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Vibrational relaxation of liquid water in ionic solvation shells

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Abstract

Femtosecond two-color pump–probe spectroscopy is used to measure the vibrational lifetime of the O–H stretch vibration in solutions of KF, NaCl, NaBr, and NaI in HDO:D_2O. We observe a slow component (roughly 2–4 times slower than in HDO:D_2O) in the decay of the absorption change, which is due to O–H groups that are hydrogen bonded to the dissolved anions. The time constant of this slow component depends on the nature of the anions and is observed to decrease with temperature, in contrast with the temperature dependence of the relaxation of the OH stretch vibration in pure HDO:D_2O.

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1. Introduction

In early studies on the effect of electrolytes on the infrared absorption bands of water, it was concluded that the hydrogen-bonded structure of water becomes disrupted upon addition of salt [1–3]. At the same time, a new type of hydrogen bond emerges, involving the anions. Seemingly, two types of O–H groups are present in an aqueous salt solution: water-bonded O–H groups, in which the hydrogen atom is hydrogen bonded to the oxygen atom of another water molecule, and anion-bonded O–H groups, where the hydrogen atom is involved in a hydrogen bond to the anion. The latter O–H group can absorb at a different frequency, because the O–H stretch frequency depends on the type and strength of the hydrogen bond [4,5]. As a result, the broad O–H stretching band in salt solutions is inhomogeneous and consists of a water-bonded part, which is almost the same for all solutions, and an anion-bonded part.

Unfortunately, the information that can be obtained on the structure and dynamics of the solvation shell by linear spectroscopy is rather limited. One can subtract the bulk-water contribution from the total spectrum in the O–D or O–H stretch region, to obtain a difference spectrum that represents the absorption of the anion-bonded O–H groups [6]. However, the possible contributions from the cations and from bulk-water disturbances are also contained in this difference spectrum. In addition, as in pure liquid water, this difference spectrum may well be inhomogeneously broadened, in which case no information on the dynamical behavior of solvation shells can be obtained from the linewidth.

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In previous publications [7–10], it was demonstrated that two-color mid-infrared pump–probe spectroscopy is a powerful tool to investigate the dynamical behavior of solvation shells. The strength of this method lies in the much longer lifetime (T_1) of the O–H stretch vibration of anion-bonded water molecules as compared to that of other water molecules, including those in the cation's solvation shells [7–9]. A different interpretation of the long-lifetime component was recently presented by Laenen et al. [10]. However, due to a poor signal-to-noise ratio, their results are doubtful, as was shown in [11].

The relatively long lifetime of the anion-bonded O–H groups enables a selective study of the water molecules in anionic solvation shells. It was shown that these shells form relatively rigid structures: the distance from the ion to a particular solvating molecule changes on a time scale that is 20–30 times longer than the intermolecular motion in pure water [7,8]. The rotational dynamics of the solvation cages were found to be similarly slow [9]. In the present work, we study the mechanism of the vibrational-energy relaxation of the anion-bonded O–H groups.

2. Experiment

We performed two-color mid-infrared pump–probe experiments on solutions consisting of 3 or 6 M of salt (KF, NaCl, NaBr, and NaI) and less than 1 M of HDO in D_2O. KF is used instead of NaF because the solubility of the latter salt is too low, approximately 1 M. In the experiment, the pump pulse excites the O–H stretch vibration of a subset of the molecules, characterized by their absorption frequency. The probe pulse measures the induced transmission change ((T/T_0), with T as the transmission with, and T_0 the transmission without the pump pulse) at a certain frequency.

The mid-infrared pulses are generated using the 800 nm pulses from a commercial 1 kHz Ti:sapphire RGA/multipass laser system (Quantronix Titan) using parametric light conversion processes. First, in an optical parametric generation and amplification stage based on a BBO crystal, part of the 800 nm is used to generate 1250 nm (signal)

and 2200 nm (idler) wavelengths. The idler is frequency-doubled in BBO, obtaining a 1100 nm pulse that is used as a seed pulse in the final conversion step, where a fresh part of the 800 nm light is converted into 1100 and 3000 nm light using a 5 mm KTP crystal.

