

Supporting Information:

Accelerated Vibrational Energy Relaxation of Water in Alkaline Environments

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This file contains: 8 pages and 4 figures.

Linear absorption signal of OH⁻-associated OH vibrations

In Figure S1 we show linear absorption spectra that result from subtracting the linear absorption spectrum of H₂O/ D₂O from the spectra of OH⁻/H₂O/D₂O with different concentrations of OH⁻ (1.5, 3, 4.5 and 6 M). The resulting difference spectra only represent the responses of the H₂O and HDO molecules that are directly interacting with OH⁻. It is seen that these molecules have a very broad absorption spectrum ranging from ~ 1000 cm⁻¹ to ~ 3000 cm⁻¹ that is assigned to the OH and OD stretch vibrations of H₂O and HDO molecules that are strongly hydrogen bonded to OH⁻, where the OH stretch vibrations of H₂O will dominate (in view of the H:D isotope ratio of 24:1). In addition to this broadband absorption, there is a narrow band at 1650 cm⁻¹ representing the absorption of the bending mode of H₂O molecules that are hydrating OH⁻. It is seen that increasing the concentration

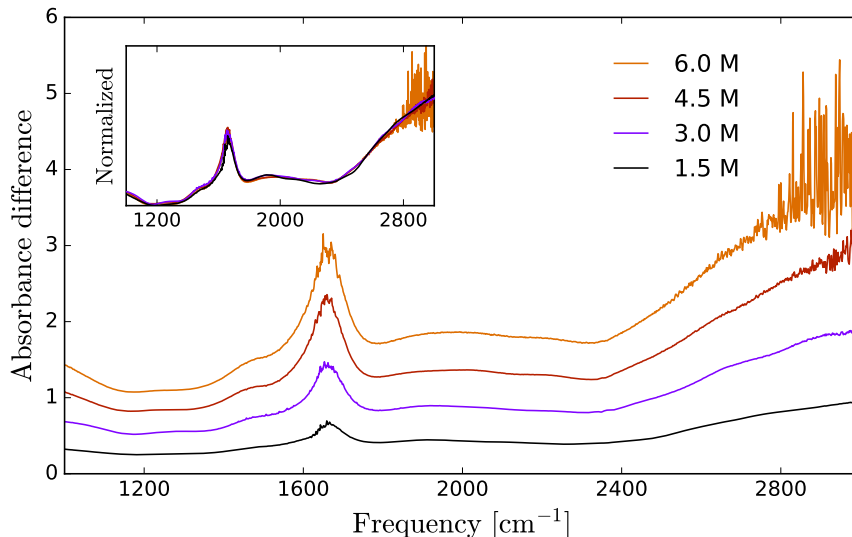


Figure S1: Linear absorption spectra difference that result from subtracting the linear absorption spectrum of $\text{H}_2\text{O}/\text{D}_2\text{O}$ from the spectra of $\text{OH}^-/\text{H}_2\text{O}/\text{D}_2\text{O}$ with different concentrations of OH^- (1.5, 3, 4.5 and 6 M).

of OH^- leads to a proportional increase of the amplitude of the absorption spectrum while the shape remains the same. The independence of the shape of the absorption spectrum on the concentration of OH^- is more clearly illustrated in the inset of Figure S1, where we show the same difference absorption spectra normalized.

Transient absorption signal of H_2O hydrating OH^-

We measured transient absorption spectra of $\text{NaOH}:\text{H}_2\text{O}$ solutions in the concentration range of 1–5 M without the addition of D_2O , in order to determine the contribution of the OH^- -associated OH groups to the transient absorption signal in an independent manner.

We model the data with a two-step relaxation model, in which the excited OH vibration relaxes rapidly within the solvation structure of the OH^- ion leading to a locally heated hydration complex with an associated intermediate state spectrum σ_{I} . This locally hot state equilibrates with the surroundings due to heat diffusion, thus creating a global hot ground state σ_{hgs} . We find the relaxation time constants $1/k_{\text{OH}} = 0.15 \pm 0.1$ ps and $1/k_{\text{I}} = 0.5 \pm 0.1$ ps. The result of the modeling is illustrated in Figure S2.

