that eq 12 cannot be used to calculate the activation energy of viscous flow for our present micellar systems, and the effect of micellar size change should be taken into account in applying this equation to other micellar solutions, which, unfortunately, was overlooked in the literature.[16,19,20]

Conclusions

1. A method for calculating the content of organic ions in micelles at the cmc using the Gibbs–Duhem equation is proposed. The results show that the content of B_4N in the alkyl sulfate micelles at the cmc and in surface adsorption layer decreases with increasing alkyl sulfate chain length, which arises from the increase of the hydrophobicity asymmetry between B_4N and the surfactants with the surfactant chain length.

2. The Krafft point of alkyl sulfate salt is reduced considerably in the presence of B_4N, which enables a practical use of the micellar solutions with a hydrophobic chain length as long as octadecyl at room temperature. The Krafft point decreases with increasing micellar concentration in the presence of inorganic salt and increases with increasing inorganic salt concentration and chain length of the surfactant.

3. The cloud point of B_4NC_nS increases with increasing surfactant chain length except for that of the hexadecyl and octadecyl chains at concentrations below 56 mM. It is interpreted in terms of the variation of the B_4N content in the micelles with the surfactant chain length by using our previously proposed model for the occurrence of the cloud point phenomenon. The addition of NaBr raises the cloud point initially, passing through a maximum, and then decreases again. The decrease of the cloud point may be relevant to the micellar growth and the reduction of electrostatic repulsion between micelles with inorganic salt.

4. $B_4NC_{18}S$ forms homogeneous micellar solutions in the temperature range from the Krafft point to the cloud point. The micellar size decreases with increasing surfactant concentration at 0.2 M NaBr in the concentration range studied and is not likely due to an overlap of the micelles. The temperature dependence of the micellar growth varies with the salinity. The micellar size increases with increasing temperature in the presence of a comparable amount of NaBr to the surfactants or in the absence of NaBr and decreases on adding excess NaBr. The micellar size increases with increasing surfactant chain length.

5. An Arrhenius type of equation cannot be used to calculate the activation energy of viscous flow of micellar solutions without considering the effect of micellar size change with temperature.

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Molecular Second Harmonic Generation Studies of Methylene Blue Chemisorbed onto a Sulfur-Modified Polycrystalline Platinum Electrode

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The resonant molecular second harmonic generation (SHG) response of a monolayer of adsorbed methylene blue is studied in situ on a polycrystalline platinum electrode modified by the deposition of a monolayer of chemisorbed sulfur. The sulfur monolayer prevents the irreversible decomposition of the dye molecules on the platinum electrode and ensures that the contributions to the surface nonlinear susceptibility from the metal and from the methylene blue remain separable. At an incident angle of 40°, the resonant molecular SHG signal from the methylene blue monolayer dominates the nonlinear optical response of the interface, and the potential dependence of the resonant SHG signal matches that expected during the electrochemical reduction and reoxidation of the chemisorbed methylene blue. The polarization dependence of SHG signal provides a picture of the average molecular orientation of the dye molecules as a function of surface coverage; this calculation of the average molecule orientation must include the complex Fresnel coefficients for the metal–electrolyte interface at the fundamental and second harmonic wavelengths and a full accounting of the various molecular nonlinear polarizability tensor elements.

Introduction

A number of research groups are currently exploring the use of the nonlinear optical process of second harmonic generation (SHG) as an in situ probe of chemisorption and structure at metal electrodes.[1–9] The sensitivity of SHG to the interfacial region when the adjacent bulk media are both centrosymmetric has led to its extensive implementation as a probe of surfaces.[10] At electrochemical interfaces, the SHG process is particularly useful due to its ability to discriminate between surface and solution species. In a recent paper[1] we used changes in the *nonresonant* optical response of the metal surface to indirectly monitor the chemisorption of species (e.g., monatomic hydrogen, bisulfate ions)

