Ion solvation in water: femtosecond spectroscopy of hydrogen-bond dynamics
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Recently, Laenen and Thaller published results on the vibrational lifetime of the O–H stretch vibration of aqueous salt solutions (LiCl, NaCl, KCl or NaI). They reported that the vibrational lifetime depends on the nature of the cation, and not on that of the anion. The variance of this finding with the results presented in chapter 3 and chapter 4, was attributed to differences in pulse characteristics. In this chapter, we present experimental results that show that the claims by Laenen and Thaller are wrong, and that the vibrational lifetime is influenced strongly by the anion, and only weakly by the cation, independent of the pulse characteristics.

5.1 INTRODUCTION

In the Letter published by Laenen and Thaller, results were presented on the vibrational and orientational relaxation of water molecules in aqueous salt solutions containing LiCl, NaCl, KCl, or NaI. It was reported that the vibrational lifetime depends on the nature of the cation and not on that of the anion (see chapter 3 and chapter 4). Unfortunately, no comparative data were supplied to support these findings (only data for NaCl solutions were shown). Since the difference with our previously published work was ascribed by Laenen and Thaller to differences in the pulse parameters, we repeated their measurements with laser pulses identical to the pulses they used. The results, which are presented in this chapter, show that the conclusions of Laenen and Thaller are incorrect.

5.2 EXPERIMENT

In order to reproduce the measurements of Laenen and Thaller, we changed our method of pulse generation slightly with respect to the previous chapters. By using two instead of only one KTP crystal in the pulse generation (section 2.3), we managed to obtain laser pulses with almost the same bandwidth, pulse duration and pump energy as the pulses used by Laenen. The spectral width of the pulses was reduced to 37 cm⁻¹, and the pulse duration was increased to 450 fs. The pump-pulse energy was limited to 10 μJ. The pump was tuned to 3420 cm⁻¹, the probe to 3150 cm⁻¹ and 3420 cm⁻¹. The sample is contained in a rotating sample cell to obtain a fresh part of the sample at every laser shot. Hence, the temperature error is limited to the effect of a single pump pulse, and is less than 1 K. The only difference with the experiment of Ref. 71 is that the pulses used in the present study have a 1 kHz repetition rate, whereas the pulses used in Ref. 71 have a repetition rate of only 50 Hz.
5.3 Results and Discussion

The pump–probe transients (isotropic transmission changes) of 2 M solutions of NaCl, KCl, KF, and NaI obtained with these pulse parameters are shown in figures 5.1 and 5.2.

First, we studied the dependence of the vibrational lifetime on the nature of the anion. In Ref. 71 it is reported that the vibrational relaxation is independent of the anion: the same time constant of $2.7 \pm 0.2$ ps is reported for NaCl and NaI at all concentrations. In figure 5.1, we present data on these solutions using the same pulse parameters as Laenen and Thaller. It is clear that, contrary to the results of Ref. 71, the vibrational relaxation in the solutions containing 2 M NaCl or NaI is different. In the figure, we also added a measurement of 2 M KF, for which the absorption change decays much faster, approximately as fast as pure HDO:D$_2$O $(0.74 \pm 0.1$ ps). We used KF instead of NaF since the latter salt is poorly soluble in water. However, exchanging Na$^+$ for K$^+$ does not have a strong effect on the lifetime, as is illustrated in figure 5.2. It is clear from the measurements presented in figure 5.1 that the anion does have a strong effect on the vibrational lifetime and that this lifetime increases going from F$^-$ to Cl$^-$ to I$^-$.

Time constants for the relaxation can be obtained by performing a biexponential fit to the data (the fit function is the sum of two exponentials, multiplied with the Heavyside function and convolved with the gaussian cross-correlation trace). For all solutions, we
find a fast component similar to that of HDO:D₂O and slow decay-time constants of $2.21 \pm 0.1$ ps (2 M NaCl) and $2.76 \pm 0.1$ ps (2 M NaI). For higher concentrations, the decay times increase to $2.6 \pm 0.2$ ps (6 M NaCl) and $3.7 \pm 0.2$ ps (6 M NaI). The decay time of KF remains $0.74 \pm 0.1$ ps at all concentrations. We found that the time constant of the slow component does not depend on the probe frequency: measurements on a 2 M NaCl solution using a pump frequency of 3420 cm⁻¹ and probe frequencies of 3100, 3150, and 3200 cm⁻¹ give the same result.

Second, we studied the dependence of the vibrational lifetime on the nature of the cation. Laenen and Thaller report a rather strong dependence of the vibrational lifetime on the cation, e.g. 2.4 ps for KCl and 2.7 ps for NaCl (2 M solutions). We also performed measurements on these solutions; the results are presented in figure 5.2. The relaxation does not differ at all. Biexponential fits of the data reveal the following lifetimes: $2.21 \pm 0.1$ ps (NaCl) and $2.18 \pm 0.1$ ps (KCl) (2 M solutions, at 3150 cm⁻¹ probe). At higher concentrations of salt, the vibrational relaxation of NaCl and KCl remain equal.

In these experiments on aqueous salt solutions, there is very little effect of spectral diffusion, at least at delay times $>2$ ps. Only if the $0\rightarrow1$ transition is excited in the wings of the absorption band, so that the initial distribution of excited molecules most strongly differs from the final equilibrium distribution, we observe a small effect (see chapter 6). In the experiments of figures 5.1 and 5.2, where the $0\rightarrow1$ transition is excited close to the

**Figure 5.2.** Isotropic transmission changes of solutions of HDO in D₂O and 2 M of NaCl, and KCl. The pump was tuned to 3420 cm⁻¹, the probe to 3150 cm⁻¹.
center of the absorption band, the dynamics after 2 ps are not at all affected by spectral diffusion, which implies that the time constants directly represent the vibrational lifetimes $T_1$ of the O–H stretch vibration. This means that the differences between the time constants we find and those of Ref. 71 cannot be attributed to differences in modeling of the transient spectral response and of the spectral diffusion.

