Supporting Information for

An Optical Voltmeter for Studying the Interaction of Cetyltrimethylammonium Bromide

Interacting with Fused Silica/Aqueous Interfaces at High Ionic Strength

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Figure S1: The experimental setup and flow cell used in SHG experiments. See experimental methods section for further details.
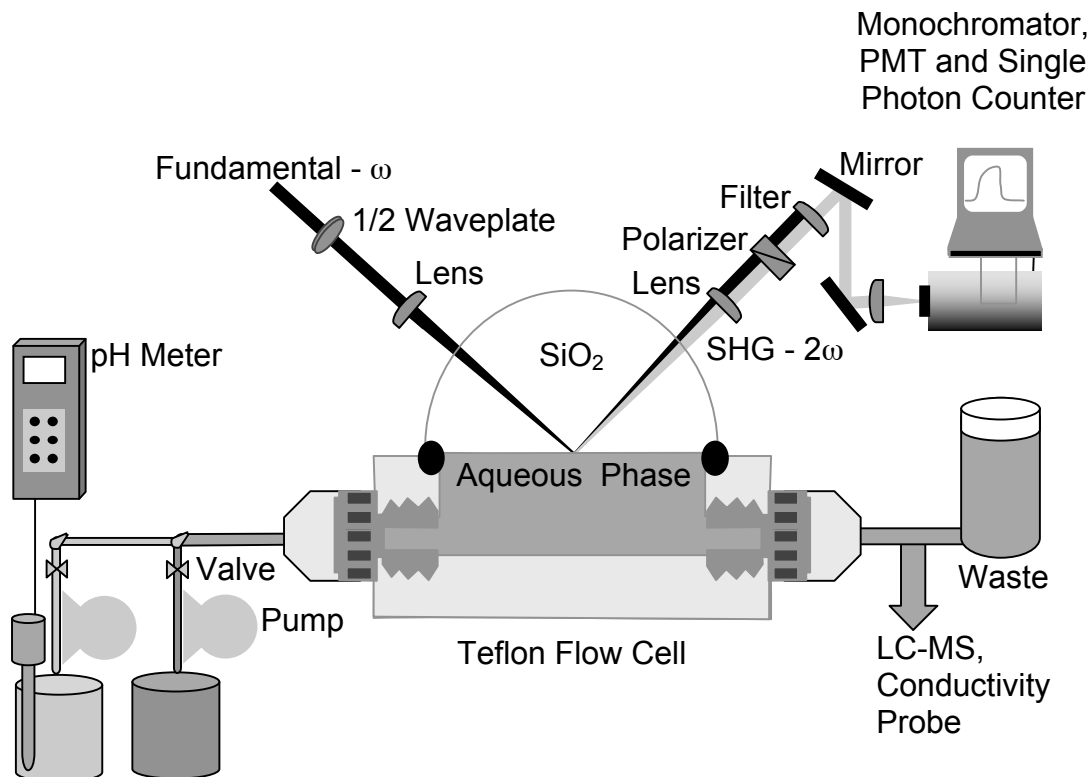
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Figure S2: LC-MS calibration curves for CTA quantification from pH 11 solutions containing **(A)** 10 mM NaCl **(B)** 100 mM NaCl **(C)** 300 mM NaCl and **(D)** 500 mM NaCl. See text for experimental conditions.
