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Hydrogen Bond Rearrangements in Water

Probed with Temperature-Dependent 2D IR

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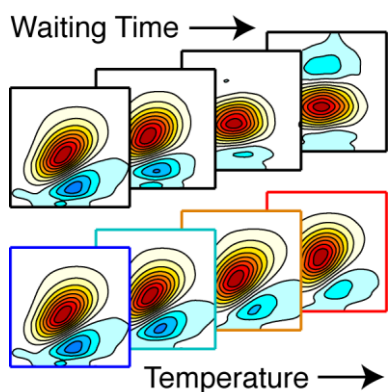
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We use temperature-dependent two-dimensional infrared spectroscopy (2D IR) of dilute HOD in H₂O to investigate hydrogen bond rearrangements in water. The OD stretching frequency is sensitive to its environment, and loss of frequency correlation provides a picture of local and collective hydrogen bond dynamics. The timescales for hydrogen bond rearrangements decrease from roughly 2 ps at 278 K to 0.5 ps at 345 K. We find the barrier to dephasing and hydrogen bond switching to be $E_a = 3.4 \pm 0.5$ kcal/mol, although the trend is slightly non-Arrhenius. The value is in good agreement with the reported barrier height for OD reorientation observed in pump-probe anisotropy measurements. This provides evidence for the proposal that hydrogen bond switching occurs through concerted large angular jump reorientation. MD simulations of temperature-dependent OD vibrational dephasing and orientational correlation functions are used to support our conclusions.

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Keywords: Water; Hydrogen-Bond Dynamics; Temperature-Dependence; Ultrafast Spectroscopy; Molecular Dynamics; Pump-Probe Geometry

Rearrangements in the hydrogen bond (HB) network of water necessarily require collective intermolecular rotations and translations. A number of recent studies using ultrafast infrared spectroscopy and molecular dynamics simulations have led to a self-consistent description of the dynamics that underlie the mechanism of hydrogen bond rearrangements. 2D IR spectroscopy of HOD in D₂O has shown that broken or strained hydrogen bonding configurations do not persist in the liquid, but reform a hydrogen bond in <150 fs.^{1 2} This observation indicates that hydrogen bond switching is a concerted process that proceeds through a bifurcated HB transition state. Independently, Laage and Hynes presented a picture for molecular jump reorientation in water, in which reorientation upon HB switching is guided by fluctuations in HB coordination.^{4 5} This is consistent with frequency-resolved pump-probe anisotropy measurements of HOD in H₂O, which reveal that non-hydrogen bonded configurations have a higher degree of inertial rotation than strong HB species,⁶ and that orientational motion accompanies the formation of a HB from an unstable configuration.⁷

To further test this proposal for hydrogen bond dynamics, we measured temperature-dependent spectral diffusion of the OD stretch of HOD in H₂O using 2D IR spectroscopy.¹¹ Hydrogen bonding fluctuations modulate the OD frequency, and water structural rearrangements dictate the picosecond spectral diffusion kinetics.⁸ Temperature-dependent studies of these processes provide information on the HB switching barrier, which can be compared to recent simulations⁵ and IR pump-probe anisotropy measurements⁹ of water reorientation to test their joint contribution to the hydrogen bond rearrangement mechanism.

FTIR spectra of dilute HOD in H₂O at 278, 295, 323, and 345 K are shown along with background H₂O spectra in Figure 1. Between 278 and 345 K, the OD stretch blue shifts linearly from 2499 to 2534 cm⁻¹ and broadens from 160 to 170 cm⁻¹ (FWHM). The blue shift in the OD stretch frequency with temperature is attributed to the increased thermal fluctuations and switching of hydrogen bonds. The observed temperature dependent trends in frequency and line width track the predictions of recent simulations.¹⁰ The absorption band is superimposed on a broad H₂O background dominated by the libration+bend combination band. In contrast to the OD stretch, the combination band absorption peak red shifts from 2143 to 2085 cm⁻¹ over the same temperature range.

