Love and fear of water: Water dynamics around charged and apolar solutes
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Hydrophobic and Coulomb Interactions Disentangled

In the previous two chapters we investigated the effect of charges on the reorientation dynamics of water: Positive charges align a different vector in the water molecules than negative charges. If they do so strongly enough, their combined effect may lead to a locked water complex in which the reorientation of water molecules is severely hindered. In chapter 7 we saw that hydrophobic groups have a pronounced effect on the dynamics of water as well, for a very different reason. Many molecular systems in nature involve both hydrophobic groups and electric charges and the purpose of this chapter is to reveal their combined effects on the dynamics of water. To that end we used salts of which the cation has hydrophobic alkyl chains. By varying the length of the alkyl chains we can tune the hydrophobicity of the cation. We find that not only the reorientation dynamics of water molecules around the hydrophobic groups are strongly retarded, also the OD-groups that are hydrogen-bonded to the anion have a much slower reorientation dynamics. The wobbling component that was found in chapter 9 becomes much slower. This observation shows that the wobbling motion is governed by the reorientation of the hydrogen-bond network outside the anion hydration shell.
10.1 Introduction

Many processes in biological systems involve a subtle interplay between hydrophilic and hydrophobic molecular groups and water. The aggregation of hydrophobic side groups of amino acids in proteins for example is a driving force for proteins to assume their native conformation in water. Charged side groups can form salt bridges to enforce the thus formed structure. A detailed understanding of the effect of hydrophobes and charges on water is therefore crucial to understand processes like protein folding and membrane formation.

Symmetrical tetra-$n$-alkylammonium (TAA, $N(C_nH_{2n+1})_4^+$) salts are good model systems for hydrophobic hydration since they are often well soluble in water and their hydrophobicity is easily increased by increasing $n$. Moreover, tetramethylammonium ($\text{Me}_4^+$) is ubiquitous in biological systems as it forms the positively charged moiety in polar head groups of a common class of phospholipids. Frank and Evans used TAA salts in their famous work in which they proposed so-called iceberg formation around hydrophobes, thereby explaining the counter-intuitive thermodynamic behavior that is common for hydrophobic solutions \cite{96}. The formation of more structured ice-like water around hydrophobic moieties provided an explanation for the increased heat capacity of solutions containing amphiphiles. In later work the iceberg theory was disputed, as hardly any changes in the hydrogen-bond structure of water were observed upon the addition of amphiphilic solutes \cite{97}. However, recent Raman spectroscopy studies did find a more ordered hydration structure around hydrophobic groups \cite{98}. In other work the dynamics rather than the structure of water were found to be affected: water molecules are observed to reorient much more slowly in solutions containing amphiphilic molecules \cite{28, 110, 17}.

The ionic nature of TAA salts offers an interesting opportunity to study the combination of coulomb and hydrophobic effects. Not only does the cation carry both charge and hydrophobic groups in different ratios depending on the length of the alkyl chains, the system also necessarily includes counter ions. The combined ionic and hydrophobic character of the TAA cations is often used to explain their influence on the conformation of proteins in terms of the concepts of structure making and breaking \cite{176, 177, 137, 178}. The $n = 1$ salts were found to be structure breakers, the $n \geq 3$ salts structure makers, and the $n = 2$ salts neutral intermediates \cite{176}. This change in character with increasing alkyl length is believed to result from the competition between coulomb and hydrophobic interactions \cite{178, 103}. Some recent studies suggested that the water structure around the TAA hydrophobic moieties is enhanced \cite{98}, and that this is less the case for $\text{Me}_4\text{NBr}$ and $\text{Et}_4\text{NBr}$ compared to $\text{Pr}_4\text{NBr}$ and $\text{Bu}_4\text{NBr}$ \cite{97, 178}.

