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

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8 THE INFLUENCE OF IONS ON THE HYDROGEN-BOND STRUCTURE OF WATER

The effects of ions on bulk properties of liquid water, such as viscosity and ionic mobility, suggest that ions alter the hydrogen-bond network of liquid water. In this chapter, measurements of the orientational-correlation time of water molecules in solutions of $NaClO_4$, $Mg(ClO_4)_2$, and Na_2SO_4 are presented. The measurements show that, even for high concentrations of ions that are believed to strongly enhance the hydrogen-bond network, there is no influence on the rotational dynamics of water molecules outside the first solvation shell. The results described in this chapter oppose the prevailing notion of structure-making or structure-breaking ions, that has been held for decennia.

8.1 INTRODUCTION

After having studied several aspects of solvations shells, we turn our attention in this final chapter to the behaviour of the bulk solvent. It is generally assumed that ions can enhance or weaken the hydrogen-bond structure in water;[28,34,38,39] as a result, ions are categorized as either 'structure makers' or 'structure breakers'. The concept of structure making and breaking was probably introduced in the 1930's.[20] The central idea of this concept is that the hydrogen-bond structure and dynamics of water in the direct environment, usually over a distance of several molecules, are changed by the electrostatic field exerted by the ion. To quote Engel in Ref. 34, 'the word structure breaking is synonymous with the characterization "causing faster motions of the water molecules".' Therefore, ions with strong electric-field density, i.e. small or highly-charged ions, will be structure makers, while larger ions will likely be structure breakers. For polyatomic ions, it is not always a priori obvious whether they will belong to the one or the other group: SO_4^{2-} is a strong structure maker, while ClO_4^- is a structure breaker. Structure breaking is sometimes called 'negative hydration'.

The concept of structure making and breaking has gained recognition when more anomalous phenomena could be explained by these ideas. First, there are the anomalous mobilities of many ions in water. The usual models use Stokes' law, that describes friction due to viscosity, and/or dielectric friction, as described by Zwanzig.[144] These models provide a poor description of the mobility. In general, ions with low charge densities (e.g. large univalent ions) move less hindered and therefore have a larger mobility than predicted by the Stokes/Zwanzig models,[39] while ions with high charge densities generally have smaller mobilities. The large tetra-alkylammonium ions also have an unexpected low mobility. The effect is much stronger if these ions are dissolved in water than if they are dissolved in some aprotic solvent, which can be explained when the tetra-alkylammonium ions are assumed to promote the degree of hydrogen bonding between the solvent molecules in the case of water.

A second argument that supports the concept of a changed hydrogen-bond structure in water due to ions, is provided by the effect of the presence of ions on the viscosity of water.[44] The phenomenological Jones–Dole expression[55] relates the viscosity of an aqueous ionic solution to the ion concentration:

$$\frac{\eta}{\eta_0} \approx 1 + A\sqrt{c} + Bc. \qquad (8.1)$$

In this equation c is the ion concentration, η is the viscosity of the solution, η_0 is the viscosity of pure water, and A and B are the 'Jones–Dole constants'. Equation (8.1) is valid for concentrations up to about 1 M, but this range can be extended by including higher-order terms in the concentration.[97] The second term on the right-hand side, $A\sqrt{c}$, results from electrostatic interactions between the ions. The constant A is due to the electrostatic interaction between the ions and can be derived from theory.[35] The third term, Bc is attributed to the influence on the hydrogen-bond structure by the ion: the ions that are considered strong structure makers have positive B coefficients, while ions with negative B coefficients are structure-breaking, since structured water, with stronger hydrogen bonds, is expected to be more viscous than nonstructured water.

The vibrational spectra of electrolyte solutions have also been studied in order to get insight in the influence of ions on the hydrogen-bond structure in liquid water.[39] Some cations with high charge density (like Al^{3+} [81] or Mg^{2+} [125]) are considered to be strong structure makers and cause a slight redshift of the spectrum, indicative of an enhanced hydrogen-bonding (see figure 8.1). However, aqueous tetra-alkylammonium solutions do not show this redshift,[39] although the tetra-alkylammonium ions would be even stronger structure makers than Mg^{2+}.

The above described effects all constitute rather indirect probes of the effect of ions on the hydrogen-bond structure of liquid water, relating macroscopic quantities to microscopic behaviour. A better way would be to probe the hydrogen-bonded network in ionic solutions directly at a microscopic level, as was done for the solvating molecules in the experiments presented in the previous chapters. The orientational-correlation time of the water molecules can be viewed as a probe for the stiffness of the hydrogen-bond network, because it is more difficult for water molecules to change their orientation if the hydrogen-bond network is more rigid.[90] Based on the hypothesis that ions influence the hydrogen-bond network, one would expect the 'bulk' water molecules around a structure-making ion to have a relatively long orientational-correlation time (compared to pure liquid water with no ions present), and those surrounding a structure-breaking ion to have a relatively short orientational correlation time. The orientational-correlation time of water molecules in ionic solutions has been measured with NMR.[96] However, as has been mentioned before, for ionic solutions NMR lacks specificity, since the pulses used in this method are very long (microseconds) compared to the time scale on which water molecules exchange between the solvation shell and the bulk solution. Hence, only the average reorientation time of all water molecules is measured.

