

since $\ln [\text{CH}_4]$ is only a weak function of temperature. Now the left-hand side of eq 10 divided by R gives E_r , the activation energy for radical formation. Thus

$$E_r \approx E_1/2 \quad (11)$$

or the activation energy for CH_3^* radical formation should be approximately half the activation energy for CH_4 conversion, which in fact was observed.

Conclusions

For the oxidative coupling of methane there is good qualitative agreement between the $(\text{C}_2 \text{ yield})^{1/2}$ and the formation of methyl radicals, either when the type of catalyst is not varied greatly or when the partial pressures of reactants and products are not significantly different. Carbon dioxide is an important variable

which must be considered when making comparisons between reactor systems and catalysts. Quantitative comparisons between the rates of radical formation and C_2 product formation provide evidence for the importance of the gas-phase coupling reaction in the formation of ethane as a primary product. The activation energies for CH_4 conversion and methyl radical formation also are consistent with a radical coupling mechanism.

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Registry No. CH_4 , 74-82-8; CH_3^* , 2229-07-4; MgO , 1309-48-4; CaO , 1305-78-8; Li^+ , 17341-24-1; Na^+ , 17341-25-2; K^+ , 24203-36-9; ethane, 74-84-0; ethylene, 74-85-1.

Second Harmonic Generation Studies of Polycrystalline Platinum Electrodes in Sulfuric and Perchloric Acid Solutions

Deborah J. Campbell and Robert M. Corn*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706
(Received: February 16, 1988)

The potential dependence of optical second harmonic generation from polycrystalline platinum electrodes is presented for aqueous sulfuric and perchloric acid solutions. The second harmonic signal from the metal surface increases dramatically during the electrochemical deposition of hydrogen; this increase is quantitatively related to the charge passed during the chemisorption of the hydrogen species. Differences in the second harmonic signal for the weakly and strongly adsorbed hydrogen occur only in the presence of sulfate and bisulfate ions. The second harmonic signal for sulfuric acid solutions also increases as a function of potential in the double-layer region; this increase is attributed to the specific adsorption of sulfate and bisulfate ions and disappears during the formation of an oxide monolayer on the platinum surface.

Introduction

The process of second harmonic generation (SHG) exhibits a unique optical sensitivity to the interface of two centrosymmetric media.¹ This sensitivity is being exploited at a variety of condensed-phase interfaces; in particular, SHG has been employed in the examination of metal electrode surfaces. In the absence of any molecular transitions at the incident laser or second harmonic wavelengths, the second harmonic intensity from these interfaces is dominated by the nonlinear susceptibility of the surface metal atoms. This second harmonic signal has been used previously to measure changes in the charge density on the electrode surface,² to optically monitor the specific adsorption of anions,³ to follow the formation of oxide,⁴ hydrogen,⁵ and underpotentially deposited metal^{2,6} monolayers, and to probe the structure of single-crystal electrode surfaces via the dependence of the second harmonic intensity on the angles between the polarization vectors of the fundamental and second harmonic beams with respect to the crystal axes.⁷ In our own studies,⁵ we have most recently examined silver electrodes in nonaqueous solvents,

using the second harmonic signal to quantitate the adsorption of hydrogen during the evolution of molecular hydrogen. In this paper we extend our SHG studies to platinum electrodes in aqueous solutions. Our interest in platinum electrodes stems from several points: (i) for comparison with our previous work, the process of hydrogen adsorption at platinum electrodes is an electrochemically reversible process that has been studied intensively; (ii) there is a large body of linear electroreflectance data⁸ at platinum electrodes in sulfuric acid solutions with which to compare the SHG measurements; and (iii) as a long term goal we wish to extend our SHG studies to molecular SHG from both electroactive and electroinactive species chemisorbed onto polycrystalline platinum electrodes.