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onto platinum electrodes. The SHG signal was shown to provide a quantitative measure of the relative surface coverage of the chemisorbed species; similar quantitative SHG studies have also been used to study the hydrogen evolution reaction at polycrystalline silver electrodes[2] and to measure surface coverages under ultrahigh vacuum.[7-9] In one recent study,[7] Heskett et al. have shown how model calculations of the changes in the SHG from metal surfaces upon adsorption can provide an estimate of molecular orientation and packing within a chemisorbed overlayer. Although these studies can in general provide a valuable in situ measure of chemisorbed intermediates in reactions occurring at the electrode surface, the indirect nature of this measurement leaves one with a minimal amount of control over the specificity of the technique.

A second large area of application of SHG to surfaces has been the study of molecular SHG at a variety of condensed-phase interfaces.[11-17] In these studies, the SHG from the interface is dominated by the molecular contributions to the surface nonlinear susceptibility. The second harmonic intensity from these systems has been used to measure relative surface coverages of interfacial species and to obtain estimates of the average molecular orientation at the surface. Although prior SHG studies at silver electrodes have shown that there can be molecular contributions to the surface nonlinear susceptibility (particularly at roughened electrodes),[18] it has been difficult to separate the molecular second harmonic response from the second harmonic response of the metal surface itself.

In this paper we demonstrate unequivocally that the *resonant* SHG response of molecules can be utilized to study chemisorption at platinum surfaces under electrochemical conditions. In particular, we present the resonant molecular SHG response of a monolayer of the thiazine dye methylene blue chemisorbed onto a sulfur-modified platinum electrode. The SHG signal is observed at the resonant wavelength from these electrodes for both p-polarized and s-polarized input light and vanishes upon the electrochemical reduction of the adsorbed methylene blue to its leuco form. The polarization dependence of the SHG signal provides a measure of the average molecular orientation at the surface; changes in the average molecular orientation are observed as a function of the surface coverage of methylene blue. A monolayer of sulfur is deposited onto the platinum surface prior to the adsorption of methylene blue; the presence of the sulfur monolayer is verified in a separate set of nonresonant SHG measurements. The sulfur modification of the platinum surface serves three purposes: (i) it controls the direct adsorption of species onto the platinum electrode, thereby fixing the nonresonant SHG signal from the metal surface to a small, constant and negligible level, (ii) it prevents the irreversible decomposition of the dye molecules at the platinum surface, and (iii) it increases the strength and specificity of the methylene blue chemisorption.

Experimental Considerations

The SHG signal measured in these experiments was created on the electrode surface from either the 10-ns pulses of light (585 and 532 nm) generated by a 10-Hz Nd:YAG-pumped dye laser system (Quantel Model 580) or the 1.6-ps pulses of light (585.0 and 610 nm) generated by a 4-MHz sync-pumped dye laser/mode-locked Nd:YAG laser system (Coherent Model 702). The

SHG signal was separated from the fundamental laser beam with two sets of UV-transmitting filters and a 0.175-m spectrometer (Jarrell Ash); the UV light was detected with a cooled Hamamatsu R928 photomultiplier tube (PMT). For the nanosecond laser system the SHG signal was obtained by integration of the PMT pulses with a boxcar averager (Stanford Research Model 280), and for the picosecond laser system the SHG signal was measured by single photon counting electronics (Stanford Research Model 600). The SHG signal is expressed in arbitrary units for the boxcar-averaged measurements and as the number of counts per second (i.e., per 4 million laser pulses) for the photon counting measurements. The SHG signal in both cases was found to be monochromatic within the resolution of the spectrometer and represented the total SHG intensity observed at that wavelength; no background level of SHG has been subtracted from the data. To ensure that the ultraviolet light was indeed produced in a nonlinear optical process, it was verified for each experiment that the SHG signal varied as the square of the input laser beam power.