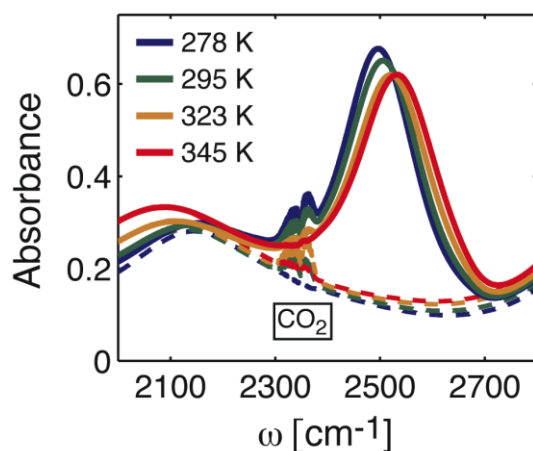


Figure 1. Temperature-dependent FTIRs of 5% D₂O in H₂O (solid) showing the OD stretch vibration of HOD (~2500 cm⁻¹) and the H₂O bend+libration combination band (~2100 cm⁻¹), in addition to the neat H₂O background (dashed). The H₂O absorption in the OD stretch frequency region is ~0.15. The absorption from atmospheric CO₂ is indicated.

Representative 2D IR absorptive and phase spectra of the OD stretching vibration as a function of waiting time are shown in Figure 2 for 278 and 345 K. Absorptive spectra provide a correlation map relating the probability of exciting a frequency ω_1 and observing a frequency ω_3 after a waiting period. At early waiting times the peaks from the positive fundamental $v=0-1$ transition (red contours) and negative $v=1-2$ induced absorption (blue contours) are diagonally elongated indicating memory of the initial excitation frequency. The pinched line shape and waiting time trends have been previously observed,¹¹ and form the basis for describing the rapid HB reformation by non-hydrogen bonded configurations.^{1 2} As the waiting time is increased, this memory is lost and the peaks become symmetric in ω_1 and ω_3 . This spectral evolution can also be characterized through the time scale at which the slope of the node between the 0-1 and 1-2 peaks, or the slope of a constant phase line, approaches zero. The initial slope and the time scale of spectral diffusion decrease with increasing temperature. We also find that the overall magnitude of the 2D signal decreases with temperature as a result of increased thermal fluctuations coupled with the non-Condon effect.¹²

The long time features of the 2D spectra are also influenced by the OD vibrational relaxation and thermalization processes.^{14 15} Vibrational relaxation decreases the amplitude of the 1-2 peak relative to 0-1, and induces a relaxation-induced spectral blue-shift in the 0-1 absorption.¹⁶ In differential-mode spectroscopy, this thermally shifted ground state (TSGS) leads to the persistence of a positive peak to long waiting times and the observation of a negative feature above the diagonal.¹⁷ This is most apparent at low temperature where the OD spectral shift is greatest. The TSGS is expected to decrease the

value of the slope of the phase lines upon sufficient vibrational relaxation and increase the observed spectral relaxation rate, as described below.

