Supporting Information

Temperature Dependence of the Air/Water Interface Revealed by Polarization Sensitive Sum-Frequency Generation Spectroscopy

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Structure of Water Slabs

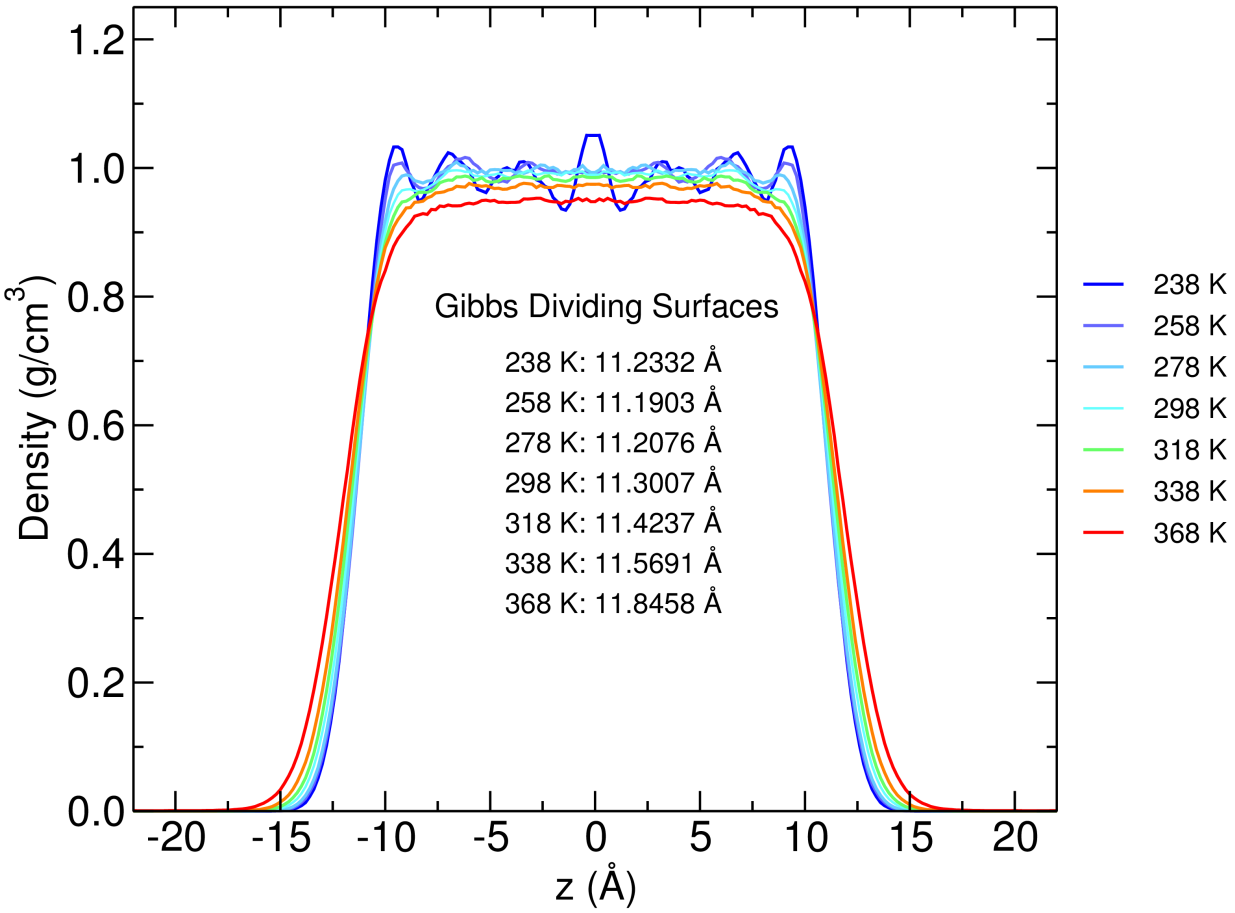

Figure S1: Density profiles of water slabs as a function of temperature. The Gibbs dividing surfaces for each temperature are also included.

