Ion solvation in water: femtosecond spectroscopy of hydrogen-bond dynamics
Kropman, M.F.

Citation for published version (APA):
4 CONCENTRATION AND CATION DEPENDENCE OF THE VIBRATIONAL RELAXATION OF ANIONIC SOLVATION SHELLS

Femtosecond two-colour pump-probe spectroscopy is used to study the dependence of the vibrational relaxation on the nature of the anion and the cation, and their concentration. The vibrational lifetime of the anion-solvating molecules has been determined for a series of salts consisting of the anions Cl\(^-\), Br\(^-\) and I\(^-\), and the cations Li\(^+\), Na\(^+\) and Mg\(^{2+}\), for a range of concentrations from 0.5 M up to 6 M (chloride salts), 9 M (bromide salts), and 10 M (iodide salts). A quantum mechanical model is presented that describes the observed dependencies. In addition to the previously found strong dependence on the nature of the anion, the lifetime is found to show a small but significant dependence on the nature of the cation and a strong concentration-dependence.

4.1 INTRODUCTION

In the previous chapter, the vibrational relaxation of water molecules in aqueous salt solutions was observed to differ drastically from that of pure liquid water. The O–H stretch lifetime was found to be much longer for the anion-bound molecules: after vibrational excitation, the bulk and cation-bonded water molecules relax in about 0.8 picoseconds, whereas the water molecules in the anion shell remain excited 3 to 6 times as long.

Notwithstanding the dominant influence of the anions, it can be expected that at high concentrations the cations should also affect the vibrational relaxation: at concentrations above approximately 6 M, almost all water molecules are involved in solvating ions, and ions are sharing water molecules in their first solvation shells.\(^56\) Between 1 and 6 M, the salt concentration becomes an important parameter because in this regime, the local environment of the anion changes drastically.

In the present chapter, 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 do change the vibrational lifetime of water molecules in the solvation shell of the anion, albeit to a lesser extent than do the anions. The experiments and modeling presented in this paper aim to understand the influence of anions and cations on the O–H stretch vibrational lifetime of water molecules in anionic solvation shells.

4.2 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\(_2\), Lil, NaI, or MgI\(_2\), dissolved in D\(_2\)O and less than 1 M of HDO. The salts were
studied at the following anion concentrations: 0.5, 1, 2, 3, 4, 6 and 9 M (bromide salts), 10 M (iodide salts). Below 0.5 M, the concentration was too low to allow for an accurate determination of the vibrational lifetime. The maximum concentrations are limited by the solubilities in each series of three salts of the same anion. The samples were kept between two CaF$_2$ windows, separated by a 200 µm teflon spacer. The transmission of the samples at the approximate center of the O–H stretch absorption band (3450 cm$^{-1}$) is generally between 5 and 20%, depending on the HDO concentration.

![Figure 4.1](https://example.com/figure4.1.png)

**Figure 4.1.** Pump-probe traces of solutions of several concentrations of NaI in HDO:D$_2$O. The measurement was performed at 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 bi-exponential function convolved with a gaussian crosscorrelation function.

The experimental methods applied in this chapter are similar to those of the previous chapter. The polarization of the probe pulse was again set at the magic angle (54.7°) with respect to the pump polarization, so that 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 probe now has a narrower spectral width, because two KTP crystals have been used instead of one for better pulse-to-pulse stability. The pump pulses have an energy of typically 20 µJ, the energy of the probe pulses is less than 1 µJ. The cross-correlation trace typically has a width of 400 fs. Variation of the pump energy leads only to a change in signal amplitude, and does not influence the dynamics.
4.3 Results

In figure 4.1, pump-probe traces of solutions of NaI are shown. The decay is non-exponential, which is most clearly seen at low concentrations. The data can be well fitted with a bi-exponential function, convolved with a gaussian cross-correlation trace (equation 2.8 with \( n = 2 \)). In this way, two time constants are obtained, the shorter of which, 0.8 ps, is approximately the same as obtained previously for pure HDO dissolved in D$_2$O.\(^{198,99}\) It originates from O–H groups that are hydrogen bonded to another water molecule, which makes them similar to the O–H groups in HDO:D$_2$O. The longer time constant ranges from roughly 2 to almost 5 picoseconds, and was found to correlate mainly with the type of anion and its concentration. The slow component of the vibrational relaxation, denoted in this chapter by \( T_1 \), is the focus of the present study.

