

Energy Relaxation Dynamics of the Hydration Complex of Hydroxide

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Abstract

We use polarization-resolved mid-infrared pump-probe spectroscopy to study the dynamics of the hydration shells of hydroxide ions (OH^-). We excite the O–H stretch vibrations of H_2O molecules solvating the OH^- ion and observe that this excitation decays with a relaxation time constant T_1 of 200 fs. This relaxation is followed by a thermalization process that becomes slower with increasing concentration of OH^- . The pre-thermalized state is observed to be anisotropic, showing that the energy of the excited O–H stretch vibrations is dissipated within the hydration complex. The anisotropy of the pre-thermalized state decays both as a result of the reorientation of the OH^- hydration complex and heat diffusion from the excited complexes to unexcited complexes. Modeling the anisotropy data at different concentrations allows for accurate estimate of the number of water molecules in the hydration shell of OH^- , the reorientation dynamics of the OH^- hydration complex, and the molecular-scale heat diffusivity.

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Introduction

The hydroxide ion OH^- and the hydronium ion H_3O^+ both form strong hydrogen bonds with their surrounding water molecules. Experimental and theoretical investigations indicate that these hydrogen bonds are rapidly exchanged with the chemical bonds of the surrounding water molecules.¹⁻⁴ This exchange results in a transfer of the charge of the proton and the hydroxide ion to the solvating water molecules, and thus effectively in the transport of the proton and hydroxide ion. Hence, these ions are not transported as particles, as in conventional Stokes diffusion, but only their charge is being conducted. This structural diffusion mechanism is highly efficient and explains the anomalously high mobility of protons and hydroxide ions in liquid water. The mechanism is often referred to as Grotthuss conduction.⁵

Density functional calculations indicate that there are two somewhat different mechanisms by which the hydroxide ion is transported through liquid water. One of these mechanisms is denoted as the “dynamical hypercoordination” mechanism,^{6,7} which involves reduction of coordination number of OH^- complex. In this mechanism $\text{OH}^-(\text{H}_2\text{O})_4$ breaks a accepting hydrogen bond between its oxygen and a water molecule in the first hydration shell, and then donates a hydrogen bond transiently to another water molecule. The other mechanism is the so-called “mirror image” mechanism,^{3,8,9} in which H_7O_4^- ions are converted to H_3O_2^- ions by cleavage of a second shell hydrogen bond. This mechanism is quite similar to the transfer mechanism of protons in liquid water, thus explaining the name “mirror image” mechanism.

The dynamics of the O–H stretch vibrations of protons and hydroxide ions in water has been investigated using femtosecond mid-infrared spectroscopy of isotopically diluted systems. For a solution of OD^- and HDO in D_2O , it was found that for part of the HDO molecules the absorption spectrum of the OH stretch vibration is broadened and shifted to lower frequencies.¹⁰⁻¹² This spectral component shows a very rapid relaxation with a time constant of 120-160 femtoseconds. The amplitude of the fast component scales with the concentration of OD^- , and is thus assigned to HDO molecules hydrating the OD^- ions. The fast relaxation has been interpreted in two different ways. In one interpretation, the fast relaxation was assigned to HDO molecules of which

the OH group is hydrogen-bonded to an OD^- ion that is showing deuteron exchange with a D_2O molecule.¹⁰ The exchange will lead to a strong modulation of the strength of the $\text{O-H}\cdots\text{O}$ hydrogen bond as this bond changes from a bond to an OD^- to a bond to a D_2O molecule. The modulation leads to a fast decay of the vibrational excitation of the HDO molecule that is a spectator at the deuteron transfer. In the other interpretation the fast relaxation component is assigned to the second excited vibrational state of a $\text{DO}\cdots\text{H}\cdots\text{OD}$ Zundel complex.¹¹ This Zundel complex forms a transition state in the transfer of the proton from HDO to OD^- . The fast vibrational relaxation is explained from the short lifetime of this transition state complex.

Here we use polarization-resolved pump-probe infrared spectroscopy to investigate the energy and reorientation dynamics of the hydration complex of the OH^- ion in H_2O . We study the energy relaxation dynamics of the O–H vibrations that are strongly hydrogen bonded to the OH^- ion. We also study the structural relaxation dynamics of the liquid following the fast local dissipation of heat and the heat diffusion from the excited hydration complexes to the surroundings.