Pump and probe pulses are independently produced using the above conversion scheme, enabling the independent tuning of their frequencies. The polarization of the probe pulse was set at the magic angle (54.7°) with respect to the pump polarization; in this way, the measured signals are not affected by the reorientational motion of the excited molecules. The spectral widths of the pump and probe pulses were approximately 80 and 60 cm^{-1}, respectively. The pump pulses have an energy of typically 20 μJ, the energy of the probe pulses is about 1 μJ. The cross-correlation trace typically has a width of 350 fs. Variation of the pump energy leads only to a change in signal amplitude, and does not influence the dynamics. A detailed description of the data acquisition can be found in [12].

3. Results

In Fig. 1, infrared spectra of the O–H stretching band of protonated heavy water (HDO:D_2O), and those of different salt solutions (KF, NaCl, NaBr, and NaI) in HDO:D_2O are shown. The O–H stretching band of the HDO:D_2O solution is centered at 3410 cm^{-1}; upon dissolution of salt this band shifts to the blue (NaCl, NaBr, and NaI), or slightly to the red (KF).

In the experiments on KF, NaCl, NaBr, and NaI, the pump frequency was tuned to the approximate center of the $0 \rightarrow 1$ transition (3450 cm^{-1}), and the probe frequency to the $1 \rightarrow 2$ transition (3200 cm^{-1}). At these particular pump and probe frequencies, the measured signals are quite insensitive to spectral diffusion of the O–H stretch vibration [13,14]. In previous work [7,8,11], we found that the spectral diffusion of the anion-bonded O–H groups is slow and only becomes observable when the pump frequency is in the wings of the absorption band and when the probe is tuned through the $0 \rightarrow 1$ absorption spectrum. If
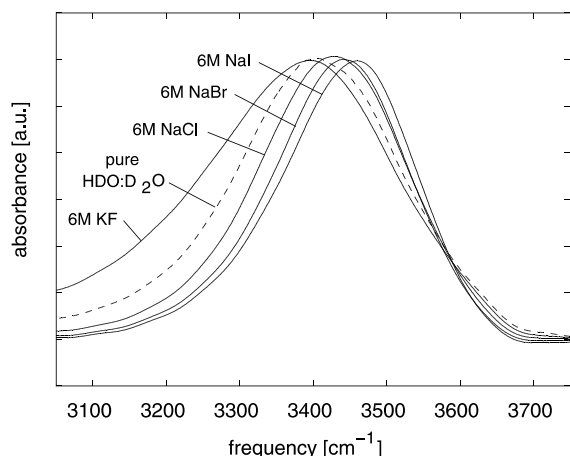
Fig. 1. The O–H stretch absorption spectrum of solutions of 6 M of NaI, NaBr, NaCl, and KF, respectively, and less than 1 M of HDO, dissolved in D_2O. Also shown is a solution containing no salt. The D_2O background is subtracted.
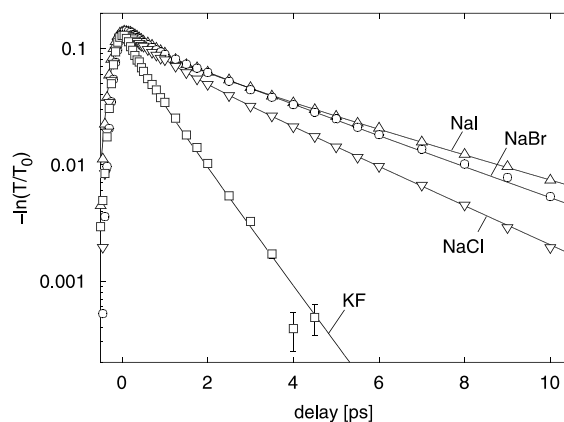

Fig. 2. Room temperature isotropic pump–probe scans of 6 M solutions of KF, NaCl, NaBr, and NaI, and bi-exponential fits described in the text. The pump frequency was 3450 cm^{-1}, the probe frequency was 3200 cm^{-1}. For a solution of KF, the decay is almost identical to that of pure HDO:D_2O.

the probe is resonant with the $1 \rightarrow 2$ absorption, spectral diffusion effects are not observed, probably because the spectral diffusion is slow, and because each particular probed $1 \rightarrow 2$ frequency corresponds to a broad distribution of $0 \rightarrow 1$ frequencies. We observed that changing the pump and probe frequencies within a range of 100 cm^{-1} did not change the results. The measured dynamics thus directly represent the vibrational relaxation of the O–H stretch vibration.