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 and cleaned in chromic acid. This working electrode was used in a three-electrode configuration with a platinum counter electrode and an isolated saturated calomel reference electrode. For the electrochemical experiments cyclic voltammograms (CVs) were obtained by cycling the electrode potential at a rate of 10 or 50 mV/s by a PAR 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 nonresonant SHG signal from the metal surface a two-window, 60° incident angle (relative to the surface normal) cell, and (ii) for the resonant SHG studies a single-window, 40.5° incident angle (60° incident to the window) cell. The single-window cell was constructed to hold only a small volume of electrolyte (ca. 4 mL). This permitted the rapid introduction and expulsion of the sulfide and methylene blue solutions used in the adsorption process.

Methylene blue (Kodak) was recrystallized twice from ethanol–water solutions prior to use. The UV–vis spectrum of methylene blue was obtained from a 1.0×10^{-5} M solution in a phosphate buffer at a pH of 7.9 with an HP diode array (Model 8452A) spectrometer. A supporting electrolyte of 0.5 M NaF or $NaNO_3$ was employed in all electrochemical solutions. The water employed in these experiments was Millipore-filtered and then doubly distilled. All other chemicals were of Puriss (Fluka) quality.

Results and Discussion

A. Platinum Electrode Preparation and Nonresonant SHG Measurements. The first step in the electrode preparation was to electrochemically clean the platinum surface by repeated electrochemical cycling in acidic solution between +1.22 and −0.26 V. The steady-state CV from the polycrystalline platinum electrode in a 0.5 M sulfuric acid solution is shown in Figure 1a. The well-documented electrochemical formations of a surface oxide monolayer and a monolayer of chemisorbed monatomic hydrogen are evident in the CV and indicate the establishment of a clean, polycrystalline surface.[19]

Further information on the state of the platinum surface was obtained by nonresonant SHG measurements performed in the 60° spectroelectrochemical cell. The SHG signal from p-polarized input light during the CV from the platinum electrode in a 0.5 M sulfuric acid solution is shown in Figure 1b. This SHG signal is a "nonresonant" response from the electrode surface in that the nonlinear susceptibility of the metal surface dominates the SHG signal and there is no strong wavelength dependence to the surface SHG. Changes are observed in the nonresonant SHG signal

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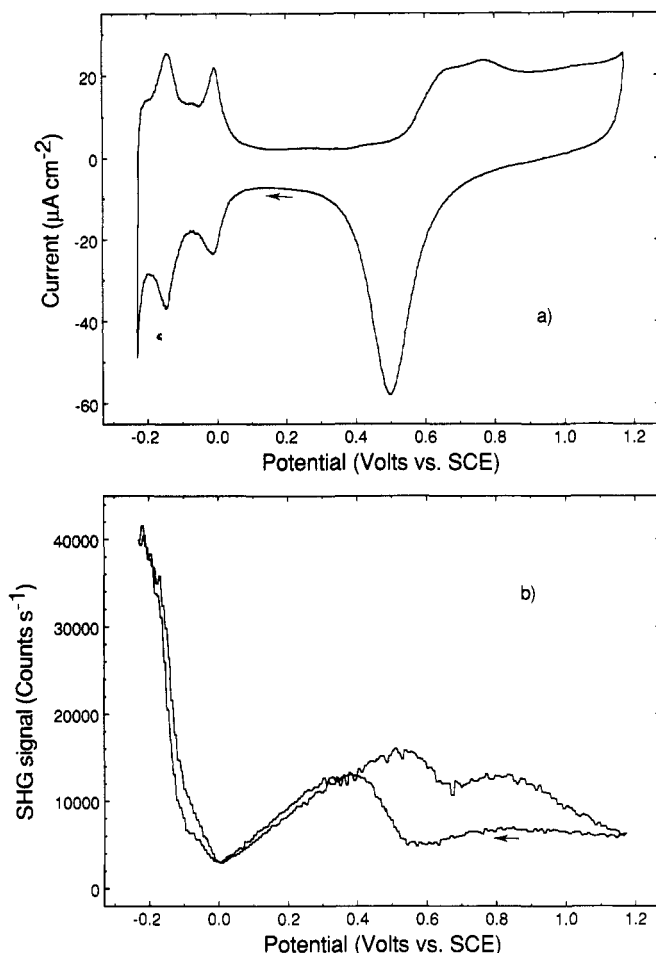
Figure 1. Cyclic voltammogram (a) and nonresonant SHG signal at 292.5 nm (b) from a polycrystalline platinum electrode in a 0.5 M H_2SO_4 solution. The 585-nm fundamental beam was p-polarized at an incident angle of 60°, and the SHG signal was observed at 58°. The scan rate is 10 mV/s.

