

Second Harmonic Generation Studies of Anionic Chemisorption at Polycrystalline Platinum Electrodes

Deborah J. Campbell, Matthew L. Lynch, and Robert M. Corn*

Department of Chemistry, University of Wisconsin—Madison, 1101 University Ave., Madison, Wisconsin 53706

Received December 14, 1989

Nonresonant optical second harmonic generation (SHG) is used to monitor the adsorption of bisulfate, chloride, bromide, and iodide anions at polycrystalline platinum electrodes in aqueous solutions. Different polarization combinations of the fundamental and second harmonic beams are used to probe changes in the surface nonlinear susceptibility tensor elements caused by adsorption, reaction, and the electrode potential. The relative surface coverages of chloride and bromide as a function of solution concentration at a fixed potential are calculated from the changes observed in the nonresonant SHG signal. The reversibility of the chloride chemisorption is demonstrated by additional SHG measurements. Unlike the chloride and bromide chemisorption, iodide solutions lead to a monolayer of zero-valent iodine that is irreversibly adsorbed onto the electrode surface over a wide potential range. For partial iodine monolayers, the relative surface coverage of iodine can be determined from the SHG signal. The adsorption of various iodine species at platinum electrodes during the oxidation and reduction of solution iodide is studied in acidic and basic media. In basic solutions, the adsorption of atomic hydrogen in the presence of iodide is confirmed.

Introduction

The chemisorption of anions onto platinum electrodes is a process that affects the reactivity of the platinum surface and strongly influences the surface's ability to catalyze the oxidation of organic species. For this reason, the adsorption of halides, sulfates, and other simple anions at polycrystalline platinum electrodes has been studied intensively by electrochemists.¹⁻⁸ Electrochemical studies have monitored anionic adsorption onto polycrystalline and single-crystal platinum electrodes by differential capacitance,¹ by the alteration or suppression of hydrogen underpotential deposition,² by the effect of anionic adsorption on oxide formation,³ and by various replacement reaction schemes.⁴ Complementing the electrochemical studies, anionic adsorption on platinum electrodes has been monitored in situ with spectroscopic techniques such as reflectance,⁵ ellipsometry,⁶ and, for anions with internal structure, Fourier transform infrared (FTIR) spectroscopy.⁷ In cases where the anions are strongly chemisorbed onto the electrode, emersion methods have been used to study the adsorption ex situ with a variety of electron spectroscopies.⁸

A relatively new in situ technique which can be applied to the study of anionic chemisorption is the nonlinear optical process of second harmonic generation (SHG).⁹⁻¹⁵ In the absence of any molecular transitions at the incident

laser or second harmonic wavelengths, the second harmonic intensity from platinum electrodes is dominated by the nonlinear susceptibility of the surface metal atoms. In a previous paper,⁹ we used changes in this "nonresonant" SHG from the metal surface to indirectly monitor the underpotential deposition of hydrogen and the chemisorption of bisulfate ions in perchloric and sulfuric acid solutions at platinum electrodes. The SHG signal was shown to provide a quantitative measure of the relative surface coverage of the chemisorbed species. In contrast to "resonant" SHG studies of molecules at electrode surfaces,¹⁶ the nonresonant SHG signal is similar to an electroreflectance or ellipsometric measurement in that it is a relatively nonspecific method of monitoring the surface. However, unlike the linear reflection measurements, the SHG signal is sensitive primarily to changes in the metal electronic structure and is therefore only capable of monitoring the adsorption of species that perturb the metal surface.

In this paper, we explore the use of the nonresonant SHG signal to study the adsorption of various anions at polycrystalline platinum electrodes in aqueous solutions. The changes in the nonlinear optical response of the surface during electrochemical adsorption are probed with the potential and polarization dependence of the SHG signal. In the double-layer region, the very weak adsorption of perchlorate anions and the stronger reversible adsorption of bisulfate, chloride, and bromide anions are monitored by changes in the SHG measurements. Adsorption isotherms for the chemisorbed chloride and bromide species are calculated from the SHG data. The reversibility of chloride adsorption is also examined in a set of flushing experiments. In contrast to the other halides, SHG studies of platinum electrodes exposed to iodide confirm that a zero-valent iodine monolayer is irreversibly adsorbed over a wide range of potentials. Changes in the SHG from the

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adsorbed monolayer with potential and surface coverage of iodine are observed. In the presence of iodide in acidic and basic solutions, additional surface species are monitored during the processes of iodide oxidation and reduction at the platinum surface. In basic solutions, the replacement of the adsorbed iodide with atomic hydrogen is confirmed by the optical measurements.

Experimental Section

The SHG signal measured in these experiments was created on the electrode surface from either the 10-ns pulses of light (585 nm) generated by a 10-Hz Nd:YAG-pumped dye laser system (Quantel Model 580) or the 1.6-ps pulses of light (604 nm) generated by a 4-MHz synchronously pumped dye laser/mode-locked Nd:YAG laser system (Coherent Model 702). The experimental optical systems are identical with those used previously.¹⁶ The SHG intensities have been normalized to a common intensity scale.

The metal surface for the SHG experiments consisted of a polycrystalline platinum rod (99.99%) that had been mechanically polished with 0.05- μm alumina. The working electrode was used in a three-electrode configuration with a platinum counter electrode and an isolated Ag/AgCl reference electrode. For the electrochemical experiments, cyclic voltammograms (CVs) were obtained by cycling the electrode potential at a rate of 10 mV/s with a Princeton Applied Research 173/175 potentiostat; all potentials are reported versus the saturated calomel electrode (SCE). The CV and potential dependence of the SHG signal from the platinum electrode were captured digitally and stored on an IBM personal computer.

Two spectroelectrochemical cells were employed in these studies: (i) for studies of the SHG in the presence of solution species and for monolayers of iodine, a two-window 60° incident angle (relative to the surface normal) cell; (ii) for the SHG studies during flushing experiments, a single-window 40.5° incident angle (60° incident to the window) cell with a solution volume of 4 mL.

The sulfuric acid, NaCl, NaBr, and NaI were of puriss quality (Fluka). The sodium hydroxide was 99.99% pure (Aldrich). The perchloric acid was doubly distilled from Vycor (GFS Chemicals). The water employed in these experiments was Millipore-filtered and then doubly distilled.

