The combined effect of cations and anions on the dynamics of water

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We studied the orientational relaxation of the OD-stretch vibration of HDO molecules in concentrated solutions of alkali-halide salts (NaCl, NaI, CsCl and KI) in isotopically diluted water (4% D_2O in H_2O), using polarization-resolved femtosecond infrared pump–probe spectroscopy (fs-IR). We were able to distinguish the orientational dynamics of the water molecules solvating the halide ions from the dynamics of the bulk water and the water solvating the cations. We found that the reorientation of the halide-bound molecules shows two strongly different components (2.0 ± 0.3 ps and 9 ± 1 ps), related to a wiggling motion of the OD group hydrogen-bonded to the anion, and rotational diffusion of the molecule over the charged anion surface, respectively. The relative amplitudes of the two components are dependent on the nature of both the anion and cation, and on the concentration. These results show that cations can have a profound effect on the solvation shell dynamics of their counter-ions.

I. Introduction

Aqueous solutions have been studied extensively over the past century due to their relevance to many processes.[1–3] It is therefore surprising that much is still unknown about the exact nature of ion hydration and the effect of ions on aqueous systems in general. One of the important disputes concerns the spatial extent over which ions affect the water around them.[4] Over a century ago, Hofmeister arranged a number of salts according to their ability to denature proteins, resulting in the so-called Hofmeister series.[5] In an attempt to explain this heuristic ordering of ions on a molecular level, the concepts of structure-making and structure-breaking were introduced.[2] It was thought that different ions either strengthen or weaken the hydrogen-bond network of water over long distances and that this effect would explain the observed (de)naturation effects.

In the past decade, more evidence was found that the effect of ions on water does not extend much further than their first hydration shell.[6–10] For most of these studies, the effect of the anion and cation on the dynamics of water was considered to be additive.[6,11] Recently it was shown that this assumption does not hold for strongly hydrated ions like Mg^{2+} and SO_4^{2-}[12,13]: a solution of $MgSO_4$ shows a very large fraction of water molecules with slower than normal dynamics, corresponding to $\sim 18 H_2O$ molecules per combination of Mg^{2+} and SO_4^{2-}. The slow water molecules in a solution of $MgSO_4$ are probably contained in a cooperatively locked hydrogen-bonded water network in between the Mg^{2+} and SO_4^{2-} ions (solvent-separated ion pair). This explains why the fraction of

slow water in this solution is much larger than the added fractions observed for solutions of Mg^{2+} and SO_4^{2-} in combination with weakly hydrating counter-ions: in the case of $Mg(ClO_4)_2$ and Cs_2SO_4 the effect of the ions on the dynamics of water was found to be limited to the first hydration shell.

In this work we study in detail the behavior of water molecules in different anionic hydration shells. We measure the reorientation of the OD-stretch vibration of HDO molecules in isotopically diluted water using polarization-resolved femtosecond infrared pump–probe spectroscopy. We studied solutions of NaCl, NaI, CsCl and KI, chosen for their high solubility and coverage of the moderately strong to weakly hydrating alkali and halide ion series.[2] We can distinguish the orientational dynamics of water solvating the halide ions from the other water molecules, thanks to the difference in the vibrational lifetime and spectral response between the anion hydration shell on one hand, and the bulk and the water molecules around the cation on the other hand.

II. Experiment

A. fs-IR pump–probe

The dynamics of water molecules are studied by monitoring the reorientation of the deuteroxyl group of HDO in isotopically diluted water (4% D_2O in H_2O) with polarization-resolved femtosecond infrared (fs-IR) pump–probe spectroscopy. To generate laser pulses of 4 μm that are resonant with the OD-stretch vibration in HDO we use a Ti:Sapphire laser (Hurricane, Spectra-Physics) that generates 800 nm pulses with a duration of 110 fs and an energy of 0.9 mJ at a repetition rate of 1 kHz. 60% of the light is used to pump an optical parametric amplifier (OPA, Spectra-Physics) for parametric down conversion to 2000 nm in a BBO crystal.

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After doubling in a second BBO crystal, the 1000 nm light is converted to 4 μm (FWHM $\sim$120 cm^{-1}) in a difference frequency mixing stage pumped by the remaining 40% output of the Ti:Sapphire laser. Most of this light (5 μJ) is used as a pump to promote the OD-stretch vibration of a subset of the HDO molecules to its first excited state. Since the transition dipole of the excited OD oscillators will be mainly parallel to the pump pulse, this excitation generates an anisotropic excited state population in the sample. After a delay-time t we probe the sample by a much lower intensity pulse (200 nJ) with its polarization either parallel or perpendicular to the pump polarization. After subtraction of the unpumped absorption spectra we obtain the delay-time dependent pump-induced transient absorption spectrum for both polarization directions, $\Delta\alpha_{\parallel}(\omega, t)$ and $\Delta\alpha_{\perp}(\omega, t)$.

The parallel and perpendicular signals contain information about the lifetime of the vibrational excitation and the orientation dynamics of the transition dipole along the OD axis. The vibrational lifetime is obtained from the isotropic signal, given by the weighted sum of the parallel and perpendicular signals,

$$\Delta\alpha_{\mathrm{iso}}(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) + 2\Delta\alpha_{\perp}(\omega, t)}{3} \qquad (1)$$

The reorientation dynamics is expressed in the anisotropy parameter R, which is essentially a normalized difference of the two signals,

$$R(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) - \Delta\alpha_{\perp}(\omega, t)}{\Delta\alpha_{\parallel}(\omega, t) + 2\Delta\alpha_{\perp}(\omega, t)} \qquad (2)$$

The denominator divides out the decay of $\Delta\alpha_{\parallel}(\omega, t)$ and $\Delta\alpha_{\perp}(\omega, t)$ due to the vibrational relaxation of the excitation. This isolates the pure reorientation dynamics.