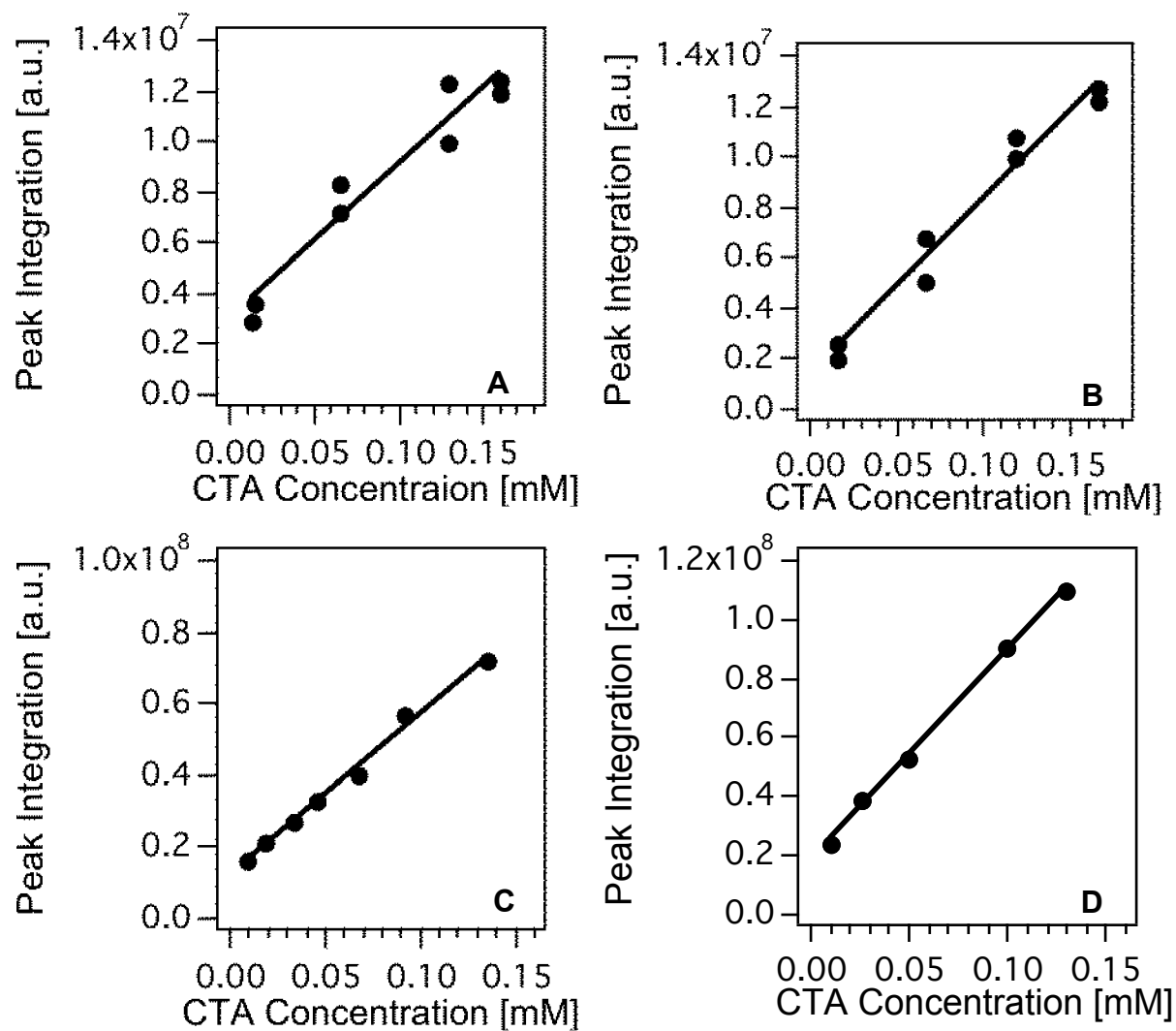
Figure S3: CMC determination from interfacial tension measurements for CTAB in the presence of **(A)** 10 mM, **(B)** 100 mM, **(C)** 300 mM, and **(D)** 500 mM NaCl. The CMCs are 2.2(2) x 10^{-4} M, 2.6(3) x 10^{-4} M, 3.8(3) x 10^{-4} M, and 5.1(5)x 10^{-4} M, respectively. For reference, the CMC for CTAB without added salt was determined to be 9.6(1) x 10^{-4} M. Values obtained in this work agree well with literature CMC values for cetyltrimethylammonium surfactants with 0 mM, 10 mM and 100 mM added salt.[1,2] To our knowledge CMCs have not been previously determined for cetyltrimethyammonium surfactants with 300 and 500 mM added salt. Interfacial tensions (IFT) were measured using the pendant drop method.[3] Following the procedure described by Rehfeld[4] the low concentration region was fitted with a third-order Taylor series with argument *ln[CTA]*. The CMC was determined from the intersection of this fit with a linear least-squares fit of the high concentration region. Errors were estimated by propagating the standard deviation of the IFT measurements through the fits and the intersection calculations.