Theoretical Considerations

Changes in the nonresonant SHG response of the platinum surface are used to study the chemical changes which occur as a function of electrode potential and adsorption. The SHG signal arising from a metal surface is treated in detail by several authors^{15,17,18} and is briefly outlined here. At a metal-solution interface, the inversion symmetry is broken, and in the limit of the electric dipole approximation, the induced surface nonlinear polarizability is given by¹⁸

$$\mathbf{P}_0^{(2)} \propto \chi_S^{(2)} \mathbf{E}(\omega) \mathbf{E}(\omega) \quad (1)$$

where $\chi_S^{(2)}$ is the surface nonlinear susceptibility and $\mathbf{E}(\omega)$ is the incident electric field. The possible contribution of higher order bulk terms to the overall nonlinear polarizability is discussed by Guyot-Sionnest et al.¹⁷ The surface nonlinear susceptibility is modified by the presence of an adsorbate to a new value $\chi'_S{}^{(2)}$:

$$\chi'_S{}^{(2)} = \chi_S^{(2)} + \chi_A^{(2)} + \Delta\chi_I^{(2)} \quad (2)$$

where $\chi_A^{(2)}$ is the inherent nonlinear susceptibility of the adsorbate independent of the surface and $\Delta\chi_I^{(2)}$ is the

change in nonlinear susceptibility of the surface and adsorbate due to any interactions. At a polycrystalline metal surface, $\chi_S^{(2)}$ is typically larger than $\chi_A^{(2)}$; however, $\Delta\chi_I^{(2)}$ can be large enough to permit the detection of submonolayer quantities of an adsorbate. In some instances, the surface can be modified to minimize $\Delta\chi_I^{(2)}$. In a previous paper, we studied molecular chemisorption by using a sulfur monolayer to minimize the contributions of $\Delta\chi_I^{(2)}$ and by choosing a molecule and experimental geometry for which $\chi_A^{(2)}$ is the dominant contribution to $\chi'_S{}^{(2)}$.¹⁶ In the present paper, we use changes in the SHG signal intensity caused by $\Delta\chi_I^{(2)}$ to determine the coverage of anions on the surface and refer to this response as nonresonant SHG.

If the nonlinear susceptibility of the interface changes only slightly in the presence of an adsorbed species, then $\chi'_S{}^{(2)}$ should vary linearly with the relative surface coverage of the adsorbate θ .^{9,19}

$$\chi'_S{}^{(2)} = \chi_S^{(2)}(1 + c\theta) \quad (3)$$

where c is a constant that can be determined by the second harmonic signal at maximum relative surface coverage ($\theta = 1$). This method of determining surface coverages from the SHG signal has been used previously for adsorbates on a metal surface under ultrahigh vacuum¹⁹ and on electrode surfaces.⁹ For cases where the changes in $\chi'_S{}^{(2)}$ are sufficiently large, eq 3 is no longer valid, and further phase shifts and modifications of the surface nonlinear susceptibility can be observed.²⁰

Since $\chi'_S{}^{(2)}$ is a third rank tensor, the different elements of the surface nonlinear susceptibility can be probed by studying the SHG signal as a function of the polarization of the fundamental and second harmonic beams. The nonlinear susceptibility for an isotropic metal surface has three non-zero tensor elements: χ_{ZZZ} , $\chi_{ZXX} = \chi_{ZYY}$, and $\chi_{XXZ} = \chi_{XXZ} = \chi_{YYZ} = \chi_{YYZ}$.¹⁷ The polarization dependence of the SHG signal is related to the light field vectors at the surface and these surface nonlinear susceptibility tensor elements. We have measured the SHG signal for three different polarization combinations: I_1 (45° in, s-out), I_2 (p-in, p-out), and I_3 (s-in, p-out). These intensities are related to surface nonlinear susceptibility tensor elements by eqs 4–6:²¹

$$I_1(2\omega) \propto |a_1 \chi_{XXZ}|^2 \quad (4)$$

$$I_2(2\omega) \propto |a_2 \chi_{XXZ} + a_3 \chi_{ZXX} + a_4 \chi_{ZZZ}|^2 \quad (5)$$

$$I_3(2\omega) \propto |a_5 \chi_{ZXX}|^2 \quad (6)$$

The complex constants a_i are defined for a given angle of incidence

$$a_1 = e_y(\omega) e_z(\omega) e_y(2\omega)$$

$$a_2 = 2e_x(\omega) e_z(\omega) e_x(2\omega)$$

$$a_3 = |e_x(\omega)|^2 e_z(2\omega)$$

$$a_4 = |e_z(\omega)|^2 e_z(2\omega)$$

$$a_5 = |e_y(\omega)|^2 e_z(2\omega) \quad (7)$$

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Table I. Optical Constants and Calculated Fresnel Coefficients Used To Determine the a Constants

| Z^a | real Z | imaginary Z |
|-----------------------------------|----------|---------------|
| $n_{\text{Pt}}(\omega)^a$ | 2.26 | 3.99 |
| $n_{\text{Pt}}(2\omega)$ | 1.47 | 2.19 |
| $n_{\text{H}_2\text{O}}(\omega)$ | 1.33 | 0 |
| $n_{\text{H}_2\text{O}}(2\omega)$ | 1.36 | 0 |
| $e_x(\omega)^b$ | 0.3338 | -0.2584 |
| $e_y(\omega)$ | 0.1517 | -0.2183 |
| $e_z(\omega)$ | 1.1539 | 0.4475 |
| $e_x(2\omega)$ | -0.5325 | 0.2533 |
| $e_y(2\omega)$ | 0.2934 | -0.3434 |
| $e_z(2\omega)$ | 0.8394 | 0.4101 |
| a_1^c | 0.0168 | -0.1477 |
| a_2 | -0.4580 | 0.4121 |
| a_3 | 0.1496 | 0.0731 |
| a_4 | 1.2859 | 0.6283 |
| a_5 | 0.0593 | 0.0290 |

^a $n(\omega)$ and $n(2\omega)$ are the complex indices of refraction at 604.0 and 302.0 nm, and the other symbols are defined in the text. ^b The e values are calculated with $\theta_\omega = 60^\circ$, $\theta_{2\omega} = 58.3^\circ$. ^c a_1 - a_5 are defined in the text.

where the different components of the complex Fresnel factors $e(\omega)$ and $e(2\omega)$ are

$$\begin{aligned} e_x(\omega) &= \cos \gamma \cos \theta_\omega [1 - r_{\parallel}(\omega)] \\ e_y(\omega) &= \sin \gamma [1 + r_{\perp}(\omega)] \\ e_z(\omega) &= \cos \gamma \sin \theta_\omega [1 + r_{\parallel}(\omega)] \end{aligned} \quad (8)$$

$$\begin{aligned} e_x(2\omega) &= \cos \gamma' \cos \theta_{2\omega} [r_{\parallel}(2\omega) - 1] \\ e_y(2\omega) &= \sin \gamma' [1 + r_{\perp}(2\omega)] \\ e_z(2\omega) &= \cos \gamma' \sin \theta_{2\omega} [1 + r_{\parallel}(2\omega)] \end{aligned} \quad (9)$$

γ and γ' are the polarization angles for the fundamental and second harmonic beams ($\gamma = 0^\circ \rightarrow$ p-polarized light, $\gamma = 90^\circ \rightarrow$ s-polarized light), θ_ω is the angle of incidence, $\theta_{2\omega}$ is the angle of the outgoing second harmonic light, $r_{\perp}(\omega)$ and $r_{\parallel}(\omega)$ are the complex Fresnel coefficients for light perpendicular and parallel to the plane of incidence at the fundamental wavelength, and $r_{\perp}(2\omega)$ and $r_{\parallel}(2\omega)$ are the complex Fresnel coefficients²² for light at the second harmonic wavelength. The use of complex Fresnel coefficients described here is similar to that employed in the phenomenological treatment of surface SHG by Sipe,²³ except that the driving fields of the nonlinear polarizability have been chosen to lie just outside the metal surface rather than just inside the metal surface.