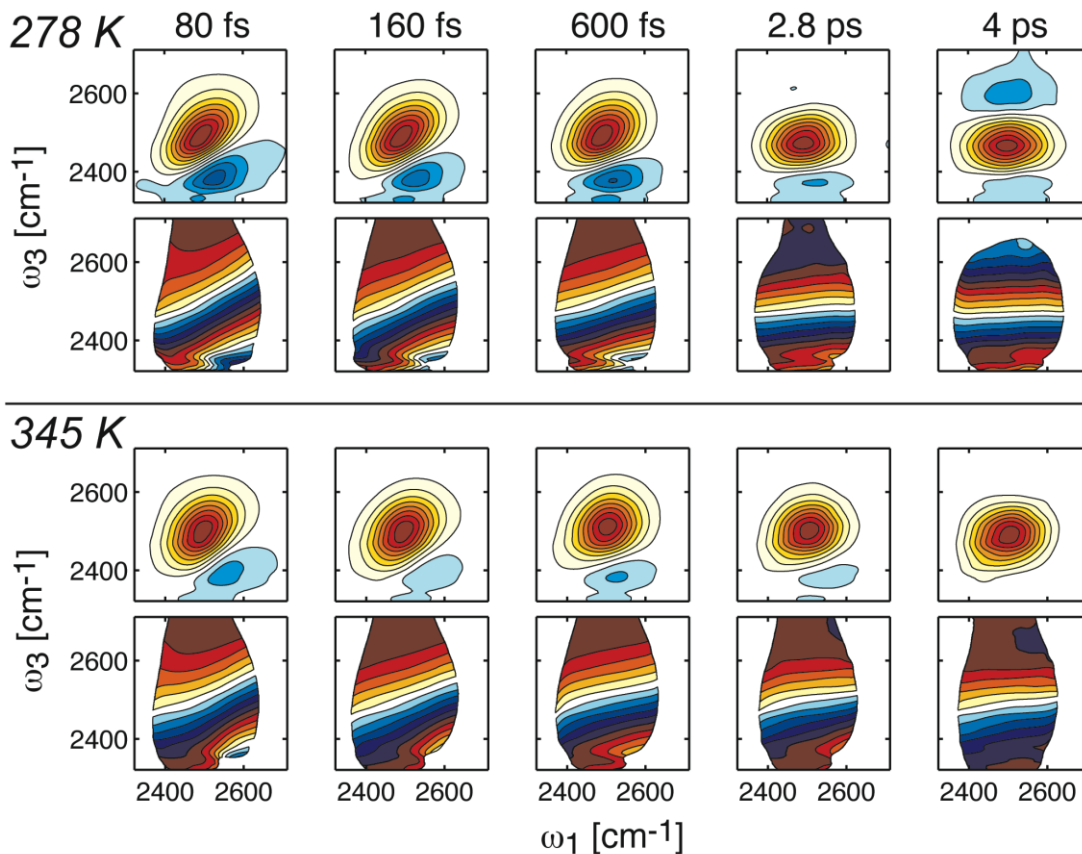


Figure 2. Absorptive and phase 2D IR spectra of HOD in H₂O for waiting times of 80 fs, 160 fs, 600 fs, 2.8 ps and 4 ps at 278 K (top) and 345 K (bottom). The amplitude and phase is distorted for $\omega \sim 2350 \text{ cm}^{-1}$ as a result of atmospheric CO₂ absorption. The contours in the absorptive 2D IR spectra each represent a 12% intervals relative to maximum. The phase spectra are plotted from $-\pi/2$ to $\pi/2$ and are windowed by 10% of the absolute value spectra.

The waiting time dependence of the spectral relaxation was analyzed by a number of metrics that have previously been described,¹⁸⁻¹⁹ including the slope of the node or line of constant phase,²⁰⁻²¹ dynamic line width,¹¹ and center line slope.²² The phase line slope $\tan(\psi) = \Delta\omega_3/\Delta\omega_1|_{\phi=0}$, which varies from one to zero is our preferred metric; however, all metrics show similar trends with temperature. The node of the imaginary surface ($\phi=0$) is preferred over the real surface node ($\phi=-\pi/2$) since at long waiting times the 1-2 peak has significantly decayed. Due to peak shifts with temperature, we averaged $\tan(\psi)$ over a box with bounds set by 90% of the peak maximum of the real surface.

Phase line slope decay is shown in Figure 3a for the five temperatures studied. The decays span from the femtosecond time scales of intermolecular fluctuations to picosecond structural reconfiguration.³ Overall, the decays in Figure 3a are non-exponential, and show a faster drop of initial amplitude and a shorter dephasing time as the temperature is increased. At the earliest measured waiting time, 40 fs, the slope varies from 0.63 at 278 K to 0.46 at 345 K. By $\tau_2 = 400$ fs the values at these temperatures have dropped by 33% and 46%, respectively. The decay of the long-time tails range from ~ 2 ps for 278 K to ~ 0.5 ps for 345 K. For waiting times greater than 400 fs, the room temperature results correspond to the fit frequency correlation function obtained by Fayer and co-workers¹¹.

