

# Vibrational dynamics of the bending mode of water interacting with ions.

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## Abstract

We studied the vibrational relaxation dynamics of the bending mode ( $\nu_2$ ) of the H<sub>2</sub>O water molecules in the presence of different salts (LiCl, LiBr, LiI, NaI, CsI, NaClO<sub>4</sub> and NaBF<sub>4</sub>). The linear and nonlinear spectra of the bending mode show distinct responses of water molecules hydrating the anions. We observe that the bending mode of water molecules that are hydrogen-bonded to an anion exhibit much slower relaxation rates ( $T_1 \sim 1$  ps) than water molecules that are hydrogen-bonded to other water molecules ( $T_1 = 400$  fs). We find that the effect of the anion on the absorption spectrum and relaxation time constant of the water bending mode is not only determined by the strength of the hydrogen-bond interaction but also by the shape of the anion.

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## I. INTRODUCTION

Water is rarely encountered as a pure liquid, and usually contains dissolved (bio)molecules and ions.<sup>1,2</sup> The interactions between water and the dissolved ions and molecules can lead to completely different molecular motions and energy dynamics of the solvating water molecules compared to water in the pure liquid.<sup>3-5</sup> In turn, these different dynamics of the water solvating will have an effect on the conformations and the (bio)chemical reactivity of the dissolved molecules and ions.<sup>1</sup>

The dynamics of the OH stretch vibrations of water molecules solvating ions have been studied extensively with femtosecond mid-infrared spectroscopic techniques.<sup>3,4,6,7</sup> For water molecules hydrating halogenic anions like  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  it was found that the vibrational lifetime of the OH stretch vibration is significantly longer than for water molecules in bulk liquid water. It was also observed that water in the hydration shells of ions often show a much slower reorientation, depending on the strength of the interaction of the ion with the water.<sup>3,4,7</sup>

In most of the experimental and theoretical studies of the properties of water hydrating ions, the dynamics are probed via the response of the OH stretch vibrations ( $\nu_1$ ,  $\nu_3$ ) of the water molecules. Here we probe the water dynamics via the bending mode ( $\nu_2$ ) of the  $\text{H}_2\text{O}$  water molecules. The bending mode exhibits similar properties as the OH stretch vibration in terms of the sensitivity of its vibrational frequency to the strength of the hydrogen bonds. Previous mid-infrared femtosecond studies of the bending mode of water focused on the vibrational relaxation mechanism of the bending mode of bulk water and its role in the vibrational relaxation pathway of the OD/OH stretch vibration.<sup>8-14</sup> It was found that the relaxation of the bending mode of bulk water (both of  $\text{H}_2\text{O}$  and HDO molecules in HDO: $\text{D}_2\text{O}$  isotopic mixture) is a two-step process consisting first of the depopulation of the excited state  $\nu=1$  of the bending mode and excitation of the lower frequency modes (librations), and second by the thermal equilibration of the vibrational energy over all intermolecular modes. The vibrational lifetime of the bending mode of  $\text{H}_2\text{O}$  in HDO: $\text{D}_2\text{O}$  was found to be  $T_1 = 380 \pm 50$  fs. The thermal equilibration had a time constant of  $\sim 1.2$  ps.<sup>9,11</sup> The same relaxation pathway was found for pure  $\text{H}_2\text{O}$ . Due to more efficient intermolecular coupling in comparison to the isotopically diluted mixture, however, both the vibrational lifetime and the thermalization are faster and show time constants  $T_1 = 170 \pm 30$  fs and  $T_{eq} = \sim 0.8$ -1 ps,

respectively.<sup>8,10</sup> No studies, however, have been reported on the vibrational dynamics of the bending mode of water in salt solutions. Since the vibrational coordinate of the bending mode is very different from that of the stretch vibrations, this mode presents an interesting, complementary probe of the interaction between water and ions.

## II. EXPERIMENT

We measure the vibrational dynamics of the bending mode of water molecules using polarization-resolved mid-infrared pump-probe spectroscopy. The femtosecond mid-infrared pulses needed for this experiment are generated by frequency conversion processes that are pumped with the near-infrared 800 nm pulses derived from a high energy Ti:Sapphire amplifier system. This system is a Coherent "Legend Duo" regenerative amplifier that delivers 40 fs pulses with a pulse energy of 7 mJ per pulse at a repetition rate of 1 kHz. We use about 5.5 mJ to pump an optical parametric amplifier (Light Conversion - High Energy TOPAS). The produced signal and idler pulses are used in a difference-frequency-mixing process in a silver-gallium-disulphide ( $\text{AgGaS}_2$ ) crystal, that generates pulses with a central wavelength of  $\sim 6000$  nm ( $\sim 1650$   $\text{cm}^{-1}$ ), a pulse duration of  $\sim 65$  fs, a pulse energy of 40  $\mu\text{J}$ , and a spectral bandwidth of  $\sim 350$   $\text{cm}^{-1}$ .

The generated infrared pulses are split into pump, probe, and reference beams. The probe and reference beams are split off from the broadband infrared pulse beam using two wedged  $\text{BaF}_2$  windows. The transmitted beam ( $\sim 92\%$ ) is used as the pump. The probe is sent into a 4 fs resolution delay stage. The pump and probe pulses are focussed onto the same spot in the sample using a gold-coated parabolic mirror. The reference pulse is also focused onto the sample by the same mirror, but not in overlap with the pump. After the sample, the probe and reference beams are dispersed with an Oriel monochromator and detected with an Infrared Associates  $2 \times 32$  pixels mercury-cadmium-telluride (MCT) detector array. The reference allows for a frequency-resolved correction of shot-to-shot fluctuations of the probe-pulse energy.