Experimental methods

In the time-resolved mid-infrared pump-probe experiment,¹³ the pump pulses excite a fraction of the molecules from the ground state ($\nu = 0$) to the first excited state ($\nu = 1$). The probe pulses measure the pump-induced absorption changes, which is the difference in probe absorption between the pumped and un-pumped sample. The typical absorption changes induced by the pump are a bleaching at the fundamental transition ω_{01} ($\nu = 0 \rightarrow 1$) and induced absorption ω_{12} ($\nu = 1 \rightarrow 2$) from the excited $\nu = 1$ state. The vibrational dynamics of the excited molecules is observed by measuring the pump-induced absorption changes at different delay times between pump and probe.

The infrared laser pulses needed for the experiments are generated via parametric nonlinear optical frequency conversion processes that are pumped by the output of a Ti:sapphire regeneratively amplified laser system (Spectra-Physics Hurricane). This system generates pulses at a wavelength of 800 nm with a pulse energy of 800 μJ and a pulse duration of 110 fs at a repetition rate of 1 kHz.

The 800 nm beam is split into two parts. The first part is coupled into a white-light seeded OPA (Optical Parametric Amplifiers). In the OPA the 800 nm pulses are split into signal (1300 nm) and idler (2000 nm) pulses. After the OPA the second harmonic of the idler is generated in a 3 mm BBO (β -barium borate) crystal. The doubled idler (1000 nm) is used as a seed for a parametric amplification process in a 5 mm KN (potassium niobate) crystal. This process is pumped by the second part of the 800 nm pulses. This process leads to amplification of the doubled idler (~ 1000 nm) and the generation of infrared pulses at the difference frequency tunable in the range $2400\text{-}2800\text{ cm}^{-1}$, with a duration of ~ 150 fs, a spectral width (FWHM) of $\sim 150\text{ cm}^{-1}$ and a pulse energy of a few μJ .

The generated mid-infrared pulses are sent onto a CaF_2 wedged window. The largest part ($\sim 92\%$) is transmitted and serves as the pump. The reflection from the front side of the wedge ($\sim 4\%$) serves as the probe, the reflection from the rear side of the wedge ($\sim 4\%$) serves as the reference. The reference beam is used to normalize the pulse to pulse fluctuations of the IR beam. All three beams (pump, probe and reference) are focused on to a sample cell by a gold coated parabolic mirror. The pump and probe are spatially overlapped. The delay time between pump and probe is varied using a motorized delay stage. Before entering the sample cell, the polarization of the pump is rotated to 45° with respect to the probe and reference polarization using a half-wave plate. Every other pump pulse is blocked by a chopper wheel to obtain pumped and unpumped signals. After the sample the probe and reference pulses pass through a rotatable polarizer to select the polarization components of them parallel and perpendicular to the polarization of the pump. The probe and reference pulses are dispersed by a spectrograph and the intensities of the different frequency components are detected by a Mercury Cadmium Telluride (MCT) detector.

The parallel and perpendicular components of the pump-induced absorption changes ($\Delta\alpha_{\parallel}$, $\Delta\alpha_{\perp}$) are used to construct the isotropic signal $\Delta\alpha_{\text{iso}}$ and anisotropic signal R :¹³

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

$$R(t) = \frac{\Delta\alpha_{\parallel}(t) - \Delta\alpha_{\perp}(t)}{\Delta\alpha_{\parallel}(t) + 2 \cdot \Delta\alpha_{\perp}(t)}. \quad (2)$$

The isotropic signal gives information on the decay of the excited vibration states and the subsequent thermalization dynamics. The anisotropy represents the normalized absorption-change difference between the parallel and perpendicular probe components.

The experiments were performed on NaOH/H₂O solutions at ten concentrations ranging from 0.5 to 10 M. The stock NaOH solution was purchased from Sigma-Aldrich. The solutions were held in a sample cell with two 4 mm thick CaF₂ windows separated by Teflon spacers of 50 μm (for 0.5 and 1.0 M), 25 μm (for 2.0 and 3.0 M) and 12 μm (for 4.0, 5.0, 6.0, 7.0, 8.6 and 10.0 M).