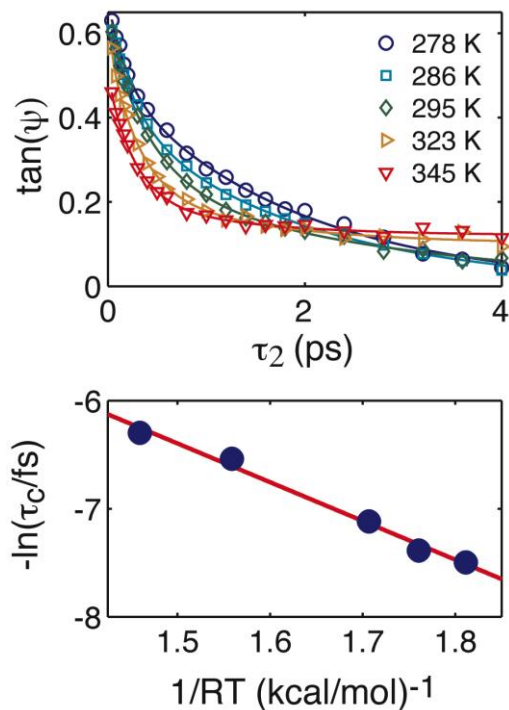


Figure 3. (a) Slope of the phase lines, $\tan(\psi)$, extracted from 2D IR spectra at temperatures 278 (circle), 286 (square), 295 (diamond), 323 (triangle) and 345 K (inverted triangle), are plotted as a function of waiting time from 40 fs to 4 ps. The lines represent triexponential fits with offsets. (b) Arrhenius plot for data in (a) for the case where τ_c was determined from one half the decay time from the initial value to $1/2e$.

For picosecond waiting times, a residual offset appears in Figure 3a. The additional slight constant tilt of the phase lines is most pronounced at 345 K and it appears constant within our experimental time window even when all apparent dynamics of the liquid have passed. The only consistent explanation for a lineshape distortion in both dimensions which is most pronounced at high temperature is an additional additive signal contribution from the sloping water background, as observed in other ultrafast

experiments.^{14 24 25} This signal contribution is a relaxation induced spectral red-shift of the water background following direct excitation of the OD stretch. The contribution appears to grow with increasing temperature because of the decreasing OD signal that arises from the non-Condon effect.¹² Our modeling indicates that this effect leads to a positive offset on the phase line slopes within the experimental time scale, whereas the TSGS of the OD stretch acts to decrease the the phase line slope. Since it induces small changes to the measured OD spectral dynamics, this offset has been subtracted in subsequent analysis of the time-dependence and uncertainty in the analysis has been taken into account in the error bars.

Based on the femtosecond time-scales involved, the non-exponential relaxation, and the non-Gaussian nature of the fast dynamics, simple Arrhenius behavior cannot be assumed and the proper method to analyze the relaxation kinetics is unclear. Our prior interpretation of the room temperature experiments indicated a modest separation of time-scales between the femtosecond fluctuations in hydrogen bond configuration and the thermally activated picosecond reorganization of the network. Such a separation does not exist for high temperatures, where spectral scrambling occurs on the time-scale of the shortest intermolecular motions. The barriers to hydrogen bond reconfiguration are low and at high temperatures adequate equilibration of a liquid configuration between switching events may not occur.