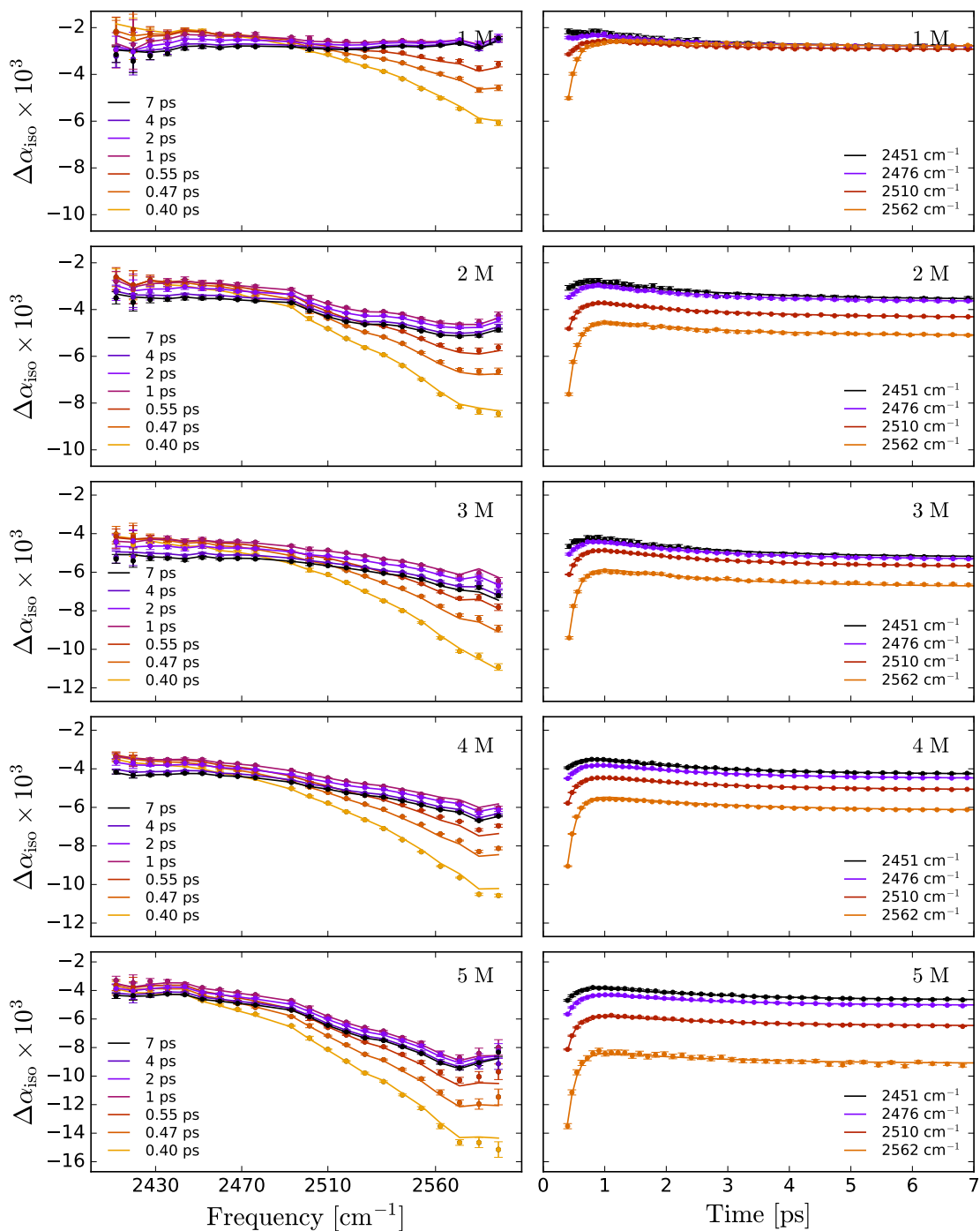


Figure S2: Transient absorption signals of solutions of NaOH in H₂O, with OH⁻ concentrations in the range of 1 to 5 M (from top to bottom). The solid circles represent the measured absorption changes, and the solid curves result from the least-squares fit described in the text.

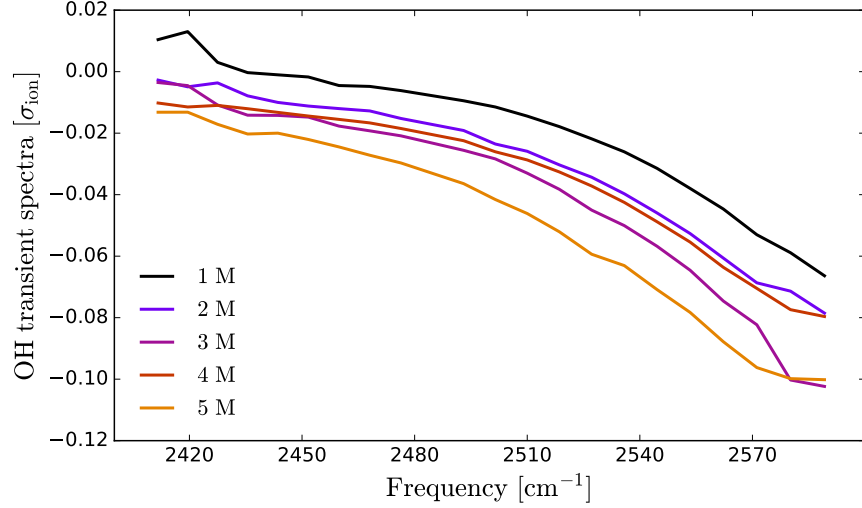


Figure S3: Transient absorption spectrum of the OH vibrations of H₂O molecules solvating OH⁻ ions for solutions with different OH⁻ concentrations.