Results and Discussion

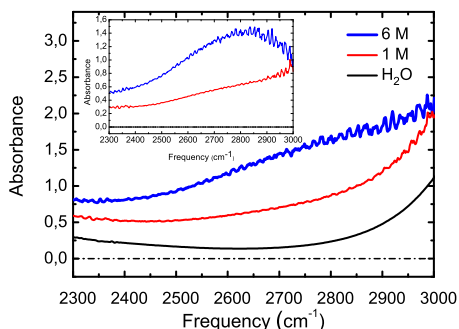


Figure 1: Absorption spectra of H₂O (black line) and NaOH/H₂O solutions of 1 M (red line) and 6 M (blue line). The inset shows the spectra of the hydroxide solutions after subtraction of the pure H₂O spectrum.

Figure 1 shows the linear absorption spectra of NaOH/H₂O solutions with two different hydroxide concentrations. It is clear that the spectra show an increasing red-shifted absorption with increasing NaOH concentration. This red-shifted absorption is assigned to the O-H stretch vibrations of water molecules that are hydrogen bonded to hydroxide ions. The hydrogen bonds

between H₂O molecules and the OH⁻ ion are much stronger than the hydrogen bonds between H₂O molecules. As a result, the (uncoupled) vibrational frequency of these oscillators is strongly red-shifted with respect to the other vibrations in the liquid making these vibrations relatively well localized. This assignment agrees with the results of some recent studies by the group of Tokmakoff.^{11,12} In these latter studies it was shown that the broad, red-shifted OH stretch vibrational spectrum of OH groups bonded to OH⁻ comprises both 0→2 transitions to Zundel states for (nearly) symmetric O···H···O systems and 0→1 transitions of OH groups that are strongly hydrogen bonded to OH⁻, but that are asymmetric in the sense that the hydrogen atom is much closer to one of the oxygen atoms.

Vibrational relaxation

We excite the OH stretch vibrations of H₂O molecules hydrating the OH⁻ ions. At all concentrations, we use pump and probe pulses with a central frequency of 2650 cm⁻¹. In Figure 2 we show transient absorption spectra at three different delay times, 0.4 ps, 1.2 ps and 40 ps, for solutions of 2 M (A), 4 M (B) and 6 M (C). At early delays, the transient spectra show a negative absorption change throughout the whole frequency region. This negative absorption change is due to the bleaching of the ground state and the stimulated emission from the excited OH stretch vibration. It is seen that the amplitude of the bleaching decays rapidly at short delay time, but it increases again at later.

In Figure 3 the isotropic absorption change $\Delta\alpha_{\text{iso}}$ at the center frequency 2650 cm⁻¹ is shown as a function of delay for three NaOH concentrations. At zero time delay, the pump excitation results in a bleaching signal that rapidly relaxes on a time scale of a few hundred femtoseconds. After reaching a minimum, the bleaching rises again on a much longer time scale. The signal no longer changes after ~5 picoseconds. At this time the energy that was put in by the excitation is completely thermal over the focus. The transient minimum in the bleaching implies that the vibrational relaxation does not immediately lead to a thermalization of the excitation energy. Figure 3 shows that the equilibration process becomes slower with increasing NaOH concentration, which

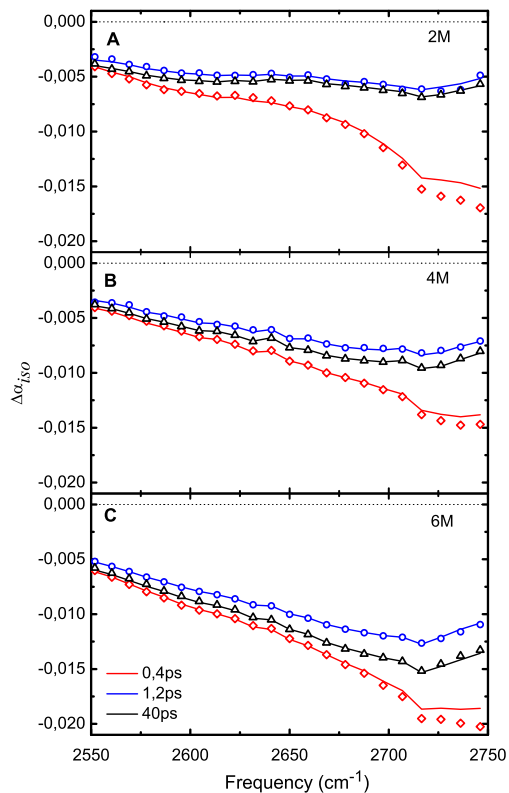


Figure 2: Transient spectra of three different NaOH solutions at pump-probe delay times of 0.4 ps (\diamond), 1.2 ps (\circ) and 40 ps (\triangle). The solid lines show the fitted result with the consecutive relaxation model.

makes the bleaching minimum more pronounced.