In this paper we report that the generation of light at 289 nm at platinum electrodes in sulfuric and perchloric acid solutions has a potential dependence that can be broken into the three different potential regions in which monolayer oxide formation, double-layer charging, and hydrogen atom chemisorption are occurring. In sulfuric acid solutions, we find that the second harmonic signal from the platinum surface increases during double-layer charging due to the contact adsorption of bisulfate and sulfate. This specific anionic adsorption depends upon the electrode potential and increases to a maximum level just prior to the commencement of monolayer oxide formation. A slow decrease in the second harmonic signal occurs during the formation of the oxide monolayer due to the desorption of the bisulfate and

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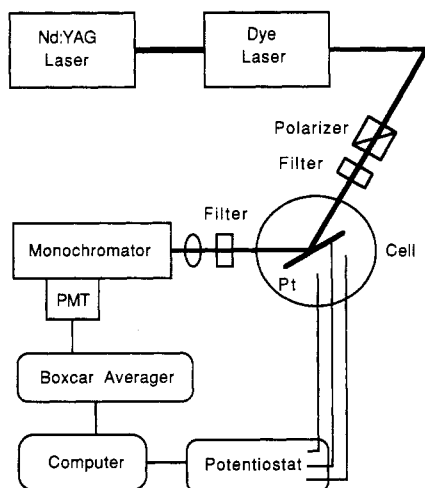


Figure 1. Schematic diagram of the experimental apparatus for second harmonic generation studies of platinum electrodes in aqueous acid solutions.

sulfate species. Upon return to the double-layer region, the platinum metal surface is regenerated, and the second harmonic signal again increases due to the anionic chemisorption.

In both sulfuric and perchloric acid solutions the second harmonic signal increases during the chemisorption of strongly and weakly bound hydrogen species onto the platinum surface. A comparison of the second harmonic signal with the amount of charge passed during the hydrogen deposition reaction reveals that the nonlinear susceptibility of the surface is linearly related to the surface coverage of the adsorbed hydrogen species. In perchloric acid media the increase in the surface nonlinear susceptibility is the same for both strongly and weakly adsorbed hydrogen, whereas in the presence of bisulfate and sulfate ions the chemisorption of the weakly adsorbed hydrogen species has a greater effect on the SHG from the platinum surface than the deposition of strongly adsorbed hydrogen.

Experimental Considerations

The SHG electrochemistry experiments were performed in a two-window Teflon cell which permitted an incident laser angle of 60° relative to the surface normal. The working electrode was a 6.35-mm-diameter platinum (99.99% purity) plug that was imbedded into a Teflon rod and then polished until optically smooth with $0.05\text{-}\mu\text{m}$ alumina. A saturated calomel electrode (SCE) or a Ag|AgCl electrode that was isolated from the acid solutions with a cracked glass frit served as the reference electrode; all potentials in this paper are reported vs SCE. A platinum wire counter electrode completed the standard three-electrode configuration that was controlled with a PAR 173/175 potentiostat. Millipore-filtered water was used in all the experiments, the perchloric acid was double-distilled (GFS Chemicals), and the sulfuric acid and all other reagents were of Puriss (Fluka Chemical Corp.) purity.

The experimental apparatus for the SHG studies is depicted schematically in Figure 1. The second harmonic light was generated at the platinum surface from a train (10 pulses/s) of 10-ns pulses of p-polarized 578-nm light from a single-stage amplified dye laser that was pumped with the doubled output of a Quantel Model 580 Nd:YAG laser. The incident and reflected fundamental beams were at 60° relative to the surface normal, whereas the second harmonic beam emerged at 58° due to the change in the index of refraction of water from 578 to 289 nm. The second harmonic light was passed through filters and a 0.156-m spectrometer to eliminate any residual fundamental laser light and any fluorescence caused by two-photon absorption; the ultraviolet light pulses were subsequently detected with a Hamamatsu R928 photomultiplier tube. The second harmonic signal was observed to be monochromatic within the bandwidth of the spectrometer (2 nm) and had a pulse shape of 15 ns, which represents a convolution of the laser pulse width and the spread

