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Proton Transfer in Concentrated Aqueous Hydroxide

Visualized using Ultrafast Infrared Spectroscopy

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Abstract

While it is generally recognized that the hydroxide ion can rapidly diffuse through aqueous solution due to its ability to accept a proton from a neighboring water molecule, a description of the OH^- solvation structure and mechanism of proton transfer to the ion remains controversial. In this report, we present the results of femtosecond infrared spectroscopy measurements of the O-H stretching transition of dilute HOD dissolved in $NaOD/D_2O$. Pump-probe, photon echo peak shift, and two-dimensional infrared spectroscopy experiments performed as a function of deuteroxide concentration are used to assign spectral signatures that arise from the OH^- ion and its solvation shell. A spectral feature that decays on a ~110 fs time scale is assigned to the relaxation of transiently formed configurations wherein a proton is equally shared between a HOD molecule and an OD^- ion. Over picosecond waiting times, features appear in 2D IR spectra that are indicative of the exchange of population between OH^- ions and HOD molecules due to deuteron transfer. The construction of a spectral model that includes spectral relaxation, chemical exchange, and thermalization processes, and self-consistently treats all of our data, allows us to qualitatively explain the results of our experiments and gives a lower bound of 3 ps for the deuteron transfer kinetics.

I. Introduction

Under ambient conditions, one in every 10^{14} water molecules will dissociate, yielding both a hydronium, H_3O^+, and a hydroxide ion, OH^-. These ions display anomalously high diffusion rates compared to ions of similar size and charge density[1] due to their ability to undergo a proton transfer (PT) reaction with a neighboring water molecule, leading to a translocation of the ion's structural motif rather than the diffusion of a specific set of covalently bound atoms.[2-5] While this process allows us to rationalize the large mobilities exhibited by these ions, many questions concerning the microscopic details of this mechanism remain. Most notably, how do we conceptualize the structure of these ions? In the case of the excess proton, researchers commonly identify two limiting configurations: the Eigen cation,[6] a triply solvated hydronium ion ($H_3O^+ \cdot 3H_2O$), and the Zundel ion,[7] a proton equally shared between two water molecules ($H_5O_2^+$ or $H_2O \cdot \cdot H^+ \cdot \cdot OH_2$). PT is often described in terms of the exchange between Eigen and Zundel species,[8,9] but the energy that separates these configurations is small (2-3 kcal/mol),[3] indicating that they are not distinct. Rather, the proton rapidly evolves through a continuum of structures that may momentarily bear similarity to an Eigen or Zundel cation.[8-10] These dynamics result from the femtosecond to picosecond fluctuations of the hydrogen bond network, which lead to changes in ion coordination and polarization fluctuations.[7,11-14]

Similar questions regarding the structure and PT dynamics of the hydroxide ion exist. An initial proposal for the ion's transport mechanism described it as the mirror image of that of the hydronium ion and postulated the existence of two limiting structures, a $H_7O_4^-$ ion ($HO^- \cdot 3H_2O$) with a triply solvated oxygen, and a $H_3O_2^-$ ion ($HO \cdot \cdot H \cdot \cdot OH^-$)

that are the analogues of the Eigen and Zundel structures of the excess proton, respectively.[15] The rate limiting step was suggested to be the cleavage of a hydrogen bond in the first solvation shell of a $H_7O_4^-$ ion, which allows the solvent around the ion to adopt a hydrogen bonding configuration conducive to the formation of a $H_3O_2^-$ ion.

Recent Car-Parrinello molecular dynamics (CPMD) simulations have called this mechanism into question.[16-19] These simulations suggest the oxygen of the hydroxide ion can accept up to four hydrogen bonds from surrounding water molecules to form a "hypercoordinated" $H_9O_5^-$ ion. The simulations also advocate that a breakage of a hydrogen bond to this 4-coordinate complex facilitates PT since the two oxygen atoms of a $H_3O_2^-$ ion can each support up to 3 hydrogen bonds (including the shared proton). While CPMD simulations provide an insightful view of PT in aqueous hydroxide solutions, care must be used when interpreting their results since they display a strong dependence on the density functional employed for the simulation.[20,21]

Debate between these conceptual views of the transport of the OH^- ion continues in part due to the lack of definitive experimental evidence that supports one picture over the other. Thermochemical measurements[22] and infrared spectra[23] of gas phase clusters show that the OH^- ion accepts only three hydrogen bonds, consistent with the formation of an $H_7O_3^-$ ion. In contrast, neutron scattering[24,25] and x-ray diffraction[26] measure a coordination number to the OH^- oxygen between 3 and 4, and found that the ion's hydrogen atom donates only a weak hydrogen bond to the surrounding liquid. Raman spectra support this conclusion, by resolving a narrow, high-frequency O-H stretching peak attributed to the weakly hydrogen bound OH^- stretch.[27,28] Recent core-level photoelectron emission measurements[29] and CPMD simulations[16] found evidence of a

transiently formed hydrogen bond by the hydrogen atom of OH⁻, and suggest this interaction may play a role in the transport of the hydroxide ion.

Time resolved spectroscopy has provided evidence for both fast and slow relaxation time scales involving the OH⁻ ion. Nienhyus et al.[30] observed a decay of 160 fs in transient hole burning measurements of the O-H stretch of HOD dissolved in a 10 M NaOD solution. This rapid decay was attributed to HOD molecules in the solvation shell of OD⁻ ions that undergo induced population relaxation when the OD⁻ ion accepts a proton from a neighboring water molecule. The lack of an observable decay of the rotational anisotropy in these experiments suggests that hydrogen bond dynamics in concentrated hydroxide solutions are quite slow. However, at much lower hydroxide ion concentrations (40 mM KOH), rotational anisotropy measurements of the charge transfer to solvent band of the OH⁻ ion track the reorientation of water at temperatures above 290 K,[31] and implies that the reorientation of the ion is dictated by the surrounding solvent.

To probe the structural diffusion of the OH⁻ ion, we have performed femtosecond two-dimensional infrared spectroscopy (2D IR) spectroscopy and related nonlinear IR experiments on an isotopically dilute solution of HOD dissolved in NaOD/D_2O. This allows us to probe the vibrational dynamics experienced by OH⁻ ions and solvating HOD in a deuterated environment. The frequency of the O-H stretching transition, ω_{OH}, is sensitive to the strength of the hydrogen bond formed by the proton. Short, linear hydrogen bonds between a HOD molecule and an OD⁻ ion appear red shifted from the main O-H stretching band whereas weak hydrogen bonds of the type formed by the proton of an OH⁻ ion appear at high frequency. Time dependent changes in ω_{OH} on femtosecond to picosecond time scales result from the dynamics of the solvent that

enable the donation of a proton from a HOD molecule to an OD⁻ ion and the subsequent solvation of the newly formed ion.

Upon the addition of NaOD, a new spectral feature appears in pump-probe (PP) measurements that relaxes in 110 fs. 2D IR experiments show that this decay corresponds to a broad component that absorbs across the entire frequency range probed by the experiments. In a previous report,[32] we demonstrated that this feature arises from Zundel-like states, wherein a proton is delocalized between a HOD molecule and a deuteroxide ion. Once the 110 fs decay is complete, photon echo peak shift (PS) measurements display an offset that increases linearly with NaOD concentration, indicating a slowing of the dynamics of the system. Beyond a waiting time of ~2 ps, this offset decays uniformly to zero, primarily as a result of non-equilibrium heating of the solvent by vibrational relaxation of HOD. 2D IR spectra measured for waiting times in this picosecond regime show the existence of chemical exchange between the center of the O-H stretching transition and the high frequency side of the lineshape, a spectral range indicative of the absorption of the OH⁻ ion.

We have built a spectral model that can self-consistently explain the behavior of the measured PP, PS, and 2D IR spectra, taking into account the effects of both chemical exchange induced by PT to the hydroxide ion and the heating of the bath upon vibrational energy relaxation. The results of this model suggest that while protons shared in Zundel-like configurations undergo rapid relaxation within 110 fs, the solvation of the newly formed hydroxide ion is much slower, occurring over a time scale of at least 3 ps.

II. Experimental Methods

Samples were prepared through the dilution of a 40% NaOD stock solution (99.5% deuteration; Cambridge Isotope Laboratories) with D_2O. Roughly 1 v% H_2O was added to each solution and allowed to exchange, giving an O-H stretch absorbance no greater than 0.4 after subtraction of the D_2O background. FT-IR measurements were performed using a 50 μm path length CaF_2 sample cell. For nonlinear experiments, samples were housed within a Teflon sample cell with a 100 μm path length. Due to the overwhelming nonresonant response of CaF_2 when all three pulses are time coincident, Si_3N_4 windows (Norcada) were used for these measurements. Multiple reflections from the high index Si_3N_4 windows were suppressed by wedging the windows at roughly 0.2° with a small piece of Parafilm. 500 nm thick windows were used for PS experiments while all other measurements were carried out using 100 nm windows. Both sets of windows gave no measurable nonresonant response.

