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Supporting Information: Orientation Independent Vibrational Dynamics of Interfacial Water

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Monolayer Preparation

Table S1: Average configuration of monolayer preparation

Lipid Unit	Concentration mmol/l	Drops Number	Coverage $Å^2$/molecule	Surface Pressure mN/m
DOPC	0.43	54 ± 5	64 ± 6	11 ± 2
DOCPe	0.43	44 ± 1	77 ± 2	13 ± 1

Stock solutions of DOPC and DOCPe were prepared with the in Table S1 given concentration of lipid, dissolved in Chloroform. The monolayers were prepared by dropping the specified amount of 0.25 μl drops of stock solution on D_2O in a rotating teflon trough. The trough has a diameter of 77 mm and is filled with 35 ml D_2O. A tensiometer was used to measure the surface pressure during monolayer preparation. To obtain similar surface pressure results through the 14 monolayer preparations the drop count of the lipid needed to be adjusted and the reason for the relative large variance of 10 % in the drop count of DOPC. [S1,S2]

Surface Pressure Measurement

Each pump probe measurement was carried out over a course of 12 h. Figure S1 shows that the surface pressure is stable throughout the complete time with a slow drift of about 10%, while the water level is kept constant using a reservoir.

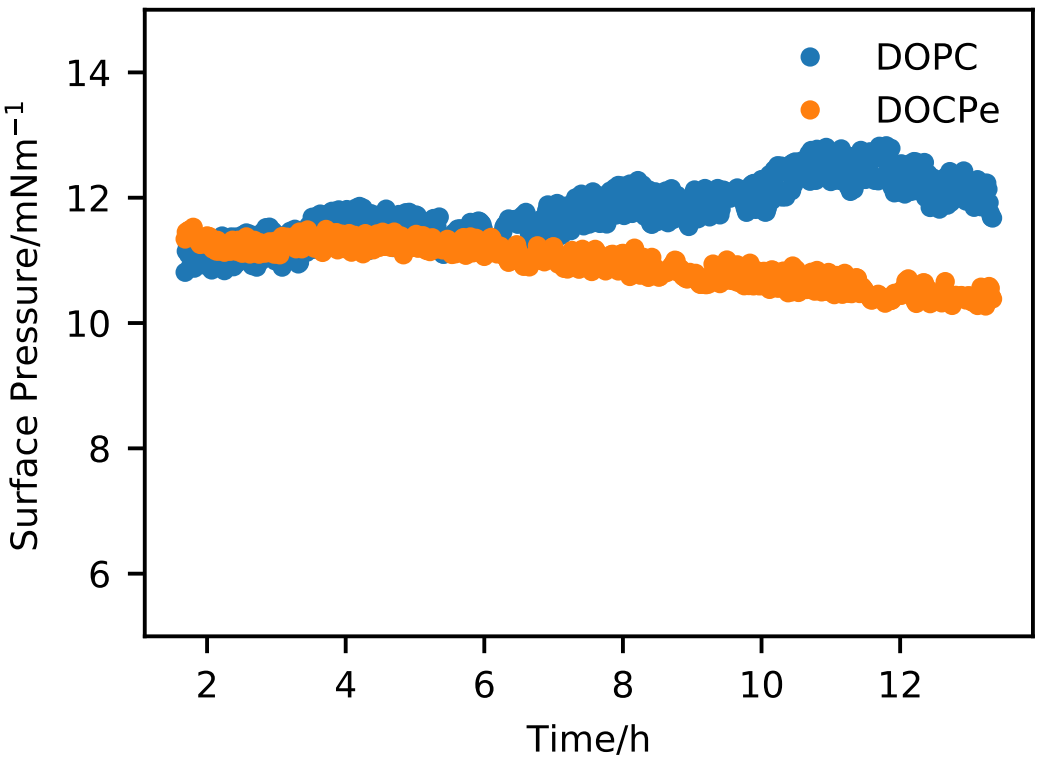

Figure S1: Surface pressure measurements on DOCPe and DOPC covered D_2O for 12 h during a pump-probe measurement.