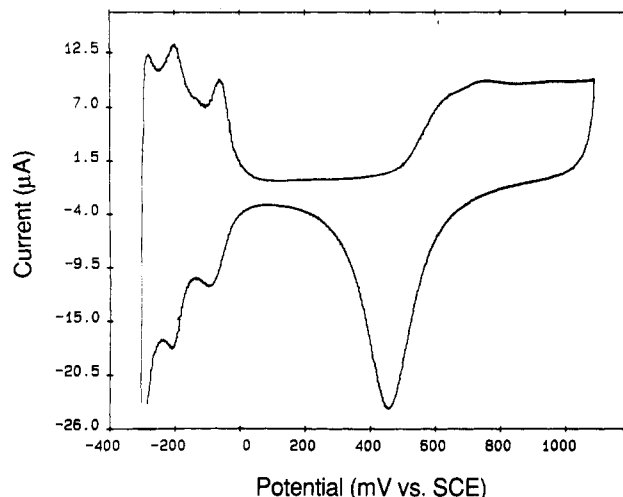


Figure 2. The cyclic voltammogram for a polycrystalline platinum electrode in a 0.5 M sulfuric acid solution. Scan rate: 10 mV/s.

time of the photomultiplier tube. The incoming train of second harmonic light pulses were averaged with a Stanford Research SR250 boxcar averager; this second harmonic signal, the current, and the electrode potential were captured simultaneously with an IBM PC computer as a function of time.

Laser-induced heating, desorption, and surface damage are significant concerns at platinum surfaces due to the lower reflectivity and thermal conductivity of platinum metal as compared to silver. In the range of laser power densities of $1\text{--}12\text{ mJ/cm}^2$, the second harmonic signal intensity from the surface was found to vary as the square of the incident power. Above these power densities, we observed laser-induced currents due to potential changes at the electrode, deviations from the quadratic dependence due to changes in the optical constants of the metal from surface heating, and eventually, at very high power densities, visible surface damage. We therefore used the onset of laser-induced currents as an experimental measure of the surface damage threshold and kept our power densities below this level in our measurements.

Results and Discussion

The cathodic and anodic currents observed from a platinum electrode in a 0.5 M H_2SO_4 solution while the potential is scanned linearly between +1.1 and -0.3 V at a rate of 10 mV/s are shown in Figure 2. The depicted currents are the steady-state response and are obtained after repeated cycling in order to destroy any impurities either adsorbed onto the surface or residing within a diffusion layer near the electrode. Similar curves were obtained from perchloric acid solutions. Three well-known regions appear in the cyclic voltammogram: (i) double-layer charging as the electrode is scanned positively from 0 to $+0.500\text{ V}$, (ii) oxide monolayer formation as the electrode is scanned from $+0.500$ to $+1.100\text{ V}$ and subsequent oxide monolayer stripping on the return sweep at a peak potential of $+0.450\text{ V}$, and (iii) hydrogen chemisorption and desorption as the potential is scanned between 0 and -0.300 V . The two reversible peaks at -0.090 and -0.208 V correspond to the electrochemical deposition of two different types of adsorbed hydrogen (denoted as strongly (H_s) and weakly (H_w) adsorbed hydrogen, respectively). Studies of single-crystal platinum electrodes^{9,10} show that these two peaks correspond to hydrogen adsorption onto different crystal faces, and electroreflectance measurements indicate that the bonding characteristics of these two hydrogen species are quite different. The chemisorption of H_s increases the reflectivity of the electrode, and the 1s electron is thought to be delocalized into the s-band of the metal surface. In contrast, H_w decreases the reflectivity of the surface upon chemisorption and is thought to form a localized H-Pt bond. As shown by other authors,¹⁰ we can calculate the charge passed