The pump pulse excites the bending mode of  $\text{H}_2\text{O}$  molecules from the ground state  $v = 0$  to the first excited state  $v = 1$  of the bending mode. This excitation leads to a bleach and stimulated emission at probe frequencies matching the  $v = 0 \rightarrow 1$  transition, and an induced absorption at probe frequencies matching the  $v = 1 \rightarrow 2$  transition. These transient changes

in absorption  $\Delta\alpha$  are monitored with the broadband IR probe pulse as a function of time delay between the pump and probe pulses.

Before entering the sample, the polarization of the probe is rotated at  $45^\circ$  with respect to the polarization of the pump using a wire-grid polarizer. After the sample the polarization component parallel or perpendicular to the pump is selected using a polarizer mounted in a motorized rotation stage. The thus obtained transient absorption changes  $\Delta\alpha_{\parallel}(t, \nu)$  and  $\Delta\alpha_{\perp}(t, \nu)$  are used to construct the so-called isotropic signal:

$$\Delta\alpha_{iso}(t, \nu) = \frac{\Delta\alpha_{\parallel}(t, \nu) + 2 \cdot \Delta\alpha_{\perp}(t, \nu)}{3} \quad (1)$$

The isotropic signal  $\Delta\alpha_{iso}(t, \nu)$  is not sensitive to depolarization of the excitation and gives information on the rate of vibrational energy relaxation and energy transfer.

The samples are solutions of LiCl, LiBr, LiI, NaI, CsI, NaClO<sub>4</sub> and NaBF<sub>4</sub> in water. We use a mixture of 1:2 H<sub>2</sub>O in D<sub>2</sub>O ( $\sim 11:44:44\%$  H<sub>2</sub>O:HDO:D<sub>2</sub>O) in order to minimize the intermolecular resonant energy transfer between water molecules while at the same time maintaining sufficient optical density for the H<sub>2</sub>O bending mode. The bending mode has a different resonant frequency for different isotopologues of water:  $\sim 1250$  cm<sup>-1</sup> for D<sub>2</sub>O,  $\sim 1450$  cm<sup>-1</sup> for HDO and  $\sim 1650$  cm<sup>-1</sup> for H<sub>2</sub>O.<sup>15</sup> This allows us to selectively excite the bending mode of the H<sub>2</sub>O molecules. We study salt solutions at the following concentrations: 10 m for solutions of LiCl, LiBr, LiI, CsI, and NaBF<sub>4</sub>, a series of 3 m, 6 m, 9 m and 12 m for LiI, and a series of 3 m, 6 m, 10 m and 14 m for NaClO<sub>4</sub>. The samples are placed between two 2 mm thick CaF<sub>2</sub> windows separated by a teflon spacer with a thickness of 50  $\mu$ m. During the experiments the experimental setup is constantly flushed with N<sub>2</sub> gas to prevent any influence of the absorption lines of ambient water vapor on the measured spectra and dynamics.

### III. RESULTS AND DISCUSSION

#### A. Linear spectra

In figure 1, we present linear absorption spectra of the OD-stretch vibration and the bending mode for solutions of 10 m of different salts in a D<sub>2</sub>O/H<sub>2</sub>O mixture. The top panel presents the linear spectra of the OD-stretch vibration of salt solutions in a 1:7 D<sub>2</sub>O/H<sub>2</sub>O

mixture, and the bottom panel shows the linear spectra of the  $\text{H}_2\text{O}$  bending mode for salt solutions in a 1:2  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture. For comparison also the spectra of the pure  $\text{D}_2\text{O}/\text{H}_2\text{O}$  mixtures are shown (without salt). For clarity all linear spectra are corrected (by subtraction) for the background signal of the broadband librational band. The addition of salts leads to a blueshift of the absorption spectrum of the OD stretch vibration. This blueshift can be explained from the fact that the hydrogen bonds between water molecules and halide anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) are weaker than between water molecules.<sup>5</sup> The hydrogen bond to the anion becomes weaker within the halogenic series  $\text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$ , and thus the blueshift increases, as illustrated in the top panel of figure 1. In the cases of the very weak hydrogen bonds between water molecules and hydrated  $\text{ClO}_4^-$  and  $\text{BF}_4^-$ , the absorption band of the OD stretch mode even splits into two, with a high frequency subband (rather than a shift) at  $\sim 2650 \text{ cm}^{-1}$ .<sup>16,17</sup> This subband corresponds to water molecules hydrating  $\text{ClO}_4^-$ .