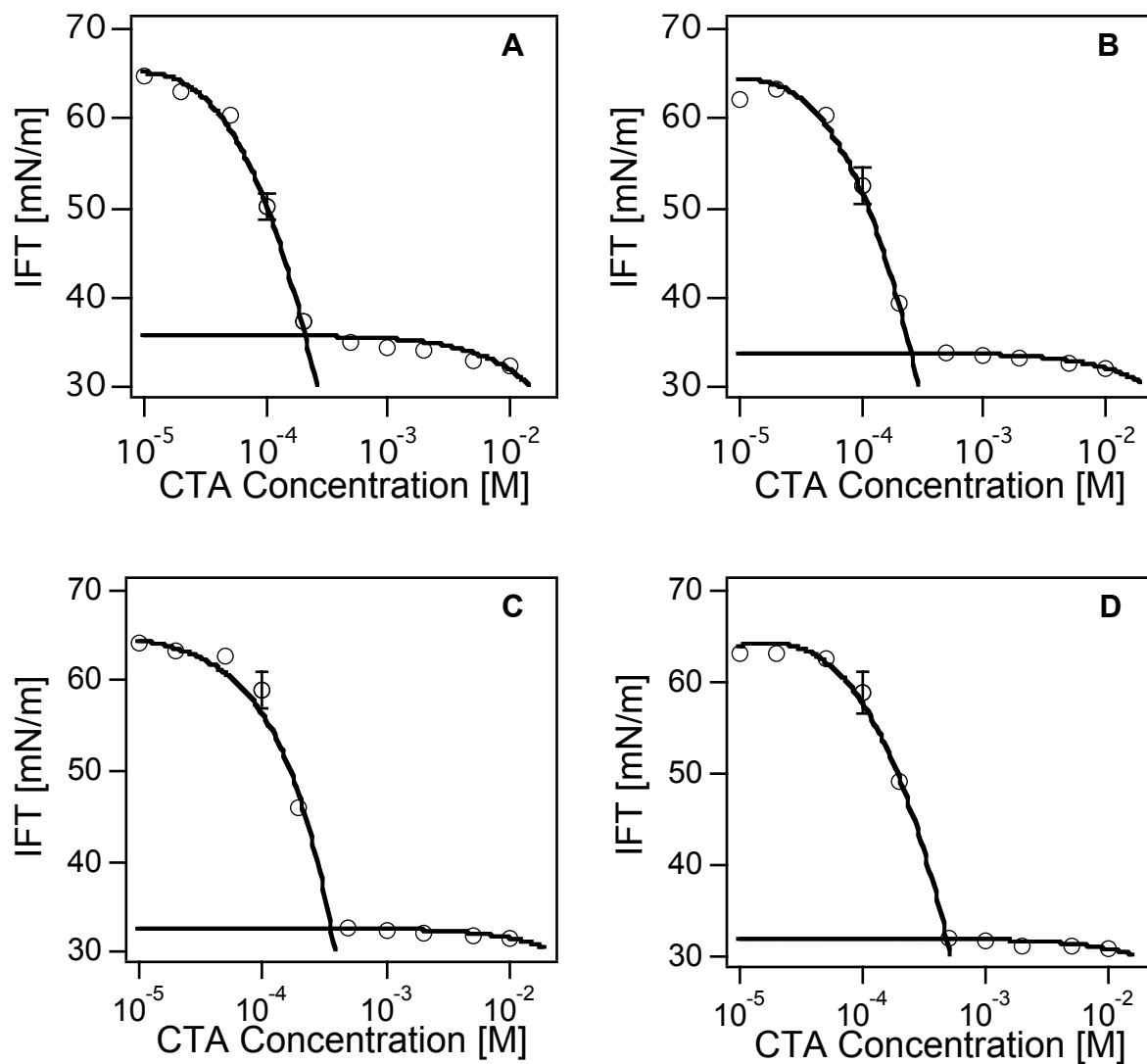
Figure S3 (Cont.):

Figure S4: FFG fits to SHG isotherms for CTA with **(A)** 10 mM, **(B)** 100 mM, **(C)** 300 mM, and **(D)** 500 mM NaCl. The solid lines represent fits to the data using the FFG equation and the dashed lines represent the corresponding fits to the Langmuir model. To allow for fitting with the FFG equation, the SHG data was converted to relative surface coverage using the following procedure. First, the data was offset so that surface saturation corresponds to zero and then normalized. Second, each data point was subtracted from one to obtain relative surface coverage. (*n.b.