Direct experimental evidence of hydration shell reorganization in water from non-linear infrared spectroscopy of the water bending mode

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Supporting information

Integrated photon echo and peak-shift

The peak-shift was obtained as follows. The 2D-IR signal $S(\omega_t, \omega_\tau; T)$ was Fourier transformed along the tau domain to give $S_T(\omega_t, \tau; T)$. This Fourier transform is useful for removing the background signal outside the specified spectral window. The selected spectral window restricts the frequency domain data to include only the region of the HDO bend including both 0-1 and 1-2 transitions. The ω_t range is from 1300 to 1550 cm⁻¹ and ω_τ range is from 1340 to 1530 cm⁻¹. The echo signal versus ω_t for each waiting time (T) is calculated as the square of the absolute value of the signal ($S_T(\tau; T)$) of the integrated signal ($|S_T(\omega_t, \tau; T)|^2$) along ω_t . The peak-shift for each *T* is determined as the τ time where the integrated signal has the maximum.

Water grating signal

It is well known that the grating signal is broad spectral signal that grows instantaneously; thus if the 2D-IR spectrum is mainly composed by the signal arising from the HDO bend, removing the first 100 fs of the data in the t and τ time domains should not affect the general features of 2D-IR spectrum at any waiting time. This is exactly what the data analysis shows and allows us to conclude that the features observed in the 2D-IR spectrum at longer waiting time are mainly due to the bending mode.



Figure S1.2D-IR spectrum for Tw=2ps. Left panel correspond to the uncut 2D-IR spectrum whereas the right panel is the 2D-IR spectrum where the first 100 fs of signal in the t and τ time domains are cut.

Cross-peak intensity determination

For the measurement of the cross-peak intensity, two different regions of the 2D-IR spectrum are used: $\omega_{\tau} = 1420 \text{ cm}^{-1}$, $\omega_t = 1520 \text{ cm}^{-1}$ and $\omega_{\tau} = 1480 \text{ cm}^{-1}$, $\omega_t = 1320 \text{ cm}^{-1}$. These spectral intensities are selected because they are parts of the cross-peaks that are well separated from other spectral components allowing us to correctly determine their dynamics. Due to the presence of the water grating signal, the intensity of the cross-peak is determined as:

$$S_{xpeak} = \frac{I_{xpeak} \left(\omega_{\tau}^{xpeak}, \omega_{t}^{xpeak} \right) - I_{grating} \left(\omega_{\tau}^{xpeak}, \omega_{t}^{grating1} \right)}{I_{dpeak} \left(\omega_{\tau}^{dpeak}, \omega_{t}^{dpeak} \right) - I_{grating} \left(\omega_{\tau}^{dpeak}, \omega_{t}^{grating2} \right)}$$

The selected frequencies are:

	Left cross-peak	Right cross-peak	
$\omega_{\tau}^{xpeak} =$	1480 cm^{-1}	1420 cm^{-1}	
$\omega_t^{xpeak} =$	1320 cm^{-1}	1520 cm^{-1}	
$\omega_t^{grating1} =$	1300 cm^{-1}	1550 cm ⁻¹	
$\omega_{\tau}^{dpeak} =$	1453 cm ⁻¹		
$\omega_t^{dpeak} =$	1460 cm ⁻¹		
$\omega_t^{grating 2} =$	1550 cm^{-1}		

Diagonal traces

Due to the "small" anharmonicity of the water bend, the points in the diagonal ($\omega_{\tau}=\omega_{t}$) were not selected for showing the diagonal traces. Instead, the points parallel to the diagonal and passing through the maximum were selected. Thus, the diagonal traces of the 2D-IR spectra were obtained using the following procedure. First, the maximum of the bleach/stimulated emission peak (positive in Figure 2 of the main text) was determined for each waiting time. Then the intensity of the points passing through the 2D-IR spectrum maximum and running parallel to the diagonal were extracted.

	Mode 1	~	Mode 2	
				2
Frequency (cm ⁻¹)	1611		1628	
Intensity (km/mole)	82		42	

FTIR of bending

Since the bend mode is either on top of combination band of D_2O or the libration band of water is modeling is not straight forward. Here, we model the brackground signal with a set of peak functions and the bend band is everything but the background.



Figure S2. FTIR of the water bend. Left and right panels show the FTIR of the HDO and H_2O bend, respectively. Red and blue lines correspond to the peaks of the bend while the green line is the background.

Anisotropy of the transient grating signal of H₂O

The anisotropy for H₂O was measured and computed as in Ref. [1].



Figure S3. Ultrafast anisotropy of H_2O determined from polarization dependent transient grating experiments at 1670 cm⁻¹.

Simulation of the 2D-IR spectrum

The simulation was performed according to the general procedures described in Ref. [2]. Only the response functions involving an uncoupled oscillator transitions and the parameters for the FFCF and lifetimes are described in the following table:

noromatara	Transition		
parameters	1	2	
ω , cm ⁻¹	1440	1455	
$\Delta_1, \mathrm{cm}^{-1}$	15	15	
Lifetime, ps	0.4		
μ	1.0		
$\left< \delta \omega_{_{i}}(t) \delta \omega_{_{i}}(0) \right>$			
Δ_1 , ps ⁻¹	2		
τ_{c1} , ps	0.1		
Δ_2 , ps ⁻¹	1.25		
τ_{c2} , ps	7		

The results of the simulation are presented in the following Figures:



Figure S4. Simulated 2D-IR spectra for two transitions.



Figure S5. CLS and Peak-shift computed from the simulated 2D-IR spectrum. In the left panel, the open circles and filled squares correspond to the CLS measured with frequencies within the full bandwidth and with ± 10 cm⁻¹ from the maximum, respectively. Both frequency ranges are shown in the two 2D-IR spectra. The formulas in the figure correspond to its fit.



Figure S6. Center line slope. Some of the 2D-IR spectra used for the determination of the CLS. The black points correspond to the maxima and the black line is the fit to a line.



Figure S7. Histogram of the computed water bend frequencies as function of the total number of hydrogen-bonds.



Figure S8. Histogram of the computed bend frequencies as function of the number of hydrogen-bonds. Left and right panels correspond to the acceptor and donor cases, respectively.

References

 Chuntonov, L.; Kuroda, D. G.; Ghosh, A.; Ma, J. Q.; Hochstrasser, R. M. Quantum Beats and Coherence Decay in Degenerate States Split by Solvation. *J. Phys. Chem. Lett.* **2013**, *4*, 1866-1871.
Ge N. H.; Zanni, M. T.; Hochstrasser, R. M. Effects of Vibrational Frequency Correlations on

[2] Ge, N. H.; Zanni, M. T.; Hochstrasser, R. M. Effects of Vibrational Frequency Correlations on Two-Dimensional Infrared Spectra. J. Phys. Chem. A **2002**, 106, 962-972.