# Supporting Materials

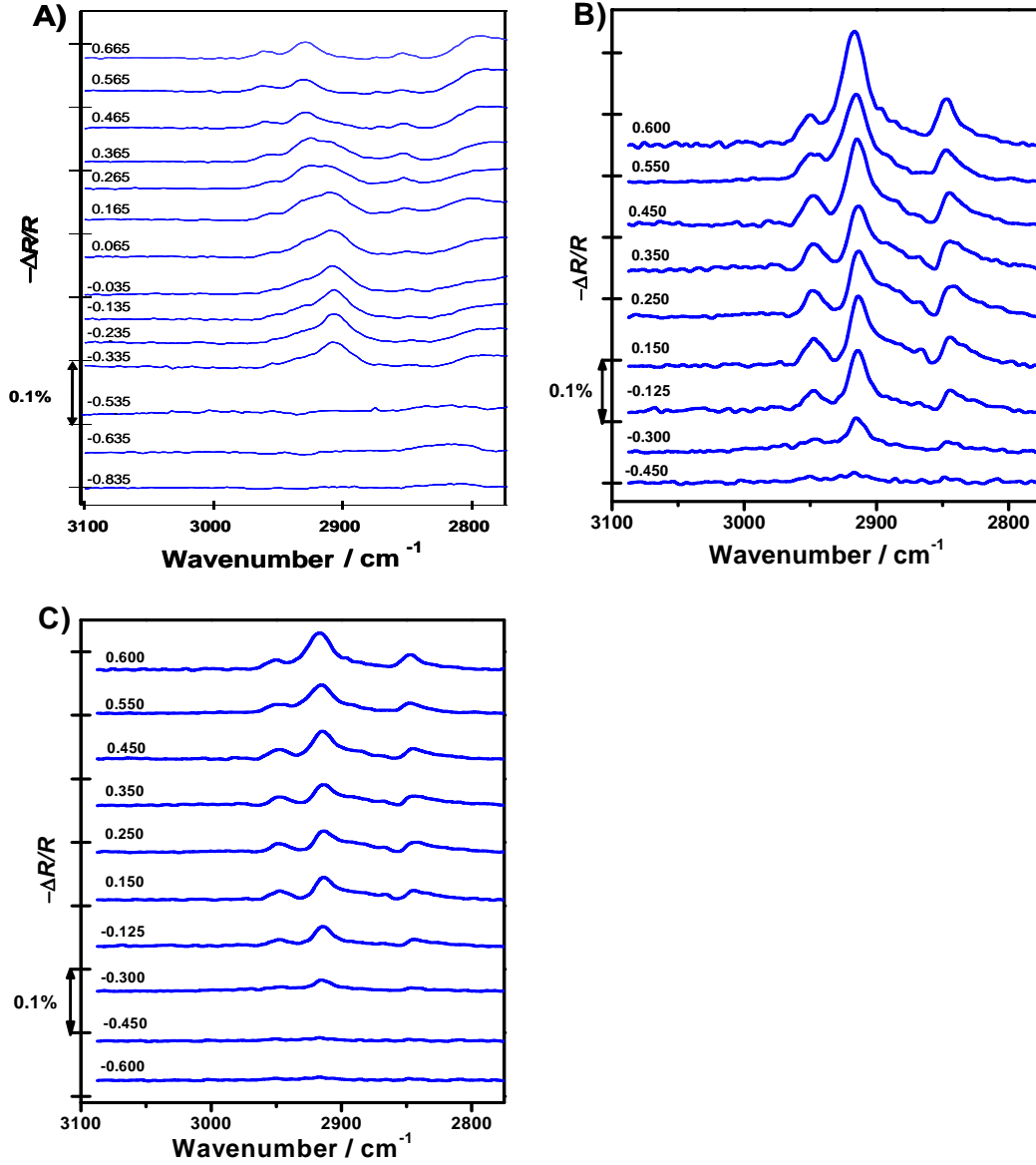## SI1. SNIFIRS Spectra of SDS Adsorbed at the Au(111) Electrode Surface

Initial SNIFTIRS experiments performed about 10 years ago are shown in Figure SI1

