Slowing Down of Vibrational and Structural Relaxation of Water Molecules in Concentrated Aqueous NaCl Solutions

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Sub-picosecond IR-spectroscopy is applied to aqueous NaCl solutions with low concentrated HDO–molecules acting as local probes for the strength of the H-bonds. We find a notable lengthening of the OH-lifetime by the presence of the dissolved ions by a factor of almost 3 up to 2.7 ps at 273 K in comparison to neat water. Simultaneously the average reorientation of the OH–dipoles slows down to 11 ps (273 K) and 4 ps (343 K) while also structural relaxation is found to proceed slower as compared to the case of neat water.

The investigation of the structural and dynamical properties of water is one of the major goals in scientific research which can be easily seen by looking at the broad literature published in this field. The fascinating features of the small water molecules are due to their ability to associate to a complicated, three dimensional network via hydrogen bonding. The hydrogen bonds between the individual water molecules are the reason for the special thermodynamical features of water as a three dimensional network is realized by hydrogen bonding resulting in strong cooperative effects. On the other hand all fundamental biological reactions proceed in aqueous solutions with strong impact of H bonding. But especially considering the latter reactions they always proceed in aqueous salt solutions and not neat water. Consequently a wealth of experiments have been conducted on aqueous salt solutions reporting on proton and dielectric relaxation, neutron and X ray scattering as well as proton mobility measurements and further more.[1] Missing is up to now a detailed understanding of the impact of salts on the vibrational and structural relaxation of the water molecules on the picosecond time scale.

For this reason we present here data of sub-picosecond IR-spectroscopy on aqueous salt solutions monitoring directly with high temporal resolution vibrational and structural relaxation within the H-bonded network of water. As the hydrogen brige bond vibrations itself are not accessible to pump-probe spectroscopy, we concentrate in the following on the dynamics of the OH-stretching mode of water. The latter one shows up as a broad structureless band in the conventional IR-spectrum of water while the OH mode acts as a local probe for the strength of the hydrogen bonding of the hydroxilic group determining its frequency position.[2] In the case of pure water the first time resolved experiments were reported by Graener et al.[3] giving evidence for discrete structural components underlying the broad OH-band utilising independently tunable pump and probe pulses of 11 ps duration. Changes of the transient OH-band shape as a function of the frequency position of the excitation pulse provided evidence for the inhomogeneous character of the OH-band of water (HDO in D_2O) at 298 K. Three major spectral components were inferred from the data and assigned to different environments.[3] These data were substantiated by additional experiments with higher temporal resolution yielding evidence for spectral holeburning in the OH-band of water and structural relaxation with a typical time constant of 1 ps[4] while the OH-lifetime was determined to be in the same order of magnitude[5–7] at room temperature.

First time-resolved experiments on pump-probe spectroscopy of aqueous salt solutions have been reported recently demonstrating vibrational lifetime lengthening of the OH-mode of HDO.[8] The authors stated an impact of anions on the dynamics, only, with no measurable effect of the cations. With the help of our sub-picosecond pulses allowing for higher spectral resolution accompanied by a sufficient temporal resolution we obtain a more detailed picture which will be outlined in the following.

Experimental

Our experimental system is described in detail elsewhere.[9] The two IR-pulses are derived from parametric oscillator-amplifier devices with independent, computer-controlled tunability in the range of 1600 to 3700 cm^{-1} (2800 to 3700 cm^{-1}; numbers in brackets refer to the pump) and typical energy of ≈ 10 nJ (≤ 10 μJ). A special feature of our laser system is the possibility to align separately pump and probe pulse duration between 0.4 ps and 2.6 ps changing the operation conditions of the parametric devices. All experimental data presented in the following are taken with pulse durations of $\simeq 0.5$ ps. The change in optical density of the sample is determined for parallel ($\|$) and perpendicular ($\perp$) polarization with respect to the linear polarization of the pump. The data are taken for variable probe frequency ν and delay time t_D and we investigate an isotropic signal, $\ln (T/T_0)_{is} = (\ln (T/T_0)_{\|} + 2 \ln (T/T_0)_{\perp})/3$ and the induced dichroism $((\ln (T/T_0)_{\|} - \ln (T/T_0)_{\perp})/ 3 \ln (T/T_0)_{is}$ of the sample.[10] For negligible energy transfer processes, the time evolution of the induced dichroism is governed by the reorientation time constant τ_{or} (second order reorientational correlation time), while the isotropic signal delivers information on the vibrational population dynamics. The samples for time-resolved spectroscopy consists of NaCl added at various concentrations in between 1 M to 5 M to a 0.8 M HDO:D_2O solution while the data are taken at three different sample temperatures of 273 K, 298 K, and 343 K. The zero-setting of the delay time scale (maximum overlap between pump and probing pulses) is determined by a two-photon absorption technique in independent measurements with an accuracy of better than ±0.2 ps.[11]