Figure 2. Cyclic voltammogram (a) and nonresonant SHG signal at 292.5 nm (b) from a polycrystalline platinum electrode in a 1 mM Na_2S + 0.5 M H_2SO_4 solution. The scan rate is 10 mV/s.

during hydrogen adsorption, oxide formation, and bisulfate chemisorption as reported in a previous paper.[1]

After electrochemical cleaning, a monolayer of zerovalent sulfur was deposited onto the platinum surface. The electrode potential was held in the double-layer region at +0.100 V, and an aliquot of sodium sulfide was added to the solution to create a 1 mM sulfide concentration in the acidic medium. The CV obtained from the resultant surface is shown in Figure 2a. As has been reported by other authors,[20,21] we find that the sulfide ions chemisorb to the Pt surface, forming a sulfur monolayer that inhibits the reversible hydrogen adsorption which normally would occur prior to hydrogen evolution.[19]

The SHG response from the platinum electrode in the 60° cell after the sulfur adsorption is plotted in Figure 2b. The SHG signal has changed to a level that is only weakly potential dependent, demonstrating that the sulfur does indeed prevent the chemisorption of other species. The SHG signal level is comparable to that observed upon chemisorption of hydrogen or bisulfate. At the wavelengths employed in this study (585.0-nm fundamental and 292.5-nm second harmonic), there are no electronic resonances with the chemisorbed sulfur atoms. This is in contrast to the studies of Heuer et al.,[8] who attributed a 65-fold increase in the SHG at 532 nm from a Pd surface upon the chemisorption of a monolayer of sulfur to a resonant enhancement at 1064 nm. At 585 nm the lack of strong wavelength dependence or large enhancements in the SHG signal establishes that the SHG from the sulfur-modified platinum electrode is, just as in the case of
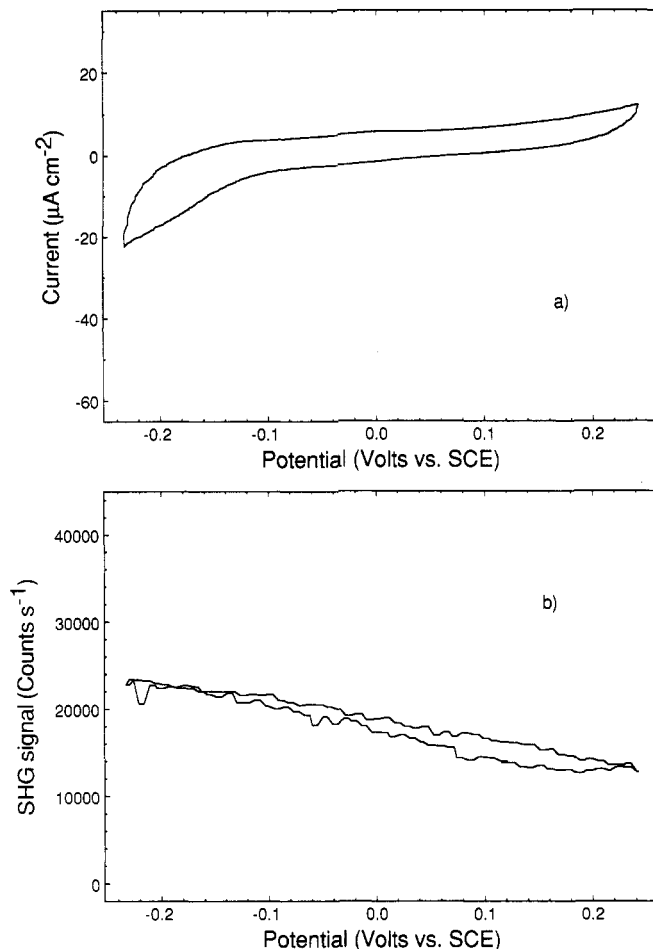
chemisorbed hydrogen or bisulfate, a "nonresonant" response due to the combined nonlinear susceptibility of the metal and adsorbate.