The transient spectra measured on neat HDO:H$_2$O contain three contributions. First, the pump induced decreased population of HDO molecules in the ground state of the OD-stretch vibrational mode leads to a reduced absorption at the $\nu = 0 \rightarrow 1$ transition frequency of this mode, which is denoted as the ground state bleach. Second, stimulated emission out of the $\nu = 1$ state contributes to the absorption decrease at the $\nu = 0 \rightarrow 1$ transition frequency. Finally, the absorption of the probe pulse due to the $\nu = 1 \rightarrow 2$ excitation of pump-excited modes leads to an induced absorption. The spectrum associated with this latter transition is red-shifted by $\sim$180 cm^{-1} due to the anharmonicity of the OD stretch vibration. With increasing pump–probe delay, an increasing number of excited HDO molecules have relaxed to their ground state, causing all three contributions to the transient spectra to decrease in amplitude.

After the vibrational energy is equilibrated over the low-frequency modes of the solution, the sample temperature has increased, leading to a somewhat different absorption spectrum of the ground state. The difference with the absorption spectrum before the pump excitation defines the thermal-difference spectrum. This thermal difference spectrum has to be subtracted from the overall transient spectral response to determine the anisotropy dynamics of the OD vibrational excitation. To determine the delay-time dependence of the ingrowing thermal difference spectrum, we fit a kinetic model to the isotropic data. The fit gives us the population dynamics and associated spectra for every state in the model. For neat 4% D$_2$O in H$_2$O it was found that the rise of the thermal difference spectrum was somewhat delayed with respect to the vibrational relaxation of the excited OD stretch vibration. This delayed response indicates the presence of an intermediate state in the relaxation. This intermediate state was found to have no spectral signature,[14] which means that its absorption spectrum is identical to that of the OD stretch before the excitation by the pump. Therefore, the intermediate state likely does not correspond to a transient excitation of the bending mode, as such an excitation would induce an anharmonic frequency shift of the OD stretch spectrum. The zero transient spectrum of the intermediate state indicates that this state represents the delayed adaptation of the coordinates of the low-energy degrees of freedom (hydrogen-bond bend and stretch) to the higher energy content resulting from the relaxation of the OD stretch vibration. The relaxation of the OD stretch vibration leads to a rapid increase of the energy content of the lower-energy degrees of freedom, and these coordinates need some time to evolve to the new equilibrium positions corresponding to their higher energy content. As a result, the observed thermal effect on the OD stretch absorption spectrum is somewhat delayed with respect to the T_1 relaxation of this vibration. After correction for the ingrowing thermal difference spectrum, eqn (2) can be used to construct the delay-time dependent anisotropy of the OD stretch excitation.[14]

B. Samples

All samples were prepared with 4% D$_2$O in H$_2$O as the solvent. NaCl, NaI, CsCl and KI salts were purchased from Sigma Aldrich and were all of $\geq$ 99.5% purity. D$_2$O was also purchased from Sigma Aldrich and has a purity of $\geq$ 99.99%. The sample cell consisted of two calcium fluoride windows of 4 mm thick which were pressed against each other with a teflon spacer in between. To keep the infrared transmission around 10% we used spacers of 25 μm for the low concentration samples and 50 μm for the high concentration samples. All concentrations in this paper are denoted in moles of solute per kilogram of solvent (molality).

The linear spectra of the halide salts show a blue-shift of the OD-stretch vibration that increases with the size of the anion and is independent of the cation (Fig. 1). The blueshift is caused by the fact that the OD$\cdots$A$^-$ between the OD group and the anion is weaker for larger anions due to the reduced surface charge density.[15]

III. Results

A. Isotropic results

In Fig. 2 transient spectra at different delay-times are shown for a 4 m solution of NaI. The spectrum at long delay-times is the thermal-difference spectrum resulting from the temperature rise due to the equilibrated pump-energy. It is clear that the signal on the blue side of the spectra decays much more slowly than on the red side, pointing to the presence of two excited species with different vibrational lifetimes. Previous work showed that the vibrational lifetime of OD oscillators forming OD$\cdots$A$^-$ (A$^-$ = Cl$^-$, Br$^-$, or I$^-$) hydrogen bonds is significantly longer than the vibrational lifetime of OD oscillators forming OD$\cdots$O hydrogen
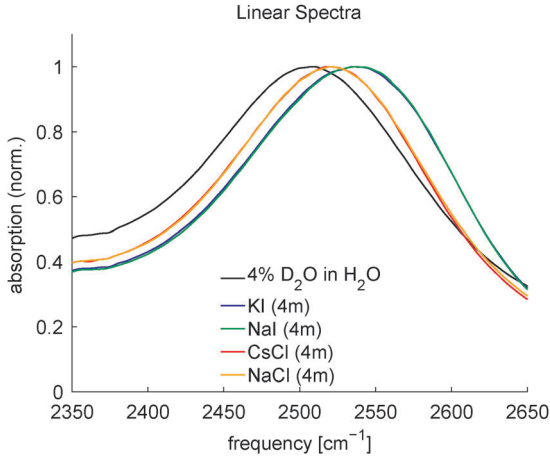
Fig. 1 Linear absorption spectra in the region of the OD-stretch vibration for concentrated solutions of the measured salts and neat 4% D_2O in H_2O. The spectra of salt solutions with the same anion are nearly identical.
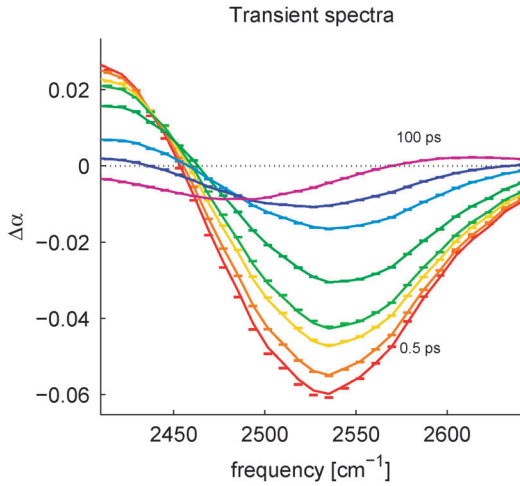

