Supporting Information for "Sulfate Adsorption at the Buried Fluorite - Solution Interface Revealed by Vibrational Sum Frequency Generation Spectroscopy"

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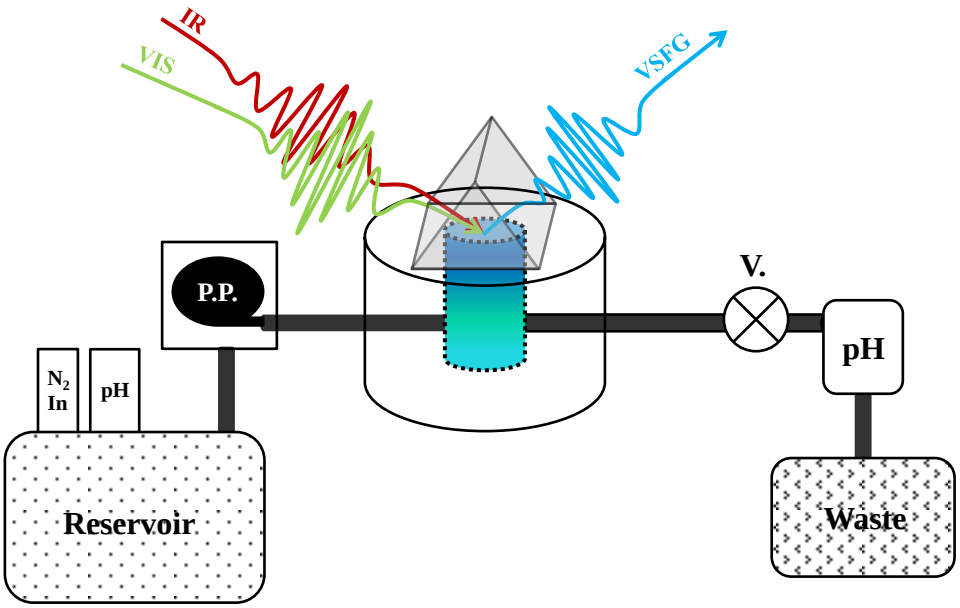

Figure S1. Experimental geometry and flow-cell schematic for the VSFG experiments. Abbreviations: P.P. – peristaltic pump, V. – valve.

$$\mathrm{I}_{VSFG} = \left| B_{NR} e^{i\phi} + \left(\sum_{\nu} \frac{A_{\nu}}{\omega_{\nu} - \omega_{\mathrm{IR}} + i\Gamma_{\nu}} \right) \right|^2$$

Equation S1. Lorentzian profile used to fit the VSFG spectra.