The properties of ionic solutions have also been studied with MD simulations, but the results obtained are inconclusive as to the long-range effect of ions on the hydrogen bonding of the water molecules. A number of MD results have been supportive of the concept of structure making and structure breaking,[17,95,123] but other MD studies do not confirm this picture.[18,143,130,74]

Until recently, it was not possible to study the very fast hydrogen-bond dynamics of water molecules experimentally. Since a few years, however, this has become possible with femtosecond nonlinear spectroscopy.[23,43,40,77,137,134] It was shown in the previous chapters that with this technique, the behaviour of O–H groups of water molecules hydrogen bonded to an anion can be distinguished from the behaviour of O–H groups of water molecules hydrogen bonded to a water molecule. Consequently, the solvation shells of negative ions and the bulk water molecules can be studied separately from each other.

8.2 EXPERIMENTAL

The experiments are similar to the ones in the previous chapter. They are polarization-resolved two-color femtosecond mid-infrared pump-probe experiments on a dilute (<1 M) solution of HDO dissolved in D_2O and several concentrations (0–6 M) of salt ($NaClO_4$, $Mg(ClO_4)_2$ or Na_2SO_4). The generated mid-infrared pulses have a pulse energy of 20 μJ and a duration of approximately 200 fs.

To study the orientational relaxation of the excited HDO molecules, the polarization of the probe pulse was rotated 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 ($\ln(T/T_o)_\parallel$) and perpendicular to the pump ($\ln(T/T_o)_\perp$) were measured as a function of the delay τ 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.

8.3 RESULTS

SEPARATION OF ABSORPTION BANDS   The absorption spectra of the O–H stretch vibration of solutions of 6 M $NaClO_4$ and 3 M $Mg(ClO_4)_2$ in $HDO{:}D_2O$ solution is shown in figure 8.1. For both solutions, two distinct peaks are seen. The peak in the $NaClO_4$ spectrum. which is centred at 3400 cm^{-1}, is attributed to O–H groups hydrogen-bonded to D_2O molecules, whereas the peak at 3575 cm^{-1} is attributed to O–H groups bonded to ClO_4^-.[39] By fitting two Gaussian functions to the absorption spectrum of $NaClO_4$, we determined the approximate centre and width (FWHM) of the O–H$\cdots ClO_4^-$ band to be 3575 cm^{-1} and 90 cm^{-1}, respectively, and of the O–H$\cdots$O band 3400 cm^{-1} and 270 cm^{-1}.

We performed pump–probe measurements to study the dynamics of these two bands. The decay of the isotropic signal is shown in figure 8.2. First, we pumped at 3575 cm^{-1} (0→1 transition of ClO_4^- bonded O–H groups) and probed at 3325 cm^{-1} (1→2 transition). The decay is clearly biexponential, where the fast component (0.8 ps) results from O–H groups that are hydrogen-bonded to D_2O, and the slow component (1.7 ps) is due to the decay of the excitation of O–H groups bonded to ClO_4^-. Then, we pumped at 3400 cm^{-1} (0→1 transition of water-bonded O–H groups) and probed at 3150 cm^{-1} (1→2 transition). At this frequency, practically no anion-bonded O–H groups are observed: the decay is fast and almost monoexponential with a time constant of about 0.8 ps (the same as observed for O–H groups in the pure liquid.[91])