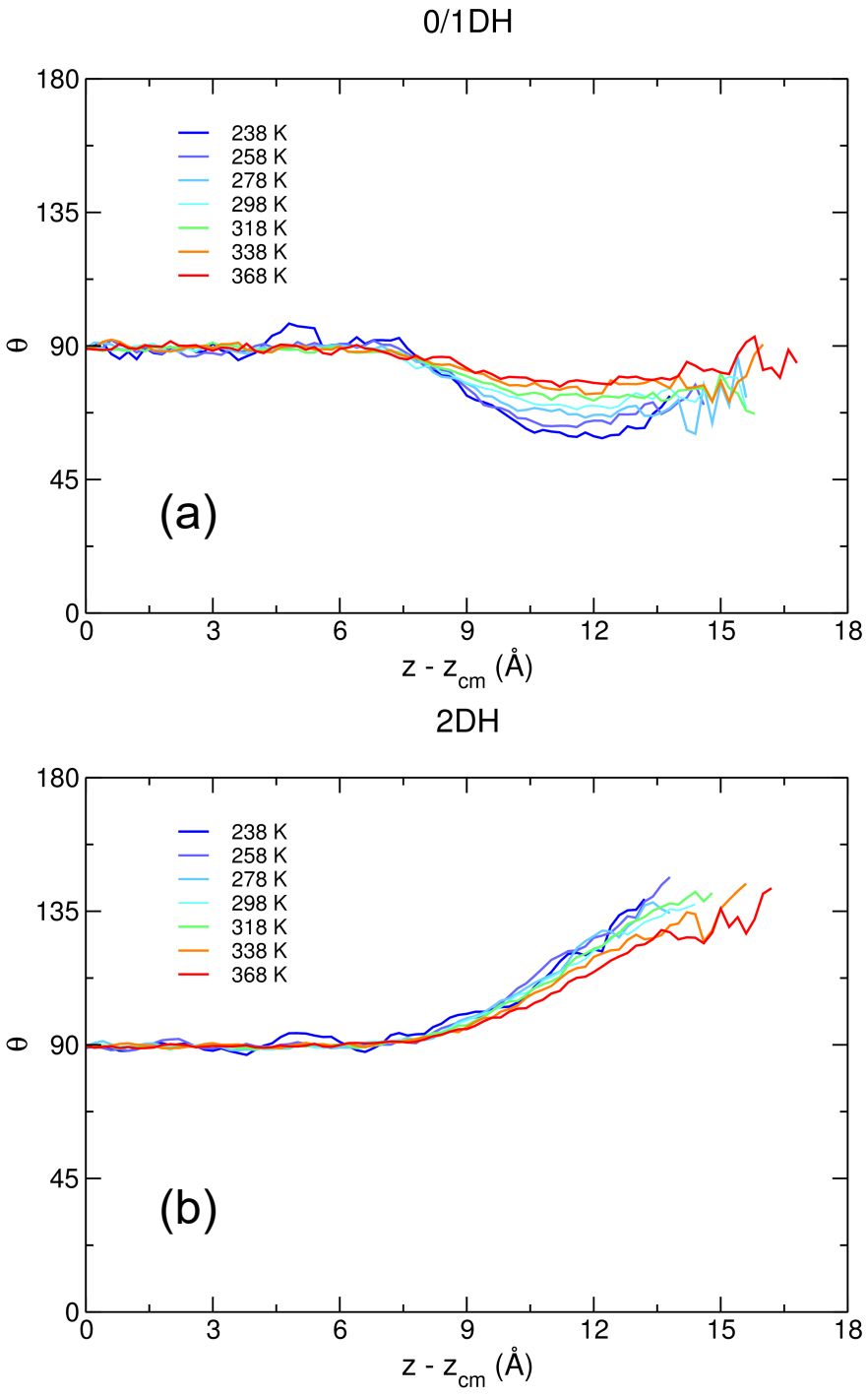

Figure S2: Temperature dependence of the average angle for water molecules as a function of distance from the center of mass of simulation slab for (a) 0/1DH and (b) 2DH.

