

Accelerated Vibrational Energy Relaxation of Water in Alkaline Environments

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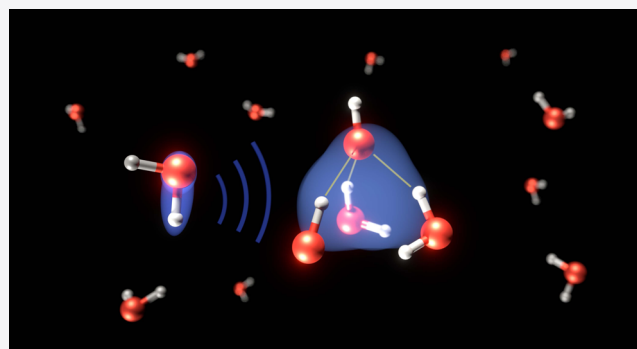


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ABSTRACT: We observe that hydrated hydroxide ions introduce an additional relaxation channel for the vibrational relaxation of the OD vibrations of HDO molecules in aqueous NaOH solutions. This additional relaxation path involves resonant (Förster) vibrational energy transfer from the excited OD vibration to OH stretch vibrations of hydrated OH⁻ complexes. This energy transfer constitutes an efficient mechanism for dissipation of the OD vibrational energy, as the accepting OH stretch vibrations show an extremely rapid subsequent relaxation with a time constant of <200 fs. We find that the Förster energy transfer is characterized by a Förster radius of 2.8 ± 0.2 Å.



INTRODUCTION

Understanding the transfer of energy in water, the most ubiquitous liquid in nature, is of fundamental importance for many chemical and biological processes. In fact, the structural and dynamical properties of water facilitate a wide range of essential interactions in nature, such as protein folding.¹ When energy is locally dissipated in an aqueous environment, the excess energy rapidly equilibrates due to structural rearrangements and intermolecular couplings.^{2–5} One of these couplings is dipole–dipole interaction leading to resonant (Förster) energy transfer.⁶ Vibrational Förster energy transfer has been observed for amide vibration of peptides,⁷ the CO vibration on metal surfaces,^{8,9} and the stretch vibrations of water and ice.^{2,5,10} In pure H₂O, Förster transfer between the OH stretch vibrations takes place on a time scale of <100 fs.²

Förster energy transfer can also occur between vibrations of different molecular species. For instance, in acidic water, a Förster-type coupling between hydrated protons and OD vibrations has been observed to accelerate the relaxation of the latter vibrations.¹⁰ Here, we investigate whether a similar effect can occur in alkaline solutions. Recent theoretical studies have shown that hydroxide ions possess a different hydration structure compared to protons.^{11–16} We use ultrafast mid-IR pump–probe spectroscopy to investigate the vibrational relaxation dynamics of the OD stretch excitations of HDO molecules dissolved in aqueous solutions of hydroxide ions of different concentrations.

EXPERIMENTAL METHODS

Aqueous hydroxide solutions were prepared by diluting a commercially available solution of 50 wt % NaOH (Sigma Aldrich) in deionized water (5.5 μS/m, Milli-Q) at

concentrations ranging between 1 and 6 M. In addition, D₂O (99.96% D, Eurisotop) was added to obtain an OD/OH ratio of 4% in all studied samples. The samples were kept between two 2 mm thick CaF₂ windows separated by Teflon spacers of 25 μm for 1–3 M NaOH solutions and 10 μm at higher concentrations. The path length did not affect the relaxation dynamics.