Results and Discussion

Conventional IR-spectra taken in the OH-stretching region are demonstrated in Fig. 1 for four different aqueous salt solutions. For three different salt concentrations ranging between 1 M and 5 M we investigated the impact of the ions on the hydroxilic stretching mode of the HDO molecules in the sample. The results for LiCl (a), NaCl (b), and KCl (d) show an increasing shift of the OH-band towards higher frequencies while the blue wing of the band steepen with increasing size of the cation. Increasing the size of the anion (NaI, c), this effect even gets more pronounced. It is concluded, that the presence of the ions results in a disturbance of the H-bonded network thereby weakening a significant amount of bonds. On the other hand it is known from NMR-experiments on the reorientational dynamics of aqueous salt solutions that Li^+ or Na^+ act like structure makers and K^+, Cl^-, I^- as structure breakers.[13,14] The latter was concluded from the respectively slowed down and enhanced reorientational motion of the water molecules affected by the ions, i.e. in the conventional IR-spectrum of the hydroxilic stretching mode at ambient temperatures it is not easily possible to identify the impact of cations and anions, respectively.

In the case of water molecules surrounding anions it has been calculated, that the OH-groups points dominantly towards the anion thereby building hydrogen bonds.[15] These special H-bonds could also be potentially observed in conventional IR-spectra and for this reason we cooled down the aqueous NaCl solution below the freezing point. An example of a FT-IR spectrum of a frozen aqueous salt solution is shown in Fig. 2 for an 5 M NaCl solution in 0.8 M $HDO:D_2O$ at 210 K. Besides the well known absorption band at 3305 cm^{-1} (dashed line) related to the presence of hexagonal ice we notice an additional absorption at 3420 cm^{-1} (dash-dotted line). The latter is most probably related to the weaker H-bonds build up between the HDO molecules surrounding the anion while the size of the anion results in a disturbance of the water network around it. The cations may also contribute to the absorption at 3305 cm^{-1} as Na^+ is known to act as a moderate structure maker with probably smaller impact on the surrounding water or the HDO molecules are at lower temperatures not statistically distributed over the two different ions but preferably bonded to the anion. To get a knowledge on the ion impact on the dynamical properties of the water, one has however to perform time-resolved IR-spectroscopy as demonstrated in the following.

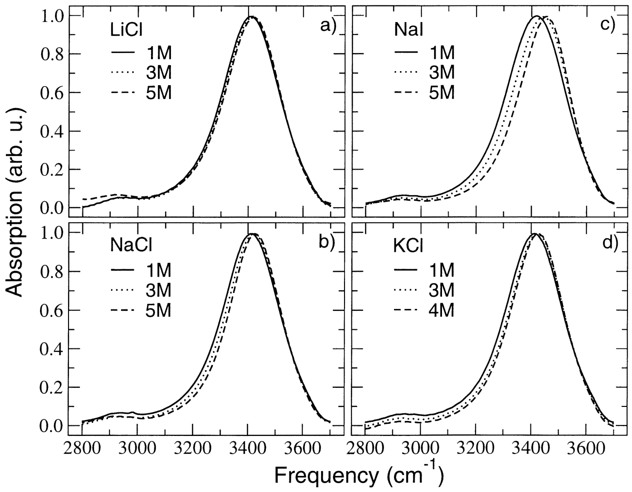

Fig. 1. Conventional IR spectra taken within the OH-stretching region of four different samples consisting of salts dissolved in an 0.8 M $HDO:D_2O$ solution. The data are shown for the three indicated different salt concentrations and are normalized to 1 ; a, LiCl; b, NaCl; c, NaI; d, KCl.

