Electrochemical Surface Science
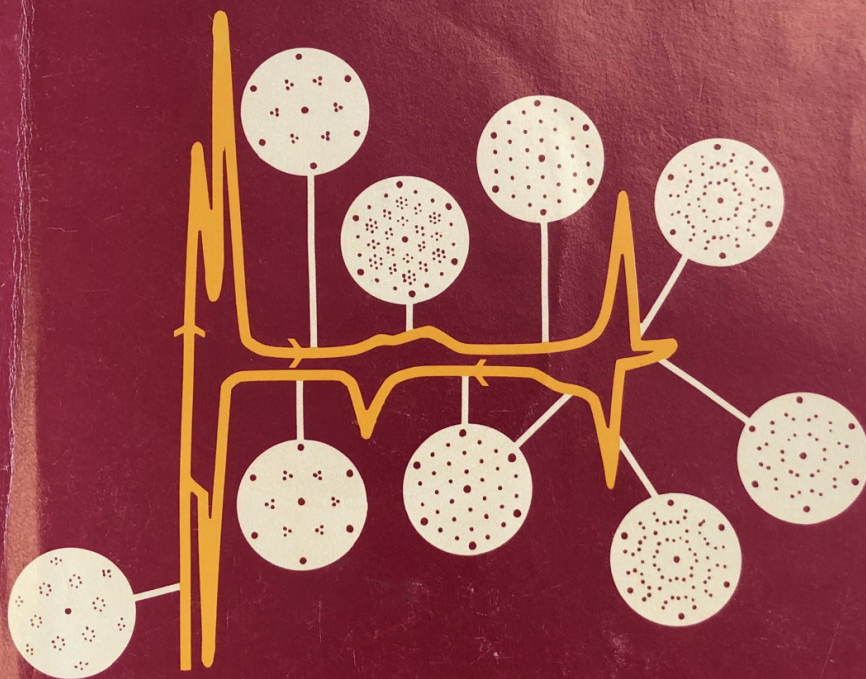
Molecular Phenomena at Electrode Surfaces

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Chapter 20

Second Harmonic Generation Studies of Chemisorption at Electrode Surfaces

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Optical second harmonic generation from electrode surfaces is employed *in situ* to study the electrochemical processes of lithium deposition and monatomic hydrogen chemisorption at silver electrodes in acetonitrile, and the reversible deposition of hydrogen at platinum electrodes in aqueous perchloric acid solutions. The changes observed in the second harmonic intensity are ascribed to modifications in the electronic structure of the metal surface upon adsorption. These studies demonstrate how the nonlinear optical response from the surface can provide both a qualitative and quantitative probe of chemisorption.

Optical second harmonic generation (SHG) is sensitive to the interface of two centrosymmetric media. At metal/electrolyte interfaces, the surface nonlinear susceptibility arising from the sharp gradients in the static electric fields have been shown to dominate the bulk magnetic dipole sources for SHG when using p-polarized light in a reflection geometry (1-2). This sensitivity of the SHG to the surface has been exploited at electrodes for measurements of charge density (3-4), anionic adsorption (5), oxide formation (6) and chemisorption (7-8). In the majority of the chemisorption studies to date, changes in the nonlinear optical response of the metal surface upon reaction have been used to indirectly follow the adsorption process. For example, the process of underpotential deposition (upd) of a monolayer of Pb or Tl has been studied through its effect on the SHG from silver surfaces (3-4,7).

In this paper we extend our SHG studies to silver electrodes in acetonitrile solutions and to platinum electrodes in aqueous solutions. Three different examples are chosen to demonstrate how SHG can be used both qualitatively and quantitatively to study the adsorption of chemical species onto

an electrode surface. The systems examined are the deposition of lithium onto a silver surface in acetonitrile, the chemisorption of monatomic hydrogen during the evolution of molecular hydrogen in nonaqueous acidic media, and the reversible deposition of hydrogen on platinum electrodes prior to the hydrogen evolution reaction in aqueous perchloric acid solutions.