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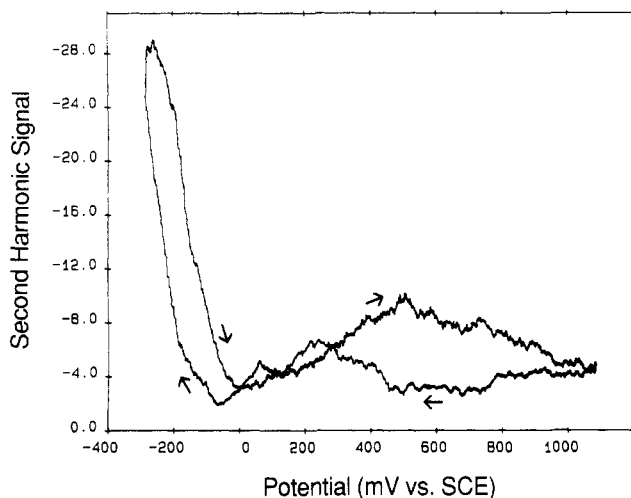


Figure 3. The second harmonic signal (arbitrary units) during a cyclic voltammogram from a polycrystalline platinum electrode in a 0.5 M sulfuric acid solution. Scan rate: 10 mV/s.

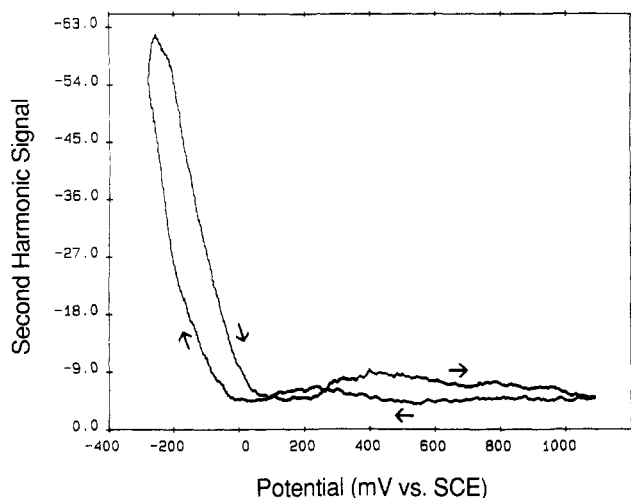


Figure 4. The second harmonic signal (arbitrary units) during a cyclic voltammogram from a polycrystalline platinum electrode in a 0.35 M perchloric acid solution. Scan rate: 10 mV/s.

during hydrogen deposition by subtraction of the currents obtained from an acid solution containing 1 mM potassium iodide (in which there is complete blocking of the hydrogen adsorption). The total charge from these corrected currents is used as a measure of the effective surface area of the electrode, assuming that there is approximately 254 and 251 $\mu\text{C}/\text{cm}^2$ for a complete monolayer of adsorbed hydrogen on platinum in sulfuric and perchloric acid solutions, respectively.¹⁰

The second harmonic signals that we observe from the platinum electrode in 0.5 M H_2SO_4 and 0.35 M HClO_4 during potential cycling at scan rates of 10 mV/s are shown in Figures 3 and 4, respectively. The second harmonic signal changes in each of the three regions mentioned above (by differing amounts depending on the acid), demonstrating that the second harmonic signal reflects the chemical processes that are occurring on the electrode surface. We address the nonlinear optical response from the surface in the three regions separately:

1. *Double-Layer Charging Region.* As the electrode potential is scanned positively from 0 to ca. +0.500 V, a small potential-independent current is observed due to the charging of the electrical double layer. On platinum electrodes the exact location of the potential of zero charge (pzc) is of some dispute but is thought to reside approximately at -0.100 V.¹¹ Figure 3 shows that the second harmonic signal reaches a minimum near that potential and rises steadily until +0.500 V. This increase in the second