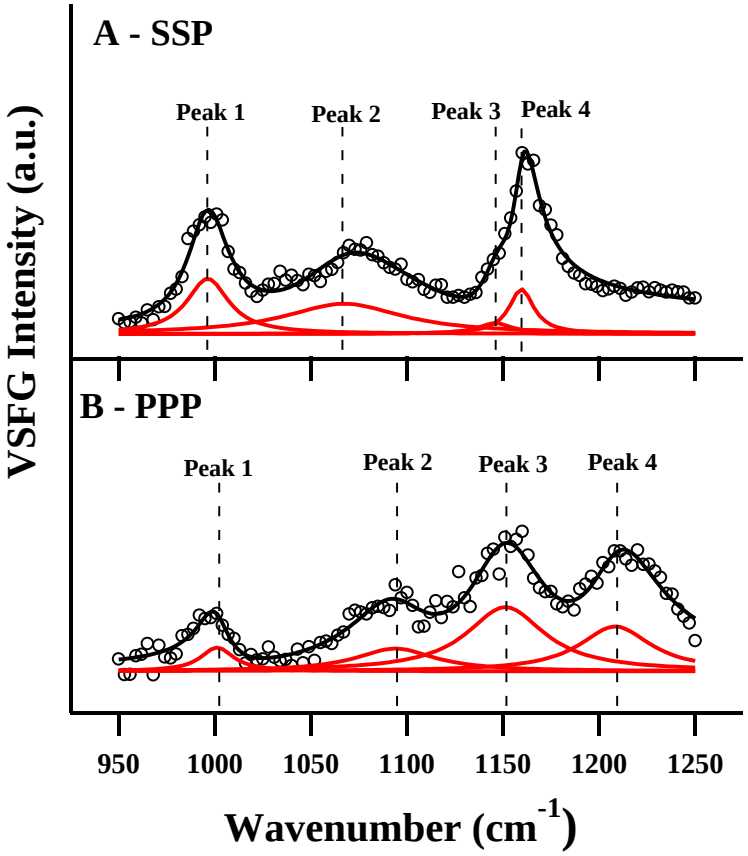

Figure S2. Representative VSFG spectra, A-SSP and B-PPP (both are the 100 mm Na_2SO_4 solution set), showing four typical Lorentzian fit components used to fit the data. Data are markers, solid black line is total fit to the data, and red solid lines are individual Lorentzian fit components. Peaks are labeled 1-4 from left to right. Complete fitting results for all VSFG spectra are listed in Table S1.

Table S1. Curve-Fitting Results for VSFG Spectra

		Non-Resonant Terms		Peak 1 (ν_{SS}-SO_4^{2-})			Peak 2 (ν_{AS}-SO_4^{2-})			Peak 3 (ν_{AS}-SO_4^{2-})			Peak 4 (ν_{AS}-SO_4^{2-})		
Na_2SO_4 Concentration	Polarization	Real	Imaginary	A	ω	HWHM	A	ω	HWHM	A	ω	HWHM	A	ω	HWHM
0.1 mm	SSP	0.02 ± 0.01	0.10 ± 0.01	N/A	N/A	N/A	N/A	N/A	N/A	4.4 ± 1.4	1121.0 ± 2.4	19.3 ± 4.2	2.3 ± 0.9	1149.6 ± 1.1	13.1 ± 2.5
	PPP	0.00 ± 0.01	-0.04 ± 0.01	N/A	N/A	N/A	1.1 ± 0.3	1095.3 ± 2.1	17.1 ± 3.7	1.0 ± 0.3	1144.6 ± 2.3	17.5 ± 4.5	N/A	N/A	N/A
1 mm	SSP	0.08 ± 0.01	-0.07 ± 0.02	1.8 ± 0.3	993.5 ± 0.8	12.4 ± 1.5	5.0 ± 1.3	1070.4 ± 2.4	46.1 ± 7.4	1.2 ± 0.5	1148.0 ±2.4	10.9 ± 2.8	0.9 ± 0.4	1159.2 ± 0.7	6.4 ± 1.4
	PPP	-0.01 ± 0.01	-0.01 ± 0.05	0.8 ± 0.6	1009.7 ± 12.3	22.3 ± 11.6	1.0 ± 0.3	1098.9 ± 2.4	12.0 ± 2.5	4.8 ± 2.1	1147.3 ± 2.0	31.2 ± 5.1	1.1 ± 0.4	1200.2 ± 2.8	16.2 ± 3.9
10 mm	SSP	0.10 ± 0.01	-0.08 ± 0.02	1.9 ± 0.3	994.2 ± 0.8	11.4 ± 1.3	5.7 ± 1.3	1069.6 ± 2.0	42.9 ± 5.9	1.7 ± 0.8	1149.8 ± 3.4	12.0 ± 2.4	1.0 ± 0.6	1158.9 ± 0.7	6.2 ± 1.5
	PPP	-0.01 ± 0.01	-0.03 ± 0.03	0.7 ± 0.3	1002.2 ± 3.2	10.7 ± 3.6	1.4 ± 0.3	1098.5 ± 1.8	13.8 ± 2.6	4.7 ± 1.1	1149.2 ± 1.8	29.6 ± 3.7	1.5 ± 0.4	1203.4 ± 1.5	15.0 ± 2.9
100 mm	SSP	0.10 ± 0.01	-0.09 ± 0.02	3.3 ± 0.4	996.2 ± 0.6	12.9 ± 1.0	6.8 ± 1.4	1067.5 ± 1.6	36.8 ± 4.2	1.0 ± 0.5	1145.3 ± 1.8	9.4 ± 3.2	2.0 ± 0.4	1159.5 ± 0.6	8.1 ± 1.0
	PPP	0.01 ± 0.02	-0.02 ± 0.03	1.2 ± 0.3	1002.1 ± 2.3	10.7 ± 2.3	3.0 ± 1.1	1094.3 ± 2.9	26.6 ± 5.6	4.7 ± 0.8	1151.3 ± 1.7	25.1 ± 2.5	3.5 ± 0.7	1207.6 ± 2.2	22.8 ± 2.9