In Fig. 2, pump–probe measurements of 6 M solutions of KF, NaCl, NaBr, and NaI are shown. Clearly, for the solutions of NaCl, NaBr, and NaI, the signals decay non-exponentially, showing a fast and a slow component. The pump–probe signal can be modeled well with a sum of two exponential functions, convolved with the crosscorrelation trace; the fits using these functions are shown in the figure. The fast component decays with a time constant of approximately 800 fs that has been observed before for pure, i.e., containing no ions, HDO:D_2O [15]; the slow component decays much slower (e.g., 2.6 ps for NaCl). The time constant of the fast component is the same for all solutions. The time constant of the slow component depends on the dissolved salt, and increases with the anion mass. The relative amplitude of the slow component scales with the salt concentration,

and agrees with the amplitude to be expected from the solvation number and the cross section of the two components. Interestingly, for the solution containing KF, no slow component is observed; the signal decays with a time constant similar to that in pure water. It is very unlikely that this absence of a slow component in the KF solution is due to the potassium cation, since we previously
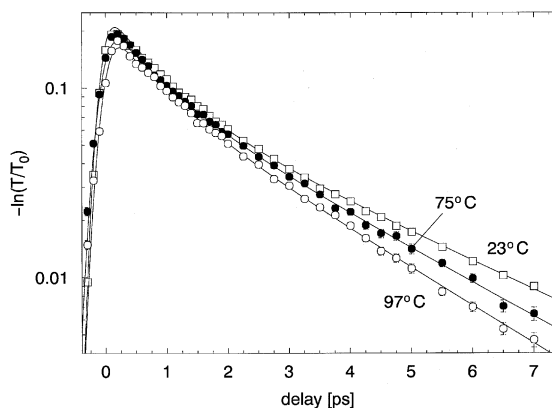

Fig. 3. Isotropic pump–probe scans of a solution of 3 M NaBr in HDO:D_2O at different temperatures, and bi-exponential fits described in the text. The pump frequency was tuned to 3450 cm^{-1}, the probe to 3200 cm^{-1}. The decay time constant (obtained by fitting to a bi-exponential function) decreases from 2.9 ps at room temperature to 2.3 ps at 97 °C.
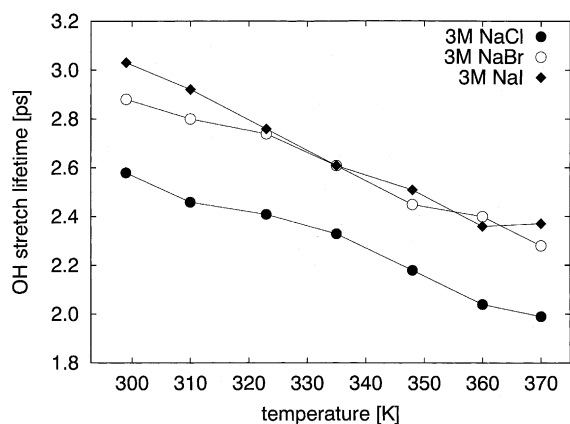
Fig. 4. The O–H stretch vibrational lifetime of anion-bound water molecules as a function of temperature for 3 M solutions of Cl⁻, Br⁻, and I⁻ in liquid water. The lifetimes are obtained by fitting the data to a bi-exponential function. The uncertainty is approximately 0.1 ps.

showed that solutions of NaCl and KCl are identical for this experiment [11].

In Fig. 3, the absorption change is plotted as a function of time delay for a 3 M solution of NaCl at several temperatures between room temperature and 106 °C. The sample was continuously rotated to avoid accumulated heating. In Fig. 4, the anion-bound O–H stretch lifetimes of Cl⁻, Br⁻, and I⁻ are shown as a function of temperature. We observe that the vibrational lifetime decreases with temperature.

4. Discussion

A few conclusions can be drawn from the data presented in Figs. 2–4. First, the slow component in the vibrational relaxation depends on the anion species (Figs. 2 and 4). Second, the slow component becomes faster when the temperature is increased (Figs. 3 and 4).

For a solution of pure HDO:D$_2$O, it was found that the hydrogen bond plays an important role in the relaxation of the O–H stretch vibration [15,16]. The excited O–H stretch relaxes via excitation of the hydrogen bond or by transferring its energy to a combination tone of the hydrogen-bond vibration and the bending vibration [14]. For the salt solutions studied here, the vibrational lifetime is found to depend on the nature of the anion, which indicates that again the hydrogen bond, in this case to the anion, plays a substantial role in the relaxation of the anion-bonded O–H groups.

