

Supporting Information for

Nitrous oxide vibrational energy relaxation is a probe of interfacial water in lipid bilayers

Logan R. Chieffo^{}, Jeffrey T. Shattuck^{*}, Eric Pinnick[†], Jason J. Amsden[†], M. K. Hong[‡], Feng
Wang^{*}, Shyamsunder Erramilli^{‡§}, Lawrence D. Ziegler^{*§}*

^{*}Department of Chemistry and the Photonics Center, Boston University, 590 Commonwealth
Avenue, Boston, MA-02215, USA. [†]Department of Physics, Boston University, 590
Commonwealth Avenue, Boston, MA-02215, USA. [‡]Department of Physics and Department of
Biomedical Engineering and the Photonics Center, Boston University, 590 Commonwealth
Avenue, Boston, MA-02215, USA.

[§]Corresponding Authors: Shyamsunder Erramilli, Department of Physics, 590 Commonwealth
Avenue, Boston University, Boston, MA 02215; TEL: 617-353-1271 FAX: 617-353-9393;
shyam@bu.edu; Lawrence Ziegler, Department of Chemistry, 590 Commonwealth Avenue,
Boston University, Boston, MA 02215 lziegler@bu.edu.

This file includes:

Figures S1 to S9

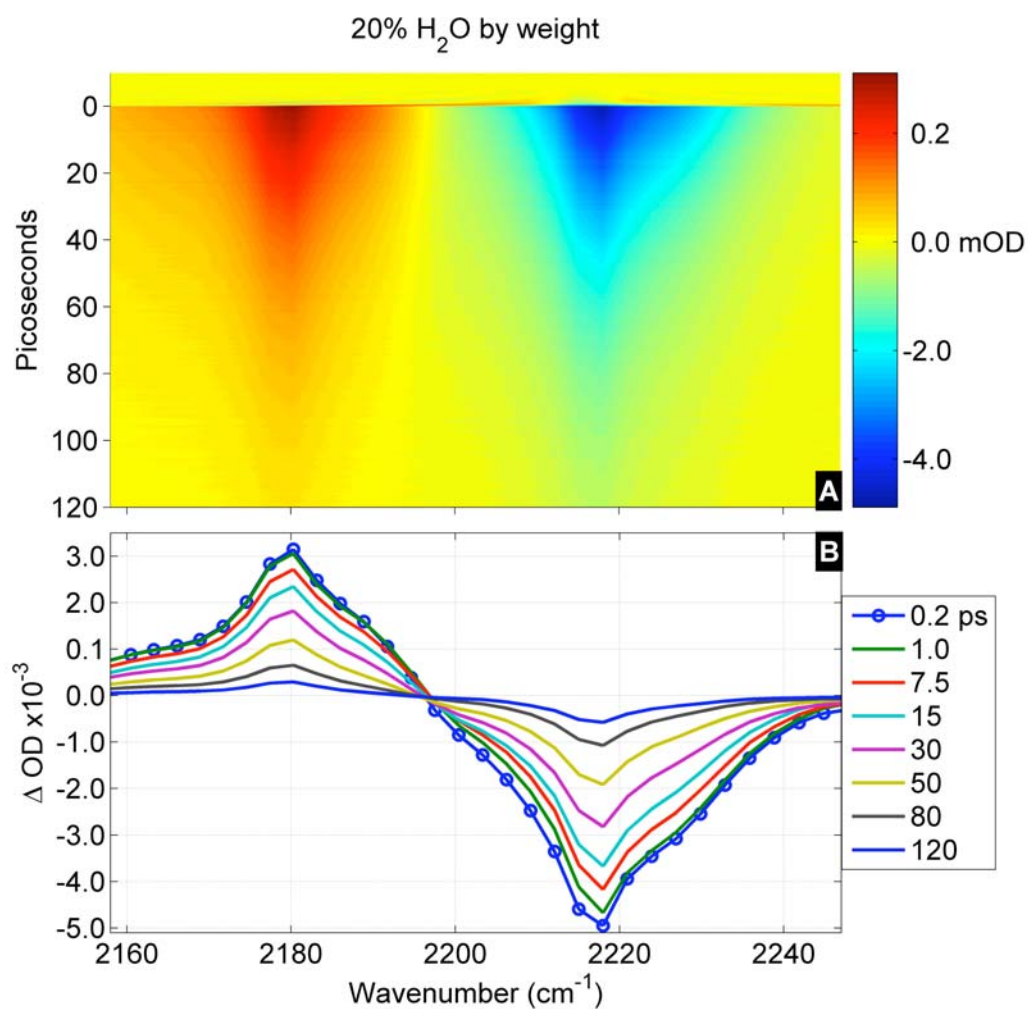


Figure S1. Frequency dispersed transient absorbance of the ν_3 band of N₂O dissolved in hydrated DOPC at 20% hydration by weight. **(A)** Infrared pump-probe measurement showing the ground state bleaching and the excited state absorption shifted by the ν_3 anharmonicity. **(B)** Transient spectrum of 20% hydrated DOPC as a function of increasing pump-probe delay.

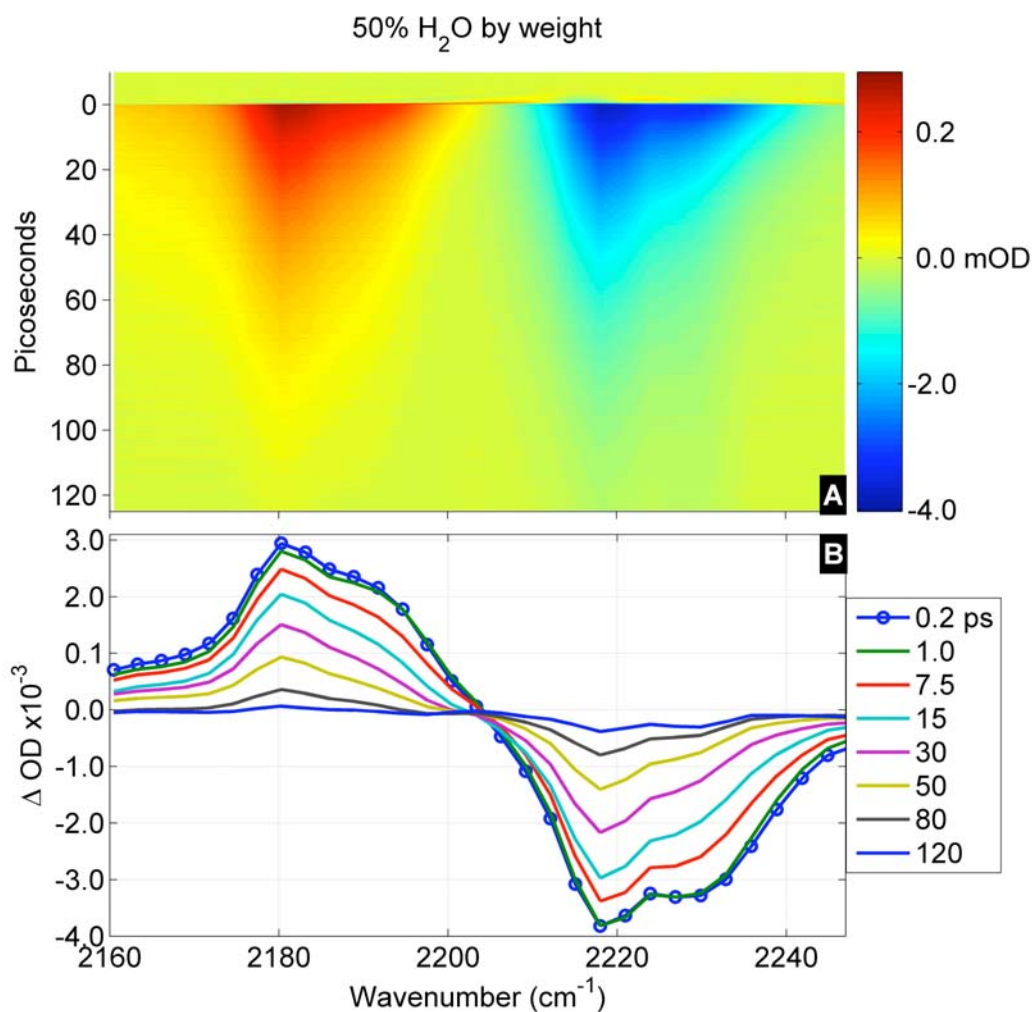


Figure S2. Frequency dispersed transient absorbance of the ν_3 band of N₂O dissolved in hydrated DOPC at 50% hydration by weight. **(A)** Infrared pump-probe measurement showing the ground state bleaching and the excited state absorption shifted by the ν_3 anharmonicity. **(B)** Transient spectrum of 50% hydrated DOPC as a function of increasing pump-probe delay.