The shape of the spectral component, $\sigma_{\text{OH}}(\omega)$, of the initially excited ion-associated OH vibration, is shown in Figure S3 and is independent of the concentration. We use this finding to identify the contribution of the ion-associated OH vibrations to the transient absorption spectra measured for solutions that also contain D₂O.

Using the transient absorption signals measured in parallel and perpendicular configurations of the pump and probe pulses, we construct the isotropic signal as:

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

We describe the transient absorption signal as the sum of the responses of different states i , with associated populations, $N_i(t)$, and transient absorption spectra, $\sigma_i(\omega)$. Therefore, the isotropic signal can be modeled as:

$$\Delta\alpha_{\text{iso}}(\omega, t) = \sum_i^n N_i(t) \cdot \sigma_i(\omega), \quad (2)$$

with n the number of energy level that characterize the relaxation mechanism. The popula-

tion dynamics of the system is described by:

$$\frac{dN_i(t)}{dt} = K_{ij}N_j(t), \quad (3)$$

where the relaxation rate matrix K_{ij} represents the relaxation mechanism of the system.

As was shown in previous experiments,^{S1} the transient absorption of NaOH:H₂O solutions following excitation of the OH stretch vibrations of the H₂O can be fitted well with a two-step relaxation model, in which the ion-associated OH vibrations relax to a locally heated hydration complex. Subsequently, the locally hot complexes equilibrate with the surroundings due to heat diffusion, creating a global hot ground state. This mechanism is described by the rate matrix:

$$K_{ij} = \begin{bmatrix} -k_{\text{OH}} & 0 & 0 \\ +k_{\text{OH}} & -k_{\text{I}} & 0 \\ 0 & +k_{\text{I}} & 0 \end{bmatrix}, \quad (4)$$

with k_{OH} the decay rate constant of the excited ion-associated OH groups, and k_{I} the decay rate constant of the intermediate locally hot state associated with heat diffusion.

The spectral components $\sigma_i(\omega)$ and the decay rates constants are obtained by a least-squares minimization process of the following χ^2 function:

$$\chi_{\text{iso}}^2 = \iint \left(\frac{\Delta\alpha_{\text{iso}}^{\text{exp}}(\omega, t) - \sum_i N_i(t, \mathbf{k})\sigma_i(\omega)}{\xi(\omega, t)} \right)^2 dt d\omega, \quad (5)$$

with $\Delta\alpha_{\text{iso}}^{\text{exp}}(\omega, t)$ the experimental signal with standard deviation $\xi(\omega, t)$.

Fitting of the transient absorption signals of the OH⁻/H₂O/D₂O solutions

The spectral shapes are obtained by fitting the following equation to the data:

$$\Delta\alpha_{\text{iso}} = \sum_{j=1}^3 N_j(t) \cdot \sigma_j(\omega), \quad (6)$$

with the σ_j corresponding to the different spectral components. σ_{OD} is the transient absorption spectrum of the OD vibration of HDO, σ_{OH} is the transient absorption spectrum of H₂O molecules interacting with OH⁻, and σ_{therm} is the thermal difference (hot ground state) spectrum observed at later delay times (>30 ps). The $N_j(t)$ represent the time-dependent populations of these components. Unlike the case where we modeled the transient absorption spectra of the OH⁻/H₂O solutions (not containing D₂O), there is not an *a priori* assumption about the time dependence of the populations $N_j(t)$, i.e. we do not describe these dynamics with rate constants.

The fitting procedure proceeds as follows. The data form a two-dimensional matrix of amplitudes as a function of frequency (column) and time delay (row) for each studied OH⁻ concentration. As we measured 5 different OH⁻ concentrations, there are 5 of these two-dimensional matrices. Each matrix is the result of the dynamics of three spectral components $\sigma_j(\omega)$ that each show a particular time dependence expressed as $N_j(t)$. Hence, the two-dimensional data matrix is fitted to a sum of three columns (representing $\sigma_j(\omega)$) that are each multiplied with a row (representing $N_j(t)$). The spectral shape of σ_{OH} is obtained from the spectral decomposition of the transient absorption signals of the OH⁻/H₂O solutions. The shape of these spectra is found to be independent of the OH⁻ concentration (as shown in Figure S3), only the amplitudes are found to be different at different OH⁻ concentrations. Hence, the shape of σ_{OH} is not a fitting parameter and only the amplitude of σ_{OH} is used as a fitting parameter in the fit of the transient absorption spectrum at each particular OH⁻

concentration.