* This procedure assumes that surface potential is linearly proportional to surface charge density, which is consistent with the constant capacitance model.) The data was fitted to the FFG model using our previously described procedure.[5]
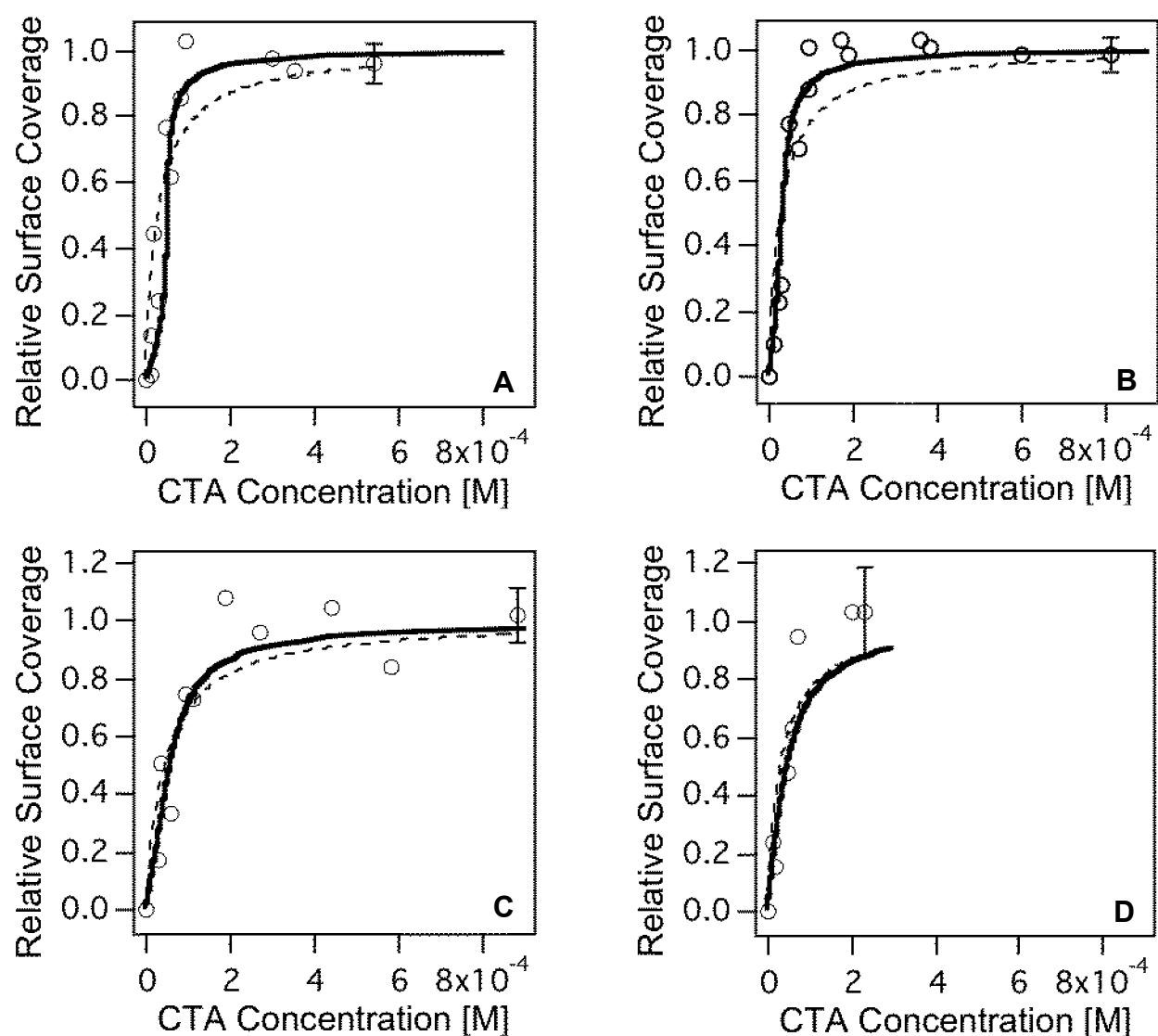
Figure S5: Summary of binding parameters obtained from Frumkin-Fowler-Guggenheim fits for CTA adsorption to the silica/aqueous electrolyte interface at pH 11 and 295 K. It should be noted that K_{ads} and ΔG_{ads} values from the FFG fits correspond to the low concentration limit. The decreasing g values with increasing NaCl concentration indicate that the binding constant at high NaCl concentrations is not influenced strongly by surface coverage.

