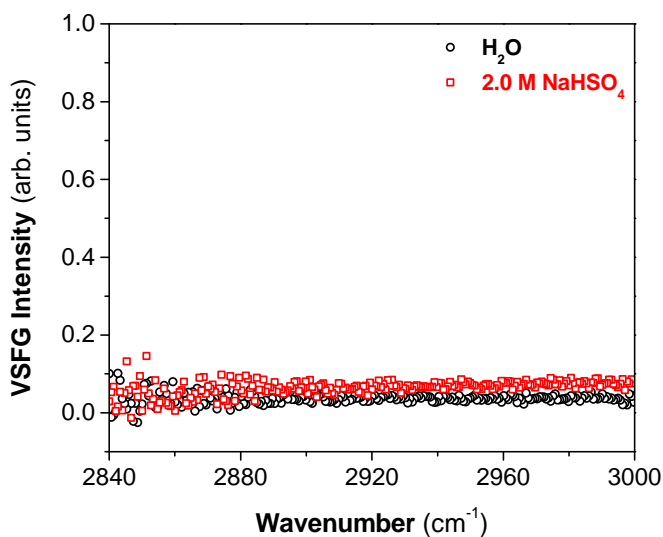


**Supporting Information to**  
**“Relative Order of Sulfuric Acid, Bisulfate, Hydronium, and Cations at the**  
**Air-Water Interface”**

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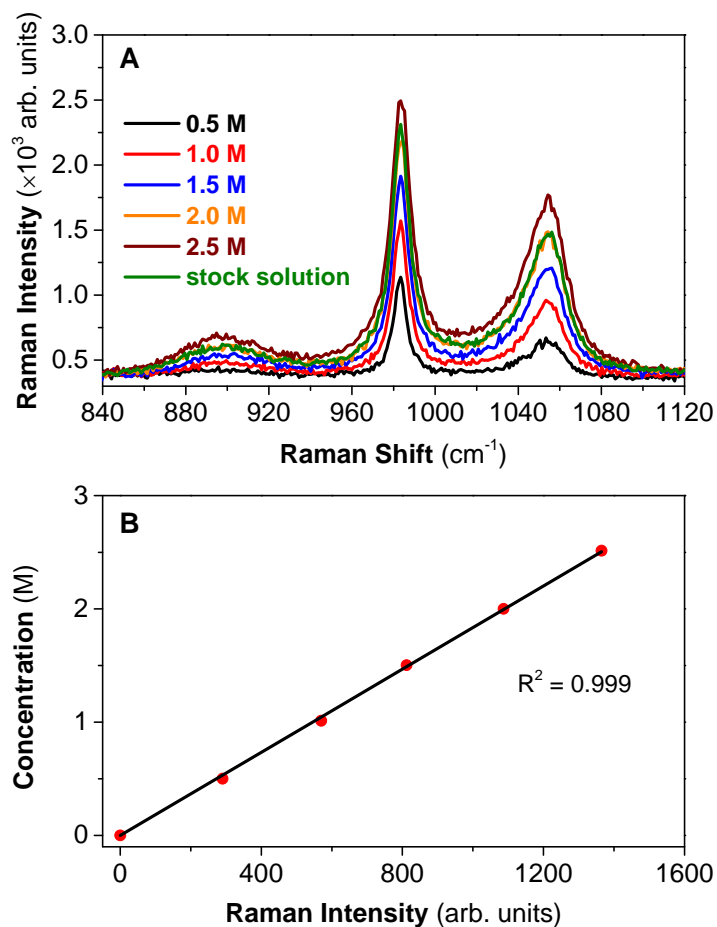
**SUPPLEMENTARY FIGURES**