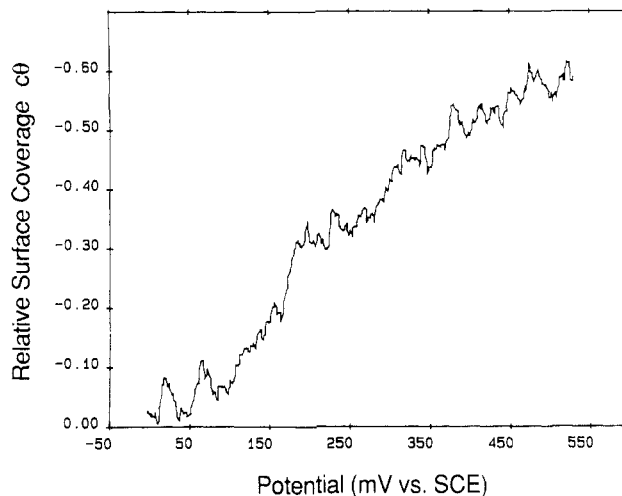


Figure 5. The optically determined relative surface coverage, $c\theta$, of adsorbed bisulfate as a function of potential in the double-layer region during a positive potential sweep in a 0.5 M sulfuric acid solution.

harmonic signal occurs to a much smaller degree in perchloric acid solutions; the addition of millimolar quantities of sulfuric acid results in a second harmonic signal analogous to that for the 0.5 M H_2SO_4 solution. We attribute the increase in the second harmonic signal to the modification of the surface nonlinear susceptibility by specific anion adsorption. We will call this anion adsorption "bisulfate adsorption" after the majority species at this pH, even though it is known from FTIR measurements that both bisulfate and sulfate ions are present on the electrode surface.¹² An increase in the surface second harmonic signal also occurs in the presence of halide ions; these results will be reported in a later paper. The lack of a large increase in the second harmonic signal from perchloric acid media is indicative of the very weak adsorption of perchlorate ions onto the platinum surface.

If the nonlinear susceptibility of the surface changes linearly with the surface coverage of chemisorbed bisulfate, then the second harmonic intensity $I(2\omega)$ should vary with the relative surface coverage θ as

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

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 ($\theta = 1$). This equation assumes that there is no phase shift in the surface nonlinear susceptibility upon chemisorption. Figure 5 plots the function " $c\theta$ " $\{= [I(2\omega)/I(2\omega)_0]^{1/2} - 1\}$ as the potential is scanned positively from -0.100 to +0.500 V. The amount of chemisorption asymptotically approaches a maximum at +0.500 V. The observation of a potential dependence for the adsorption of bisulfate agrees with the qualitative findings of FTIR measurements.¹²

2. *Oxide Formation Region.* As the potential is scanned positively beyond +0.500 V, we observe an anodic current due to the formation of a monolayer of oxide on the platinum surface. The chemical composition of the oxide layer is not known exactly but is thought to have a stoichiometry of two oxygen atoms for every surface platinum atom.¹³ As evidenced by the cyclic voltammogram (Figure 2), the formation of this chemisorbed layer is a kinetically slow process. Large changes are observed in the ellipsometric¹⁴ and electroreflectance⁸ data from platinum electrodes during the formation of this oxide layer. In sulfuric acid solutions (Figure 3) we observe a decrease in the second harmonic signal during this potential range as the bisulfate ions slowly desorb. The lack of large increases in the second harmonic signal

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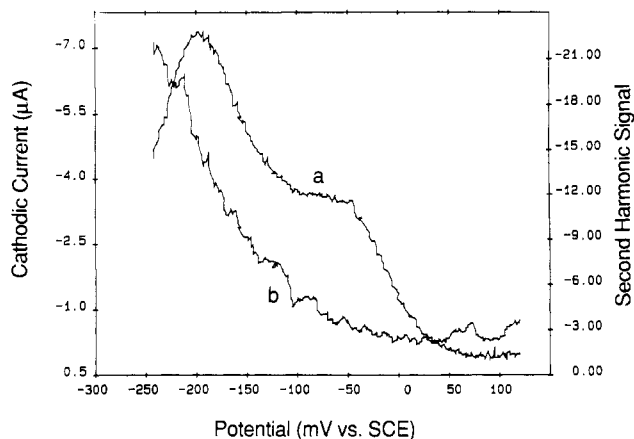


