Molecular motions of water: The effect of charged and hydrophobic solutes
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6 Semi-rigid hydration and cooperativity in ion solutions

Despite prolonged scientific efforts to unravel the effects of ions on the structure and dynamics of water, many open questions remain, in particular concerning the spatial extent of this effect (how many water molecules are affected) and the origin of ion-specific effects. A combined terahertz and femtosecond infrared spectroscopic study of water dynamics around different ions reveals that the effect is usually limited to the first hydration shell of water molecules surrounding an ion, where cations and anions lock different degrees of freedom: semi-rigid hydration. In certain cases – when strongly hydrated cations and anions are combined – large structures (∼18 H$_2$O’s) are formed in between the ions, where the water dynamics are locked. This shows that the effect of ions and counterions on water can be strongly interdependent and non-additive.

6.1 Introduction

The properties of solutions of ions in water are of relevance for a wide range of systems, including biological environments [78] and atmospheric aerosols [65]. Interestingly, even for simple binary solutions the effect of ions on the structure and dynamics of water has been the subject of ongoing debate [45, 101, 166]. Key questions concerning ion effects on water pertain to the number of water molecules that are affected, and how the different degrees of freedom of these water molecules are influenced.

During the last decade a variety of measurement techniques has provided evidence that ions primarily have an effect on the structure and dynamics of the first solvation shell of water molecules directly surrounding the ion. This evidence consists of structural measurements of ion hydration using neutron and X-ray diffraction [36, 100], X-ray absorption spectroscopy [29] and infrared and Raman spectroscopy [150]. Information on the ion effects on water dynamics has been mainly obtained from femtosecond time-resolved infrared vibrational spectroscopy (fs-IR) [112, 119, 121] and optical Kerr effect spectroscopy [169].
These reports support the notion that the effect of ions on water is largely limited to the first solvation shell. A different dynamical technique, dielectric relaxation (DR), also showed that for many different cations and anions, the effect is limited to the first solvation shell [26,34,66,176]. However, for certain ion combinations an effect beyond the first solvation shell was observed [24,25,175].

Here, we study the effect of ions on water using terahertz dielectric relaxation (DR) spectroscopy and femtosecond vibrational infrared spectroscopy (fs-IR). It turns out that these techniques are complementary, in that they are sensitive to water reorientation dynamics along different axes of the water molecule. Moreover, the ability to independently resolve water reorientation along different directions helps to uncover previously unappreciated cooperativity between hydrated cations and anions. We study dissolved salts, containing various combinations of ions that have different charge densities and water affinities. For specific combinations of cations and anions we observe dynamic hydration effects that extend well beyond the first structural solvation shell.

6.2 Experiment and analysis

6.2.1 THz spectroscopy

We perform dielectric relaxation (DR) spectroscopy using a terahertz time-domain spectroscopy (THz-TDS) setup. This setup (see Chapter 3, Fig. 3.4) is based on THz generation and detection in ZnTe non-linear crystals, using 800 nm pulses with a duration of \( \sim 150 \) fs. The time-dependent electric field strengths of the THz pulses (\( \sim 3 \) ps) that are transmitted through the sample are measured by means of electro-optic sampling with a variably delayed pulse of 800 nm light with a duration of \( \sim 150 \) fs in a second ZnTe crystal. By comparison of the THz pulse that is transmitted through an empty cuvette and through a cuvette filled with the sample, we can extract the complex refractive index \( \hat{n} = n - i\kappa \). Here \( n \) is the regular refractive index and \( \kappa \) is the extinction coefficient. We determine the frequency-dependent complex dielectric response \( \hat{\epsilon}(\omega) = \hat{n}^2 \) for a number of salt solutions. In each measurement a sample is measured quasi-simultaneously with a reference sample. We employ a mechanical device that alternatively positions the sample and the reference sample (contained in cuvettes that have chambers with an optical path length of \( 103\pm0.5 \) \( \mu m \)) in the THz beam. This approach minimizes the effect of fluctuations in THz intensity and temperature as noise sources. We measure the following combinations of salt solutions: MgCl\(_2\)-CsCl, LiCl-CsCl, Cs\(_2\)SO\(_4\)-CsCl, Mg(ClO\(_4\))\(_2\)-CsCl and MgSO\(_4\)-Cs\(_2\)SO\(_4\). In most cases, the salt CsCl is chosen as a reference sample, since its dielectric properties are known and the ions Cs\(^+\) and Cl\(^-\) have a negligible hydration effect according to GHz dielectric relaxation measurements [34]. We have measured other additional combinations of samples and reference samples, to assure consistency. We
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compare samples with similar concentrations.