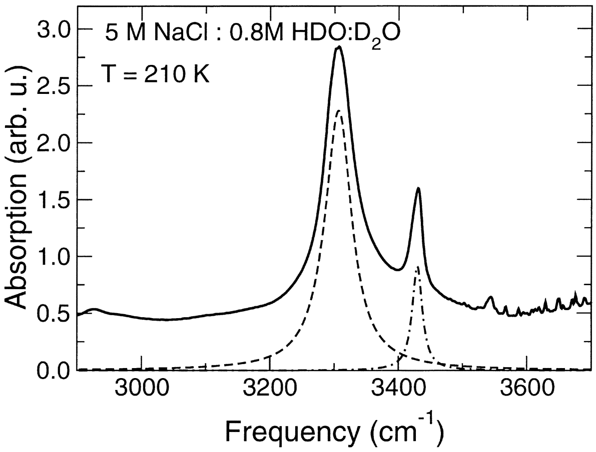

Fig. 2. The same as shown in Fig. 1, this time however for an ice sample taken at a temperature of 210 K. Clearly two different ice structures show up, indicated by the broken lines.

Time resolved data taken at fixed pump and probing frequencies are depicted in Figs. 3a,b and 4, concentrating on vibrational relaxation and reorientational dynamics, respectively. In Figs. 3a and b measured data are plotted for a 3 M NaCl solution of the partially deuterated water sample at $T = 343$ K and $\nu_{pu} = 3440$ cm^{-1}. Probing is demonstrated at the frequency of excitation (a) and within the excited-state absorption at 3150 cm^{-1} (b). For the OH-stretch with strong anharmonic character the excited-state absorption is notably red-shifted in respect to the 01-transition and is for this reason spectrally well separated. As the higher lying excited-states of the OH-mode are thermally almost not occupied at ambient temperatures, T_1 can be directly determined from monitoring the relaxation of the population in the first excited state.

The data are fitted by numerically solving two independent sets of energy level schemes consisting of 3-levels each, respectively, and depicted in Fig. 3c. The latter considers the vibrational ground state of the OH-stretching mode (0) of HDO, a joint first excited level $v = 1$ (1) of the respective spectral component(s) directly pumped by the excitation pulse, and population redistribution to an intermediate state (2) representing the other spectral components involved in the dynamics and grouped together in only one level. Energy redistribution between levels (1) and (2) is described by a time constant τ_s, while population decay out of levels (1) and (2) proceeds back