Figure 6. The cathodic current after iodide background subtraction (a) and the second harmonic signal (b) as a function of potential in the hydrogen adsorption region for a 0.35 M perchloric acid solution.

during oxide formation eliminates the possibility of a noncentrosymmetric bulk oxide layer existing on the surface. The differences between the electroreflectance data and the second harmonic signal emphasize that at electrode surfaces the changes in the second harmonic intensity are dominated by contributions from the metal surface atoms. The electroreflectance data, however, are a combination of the index of refraction changes of the metal, chemisorbed layer, and double layer.

As the potential is swept negatively, the oxide is eventually stripped off of the surface with a peak potential of +0.450 V. Upon renewal of the platinum surface, the second harmonic signal returns at a potential of +0.300 V to a level that is dictated by the chemisorption of bisulfate. This return occurs at +0.400 V for a scan rate of 1 mV/s; the observed scan rate dependence indicates that the reduction of the oxide monolayer is kinetically limited. The pattern of loss and subsequent return of second harmonic signal is reproducible throughout cycling of the potential. The stability of the second harmonic signal indicates that the optical signal, like the current, is not sensitive to any "roughening" (on the one- to two-monolayer level) that occurs during oxide formation. This insensitivity is in contrast to the changes that have been observed at silver surfaces.¹⁵

3. Hydrogen Atom Adsorption Region. As the potential scan continues negative of the *pzc*, a monolayer of hydrogen atoms is adsorbed onto the platinum surface prior to H₂ evolution. As seen in Figures 3 and 4, the second harmonic signal increases dramatically as the hydrogen layer is formed for both sulfuric and perchloric acid solutions. The signal increase in perchloric acid is larger than that for sulfuric acid; this difference can be attributed to the presence of the bisulfate ion during hydrogen deposition. In both acids the observed increase is not totally reversible at a scan rate of 10 mV/s (as evidenced by the hysteresis loop observed in both figures); however, at a scan rate of 1 mV/s the hysteresis is diminished. In the presence of iodide, there is blocking of the hydrogen adsorption and the second harmonic signal is greatly diminished in this potential region. Figures 6 and 7 plot the corrected currents (curve a) and the second harmonic signal (curve b) during the deposition of hydrogen for a 0.35 M HClO₄ solution and a 0.5 M H₂SO₄ solution, respectively. As seen in Figure 7, in sulfuric acid solutions there is no immediate increase in the second harmonic signal with the commencement of hydrogen adsorption. This delay can be attributed to the remaining presence of chemisorbed bisulfate.

From the corrected currents we can quantitate the amount of charge passed during the chemisorption of monatomic hydrogen, and from this charge we get an estimate of the surface coverage of hydrogen atoms. As in the case of bisulfate adsorption, we can also calculate the function $c\theta$ for adsorbed hydrogen from the second harmonic signal. These optically measured surface coverages can be compared with the electrochemically determined

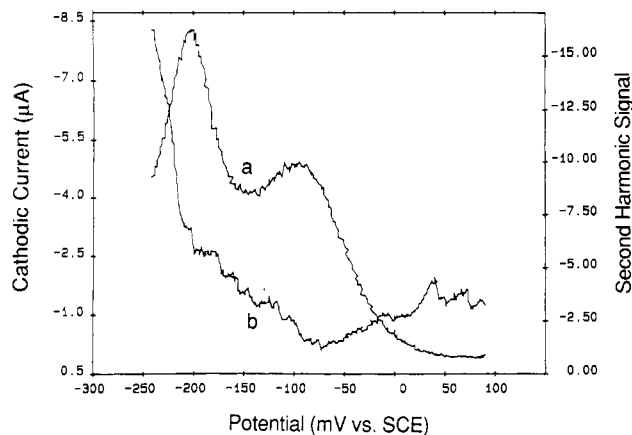


Figure 7. The cathodic current after iodide background subtraction (a) and the second harmonic signal (b) as a function of potential in the hydrogen adsorption region for a 0.5 M sulfuric acid solution.