In this chapter we study the reorientation of water in solutions of TAABr salts for four different chain lengths ($n = 1, 2, 3, 4$) using polarization-resolved femtosecond pump-probe spectroscopy. In line with what was shown in the previous chapters we will demonstrate that this technique also allows to disentangle the effects of the hydrophobic cation on water from those of the anion. We compare the data with results on solutions of NaBr, for which the coulomb effects will dominate.
10.2 Experiment

For our experiments we use the one-color setup described in section 3.1.1. The pump-probe spectrum was centered around 2525 cm\(^{-1}\). We prepared solutions containing different concentrations (0.25, 0.5, 1, 2, 3, 4 and 6 molal, mol/kg solvent) of tetra-\(n\)-alkylammonium bromide in isotopically diluted water (4% D\(_2\)O in H\(_2\)O). We used bromide salts with tetra-\(n\)-alkylammonium cations with four different alkyl chain lengths: 4-methylammonium (Me\(_4\)NBr), 4-ethylammonium (Et\(_4\)NBr), 4-propylammonium (Pr\(_4\)NBr) and 4-butylammonium (Bu\(_4\)NBr). We use solutions of NaBr as a reference, since the sodium cation has no hydrophobicity and we expect only coulomb interactions in its hydration shell. We did not choose the ammonium salt as a reference since the protons of the ammonium cation exchange with the deuterium in the solvent. The thus formed ND-groups absorb at nearly the same frequency as the OD-groups in the solvent. As a result, the observed dynamics would no longer exclusively represent the dynamics of the water molecules. All salts were purchased from Sigma Aldrich and had a purity of \(\geq 98\%\). The sample cell consisted of two calcium fluoride windows (dimensions WxHxD 20x39x4 mm\(^3\)) pressed against each other with a teflon spacer in between. The thickness of the spacer was varied between 25 \(\mu\)m and 100 \(\mu\)m for different compounds and concentrations to obtain about 10 % transmission in the OD stretch region in all measurements. To prevent heat accumulation during the measurements the sample cell was slowly moved up and down with an oscillation period of a few seconds.

10.3 Results and Analysis

10.3.1 Experimental Results

Fig. 10.1A displays linear spectra of the OD-stretch absorption band of neat 4% D\(_2\)O in H\(_2\)O and 4 molal solutions of the different salts. The TAA salt solutions show a blue-shift with respect to neat HDO:H\(_2\)O, without any clear dependence on the nature of the cation. The blue-shift increases with concentration. Analog to what was discussed in the previous chapter, we can assign this blue-shift to the OD oscillators of HDO molecules that are hydrogen-bonded to the anions (OD\(\cdots\)Br\(^-\)) \[128\]. Since this bond is weaker than water-water hydrogen bonds (OD\(\cdots\)O), the coupled OD-stretch resonance frequency is blue-shifted. We centered the pump and probe spectrum in our experiment at 2525 cm\(^{-1}\) to have them optimally overlapping with both contributions to the absorption band. The linear spectrum of the same concentration NaBr shows a significantly larger blue-shift of the OD-stretch compared to the TAA salt solutions. We will come back to this observation in the discussion section of this chapter.

Fig. 10.1B shows transient spectra at different pump-probe delay times for a 2 molal solution of Bu\(_4\)NBr. For early delays, a bleach due to the depleted ground state and stimulated emission is observed in the center and at the blue side of the spectrum. The positive feature at lower frequencies is the onset of the induced absorption \(\nu = 1 \rightarrow 2\). For increasing delay times, the absorption changes decay to a spectral feature that remains constant on the timescale of the
Figure 10.1. A Comparison of the linear spectra of 4 molal TAABr solutions in the OD-stretch region in isotopically diluted water (4% D$_2$O in H$_2$O). The spectra are blue-shifted compared to neat 4% D$_2$O in H$_2$O due to the bromide ions, but not as much as for 4 molal NaBr. Panel B shows the transient spectra measured for different delay times for a 2 molal solution of Bu$_4$NBr. The solid lines represent a fit of the kinetic model described in section 10.3.2.