We perform polarization-resolved transient absorption measurements using femtosecond mid-infrared light pulses with a repetition rate of 1 kHz and centered at a frequency of 2510 cm⁻¹ that are resonant with the OD stretch vibration of HDO molecules in aqueous solution. These pulses are generated via parametric down-conversion of Yb:KGW laser pulses in a KTA crystal. At 2510 cm⁻¹, the generated pulses have an energy of 12 μJ, a bandwidth of 120 cm⁻¹, and a pulse duration of 200 fs. At 3390 cm⁻¹, the pulse energy is 25 μJ, the bandwidth is 90 cm⁻¹, and the pulse duration is 280 fs. A ZnSe window at an incident angle of 45° is used to create the pump (transmission), while the reflected beam is sent over a second ZnSe window to generate the probe and reference pulses. The pump pulse is sent over a delay stage to vary the pump–probe time delay and sent through a λ/2 plate to set its polarization at π/4 with respect to the polarization of the probe. A rotating wire grid polarizer is used after the sample to selectively

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measure the polarization component of the probe that is parallel or perpendicular to the pump polarization.

We measure the pump-induced transient absorption changes ($\Delta\alpha$) as a function of time delay between the pump and the probe. At $t = 0$, the pump pulse excites OD stretches from the ground state to the first excited state, $|0\rangle \rightarrow |1\rangle$. This excitation leads to a reduced density of absorbers in the ground state and stimulated emission out of the excited state, both contributing to an absorption decrease (bleach). The excitation also leads to absorption at lower frequencies, associated with the $|1\rangle \rightarrow |2\rangle$ transition. The vibrational relaxation of the excited state eventually results in heating of the sample, which induces an absorption change that decays on a time scale (tens to hundreds of picoseconds) much slower than that of the pump-probe experiment.

The experimentally obtained parallel and perpendicular transient absorption signals are used to construct the isotropic transient response

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

where ω and t are the probe frequency and time delay, respectively. The isotropic signal provides information on the rate of vibrational energy relaxation and is insensitive to molecular reorientation.

RESULTS

Linear IR Absorption. Figure 1 displays the linear absorption spectra of solutions of 8% HDO and different

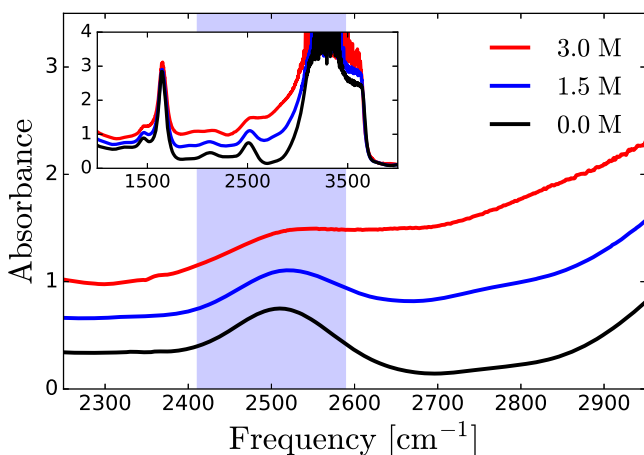


Figure 1. Linear IR spectra of 8% HDO and different concentrations of NaOH in H_2O . The blue shaded area indicates the region where transient absorption is recorded.

concentrations of NaOH in H_2O . The spectra show a band centered at 2510 cm^{-1} that is assigned to the OD stretch vibration of HDO molecules that are hydrogen-bonded to neighboring water molecules. With increasing OH^- concentration, a broad background absorption rises, which is attributed to the OH stretch vibrations of H_2O molecules donating strong hydrogen bonds to OH^- ions. The spectral responses of the OD/OH stretch vibrations are negligibly affected by Na^+ ions.

Isotropic Transient Spectra. Figure 2 shows isotropic transient absorption spectra for neat HDO/ H_2O and two NaOH/ H_2O solutions. All solutions contain 8% HDO: D_2O . The isotropic transient spectra show a pump-induced

