

Accepted Manuscript

A Microscopic Model of the Electrochemical Vibrational Stark Effect:
Understanding VSF Spectroscopy of (bi)Sulfate on Pt(111)

Gregor Zwaschka, Martin Wolf, R. Kramer Campen, Yujin Tong

PII: S0039-6028(18)30228-0
DOI: [10.1016/j.susc.2018.05.009](https://doi.org/10.1016/j.susc.2018.05.009)
Reference: SUSC 21260

To appear in: *Surface Science*

Received date: 8 March 2018
Revised date: 15 May 2018
Accepted date: 16 May 2018

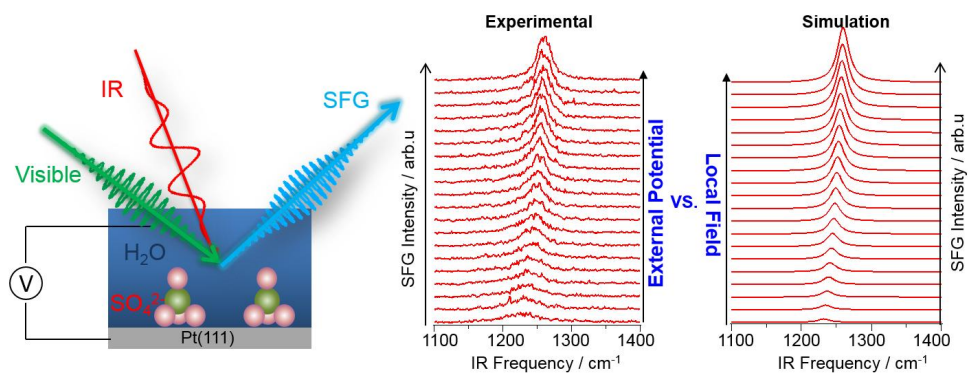
Please cite this article as: Gregor Zwaschka, Martin Wolf, R. Kramer Campen, Yujin Tong, A Microscopic Model of the Electrochemical Vibrational Stark Effect: Understanding VSF Spectroscopy of (bi)Sulfate on Pt(111), *Surface Science* (2018), doi: [10.1016/j.susc.2018.05.009](https://doi.org/10.1016/j.susc.2018.05.009)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Highlights

- Sulfate acid anions adsorbed on Pt(111) electrode can be studied by SFG spectroscopy
- Linear changes in potential lead to nonlinear changes in peak frequency and intensity
- The nonlinear potential dependent behaviors can be modeled with electrodynamic theory
- The proposed electrodynamic theory is based on microscopic dipole-dipole coupling



A Microscopic Model of the Electrochemical Vibrational Stark Effect: Understanding VSF Spectroscopy of (bi)Sulfate on Pt(111)

Gregor Zwaschka^a, Martin Wolf^a, R. Kramer Campen^a, Yujin Tong^{a,*}

^a*Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, D-14195 Berlin, Germany*

Abstract

Much work over the past several decades has demonstrated that the vibrational frequencies of adsorbates on metal surfaces in ultra-high vacuum (UHV) shift with changing surface coverage. Extensive theoretical efforts have shown that this shift can be quantitatively understood as the result of dipole-dipole interaction. A similar phenomenon is known from spectro-electrochemistry (the so-called electrochemical Vibrational Stark Effect (VSE)): the vibrational frequency of the adsorbate is observed to change as a function of applied external potential. Typically this potential-dependent change in adsorbate frequency is assumed to be linear (or piece-wise linear) with applied bias and thus changes in slope are assigned to changes in adsorbate structure or chemical reactions. Here we measure the change in spectral response of the (bi)sulfate anion adsorbed on a Pt(111) working electrode with changes in applied bias and quantitatively interpret the results using a microscopic model of the VSE that explicitly accounts for the effect of dipole-dipole interaction. Using this model we show that changes in external bias that cause a *linear* change in molecular polarizability **can** induce a *nonlinear* change in the center frequency and intensity of the spectral response of the adsorbed (bi)sulfate: **the nonlinearity of the VSE depends both on the local field at potential of zero charge and also the relative change induced by**

*Corresponding author

Email address: tong@fhi-berlin.mpg.de (Yujin Tong)

URL: <http://www.fhi-berlin.mpg.de/pc/NSECh/> (Yujin Tong)

external bias. These results imply that essentially all spectroelectrochemical studies that have attributed chemical significance to changes in slope of spectral parameters with applied bias should be revisited, as potential dependent dipole-dipole interaction can induce such changes independent of any structural or chemical change.

Keywords: Vibrational Stark effect, Dipole-dipole coupling, Vibrational sum frequency spectroscopy, (Bi)sulfate adsorption, Pt(111) electrode
2000 MSC: 92E10, 78A60

1. Introduction

The interaction of small, often polar, molecules with solid surfaces underlies much gas phase heterogeneous catalysis. Understanding the structure of such adsorbates (and any surface reconstruction they induce) is thus a prerequisite to gaining mechanistic insight into much important chemistry. So motivated several decades of work have probed the structure of such molecules on solid surfaces in UHV using various techniques. One powerful structural probe of di- and polyatomic molecules is the vibrational response of the adsorbed species. Reflecting the relative ease of measurement of this observable, the vibrational response of small molecules on metal single crystal surfaces in ultra-high vacuum (UHV) has been studied extensively with a variety of different approaches [1, 2, 3, 4]. Because CO is important both as a product and poison in a wide variety of heterogeneous catalytic processes, the vibrational response of CO has been particularly well studied.

Perhaps the most striking observable from the CO work is that, as coverage increases, the frequency of the CO stretching mode blueshifts and the work function decreases significantly [3]. The blueshift has been quantitatively reproduced within classical electrodynamic theory that explicitly describes electrostatic interaction between a dipole, its image dipole and its neighboring dipoles and image dipoles [2, 1, 5, 4]. At this level of approximation a surprisingly simple analytical expression has been derived that satisfactorily reproduces experimental data by

combining all dipolar interaction into a single local interaction potential that is a linear function of surface coverage. Importantly, as will be discussed in detail below, the resulting model suggests that over a sufficiently large range in surface coverage the relationship of surface coverage and center frequency will be nonlinear.

A similar phenomenon to this coverage induced change in adsorbate vibrational frequency has also been observed in electrochemistry: the frequencies of vibrational modes of adsorbates have been observed to shift with applied macroscopic bias (known as the Vibrational Stark Effect, VSE) [6, 7, 3, 8, 9, 10]. Although the electrochemical VSE seems more complicated – coverage, type of adsorbate, and structure of the solvent or electrolyte may all change with applied bias – in the great majority of studies a linear relationship between the frequency shift and the applied bias has been used to rationalize the data [6, 7, 3, 8, 9, 10]. While the microscopic basis of this linear relationship has not been well explored, it has typically been taken to suggest potential independent structures of the solvent, electrolyte and adsorbate in the potential region over which the center frequency linearly shifts. As a result, changes in slope with potential are typically justified as the result of interfacial chemical or structural change.