$\chi^{(2)}_{ijk}$ Spectra - No Fresnel Factors

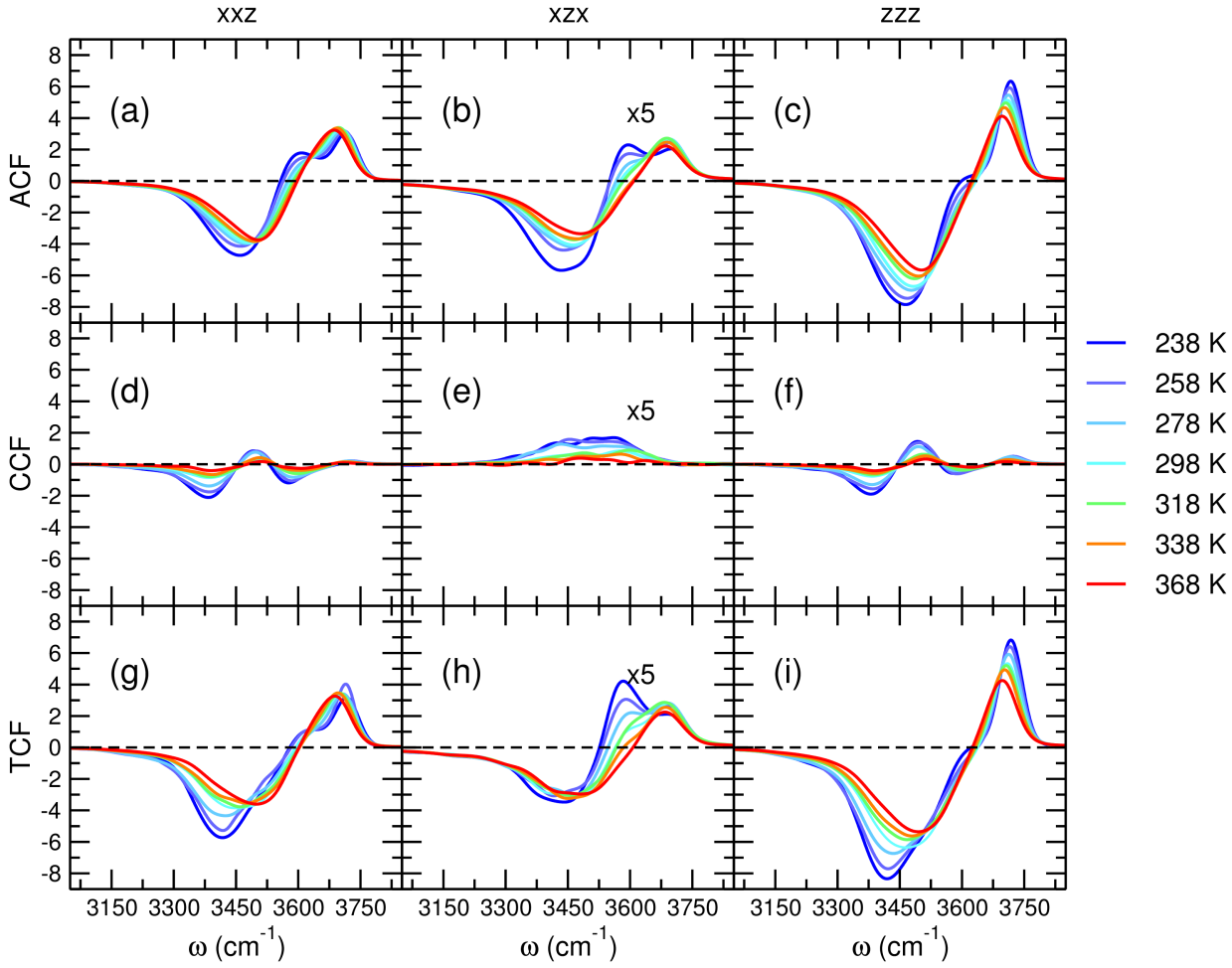

Figure S3: Polarization and temperature dependent vSFG spectra of the OH stretching region at the air/water interface. From top-to-bottom: auto-correlation contribution (ACF, a-c), cross-correlation contribution only (CCF, d-f), and total contribution (TCF, g-i) to the vSFG spectra with intermolecular cut-off of 4.0 Å. From left to right: imaginary components of $\chi^{(2)}_{xxz}(\omega)$, $\chi^{(2)}_{xzx}(\omega)$, and $\chi^{(2)}_{zzz}(\omega)$. All $\chi^{(2)}_{pqr}(\omega)$ were calculated according to Eq. 2 in the main text and normalized relative to $k_B T_{298}$ (see Table S1).

