Effect of Ions on the Vibrational Relaxation of Liquid Water

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Abstract: We study the relaxation of the O−H stretch vibration of water in aqueous salt solutions using femtosecond two-color pump−probe spectroscopy. The vibrational lifetimes are measured for a series of salts consisting of the anions Cl⁻, Br⁻, and I⁻ and the cations Li⁺, Na⁺, and Mg²⁺, for a range of concentrations from 0.5 M up to 6 M (chloride salts), 9 M (bromide salts), and 10 M (iodide salts). In addition to the previously found dependence of the vibrational lifetime on the nature of the anion, the lifetime is found to depend on concentration and is observed to show a small but significant dependence on the nature of the cation. We present a model in which all the effects of ions on the vibrational relaxaton of liquid water are accounted for.

1. Introduction

Since the beginning of chemistry, there has been an enormous interest in the microscopic properties of electrolyte solutions.[1] One of the major problems in studying solvation interactions is the necessity to separate the response of the solvating water molecules from that of the bulk solvent. In principle, this distinction can be achieved using nuclear magnetic resonance or Raman-scattering techniques. However, these techniques do not provide sufficient temporal resolution to study dynamical processes on a time scale of picoseconds. Another way to avoid bulk solvent molecules to interfere with the experiment is by solvating a specific probe molecule, that can be excited to study its response, e.g., fluorescence.[2−4] It is hereby assumed that the response of the probe molecule directly reflects the response of the solvating molecules to the excitation of the probe molecule. However, other dynamical processes of the probe molecule can also contribute, thus complicating the interpretation.

The past decade has brought powerful femtosecond mid-infrared laser sources, which enabled the study of the dynamics of liquids with subpicosecond time resolution. Ultrafast processes such as spectral diffusion in liquid water, previously only surmised, were accurately studied.[5−7] Other studies on liquid water addressed the orientational dynamics,[8−11] the O−H stretch vibrational lifetime,[11−13] and intermolecular vibrational energy transfer.[14]

For aqueous salt solutions, the behavior of water molecules in the anion's solvation shell was observed to differ drastically from pure liquid water. After vibrational excitation, the bulk and cation-bonded water molecules relax in about 0.8 ps, whereas the water molecules in the anion shell remain excited 3 to 6 times as long.[19] This difference in lifetime provides a means to discriminate between the response from the molecules solvating the anions and the response from the bulk and cation-solvating molecules and, thus, to specifically study the anion's solvation shell. It was found, for example, that the time scales of spectral diffusion[15,16] and orientational dynamics[17] are significantly longer for water molecules in an anion's solvation shell than in the bulk liquid. An old paradigm, according to which ions are capable of changing the hydrogen-bond structure of the bulk solution (structure-making or -breaking), has been rejected, since outside the solvation shell no sign of a change in dynamics could be found.[20] Although these experiments only concerned the anion's solvation shell, the results are expected to apply to the cation as well.

Notwithstanding the dominant influence of the anions, it can be expected that at high concentrations the cations should affect the (slow component of the) vibrational relaxation: at concen-

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trations above approximately 6 M, almost all water molecules are involved in solvating ions, and ions are starting to share water molecules in their first solvation shells.[21] In the present study, the effect of the cation on the vibrational relaxation of the anion-bonded O−H stretch vibration is studied. It is observed that the cations indeed change the vibrational lifetime of water molecules in the solvation shell of the anion, albeit to a lesser extent than do the anions. In addition, we study the effect of the concentration of the ions on the vibrational lifetime. In combination with the previous work on the effects of the anions, the results obtained provide a complete picture of the influence of anions and cations on the O−H stretch vibrational lifetime of water in aqueous salt solutions. This picture is incorporated in a model for the vibrational relaxation in which all the effects of cations, anions, and their concentration are accounted for.

2. Experiment

We performed two-color mid-infrared pump−probe experiments on the O−H stretch vibration in several salt solutions. The salt solutions were LiCl, NaCl, MgCl$_2$, LiBr, NaBr, MgBr$_2$, LiI, NaI, or MgI$_2$, dissolved in D$_2$O and less than 1 M of HDO. The hydrogen concentration was kept low enough to prevent Förster-energy transfer between nearby O−H groups. The salts were studied at the following anion concentrations: 0.5, 1, 2, 3, 4, 6, and 9 M (bromide salts) and 10 M (iodide salts). Below 0.5 M, the concentration was too low to allow for an accurate determination of the vibrational lifetime of the anion-solvating HDO molecules. The maximum concentrations are limited by the solubility in water. The samples were kept between two CaF$_2$ windows that are held apart by a 200 μm Teflon spacer. The transmission of the samples at the center of the O−H stretch absorption band (approximately 3450 cm^{-1}) is generally between 5% and 20%, depending on the HDO concentration.