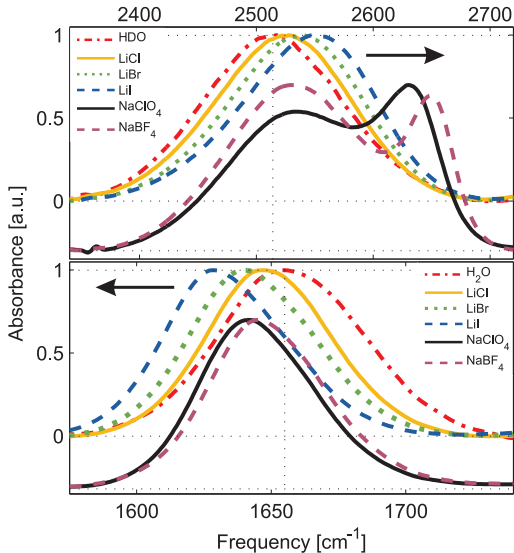


FIG. 1: Normalized linear absorption spectra of the OD stretch vibration of HDO molecules in 10 m salt solutions of LiCl, LiBr, LiI, NaClO<sub>4</sub>, NaBF<sub>4</sub> in a  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (1:7) mixture (top panel), and of the  $\text{H}_2\text{O}$  bending mode in 10 m salt solutions of LiCl, LiBr, LiI, NaClO<sub>4</sub>, NaBF<sub>4</sub> in a  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (1:2) mixture (bottom panel).

The lower panel of figure 1 shows that the addition of salts leads to a red shift of the vibrational frequency of the bending mode of  $\text{H}_2\text{O}$ . This redshift demonstrates the opposite effect of hydrogen-bond formation on the frequencies of the stretch vibrations and the bend vibration of water. The redshift of the bending mode increases in the halogenic series

$\text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$ , in line with the weakening of the  $\text{O}-\text{H} \cdots \text{X}^-$  hydrogen bond in this series. Interestingly, for the multiatomic  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  anions, the bending mode frequency is similarly affected as for the other salts and shifts towards lower frequency. However, in contrast to the observations for the OD-stretch vibration, the  $\text{H}_2\text{O}$  bending mode spectrum remains a single band. In fact the absorption spectra of the  $\text{H}_2\text{O}$  bending mode in  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  solutions resembles very much that of a  $\text{Br}^-$  solution, and is less redshifted in comparison to that of an  $\text{I}^-$  solution.

In figure 2 we show absorption spectra for pure water, LiI and  $\text{NaClO}_4$  solutions as a function of salt concentration. With increasing salt concentration, the bending mode spectra show a progressive redshift with respect to the pure  $\text{H}_2\text{O}$  bending mode spectrum. The bending mode spectrum of pure  $\text{H}_2\text{O}$  possesses a slight asymmetry that in previous studies has been described with two gaussians.<sup>18,19</sup> This asymmetry is however small compared to the asymmetry resulting from the addition of salts. Here we neglect the asymmetry of the pure  $\text{H}_2\text{O}$  bending mode spectrum and we fit the linear spectra of the salt solutions to a sum of two gaussian spectral profiles. In this fit the position of the two bands and their spectral widths are kept constant for spectra at different concentrations and only the amplitudes are varied. This approach provides an excellent fit of the spectra at all salt concentrations. This implies that the redshift of the overall absorption spectrum can be fully described in terms of two inter-converting water species that we tentatively assign to bulk and anion-bound water molecules.

The two gaussian bands used to describe the linear spectra at all concentrations are shown in figure 2 as solid black lines. For iodide associated water molecules we find a redshift of  $28 \text{ cm}^{-1}$ , and for water molecules interacting with perchlorate the redshift is  $21 \text{ cm}^{-1}$ . This observation is surprising, in view of the effect these two anions have on the frequency of the stretch vibrations of water (the blueshift for the perchlorate solution is larger than for the iodide solution). The bending mode frequency of  $\text{H}_2\text{O}$  appears to be less affected by the formation of a very weak hydrogen bond to  $\text{ClO}_4^-$  than by the formation of a less weak hydrogen bond to  $\text{I}^-$ .

By integrating the bands resulting from the global fit we obtain the populations of the bulk-like and anion-bound waters. In figure 3 we show the fraction of bulk-like water as a function of concentration for both LiI and  $\text{NaClO}_4$ . The population of the bulk-like water decreases with increasing salt concentration, whereas the anion-bound population increases

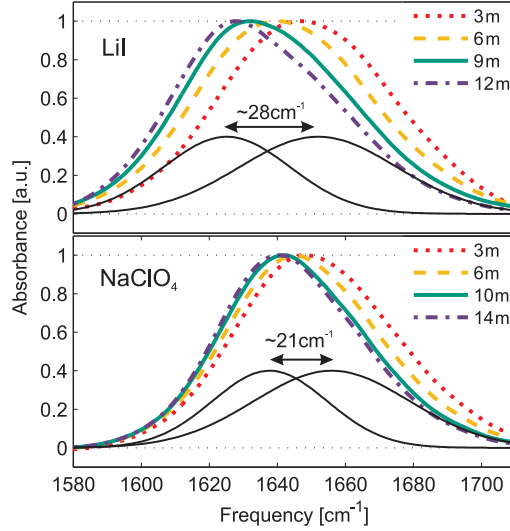


FIG. 2: Absorption spectra of the  $\text{H}_2\text{O}$  bending mode for different concentrations of LiI and  $\text{NaClO}_4$  in a  $\text{H}_2\text{O}/\text{D}_2\text{O}$  ( $\sim 1:2$ ) mixture.

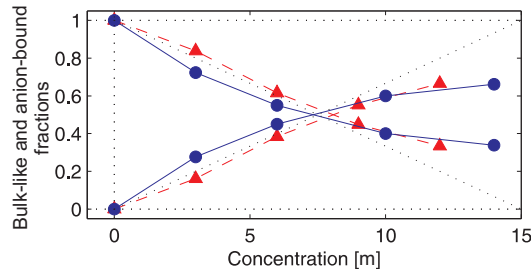


FIG. 3: Fractions of bulk and anion-bound water molecules for LiI (triangles, red) and  $\text{NaClO}_4$  (dots, blue), extracted from a global fit of the linear absorption spectra at different concentrations. The lines are guide to the eyes.

with increasing salt concentration.