A. These experiments were performed using a thin layer configuration with a 1″ equilateral $CaF_2$ prism, $D_2O$ electrolyte and Au(111) electrode. The results from these previous experiments were only qualitative in nature since the precise thickness of the thin layer cavity was not known as the methodology for calculating the thin layer thickness was not developed. Furthermore, the intensity of the SNIFTIRS bands shows no apparent trend as a function of the electrode potential. This is likely due to poor background subtraction since the IR absorbance bands of the SDS film are very weak and the electric field enhancement at the Au(111) surface for the $CaF_2$ setup is approximately 3.2X less than that of the ZnSe setup (Note: this assumes that a thin layer cavity thickness of 4.3 μm and incidence angle of $54^o$ was used in the $CaF_2$ experiments). Figure SI1 B shows the SDS SNIFTIRS spectra obtained in this work using the ZnSe hemispherical prism setup. The mean square electric field strength at the Au(111) surface was calculated for the two setups (i.e. $CaF_2$ and ZnSe) using the

Fresnel program, and the ratio of the MSEFSs for the *p*-polarized radiation, $\left( \dfrac{E_{p_{CaF_2}}}{E_{p_{ZnSe}}} \right)$,

was multiplied by the spectra obtained using the ZnSe hemisphere setup for comparison. The resulting intensities of the CH stretching vibrations for the ZnSe experiments are shown in SI1 C. After correcting for the differences in the electric field strengths, the magnitudes of the CH band intensities are very similar, however, the shape and position of these bands are quite different due to the superior sensitivity and improved signal-to-noise that is achieved when using a ZnSe hemispherical prism.

SI1: SNIFTIR spectra of SDS adsorbed at the Au(111) electrode surface using a A) CaF$_2$ equilateral prism, $-\left(\dfrac{\Delta R}{R}\right)_{CaF_2}$, B) ZnSe hemispherical prism, $-\left(\dfrac{\Delta R}{R}\right)_{ZnSe}$, and C)

$-\left(\dfrac{\Delta R}{R}\right)_{ZnSe} \times \left(\dfrac{E_{p_{CaF_2}}}{E_{p_{ZnSe}}}\right)$. The potentials are referenced using a saturated calomel electrode.

(Note: the SNIFTIR spectra from the CaF$_2$ experiments, presented in SI1 A, were originally plotted as –$\Delta R/R$. Unfortunately, the raw data for these experiments is no longer available, therefore, the SNIFTIR spectra from the ZnSe experiments presented in this work have also been replotted as –$\Delta R/R$ in the supporting information for comparative purposes.)

## SI2. Critical Micelle Concentration for SDS in 0.1 M NaF Electrolyte

The critical micelle concentration for SDS was determined by filling a 250-mL beaker containing a magnetic stir bar with 100 mL of a 0.1 M NaF electrolyte solution. A Wilhelmy balance cut from filter paper was used to measure the surface pressure of the electrolyte solution. The Wilhelmy balance was removed from the solution and 20 µL of the SDS stock solution (60 mM) dissolved in a 0.1 M NaF aqueous electrolyte was injected into the beaker (Note: the high concentration ensures that the change in total electrolyte volume is less than 2%). The SDS solution was stirred for 1 minute before taking all readings. The stirrer was turned off after 1 minute and the Wilhelmy balance was lowered to the same height inside the 250-mL beaker. The concentration of SDS at the air-water interface was allowed to reach equilibrium before recording the surface pressure. In Figure SI2 we plot the change in the surface pressure with respect to the SDS concentration. Each point on the curve is an average of three individual measurements and the critical micelle concentration (cmc) for SDS is determined from the intersection of the plateau region (formation of micelles) with the linear slope from the increasing monomer concentration. According to Figure SI2, the cmc for SDS in a 0.1 M NaF aqueous electrolyte is 0.64 mM.
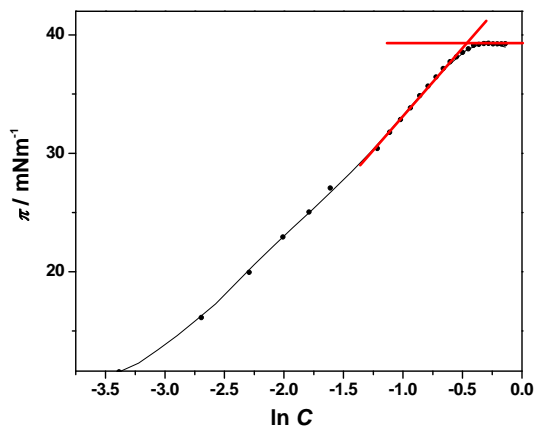


SI2: Determination of the critical micelle concentration for SDS in a 0.1 M NaF aqueous electrolyte by monitoring the change in surface pressure with respect to the SDS concentration.