The isotropic signals were fitted by least-square method with a consecutive relaxation model.¹⁴ In this model, the excited state relaxes with a time constant T_1 to an intermediate state. This intermediate state relaxes to the final thermal equilibrium with a time constant T_{eq} . The fitted results are represented by the solid lines in Figure 2 and Figure 3. The time constants T_1 and T_{eq} resulting from the fit are plotted as a function of concentration in Figure 4. As shown in Figure 4, the concentration dependencies of T_1 and T_{eq} are quite different.

The transient spectrum of the intermediate state has the form of a thermal difference spectrum, which means that the fast relaxation process corresponds to the vibrational relaxation of the O–H

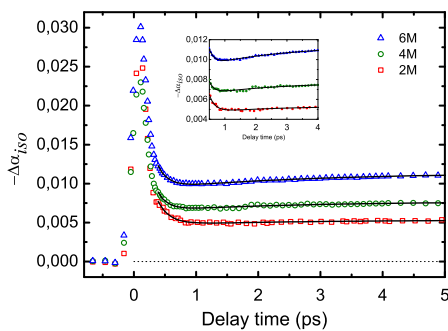


Figure 3: Isotropic absorption change $-\Delta\alpha_{ISO}$ as a function of delay time for three different concentrations of NaOH, measured at frequency of 2650 cm^{-1} . The solid lines represent fits to the data with the consecutive relaxation model. Inset, zoom-in from 0.5 ps to 4 ps

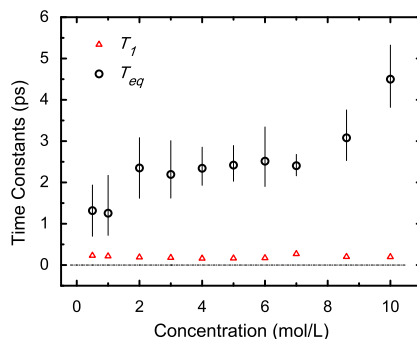


Figure 4: Vibrational lifetime constant T_1 and equilibration time constant T_{eq} as a function of concentration. The error bars of T_{eq} are estimated by increasing the chi-square up to 10% of the minimum. The error bars of T_1 are comparable with the triangle size

stretch vibration of H_2O molecules hydrating OH^- . The time constant T_1 has a value of 200 fs, and is independent of OH^- concentration (see Figure 4). The lack of concentration dependence of T_1 indicates that the vibrational relaxation is a local process in which the energy of the excited O–H stretch vibration relaxes to lower-frequency degrees of freedom within the same OH^- hydration complex. The value of T_1 is quite similar to the relaxation time constant T_1 of the O–H stretch vibrations in pure H_2O .^{15,16} The relaxation time of 200 fs is also quite similar to the time constant of 120–160 fs that was observed for HDO hydrating an OD^- ion.^{10–12}

The character of the intermediate state (being a local heated state) differs from that of the intermediate state of the relaxation observed in studies of isotopically diluted water, i.e. for the O–D/O–H stretch vibration of HDO molecules in $\text{H}_2\text{O}/\text{D}_2\text{O}$.¹⁷ The intermediate state of the latter

relaxation process does not have an associated transient spectrum, and its relaxation likely represents the delayed adaptation of the coordinates of the hydrogen bond network to the higher energy content of the low-frequency modes (librations, hydrogen-bond stretch and bend vibrations) that results from the relaxation of the O–D/O–H stretch vibration.

The equilibration time strongly varies with concentration, and increases from 1.3 ± 0.5 ps at low concentrations to 4.5 ± 0.7 ps for a solution of 10 M NaOH. The lack of concentration dependence of T_1 indicates that the vibrational relaxation is a local process in which the energy of the excited O–H stretch vibration relaxes to other vibrations within the same OH^- hydration complex. In contrast, the equilibration time T_{eq} is a more global parameter and very sensitive to the structural dynamics of the hydrogen bond network of the solution. For higher OH^- concentrations the restructuring takes more time, probably as a result of the stiffer hydrogen-bond network.

The intermediate state relaxes with an equilibration time constant that increases from 1.3 ± 0.5 ps at low concentrations to 4.5 ± 0.7 ps for a solution of 10 M NaOH. This strong concentration dependence can be understood from the fact the equilibration time T_{eq} is not a local parameter and will be strongly related to the collective structural dynamics of the hydrogen bond network of the solution. At higher OH^- concentrations the hydrogen-bond network will be stiffer, which will make the restructuring and thus full equilibration of the solution slower.

