

Supporting Information

Capturing the Ultrafast Vibrational Decoherence of Hydrogen Bonding in Interfacial Water

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FID-SFG simultaneous fit using one vibrational oscillator

To confirm that the sum-frequency generation (SFG) spectrum at the H₂O/CaF₂ interface contains two vibrational oscillators instead of one, we attempted to perform the simultaneous fit of frequency and time domain measurements, using equations 2 and 3 in the main text, but considering only one oscillator. Based on their experimental values, $\Delta\omega_{\text{mid-IR}}$ and $\Delta\omega_{\text{vis}}$ are kept fixed at 600 cm⁻¹ and 16 cm⁻¹, respectively. The resulting fits are shown in **Figure 1S**, and the parameters returned by the converged fit are listed in **Table S1**.

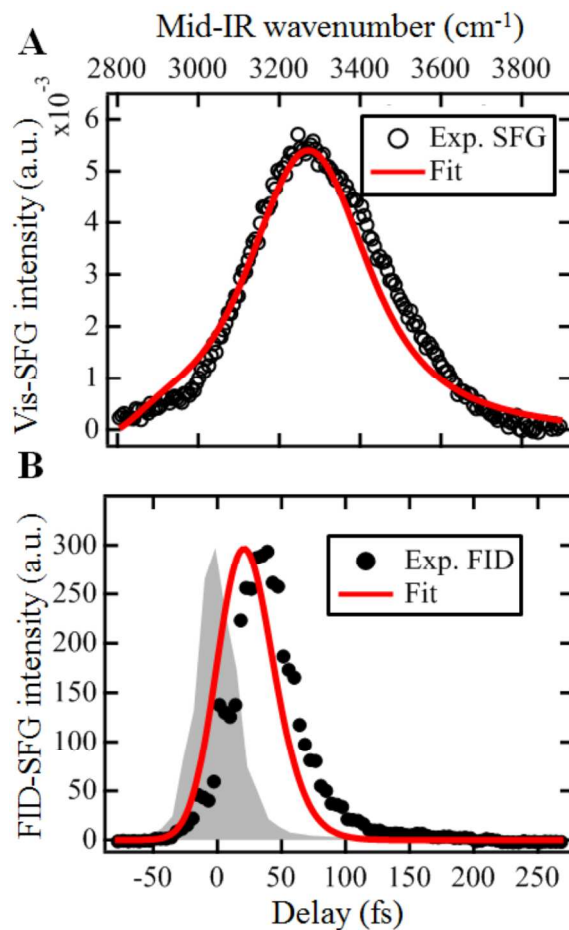


Figure S1. **A.** Normalized Vis-SFG spectrum of the OH vibrational stretch at the CaF₂/H₂O interface (symbols). **B.** FID-SFG dynamics at the CaF₂/H₂O interface (symbols). The solid lines in A and B are the result of a simultaneous fit to spectral and time domain data using one vibrational oscillator. The shaded area in B is the instrument response function measured at the CaF₂/Au interface.

Table S1: Amplitude A_n , frequency ω_n , Lorentzian half-width at half maximum (HWHM) Γ_n , dephasing time $T_{2,n}^*$, and inhomogeneous broadening $\Gamma_{inh,n}$ extracted from the simultaneous fit of the SFG spectrum and the FID-SFG^a

A_n	$\omega_n(\text{cm}^{-1})$	$\Gamma_n(\text{cm}^{-1})$	$T_{2,n}^*(\text{fs})$	$\Gamma_{inh,n}(\text{cm}^{-1})$
1.00±0.05	3269.7±16.3	116.2±5.2	45.7±2.2	90.9±16.9

^aDephasing time $T_{2,n}^*$ is extracted from Γ_n as $T_{2,n}^*=1/(2\pi c\Gamma_n)$.^{1,2} The values of the non-resonant susceptibility, A_{NR} , and the phase, ϕ , were 0.1 and 0, respectively. The uncertainty values are based on the standard deviation determined from multiple experiments.