If not from the pulse parameters or from differences in spectral modeling, how can the qualitative differences between the present findings and those of Ref. 71 be explained? The answer to this question can be found in the quality of the data. For comparison of the data quality, similar experimental data from Laenen’s work (figure 5.3) and measured with our setup (figure 5.4) are presented.

The difference in quality of the data can be quantized by calculating the value of $\chi^2$. The value of $\chi^2$ calculated from the data of figure 5.3 (figure 2 of Ref. 71) is $2 \times 10^{-4}$ (with respect to their own fit), whereas for the data we obtained (figure 5.4), $\chi^2 = 3 \times 10^{-6}$ (with respect to a biexponential fit). The difference is almost two orders of magnitude. This difference in quality of the data leads to a large difference in dynamic range of the data: the data of figures 1 and 2 have a 20 times larger dynamic range than the measurements of Ref. 71. As a result, the uncertainties in the time constants reported in Ref. 71 must be quite substantial. As such, the statement of Ref. 71 that “increasing the size of the anion results in no measurable effect on $T_1$ for the investigated anions [...] within our measurement accuracy” is more informative on this accuracy than on the true physical.

Figure 5.3. Experimental data published by Laenen and Thaller (figure 2 of Ref. 71). In the experiment, the pump was tuned to 3420 cm$^{-1}$, the probe to 3150 cm$^{-1}$. The sample was a solution of 5 M of NaCl.
5.3 COMMENT ON LAENEN AND THALLER

properties of these solutions. In view of the poor quality of the data, it is also questionable whether a decomposition of the absorption band in no less than six exchanging spectral components, as is done by Laenen and Thaller, is required and justified.

In their discussion of the data, Laenen and Thaller propose a correlation between the vibrational lifetime $T_\nu$ and the redshift of the O–H-stretch frequency with respect to the gas-phase value. This correlation is in agreement with experiment\textsuperscript{84} and with theory, e.g. Ref \textsuperscript{117}, where the vibrational lifetime has been calculated as a function of O–H stretch frequency (hydrogen-bond strength) for an O–H⋯O system. In Ref. \textsuperscript{71} this correlation is illustrated with a figure in which $T_\nu$ is presented as a function of the redshift for three previously measured systems. Indeed, these results neatly fall on a straight line. This figure is used by Laenen and Thaller to explain the observed long vibrational lifetimes of solutions containing Cl\textsuperscript{−} and I\textsuperscript{−}. Curiously, however, the data measured for the salt solutions are not at all included in this figure. If one would include these data one would see that they are far above (larger $T_\nu$) the line representing the correlation between $T_\nu$ and the redshift.

The work in chapter 3 and chapter 4 provides a rather straightforward explanation for this observation. In short, the vibrational lifetime $T_\nu$ is indeed correlated to the O–H-stretch redshift via the empirical relation $T_\nu \propto (\Delta \omega_{\text{OH}})^{-1.8,117}$ for all hydrogen-bonded O–H groups, the vibrational lifetime will decrease with increasing redshift. However, the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.4}
\caption{Data obtained at our setup, using the same sample and pulse characteristics as in the experiment of Laenen and Thaller, shown in figure 5.3. Comparison of the variances between the data set and its fitted curve leads to a value of $\chi^2$ that is two orders of magnitude smaller in our case.}
\end{figure}
Figure 5.5. The data points connected by the straight line were used in Ref. 71, figure 5, to explain the lifetimes of the measured data, which we added here to show that these data are not at all on this line.

The precise value of the lifetime will also depend on the nature of the hydrogen-bond acceptor, i.e., O, Cl\(^{-}\), or I\(^{-}\). In previous Raman\(^{26}\) and infrared spectroscopic studies,\(^9\) it was found that a substantial part of the O-H-stretch absorption spectrum of salt solutions containing X\(^{-}\) halogenic anions results from O-H\(\cdots\)X\(^{-}\) hydrogen-bonded groups. The observed long vibrational lifetimes of solutions containing Cl\(^{-}\) and I\(^{-}\) can thus be well explained if these lifetimes represent the relaxation of O-H\(\cdots\)Cl\(^{-}\) and O-H\(\cdots\)I\(^{-}\) systems, and not of O-H\(\cdots\)O systems. The longer O-H-stretch vibrational lifetimes of O-H\(\cdots\)Cl\(^{-}\) and O-H\(\cdots\)I\(^{-}\) in comparison to O-H\(\cdots\)O at the same redshift can be well explained from the larger mass of the hydrogen-bond acceptor. This explanation also agrees with the observation that the O-H-stretch vibrational lifetime of O-H\(\cdots\)F\(^{-}\) is comparable to that of O-H\(\cdots\)O, since the mass of F\(^{-}\) is very similar to that of a water molecule.

5.4 Conclusions

In this chapter, we presented experimental data on the salt solutions studied in Ref. 71 using the same experimental parameters, but with a much better signal-to-noise ratio. It is found that the vibrational lifetime strongly depends on the nature of the anion and only weakly on the nature of the cation, in strong contrast to the claims of Laenen and Thaller, and in agreement with the results of chapter 3 and chapter 4.