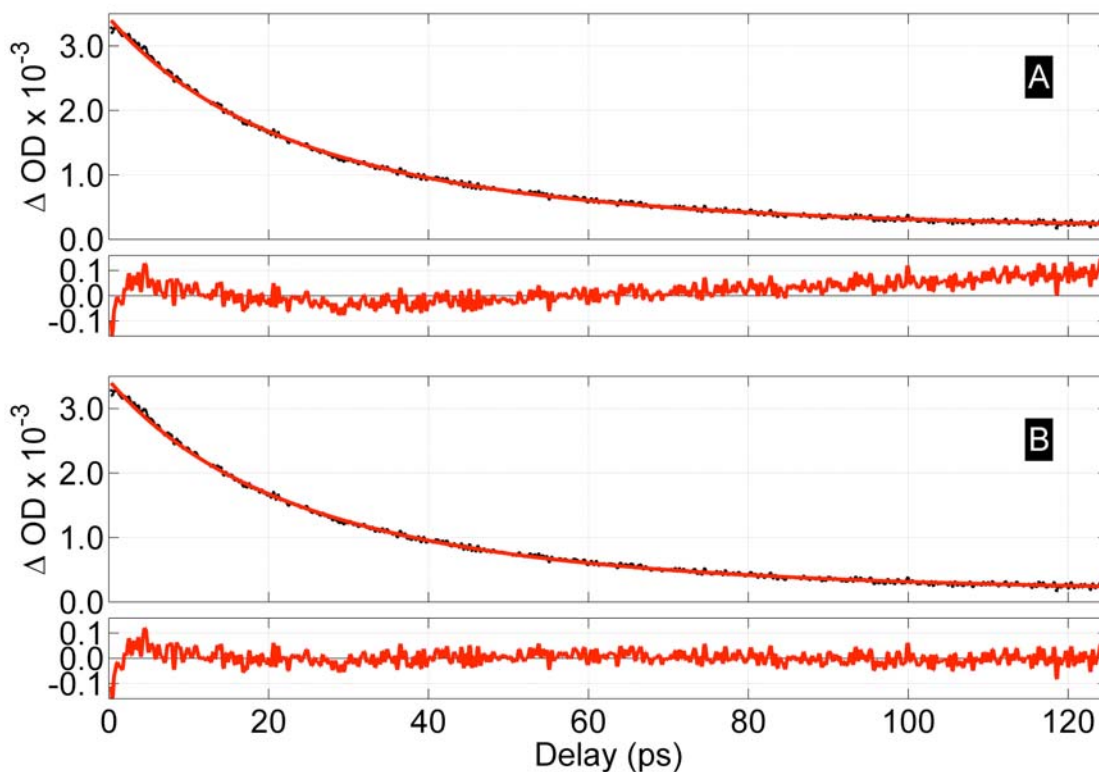


Figure S3. Comparison of bi-exponential (A) and tri-exponential (B) fits to the dispersed transient absorption response at 2230 cm^{-1} for 50% water-DOPC mixture. The plots show the best-fits (red line) to the data (black dots) along with residuals in the bottom panel. The resulting time constants are: (A) 13 ps and 47 ps, (B) 9 ps, 20 ps and 51 ps. The three decay rates for B are attributed to N_2O in bulk water pools, interfacial water and acyl chain regions respectively. A small constant component, corresponding to bulk water heating effects, is required to capture the longer time decay of this response as described in the text. The tri-exponential fit results in a much improved fit to the observed response at 2230 cm^{-1} for this hydrated lipid system.