Table S1. Fitting results for the fluorite/Na_2SO_4 solution interface VSFG spectra using Equation S1 with plus/minus one standard deviation noted. A – peak amplitude, ω – peak frequency in wavenumbers, HWHM – peak half-width at half-max in wavenumbers.

$$\left[\frac{d(\frac{1}{\theta_{rel}})}{d(\frac{1}{[SO_4^{2-}]})}\right]^{-1} = \frac{1}{55.5M}\exp^{(\frac{-\Delta G^{\circ}_{ads}}{RT})}$$

Equation S2. Equation relating the slope of the line of one over relative surface coverage (θ_{rel}) versus one over sulfate solution concentration to the surface free energy of adsorption ($\Delta G°_{ads}$). A concentration for water of 55.5 M is used to normalize the aqueous solutions.[1,2]

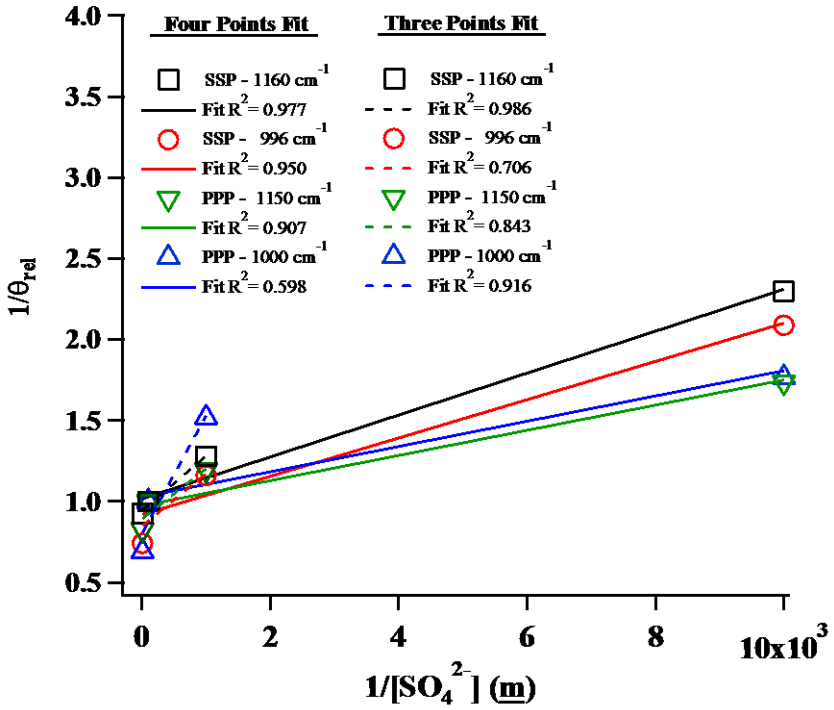

Figure S3. One over relative surface coverage (θ_{rel}) versus one over sulfate solution concentration from Langmuir adsorption analysis for the four isotherms shown in manuscript Figure 4. Data are markers, solid lines are fits to all four Na_2SO_4 concentrations, and dashed lines are fits to three highest (100, 10, and 1 mm) Na_2SO_4 concentrations with R^2 values for the fits are indicated in the legend. From the slope of the lines it is possible to calculate the surface free energy of adsorption using Equation S2.

References.

(1) Mifflin, A. L.; Gerth, K. A.; Weiss, B. M.; Geiger, F. M. *J. Phys. Chem. A* **2003**, *107*, 6212-6217.

(2) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; 6th ed.; Wiley-Interscience: New York, New York, 1997.