The SHG studies at silver electrodes employed a p-polarized fundamental beam at 1064 nm from a Q-switched Nd:YAG laser (10 Hz repetition rate, 8 ns pulse width) with an incident angle of 30° relative to the surface normal, and the platinum electrode experiments used p-polarized light at 578 nm from a pulsed dye laser (10 Hz repetition rate, 6 ns pulse width) with an incident angle of 60°. The current and second harmonic signal observed during the cycling of the electrode potential were recorded simultaneously and stored on computer. In the two nonaqueous studies, potentials are reported versus a $Ag|0.100M\ AgNO_3$ reference electrode, and in the aqueous study the potentials are reported versus a saturated calomel electrode (SCE). Further experimental details are published elsewhere (8).

Lithium Deposition on Silver Electrodes in Acetonitrile

The cyclic voltammogram for a silver electrode in 0.1M $LiClO_4$ acetonitrile solution is shown in Figure 1 (curve a). At a potential of -1.5 V, cathodic current due to the reduction of Li^+ ions commences. The upd of lithium has been reported previously by Kolb et al. for positive potential sweeps after substantial lithium reduction (9); however, due to the reactivity of the metallic lithium with impurities in solution, the adsorbed layer formed on the negative potential sweep is not as stable as other upd monolayers (9). An additional cathodic wave due to the reduction of lithium is observed at approximately -2.5V, and on the return sweep the lack of an anodic wave is indicative of the reactivity of the chemisorbed atoms.

The second harmonic signal at 532 nm obtained from the electrode during this cyclic voltammogram is also shown in Figure 1 (curve b). The second harmonic signal steadily increases as the potential is swept negatively through the lithium reduction region, and decreases back to its original level on the positive scan. The independence of the second harmonic signal on the scan direction suggests that the surface undergoes a change that is solely a function of potential. We attribute the increase in second harmonic signal from the surface to the presence of a potential-dependent surface coverage of chemisorbed lithium. The amount of adsorbed lithium at a given potential is determined by the rates of formation and destruction of the reactive metal overlayer. The nonlinear susceptibility of the electrode surface increases upon lithium deposition due to the increase in free electron density on the surface through the delocalization of the lithium 2s electron.

Similar increases of the surface second harmonic intensity have been observed during the formation of alkali metal monolayers on Ge and Rh surfaces *in vacuo* (10-11).

Hydrogen Adsorption and Evolution at Silver Electrodes in Acetonitrile

The cyclic voltammogram and the second harmonic signal at 532 nm for a silver electrode in a 0.1M LiClO4 + 3.5mM HClO4 acetonitrile solution is shown in Figure 2. At a potential of - 0.83V there is a cathodic current peak due to the irreversible evolution of molecular hydrogen. A reversible decrease is observed in the second harmonic signal that starts prior to the cathodic current wave. We attribute this decrease in the optical signal to the modification of the nonlinear susceptibility of the silver surface by the steady state formation of a monatomic hydrogen intermediate on the electrode during the hydrogen evolution reaction.

The cyclic voltammogram and the second harmonic signal at 532 nm for a silver electrode in a 0.1M TBABF4 (tetrabutylammonium tetrafluoroborate) + 35mM acetic acid acetonitrile solution is shown in Figure 3. A reversible loss of second harmonic signal and an irreversible current wave from hydrogen evolution are present just as in the perchloric acid solution. However, the potentials for these processes have been shifted by approximately -1V. These shifts are directly related to the pH of the solution; millimolar solutions of other acids show shifts of varying magnitude in accordance with their acidity (8).

We can quantitate the relative surface coverage of adsorbed hydrogen, θ, from the second harmonic signal, $I(2\omega)$:

$$I(2\omega) = I(2\omega)_0 (1 + c\theta)^2 \qquad (1)$$

where $I(2\omega)_0$ is the second harmonic signal from the surface in the absence of chemisorption, and c is a constant that can be determined by the second harmonic signal at maximum surface coverage ($\theta = 1$). Equation 1 assumes that there is no change in phase of the nonlinear susceptibility from the surface. The relative surface coverage calculated from the second harmonic signal using Equation 1 for the case of acetic acid is shown as the solid circles in Figure 4. The potential at which the relative surface coverage is one half, $E_{1/2}(\theta)$, is -1.51V. For the perchloric acid solution a similar curve can be constructed, and $E_{1/2}(\theta)$ is found to be -0.45V.