In the experiment, the pump pulse excites the O−H stretch vibration of a subset of the water molecules, characterized by their absorption frequency. This subset of excited molecules will contain molecules in all possible environments: although the different environments of the liquid (near a cation, anion, or only near other water molecules) affect the O−H stretch frequency of the water molecule differently, the resulting difference is not large enough to separate the different environments spectrally. The probe pulse measures the induced transmission change ((T/T_0), with T as the transmission with the pump pulse and T_0 as the transmission without). The probe frequency can be tuned either to the fundamental 0→1 transition or to the 1→2 transition, which absorbs at a lower frequency than the fundamental because of the anharmonicity of the O−H stretch vibration. In the experiments presented here, the excitation frequency was at 3450 cm^{-1}, where the absorption of the 0→1 transition is maximal, and the probe frequency was tuned to 3200 cm^{-1}, the maximum absorption of the 1→2 transition. The transmission change is measured as a function of time delay between pump and probe pulses, to measure the dynamics of the excitation.

The mid-infrared pulses used to pump and probe the O−H stretch vibration are generated from the 800 nm pulses delivered by a commercial 1 kHz Ti/sapphire RGA/multipass laser system (Quantronix Titan) using parametric light conversion processes. The 800 nm light is split into two branches to generate independently tunable pump and probe pulses by the following method. First, in an optical parametric generation and amplification process in a β-barium borate (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 a second BBO crystal to obtain 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 potassium titanyl phosphate (KTP) crystal. In the probe branch, two KTP crystals are

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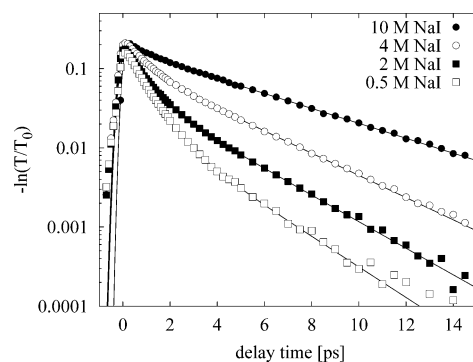
Figure 1. Pump−probe measurements of solutions of several concentrations of NaI in HDO/D$_2$O. The measurements are performed using a pump frequency of 3450 cm^{-1} and a probe frequency of 3200 cm^{-1}. The lines are fits to the data. The fit function is a biexponential function convolved with a Gaussian cross-correlation function.
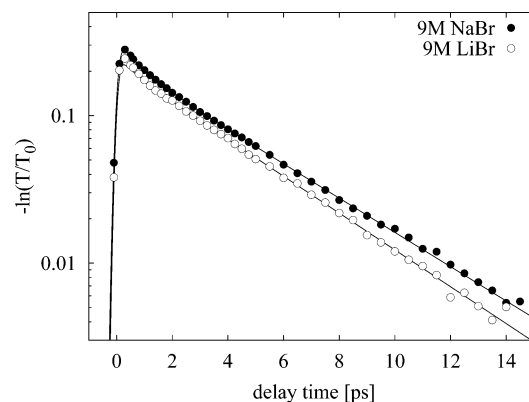
Figure 2. Pump−probe measurements of 9 M solutions of LiBr and NaBr in HDO/D$_2$O. The measurements are performed using a pump frequency of 3450 cm^{-1} and a probe frequency of 3200 cm^{-1}. The lines are fits to the data.

used instead of one, to increase the pulse-to-pulse stability. The resulting narrower spectrum and longer pulse duration are not disadvantages in the present experiment.

The polarization of the probe pulse was set at the magic angle (54.7°) with respect to the pump polarization. As a result, 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 40 cm^{-1}, respectively. The pump pulses have an energy of typically 20 μJ, and the probe pulses, that of less than 1 μJ. Variation of the pump energy leads only to a change in signal amplitude and does not influence the dynamics. The cross-correlation trace has a typical width of 400 fs. A detailed description of the data acquisition method can be found in ref 9.

3. Results

In Figure 1, pump−probe traces of solutions of NaI are shown. The decay is nonexponential, which is most clearly seen at low concentrations. The decay rate of the signals shows a dependence on concentration. In Figure 2, two measurements are shown where the dissolved salts differ in the nature of the cation. It is observed that the solution containing Li$^+$ ions shows a somewhat faster decay than the solution containing Na$^+$ ions.

