
Supporting Information for *Resolving the Chemical Identity of H_2SO_4 Derived Anions on Pt(111) Electrodes: They're Sulfate*

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Contents

1 Experimental Details

1.1 Electrochemistry

All measurements were conducted in a homebuilt thin-film spectroelectrochemical cell previously described [1,2]. To allow sufficient IR light to reach the Pt surface we reduced the thickness of the electrolyte film to ≈ 1μm (quantified by IR absorption). Glassware was cleaned by immersion in an alkaline $KMnO_4$ solution for 24 h, subsequent immersion in Piranha (0.05 M H_2O_2 and 1 M H_2SO_4 in H_2O) etch for 2 h, followed by rinsing with Milli-Q water. Subsequently, we placed the glassware in Milli-Q water in a supersonic bath for at least 5 min three times (after each cycle fresh Milli-Q was added). After the cleaning cycles the glassware was rinsed thoroughly a final time with Milli-Q water. The CaF_2 window and O-rings that contacted electrolyte were first cleaned by immersion in acetone p.a. (AppliChem) and placed inside a supersonic bath for 5 min and then treated like the glassware: with supersonic baths and rinsing in Milli-Q. Solutions were prepared from Suprapur sulfuric acid (Merck) and Milli-Q water. The Pt(111) working electrode (5 mm diameter, 3 mm thick, MaTeck) was flame annealed in a butane air flame, cooled in a water saturated N_2 atmosphere, quenched in and covered with a droplet of Milli-Q water (after all 5 annealing steps) that was deaerated for 45 min. Quenching water and electrolyte were deaerated with N_2 evaporated from liquid. Curved surface of the WE was wrapped in Teflon after flame annealing and transferred to the cell after the Teflon wrapping was rinsed thoroughly with Milli-Q water. A homebuilt reversible hydrogen electrode (RHE), a Pt wire in deaerated and $H_2(D_2)$ saturated 0.5 M $H_2SO_4(D_2SO_4)$, was used as a reference electrode [3].

1.2 VSF Spectroscopy

To collect VSF spectra we overlap infrared and visible laser pulses spatially and temporally on the working electrode and measure the frequency dependent intensity of the emitted sum frequency (SF) field. The laser system and optical setup have been described in detail in our previous work [1]. For the experiments described in the text of this paper the IR pulse was centered near 1300 cm^{-1}, had a full width at half maximum (FWHM) of ≈ 300 cm^{-1}, was ≈ 100 fs in length, and had a power of 3.6 mW controlled by a $\lambda/2$ plate and polarizer combination just before the sample. We generated the 800 nm narrowband upconversion pulse (VIS, 3.2 mW, FWHM of 5 cm^{-1}) with a homebuilt pulse-shaper by dispersing 600 mW of the amplifier output on a grating and focusing the dispersed beam on a slit. Unwanted frequencies were filtered out with a band pass filter centered at 800 nm. The beams were focused onto the sample using lenses with focal lengths of 100 and 500 mm and incident angles of $62° \pm 0.5$ and $45° \pm 0.5$ for the IR(KBr lens) and VIS(N-BK7 lens), respectively. After the sample the emitted VSF signal was collimated with a 500 mm N-BK7 lens, dispersed in a spectrograph (SR303i, Andor Technology) and imaged using an emICCD camera (PI-MAX4, Princeton Instruments). All measurements were taken under ambient conditions at room temperature with the *ppp* polarization condition (*p*-polarized SF, *p*-polarized VIS, and *p*-polarized IR where *p* is polarization in the plane of incidence). The acquisition time for a gold reference was 30 sec and for the sample 10 sec. For every measurement, spectra were collected during multiple voltrammetric scans at 2 mV/s. The spectra at identical potentials during different voltammetric cycles did not differ from one another and were later averaged. Spectra at identical potentials in the positive and negative going scan of one voltammetric cycle were identical and suggest that the scan rate is sufficiently slow to avoid mass transport limitations.

2 Potential dependent series of VSF spectra of Pt(111) in $D_2SO_4(D_2O)$ solution

Figure S1 shows the potential dependent VSF spectra of Pt(111) in $D_2SO_4(D_2O)$ solution. As we show in Figure 2 of the main text, quantitatively similar spectra, at a given potential, are observed in both $H_2SO_4(H_2O)$ and $D_2SO_4(D_2O)$.