Since the water band at 3400 cm^{-1} is much broader (270 cm^{-1} compared to 90 cm^{-1}), these bulk-water molecules still can absorb at 3575 cm^{-1}. The reverse is not the case:
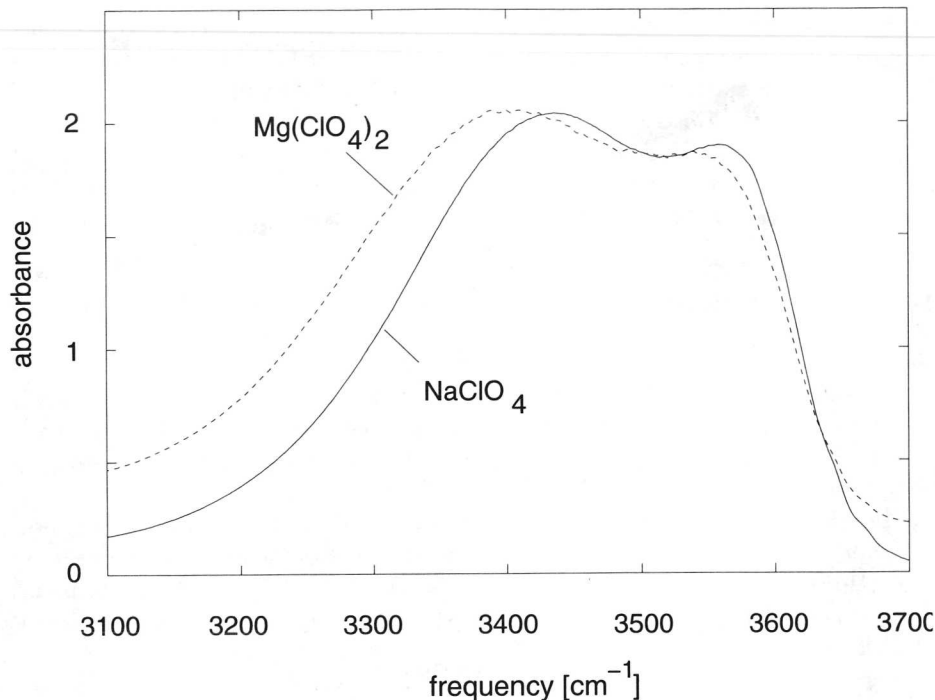
FIGURE 8.1. Absorption band of the O–H stretching vibration in a 6 M NaClO$_4$ and in a 3 M Mg(ClO$_4$)$_2$ ($\equiv$ 6 M ClO$_4^-$) in HDO:D$_2$O solution. For both solutions there are two distinct peaks meaning that the O–H$\cdots$ClO$_4^-$ band is well separated from the O–H$\cdots$O band. Therefore, the O–H$\cdots$O band could be pumped and probed selectively.

pumping at 3400 cm^{-1} will not excite anion-bound water molecules. The difference in vibrational relaxation times of the two absorption bands confirm what was already concluded from the linear spectra, namely that the high-frequency absorption peak corresponds to the O–H$\cdots$ClO$_4^-$ groups, while the rest of the molecules, all forming O–H$\cdots$O hydrogen bonds to other water molecules, give rise to the broad absorption at 3400 cm^{-1}.

ORIENTATIONAL MOBILITY   In the previous chapter, we studied the anisotropy decay of the anion-bound water molecules. The specificity was obtained by the difference in vibrational lifetime. We could not look in detail to the dynamics of the other water molecules, since all pump–probe responses were dominated by the response of the anion-bound molecules. In the case of ClO$_4^-$, the absorption frequencies are well separated, which enables the study of the other molecules, i.e. all molecules with the exception of the anion-bound ones. These include pure bulk molecules and water molecules in the cations' solvation shells, that may show some redshift (stronger hydrogen bonds) in the absorption spectrum (chapter 4). It is known that the stiffness of the hydrogen bonds affects the orientational-correlation time.[90] Since we are interested in the hydrogen-bond network outside the anion's solvation shell, we performed measurements of the anisotropy
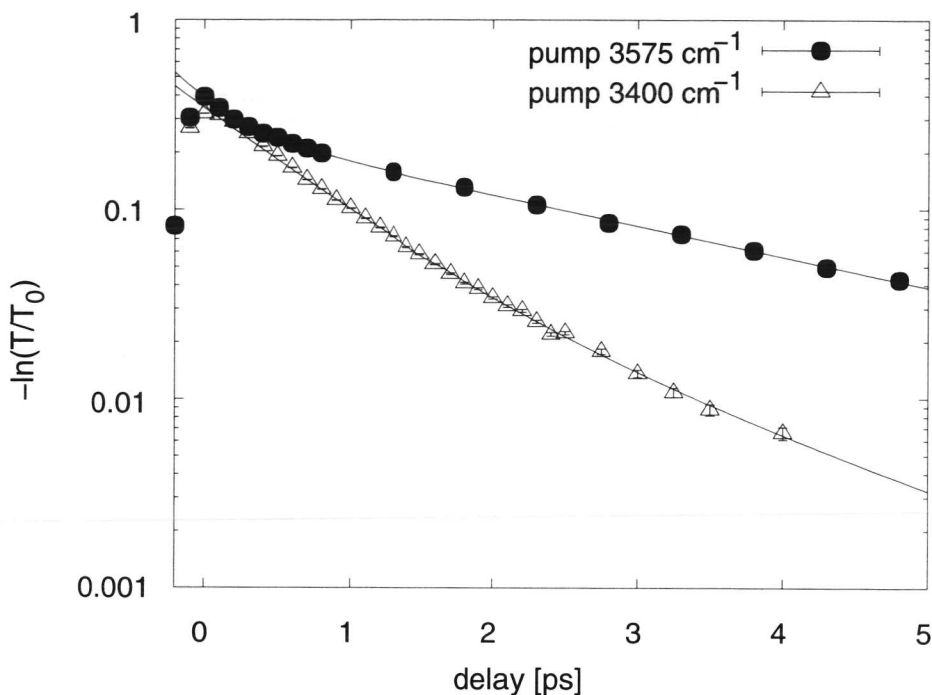
FIGURE 8.2. A logarithmic plot of the induced absorption measured as a function of time delay for a 6 M NaClO$_4$ solution for two different pump and probe frequencies. The decay has been fitted biexponentially. When the pump frequency is 3575 cm^{-1} and the probe frequency is 3325 cm^{-1}, the decay is biexponential, whereas the decay is almost monoexponential when the pump frequency is 3400 cm^{-1} and the probe frequency is 3150 cm^{-1}.