The nonresonant SHG signal that we observe from the sulfur-modified platinum electrodes in the absence of dye adsorption agrees with previous electrochemical studies which indirectly find that a full monolayer of chemisorbed sulfur is present at the electrode potentials employed here[21] and that the sulfur chemisorption blocks hydrogen and bisulfate chemisorption. Although the adsorbed sulfur is present in a full monolayer, the electrode is still electroactive. Indeed, the presence of an adsorbed sulfur monolayer is thought to act as an electrocatalyst on platinum.[22] In addition, it has been suggested that the chemisorbed sulfur can form sulfur–sulfur bonds with any sulfur-containing solution species (e.g., methylene blue).[23,24] This type of adsorption is preferable on platinum electrodes because it inhibits any irreversible adsorption of organic molecules observed by other authors[25] that might in our case destroy the optical and electrochemical properties of the thiazine dyes. Sulfur modification has been used previously on gold electrodes to form a monolayer of chemisorbed methylene blue;[24] the method of chemisorption that we utilize in this paper is an extension of that work to sulfur-modified platinum electrodes. The sulfur chemisorption therefore serves three functions in this study: (i) it fixes the nonresonant SHG signal of the metal surface to a constant and low level, (ii) it prevents the irreversible adsorption of the organic molecules

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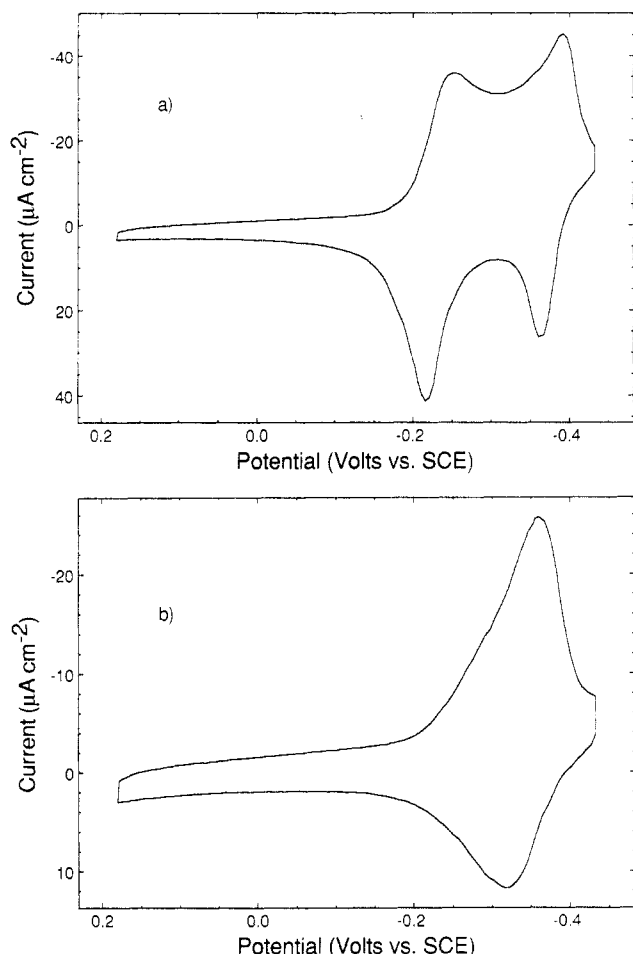
Figure 4. UV–vis absorption spectrum of a dilute methylene blue solution in a phosphate buffer at a pH of 7.9. The fundamental and second harmonic wavelengths employed in this study are shown in the figure.