The Fresnel coefficients differ substantially for s-polarized and p-polarized light at a platinum-water interface with an angle of incidence of 60° . By use of tabulated optical constants for the Pt-water interface,²⁴ the Fresnel coefficients and a_i constants calculated for this experimental geometry are listed in Table I. The magnitudes of the a_i constants indicate that $I_2(2\omega)$ will be much larger than $I_1(2\omega)$ or $I_3(2\omega)$.

A final contribution to the SHG from an electrode surface that must be considered is the second-order nonlinear susceptibility induced by the presence of the DC electric field. This contribution to the surface nonlinear susceptibility can be written as^{11,25}

$$\chi_{\text{DC}}^{(2)} = \chi^{(3)}[\omega, \omega, 0] E_{\text{DC}} \quad (10)$$

where $\chi^{(3)}[\omega, \omega, 0]$ is the third-order nonlinear hyperpolar-

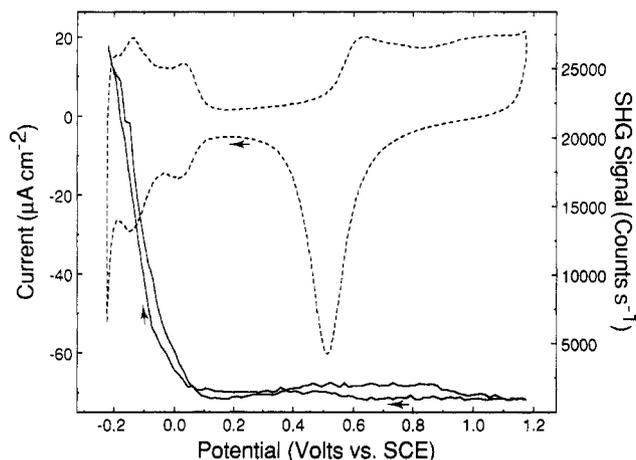


Figure 1. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 304 nm (—) from a polycrystalline platinum electrode in a 0.5 M HClO_4 solution.

izability tensor for the metal surface and E_{DC} is the static electric field at the interface. In the initial studies on weakly adsorbed anions, it was observed that this hyperpolarizability effect led to a SHG signal that varied as the square of the charge on the electrode surface.¹¹ However, for strongly adsorbed anions such as sulfide and halides, a linear change in the p-polarized SHG signal with electrode potential is observed.^{16,26} This linear change in the SHG signal has been attributed to either an interference between $\chi_{\text{S}}^{(2)}$ and $\chi_{\text{DC}}^{(2)}$ ²⁰ or a change in the surface electronic structure with potential.²⁶ Actually, there is very little distinction between a hyperpolarizability term that changes the surface nonlinear susceptibility and a reorganization of the electronic structure of the bonding between the surface and adsorbate that leads to changes in $\chi_{\text{S}}^{(2)}$. Therefore, in principle any changes in the SHG response of the platinum electrode as a function of potential must be considered to be a combination of changes in the surface electronic structure and changes in the state of chemisorption for the surface. In practice, we will show that in cases where the state of chemisorption at the platinum surface is fixed (e.g., irreversibly adsorbed sulfide and iodide monolayers) the SHG measurements from the platinum surface vary linearly with potential.

Results and Discussion

1. Perchloric Acid Solutions. Figure 1 shows the cyclic voltammogram (CV) and the SHG signal for the $I_2(2\omega)$ polarization combination from a polycrystalline platinum electrode immersed in a 0.5 M perchloric acid solution. The platinum surface has three different chemical states throughout the course of the CV: (i) the hydrogen adsorption region where a monolayer of reversibly adsorbed atomic hydrogen covers the surface, (ii) the double-layer region, and (iii) the oxide region where a monolayer of oxide species exists on the surface. The small change observed in $I_2(2\omega)$ in the double-layer region is attributed to the very weak adsorption of the perchlorate anion. The SHG signal increases significantly only in the region where atomic hydrogen is adsorbed onto the surface. We have shown previously that this increase intensity can be used to quantify the relative surface coverage of adsorbed hydrogen through eq 3.⁹

2. Sulfuric Acid Solutions. Figure 2 shows the CV

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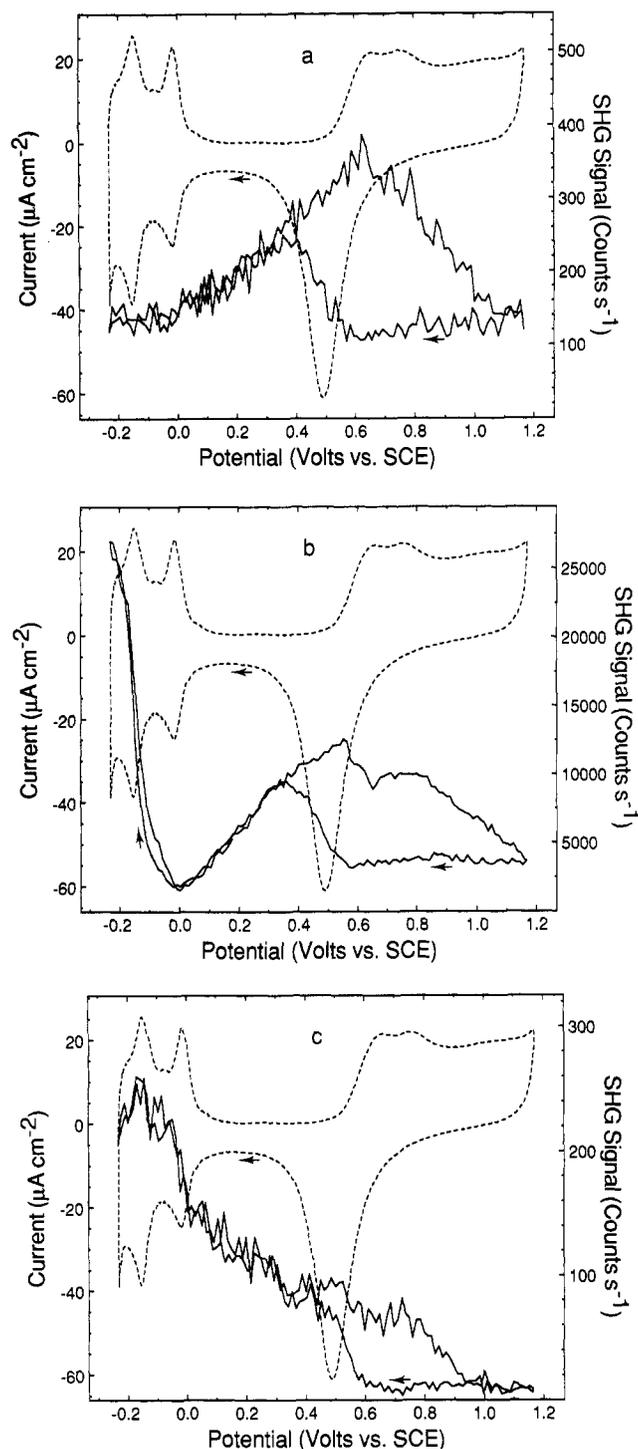