![Figure 4.2](image)

**Figure 4.2.** Pump-probe traces of 9 M solutions of LiBr and NaBr in HDO:D$_2$O. The measurement was performed at 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 bi-exponential function convolved with a gaussian crosscorrelation function.

\( T_1 \) shows a clear concentration dependence, that can already be seen from the raw data (figure 4.1). Less well pronounced are the differences in \( T_1 \) for different cations: in figure 4.2, raw data are shown for 9 M solutions of NaBr and LiBr.

In figure 4.3, \( T_1 \) 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
of anion concentration, the lifetimes of $\text{Br}^-$ and $\text{I}^-$ are almost the same; $\text{Cl}^-$ is faster at all measured concentrations. The sodium and magnesium salts show the same features.

In figures 4.4, 4.5 and 4.6, $T_1$ 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 in figure 4.3, in which the anion was varied. For example, at a concentration of 6 M, $T_1$ of an iodide salt is 50% longer than for a chloride salt, whereas the change of the cation from $\text{Mg}^{2+}$ to $\text{Na}^+$ leads to an increase of $T_1$ of at most 10%. The lithium salts have $T_1$'s in between sodium and magnesium salts.

### 4.4 Model

In this section we will develop a model for the vibrational relaxation of HDO molecules in the solvation shells of $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ that can explain the trends observed in the previous section. The relaxation rate of the initially excited state of the O–H stretch vibration with wave function $\varphi_{\text{OH},v=1}$ can be described by a Fermi 'golden rule' expression:

$$
\frac{1}{T_1} = \int dE_f |\langle \varphi_{\text{acc},E_f,\varphi_{\text{OH},v=0}} | V_{\text{anh}} | \varphi_{\text{acc},E_i,\varphi_{\text{OH},v=1}} \rangle|^2 \delta(E_f - E_i) \rho(E_f),
$$

(4.1)

with $E_f$ the energy of the final combination state of accepting modes, represented by the wavefunction $\varphi_{\text{acc},f,\varphi_{\text{OH},v=0}}$, $E_i$ the energy of the initial state $\varphi_{\text{acc},i,\varphi_{\text{OH},v=1}}$, and $\rho(E_f)$ the
density of states.

In the condensed phase, the combination of accepting modes will contain both high-frequency intramolecular modes and low-frequency intermolecular (bath) modes. The latter modes often play an important role in making the energy transfer resonant, i.e. making the $\delta(E_f - E_i)$ function different from zero. Two different cases can be distinguished. In the first, the anharmonic coupling only depends on high-frequency intramolecular coordinates. Then the energy transfer gets resonant because the energies of the initially excited mode and the combination of intramolecular accepting modes are both subject to fluctuations induced by the interactions with the bath modes. In the second case, the anharmonic coupling depends explicitly on the bath coordinates. In this case, the anharmonic coupling $V_{\text{anh}}$ is often assumed to be a product of an intramolecular system part $V_{\text{anh},S}$ and a bath part $V_{\text{anh},B}$. By representing the delta function in the time domain, the transition rate can be written in the form of a product of an intramolecular anharmonic coupling and a Fourier transform of a $\langle V_{\text{anh},B}(t)V_{\text{anh},B}(0) \rangle$ bath correlation function. The latter is often evaluated with molecular dynamics simulations.

For polyatomic molecules in the condensed phase, it is not possible to evaluate the transition rate exactly. In most cases only the trends, e.g. the dependencies on certain parameters like pressure, temperature or solvent, can be described. These dependencies often result from changes in the character, energy and density of states of the low-frequency bath modes.

In the relaxation of the O–H stretch vibration of HDO:D$_2$O, at least part of the energy has to be accepted by the hydrogen bonds, because in contrast to H$_2$O, 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 not only dependent 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. Hence, the donated hydrogen bond is not a pure local O–H⋯X⁻ (X=Cl⁻, Br⁻, I⁻) mode, but in fact will be 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 wavefunction of this delocalized hydrogen bond.