Fig. 2 Transient spectra measured for a 4 m NaI solution for delay times of 0.5, 0.7, 1.1, 1.4, 2.5, 5.1, 8.1 and 100 ps. The lines result from a fit to the kinetic model described in the text. The transient spectra of the different components and their population dynamics resulting from this fit are presented in Fig. 4.

bonds to water.[16] These OD$\cdots$A$^-$ oscillators absorb in the blue wing of the spectrum and their vibrational relaxation is modeled by adding a second excited state to the kinetic model for neat HDO : H_2O. The two excited states will exchange, since the HDO molecules bound to an anion can rotate out of the anion-hydration shell and become OD$\cdots$O hydrogen-bonded and *vice versa*. The exchange time constant τ_{AO} for this process is fixed to the literature value of 9 ps that was recently found for NaClO$_4$ solutions.[19] We use this value since the exchange rates for chloride and iodide are very difficult to obtain experimentally due to the smaller blue-shift of OD$\cdots$Cl$^-$ and OD$\cdots$I$^-$ in comparison to OD$\cdots$ClO$_4^-$. The back-process time constant τ_{OA} is obtained by using the fact that the anion hydration number should be conserved in the exchange processes. The complete kinetic model is schematically displayed in Fig. 3. In the analysis we neglect the effects of spectral diffusion within the OD$\cdots$O and OD$\cdots$A$^-$ bands. This is a good approximation as we use relatively broad-band excitation
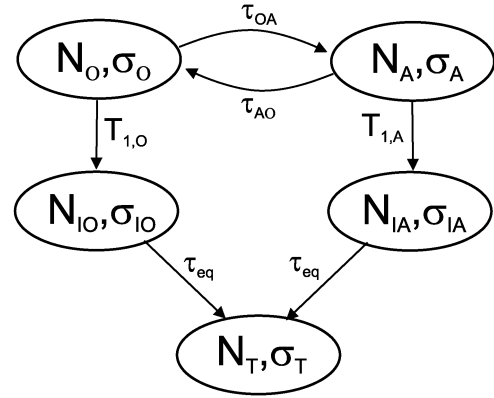

Fig. 3 Schematic representation of the kinetic model used for fitting the vibrational decay processes. The populations N_O and N_A represent the excitation of the OD$\cdots$O and OD$\cdots$A$^-$ oscillators, respectively. These populations decay with respective time constants $T_{1,O}$ and $T_{1,A}$, and exchange with time constants τ_{OA} and τ_{AO}. The transient spectra σ_O and σ_A comprise the $1 \rightarrow 2$ excited-state absorption, the $1 \rightarrow 0$ stimulated emission and the bleaching of the $0 \rightarrow 1$ ground-state absorption. The presence of the latter contribution in σ_O and σ_A implies that the exchange dynamics of the ground states of the OD$\cdots$O and OD$\cdots$A$^-$ oscillators are contained in the exchange of N_O and N_A. The transient spectra σ_{IO} and σ_{IA} of the intermediate states are equal to zero at all frequencies, which means that the absorption spectrum of the intermediate states is the same as that of the ground states of the OD$\cdots$O and OD$\cdots$A$^-$ oscillators. The shape of the transient spectrum σ_T of the final heated ground state is assumed to be independent of the type of oscillator that was originally excited.

pulses (FWHM ~ 120 cm^{-1}), and because we only model the dynamics for delays ≥ 0.5 ps, for which the spectral diffusion is nearly complete.[17,18]

Fig. 4A shows the spectra that result from a fit of the kinetic model to the data. The spectrum around 2500 cm^{-1} represents excited OD groups hydrogen-bonded to other water molecules (OD$\cdots$O) and the spectrum around 2550 cm^{-1} represents excited OD groups solvating the anion (OD$\cdots$I$^-$). Neither of the two spectral shapes changes significantly when the concentration or the nature of the cation is changed. The transient spectrum of the OD$\cdots$I$^-$ absorption component shows a clear $\nu = 1 \rightarrow 2$ excited state absorption at frequencies <2490 cm^{-1}. This excited state absorption is blue-shifted with respect to the $\nu = 1 \rightarrow 2$ absorption of the OD$\cdots$O component (that is outside the probed spectral window), because the $\nu = 0 \rightarrow 1$ fundamental transition of the OD$\cdots$I$^-$ is blueshifted, and because the anharmonic shift between $\nu = 0 \rightarrow 1$ and $\nu = 1 \rightarrow 2$ is somewhat smaller for OD$\cdots$I$^-$ than for OD$\cdots$O.

For the chloride salt solutions the anion-bound spectra show a smaller blue-shift compared to the iodide salt solutions. This is in line with the linear absorption spectra (Fig. 1). The population dynamics resulting from the fit to the data obtained for a 4 m NaI solution (Fig. 2) are shown in Fig. 4B, from which it is clear that the OD$\cdots$I$^-$ spectrum decays much more slowly than the OD$\cdots$O spectrum.