Figure 2. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 304 nm (—) for the polarization combinations (a) $I_1(2\omega)$, (b) $I_2(2\omega)$, and (c) $I_3(2\omega)$ from a polycrystalline platinum electrode in a 0.5 M sulfuric acid solution.

and SHG signals $I_1(2\omega)$, $I_2(2\omega)$, and $I_3(2\omega)$ from a polycrystalline platinum electrode immersed in a 0.5 M sulfuric acid solution. The potential dependence of the SHG measurements correlates with the various electrochemical processes occurring on the platinum surface. $I_1(2\omega)$ (which is proportional to $|\chi_{XXX}|^2$) is at a constant low level in the hydrogen region, rises throughout the double-layer region, and falls back down to a lower level upon formation of the surface oxide. In contrast, $I_3(2\omega)$ (which is proportional to $|\chi_{ZZX}|^2$) is at a constant high level in the hydrogen region, decreases with the desorption of the strongly adsorbed hydrogen (H_s) at -0.02 V, decreases monotonically throughout the double-layer region, and then drops to zero

after the second oxide peak at 0.76 V. The third SHG measurement, $I_2(2\omega)$, is related to χ_{ZZZ} as well as χ_{XXZ} and χ_{ZXX} (eq 5) and has a combined response similar to $I_1(2\omega)$ and $I_3(2\omega)$ in the double-layer and oxide regions with an additional large increase in signal upon adsorption of hydrogen. $I_2(2\omega)$ increases the most upon adsorption of the weakly adsorbed hydrogen (H_w) at -0.16 V.

The potential dependence of the three SHG measurements can be used to derive information on the presence of adsorbates at the interface. Of course, one always needs to distinguish the changes due to surface chemisorption from changes which occur due to changes in the surface electronic structure with potential. We can distinguish between these two effects experimentally by comparing the potential dependence of the SHG measurements in the presence and absence of the chemisorbing species. For example, $I_1(2\omega)$ is relatively constant after oxide formation and hydrogen adsorption. The increase that occurs in the double-layer region does not occur to the same extent in perchloric acid solution. We can therefore attribute the rise and fall with potential of $I_1(2\omega)$ to the adsorption of bisulfate and sulfate ions. The potential dependence of this adsorption matches the potential dependence that we obtained in a previous paper by monitoring changes in $I_2(2\omega)$.⁹

In contrast, the potential dependence of $I_3(2\omega)$ in the double-layer region is very similar to that observed in perchloric acid. In this case, we must attribute the changes observed in the SHG signal in the double-layer region to changes in the surface electronic structure. $I_3(2\omega)$ is proportional to $|\chi_{ZXX}|^2$ and represents the nonlinear optical response of the surface to parallel-polarized fundamental light. This response increases abruptly with the deposition H_s but is not affected by the adsorption of H_w . However, $I_2(2\omega)$, which contains χ_{ZZZ} , is very sensitive to the weakly adsorbed hydrogen. Therefore, in sulfuric acid solutions we observe large changes in the perpendicular nonlinear optical response of the surface when weakly adsorbed hydrogen is present and changes in the parallel nonlinear optical response of the surface upon deposition of H_s . These observations are in agreement with FTIR and reflectance measurements, which have suggested that the bonding for H_s is delocalized whereas the bonding for H_w is more directional and perpendicular to the surface.²⁷

3. Chloride Solutions. The CV and $I_2(2\omega)$ SHG signal from a polycrystalline platinum electrode immersed in a 0.5 M perchloric acid solution that contains 0.1 mM sodium chloride are shown in Figure 3. As noted previously by other authors, the currents due to hydrogen adsorption and oxide formation are modified by the presence of the chloride species.¹⁻³ These modifications indicate that there is a chemisorbed chloride species on the platinum surface in the double-layer region that must desorb concurrently with the formation of the hydrogen or oxide monolayer. The inhibition of both hydrogen and oxide deposition can be seen in the SHG signal in Figure 3; the changes in the SHG signal denoting the displacement of chemisorbed chloride occur at potentials that are more negative for hydrogen adsorption and more positive for oxide formation than those observed in the perchloric acid solutions (Figure 1). In the double-layer region, the SHG signal is at a nonzero value that is independent of potential; this level of the SHG signal was found to depend on the chloride solution concentration. As the chloride is replaced by either oxide or adsorbed hydrogen the SHG signal changes, signaling the desorption of the chloride. Upon return to

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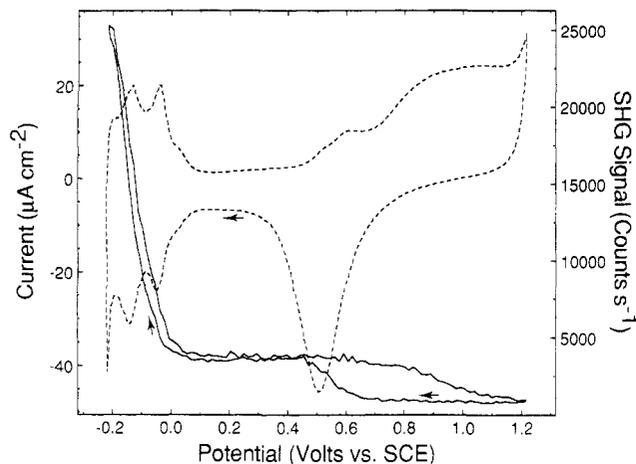


Figure 3. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 304 nm (—) from a polycrystalline platinum electrode in a 0.1 mM NaCl + 0.5 M HClO₄ solution.

