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The Dynamics of Aqueous Hydroxide Ion Transport Probed via Ultrafast Vibrational Echo Experiments

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Abstract: We use peakshift, transient grating, and 2D IR measurements to probe the dynamics of NaOD solutions. Our experiments suggest that OD⁻ possesses a stable solvation shell and signatures of fast intermolecular proton transfer are observed.

1. Introduction

Compared to ions of similar size and charge density, the aqueous hydroxide ion possesses an anomalously fast diffusion constant due to its ability to accept a proton from a neighboring water molecule, leading to the translocation of the ion. Despite this being a fundamental reaction of acid-base chemistry, the mechanism by which hydroxide ions are conducted through water is still highly contested and poorly understood. Lewis dot diagrams predict that the hydroxide oxygen has three lone pairs and hence can accept three hydrogen bonds. To date only three coordinate structures have been observed in gas phase clusters [1]. In contrast, neutron scattering [2] experiments suggest that OH⁻ is hypercoordinated in the liquid, accepting four hydrogen bonds from its neighbors. *Ab initio* molecular dynamics simulations have observed both three and four coordinate structures and suggest that proton transfer proceeds only when OH⁻ forms three hydrogen bonds [3]. Moreover, proton transfer in the three coordinate state proceeds very rapidly, on the order of 180 fs, but is gated by the exchange between three and four coordinate structures which occurs over a few ps. As of yet, no direct evidence of this exchange exists due to the difficulty of developing a probe that is both structurally sensitive and has adequate time resolution.

Femtosecond infrared spectroscopy is a powerful tool to study proton transfer since short pulses on the order of ~50 fs can be generated and the OH stretching frequency of water molecules, ω_{OH} , is sensitive to its hydrogen bonding partner. Short, linear hydrogen bonds of the type formed between water and an OH⁻ ion appear red shifted from the main OH stretching band whereas weak hydrogen bonds of the type formed by the proton of the OH⁻ ion appear at high frequency (see Fig 1A). Time dependent changes in ω_{OH} result from the dynamics of the solvent that drive molecules into and out of the solvation shells of OH⁻ ions.

We present the results of multiple of third order IR spectroscopy measurements of the OH stretch of dilute HOD (~1%) dissolved in NaOD:D₂O solution. By using an isotopically dilute system, we break the symmetry of the HOD molecule, creating a localized stretching coordinate and eliminate resonant energy transfer between molecules. With increasing NaOD concentration, photon echo peakshift measurements indicate the environment surrounding HOD molecules is static up to ~1.5 ps, suggesting that OD⁻ ions possess a stable solvation shell over this timescale. Pump probe and transient grating measurements show the appearance of fast vibrational relaxation attributable to HOD molecules hydrogen bonded to OD⁻ ions. 2D IR measurements display a large off diagonal intensity that relaxes on a ~100 fs timescale, and may be an indicator of rapid proton exchange.

2. Nonlinear Infrared Spectroscopy of HOD in NaOD Solution

Shown below are the results of both linear and nonlinear IR spectroscopy measurements of dilute HOD dissolved in various concentrations of NaOD. With increasing concentration, the FT-IR spectrum shown in Fig. 1A undergoes a number of changes, including a large increase of intensity on the red side of the spectrum from the formation of strong hydrogen bonds between HOD molecules and the oxygen of OD⁻ ions [4]. Also, a small shoulder appears near 3600 cm⁻¹ which has been attributed to the OH⁻ ion since its hydrogen atom can only form weak hydrogen bonds due to the ion's overall negative charge.

The three pulse photon echo peakshift (PS) taken using 45 fs pulses centered at 3350 cm⁻¹ is seen in Fig. 1B. Although the initial decay of the PS remains fairly independent of NaOD concentration, the offset at long waiting times increases linearly with concentration. The increasing offset is consistent with a slowing of the dynamics of the hydrogen bonding network, which agrees with the fact that solution viscosity increases with NaOD concentration. Given the local nature of the probe in our experiments, this result suggests that OD⁻ ions possess a stable solvation shell up to ~1.5 ps.