B. Anisotropy

To obtain the correct anisotropy dynamics, the anisotropy decays for both OD$\cdots$O and OD$\cdots$A$^-$ species should be
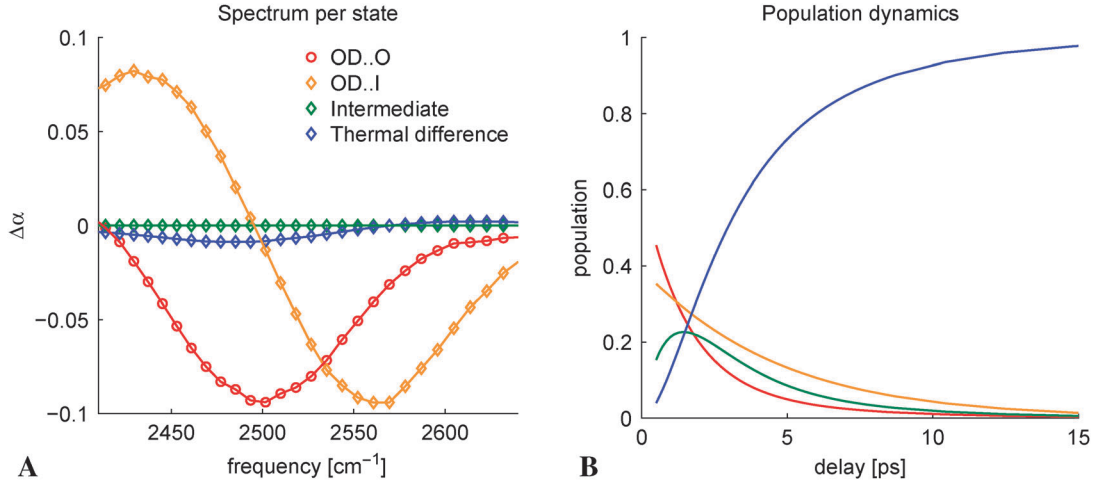
Fig. 4 (A) Spectral components obtained from fitting the spectra measured for a 4 m NaI solution presented in Fig. 2. (B) Time dependence of the normalized populations corresponding to the spectral components of figure A. At any given delay-time the fitted total transient spectrum is the weighted sum of the spectra shown in A, the weight factors given by the population values in B.

resolved separately, which is possible due to the spectral separation of their response. We therefore consider the difference signal D:

$$D(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) - \Delta\alpha_{\perp}(\omega, t)}{3} = \sum_{i=1}^{n} R_i(t) N_i(t) \sigma_i(\omega) \quad (3)$$

where R_i is the anisotropy decay, N_i the population dynamics and σ_i the associated transient spectrum of the ith species or state. The associated state spectra and population dynamics were already obtained from fitting the isotropic data and we thus can resolve from $D(\omega, t)$ the anisotropy dynamics of the different states. This formalism implicitly assumes that the anisotropy decay within the absorption band of a certain species does not show any significant frequency dependence, as is the case for neat 4% D_2O in H_2O.[14] Since the intermediate state does not have an associated transient spectrum and the final heated ground state has no anisotropy, only the excited states of the OD$\cdots$O and OD$\cdots$A$^-$ species contribute to $D(\omega, t)$ and thus n equals 2. To resolve the OD$\cdots$O anisotropy R_O and OD$\cdots$A$^-$ anisotropy

R_A separately, we decompose the difference spectrum D at every delay-time t in the two spectra σ_O and σ_A obtained from the isotropic fit. The resulting time-dependent amplitudes are products of N_i and R_i and the latter is obtained through division by the fitted isotropic population dynamics N_i. As implied by the kinetic model, R_A now only represents the anisotropy of water molecules that are hydrogen bonded to the anion at time t, *i.e.* the water molecules that have kept their hydrogen bond with the anion intact or that have rotated from the bulk into the anion solvation shell. In Fig. 5 a typical example of a decomposition for a 4 m NaI solution is shown. The reorientation of the OD$\cdots$O component occurs with a time constant of $\sim$2.6 ps, a behavior identical to that found for neat HDO:H_2O.[14] The OD$\cdots$I$^-$ anisotropy decay is clearly not mono-exponential: after a rapid decay, faster than in bulk water, the anisotropy R_A decays *via* a much slower component.

Fig. 6 shows a collection of OD$\cdots$A$^-$ anisotropy curves from measurements of 4 m solutions of four different salts, all obtained with the pump-spectrum centered at around 2500 cm^{-1}. The curves show a strong non-mono-exponential decay with a fast and slow component. The relative amplitudes of the two decay processes change when varying the nature of the ions: larger anions or cations induce a larger fast decay component of the anisotropy. Fig. 7 presents the OD$\cdots$I$^-$ anisotropy for different concentrations of NaI and KI. The amplitude of the slow process increases with concentration for NaI, while the KI solutions show no change up to 6 m.

From the decomposition we also obtain the OD$\cdots$O anisotropy curves, which are shown for NaCl and NaI solutions in Fig. 8. For low concentrations the curves have a mono-exponential character with a time constant that resembles that of neat HDO:H_2O. For the more concentrated solutions the reorientation slows somewhat down, the onset of this slowing down occurring at a higher concentration for NaI than for NaCl. In contrast, the OD$\cdots$O anisotropy decays for the KI and CsCl solutions behave like neat HDO:H_2O up to the highest concentration measured (data not shown).

The data shown so far were obtained with the pump–probe spectrum centered at the OD$\cdots$O resonance at 2500 cm^{-1}.
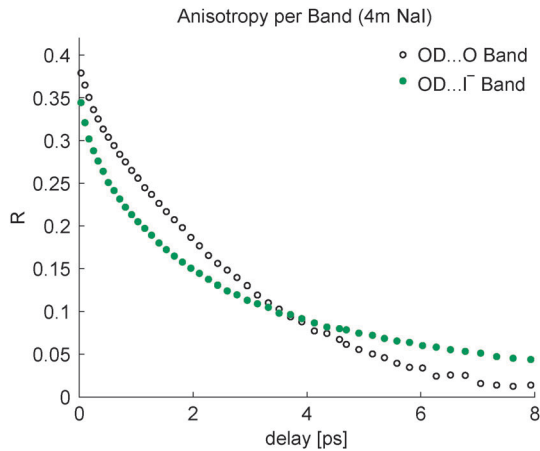

Fig. 5 Anisotropy dynamics of the OD$\cdots$O spectral component (open circles) and the OD$\cdots$I$^-$ spectral component (solid circles) resulting from the analysis of the data measured for a 4 m NaI solution.
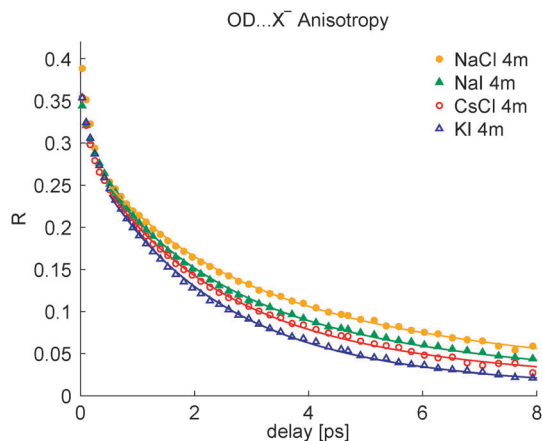
Fig. 6 Orientational dynamics of anion-bound water of four different 4 m salt solutions. All curves show a fast and slow decay component, of which the amplitudes are dependent on the nature of both the anion and the cation.