These two facts, (i) the shape of the relative surface coverage-potential curve and (ii) the pH dependence of $E_{1/2}(\theta)$ can both be accounted for by the following reaction mechanism:
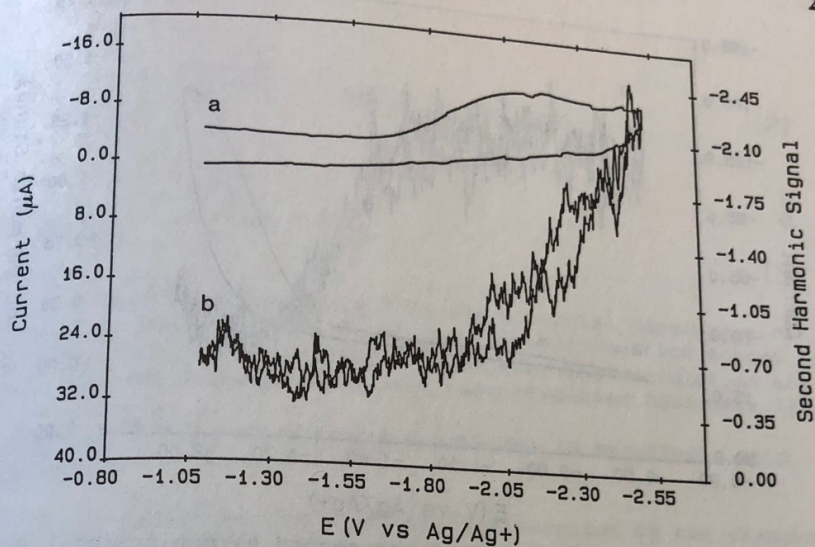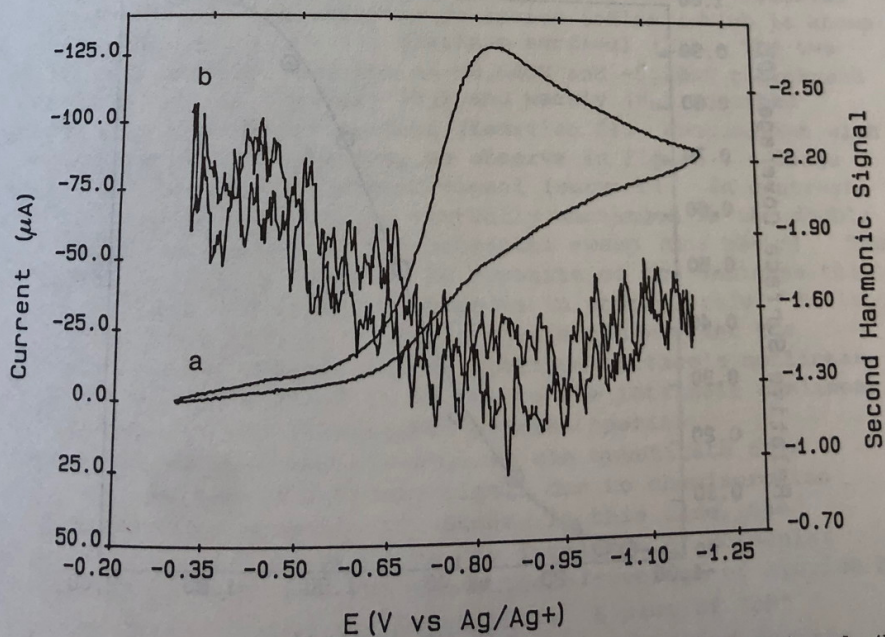
Figure 1.   The current (a) and the second harmonic signal (b) obtained during the potential cycling (10 mV s^{-1} scan rate) from a polycrystalline silver electrode in a 0.1M LiClO$_4$ acetonitrile solution.