Fig. 1C shows the concentration dependence of the magic angle transient grating (TG) decay. The TG for HOD:D₂O is fit well by a single squared exponential with a time constant of 600 fs. This is somewhat shorter than the previous estimated value of 700 fs for the HOD lifetime. However, it is well known that the observed timescale

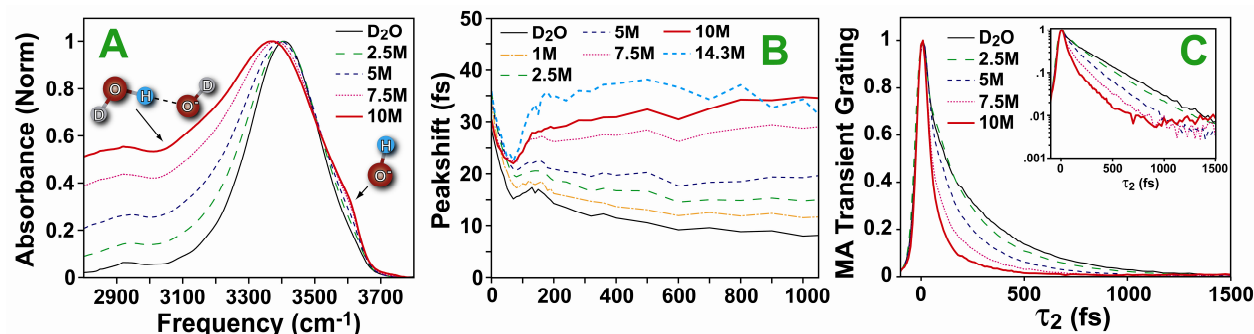


Fig. 1. Linear and nonlinear infrared measurements of the OH stretch of HOD:NaOD solution as a function of NaOD concentration. (A) FT-IR. (B) Three Pulse Photon Echo Peakshift. (C) Magic Angle Transient Grating (inset: log scale).

for the TG decay will vary depending on where the pulse spectrum is centered relative to the sample absorption maximum due to absorption induced heating effects [5]. As the concentration increases the decay becomes bi-exponential and can be fit well with a squared sum of exponentials with time constants of 120 and 600 fs for all concentrations. This result is similar to that of Nienhuys et. al. [6] who reported transient hole burning measurements on dilute HOD in 10M NaOD solution showed the existence of two decay components with timescales similar to those reported here.

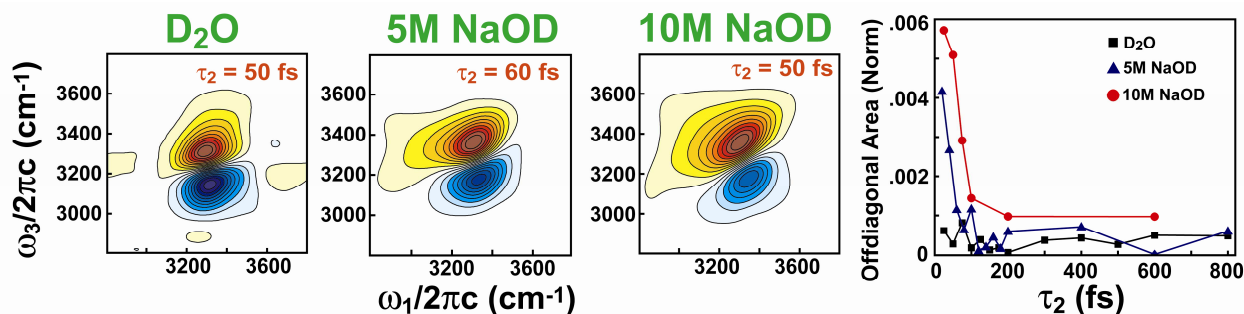


Fig. 2. 2D IR spectra at short waiting times as a function of NaOD concentration. To the right is the integrated area between $\omega_1 = 3000$ & 3100 cm^{-1} and $\omega_3 = 3500$ & 3600 cm^{-1} normalized by the integrated absolute value spectrum.

The origin of the fast decay seen in the TG measurement is displayed in the 2D IR spectra shown in Fig. 2. The antidiagonal linewidth at a particular value along the diagonal of the 2D spectrum is related to the homogeneous linewidth for molecules at that frequency. With increasing concentration the initial antidiagonal linewidth of the red side of the 2D spectrum, which corresponds to molecules hydrogen bonded to OD⁻, increases dramatically. As the waiting time increases the offdiagonal intensity relaxes over ~ 100 fs, consistent with the fast decay seen in the TG measurement. This differs greatly from the 2D lineshape for HOD:D₂O which instead broadens on the blue side of the spectrum with waiting time due to the transient nature of broken hydrogen bonds [7]. The ability to sequentially drive transitions at 3600 cm^{-1} and 3100 cm^{-1} within a 50 fs window is suggestive of probing the localization of motion during a proton transfer process.

3. References

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