Second Harmonic Generation Studies of Anionic Chemisorption at Polycrystalline Platinum Electrodes

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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. Electrochemical studies have monitored anionic adsorption onto polycrystalline and single-crystal platinum electrodes by differential capacitance, by the alteration or suppression of hydrogen underpotential deposition, by the effect of anionic adsorption on oxide formation, and by various replacement reaction schemes. Complementing the electrochemical studies, anionic adsorption on platinum electrodes has been monitored in situ with spectroscopic techniques such as reflectance, ellipsometry, and, for anions with internal coordination, Fourier transform infrared (FTIR) spectroscopy. 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.

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). 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, 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, 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...
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. 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 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 polarization is given by

$$P_0^{(2)} = x_S^{(2)} E(\omega) E(\omega)$$  \hspace{1cm} (1)

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

$$x_S^{(2)} = x_S^{(2)} + x_A^{(2)} + \Delta x^{(2)}$$  \hspace{1cm} (2)

where $x_A^{(2)}$ is the inherent nonlinear susceptibility of the adsorbate independent of the surface and $\Delta x^{(2)}$ is the change in nonlinear susceptibility of the surface and adsorbate due to any interactions. At a polycrystalline metal surface, $x_S^{(2)}$ is typically larger than $x_A^{(2)}$; however, $\Delta x^{(2)}$ can be large enough to permit the detection of submonolayer quantities of an adsorbate. In some instances, the surface can be modified to minimize $\Delta x^{(2)}$. In a previous paper, we studied molecular chemisorption by using a sulfur monolayer to minimize the contributions of $\Delta x^{(2)}$ and by choosing a molecule and experimental geometry for which $x_A^{(2)}$ is the dominant contribution to $x^{(2)}$. In the present paper, we use changes in the SHG signal intensity caused by $\Delta x^{(2)}$ to determine the coverage of anions on the surface and to 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 $x_S^{(2)}$ should vary linearly with the relative surface coverage of the adsorbate $\theta$,

$$x_S^{(2)} = x_S^{(2)} (1 + \theta)$$  \hspace{1cm} (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 vacuum and on electrode surfaces. For cases where the changes in $x^{(2)}$ are sufficiently large, eq 3 is no longer valid, and further phase shifts and modifications of the surface nonlinear susceptibility can be observed.

Since $x^{(2)}$ 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: $x_{ZZZ}, x_{XXZ} = x_{ZYY},$ and $x_{XXZ} = x_{YYZ} = x_{ZYZ}$. 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:

$$I_1(2\omega) = |a_1 x_{XXZ}|^2$$  \hspace{1cm} (4)

$$I_2(2\omega) = |a_2 x_{XXX} + a_4 x_{ZZZ}|^2$$  \hspace{1cm} (5)

$$I_3(2\omega) = |a_3 x_{ZXX}|^2$$  \hspace{1cm} (6)

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

$$a_1 = e_1(\omega) e_1(\omega) e_1(2\omega)$$  \hspace{1cm} (19)

$$a_2 = 2 e_1(\omega) e_1(\omega) e_1(2\omega)$$  \hspace{1cm} (20)

$$a_3 = |e_1(\omega)|^2 e_1(2\omega)$$  \hspace{1cm} (21)

$$a_4 = |e_1(\omega)|^2 e_1(2\omega)$$  \hspace{1cm} (22)

References:

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

$$
\epsilon_x(\omega) = \cos \gamma \cos \theta_0 [1 - r_1(\omega)]
$$

$$
\epsilon_y(\omega) = \sin \gamma [1 + r_1(\omega)]
$$

$$
\epsilon_x(2\omega) = \cos \gamma' \cos \theta_0 [r_1(2\omega) - 1]
$$

$$
\epsilon_y(2\omega) = \sin \gamma' [1 + r_1(2\omega)]
$$

$\gamma$ and $\gamma'$ are the polarization angles for the fundamental and second harmonic beams ($\gamma = 0^\circ$ = p-polarized light, $\gamma = 90^\circ$ = s-polarized light), $\theta_0$ is the angle of incidence, $\theta_0$ is the angle of the outgoing second harmonic light, $r_1(\omega)$ and $r_1(2\omega)$ are the complex Fresnel coefficients for light perpendicular and parallel to the plane of incidence at the fundamental wavelength, and $r_1(2\omega)$ and $r_1(2\omega)$ are the complex Fresnel coefficients 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, except that the driving fields of the nonlinear polarization 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, 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 $I_2(2\omega)$.