To translate the spectral amplitudes to relative fractions of bulk-like and anion-bound water molecules, we need to know the ion concentration dependence of the bending-mode spectra of these species. We found that the cross-section of both species is larger by  $\sim 95\%$  for a solution of 12 m LiI and by  $\sim 110\%$  for a solution of 14 m  $\text{NaClO}_4$ . As the cross-section increase is the same for both species, the ratio of the spectral amplitudes directly represents the ratio of the bulk-like and anion-bound water at all salt concentrations.

For the highest concentrations measured (12 m for LiI and 14 m for  $\text{NaClO}_4$ ) we find that approximately 35% of the water molecules behave bulk like and do not form hydrogen

bonds with the anions. This means that for  $\sim 35\%$  of the water molecules both OH groups are bonded to other water molecules ( $\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{O}$ ), even at these very high concentrations. Assuming a statistical distribution of hydrogen bonds, this implies that  $\sim 60\%$  of the hydroxyl groups form  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds to a water molecule and  $\sim 40\%$  of the hydroxyl groups form  $\text{O}-\text{H}\cdots\text{X}^-$  hydrogen bonds to an  $\text{X}^-$  anion. From this distribution it follows that for  $\sim 48\%$  of the water molecules one O-H group is hydrogen bonded to an anion and the other O-H group is hydrogen bonded to a water molecule ( $\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{X}^-$ ). For  $\sim 16\%$  of the water molecules both O-H groups are hydrogen bonded to anions ( $\text{X}^-\cdots\text{H}-\text{O}-\text{H}\cdots\text{X}^-$ ). Hence, even at the highest salt concentrations, the bulk-like waters ( $\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{O}$ ) and the water molecules that are only singly hydrogen bonded to an anion ( $\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{X}^-$ ) dominate. The water molecules that are doubly hydrogen bonded to anions form a minority at all studied salt concentrations. This explains why at all concentrations the absorption spectrum of the water bending vibrations can be well described with only two interconverting bands. If the water molecules with two hydrogen bonds to anions had become important at high salt concentrations, a third, even more redshifted absorption component would have been expected to show up in the absorption spectrum.

Based on this estimation and the salt concentration we find that at high salt concentrations there are  $\sim 3 - 3.5$  H-bonds per anion. For the lowest concentration of 3 m approximately 85% (LiI) and 75% ( $\text{NaClO}_4$ ) of water molecules behave bulk like implying that  $\sim 8\%$  and  $\sim 13\%$  of hydroxyl groups are bonded to anion for LiI and  $\text{NaClO}_4$ , respectively. The hydration numbers for the low salt concentration are thus somewhat higher and amount to  $\sim 4$  and  $\sim 5$  H-bonds for LiI and  $\text{NaClO}_4$ , respectively.

## B. Vibrational energy relaxation dynamics

Figure 4 shows transient spectra at different delays after the excitation. The excitation is observed to result in a transient absorption decrease of the fundamental  $\nu = 0 \rightarrow 1$  transition between 1620 and 1680  $\text{cm}^{-1}$ , due to the depopulation of the  $\nu = 0$  state of the bending mode and  $\nu = 1 \rightarrow 0$  stimulated emission out of the excited  $\nu = 1$  state. At lower frequencies the signal changes sign and we observe the induced  $\nu = 1 \rightarrow 2$  absorption. The shape of the bleaching signal of the transient spectra follows the lineshape of the linear absorption spectrum. The nonlinear spectra of LiI clearly show the two subbands that were extracted



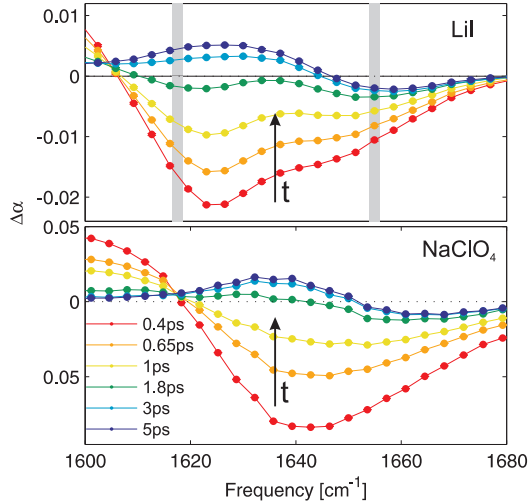


FIG. 4: Transient spectra of solutions of 12 m LiI and 14 m NaClO<sub>4</sub> as a function of delay time between the pump and probe pulses. The arrows indicate the time evolution of the amplitude of the spectra. The solid lines represent fits to the model described in the text. The two gray bars in the top panel indicate the frequencies for which the two delay traces in figure 5 are shown.

from the linear spectra. In the case of NaClO<sub>4</sub>, the overlap between the two subbands is larger, making the transient spectra appear as a broad single band. With increasing delay time the signals decay and the shape of the transient spectra invert. After  $\sim 5$  ps the spectrum does not change anymore and the observed spectral shape is a signature of an increase in sample temperature. An increase in sample temperature leads to a redshift of the fundamental absorption spectrum.<sup>15,20</sup> As a result we observe a negative signal at the blue side of the spectrum ( $>1650$  cm<sup>-1</sup>) and a positive signal at the red side of the spectrum ( $<1650$  cm<sup>-1</sup>). The increase in temperature reflects the equilibration of the bending mode excitation energy over the low-frequency librational and translational modes.