decay in several solutions known for their structure-making quality.

First, we performed two anisotropy measurements on a solution of NaClO$_4^-$ in HDO:D$_2$O. In the first, we pumped the 'water' peak at 3400 cm^{-1}, in the second, the 'anion' peak at 3575 cm^{-1}. In both experiments, the 1→2 induced absorption was probed, by tuning the probe frequency 250 cm^{-1} redshifted with respect to the pump. By pumping the different subbands, mostly O–H groups of one type are excited. However, since the water band is quite broad, it is inevitable that these O–H groups are also excited when pumping at 3575 cm^{-1}. Fortunately, the latter O–H groups have a shorter vibrational lifetime, and the ratio between excited O–H$\cdots$ClO$_4^-$ and O–H$\cdots$O groups rapidly decreases. Thus, by analyzing the anisotropy at delays larger than 2.5 ps, only O–H$\cdots$ClO$_4^-$ groups are probed. The results of the two experiments are shown in figure 8.3. The anisotropy clearly decays at different rates. For the O–H$\cdots$O groups, a decay of 3.2±0.3 ps is measured, similar to pure liquid water. For the O–H$\cdots$ClO$_4^-$ groups, a slower decay is observed, 7.6±0.3 ps. This is in qualitative agreement with the results of chapter 7. In this case, separation between O–H$\cdots$O and O–H$\cdots$ClO$_4^-$ groups has been achieved by 'spectral selection', rather than separation based on vibrational lifetime.
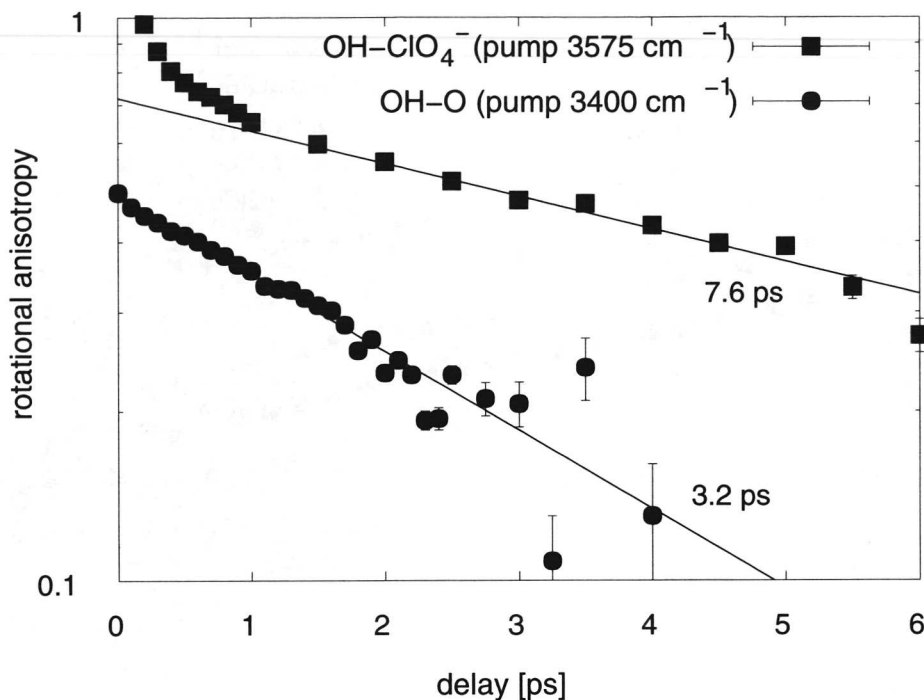
FIGURE 8.3. A logarithmic plot of the anisotropy parameter R as a function of time delay for a solution of 6 M $NaClO_4$ in $HDO:D_2O$ for two different pump and probe frequencies. When the pump frequency is 3575 cm^{-1} and the probe frequency is 3325 cm^{-1}, the anisotropy decay is much slower than if the pump frequency is 3400 cm^{-1} and the probe frequency is 3150 cm^{-1}. In the former case, initially a rapid decay is seen, which can be attributed to $O–H\cdots O$ groups. After a few picoseconds, these molecules have relaxed and the anisotropy is purely determined by the solvation shell water molecules, forming $O–H\cdots ClO_4^-$ hydrogen bonds that have a much longer orientational-correlation time. The 3575 cm^{-1} pump data have been fitted monoexponentially between 2.5 ps and 6 ps delay, the 3400 cm^{-1} pump data have been fitted monoexponentially between 0.5 ps and 3 ps delay.