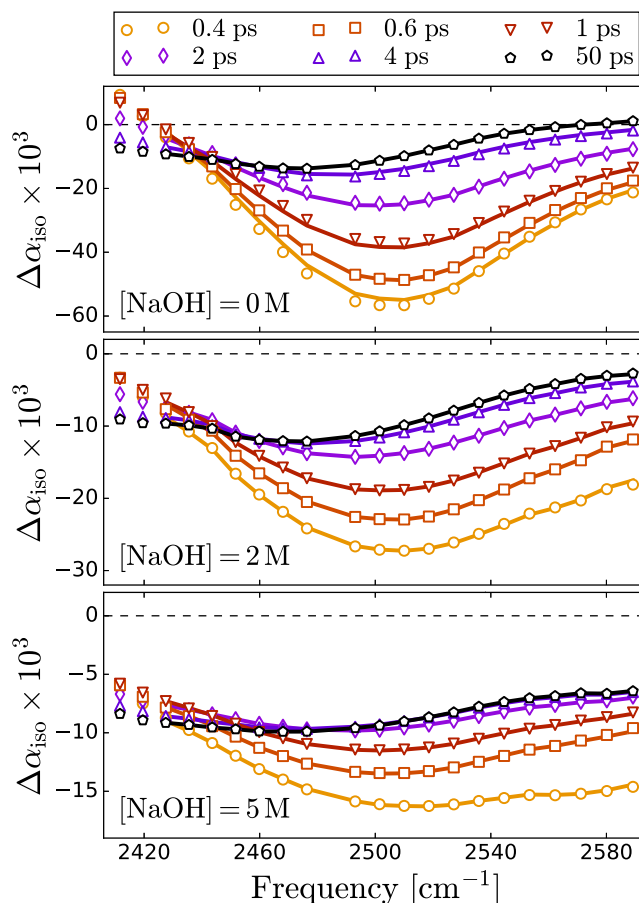


Figure 2. Isotropic transient absorption spectra for neat HDO/ H_2O (upper panel) and HDO dissolved in 2 M (middle panel) and 5 M (lower panel) NaOH/ H_2O solutions. The solid lines represent the results of a fit using the kinetic model described in the text.

bleaching signal at around 2510 cm^{-1} due to the excitation of the OD stretch vibration of the HDO molecules. At frequencies $<2420\text{ cm}^{-1}$, the upper panel also shows the high-frequency wing of the induced $|1\rangle \rightarrow |2\rangle$ absorption. The lower panels show that the amplitude of the bleaching signal of the OD stretch vibration decreases upon the addition of NaOH because an increasing part of the energy of the excitation pulse is absorbed by OH vibrations of H_2O molecules that are hydrogen-bonded to OH^- . In addition, with increasing OH^- concentration, the OD groups of an increasing fraction of the HDO molecules will be directly hydrogen-bonded to OH^- , which shifts their absorption to lower frequency. As a result, these OD groups no longer contribute to σ_{OD} , thus decreasing the amplitude of this spectral component in comparison to σ_{OH} and σ_{therm} .

To elucidate the transient spectral response of the excited OH stretch vibrations of H_2O solvating OH^- , we measure the transient absorption spectra of NaOH/ H_2O solutions in a concentration range of 1–5 M without the addition of D_2O (see the Supporting Information). In these experiments, we only probe the vibrational relaxation dynamics of the ion-associated OH groups. The signal can be well described using 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_1 . This locally hot state equilibrates with the surroundings due to heat diffusion,

thus creating a global hot ground state σ_{hgs} . This relaxation mechanism has been observed in a previous study on heat diffusion and molecular reorientation in aqueous hydroxide solutions.¹⁷

From a least-square fit of the isotropic data, we find that the two subsequent relaxation processes take place with time constants of 0.15 ± 0.1 and 0.5 ± 0.1 ps, both independent of the concentration. The uncertainty in a time constant of 0.15 ps is relatively large as a result of the relatively long pulse duration of 0.2 ps. The spectral signature σ_{OH} of the excited state does not depend on concentration. The spectral shape of the intermediate state σ_{i} is very similar to that of the hot ground state σ_{hgs} . The main difference is that σ_{i} has a much larger amplitude.

Spectral Decomposition and Population Dynamics.