In figure 5 we show the transient absorption changes as a function of delay time for the frequencies indicated by the gray bars in the transient spectra of the LiI solution shown in figure 4. The dynamics at these frequencies are representative for the dynamics of the two subbands for LiI. Clearly the excitation at the red side of the spectrum (red) decays more slowly than the transient signal at the high-frequency edge of the spectrum (black). The vibrational relaxation of the anion-bound water molecules is thus approximately twice as slow as the vibrational relaxation of the bulk water species. The inset in figure 5 shows the same time traces on a logarithmic scale. For delays  $>300$  fs the data can be fit well with a

straight line, which implies that from this delay on the decays are single exponential.

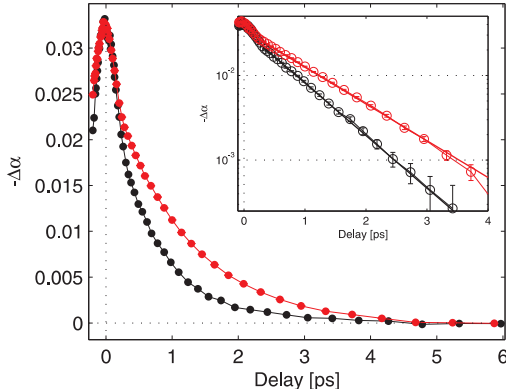


FIG. 5: Transient absorption change as a function of delay time between pump and probe for a solution of 12 m LiI at frequencies of  $1618\text{ cm}^{-1}$  and  $1655\text{ cm}^{-1}$  (indicated by the gray bars in figure 4). The inset shows the same delay traces on a logarithmic scale - the lines are single-exponential functions that serve as a guide to the eye.

Based on these observations we model the data with a model containing three transient spectral components: two spectra reflect the bulk-like and anion-bound water and one spectrum represents the change in the spectral response due to the thermal equilibration. Each of the spectral components is described as a product of its population dynamics  $N(t)$  and its associated spectral signature  $\sigma(\nu)$ . The isotropic data ( $\Delta\alpha_{iso}$ ) at all times and frequencies are thus described with the following equation:

$$\Delta\alpha_{iso}(t, \nu) = N_b(t) \cdot \sigma_b(\nu) + N_a(t) \cdot \sigma_a(\nu) + N_{0^*}(t) \cdot \sigma_{0^*}(\nu) \quad (2)$$

where the symbols in the subscript refer to bulk-like water ( $b$ ), anion-bound ( $a$ ) water band, and the heated final state ( $0^*$ ). We assume that the bulk and anion-bound water molecules relax independently with a single rate constant to the common final heated state. We find that this model describes the experimental data very well for LiI and  $\text{NaClO}_4$  solutions at all concentrations. The results of the fits are represented in figure 4 by the solid lines.

From the fit we can extract the transient spectra associated with each state. In figure 6 we show these spectra for a 12 m solution of LiI (top panel) and a 14 m solution of  $\text{NaClO}_4$ . The blueshifted (solid line) and redshifted (dashed line) spectra reflect the bulk-like and

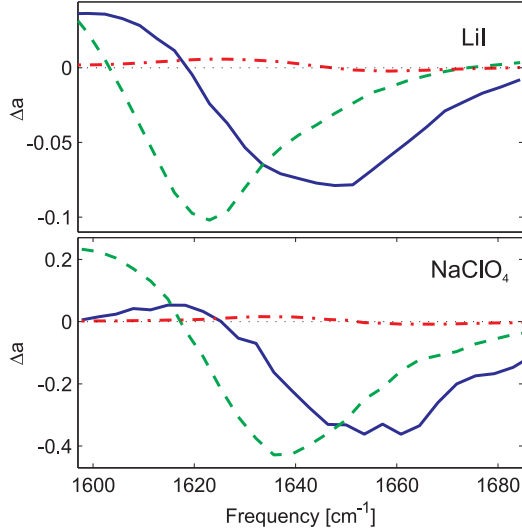


FIG. 6: Spectra extracted from the fit of the isotropic data to the three-level kinetic model. The solid line (blue) represents bulk-like water, the dashed line (green) represents anion-bound water, and the dash-dotted line (red) represents the final heated spectrum.

anion-bound water molecules respectively. The dashed-dotted line represents the transient spectrum of the final heated state. The frequency difference between the maxima of the bulk-like and anion-bound water bands is consistent with the frequency differences extracted from the analysis of the linear spectra ( $\sim 30 \text{ cm}^{-1}$  for LiI and  $\sim 20 \text{ cm}^{-1}$  for NaClO<sub>4</sub>).

In figure 7 we show the initial populations  $N_a(t = 0)$  and  $N_b(t = 0)$  as a function of concentration (triangles). Here it should be noted that we have assumed that the bulk-like and anion-bound water molecules have the same absorption cross section (defined as the integral of the bleaching component of the corresponding spectra). For comparison we also show the populations obtained from the fits of the linear absorption spectra at different concentrations (dots). The populations  $N_a(t = 0)$  and  $N_b(t = 0)$  are observed to correlate very well with the amplitudes of the subbands.