[NaCl] (mM)	K_{ads} (M^{-1})	$-\Delta G_{ads}$ (kJ/mol)	g
10	$0.4(1) \times 10^4$	30.2(7)	3.7(5)
100	$0.7(2) \times 10^4$	31.6(9)	2.6(6)
300	$0.7(2) \times 10^4$	32(1)	1.7(8)
500	$1.3(6) \times 10^4$	33(1)	0.9(8)

Figure S6: SHG adsorption isotherms for CTA with **(A)** 10 mM , **(B)** 100 mM, **(C)** 300 mM, and **(D)** 500 mM NaCl as a background electrolyte concentration. Each trace is a fit of the triple layer model to a separate isotherm experiment. Triangles and dashed lines are offset for clarity. See text for fitting details. From fitting the data at the four NaCl concentrations, an average surface density of 2.8(3) x 10^{13} charges/cm^2 was determined.
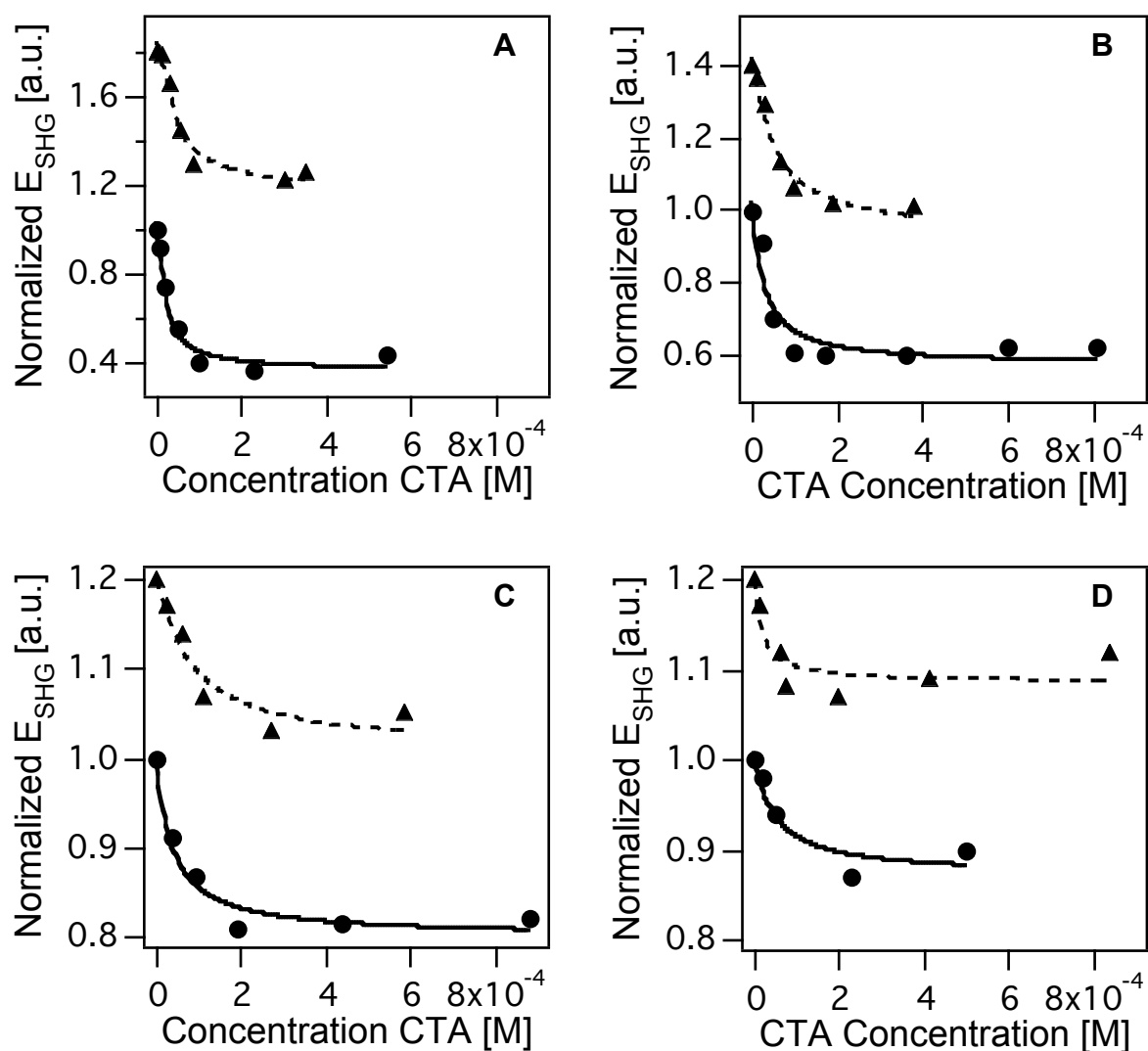
Figure S7: Surface charge densities, as determined from the triple layer fits described in Figure
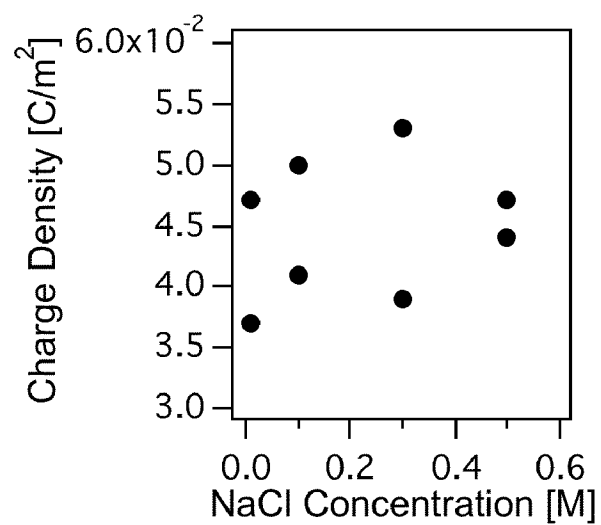
5, displayed versus the corresponding NaCl concentrations.

Figure S8: ssp-polarized SFG spectra obtained from the silica/aqueous interface at pH 11 in the presence of **(A)** 0.025 mM, **(B)** 0.05 mM, **(C)** 0.1 mM CTA, and **(D)** 0.5 mM CTA. All spectra were collected with 10 mM NaCl and under non-flowing conditions. Peak assignments are given in the main text. The broad shoulder above 3000 cm^{-1} is due to the vibrational resonances of interfacial water. In spectrum A, the CTA surface coverage is low enough that the surface is still negatively charged and orients water molecules giving rise to the observed shoulder. In spectrum B, the net charge at surface is near zero, and thus the water signal is not observed. In spectra C and D, the shoulder reappears as the surface becomes more positively charged with increasing CTA surface coverage and water is again oriented relative to the interface.