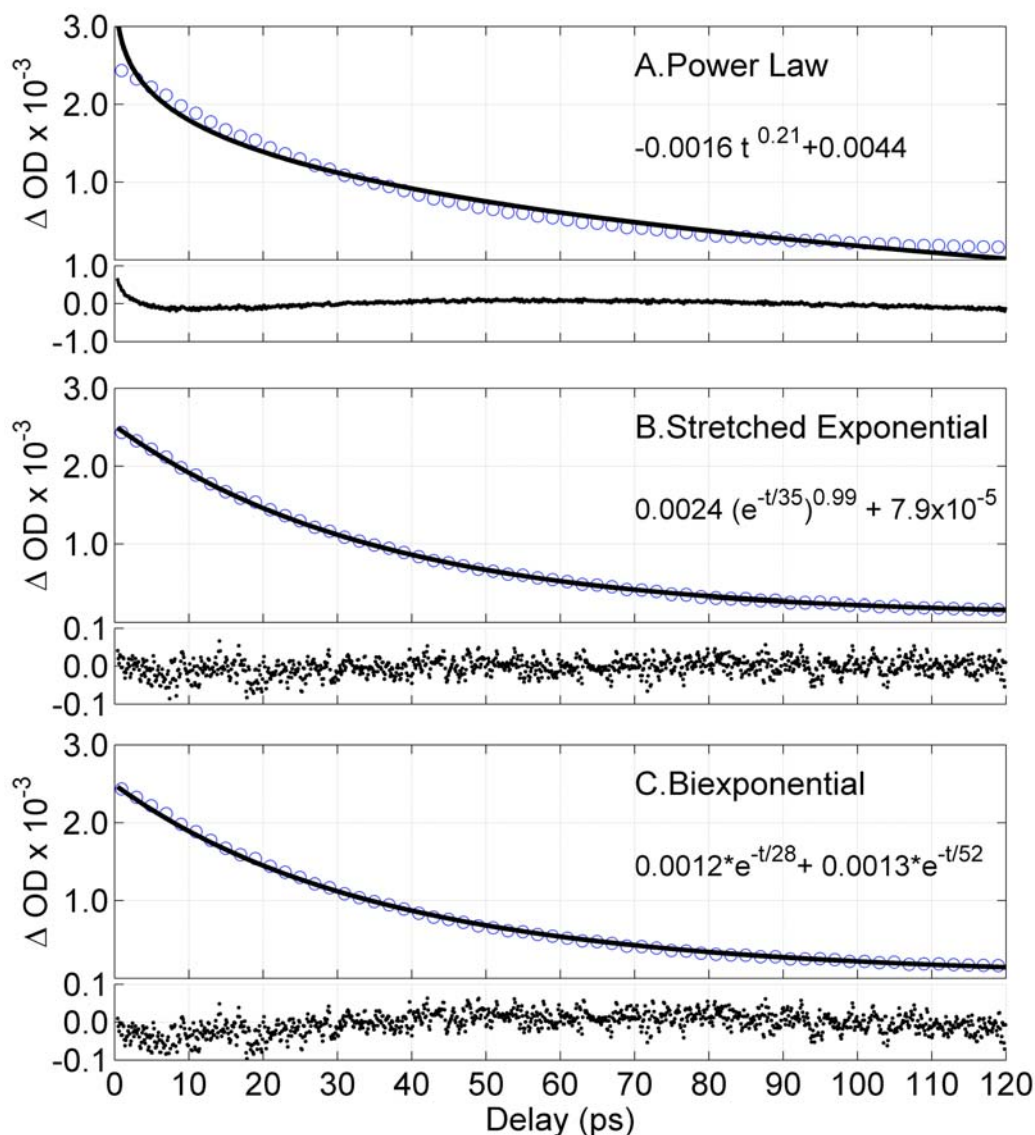


Figure S4. Comparison of best-fit results for different fitting models. The experimental results (blue circles) from single wavelength slice at 2230cm^{-1} for the 20% hydration by weight DOPC-water sample are shown with best-fits (black lines) for different fitting models. The residuals are shown directly below each best-fit. **(A)** Shows the resulting best-fit with a power law, **(B)** shows the resulting best-fit with a stretched exponential, and **(C)** shows the resulting best fit with a biexponential. The power law model (A) does not fit the data. The stretched exponential model (B) is fit with a $\beta = 0.99$, and thus is not a useful model for describing the observed kinetics. An excellent fit is found for the biexponential model (C).