Since the pump spectrum has a bandwidth slightly smaller than the absorption band at hand, one may wonder what effect different pump frequencies have on the results of this analysis. To further investigate the nature of the $OD\cdots I^-$ component we therefore shift the pump–probe spectrum to be centered around 2535 and 2570 cm^{-1} to have a better overlap with the $OD\cdots I^-$ resonance for the iodide salt solutions. The resulting decomposed anion-bound anisotropy decays of a 4 m NaI solution are presented in Fig. 9A, showing a smaller initial decay when the pump has a better overlap with the iodide band.

The differences depending on the center frequency of the pump spectrum can be further examined by repeating this experiment for aqueous $NaClO_4$ (Fig. 9B). A decomposition of the anisotropy is, for this system, not needed due to the large frequency shift of $OD\cdots ClO_4^-$ (~ 140 cm^{-1}), making it ideal for studying the effect of the pump frequency on the anion-bound anisotropy. The anisotropy probed at 2620 cm^{-1} shows a larger fast decay component with the pump spectrum centered around 2560 cm^{-1} than with the pump spectrum centered around the probed frequency of 2620 cm^{-1}. A similar effect is observed when the anisotropy decay at 2500 cm^{-1} is

compared for pump frequencies around 2500 cm^{-1} and 2560 cm^{-1}. For the latter pump frequency the anisotropy decay shows a larger faster component than for the 2500 cm^{-1} pumped and probed case.

IV. Discussion

In contrast to previous femtosecond measurements on water reorientation in salt solutions, we resolved the dynamics of $OD\cdots O$ and $OD\cdots A^-$ groups separately. The $OD\cdots I^-$ curve shown in Fig. 5 therefore represents the orientation dynamics of water bound to iodide *only*. The features in the first 200 fs lie within the cross correlate of the pump and probe pulse and the effects of spectral diffusion are not negligible. Nonetheless, it is clear that an extremely rapid decay makes the anisotropy drop to about 75% of its theoretical maximum of 0.4, likely due to fast librational motions.[20] The behavior after 0.5 ps has a non-mono-exponential character with a fast decay component and a slower component at later delay times. In the following, when mentioning the fast process we refer to the fast decay of the bi-exponential behavior after 0.5 ps, not the quick drop within the first 200 fs. We will first discuss the nature of the $OD\cdots I^-$ anisotropy decay with the help of the results from different pump frequencies, after which we view it in a bigger picture including the results at different concentrations from all measured salts. Eventually we will discuss the $OD\cdots O$ anisotropy decays and combine the results.

A. Role of exchange

To model the vibrational relaxation we used a kinetic model that incorporates exchange events between water molecules in the anion hydration shell and water molecules hydrogen-bonded to other water molecules. Exchange events are thought to occur with a time constant between 5 and 20 ps, depending on the anion.[19,23–26] The way in which exchange affects the anisotropy can be understood as follows. When an OD group rotates into the solvation shell of the anion, the event involves a large angular jump, causing it to lose its directionality almost completely.[21,22] The vibration remains excited, though, and will contribute to the blue-shifted $OD\cdots A^-$ component of the transient spectrum and hence to the decay of the $OD\cdots A^-$
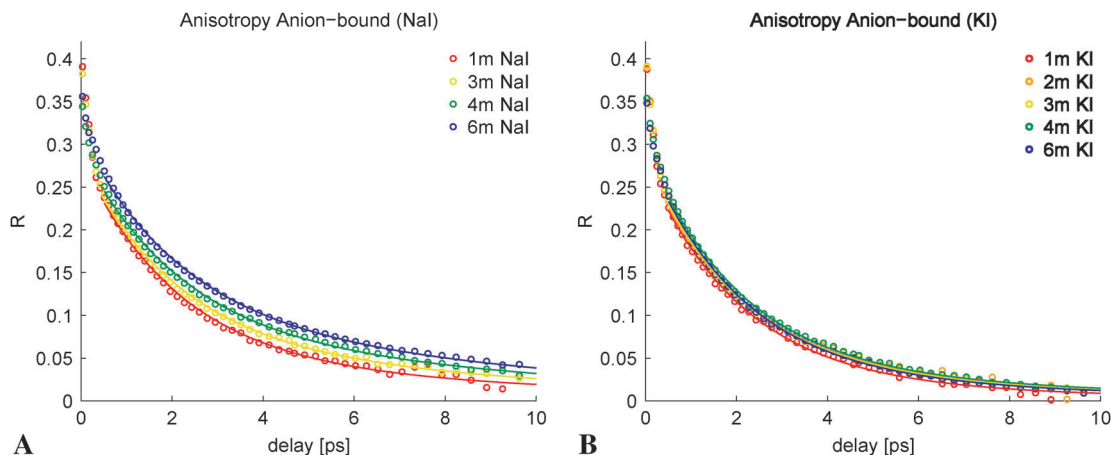