Figure 10.2. The results of a fit of the kinetic model described in the text to the data obtained for a 2 molal solution of TBABr. Panel A shows the fitted state spectra and panel B the fitted population dynamics. The vibrational decay is very slow and has at 15 ps not yet come to a complete end.

experiment (<100 ps). This final spectrum is a thermal-difference spectrum that results from the heating of the sample by a few degrees due to the thermalization of the excitation energy [179]. To calculate the anisotropy dynamics of the excited OD oscillators we subtract this thermal contribution by fitting a kinetic model for the vibrational decay to the isotropic data.
10.3.2 MODELING

Analogous to what we found for the alkali-halide solutions in chapters 8 and 9 we expect that the transient spectra contain contributions of OD····O and OD····Br− oscillators that are spectrally shifted with respect to each other. We therefore assume the same kinetic model as brought forward in section 4.3.1, in which the two contributions are fitted as separate excited states. In this chapter we neglect the exchange discussed in chapter 8, as these effects are very small.

Both OD····O and OD····Br− oscillators have different reorientation dynamics [30] and therefore we assume a functional form for the anisotropy decays of these two species. Several studies showed that in solutions containing amphiphilic solute molecules the reorientation of water takes place on two different timescales [103, 28, 17]. The fast timescale is associated with OD-groups that have bulk-like reorientation dynamics and the slow timescale with OD-groups hydrating the hydrophobic group of the solute. We thus model the OD····O anisotropy decay by,

\[ R_{OD···O}(t) = A_f e^{-t/\tau^O_f} + A_s e^{-t/\tau^O_s} \]  

(10.1)

where \( A_f \) and \( A_s \) are the relative amplitudes of the fast and slow relaxation processes and \( \tau^O_f \) and \( \tau^O_s \) are the fast and slow relaxation time constants.

In other work, the anisotropy of OD groups bound to anions was found to decay by a number of processes [132, 150, 104]: (1) a very fast decay due to librational motions (\( \sim 150 \) fs), (2) a contribution due to a wobbling motion that is caused by the reorganization of the hydrogen-bond network outside the first solvation shell (\( \sim 2 \) ps) and (3) a much slower decay due to rotational diffusion of the solvating water over the anion surface or frame reorientation (\( \sim 10 \) ps). Therefore, we choose the following functional form for the OD····Br− anisotropy decay,

\[ R_{OD···Br−}(t) = B_f \left( C e^{-t/\tau^{Br}_{lib}} + (1 - C)e^{-t/\tau^Br_f} \right) + B_s e^{-t/\tau^Br_s} \]  

(10.2)

where \( B_f \) and \( B_s \) are the relative amplitudes of the fast and slow orientational relaxation processes described above and \( \tau^{Br}_{lib} \), \( \tau^Br_f \) and \( \tau^Br_s \) are their corresponding time constants. The anisotropy dynamics in (10.2) thus contains a fast decaying part and a slow decaying part analogous to the OD····O anisotropy decay in equation (10.1). Both the librational decay and wobbling motion are included in the fraction of the fast decaying part, with relative weighting given by the parameter \( C \).

Both the kinetic model for the vibrational decay and the functions for the two excited state anisotropy decays are fitted to the data simultaneously in a self-consistent fit (see also section 4.4.2). To limit the freedom in the fit we fix several parameters entering Eq. (10.1) and Eq. (10.2). Since the vibrational lifetime of OD····O oscillators in pure HDO:H2O is 1.8 ps [22], the OD····O anisotropy can only be measured accurately up to about 10 ps. The long delay time dynamics of the OD····O anisotropy in the TAA solutions is even more obscured by the response of the OD····Br− oscillators that have a much longer
The vibrational lifetime. We therefore model the slow component of the OD···O reorientation as an endlevel of the anisotropy, i.e. we set the slow time constant to $\tau^{O}_{s} = \infty$ ps. In previous work on solutions of amphiphiles in water it was found that up to high concentrations a fast reorientation process is present in $R_{OD···O}(t)$ with a time constant of $\tau^{f}_{O} = 2.5$ ps [24]. Similarly it was found in aqueous solutions of alkali-halide salts that a fast reorientation process is present in the anion-bound reorientation dynamics with a time constant of $\tau^{f}_{Br} = 2$ ps [30]. In our fit we fix those constants accordingly. Finally, the time resolution of our experiment is limited to the cross correlate of the pump and probe pulses ($\sim 250$ fs). For this reason we fix the amplitude $C = 0.25$ and the time constant of the librational decay $\tau^{lib}_{Br} = 170$ fs, corresponding to the values found in previous work on alkali halide solutions [104]. The freely fitted parameters are thus the parameters of the kinetic model describing the isotropic decay, the amplitudes $A_f, A_s, B_f$ and $B_s$ and the slow reorientation time $\tau^{Br}_{s}$ of bromide bound water.