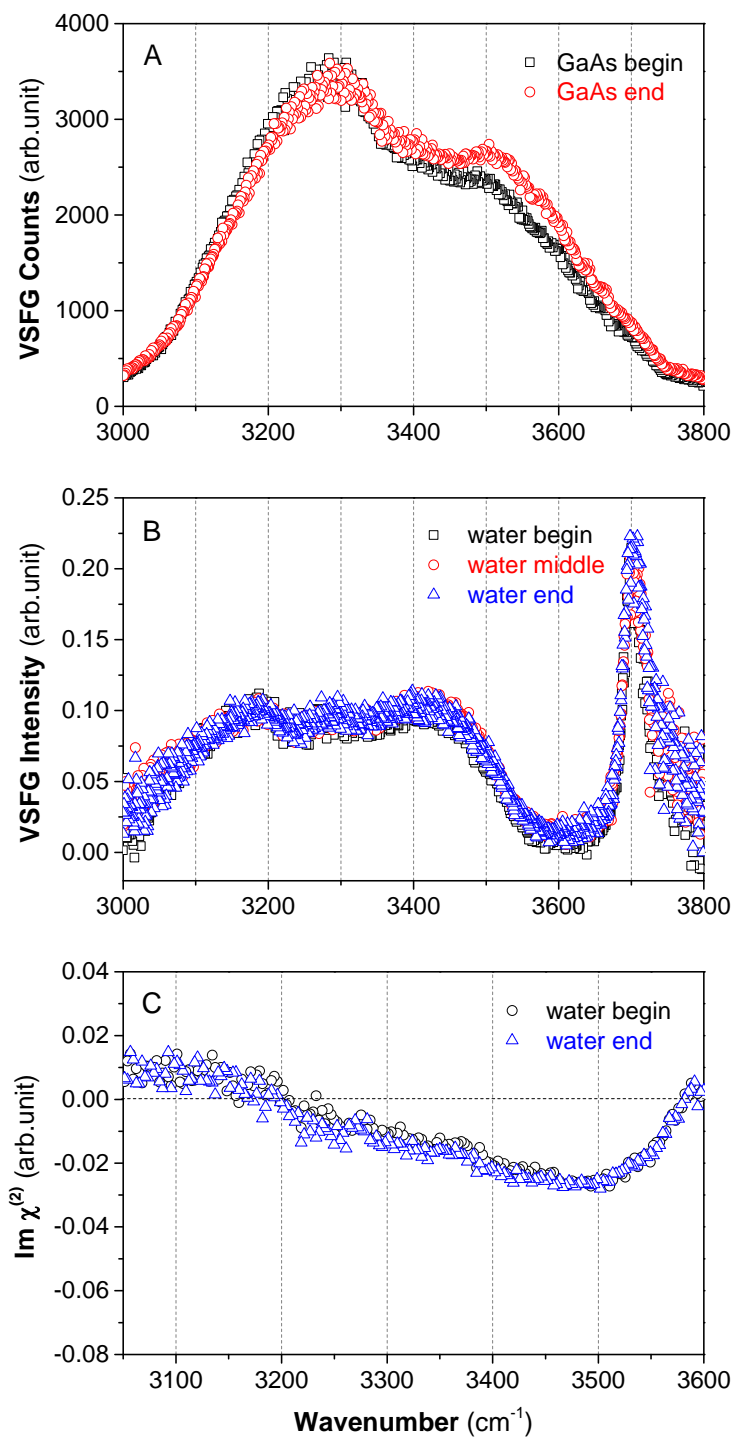
**Figure S1.** VSGF spectra of neat water and NaHSO<sub>4</sub> stock salt solution after filtration (2.0 M) in the surfactant CH stretching region (2800–3000 cm<sup>-1</sup>).

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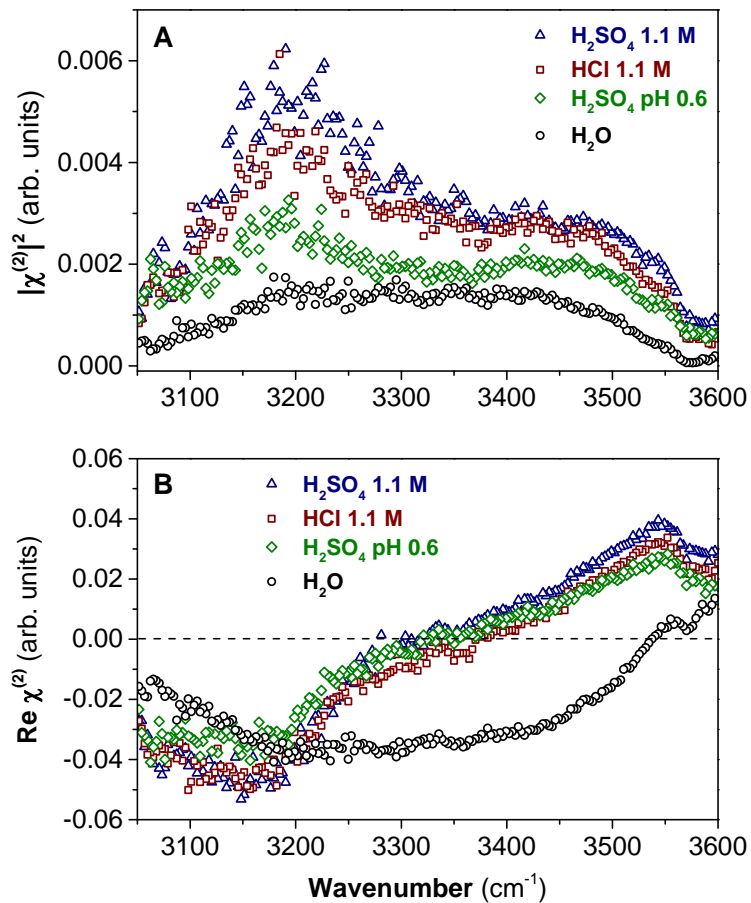
\* To whom correspondence should be addressed. E-mail: allen@chemistry.ohio-state.edu.