Molecular reorientation processes lead to dielectric relaxation, i.e. the anomalous dispersion of the dielectric constant and the accompanying absorption of electromagnetic energy [19, 20], as explained in Section 2.2. The dielectric response of pure water has shown evidence for two molecular reorientation processes [46, 68, 138–140, 186]

\[
\hat{\epsilon}(\omega) = \frac{S_{1,\text{pure}}}{1 + i\omega\tau_{D,\text{pure}}} + \frac{S_{2,\text{pure}}}{1 + i\omega\tau_{2,\text{pure}}} + \epsilon_\infty .
\] (6.1)

At room temperature, \(S_{1,\text{pure}} \approx 75\) and \(S_{2,\text{pure}} \approx 1.8\) and the corresponding time constants are \(\tau_D \approx 8\) ps and \(\tau_2 \approx 250\) fs [186]. The former time constant is associated with the reorientation of water, which is a concerted process that occurs through a molecular jump mechanism [81, 83]. The latter time constant is generally ascribed to the reorientation of undercoordinated water molecules [186]. The dielectric constant in the high frequency limit is given by \(\epsilon_\infty\).

In previous dielectric relaxation studies of aqueous salt solutions, it was observed that a certain number of water molecules shows very slow reorientation dynamics, whereas for the remaining water molecules the orientational dynamics are similar to bulk liquid water [24–26, 34, 66, 175, 176]. Also in computer simulations it was found that a fraction of water remains that is unaffected by the presence of the ions [82, 92]. In analyzing the THz data, we thus follow the literature and identify two sub-ensembles of water molecules in ionic solution: those whose dynamics are predominantly unaffected by the presence of ions (bulk-like water), and those whose dynamics are affected (hydration shell water). Including the conductivity \(\sigma\) due to ions (see Eq. 2.13), we obtain the following dielectric function of the ionic solution

\[
\hat{\epsilon}(\omega) = \frac{S_1}{1 + i\omega\tau_D} + \frac{S_2}{1 + i\omega\tau_2} + \frac{\sigma}{i\omega\epsilon_0} + \epsilon_\infty .
\] (6.2)

The addition of ions to water has an effect on the relaxation strength \(S_1\), since fewer water molecules contribute to this process. In total, there are three effects by which ions can lead to a lowering of \(S_{1,\text{pure}}\) by an amount \(\Delta S_1\) (depolarization): (i) the solution’s water concentration is slightly lower than the pure water case, resulting in a small overall lowering of the dielectric response (dilution effect); (ii) due to the interaction of the electric field of an ion with a number of water molecules in the vicinity of an ion, these water molecules can no longer participate in the relaxation process with \(\tau_D\) (static depolarization); and (iii) due to ions that move in the driving field, water molecules are caused to reorient in a direction opposite to the driving field (kinetic depolarization) [60, 66]. The static and kinetic depolarization effects
are schematically depicted in Fig. 6.1.

In ionic solutions the Debye time $\tau_D$ might be somewhat different from the value in pure water $\tau_{D_{\text{pure}}}$. However, this effect was found to have a negligible dependence on the nature of the ions [34,175,176]. The effect is furthermore small: it results in a $\tau_D$ that is $\sim 10\%$ lower for a 1 molar solution, compared to pure water.

In analyzing the data, we use the parameter $S_{1,\text{ref}}$ for the reference salt solution of CsCl from Ref. [34] and literature values for the ion conductivities of the solutions CsCl, MgCl$_2$, LiCl, Cs$_2$SO$_4$, MgSO$_4$ and Mg(ClO$_4$)$_2$ from Refs. [4,17,24,25,34,170,175]. For each sample, we fix $\tau_D$ to the value that was found for the accompanying reference sample. This allows us to extract the relaxation strength $S_1$ of a salt solution. For details on the extraction and modeling of the dielectric data from THz measurements, see Section 4.1.2. Finally, through the relaxation strength $S_1$ of a salt solution, we calculate the hydration number of the ions in the solution.

The hydration number of an ion, is defined as the number of moles of water molecules per mole dissolved salt, which no longer participate in dielectric relaxation due to the presence of the ion (effect ii above). These hydration numbers have been extracted successfully for a large number of ionic solutions by Buchner et al. [24–26,34,175,176]. We start with the extracted relaxation strength $S_1$ of a salt solution and obtain the total decrease of the relaxation strength of a salt solution compared to pure water: $\Delta S_1 = S_1 - S_{1,\text{pure}}$. This number is negative, since it is a reduction of the induced polarization, i.e. a depolarization. This depolarization is subsequently corrected for the effect of kinetic depolarization (effect iii mentioned above), which is proportional to the conductivity $\sigma$ and depends on the salt concentration $c$ [26,66]
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\[
\Delta S_{1, \text{kin, dep.}}(c) = -\sigma(c) \cdot \frac{2\tau_D, \text{pure} \epsilon_{s, \text{pure}} - \epsilon_\infty(c)}{\epsilon_{s, \text{pure}} \epsilon_0}.
\] (6.3)

