

**Supporting Information to**  
**“Surface Prevalence of Perchlorate Anions at the Air/Aqueous Interface”**

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**EXPERIMENTAL DETAILS**

**Materials.** NaClO<sub>4</sub>·H<sub>2</sub>O (Fisher Scientific, Crystalline/Laboratory) was used as-received. Ultrapure water (not purged of CO<sub>2</sub>) with a resistivity of 18.2–18.3 MΩ·cm and a measured pH of 5.6 was obtained from a Barnstead Nanopure system (model D4741, Thermolyne Corporation) equipped with additional organic removing cartridges (D5026 Type I ORGANICfree Cartridge Kit; Pretreat Feed). Because the ultrapure water was not degassed, its pH was slightly acidic due to the dissolution of gaseous CO<sub>2</sub>.

**Preparation of Salt Solutions.** NaClO<sub>4</sub> stock salt solution for VSFG measurements was prepared by dissolving salt in ultrapure water. Owing to its ultrahigh sensitivity, VSFG spectra obtained in the surfactant CH stretching region (2800–3000 cm<sup>-1</sup>) were utilized as a probe to verify the presence of trace amount organic contaminants. As revealed in these spectra, organic contamination was found in NaClO<sub>4</sub> stock salt solution prior to any pretreatment (data not shown). To completely eliminate organic impurities, NaClO<sub>4</sub> stock solution was filtered four times using activated carbon filters (Whatman Carbon Cap 75, Fisher Scientific). After thorough removal of organic contaminations, for the same inorganic salt, solutions made from ACS and

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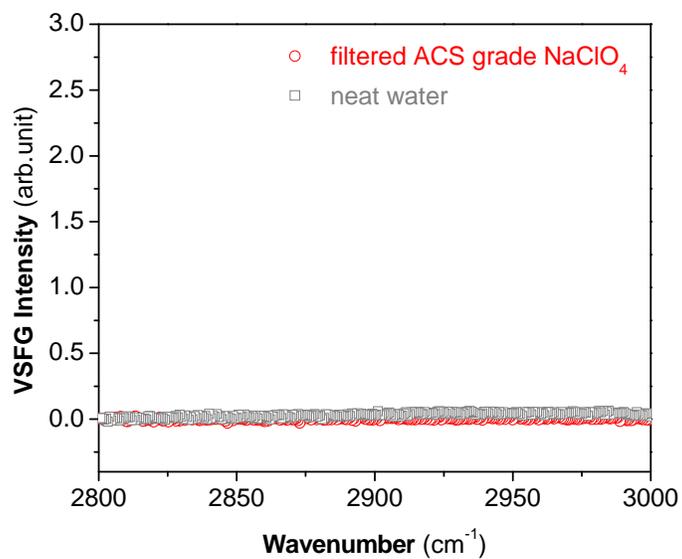
ultrapure grade salts (trace metal basis, purities ranging from 99.99% to 99.9999%) perturb the conventional and HD-VSFG spectra in the water OH stretching region mostly to the same extent.<sup>1</sup> Raman calibration curves were obtained to determine the concentration of perchlorate after filtration based on vibrational symmetric stretch mode of  $\text{ClO}_4^-$  ion ( $\sim 935 \text{ cm}^{-1}$ ). The measured pH of 1.7 M  $\text{NaClO}_4$  was  $\sim 5.9$ . The pretreated (filtered)  $\text{NaClO}_4$  stock salt solution was shown to be free of organic impurities as revealed by the conventional VSFG spectra obtained in the CH stretching region (Figure S1). All solutions were thermally equilibrated to room temperature ( $23 \pm 1 \text{ }^\circ\text{C}$ ) over 24 h before use. No degassing or  $\text{N}_2$ -purging has been applied on them.