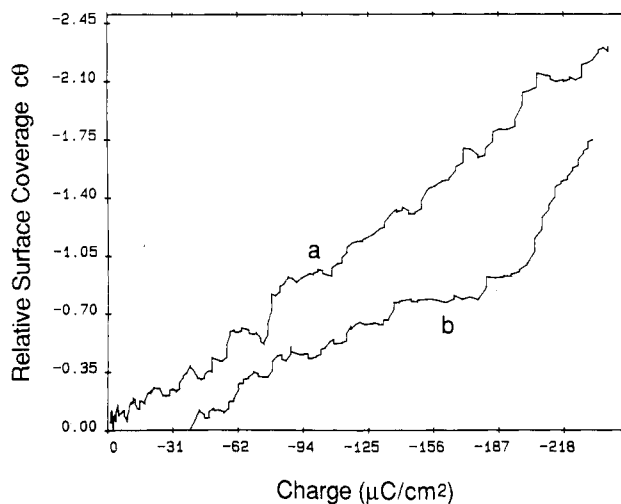


Figure 8. The relative surface coverage of hydrogen, $c\theta$, as a function of charge, q , for a 0.35 M perchloric acid solution (a) and a 0.5 M sulfuric acid solution (b). The constant c is different for each acid.

values. Figure 8 plots $c\theta$, the relative surface coverage of adsorbed hydrogen, versus q , the charge passed due to hydrogen chemisorption, for the two acid solutions. For the 0.35 M HClO₄ solution, the function $c\theta$ is linear with respect to q throughout the hydrogen adsorption region. For the 0.5 M H₂SO₄ solution, a break is observed in $c\theta$ at a charge that coincides with the peak current due to the chemisorption of H_w. A similar break is also observed when small amounts of bisulfate are added to 0.5 M perchloric acid solutions. This break can be seen clearly in the second harmonic signal plotted in Figure 7 and is attributed to the desorption of bisulfate ions.

The increase in second harmonic signal during the hydrogen adsorption is in direct contrast with the decrease that we observed previously from silver electrodes in nonaqueous solvents.⁵ This increase could be due to one of three possibilities: (i) a contribution from the intrinsic nonlinear susceptibility of the adsorbed hydrogen species, (ii) an increase in the free electron charge density on the platinum surface, or (iii) a change with adsorption in the platinum d-band contribution to the nonlinear susceptibility. The fact that we see increases in the second harmonic signal for both H_s and H_w makes the first and second cases unlikely since the electronic structure of the two hydrogen species is thought to vary substantially. This suggests that the nonlinear susceptibility of the surface metal atoms is dominated by the bound (d-band) electrons. In the two different metals, platinum and silver, hydrogen adsorption could affect the d-band contribution to the nonlinear polarizability in a different manner. We will reserve judgment on this problem until we can monitor the SHG from these electrodes at a variety of wavelengths. However, these results and those of other authors⁷ suggest that the wavelength dependence

of the SHG from a variety of metal electrodes (e.g., Au, Pt, Cu, Ag) should vary sharply.

Conclusions

In summary, we have demonstrated that the second harmonic signal from platinum electrodes is sensitive to the surface changes which occur during an electrochemical cycle. The processes of specific anion adsorption and hydrogen atom chemisorption both increase the second harmonic signal from the platinum surface. The SHG measurements show that the chemisorption of bisulfate ions in the double-layer region varies with potential, reaching a minimum near the pzc. In the oxide region, the second harmonic signal slowly decreases during the replacement of the chemisorbed bisulfate with the oxide monolayer. In the hydrogen adsorption region, the second harmonic signal quantitatively increases during the chemisorption of strongly and weakly bound hydrogen; this increase also detects the desorption of bisulfate ions during the deposition process. These results, along with our studies on silver electrodes, suggest that the changes in the nonlinear susceptibility of the metal surface during chemisorption are dominated by changes in the contributions from the bound (d-band) electrons. The measurements reported here demonstrate that for certain adsorbates (e.g., hydrogen, anions) it is possible to quantitatively follow the chemisorption process by indirectly monitoring changes