Our approach here is to obtain characteristic relaxation times for loss of frequency correlations, τ_c , at each temperature from a number of methods and test for Arrhenius behavior, $1/\tau_c = A \exp(-E_a/RT)$. We used a number of single and multi-exponential forms, a power law decay, and a stretched exponential function. From the fits we

obtained correlation times either from the fit directly, by integrating the normalized relaxation function, or from the $1/e$ period. As an example, Figure 3a shows triexponential fits between $\tau_2 = 40$ fs and 4 ps allowing for an offset. Figure 3b shows a plot of $-\ln(\tau_c)$ vs. $1/RT$ for the case where τ_c was determined from one half the decay time from the initial value to $1/2e$. The slope observed in this plot and slight quadratic deviations from linear behavior were observed for all of the fitting methods employed. A linear fit to all methods of analyzing the data gives $E_{a,\omega} = 3.4 \pm 0.5$ kcal/mol and $1/A_\omega = 3.4 (+3.0, -1.5)$ fs, where error bars reflect 95% confidence limits. This activation barrier is roughly equal to $-\Delta H_f$ for a medium strength hydrogen bond,²⁷ and lies within a range of values (1.5-4.9 kcal/mol) observed in various structural relaxation measurements on water.^{28 30 31}

An important comparison of our experimental results is to the temperature-dependent anisotropy of HOD in H₂O, for which the barrier height for reorientational motion was found to be $E_{a,\text{rot}} = 4.1$ kcal/mol.⁹ This value lies close to our value of $E_{a,\omega}$, especially when restricting the comparison to temperatures < 323 K. If, as experimental^{2 3} and theoretical findings suggest,^{4 5} large angle reorientation is a key component of hydrogen bond rearrangements, then the OD dephasing and OD reorientation should be strongly correlated. Although the timescale of orientational correlations cannot be trivially compared to isotropic observables, the temperature dependence should scale similarly. The close agreement between the two barrier heights is another key piece of evidence for this picture.

This barrier also reinforces our earlier conclusion that the picosecond decay of frequency correlations occurs as a result of hydrogen bond rearrangements that switch

hydrogen bonds, not merely fluctuations about a HB. The correlation between many internal and spectroscopic variables is a result of the collective nature of the structural rearrangements.³² This conclusion also suggests that the loss of OH frequency memory and the bulk transport coefficients of the liquid are correlated. Fitting the viscosity of H₂O³³ over the experimental temperature range results in a similar $E_{a,\eta}$ of 3.8 kcal/mol, and the Arrhenius plots for these curves show a remarkably similar quadratic deviation from the linear behavior.

As another point of contact to the concerted hydrogen bond switching mechanism, we have used MD simulations to calculate temperature-dependent OD frequency and reorientational correlation functions. Our model uses the SPC/E water potential that was used to illustrate concerted hydrogen bond switching, and calculate electric field induced vibrational frequency shifts. The method only differs from previous applications in that HOD is placed in a bath of H₂O rather than D₂O and the OD stretching frequency is calculated. Trajectories were calculated at four temperatures (273, 298, 310, and 330 K) with the density chosen to match experiments. The OD frequency correlation functions, $C_\omega(\tau) = \langle \delta\omega_{\text{OD}}(0) \delta\omega_{\text{OD}}(\tau) \rangle$, and OD bond reorientational correlation functions, $C_2(\tau) = \langle P_2(\hat{\mathbf{r}}_{\text{OD}}(0) \cdot \hat{\mathbf{r}}_{\text{OD}}(\tau)) \rangle$, are shown in Figures 4a and 4b, respectively. For $C_\omega(\tau)$, the sub-100 fs decays are indistinguishable, but the picosecond tails show relaxation times that decrease from roughly 1.4 ps at 273 K to 450 fs at 330 K. Similarly for $C_2(\tau)$, beyond the early librational time scales, the correlation functions decay faster with temperature, from a value of 4.5 ps for 273 K to 1.4 ps for 330 K. An Arrhenius plot (Figure 4c) for the temperature-dependent correlation times gives a barrier to frequency

randomization of $E_{a,\omega} = 3.6$ kcal/mol and a barrier of $E_{a,\text{rot}} = 3.6$ kcal/mol for reorientation. The latter number is in agreement with the 3.5 kcal/mol value previously calculated by Laage and Hynes for the OH stretch.⁵ Although SPC/E water was not parameterized for temperature dependent work, we feel that this will not affect the important close correspondence between $E_{a,\omega}$ and $E_{a,\text{rot}}$.