We assume that the anharmonic coupling $V_{an}$ can be written as $V_{OH} V_{dbb} V_{oth}$, with $V_{OH}$ the dependence of the anharmonic coupling on the O–H stretch coordinate, $V_{dbb}$ the dependence on the delocalized hydrogen-bond coordinate, and $V_{oth}$ the dependence on all other coordinates including intramolecular coordinates (bending mode, O–D stretch vibration) and intermolecular modes (librational modes, other hydrogen bond stretch and bend vibrations). The wavefunction $\psi_{acc,f}$ can then be written as the product $\psi_{oth,f} \psi_{dbb,f}$. The wavefunction $\psi_{dbb,f}$ has contributions from four different hydrogen
bonds: the local anionic (O-H···X\(^-\)) mode, other anionic hydrogen bonds (O-D···X\(^-\)), bulk (O-D···O), and cationic (Y\(^+\)-O-D···O) hydrogen bonds. Since almost all solvent molecules are D\(_2\)O molecules, the latter hydrogen bonds are actually deuterium bonds. This does not hold of course for the donated hydrogen bond next to the excited O-H group. The stretching frequency of a deuterium bond is almost the same as for a hydrogen bond, because the reduced mass of the hydrogen-bond vibration does not change very much when hydrogen is substituted by deuterium. The delocalized hydrogen bond wavefunction \(\varphi_{\text{dhh,f}}\) can be written as:

\[
\varphi_{\text{dhh,f}} = C_{a'} \varphi_{\text{O-H···X}} + \sum_{a''} C_{a''} \varphi_{\text{O-D···X}} + \sum_{b} C_{b} \varphi_{\text{O-D···O}} + \sum_{c} C_{c} \varphi_{\text{Y+O-D···O}}.
\]

The contribution of each hydrogen-bond mode is denoted by the coefficients \(C_{a'}, C_{a''}, C_{b},\) and \(C_{c}\), where the subscripts \(a, b, c\) denote anion (single prime for O-H···X\(^-\)), double prime for admixing O-D···X\(^-\)), bulk water and cation, respectively. The wavefunction likely will be dominated by the local anionic hydrogen bond. Hence, \(C_{a'}\) will be greater than \(C_{a''}\), \(C_{b}\) and \(C_{c}\) at all concentrations. The coefficients further depend on the components' abundance, which changes with concentration; they will be calculated below.

If we now substitute the expression for \(\varphi_{\text{dhh,f}}\) of equation (4.2) in \(\varphi_{\text{acc,f}}\) and \(\varphi_{\text{acc,i}}\) in equation (4.1), and use the product form of the anharmonic coupling, we get:
\[ \frac{1}{T_i} = \left\{ \left| C_{a'}\langle \varphi_{O-H-X,i}|V_{dhh}|\varphi_{O-H-X,i}\rangle \right|^2 \right. \]
\[ + \sum_{a''} \left| C_{a''}\langle \varphi_{a'',O-D-X,i}|V_{dhh}|\varphi_{a'',O-D-X,i}\rangle \right|^2 + \]
\[ + \sum_b \left| C_b\langle \varphi_{b,O-H-O,i}|V_{dhh}|\varphi_{b,O-H-O,i}\rangle \right|^2 \}
\[ + \sum_c \left| C_c\langle \varphi_{c,Y+O-H-O,i}|V_{dhh}|\varphi_{c,Y+O-H-O,i}\rangle \right|^2 \times \]
\[ \left. \left| \langle \varphi_{odd,i}|V_{oth}|\varphi_{odd,i}\rangle \right|^2 \left| \langle \varphi_{OH,v=0}|V_{OH}|\varphi_{OH,v=1}\rangle \right|^2 \right\} \quad (4.3) \]

In this expression all cross terms have been neglected. The reasoning behind this is that the different \( C_{a''}, C_b, C_c \) will have different signs. Hence, the terms proportional to \( C_{a''} \sum_b C_b, C_{a''} \sum_c C_c, \sum_{a''} C_{a''} \sum_b C_b, \sum_{a''} C_{a''} \sum_c C_c, \sum_b C_b \sum_{c'} C_{c'} \) (\( b \neq b' \)), and \( \sum_{c'} C_{c'} \sum_{c''} C_{c''} (c \neq c') \), are all expected to be negligibly small.

We can write equation (4.3) as

\[ \frac{1}{T_i} = \sum_a \left| C_a \right|^2 / T_{1a} + \sum_b \left| C_b \right|^2 / T_{1b} + \sum_c \left| C_c \right|^2 / T_{1c}, \quad (4.4) \]

where the term \( \sum_a \left| C_a \right|^2 \) is equal to \( \left| C_{a'} + \sum_{a''} C_{a''} \right|^2 \) of equation (4.3). In this expression it is assumed that the coupling to the \( O-H \cdots X^- \) hydrogen bond is the same as to the \( O-D \cdots X^- \) hydrogen bond. The relaxation rate is now 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 \( \varphi_{dhh,f} \) would be purely anionic, bulk, or cationic in character. In the case of bulk, this corresponds to the situation of pure liquid \( HDO:2D_2O \) with no ions added.