10.3.3 MODELING RESULTS

The solid lines in Fig. 10.1B represent the isotropic results of a fit of the model to the data obtained for a 2 molal Bu$_4$NBr solution. Fig. 10.2A presents the fitted state spectra $\sigma_i(\omega)$ and the corresponding population dynamics $N_i(t)$ are shown in Fig. 10.2B. The excited OD···Br$^-$ spectrum shows a blue-shift of about 30 cm$^{-1}$ with respect to the excited OD···O spectrum, significantly smaller than the value of 50 cm$^{-1}$ that was found for alkali bromide salts [128]. The vibrational decay time of the OD···Br$^-$ is slow, as is the decay of the intermediate state, leading to a long delay of the heat ingrowth. Delay traces show that the vibrational decay becomes slower with increasing concentration.
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Figure 10.4. For all measured salts and concentrations the vibrational decay time of the OD···Br$^-$ oscillators (A) and the decay time of the intermediate state (B). The vibrational lifetime of bromide-bound water becomes very slow for high concentrations of the salts with longer alkyl chains. The solid lines are guides to the eye.

(Fig. 10.3). Equal concentrations of different TAA salts show the same trends.

The fit results of the isotropic model are summarized for all measured data sets in Fig. 10.4. The vibrational lifetime of OD···Br$^-$ increases both with TAA Br salt concentration and with alkyl chain length and becomes as long as 7.3±3 ps for the highest concentration of Bu$_4$NBr. The dynamics of the ingrowing heat strongly depends on the decay time of the intermediate state, which is found to increase strongly for increasing concentrations and longer alkyl chain lengths. The right panel shows the population of OD···Br$^-$ relative to that of OD···O. When calculating these values we took into account that the cross section of OD···Br$^-$ is ~1.5 times higher than the cross section of OD···O. This ratio is obtained from an analysis of the linear absorption spectra. From the slope we determine a hydration number of 7±2, consistent with earlier work [150, 180], and without clear dependence on the nature of the counterion (Fig. 10.2C). For the 3 molal solutions all fitted spectra are shown in Fig. 10.5. The blue-shift of the OD···Br$^-$ spectrum clearly depends on the nature of the cation, while the OD···O spectrum is the same for all cations. This is surprising since the linear spectra of the solutions do not show a clear dependence on the length of the alkyl chains.

Fig. 10.6 shows the OD···O and OD···Br$^-$ anisotropy decays and corresponding fits for different concentrations of Bu$_4$NBr (a detailed description of how the data-points of the anisotropy decays were obtained can be found in section 4.4.2). Both $R_{OD···O}(t)$ and $R_{OD···Br^-}(t)$ show a bi-exponential behavior with a slow component of which the amplitude increases with increasing concentration. The fraction of this component is determined from the fitted amplitudes. More specifically, we determine the fraction of slow OD-groups $f_A = A_s/(A_f + A_s)$ in the case of OD···O. For the OD···Br$^-$ anisotropy de-
Figure 10.5. The spectra of OD···O (A) and OD···Br⁻ (B) oscillators obtained by fitting the kinetic model to all 3 molal solutions. Depending on the alkyl chain length the resonance frequency of the bromide-bound oscillators blue-shifts less compared to that of aqueous NaBr.