in the second harmonic signal from the platinum surface atoms. Having quantified the "nonresonant" second harmonic signal from platinum electrodes, we are now in a position to analyze the "resonant" molecular SHG contribution¹⁶ from chemisorbed species (for which there is a wealth of electrochemical data available at platinum electrodes);¹⁷ this contribution can potentially provide a direct measurement of surface coverage and molecular orientation with molecular specificity obtained by the proper selection of second harmonic wavelength.

Acknowledgment. The authors gratefully acknowledge the assistance of Matt Lynch and Eric Miller in the construction of the experimental apparatus for these experiments. This work was supported by the National Science Foundation.

Registry No. Pt, 7440-06-4; H₂SO₄, 7664-93-9; HClO₄, 7601-90-3; H₂, 1333-74-0; H⁺, 12184-88-2; SO₄²⁻, 14808-79-8; HSO₄⁻, 16057-15-1; platinum oxide, 11129-89-8.

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An Infrared Study of Trimethylgallium Adsorbed on Alumina and the Lewis/Hydroxyl Site Ratio

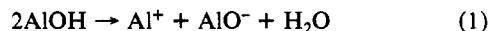
Richard A. McFarlane and B. A. Morrow*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5
(Received: February 22, 1988)

Infrared spectroscopy has been used to show that trimethylgallium, Ga(CH₃)₃, reacts with the AlOH groups on alumina to yield AlOGa(CH₃)₂ (I) and CH₄. The number of Lewis acid/base sites increases with the temperature of activation, and the Lewis acid sites react with Ga(CH₃)₃ to yield AlCH₃ (II) while the base sites yield species I. Spectral subtraction techniques have permitted the determination of the relative extinction coefficients of I and II which in turn has allowed us to determine simultaneously the ratio of the number of molecules that react with Lewis acid/base sites to those that react with AlOH sites, as a function of the temperature of activation of alumina. The results for the Lewis/OH site ratio have been compared with those that have been obtained from the water loss method, and we have found that the site ratio is lower at higher temperatures. Therefore, the data are probably a more accurate measure of the number of accessible sites that can react with molecules having dimensions similar to those of Ga(CH₃)₃.

Introduction

Alumina is widely used as a catalyst and as a catalyst support,¹⁻³ and it is generally accepted that there can be as many as five types of surface hydroxyl groups. Dehydroxylation produces Lewis acid and base sites as follows:

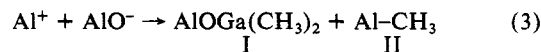


Because the catalytic activity of alumina can be related to the numbers of hydroxyl groups and Lewis acid/base sites, it is, therefore, of interest to know the relative numbers of these types of sites.

We have recently shown⁴ that trimethylgallium (TMG) reacts with silanol (SiOH) groups on silica to yield SiOGa(CH₃)₂ and CH₄. A similar reaction could be envisaged with AlOH groups on Al₂O₃:



Additionally, a reaction with the Lewis acid/base sites created via the dehydroxylation process in reaction 1 might occur as follows:



Although species I would be produced via reactions 2 and 3, species II would be created by only reaction 3. The present investigation was undertaken in order to see whether an infrared study of the reaction of TMG with Al₂O₃ could be used to verify that reaction 3 occurs and to use this data to determine simultaneously the ratio of surface AlOH groups to Lewis acid/base sites by quantitatively determining the relative proportions of species I and II produced from reactions 2 and 3. The results are compared with those obtained from other methods (see below).^{1,5-9}

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