In contrast to the solutions of chapter 7, we can now study the bulk $O–H\cdots O$ groups separate from the anion-bound O–H groups.

To investigate the influence of ions on the hydrogen-bond network in bulk liquid water, we determined the orientational-correlation time of bulk water molecules in aqueous solutions of $NaClO_4$, $Mg(ClO_4)_2$ and Na_2SO_4. We performed measurements of the decay of the anisotropy parameter R at different concentrations of $NaClO_4$ in which the $O–H\cdots O$ band was pumped at 3400 cm^{-1} and probed at 3150 cm^{-1}.

The measured anisotropy decay for 0 M, 0.5 M, 1 M, 3 M and 6 M $NaClO_4$ in $HDO:D_2O$ solutions is shown in figure 8.4, where R is plotted against the time delay between the pump and probe pulses. The anisotropy decay, at pump and probe frequencies of 3400 cm^{-1} and 3150 cm^{-1} respectively, turns out to be independent of the $NaClO_4$
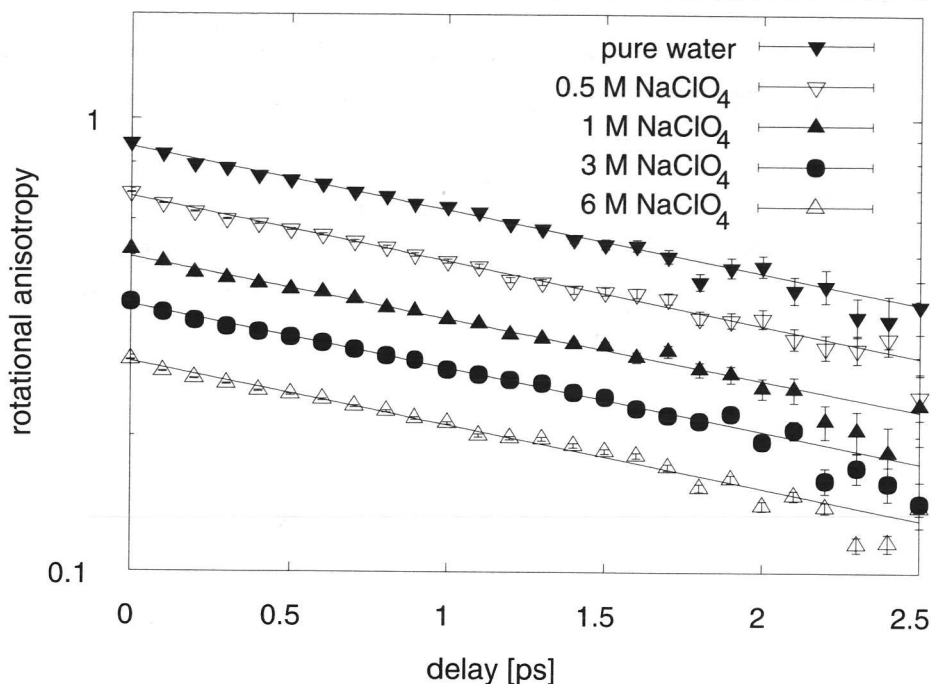
FIGURE 8.4. A logarithmic plot of the anisotropy parameter R measured as a function of delay for different concentrations of $NaClO_4$. The pump frequency was tuned to 3400 cm^{-1}, the probe to 3150 cm^{-1}. The data have been fitted monoexponentially and shifted vertically with respect to each other for clarity. As can be seen, the orientational correlation time is the same for each concentration.

concentration, which means that the orientational correlation time τ_{or} for the bulk water molecules is independent of the salt concentration, its value is 3.4±0.1 ps.