The data are fitted with a biexponential function, convolved with a Gaussian cross-correlation trace $CC(t)$:

$$S_{PP}(t) = A \times CC(t)(A_f e^{-t/T_{1,f}} + A_s e^{-t/T_{1,s}}) \quad (1)$$

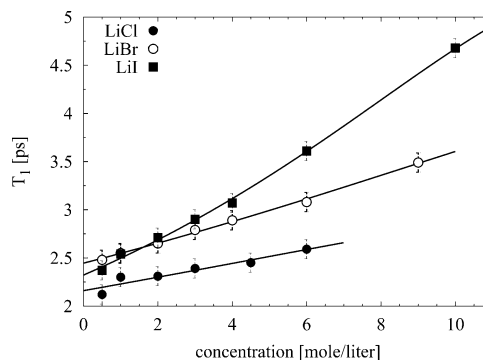with $A_f + A_s = 1$, so that A_f and A_s represent the fractional
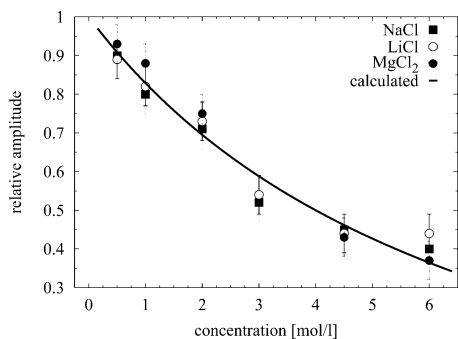
**Figure 3.** Value of A_f, representing the relative abundance of the fast component in the biexponential fit, for a series of Cl^- salts as a function of concentration. The line is obtained from a simple calculation of the relative abundance of the fast component, assuming a coordination number of 6 of the Cl^- ion and a cross-sectional ratio of the Cl^-- and water-bound HDO molecules of 2.2.

contributions of the fast and slow components to the total biexponential function. Two time constants are obtained, the shorter of which, $T_{1,f}$, is approximately 0.8 ps. The same time constant was observed for pure HDO dissolved in D_2O.[12,13] The fast component originates from O–H groups that are hydrogen bonded to a D_2O molecule, thus making them similar to the O–H groups in HDO/D_2O. The longer time constant, $T_{1,s}$, ranges from roughly 2 to almost 5 ps and was found to correlate with the type of anion.[18,19]

Especially at high concentrations, the parameters A_f, $T_{1,f}$, A_s, and $T_{1,s}$ will all be influenced by the cations present. However, due to the dominance of the long-living component, we cannot determine the time constant of the fast component very precisely; we therefore set $T_{1,f} = 0.74$ ps in all fits (see section 5). The parameters A_f, A_s, and $T_{1,s}$ are all treated as fit parameters in fitting the pump–probe measurements. In Figure 3, the resulting value of A_f is shown as a function of concentration for a series of Cl^- salts. The concentration dependence of A_f can be described by assuming a cross-sectional ratio between the two components and a coordination number of the anion. If the absorption cross sections are independent of the concentration, the value of A_f is then completely determined by the relative abundance of the D_2O-bound HDO molecules, which is easily calculated. In Figure 3, the calculated concentration dependence of A_f is represented by the solid line. In this calculation, the coordination number of Cl^- is taken to be 6, and the cross-sectional ratio of the anion-bound and water-bound water molecules is 2.2. The fitted A_f are all close to the calculated line. The deviations seem to be real; i.e., forcing the A_f to lie on the calculated line results in bad fits. The deviations can be explained from variations in the pump and probe spectra and the fact that the anion-bound and water-bound O–H groups absorb at slightly different frequencies, which makes the cross-sectional ratio frequency-dependent.[25,26,35]

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Figure 4. T_1 as a function of concentration for three salts containing the same cation: LiCl, LiBr, and LiI. The lines are calculated using the model described in section 4.
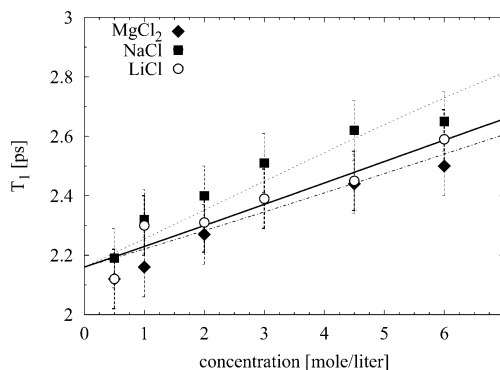
Figure 5. T_1 as a function of concentration for three salts containing Cl^-. The lines are calculated using the model described in section 4.
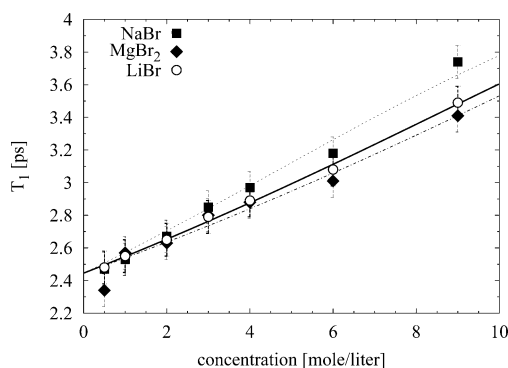
Each salt at each concentration has been measured at least twice. The typical variation between two measurements taken at different days is larger than the error estimated from the fitting procedure. Therefore, we use the variation in different measurements to estimate the error in the obtained values of T_1 of the slow component. We estimate the error in T_1 to be 0.1 ps. Within one series of experiments, the errors are smaller than these values. For this reason, the main trends, i.e., the dependences of T_1 on the nature of the cation and the concentration, have always been determined in single measurement runs.