Based on these observations, we consider the transient absorption signal to be composed of the responses of two excited states and a thermal spectrum σ_{therm} . This latter spectrum σ_{therm} represents both the spectral response σ_{i} of the intermediate state of the relaxation of the OH vibration of H₂O molecules solvating OH⁻ and the spectral response σ_{hgs} of the final hot ground state. We describe the responses of the intermediate state and the hot ground state with a single spectral component σ_{therm} because these states have very similar spectral shapes. The time evolution of σ_{therm} thus represents the population dynamics of both the intermediate state and the hot ground states. The transient absorption signal can thus be described as a linear combination of three states with associated transient spectra σ_j and time-dependent populations N_j

$$\Delta\alpha_{\text{iso}} = \sum_{j=1}^3 N_j(t) \cdot \sigma_j(\omega) \quad (2)$$

To determine the relaxation dynamics of the OD stretch vibration, we perform a spectral decomposition of the transient absorption spectra at all delay times and all concentrations. In this analysis, we fix the shape of the independently measured concentration-independent σ_{OH} band, and we fix the shape of the thermal spectrum σ_{therm} at each studied OH⁻ concentration to the transient absorption spectrum measured at long delay times (>30 ps). We treat the spectral shape of the excited OD vibration σ_{OD} as a global fit parameter across all OH⁻ concentrations. The global fit yields the spectral shape of σ_{OD} and the time-dependent population dynamics $N_j(t)$ of all three states without any assumption about the relaxation mechanism. The fitting procedure is described in detail in the Supporting Information. For a 2 M NaOH/H₂O solution, the χ^2 -minimization process yields the spectral components shown in Figure 3 and the population dynamics displayed in Figure 4. The solid red line in Figure 4 shows the dynamics of the thermal state, which represents the decay of the intermediate state of the relaxation of the OH vibration of H₂O molecules solvating OH⁻ at short delay times, and the ingrowing signal of the hot ground state at late delay times (>2 ps). The solid curves displayed in Figure 2 show that the spectral components shown in Figure 3 fit our experimental data well, even at the highest OH⁻ concentration of 5 M.

In Figure 5, we show the normalized population dynamics of the excited OD vibration for five different NaOH concentrations. We observe that the relaxation becomes faster and increasingly nonexponential with increasing ion concentration. This ion-induced change of the relaxation can be explained by

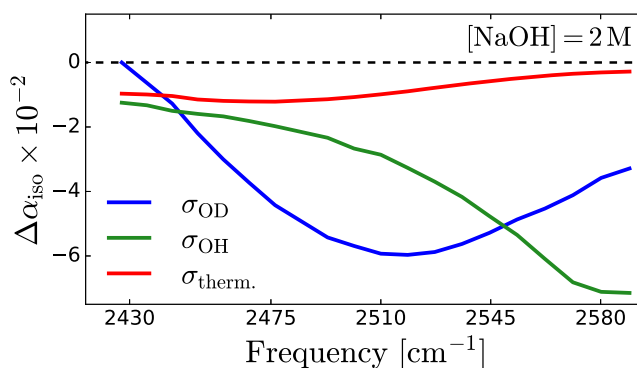


Figure 3. Spectral decomposition of the transient absorption spectrum of a solution of HDO and 2 M NaOH in H₂O. The spectra σ_{OH} and σ_{therm} have been fixed in a least-squares optimization process of eq 2 to the data, while the spectral shape σ_{OD} of the OD vibrations is fitted as a global parameter across all OH⁻ concentrations.

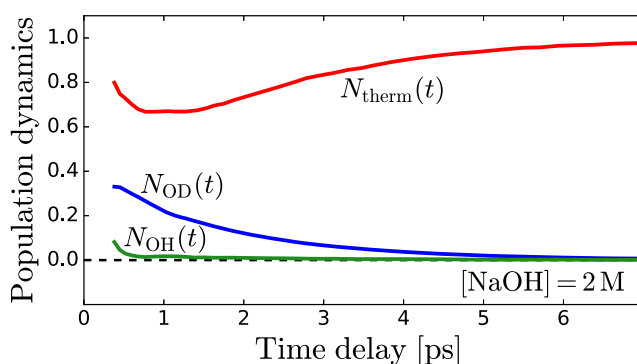


Figure 4. Fitted population dynamics of the different spectral components of Figure 3 of a solution of HDO and 2 M NaOH in H₂O. The population dynamics of the thermal spectrum represents both the decay of the intermediate state of the relaxation of the OH vibration of H₂O molecules solvating OH⁻ and the ingrowing signal of the hot ground state.