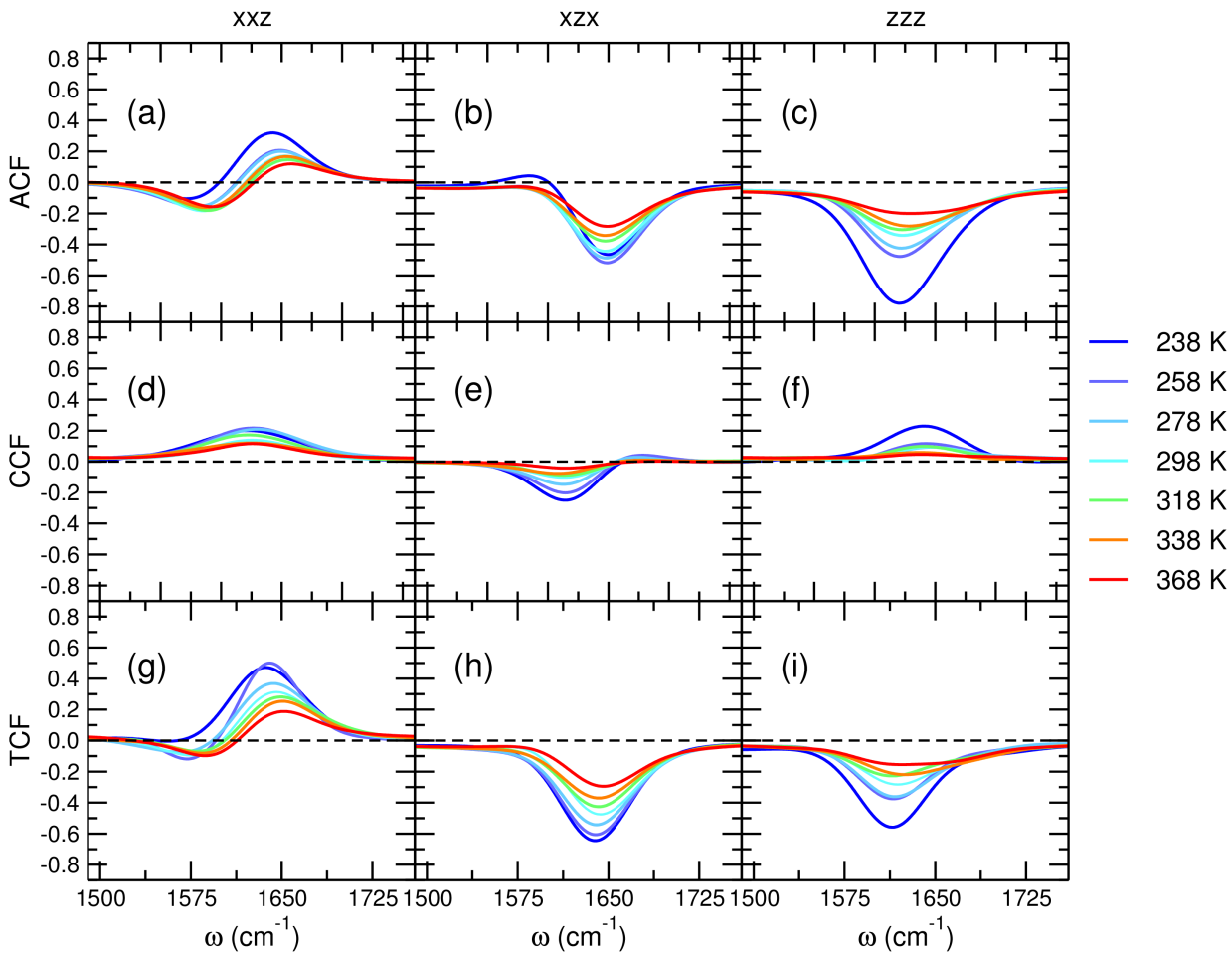

Figure S4: Polarization and temperature dependent vSFG spectra of the OH bending region at the air/water interface. From top-to-bottom: auto-correlation contribution (ACF, a-c), cross-correlation contribution only (CCF, d-f), and total contribution (TCF, g-i), to the vSFG spectra with intermolecular cut-off of 4.0 Å. From left to right: imaginary components of $\chi^{(2)}_{xxz}(\omega)$, $\chi^{(2)}_{xzx}(\omega)$, and $\chi^{(2)}_{zzz}(\omega)$. All $\chi^{(2)}_{pqr}(\omega)$ were calculated according to Eq. 2 in the main text and normalized relative to $k_B T_{298}$ (see Table S1).