Fig. 7 Anion-bound anisotropy decays for different concentrations of NaI (A) and KI (B) solutions, measured with a pump pulse centered at 2500 cm^{-1}. The anisotropy dynamics of the OD groups hydrogen-bonded to the iodide anion show a clear dependence on the nature of the cation.
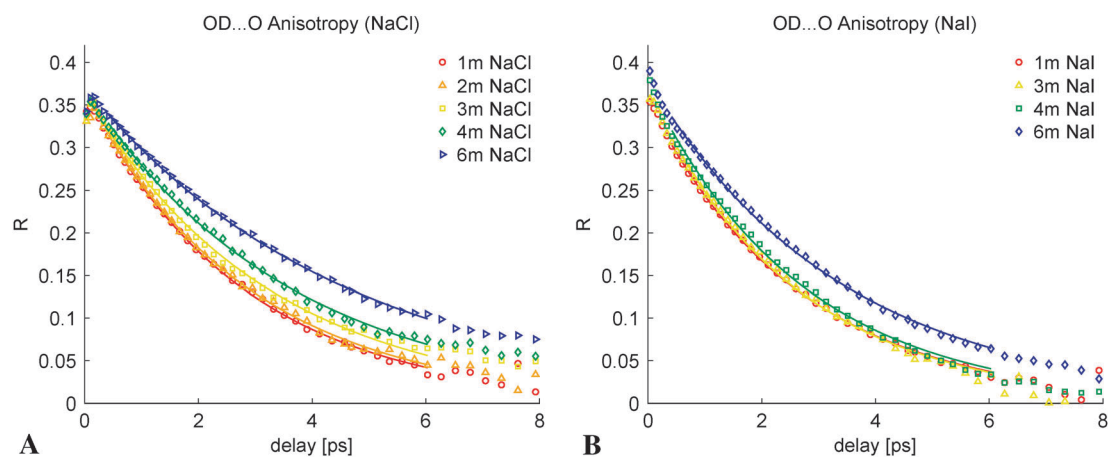
Fig. 8 OD$\cdots$O anisotropy decay for different concentrations of NaCl (A) and NaI (B) solutions. The reorientation becomes slower for more concentrated solutions, in the case of NaI the slowing down is much weaker and occurs at higher concentrations.
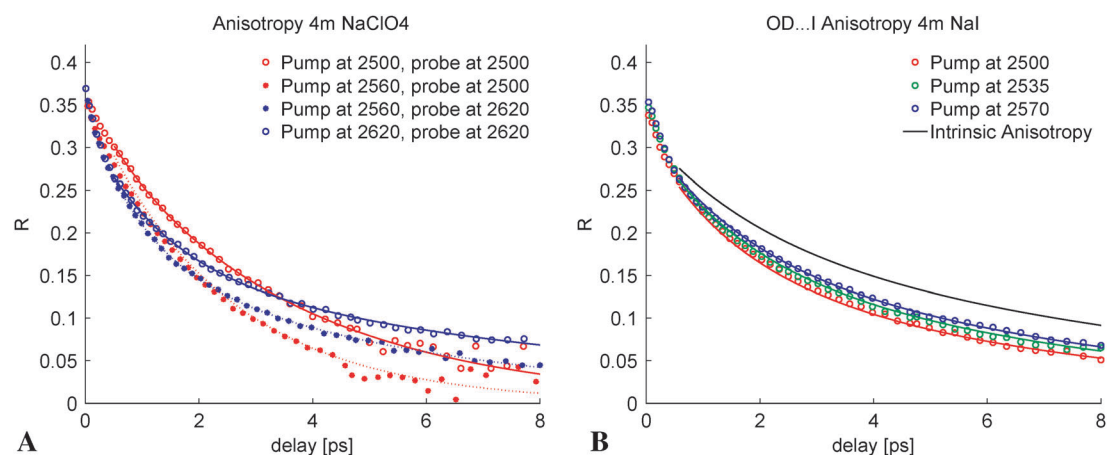

Fig. 9 (A) The total anisotropy decay of a 4 m NaClO$_4$ solution measured at different pump and probe frequencies. If the pump and probe frequencies are not the same, the anisotropy decays faster due to the contribution of exchange events between the bulk and the anion hydration shell. (B) Anisotropy decay of the anion-bound water for a solution of 4 m NaI measured with different pump frequencies. The lines going through the points are obtained from a fit in which the exchange between the bulk and the I$^-$ hydration shell is included. The solid line above the points represents the intrinsic anisotropy, *i.e.* the anisotropy dynamics of the OD$\cdots$I$^-$ groups if there were no exchange events.

anisotropy. The results for NaClO$_4$ presented in Fig. 9A show the effect of exchange very clearly. Here the two bands are well separated, allowing for excitation of almost exclusively OD$\cdots$ClO$_4^-$ or OD$\cdots$O oscillators. In case the pump spectrum is centered at around 2560 cm^{-1}, oscillators in both bands are excited. The exchange events then cause the anisotropy probed at 2500 cm^{-1} and 2620 cm^{-1} to decay considerably faster compared to the situation where pumped at 2500 cm^{-1} and 2620 cm^{-1}, respectively.

The exchange between bulk and the anion hydration shell explains the behavior of the anisotropy decay of the anion-bound water for different pump frequencies: when the pump spectrum is centered around the OD$\cdots$O resonance at 2500 cm^{-1}, relatively more water molecules *outside* the anion hydration shell are excited compared to an experiment with a blue-shifted pump spectrum. For a pump frequency of 2500 cm^{-1}, the anisotropy of the OD$\cdots$I$^-$ band will thus show a larger contribution of originally excited OD$\cdots$O groups that rotated into the hydration shell of I$^-$. As a result, the amplitude of the fast decay is larger when the pump frequency is centered at 2500 cm^{-1} than when the pump frequency is centered at 2570 cm^{-1} (see Fig. 9B).

To fit all three anisotropy curves shown in Fig. 9B, we assume a single bi-exponential functional form for the intrinsic OD$\cdots$I$^-$ anisotropy decay and include exchange effects. From the fitted vibrational decay constants and exchange rates we obtain the population dynamics of OD oscillators that remain OD$\cdots$A$^-$ or OD$\cdots$O bonded and those that exchange. The exchanging molecules are assumed to lose their orientation completely in the event, which is a slight overestimation compared to the decrease of $\sim$75% found by Gaffney *et al.* for perchlorate solutions.[19] The resulting curves including exchange are fitted simultaneously to the curves obtained with different pump frequencies. The solid lines in Fig. 9B are the result of the fit, the black line being the intrinsic anisotropy if no exchange would occur. The single intrinsic anisotropy decay can indeed describe all three measurements, thus confirming that the differences between the data obtained with different pump frequencies can be well explained from exchange events. We performed a similar analysis for all measured salt solutions at all concentrations. The analysis yields the intrinsic anisotropy dynamics of the anion-bound water, *i.e.* the anisotropy dynamics in the absence of exchange.

