

SI Methods

The 2D experiments were performed using pulses centered at 3400 cm^{-1} with a bandwidth spanning the OH-stretching band. The pulses were generated in an optical parametric amplifier, pumped by a regeneratively amplified Ti:sapphire laser at a repetition rate of 1 kHz to provide $5\ \mu\text{J}$ of energy and a near transform limited 70-fs pulse width. The high quality of the pulses was confirmed by a transient grating infrared frequency resolved optical gating method described previously [1]. The setup of the photon echo experiment is shown schematically in Fig. 7. The heterodyne detected photon echo and pump probe signals were recorded with a scanning monochromator and HgCdTe array detector (16 elements). The photon echoes were measured as a function of the coherence time, τ , and the population time T, using a diffractive optic technique [2]. A beam splitter (BS) is used to introduce a delay, t_{13} , between two beams that are focused onto a reflective diffractive optic designed to image a grating pattern with maximal diffraction efficiency in the first order. The boxcar geometry was selected with a spatial mask, with over 70 % diffraction efficiency of the incident light into the four resulting beams. A second time delay, t_{12} , is introduced between the bottom pulses to create a pulse sequence of two pump beams (k_1, k_2) separated by τ , and a probe beam (k_3) separated by time T. The fourth beam (k_{ref}) is attenuated and delayed by ~ 900 fs to be used as a local oscillator for heterodyne detected spectral interferometry [3]. All the beams generated from the diffractive optic are relay imaged with off-axis parabolic mirrors in a 1:1 imaging system to give a beam focus of $150\ \mu\text{m}$ diameter at the sample. To observe the decay in the frequency correlation and spectral diffusion within the time T, correlation spectra were recorded by scanning coherence time τ over both negative and positive times in order to measure both non-rephasing and rephasing pathways. A Fourier-transform of the τ dimension results in the excitation frequency dimension, ν_1 , as a function of the detected frequency dimension, ν_3 . The absolute phase of the detected signal is determined by adjusting the phase parameter, matching the real part of the echo signal to independently measured spectrally resolved pump-probe spectra. This procedure enables the separation of the pure absorptive part of the 2D spectrum.

The extremely thin pathlengths required for these studies were provided by a nanofluidic cell based on design concepts previously reported with a number of important improvements [4]. The basic design is shown in Fig. 8. The cell was designed to support a 400 nm thick water layer. The flow channel is provided by an etched Si layer that leaves two SiN windows to confine the laminar flow. The windows have a 1 mm x 1 mm clear aperture to avoid diffraction effects on the laser beam inputs and 800 nm thickness to avoid nonresonant background signals from the windows themselves. This latter design feature is very important. Conventional cell designs use windows that are orders of magnitude thicker than the water layer, leading to a very significant nonresonant background signal from the windows. In the 2D experiment, the removal of the nonresonant background is essential as otherwise the 10-100 fs dynamics of water would be masked by a large pulse width limited nonresonant contribution. There was no detectable signal from the very thin SiN windows of the nanocell [5].

For the temperature control studies, the nanofluidic cell was mounted inside a copper enclosure with small access holes for the input beams. The enclosure itself was thermally isolated and maintained at the desired temperature set point to ensure a spatially uniform temperature profile throughout the sample. The experimental setup was purged with nitrogen gas to avoid condensation while the temperature of the sample holder was adjusted between 263 and 353 K. Without laser excitation the sample temperature was estimated based upon measurements using a thermocouple in thermal contact with the sample. The temperature under experimental conditions was calibrated by repeated measurements of the observed melting point of the water under laser excitation. A steady state temperature rise of 6 ± 1 K. was observed due to the laser excitation. An initial transient temperature rise of 10 K is estimated based on pump probe signal at long time delays, $T > 2\text{ps}$, calibrated using independently measured temperature dependent linear absorption spectra. The thermal profile was also previously determined for these same conditions using a thermal imaging camera that further confirm the steady state temperature rise in the laser irradiated volume [4].

