

Real-Time Investigations of Pt(111) Surface Transformations in Sulfuric Acid Solutions

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Abstract: We present the first broadband sum-frequency generation (SFG) spectra of adlayers from sulfuric acid solutions on Pt(111) surfaces and reveal surface transformations of (bi)sulfate anions in unprecedented detail. SFG amplitudes, bandwidth, and electrochemical Stark tuning of (bi)sulfate vibrational bands centered at 1250–1290 cm^{-1} strongly depend on the applied potential and are correlated with prominent voltammetric features. (Bi)sulfate adlayers on Pt(111) are important model systems for weak, specific adsorption of anions on catalytically active surfaces. Although the existence of surface transformations on Pt(111) in dilute H_2SO_4 solutions has been established by previous studies, so far they have not been observed with surface vibrational spectroscopy. Our results confirm previous reports of a surface transformation at 0.21 V and provide new information on a second transformation at 0.5 V due to surface hydroxyl formation and rearrangement of the electric double layer.

In this Communication, we present the first vibrational sum-frequency generation (SFG) spectra of adlayers from sulfuric acid solutions on Pt(111) surfaces and reveal surface transformations of sulfuric acid anions in unprecedented detail. SFG amplitudes, bandwidth, and electrochemical Stark tuning of the observed vibrational bands strongly depend on the applied potential and are correlated with prominent voltammetric features. Although the existence of surface transformations on Pt(111) in H_2SO_4 solutions was established by previous studies, so far they have not been observed with surface vibrational spectroscopy. Our results confirm previous reports of a surface transformation at 0.21 V and provide new information on a second transformation at 0.5 V.

The specific adsorption of bisulfate and sulfate anions on Pt(111) single-crystal surfaces represents an important model system in electrochemical surface science^{1,2} and has been shown to change the reaction pathways and efficiency of electrochemical reactions significantly.^{2,3} Nafion-based fuel cell technology represents an example where sulfate-type interfaces are of great interest, since the sulfonic acid head-groups of Nafion form very similar double-layer structures at Pt interfaces.^{4,5}

The surface structure of Pt(111) in the potential range of sulfate and bisulfate adsorption has been studied previously with scanning tunneling microscopy (STM)^{6,7} and theoretical simulations.^{4,8} Adlayers with co-existing domains of $(\sqrt{3} \times \sqrt{7})\text{R}19.1^\circ$ superstructures and with different rotational domains are established at potentials higher than the sharp spike in the cyclic voltammogram (CV) (Figure 1a). These structures undergo reversible surface transformations at 0.21 and 0.5 V, where a disordered layer is transformed into an ordered layer and vice versa.^{6–8} For potentials $E > 0.21$ V, domains with $(\sqrt{3} \times \sqrt{7})\text{R}19.1^\circ$ structures consist of sulfate anions locked to three-fold hollow sites of Pt(111) and co-adsorbed water molecules.^{6,7,9} H_2O co-adsorption leads to the

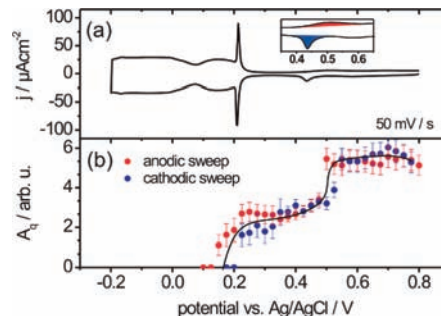


Figure 1. (a) Hanging-meniscus cyclic voltammogram of a well-ordered Pt(111) electrode in 0.1 M H_2SO_4 . The CV was recorded in the SFG spectroelectrochemical cell. (b) SFG amplitude A_{SFG} of the vibrational band in Figure 2a as a function of the applied potential E .

formation of hydrogen bonds to adsorbed sulfate, reduces the Coulomb repulsion among adjacent anions, and, consequently, stabilizes the asymmetric $(\sqrt{3} \times \sqrt{7})\text{R}19.1^\circ$ superstructure.^{6,7,9} For $E < 0.21$ V, DFT calculations show a bidentate configuration of sulfuric acid anions, with two oxygen atoms pointing toward the Pt(111) surface, which is transformed for $E > 0.21$ V into a three-fold-coordinated state with three oxygens of the anion binding to Pt atoms.⁹ It should be noted that the chemical identity of the molecular adsorbate — HSO_4^- , SO_4^{2-} , or a $\text{SO}_4^{2-} + \text{H}_3\text{O}^+$ complex — on Pt(111) in H_2SO_4 solutions has been highly debated in the past^{4,6,7,10–15} and is denoted henceforth as (bi)sulfate.