Na^+ is known as a very weak structure maker and ClO_4^- is known as a weak structure breaker,[39,80] so maybe there *is* an effect of ions on the hydrogen-bond network of bulk water but for $NaClO_4$ the effect is just too small to have a measurable effect on the orientational-correlation time. Therefore, we also performed measurements on solutions that contained supposed strong structure makers, like Mg^{2+} and SO_4^{2-}. Thus, anisotropy measurements were performed for bulk water molecules in $Mg(ClO_4)_2$ and Na_2SO_4 solutions. The Jones–Dole B coefficients at room temperature of $Mg(ClO_4)_2$ and Na_2SO_4 solutions are 0.3 and 0.4 respectively.[80] With these values, the viscosity of 1 M $Mg(ClO_4)_2$ is about 30 % higher than the viscosity of pure water and the viscosity of 1 M Na_2SO_4 is even about 40 % higher.[1] Because the O–H$\cdots$O and O–H$\cdots ClO_4^-$ bands are also well separated in the $Mg(ClO_4)_2$ solution (see figure 8.1), the O–H$\cdots$O groups can be studied selectively in a $Mg(ClO_4)_2$ solution as well. In the case of Na_2SO_4, the anion-bonded O–H groups absorb near 3400 cm^{-1}, like the bulk water molecules, but at low concentrations, the contribution of the water-bonded O–H groups will be much larger. Therefore, even for a solution of Na_2SO_4, mainly the water-bonded O–H$\cdots$O groups are probed as
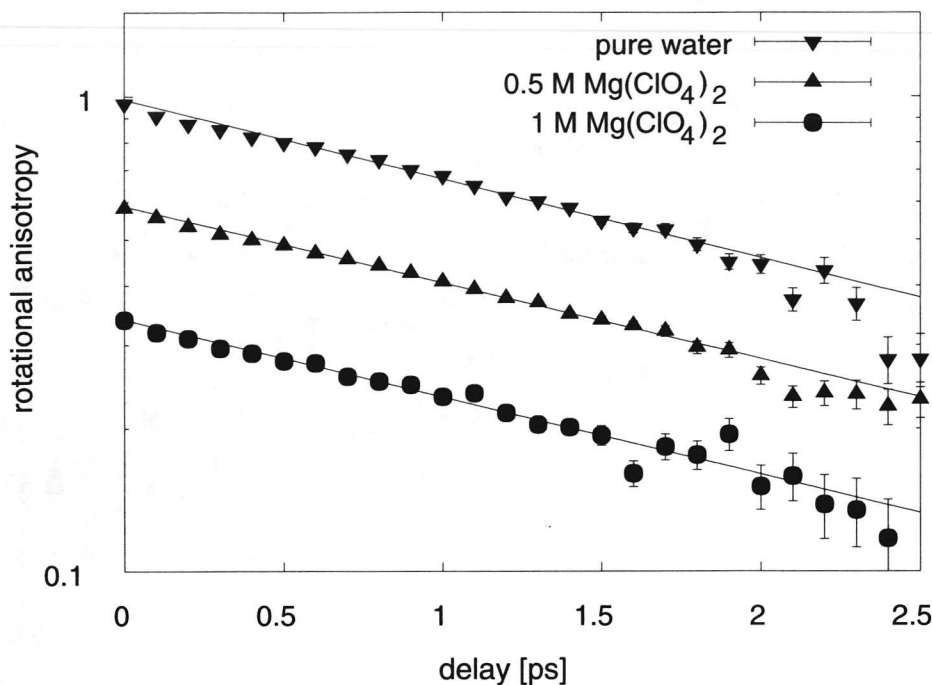
FIGURE 8.5. A logarithmic plot of the anisotropy parameter R as a function of time delay for different concentrations of $Mg(ClO_4)_2$. Again, the data have been fitted monoexponentially and are shifted vertically with respect to each other for clarity.

long as the salt concentration is sufficiently low. The results for $Mg(ClO_4)_2$ are shown in figure 8.5, for Na_2SO_4 in figure 8.6. Again, the decay of R turns out to be independent of the salt concentration (at least for concentrations up to 1 M): the orientational-correlation time is 3.2±0.2 ps for each solution. The difference with the $NaClO_4$ solutions of figure 8.4 is within the experimental error.