Excluding the inhomogeneous broadening

To investigate the role of the inhomogeneous contribution to the vibrational linewidth, we carried out the simultaneous fit of frequency and time domain SFG measurements but we excluded the inhomogeneous terms in **eqs. 2** and **3d** in the main text. Based on their experimentally determined values, $\Delta\omega_{\text{mid-IR}}$ and $\Delta\omega_{\text{vis}}$, they are kept fixed at 600 cm^{-1} and 16 cm^{-1} , respectively. The parameters are listed in **Table S2**, and they are kept fixed as obtained in the main text. The resulting fits are plotted in **Figure S2**.

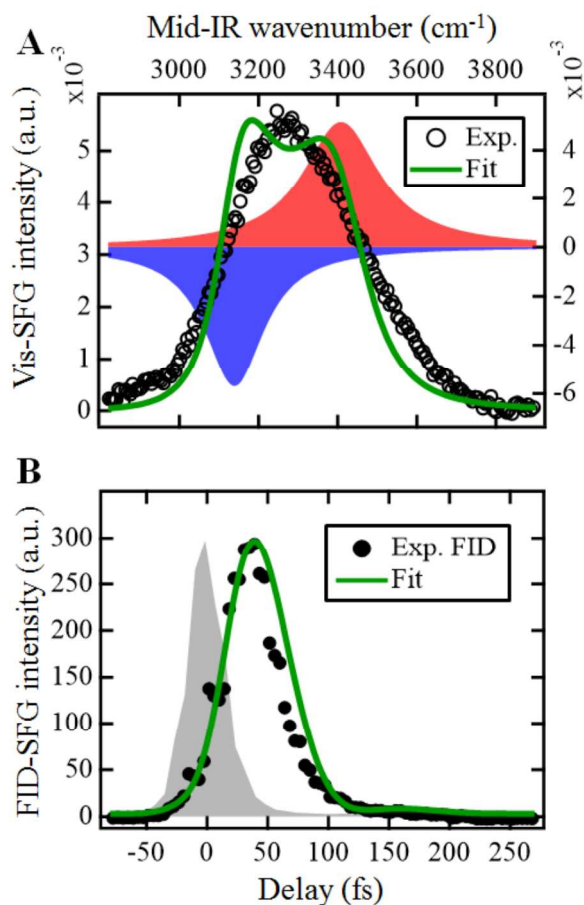


Figure S2. A. Normalized Vis-SFG spectrum of the OH vibrational stretch at the CaF₂/H₂O interface (symbols) with the intensity axis on the right side. The two shaded areas indicate the two spectral components of the fit, with the intensity axis on the left side. Each component is obtained making the amplitude of the other peak zero while fixing all the other parameters as obtained by the converged fit. **B.** FID-SFG dynamics at the H₂O/CaF₂ interface (symbols). The solid lines in A and B are the result of a simultaneous fit to spectral and time domain data considering there is no inhomogeneous broadening. The shaded area in B is the instrument response function measured at the CaF₂/Au interface.

Table S2: Amplitude A_n , frequency ω_n , Lorentzian half-width at half maximum (HWHM) Γ_n , dephasing time $T_{2,n}$, and inhomogeneous broadening $\Gamma_{inh,n}$ extracted from the simultaneous fit of the SFG spectrum and the FID-SFG^a

A_n	$\omega_n(\text{cm}^{-1})$	$\Gamma_n(\text{cm}^{-1})$	$T_{2,n}(\text{fs})$	$\Gamma_{inh,n}(\text{cm}^{-1})$
-0.43±0.04	3138.9±11.1	75.1±6.1	70.7±6.9	0
+0.53±0.11	3408.3±11.9	102.1±9.9	51.9±5.9	0

^aThe dephasing time $T_{2,n}$ is extracted from Γ_n as $T_{2,n}=1/(2\pi c\Gamma_n)$.^{1,2} The values of non-resonant susceptibility A_{NR} and phase ϕ were 0.1 and 0, respectively. The error bars are based on the standard deviation determined from multiple experiments.