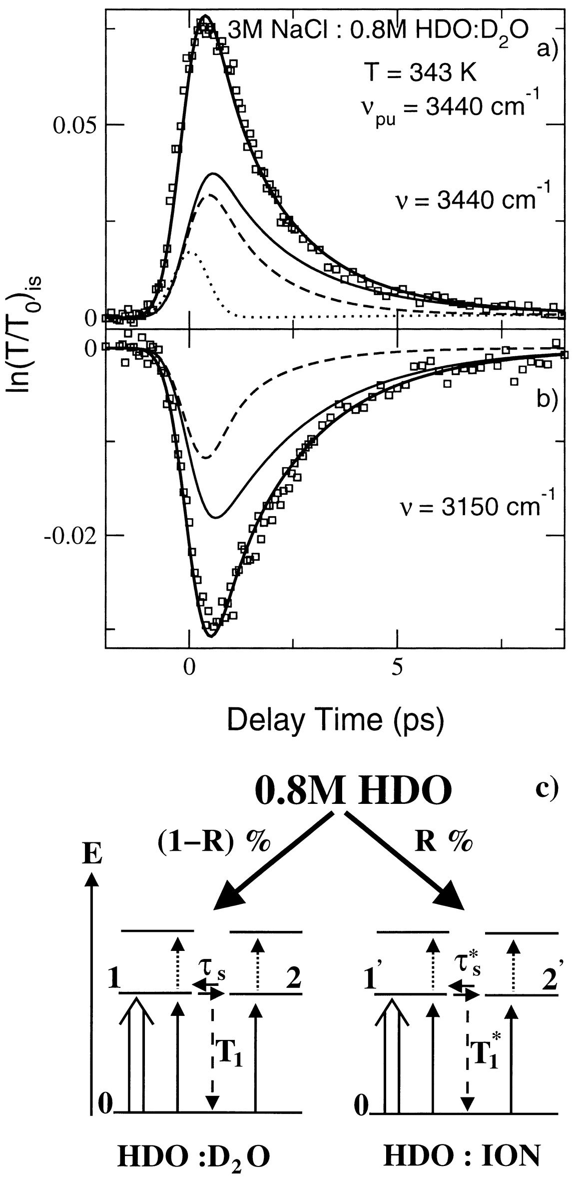

Fig. 3. Isotropic signal transients taken at 343 K, ν_{pu} = 3440 cm^{-1} and fixed probing at $\nu = \nu_{pu}$ (a) and ν = 3150 cm^{-1} (b); experimental points, calculated lines. Dotted line: coherent signal contribution, thin solid and dashed line: HDO close to and more distant to the solvated ions. (c): Energy level scheme used for the fitting of the measured signal transients taken at fixed probing frequencies. R% of the HDO molecules are considered to be close to the ions. Vibrational relaxation is calculated to proceed with one average time constant T_1* (dashed arrows). Thick arrow, excitation; thin solid and dotted arrows, probing transitions from the ground and first excited-state, respectively.

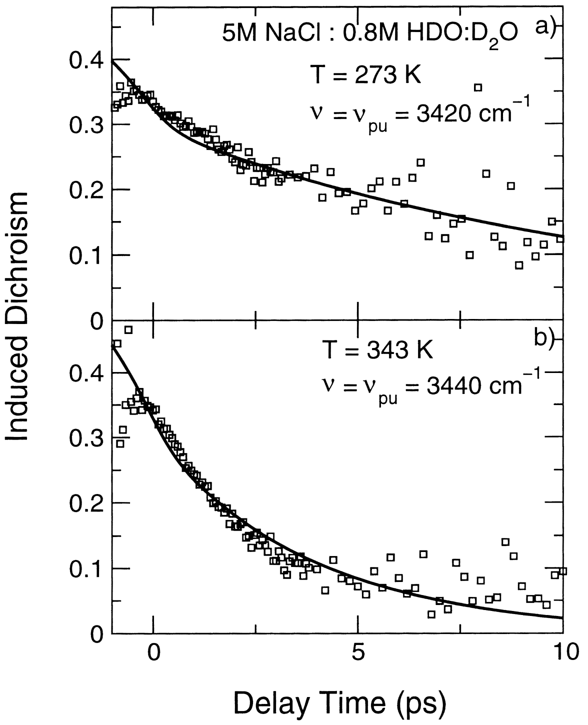

Fig. 4. Induced dichroism of an 5 M NaCl in 0.8 M HDO:D$_2$O sample with probing at the pump frequency of ν_{pu} = 3420 cm^{-1} (a, 273 K) and ν_{pu} = 3440 cm^{-1} (b, 343 K); experimental points, calculated lines.

to the ground state as the long time heating of the sample due to the deposited energy appears to be negligible. The redistribution time τ_s from level (1) to (2) is consistently attributed to spectral relaxation of the primarily excited molecules selected in their specific environment by the frequency position of the pump pulse. The reverse process (2) → (1) is included assuming detailed balance. τ_s is inferred from additional transient spectra (data not shown) taken at the same excitation frequency and different delay times. From consistently fitting of the transient spectra with a set of Gaussians related to preferred spectral components[5] and plotting the peak amplitudes of the latter versus delay time, we obtain τ_s. Due to spectral relaxation distinct spectral components show different temporal evolutions which can be determined by fitting of these data with the help of the mentioned energy level scheme. The simplification $\tau_{10} \simeq \tau_{20} = T_1$ is introduced in general in the data analysis while the latter time constant denotes an average population lifetime of the OH-stretching mode of HDO. In a simplified picture our signals now consists of two contributions: HDO in a modified structure around the ions and HDO in the neat, deuterated water structure. Consequently R% of the HDO molecules are considered to be affected by the presence of the close by ion with corresponding energy levels 1′, 2′ and time constants T_1^*, τ_s*. The remainder equals HDO molecules in an D$_2$O environment with already known dynamical properties.[5–7,12] The latter data are listed in the first and fifth row of Table 1. From fitting of the data (solid line) with the help of the mentioned energy level scheme depicted in Fig. 3c we determine T_1^* = 2.4±0.2 ps. This demonstrates a significant vibrational lifetime lengthening for the OH-stretch of HDO due to the impact of the close by ions.