Now it is still possible that some of the water molecules can rotate freely in some directions while being hindered in others. This would lead to relaxation of R to some permanent or longer-living end level. Unfortunately, the anisotropy decay of the bulk O–H···O oscillators can only be followed during a few picoseconds, because of the short relaxation time of the O–H stretch vibration. To investigate the possible presence of such a small slow component in the anisotropy, we also probed the O–D stretch vibration of salt solutions using $HDO:H_2O$ as solvent. The vibrational-relaxation time of the O–D stretch vibration in $HDO:H_2O$ is 1.7±0.3 ps,[67] which is more than twice as long as the vibrational-relaxation time of the O–H stretch vibration. Consequently, the anisotropy decay can be followed twice as long (over 5 ps instead of 2.5 ps). We performed measurements on the anisotropy decay in solutions of different concentrations (1 M and 3 M) of $Mg(ClO_4)_2$ in $HDO:H_2O$. The O–D stretch vibration is pumped and probed at
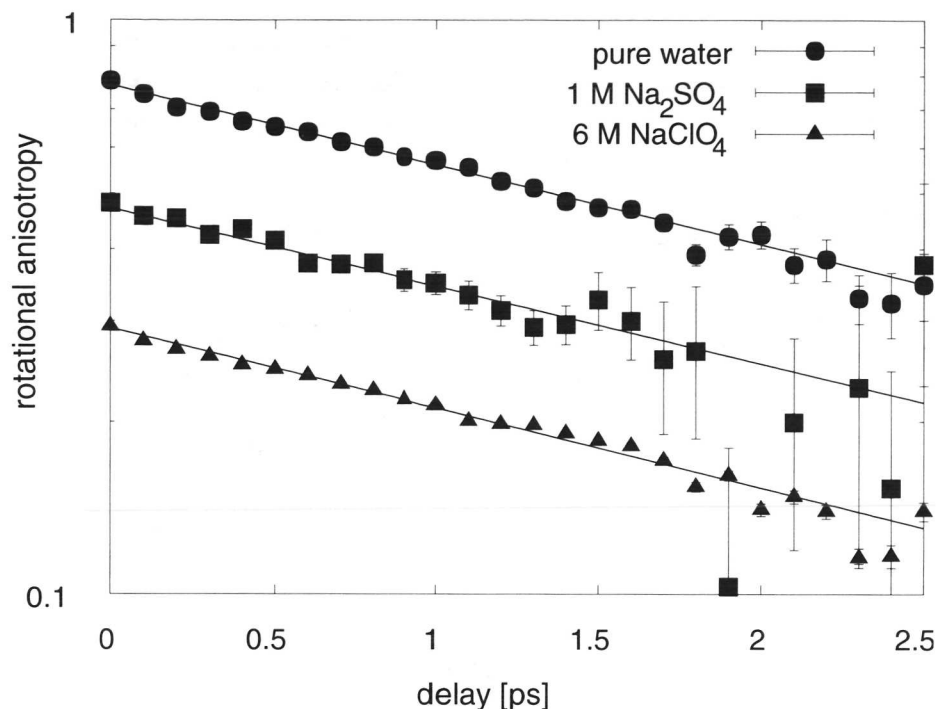
FIGURE 8.6. A logarithmic plot of the anisotropy parameter R as a function of time delay for pure water, for 1 M Na_2SO_4 and for 6 M $NaClO_4$. The data have been fitted monoexponentially and are shifted vertically with respect to each other for clarity.

2500 cm^{-1} (0→1 transition).[*] The results are shown in figure 8.7. Again, no concentration dependence is found, which shows once more that the addition of $Mg(ClO_4)_2$ has a negligible effect on the orientational dynamics of bulk water molecules. For each solution, the orientational-correlation time of the bulk water molecules is 2.5±0.1 ps. This orientational-correlation time agrees well with the orientational-correlation time of 2.6 ps found by Nienhuys et al.[90] for pure HDO:D_2O, with NMR measurements,[49,115] and with terahertz spectroscopy.[60,111] The difference between τ_{or} of 3.4 ps of figures 8.4, 8.5, and 8.6 and the τ_{or} of 2.5 ps of figure 8.7 can be understood in the following way. When the 0→1 transition is probed as in figure 8.7, the signal is caused partly by a depletion of the ground state ('hole contribution') and partly by a population of the first excited state ('particle contribution'). The hydrogen bond in the first excited state of the O–H (O–D) stretch vibration is stronger than in the vibrational ground state.[134] Hence, when probing the 0→1 transition relatively weakly hydrogen-bonded O–H (O–D) groups in the ground state as well as relatively strongly hydrogen-bonded O–H (O–D) groups in the