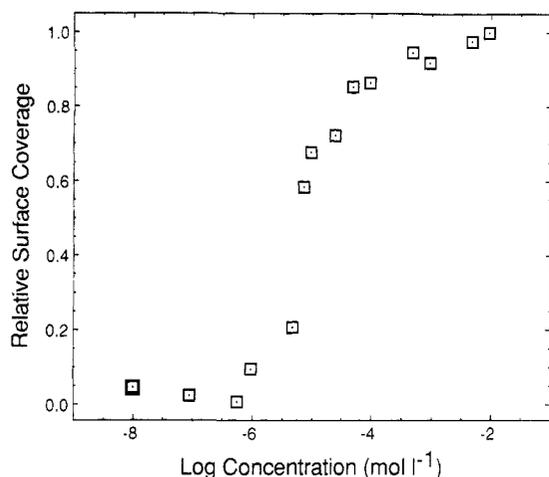


Figure 4. Optically determined relative surface coverage θ of chemisorbed chloride as a function of concentration at 0.20 V vs SCE.

the double-layer region, chloride ions are readsorbed and the SHG signal returns to its previous level.

With the SHG signal, we can obtain a direct measure of the relative surface coverage of chemisorbed chloride in the double-layer region. In Figure 4, we have chosen the potential of 0.20 V vs SCE and calculated the relative surface coverage of chloride from the SHG signal (using eq 3) as a function of concentration. The adsorption isotherm obtained from the SHG signal agrees qualitatively with that obtained in perchloric acid solutions by Novak et al., who measured the adsorption isotherm for chloride in both sulfuric and perchloric acid media via the suppression of oxide formation.³

The SHG signal in Figure 3 is only very weakly dependent on potential in the double-layer region. This lack of potential dependence can be described either by a chloride chemisorption that is independent of electrode potential in the double-layer region or by a combination of changes in chloride adsorption and surface electronic structure with potential that cancel out. A lack of potential-dependent SHG in the double-layer region agrees with the nearly potential independent chloride coverage observed in potential step measurements² but is in disagreement with other spectroscopic and electrochemical measurements, which have shown that chloride exhibits a potential dependence similar to that observed for the adsorption of bisulfate.^{4,5} It is possible that the SHG measurements are only sensitive to the chemisorbed

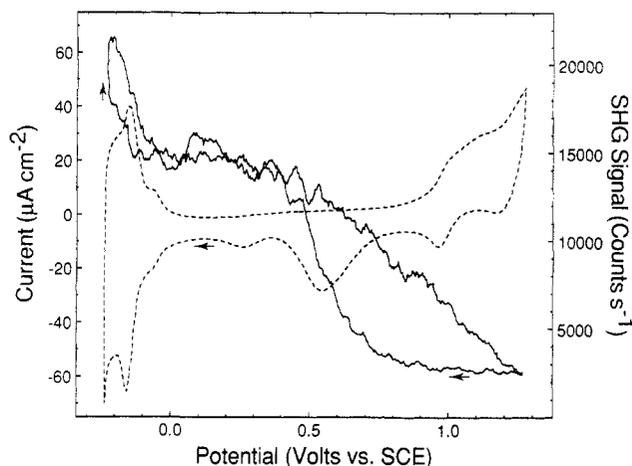


Figure 5. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 292.5 nm (—) from a polycrystalline platinum electrode in a 0.1 mM NaBr + 0.5 M HClO₄ solution.

chloride that interacts directly with the platinum surface, as compared to other measurements which are sensitive to the total surface excess of chloride.

The reversibility of chloride chemisorption has been addressed in a number of studies.^{4,28} The radiotracer results of Horanyi et al.⁴ and the thin-layer electrochemistry experiments of Lane and Hubbard²⁸ differ as to whether the chemisorbed chloride can be rapidly displaced by iodide from solution. Our SHG measurements of chloride reversibility demonstrated that the sequential exposure of a platinum electrode to a 1 mM chloride solution, a 1 mM Cl + 0.1 mM iodide solution, and finally a perchloric acid solution led to a surface SHG signal that was identical with that obtained when the electrode was covered with an irreversibly adsorbed iodine monolayer. The SHG signal from this monolayer is discussed in greater detail below. We therefore conclude that the chloride can be rapidly displaced by iodide from solution.

4. Bromide Solutions. The CV and p-polarized SHG signal from a polycrystalline platinum electrode immersed in a 0.5 M perchloric acid solution that contains 0.1 mM sodium bromide are shown in Figure 5. The chemisorbed bromide caused changes in the CV and SHG similar to those observed for chloride in the hydrogen adsorption and oxide formation regions. Additional solution chemistry of the bromide is also present in the CV;²⁹ this solution electrochemistry does not affect the SHG response of the surface. In the hydrogen region, the current and SHG response indicate that the first hydrogen wave has been greatly suppressed by the presence of bromide and that the majority of the hydrogen adsorption occurs during the second hydrogen wave. For bromide solutions, hydrogen adsorption is suppressed to a much larger extent than in the chloride solutions of equivalent concentration.

Throughout the double-layer region the SHG signal remains at a constant value which varies as a function of solution bromide concentration. From $I_2(2\omega)$, we can calculate the surface coverage of chemisorbed bromide. In Figure 6, the optically determined relative surface coverage of bromide at an electrode potential of 0.20 V is plotted as a function of solution concentration. This bromide adsorption isotherm agrees qualitatively with the electrochemical measurements of Novak et al.³

In the potential range of -0.05 to 0.35 V, the SHG signal from the surface is fairly constant. Above 0.35 V, $I_2(2\omega)$

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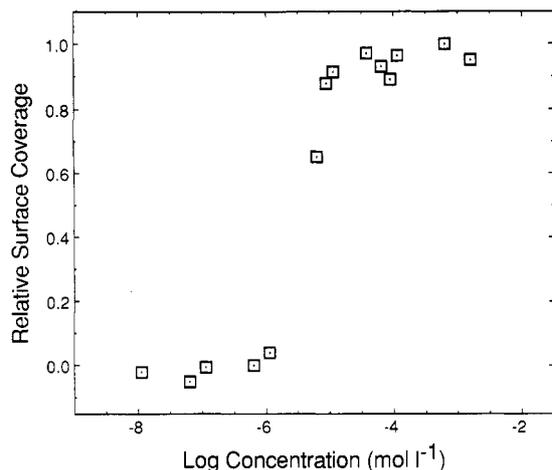


Figure 6. Optically determined relative surface coverage θ of chemisorbed bromide as a function of concentration at 0.20 V vs SCE.