Mid-infrared pulses resonant with the O-H stretch of HOD were generated by a homebuilt $BBO/KNbO_3$ based OPA[33] pumped with the output of a multipass Ti:sapphire amplifier. Many of the experimental methods for measuring PP, PS, and 2D IR spectra have been described previously,[32,34-36] the salient features of which we describe below.

PP experiments were carried out using 45 fs pulses peaked at 3325 cm^{-1} with a bandwidth of 350 cm^{-1} FWHM. Half-wave plates (Alphalas) and CaF_2 wire-grid polarizers (Molectron) were used orient the pump and probe polarizations at the magic angle (54.7°) with respect to one another to remove effects due to molecular reorientation. After the sample, the probe was passed through an analyzing polarizer and a narrow band-pass filter (FWHM ~50 cm^{-1}, Spectrogon) centered at 3400 cm^{-1}. The filter reduced

contributions to the spectrally integrated signal due to the anharmonically shifted $v = 2 \leftarrow 1$ transition. PP and other spectrally integrated signals were detected with liquid nitrogen cooled InSb detectors.

PS measurements were made in a box geometry using 45 fs pulses centered at 3375 cm^{-1} and were carried out at parallel polarization (zzzz). To calibrate the zero timing position of the τ_1 time axis, the time-symmetric pair of two-pulse echo signals stimulated by the first two excitation pulses were recorded simultaneously, allowing us to determine $\tau_1 = 0$ to <5 fs.

2D IR signals were generated by three incident fields in the box geometry and detected using either of two heterodyne methods, time-time and time-frequency detection. In time-time detection, the signal is overlapped with a local oscillator (LO), the τ_1 (pulse 1-2) and τ_3 (3-LO) delays are scanned, and the interference between signal and LO is measured using a single channel detector. A 2D Fourier transform of the time domain data yields the frequency domain 2D spectrum. In time-frequency detection, the signal and LO are spectrally dispersed onto a multichannel array detector, which directly observes data along the ω_3 axis. In practice time-time data was preferred for picosecond waiting time (τ_2) delays where the integrated signal level had fallen significantly.

The interferometers and methods used for acquiring 2D IR data for the time-frequency[35] and time-time[36] spectra have been described in detail elsewhere. For time-frequency data, τ_1 was acquired in 2 fs steps to 250 fs for rephasing and non-rephasing scans, giving an ω_1 resolution of 10.6 cm^{-1}. The signal was sampled using balanced detection on a liquid nitrogen cooled HgCdTe array detector with 8 cm^{-1} resolution in ω_3. For time-time detection, τ_1 was sampled with 2 fs steps to 250 fs and τ_3 was determined

to 0.4 fs resolution over a range of 500-600 fs in a rapid sweeping measurement.[36] Similar to the time-frequency approach, balanced detection of the signal field is employed using two single channel liquid nitrogen cooled InSb detectors. All spectra were recorded using ~45 fs pulses and zzzz polarization. The excitation pulses were centered within the range of 3375 - 3400 cm^{-1} for all presented data sets.

III. Infrared Spectroscopy of Isotopically Dilute Hydroxide Solutions

Fig. 1 displays linear absorption spectra of ~1% HOD dissolved in NaOD/D$_2$O solutions with varying deuteroxide concentration. As the NaOD concentration is increased, the spectra broaden significantly to low frequency. This feature is attributed to water O-H stretching vibrations in which the proton is bound to the oxygen atom of deuteroxide. Hydrogen bonding in water causes the O-H resonance to decrease in frequency by ~300 cm^{-1} relative to the gas phase value of 3707 cm^{-1}.[37] However, in the case of a hydrogen bond formed between a HOD molecule and an OD$^-$ ion, the interaction between the two species is much stronger, yielding larger frequency shifts. The broadening pictured is the high frequency region of the continuum absorption observed in infrared spectra of strong acids or bases,[7,38-40] which spans the entire mid-infrared region below the peak of the O-H stretching transition. In the liquid, Zundel hypothesized that the stretching potential of a shared proton will be modulated by the fluctuations of the surrounding solvent, resulting in the broad absorption that appears across the mid-infrared range.[7]

In addition, a peak at 3600 cm^{-1} appears with increasing NaOD concentration that is attributed to the OH$^-$ stretch. Because of the negative charge on the OH$^-$ ion, its proton can only donate a weak hydrogen bond. This leads to a blue shift of the ion's O-H

stretching frequency relative to the main HOD absorption peak. To aid in the description of the nonlinear spectra that follows, we denote the frequency range indicative of the stretch of the OH$^-$ ion by ω_{Ion} (~3600 cm^{-1}), that of HOD molecules hydrogen bonded to D$_2$O by ω_W (3300-3500 cm^{-1}), and that of HOD molecules that donate a hydrogen bond to a deuteroxide ion but are not engaged in proton transfer by ω_{Sol} (<3200 cm^{-1}).

In Fig. 2, we present the results of pump-probe transient absorption measurements of the O-H stretch measured as a function of NaOD concentration. The addition of deuteroxide leads to the appearance of a fast decay component whose amplitude grows with hydroxide concentration. Previously, we demonstrated that each decay trace could be well characterized by two decay components (710 fs and 110 fs) whose amplitudes vary in proportion to NaOD concentration.[32] The slower decay component of 710 fs is similar to time scales measured for the vibrational relaxation of a HOD molecule interacting with a bath of D$_2$O.[41-43] while the fast decay time scale of 110 fs describes the structural relaxation of Zundel-like DO··H··OD$^-$ configurations wherein the hydrogen atom of the HOD molecule is equally shared with a neighboring OD$^-$ ion. Spectroscopic calculations based on a multistate empirical valence bond model of aqueous hydroxide show that as the O-H potential broadens to form a shared proton transition state, the v = 2←0 overtone transition of the shared proton complex red-shifts significantly, falling in the range of 3 μm, and experiences a strong increase in its transition dipole moment.[32] Feynman pathways involving this transition and other overtones thus contribute to the spectra at short delay times. As the proton localizes on either oxygen atom of the unstable Zundel-like transition state, these overtone transitions move out of resonance with our 3

μm excitation pulses. Thus, the 110 fs time scale results not from population relaxation, but rather from rapid spectral sweeping that occurs as a result of proton transfer.[32]

To determine how the presence of OD$^-$ ions influences the spectral dynamics of the surrounding water, we measured the decay of the three pulse photon echo peak shift of ω_{OH} for differing NaOD concentrations (Fig. 3A). For an isolated hydroxyl stretch, the PS decay is related to the frequency correlation function for ω_{OH},

$$C(\tau) = \langle \delta\omega_{OH}(\tau)\delta\omega_{OH}(0) \rangle, \text{ where } \delta\omega_{OH}(\tau) = \omega_{OH}(\tau) - \langle \omega_{OH} \rangle \text{ .}^{[44\text{-}47]} \text{ In the case of}$$

HOD/D$_2$O, the PS displays a sub-100 fs decay, a recurrence at 160 fs due to an underdamped hydrogen bond oscillation, and a longer 1.2 ps decay time scale.[34] With increasing NaOD concentration, the initial decay of the PS appears similar to that of HOD/D$_2$O; however, its offset at longer waiting times is found to increase. Fig. 3B plots the value of the peak shift at a waiting time of 600 fs and shows that this offset increases linearly with NaOD concentration. The lack of an observed decay over this range of waiting times ($\tau_2 < 1$ps) suggests that the addition of NaOD slows down the average dynamics of the system. This is not surprising given that the viscosity of alkali hydroxide solutions strongly increases with the number of dissolved hydroxide ions.[48]

More interesting is the fact that at concentrations greater than 5.3 M, after a waiting time of ~80 fs the PS undergoes a large increase before reaching its offset. If the PS decay originated from a single vibrational transition, an increase in the PS would indicate that memory of the initially excited frequency returns with waiting time - a counterintuitive result. More likely, this recurrence results from the disappearance of contributions to the third-order signal due to Zundel-like configurations. Modulations of the O-H stretching potential cause these configurations to undergo rapid spectral

sweeping, leading to an overall small value of the PS. As this component relaxes, the contribution to the PS due to the slower dynamics of the solvent will dominate the signal, causing the observed rise in the PS after $\tau_2 = 80$ fs.

Fig. 4 expands the time axis of Fig. 3A and plots the decay of the PS out to 10 ps. Unexpectedly, at a waiting time of ~2 ps each measured PS trace decays uniformly to zero independent of deuteroxide concentration. One possible explanation for this decay is that it is due to PT. As spectral diffusion slows due to the increased viscosity of the solution, PT can serve as a means of converting a high frequency free OH^- stretch into a lower frequency, water-like stretch. The large shift in frequency from this exchange would cause a decrease in the measured PS. CPMD simulations have suggested that in deuterated solutions, the structural diffusion of the OD^- ion occurs on a 1.7 ps time scale,[21] which agrees well with our experimental results provided the decay of the PS is due to PT.