Pump Positions

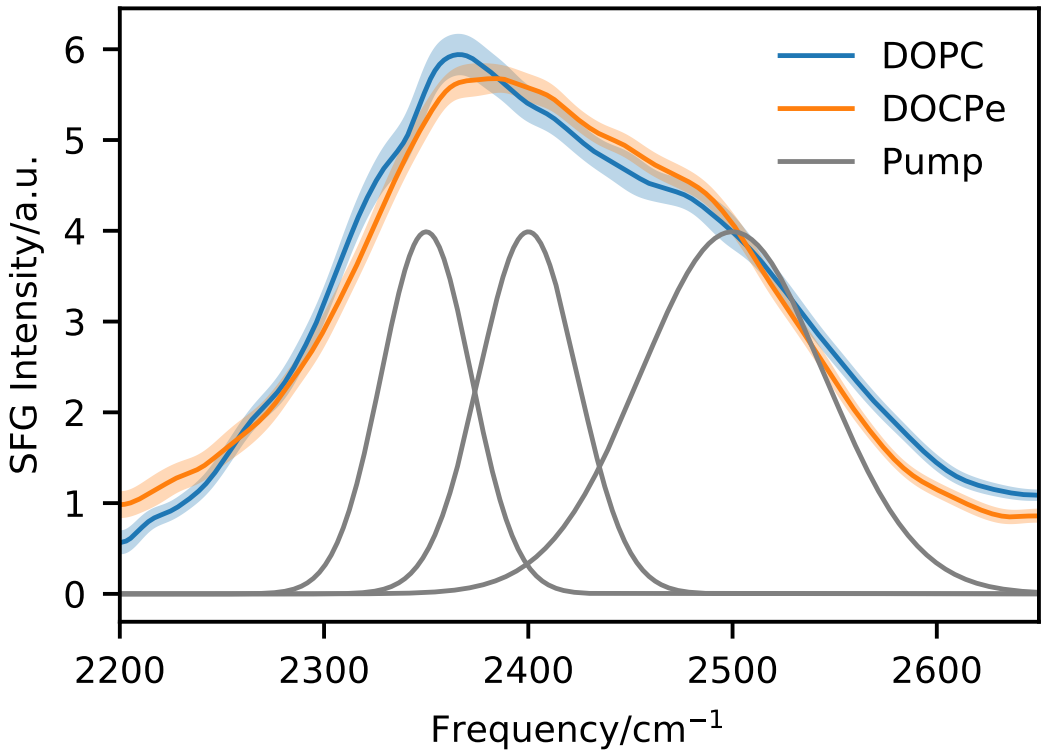

Figure S2: SFG spectrum of the OD Stretch vibration of the lipid-D_2O interface. The grey curve shows the spectrum of the IR pump laser beam.

Table S2: Mean frequency of the pump IR spectrum and the width (1σ) of a gaussian fit to the Pump IR spectrum.

Mean Frequency/cm^{-1}	2350	2400	2500
Width/cm^{-1}	22	24	45

Three different center pump frequencies were used. The center frequency of the pump spectrum is determined by measuring the non resonant Pump-Visible SFG response from a gold sample and the mean position and width is given in Table S2.

Heat Correction

Typically D_2O relaxation dynamics are described using a four-level-model[S3,S4] with two lifetimes $\tau_1 \approx 0.2\,\text{ps}$ - $0.8\,\text{ps}$ and $\tau_2 \approx 0.7\,\text{ps}$. We approximate the ingrowth of heat using Equation 1, with $\tau_{\text{heat}} = 1\,\text{ps}$ and $A(\omega)$ as bleach at $t = 20\,\text{ps}$ at probe frequency ω.

$$H(\omega, t) = A(\omega) \cdot (1 - e^{-t/\tau_{\text{heat}}}) \tag{1}$$

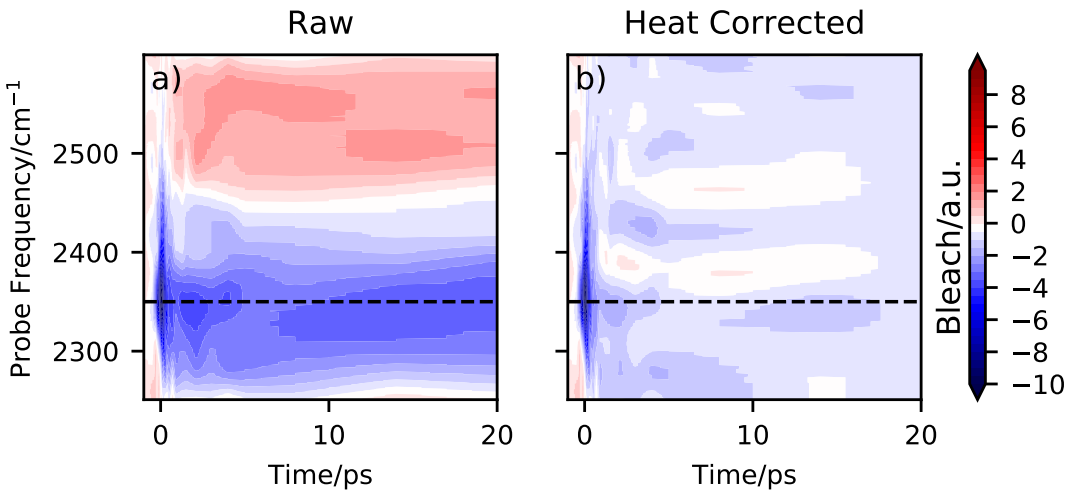

Figure S3: Effect of heat correction on Pump-Probe spectra. a) bleach spectrum of DOPC-D_2O interface without heat correction. b) same spectrum after heat correction.