Viewed from the perspective of chemical bonding of the adsorbate, adsorption on a metal surface in UHV or on a metal working electrode seems similar. In both cases we are interested in understanding the vibrational response of a small molecule in a spatial region where local potential is changing significantly (see Figure 1). Because of this similarity it seems natural to ask whether insight into vibrational response, and local potential, gained from the study of small molecules adsorbed in UHV may also be useful in understanding small molecules adsorbed on metal electrodes. Several pioneering studies [11, 12] using this “UHV double layer (or electrochemical) modeling” strategy, have proposed that, if changing the surface coverage in UHV produces a change in frequency ($\Delta\omega$) and a change in work function ($\Delta\Phi$), within an electrochemical cell the change in bias (ΔV) that produces the same change in frequency ($\Delta\omega$) will be such

that $\Delta\Phi/e = \Delta V$ [13]. Given this insight the different contributions to the potential drop within the double layer can be disentangled by starting with a bare metal surface and then adding ions and solvent molecules consecutively while monitoring the work function.

Inspired by this approach, in the current study we extend the microscopic model developed to explain the coverage dependent change in vibrational frequency of adsorbates on metal surfaces in UHV to explain the electrochemical VSE for the case of (bi)sulfate adsorbed on Pt(111). In particular, we employ the interface-specific, laser-based probe, vibrationally resonant sum frequency spectroscopy (VSFS) and monitor the S-O spectral response as a function of potential. **This technique has been previously employed to study different types of adsorbates at various electrode/solution interfaces.**[9, 10, 14, 15, 16, 17, 18, 7, 19, 20, 21]

The S-O vibrational stretching property has been previously studied using electrochemical [22], spectroscopic (infrared reflection-absorption spectroscopy, IRRAS, and VSFS) [23, 24, 7] and theoretical approaches [8]. For our purposes here it has the particular advantage that there is a fairly large potential range in which this previous work makes clear that (bi)sulfate coverage is potential independent: we can assess the influence of the applied bias on the VSE without accounting for change in coverage. Because we perform these measurements at higher potential resolution than previous studies we are able to show that the relationship between the applied bias and center frequency is clearly nonlinear (and, in particular, not piece-wise linear) over chemically important changes in bias. We further show, by applying a model inspired by these previous UHV studies that this nonlinear dependence of S-O stretch frequency on applied bias can be straightforwardly understood as a potential induced change in local, interfacial field. It is not necessary to invoke potential dependent chemical or structural changes to rationalize this data.

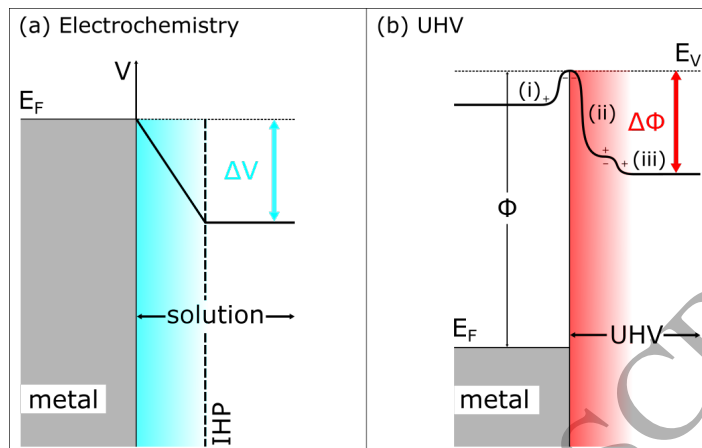


Figure 1: Schemes for (a) the potential drop in the inner Helmholtz plane (IHP, a layer consisting of a monolayer of adsorbates) of an electrochemical bilayer and (b) the work function change as a function of adsorbate coverage in UHV. The potential drop ΔV in the electrochemical system can be adjusted via the applied potential, which effectively shifts the Fermi level E_F . The work function of a surface in UHV is affected by different surface contributions, including (i) surface dipole; (ii) charge double layer and (iii) dipole contribution, of which (ii), (iii) and consequently $\Delta\phi$ can be modulated by the nature and coverage of the adsorbates. A linear correlation has been found between ΔV and $\Delta\phi/e$ in a previous UHV electrochemical modeling experiment [13].

2. Experimental

2.1. Electrochemistry

All measurements were conducted in a homebuilt thin-film spectroelectrochemical cell that has been described elsewhere [25, 26]. For this system we found it necessary, due to absorption of the incident IR beam when passing through the electrolyte, to reduce the thickness of the electrolyte film overlying the electrode to $\approx 1\mu\text{m}$ to ensure sufficient IR power reached the working electrode surface¹. Prior to measurement, the glassware was cleaned by immersion in an alkaline

¹We created a film with thickness of $1\mu\text{m}$ by removing the teflon spacer used in the previous studies. We quantified the film thickness in the absence of the spacer by the absorbance of the reflected IR.

KMnO₄ solution for 24 h, subsequent immersion in Piranha (composed of 0.05 M H₂O₂ and 1 M H₂SO₄ in H₂O) etch for 2 h, followed by thorough rinsing with Milli-Q water. Subsequently, the glassware was immersed in Milli-Q water and placed inside a supersonic bath for at least 5 min; this was repeated for 3 times with the water replaced by fresh Milli-Q after each wash. Finally, the glassware was rinsed thoroughly again with Milli-Q water. The CaF₂ window and O-rings that come into contact with electrolyte were first cleaned by immersion in acetone p.a. (AppliChem) and placed inside a supersonic bath for 5 min and then treated according to the two last steps of the glassware cleaning (supersonic bath and rinsing). 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 (4 × 1 min plus 1 × 15 min), cooled in a water saturated N₂ 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 pure N₂ that was evaporated off of liquid N₂. 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 H₂ saturated 0.5 M H₂SO₄, was used as a reference electrode [27].

2.2. VSF spectrometer

To collect VSF spectra we overlapped infrared and visible laser pulses spatially and temporally on the working electrode surface and measured the frequency dependent intensity of the emitted sum frequency (SF) field. The laser system and optical setup have been described elsewhere [25]. For this study the IR pulse was centered around 1300 cm⁻¹, had a full width at half maximum (FWHM) of ≈ 300 cm⁻¹, was ≈ 100 fs in length, and was adjusted to a power of 3.6 mW by a λ/2 plate and polarizer combination just in front of the sample. The 800 nm narrowband upconversion pulse (VIS, 3.2 mW with a FWHM of 5 cm⁻¹) was generated in a homebuilt pulse-shaper by dispersing 600 mW of the amplifier output on a grating and focusing the dispersed beam on a slit

(with the focus direction orthogonal to the slit) with μm precision. Unwanted frequencies were filtered out with a band pass filter centered at 800 nm. Both beams were propagated to the sample and focused onto the sample using lenses with focal lengths of 100 and 500 mm and incident angles of $62^\circ \pm 0.5$ and $45^\circ \pm 0.5$ for the IR (KBr lens) and VIS (N-BK7 lens), respectively. The 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 combination (*p*-polarized SF, *p*-polarized VIS, and *p*-polarized IR where *p* is the polarization in the plane of incidence). The acquisition time for a gold reference was 30 sec and 10 sec per spectrum for the sample. For every measurement, spectra were collected during multiple voltammetric scans of 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 problems.