In Figure 4, T_1 is plotted as a function of anion concentration, for a series of lithium salts. For all anions, the lifetime increases with concentration, but different slopes are observed for different anions; the slope increases going from Cl^- to Br^- to I^-. Below 3 M anion concentration, the lifetimes of HDO in the solvation shells of Br^- and I^- are almost the same; HDO in the solvation shell of Cl^- relaxes faster at all measured concentrations. The sodium and magnesium salts show the same concentration dependences as the Li^+ salts.
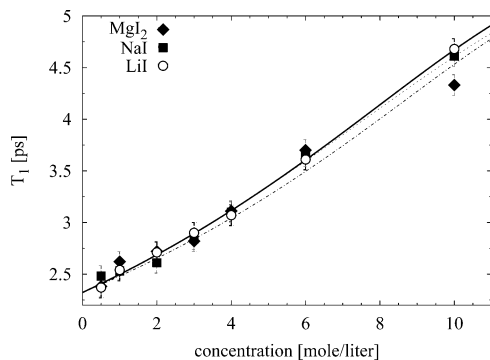
In Figures 5–7, T_1 is plotted for solutions of salts containing chloride, bromide, and iodide, respectively. Each anion is combined with lithium, sodium, and magnesium. The difference between the data in these figures, in which the cation is varied, is much smaller than that in Figure 4, where the anion was varied. For example, at a concentration of 6 M, the value of T_1 for an iodide salt is 50 times larger than that for a chloride salt, whereas the change of the cation from Mg^{2+} to Na^+ leads to

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Figure 6. T_1 as a function of concentration for three salts containing Br⁻. The lines are calculated using the model described in section 4.

Figure 7. T_1 as a function of concentration for three salts containing the same I⁻. The lines are calculated using the model described in section 4.

an increase of T_1 of at most 10%. The sodium salts have slightly longer T_1's than the lithium and magnesium salts.

4. Model

In this section, we will present a model for the vibrational relaxation of HDO molecules in the solvation shells of Cl⁻, Br⁻, and I⁻ that can explain the trends observed in the previous section. In the relaxation of the O−H stretch vibration of HDO/D₂O, at least part of the energy has to be accepted by the hydrogen bonds because, in contrast to H₂O, there is no combination of intramolecular modes that is resonant with the O−H stretch vibration. A special role is expected to be played by the hydrogen bond that involves the hydrogen atom of the excited O−H group. In the following, we will denote this hydrogen bond as the donated hydrogen bond. The present experiments indeed demonstrate that this hydrogen bond plays an essential role, because the change of this hydrogen bond from O−H···O to O−H···Cl⁻ to O−H···Br⁻ to O−H···I⁻ leads to a significant slowing down of the vibrational relaxation. However, it should be realized that the hydrogen bonds in liquid water form a strongly coupled network. This means that the energy of the excited O−H stretch vibration in the solvation shell of the anion is dependent not only on the local O−H···X⁻ coordinate but also on the O−D···X⁻, O−D···O, and Y⁺O−D···O coordinates of the other hydrogen bonds in the liquid. As a result, the donated hydrogen bond is not a pure local O−H···X⁻ (X = Cl⁻, Br⁻, I⁻) mode but a delocalized mode showing admixture of surrounding hydrogen bonds. We therefore anticipate that the small but significant influences of the cations and concentration on the relaxation rate result from changes in the wave function of this delocalized hydrogen bond. Hence, we describe the relaxation rate as a sum of three

contributions representing the O−H···X⁻/O−D···X⁻, the O−D···O, and the Y⁺O−D···O character of the accepting hydrogen bond (this equation can simply be derived from Fermi's golden rule, using the random-phase approximation):

$$1/T_1 = F_a/T_{1a} + F_b/T_{1b} + F_c/T_{1c} \tag{2}$$

with $F_a + F_b + F_c = 1$. The relaxation rate is thus given by a sum of three contributions corresponding to the different characters of hydrogen bonds present in the solution. The T_{1i} (i = a,b,c) are the lifetimes of the O−H groups, in the case where the accepting hydrogen bond would be purely anionic, bulk, or cationic in character. In the case of bulk, this corresponds to the situation of pure liquid HDO/D₂O with no ions added.