Figure 3. (a) Cyclic voltammogram of a sulfur-modified platinum electrode in a 100 μM methylene blue solution buffered at a pH of 7.9. (b) Cyclic voltammogram of the chemisorbed methylene blue monolayer after flushing the electrochemical cell with phosphate buffer. Integration of the reduction peak yields on average a surface charge density for the chemisorbed methylene blue of 32 μC/cm^2. The scan rate is 50 mV/s in both voltammograms.

onto the platinum surface, and (iii) it specifically enhances the chemisorption of the methylene blue molecules.

The nonresonant SHG signal from the sulfur monolayer was observed with p-polarized fundamental light at an incident angle of 60°. With s-polarized fundamental light the nonresonant SHG signal from the sulfur-modified platinum surface was observed to be approximately 30 times smaller. The difference in SHG signal from p-polarized and s-polarized light is due in part to the difference in Fresnel factors for the two polarizations at the metal surface and in part from the dominance of the surface terms that contribute to the nonlinear susceptibility of the metal surface. We have noted previously that the choice of p-polarized light at a 60° angle of incidence is appropriate for nonresonant SHG studies of chemisorption at platinum electrodes.[1] However, for molecular SHG studies we employ a 40.5° incident angle cell geometry. At this incident angle the nonresonant SHG signal is substantially reduced and will be shown to be negligible when compared with the molecular SHG response.

B. Electrochemical Formation of a Chemisorbed Methylene Blue Monolayer. The molecular SHG studies were performed on a monolayer of methylene blue molecules that were chemisorbed electrochemically onto a sulfur-modified platinum electrode. First, a monolayer of chemisorbed sulfur was created as described above on a platinum electrode in the small volume spectroelectrochemical cell. Following the flushing of the cell with a phosphate buffer at a pH of 7.9, a 100 μM methylene blue solution is introduced; Figure 3a displays the CV that is obtained. On the cathodic sweep the first wave corresponds to the two-electron reduction of solution species to the leuco form, and the second
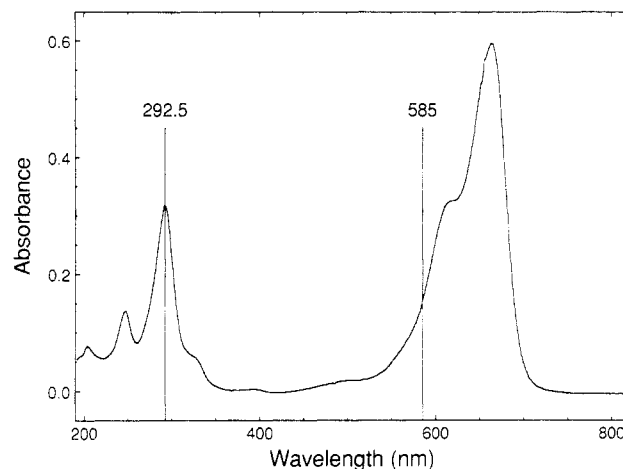
peak is the adsorption postwave due to the subsequent reduction of the chemisorbed monolayer of methylene blue. The difference in peak potentials between the solution and surface species is a measure of the strength of the adsorption of methylene blue; the difference at a sulfur-modified platinum surface is greater than that observed in the absence of chemisorbed sulfur.[23] (However, the observed difference is not as great as that realized during the adsorption of methylene blue onto sulfur-modified gold electrodes.) The shift of the adsorption postwave verifies that the presence of the sulfur monolayer has enhanced the strength of the methylene blue chemisorption. Clavilier et al.[24] have attributed this increase in chemisorption strength to a specific sulfur–sulfur interaction at the surface.