The dynamics of the HDO within the vicinity of the solvated ions is consequently known from fitting of the data taken on the saturated NaCl solution (data not shown, see row 4 and 9 of Table 1) and the only adjustable parameter for the fitting of samples with intermediate salt concentrations is the ratio R of HDO (R = 1: all HDO molecules are close by the ions). The

Table 1. The Vibrational Lifetime T_1^* of the OH-Stretching Vibration, the Time Constants for Spectral Relaxation (τ_s^*) and Reorientational Relaxation τ_{or}^* As Well as the Percentage R or HDO Molecules R Affected by the Ions Are Summarized Here. The Numbers Are Inferred from Numerically Fitting of the Data Taken at the Respective Samples and Temperatures. Accuracy of the Numbers: T_1^*±0.2 ps; τ_s^*±0.5 ps; τ_{or}^*±15%; R±20%

Sample	T_1^*/ps	τ_s^*/ps	τ_{or}^*/ps	R/%
0 M NaCl (273 K)	1.0	1.5	11	0
1 M NaCl (273 K)	2.7	2.0	12	16
3 M NaCl (273 K)	2.7	2.0	12	56
5 M NaCl (273 K)	2.7	2.0	12	100
2 M NaCl (298 K)	2.7	2.0	10	40
0 M NaCl (343 K)	1.4	1.0	3	0
1 M NaCl (343 K)	2.4	2.0	4	8
3 M NaCl (343 K)	2.4	2.0	4	50
5 M NaCl (343 K)	2.4	2.0	4	100

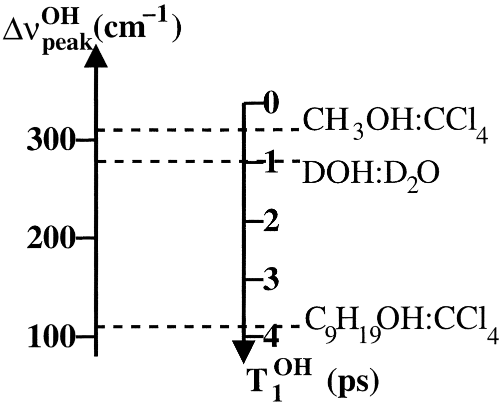

Fig. 5. Here we depict the lifetime of the OH-stretching mode for three different examples together with the OH-band peak shift $\Delta\nu_{peak}^{OH}$ between monomeric and associated species. Clearly a corresponding decrease of T_1 is noted with increasing overall strength of the H-bonds.

fitting of the data is indicated in Figs. 3a,b by the lines in different styles. Dotted line: coherent coupling artefact, dashed line and thin solid line: HDO more distant to and close to the ions. The best fit of the data is achieved with $R = 0.5$, $T_1^* = 2.4\pm0.2$ ps and $\tau_s^* = 2\pm0.5$ ps ($T_1 = 1.4\pm0.2$ ps and $\tau_s = 0.8\pm0.4$ ps for the corresponding partially deuterated water sample without NaCl).[12]

In the following we want to focus on the reorientational dynamics of the excited and probed OH-dipole, which can be investigated by determination of the induced dichroism of the sample. Corresponding data are depicted in Fig. 4 for a 5 M NaCl solution in 0.8 M $HDO:D_2O$. The data are plotted for probing at the excitation frequency at the center of the OH-band for sample temperatures of 273 K (a) and 343 K (b), respectively. At early delay times the same coherent artefact which is already indicated in Fig. 3a contributes to the measured induced dichroism resulting in a non-exponential decay of the signal. Clearly a remarkable speed up of the overall reorientational dynamics is concluded with increasing temperature from 12±2 ps (273 K) to $\tau_{or}^* = 4\pm0.5$ ps. Similar data have been taken at concentrations ranging from 1 M to 5 M for the two already mentioned sample temperatures of 273 K and 343 K and the results of the fitting procedure of the signal transients are summarized in Table 1.

