Supporting Information

Interfacial water structure associated with phospholipid membranes studied by phase-sensitive vibrational sum frequency generation spectroscopy

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The experimental configuration of the phase-sensitive vibrational sum frequency generation (PS-VSFG) probe and detection portion of the system is illustrated in Figure S1.

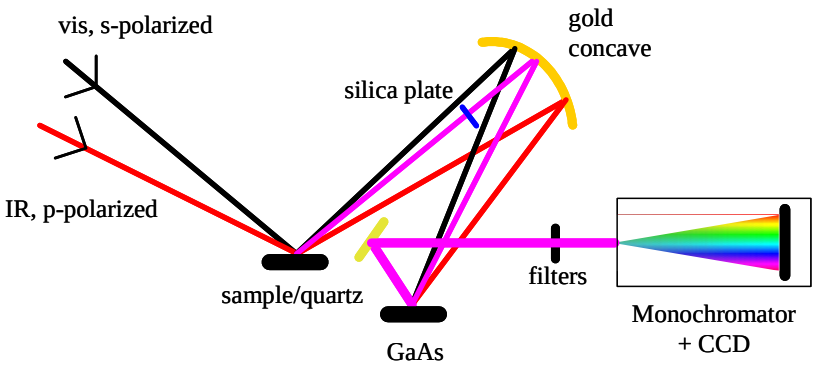

Figure S1. Schematic of the PS-VSFG experiment configuration.

The total detected intensity can be described as:[1]

$$I_{HD-SFG} \propto \left|E_{tot}\right|^2 = \left|E_{sample} + E_{LO}\right|^2$$

$$= \left|E_{sample}\right|^2 + \left|E_{LO}\right|^2 + E_{sample}E_{LO}^{*}\exp(i\omega\Delta t) + E_{sample}^{*}E_{LO}\exp(-i\omega\Delta t)$$

E_{sample} denotes the sum frequency beam from samples or quartz and E_{LO} denotes the sum frequency beam from GaAs. Δt is the 2.5 ps time difference between two sum frequency beams.

The raw interferograms (Figure S2) were inverse Fourier transformed to the time domain using OriginPro software (version 7.5). The $|E_{sample}|^2$ and $|E_{LO}|^2$ signals at t = 0 in time domain were filtered out and only the cross terms were kept and followed by Fourier transform back to the frequency domain. The resulting frequency spectra contain phase information (φ) of the complex $E_{sample}E_{LO}^{*}exp(i\omega\Delta t)$ (Figure S2). Because quartz does not have any resonance in this infrared region, the phase of quartz can be used as a reference. Therefore, the real and imaginary $\chi^{(2)}$ spectra can be obtained by dividing the sample interferogram by the quartz reference, through which the contribution from E_{LO} is completely removed. Moreover, the final spectra were normalized to the different reflectivities of the incident visible and IR beams on quartz and on samples. The expression of the Im $\chi^{(2)}$ spectrum is as follows:

$$\mathrm{Im}\,\chi^{(2)} \propto \frac{r_{vis,quartz}\, r_{IR,quartz} \left| E_{sample} E_{LO} \right|}{r_{vis,sample}\, r_{IR,sample} \left| E_{quartz} E_{LO} \right|} \sin(\varphi_{sample} - \varphi_{quartz})$$

r is the reflectivity of the incident visible or IR beams on quartz or the sample. The phases of the quartz and sample (φ) are obtained directly from the Fourier transformation.

Our current IR profile is lower near 3200 cm^{-1} as compared to 3400 cm^{-1} (Figure S2, bottom panel), which can slightly distort the normalized intensity near 3200 cm^{-1}.

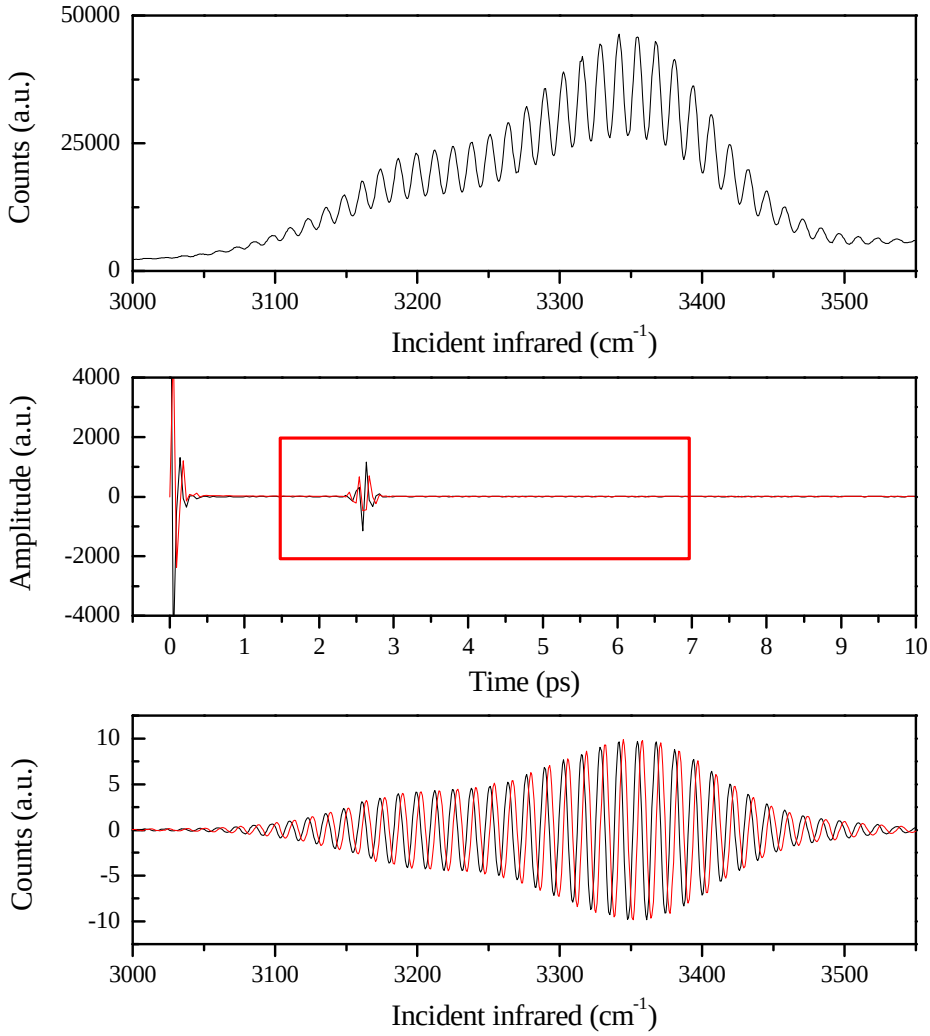

Figure S2. Upper panel: Raw interferogram of z-cut quartz with GaAs. Middle panel: Time domain real (black) and imaginary (red) signals. The cross term at ~ 2.5 ps is extracted to yield the heterodyne frequency spectra. Lower panel: Real (black) and imaginary (red) parts of heterodyne frequency spectra of z-cut quartz with GaAs. Phase information (φ) is therefore obtained.

References

1. Yamaguchi, S.; Tahara, T., *J. Chem. Phys.* **2008,** 129, (10), 101102.