A second potential explanation is that the PS's decay is due to a non-equilibrium heating of the solvent. Following vibrational relaxation, the energy lost by an excited HOD molecule funnels down to the low frequency modes of the bath, making the local environment surrounding the molecule appear as if it has been heated.[49] This can shift the absorption frequency of the molecule, preventing the photobleach of the O-H stretch from refilling upon population relaxation. In PP measurements of HOD/D_2O, this "hot ground state" absorption contributes a static offset to the decay that persists over 10's of picoseconds[34,50] while in PS measurements, both recurrences and decays of the PS at time delays corresponding to a few ps can be observed depending on the bandwidth and center frequency of the excitation pulses.[49,51]

To help explain the origin of the features in our PP and PS experiments, we carried out 2D IR measurements. Representative 2D IR and 2D IR difference spectra are presented in Fig. 5-8. A 2D IR spectrum plotted in the frequency domain is related to the joint probability of exciting a molecule at a given initial frequency, ω_1, and detecting it at a second frequency, ω_3, after a waiting period τ_2. As τ_2 is increased, peaks due to rapidly dephasing transitions take on homogeneous, round shapes, whereas peaks comprised of an inhomogeneous distribution of transition energies remain diagonally elongated. Additionally, as τ_2 is stepped cross peaks can appear that indicate the flow of population from one vibrational state to another.[52] Since vibrational systems are inherently multilevel, for each positive peak in a 2D IR spectrum, a matching negative peak appears that is anharmonically shifted along the ω_3 axis and corresponds to a photoinduced absorption involving a $v = 2 \leftarrow 1$ transition.

For the earliest waiting times, 2D IR spectra for $\tau_2 = 60$ fs and 200 fs are plotted in Fig. 5 as a function of NaOD concentration. More extensive waiting time data has previously been presented.[32] Strong off-diagonal broadening is present in the NaOD spectra at $\tau_2 = 60$ fs whose intensity grows with increasing NaOD concentration. This broadening is observed at all probed frequencies and quickly relaxes as τ_2 increases, nearly disappearing from the spectra by a waiting time of 100 fs.[32] We can better isolate the short time spectral features due to hydroxide by calculating difference spectra between surfaces for NaOD/D_2O and neat HOD/D_2O solution.[53] Fig. 6A plots difference spectra calculated at two waiting times, 60 and 200 fs. At all concentrations, difference spectra at a given waiting time appear similar, but decrease in signal-to-noise as the NaOD concentration lessens.

At $\tau_2 = 60$ fs, positive intensity appears throughout most of the pictured spectral range. We can quantify this contribution to the 2D surfaces by integrating an off-diagonal region of the spectra (Fig. 6B).[54] At $\tau_2 = 60$ fs, the offdiagonal amplitude grows linearly with concentration, but disappears by $\tau_2 = 200$ fs. Off-diagonal intensity is commonly observed in systems containing coupled oscillators,[55] but given that the solutions under investigation are isotopically dilute, the probability of two separate O-H oscillators encountering each other is small. Off-diagonal intensity can also appear in 2D IR chemical exchange experiments;[56] however, the observed collapse of intensity with waiting time is the opposite of what is expected. In a previous report,[32] we assigned the large broadening at early waiting times to Zundel-like configurations. The O-H stretching potentials of these species are strongly modulated during proton transfer events, allowing their vibrational transitions of the shared proton to rapidly sample the frequency range probed by our experiments.

As the concentration is raised, we find that the spectrum recorded at $\tau_2 = 200$ fs becomes increasingly elongated along the diagonal frequency axis. This increase in the ellipticity of the lineshape is consistent with the conclusions drawn from the PS data and indicates a slowing of spectral diffusion. The difference spectra calculated at $\tau_2 = 200$ fs shows that the intensity of the NaOD 2D spectra is increased relative to D_2O along the diagonal axis, but decreased in the regions above and below the diagonal. A difference spectrum of this type is expected for the subtraction of a homogenous 2D lineshape from an inhomogeneous one. The difference spectra at $\tau_2 = 60$ fs reflect these features related to the slowing of spectral diffusion in addition to the broad positive offset that absorbs across the entire plotted frequency region.

Picosecond relaxation processes are observed in the 2D IR surfaces and difference spectra in Fig. 7 and 8. For reference we first consider the spectra recorded for HOD in D_2O, at $\tau_2 = 1$ ps. We find that the nodal line separating the $v = 1 \leftarrow 0$ and $v = 2 \leftarrow 1$ transitions has rotated to be nearly parallel to the ω_1 axis, indicating that spectral diffusion is largely complete by this waiting time. As τ_2 increases, the negative peak corresponding to the $v = 2 \leftarrow 1$ transition disappears from the 2D spectra due to the rise of the "hot ground state" absorption[35] described above.

In contrast, as the $v = 2 \leftarrow 1$ transition disappears in 2D spectra of 10.6 M NaOD due in part to vibrational relaxation, we observe a shift of negative amplitude along the direction of the diagonal axis to frequencies near $\omega_1 = 3600$ cm^{-1}/$\omega_3 = 3450$ cm^{-1}, as is prominently seen in spectra for $\tau_2 = 3$ ps. This location along the ω_1 axis corresponds to the free OH$^-$ stretch (ω_{Ion}) present in the FT-IR spectra in Fig. 1. The persistence of the induced absorption of ω_{Ion}'s $v = 2 \leftarrow 1$ transition at this waiting time suggests that the vibrational lifetime of the OH$^-$ stretch is longer than the 710 fs lifetime of the HOD molecule. This result is not unexpected since the OH$^-$ ion can only undergo vibrational relaxation through intermolecular pathways. Vibrational lifetimes for similar diatomic molecules in D_2O that relax via intermolecular energy transfer can be quite slow, reaching time scales as long as 71 ps in the case of the CN$^-$ ion.[57] Given the low density of high frequency acceptor modes present in an isotopically dilute solution of HOD/NaOD, we expect the vibrational lifetime of the OH$^-$ ion in these solutions to be longer than that of the HOD molecule. Fits to the data based on our spectral model (see below) place the lifetime of the ion's stretch at 1.3 ps, significantly faster than that of the CN$^-$ ion, but only roughly double that of HOD molecule. This raises the possibility that

PT to the ion, resulting in the reformation of a HOD molecule, may be a dominant vibrational relaxation process for the ion.

Additional examination of the $\tau_2 = 3$ ps 2D spectrum of 10.6 M NaOD shows the growth of a positive feature below the v = 2←1 peak of the OH⁻ stretch at $\omega_1 = 3600$ cm⁻¹/$\omega_3 = 3300$ cm⁻¹. The appearance of this feature coincides with an intensification of the ridge extending away from the diagonal axis along $\omega_3 = 3600$ cm⁻¹, suggesting that these features signal the growth of cross peaks due to the exchange of population between ω_W and ω_{Ion}. To highlight the growth of these features, we have calculated difference spectra of the 2D surfaces measured for 10.6 M NaOD and D_2O solutions (Fig. 8A).[58] At $\tau_2 = 600$ fs, the 10.6 M NaOD spectrum is more intense along the diagonal axis between 3300 and 3600 cm⁻¹, reflecting both the absorption of ω_{Ion} near 3600 cm⁻¹ and the slowing of spectral diffusion with increasing NaOD concentration. Near a waiting time of 2 ps, a ridge begins to extend horizontally along the ω_1 axis at $\omega_3 = 3600$ cm⁻¹ that strengthens over time. Likewise, over a similar time scale the region below the diagonal at $\omega_1 = 3600$ cm⁻¹ changes from negative to positive. Together, these features support the appearance of a cross peak between ω_W and ω_{Ion}. While the growth of intensity in these regions does not have the same asymptotic limit due to interference with the v = 2←1 transition below the diagonal axis, the intensity in both off-diagonal regions can be well described by a rising exponential with a time constant of 1.9 ps (Fig. 8B).

IV. Modeling of Chemical Exchange in 2D IR Lineshapes

From the discussion of the experimental data above, it is clear that a number of processes contribute to the presented PP, PS, and 2D IR surfaces, including molecular

reorientation, vibrational relaxation, and non-equilibrium heating. To determine how each of these effects influence our measured spectra, we apply a fitting model that accounts for the varying population relaxation of different hydride species, their exchange, and the effects of non-equilibrium heating. Since our nonlinear experiments primarily focus on the spectral region centered near 3 μm, we will only distinguish states with O-H vibrations that absorb in this range: ω_W, ω_{Ion}, and ω_{Sol}. We self-consistently model all of our experiments by treating these as distinct states, free energy minima that experience Gaussian fluctuations and undergo uncorrelated exchange kinetics as a result of PT over picosecond time scales. In addition to these stable configurations, we also account for spectral signatures associated with unstable Zundel-like PT transition states that appear over femtosecond time scales. This model can adequately reproduce our measured FT-IR, PP, PS, and 2D IR data, and allows us to estimate a lower bound for the exchange of the free OH^- stretch and the main HOD absorption band due to PT.