After the chemisorption of methylene blue from solution, the cell is again flushed with buffer and a CV in which the solution wave is absent is obtained (Figure 3b). Integration of the re-maining current peak due to the chemisorbed methylene blue typically yielded a total surface charge density of 32 $\pm$ 3 μC/cm^2. Previous calculations have suggested that a surface charge density of 25 μC/cm^2 roughly corresponds to a close-packed monolayer of dye molecules with aromatic rings parallel to the electrode surface, and a surface charge density of 50 μC/cm^2 corresponds to a monolayer of methylene blue oriented perpendicular to the surface.[24]

A partial monolayer of methylene blue could be formed by cyclically reducing and reoxidizing the chemisorbed dye molecules. The reduced form of the molecule is not strongly chemisorbed to the surface and desorbs to some extent during a CV. For example, after five electrochemical cycles at 50 mV/s followed by a flushing with phosphate buffer, a subsequent CV revealed that the surface methylene blue concentration was reduced to 18 μC/cm^2, or 56% of the original value. After additional CV/flushing cycles the surface charge density was further reduced. This electrochemically induced decrease in the surface coverage can be used to create partial methylene blue monolayers for the molecular SHG studies. A second technique that reduced the surface concentration of chemisorbed methylene blue was to lower the concentration of the adsorption solution. For example, adsorption from a 0.5 μM methylene blue solution led to a surface charge density of 11 μC/cm^2, or 33% of the maximum surface charge density observed.

C. Molecular SHG Response from the Chemisorbed Methylene Blue Monolayer. Following electrochemical deposition, surface SHG experiments were performed at 585 nm on the full monolayer methylene blue coated electrode. The absorption spectrum of a dilute solution of methylene blue in a pH 7.9 buffer is shown in Figure 4; the spectrum has a broad absorption centered at 660 nm and a narrower absorption at 290 nm. By choosing a fundamental wavelength of 585 nm for the SHG experiments, the SHG process is resonance-enhanced at both the fundamental and second harmonic wavelengths. Such a double resonance has

TABLE I: Magnitudes of the SHG Signal as a Function of Surface Conditions and Input Polarization

surface[a]	SHG measurement	expt[b]	calcd[c] A	calcd[c] B
Pt-S-MB	I_1 (45° in, s out)	0.52	0.1	0.6
Pt-S-MB	I_2 (p in, p out)	11.9	11.9	11.9
Pt-S-MB	I_3 (s in, p out)	1.0	1.0	1.0
Pt-S-MB	I_4 (45° in, p out)	3.4	4.9	4.6
Pt-S	I_1	0.045		
Pt-S	I_2	0.440		
Pt-S	I_3	0.015		
Pt-S	I_4	0.076		

[a] Pt-S refers to a sulfur-modified polycrystalline platinum surface, and Pt-S-MB corresponds to a full methylene blue monolayer (32 $\mu C/cm^2$) adsorbed from a 100 μM deposition solution onto a sulfur-modified polycrystalline platinum surface. [b] The SHG signal intensities were obtained from photon counting measurements on a 4-MHz pulsed picosecond laser system at 585/292.5 nm and are listed on a scale which sets $I_3 = 1$. The largest SHG signal observed, I_2 from the methylene blue monolayer, was typically on the order of 20 000 counts per second. The SHG signal levels are accurate to approximately 10%. [c] Two calculations of the relative SHG signal intensity are listed in the table and correspond to different theoretical assumptions and parameters. A: $\beta_{x'x'x'} = 0$ and either $\alpha = 0°$, $\phi = 20°$ or $\alpha =$ random, $\phi = 29°$. B: $\beta_{x'x'x'}/\beta_{z'xx} = -0.3$ and either $\alpha = 0°$, $\phi = 24°$ or $\alpha =$ random, $\phi = 35°$.

been exploited previously in SHG studies of the similar oxazine dye molecule Nile Blue while adsorbed onto fused silica surfaces;[16] the SHG response of that molecular monolayer was observed to be quite strong in comparison with species that are only resonant at one wavelength.