## SI3. Determining the Angle of Incidence and Thin Layer Cavity Thickness

The electrochemical IR cell was filled with the aqueous electrolyte and the angle of incidence was adjusted to $30\pm2^{o}$. After purging the electrolyte with argon for about 1 hour, the gold electrode was pressed up against the IR window to form the thin layer configuration. The IR reflectivity spectrum (black curve shown in SI3) of the ZnSe|electrolyte|Au interface was obtained experimentally. A reflectivity spectrum was then calculated from the optical constants for the ZnSe prism, aqueous electrolyte and Au electrode using the Fresnel matrix method. The angle of incidence and thin layer cavity thickness are two adjustable parameters in the Fresnel matrix, which are used to create the calculated spectrum (red curve) that best fits the experimental data.
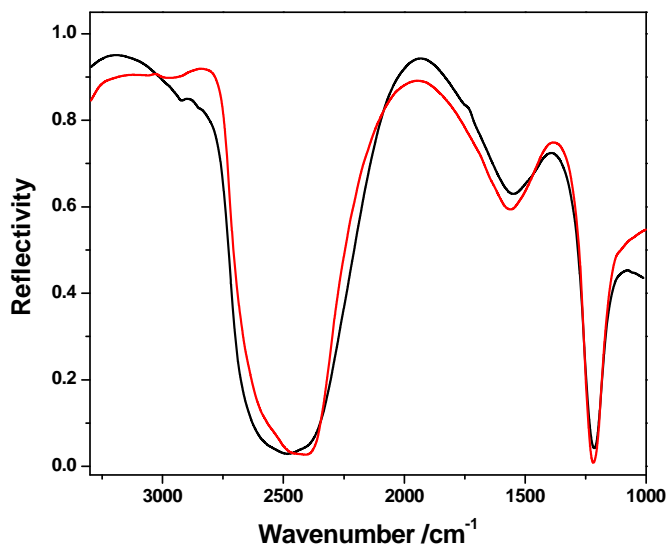


SI3: Experimental (black) and theoretical (red) reflectivity spectra for the thin layer of electrolyte for the experimental setup in which the thin layer cavity is composed of ZnSe|$D_2O$|Au. The theoretical spectrum is calculated using an incidence angle of $31.2^{o}$ and a thin layer thickness of 2.2 μm.

## SI4. Optical Constants for the Various Stretching Vibrations of SDS Used to Calculate the IR Absorbance Spectrum of a Randomly Oriented Film