B. Reorientation dynamics of water in the anion hydration shell

The intrinsic anisotropy decays show a bi-exponential behavior. We assign the slow decay component to the rotational diffusion of hydration shell water molecules on the anion surface. In this diffusion the OD···A$^-$ hydrogen bond remains intact. The fitted timescale is 9 ± 1 ps, in good agreement with the value that was found previously for the long delay-time behavior of halide bound water.[27] For the fast component we found a timescale of 2.0 ± 0.3 ps that we assign to a wiggling motion of the OD bound to the anion. Since the iodide anion is substantially larger than a water molecule, the OD···I$^-$ bond is less directional than the OD···O hydrogen-bond. The angle between the O···I$^-$ vector and the OD transition dipole moment $\vec{\mu}$ can therefore assume larger values than in bulk water, without significantly weakening this bond. The variation of this angle—while keeping the bond to the anion intact—will be influenced by the environment of the water molecule. In principle this contribution will therefore show a similar decay time as the bulk reorganisation/reorientation. However, as the wiggling within the anionic hydration shell does not necessarily require a completed bulk reorientation event, its time constant can be somewhat shorter. This mechanism was previously proposed for water solvating bromide ions in cationic micelles.[28] For small micelles the bromide concentration in the interior becomes extremely high and the total anisotropy will be dominated by the behavior of water solvating the anions. For this system, an initially rapidly decaying anisotropy was observed, assigned to the angular freedom of the OD···Br$^-$ hydrogen bond.

The relative amplitude of the fast process of the intrinsic anisotropy decay is presented for all salts in Fig. 10A. In the fits, the rate constants of the slow and the fast processes are kept fixed for all concentrations of all the salts measured. With decreasing size of the anion from I$^-$ to Cl$^-$, the amplitude of the fast process decreases. This decrease in amplitude can be explained from the fact that the smaller chloride ion allows for a more restricted angular freedom of motion than the larger iodide ion. As a result, the anisotropy of chloride-bound water shows a smaller amplitude of its fast decay component than iodide-bound water.[29,30] The amplitude of the fast component can be translated to a cone angle using the expression $f_{\text{fast}} = 1 - [^1/_2 \cos\theta_c \cdot (1 + \cos\theta_c)]^2$, where f_{fast} is the fraction of the anisotropy decay resulting from the complete diffusion of a vector within a cone with a maximum angle θ_c. When the salt concentration is increased from 1 to 6 m, the cone angle decreases for KI from ∼60° to ∼55°, for CsCl from ∼55° to ∼45°, for NaI from ∼55° to ∼35°, and for NaCl from ∼45° to ∼20°.

C. Effect of the cations

Femtosecond mid-infrared spectroscopy enables the distinction of the anisotropy dynamics of the anion-bound water molecules from that of the other water molecules. The orientational dynamics of the water molecules hydrating the cation are included in the anisotropy dynamics of the OD···O band. For all measured salt concentrations, we fitted the anisotropy dynamics of the OD···O groups to a mono-exponential

function of which the time constants are shown in Fig. 10B. The data in Fig. 10B show that for most salt solutions the reorientation time constant is very similar to that of pure water. Only for the higher concentrations of the sodium salts there is an increase of the reorientation time constant. This implies that up to concentrations of 3 m the cation does not affect the reorientation of the hydroxyl groups of water molecules in its solvation shell, which was shown before even for strongly hydrated cations like Mg^{2+}.[6,12]

This result strongly contrasts with the findings of dielectric relaxation studies that found a very strong slowing down effect of the water dynamics in the first hydration shells of the cation.[31,32] However, in the present experiments we probe the reorientation of the OD groups, whereas in dielectric relaxation studies the orientational dynamics of the water dipoles is probed. The electric field of the cation will strongly orient the water dipoles in the first hydration shell, thus preventing these water molecules to contribute to the polarization response to an applied electric field. Hence, the dipolar motion in the first hydration shell of the cation is more or less immobilized. However, the O–D groups of these water molecules can still reorient in a propeller-like motion around the fixed dipole (bisectrix of the water molecule), which explains why the femtosecond mid-infrared experiments show little effect of the cations on the orientational mobility of the OD groups.

The solutions containing a high concentration of sodium ions (≥ 4 m) do show a somewhat slower reorientation of the OD···O molecules, and this effect is more pronounced for NaCl than for NaI. The difference between NaI and NaCl indicates that the hydration shell dynamics of the cation is dependent on the nature of the counter-ion. For the weaker hydrated Cs$^+$ and K$^+$ cations we observe no strong dependence on concentration and/or the nature of the anion, from which we conclude that the importance of this effect also increases with cation hydration strength. It follows that the reorientation of the OD···O groups is highly dependent on the interplay of the cations and the anions. The observed reorientation time constant of the OD···O groups scales in fact quite well with the viscosity of the solution, which suggests that the propeller-like reorientation of OD···O groups in the cation hydration shell is governed by the collective translational mobility of the water molecules and ions in the solution, as is reflected in the value of the viscosity. As a result, the reorientation time constant of the OD···O groups can be described with a Stokes–Einstein–Debye equation.

We did not report a slowing down of the reorientation of the OD···O groups at concentrations >3m in a previous study,[33] because we could not distinguish the dynamics of the OD···O groups from the dynamics of the OD groups that are hydrogen bonded to the anion. As a result, at high salt concentrations the dynamics of the OD···O groups were hidden under the dominant signal of the OD groups bonded to the anions. In the present study we are able to discern the dynamics of the OD···O groups from the dynamics of the OD groups bonded to the anion at all concentrations and for all delay times. As a result we can now determine the reorientation time of the OD···O with much more accuracy, even at high salt concentrations.