In the following we will determine the values of the \( \sum_i \left| C_i \right|^2 \) 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 \( \epsilon \) of the anion. We assume that there is an equilibrium between unoccupied anion binding sites (the concentration of empty anion binding sites is denoted \( [A^-] \)), the actual concentration of anion-bonded O-D groups \( ([A \cdot OD]) \) and the concentration of O-D groups that are not bound to the anion solvation shell \( ([O-D \cdots O]) \). With the equilibrium an equilibrium constant \( K_s \) is associated defined by

\[ K_s = \frac{[A \cdot OD]}{[A^-][OD \cdots O]}. \quad (4.5) \]

We now identify \([A \cdot OD]\) with \( N_{OD,a}(\epsilon)\). It can be written in terms of \( K_s \) and \( \epsilon \) using the following 'conservation laws':

\[ [A^-] + [A \cdot OD] = N_s \epsilon, \]
\[ [A \cdot OD] + [OD \cdots O] = N_{OD}. \quad (4.6) \]
$N_a$ is the maximum number of water molecules in the anion's solvation shell, called the coordination number. $N_{OD}$ is the concentration of O–D groups, equal to twice the molarity of water, 110 M.

An expression for the concentration 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:

$$K_c = \frac{[C \cdot OD_2]}{[C_\cdot][D_2 O]},$$

(4.7)

and the conservation laws

$$[C_\cdot] + [C \cdot OD_2] = N_c \epsilon,$$

$$[C \cdot OD_2] + [D_2 O] = N_{OD}/2.$$  

(4.8)

$N_c$ is the cation's coordination number, $[D_2 O]$ is the concentration of water molecules that are not in the cation's solvation shell.

The concentration of O–D groups that are 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 and Raman spectroscopy. Hence, to arrive at $N_{OD,c}(\epsilon)$, the concentration of cation-affected O–D groups, $2[C \cdot OD_2]$, is multiplied with the fraction that binds to another water molecule and not to an anion. Hence,

$$N_{OD,c}(\epsilon) = 2[C \cdot OD_2] \left(1 - \frac{N_{OD,a}(\epsilon)}{N_{OD}}\right)$$

(4.9)

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

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

(4.10)

The dominant character of $\varphi_{acc}$ is that of O–H−X−. The admixture of bulk and cation behaviour is assumed to scale with $N_{OD,b}(\epsilon)$ and $N_{OD,c}(\epsilon)$, respectively. We assume that the coefficients $|C_b|^2$ and $|C_c|^2$ depend linearly on these concentrations. The coefficient $|C_a|^2$ then follows from the normalization of $\varphi_{acc}$. As a function of concentration, the coefficients are now defined as follows:
\[
\begin{align*}
\sum_b |C_b|^2(e) &= k_b \frac{N_{OD,b}(e)}{N_{OD}}, \\
\sum_c |C_c|^2(e) &= k_c \frac{N_{OD,c}(e)}{N_{OD}}, \\
\sum_a |C_a|^2(e) &= \left(1 - \sum_b |C_b|^2(e) - \sum_c |C_c|^2(e)\right),
\end{align*}
\]  

(4.11)

with \(k_b\) and \(k_c\) proportionality constants that depend on the nature of the cation and the anion. Equations (4.4) to (4.11) fully describe the dependence of the vibrational lifetime on anion, cation and their concentration. Note that \(N_{OD,b}(e)\) and \(\sum_b |C_b|^2\) reach their maximum value at \(e = 0\), while \(N_{OD,c}(e)\) and \(\sum_c |C_c|^2\) are equal to zero at \(e = 0\).

### 4.5 Fit Results

In the previous section, we obtained an expression for the lifetime of the anion-bound O–H stretch vibration, as a function of concentration and composition of dissolved salt, in terms of the lifetimes of anionic (\(T_{ia}\)), bulk (\(T_{ib}\)) and cationic (\(T_{ic}\)) components. \(T_{ib}\) is known from previous studies on pure HDO:D\(_2\)O and equals 0.74 ps. For the \(T_{ic}\), no data are available, and their contribution to the measured \(T_i\) 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 \(T_{ic}\) 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:

\[T_i = k(\Delta \omega_{OH})^{-1.8}.
\]  

(4.12)