The shape and amplitude of σ_{therm} are defined by the averaged transient absorption spectrum measured at long delay times (>30 ps), so neither the shape nor the amplitude of σ_{therm} are fitting parameters. For the third spectral component, σ_{OD} , both the shape and the amplitude are fitted. The shape of σ_{OD} is set to be the same shape at all OH^- concentrations, while the amplitude of σ_{OD} is allowed to be different at different OH^- concentrations. The shape of σ_{OD} is thus a global fit parameter while the amplitude of σ_{OD} is a local fit parameter. The experimental data and the results of the fit for OH^- concentrations of 0, 2 and 5 M are shown in Figure 2 of the main manuscript.

Frequency dependence of the relaxation of the OD vibration of HDO in $\text{OH}^-/\text{H}_2\text{O}$ solutions

A possible origin of the non-exponential character of the relaxation of σ_{OD} is that the relaxation of the OD vibration depends on frequency, with the result that the relaxation of the transient absorption spectral component σ_{OD} is in fact a sum of exponential functions with different time constants. To investigate the frequency dependence of the relaxation of the OD vibration, we subtract the σ_{OH} component and the σ_{therm} component from the total measured transient absorption spectra at different delays. The remaining signal only represents the transient absorption signal of the OD vibrations. In Figure S4 we show the resulting transient absorption spectra of the OD vibrations at different delays (left panel), and we show the transient absorption signal as a function of delay at three different frequencies within the OD absorption band (right panel). It is seen in this figure that the spectral shape of the transient absorption signal of the OD vibrations does not change as a function of delay. We also observe that the relaxation dynamics are the same in the red wing, the center, and the blue wing of the OD transient absorption band. These results show that the non-exponential character of the vibrational relaxation of σ_{OD} is not due to

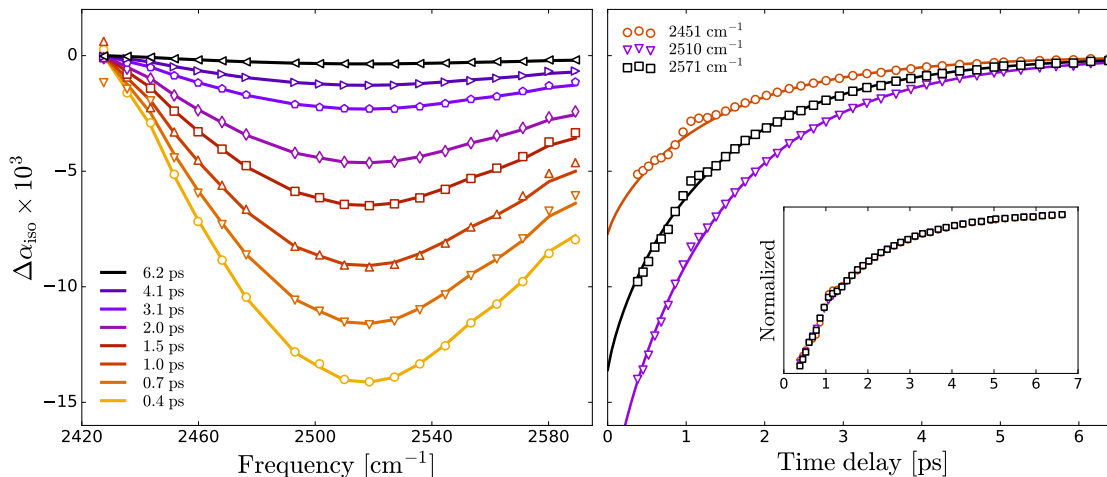


Figure S4: Transient absorption signal of the OD vibration of HDO in a solution of H_2O and 3 M NaOH. The left panel shows the transient absorption spectrum of the OD vibration at different delays. The right panels shows the transient absorption signal at frequencies in the red wing, the center and the blue wing of the absorption band. The solid lines in the right panel represent fits of equation (5) of the main manuscript to the data, and include the effect of Förster energy transfer to the vibrations of OH groups hydrating OH^- .

a frequency-dependence of the OD relaxation, but must be due to an effect that is equally strong at different OD frequencies, e.g. Förster energy transfer to the vibrations of OH groups hydrating OH^- with a broad absorption band that overlaps with the OD absorption band.

References

- (S1) Liu, L.; Hunger, J.; Bakker, H. J. Energy Relaxation Dynamics of the Hydration Complex of Hydroxide. *J. Phys. Chem. A* **2011**, *115*, 14593–14598.