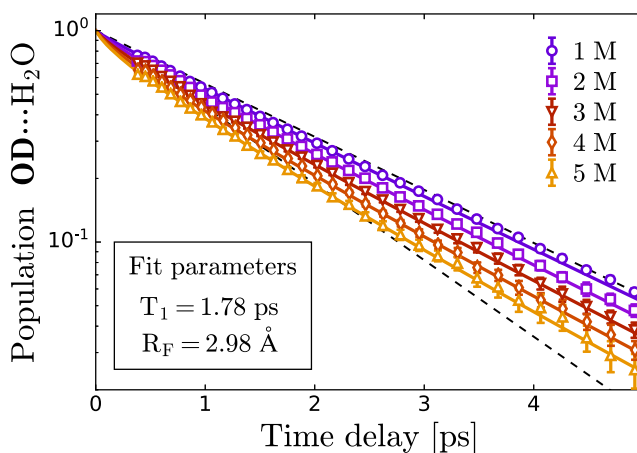


Figure 5. Time-evolving population probability of excited OD stretch vibrations at five different NaOH concentrations. The markers show the temporal decomposition described in the main text. The solid lines show the least-square fit of eq 5, which results in 1.78 ps for the OD vibrational lifetime and 2.98 Å for the Förster radius. The dashed lines represent two single-exponential decays with time constants of 1.75 and 1.2 ps. The difference between the latter curve and the data illustrates that the observed decay is nonexponential.

three possible scenarios: (i) the addition of OH^- to the solution leads to inhomogeneous broadening of the OD absorption band with a faster relaxation rate at low OD frequencies than at high OD frequencies, thus yielding a nonexponential decay for σ_{OD} ; (ii) hydroxide ions affect the binding dynamics of the hydrogen-bond network, which in turn changes overall the vibrational relaxation process; (iii) the spectral overlap between the OD band and the hydroxide continuum enables resonant Förster energy transfer from excited OD vibrations to unexcited hydroxide complexes. To investigate scenario (i), we investigated the frequency dependence of the relaxation of the OD stretch vibration (see Figure S4 in the Supporting Information). We observe this relaxation to be uniform over the OD absorption band, thus ruling out the possibility that the nonexponential relaxation would originate from a frequency dependence of the OD relaxation rate.

To discriminate between scenarios (ii) and (iii) as origins of the ion-induced increase in the relaxation rate, we performed the same experiment on H/D-reversed isotope solutions, i.e., H_2O diluted in D_2O . We thus measure the transient spectral response of solutions of HDO and OD^- in D_2O , following the excitation of the OH stretch vibration of the HDO molecules near 3400 cm^{-1} . Since the OH stretch vibration band does not overlap with the deuterioxide-induced continuum, as the inset in Figure 6 shows, the possibility of Förster energy transfer can be ruled out for these samples.

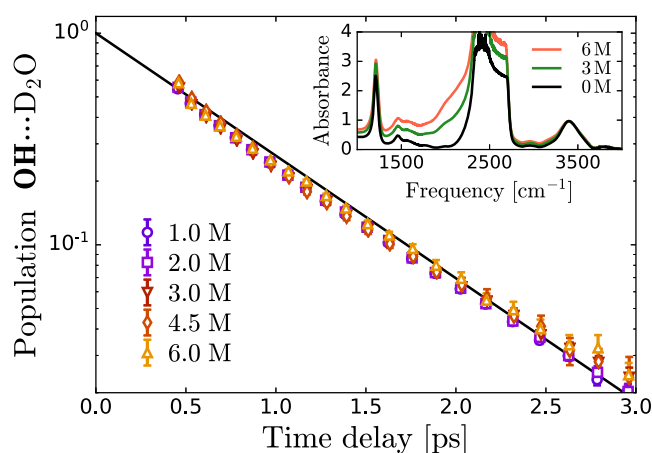


Figure 6. Time-evolving population probability of excited OH stretch vibrations at five different NaOD concentrations. The markers show the temporal decomposition described in the main text. The solid line represents a monoexponential decay with a time constant of 0.75 ps, similar to that in the neat HDO/ D_2O solvent.¹⁹