Next we kept the fit parameters free and attempted to carry out the simultaneous fit but with the inhomogeneous broadening terms in **eqs. 2** and **3d** excluded. Based on their experimentally determined values, $\Delta\omega_{\text{mid-IR}}$ and $\Delta\omega_{\text{vis}}$, they are kept fixed at 600 cm^{-1} , and 16 cm^{-1} , respectively. The resulting fits are plotted in **Figure S3**, and the parameters returned by the converged fits are listed in **Table S3**.

Although the fit acceptably described the frequency-domain SFG spectrum, the simulation did not well describe the time-domain FID dynamics. In fact, the fit was off both at the negative and positive time-delays.

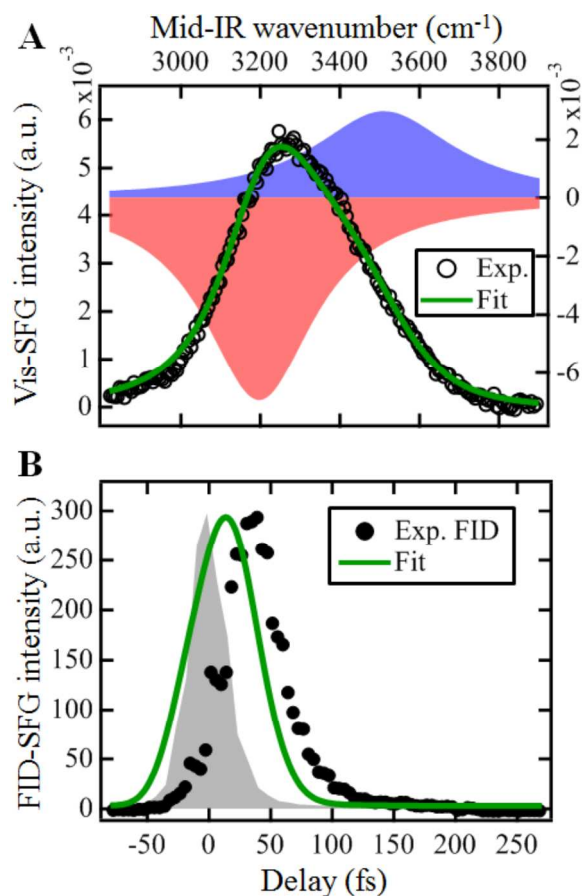


Figure S3: **A.** Normalized Vis-SFG spectrum of the OH vibrational stretch at the H₂O/CaF₂ interface (symbols), with the intensity axis on the left side. The two shaded areas indicate the two spectral components of the fit, with the intensity axis on the right side. Each component is obtained making the amplitude of the other peak zero while fixing all the other parameters as obtained by the converged fit. **B.** FID-SFG dynamics at the CaF₂/H₂O interface (symbols). The solid lines in A and B are the result of a simultaneous fit to spectral and time domain data considering there is no inhomogeneous broadening. The shaded area in B is the instrument response function measured at the CaF₂/Au interface.

Table S3: Amplitude A_n , frequency ω_n , Lorentzian half-width at half maximum (HWHM) Γ_n , dephasing time $T_{2,n}$, and inhomogeneous broadening $\Gamma_{inh,n}$ extracted from the simultaneous fit of the SFG spectrum and the FID-SFG^a

A_n	$\omega_n(\text{cm}^{-1})$	$\Gamma_n(\text{cm}^{-1})$	$T_{2,n}(\text{fs})$	$\Gamma_{inh,n}(\text{cm}^{-1})$
-0.18±0.01	3196.7±12.7	153.1±35.1	34.7±14.6	0
+0.15±0.01	3510.5±44.1	199.5±31.0	26.6±6.0	0

^aThe dephasing time $T_{2,n}$ is extracted from Γ_n as $T_{2,n}=1/(2\pi c\Gamma_n)$.^{1,2} The values of the non-resonant susceptibility (A_{NR}) and the phase (ϕ) were 0.1 and 0, respectively. The error bars are based on the standard deviation determined from two independent experiments.

