Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface-Specific Vibrational Spectroscopy of the Water/Silica Interface: Screening and Interference

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S1. Normalized SFG spectra of water at the silica surface

In the manuscript, we show the raw SFG spectra taken from the silica/water interface. For comparison, Figure S1 presents the same spectra shown in Figure 1, after normalization by the non-resonant signal from a chromium-free gold coated silica window. The double feature in the O-H stretch region reported previously[1] is reproduced.

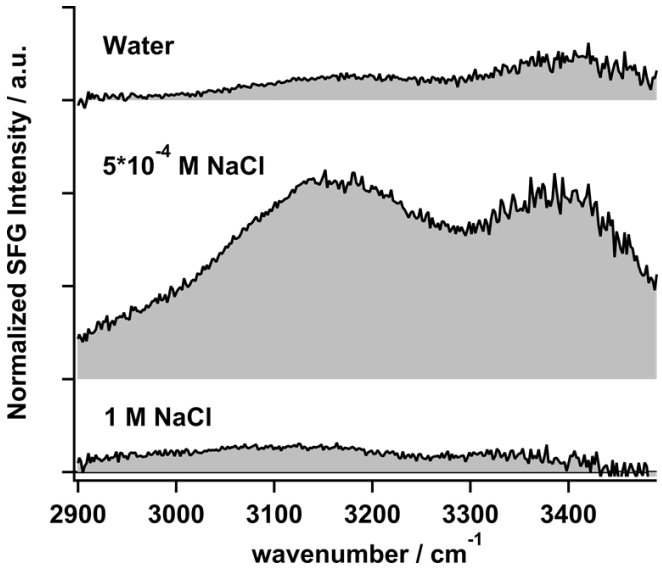

Figure S1: Normalized SFG spectra of the silica / water interface obtained from the raw data shown in Figure 1, normalized by the non-resonant signal from a chromium-free gold coated silica window

S2. Expression for the potential, Debye length and wave-vector mismatch

Based on the previously reported theoretical model[2], we determined the ratios between the non-linear susceptibilities $\chi^{(3)}/\chi^{(2)}$. For a 1:1 electrolyte solution, the explicit definitions of the surface potential ϕ_0, Debye length κ and wave vector Δk_z are given in equation S1-S3.

$$\phi_0(c) = \frac{2k_BT}{e_c}\sinh^{-1}\left(\frac{\sigma_0}{\sqrt{8000k_BTN_Ac\varepsilon_0\varepsilon_r}}\right) \quad \text{(S1)}$$

$$\kappa(c) = \sqrt{\frac{2000e_c^2N_Ac}{\varepsilon_0\varepsilon_rk_BT}} \quad \text{(S2)}$$

$$\Delta k_z = \frac{\sqrt{n_{SFG}^2 - \sin^2(\theta_{SFG})}}{\omega_{SFG}} + \frac{\sqrt{n_{VIS}^2 - \sin^2(\theta_{VIS})}}{\omega_{VIS}} + \frac{\sqrt{n_{IR}^2 - \sin^2(\theta_{IR})}}{\omega_{IR}} \quad \text{(S3)}$$

where k_B is the Boltzmann constant, T the temperature, e_c the elementary charge, σ_0 the surface charge density, N_A Avogadro's number, c the electrolyte concentration, ε_0 the vacuum permittivity, ε_r the relative permittivity of water, n_i the refractive index, ω_i the frequency and θ_i the angle between the beam and the surface normal.

S3. Uncertainty on the non-linear susceptibility ratio

Surface charge densities, σ_0, as reported for silica around neutral pH silica are $-0.06\ C/m^2 < \sigma_0 < -0.02\ C/m^2$.[3-7] Here, we compare the effect of the different values of σ_0 on the shape of the SFG intensity and obtain for the $\chi^{(3)}/\chi^{(2)}$ values ranging from $-16.50\ V^{-1}$ to $-22.25\ V^{-1}$. The resulting curves are shown in Figure S2

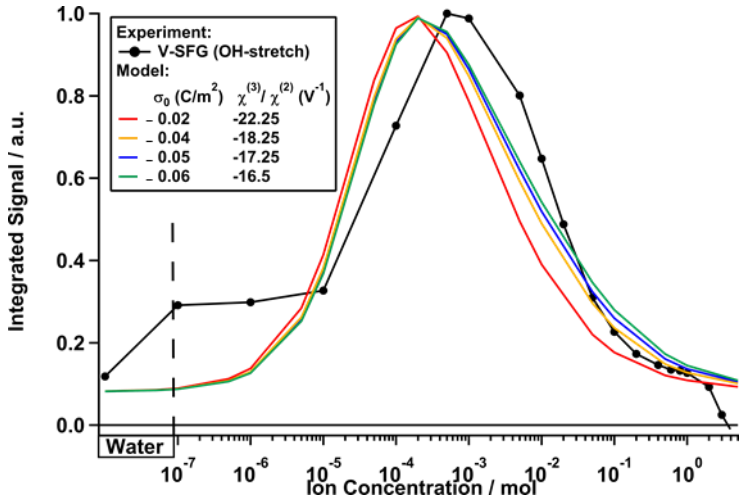

Figure S2: Intensity curves resulting from equation 4, assuming different surface charge densities σ_0 and adjusting the $\chi^{(3)}/\chi^{(2)}$, compared to the experimental data for solutions with varying NaCl concentrations.

References

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