In the discussion of the experimental results we will first concentrate on the lifetime of the OH-stretching mode of HDO. A clear vibrational lifetime lengthening is concluded for this vibrational mode as HDO molecules becomes neighbours of solvated ions: T_1 increases from 1 ps (neat water, 273 K) up to 2.7 ps (data not shown) by adding NaCl to the investigated water sample. In the case of the higher experimentally examined sample temperature of 343 K this lifetime lengthening reduces to a factor of 1.7 from 1.4 ps (neat water) up to 2.4 ps for a 5 M aqueous NaCl solution. Interestingly we find no impact of the concentration of the solvated ions on T_1: for all investigated samples with NaCl concentrations in between 1 M and 5 M we were able to fit the measured transients with the mentioned OH-lifetime within the experimental accuracy. In order to fit the data with the energy level scheme depicted in Fig. 3c we had however to adjust the fraction R of HDO molecules which are affected by the ions. R increases by addition of NaCl to the water sample from 16% (1 M, 273 K) up to 100% for an aqueous 5 M NaCl solution at 273 K. Somewhat smaller numbers are found for non-saturated salt solutions at the higher sample temperature of 343 K. The numbers stated here for the lifetime of HDO in partially deuterated water samples with NaCl are slightly longer compared to the ones published recently[8] and investigated by the same experimental technique at room temperature which may be due to the significantly higher excitation level adjusted in the latter experiments as well as the poorer spectral resolution. We propose the following relaxation scheme for the excited OH-stretching mode to account for the observed lifetime lengthening in aqueous salt solutions: the excited hydroxilic stretching mode relaxes dominantly via excitation of hydrogen bridge bond vibrations ν_{HB}. The stronger the H-bonds, the stronger the anharmonic coupling of the bridge bond vibrations to the OH-mode and the more effective this relaxation channel is. This can be seen for HDO and alcohols in solution as illustrated in Fig. 5. In this figure the experimentally determined T_1 is shown together with the corresponding peak shift $\Delta\nu_{peak}^{OH}$ between the OH-absorption of the monomeric and associated species in the respective solvent. The alcohol $C_9H_{19}OH$ diluted in the solvent CCl_4 exhibits the smallest peak shift of the OH-band of 120 cm^{-1} as it associates to dimers, only.[16] For the proton donor a corresponding long T_1 of 3.6 ps has been reported.[17] In the case of the remarkably stronger H-bonded water sample $HDO:D_2O$ we find $\Delta\nu_{peak}^{OH} = 280$ cm^{-1} and a notably shorter $T_1 = 1$ ps.[5] Looking at the even stronger H-bonds present in associated methanol we find respective numbers[18] of 310 cm^{-1} and $T_1 = 0.6$ ps. Although there are only a few examples investigated of the impact of hydrogen bonds on T_1 of simple molecules as shown in Fig. 5, there is nevertheless a clear trend for OH-lifetime shortening with increasing H-bond strength. This can not be understood by simple Fermi-resonance arguments of relaxation of the excited OH-stretch to other accepting modes like overtones of OH-bend or CH-stretch in the case of alcohols. It is more likely that the incresing strength of the anharmonic coupling of the OH-stretch to the low frequency hydrogen bridge bond vibration results in the latter being a more effective relaxation channel for the excited OH-stretch which was clearly shown[19] in the case of alcohol dimers. Further experiments are needed to clarify this interesting question into more detail. Looking at Fig. 2 it is clearly seen, that the OH-absorption related to H-bonds towards the anions and centred at 3420 cm^{-1}, are 115 cm^{-1} blue shifted in comparison to the neat water, i.e. the H-bonds between HDO and the anions are really notably weaker in respect to the situation in bulk water giving rise for the longer T_1 in the NaCl sample. The decreasing effect of the ions on T_1 of the neighbouring HDO molecules at higher sample temperatures of 343 K can be understood in the following way recalling results from for example NMR-experiments on respective samples. With increasing temperature the disturbance of the H-bonded water network around the structure breaking anion Cl^- reduces as the water network itself gets weaker. This results first in the lengthening of T_1 up to 1.4 ps at 343 K for the neat water as hydrogen bridge bond vibrations display a not so effective relaxation channel for the excited OH-mode any more due to the overall weakening of the H-bonds. Consequently the anions introduces at higher temperatures only a minor disturbance to the surrounding water molecules: from NMR-experiments it is even known that at higher temperatures the structure breaking Cl^- can change in function to a structure maker for the water above $\approx$310 K.[14] At the end of this discussion we have however to recall, that from our investigations it is not really clear, what is the impact of the cation on the vibrational dynamics of the OH and this will be subject to further investigations.[20]