cay the fraction \( f_B = B_s / (B_f + B_s) \) represents the part of the anisotropy that decays by the slow process. The fractions are plotted for all measured data in Fig. 10.7. \( f_A \) and \( f_B \) increase with increasing alkyl chain length and with concentration. Towards infinite dilution, the OD···Br⁻ slow fraction extrapolates to a non-zero value that is roughly 0.25 for all salts. In Fig. 10.9 \( f_A \) and \( f_B \) are plotted against the number of carbons in the cation alkyl chains for two concentrations. The increase of the alkyl chains is shown to increase the fraction of water with slower dynamics, both for the OD···O and the OD···Br⁻ oscillators.

The time constant \( \tau_s^{Br} \) was a free parameter in the model and its fitted values are shown in Fig. 10.8. The slow reorientation time of water bound to bromide is 14±2 ps for Me₄NBr, independent of the concentration. This time constant can be well determined thanks to the very slow vibrational relaxation of the OD···Br⁻ oscillators \( (T_1 \) up to 5.5 ps for the highest concentration of Me₄NBr). The value of \( \tau_s^{Br} \) for Et₄NBr \( \tau_s^{Br} \) depends strongly on the concentration, increasing from 20±2 ps for the lowest concentrations up to 41±13 ps for the highest concentration. In the case of the cations with the longest alkyl chains (Pr₄NBr and Bu₄NBr) the slow reorientation time exceeds 40 ps already at low concentrations.
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Figure 10.6. The anisotropy decay in solutions of different concentrations Bu$_4$NBr, decomposed in its components OD····O (A) and OD····Br$^-$ (B). Already for 250 mmolal Bu$_4$NBr the anisotropy decay shows a substantial slow component compared that of neat water (black circles). The OD····Br$^-$ anisotropy decay shows a saturation effect for the higher concentrations.

Figure 10.7. The fractions of OD-groups with slow reorientation for OD····O (A) and OD····Br$^-$ (B) oscillators. Bromide-bound OD-groups have an intrinsic slow fraction, which becomes more retarded in solutions with many or large hydrophobic cations. The solid lines are guides to the eye.

10.4 Discussion

10.4.1 Hydrophobic Effects on the Anion Hydration Shell

The blue-shift of OD····Br$^-$ oscillators relative to OD····O oscillators enables us to disentangle the anisotropy dynamics of these two species, similar to our
Figure 10.8. (A) A comparison of the anisotropy decay of bromide-bound OD-groups for salts with different alkyl chain lengths. The vertical axis is logarithmic. (B) The slow reorientation time becomes slower for higher concentrations of Et$_4$NBr. All fitted time constants for Pr$_4$NBr and Bu$_4$NBr were longer than 40 ps (data-points not shown). At such long timescale our experiment is not sensitive enough to determine this time constant accurately.

The slow fraction of water around the bromide ion $f_B$ (Fig. 10.7B) shows the same qualitative behavior compared to water outside the bromide hydration shell. Extrapolation of $f_B$ towards infinite dilution suggests that there is an intrinsic effect of the bromide on the reorientation dynamics. This fits the picture sketched in chapter 9, where the reorientation dynamics of OD-groups bound to an anion were found to have two main contributions on a fast and slow timescale. A fast decay process ($\sim 2$ ps) is caused by the wobbling motion of a water molecule while keeping its hydrogen bond to the anion intact. As
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Figure 10.9. The fraction of slow water for different alkyl chain lengths decomposed in its components for 1 molal and 4 molal solutions. The solid lines are guides to the eye.