We also observe that the cation can have an effect on the orientational mobility of the OD groups that are hydrogen
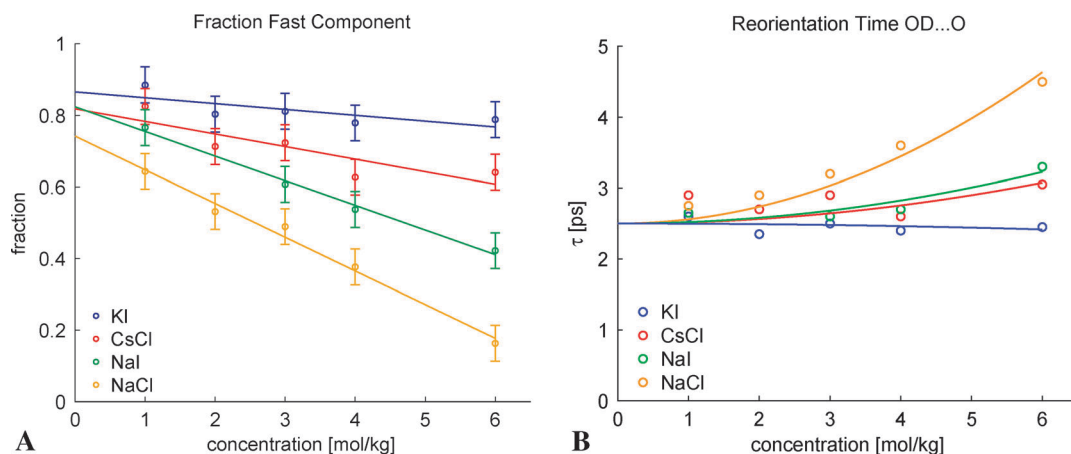
Fig. 10 (A) The fraction of the fast component in the anisotropy decay of the OD groups that are hydrogen-bonded to the anion (the lines are guides to the eye). The fractions result from a global fit to all measured concentrations of a particular salt, with the fast and the slow reorientation times as global (constant) parameters. (B) Reorientation time constants for different salts at different concentrations as obtained from an exponential fit to the anisotropy decay of the OD⋯O groups. The lines are guides to the eye.

bonded to the anion. From the faster OD⋯I$^-$ anisotropy decay for KI compared to NaI solutions, shown in Fig. 7, it is clear that the orientational relaxation of water molecules around the *anions* depends on the nature of the *cations*. The sodium induces a decrease in the amplitude of the fast relaxation process, which is absent for the larger cations (see also Fig. 6). We explain this observation from the electric field between cations and anions, which is larger in the case of a smaller anion with larger surface charge density. If the field is strong enough it partly aligns the static dipole of the water molecules around the anion, hindering the fast reorientation process by decreasing the angle of the cone over which the OD can wiggle. Fig. 10A shows that the amplitudes of the fast process are diminished by the presence of the stronger hydrated sodium for all measured concentrations of iodide and chloride salts.

We thus observe that for both cations and anions the reorientation dynamics of the OD groups in the hydration shell can be dependent on the nature of the counter-ion, especially at high concentrations and for ions that have a strong interaction with water. Following this line of thought, in the limit where both ions are very strongly hydrated (like the case for MgSO$_4$), we expect a strong cooperative retardation of water ($\bar{\mu}$) in both hydration shells, as was indeed recently shown.[12,13] For relatively weakly hydrated ions, like those considered in this paper, the effect on the water dynamics is more subtle and limited to their first hydration shell, but nonetheless we find that these ions should always be considered in the context of their counter-ion. The results presented here emphasize that the mutual influence of ions on each other's hydration shell dynamics is a very general effect and this notion likely also applies to charged side groups found in proteins or the head groups of polar surfactants.

V. Conclusions

We studied the reorientation dynamics of water in aqueous solutions of different alkali-halide salts (NaCl, NaI, CsCl and KI) by measuring the anisotropy dynamics of the excitation of the OD stretch vibration of HDO molecules. We were able to distinguish the response of the HDO molecules forming OD⋯A$^-$ hydrogen bonds to the halide (A$^-$ = Cl$^-$, I$^-$) anions from the other water molecules. We corrected the anisotropy dynamics of these OD groups for the effects of exchange between the bulk and the hydration shell by measuring the dynamics for different excitation frequencies. Thereby we obtained the intrinsic anion hydration-shell dynamics, *i.e.* the reorientation of the water molecules that keep their hydrogen bond with the anion intact. For all measured salts we found that the anisotropy dynamics of the anion-bound water comprises a fast and a slow decay process (2.0 ± 0.3 ps and 9 ± 1 ps). The fast component is associated with the wiggling motion of the OD while keeping its hydrogen-bond to the anion intact. An anion with a smaller radius and higher surface charge density exerts a stronger restriction on the maximum cone angle of this wiggling motion, thus explaining the decrease of the amplitude of this process for smaller anions. We found that a strongly hydrating cation like Na$^+$ has the tendency to align the water molecules in the anion hydration shell, thereby restricting the angular cone.

For most studied solutions, the OD groups that are hydrogen-bonded to other water molecules, forming OD⋯O hydrogen bonds, show similar reorientation dynamics as is observed for bulk liquid water. However, at concentrations >3 m, and in the case of a relatively strongly hydrating cation like Na$^+$, the dynamics of the OD groups bonded to other water molecules is observed to slow down. These OD groups likely belong to water molecules hydrating the cation and are restricted in their reorientation by the influence of the anion. The slowing down is more pronounced in the case of a stronger hydrating anion and can be seen as the onset of cooperative locking outside the hydration shells that was recently observed for strongly hydrating cations and anions like Mg^{2+} and SO$_4^{2-}$. This work demonstrates that cations and anions affect each other's hydration shell dynamics in a subtle way, even if the ions are not strongly hydrated.

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