3. Theory

3.1. Modeling the VSF line shape in the absence of surface charge

The measured SF signal intensity I_{sf} is proportional to the intensities of the incident infrared (I_{ir}) and visible beams (I_{vis}) and the squared modulus of the macroscopic, second-order nonlinear susceptibility $\chi^{(2)}$ [28, 5, 29]:

$$I_{\text{sf}} \propto \left| \chi^{(2)} \right|^2 I_{\text{ir}} I_{\text{vis}} \quad (1)$$

For systems that contain bulk phases with inversion symmetry $\chi^{(2)}$ is nonzero (in the dipole approximation) at the interface between the two bulk phases. Because we choose the visible and infrared frequencies such that only the incident infrared beam is resonant with the material, $\chi^{(2)}$ is a function of the incident IR frequency and this frequency dependence furnishes the vibrational response of molecules with interfacial specificity.

$\chi^{(2)}$ is the macroscopic nonlinear susceptibility of the system. In the limit of a local mode it can be related to the frequency dependent nonlinear response of a single molecule, *i.e.* the hyperpolarizability $\beta^{(2)}$:

$$\chi^{(2)} \propto N_s \beta^{(2)} \quad (2)$$

where N_s is the number of molecules in the laser spot. In turn the $\beta^{(2)}$ can be related to the molecule's transition dipole $\left(\frac{\partial \mu}{\partial Q}\right)$ and polarizability $\left(\frac{\partial \alpha}{\partial Q}\right)$ both taken with respect to normal mode Q :

$$\beta^{(2)} = \frac{\partial \mu}{\partial Q} \frac{\partial \alpha}{\partial Q} \quad (3)$$

The frequency dependence of $\beta^{(2)}$ can be described as the coherent sum of a nonresonant and resonant interaction:

$$\beta^{(2)} = \beta_{nr}^{(2)} e^{i\phi} + \frac{\beta_{r,pzc}^{(2)} \cdot \Gamma_{pzc}}{1 - \omega_{ir}/\omega_{pzc} - i\Gamma_{pzc}/\omega_{pzc}} \quad (4)$$

where $\beta_{nr}^{(2)}$ and ϕ are the nonresonant amplitude and phase, $\beta_{nr}^{(2)}$, $\beta_{r,pzc}^{(2)}$ is the, complex, amplitude of the (bi)sulfate vibration we probe at the potential of zero charge, ω_{pzc} is the vibrational frequency of the adsorbed (bi)sulfate at the pzc (pzc), and Γ is the vibrational dephasing time constant also at the pzc.

3.2. Modeling the VSF response with applied bias

Using equations 1 - 4 one can construct a lineshape model where all spectral parameters are independent of applied bias. To describe the electrochemical vibrational Stark effect, however, we need a model that connects each of these parameters to the external field. As we have discussed in the Introduction, previous workers have shown that the change in frequency of the CO stretch vibration on a metal surface in UHV as a function of surface coverage can be written:

$$\chi^{(2)} \propto \frac{\theta \times \beta^{(2)}}{[1 + \alpha_{ir}\theta U_0][1 + \alpha_{vis}\theta U_0][1 + \alpha_{sf}\theta U_0]} \quad (5)$$

where θ is surface coverage, α_i is the polarizability of CO at frequency i and U_0 which was termed as "dipole sum factor" [5] and is defined $U_0 \propto \sum_{j,k} \frac{1}{(r_j - r_k)^3} + \dots$,

in which the r_j or r_k denote the the adsorption site of the adsorbate[2]. Note that the expression in Equation 5 assumes that $\beta^{(2)}$, the *molecular* response, is independent of coverage: the local field induced by dipole-dipole interaction is too small to induce coverage dependent structural changes in CO that would change its second order response. Our study of the adsorption of (bi)sulfate on the Pt(111) electrode differs from CO adsorption in UHV in two important ways: the vibrational response of the adsorbate changes as a function of applied bias but *coverage is constant* and the permanent dipole of the (bi)sulfate is small relative to that of CO. The former implies we need an expression for the relationship developed in equation 5 where external bias appears explicitly and, as we show below, the latter implies that to reproduce our data the molecular response must also be a function of the applied field.

As we have described above, given a perfect surface and independent insight into adsorbate structure U_0 can be calculated, by summing over all adsorbate positions and accounting for the local electric field due to all other dipoles and image dipoles. For the electrochemistry problem we require a similar physical description: we would like to relate the applied external field to the local field sensed by the adsorbate. For small applied external fields we expect the effect of macroscopic bias on α_i , *i.e.* molecular polarizability at frequency i , to be linear [13]. This suggests that we might replace the cU_0 term in equation 5 with a local field parameter L :

$$L = [L_{pzc} + L_{ext}(V - V_{pzc})] \quad (6)$$

in which L_{pzc} is the local field proportionality constant in the absence of net surface charge, V is the applied external bias, and V_{pzc} is the applied bias at the potential of zero charge. From a microscopic perspective the quantity $L_{ext}(V - V_{pzc})$ is the local field normalized by the single molecule dipole moment in the monolayer in the absence of the applied bias, sensed by an adsorbed (bi)sulfate. In what follows we refer to this quantity as the *local field* for convenience. We here follow prior work and take 0.3 V, with respect to the RHE, to be the potential of zero charge of the Pt(111) electrode in 0.5 M H_2SO_5 [30].

As a practical matter we make two simplifying assumptions in analyzing our data. First, because we consider a mode of (bi)sulfate that is only VSF active in the presence of an applied field ($L_{\text{pzc}} \ll L_{\text{ext}}(V - V_{\text{pzc}})$). Second, because (bi)sulfate surface concentration does not change over our potential range of interest our model of the local field does not explicitly account for concentration dependent effects.

This still leaves the question of the effect of the applied bias on the $\beta^{(2)}$. If polarizability changes linearly with the applied macroscopic field, *i.e.* $\alpha(E) \propto \alpha \times E$, the induced dipole will change quadratically, $\mu(E) \propto \alpha(E) \times E$. Given equation 3 we thus expect that the $\beta^{(2)}$ of the isolated (bi)sulfate should be cubic with the respect to the applied, macroscopic field. Because small deviations from linearity with respect to the influence of the external field on the applied potential will have large effects on the $\beta^{(2)}$, in practice we will treat this as a fit parameter and test the cubic prediction from the data. Given these assumptions the version of equation 5 appropriate for description of the electrochemical vibrational Stark Effect is (where $\Delta V = (V - V_{\text{pzc}})$):

$$\chi^{(2)} \propto \frac{\beta^{(2)} [L_{\text{ext}} \Delta V]^n}{[1 + \alpha_{\text{ir}} L_{\text{ext}} \Delta V] [1 + \alpha_{\text{vis}} L_{\text{ext}} \Delta V] [1 + \alpha_{\text{sf}} L_{\text{ext}} \Delta V]} \quad (7)$$

Note that we have implicitly assumed, in writing equation 7, that the orientation of (bi)sulfate anions is potential independent over our range of interest (if it were not, per equation 2, we would expect that the potential dependent $\chi^{(2)}$ would be a function of (bi)sulfate orientation). We make this simplifying assumption because previous in situ-electrochemical STM measurements have shown that the adsorption geometry of sulphate in the potential region that is investigated in the current study is independent of the externally applied potential [31, 32].