In the following, we will determine the values of the fractions F_i from the concentrations of the different types of hydrogen bonds present in a particular salt solution. We will calculate the concentration $N_{OD,i}(\epsilon)$ of the three different types of hydrogen bonds as a function of the concentration ϵ of the anion. We assume that there is an equilibrium between unoccupied anion binding sites X⁻· and occupied anion binding sites O−D···X⁻ with an equilibrium constant K_a defined by

$$K_a = \frac{[\text{O}-\text{D}\cdots\text{X}^-]}{[\text{X}^-\cdot][\text{O}-\text{D}\cdots\text{O}]} \tag{3}$$

where O−D···O represents the concentrations of O−D groups that are not bound to the anion solvation shell. These concentrations fulfill the following "conservation laws":

$$[\text{X}^-\cdot] + [\text{O-D}\cdots\text{X}^-] = S_a\epsilon$$

$$[\text{O-D}\cdots\text{X}^-] + [\text{O-D}\cdots\text{O}] = N_{OD} \tag{4}$$

S_a is the maximum number of water molecules in the anion's solvation shell, which we will call here the hydration number. N_{OD} is the concentration of O−D groups, equal to twice the molarity of water, 110 M. We identify [O−D···X⁻] with $N_{OD,a}(\epsilon)$.

An expression for the number density of cation-affected O−D groups, $N_{OD,c}(\epsilon)$, can be obtained in a similar way. We describe these O−D groups in terms of water molecules, since in the solvation shell of the cation the water molecules are closest with their oxygen atom to the cation. The equilibrium is written as

$$K_c = \frac{[\text{Y}^+\cdot\text{OD}_2]}{[\text{Y}^+\cdot][\text{D}_2\text{O}]} \tag{5}$$

and the conservation laws are

$$[\text{Y}^+\cdot] + [\text{Y}^+\cdot\text{OD}_2] = S_c\epsilon \tag{6}$$

$$[\text{Y}^+\cdot\text{OD}_2] + [\text{D}_2\text{O}] = N_{OD}/2$$

S_c is the maximum number of water molecules in the cation's solvation shell (called the hydration number), and [D₂O] is the concentration of water molecules that are not in the solvation shell of a cation.

The concentration of O−D groups that is affected by the cation is equal to twice (two O−D groups per water molecule) the concentration of occupied cation bonding sites. However, a fraction of these O−D groups will bind to the anion (especially

at high concentrations); these are considered to be anion-bound O−D groups, since the anion has a much stronger effect on the hydrogen bond than the cation. This is illustrated by the O−D stretch absorption spectra obtained from infrared spectroscopy[24−27] and Raman spectroscopy.[28] Hence, to arrive at $N_{OD,c}(\epsilon)$, the concentration of cation-affected O−D groups, $2[Y^+ \cdot OD_2]$, is multiplied with the fraction that binds to another water molecule and not to an anion. Hence,

$$N_{OD,c}(\epsilon) = 2[Y^+ \cdot OD_2]\left(1 - \frac{N_{OD,a}(\epsilon)}{N_{OD}}\right) \qquad (7)$$

Neglecting changes in N_{OD} due to dissolution of salt, the concentration of bulk O−D groups, i.e., the ones that are affected neither by the anion nor by the cation, is given by

$$N_{OD,b}(\epsilon) = N_{OD} - N_{OD,a}(\epsilon) - N_{OD,c}(\epsilon) \qquad (8)$$

The dominant character of the accepting hydrogen bond is that of O−H···X$^-$. The admixture of bulk and cation behavior is assumed to scale with $N_{OD,b}(\epsilon)$ and $N_{OD,c}(\epsilon)$, respectively. We assume that the fractions F_b and F_c depend linearly on these concentrations. The coefficient F_a then follows from the normalization of the hydrogen bond mode ($F_a + F_b + F_c = 1$). The fractions thus show the following dependences on concentration:

$$F_b(\epsilon) = k_b \frac{N_{OD,b}(\epsilon)}{N_{OD}}$$

$$F_c(\epsilon) = k_c \frac{N_{OD,c}(\epsilon)}{N_{OD}}$$

$$F_a(\epsilon) = (1 - F_b(\epsilon) - F_c(\epsilon)) \qquad (9)$$

with k_b and k_c proportionality constants that depend on the nature of the cation and the anion. Equations 2 and 9 fully describe the dependence of the vibrational lifetime on anion, cation, and their concentration.