Fig. 9 displays exchange processes that may be observed in 2D IR experiments while Fig. 10 highlights regions where their signatures are expected to appear. In Fig. 9A, the deuteron of a HOD molecule is transferred to an OD^- ion, creating a new OH^- ion. Exchange of this type will result in a cross peak between ω_W and ω_{Ion} and is included in our model. In the scenario shown in Fig. 9B, the positions of the proton and transferring deuteron have been exchanged. In this case, since the two configurations formed as a result of the pictured PT event are identical, no cross peaks are expected to form as a result of this process over picosecond time scales. However, the transition state associated with the PT process in Fig. 9B can make a strong contribution to the third-order signal at short waiting times,[32] which we account for in our spectral model.

In Fig. 9C we see a scenario that would lead to a cross peak between ω_{Sol} and ω_W, wherein a HOD molecule initially hydrogen bonded to an OD⁻ ion migrates out of the ion's solvation shell. Likewise, Fig. 9D pictures an exchange process involving two separate OD⁻ ions that we only expect to take place at high deuteroxide concentration, but would lead to an exchange cross peak between ω_{Sol} and ω_{Ion}. Unlike the process pictured in Fig. 9A however, these processes involve the transfer of a proton instead of a deuteron. Due to the isotopically dilute nature of the investigated solutions, cross peaks associated with the exchange process pictured in Fig. 9A are expected to be more intense than those due to the processes in Fig. 9C & 9D. Hence, we neglect these two processes in our analysis.

An additional process that can give rise to a cross peak between ω_{Sol} and ω_W is shown in Fig. 9D, wherein a deuteron is transferred to an OD⁻ ion whose solvation shell contains a HOD molecule. While cross peaks due to this process may contribute to our measured 2D spectra, the bandwidth of the excitation pulses used to measure the spectra in Fig. 5-8 was tuned to span ω_W and ω_{Ion}. Thus, in the model we present below we neglect this process from our analysis. In the supporting information, we include a more detailed model that accounts for this process, but the results obtained with this model are similar to those found with the simpler model presented below.

Recently, kinetic models have been developed that allow chemical exchange processes to be incorporated into the commonly used phenomenological modeling of 2D IR spectra.[59,60] These models assume that exchange occurs on time scales long compared to dephasing during τ_1 and τ_3, and that the exchange reaction is described by first order kinetics. We expect these assumptions to be appropriate for times longer than ~500 fs.

We describe exchange between two states, "A" and "B", by a rate constant $k_{A \to B}$. Rate constants are related by detailed balance, $N_A(0)k_{A \to B} = N_B(0)k_{B \to A}$. The model also assumes that exchange processes leave no correlation in frequency to the initial state. These models neglect the variation of the O-H transition dipole with vibrational frequency (non-Condon effects) and asymmetries that appear in the shape of peaks of 2D spectra, which we have emphasized in our studies of HOD/D_2O for short times.[32,61-63] However, these assumptions should be valid for long times, and we apply it to obtain an exchange time scale between the free OH^- stretch and the main HOD/D_2O transition. We make a further simplifying approximation and neglect the reorientation of molecules since both PP anisotropy[30] and *ab initio* simulations[19] have shown a strong retardation of orientational dynamics for water molecules located in a hydroxide ion's solvation shell. Expressions governing the time dependent populations of vibrationally excited molecules that contribute to nonlinear signals involving ω_{Sol}, ω_W, and ω_{Ion} appear in the supporting information.

Within these approximations, it is possible to describe the third-order response in our experiments, S^{Total}, by writing it as a sum of three separate terms:

$$S^{Total} = S^{OH} + S^Z + S^{Therm} \tag{1}$$

S^{OH} denotes signal contributions from all three O-H oscillator states, including exchange kinetics, S^Z corresponds to the transient signature of Zundel-like configurations that appears at waiting times <200 fs, and S^{Therm} describes the thermalization of the sample upon vibrational relaxation.

IVa. Description of Vibrational Dephasing

The dominant signal contributions to the O-H species and exchange kinetics are written as

$$S^{OH} = \sum_{A=Ion,W,Sol} S^A + \sum_{A,B=Ion,W} S^{A,B} \tag{2}$$

The indices A and B refer to the W, Ion, or Sol states. (In the description that follows, we will use capital letters to denote different chemical species and lower case letters to denote the vibrational eigenstates of these species.) S^A terms refer to vibrational dynamics within state A, and $S^{A,B}$ terms describe exchange kinetics initiating in state A and ending in state B. We include exchange terms for the probability of returning to the initial state after a series of exchange reactions, $S^{A,A}$. As per Ref. 60, we assume that the initial exchange process leads to a loss of frequency correlation.

The general form of the set of response functions, S^A, can be written as

$$S^A_{\pm}(\tau_3,\tau_2,\tau_1) = N_A(\tau_2)\left|\mathbf{\mu}^A_{10}\right|^2 \exp\left[\mp i\left\langle\omega^A_{10}\right\rangle\tau_1 - \tau_1/2T^A_1\right]$$
$$\times\left\{\left|\mathbf{\mu}^A_{10}\right|^2 \exp\left[-i\left\langle\omega^A_{10}\right\rangle\tau_3 - \tau_3/2T^A_1\right]F^A_{\pm}(\tau_3,\tau_2,\tau_1)\right. \tag{3a}$$
$$\left.-\left|\mathbf{\mu}^A_{21}\right|^2 \exp\left[-i\left\langle\omega^A_{21}\right\rangle\tau_3 - 3\tau_3/2T^A_1\right]F^A_{\pm2}(\tau_3,\tau_2,\tau_1)\right\}$$

where

$$\begin{aligned}
F^A_- &= F^{(3)A}_{0101} + F^{(4)A}_{0101} \\
F^A_{-2} &= F^{(2)A}_{0121} \\
F^A_+ &= F^{(1)A}_{0101} + F^{(2)A}_{0101} \\
F^A_{+2} &= F^{(4)A}_{0121}.
\end{aligned} \tag{3b}$$

Likewise, the set of functions, $S^{A,B}$, can be described by

$$S_{\pm}^{A,B}(\tau_3,\tau_2,\tau_1) = N_{A,B}(\tau_2)\left|\boldsymbol{\mu}_{10}^{A}\right|^2 \exp\left[\mp i\left\langle \omega_{10}^{A}\right\rangle \tau_1 - \tau_1/2T_1^{A}\right]$$

$$\times \left\{\left|\boldsymbol{\mu}_{10}^{B}\right|^2 \exp\left[-i\left\langle \omega_{10}^{B}\right\rangle \tau_3 - \tau_3/2T_1^{B}\right] F_{\pm}^{A,B}(\tau_3,\tau_2,\tau_1)\right. \tag{3c}$$

$$\left.-\left|\boldsymbol{\mu}_{21}^{B}\right|^2 \exp\left[-i\left\langle \omega_{21}^{B}\right\rangle \tau_3 - 3\tau_3/2T_1^{B}\right] F_{\pm2}^{A,B}(\tau_3,\tau_2,\tau_1)\right\}$$

where

$$F_{\pm}^{A,B} = \exp\left[-h_{10}^{A}(\pm\tau_1) - h_{10}^{B}(\tau_3)\right] + \exp\left[-h_{10}^{A}(\pm\tau_1) - h_{10}^{B}(-\tau_3)\right]$$

$$F_{\pm2}^{A,B} = \exp\left[-h_{10}^{A}(\pm\tau_1) - h_{21}^{B}(\tau_3)\right] \tag{3d}$$

Here "−" and "+" refer to the rephasing and nonrephasing contributions to the third-order response, $\{\boldsymbol{\mu}_{10}^{A}, \boldsymbol{\mu}_{21}^{A}\}$ and $\{\omega_{10}^{A}, \omega_{21}^{A}\}$ denote the transition dipole matrix elements and frequencies of the v = 1←0 and v = 2←1 transitions for oscillator A, and T_1^{A} denotes the vibrational lifetime of state A. The set of dephasing functions, F, in Eq. 3 can be further expressed in terms of line-shape functions $h_{nm}^{A}(\tau)$ that are listed in the supporting information. These lineshape functions are each described using a set of frequency correlation functions, $C_{nm}^{A}(\tau) = \left\langle \delta\omega_{n0}^{A}(\tau)\delta\omega_{m0}^{A}(\tau)\right\rangle$. By assuming that harmonic scaling relationships hold (see supporting information), only three unique correlation functions, $C^{Ion}(\tau)$, $C^{W}(\tau)$, and $C^{Sol}(\tau)$, which describe ω_W, ω_{Ion}, and ω_{Sol} respectively, are needed to describe vibrational dephasing.