The molecular polarizability at the i^{th} frequency, α_i in equation 7, can be written as a sum of the electronic and vibrational contributions [5]²:

$$\alpha_i = \alpha_e + \frac{\alpha_v}{1 - (\omega_{\text{ir}}/\omega_0^2) (\omega_{\text{ir}} + i\Gamma)} \quad (8)$$

²In reference [5], there is an factor of 2 attached to the last term of the denominator. This factor is absent from the derivation in the original reference[2]

in which the vibrational and electronic polarizabilities at the pzc are denoted as α_v and α_e . Since both the sf and vis fields are far off an electronic transition and their frequencies much larger than those of the vibrational transition we approximate the molecular polarizability at these frequencies as $\alpha_{\text{sf}} \approx \alpha_{\text{vis}} \approx \alpha_e = 1.775 \text{ \AA}^3$ [33]³

4. Results and Discussion

The cyclic voltammetry (CV) of Pt(111) in contact with 0.5 M H_2SO_4 , recorded at a scanning speed of 50 mV/s in a hanging meniscus geometry, is shown in Figure 2(a). Moving from a potential of 0 V in a positive direction, the plateau from 0.05 to 0.3 V is assigned to the adsorption of so-called underpotentially deposited hydrogen (H_{UPD}) on (111) terraces [22]. Continuing to still more positive potentials, the two current features in the region between 0.3 - 0.45 V, often called the “butterfly” feature, are thought to be the result of (bi)sulfate adsorption [22]. The broad feature in the lower potential portion of the *butterfly* is thought to result from formation of an unordered layer of (bi)sulfate that adsorbs in a bidentate fashion and the large current spike at 0.45 V from a disorder - order phase transition [31]. At potentials positive of the spike STM studies have shown that the (bi)sulfate adlayer has a $(\sqrt{3}\times\sqrt{9})\text{R}19.1^\circ$ structure and a coverage of 0.2 ML (3×10^{14} ions/cm²) [34, 35, 32]. The low coverage has lead to the conclusion that a co-adsorbate must also be present over this potential range. The identity of this co-adsorbate is unknown but is typically argued to be either water or perhaps adsorbed OH [36]. Going to still more positive potentials, a small positive current is apparent at ≈ 0.7 V. The assignment of this feature has been strongly debated. Amongst other possibilities it has been argued to be the result of the conversion of bisulfate to sulfate [37], a second order to disorder transition of the adsorbed anions [31], OH coadsorption and/or

³The numerical value of α_e we adapt here was taken from a DFT simulation of a solvated sulfate anion [33]. We found that our results are relatively insensitive to the precise value chosen: a change of α_e from 1.775 to 2.0 Å^3 cause a change of the α_v from 0.4 to 0.45 Å^3 .

the possible desorption of (bi)sulfate anions [38, 39].

Figure 2(b) shows Cyclic voltammeters collected from a Pt(111) working electrode within our spectroelectrochemical cell with the electrode retracted (this is labelled *bulk*) and in measurement position. The CVs clearly show similar current features to that in the meniscus geometry⁴. It is finally worth noting that the small current feature around 0.7 V that is observed in the hanging meniscus geometry is absent in the electrochemical cell used for the optics measurements. We will return to this point when discussing the optical response.

Figure 3(a) shows the measured VSF spectra as a function of applied external potential during the positive going scan. The CV in the experimental geometry for the VSFS measurement is shown in Figure 2(b). Only spectra after reaching full coverage of (bi)sulfate are shown (0.5 - 0.9 V). As discussed above, and is apparent from Figure 2(b), over this potential range there is no change in (bi)sulfate surface population. It is clear from inspection of Figure 3(a) that at a potential of 0.5 V, a weak and broad resonance centered at $\approx 1225 \text{ cm}^{-1}$ appears whose center frequency blue shifts, intensity increases and line width narrows with increasing potential. This peak has been assigned by prior workers to the stretching of the S-O_{uncoord.} bond of tridentate adsorbed sulfuric acid anions. Because sulfuric acid is diprotic this anion may, in principal be either SO_4^{2-} or HSO_4^- . The identity of this species has been extensively debated in the literature. While the issue has not yet been definitively resolved, most recent theoretical studies assign this mode to the S-O_{uncoord.} stretching vibration of a tridentate adsorbed SO_4^{2-} [8, 40, 36]. In any case, since the assignment of this mode does not affect the conclusions of the current study, both the potential dependent spectra and CV suggest that the adsorbed species does not (de)protonate in our 400 meV potential range, hereafter we will simply call this mode S-O stretching (S-O_{str}) for convenience.

⁴We take the asymmetry in current features between the cathodic and anodic scans to be due to leakage of small amounts of O₂ into the cell and/or contaminants from the CaF₂ window (note that CaF₂ dissolves in strong acid or base).

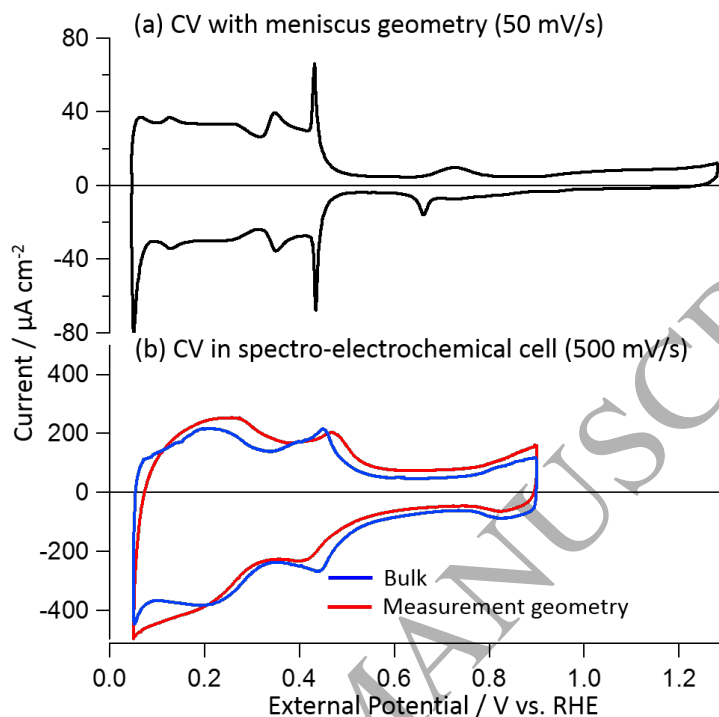


Figure 2: (a) Cyclic voltammograms of a Pt(111) electrode in 0.5 M H₂SO₄ in meniscus geometry, the scanning speed was 50 mV/s. (b) Voltammograms (500 mV/s) recorded in the spectro-electrochemical cell. The blue line was recorded in bulk electrolyte within the spectroelectrochemical cell, the red line with a film of $\approx 1\mu\text{m}$ between the working electrode and a CaF₂ window.