5. Fit Results

In the previous section, we obtained an expression for the lifetime of the anion-bound O−H stretch vibration in terms of the lifetimes of anionic (T_{1a}), bulk (T_{1b}), and cationic (T_{1c}) components. T_{1b} is known from previous studies on pure HDO/D$_2$O and equals 0.74 ps. For T_{1c}, no data are available, and their contribution to the measured T_1 turned out to be too small to allow for an accurate determination of their values in the present work. Hence, we determine the value of T_{1c} using a phenomenological relation between the O−H stretch redshift (with respect to the gas-phase value of 3700 cm^{-1}) and the vibrational lifetime:[29,30]

$$T_1 = k(\Delta\omega_{OH})^{-1.8} \qquad (10)$$

The form of this relation can be intuitively understood by appreciating that both quantities rely on the hydrogen-bond strength. The first spectral moment of the component of the O−D stretch absorption band due to several cations has been measured in ref 24. After multiplication by a factor of 1.36[31] to obtain the O−H stretch frequencies, the values are 3325 cm^{-1} (Li$^+$O−H···O), 3456 cm^{-1} (Na$^+$O−H···O), and 3340 cm^{-1}

Table 1. Fit Values of T_{1a}, k_b, and k_c[a]

	T_{1a} (ps)	k_b	k_c
LiCl	3.5	0.17	0.07
NaCl	3.5	0.17	0.10
MgCl$_2$	3.5	0.17	0.07
LiBr	5	0.18	0.08
NaBr	5	0.18	0.14
MgBr$_2$	5	0.18	0.07
LiI	6	0.22	0.08
NaI	6	0.22	0.19
MgI$_2$	6	0.22	0.06

[a] T_{1a} and k_b depend only on the nature of the anion. The fits are shown in Figures 4−7.

(Mg^{2+}O−H···O). Compared to a frequency of 3410 cm^{-1} for HDO/D$_2$O without salt,[32] the Na$^+$ affected O−H stretch band is blueshifted, and the Mg^{2+} and Li$^+$affected O−H bands are redshifted. The constant k in eq 10 is determined using a lifetime of 0.74 ps for pure HDO/D$_2$O.[12,13] For T_{1c} the following values are obtained: 0.5 ps (Li$^+$), 1.0 ps (Na$^+$), and 0.5 ps (Mg^{2+}). For the determination of T_{1a}, we cannot use eq 10, since this equation is only valid for O−H···O hydrogen bonds. For O−H···X$^-$ hydrogen bonds the frequency dependence of T_1 will be different.

Values for the hydration numbers can be found in the literature.[33−38] We use hydration numbers of 4 for Li$^+$; 6 for Na$^+$, Mg^{2+}, Cl$^-$, and Br$^-$; and 9 for I$^-$. The description using chemical equilibria, eqs 3 and 5, allows for a time-averaged hydration number that is different from S_a and S_c and also for a smooth transition to higher concentrations. The values of K_a and K_c appeared not to be very critical in the fit. We used values of 0.25; in a 1 M NaCl solution, the Cl$^-$ ion will then have on the average 5.8 water molecules in its first shell and 0.2 free sites, in agreement with MD similations.[38]

The remaining fit parameters are T_{1a}, k_b, and k_c. Of these parameters, T_{1a} should only depend on the nature of the anion. Furthermore, at zero concentration, the value of T_1 should not depend on the nature of the cation. Hence, at $\epsilon = 0$, $F_c = 0$, $F_b = k_b$, and $F_a = 1 - k_b$. Therefore, the nature of the anion defines the values of T_{1a} and k_b. This means that, for a particular combination of cation and anion, only k_c is left as an independent fit parameter. The results of the fits to the measured values of T_1 are represented by the lines in Figures 4−7. The fit values of T_{1a}, k_b, and k_c are shown in Table 1.

6. Discussion

The model of section 4 provides a good description of the trends observed in section 3. Using the model, we can identify the origins of these trends. The increase in T_1 going from Cl$^-$ to Br$^-$ to I$^-$ finds its origin in an increase in T_{1a}. This increase implies that the coupling of the excited O−H stretch vibration to the local O−H···X$^-$ mode decreases in the series Cl$^-$ to Br$^-$ to I$^-$, which can be understood as follows. Within the halogenic series (F$^-$, Cl$^-$, Br$^-$, I$^-$), the absorption spectrum of the O−H stretch vibration shifts to higher frequencies, which indicates that the strength of the hydrogen-bond interaction decreases.[39,40] The weaker hydrogen-bond interaction in turn leads to a decrease of the anharmonic interaction between the O−H stretch
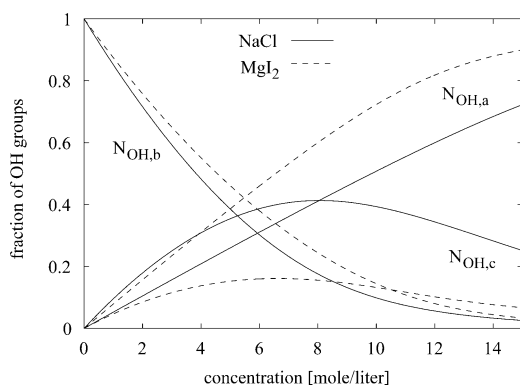
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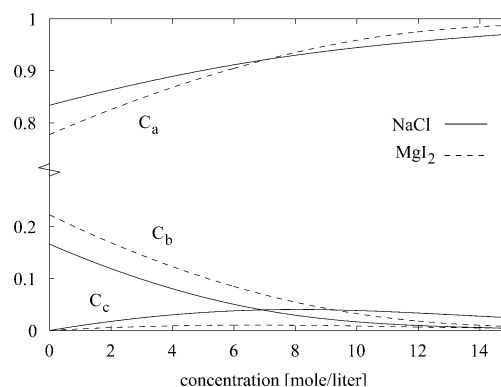(40) Mikenda, W. *J. Mol. Struct.* **1986**, *147*, 1−15.