the anion restricts the wobbling motion to a certain angle, this process does not lead to a full decay of the anisotropy and the remaining part decays by the much slower process of rotational diffusion of the molecules over the anionic surface [149, 30]. The latter slow component is the intrinsic anionic effect that is present in Fig. 10.7B. For increasing alkyl chain lengths and concentrations the amplitude of the slow process becomes larger (see also Fig. 10.9). $R_{OD...Br}(t)$ must therefore be interpreted as a combination of an anionic effect and a hydrophobic effect and the latter can be understood as follows. The wobbling motion of an OD group bound to the bromide anion is caused by the reorganization of the hydrogen-bond network outside the first solvation shell. For this reason, the wobbling reorientation time ($\sim 2$ ps) is close to that of normal hydrogen-bond network reorganization ($\sim 2.5$ ps). In the TAABr solutions, the dynamics of the hydrogen-bond network is dramatically retarded by the presence of the hydrophobic cations. This decreased mobility is reflected in the dynamics of the OD-groups that are hydrogen bonded to the bromide ion. The OD···Br$^-$ wobbling motion thus becomes slower for increasing alkyl chain lengths and concentrations.

The vibrational lifetime of the OD-stretching mode of anion bound water is in general observed to be longer than for bulk water [182, 183]. It depends on the salt concentration and was reported to be as long as 4.8 ps for a 6 molal NaBr solution [130], in agreement with our current findings (Fig. 10.4). The increased vibrational lifetime is generally caused by a decrease of the hydrogen bond interaction [182]. Typically we observe that the vibrational lifetime becomes slower with increasing concentration. This dependence may in part be due to exchange events between OD···Br$^-$ and OD···O species [184]. An initially excited OD···Br$^-$ oscillator can rotate out of the solvation shell and become
OD· · · O, thereby decreasing the effective vibrational lifetime. We have seen in chapter 8 that in salt solutions these exchange effects take place on a timescale of \( \sim 10 \text{ps} \) depending on concentration \([126, 127]\). For the TAABr salts, the OD· · · Br\(^-\) vibrational lifetime becomes even longer than for NaBr, up to 7.3 ps for a 6 molal concentration of Bu\(_4\)NBr (Fig. 10.4). We interpret this long lifetime as a result of a considerably slower exchange rate out of the bromide solvation shell in solutions with big hydrophobic cations. This picture is consistent with the decreased mobility of the OD· · · Br\(^-\) wobbling component: a more slowly wobbling OD-group will jump out of the solvation shell at a lower rate.

For all solutions we observe that the thermalization is delayed with respect to the vibrational relaxation. This delay is \( \sim 800 \text{fs} \) in pure water and was interpreted to reflect the adaptation of the hydrogen-bond network to the new energy distribution after vibrational relaxation \([185, 22]\). Fig. 10.4B shows that the thermalization dynamics, expressed in the decay time of the intermediate state, becomes very slow upon the addition of Bu\(_4\)NBr. Apparently, at high concentrations the hydrogen bond network is less capable of adapting to the new energy distribution after the vibrational excitation has relaxed into thermal modes. The effect is weaker for the shorter alkyl chains, indicating that this effect is correlated with the hydrophobicity in the solution.

The OD· · · Br\(^-\) oscillators shows a smaller blue-shift in solutions of TAABr than in solutions of NaBr as seen in both the linear spectra (Fig. 10.1) and the transient spectra (Fig. 10.5). A smaller blue-shift means relatively stronger OD· · · Br\(^-\) hydrogen-bonds, which in this case appears to be induced by the presence of the hydrophobic cations. The stronger OD· · · Br\(^-\) interaction can be explained if on average less OD groups are hydrogen-bonded to bromide per anion, as the anion charge is in such case less screened. The depletion of the bromide solvation shell can be caused by the large hydrophobic chains of the cations that stick into the bromide solvation shell. This explanation is supported by the OD· · · Br\(^-\) populations that show that the number of OD groups in the bromide solvation shell is systematically lower in solutions of TAABr than in solutions of NaBr. This interpretation is also in agreement with recent findings of a tendency of weaker hydrated halide anions to form ion pairs with TAA cations \([186]\).