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. 118. After multiplication by a factor of 1.36\(^{39}\) 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\(^{-1}\) (Mg\(^{2+}\)O–H⋯O). Compared to a frequency of 3410 cm\(^{-1}\) for HDO:D\(_2\)O without salt,\(^{36}\) the Na\(^+\) affected O–H stretch band is blueshifted with respect to pure water, whereas Mg\(^{2+}\) and Li\(^+\), that have stronger electric fields, are redshifted. The constant \(k\) in equation (4.12) is determined using a lifetime of 0.74 ps for pure HDO:D\(_2\)O.\(^{38,91}\) For \(T_{ic}\) the following values are obtained: 0.5 ps (Li\(^+\)), 1.0 ps (Na\(^+\)) and 0.5 ps (Mg\(^{2+}\)). For the determination of \(T_{ia}\) we cannot use equation (12) since it is only valid for O–H⋯O hydrogen bonds. For O–H⋯X\(^-\) hydrogen bonds the frequency dependence will be different.

Values for the coordination numbers can be found in the literature.\(^{96,80,9,30,107}\) We use coordination numbers of 4 for Li\(^+\), 6 for Na\(^+\), Mg\(^{2+}\), Cl\(^-\)and Br\(^-\), and 9 for I\(^-\). The values of \(K_a\) and \(K_c\) appeared not to be very critical in the fit. We used a value of 0.25; a 1 M NaCl solution will then have 5% of the available anion-binding sites unoccupied. At 6 M, this fraction is 7%.
The remaining fit parameters are $T_{1a}$, $k_b$, and $k_c$. Of these parameters $T_{1a}$ and $k_b$ should only depend on the nature of the anion. At zero concentration $N_{OD,B} = N_{OD}$ and $|C_e| = 1 - k_b$. Therefore, for a given anion, $k_b$ should be the same for all cations. Hence, for a particular combination of cation and anion only $k_c$ is left as a fit parameter.

The fit values of $T_{1a}$, $k_b$, and $k_c$ are shown in table 4.1.

### Table 4.1

<table>
<thead>
<tr>
<th></th>
<th>$T_{1a}$</th>
<th>$k_b$</th>
<th>$k_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>3.5 ps</td>
<td>0.17</td>
<td>0.07</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.5 ps</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>3.5 ps</td>
<td>0.17</td>
<td>0.07</td>
</tr>
<tr>
<td>LiBr</td>
<td>5 ps</td>
<td>0.18</td>
<td>0.08</td>
</tr>
<tr>
<td>NaBr</td>
<td>5 ps</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>MgBr$_2$</td>
<td>5 ps</td>
<td>0.18</td>
<td>0.07</td>
</tr>
<tr>
<td>LiI</td>
<td>6 ps</td>
<td>0.22</td>
<td>0.08</td>
</tr>
<tr>
<td>NaI</td>
<td>6 ps</td>
<td>0.22</td>
<td>0.19</td>
</tr>
<tr>
<td>MgI$_2$</td>
<td>6 ps</td>
<td>0.22</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The fit model of section 4.4 provides a good description of the trends observed in section 4.3. From the comparison of the fit results with the experimental data we can now identify the origins of the trends observed. Within the framework of the model, 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$^-$. This can be understood in the following way. 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.$^{94,82}$ The weaker hydrogen-bond interaction in turn leads to a decrease of the anharmonic interaction between the O-H stretch vibration and the hydrogen-bond mode,$^{107}$ and thereby to a slow-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$^6$: 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.$^{93}$

A second important effect 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 delocalized hydrogen bond wavefunctions $\varphi_{dhh,f}$ and $\varphi_{dhh,l}$. In figure 4.7, the fractions of the different types of hydrogen bonds are shown for NaCl and MgI$_2$. It is clearly
seen that with increasing concentration of dissolved salt, the fraction of O–D···O hydrogen bonds decreases while the fraction of O–D···X⁻ hydrogen bonds increases. The fraction of cationic hydrogen bonds Y⁺O–D···O first increases with concentration 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 4.8, the corresponding coefficients are shown for the same two salts. It is clearly seen that at low concentration the delocalized hydrogen bond is already dominated by the anionic hydrogen bond modes. 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 short $T_{1b}$.