Figure 8. Functions $N_{OD,a}(\epsilon)/N_{OD}$, $N_{OD,b}(\epsilon)/N_{OD}$, and $N_{OD,c}(\epsilon)/N_{OD}$, defining the normalized number densities of the different O−D groups present in solution, for NaCl (solid lines) and MgI$_2$ (dashed lines).

Figure 9. Fractions $F_a(\epsilon)$, $F_b(\epsilon)$, and $F_c(\epsilon)$, representing the anionic, bulk, and cationic hydrogen-bond character of the accepting hydrogen-bond mode, for NaCl (solid lines) and MgI$_2$ (dashed lines). The fractions depend on the functions $N_{OD,a}(\epsilon)/N_{OD}$, $N_{OD,b}(\epsilon)/N_{OD}$, and $N_{OD,c}(\epsilon)/N_{OD}$ shown in Figure 8 and are defined in eq 9.

vibration and the hydrogen-bond mode[30] and, thereby, to a slowing-down of the vibrational relaxation. In addition, the reduced mass of the O−H···X$^-$ hydrogen-bond stretch vibration, which determines the energy spacing of the levels of this mode, increases within the halogenic series Cl$^-$, Br$^-$, I$^-$. The hydrogen-bond frequencies have been measured:[41] 210 cm^{-1} for O−H···Cl$^-$, 158 cm^{-1} for O−H···Br$^-$, and 135 cm^{-1} for O−H···I$^-$. As a result, the dissipation of the excitation energy of the O−H stretch vibration will involve a higher level of excitation of the hydrogen-bond vibration for I$^-$ than for Cl$^-$, which also decreases the anharmonic interaction.[42]

A second important trend is the increase of T_1 with concentration. According to the model, this increase mainly results from the decreased contribution of bulk O−D···O bonds to the accepting hydrogen-bond mode. In Figure 8, the normalized concentrations of the different types of O−D groups are shown for NaCl and MgI$_2$. It is clearly seen that with increasing concentration of dissolved salt the concentration of O−D···O hydrogen bonds decreases, while the concentration of O−D···X$^-$ hydrogen bonds increases. The concentration of cationic hydrogen bonds Y$^+$O−D···O first increases with the concentration of dissolved salt because more ions are present but, at high concentration, decreases again because an increasing part of the water molecules in the first solvation shell of the cation are simultaneously bound to an anion via an O−D···X$^-$ hydrogen bond. In Figure 9, the corresponding fractions of the anionic, cationic, and bulk hydrogen-bond character of the accepting hydrogen bond are shown. At low concentration, the character of the accepting hydrogen bond is already dominated by the anionic hydrogen bond mode. With increasing concentration, this character gets even stronger, making the hydrogen bond into an almost purely anionic hydrogen bond at high concentrations. Hence, the overall relaxation time T_1 increases with concentration because of the increase of the contribution of the long T_{1a} and the decrease of the contribution of the shorter T_{1b}.

The slope of the concentration dependence is largest for I$^-$ salts. The slope of the concentration dependence of T_1 is mainly determined by the difference between T_{1a} and T_{1b}. This difference increases going from Cl$^-$ to Br$^-$ to I$^-$, thus largely explaining the observed increase in slope in this series. In addition, the hydration number is higher for I$^-$ than for Cl$^-$

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and Br$^-$. As a result, the fraction of anion-affected O−D groups increases faster with concentration for I$^-$ than for Cl$^-$ and Br$^-$. In Figure 8, it is indeed seen that for MgI$_2$ the relative fraction of anionic hydrogen bonds rises faster with anion concentration than for NaCl. The faster rise of the fraction of anionic hydrogen bonds for I$^-$ leads to a faster rise of the contribution of the anionic hydrogen bonds to the accepting hydrogen-bond mode, which in turn results in a faster increase of T_1.

Another important trend is the small but significant dependence of T_1 on the nature of the cation: the sodium salts have a longer T_1 than the magnesium and lithium salts. This results primarily from the difference in the value of T_{1c}. The different values of T_{1c} can be explained from the different strengths of the electric fields around the cations: Li$^+$ is smaller than Na$^+$, while Mg^{2+} has the same size as Na$^+$ but twice the charge. The electric field serves to polarize the hydrogen bonds of water molecules adjacent to the cation which leads to a strengthening of these bonds. This strengthening in turn leads to an increase of the anharmonic interaction with the O−H vibration. The influence of the very short (0.5 ps) T_{1c} of lithium and magnesium is somewhat tempered by the fact that there are fewer cationic O−H groups compared to sodium at the same concentration: for lithium because the hydration number is lower (4), for magnesium because of the double charge, halving its concentration with respect to the anion.