We describe the data with a similar model that we used to describe the vibrational dynamics of the OD stretch vibration of HDO in $\text{OH}^-/\text{H}_2\text{O}$ solutions and that we reported before.¹⁸ In this model, we consider two different types of excited OH stretch vibrations that relax via an intermediate state to a final hot ground state. The first type is formed by the OH vibration of HDO molecules that are not directly interacting with the OD^- ions. The second type is formed by the OH vibrations of HDO molecules that are forming hydrogen bonds with OD^- . These latter OH vibrations have a broad red-shifted spectral response centered at 3340 cm^{-1} . Both types of OH vibrations relax to an intermediate state that subsequently relaxes to a hot ground state.

We find that for all studied OD^- concentrations, the vibrationally excited OH groups that are directly hydrogen-bonded to OD^- ions relax with a time constant T_1 of 0.27 ± 0.05 ps and that the intermediate state relaxes with a time constant 0.9 ± 0.3 ps. The OH stretch vibrations of the HDO molecules that are not directly hydrogen-bonded to OD^- ions relax with a time constant that shows negligible dependence on the OD^- concentration, as illustrated in Figure 6. At all concentrations, the relaxation can be well described with an exponential function with a decay time constant of 0.75 ps. This relaxation time is similar to the previously reported time constant of 0.7 ps for the excited OH stretch vibration of HDO in neat HDO/ D_2O .¹⁹

In a previous study of the reorientation dynamics of the OD and OH vibrations of HDO molecules in aqueous hydroxide solutions, we did not explicitly include the vibrational relaxation of the OH groups that form hydrogen bonds with OD^- , and we only considered the thermal effect following the relaxation of these vibrations.²⁰ As a result, the observed relaxation rate represented the average relaxation dynamics of all OH vibrations, and this averaged relaxation becomes faster with increasing OD^- concentration, as the contribution of OH groups directly bonded to OD^- increases. In the present study, we investigate the OH stretch relaxation over a larger spectral range and we include the vibrational relaxation of the OH groups that form hydrogen bonds with OD^- . We thus observe that for both the OH groups hydrating OD^- and the OH groups that are not hydrating OD^- , the vibrational relaxation rate shows negligible dependence on the OD^- concentration. This means that there is no acceleration of the relaxation of the OH of HDO in $\text{OD}^-/\text{D}_2\text{O}$ solutions with increasing OD^- concentration, only the relative contributions of the two OH species change.

It is interesting that for the OH vibration of HDO in $\text{OD}^-/\text{D}_2\text{O}$, we observe a fast relaxation component in the red wing of the OH absorption band, associated with OH groups that directly hydrate OD^- ions, whereas for the OD vibration of HDO in $\text{OH}^-/\text{H}_2\text{O}$ solutions, we do not see a similar component associated with OD groups directly hydrating OH^- (see Figure S4 in the Supporting Information). This observation suggests that these latter OD groups have a similar vibrational relaxation time constant as the OD groups that are further away from the OH^- ions. A possible explanation for this difference between OD and OH vibrations is that the relaxation mechanisms differ, with the result that the relaxation of the OH vibration could be much more sensitive to the local hydrogen-bond strength than the relaxation of the OD vibration.

The absence of the concentration dependence of the relaxation of the OH vibrations of HDO molecules further away from OH^- shows that the change of the hydrogen-bond network resulting from the addition of hydroxide ions has a negligible effect on the vibrational relaxation. Hence, the observed acceleration of the vibrational relaxation for the OD vibrations of HDO in $\text{OH}^-/\text{H}_2\text{O}$ solutions can only be explained with the third scenario, i.e., Förster energy transfer from the excited OD vibration to OH vibrations of H_2O molecules hydrating the OH^- ions. This energy transfer is enabled by the spectral overlap of the OD stretch absorption spectrum and the wing of the broad and strong absorption band of the OH stretch vibrations of H_2O molecules hydrating OH^- ions.