Here, \(\epsilon_{s, \text{pure}}\) is the static permittivity of pure water and \(\epsilon_\infty(c)\) the high-frequency limit of the permittivity for the salt solution. After having corrected the total depolarization \(\Delta S_1\) for the kinetic depolarization, we obtain the corrected depolarization \(\Delta S'_1\). This number can subsequently be translated into the hydration number, as measured with THz DR spectroscopy, \(N_{\vec{p}}\), using [54]

\[
N_{\vec{p}}(c) = \left( c_s - \frac{S_{1, \text{pure}} + S_{2, \text{pure}} + \Delta S'_1}{S_{1, \text{pure}} + S_{2, \text{pure}}} c_0 \right) / c
\] (6.4)

In this equation, \(c_s\) is the concentration of solvent water molecules in the solution and \(c_0\) represents the concentration of water molecules of pure water (\(\sim 55\) mol/L). The subscript \(\vec{p}\) refers to the molecular vector whose reorientation is monitored: the dipole moment of the water molecules. In Eq. 6.4, the dilution effect of the ionic solution (effect i mentioned above) is taken into account through the concentrations \(c, c_s\) and \(c_0\). We point out that the hydration number is a dynamics property and is therefore distinct from the structural concept of solvation shells. Solvation shells are often defined in terms of the distance distribution of the water molecules from the center of the ion, but as such do not present information on the dynamics of the water molecules.

6.2.2 fs-IR spectroscopy

Complementary to DR measurements, we use femtosecond time-resolved infrared vibrational spectroscopy (fs-IR) measurements. The setup of these experiments is schematically depicted in Chapter 3, Fig. 3.5. This technique allows the direct study of the reorientational dynamics of individual water molecules with high temporal resolution (\(\sim 150\) fs). In these experiments, we excite the OD-stretch vibration of a subset of HDO molecules in H_2O (4% D_2O in H_2O). Molecules with their OD group preferentially aligned along the polarization axis of the excitation (pump) pulse are most efficiently tagged. By interrogating, using a second laser (probe) pulse, the number of tagged OD groups that are oriented parallel and perpendicular to the excitation axis, the rotation of these groups can be followed in time. To this purpose, we measure the pump-induced absorption change as a function of frequency and pump-probe delay for a probe pulse that is polarized parallel (\(\Delta \alpha_{||}\)) and a probe pulse that is polarized perpendicular (\(\Delta \alpha_{\perp}\)), with respect to the pump pulse. We use \(\Delta \alpha_{||}\) and \(\Delta \alpha_{\perp}\) to construct the isotropic signal, which is independent of reorientation

\[
\Delta \alpha_{\text{iso}} = \frac{1}{3} (\Delta \alpha_{||} + 2 \Delta \alpha_{\perp})
\] (6.5)
To obtain the anisotropy dynamics of the excited OD-stretch dipole vectors, the measured data $\Delta \alpha_{\parallel}$ and $\Delta \alpha_{\perp}$ are corrected for the time-dependent thermalization signal. The temporal evolution of this contribution to the signal is obtained from a detailed investigation of the spectral dynamics of the isotropic signal. All data are modeled with the cascading energy relaxation model described in Section 4.2.1 and Ref. [134]. In this model the energy from the OD-stretch vibration is transferred through an intermediate state (presumably the bending mode) to a thermal end level (lower energy modes). The model contains two main fit parameters: $\tau_1$ (first excited state OD-stretch $\rightarrow$ intermediate state) and $\tau_2$ (intermediate state $\rightarrow$ thermal end state). A least squares fit is conducted for the whole spectrum at each delay time to find the two time scales that constitute the best fit. In Fig. 6.2, we show measurements and the results of the fitting procedure for the isotropic data of different sulfate-containing salt solutions. Clearly, the vibrational lifetime depends only weakly on the salt concentration.

$$R(t) = \frac{\Delta \alpha_{\parallel}'(t) - \Delta \alpha_{\perp}'(t)}{\Delta \alpha_{\parallel}'(t) + 2\Delta \alpha_{\perp}(t)}.$$  \hspace{1cm} (6.6)

The decay of the anisotropy represents the orientational relaxation of the OD groups of the water molecules in the system. In neat HDO:H$_2$O, the time scale of the decay of the anisotropy corresponds well within a constant scaling factor to the relaxation time $\tau_{D,\text{pure}}$ of pure water, as measured with THz DR.
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spectroscopy. This was shown for a large range of temperatures in Chapter 5.