To understand the potential induced spectral changes in Figure 3(a) we first quantified the line shape changes using the model in Equations 1 - 4: using different parameters to describe the resonance at each potential. This approach allows us to extract the center frequency, $\beta_r^{(2)}$ and Γ for the S-O_{str} vibration *at each* potential. The extracted center frequencies, plotted as a function of applied bias in Figure 4, clearly illustrate that as potential is changed from 0.5 - 0.9 V the center frequency of the S-O_{str} spectral feature changes from 1225 to 1260 cm⁻¹. As described in the Introduction, a number of prior studies of this system have observed a similar potential dependence of the center frequency. Typically

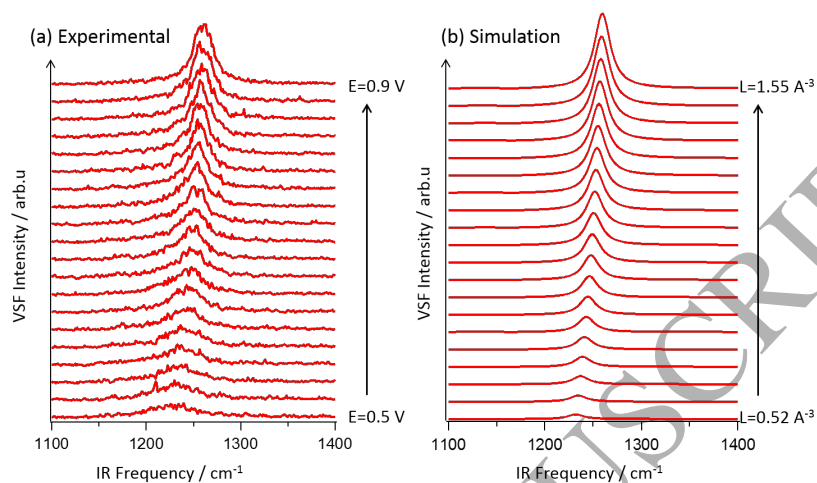


Figure 3: (a) Experimentally observed VSFS spectra of the S-O_{str} on a Pt(111) electrode in 0.5 M H₂SO₄ solution as a function of applied potential; (b) Corresponding simulated spectra using the parameters that determined from the fit of the center frequency (Figure 4) and peak intensity (Figure 5), plotted as a function of local field factors L (see Equation. 6 and the relevant text for details).

this observation has been rationalized by assuming that the change in frequency with applied bias is linear, or composed of multiple linear segments, and a slope extracted. Inspection of Figure 4 suggests that at least two such line segments would be necessary to fit our data. If we choose to have one line segment from 0.5-0.7 and one from 0.7-0.9 V we find slopes of $118 \pm 6 \text{ cm}^{-1}/\text{V}$ and $56 \pm 3 \text{ cm}^{-1}/\text{V}$ respectively. Prior VSF studies of have found slopes of $75 \text{ cm}^{-1}/\text{V}$ and $56 \text{ cm}^{-1}/\text{V}$ over the same regions [7]. The low slope from 0.5-0.7 V is particularly surprising because earlier IR studies of the same potential region found a slope of $120 \text{ cm}^{-1}/\text{V}$ [6]. We found in preliminary measurements that the slope of the change in center frequency with potential, for the potential region between 0.5 and 0.7 V was extremely sensitive to IR power. IR energies above $3.6 \mu\text{J}$ per pulse lead to apparent slopes consistent with the earlier VSF studies (see supplementary information for one additional data set with IR power of 4.2 mW), presumably because irradiating the surface with high enough peak power leads to laser

induced (bi)sulfate desorption and a new, dynamic (bi)sulfate coverage that now depends on laser power. As has been demonstrated previously and discussed above, changes in surface coverage would be expected to change the slope of the VSE [1, 2, 5].

While our data thus appears to be qualitatively consistent with both prior IR and VSF studies, it is clear that simply fitting the extracted center frequencies (or line widths or intensities) with a line provides little insight into the *mechanism* by which the external field affects the spectral response nor is there any electrochemical justification (see Figure 2) for choosing to break this potential range into two segments at 0.7 V. Combining equations 7 and 8 allows the derivation of an expression for the potential dependent peak center frequency (see Supplementary Information for detailed discussion of the derivation):

$$\omega_{\Delta V} = \omega_{pzc} \sqrt{1 + \frac{\alpha_v L_{ext} \Delta V}{1 + \alpha_e L_{ext} \Delta V}} \quad (9)$$

where the electronic polarizability α_e is set to be 1.775 \AA^3 as mentioned in the theory section. The three unknown parameters in equation 9 are the center frequency (ω_{pzc}) and vibrational polarizability (α_v) at the pzc and the scaling factor L_{ext} between the local field and the externally applied potential.

As demonstrated in Figure 4 the VSE can be well reproduced by this model. We find, given the fit displayed in Figure 4, $\alpha_v = 0.4 \text{ \AA}^{-3}$. While no independent insight into the vibrational polarizability of interfacial (bi)sulfate exists, our extracted value is similar to other strongly interacting adsorbates on metal surfaces: for CO on Pt(111) $\alpha_v = 0.52 \text{ \AA}^3$ [5]. While independent evaluation of L_{ext} is challenging, we can at least compare the product: $L_{ext} \Delta V$. This quantity varies from 0.52 to 1.55 \AA^{-3} with a change in external bias of 0.5 - 0.9 V. This local field is of the same order of magnitude as that sensed by a single sulfate anion on Pt(111) in a recent DFT simulation [8]. Finally, from the fit $\omega_{pzc} = 1168 \text{ cm}^{-1}$. With these parameters in mind the physics of the problem become clear: a linear perturbation of molecular polarizability with changing bias leads to a change in center frequency with bias that is nonlinear, as predicted in Equation 9. In this picture the slope of the change in frequency

with external bias continually decreases due to the increasing polarization of interfacial (bi)sulfates ⁵.

It is worth pointing out that this kind of nonlinearity only becomes obvious when two conditions are met: (1), the net local field (L_{pzc} in 6) is small at potential of zero charge; (2), change of the potential is sufficiently large (the second terms in the denominator and the numerator of 9 are close to unity). As shown in the supplementary information, too large net local field at pzc or too small change of the local field as a function of the external bias will only cause apparently linear change of the stark shifting rate (see Supporting Information for a numerical exploration of this effect). We thus expect that the extent to which a particular system has a nonlinear shift in center frequency with applied bias will depend sensitively on local structural parameters (coverage, dipole moment, etc). Presumably it is this relationship which explain why similar studies of other systems, particularly recent, high resolution work by Lian and coworkers and Dawlaty and coworkers, see only a linear dependence of center frequency on applied field[9, 10, 6, 7, 3, 14, 15, 16, 18, 21]

The potential dependent peak amplitude of the data in Figure 3 are shown as black triangles in Figure 5, and the corresponding fit of the model to the data shown as a solid red line. The parameter n in the numerator of equation 7, which describes the dependence of the hyperpolarizability on the external bias, is determined from a global fit of both the peak center frequency and the peak amplitude by linking the vibrational polarizability, α_v , and the local factor, L_{ext} , as described above. The n was determined to be 3.3, quite similar to that expected if the polarizability is linearly modulated by the applied field (as discussed in the Theory section). It is clear from inspection that our model overestimates amplitudes from 0.8-0.9 V. We cannot offer a definitive explanation for this discrepancy but note that the CVs in Figure 2(b) also show small oxidation (positive going scan) and reduction (negative going scan) currents over this

⁵Note that a nonlinear relationship of polarizability to applied bias would only serve to amplify this trend: small changes in external bias would lead to even larger decreases in slope.

