that represent the O–H⋯O and O–H⋯X$^-$ components. The signals of each component can simply be added, similar to equation 2.8. In table 6.1, the central frequency $\omega_{eg}$, the spectral width $\Delta \omega$ (full width at half maximum: $\Delta \omega = \sqrt{8 \ln 2} \Delta$), the vibrational lifetime $T_v$ and the correlation time $\tau_c$ that result from these fits are presented for the different absorption components.

For all solutions, we find the same set of parameters for the O–H⋯O component. The parameters of this oscillator are quite similar to those of HDO dissolved in D$_2$O. Only the width of the absorption band appears to be slightly larger, which can be explained from the contribution of HDO molecules solvating the cations. The results of the calculations are shown in figures 6.1–6.5 by the solid curves. The measurements are sensi-
Table 6.1. The central frequency $\omega_0$, width $\Delta \omega$, vibrational lifetime $T_1$, and spectral-diffusion time $\tau_c$ of the O-H stretch vibration of different hydrogen-bonded O-H groups, obtained by fitting the data using a two-component Brownian-oscillator model, described in the text. The values are obtained for 6 M solutions of NaCl, NaBr, and NaI. For all solutions, the same set of values for the O-H···O component was used.

<table>
<thead>
<tr>
<th></th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$\Delta \omega$ (cm$^{-1}$)</th>
<th>$T_1$ (ps)</th>
<th>$\tau_c$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H···O</td>
<td>3420±10</td>
<td>280±20</td>
<td>0.8±0.1</td>
<td>0.5±0.2</td>
</tr>
<tr>
<td>O-H···Cl$^-$</td>
<td>3440±15</td>
<td>160±15</td>
<td>2.6±0.2</td>
<td>12±3</td>
</tr>
<tr>
<td>O-H···Br$^-$</td>
<td>3470±15</td>
<td>130±15</td>
<td>3.0±0.2</td>
<td>25±5</td>
</tr>
<tr>
<td>O-H···I$^-$</td>
<td>3490±15</td>
<td>105±15</td>
<td>3.7±0.3</td>
<td>18±5</td>
</tr>
</tbody>
</table>

We find $\tau_c = 12±3$ for Cl$^-$, $\tau_c = 25±5$ for Br$^-$, and $\tau_c = 18±5$ for I$^-$. For comparison, in figures 6.2–6.4 also results obtained with $\tau_c = \infty$ are shown (dashed curves). The calculated dashed curves run parallel at large delays, because for $\tau_c = \infty$ the transients are no longer affected by spectral diffusion. This behaviour is in clear contrast to the experimental observations and the calculated solid curves. The value of $\tau_c$ of 25±5 ps for Br$^-$ is in good agreement with recent Car–Parrinello simulations, in which a value for the residence time of a water molecule in the solvation shell of Br$^-$ of 19±5 ps was found.

The frequencies of the O-H···Cl$^-$, O-H···Br$^-$ and O-H···I$^-$ absorption components are in quite good agreement with the results from a study in which a double-difference spectroscopic technique was used to obtain the change in O–D stretch frequency due to salt addition. After multiplying by 1.36 to convert O–D into O–H stretch frequencies, the central absorption frequencies they found are 3441 cm$^{-1}$ (O–H···Cl$^-$), 3476 cm$^{-1}$ (O–H···Br$^-$) and 3495 cm$^{-1}$ (O–H···I$^-$).

The central frequency of the absorption band of the O-H···X$^-$ component increases in the halogenic series Cl$^-$, Br$^-$, I$^-$, whereas the width of the absorption band decreases within this series. Both trends reflect the decrease of the strength of the hydrogen-bond interaction between the solvating HDO molecule and the anion in the halogenic series. The relation between the O-H stretch vibrational frequency and the length of the O-H···X$^-$ has been measured for many hydrogen-bond acceptors X including the halogenic anions. This relation can be used to determine the distribution of O-H···X$^-$ hydrogen-bond lengths from the width of the O-H···X$^-$ absorption components. For the O-H···Cl$^-$, O-H···Br$^-$, and O-H···I$^-$ hydrogen-bonds, we obtain widths of the length distribution of 0.20±0.05 Å, 0.21±0.05 Å and 0.12±0.04 Å, respectively. These widths are relatively small compared to the width of the O-H···O absorption band of HDO:D$_2$O of 0.36±0.02 Å. It should be noted that, because of additional homogeneous broadening, the widths of the obtained distributions form upper limits; the true widths may be even narrower. Homogeneous broadening can be expected to be significant, since for pure water it is between 60 and 120 cm$^{-1}$. The narrow width and long $\tau_c$ of the O-H···X$^-$ absorption component imply that the water molecules that directly bind to the X$^-$ halogenic anion form a relatively stable and well-defined structure. The solvation shells of F$^-$ and of the cations likely show similar dynamics as the solvation shells of Cl$^-$, Br$^-$ and I$^-$, but unfortunately these dynamics could not be measured because the O-H...
The value of $\tau_c$ is observed to be somewhat longer for the solvation shells of $\text{Br}^-$ and $\text{I}^-$ than for the solvation shell of $\text{Cl}^-$ and $\tau_c$ is observed to increase with temperature from $12\pm3$ ps at $25\,^\circ\text{C}$, to $24\pm5$ ps at $65\,^\circ\text{C}$, to $30\pm6$ ps at $85\,^\circ\text{C}$ (figure 6.5). These observations can be well explained within the framework of the Brownian-oscillator model, in which the time constant $\tau_c$ is related to the frequency $\omega_{\text{HB}}$ of the hydrogen-bond stretch vibration via $\tau_c = \gamma/\omega_{\text{HB}}^2$, with $\gamma$ the damping of the hydrogen-bond stretch vibration. The dependence of $\tau_c$ on $\omega_{\text{HB}}$ can be understood from the fact that tight bonds (high $\omega_{\text{HB}}$) show faster dynamics than weak bonds (low $\omega_{\text{HB}}$), leading to a faster decay of $\langle R_{\text{HB}}(t)R_{\text{HB}}(0) \rangle \propto e^{-t/\tau_c}$.