In aqueous salt solutions, we describe the anisotropy decay using a bimodal model, analogous to the DR measurements: the slow time constant and the associated fraction of slow hydration shell water are obtained from a double exponential fit to the anisotropy decay. Here the bulk-like time constant is determined from independent measurements of the reorientation time of neat water ($\tau_{\text{bulk}} = 2.6 \pm 0.1$ ps at room temperature). The slow component represents a weighted average of water molecules that have in common that they reorient more slowly than the water molecules in bulk liquid water. Hence, the data are fit with the following model

$$R(t) = A_{\text{bulk}} \cdot e^{-t/\tau_{\text{bulk}}} + A_{\text{shell}} \cdot e^{-t/\tau_{\text{shell}}} . \quad (6.7)$$

For all studied solutions (Mg(ClO$_4$)$_2$ up to 2 mol/kg, LiI up to 4 mol/kg, LiCl up to 4 mol/kg, Cs$_2$SO$_4$ up to 4 mol/kg, Na$_2$SO$_4$ up to 3 mol/kg and MgSO$_4$ up to 2 mol/kg), we found good agreement with a fixed slow water time constant of $\tau_{\text{shell}} = 10$ ps. We point out that exchange of water molecules inside and outside the hydration shell can occur. However, this time scale is slow (tens of picoseconds [74]) in comparison to the time scale of the molecular reorientation of neat water [134]. Hence, a water molecule outside the solvation shell has long reoriented before it is exchanged with a water molecule in the solvation shell. As a result, the dynamics of the water molecules outside the solvation shells are observed well separated from the dynamics of the water molecules inside the solvation shell. For water in the solvation shell, the exchange time is also too long to obtain an averaging of solvation shell and bulk behavior. The residence time of the solvation shell may however contribute to the measured reorientation time scale. When the water molecule leaves the shell, it will likely also reorient. Hence the reorientation time of the hydration shell does present a lower limit for the residence time of the water molecules in the solvation shell. For all studied ions the residence time is too long [74] to make the slowly reorienting water molecule into a bulk-like water molecule. Hence, the value of the hydration number is not dependent on the time scale of the exchange.

In analogy to the DR measurements, the slow water fraction as measured with fs-IR can be translated into a hydration number $N_{\vec{\mu}}$. This corresponds to the number of moles of slowly reorienting OD groups (with transition dipole moment $\vec{\mu}$) per mole dissolved salt

$$N_{\vec{\mu}} = \frac{A_{\text{shell}}}{A_{\text{bulk}} + A_{\text{shell}}} \times 2c_s , \quad (6.8)$$

where the factor 2 is due to the fact that there are two OD groups per water molecule.
6.3 Results

We first present the results of DR spectroscopy of different dissolved salts. In the inset of Fig. 6.3A, we show THz pulses as transmitted through 0.5 mol/kg solutions of Cs$_2$SO$_4$, MgSO$_4$ and through a reference solution of CsCl [34]. Generally, THz pulses are delayed as a result of refraction and experience a decrease in amplitude as a result of absorption (see also Chapters 2 and 4). In Fig. 6.3A, we show the imaginary part of the extracted dielectric function $\epsilon$, which is associated with absorption of electromagnetic radiation by water molecules.

![Figure 6.3. Results of DR spectroscopy.](image)

Figure 6.3. Results of DR spectroscopy. (A) The imaginary part of the dielectric function for 0.5 mol/kg solutions of CsCl, Cs$_2$SO$_4$ and MgSO$_4$ and the corresponding transmitted THz pulses (inset). (B) The depolarization (corrected for kinetic depolarization due to conductivity, according to Eq. 6.3) and the fraction of slow water as a function of concentration for the salt solutions CsCl (from Ref. [34]), Cs$_2$SO$_4$, NaCl (from Ref. [26]), LiCl and MgSO$_4$. The fraction of slow water is calculated from Eq. 6.4. The lines are linear fits to the depolarization values and serve to distinguish the studied salts. Error bars represent the 95% confidence interval and are derived through error propagation of the experimental uncertainty in the dielectric function.