As a functional form for $C^{W}(\tau)$ and $C^{Sol}(\tau)$, we will use a sum of two exponentially decaying functions, a static offset, and an underdamped oscillatory decay to account for the hydrogen bond oscillation that appears in the data at early delay times:

$$C(\tau) = \Delta_{static} + A_{fast}\exp\left[-\tau/\tau_{fast}\right] + A_{slow}\exp\left[-\tau/\tau_{slow}\right]$$

$$+ A_{osc}\exp\left[-\tau/\tau_{osc}\right]\left(\cos(\omega_{osc}\tau) + (\tau_{osc}/\omega_{osc})\sin(\omega_{osc}\tau)\right). \tag{4}$$

The choice of this functional form is motivated by our previous PP and PS measurements on HOD/D_2O,[34] and assumes that the time scale of fluctuations experienced within each state are similar, although their amplitudes may vary. Since the hydroxide ion can only donate a weak hydrogen bond, we simply use a biexponential function plus a static offset for $C^{Ion}(\tau)$. These correlation functions serve as a set of fitting parameters that are optimized to match the experimental data.

To account for the broad, transient contribution to the 2D IR data at early waiting times, we include an additional transition along the diagonal axis that is centered at the same frequency as ω_W, and whose linewidth is set such that it covers the total experimental frequency range:

$$S_{\pm}^{Z}(\tau_3, \tau_2, \tau_1) = K_Z \exp\left[\mp\langle\omega_{10}^{Z}\rangle\tau_1 - i\langle\omega_{10}^{Z}\rangle\tau_3 - (\tau_1 + 2\tau_2 + \tau_3)/2T_1^{Z}\right]F_{\pm}^{Z} \qquad (5)$$

We describe the intensity of this feature using an empirical scaling factor, K_Z, whose value is set based on the scaling between the relative contributions of the fast and slow components of the PP signal (Fig. 2). The frequency fluctuations of this transition are described using a single exponential decay with a correlation time of 35 fs, as determined from our fits to the PS data. To ensure that this feature does not contribute to the signal at delay times where chemical exchange is believed to occur, we input a relaxation time of $T_1^{Z} = 110$ fs, consistent with our PP measurements. This choice is purely to match the behavior of the PS and PP data at short delay times in our spectral window, and is not meant to suggest the disappearance of S^Z is a result of population relaxation.

IVb. Treatment of Thermal Effects

The thermalization response that appears due to fast vibrational relaxation has contributions from each of the O-H species and the solvent:

$$S^{Therm} = S_{D_2O}^{Therm} + \sum_{A=Ion,W,Sol} S^{A,Therm}. \tag{6}$$

$S^{W,Therm}$, $S^{Ion,Therm}$, and $S^{Sol,Therm}$ each describe signal contributions related to a nonequilibrium heating of the bath following the vibrational relaxation of ω_W, ω_{Ion}, and ω_{Sol}, while $S_{D_2O}^{Therm}$ describes a thermal signal generated by the D_2O solvent.[51,64] PP and vibrational echo experiments on dilute HOD in D_2O and H_2O have shown that $S^{W,Therm}$ consists of a ground state bleach that persists over picosecond time scales.[34,50,51,64,65] The lineshape of this bleach resembles the linear absorption spectrum of the sample when projected along the ω_1 frequency axis and the difference of the linear absorption spectrum measured at room temperature and a temperature elevated by a few degrees when projected along the ω_3 frequency axis.[34,35] To describe this heating effect for $S^{W,Therm}$, $S^{Ion,Therm}$, and $S^{Sol,Therm}$, we write:

$$\begin{aligned} S_{\pm}^{A,Therm}(\tau_3,\tau_2,\tau_1) = K_A^{Therm} \left|\mathbf{\mu}_{10}^A\right|^4 N_A(0) N_A^{Therm}(\tau_2) \exp\left[\mp i\left\langle\omega_{10}^A\right\rangle\tau_1 - i\left\langle\omega_{10}^A\right\rangle\tau_3\right] \\ \times \exp\left[-h_{10}^A(\mp\tau_1) - h_{10}^A(\tau_3)\right]\left(1 - \left|\Delta\mathbf{\mu}_{10}^A\right|^2 \exp\left[-i\Delta\omega_3^A\tau_3\right]\right) \end{aligned} \tag{7}$$

Eq. 7 represents a difference spectrum between the product of the linear absorption spectrum of ω_W multiplied along both the ω_1 and ω_3 axes and this same quantity which has been shifted by $\Delta\omega_3^A$ along the ω_3 axis and decreased in intensity by $\left|\Delta\mathbf{\mu}_{10}^A\right|^2$. These two fitting parameters are set such that the projection of the thermal response onto the ω_3 axis at a waiting time of 10 ps matches the experimentally measured dispersed PP signal.

K^{Therm} is an adjustable parameter that sets the intensity of the thermal signal relative to the resonant contributions to the third-order response. This parameter is determined by matching the offset of the experimental PP signal.

The growth of $S^{A,Therm}$ with waiting time is described by $N_A^{Therm}(\tau_2)$ in Eq. 7, and researchers have postulated different functional forms for the growth of this thermal response. Yeremenko et. al.[64] and Fecko et. al.[34] have assumed that $N_W^{Therm}(\tau_2)$ can be well described by an exponential growth towards an asymptotic limit. Since the relaxation of the HOD molecule is believed to proceed through a series of intramolecular modes before populating the low frequency modes of the bath,[66,67] Rezus and Bakker[65] postulated that the growth of the thermal signal can be described by assuming that the O-H stretch first relaxes to an intermediate state before reaching the low frequency modes of the system. We have chosen to describe $N_A^{Therm}(\tau_2)$, using this latter, more physically reasonable approach. The analytical solution for the growth of the thermal signal is then given by:[1]

$$N_A^{Therm}(\tau_2) = 1 + \frac{\left(1/T_1^A\right)\exp\left[-\tau_2/T_1^{Int}\right] - \left(1/T_1^{Int}\right)\exp\left[-\tau_2/T_1^A\right]}{1/T_1^A - 1/T_1^{Int}} \tag{8}$$

where T_1^{Int} is the lifetime of the intermediate state, which will be adjusted to properly fit the experimental data.

As a final contribution to the third-order response, we note that Yeremenko and coworkers[51,64] have found that a thermal signal can also originate from direct excitation of the D_2O solvent. Although the absorptive component of the O-D stretch is well detuned from the 3 μm region of the mid-infrared spectrum that we are probing, the dispersive component of this transition has a large tail that extends towards 3 μm and

facilitates the non-resonant excitation of the O-D stretch. Since this excitation process is non-resonant, we expect the thermal signal that arises from the relaxation of the O-D stretch to be $\pi/2$ phase shifted from the signal field, and should not contribute to the absorptive third-order response measured in heterodyne detected experiments such as PP and 2D IR spectroscopy. However, homodyne measurements such as the PS, which contain contributions from both absorptive and dispersive changes of the sample, will be sensitive to this thermal signal. We add the following term used by Yeremenko and coworkers[51,64] to account for the non-resonant absorption of D_2O:

$$S_{D_2O}^{Therm}\left(\omega_3,\tau_2,\omega_1\right)=e^{i\pi/2}K_{D_2O}\left(1-\exp\left[-\tau_2/T_1^{D_2O}\right]\right)S_{pulse}\left(\omega_3,\omega_1\right) \qquad (9)$$

where K_{D_2O} is a scaling factor that is determined by matching the decay of the PS, and $T_1^{D_2O}$ is the vibrational lifetime of the O-D stretch of D_2O, which is set to the experimentally determined value of 400 fs.[68] The phase factor at the start of this term ensures that it is $\pi/2$ phase shifted from the signal field. Since the O-D stretch is largely detuned from the frequency range probed by our experiments, the spectral shape of the thermal signal is simply given by the product of the experimental pulse spectrum along the ω_1 and ω_3 dimensions, $S_{pulse}\left(\omega_3,\omega_1\right)$, normalized to its maximum value.

IVc. Constraints for Fitting Parameters

Admittedly, this model contains a large number of fitting parameters, but many of these values have been independently determined or can be constrained based on measurements. Each experimental observable (FT-IR, PP, PS, & 2D IR) differs in its sensitivity to the parameters contained by our model. Thus, to fit our measured spectra we have adopted an iterative approach wherein only a subset of the model's parameters

are floated at a given time to fit the observables that are most sensitive to those parameters. These parameters are then constrained while fitting the remaining pieces of data, and this process is looped over until the fit to the full experimental data set. Where possible, we have taken parameter values from the literature.