Figure S3 shows an example for heat corrected pump probe data. Note that this heat correction is only used in Figure 2, Figure S4 and Figure 3, but not in Figure 4, where the four-level-model accounts for heating effects.

Determination of the Spectral Weight Line

The spectral weight is determined by taking vertical slices of Figure 2 at a given pump beam frequency. The slice is fitted with the sum of two Gaussians and examples for three different pump beam frequencies, at a pump-probe time delay of $-0.1\,\text{ps}$ are shown in Figure S4.

In Figure S4 the vertical difference of the dotted lines equals the central pump frequency

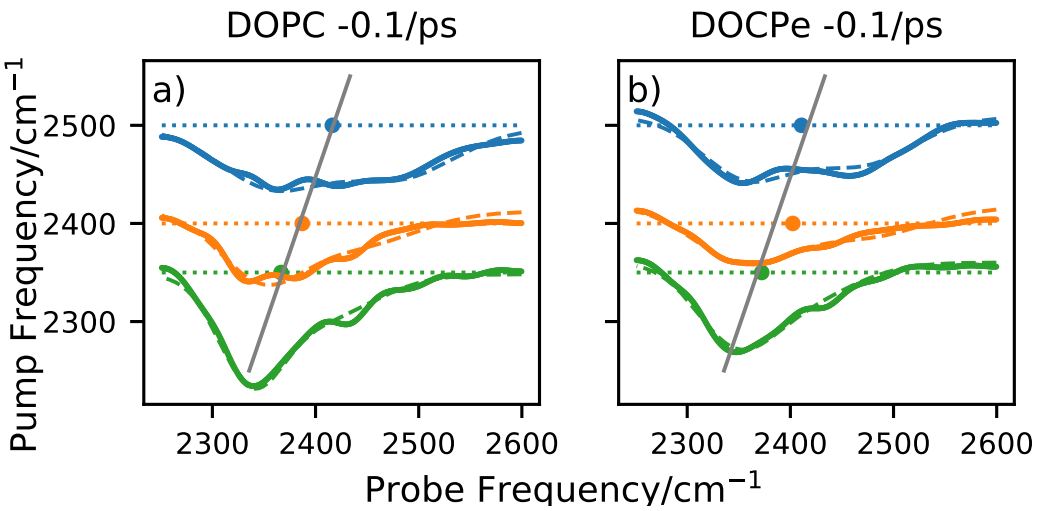

Figure S4: Transient SFG spectra of DOPC and DOCPe. The X-Axis shows the probe frequency, while the dotted line on the Y-Axis corresponds to the pump frequency. The distance between dotted and colored line denotes the Δ intensity in a.u. Each point on the dotted line illustrates the SW of Equation 3. The grey line is a linear fit through the SW points and corresponds to the white line of Figure 2.

difference and the distance between the dotted and the solid line corresponds to the ΔI of Figure 2: e.g. the difference in SFG intensity with pump beam on and pump beam off. The double peak like structure for a pump frequency of 2500 cm^{-1} illustrates, that at least two peaks are needed to describe the data. The fit function has the form:

$$t(\omega) = \sum_{n}^{2} A_n e^{-(\omega-\omega_n)^2/(2\sigma_n^2)} + c_n \tag{2}$$

with Amplitude A_n, the central frequency ω_n, the offset c_n and the width σ_n of the feature n. The spectral weight is defined as the average of ω_n weighted with A_n. e.g:

$$SW = \frac{\sum_n^2 A_n \cdot \omega_n}{\sum_n^2 A_n} \tag{3}$$

SW is shown as a dot in Figure S4. By plotting SW vs the central pump beam frequency, the spectral width line (SWL) can be determined. The SWL is shown as a grey line in Figure S4 and as a white line in Figure 2.