The scaling of $\tau_c$ with the damping parameter $\gamma$ reflects the fact that the motion in the hydrogen-bond coordinate $R_{\text{HB}}$ will slow down when $\gamma$ increases. Exchanging $\text{Cl}^-$ for $\text{Br}^-$ or $\text{I}^-$ leads to a decrease of $\omega_{\text{HB}}$, because the hydrogen bond becomes weaker and because the reduced mass of the hydrogen-bond vibration increases. An increase in temperature also leads to a decrease of $\omega_{\text{HB}}$, because the hydrogen-bond interaction decreases with temperature. Hence, if the damping $\gamma$ of the hydrogen-bond stretch vibration is similar for $\text{O-H} \cdots \text{Cl}^-$, $\text{O-H} \cdots \text{Br}^-$ and $\text{O-H} \cdots \text{I}^-$ hydrogen bonds, and if $\gamma$ does not depend strongly on temperature, the observed increase of $\tau_c$ with temperature and variation of the anion from $\text{Cl}^-$ to $\text{Br}^-$ or $\text{I}^-$, can be well explained from a decrease of the hydrogen-bond stretch frequency $\omega_{\text{HB}}$.

The large difference between the values of $\tau_c$ of the $\text{O-H} \cdots \text{O}$ and the $\text{O-H} \cdots \text{X}^-$ oscillators cannot simply be explained from a difference in $\omega_{\text{HB}}$, because the frequency $\omega_{\text{HB}}$ of the $\text{O-H} \cdots \text{X}^-$ hydrogen-bond stretch vibration is only 1-2 times lower than the frequency of the $\text{O-H} \cdots \text{O}$ hydrogen-bond stretch vibration, which can account for an increase of $\tau_c$ of almost a factor of 4. Hence, the difference in $\tau_c$ must be explained from differences in microscopic structure.

For a solvation shell, the value of the hydrogen-bond coordinate $R_{\text{HB}}$ will be largely determined by strongly damped deformational vibrations of this shell. The frequency of these deformations will be much lower than $\omega_{\text{HB}}$ of the $\text{O-H} \cdots \text{X}^-$ hydrogen-bond stretch vibration between a single water molecule and the $\text{X}^-$ halogenic ion, because, in the liquid phase, the deformation of a relatively large solvation structure requires a reorganization of a large part of the local liquid structure. These deformational modes effectively take the role of the Brownian oscillator in the above described model. Because the deformations are slow, the autocorrelation function $\langle R_{\text{HB}}(t)R_{\text{HB}}(0) \rangle$ will decay slowly, i.e. $\tau_c$ is large. Bulk liquid water possesses a disordered 3-dimensional structure and the fluctuations that affect a local $\text{O-H} \cdots \text{O}$ hydrogen-bond length will involve a reorganization of only a small part of the local liquid structure. As a result, the time scale of these fluctuations will be much shorter, leading to a much faster decay of $\langle R_{\text{HB}}(t)R_{\text{HB}}(0) \rangle$. 

6.4 HYDROGEN-BOND DYNAMICS OF AQUEOUS SOLVATION SHELLS

stretch vibrational lifetime of the water molecules in these solvation shells is comparable to that of bulk HDO:D$_2$O.

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6.5 Conclusions

In this chapter, we presented two-color femtosecond mid-infrared spectroscopic measurements of the dynamics of the aqueous solvation shells of the halogenic anions Cl\(^-\), Br\(^-\) and I\(^-\). A few picoseconds after excitation, only HDO molecules in the solvation shells of the anions remain excited, which allows for a highly selective study of the spectral dynamics of these molecules.

The spectral dynamics was studied by measuring pump–probe transients at different probe frequencies. From this study, we found that the stochastic modulation of the length of the hydrogen bond between the water molecules and the halogenic anions has a characteristic time constant \(\tau_c\) of 15–25 ps which is 30–50 times longer than the \(\tau_c\) of the O–H···O hydrogen bonds of bulk liquid water. In addition, the distribution of lengths of the hydrogen bond between the water molecules and the halogenic anions was observed to be relatively narrow. Both the long \(\tau_c\) and the narrow distribution of hydrogen-bond lengths indicate that the aqueous solvation shell forms a relatively long-living, well-defined structure. The value of \(\tau_c\) is larger for the aqueous solvation shells of Br\(^-\) and I\(^-\) than for the solvation shell of Cl\(^-\) and was observed to increase with temperature. These observations can be well explained from the dependence of \(\tau_c\) on the frequency of the hydrogen-bond vibrations between the HDO molecules and the solvated anions.

The large difference between the values of \(\tau_c\) of aqueous solvation shells and bulk liquid water likely results from a strong difference in the time scale of the fluctuations that affect the length of the hydrogen bond. For an aqueous solvation shell, these fluctuations can be identified with slow deformations of the solvation shell that involve a relatively large reorganization of the local liquid structure. For bulk liquid water, the fluctuations that affect the hydrogen-bond length likely are more local in nature which makes them much faster.