Anisotropy Dynamics

Figure 5 shows the anisotropy decay for five different concentrations (0.5, 1.0, 2.0, 4.0, and 6.0 M). At time zero the anisotropy signals are roughly 0.35. The initial partial decay of this anisotropy from 0.4 to 0.35 may be due to rapid resonant intermolecular energy transfer between OH vibrations within the OH^- hydration complex and/or due to librational motions. The anisotropy dynamic shows a rapid initial drop (200 fs) followed by a much slower decay on a time scale of ~ 10 ps. With increasing NaOH concentration the initial drop becomes larger and the subsequent decay becomes faster. In view of the short T_1 of the relaxation of the O–H stretch vibrations of 200 fs, it is clear that the signal conserves its anisotropy after the vibrational relaxation is complete,

which implies that the influence of the heat resulting from the vibration relaxation on the transient spectral response is anisotropic. After the fast vibrational relaxation, the resulting localized heat primarily affects the originally excited O-Hs whose transition dipole moments direction have not changed during this short time. Therefore the transient spectrum resulting from this local heating effect is anisotropic. In fact, if the heating effect resulting from the vibrational relaxation would only influence the absorption spectrum of the originally excited OH vibration, the anisotropy of the original excitation would be conserved fully. However, the dissipated heat will also affect the absorption spectra of other O–H vibrations in the same hydration complex of the OH⁻ ion that will have different orientations. Nevertheless, as the number of O–H vibrations absorbing at 2650 cm⁻¹ within the complex will be limited, a net non-zero anisotropy is retained.

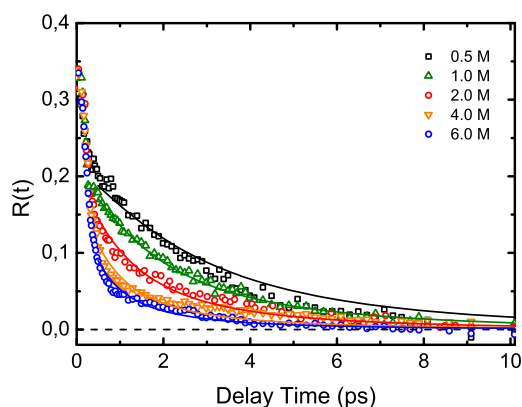


Figure 5: Anisotropy as a function of delay for five different concentrations of NaOH. The data are measured at a frequency of 2650 cm⁻¹. The solid lines are fits to the data of the heat diffusion model.

The ultrafast excitation and vibrational relaxation of the OH vibrations result in a strongly heated OH⁻ hydration complex that is hotter than its surroundings. Hence, the complex itself is in (hot) thermal equilibrium but the whole solution is in a non-equilibrium state. The complex then cools via heat diffusion to its surroundings. Given the probe frequency of 2650 cm⁻¹, we only observe the effects of heat reaching other excited and unexcited hydration complexes. Over time the unexcited complexes will become heated and, as the solvating water OH groups in these complexes have different (random) orientations, the overall distribution of the thermally affected

O-H vibrations becomes isotropic.

The anisotropy dynamics of hydroxide solutions have been studied before for isotopically diluted solutions of HDO in D_2O/OD^- .¹⁰ In this latter study, the dynamics of the isotropic signal contained a strong slow component associated with the vibrational relaxation of HDO molecules that are not directly interacting with OD^- ions. In addition, the heating effect of the vibrational relaxation was much smaller, because the probed hydroxyl groups are isotopically diluted. As a result, the anisotropy dynamics observed in Ref.10 were dominated by the orientational dynamics of the still excited OH vibrations of HDO molecules that are not in the first hydration shell of the hydroxide ion. In the present study the anisotropy dynamics are dominated by the heat diffusion and reorientation of the hot OH^- hydration complexes.