3 CV collected in the measurement position of the spectroelectrochemical cell.

Cyclic voltammograms (CV) of a Pt(111) electrode in 0.5 M H_2SO_4/H_2O (red trace) and D_2SO_4/D_2O (blue trace) in the spectroelectrochemical cell with scanning speed of 500 mV/s are shown in Figure S2. The CVs clearly show similar current features to that in the meniscus geometry (Figure 1a) in the main text. The small asymmetry in current in the positive and negative going directions we take to be the result of reduction of a small amount of O_2 that has diffused into the cell or trace contaminants from the dissolving CaF_2 cell window. The smaller current in the anion desorption and adsorption region in D_2O in comparison that in H_2O solution should be due to the impurities from the D_2O.

4 Effect of IR absorption on measured VSF spectral features in D_2O

While the interface specificity of VSF spectroscopy means no subtraction is necessary to account for the effect of IR absorption in bulk electrolyte before the sample, such absorption *can* be reflected in the spectrum if a sufficient number of photons are lost before reaching the interface: to generate an SF photon an IR photon is required. Figure S3 shows that this effect is negligible in our

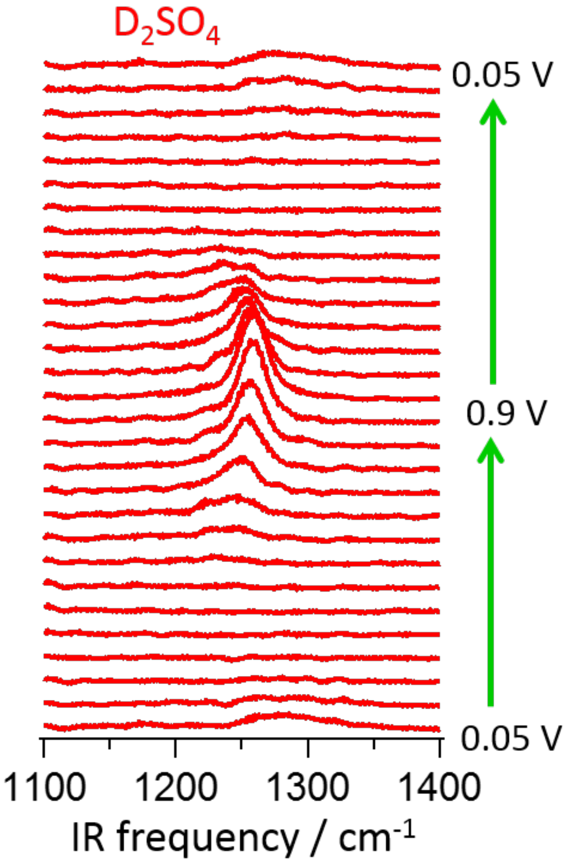

Figure S1. Potential dependent VSF spectra of the adsorbed sulfuric acid anions in the 0.5 M $D_2SO_4(D_2O)$ system on a Pt(111) electrode; the green line indicates the potential limits for spectroscopic measurement. Note that the potential in this measurement is defined with respect to a D_2 saturated 0.5 M solution of D_2SO_4.

experiment. At 0.05 V, whether in D_2O or H_2O, there is no resonant feature. Comparison of the two spectra, however, shows a ≈ 30% loss of intensity in the spectra in D_2O centered at ≈ 1240 cm^{-1} but that is quite broad. This loss in intensity is the result of absorption of IR photons before the Pt electrode through absorption by the D_2O bend. In comparison, at 0.9 V, a clear resonant feature is apparent both in D_2O that is 8× larger in intensity and whose line shape is not effected by the background.

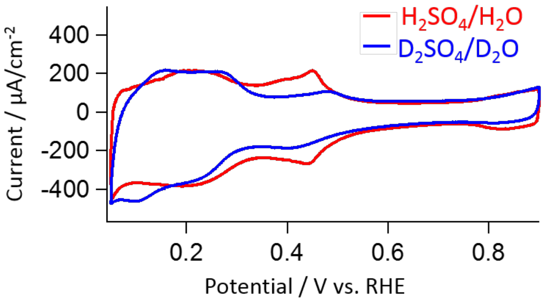

Figure S2. Cyclic voltammograms of a Pt(111) electrode in 0.5 M H_2SO_4/ceH2O (red trace) and in D_2SO_4/ceD2O (blue trace) in the spectroelectrochemical cell, the scanning speed was 500 mV/s, the thickness between the working electrode and a CaF_2 window is ≈ 1µm.