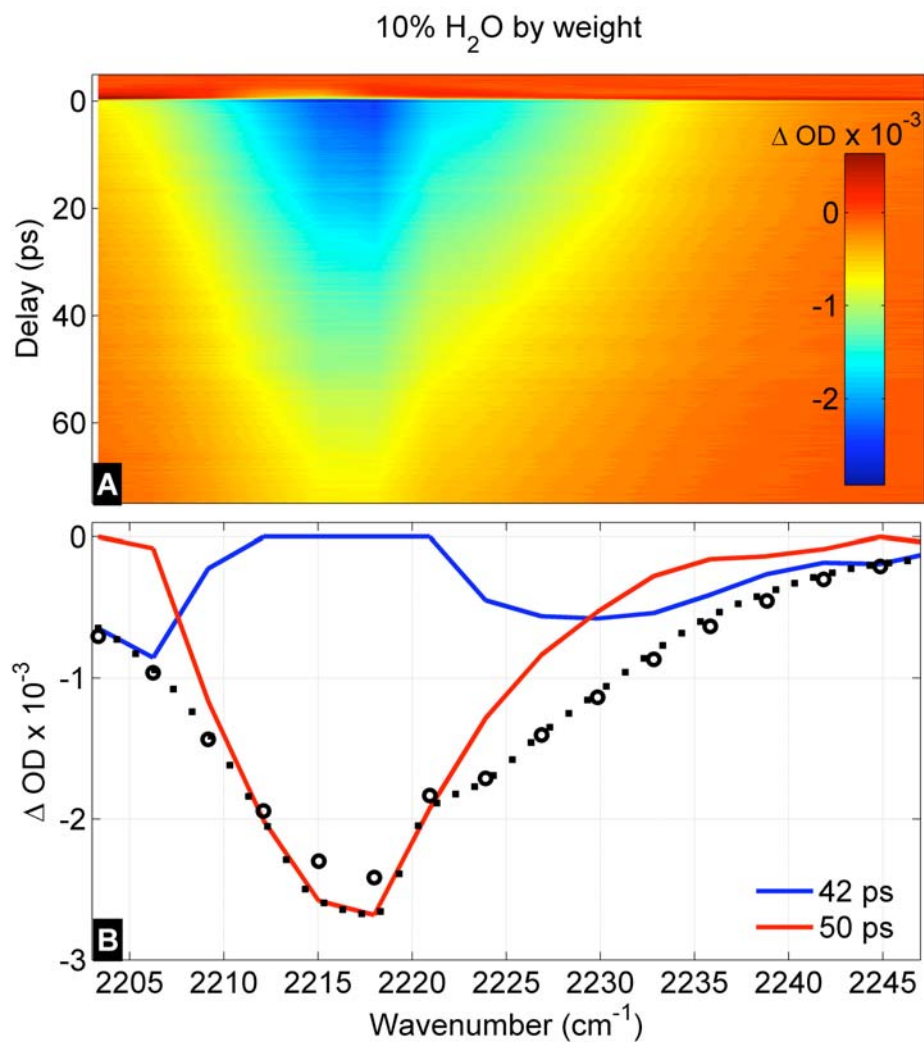


Figure S5. (A) Infrared pump induced transient differential probe spectrum of N₂O in DOPC bilayers at 10% hydration by weight. (B) Decay Associated Spectra (DAS) obtained by global fitting the spectrum shown above. The solid lines show the different components of the DAS, the dotted black line is comprised of the sum of all DAS and the black circles are the observed spectrum at 200fs.