To calculate the anisotropy decay due to heat diffusion, we assume that the hydration complex of OH^- is a sphere with radius R and we neglect the interactions between different excited complexes. Under these assumptions, the time-dependent distribution of the temperature inside and outside the hot complex is expressed by the following equation,¹⁸ that describes the heat diffusion from a hot sphere to an infinitely large cold environment without any source:

$$T(R, r, t) = T_{\max} \cdot \left\{ \frac{1}{r} \sqrt{\frac{\chi}{\pi}} t [\exp(-\varepsilon_+^2) - \exp(-\varepsilon_-^2)] + \frac{1}{2} [\operatorname{erf}(\varepsilon_+) + \operatorname{erf}(\varepsilon_-)] \right\} \quad (3)$$

where $\varepsilon_{\pm}(R, r, t) = (R \pm r) / (2\sqrt{\chi t})$, $\operatorname{erf}(x)$ is the Gaussian error function, T_{\max} denotes the initial temperature of the hot sphere, χ represents the thermal diffusivity of the medium surrounding the complex respectively, and r is the distance away from the center of the hot complex.

The thermal energy that diffuses out of the excited complex will heat other unexcited complexes and solvent water molecules. The fraction f of the thermal energy contained in these other complexes is equal to the volume fraction of the OH^- hydration complex $f = 4\pi\rho R^3/3$, where ρ is the number density expressed in number of hydration complexes per nm^3 . After the vibrational

relaxation, the thermal energy still present in the excited complex and the thermal energy contained in the other complexes is governed by following equations:

$$E_{\text{in}}(t) = \int_0^R 4\pi r^2 T(R, r, t) dr \quad (4)$$

$$E_{\text{out}}(t) = f \cdot \int_R^\infty 4\pi r^2 T(R, r, t) dr \quad (5)$$

The anisotropy due to the heating effect $R_h(t)$ is proportional to the ratio of the part of the excitation energy that is still in the excited complex $E_{\text{in}}(t)$, and the total dumped energy contained in all OH^- hydration complexes which is the sum of the energy in the excited complex and the energy contained in all other complexes outside the excited complex E_{out} :

$$R_h(r, t) = a \cdot \frac{E_{\text{in}}(t)}{E_{\text{in}}(t) + E_{\text{out}}(t)} \quad (6)$$

where a is a scaling factor. Substituting the expressions for $E_{\text{in}}(t)$ and $E_{\text{out}}(t)$ we obtain:

$$R_h(r, t) = \frac{a \cdot \int_0^R r^2 T(R, r, t) dr}{\int_0^R r^2 T(R, r, t) dr + f \cdot \int_R^\infty r^2 T(R, r, t) dr} \quad (7)$$

The anisotropy not only decays as a result of heat diffusion but also as a result of the reorientation of the OH^- hydration complexes. These anisotropy dynamics $R_r(t)$ are described by an exponential function:

$$R_r(t) = e^{-\frac{t}{\tau_r}} \quad (8)$$

As the total anisotropy dynamics of the hydroxide complexes is described by $R(t) = R_h(t)R_r(t)$, we obtain:

$$R(t) = \frac{a \cdot \int_0^R r^2 T(R, r, t) dr}{\int_0^R r^2 T(R, r, t) dr + f \cdot \int_R^\infty r^2 T(R, r, t) dr} \cdot e^{-\frac{t}{\tau_r}} \quad (9)$$

The three parameters R , χ and τ_r that enter Eq. (9) are assumed to be independent of concentration, which is not necessarily true. However, it was shown in neutron scattering studies that

the spatial distribution of water molecules hydrating hydroxide remains the same, even at very high concentrations, which indicates that the radius R of hydration complex is quite independent of concentration.^{19,20} Likewise, the thermal diffusivity of aqueous salt solutions shows very little dependence on the salt concentration: the χ of pure water is $0.1435 \text{ nm}^2/\text{ps}$ and the χ of 6 M NaOH/H₂O is $0.1495 \text{ nm}^2/\text{ps}$ both at 25 °C.²¹

We fitted the anisotropy signals globally with, and find that the heat diffusion model provides a very good description of the anisotropy decay at all hydroxide concentrations, as illustrated by the solid lines in Figure 5. The speed up of the anisotropy decay with concentration can thus be well explained from the fact that with increasing NaOH concentration the nearest unexcited hydration complexes are located at smaller values of r . From the fitting we obtain $a=0.22\pm0.02$, $R=0.36\pm0.03 \text{ nm}$, $\chi=0.05\pm0.01 \text{ nm}^2/\text{ps}$ and $t_f=12\pm2 \text{ ps}$. The errors are estimated when chi-square increases up to 1.5 times the minimum value.