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[*]To generate these pulses, the KTP crystal was exchanged for a LiNbO$_3$ crystal in figure 2.3.5, and all other crystals were adjusted to a slightly different frequency. Since LiNbO$_3$ starts to absorb below 2500 cm^{-1}, we could not make the laser pulses necessary to probe the 1→2 transition without rather drastically changing the pulse-generation setup.
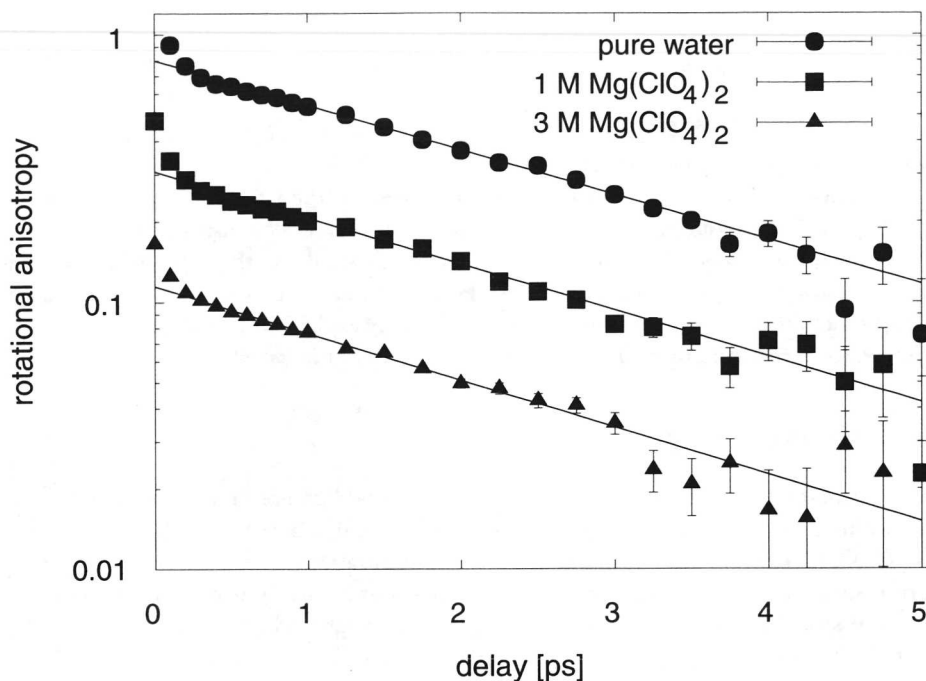
FIGURE 8.7. A logarithmic plot of the anisotropy parameter R as a function of time delay for different concentrations of $Mg(ClO_4)_2$ dissolved in H_2O with 4 % HDO. The data have been fitted with a mono-exponential function and are shifted vertically with respect to each other for clarity.

excited state contribute to the observed (orientational) dynamics. However, if the $1 \rightarrow 2$ transition is probed as in figures 8.4, 8.5, and 8.6, the signal is caused by a population of the first excited state only, and therefore only stronger hydrogen-bonded O–H (O–D) groups contribute to the measured dynamics.

8.4   DISCUSSION

The measurements of the orientational mobility of water molecules in salt solutions oppose the idea of enhanced or weakened hydrogen bonds around ions, outside their first solvation shell: no structure-making or structure-breaking effect of ions on the hydrogen-bond structure could be found, even for ions that are particularly known for their supposed structure-making capacity. With respect to reorientation rate, i.e. average hydrogen-bond strength, there are only two types of water molecules: anion-bonded or water-bonded. This result indicates that an aqueous salt solution should not be viewed as a homogeneous liquid with a modified hydrogen-bond structure, but rather as a colloidal suspension of inert particles (hard spheres) in pure liquid water, that consist of the ion and its first hydration shell. The viscosity at low concentration can then be described by the Einstein equation:[50]

$$\frac{\eta}{\eta_0} \approx 1 + 2.5\phi,$$

with ϕ the volume fraction of the spheres.

It follows from this equation that a 30 % increase of the viscosity, as observed for a 1 M $Mg(ClO_4)_2$ solution, can be obtained with a solution of 1 M suspended spheres that have a radius of about 3.6 Å. This radius is surprisingly similar to the radius of an ion and its first solvation shell of water molecules. Hence, the increase in viscosity upon adding small spherical ions to liquid water can indeed be fully explained from the rigid nature of the solvation structure formed by the ion and its first solvation shell.

8.5 CONCLUSIONS

The orientational-correlation time was measured for O–H groups of bulk water molecules in various ionic solutions [$NaClO_4$, $Mg(ClO_4)_2$ and Na_2SO_4 in HDO:D_2O and $Mg(ClO_4)_2$ in HDO:H_2O] at different salt concentrations with femtosecond pump–probe spectroscopy. It is found that the addition of ions has no influence on the rotational dynamics of the bulk water molecules, even at very high concentrations (up to 6 M). For all the ionic solutions the orientational-correlation time of the bulk water molecule (measured at the 1→2 transition) is 3.4±0.2 ps. Only for the O–H groups in the first solvation shell of the ClO_4^- ion, a different orientational-correlation time was found, its value is 7.6±0.3 ps. Therefore, we conclude that ions do not enhance or break the hydrogen-bond network outside their direct vicinity (probably only their first solvation shell). As a result, there is no long-range structure-making effect or structure-breaking effect. The origin of the strong influence on the viscosity of water is not the ability of the ions to enhance the bulk hydrogen-bond network, but rather the rigidity of the first solvation shell, that increases the effective radius of the dissolved ion.