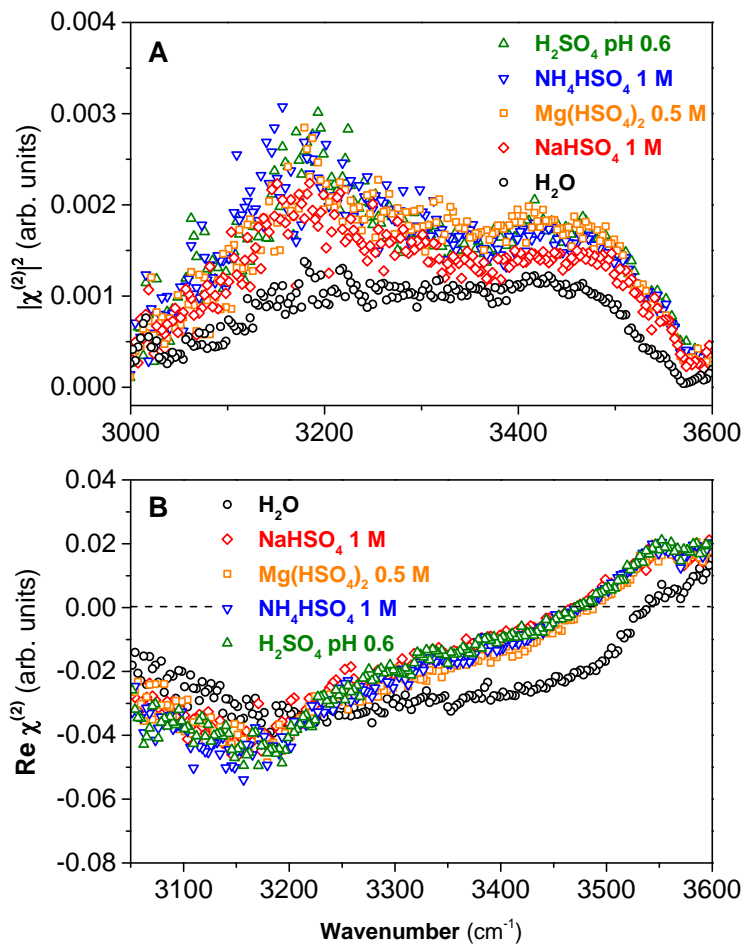
**Figure S2.** (A) Raman spectra of 0.5, 1.0, 1.5, 2.0, and 2.5 M unfiltered NaHSO<sub>4</sub> calibration solutions, as well as filtered VSGF stock solution (2.0 M), (B) calibration curve of NaHSO<sub>4</sub> solutions using the peak height of the HSO<sub>4</sub><sup>-</sup> stretching mode ( $\sim 1052$   $\text{cm}^{-1}$ ) from each individual Raman spectrum. The concentrations of MgSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> VSGF stock solutions were determined in the same manner.



**Figure S3.** Stability of the SFG system in the course of a typical experiment exemplified by the (A) GaAs profile, (B) VSGF and (C) HD-VSGF ( $\text{Im } \chi^{(2)}$ ) spectra of neat water in the OH stretching region (3000–3800 cm<sup>-1</sup> and 3000–3600 cm<sup>-1</sup>, respectively).



**Figure S4.** (A) Power spectra  $|\chi^{(2)}|^2$  and (B)  $\text{Re } \chi^{(2)}$  spectra extracted from HD-VSFG results of 1.1 M H<sub>2</sub>SO<sub>4</sub>, 1.1 M HCl, pH 0.6 (0.26 M) H<sub>2</sub>SO<sub>4</sub> acid solutions in the OH stretching region (3050–3600 cm<sup>-1</sup>). Neat water spectra are shown as reference.



**Figure S5.** (A) Power spectra  $|\chi^{(2)}|^2$  and (B)  $\text{Re } \chi^{(2)}$  spectra extracted from HD-VSFG results of pH 0.6 H<sub>2</sub>SO<sub>4</sub> acid solution, and 1 M NH<sub>4</sub>HSO<sub>4</sub>, 0.5 M Mg(HSO<sub>4</sub>)<sub>2</sub>, and 1 M NaHSO<sub>4</sub> salt solutions in the OH stretching region (3050–3600 cm<sup>-1</sup>). Neat water spectra are shown as reference.