Table 1 provides a list of the parameters that were floated and the experimental observables used to determine their values. Center frequencies and transition dipole strengths of ω_W, ω_{Ion}, and ω_{Sol} are found by fitting FT-IR spectra as a function of NaOD concentration. Based on these values, we calculate the transition dipole matrix elements and center frequencies for the v = 2$\leftarrow$1 transitions of ω_W, ω_{Ion} and ω_{Sol} using anharmonic DFT generated frequency maps described in a previous report.[32]

To determine the frequency-frequency correlation functions that describe the spectral diffusion of ω_W, ω_{Ion}, and ω_{Sol}, we used our previously determined $C(\tau)$ for HOD/D$_2$O[34] as an initial guess for $C^W(\tau)$, $C^{Ion}(\tau)$, and $C^{Sol}(\tau)$, and varied these functions to match our experimental PS data set. While iteratively fitting the data, we found that the relative amplitudes of the components of $C^W(\tau)$ and $C^{Sol}(\tau)$ often converged to similar values. To eliminate superfluous fit parameters from our model we have constrained both of these functions to vary only in terms of their time zero values to properly fit the linear absorption spectrum. Likewise, the relative scaling of the fast and slow components of $C^{Ion}(\tau)$ matched that of $C^W(\tau)$ and $C^{Sol}(\tau)$, so we also set this ratio to be the same. This enabled us to describe spectral diffusion through the use of a single frequency-frequency correlation function for each NaOD concentration. The initial values of $C^W(\tau)$, $C^{Ion}(\tau)$, and $C^{Sol}(\tau)$ were set to match the linewidth of the

experimental FT-IR spectra. We found that we did not need to vary these linewidths with the concentration of NaOD.

Time scales for population relaxation were determined from magic angle PP experiments. Parameters describing thermalization effects were initially unknown, but the amplitude and rate of growth of the thermal signal was found to be sensitive to the asymptotic behavior of the PS and PP signals. Parameters that govern the shape of the "hot ground state" absorption were set to match the results of dispersed PP measurements carried out at $\tau_2 = 10$ ps. At this waiting time well past the vibrational lifetime of the O-H stretch, thermal effects are expected to dominate the third-order signal.

On the basis of our 1D measurements alone (FT-IR, PP, and PS), we can constrain all of the parameters that enter into our fitting model except for two, the vibrational lifetime of the OH$^-$ stretch, T_1^{Ion}, and the exchange time scale between ω_{Ion} and ω_W, $\tau_{Ion \rightarrow W}$. These two parameters were adjusted iteratively to fit our experimental 2D IR spectra at a NaOD concentration of 10.6M. A set of tables containing the parameters used to fit each of our experimental observables appears in the supporting information. The results of these fits are plotted together with the data in Fig. 1, 2, 3, 4, and 7.

V. Comparison Between Model Calculations and Experiment

Va. FT-IR and Magic Angle Pump-Probe Experiments

In Fig. 1 we present a comparison between our experimental FT-IR spectra and those calculated using our spectral model as a function of NaOD concentration. In fitting the FT-IR data, the transition dipole matrix elements, linewidths of each transition, and

the center frequencies were held constant across the entire data series. Good agreement with the measured spectra is obtained for frequencies above 3100 cm^{-1} except in the case of 10.6 M NaOD solution, where the peak corresponding to ω_W appears at too high a frequency since our model does not allow its center frequency to vary with concentration. Below 3100 cm^{-1}, our model fails to match the FT-IR data due to the broad continuum absorption that appears across the mid-infrared in spectra of strong bases. We expect our spectroscopic model, which assumes Gaussian fluctuations and does not treat transition dipole variation (non-Condon effect), to fail in this region. However, this region lies outside of the frequency range probed by our nonlinear experiments.

The relative populations of each of the species that contribute to ω_W, ω_{Ion}, and ω_{Sol} as a function of NaOD concentration was needed as an input to the fitting routine. These values were obtained from a combination of the known densities of NaOH solutions[48] and neutron scattering results,[25] which estimate changes in the coordination number of the OH$^-$ ion changes with NaOH concentration. Since values for the density of NaOD solutions are not readily available, we assumed that the spatial composition of an isotopically dilute HOD in NaOD/D_2O solution is identical to that of a NaOH solution of equivalent concentration. Given that the molarity of pure D_2O only varies by ~0.5% from that of pure H_2O, we believe that this assumption is valid. Table 2 displays our estimates of the relative populations of hydrogen atoms whose nearest neighbor is a D_2O molecule, an OD$^-$ ion, or exist as an OH$^-$ ion as a function of NaOD concentration. In determining these values, we have assumed that no hydrogen bonds are donated to the Na$^+$ ion, that only O-H bonds that are directly hydrogen bonded to the oxygen atom of an OD$^-$ ion contribute to ω_{Sol}, and that on average, only a negligible amount of ion pairing occurs in

solution. This last assumption is expected to break down at concentrations near 10.6 M and above, where only 4.8 water molecules exist per OD^- ion.

Displayed in Fig. 2 is a comparison between PP spectra calculated from our spectral model and our experimental results. In general, the agreement is quite good and the fits reproduce both the magnitude of the fast decay component of the PP and the offset at large values of τ_2 that is determined by the magnitude of the thermal contribution to the third-order response. However, in each experimental PP trace, the decay of the signal is preceded by a slight rise that is not captured by our model since it does not take into account the finite time duration of the excitation pulses.

Vb. Photon Echo Peak Shift

Alongside the experimental PS data pictured in Fig. 3 and 4, we plot the results calculated from our spectral model. Examining the behavior of the PS in the waiting time range below 1 ps (Fig. 3), at all concentrations smaller than 5.3 M NaOD we observe an initial fast decay followed by a recurrence due to an underdamped hydrogen bond oscillation that is reproduced by our fitting model. At higher concentrations, the initial fast decay is still present, but then gives way to a rise in the PS. This rise is due to the relaxation of the broad, transient contribution to the third-order response from Zundel-like states (S^Z) and is captured by our fitting model at concentrations of 7.9 and 10.6 M NaOD. While our model is unable to match the initial value of the PS of the 15.1 M NaOD data, presumably due to an improper treatment of the lineshape of the Zundel-like feature, it is able to describe the rise in the PS between $\tau_2 = 0.2 - 1$ ps.

When fitting the data for waiting times between $0.2 - 2$ ps (Fig. 4), we could not reproduce the increase in the value of the PS with NaOD concentration by simply changing the time scales and amplitudes of the exponentially decaying functions that comprise $C(\tau)$. The data could only be properly fit when a static offset was included in $C(\tau)$. The relative contribution of this static component to $C(\tau)$ is plotted in Fig. 11. Although this variation with NaOD concentration is nonlinear, we find that it correlates with the increase in the viscosity of aqueous NaOH[48] with concentration.

At a waiting time of ~2 ps we observe a decay of the PS to zero that is independent of NaOD concentration. This decay is suggestive of chemical exchange but may also be explained by solvent induced heating. The fits from our model show that both of these processes contribute to the decay of the PS, but that the solvent induced heating effect forms the dominant contribution to the decay. At $\tau_2 = 1$ ps and a concentration of 10.6 M, varying the exchange time scale $\tau_{Ion \rightarrow W}$, defined as $\tau_{Ion \rightarrow W} = 1/k_{Ion \rightarrow W}$, from 500 fs to 1 ns changed the value of the PS by only 1.5 fs. At all other values of τ_2 at this concentration, the variation of the calculated PS with $\tau_{Ion \rightarrow W}$ was generally smaller than 2 fs, leading us to conclude that the PS is relatively insensitive to frequency shifts induced by the exchange process in Fig. 9A. As shown in Table 2, even at high concentration, the number of hydrogen atoms that form OH$^-$ ions is small relative to the number of HOD molecules hydrogen bonded to D$_2$O. This means that the contribution of exchange events to the total third-order signal will be small relative to the signals due simply to the isolated dynamics of ω_{Ion} and ω_W. However, since exchange

events appear as spectrally separated cross peaks in 2D IR experiments, measurements of this type are better suited to the determination of $\tau_{Ion \rightarrow W}$.

It is worth noting that while we can reproduce the overall decay of the PS near ~2 ps, our model cannot well reproduce the recurrence near 1.5 ps at concentrations of 5.3 M and below. A recurrence of this type has been shown to arise in PS measurements of HOD in D_2O using pulses that are somewhat longer than ours (90 fs) and are tuned toward the red edge of the O-H absorption spectrum.[49] Yeremenko and coworkers[51,64] demonstrated that this recurrence grows in intensity as the experimental pulse spectrum is narrowed and detuned farther from resonance with the O-H stretch, and that this feature can be reproduced by taking into account both the thermal redistribution term displayed in Eq. 9 and a change in the refractive index of the D_2O solvent upon the transfer of vibrational energy to the low frequency modes of the bath. In an earlier version of our model, we included this change in the solvent refractive index but found that it only had a minimal effect on the calculated PS. However, we have found that by artificially narrowing and red shifting our experimental pulse spectrum, we can better reproduce the recurrence near 1.5 ps at low NaOD concentration. It is known that the transition dipole of the O-H stretch of the HOD molecule increases with the strength of the hydrogen bond to the proton.[61,69-71] This non-Condon effect can bias our experimental measurements in favor of signals that arise from the low frequency side of the O-H absorption lineshape despite the fact that our pulses span a large portion of ω_{OH}. The lack of inclusion of these effects in our spectral model may explain our inability to properly reproduce the recurrence present in our experimental results.