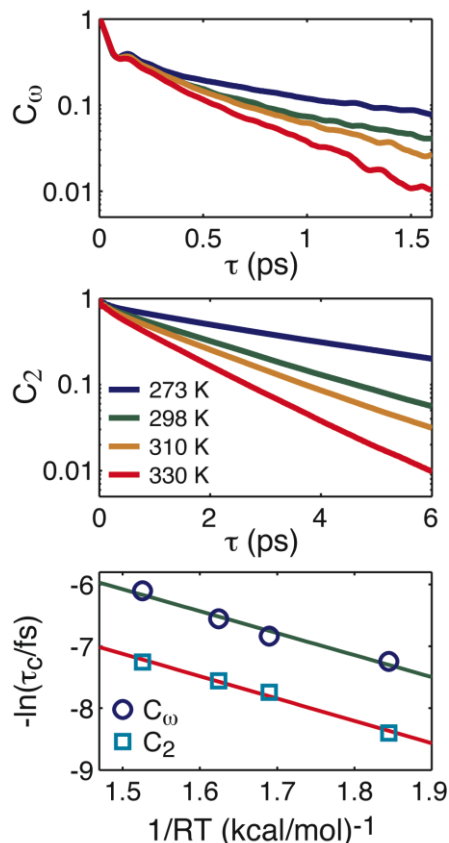


Figure 4. Normalized temperature-dependent correlation functions for (a) the OD stretch vibrational frequency, $C_\omega(\tau)$, and (b) OD bond reorientation, $C_2(\tau)$, from MD simulations. (c) Arrhenius plots of correlation times in femtoseconds obtained from simulation. Vibrational dephasing rates and reorientation rates were obtained from mono-exponential fits to picosecond data. Linear fits give $E_{a,\omega} = 3.6$ kcal/mol, $1/A_\omega = 2.1$ fs and $E_{a,\text{rot}} = 3.6$ kcal/mol, $1/A_{\text{rot}} = 5.5$ fs.

To summarize, analysis of the temperature-dependent 2D IR spectroscopy of the OD stretch in water indicates that the mechanism of vibrational dephasing, reorientational motion, and hydrogen bond rearrangement are all strongly correlated. This is based on the same temperature dependent scaling for these different rate processes, and from close agreement to the frequency changes, orientational motion, and hydrogen bond switching in MD simulations.

Experimental

2D IR spectra were acquired with a Fourier transform pump-probe 2D spectrometer that has been described previously.³⁴ Experiments were performed with 70 fs pulses whose spectrum was centered at 2500 cm^{-1} with a FWHM of $\sim 250\text{ cm}^{-1}$. The excitation fields were generated with a Mach-Zehnder interferometer, and translating ZnSe wedges controlled pulse delays. The τ_1 axis was created by moving the non-chopped pump arm in 2 fs steps to 600 fs. The probe beam was spectrally dispersed onto a 64-channel MCT array with $\sim 6\text{ cm}^{-1}/\text{pixel}$ resolution, and difference spectra were acquired by chopping. In order to extract phase information, we recover the complex 2D IR spectrum from the raw absorptive data on the basis of a Kramers-Kronig assumption.³⁶

The sample of 3% D₂O in H₂O with a path length of 6 μm was contained between CaF₂ windows in a temperature regulated brass cell. 2D IR surfaces were collected at 278, 286, 295, 323 and 345 K in the parallel (ZZZZ) polarization geometry. At each temperature, surfaces were collected for 20 to 21 waiting times between 40 fs and 4 ps. Distortions to the 2D spectrum from non-resonant response are observed for waiting

times <80 fs. Although the FTIR and 2D IR data was acquired with purged air, residual atmospheric CO₂ absorption is still observed from 2300-2380 cm⁻¹.

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