There exists a strong correlation between the frequency of the O–H stretch vibration and the vibrational lifetime: the O–H stretch lifetime has been found experimentally to increase with frequency [17]. The relation between the frequency and lifetime of the O–H stretch vibration has also been studied theoretically [18–20]. The existing theories are not capable of fully describing vibrational relaxation, but they may be used in the present context to elucidate the trends we observe in our data.

In the analytical theory developed by Staib and Hynes [19], vibrational relaxation in an isolated O–H···O system is described with Fermi's 'golden rule', using Lippincott–Schroeder potentials for the covalent bond and for the hydrogen bond. The coupling between the hydrogen bond and the O–H stretch vibration is described adiabatically, with a non-adiabatic coupling term giving rise to vibrational relaxation. This non-adiabatic coupling is smaller for longer and weaker hydrogen bonds, resulting in longer O–H stretch lifetimes. The linear spectra in Fig. 1 show that the O–H stretch frequency increases going from pure water to solutions containing F⁻, Cl⁻, Br⁻, or I⁻, which indicates that the hydrogen-bond interaction decreases in this series. Hence, the observed increase of T_1 in the series F⁻, Cl⁻, Br⁻, I⁻ can be explained qualitatively from a decrease of the anharmonic interaction between the O–H stretch and the O–H···X⁻ hydrogen bond.

An additional effect is that the reduced mass increases in the series F⁻, Cl⁻, Br⁻, I⁻. In the theory of Staib and Hynes, the non-adiabatic coupling responsible for the energy transfer is inversely proportional to this reduced mass. Thus, the increase of T_1 in the series F⁻, Cl⁻, Br⁻, I⁻ can be explained from a decreased anharmonic coupling due to a weakening of the hydrogen bond, and from the reduced mass of the hydrogen-bond oscillator. For O–H···F⁻ both the O–H stretch frequency and the reduced mass of the hydrogen bond are similar to those of the O–H···O system, which explains why T_1 of O–H···F⁻ is observed to be similar to that of HDO:D$_2$O.

For the temperature dependence of the relaxation rate of the O–H stretch vibration in hydrogen-bonded systems, two counteracting effects are important. First, the hydrogen bond becomes longer and weaker (as indicated by the blue shift of the O–H stretch frequency) when the temperature increases, which leads to an increase of the vibrational lifetime [19]. Second, increasing the temperature leads to a higher average occupation number of the accepting modes. The relaxation rate is, applying Fermi's 'golden rule', proportional to $|\langle f|H_c|i\rangle|^2$, where i, f denote the initial and final states of the system, and H_c denotes the coupling terms in the Hamiltonian. For a single accepting harmonic oscillator with vibrational coordinate x that takes k quanta in the relaxation process, the matrix element $\langle n|x^k|n+k\rangle$ increases with n, because the wavefunctions for higher n are more spatially extended. If the frequency of the accepting mode is smaller than, or of the order of, kT, as is the case for the hydrogen-bond mode, n will show a significant temperature dependence. In this case, a temperature increase leads to a decreased lifetime of the vibration.

Previous work on liquid water (i.e., HDO:D$_2$O) [15] showed that the non-salted O–H stretch lifetime increases with temperature. Apparently, for liquid water, the effect of the weakening of the hydrogen-bond interaction with temperature is dominant in the temperature dependence of the relaxation rate. In [15], the O–H stretch frequency (as a measure for the hydrogen-bond strength) as a function of temperature was used in combination with the theoretical dependence of the vibrational lifetime on the O–H stretch frequency by Staib and Hynes [19]. By using only the frequency shift of the O–H stretch with temperature, the data could be quite well described over the whole temperature range (30–363 K). However, a close observation of the data of [15] shows that the measured increase of the lifetime with temperature is somewhat less steep than what the theory predicts based on the frequency shift alone. This difference may be attributed to the neglect of the change of accepting-mode occupation numbers with temperature.