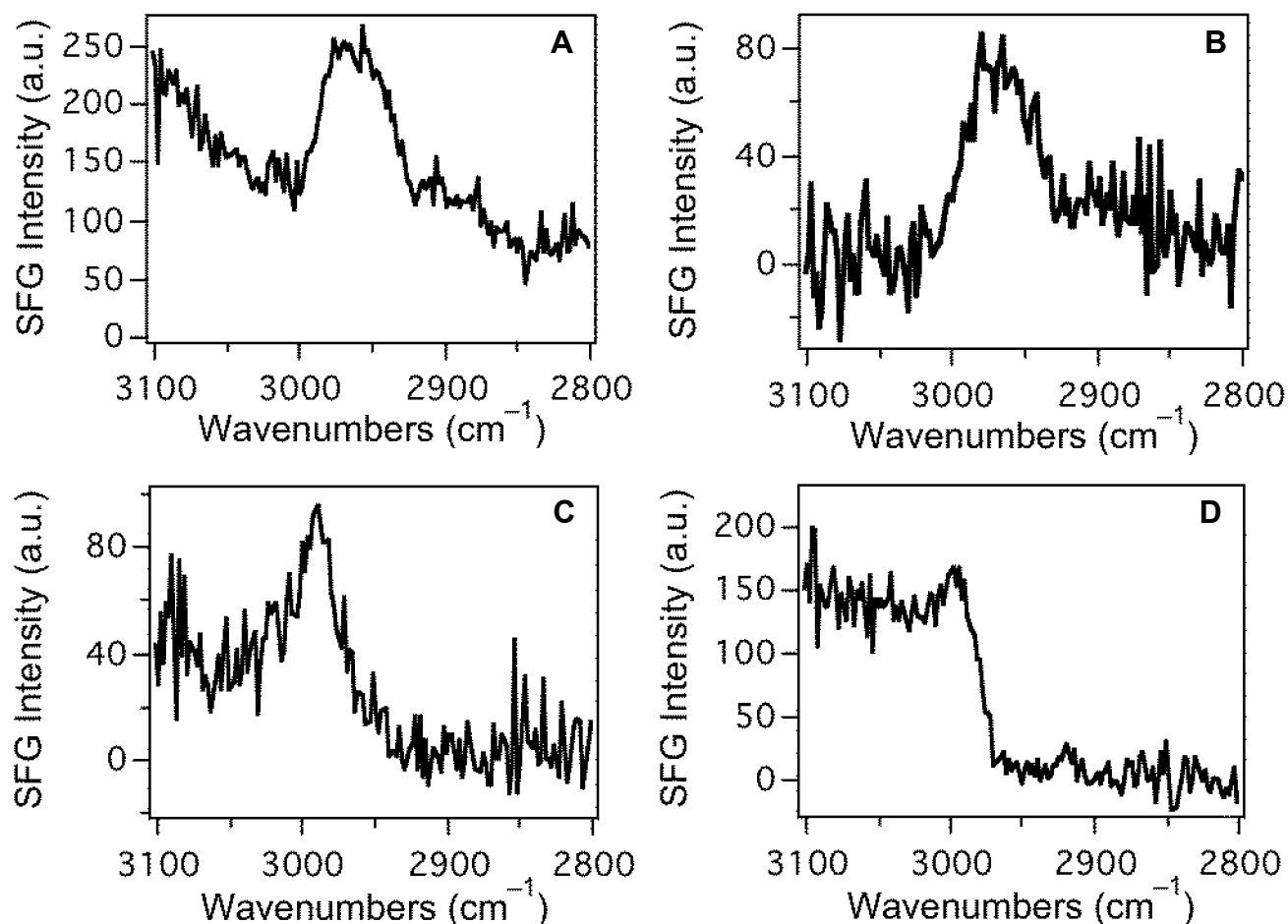
Figure S9: Normalized time-resolved SFG spectra of 30 μM CTA adsorbing to the silica/aqueous interface in 10 mM NaCl at **(A)** t = 30s, **(B)** t = 330s, **(C)** t = 20 min. The dashed and dotted lines in each panel represent where the nonresonant and resonant signals were measured, respectively. Spectra are truncated to only include region where IR laser pulse intensity is greater than 50% of maximum.