In Fig. 6.3B, we show the concentration-dependent depolarization (corrected for kinetic depolarization, as described in the previous section) and corresponding slow water fraction for five different salts. It is typically found that ions with a larger charge density (small, multivalent ions) affect the dynamics of a larger number of water molecules, i.e. have a higher hydration number, than ions with a lower charge density (large, monovalent ions) [24–26,34,36,66,100,175]. This is caused by the larger local electric field around these ions, which affects the orientation of a larger number of surrounding water molecules. The results for CsCl, NaCl and LiCl are in good agreement with this general rule, since the cation Cs$^+$ is larger than Na$^+$, which is in turn larger than Li$^+$. The extracted hydration numbers $N_p$ for these salt solutions are $\sim 0$, $\sim 4$ and $\sim 9$, respectively. This shows that the water molecules in the solvation shell of
Cs\(^+\) show reorientational dynamics similar to bulk liquid water [34], probably because the positive charge of the Cs\(^+\) ion is distributed over a large volume. It also shows that water surrounding the anion Cl\(^-\) is not slowed. Therefore, the observed slowly reorienting water molecules are likely located in the first geometrically surrounding solvation shell of the cations Na\(^+\) and Li\(^+\). Indeed, it is generally considered that the cationic hydration strengths are related as Li\(^+\) > Na\(^+\) > Cs\(^+\) [77]).

For Cs\(_2\)SO\(_4\) we find that \(N_{\overrightarrow{p}} \approx 1\), where the slowly reorienting water can be attributed to a water molecule located within the solvation shell of strongly hydrated SO\(_4^{2-}\), possibly forming hydrogen bonds with both OH groups to two oxygen atoms of the SO\(_4^{2-}\) ion. This result is surprising, since sulfate is a strongly hydrated anion ([77]). Hence the low value of \(N_{\overrightarrow{p}}\) found for Cs\(_2\)SO\(_4\) indicates that the effect of anions on water reorientation is either negligible or not measurable by DR measurements. Similarly, a previous GHz DR measurement of the anions Br\(^-\), I\(^-\), NO\(_3^-\), ClO\(_4^-\) and SCN\(^-\) found that the impact of these anions on water dynamics is remarkably small and similar, despite the different water affinities of these ions [176]. The results for MgSO\(_4\) form an exception and will be discussed in detail in Section 6.5.

The results of the fs-IR measurements for four aqueous salt solutions are shown in Fig. 6.4. Here, we show the anisotropy decay for the dissolved salts Mg(ClO\(_4\))\(_2\), LiI, LiCl and Cs\(_2\)SO\(_4\). These measurements show very different behavior from the THz DR measurements: for water around the anion SO\(_4^{2-}\) a slowing down of the reorientation dynamics is observed, while for the other solutions, which contain the strongly hydrated cations Li\(^+\) and Mg\(^{2+}\), there is surprisingly little effect. This indicates that the effect of cations on water reorientation is either negligible or not measurable by fs-IR measurements.

### 6.4 Semi-rigid hydration

As we have seen, there is an apparent discrepancy between the DR measurements and the fs-IR measurements: Li\(^+\) shows a large slow fraction when measured with DR, but the fs-IR measurements of LiI and LiCl show a negligible slow fraction. For the hydrated anion SO\(_4^{2-}\), the opposite is the case: no slow fraction is observed with DR spectroscopy, whereas fs-IR measurements show the existence of a significant slow water fraction. These apparently contradictory results are shown in Fig. 6.5.

The differences between the results of DR and fs-IR can however be understood by noting the different molecular vectors that the two measurement techniques probe: the permanent dipole moment \(\overrightarrow{p}\) of water molecules in the case of DR and the OD-stretch transition dipole moment \(\overrightarrow{\mu}\) in the case of fs-IR (see Fig. 6.6). The local electric field around the ions causes the dipole vector \(\overrightarrow{p}\)
of water molecules in the solvation shell of a cation to point radially away from the cation, whereas for an anion one of the OD groups of a hydrogen-bonded water molecule linearly points towards the anion [117,150]. Fig. 6.6 shows that the observed rotational motion of water molecules in the cationic solvation shell does not lead to reorientation of the vector $\vec{p}$, but does result in randomization of the transition dipole vector $\vec{\mu}$. For the case of anions, the reverse effect occurs: for water molecules in the anionic solvation shell, the motion of $\vec{p}$ is unrestricted within a cone with fixed axis $\vec{\mu}$, where $\vec{\mu}$ corresponds to the vector of the OD that is hydrogen-bonded to the anion.

Reorientation in a cone with a semi-cone angle between $\vec{\mu}$ and $\vec{p}$ of $\theta \approx 52^\circ$ (half the HOD-bond angle) leads to a complete randomization of a vector whose motion is unrestricted within the cone (see Fig. 6.7). This explains the insensitivity of DR towards anionic, and of fs-IR towards cationic hydration. For both cations and anions, these observations lead to a molecular picture
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Figure 6.5. Discrepancy between THz DR and fs-IR spectroscopy. The left figure shows the slow water fractions for LiCl and Cs$_2$SO$_4$ as extracted with THz DR spectroscopy; the right figure shows the slow water fractions for the same salts as extracted with fs-IR spectroscopy.

of “semi-rigid hydration”, i.e. water molecules in ionic solvation shells that reorient in a propeller-like manner, giving rise to anisotropic reorientation, along a distinct axis.