### 10.4.2 Formation of Aggregated Ion Clusters

The fraction of slow water \( f_A \) in Fig. 10.7 saturates for increasing concentrations Et\(_4\)NBr, Pr\(_4\)NBr and Bu\(_4\)NBr, which means that there is a decreasing number of slow OD groups per solute molecule. This can partly be explained by overlapping hydration shells: with 34 OD groups per Bu\(_4\)N\(^+\) solvation shell this overlap is bound to happen already at concentrations of 2 molal. In addition, MD simulations and neutron diffraction experiments show that large hydrophobic cations tend to aggregate strongly \([187, 177]\). The aggregation leads to a reduced hydrophobic surface that is exposed to water and hence effectively decreases the slow fraction. Me\(_4\)NBr does not seem to aggregate much, which was also predicted by MD simulations \([188]\). A very similar situation occurs when aqueous
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solutions of TMU or TBA are compared to solutions of TMAO. TMU and TBA show saturation behavior due to aggregation starting at concentrations of 3 molal [189]. The very polar TMAO molecule, on the contrary, has little tendency to aggregate and the slow water fraction for TMAO solutions is accordingly observed to saturate only at very high concentrations (>8 molal) due to inevitable overlap of the hydration shells at these high concentrations [189, 152]. The lack of aggregation for Me$_4$NBr solutions is therefore attributed to the charged nature of the Me$_4$N$^+$ cation. In spite of this charged nature, we observe a fraction of slowly reorienting water molecules around the Me$_4$N$^+$ that we associate with the hydration of the hydrophobic methyl groups. This observation agrees with the results of NMR studies in which it was found that Me$_4$N$^+$, other than Na$^+$, is not capable of aligning the static dipoles of its solvating water molecules, in agreement with its qualification as a hydrophobe [176, 190, 100, 191].

We observe that the slow reorientation time of OD····Br$^-$ ($\tau_{sBr}^r$) has a constant value of 14 ± 2 ps for all measured concentrations of Me$_4$NBr, while for Et$_4$NBr $\tau_{sBr}^r$ increases from 20 ps to more than 40 ps (Fig. 10.8). The reorientation time constants $\tau_{sBr}^r$ of Pr$_4$NBr and Bu$_4$NBr are longer than 40 ps for all concentrations. For alkali-halide salts the slow reorientation was found to occur with a time-constant of ~10 ps and is primarily due to rotational diffusion of OD-groups over the anionic surface while keeping their OD····Br$^-$ hydrogen-bond intact [125, 30]. The exchange of water between the hydration shell and the bulk can also contribute to the anisotropy dynamics, but this will be a minor contribution [30]. The exchange mainly affects the amplitude of the anion-bound spectral component, i.e. the $T_1$ time constant. We observe that the presence of the hydrophobic cations leads to a severe retardation effect in the anisotropy dynamics. Rotational diffusion over the anionic surface requires the reorganization of the hydrogen bond network outside the solvation shell. The hydrophobic cations appear to slow down this reorganization and thereby slow down the rotational diffusion.

The results for Me$_4$NBr are distinct from the other TAABr salts in the sense that no concentration dependence for the slow reorientation time of OD····Br$^-$ is found. This is related to the previous observation that Me$_4$NBr has no tendency to aggregate. From classical MD simulations it was shown that whether amphiphilic solute molecules tend to aggregate or not has a strong effect on the dynamics of the solvating water molecules [107]. Weakly aggregating molecules like TMAO mix better with the solvent, resulting in water molecules confined in thin films in between the big solute molecules. Aggregating molecules like TMU form clusters at higher concentrations, with nanopools of bulk-like water in between. In the case of water films around TMAO, the reorientation time is further slowed down due to the nano-confinement in addition to a hydrophobic effect. With this in mind we can interpret our results on $\tau_{sBr}^r$ as follows. For increasing concentrations of Et$_4$NBr the slow water fraction saturates, which points towards a decrease in the exposed hydrophobic surface and hence aggregation. At the same time we find increasing values of $\tau_{sBr}^r$, which point towards an increasingly slower reorientation of the hydrogen-bond network around the anions. The distortion of the hydrogen-bond network can
be caused by nano-confinement of the solvating water in between the clustering cations. In concentrated solutions of Et$_4$NBr domains are likely formed in which bromide anions and Et$_4$N$^+$ cations cluster together with a restricted number of water molecules in between. For Pr$_4$NBr and Bu$_4$NBr this type of clustering already happens at the lowest concentrations measured. The affinity of large halide anions for TAA cations was shown in MD simulations [186]. In the case of Me$_4$NBr there is no decrease in the exposed hydrophobic surface and hence no aggregation. The values of $\tau_{sBr}^-$ remain constant up to 6 molal, similar to the results for NaBr, indicating that aggregation and confinement does not play a role. The Me$_4$N$^+$ cation is thus unique in the sense that the coulomb interactions are strong enough to prevent it from aggregating, but the hydrophobic nature is still slowing down the reorientation of the water molecules hydrating the methyl groups. The reason why even at low concentrations the slow reorientation time of bromide bound OD groups is affected by the cations may find its origin in ion-pair formation, which is indeed observed for these solutions [103, 186].