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 addition, the coordination number is higher for I⁻ than for Cl⁻ 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 4.7, it is indeed seen that for MgI₂ the relative fraction of anionic hydrogen bonds rises much faster with anion concentration than for NaCl. The faster rise of the fraction of anionic hydrogen bonds for I⁻ leads to a

![Diagram](image-url)
faster rise of the contribution of the anionic hydrogen bonds to the delocalized hydrogen-bond wavefunctions $\varphi_{dbh,f}$ and $\varphi_{dbh,i}$, 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 $T_{ic}$. The different $T_{ic}$ 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 such that they are strengthened, thereby increasing the anharmonic interaction with the O–H vibration. The influence of the very short (0.5 ps) $T_{ic}$ of lithium and magnesium is somewhat tempered by the fact that there are less cations around compared to sodium; for lithium because the coordination 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–I$^-$ and Mg$^{2+}$O–D–Cl$^-$ hydrogen bonds to the delocalized $\varphi_{dbh,f}$ and $\varphi_{dbh,i}$ wavefunctions. This can be seen from the coefficients $k_c$ of the iodide salts shown in table 4.1. A possible explanation for the small admixture of cationic hydrogen bonds is the large frequency difference between the Li$^+$O–D–I$^-$ and Mg$^{2+}$O–D–Cl$^-$ hydrogen bonds and the O–H–I$^-$ hydrogen bond. The Li$^+$O–D–Cl$^-$
4.7 CONCENTRATION AND CATION DEPENDENCE OF THE VIBRATIONAL RELAXATION

and Mg$^{2+}$O-D$\cdash$O hydrogen bonds are relatively strong and will have high frequencies, whereas the O-H$\cdash$I$^-$ hydrogen bond is relatively weak, resulting in a rather low frequency. Within a perturbative approach of the description of the wavefunction, the admixture is inversely proportional to the frequency difference, thus explaining why the Li$^+$O-D$\cdash$O and Mg$^{2+}$O-D$\cdash$O hydrogen bonds are only weakly contributing to the hydrogen bond of dominant O-H$\cdash$I$^-$ character.

From the above it is clear that the observed trends can be well explained from changes in the delocalized hydrogen-bond mode involving the hydrogen atom of the excited O-H vibration. However, this hydrogen bond is not the only accepting mode. The accepting combination tones likely also contain excitations of the bending mode and/or the O-D stretching vibration, and other hydrogen-bond modes. These modes can also be affected by a change in concentration and nature of the dissolved cations and anions, and these effects can also contribute to the observed trends. However, the influence of the dissolved ions on the intramolecular modes will not be as strong as on the $\varphi_{\text{dbh}}$ hydrogen-bond. Hence, the effects on the intramolecular modes are not expected to have a large influence on the overall relaxation rate. The other hydrogen bond modes certainly do depend on the nature and concentration of dissolved salt. These other 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. The interaction with the bulk O-D$\cdash$O and cationic $Y^+$O-D$\cdash$O hydrogen bonds is therefore expected to occur mainly via the coupling of these modes with the local O-H$\cdash$X$^-$ mode, which forms the basis of the model of section 4.4.

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$^{+2}$ and Mg$^{2+}$, and the anions Cl$^-$, Br$^-$ and I$^-$ . The concentration was varied between 0.5 M and 6 M (Cl$^-$), 9 M (Br$^-$), or 10 M (I$^-$). We found that the vibrational lifetime $T$, 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 $T$, on the nature of the cation: for the same type of anion and concentration, $T$, increases in the cationic series Mg$^{2+}$, Li$^+$, Na$^{+2}$.

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$\cdash$X$^-$ (X=Cl$^-$, Br$^-$, or I$^-$) bond, but a delocalized mode showing admixture of other anionic O-D$\cdash$X$^-$ hydrogen bonds, bulk O-D$\cdash$O hydrogen bonds and O-D$\cdash$O hydrogen bonds of water molecules in the first solvation shells of the cations, denoted as $Y^+$O-D$\cdash$O hydrogen bonds.

With increasing concentration, the O-D$\cdash$X$^-$ character of the delocalized hydrogen bond increases while the bulk O-D$\cdash$O character decreases, leading to an increase of $T$, (slower relaxation), because the coupling to an O-D$\cdash$O hydrogen bond is much stronger than to an O-D$\cdash$X$^-$ 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 coupling of the excited O–H stretch vibration to the part of the delocalized hydrogen-bond wavefunction representing the cationic $Y^+\cdot\cdot\cdot O$ bonds. The strength of the cationic hydrogen bond increases going from $Na^+\cdot\cdot\cdot O$ to $Li^+\cdot\cdot\cdot O$ to $Mg^{2+}\cdot\cdot\cdot O$. 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 delocalized hydrogen bond mode.