The observed uniform relaxation of the OD vibration at different frequencies (see Figure S4 in the Supporting Information) is also consistent with a mechanism in which the nonexponential character of this relaxation is caused by Förster energy transfer, as the coupling with the very broad absorption of hydrated OH⁻ complexes will not strongly depend on the OD frequency. In principle, the reverse Förster process from hydroxide complexes to OD vibrations can also occur. However, this interaction will have a negligible effect since vibrationally excited OH groups of H₂O molecules hydrating OH⁻ ions quickly relax with a time constant <200 fs.

Förster Energy Transfer. The comparison between Figures 5 and 6 shows that Förster energy transfer to the hydrated OH⁻ complexes serves as an effective additional relaxation channel for the excited OD vibrations. In the following, we will model the effect of this additional channel using the Förster formalism.

Within the Förster model, the rate of energy transfer between two dipoles is given by⁶

$$k_F(r) = \frac{1}{T_1} \left(\frac{R_F}{r} \right)^6 \quad (3)$$

where T_1 is the intrinsic lifetime of the excited state and r is the distance between the two interacting oscillators. The Förster radius R_F determines the distance at which 50% of the excitation energy is transferred via the Förster mechanism within the lifetime T_1 of the excitation. It thus follows that the Förster process becomes significant if the mean donor–acceptor distance is comparable or smaller than R_F , as will be the case at high OH⁻ concentrations. Using eq 3 and assuming a radially uniform distribution of receiving oscillators, the survival probability of donors is given by⁶

$$S(t, \rho) = \exp \left(-4\pi\rho \int_{a_0}^{\infty} dr r^2 [1 - e^{-k_F(r)t}] \right) \quad (4)$$

where ρ is the density number of OH⁻ ions and a_0 is the minimal approach distance, which is the excluded volume of a water molecule (in the limit of $a_0 = 0$, we recover the original formula reported by Förster). This expression can be used under the condition that the shapes of the absorption spectra of the donor and acceptor, i.e., of the OD vibration of HDO (σ_{OD}) and the OH vibrations of H₂O hydrating OH⁻ (σ_{OH}), do not significantly change when the concentration of OH⁻ increases. Indeed, we find strong evidence that the shapes of these spectra hardly change. For σ_{OH} , this can be seen in the inset of Figure 1 and in Figure S1 in the Supporting Information where we show the difference absorption spectra obtained by subtracting the absorption spectrum of H₂O/D₂O from the spectra of OH⁻/H₂O/D₂O for different OH⁻ concentrations. The inset of Figure 1 and the normalized difference spectra of Figure S1 show that the shape of the low-frequency tail of the absorption spectrum of H₂O molecules hydrating OH⁻ is independent of the concentration of OH⁻. For the OD vibration of HDO (σ_{OD}), we find that we can accurately model the transient absorption spectra using the same shape of σ_{OD} at all studied OH⁻ concentrations. This latter observation also implies that the dipole–dipole (Förster) coupling of the OD vibrations and the OH vibrations does not lead to strong mixing of these vibrations and that the perturbative Förster approach remains valid even at high OH⁻ concentrations.

Using the Förster model to describe the data implies that we assume that all of the acceptors have the same absorption spectrum and that the acceptors are statistically distributed. The absorption spectrum of the OH stretch vibrations of H₂O will be inhomogeneously broadened, meaning that different acceptors have different spectra. However, it is not a priori clear whether the species for which the spectra better overlap with the OD band of HDO are closer or further away from the energy donating the OD stretch vibration of HDO, so these effects may well average out. Probably the strongest approximation in using the Förster expression for energy transfer in aqueous environments is that the distribution of distances and relative angles of donors and acceptors is assumed to be statistical. In view of the hydrogen-bond structure of water and hydroxide solutions, this assumption is not valid for short donor–acceptor distances. Hence, the Förster model is expected to break down at high concentrations where short donor–acceptor distances are important.