Figure 2.   The current (a) and the second harmonic signal (b) obtained during the potential cycling (20 mV s^{-1} scan rate) from a polycrystalline silver electrode in a 0.1M LiClO$_4$ + 3.5mM HClO$_4$ acetonitrile solution.
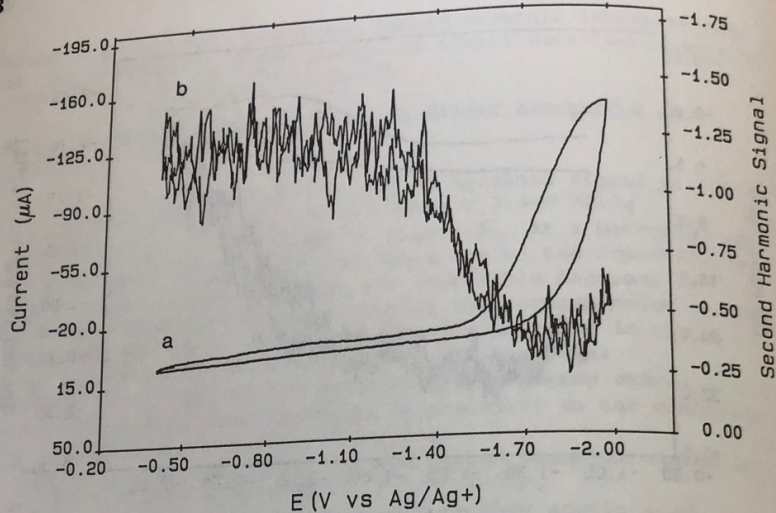
Figure 3. The current (a) and the second harmonic signal (b) obtained during the potential cycling (10 mV s^{-1} scan rate) from a polycrystalline silver electrode in a 0.1M TBABF$_4$ + 35mM acetic acid acetonitrile solution.
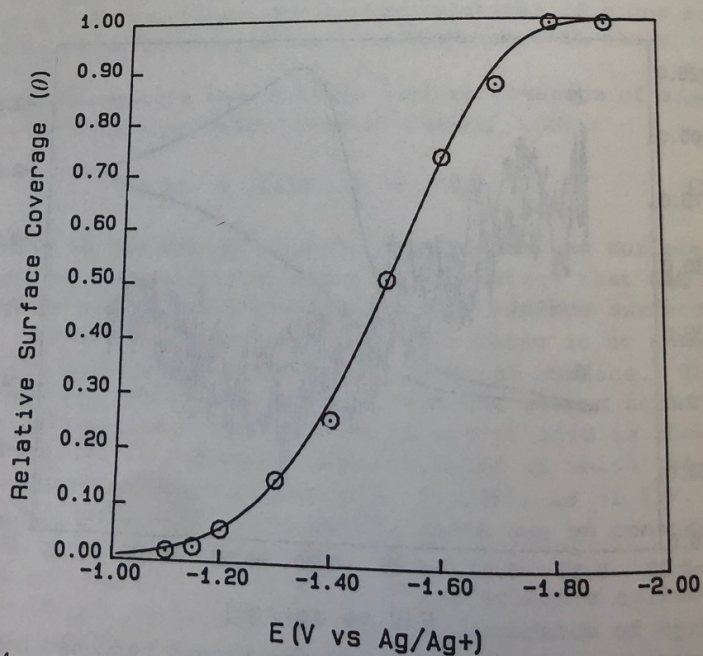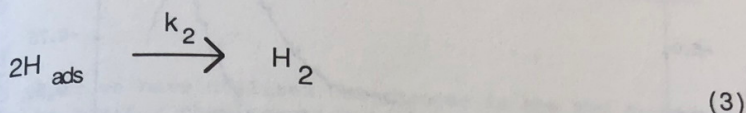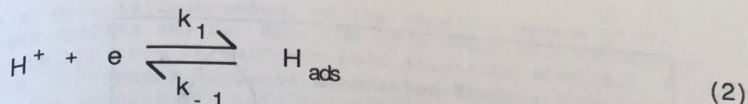