Vc. Determining an Exchange Time Scale from 2D IR Measurements

In Fig. 7 we plot a comparison between our experimental 2D IR data measured for 10.6 M NaOD solution and the spectra calculated from our model using a value of $\tau_{Ion \to W} = 3$ ps, the optimum value of the exchange time determined from a least squares fitting of the 2D IR data. The simulation model reproduces many of the features found in the experiment, such as the appearance of the OH$^-$ stretch's v = 2$\leftarrow$1 transition with increasing waiting time, and the asymmetry of the 2D spectra along the diagonal axis that persists at large values of τ_2. Also reproduced are the elongation of the diagonal OH$^-$ peak near 3600 cm^{-1} along the ω_1 axis and the appearance of a positive feature below the diagonal at $(\omega_1, \omega_3) = (3600$ cm^{-1}, 3300 cm$^{-1})$. These two features were postulated in Section III to correspond to cross peaks denoting chemical exchange. By plotting different contributions to our model, we indeed find that enhancement in these regions is due to cross peaks that appear as a result of chemical exchange. While the elongation of the 2D spectra above the diagonal axis is primarily due to chemical exchange, the peak that appears below the diagonal results from both exchange and the growth of the hot ground state absorption, which complicates the determination of $\tau_{Ion \to W}$ from our spectral model. Interference between these features as well as the fact that the vibrational relaxation time scales of the system are faster than the determined exchange rate can explain why the optimum exchange time scale differs from the 1.9 ps rise observed in the experimental 2D data (Fig. 8B).

Although it was not added in the modeling in Fig. 8, we have also investigated how the extracted deuteron transfer rate is influenced by also treating the $S^{Sol,W}$ exchange processes in Fig. 9E. This work is presented in the supplementary material. Although our

spectral bandwidth in exchange experiments was centered at high enough frequencies as to make signal contributions from the ω_{Sol} species negligible, the additional exchange processes will add additional decay channels for ω_W species, thereby lengthening the extracted $\tau_{Ion \to W}$. Indeed we do find a slight increase of our predicted value of $\tau_{Ion \to W}$ to 4.3 ps, but makes the model highly sensitive to the treatment of ω_{Sol}. Since ω_{Sol} represents the high frequency side of a largely featureless continuum band, different values for its center frequency, transition dipole, and linewidth may give similar fits to the FT-IR spectra in Fig. 1. Thus, without further experiments that allow better constraints to be placed on the treatment of ω_{Sol}, we are wary of relying on a model that accounts for exchange processes involving this transition.

Beyond a waiting time of ~6 ps, the 2D spectrum predicted by our model is no longer observed to change, indicating a completion of the growth of the thermal response. This calls into question our ability to determine if the optimum value of $\tau_{Ion \to W}$ instead corresponds to a value that is larger than 3 ps. In light of this observation as well as the discussion of the treatment of ω_{Sol} above, we view our optimal fit value of $\tau_{Ion \to W} = 3$ ps as a *lower bound* for the solvation time scale of a newly formed OH$^-$ ion upon proton transfer. (See the supporting information for further justification of this conclusion).

Vd. Implications of the Exchange Time Scale

While this result only provides a lower bound for the time scale of hydroxide ion solvation following PT, it still provides insight into the structural diffusion of the ion. PT is commonly discussed as a hopping event between a water molecule and a hydroxide ion pair, and the subsequent solvation of the products of this reaction. However, given that

protons are believed to be able to rapidly transfer along hydrogen bonded chains, it is possible that correlated PT across multiple solvation shells may be possible.[72-74] The diffusion constant for a three dimensional random walk is $D = \langle L^2 \rangle / 6\Delta t$, where L denotes the hopping distance and Δt is the time between hops.[75] The diffusion constant of the deuteroxide ion determined from mobility measurements is 0.32 $\text{Å}^2/\text{ps}$.[76,77] Using this value for D and our estimate of the exchange time scale of 3 ps for Δt, we estimate a value of 2.4 Å for $\sqrt{\langle L^2 \rangle}$. This distance nearly matches the experimentally determined value of 2.3 Å for the oxygen-oxygen separation between the hydroxide ion and the water molecules in its first solvation shell from neutron scattering data.[25] This result implies that the correlation length for the transport of the hydroxide ion does not extend past its first solvation shell. Correlated proton or deuteron shifting events appear to be unlikely in aqueous hydroxide, at least in these isotropically dilute systems.

We can also ask questions regarding the solvation process that leads to the formation of a cross peak. Given that the frequency of an O-H bond is largely determined by the hydrogen bonding configuration at the proton, the observed time scale for the growth of the cross peak must be related to how long it takes an OH^- ion to form a new hydrogen bond once it has accepted a deuteron from a neighboring water molecule. The 3 ps exchange time scale we observe is related to the reincorporation of the OH^- charge defect into water's hydrogen bonding network upon PT. Previously, we found that the fluctuations that drive the structural rearrangement of water's hydrogen bonding network occur over a time scale of ~1.4 ps.[34] Our observed lower limit of 3 ps for charge migration is at least twice as long. This result is not unexpected since the transport of a

proton requires not only the solvation of the new OH⁻ ion, but also that of the newly formed water molecule. This requires the loosely correlated motion of water molecules at least as far away as the second solvation shell of the new ion.

Our observation of a long relaxation time scale is reminiscent of other measurements of water slowing in electrolyte solutions. 2D IR measurements of the O-D stretch of HOD in NaBr solution display slowing spectral diffusion with increasing NaBr concentration.[78] Likewise, recent infrared pump-probe anisotropy and dielectric relaxation measurements show that water reorientation slows in concentrated salt solutions and suggests that the influence of ions on water's hydrogen bonding network may extend beyond the ion's solvation shell.[79] In contrast, pump-probe studies[80,81] have suggested that the water dynamics outside of anionic solvation shells are only weakly affected by the ion's presence. Similarly, molecular dynamics simulations[82-84] have shown that the initial behavior of water molecules near anionic solvation shells are similar to that of bulk water. Recent simulations[85] of aqueous NaBr have found the existence of an additional slow time scale in the $6 - 40$ ps range associated with the exchange of bulk water molecules with those in the ion's solvation shell. Likewise, 2D IR exchange experiments of HOD in $NaBF_4$ solution[86], and $NaClO_4$ solution[87], show that water molecules leave the anions' solvation shells with time constants of 7 ps and 6 ps, respectively. In comparison to hydroxide, the other water-ion hydrogen bonding interactions are significantly weaker, and yet have longer time scales. This argument suggests that the PT event is itself the fundamental step to reorganization of the solution structure.

These results clarify that the hydroxide ion exists in an a solvated OH⁻ form, rather than a Zundel analog (DO··H··OD)⁻, but they do not provide definitive evidence for a unique coordination structure within the OH⁻ solvation shell. In principle, three and four coordinate structures are separable by their O-H stretch spectrum,[88] since water hydrogen bonds to the ion are significantly stronger in the three-coordinate state. In practice we see a continuous band over this range of frequencies within the red wing of the spectrum in 1D and 2D IR measurements. This is at least suggestive that there is no preferred solvation structure, and that three- and four-coordinate structures are rapidly interconverting. If so, is coordination number the best reaction coordinate for PT to hydroxide? Perhaps other collective variables such as the solvent electric field are more useful? We will explore these questions in a future publication.

VI. Conclusions

Through the use of a systematic series of ultrafast, nonlinear infrared measurements performed on the O-H stretching transition of a dilute solution of HOD in NaOD/D$_2$O, we have demonstrated the existence of at least two unique time scales associated with the structural diffusion of deuteroxide ions. At very early delay times, we observe a feature that rapidly decays on a 110 fs time scale that we attribute to protons that are shared in Zundel-like configurations. Protons that we excite in such configurations are near the barrier for PT, and the rapid disappearance of their spectral signature indicates the time needed for these protons to commit to the formation of a new, stable covalent bond. At longer time scales, we find evidence for a slow relaxation process that leads to an increase of the PS in the 0.2 − 2 ps waiting time regime. While

we cannot resolve the time scale of this process, we have found that its amplitude appears to scale linearly with the increase in solvent viscosity.

2D IR spectra show the appearance of spectral features that are consistent with a cross peak between the O-H stretch of HOD molecules that participate in hydrogen bonds with D_2O and the non-hydrogen bonded OH^- stretch. The growth of these features is best reproduced by our spectral model when a time constant of 3 ps is used for the exchange rate between an OH^- like stretch and a HOD molecule hydrogen bonded to D_2O, and suggests that this corresponds to the time it takes the bath to solvate a newly formed HOD/OD^- pair following PT. However, due to interference effects that arise from a thermal signal generated by the bath, the time scale we determine for this process should be viewed as a lower limit of its potential value.