For the O–H$\cdots$X$^-$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$) hydrogen-bonded systems, we observe that the lifetime *decreases* with temperature. In order to

understand this opposite temperature dependence of the lifetime, we compared the temperature dependence of the O–H stretch absorption spectrum of the O–H$\cdots$O oscillators measured for HDO:D$_2$O (without the D$_2$O background) with that of the O–H$\cdots$I$^-$ oscillators measured for a solution containing 6 M NaI. The latter spectrum is a difference spectrum of a solution of 6 M NaI, 1 M HDO and D$_2$O, and D$_2$O containing 6 M of NaI and pure D$_2$O, from which the difference spectrum of HDO in D$_2$O and pure D$_2$O was subtracted. A small residual broadening due to bulk-water disturbance, or due to cation solvation may still be present [7,8]. The spectra are shown in Fig. 5. For the O–H$\cdots$O oscillators of pure water, the O–H band shows a strong blueshift of about
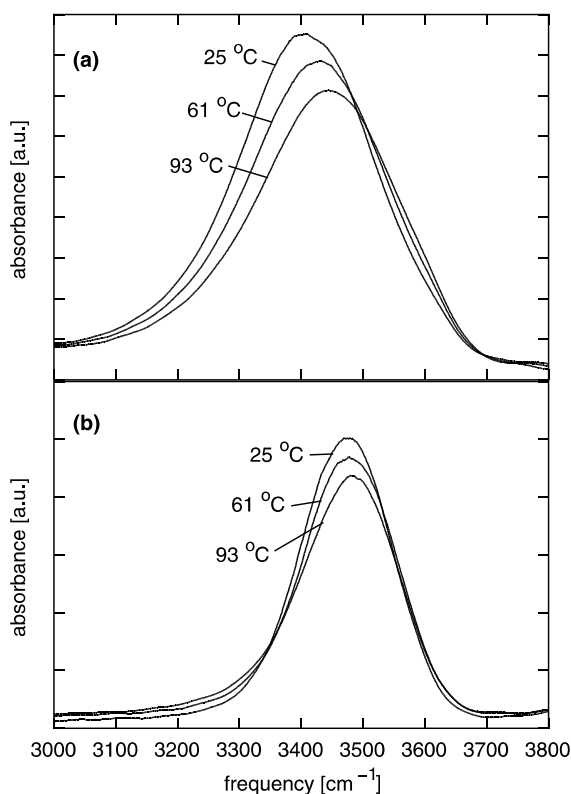

Fig. 5. Spectra of the O–H stretch vibration of HDO:D$_2$O (the D$_2$O background was subtracted, panel A) and of a solution of 6 M NaI in HDO:D$_2$O (background D$_2$O and bulk O–H band were subtracted, panel B) at three temperatures. For HDO:D$_2$O the band shifts to the blue by about 50 cm^{-1}, the O–H$\cdots$I$^-$ band shifts only by approximately 10 cm^{-1}.

50 cm^{-1} when the temperature is increased from room temperature to 93 °C. In contrast, the O–H stretch band of O–H$\cdots$I$^-$ oscillators shifts by only 10 cm^{-1} in this temperature range. Hence, the lifetime-increasing effect of the O–H stretch frequency shift is much weaker for the salt solution, so that the dominant effect in the temperature dependence of the O–H stretch lifetime is now formed by an increased occupation number of the accepting hydrogen-bond mode, which leads to a decrease of the lifetime.

5. Conclusions

We performed femtosecond mid-infrared pump–probe spectroscopy on the O–H stretch vibration of water molecules in aqueous salt solutions. The transients decay in a bi-exponential manner, with a fast component that originates from O–H$\cdots$O groups (all O–H groups that are hydrogen bonded to another water molecule), and a slow component due to O–H$\cdots$X$^-$ groups (i.e., O–H groups that are hydrogen bonded to Cl$^-$, Br$^-$ or I$^-$). For F$^-$, no slow component was observed. The increase in vibrational lifetime of the O–H$\cdots$X$^-$ group (X$^-$ = F$^-$, Cl$^-$, Br$^-$, or I$^-$) results from the decreased hydrogen-bond interaction, and from the decreased frequency of the hydrogen-bond mode.

We observe that the O–H$\cdots$X$^-$ lifetime becomes shorter when the temperature is raised. This behavior is expected on theoretical grounds, and is observed for most molecular vibrations, except for the O–H stretch in bulk water, for which the vibrational lifetime increases with temperature. This opposite behavior can be explained from the much stronger temperature dependence of the hydrogen-bond interaction for bulk water than for water in an ionic solvation shell.

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