Figure 6.6. Semi-rigid hydration. A water molecule in the solvation shell of a cation (left) and an anion (right). Dielectric relaxation measurements probe the reorientation of the permanent dipole vector $\vec{p}$. Femtosecond infrared spectroscopy is sensitive to the reorientation of the OD-stretch transition dipole moment $\vec{\mu}$. The dotted arrows indicate reorientation in a cone, in the case of semi-rigid hydration.

To show that reorientation around a fixed axis leads to complete randomization of the vector whose motion is unrestricted within the cone, we calculate the expected end level of the anisotropy $R_{t\rightarrow \infty}$ for a water molecule that can rotate with a fixed angle around a certain axis. The geometry is given in Fig. 6.7, where it is generalized to the rotation of a vector around an axis with an angle $\theta$ between vector and axis. The initial orientation $\mu_i$ corresponds to an angle $\phi_i$ in the circular plane in which the vector will precess. The final orientation is associated with angle $\phi_e$. We take $\phi_i = 0$ and integrate over $\phi$ to allow the final orientation to have a randomly distributed angle $\phi = \{0, 2\pi\}$. We find
\[
R_{t \to \infty} = \frac{2}{5} \int_0^{2\pi} P^{(2)}(\mu_i \cdot \mu_e) d\phi . \tag{6.9}
\]

with \( P^{(2)}(x) = \frac{1}{2}(3x^2 - 1) \), the second order Legendre polynomial, \( \mu_i = (\sin(\theta), 0, \cos(\theta)) \) and \( \mu_e = (\sin(\theta) \cos(\phi), \sin(\theta) \sin(\phi), \cos(\theta)) \). The result for the anisotropy end level is shown in Fig. 6.7 as a function of the angle \( \theta \). The angle between the rotating vector and the rotational axis in the case of a water molecule that rotates around its permanent dipole is half the HOD bond angle and hence \( \sim 52^\circ \). It is clear that the anisotropy end level is very small (<0.005), indeed confirming that such reorientation leads to complete randomization of the vector.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{fig6_7}
\caption{Rotation in a cone. Graphical representation of the geometry, where a water molecule can rotate around the axis of its permanent dipole \( \vec{p} \). The initial and final state of the OD-stretch dipole moment are given by \( \vec{\mu}_i \) and \( \vec{\mu}_e \), respectively. The graph on the right shows the anisotropy end level as a function of the angle \( \theta \) between \( \vec{\mu} \) and the axis of rotation.}
\end{figure}

6.5 Cooperativity

The molecular picture of semi-rigid hydration explains the ion effect on water molecules directly surrounding the ion. This picture holds for salts for which one of the counterions is weakly hydrated. However, when both ions are strongly hydrated, we find that the effect on water dynamics can be much stronger and non-additive. In Fig. 6.8, we show the normalized anisotropy for \( \text{Mg(ClO}_4\text{)}_2 \), \( \text{Cs}_2\text{SO}_4 \) and \( \text{MgSO}_4 \), each for concentrations ranging from 0 to 2 mol/kg. A remarkable conclusion can be drawn from these three measurements: \( \text{MgSO}_4 \) shows a very large slow reorientation component, whereas \( \text{Mg}^{2+} \) and \( \text{SO}_4^{2-} \) individually, in combination with other ions (\( \text{ClO}_4^- \) and \( \text{Cs}^+ \), resp.) do not. In Fig. 6.9B, we show the slow water fraction as a function of salt concentration. Clearly, \( \text{MgSO}_4 \) has a much larger fraction of slowly reorienting
water molecules (corresponding to a hydration number $N_{\mu} = 32$, extracted using Eq. 6.8) than Mg(ClO$_4$)$_2$ and Cs$_2$SO$_4$ (with hydration numbers $N_{\mu}$ of 4 and 9, respectively). This means that the dynamics of a large number of water molecules are affected, due to a cooperative effect of the cation and the anion. The size of most ions allows them to be structurally surrounded by $\sim$6 water molecules. Hence, a value of $N_{\mu} > 6$ and $N_{\pi} > 12$ implies that the effect of the ion on the orientational dynamics of water extends well beyond the first structurally surrounding shell of water molecules.

![Graphs showing normalized decay of anisotropy $\mathcal{R}(t)$ for various concentrations of Mg(ClO$_4$)$_2$, Cs$_2$SO$_4$, and MgSO$_4$.](image)

Figure 6.8. The normalized decay of the anisotropy $\mathcal{R}(t)$ for a number of concentrations of Mg(ClO$_4$)$_2$ (A), Cs$_2$SO$_4$ (B) and MgSO$_4$ (C).