**Conventional and Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy.** Conventional VSFG spectroscopy measurements were performed on a broad-bandwidth VSFG spectrometer setup which has been described in detail elsewhere.<sup>2,3</sup> The heterodyne-detected (HD-) VSFG spectroscopy setup is mostly based on the conventional one, with the optical configuration in the sample stage area redesigned for the new application.<sup>4,5</sup> The latter setup is similar to the system reported by Tahara and co-workers,<sup>6</sup> which is based on heterodyne detection of broad bandwidth signals and Fourier transform analysis. The HD-VSFG setup and the data processing procedure have been described elsewhere in detail.<sup>4,5,7</sup> Here, only the modifications made to the experimental setup and calculated parameters are presented. Briefly, the full spectral bandwidth of the generated broadband infrared beam has been expanded from  $3000$  to  $3600 \text{ cm}^{-1}$  ( $\sim 600 \text{ cm}^{-1}$ ) in the current HD-VSFG setup in the OH stretching region. The average incident energy of the visible (*s*-polarized,  $800 \text{ nm}$ ) and infrared (*p*-polarized, OH stretching region) beams prior to the sample stage was reduced to  $260 \mu\text{J}$  and  $8 \mu\text{J}$ , respectively. The primary SF beam is time-delayed by  $1.7 \text{ ps}$  by its passage through a thin silica plate ( $<1$  Neat water spectra were used as a reference for salt comparison to assess reproducibility during

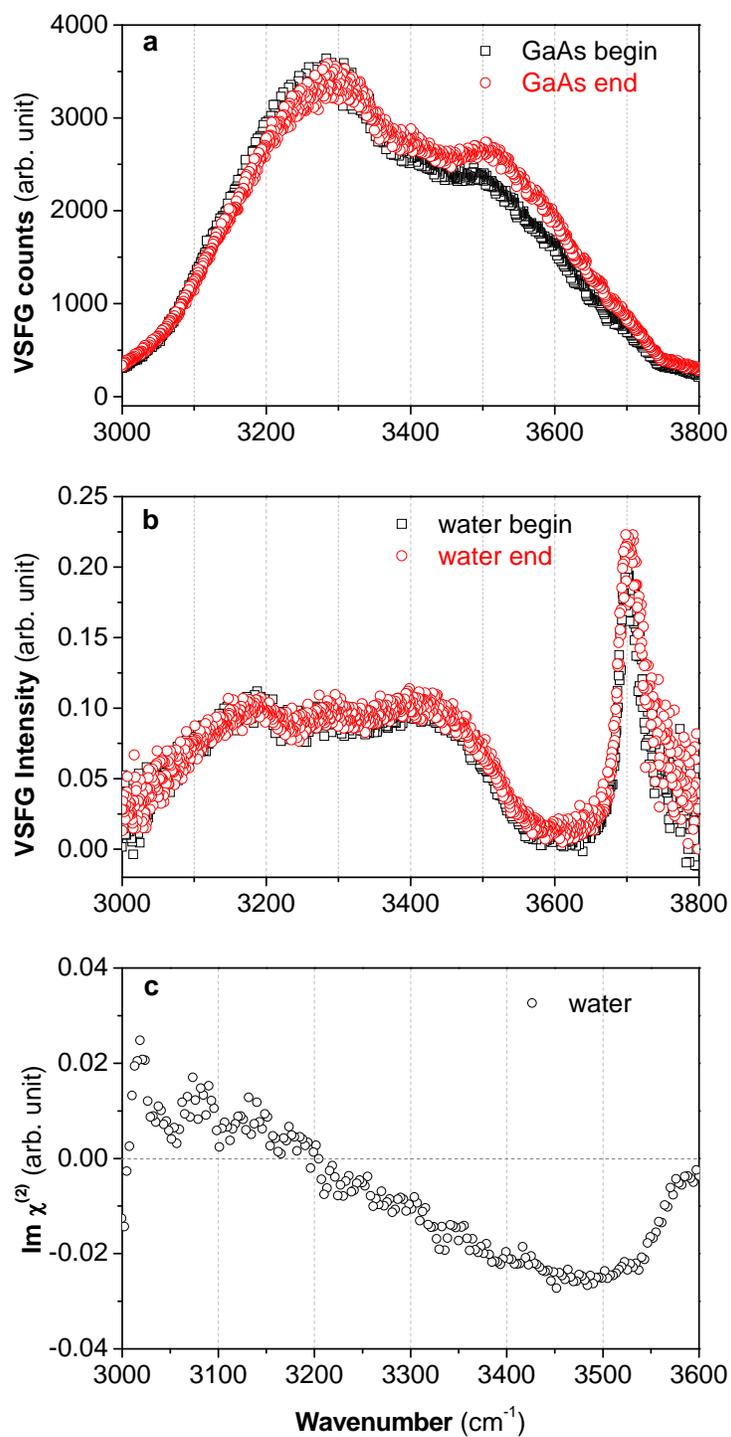
the whole experimental period. The reproducibility for both conventional and HD-VSFG ( $\text{Im } \chi^{(2)}$ ) spectra of neat water is demonstrated in the Figure S2. Critical here is that all  $\text{Im } \chi^{(2)}$  spectra of salt solutions are compared to that of neat water. Thus our interpretation is based on the *relative* difference between neat water and the salt solutions. To check the validity in the general trend of these spectra, the deduced  $|\chi^{(2)}|^2$  power spectra of each salt solution (Figure S3a) reconstructed from the HD-VSFG results are compared to those measured directly by conventional VSFG spectroscopy. Only every fourth data points are plotted in the HD-VSFG spectra to avoid spectral clutter.