The fully enclosed nanofluidic cell offers a distinct advantage over other potential approaches involving free flowing films or jets that necessarily involve much thicker path lengths. It is relatively straightforward with the nanocell to maintain a constant background temperature of the entire volume at a particular set point. The uniform temperature throughout the flow channel avoids thermal gradients in the flow to the region sampled by the laser and the position at which the temperature is measured. The small volume and high thermal conductivity of the Si/SiN nanocell also ensure rapid equilibration with the thermally controlled mass. In order to accurately compare spectra, the optical density needs to be maintained constant throughout the full temperature range and should be maintained at low enough values to avoid complicating optical density effects or pulse and signal propagation effects on the 2D spectrum [6]. The pathlength of the nanocells can be maintained fairly constant, however, the extremely thin walls do flex with changes in applied pressure in clamping the cell that is variable from cell to cell. In the present experiments, a computer controlled syringe pump is used to flow the liquid and actively stabilize the water layer thickness, based on the dynamically measured transmission of the sample. Stabilities of the optical density in the OH stretch spectral region of $\sim 5\%$ could be achieved over several hours for an average optical density of ~ 0.2 .

Eccentricity Analysis

For a more quantitative analysis of the shape of the 2D spectra, we consider the eccentricity M which is defined as $M = (a^2 - b^2) / (a^2 + b^2)$ for an elliptic shape of the spectrum, where a and b are the diagonal and anti-diagonal width of the spectrum [7]. This quantity is related to the slope of the peak lines of the spectra derived in the following way: The points in (ν_3, ν_1^o) and (ν_3^o, ν_1) in (ν_3, ν_1) space where the gradient of the response function for a given population time T

$$\nabla S(\nu_1, T, \nu_3) = 0 \quad (1)$$

corresponds to the maxima of each slice of the spectra parallel to the ν_1 and ν_3 axes.

$$\frac{\partial S(\nu_1^o, T, \nu_3)}{\partial \nu_3} = 0; \frac{\partial S(\nu_1, T, \nu_3^o)}{\partial \nu_1} = 0 \quad (2)$$

These maxima are connected by two paths on the surface of the response function, the peak lines. The slope of these peak lines gives the eccentricity function,

$$\frac{\partial \nu_1^o}{\partial \nu_3} = \frac{\partial \nu_3^o}{\partial \nu_1} = \frac{1}{M} \quad (3)$$

More generally, one finds that the slope of the peak lines is a measure of the instantaneous value of the eccentricity function. For a purely single component feature, the peak lines are straight, $\frac{\partial M}{\partial \nu} = 0$, $\frac{\partial \nu_1^o}{\partial \nu_3} = \frac{\partial \nu_3^o}{\partial \nu_1}$ and have identical slope. To get an overall measure of the diagonal elongation of the spectra, without considering the asymmetry about the diagonal, we define an average eccentricity parameter as a function of the slopes of the peaklines.

$$\bar{M}(\nu_1^*, \nu_3^*, T) = \left(\frac{\partial \nu_3^o}{\partial \nu_1} \Big|_{\nu_1^*} \right)^{-\frac{1}{2}} \left(\frac{\partial \nu_1^o}{\partial \nu_3} \Big|_{\nu_3^*} \right)^{-\frac{1}{2}} \quad (4)$$

In the analysis of the experimental data, only the shape of the 0-1 transition was considered. There is strong overlap between the positive peak of $v=0$ to 1 and $v=1$ to 0 transitions

and the negative $v=1$ to 2 peak resulting in a shift of the $v=0$ to 1 peak line that needs to be considered. To account for this effect, a double Gaussian fit was performed on slices of ν_3 and a negative Gaussian was subtracted from the data (Fig 3a (upper)). The eccentricity analysis was performed on the remaining peak using the center of mass as the maxima of the slice to minimize the effects of noise on the peak position. The peaklines were fit with a polynomial to extract the instantaneous slopes, $\bar{M}(\nu_1, \nu_3)$. This was used to reconstruct the spectrum giving a good first order approximation; the deviation of the reconstructed response function was used as the uncertainty of the measurement. To determine values for the eccentricity at the opposite ranges of the spectrum, the average slope of the peaklines was used. In the right panel of Fig. 3, such quantities are plotted as a function of population time T for the different temperatures of the water sample. The eccentricity for frequencies below 3400 cm^{-1} shows the slowing down of spectral diffusion with decreasing temperature. The values derived from the T=274 K spectra display a slower decrease than the data for higher temperatures. At high frequencies, this effect is less pronounced.

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