The THz DR data in Fig. 6.9A show the same cooperative effect as the fs-IR measurements: Mg(ClO$_4$)$_2$ has a hydration number $N_{\pi} = 6$ and Cs$_2$SO$_4$ has a hydration number $N_{\pi} = 1$, respectively associated with water molecules directly adjacent to the Mg$^{2+}$ ion and a water molecule hydrating the SO$_4^{2-}$ ion. For MgSO$_4$ $N_{\pi} = 18$, which is much larger than the sum of the hydration numbers of Mg(ClO$_4$)$_2$ and Cs$_2$SO$_4$. For MgSO$_4$, there are approximately twice as many slowly rotating OH groups ($N_{\mu}$) as slowly rotating dipoles ($N_{\pi}$), indicating that the same collection of slow water molecules is observed by fs-IR and THz DR. Even the combination of the moderately strongly hydrated cation Na$^+$ with the strong anion SO$_4^{2-}$ is observed to affect the dynamics
of a large number of water molecules ($N_{\mu} = 24$; see Fig. 6.9B). The same is true for the combination of the moderately strongly hydrated anion Cl$^-$ with the strong cation Mg$^{2+}$ (see Fig. 6.9A). In these cases, however, the hydration numbers are also increased because there are three instead of two ions per dissolved salt molecule. These results lead to the conclusion that the effects of ions and counterions can be strongly interdependent and non-additive. The key parameter determining how strongly ions affect water dynamics is thus the combination of the solvated cation and anion.

![Figure 6.9](image.png)

**Figure 6.9. Cooperativity.** The fraction of slow water compared to bulk-like water as a function of salt concentration as measured by THz spectroscopy (A) and by fs-IR spectroscopy (B). The lines are linear fits and serve as guides to the eye to distinguish the studied salts. The error bars are based on at least three measurement runs and represent the 95% confidence interval.

It is clear that the effect of MgSO$_4$, Na$_2$SO$_4$ and MgCl$_2$ on water extends well beyond the first solvation shell of the ions and that the ions show strong cooperativity in affecting the dynamics of water molecules. Previous GHz DR studies by Buchner et al. showed the presence of a certain amount of (contact and solvent-separated) ion pairs for solutions of MgSO$_4$ and Na$_2$SO$_4$ [24, 25]. Our THz DR measurements are not directly sensitive to the reorientation of ion pairs, since ion pairs lead to additional dielectric loss peaks at very low frequencies ($<5$ GHz), located well outside our THz measurement window (0.4 – 1.2 THz). For the fs-IR measurements we can neglect the contribution of contact ion pairs to the anisotropy data, since this technique excites and probes specifically the OD vibrations of water molecules. Hence, the dramatic slowing down of the anisotropy decay for MgSO$_4$ and Na$_2$SO$_4$ corresponds to slow reorientation of water molecules, not the slow reorientation of contact ion pairs. A remaining question is whether the observed slow water molecules could be water hydrating ion pairs. In the case of contact ion pairs, this is very unlikely because the concentration of contact ion pairs is generally small – less than
10% for MgSO$_4$, even at high salt concentrations [25] – whereas the observed cooperative effect leads to a slowing down of a large fraction of the water (up to 70% of all water molecules in the solution; see Fig. 6.9). In the case of solvent separated ion pairs, it is likely that the water molecules that separate the ions have slow reorientation dynamics. The large hydration number for MgSO$_4$ indicates that there are large extended structures of slowly reorienting water molecules in between Mg$^{2+}$ and SO$_4^{2-}$ ions (see Fig. 6.10).

The cooperativity in ion hydration can be explained from the fact that the cation and anion lock different degrees of freedom of the water molecules, i.e. the direction of the bisectrix ($\vec{p}$) and the direction of OD ($\vec{\mu}$), respectively. The nearby presence of both ions can thus lead to a locking in both directions of the hydrogen-bond structure of several intervening water layers, giving rise to the observation in DR and fs-IR of slowed down water molecules well beyond the first solvation shell. This cooperativity is schematically illustrated in Fig. 6.10. As illustrated in this figure, we expect the solvation structures to be quite directional in between the ions. If an ion forms $\sim$4 of these structures with surrounding counterions, the value of $N_{\vec{p}}$ of 18 implies that each of these structures consist, on average, of 4-5 water molecules. This interpretation also means that for solutions like MgSO$_4$ and Na$_2$SO$_4$ the slowly reorienting water molecules are not arranged in a spherically symmetric way around the ions.