Assuming that the intrinsic vibrational relaxation process and the Förster energy transfer are independent of each other, the time dependence of the excited population is given by

$$N(t, \rho) = \exp \left(-\frac{t}{T_1} - 4\pi\rho \int_{a_0}^{\infty} dr r^2 [1 - e^{-k_F(r)t}] \right) \quad (5)$$

We fit this expression to the experimental data shown in Figure 5 with T_1 and R_F as global parameters. We fix a_0 to the previously reported value of 1.5 Å for OD vibrations in aqueous solutions.¹⁰ The resulting fits are represented by the solid curves in Figure 5. The intrinsic vibrational lifetime T_1 of the OD vibration obtained from the fit is 1.78 ± 0.05 ps, which agrees well with the results of previous studies.^{5,21} We find a Förster radius of 2.8 ± 0.2 Å, which is similar to the characteristic intermolecular distance of liquid water.^{22,23}

DISCUSSION

We find that the hydration complexes of OH⁻ can act as antennae receiving energy from nearby excited vibrations. Because of their broad, nearly continuous absorption spectrum, we can expect that hydrated hydroxide ions can quench the energy of any IR-active vibration between 1000 and 3400 cm⁻¹, like amide and carbonyl vibrations (~1700 cm⁻¹) that are ubiquitous in (bio)chemistry. As such, hydrated hydroxide ions can act as effective dissipators of excess vibrational energy in aqueous chemical reactions.

Our findings are in line with previous observations for protonated aqueous solutions.¹⁰ The hydrated proton shows a similar continuum absorption band as the hydrated hydroxide ion²⁴ and is also observed to accept energy from excited OD vibrations, thereby accelerating their relaxation.¹⁰ For the coupling between OD vibrations and hydrated protons, a larger Förster radius of ~4 Å was found, showing that hydrated protons are even more efficient acceptors of vibrational energy than hydrated hydroxide ions. This difference in the efficiency of Förster energy transfer between acidic and basic solutions is consistent with the stronger absorption of low-frequency OH stretch vibrations in acidic solutions compared to the absorption of these vibrations in basic solutions, at corresponding H⁺/OH⁻ concentrations. This difference in absorption strength indicates that the number density and/or transition dipole of low-frequency OH species is higher in acidic solutions than in basic solutions, thus providing more

(efficient) acceptors of the energy of the OD stretch vibrational excitation of the HDO molecules.

CONCLUSIONS

We studied the vibrational relaxation mechanism of OD stretch excitations of HDO molecules in NaOH/H₂O solutions using femtosecond mid-infrared transient absorption spectroscopy. We decomposed the measured transient spectra into spectral components corresponding to the excited OD stretch vibration of the HDO molecules, the excited OH stretch vibrations of H₂O molecules hydrating OH⁻ ions, and the hot ground state that results after the vibrational relaxation is completed. This analysis yielded the population dynamics of all three states. With increasing concentration of OH⁻ ions in solution, we found the decay of the excited OD vibration to become faster and to deviate increasingly from a single-exponential decay. These observations indicate the presence of an additional relaxation channel for the OD vibrations. This additional path is assigned to Förster resonance energy transfer from OD stretches to the OH stretch vibrations of hydrated OH⁻ complexes. From a global analysis of the relaxation dynamics at different OH⁻ concentrations, we determined the intrinsic vibrational lifetime of the OD stretch vibration to be 1.78 ± 0.05 ps, and the Förster radius to be 2.8 ± 0.2 Å. Our results show that hydrated OH⁻ complexes can serve as effective antennae and dissipators of excess vibrational energy in aqueous chemical reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.1c02730>.

Linear absorption spectra; transient absorption signals of solutions of NaOH in H₂O; detailed description of the fitting procedure (PDF)

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Notes

The authors declare no competing financial interest.

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