Figure 4. The relative surface coverage of adsorbed hydrogen as a function of electrode potential for acetic acid. The circles are calculated from the second harmonic signal using Equation 1, and the solid line is the theoretical curve predicted from the reaction mechanism (Equations 2 and 3).

$$H^+ + e \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_{ads} \qquad (2)$$

$$2H_{ads} \overset{k_2}{\longrightarrow} H_2 \qquad (3)$$

The solid line in Figure 4 is the potential dependence of the relative surface coverage of H_{ads} by this reaction scheme in the steady state approximation. Details of the calculation and reaction scheme determination have been presented elsewhere (8).

Hydrogen adsorption on platinum electrodes in perchloric acid solutions

As a final example of the study of chemisorption by the changes in the SHG from metal surfaces, Figure 5 depicts the corrected current and the second harmonic signal at 289 nm from a platinum electrode in a 0.35M $HClO_4$ aqueous solution during a cathodic potential sweep in the hydrogen adsorption region. The current waveform has been corrected for double layer and hydrogen evolution contributions by subtraction of the current observed in the presence of 1 millimolar potassium iodide (which is known to block hydrogen upd on the platinum surface) (12). The two peaks in the current waveform at -0.045V and -0.200V correspond to the formation of strongly (H_S) and weakly (H_W) adsorbed hydrogen on the platinum surface (Equation 2). Concomitant with the chemisorption of hydrogen, we observe in Figure 5 a large increase in the second harmonic signal (curve b). In contrast, the second harmonic signal is virtually unchanged in the double layer and oxide regions of the potential sweep (not shown). The increase in signal is exactly the opposite of the decrease that was observed for the silver electrodes in acetonitrile. It is unclear from this data at a single wavelength whether the increase is due to changes in the platinum surface's nonlinear susceptibility, or whether it is due to the intrinsic nonlinear susceptibility of the chemisorbed hydride species.