In addition to the data shown in **Figure 3** in the main text, we also carried out a similar independent experiment. The corresponding SFG spectrum and FID dynamics and their fits are shown in **Figure S4**, and the parameters returned by the converged simultaneous fit are listed in **Table S4**.

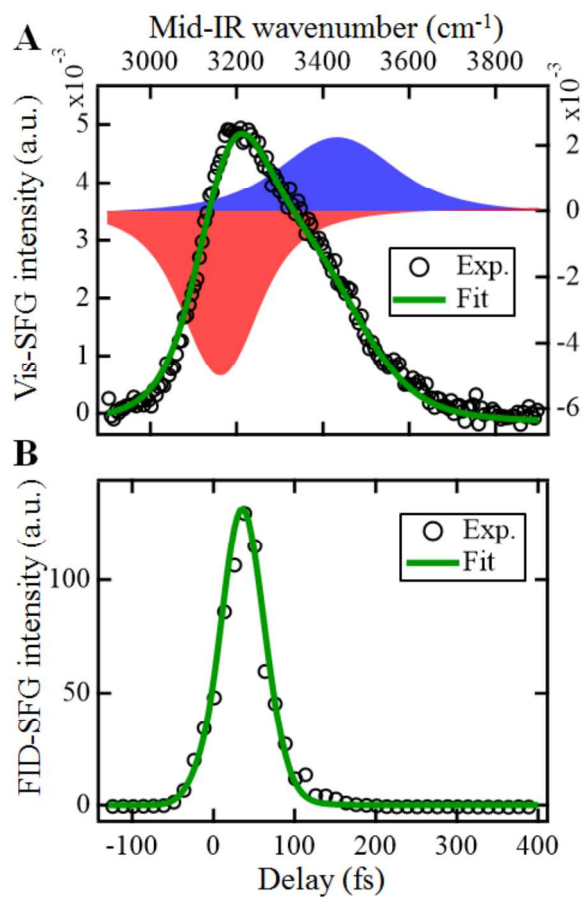


Figure S4. Normalized Vis-SFG spectrum of the OH vibrational stretch at the $\text{CaF}_2/\text{H}_2\text{O}$ interface (symbols) with the intensity axis on the left side. The two shaded areas indicate the two spectral components of the fit with the intensity axis on the right side. Each component is obtained making the amplitude of the other peak zero while fixing all the other parameters as obtained by the converged fit. **B.** FID-SFG dynamics at the $\text{CaF}_2/\text{H}_2\text{O}$ interface (symbols). The solid lines in A and B are the result of a simultaneous fit to spectral and time domain data.

Table S4: Amplitude A_n , frequency ω_n , Lorentzian half-width at half maximum (HWHM) Γ_n , dephasing time $T_{2,n}^*$, and inhomogeneous broadening $\Gamma_{inh,n}$ extracted from the simultaneous fit of the SFG spectrum and the FID-SFG^a

A_n	$\omega_n(\text{cm}^{-1})$	$\Gamma_n(\text{cm}^{-1})$	$T_{2,n}^*(\text{fs})$	$\Gamma_{inh,n}(\text{cm}^{-1})$
-0.34 ± 0.04	3161.1 ± 11.1	62.9 ± 6.1	84.4 ± 6.8	71.6 ± 17.8
$+0.30 \pm 0.11$	3432.2 ± 11.9	83.4 ± 9.3	63.6 ± 5.8	107.9 ± 12.2

^aThe pure dephasing time $T_{2,n}^*$ is extracted from Γ_n as $T_{2,n}^* = 1/(2\pi c\Gamma_n)$.^{1,2} The values of non-resonant susceptibility A_{NR} and phase ϕ were 0.1 and 0, respectively. The error bars are based on the standard deviation determined from two independent experiments.

Supplementary References

- (1) Nihonyanagi S.; Eftekhari-Bafrooei A.; Borguet E. *J. Chem. Phys.* **2011**, 134, 084701-084707
- (2) Boulesbaa A.; Borguet E. *J. Phys. Chem. Lett.* **2014**, 5, 528-533