The optical constants for SDS were obtained using a thin layer IR transmission cell. The cell consists of two plano $BaF_2$ windows that are separated by a 25-µm Teflon spacer. The transmission IR cell was filled with a sodium fluoride electrolyte and the IR background spectrum was collected. Next, the IR cell was filled with a 1% SDS electrolyte solution and the ratio between the SDS IR spectrum and the background spectrum was calculated to obtain the transmittance of SDS. This transmission spectrum is used to determine the refractive index ($n$) and attenuation coefficient ($k$) with the aid of a custom computer program written by Dr. Zamlynny[1]. In Figure SI4 we plot the optical constants for the sulfate asymmetric stretching region (SI4 A) obtained in a 0.1 M $NaF/H_2O$ electrolyte, as well as for the symmetric stretching (SI4 B) and C-H stretching (SI4 C) regions obtained in a 0.1 M $NaF/D_2O$ electrolyte.
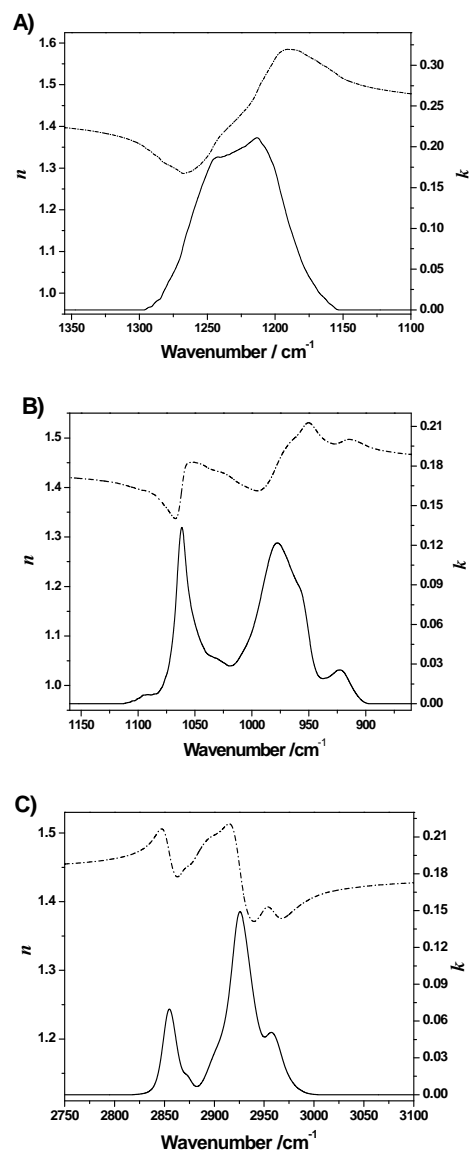
SI4: The optical constants for the sulfate asymmetric (A) and symmetric (B) stretching and CH stretching (C) regions of SDS obtained from transmission IR experiments.

## SI5. Normalization of Electric Field Strength

The gap thickness and angle of incidence between each SNIFTIRS experiment is extremely difficult to reproduce precisely. As a result, the mean squared electric field strength at the Au surface is different for each experiment. Therefore, in order to improve the signal-to-noise ratio and obtain the average IR absorbance intensity for an adsorbed SDS film, the electric field at the electrode surface must first be normalized. First, the decoupling procedure must be used to determine the IR absorbance of each individual experiment. Figure SI5 A shows the IR absorbance spectra for SDS films from four different experiments. Note that the IR absorbance intensity between each experiment is different due to the varying mean squared electric field strength (MSEFS) at the surface. In order to average the different results, the MSEFS must be determined for each spectrum using the Fresnel matrix method with the appropriate experimental parameters. After calculating the enhancement factor at the surface, the different spectra can be normalized using the following equation:

$$\left(\frac{\Delta R}{R}\right)_{B'} = \left(\frac{\Delta R}{R}\right)_{B} \times \left(\frac{\left\langle E_{p_{z=0}}\right\rangle_{A}}{\left\langle E_{p_{z=0}}\right\rangle_{B}}\right) \tag{1}$$

where $\left(\frac{\Delta R}{R}\right)_{B}$ $\left(\frac{\Delta R}{R}\right)_{B'}$ represent the spectra before and after normalizing the electric field enhancement, $\left\langle E_{p_{z=0}}\right\rangle_{A}$ and $\left\langle E_{p_{z=0}}\right\rangle_{B}$ are the reference and experimental electric field strengths, respectively. In this paper, the experiment with a gap of 4.3 μm and angle of 28.2$^{\circ}$ was selected as the reference spectrum. The electric field strengths of the other three experiments were normalized to this spectrum. SI5 B shows the resulting spectra after normalizing for the MSEFS. The relative standard deviation after normalization is ~ 9%. This normalization procedure was also used for the sulfate asymmetric and symmetric stretching regions.
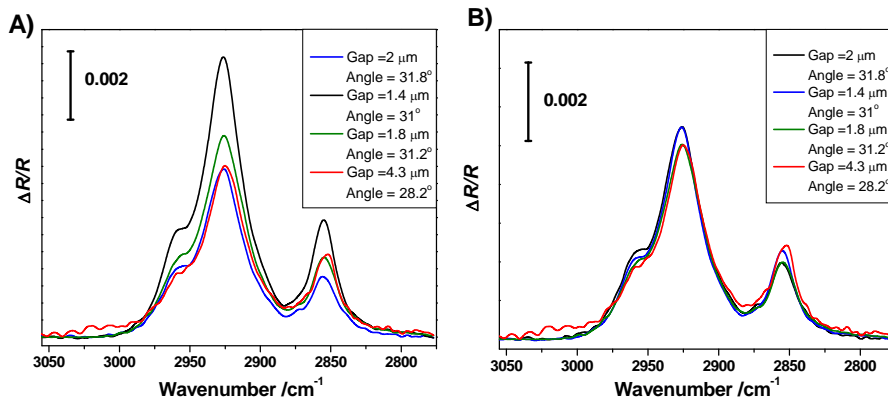
SI5: The IR absorbance spectra of SDS films adsorbed on the Au(111) electrode surface at a potential of 400 mV for four separate experiments before (A) and after (B) normalizing the mean squared electric field strength at the gold surface.