Further on we will concentrate in our discussion on the data inspecting the reorientational motion of the excited OH-dipole. Looking at the results for the different partially deuterated water samples listed in Table 1, one infers only a slight lengthening of τ_{or} while adding NaCl to the sample. An increase is found from an average number of 11 ps determined at 3420 cm^{-1} for the neat water up to 12 ps for the aqueous salt solutions ($T = 273$ K) and from 3 ps to 4 ps at 343 K, respectively. These numbers correspond to an average value of the reorientational motion of the OH-group as it most probably represent a mix up of slower and faster reorienting OH-groups in hexagonal and weak hydrogen bonding situations.[5,12] Comparison of the shorter time constant measured at higher temperatures of 343 K is possible with results of transient IR-spectroscopy on water monomers in different solutions, where $\tau_{\mathrm{or}} \simeq 2$ ps was reported in the case of weak hydrogen-bonds,[21] i.e. at the higher sample temperature investigated here a significant portion of the water molecules exhibits weak H-bonds which do not effectively hinder reorientational motion. The slight increase of τ_{or} with the presence of Na^+ and Cl^- ions is best understood by comparison of our results with data of NMR-spectroscopy of aqueous salt solutions.[22,23] From the latter investigations for the structure breaking Cl^- a decrease of τ_{or} is inferred[23] by 10% while the structure making Na^+ results in a slowed down reorientational dynamics of the close to water molecules by a factor[22] of 1.4. Our results on τ_{or} of HDO close by the ions is consequently the sum over HDO molecules close to the two different ions with opposite effect on this time constant. From our data obviously the impact of the structure making Na^+ ions on τ_{or} is more pronounced than the one of the anions. We will perform in the near future further investigations to unravel the two opposite influences of the added salts on τ_{or} of water more clearly. Closely related to the slowing down of reorientational motion of the HDO affected by the ions in the water we find a similar increase of τ_{s} describing structural relaxation between the two preferred local structures seen in the partially deuterated water sample.[5,12] This time constant is a result of the decomposition of transient spectra taken on the mentioned samples at different delay times with Gaussian spectral bands (data not shown). Plotting the maximum peak amplitudes of the latter spectral components versus delay time and fitting of the data with numerical calculations as shown in Fig. 3c yields the time constant for spectral relaxation,[5] which equals in our case structural relaxation between two preferred local structures.[12] Correspondingly to the case of reorientational motion described above, we find an increase of τ_{s} by addition of salts to the partially deuterated water sample by about 30% while one has to keep in mind the limited accuracy for the latter time constant of ± 0.5 ps. Again the impact of the structure making Na^+ cations is better seen in this kind of experiments with respectively slowed down local dynamics of the water molecules surrounding the cation. In principle the larger reorientation times compared to τ_{s} suggest that the rearrangement of the water structure is only partially due to angular changes but considerably supported by translational motion, i.e., variation of O···O distances of H-bonds.

Finally we want to comment on the ratio R, describing the percentage of HDO molecules affected by the added ions to the water sample. This number is a fit parameter in order to adjust the faster populational dynamics seen in the neat water sample in respect to the slower dynamics for HDO close to the ions. The corresponding energy level scheme is depicted in Fig. 3c and results of the fitting procedure are shown in Figs. 3a and b as thin dashed (neat water) and solid (HDO in the surrounding of the ions) lines. At the mentioned concentration of 3 M NaCl and $T = 343$ K half of the HDO molecules are in the vicinity of the solvated ions. For almost saturated NaCl solutions of 5 M we can not identify any contribution of HDO which is not affected by the ions from our experimental accuracy and this is in well correspondence to a most probable coordination number of 6 and 7 for Na^+ and Cl^-, respectively, as deduced from neutron scattering[13] and theoretical calculations.[15,24] An open question is a possible preference of the HDO to the cations or anions which could result in a non-statistical distribution of HDO in the aqueous salt solution. We found however from our investigations no hints towards this.

Conclusions

In conclusion we have demonstrated an overall slowed down dynamics of HDO which is in the vicinity of Na^+ and Cl^- ions in a $\mathrm{D_2O}$ sample. T_1 increases up to 2.7 ps at 273 K and 2.4 ps at 343 K for an aqueous NaCl solution while simultaneously reorientational motion and structural relaxation slows down from 11 ps (3 ps) to 12 ps (4 ps) for the two investigated sample temperatures of 273 and 343 K, respectively. The vibrational lifetime lengthening is most probably related to an overall weakening of the H-bonds of the water molecules surrounding the anions while the slower reorientation shows clearly the impact of the structure making cations on the surrounding HDO.

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