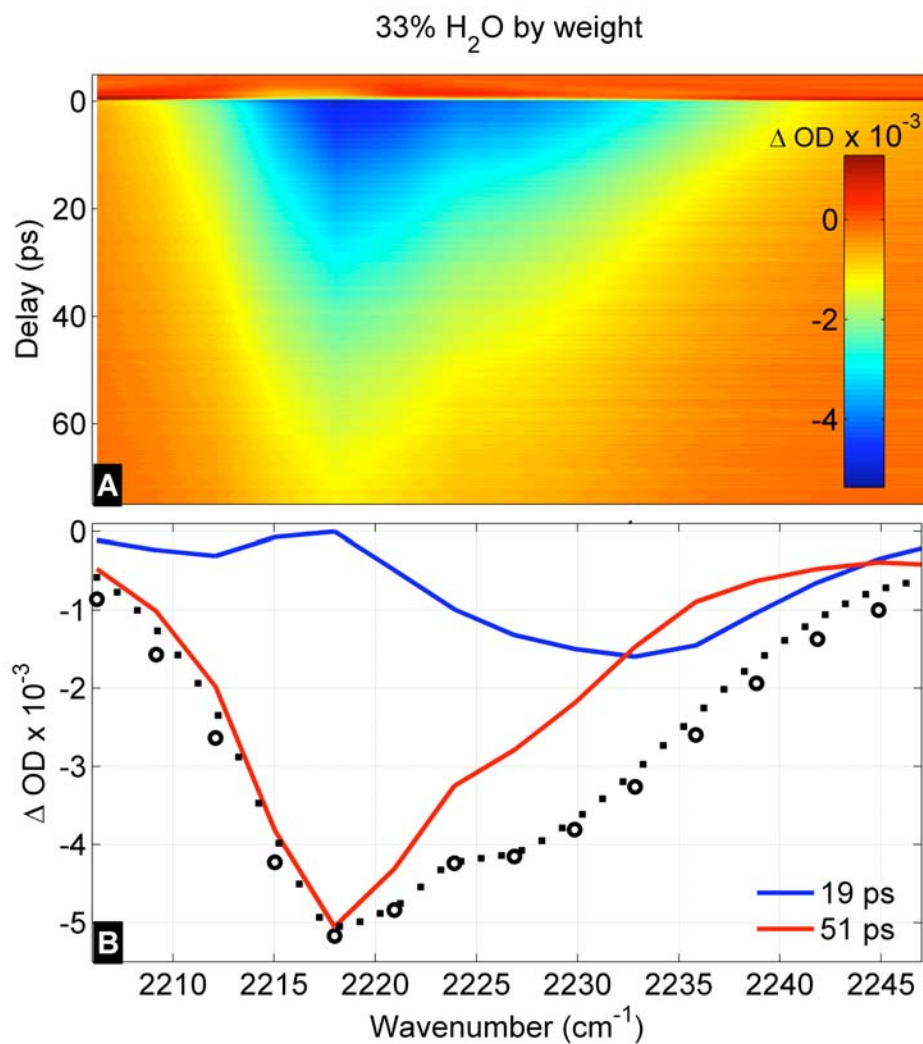


Figure S6. (A) Infrared pump induced transient differential probe spectrum of N₂O in DOPC bilayers at 33% hydration by weight. (B) Decay Associated Spectra (DAS) obtained by global fitting the spectrum shown above. The solid lines show the different components of the DAS, the dotted black line is comprised of the sum of all DAS and the black circles are the observed spectrum at 200fs.