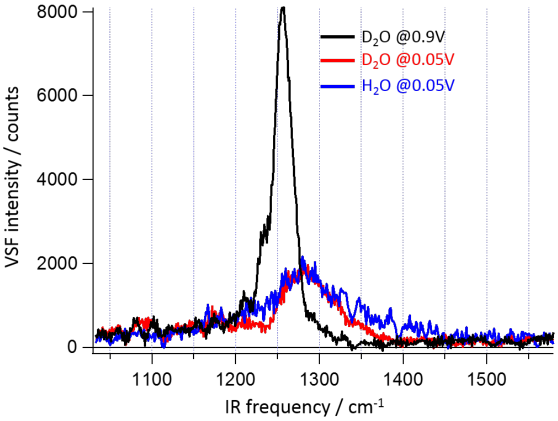

Figure S3. VSF spectra of Pt(111) electrode in 0.5 M H_2SO_4 (H_2O) at 0.05 V (blue line) and in 0.5 M D_2SO_4(D_2O) at 0.05 V (red line) and at 0.9 V (black line).

5 Frequencies from charged and uncharged models

In the simplified model we address theoretically it is necessary to decide whether the adsorbate should be charged or neutral (we do not simulate the adsorption of the anion at a defined potential and thus do not *calculate* the extent to which the sulfuric acid derived anion discharges on adsorption). As discussed in the main text we performed optimizations and calculated normal mode frequencies for both the fully charged and fully discharged model. Because measurements of electrosorption valency suggest the adsorbing anion is continuously discharged as a function of potential in the 0.5 M H_2SO_4(H_2O) system we report the structures and frequencies of the charged model in the main text. Figure S4 shows the normal mode frequencies for the uncharged anions adsorbed on the Pt(111) surface. While the frequencies are blue shifted relative to those obtained for charged anions (see Figure 3 in the main text) the trends for isotope exchange are identical. It is thus clear that the degree of anion (dis)charging has little effect on our principle conclusions.

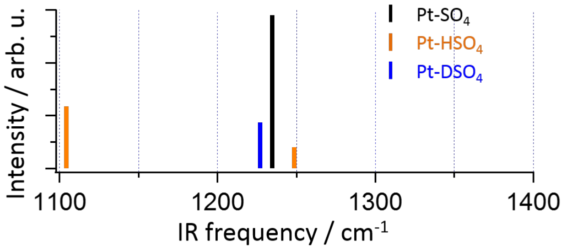

Figure S4. vibrational normal modes for SO_4, HSO_4 and DSO_4 adsorbed on Pt(111) surface that calculated by DFT

6 Orientation of the transition dipole moment of the vibrational modes

Arrows in the schemes in Figure S5 show the orientation of the transition dipole moment of the calculated vibrational modes. Only the modes around 1250 cm^{-1} have transition dipole ment that is parallel to the surface normal, which can be probed by VSFS.

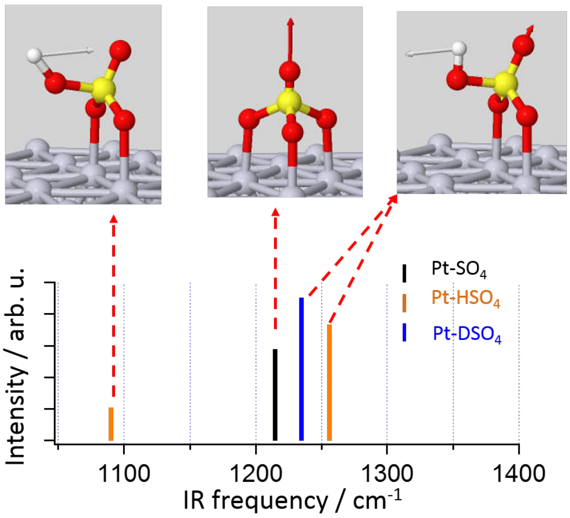

Figure S5. Schemes show the corresponding orientation of the transition dipole moment of the modes calculated in Fig. 3 in the main text for SO_4^{2-}, HSO_4^- and DSO_4^- adsorbed on a Pt(111) surface calculated by DFT

References

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