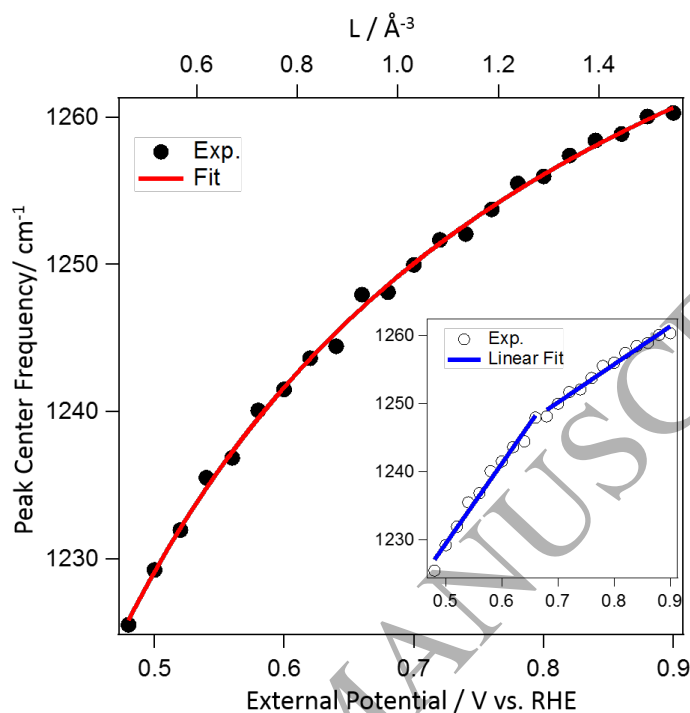


Figure 4: Peak center frequency as a function of applied external potential. The black dots represent the experimental data, while the red line shows the fit to Equation 9 of the theory section. The inset shows that the experimental observations can be also fitted with two linear functions with slopes of $118 \pm 6 \text{ cm}^{-1} / \text{V}$ and $56 \pm 3 \text{ cm}^{-1} / \text{V}$ for the low and high potential region, respectively. **The full data set of the peak center frequencies and other parameters as a function of external bias that obtained from the fit is given in the supplementary information.**

potential range. These currents are consistent with a change in surface structure, or chemical reaction, occurring over this potential range that is clearly not accounted for in our model.

In the model developed in the Theory Section we, implicitly, treated the bandwidth as a potential-independent. However inspection of the data, and the bandwidth extracted from the data and plotted in the inset of Figure 5, clarifies that the bandwidth decreases monotonically with increasing potential from 0.5-0.8 V **and that at potentials above 0.8 V it is potential independent.**

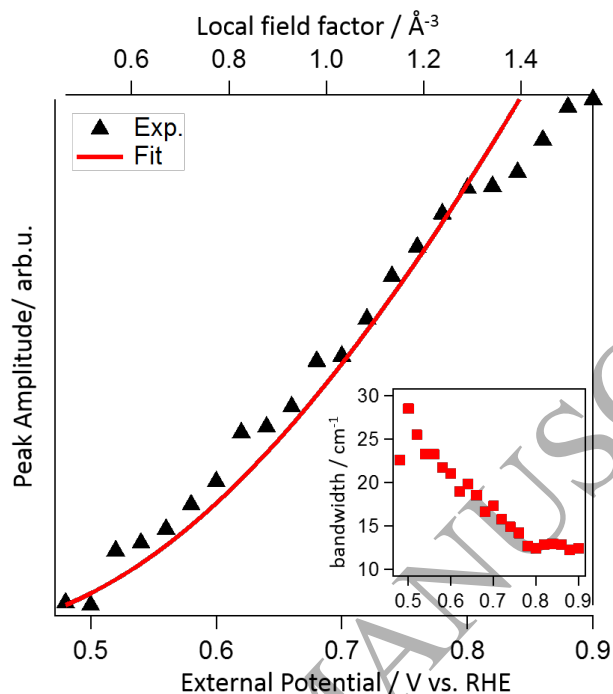


Figure 5: Normalized peak amplitude as a function of applied external potential. The black triangles represent the experimental data, while the solid red line shows the simulated peak strength as a function of local field factor according to Equation 7. The inset displays the peak bandwidth as a function of the external electrode potential. **The full data set of the normalized peak amplitude and other parameters as a function of external bias that obtained from the fit is given in the supplementary information.**

Also at 0.8 V the amplitude starts to deviate from the monotonic behavior it showed from 0.5-0.8 V. The observed change in bandwidth from 0.5-0.8 V can be rationalized within the framework of the so-called electronic friction theory, if we assume that the bandwidth is mostly determined by lifetime broadening, as is the case for CO adsorbed on Pt(111) and Cu(100) both in UHV and in electrochemical systems.[41, 42] Within the electronic friction theory, the spectral bandwidth of an adsorbate vibration is proportional to rapid, thermal, charge density oscillations between the Fermi level of the metal surface and an antibonding orbital of the adsorbate during the vibrational

period [41, 42]. Applying a positive potential to an electrode shifts its Fermi level downwards in energy thus causing the (bi)sulfate antibonding orbital to be populated less frequently during the vibrational period, and, therefore, the linewidth to narrow. This linewidth narrowing has also been observed by others and attributed to a surface reconstruction, or chemical reactions [6, 7]. We show in this study that it is not necessary to invoke such effects to rationalize the potential dependent center frequency and intensity of adsorbed (bi)sulfate and so strongly suggest any conclusions about potential dependent line widths should be revisited. Quantifying the potential dependent change in line width requires detailed insight into the electronic structure of the electrode/electrolyte interface beyond that accessible from time averaged VSF spectroscopy of the Pt(111) electrode/electrolyte interface. We are currently engaged in electronically resonant pump-probe VSF spectroscopy to help us clarify this problem.

5. Summary and Conclusions

We have employed VSF spectroscopy to study the VSE of (bi)sulfate adsorbed on Pt(111) under electrochemical conditions. Pt single crystal working electrodes in H_2SO_4 electrolyte are both of practical interest, as Pt is an extremely efficient electrocatalyst for a wide variety of reactions, and a commonly employed model systems for study of the electrode/aqueous electrolyte interface. For purposes of understanding the electrochemical VSE it has the particular advantage that there is a relatively large potential range over which the CV makes clear that there is effectively no change in population but adsorbate line shape significantly evolves. One might thus expect to be able to use this range to understand the effect of the applied, macroscopic bias, independent of any change in surface density. Prior studies have examined this system, using VSF spectroscopy and infrared absorption, and fit the potential dependent spectral changes using an empirical form, typically a line. This relationship is generally not justified microscopically and changes in the slopes of the resulting spectral parameters with potential are usually inferred to indicate changes in surface structure or surface chemistry.