10.5 Conclusions

We studied the dynamics of water in aqueous tetra-$n$-alkylammonium bromide solutions for different lengths of the alkyl chains (Me$_4$NBr, Et$_4$NBr, Pr$_4$NBr and Bu$_4$NBr). Using the blue-shift of the OD stretch resonance of HDO molecules bound to bromide (OD···Br$^-$), we can distinguish the dynamics of the bromide solvation shell from the bulk water dynamics (OD···O). The number of slow water molecules increases with the length of the alkyl chains and corresponds to the solvation numbers of these ions found in other work. For Me$_4$NBr we find that about 12 OD-groups per cation have slower dynamics, consistent with the picture of hydrophobic hydration. This means that not the charged nature but the hydrophobic nature of the cation governs the water dynamics of its solvation shell. For the larger tetra-$n$-alkylammonium ions this dominance of the hydrophobic effect is even stronger.

The slower dynamics of the hydrogen bond network is reflected in the solvation shell of the bromide anion as well. The dynamics of OD-groups that remain hydrogen bonded to bromide is partially governed by a wobbling motion that roughly follows the reorganization of the hydrogen bond network outside the solvation shell. We find that this wobbling motion acquires a slow component due to the presence of the hydrophobic cations. We also find that the blue-shift of both the linear and transient spectra of OD···Br$^-$ compared to OD···O is much smaller for solutions of TAABr compared to NaBr solutions. This observation can be explained from the partial hydration of the Br$^-$ hydration shell by the protruding hydrophobic chains of the TAA cations. This picture also explains the increase of the vibrational lifetime for the OD-stretch excitation of OD···Br$^-$ with increasing TAA concentration and increasing alkyl chain length: For alkali-halide salt solutions this lifetime is partly determined by exchange events between OD groups bound to bromide and water outside
the solvation shell. These exchange events typically take place on a timescale of \( \sim 10 \text{ ps} \), but will be much slower in concentrated TAABr solutions due to the effect of the nearby hydrophobic TAA cations on the dynamics of the surrounding liquid.

From the saturation behavior of the fraction of water decaying by the slow process and the increasing reorientation time of OD\( \cdots \)Br\(^-\) oscillators we infer that cations with long alkyl chains form clusters with bromide ions and water molecules. The clustering effectively decreases the total exposed hydrophobic surface which leads to a saturation effect in the observed slow water fraction. The water molecules inside these clusters are highly confined, causing the reorientation of OD groups bound to the bromide ions that penetrated such a cluster to become even slower than 30 ps. Normally such slow reorientation processes are difficult to probe in this type of experiments due to the short lifetime of the OD-stretch vibration. However, the long OD\( \cdots \)Br\(^-\) vibrational lifetime allows for an accurate determination of such long reorientation time constants. The aggregation effect is not observed for Me\(_4\)NBBr even at concentrations of 6 molal, probably because for this ion the repulsive coulomb interaction is just strong enough to prevent the formation of large aggregated ion clusters.