Finally, the influence of the cations on T_1 is much smaller for the iodide salts than for the bromide and chloride salts. In the model this effect is reflected in the relatively small contribution of the Li$^+$O−D···O and Mg^{2+}O−D···O hydrogen bonds to the accepting hydrogen-bond mode. This can be seen from the coefficients k_c of the iodide salts shown in Table 1. A possible explanation for the small admixture of cationic hydrogen bonds is the large frequency difference between the Li$^+$O−D···O and Mg^{2+}O−D···O hydrogen bonds and the O−H···I$^-$ hydrogen bond. The Li$^+$O−D···O and Mg^{2+}O−D···O hydrogen bonds are relatively strong and will have high frequencies, whereas the O−H···I$^-$ hydrogen bond is relatively weak, resulting in a rather low frequency. Within a perturbative approach of the description of the wave function, the admixture is inversely proportional to the frequency difference, explaining why the Li$^+$O−D···O and Mg^{2+}O−D···O hydrogen bonds are only weakly contributing to the hydrogen bond of dominant O−H···I$^-$ character.

From the above it is clear that the observed trends can be well explained from changes in the character of the accepting hydrogen-bond mode involving the hydrogen atom of the excited O−H vibration. However, this hydrogen bond is not the only possible accepting mode. It is to be expected that the accepting combination tones also contain excitations of the bending mode and/or the O−D stretching vibration,[7] as well as other hydrogen-bond modes. The intramolecular modes can also be affected by a change in concentration and nature of the dissolved cations and anions. However, this effect will be small, since the intramolecular potentials of the HDO molecule are only weakly dependent on the nature and concentration of the ions. The bulk O−D···O and the cationic Y$^+$O−D···O hydrogen bond modes also depend on the nature and concentration of dissolved salt. However, these hydrogen bonds are not expected to couple directly with the excited O−H stretch vibration, because they are shielded from the excited vibration by an oxygen atom or a heavy anion. These hydrogen bonds mainly affect the relaxation by changing the character of the donated O−H···X$^-$ hydrogen bond, which is the basis of the model of section 4.

7. Conclusions

We studied the mechanism of vibrational relaxation of water molecules in the solvation shells of Cl$^-$, Br$^-$, and I$^-$ halogenic anions. To this end we performed measurements on the vibrational relaxation of HDO/D$_2$O solutions of a series of salts formed by the cations Li$^+$, Na$^+$, and Mg^{2+} and the anions Cl$^-$, Br$^-$, and I$^-$. The concentration was varied between 0.5 and 6 M (Cl$^-$), 9 M (Br$^-$), or 10 M (I$^-$). We found that the vibrational lifetime T_1 of HDO molecules in the solvation shell of the anions increases in the halogenic series Cl$^-$, Br$^-$, I$^-$ and with increasing concentration of dissolved salt. In addition, we found a small but significant dependence of T_1 on the nature of the cation: for the same type of anion and concentration, T_1 increases in the cationic series Mg^{2+}, Li$^+$, Na$^+$.

The observed trends in the relaxation can be well described with a model in which one of the accepting modes is the hydrogen bond involving the hydrogen atom of the excited O−H group. Due to the coupling between the hydrogen bonds in the liquid, this hydrogen bond is not a pure O−H···X$^-$ (X = Cl$^-$, Br$^-$, or I$^-$) bond but acquires character of other anionic O−D···X$^-$ hydrogen bonds, bulk O−D···O hydrogen bonds, and O−D···O hydrogen bonds of water molecules in the first solvation shells of the cations, denoted as Y$^+$O−D···O hydrogen bonds.

With increasing concentration, the O−D···X$^-$ character of the accepting hydrogen bond increases, while the bulk O−D···O character decreases, leading to an increase of T_1 (slower relaxation), because the O−H stretch vibration is more strongly coupled to an O−D···O hydrogen bond than to an O−D···X$^-$ hydrogen bond. For the iodide salts, this difference in coupling is largest, thus explaining the relatively steep increase of T_1 with concentration for solutions containing I$^-$. The value of T_1 is also affected by the cationic Y$^+$O−D···O hydrogen bonds. The strength of the cationic hydrogen bond increases going from Na$^+$O−D···O to Li$^+$O−D···O to Mg^{2+}O−D···O. Hence, the anharmonic interaction increases in this series, thus explaining the observed decrease in T_1. The latter effect is small (maximum = 10%) because for all salt solutions the cationic hydrogen bonds only form a small contribution (<7%) to the accepting hydrogen bond mode.