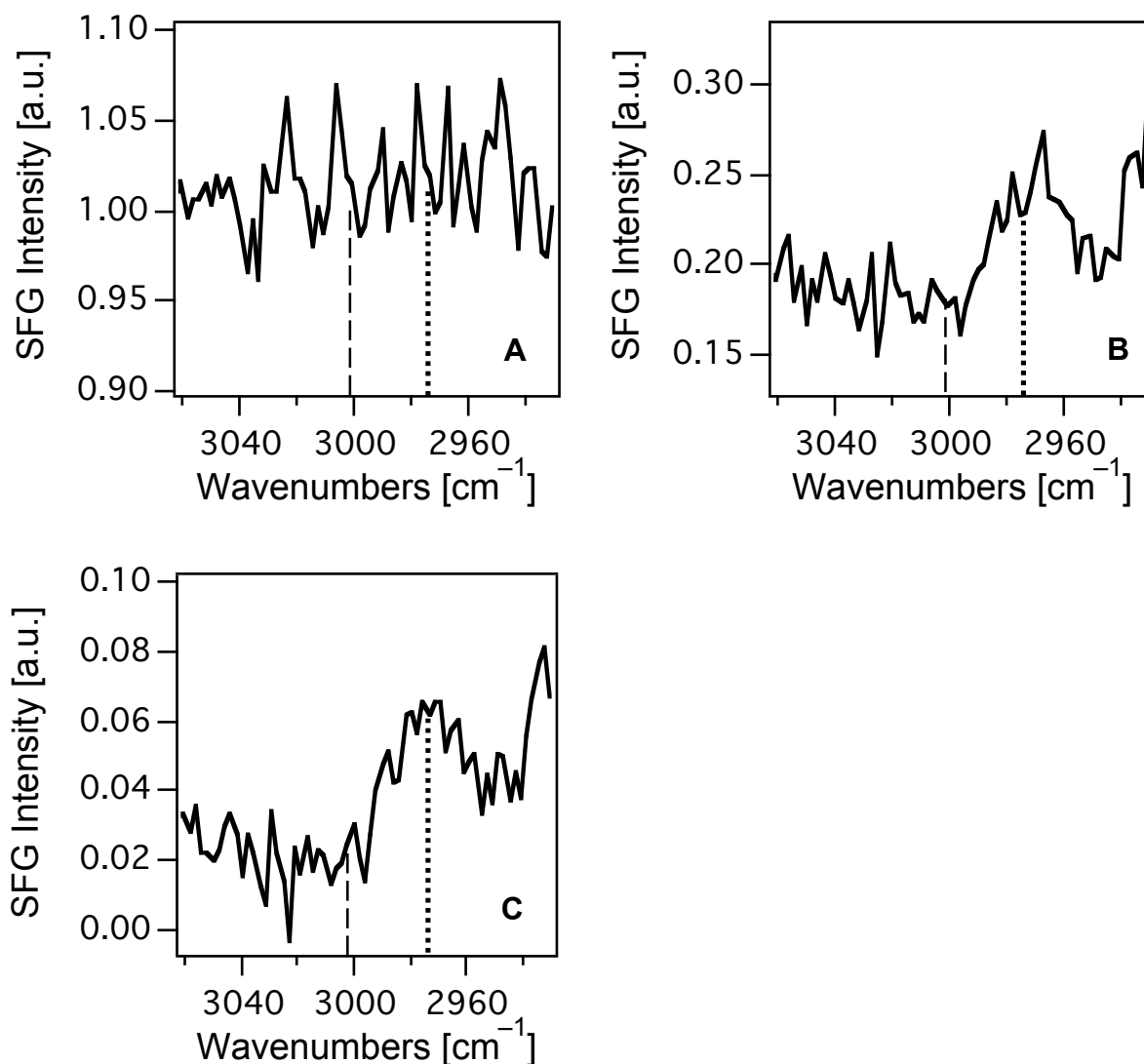
References:

(1)   Velegol, S. B.; Fleming, B. D.; Biggs, S.; Wanless, E. J.; Tilton, R. D. *Langmuir* **2000**, *16*, 2548.

(2)   Goloub, T. P.; Koopal, L. K.; Bijsterbosch, B. H.; Sidorova, M. P. *Langmuir* **1996**, *12*, 3188.

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(4)   Rehfeld, S. J. *J. Phys. Chem.* **1967**, *71*, 71.

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