## SI6. Fourier Self-Deconvolution of IR Absorbance Spectra for the Adsorbed SDS Films

The IR absorbance spectra for the adsorbed SDS films contain many overlapping bands with different directions in their transition dipole moments. Therefore, in order determine the orientation of the film, the IR absorbance bands must be deconvoluted into the individual band components. Unfortunately, many of these bands overlap with one another making it difficult to identify the precise location and number of the individual peaks within the spectral band. In order to help resolve these peaks, a Fourier Self-Deconvolution (FSD) was applied to all spectral regions. The results of the FSD function for the sulfate asymmetric and symmetric stretching and CH stretching regions are shown in Figure SI6. The FSD for the asymmetric sulfate region reveals two prominent bands at 1252 $cm^{-1}$ and 1214 $cm^{-1}$ while the sulfate symmetric region shows five bands located at 922 $cm^{-1}$, 962 $cm^{-1}$, 982 $cm^{-1}$, 1037 $cm^{-1}$ and 1063 $cm^{-1}$. Six IR bands were observed from the FSD of the CH stretching region where the peak centers are located at 2856 $cm^{-1}$, 2873 $cm^{-1}$, 2904 $cm^{-1}$, 2926 $cm^{-1}$, 2934 $cm^{-1}$ and 2960 $cm^{-1}$. The peak centers from the FSD merely provide starting values for the peak centers within the specific spectral band, however, the true values for the peak centers were obtained using spectral band decovolution.
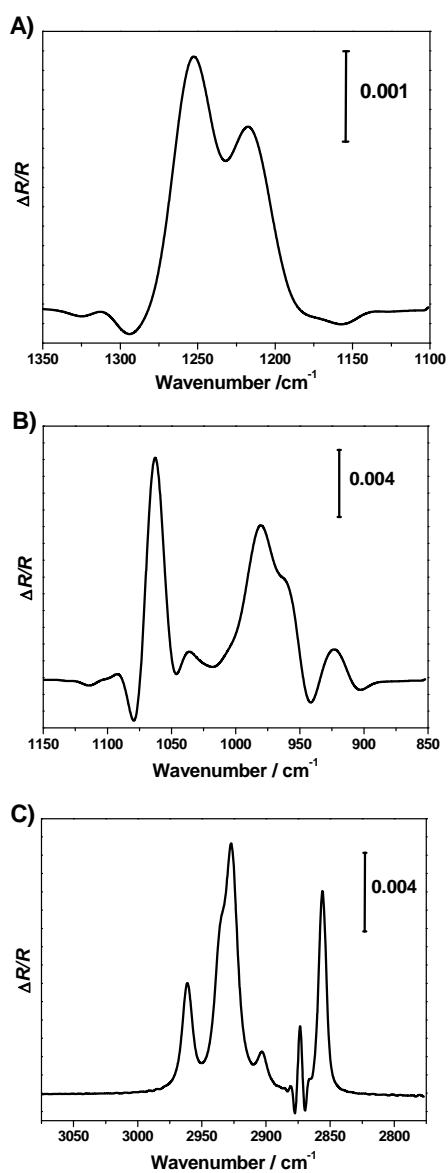
SI6: Fourier Self Deconvolutions of the asymmetric (A) and symmetric (B) sulfate stretching and CH stretching (C) regions of the SDS spectra.

**References:**

1. Zamlynny, V.  *PhD thesis*, University of Guelph, **2002**.