The decay rates of the bulk-like and anion-bound bands directly reflect the vibrational lifetimes of the two species. For all salt solutions, the bending mode of the anion-bound water molecules is observed to relax slower than the bending mode of the bulk-like water molecules. Water molecules bonded to Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> anions relax on a  $\sim 1 \pm 0.1$  ps timescale, whereas bulk-like water molecules have a lifetime of  $\sim 400 \pm 0.08$  fs. The water molecules bound to ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions relax slower ( $\sim 750 \pm 0.08$  fs) than bulk-like water molecules, but not

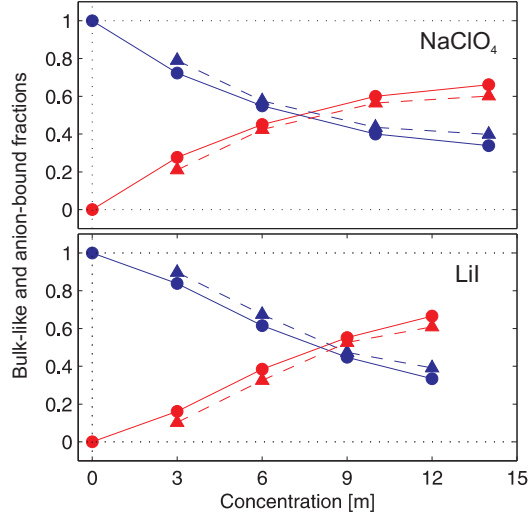


FIG. 7: Concentration dependent populations of the bulk-like (blue) and anion-bound (red) water for LiI and NaClO<sub>4</sub> solutions. The points (dots) connected by the solid lines represent the spectrally integrated absorption bands of each of the species that followed from the decomposition of the linear absorption spectra. The dashed lines connect the points (triangles) that are obtained from the fitting the transient spectra with the kinetic model described in the text.

as slow as water molecules bound to monoatomic anions. We also compared the vibrational relaxation dynamics of the bending mode for NaI and CsI salt solutions and we found no effect of the cation on the vibrational relaxation rates. As a reference we have also analyzed a pure H<sub>2</sub>O/D<sub>2</sub>O mixture (1:2), for which we find a vibrational lifetime of  $380 \pm 0.05$  fs, in excellent agreement with previous experimental results<sup>11,13</sup> and theoretical predictions.<sup>21</sup> Table I summarizes the vibrational lifetimes of both bulk ( $T_{1 \text{ HOH}\cdot\text{O}}$ ) and anion-bound ( $T_{1 \text{ HOH}\cdot\text{X}^-}$ ) water for all the studied salt solutions.

### C. Discussion

Both the linear and the transient spectra show that the addition of the multiaatomic ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions has less effect on the bending mode frequency than the addition of I<sup>-</sup>. For H<sub>2</sub>O hydrating ClO<sub>4</sub><sup>-</sup>, the bending mode shows a redshift of 20 cm<sup>-1</sup> with respect to bulk liquid water, whereas for H<sub>2</sub>O hydrating I<sup>-</sup> this redshift is 30 cm<sup>-1</sup>. This observation is surprising as ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> are observed to have a much stronger effect on the OD stretch vibrational frequency than I<sup>-</sup>. To understand this difference we need to look in more detail

TABLE I: Vibrational lifetimes of the bending mode of H<sub>2</sub>O in different salt solutions.

Sample	C [m]	T <sub>1</sub> <i>HOH...O</i> [ps]	T <sub>1</sub> <i>HOH...X-</i> [ps]
H <sub>2</sub> O	-	T <sub>1</sub> =0.38±0.05	-
	-	T <sub>eq</sub> =1.3±0.1	-
LiCl	10	0.40±0.08	0.94±0.12
LiBr	10	0.39±0.09	0.86±0.08
LiI	3	0.45±0.08	1.0±0.13
	6	0.42±0.06	1.03±0.1
	9	0.45±0.1	1.06±0.12
	12	0.47±0.08	1.10±0.09
NaI	10	0.35±0.07	1.03±0.08
CsI	10	0.43±0.05	0.97±0.1
NaClO <sub>4</sub>	3	0.35±0.08	0.81±0.1
	6	0.36±0.11	0.75±0.08
	10	0.41±0.08	0.72±0.07
	14	0.40±0.05	0.75±0.1
NaBF <sub>4</sub>	10	0.48±0.08	0.83±0.08

at the effect of the hydrogen-bond interaction on the frequencies of the OD/OH stretch vibrations and the bending mode of water.

For the stretch vibration, hydrogen-bond formation leads to a lowering of the vibrational frequency because the hydrogen bond weakens the O–H chemical bond within the water molecule. As a result of this weakening, the restoring force associated with stretching or compressing the O–H bond coordinate decreases, and thus the frequency of the stretch vibration decreases. For the bending mode, hydrogen-bond formation introduces an additional restoring force because the hydrogen bond will resist a rotation of the O–H group out of the linear O–H···O hydrogen-bonded system. An increase of the angle of the O–H group with respect to the O···O hydrogen-bond coordinate will weaken the hydrogen bond and thus has an associated energy cost that adds up to the potential energy curve of the bending mode of the unbonded H<sub>2</sub>O molecule. The presence of the hydrogen bond thus leads to a blueshift of the vibrational frequency of this mode. Due to this effect the frequency of the bending mode of H<sub>2</sub>O shifts from  $\sim 1600$  cm<sup>-1</sup> in the gas phase to  $\sim 1650$  cm<sup>-1</sup> in the liquid phase.