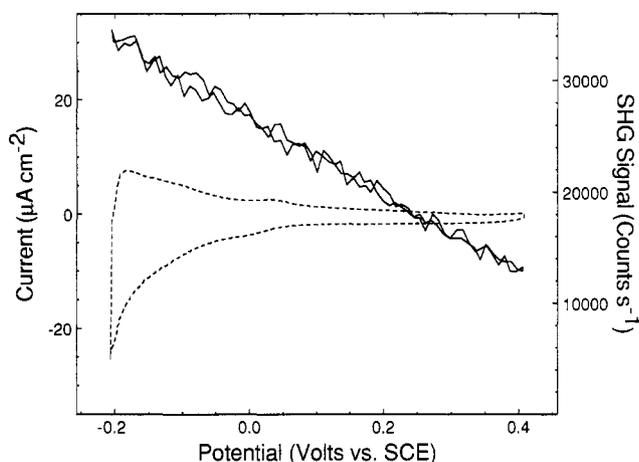


Figure 7. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 304 nm (—) from a polycrystalline platinum electrode coated with a monolayer of iodide in a 0.5 M HClO_4 solution.

decreases due to a combination of bromide desorption/oxidation and changes in the surface electronic structure. The potential dependence of bromide adsorption on platinum electrodes has been studied by potential step,² radiotracer,³⁰ ellipsometric,^{6,31} and electroreflectance⁵ measurements as well as Auger spectroscopy.³² The electroreflectance measurements suggest a large change in bromide coverage in the double-layer region, whereas the other measurements indicate that, in agreement with our observations, the adsorption of bromide in the double-layer region is nearly independent of potential.

5. Iodine Monolayer in Acidic Solution. In contrast to chloride or bromide, iodide solutions will spontaneously form an irreversibly chemisorbed monolayer of zero-valent iodine on a platinum electrode surface.²⁸ This monolayer strongly inhibits hydrogen adsorption and is stable over a wide potential range. The CV and $I_2(2\omega)$ signal in 0.5 M perchloric acid from a platinum electrode that was first exposed to a 0.1 mM iodide solution in the small volume flushing cell are shown in Figure 7. The presence of the iodide throughout this potential region is

evident in the CV by the strong suppression of the hydrogen adsorption waves and in the SHG signal by the large value of $I_2(2\omega)$ as compared to the bare platinum surface (Figure 1). There are no abrupt changes in the SHG signal that would indicate a change in the state of chemisorption on the electrode; only a linear decrease of $I_2(2\omega)$ as a function of potential is observed. Similar linear changes with electrode potential have been observed for a chemisorbed sulfur monolayer on platinum electrodes¹⁶ and adsorbed halides on silver electrodes.³³ The other SHG polarization measurements $I_1(2\omega)$ and $I_3(2\omega)$ displayed a similar potential dependence. $I_3(2\omega)$ is constant at 325 counts s^{-1} throughout this potential range, and $I_1(2\omega)$ varies linearly from 271 counts s^{-1} at 0.0 V to 340 counts s^{-1} at 0.3 V.

The linear change in the SHG response with potential for a monolayer of iodine is solely due to changes in the surface electronic structure. As discussed earlier in this paper, this potential dependence can be due to both $\chi_{\text{DC}}^{(2)}$ and changes in $\chi_s^{(2)}$. For strongly adsorbed anions such as sulfur and iodine, we suspect that changes in the non-linear optical response at visible wavelengths depend more on shifts of the electronic states of the interface than the hyperpolarizability effects. Studies of the SHG signal over a wide range of wavelengths will determine the relative contribution of these two sources of nonlinear polarization.

When the electrode potential is cycled in perchloric acid solution to 1.06 V, the iodine monolayer is oxidized to iodate (Figure 8). The CV and SHG signal return to levels close to that of a clean platinum surface (Figure 1); however, a small amount of iodine is reformed on the return scan and remains present in the solution and on the electrode surface. One can gradually strip the full iodine monolayer from the surface by only cycling part of the way into the iodine oxidation peak. Upon return to the double-layer region, the amount of iodine remaining on the surface can be determined electrochemically through the growth of the hydrogen adsorption waves. Figure 8 plots the CVs and SHG signal $I_2(2\omega)$ for a series of iodine stripping cycles. The SHG signal decreases with each subsequent stripping scan; the relative amount of adsorbed iodine left on the surface can be determined from the SHG signal by using eq 3. This optically determined surface coverage can be compared with the surface coverage determined electrochemically by the increase in charge from hydrogen adsorption. Figure 9 plots these two quantities for a series of electrochemical cycles. At an adsorbed hydrogen coverage of $240 \mu\text{C cm}^{-2}$ there is assumed to be no iodide remaining on the surface.³⁴ For partial monolayers of iodide, there are two linear regimes with a break at a hydrogen surface charge density that corresponds to approximately 50% iodine coverage. This break may be due to a reorganization of the iodide during surface oxidation; similar effects have been observed on single-crystal surfaces at partial iodine coverages.³⁵

6. Acidic Iodide Solutions. The electrochemistry at the platinum electrode surface becomes very complex in the presence of iodide solution species.^{36,37} A number of iodine and iodide species with different electroactivities are adsorbed on the surface, and the relative surface concentrations of these species depends critically on the

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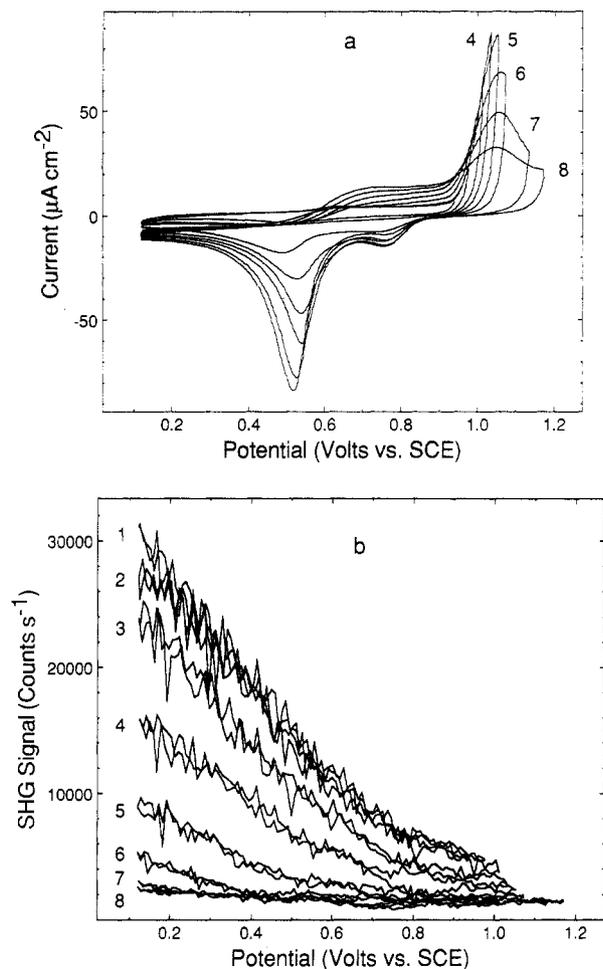


Figure 8. Cyclic voltammogram (a) and nonresonant SHG signal $I_2(2\omega)$ at 304 nm (b) from a polycrystalline platinum electrode showing the change in SHG signal as the iodide monolayer is gradually stripped from the surface in a 0.5 M HClO_4 solution. Each successive scan was taken to a more positive potential and is labeled by a scan number. (In Figure 8a, all eight scans are plotted, but only scans four through eight are labeled to avoid cluttering the figure.)