Theoretical simulations^{4,8,11} as well as radiotracer¹³ and combined STM and voltammetric experiments^{6,7} suggest a predominant adsorption of sulfate, which is in contrast to most infrared studies of this system, where a predominant adsorption of bisulfate is reported.^{12,14}

The CV of a Pt(111) single crystal immersed in 0.1 M H_2SO_4 is presented in Figure 1a. The reversible CV is comprised of four potential regions and is indicative of a well-ordered surface with large, atomically flat terraces.^{6–8,15} The pair of plateau-like current features at -0.2 to 0.07 V is due to hydrogen deposition on (111) surface sites and hydrogen stripping for cathodic and anodic sweeps, respectively. (Bi)sulfate adsorption on Pt(111) leads to a broad feature centered at 0.16 V and a subsequent sharp spike at 0.21 V. The neck-like current feature for potentials higher than the sharp spike arises from double-layer charging only and is followed by a broad current wave centered at 0.5 V, with a much narrower desorption feature at 0.43 V (Figure 1a, inset). The assignment of these features has been highly controversial, and attributions to OH adsorption^{6–8,14} or to a further ordering of (bi)sulfate adlayers with higher coverage¹⁶ have been reported.

Potentiodynamic SFG spectra of Pt(111) in 0.1 M H_2SO_4 solution which were synchronized with a CV from -0.2 to 0.8 V are presented in Figure 2a. At potentials $E < 0.2$ V, featureless SFG spectra are observed, while for $E > 0.2$ V, a vibrational band

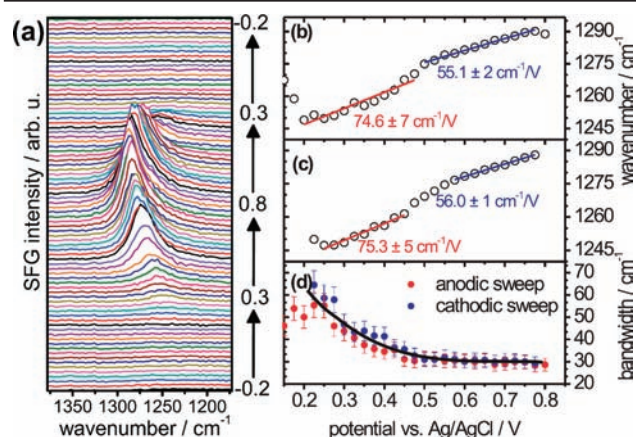


Figure 2. (a) Consecutive series of broadband SFG spectra of (bi)sulfate adsorption on Pt(111) in 0.1 M H₂SO₄. Electrode potentials E/V are indicated on the right-hand side. (b,c) Stark tuning for anodic and cathodic sweeps of the band in (a), respectively. (d) Bandwidth Γ_q of the (bi)sulfate band in (a). SFG spectra were recorded with 5 s acquisition time and during a 5 mV/s potential sweep.

dominates the SFG spectra and is assigned to symmetric S–O stretching vibrations of adsorbed (bi)sulfate. Frequency ω_q (1245–1290 cm⁻¹), bandwidth Γ_q , and amplitude A_q of this vibrational band strongly depend on the applied potential (Figure 2a). Further analysis of our SFG spectra was performed by fitting the SFG spectra presented in Figure 2a with model functions of the interfacial second-order susceptibility $\chi^{(2)}$ ¹⁷ and with A_q , ω_q , and Γ_q as adjustable parameters. The potential dependence of A_q is presented in Figure 1b, while A_q is only weakly dependent on potential in the double-layer region, and for $E > 0.5$ V, two abrupt changes occur at 0.21 and 0.5 V. These changes in A_q are accompanied by similarly abrupt changes in the Stark tuning of the frequency ω_q (Figure 2b,c) and in the bandwidth Γ_q (Figure 2d). In particular, the tuning of ω_q decreases from 75 cm⁻¹/V at potentials $E < 0.5$ V to 55 cm⁻¹/V at $E > 0.5$ V.

The notable change in Stark tuning is consistent with previous infrared studies,¹⁰ in which the crystal was pressed against an optical window; however, in our SFG study using a thick and well-defined electrolyte gap of 25 μ m, we find tuning rates that are systematically lower. In addition to the modified Stark tuning, a sudden blue-shift of ω_q by 5 cm⁻¹ at 0.5 V is revealed by a close inspection of Figure 2b,c. The bandwidth Γ_q decreases considerably for potentials $E < 0.5$ V but is constant for $E > 0.5$ V (Figure 2d). Here, a bandwidth of 30 cm⁻¹ is established and is notably higher than the experimental resolution of < 10 cm⁻¹.

All parameters in Figures 1b and 2b–d show, within the experimental scatter, a reversible behavior for anodic and cathodic sweeps. Note that the observed changes of A_q , ω_q , and Γ_q at 0.21 and 0.5 V occur at potentials of prominent current features in the CV (Figure 1a).