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:

$$
\chi^{(2)} = \chi^{(0)}[\omega, \omega, 0]E_{DC}
$$

where $\chi^{(0)}[\omega, \omega, 0]$ is the third-order nonlinear hyperpolarizability 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. However, for strongly adsorbed anions such as sulfide and halides, a linear change in the p-polarized SHG signal with electrode potential is observed. This linear change in the SHG signal has been attributed to either an interference between $\chi^{(2)}$ and $E_{DC}$ or a change in the surface electronic structure with potential. 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 $\chi^{(2)}$. 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 HClO$_4$ 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.

#### 2. Sulfuric Acid Solutions

Figure 2 shows the CV
In contrast, measurements correlate with the various electrochemical electrode in a 0.5 M sulfuric acid solution.

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 $I_2(2\omega)$ 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 $I_3(2\omega)$.

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 $|\chi_{XXX}|^2$ and represents the nonlinear optical response of the surface to parallel-polarized fundamental light. This response increases abruptly with the deposition $H_2$, but is not affected by the adsorption of $H_2^+$. However, $I_3(2\omega)$, which contains $\chi_{ZZZ}$, 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 $H_2$. These observations are in agreement with FTIR and reflectance measurements, which have suggested that the bonding for $H_2$ is delocalized whereas the bonding for $H_2^+$ is more directional and perpendicular to the surface.

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. 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

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) $I_3(2\omega)$, and (c) $I_2(2\omega)$ from a polycrystalline platinum electrode in a 0.5 M sulfuric acid solution.
measurements are only sensitive to the chemisorbed a potential dependence similar to that observed for the adsorption of bisulfate. It is possible that the SHG potential-dependent SHG in the double-layer region agrees with that obtained in perchloric acid solutions by Novak et al., who measured the adsorption isotherm for chloride in the double-layer region or by a combination 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, $I_2(2\omega)$


the double-layer region, chloride ions are readsoorbed 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 measurements 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. It is possible that the SHG measurements are only sensitive to the chemisorbed 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. The radiotracer results of Horanyi et al. and the thin-layer electrochemistry experiments of Lane and Hubbard 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; 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.

In the potential range of −0.05 to 0.35 V, the SHG signal from the surface is fairly constant. Above 0.35 V, $I_2(2\omega)$
Figure 6. Optically determined relative surface coverage \( \theta \) 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 HClO₄ solution.

developed 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 electrodes and adsorbed halides on silver electrodes.\(^{33} \) The other SHG polarization measurements \( I_3(2\omega) \) and \( I_1(2\omega) \) 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 0.9 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 \( X_{DC}^{(2)} \) and changes in \( X_s^{(2)} \). For strongly adsorbed anions such as sulfur and iodide, we suspect that changes in the nonlinear 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 \( \mu \)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% iodide 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.\(^{35} \)

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 \( I_3(2\omega) \) 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

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Acknowledgments

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 iodide concentration was sufficiently low to avoid I$_2$ film formation). 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 $I_d(2\omega)$ 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 \( I_3(2\omega) \) at 296.5 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 \(^{27} \) 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 reabsorb 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 \( I_3(2\omega) \) SHG signal are plotted in Figure 11. Three differences are observed in comparison to studies in acidic media: (i) the 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 chemisorption), 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 electrochemical measurements.

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 nonlinear susceptibility tensor elements. Additional structural information during chemisorption can be obtained from SHG studies of single-crystal surfaces; the application of the nonresonant SHG measurements to single-crystal platinum electrodes prepared by flame annealing is currently being pursued in our laboratory.

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