In spite of this uncertainty, we can quantitate this increase in the second harmonic signal due to chemisorption through the use of Equation 1. Since, in this case, the hydrogen is chemisorbed prior to the formation of molecular hydrogen, we can also monitor the surface coverage of hydride by the charge passed during the deposition. A plot of "$c\theta$" { $= [I(2\omega)/I(2\omega)_0]^{1/2} - 1$ } vs. q, the charge passed due the hydrogen deposition, is shown in Figure 6. A full monolayer corresponds to approximately 251 $\mu C/cm^2$ (12). As predicted by Equation 1, the nonlinear susceptibility of the surface depends linearly upon the amount of chemisorbed hydrogen, and
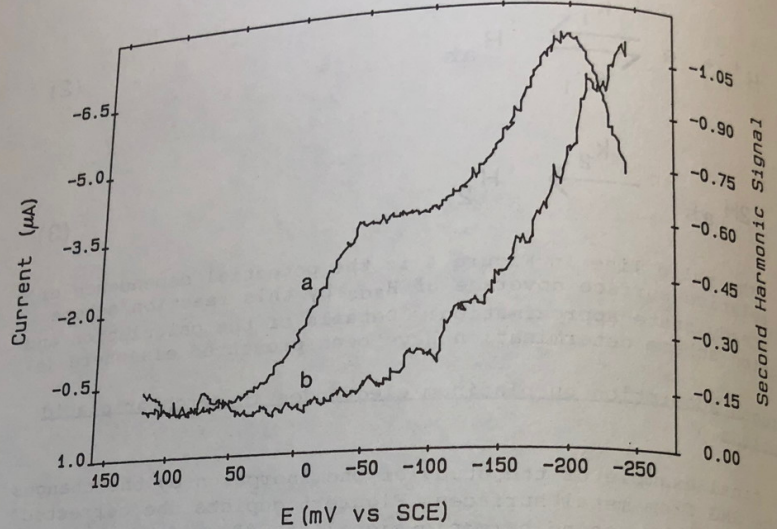
Figure 5.   The corrected current (a) and the second harmonic signal (b) obtained during cathodic sweep (10 mV s^{-1} scan rate) from a polycrystalline platinum electrode in a 0.35M HClO$_4$ aqueous solution.
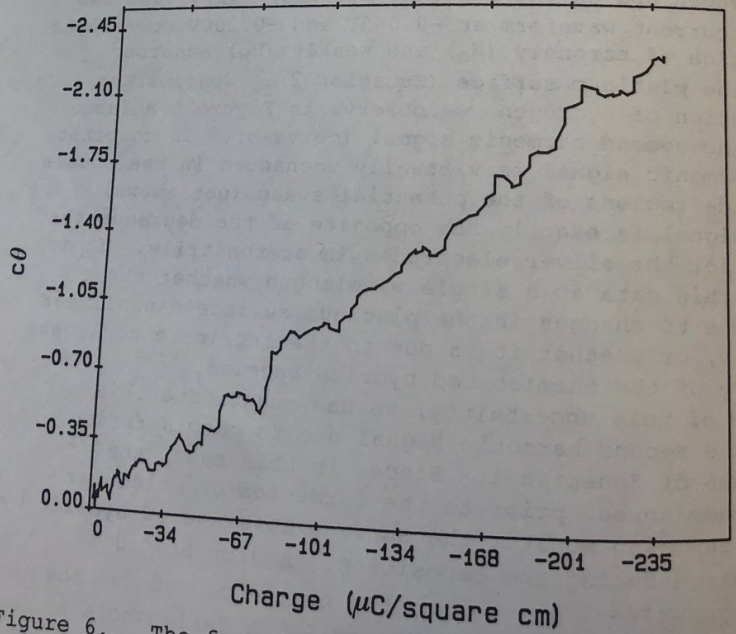
Figure 6.   The function cθ (= $[I(2\omega)/I(2\omega)_0]^{1/2} - 1$) determined from the second harmonic signal plotted versus the charge passed due to hydrogen chemisorption on the platinum electrode.

Summary

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surprisingly, is independent of the chemical nature of the hydrogen species (H_S vs. H_W). We have found this latter fact not to be the case in sulfuric acid solutions (Campbell, D. J.; Corn, R. M. "Second Harmonic Generation Studies from Platinum Electrodes in Sulfuric Acid Solutions", submitted to J. Phys. Chem.).

Summary

In this paper we have utilized the changes in the SHG from metal surfaces to monitor chemisorption processes at electrode surfaces. In particular, we have seen that:

i)   During the deposition of lithium onto silver electrodes in acetonitrile there is a potential dependent increase in the second harmonic signal from the silver surface due to a steady state coverage of unreacted metallic lithium. This increase in the second harmonic signal is thought to arise from the delocalization of the electrons associated with the metallic lithium overlayer.

ii) The chemisorption of a monatomic hydrogen species onto silver electrodes in acetonitrile is found to decrease the SHG from the surface during the irreversible process of molecular hydrogen evolution. The quantitation of the second harmonic signal for this process yields the relative surface coverage of chemisorbed hydrogen as a function of electrode potential, and the shape and pH dependence of this relative surface coverage-potential curve can be used to ascertain the reaction mechanism for hydrogen evolution at silver electrodes in acetonitrile.

iii) On platinum electrodes in perchloric acid solutions the second harmonic signal quantitatively increases during hydrogen atom underpotential deposition, and this increase is independent of the type of chemisorbed hydrogen.

Although use of the second harmonic signal from metal surfaces as an indirect probe of chemisorption lacks structural specificity, the utility of the technique is clearly demonstrated by the experiments reported here. The next step in our studies will be to demonstrate how one can directly monitor chemisorption with some degree of molecular specificity via the resonant second harmonic signal from the nonlinear susceptibility of adsorbed species.

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