### 6.6 Temperature Dependence

The reorientation of water molecules in the rigid, locked hydrogen-bond structure occurring for MgSO$_4$ can be expected to show a different temperature
dependence compared to neat liquid water. We measure the temperature dependence of the anisotropy decay for 1.5 mol/kg MgSO$_4$ (Fig. 6.11A) over an interval of about 50 °C. We compare the temperature dependence to that of a 4 mol/kg Cs$_2$SO$_4$ solution (Fig. 6.11B) with the same hydration level (Fig. 6.8D), but no cooperativity. At room temperature, the anisotropy for MgSO$_4$ decays more slowly than for Cs$_2$SO$_4$, but with increasing temperature the situation reverses. To quantify the results, we fit the anisotropy data at different temperatures with a single averaged time scale for all water molecules in the system. This means that a change in this time scale represents both the changes in time scales and changes in the relative fractions of bulk-like and slow water molecules. Figure 6.11C shows a much stronger temperature dependence of this average time scale for a solution of 1.5 mol/kg MgSO$_4$ than for a solution of 4 mol/kg Cs$_2$SO$_4$.

![Figure 6.11. Temperature dependence of the reorientation. The temperature-dependent anisotropy decay data for MgSO$_4$(A) and Cs$_2$SO$_4$(B) with fits as explained in the text. (C) Average reorientation times of solutions of 1.5 mol/kg MgSO$_4$, 4 mol/kg Cs$_2$SO$_4$ and neat HDO:H$_2$O (from Ref. [164]) as a function of temperature.](image)

The difference in temperature dependence of the reorientation of MgSO$_4$ and Cs$_2$SO$_4$ solutions indicates that the reorientation within the hydration structures involves a different mechanism. For pure water it was found from
MD simulations that the reorientation of water follows a concerted mechanism and that the rate-limiting step for reorientation of a water molecule is the motion of a second water molecule in and out of the solvation shell of the first [81,83]. For the Cs₂SO₄ solution the hydration number $N_{\overrightarrow{H}}$ has a value of 9, which is likely associated with the OH groups of water molecules that are hydrogen bonded to the SO$_4^{2-}$ ion. In view of the small value of $N_{\overrightarrow{H}}$, these water molecules are surrounded by water molecules that show bulk-like dynamics. Hence, although the reorientation of the water molecules hydrating the SO$_4^{2-}$ is slow, the temperature dependence of this reorientation is similar to that of pure liquid water, because the reorientation is governed by hydrogen-bond interactions to water molecules that show bulk-like behavior. Correspondingly, the temperature dependence of the reorientation time of Cs₂SO₄ has the same slope as for bulk water. In contrast, for MgSO₄ the solvation structures are large, as expressed by the large values of the hydration numbers $N_{\overrightarrow{H}} = 18$ and $N_{\overrightarrow{H}} = 32$. Hence, the reorientation of a water molecule in the solvation structure relies on the motions of water molecules that are contained in the same solvation structure. These motions are substantially slowed down, and reorientation thus involves a collective reorganization of the extended solvation structure, which explains the difference in temperature dependence with a solution of Cs₂SO₄ and pure liquid water.

6.7 Conclusion and outlook

In conclusion, we have found that the hydration structure of a strongly hydrated ion depends critically on the nature of its counterion. If the counterion is weakly hydrated, the strongly hydrated ion is surrounded by a semi-rigid solvation shell, where reorientation is restricted only in a certain direction, but is still allowed in other directions. If, however, strongly hydrated cations and anions are combined, the dynamics of water molecules well beyond the first solvation layer are affected through a cooperative effect of the ions. In this case, the hydrogen-bond network in between the ions is locked in multiple directions. These findings show that the effect of ions on water dynamics can be strongly interdependent and non-additive.

The observed cooperativity in ion hydration has implications for the Hofmeister series, where an ordering is given for the relative strength of cations and ions to affect properties (such as solubility) of a biomolecular solution (see Chapter 1). Due to the cooperative effects, the Hofmeister series should be considered in terms of salts, instead of individual ions$^a$. Furthermore, it is likely that the molecular origin of the Hofmeister series is related to cooperative effects between ions, e.g. Ca$^{2+}$, and biomolecules, e.g. DNA and

$^a$In his original work (published at the end of the 19th century), Franz Hofmeister described the effect of salts on biological solutions. The interpretation in terms of the effect of individual ions was given later [57,77,78].
proteins, which contain negative charges. Due to this cooperativity between ions and biomolecules, the water dynamics can be affected, which in turn leads to changes in the properties of the solution. This explanation of the molecular origin of the Hofmeister series forms an alternative to the direct ion-biomolecule effects or the pure ion-water effects.