The a value of 0.22 ± 0.02 represents the anisotropy of the heated excited complex, which is smaller than the initial value of the anisotropy of 0.4. This decrease in anisotropy can be explained from the presence of other differently oriented O–H groups with the excited hydration complex that are also hydrogen-bonded to the OH⁻ ions. The absorption frequencies of these other O–H groups can be close to $\sim 2650 \text{ cm}^{-1}$, and the heating of these other differently oriented O–H groups results in an anisotropy of the heated excited complex that is smaller than 0.4. In view of this picture the a value of 0.22 ± 0.02 may be considered to be relatively high. However, it should be noted that the anisotropy will only decay due to the heating of O–H groups that possess a non-negligible absorption at the probe frequency of 2650 cm^{-1} . The transfer of energy to O–H groups that do not absorb at 2650 cm^{-1} will decrease the magnitude of the isotropic (heating) signal at 2650 cm^{-1} , but not its anisotropy. Nevertheless, the high value of a of 0.22 ± 0.02 indicates that the initially excited O–H strongly contributes to the heated excited complex that results directly after the vibrational relaxation.

Using the radius R of the complex of $0.36\pm0.03 \text{ nm}$ and the average volume of water molecule at room temperature, we calculate the number of water molecules contained in the hydration com-

plex to be ~ 4.5 . This value agrees well with the results of *ab-initio* molecular dynamic (MD) simulations that found respective coordination numbers of 4.2, 4.8 and 4.7 respectively for mirror mechanism, dynamical hypercoordination mechanism and static hypercoordination mechanism.⁷ The thermal diffusivity of $0.05 \text{ nm}^2/\text{ps}$ is approximately three times lower than the macroscopic thermal diffusivity.²² This difference may be due to the different character of the excitations of which the energy has to be transferred. The reorientation time constant t_r of the hydration complex of $12 \pm 2 \text{ ps}$ is significantly longer than the reorientation time constant of 2.5 ps of O–D groups of HDO molecules in H_2O .^{14,17} This larger reorientation time constant indicates that the reorienting hydration complex forms a relatively large and rigid structure that has to reorient as a whole.²³

Conclusions

We study the vibrational relaxation dynamics and anisotropy dynamics of the hydration shells of OH^- ions with polarization-resolved femtosecond vibrational spectroscopy. We study the dynamics for solutions of NaOH in H_2O with concentrations ranging from 0.5 to 10 M. The relaxation of O–H stretch vibrations of water molecules hydrating the OH^- ion is observed to proceed via two subsequent processes. In the first process, the excited O–H vibrations relax to an intermediate state with a concentration independent time constant 200 fs. The intermediate state represents a state in which the relaxed energy of the excited O–H vibration has led to a local heating of the hydration complex. In the second process, the intermediate state decays to a final thermal equilibrium in which the energy is thermally distributed over the focus of the exciting laser pulse. The time constant of the equilibration process rises with increasing concentration, from 1.2 ps for a 0.5 M solution to 4.5 ps for a 10 M solution.

The locally heated hydration complex possesses a significant nonzero anisotropy which shows that this state contains a large contribution of the initially excited O–H group. We describe the decay of the anisotropy of the intermediate state with a model in which we include the heat diffusion from the excited hydration complexes to non-excited complexes and the reorientation of the hydra-

tion complexes. We find that this model provides a quantitative description of the anisotropy decay at all measured concentrations using concentration independent values for the initial anisotropy a of the intermediate state, the radius R of the hydration complex, the heat diffusivity χ , and the reorientation time t_r of the hydration complex. We find $a=0.22\pm 0.02$, $R=0.36\pm 0.03$ nm, $\chi=0.05\pm 0.01$ nm²/ps, and $t_r=12\pm 2$ ps.

The initial anisotropy a of the intermediates state of 0.22 ± 0.02 is relatively high, which indicates that there is no resonant energy transfer within the H₂O molecule to which the excited O–H group belongs.²⁴ This result shows that the two O–H groups of this H₂O molecule are shifted far out of resonance, because only one of the O–H groups is hydrating the OH[−] ion. The high value of a also implies that the intermediate state possesses a strong contribution of the initially excited O–H group, which means that the initial heating is truly a very local effect and/or there are very little O–H vibrations within the hydration complex absorbing near 2650 cm^{−1}. The value of R corresponds to a hydration shell of 4.5 water molecules, in excellent agreement with the results of *ab-initio* molecular dynamics calculations. The reorientation time of the hydration complex is significantly longer than the reorientation time of 2.5 ps of water molecules in bulk liquid water, which indicates that this complex forms a relatively large and rigid structure.