When the hydrogen bond between H<sub>2</sub>O molecules is replaced by the weaker hydrogen bonds between H<sub>2</sub>O and an anion, the redshift of the OD/OH stretch vibrations will be

smaller. Hence, the addition of halogenic anions that form weak hydrogen bonds to  $\text{H}_2\text{O}$  will lead to a blueshift of the vibrational frequency of OD stretch vibration, as is observed in the upper panel of figure 1. The hydrogen bonds to  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  are even weaker leading to an even larger blueshift. For the bending mode, the replacement of a hydrogen bond to  $\text{H}_2\text{O}$  by a weaker hydrogen bond to an anion will lead to a redshift of the vibrational frequency. The reason that the redshift of the bending mode is smaller for  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  than for  $\text{I}^-$  is most likely related to the geometry of the ions. The overall charge density of these anions will be rather similar, they are similar in size and the only parameter in which they truly differ is their shape:  $\text{I}^-$  is a sphere, whereas  $\text{ClO}_4^-$  has a tetrahedral shape.

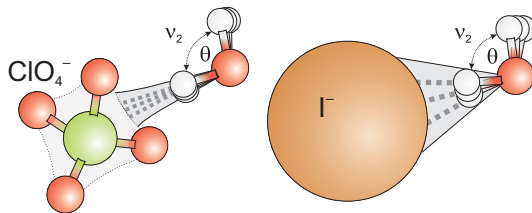


FIG. 8: Schematic representation of a water molecule binding to  $\text{I}^-$  and to  $\text{ClO}_4^-$ . The spherical shape of the  $\text{I}^-$  ion allows for a much larger angular freedom of the hydrogen bond than the tetrahedral shape of the  $\text{ClO}_4^-$  ion.

The large spherical shape of  $\text{I}^-$  implies that the strength of the hydrogen bond is not very sensitive to the angle between the  $\text{O-H}$  group and the  $\text{O}\cdots\text{I}^-$  hydrogen-bond coordinate. When the  $\text{O-H}$  group bends out of the  $\text{O-H}\cdots\text{I}^-$  system, it will still interact favorably with another part of the large negatively charged sphere of the  $\text{I}^-$  ion.<sup>22</sup> This means that the energy penalty for bending the  $\text{O-H}$  group out of the  $\text{O-H}\cdots\text{I}^-$  is low. Hence, this hydrogen bond will provide very little additional restoring force to the bending mode vibration. The replacement of the strong, highly directional  $\text{O-H}\cdots\text{O}$  hydrogen bond between two water molecules by the  $\text{O-H}\cdots\text{I}^-$  hydrogen bond will thus lead to a strong decrease of the restoring force of the bending mode vibration, and thus to a relatively large redshift of the frequency of this vibration.

For  $\text{ClO}_4^-$  it has been shown that the solvating water molecules preferentially form hydrogen bonds towards the oxygen-oxygen “ridges” of the tetrahedron (see figure 8) with the hydrogen bond being mostly parallel to the  $\text{O-Cl-O}$  angle bisector<sup>23,24</sup>. Due to the much more structured charge density of the  $\text{ClO}_4^-$  ion, the strength of the  $\text{O-H}\cdots\text{ClO}_4^-$  hydrogen

bond will be quite sensitive to the angle between the O–H group and the O–Cl–O angle bisector. Hence, the energy penalty for creating a non-zero angle between the O–H group and the O–Cl–O angle bisector will be high, which means that the O–H $\cdots$ ClO $_4^-$  hydrogen bond provides a relatively large restoring force to the bending mode vibration of the water molecule. Hence, in spite of the fact that the O–H $\cdots$ ClO $_4^-$  hydrogen bond is weaker than the O–H $\cdots$ I $^-$ , its contribution to the restoring force of the bending mode is higher, as this contribution to the restoring force is not determined by the strength of the hydrogen bond interaction, but rather by the change in this strength when bending the O–H group with respect to the hydrogen-bond coordinate. This difference between ClO $_4^-$  and I $^-$  is illustrated in figure 8.

The vibrational lifetime of the bending mode is longer for H $_2$ O molecules hydrating an anion than for H $_2$ O molecule in the pure liquid. This observation is in line with the results of previous studies on the lifetime of the OD/OH stretch vibrations of HDO molecules in isotopically diluted salt solutions. The lifetime of the OD/OH stretch vibrations was observed to increase by a factor of 3 (Cl $^-$ ) to 5 (I $^-$ ).<sup>25</sup> This increase has been explained from the relatively low frequency of the O–H $\cdots$ X $^-$  hydrogen bond stretch vibration. The frequency of this vibration is lower than that of the O–H $\cdots$ O hydrogen-bond stretch vibration in liquid water, because the hydrogen bond is weaker and because of the relatively large mass of the halogenic anion. The hydrogen-bond stretch vibration likely plays an important role in the relaxation of the OD/OH stretch vibration and likely takes up part of the vibrational energy. The lower frequency of the vibration implies that the same amount of energy corresponds to more vibrational quanta which decreases the anharmonic coupling. A similar effect may be responsible for the longer vibrational lifetime of the bending mode of H $_2$ O molecules hydrating an anion. It is interesting to note that the increase in lifetime is smaller than observed for the OD/OH stretch vibration. This can be explained from the fact that the bending mode involves both OH groups of the H $_2$ O molecule, and one of these OH groups will remain hydrogen bonded to another water molecule.