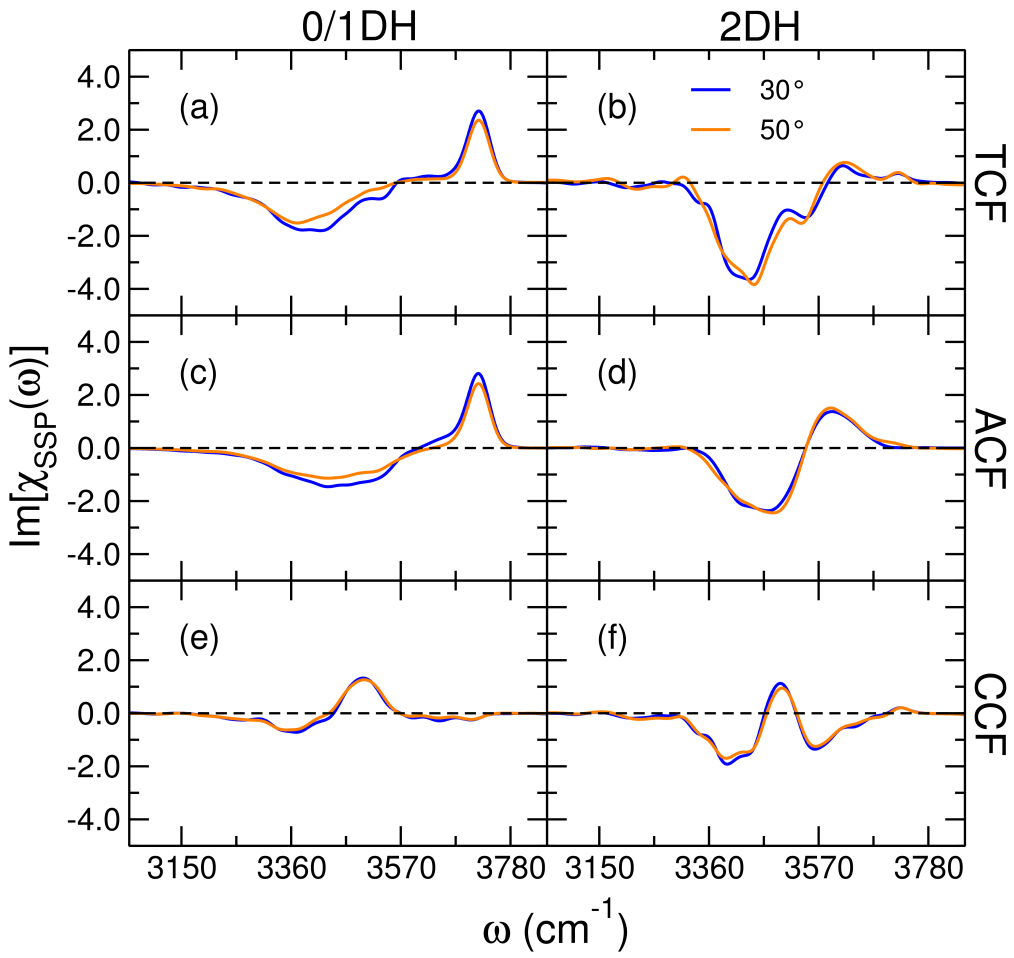

Figure S5: Comparison of (a, c, e) 0/1DH and (b, d, f) 2DH spectra using hydrogen bond angle cutoffs of 30° and 50° at 238 K. The top row contains the total correlation functions, the second row contains the autocorrelation function, and the third row contains cross-correlation function contributions. All $\chi^{(2)}_{pqr}(\omega)$ were calculated according to Eq. 2 in the main text and normalized relative to $k_B T_{298}$ (see Table S1).

Table S1: Redshift applied to each spectrum in the stretching region based on a linear fit to difference between classical and centroid molecular dynamics simulations performed in Ref. 1.

Temperature (K)	Stretching redshift (cm^{-1})	Bending redshift (cm^{-1})
238	155.96	59.39
258	157.62	57.97
278	159.27	56.56
298	160.93	55.14
318	162.59	53.73
338	164.24	52.31
368	166.73	50.19

References

(1) Reddy, S. K.; Moberg, D. R.; Straight, S. C.; Paesani, F. Temperature-Dependent Vibrational Spectra and Structure of Liquid Water from Classical and Quantum Simulations with the MB-pol Potential Energy Function. *J. Chem. Phys.* **2017**, *147*, 244504.