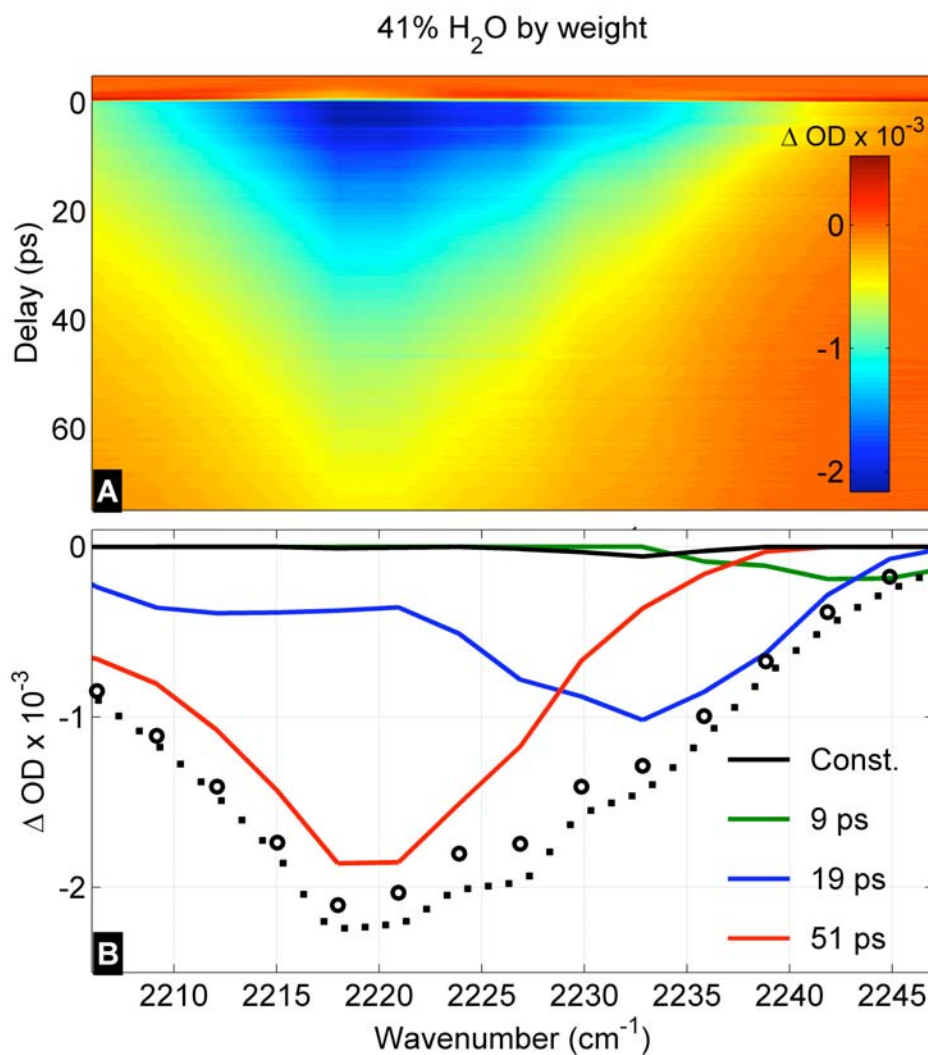


Figure S7. (A) Infrared pump induced transient differential probe spectrum of N₂O in DOPC bilayers at 41% hydration by weight. (B) Decay Associated Spectra (DAS) obtained by global fitting the spectrum shown above. The solid lines show the different components of the DAS, the dotted black line is comprised of the sum of all DAS and the black circles are the observed spectrum at 200fs.