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References

- [1] Rini, M.; Magnes, B. Z.; Pines, E.; Nibbering, E. T. J. *Science* **2003**, *301*, 349–352.
- [2] Woutersen, S.; Bakker, H. J. *Phys. Rev. Lett.* **2006**, *96*, 138305.
- [3] Agmon, N. *Chem. Phys. Lett.* **1995**, *244*, 456–462.
- [4] Mohammed, O. F.; Pines, D.; Dreyer, J.; Pines, E.; Nibbering, E. T. J. *Science* **2005**, *310*, 83–86.
- [5] Grotthuss, C. J. T. *Annales, de Chimie* **1806**, *58*, 54.
- [6] Tuckerman, M. E. *Nature* **2002**, *417*, 925–929.
- [7] Tuckerman, M. E.; Chandra, A.; Marx, D. *Acc. Chem. Res.* **2006**, *39*, 151–158.
- [8] Asthagiri, D.; Pratt, L. R.; Kress, J. D.; Gomez, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 7229–7233.
- [9] Agmon, N. *Chem. Phys. Lett.* **2000**, *319*, 247–252.
- [10] Nienhuys, H. K.; Lock, A. J.; van Santen, R. A.; Bakker, H. J. *J. Chem. Phys.* **2002**, *117*, 8021–8029.
- [11] Roberts, S. T.; Petersen, P. B.; Ramasesha, K.; Tokmakoff, A.; Ufimtsev, I. S.; Martinez, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 15154–15159.
- [12] Roberts, S. T.; Ramasesha, K.; Petersen, P. B.; Mandal, A.; Tokmakoff, A. *J. Phys. Chem. A* **2011**, *115*, 3957–3972.
- [13] Piatkowski, L.; Eienthal, K. B.; Bakker, H. J. *Physical Chemistry Chemical Physics* **2009**, *11*, 9033–9038.
- [14] Rezus, Y. L. A.; Bakker, H. J. *J. Chem. Phys.* **2005**, *123*, 114502.

- [15] Lock, A. J.; Bakker, H. J. *J. Chem. Phys.* **2002**, *117*, 1708–1713.
- [16] Cowan, M. L.; Bruner, B. D.; Huse, N.; Dwyer, J. R.; Chugh, B.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. *Nature* **2005**, *434*, 199–202.
- [17] Rezus, Y. L. A.; Bakker, H. J. *J. Chem. Phys.* **2006**, *125*, 144512.
- [18] Seifert, G.; Patzlaff, T.; Graener, H. *Phys. Rev. Lett.* **2002**, *88*, 147402.
- [19] Botti, A.; Bruni, F.; Imberti, S.; Ricci, M. A.; Soper, A. K. *J. Chem. Phys.* **2004**, *120*, 10154–10162.
- [20] McLain, S. E.; Imberti, S.; Soper, A. K.; Botti, A.; Bruni, F.; Ricci, M. A. *Phys. Rev. B* **2006**, *74*, 094201.
- [21] GmbH, L. V. Properties of Sodium Hydroxide (NaOH). <http://www.lv-soft.com/software/fachbereiche/stoff/naoh-e.htm>.
- [22] Yamakata, A.; Uchida, T.; Kubota, J.; Osawa, M. *J. Phys. Chem. B* **2006**, *110*, 6423–6427.
- [23] Kropman, M. F.; Nienhuys, H. K.; Bakker, H. J. *Phys. Rev. Lett.* **2002**, *88*, 077601.
- [24] Woutersen, S.; Bakker, H. J. *Nature* **1999**, *402*, 507–509.

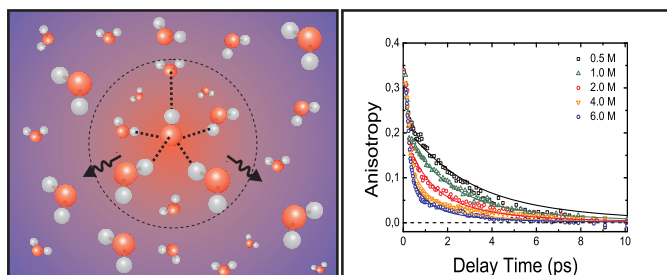


Table of Contents: Left: Illustration of heat diffusion out of the hydration complex of OH^- (The hydrogen bonds in the complex are indicated by the dashed lines, and the dotted circle indicates the excited complex). Right: Anisotropy as a function of delay for five different concentrations of NaOH. The solid lines are fits to the data of the heat diffusion model.