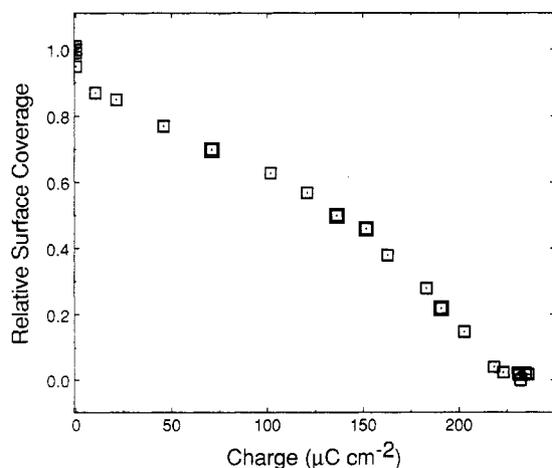


Figure 9. Optically determined relative surface coverage θ of chemisorbed iodide at 0.22 V vs SCE during a series of stripping cycles plotted against the electrochemically determined surface charge density due to hydrogen adsorption.

solution iodide concentration as well as the past history of the electrode potential. The CV and the three SHG signal measurements from a polycrystalline platinum electrode immersed in a 0.5 M perchloric acid solution that contains 0.1 mM sodium iodide are shown in Figure 10 (this

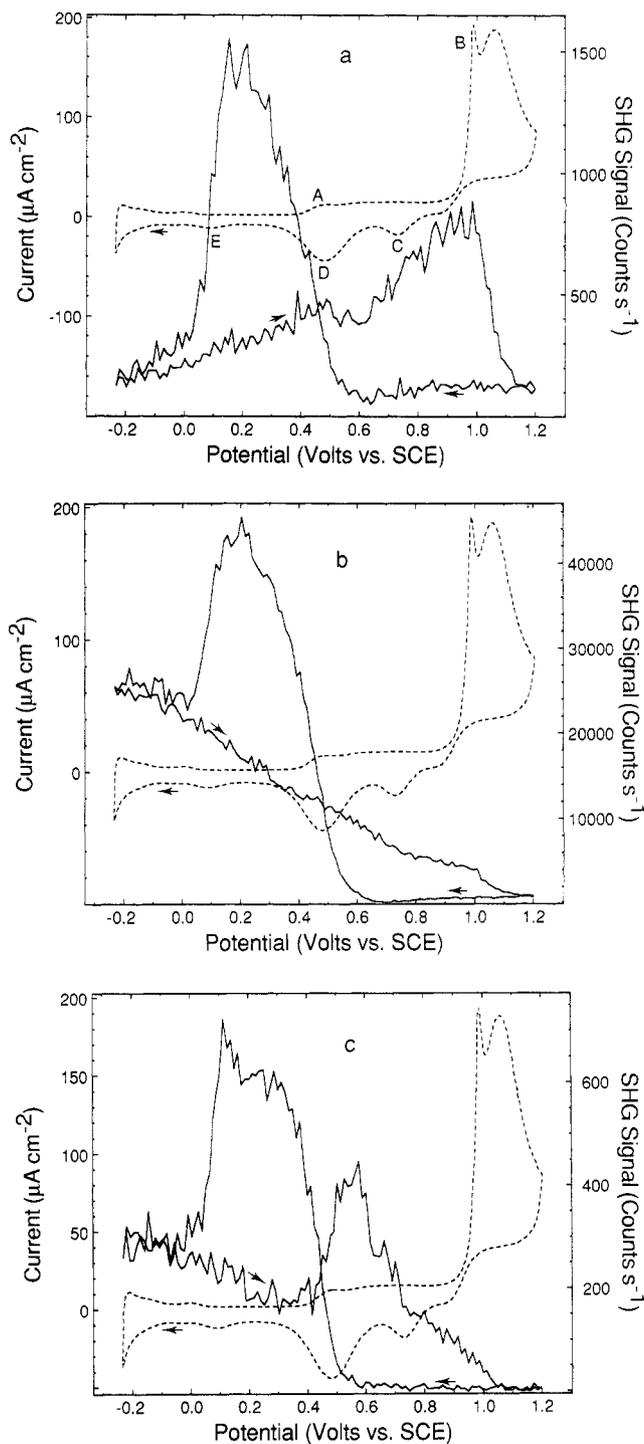


Figure 10. Cyclic voltammogram (---) and nonresonant SHG signal at 304 nm (—) for the polarization combinations (a) $I_1(2\omega)$, (b) $I_2(2\omega)$, and (c) $I_3(2\omega)$ from a polycrystalline platinum electrode in a 0.1 mM NaI + 0.5 M HClO_4 solution.

iodide concentration was sufficiently low to avoid I_2 film formation).³⁸ There are a number of current waves in the steady-state CV that correspond to different surface and solution reactions; these waves are labeled for convenience in Figure 10a.

On the anodic scan from -0.23 to 0.3 V, the SHG measurements and currents are similar to those observed for an adsorbed iodine monolayer. The linear decrease with potential of $I_2(2\omega)$ is relatively unaffected by wave A at 0.46 V and continues out to 0.98 V, where the surface oxidation of the monolayer occurs (wave B). However,

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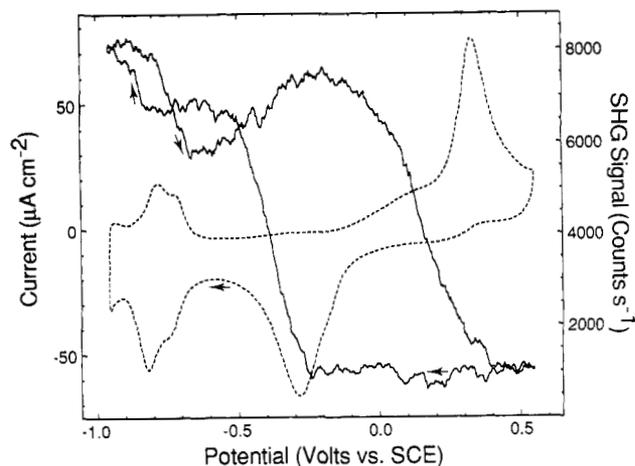


Figure 11. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 292.5 nm (—) from a polycrystalline platinum electrode in a 0.1 mM NaI + 0.5 M NaOH solution.

$I_3(2\omega)$ exhibits a large increase in the region of wave A before decreasing to zero after wave B. $I_1(2\omega)$ has a slight break at wave A but for the most part increases linearly with potential until the surface oxidation at 0.98 V. Wave A has been attributed to the oxidation of iodide to form a molecular iodine species;³⁷ the increase of $I_3(2\omega)$ at 0.46 V demonstrates that some surface modification/adsorption must occur during this process.