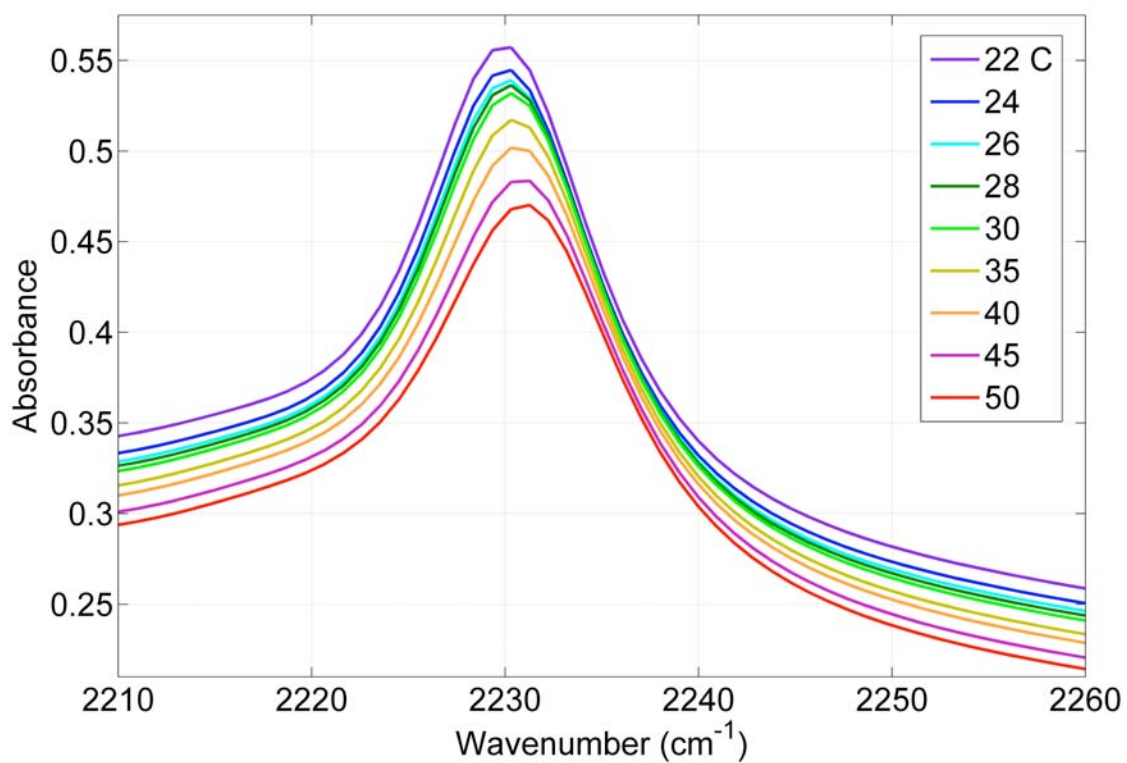


Figure S8. FTIR spectra of the ν_3 antisymmetric stretch of N_2O (10atm) in H_2O as a function of temperature. This N_2O band is seen to blue shift as the solution is heated.

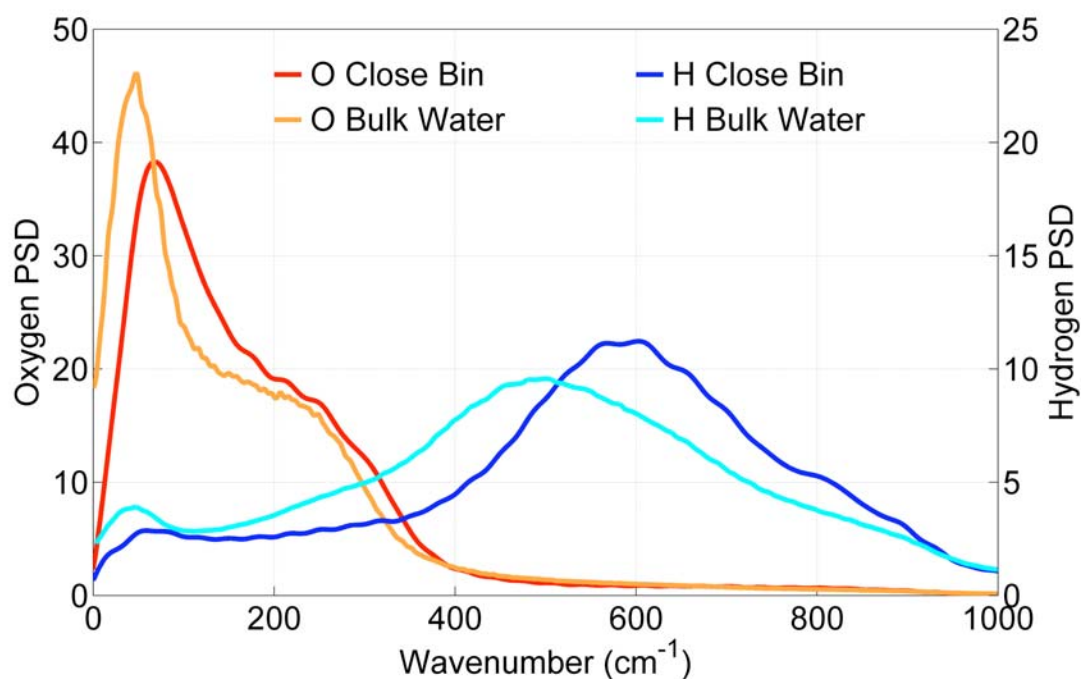


Figure S9. Power spectral density (PSD) for oxygen atoms and hydrogen atoms in SPC/Fw water for the frequency range from 0 to 1000 cm^{-1} resulting from Fourier transform of the velocity autocorrelation function. The close bin is centered at the density maximum of the phosphorus atom of the phosphocholine head group. A bin thickness of 0.3 nm is used. Only water molecules which stay in the bin for more than 80% of the time during the 25ps sampling interval were included. The bulk water PSD calculated without the lipid bilayers is included as a comparison. Interestingly the near phospholipid interfacial waters spectral densities blue shifted relative to the bulk waters. More sophisticated force fields and explicit treatment of the quantum mechanical nature of the vibrations are needed to reliably model the higher frequency (short-time) spectral densities corresponding to the tail of the librational bands and the libration-combination degrees of freedom most directly of interest to the dynamics reported here.