**Infrared and Raman Spectroscopy.** Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and Raman spectroscopy for bulk solution measurements were also performed. The setups for both measurements have been described in detail elsewhere.<sup>8</sup> The Raman and IR spectra of 1.0 and 1.7 M  $\text{NaClO}_4$  salt solutions are shown in Figure S4.

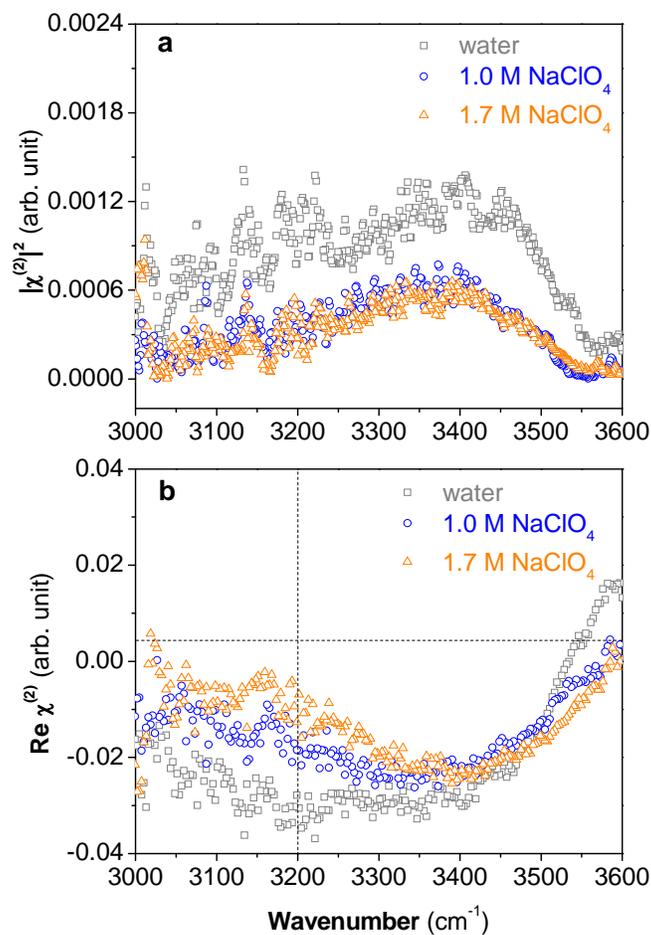
## SUPPLEMENTARY FIGURES



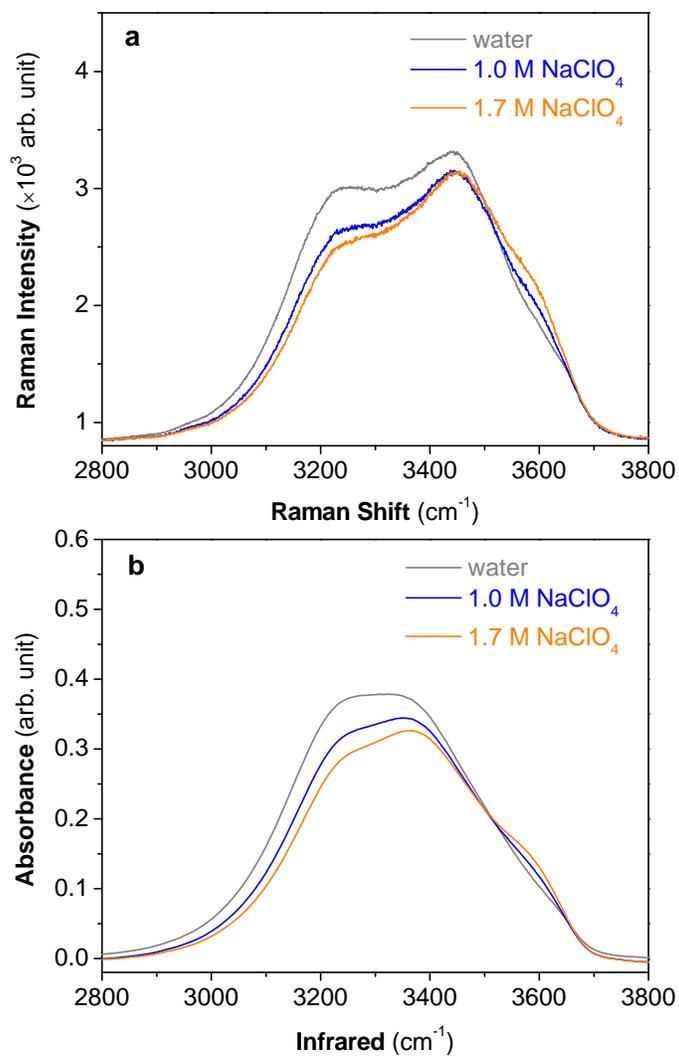
**Figure S1.** Conventional VSFG spectra in the CH stretching region (2800–3000 cm<sup>-1</sup>) of the air/aqueous interface of neat water and filtered NaClO<sub>4</sub> stock salt solution.



**Figure S2.** Stability of the SFG system shown by the GaAs profile, conventional VSF and HD-VSF  $\text{Im } \chi^{(2)}$  spectra of neat water in the OH stretching region (3000–3800  $\text{cm}^{-1}$ ). (a) GaAs profile and (b) conventional VSF spectra in the OH stretching region, and (c)  $\text{Im } \chi^{(2)}$  spectra in the OH stretching region from 3000 to 3600  $\text{cm}^{-1}$ .



**Figure S3.** (a) Deduced power spectra  $|\chi^{(2)}|^2$  and (b)  $\text{Re } \chi^{(2)}$  spectra from HD-VSFG results of 1 and 1.7 M NaClO<sub>4</sub> salt solutions in the OH stretching region (3000–3600 cm<sup>-1</sup>). Neat water spectra are shown as reference. (Note that the similarity between the reconstructed intensity spectra in Figure S3(a) and the difference of their corresponding  $\text{Im } \chi^{(2)}$  spectra (Figure 1b) can be explained by the presence of interference effects (e.g. interference with the non-resonant background, convolution effects with the real part of the nonlinear susceptibility ( $\text{Re } \chi^{(2)}$ ), etc.) (see *J. Am. Chem. Soc.* **2008**, *130*, 13033 for a detailed discussion).



**Figure S4.** (a) Raman spectra and (b) IR spectra of 1.0 and 1.7 M  $\text{NaClO}_4$  salt solutions. Neat water spectrum is shown as a reference.

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