A recent theoretical study by the Hynes group showed that the vibrational energy relaxation of the bending mode of water involves the transfer of vibrational energy to the librational modes of the initially excited water molecule, and to the four nearest neighbours of the excited water molecule (with a ratio of  $\sim 2/1$ ).<sup>26,27</sup> This transfer is followed by a second transfer to the second hydration shell. The water molecules that are hydrogen bonded to

an anion will have less water molecules as direct neighbours. Hence, the density of water librational modes in the first hydration shell of the excited water molecule will be lower which may explain the lengthening of the vibrational lifetime.

It is interesting to note that the vibrational lifetime is less lengthened for H<sub>2</sub>O hydrating ClO<sub>4</sub><sup>-</sup> than for H<sub>2</sub>O hydrating a halogenic anion. This can be due to the stronger dependence of the hydrogen bond on the angle between O–H and the hydrogen-bond coordinate. This stronger dependence may also lead to a stronger anharmonic coupling of the bending mode with the librations, thus also leading to a faster vibrational relaxation. Another explanation is that the vibrational energy of the bending mode can be partially transferred to the intramolecular vibrations of the ClO<sub>4</sub><sup>-</sup> anion. The ClO<sub>4</sub><sup>-</sup> anion possesses 9 intramolecular vibrations that can take up part of the vibrational energy of the bending mode and thereby provide additional pathways of vibrational energy relaxation in comparison to the monoatomic halogenic anions.<sup>28,29</sup> The latter explanation agrees with the observation that the vibrational relaxation of the OH stretch vibration of HDO is also somewhat faster in case the OH is hydrogen bonded to ClO<sub>4</sub><sup>-</sup> ( $\sim 2.2$  ps<sup>6</sup>) than in case the OH is bonded to I<sup>-</sup> ( $\sim 4$  ps<sup>25</sup>), in spite of the fact that the hydrogen bond to I<sup>-</sup> is stronger. Probably, the internal vibrations of the ClO<sub>4</sub><sup>-</sup> also assist in the vibrational relaxation of the OH stretch vibration.

The relaxation of the bending mode appears to be negligibly affected by the cations. We have tested the effect of the cation on the dynamics of the bulk-like and anion-bound water. Changing the cation for the iodide salt from Li to Na and Cs did not have any effect on the lifetimes of the two water species. This notion likely follows from the fact that the cation and the hydrogen atoms of the water molecule are located at opposite sides of the oxygen atom of the water molecule, even at very high salt concentrations. Hence, there will be very little interaction between the cations and the hydrogen atoms, and as the bending mode involves the motion of the hydrogen atoms, it can be understood that the cation has very little effect on its relaxation.

#### IV. CONCLUSIONS

We studied the vibrational absorption spectra and the vibrational energy relaxation dynamics of the bending mode of H<sub>2</sub>O interacting with different ions. With increasing salt concentration, the overall absorption spectrum of the bending mode shows a redshift, and this



redshift can be fully accounted for by the interconversion of two gaussian-shaped bands with concentration-independent central frequencies and spectral widths. One of these bands is associated with bulk-like H<sub>2</sub>O molecules that form hydrogen bonds with other H<sub>2</sub>O molecules, the other band is associated with the anion-bound H<sub>2</sub>O molecules of which at least one O–H group is hydrogen bonded to an anion. The latter band is redshifted with respect to the bulk-like band, and this redshift increases in the halogenic series Cl<sup>−</sup> → Br<sup>−</sup> → I<sup>−</sup>.

For H<sub>2</sub>O hydrogen bonded to the multiatomic, tetrahedral anions ClO<sub>4</sub><sup>−</sup> and BF<sub>4</sub><sup>−</sup> the redshift of the bending mode is smaller than that for H<sub>2</sub>O hydrogen bonded I<sup>−</sup>, even though the hydrogen bonds to ClO<sub>4</sub><sup>−</sup> and BF<sub>4</sub><sup>−</sup> are weaker than to I<sup>−</sup>. This observation can be explained from the difference in structure of the ions. For ClO<sub>4</sub><sup>−</sup> and BF<sub>4</sub><sup>−</sup> the hydrogen bond is formed towards the narrow O–O and F–F ridges of the ions, which makes this bond more directional than the hydrogen bond to the large spherical I<sup>−</sup> anion. Due to the stronger directional character, the energy penalty of bending the hydrogen-bonded O–H group is larger and thus this bond contributes a stronger restoring force to the bending mode vibration. Hence, the bending mode frequency of H<sub>2</sub>O hydrogen bonded to ClO<sub>4</sub><sup>−</sup> or BF<sub>4</sub><sup>−</sup> is higher than for H<sub>2</sub>O hydrogen bonded to I<sup>−</sup>.

We find that the bending mode vibrational lifetime  $T_1$  of the bending mode is longer for water bound to halogenic anions ( $\sim 1 \pm 0.1$  ps) than for bulk liquid water ( $\sim 380 \pm 0.05$  fs). For ClO<sub>4</sub><sup>−</sup> the  $T_1$  lifetime is not as long ( $\sim 750 \pm 0.08$  fs) as for H<sub>2</sub>O hydrogen bonded to the halogenic anions. This somewhat shorter  $T_1$  lifetime likely results from the participation of the internal vibrations of the ClO<sub>4</sub><sup>−</sup> anion in the vibrational relaxation of the H<sub>2</sub>O bending mode.

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