Supporting Information Available:

We display transient grating measurements of HOD in $NaOD/D_2O$ and KOD/D_2O and give a description of some of the experimental details related to the measurement of absorptive 2D IR lineshapes. We also provide a further description of our spectral model, including kinetic equations that govern the populations of different states, expressions for

the calculated 1D lineshapes in Fig. 1, and the best fit parameters obtained from the model. Lastly, a discussion regarding the accuracy of our exchange time scale and its sensitivity to the parameters contained in our model is given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1: Summary of the parameters contained by our spectral model and a description of their principle means of determination. Many of the parameters can be constrained on the basis of either our 1D measurements (PP, PS, and FT-IR data) or literature values. This leaves only two free parameters when fitting the 2D IR spectra.

Parameter	Experiment/ Reference Used For Determination	Comments
$\left\langle \omega_{10}^{W} \right\rangle$, $\left\langle \omega_{10}^{Ion} \right\rangle$, $\left\langle \omega_{10}^{Sol} \right\rangle$, $\left\|\mathbf{\mu}_{10}^{W}\right\|$, $\left\|\mathbf{\mu}_{10}^{Ion}\right\|$, $\left\|\mathbf{\mu}_{10}^{Sol}\right\|$	FT-IR	Not varied with [NaOD]
$\left\langle \omega_{21}^{W} \right\rangle$, $\left\langle \omega_{21}^{Ion} \right\rangle$, $\left\langle \omega_{21}^{Sol} \right\rangle$, $\left\|\mathbf{\mu}_{21}^{W}\right\|$, $\left\|\mathbf{\mu}_{21}^{Ion}\right\|$, $\left\|\mathbf{\mu}_{21}^{Sol}\right\|$	Ref. 32	Calculated using DFT based frequency and transition dipole maps
$\left\langle \omega_{10}^{Z} \right\rangle$	NA	Constrained to match $\left\langle \omega_{10}^{W} \right\rangle$
T_1^{W}, T_1^{Z}, K_Z	PP	Determined from a bi-exponential fit to the PP data
T_1^{Sol}	NA	Constrained to match T_1^{W}
T_1^{Int}, K_{Therm}^{W}, K_{Therm}^{Ion}	PP	Determined from the PP amplitude at $\tau_2 > 1.5$ ps
$T_1^{D_2O}$	Ref. 68	--
K_{D_2O}	PS	Determined from the PS decay at $\tau_2 > 1.5$ ps
$\Delta\omega_3$, $\left\|\Delta\mathbf{\mu}_{10}\right\|$	PP	Determined from fits to dispersed PP data at $\tau_2 = 10$ ps
τ_C^{Z}	PS	Determined from fits to the PS at $\tau_2 < 200$ fs, held constant for all [NaOD]
$C^{W}(0)$, $C^{Ion}(0)$, $C^{Sol}(0)$, $C^{Z}(0)$	FT-IR	Held constant for all [NaOD]
A_{fast}, A_{slow}, A_{osc}, Δ_{static}	PS	Determined from fits to the PS
τ_{fast}, τ_{slow}, τ_{osc}, ω_{osc}	Ref. 34	Constrained from our previous work on HOD/D$_2$O, held constant for all [NaOD]
T_1^{Ion}	2D IR	--
$\tau_{Ion \to W}$	2D IR	--

Table 2: Percentage of hydrogen atoms that neighbor D_2O (% N_W), an OD^- ion (% N_{Sol}), or exist as OH^- (% N_{Ion}) as estimated from the known densities of NaOH solutions at different concentrations[48] and from neutron scattering data.[25] Also included is the density of NaOD solutions under the assumption that their spatial composition is identical to that of NaOH at an equivalent concentration.

[NaOD] (M)	% N_W	% N_{Sol}	% N_{Ion}	Density (g/mL)
0.0	100	0	0	1.10
1.1	95.3	3.7	1.0	1.16
2.6	88.5	9.2	2.3	1.21
5.3	77.2	18.1	4.6	1.30
7.9	67.8	25.3	7.0	1.38
10.6	59.1	31.4	9.4	1.45
15.1	46.9	39.2	13.9	1.55

Figure Captions

Fig. 1: FT-IR spectra of ~1% HOD in varying concentrations of NaOD/D_2O normalized to the absorption maximum (solid black). Subsequent plots are offset by 0.4. For each presented spectrum, a background of the appropriate concentration of NaOD/D_2O was subtracted before normalization so that only contributions to the spectra due to proton (H) vibrations are pictured. We can broadly label the frequency regions corresponding to the OH^- stretch, HOD molecules hydrogen bonded to D_2O, and HOD molecules that donate a hydrogen bond to an OD^- ion by ω_{Ion} (3600 cm^{-1}), ω_W (3400 cm^{-1}), and ω_{Sol} (~2900 – 3100 cm^{-1}), respectively. Plotted on top of each trace is a fit generated by our spectral model (red dashed).

Fig. 2: Pump-probe decay traces of the O-H stretching region for differing concentrations of NaOD. Each trace is normalized to the maximum signal and is offset from the previous trace by 0.6. The cyan line that runs through each trace represents a fit calculated from our model.

Fig. 3: (A) Photon echo peak shifts of HOD in NaOD/D_2O measured for solutions of increasing NaOD concentration. Each subsequent PS profile is offset by 10 fs. As with Fig. 2, the cyan trace plotted through each data set represents a fit from our spectral model. (B) The value of the PS at $\tau_2 = 600$ fs increases linearly with NaOD concentration and suggests that the presence of NaOD slows the overall dynamics of the system.

Fig. 4: The photon echo peak shift data of HOD in NaOD/D_2O displayed in Fig. 3A, but now plotted for waiting times up to 10 ps. Traces measured for different concentrations

are offset by 20 fs for clarity. Near $\tau_2 = 2$ ps, all measured traces return to zero independent of deuteroxide concentration.

Fig. 5: 2D IR spectra of HOD in NaOD/D$_2$O measured as a function of NaOD concentration for two waiting times, 60 and 200 fs. The shaded green box plotted on top of each surface denotes the frequency range integrated to yield the data in Fig. 6B.

Fig. 6: (A) Difference spectra for the O-H stretch of HOD between NaOD/D$_2$O solutions and neat D$_2$O for waiting times of 60 and 200 fs. Contours are plotted in equal increments relative to the maximum of each computed spectral difference. At $\tau_2 = 60$ fs, a broad positive signal is observed across the entire 2D IR lineshape due to transient shared proton configurations. (B) The integrated area $\omega_1 = 3050 - 3150$ cm^{-1} and $\omega_3 = 3450 - 3550$ cm^{-1} (green shaded region in Fig. 5A & 6A) for $\tau_2 = 60$ and 200 fs. Each data point is normalized by the integrated absolute value spectrum of the corresponding surface.

Fig. 7: 2D IR spectra for neat HOD/D$_2$O and 10.6 M NaOD for waiting times from 1 - 6 ps. Over this range of τ_2, 2D spectra of HOD/D$_2$O simply display signatures of non-equilibrium heating. Spectra for NaOD solution show similar signatures of heating, but are also suggestive of exchange between the free OH$^-$ stretch near 3600 cm^{-1} and the main HOD/D$_2$O absorption band near 3400 cm^{-1}. Surfaces calculated from our spectral model for 10.6 M NaOD are displayed below the experimental data.

Fig. 8: (A) Difference 2D IR spectra of HOD in 10.6 M NaOD and D$_2$O. (B) Plots of the integrated difference in the off-diagonal regions highlighted by the shaded green squares

above and below the diagonal axis ($\omega_1 = 3300 - 3400$ cm^{-1}, $\omega_3 = 3550 - 3600$ cm^{-1} and its reflection about the diagonal). The growth of excess intensity in these regions can be well described by an exponential rise with a 1.9 ps time constant and is suggestive of exchange between ω_W and ω_{Ion}.

Fig. 9: Different types of proton transfer exchange processes for HOD in NaOD/D$_2$O.

Fig. 10: Illustration highlighting the regions where spectral signatures due to the exchange process in Fig. 9 are expected to appear. The top panel plots FT-IR spectra of HOD in 10.6M NaOD (red) and D$_2$O (black) on top of the spectrum of a typical excitation pulse used for 2D IR measurements (blue dash-dotted). The lower panel plots a 2D IR spectrum of HOD in 10.6 M NaOD at a waiting time of 3 ps. On top of this spectrum, we have plotted two contours taken at 5% of the maximum value of the $\tau_2 = 60$ fs surface recorded for this sample and displayed in Fig. 5. The labels A-E correspond to those used in Fig. 9. As τ_2 increases, we observe a rapid collapse of intensity in the off-diagonal regions followed by the appearance of features indicative of cross peaks between ω_{Ion} and ω_W. Cross peaks between ω_{Sol} and these two transitions are not observed due in part to the limited bandwidth of our excitation pulses. Hence, only exchange processes of the type pictured in A and B are included within our spectral model.

Fig. 11: The static contribution to the frequency-frequency correlation function (Δ_{static}) determined from our spectral model. Δ_{static} is found to follow the change in solvent

viscosity with NaOH concentration. (Inset) A plot of Δ_{static} vs. viscosity, highlighting the observation that these two parameters appear to be linearly correlated.