In this study we described the potential-dependent shift in (bi)sulfate center frequency and intensity that explicitly accounts for the effects of dipole-dipole interaction. This approach is inspired by many prior studies of the coverage dependent shift in adsorbate spectral response of small molecules adsorbed on metal surfaces in UHV [1, 2, 5] and prior conclusions that the local field ‘sensed’ by adsorbates on an electrode will vary linearly with applied bias [11, 13]. The critical insight that the application of this approach offers is that if changes in applied macroscopic bias are linearly related to changes in local field *sensed* by individual adsorbates dipole/dipole coupling may cause them to be *nonlinearly* related to adsorbate center frequencies and intensities. Thus changes in adsorbate center frequency or intensity that are nonlinear with potential do not, necessarily, imply changes in interfacial structure or chemistry.

The physics we have described is applicable to adsorbates on all electrochemical interfaces. While systems in which both bias and interfacial population are changing will complicate interpretation, by collecting VSF spectra in multiple spectral windows and simultaneously collecting in-situ CVs it should be possible to quantitatively account for changes in interfacial population or co-adsorption and unambiguously extract the molecular-level structural insight within the spectral observable. Our work implies that spectroelectrochemical studies that have attributed chemical significance to changes in slopes of spectral parameters with potential need to be revisited. Dipole/dipole interaction can induce such changes independent of any chemical or structural change.

References

- [1] M. Scheffler, The influence of lateral interactions on the vibrational spectrum of adsorbed CO, *Surface Science* 81 (2) (1979) 562–570. doi:10.1016/0039-6028(79)90120-1.
- [2] B. Persson, R. Ryberg, Vibrational interaction between molecules adsorbed on a metal surface: The dipole-dipole interaction, *Physical Review B* 24 (12) (1981) 6954. doi:10.1103/PhysRevB.24.6954.

- [3] I. Villegas, M. Weaver, Infrared spectroscopy of model electrochemical interfaces in ultrahigh vacuum: roles of solvation in the vibrational stark effect, *Journal of Physical Chemistry B* 101 (30) (1997) 5842–5852. doi:10.1021/jp9709058.
- [4] E. Backus, M. Bonn, A quantitative comparison between reflection absorption infrared and sum-frequency generation spectroscopy, *Chemical Physics Letters* 412 (1) (2005) 152–157. doi:10.1016/j.cplett.2005.06.118.
- [5] M. Cho, C. Hess, M. Bonn, Lateral interactions between adsorbed molecules: Investigations of CO on Ru(001) using nonlinear surface vibrational spectroscopies, *Physical Review B* 65 (20) (2002) 205423. doi:10.1103/PhysRevB.65.205423.
- [6] V. Climent, N. Garcia-Araez, J. Feliu, Influence of alkali cations on the infrared spectra of adsorbed (bi)sulphate on Pt(111) electrodes, *Electrochemistry Communications* 8 (10) (2006) 1577–1582. doi:10.1016/j.elecom.2006.07.027.
- [7] B. Braunschweig, P. Mukherjee, D. Dlott, A. Wieckowski, Real-time investigations of Pt(111) surface transformations in sulfuric acid solutions, *Journal of the American Chemical Society* 132 (40) (2010) 14036–14038. doi:10.1021/ja106618z.
- [8] R. Jinnouchi, T. Hatanaka, Y. Morimoto, M. Osawa, Stark effect on vibration frequencies of sulfate on Pt(111) electrode, *Electrochimica Acta* 101 (2013) 254–261. doi:10.1016/j.electacta.2012.12.104.
- [9] A. Ge, P. E. Videla, G. L. Lee, B. Rudshiteyn, J. Song, C. P. Kubiak, V. S. Batista, T. Lian, Interfacial structure and electric field probed by in situ electrochemical vibrational stark effect spectroscopy and computational modeling, *Journal of Physical Chemistry C* 121 (34) (2017) 18674–18682. doi:10.1021/acs.jpcc.7b05563.

- [10] J. G. Patrow, S. A. Sorenson, J. M. Dawlaty, Direct spectroscopic measurement of interfacial electric fields near an electrode under polarizing or current-carrying conditions, *Journal of Physical Chemistry C* 121 (21) (2017) 11585–11592. doi:10.1021/acs.jpcc.7b03134.
- [11] J. Sass, D. Lackey, J. Schott, B. Straehler, Electrochemical double layer simulations by halogen, alkali and hydrogen coadsorption with water on metal surfaces, *Surface Science* 247 (2-3) (1991) 239–247. doi:10.1016/0039-6028(91)90132-C.
- [12] I. Villegas, M. Weaver, Modeling electrochemical interfaces in ultrahigh vacuum: molecular roles of solvation in double-layer phenomena, *Journal of Physical Chemistry B* 101 (49) (1997) 10166–10177. doi:10.1021/jp972441j.
- [13] M. Weaver, S. Wasileski, Influence of double-layer solvation on local versus macroscopic surface potentials on ordered platinum-group metals as sensed by the vibrational stark effect, *Langmuir* 17 (10) (2001) 3039–3043. doi:10.1021/1a0014712.
- [14] S. Yang, H. Noguchi, K. Uosaki, Broader energy distribution of CO adsorbed at polycrystalline pt electrode in comparison with that at Pt(111) electrode in H₂SO₄ solution confirmed by potential dependent IR/visible double resonance sum frequency generation spectroscopy, *Electrochimica Acta* 235 (2017) 280 – 286. doi:https://doi.org/10.1016/j.electacta.2017.03.113.
- [15] J. Wang, M. Xu, Z. Huangfu, Y. Wang, Y. He, W. Guo, Z. Wang, Observation of gold electrode surface response to the adsorption and oxidation of thiocyanate in acidic electrolyte with broadband sum-frequency generation spectroscopy, *Vibrational Spectroscopy* 85 (2016) 122 – 127. doi:https://doi.org/10.1016/j.vibspec.2016.04.001.
- [16] S. Xu, S. Xing, S.-S. Pei, V. Ivaništšev, R. Lynden-Bell, S. Baldelli, Molecular response of 1-Butyl-3-Methylimidazolium Dicyanamide ionic liquid at the