After the monolayer of iodine on the platinum surface is converted to iodate at 0.98 V, the platinum surface itself can oxidize. The formation of this oxide layer contributes to the current of peak B and is not electrochemically reversible; the reduction of the electrode back to a platinum surface occurs on the return scan at approximately 0.48 V (wave D). Prior to this reduction, some of the iodate formed on the anodic scan is reduced to molecular iodine at approximately 0.73 V (wave C). All three SHG measurements are insensitive to this reaction, suggesting that it occurs in solution and not at the surface.

Concurrent with wave D on the cathodic scan, all three SHG measurements show a very large increase. Wave D has been shown to be actually two waves:²⁸ one due to reduction of the oxide layer and one which is the reversible return wave of the iodine formation at 0.46 V (wave A). Thus, three processes are occurring in wave D: first the surface oxide layer is reduced, then iodide and iodine readorb onto the bare metal surface, followed by the reduction of any remaining nonchemisorbed molecular iodine to iodide. By varying the limits of the CV, we found that the increase in the SHG after wave D depended upon the amount of molecular iodine generated at higher electrode potentials. We therefore attribute the large SHG signal increase at 0.48 V to the increased adsorption of zero-valent iodine due to the presence of molecular iodine. This surface contains a larger amount of adsorbed iodine than the surface created in the monolayer studies and could be a combination of atomic iodine, I_2 and I_3^- . The mixed monolayer is partially reduced to iodide at 0.08 V (wave E) and leaves the surface coated with the original zero-valent iodine monolayer observed in the flushing experiments.

7. Basic Iodide Solutions. To further probe iodine oxidation-reduction chemistry at platinum surfaces, we performed additional spectroscopic and electrochemical studies of a polycrystalline platinum electrode in a 0.1 mM iodide + 0.5 M NaOH solution. The CV and $I_2(2\omega)$ SHG signal are plotted in Figure 11. Three differences are observed in comparison to studies in acidic media: (i) the

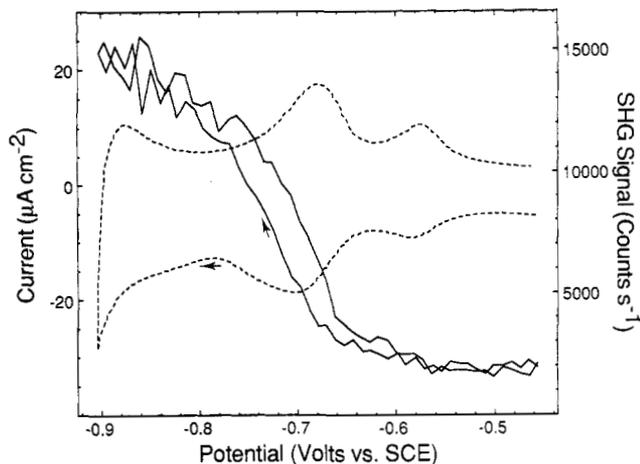


Figure 12. Cyclic voltammogram (---) and nonresonant SHG signal $I_2(2\omega)$ at 304 nm (—) from a polycrystalline platinum electrode in a 0.5 M NaOH solution.

SHG signal from the zero-valent iodine monolayer does not linearly decrease with electrode potential, (ii) the SHG signal from the surface drops precipitously before the solution iodate formation wave at 0.33 V, and (iii), the zero-valent iodine monolayer is replaced by adsorbed hydrogen at -0.825 V. The change in the potential dependence of $I_2(2\omega)$ from the zero-valent iodine monolayer in basic solution can be attributed to either the fact that the surface electronic structure is different since we are in a different potential region due to the large change in pH or that a change in the bonding of the chemisorbed iodine has occurred. The loss of SHG signal at approximately 0.1 V due to oxidation of the surface iodine monolayer prior to the oxidation of solution iodide to iodate and the adsorption of iodine at cathodic potentials also indicates that the strength of the iodine chemisorption in basic solution is much less than in acidic solution.

The cathodic desorption of the iodide and the adsorption of hydrogen in basic solutions have been discussed by a number of authors.^{39,40} To explore the nature of the current peaks at -0.825 V in Figure 11, we performed a series of flushing experiments. The CV and $I_2(2\omega)$ SHG signal for the hydrogen adsorption region in 0.5 M NaOH are shown in Figure 12. A reversible increase was observed with the adsorption of atomic hydrogen at -0.7 V. The surface was then exposed to a solution of iodide for 3 min, open circuit, and then flushed out with NaOH. The SHG signal from this surface started at a high level in the double-layer region (indicative of iodine adsorption), and then after scanning into the hydrogen region to a potential dependence identical with that in Figure 12. We conclude therefore that although zero-valent iodine does chemisorb onto the electrode surface in basic solution, it can be replaced by adsorbed hydrogen in much the same way as chloride or bromide can be replaced in acidic media.

Conclusions

In summary, we have demonstrated that the changes in the SHG signal from platinum electrodes can be used to indirectly monitor the chemisorption of anionic species. Quantitative information regarding the chemisorption of bisulfate, chloride, bromide, and iodide at polycrystalline platinum electrodes can be obtained by monitoring the SHG signal simultaneously with standard electro-

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chemical measurements (e.g., cyclic voltammetry). If a series of SHG measurements are made with different input and output polarizations, additional information can be obtained on the state of chemisorption of the electrode surface.

In comparisons between the SHG signal from platinum electrodes in perchloric and sulfuric acid solutions, we have demonstrated that bisulfate and sulfate are present at the electrode surface in the double-layer region. In chloride and bromide solutions, the SHG experiments yielded adsorption isotherms that agree with previous electrochemical measurements. The reversibility of chloride chemisorption and the irreversibility of iodide chemisorption were demonstrated by the changes in the SHG signal during a series of flushing experiments. The SHG signal from an irreversibly adsorbed zero-valent iodine monolayer exhibited a linear potential dependence that must be attributed to changes in the surface electronic structure with potential. This iodine monolayer can be gradually stripped and the coverage monitored both optically and electrochemically. In acidic iodide solutions, the SHG measurements reveal the presence of both atomic and molecular iodine adsorbed on the platinum surface. Further iodide studies in basic solutions verify the replacement of chemisorbed iodine with adsorbed atomic hydrogen at negative potentials.

In general, the sensitivity of the nonresonant SHG process to the metal surface makes it a valuable in situ measurement which complements the linear optical measurements of electroreflectance and ellipsometry (which are sensitive to changes in the optical constants of all of the interfacial layers) and provides an optical alternative to the experimentally difficult radiotracer measurements of chemisorbed species at smooth electrodes. The use of several input and output polarization combinations is necessary for the measurement of the various surface non-linear susceptibility tensor elements. Additional structural information during chemisorption can be obtained from SHG studies of single-crystal surfaces;^{26,41} the application of the nonresonant SHG measurements to single-crystal platinum electrodes prepared by flame annealing⁴² is currently being pursued in our laboratory.⁴³

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation in these studies.

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