Time Dependency of the Slope of the Spectral Width Line

By plotting the slope of the SWL vs the pump-probe time delay, Figure 3 is obtained. Figure 3 is fitted with the convolution of a Gaussian function and an exponential decay. The function has the form of Equation 4. The Gaussian accounts for the finite instrument response function and has a fixed with of $\sigma = 0.16\,\mathrm{ps}$. The start time μ (center of the Gaussian) is fixed to $-0.2\,\mathrm{ps}$ to reduce the amount of free parameters. The $-0.2\,\mathrm{ps}$ offset corrects roughly for the different definitions of time zero throughout the experiment and the fit. As Equation 4 contains the product of a gaussian and an errorfunction, the amplitude of Equation 4 at t=0 is 50 % of the maximum amplitude. However t=0 is experimentally defined by the maximum bleach on gold, as this is easier to determine during the experiment. The exponential decay has a lifetime of τ and is varied together with the Amplitude A to obtain the best fit. The maximum of the CLS is slightly different for the two lipids with DOPC : 0.34 ± 0.04 and DOCPe : 0.25 ± 0.05.

$$CLS(t, \mu, \sigma, \tau, A) = \frac{1}{2} A \exp\left(\frac{2\tau(\mu - t) + \sigma^2}{2\tau^2}\right) \mathrm{erfc}\left(\frac{\sigma^2 + \tau(\mu - t)}{\sqrt{2}\sigma\tau}\right) \tag{4}$$

Temporal Chirp

By assuming gold to have a quasi instantaneous response, the minimal resolvable lag time $\Delta\mu$ can be measured. The lag time $\Delta\mu$ is for a central pump frequency of $2350\,\mathrm{cm}^{-1}$ given by the difference of the start times of the trace at the probe frequency of $2500\,\mathrm{cm}^{-1} \pm 30\,\mathrm{cm}^{-1}$ and $2350\,\mathrm{cm}^{-1} \pm 30\,\mathrm{cm}^{-1}$. In analogy for a central pump frequency of $2500\,\mathrm{cm}^{-1}$ it is given by the start time difference of the trace at a probe frequency of $2350\,\mathrm{cm}^{-1} \pm 30\,\mathrm{cm}^{-1}$ and $2500\,\mathrm{cm}^{-1} \pm 30\,\mathrm{cm}^{-1}$. Without temporal chirp a gold sample is expected to have a lag time $\Delta\mu$ on the sub fs time scale. Thus by measuring the lag time on gold, one can estimate the instrumental resolution limit, that is expected to be on the order of tens of fs.

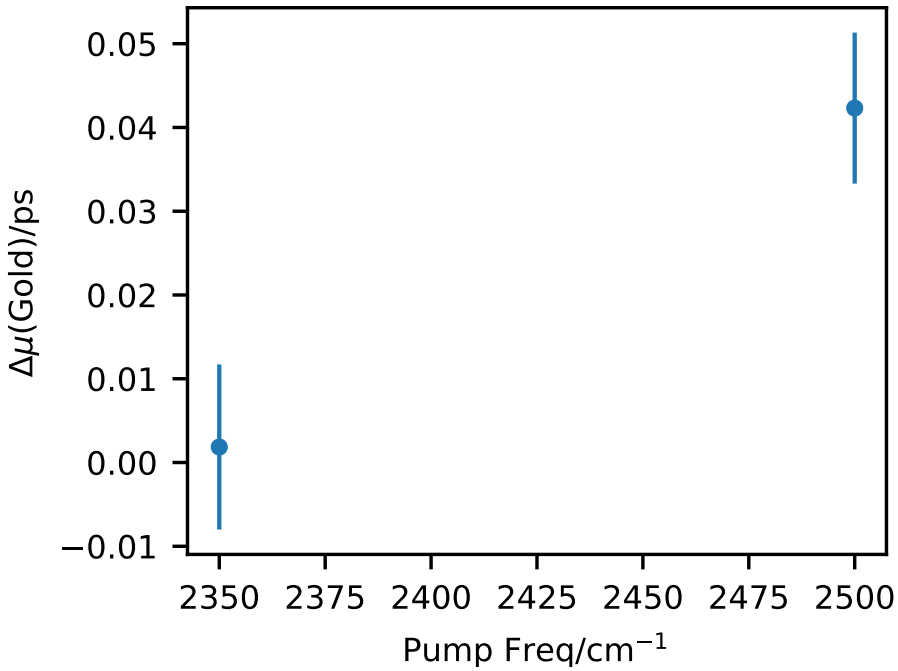

Figure S5: $\Delta\mu$ lag time on a gold sample with central pump frequencies at $2500\,\mathrm{cm}^{-1}$ and $2350\,\mathrm{cm}^{-1}$.

Figure S5 shows the lag time $\Delta\mu$ on gold to be below 0.05 ps. This is significantly below the $\Delta\mu$ lag times of 0.2 ps and 0.1 ps for the downhill and uphill crosspeaks of Figure 4 respectively.

Bibliography

References

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