- graphene electrode interface investigated by sum frequency generation spectroscopy and molecular dynamics simulations, *Journal of Physical Chemistry C* 119 (46) (2015) 26009–26019. doi:10.1021/acs.jpcc.5b08736.
- [17] W.-T. Liu, Y. R. Shen, In situ sum-frequency vibrational spectroscopy of electrochemical interfaces with surface plasmon resonance, *Proceedings of the National Academy of Sciences* 111 (4) (2014) 1293–1297. doi:10.1073/pnas.1317290111.
- [18] P. Koelsch, M. I. Muglali, M. Rohwerder, A. Erbe, Third-order effects in resonant sum-frequency-generation signals at electrified metal liquid interfaces, *Journal of the Optical Society of America B* 30 (1) (2013) 219–223. doi:10.1364/JOSAB.30.000219.
- [19] H. Liu, Y. Tong, N. Kuwata, M. Osawa, J. Kawamura, S. Ye, Adsorption of Propylene Carbonate(PC) on the LiCoO₂ Surface Investigated by Nonlinear Vibrational Spectroscopy, *Journal of Physical Chemistry C* 113 (48) (2009) 20531–20534. doi:10.1021/jp907146n.
- [20] Z. D. Schultz, S. K. Shaw, A. A. Gewirth, Potential dependent organization of water at the electrified metal/liquid interface, *Journal of the American Chemical Society* 127 (45) (2005) 15916–15922, PMID: 16277535. doi:10.1021/ja0543393.
- [21] F. Vidal, B. Busson, A. Tadjeddine, A. Peremans, Effect of a static electric field on the vibrational and electronic properties of a compressed CO adlayer on Pt(110) in nonaqueous electrolyte as probed by infrared reflection-absorption spectroscopy and infrared-visible sum-frequency generation spectroscopy, *Journal of Chemical Physics* 119 (23) (2003) 12492–12498. doi:10.1063/1.1626640.
- [22] J. Feliu, J. Orts, R. Gomez, A. Aldaz, J. Clavilier, New information on the unusual adsorption states of Pt(111) in sulphuric acid solutions from potentiostatic adsorbate replacement by CO, *Journal of Electroanalytical Chemistry* 372 (1-2) (1994) 265–268. doi:10.1016/0022-0728(93)03259-R.

- [23] P. Faguy, N. Markovic, R. Adzic, C. Fierro, E. Yeager, A study of bisulfate adsorption on Pt(111) single crystal electrodes using in situ fourier transform infrared spectroscopy, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 289 (1-2) (1990) 245–262. doi:10.1016/0022-0728(90)87220-E.
- [24] Y. Sawatari, J. Inukai, M. Ito, The structure of bisulfate and perchlorate on a Pt(111) electrode surface studied by infrared spectroscopy and ab-initio molecular orbital calculation, *Journal of Electron Spectroscopy and Related Phenomena* 64 (1993) 515–522. doi:10.1016/0368-2048(93)80117-5.
- [25] Y. Tong, K. Cai, M. Wolf, R. Campen, Probing the electrooxidation of weakly adsorbed formic acid on Pt(100), *Catalysis Today* 260 (2016) 66–71. doi:10.1016/j.cattod.2015.08.015.
- [26] Y. Tong, F. Lapointe, M. Thaemer, M. Wolf, R. Campen, Hydrophobic water probed experimentally at the gold electrode/aqueous interface, *Angewandte Chemie International Edition* 56 (15) (2017) 4211–4214. doi:10.1002/anie.201612183.
- [27] P.-O. Eggen, A simple hydrogen electrode, *Journal of Chemical Education* 86 (3) (2009) 352. doi:10.1021/ed086p352.
- [28] Y. R. Shen, *The Principles of Nonlinear Optics*, John Wiley & Sons Inc., New York, 1984.
- [29] Y. Tong, Y. Zhao, N. Li, M. Osawa, P. Davies, S. Ye, Interference effects in the sum frequency generation spectra of thin organic films. i. theoretical modeling and simulation, *Journal of Chemical Physics* 133 (3) (2010) 034704–13. doi:10.1063/1.3428668.
- [30] M. Weaver, Potentials of zero charge for Platinum(111)- aqueous interfaces: A combined assessment from in-situ and ultrahigh-vacuum measurements, *Langmuir* 14 (14) (1998) 3932–3936. doi:10.1021/1a9801054.

- [31] A. Funtikov, U. Linke, U. Stimming, R. Vogel, An in-situ STM study of anion adsorption on Pt(111) from sulfuric acid solutions, *Surface Science* 324 (1) (1995) L343–L348. doi:10.1016/0039-6028(94)00774-8.
- [32] B. Braunschweig, W. Daum, Superstructures and order-disorder transition of sulfate adlayers on Pt(111) in sulfuric acid solution, *Langmuir* 25 (18) (2009) 11112–11120. doi:10.1021/la901399j.
- [33] P. Jungwirth, J. Curtis, D. Tobias, Polarizability and aqueous solvation of the sulfate dianion, *Chemical Physics Letters* 367 (5) (2003) 704–710. doi:10.1016/S0009-2614(02)01782-7.
- [34] A. Kolics, A. Wieckowski, Adsorption of bisulfate and sulfate anions on a Pt(111) electrode, *Journal of Physical Chemistry B* 105 (13) (2001) 2588–2595. doi:10.1021/jp003536f, [link].
- [35] E. Herrero, J. Mostany, J. Feliu, J. Lipkowski, Thermodynamic studies of anion adsorption at the Pt(111) electrode surface in sulfuric acid solutions, *Journal of Electroanalytical Chemistry* 534 (1) (2002) 79–89. doi:10.1016/S0022-0728(02)01101-4.
- [36] A. Comas-Vives, J. Bandlow, T. Jacob, Ab initio study of the electrochemical H₂SO₄/Pt(111) interface, *Physical Chemistry Chemical Physics* 15 (3) (2013) 992–997. doi:10.1039/C2CP43054A.
- [37] C. Nishihara, H. Nozoye, Note on the hydrogen adsorption-desorption voltammogram on Pt(111) in sulfuric acid solution, *Journal of Electroanalytical Chemistry* 379 (1-2) (1994) 527–530. doi:10.1016/0022-0728(94)87182-5.
- [38] N. Garcia-Araez, V. Climent, P. Rodrigues, J. Feliu, Thermodynamic analysis of (bi)sulfate adsorption on a Pt(111) electrode as a function of pH, *Electrochimica Acta* 53 (23) (2008) 6793–6806. doi:10.1016/j.electacta.2007.12.086.

- [39] N. Garcia-Araez, V. Climent, P. Rodriguez, J. Feliu, Elucidation of the chemical nature of adsorbed species for Pt(111) in H₂SO₄ solutions by thermodynamic analysis, *Langmuir* 26 (14) (2010) 12408–12417. doi:10.1021/1a101112b.
- [40] K.-Y. Yeh, N. Restaino, M. Esopi, J. Maranas, M. Janik, The adsorption of bisulfate and sulfate anions over a Pt(111) electrode: A first principle study of adsorption configurations, vibrational frequencies and linear sweep voltammogram simulations, *Catalysis Today* 202 (2013) 20–35. doi:10.1016/j.cattod.2012.03.011.
- [41] B. N. J. Persson, M. Persson, Vibrational lifetime for CO adsorbed on Cu(100), *Solid State Communications* 36 (2) (1980) 175 – 179. doi:10.1016/0038-1098(80)90677-8.
- [42] M. E. Schmidt, P. Guyot-Sionnest, Electrochemical tuning of the lifetime of the CO stretching vibration for CO/Pt(111), *Journal of Chemical Physics* 104 (6) (1996) 2438–2445. doi:10.1063/1.470938.