We will now address the apparent changes and reveal their relation to Pt(111) surface transformations. The broad (bi)sulfate adsorption feature in Figure 1a indicates that near-saturation coverages of the (bi)sulfate layer are established if E is increased to potentials close to the sharp spike (Figure 1a), yet this adlayer does not give rise to measurable SFG intensities (Figures 1b and 2a). (Bi)sulfate, however, adsorbs in a bidentate geometry and has a negligible dipole moment perpendicular to the Pt surface if strong anion–surface interactions are absent. This two-fold-coordinated state is SFG inactive by virtue of the dipole selection rule at metal surfaces. It is, therefore, reasonable to conclude that our SFG spectra at potentials of ~ 0.21 V reveal an abrupt transformation of the

two-fold- into a three-fold-coordinated state of (bi)sulfate anions. Apparently this transformation is associated with the sharp spike in CV (Figure 1a) and accompanied with a similarly abrupt transformation from a disordered (bi)sulfate adlayer into the ordered ($\sqrt{3} \times \sqrt{7}$)R19.1° layer reported previously.

Once the ordered (bi)sulfate layer is established, changing the electrode potential shifts the frequency of the (bi)sulfate band considerably (Figure 2a), indicative of a pronounced Stark tuning of (bi)sulfate stretching vibrations. The dramatic decrease of Γ_q from 60 to 30 cm⁻¹ (Figure 2d) and the slight increase of A_q (Figure 1b) could be indicative of a further ordering of (bi)sulfate structures on the Pt(111) surface and, consequently, a decrease in inhomogeneous line width. Increasing the electrode potential could induce an increase of interfacial long-range order with a transformation of different rotational ($\sqrt{3} \times \sqrt{7}$)R19.1° domains into to a nearly single-domain adlayer, which is in agreement with a thermodynamic analysis of this system.¹⁶

The second abrupt increase in SFG amplitude at 0.5 V suggests that the (bi)sulfate coverage increases further, in agreement with ref 16. Such a scenario is, however, unlikely since a closed-packed (bi)sulfate adlayer has already been established at lower potentials^{6,7} and the adsorption feature in the CV (Figure 1a) at 0.5 V involves only a very low charge transfer, which is inconsistent with the magnitude of the change in SFG amplitude (Figure 1b). It is more likely that co-adsorbed water molecules in the ($\sqrt{3} \times \sqrt{7}$)R19.1° layer^{6,9,11} are transformed into surface hydroxyl (Pt–OH) via the reaction $2\text{H}_2\text{O} + \text{Pt} \rightarrow \text{Pt–OH} + \text{e}^- + \text{H}_3\text{O}^+$. The latter is in agreement with the blue-shift of the vibrational band at ~ 0.5 V (Figure 2b,c) due to a weaker hydrogen-bonding of Pt–OH species compared to the hydrogen-bonding of co-adsorbed H₂O with the (bi)sulfate adsorbate.

Furthermore, Pt–OH and additional H₃O⁺ cations from the Pt–OH formation can be incorporated into the double layer and screen the interfacial electric field while the (bi)sulfate layer persists on the Pt(111) surface. As a result of a decreased interfacial electric field, the electrochemical Stark tuning for potentials $E > 0.5$ V (Figure 2b,c) is reduced. The origin of the substantial increase in amplitude, $A_q \propto \langle \alpha_q \mu_q \rangle$, must be related to modifications of the polarizability α_q and the dynamic dipole moment μ_q of (bi)sulfate vibrations due to a different local electric field and an increase of charge density in the S–O bond induced by decreased hydrogen-bonding. While at higher pH > 1.4 , OH and (bi)sulfate adsorption is competitive,^{14,16} our results at a lower pH indicate cooperative adsorption. A loss in long-range order at $E > 0.5$ V reported previously^{6,7} might be caused by the absence of stabilizing co-adsorbed water molecules and is in agreement with our results.

In summary, we have presented the first vibrational SFG spectra of an ordered (bi)sulfate adlayer with domains of closed-packed ($\sqrt{3} \times \sqrt{7}$)R19.1° superstructures on Pt(111). (Bi)sulfate adsorbed in a bidentate configuration has negligible SFG intensities, while a potential-induced transformation from two-fold to three-fold coordination at 0.21 V gives rise to an intense vibrational band at 1245–1290 cm⁻¹. Changing the electrode potential leads to significant Stark tuning of the (bi)sulfate band and to a second dramatic change in SFG amplitude, bandwidth, and tuning at 0.5 V. The reported changes are related to surface transformations of (bi)sulfate on Pt(111), confirm previous results at 0.21 V, and provide new information on the formation of surface hydroxyl and rearrangement of the electric double layer at 0.5 V.

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Supporting Information Available: Experimental details and procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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