How strong is the SHG signal from the methylene blue monolayer relative to the nonresonant response of the sulfur-modified platinum surface? A comparison of the SHG signal obtained from the methylene blue coated electrode with the magnitude of the nonresonant SHG background in the absence of methylene blue chemisorption is shown in Table I for different input and output polarizations at 585.0 nm. The SHG signal from the methylene blue monolayer was approximately 45 times greater than the SHG signal from the sulfur-modified platinum surface for both p-polarized and s-polarized input light. It is doubtful that this increase occurred from any changes induced in the nonlinear susceptibility of the platinum surface atoms by the dye molecules because of the presence of the interceding chemisorbed sulfur monolayer. Moreover, this large enhancement in SHG signal was not observed at fundamental wavelengths of 532 or 610 nm. The increase in the surface nonlinear susceptibility can therefore be attributed to the "resonant" response of the adsorbed dye molecules.

The conclusion that the SHG from this electrode occurs from the resonant nonlinear response of the methylene blue monolayer is supported by the potential dependence of the SHG signal. The steady-state p-polarized SHG signal at 292.5 nm from p-polarized 585-nm input light for a monolayer of chemisorbed methylene blue as a function of electrode potential during the electrochemical cycling of the methylene blue monolayer is shown in Figure 5. A similar potential dependence is observed with s-polarized input light. Also shown in the figure is the CV obtained simultaneously with the optical measurement. For both input polarizations the potential dependence of the resonant SHG signal reaches a maximum level just prior to the reduction of the adsorbed dye molecules, undergoes a very large decrease as the adsorbed molecules are reduced to the leucomethylene blue form, and then returns to the original signal level upon reoxidation of the monolayer back to methylene blue. The large loss in the SHG signal from both p-polarized and s-polarized input light upon reduction of the methylene blue dye monolayer confirms that the molecular contributions to the nonlinear susceptibility dominate the SHG signal response of the interface.

Figure 6 plots the p-polarized SHG during a series of CV/ flushing cycles which reduce the surface coverage of chemisorbed methylene blue versus the electrochemically measured surface charge density. As expected, the SHG signal from the interface
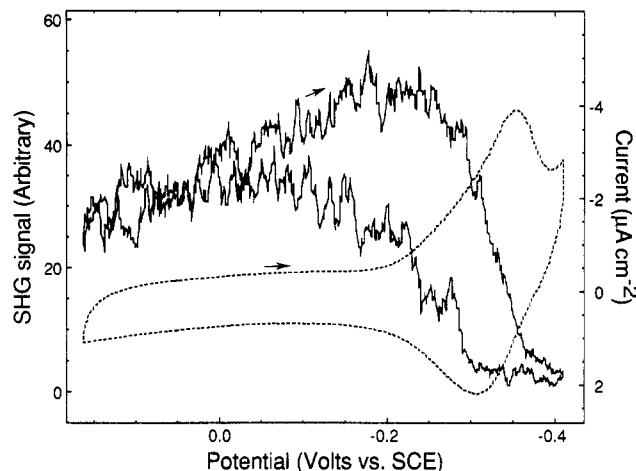

Figure 5. Potential dependence of the in situ resonant SHG signal at 292.5 nm from a monolayer of methylene blue chemisorbed onto a sulfur-modified platinum electrode during reduction of the monolayer at a scan rate of 10 mV/s. The monolayer is chemisorbed onto the sulfur-modified platinum electrode in a phosphate buffer solution at pH 7.9. The SHG signal was obtained from a p-polarized fundamental 585-nm beam at an incident angle of 40.5°. The SHG signal from s-polarized fundamental light had an identical potential dependence.
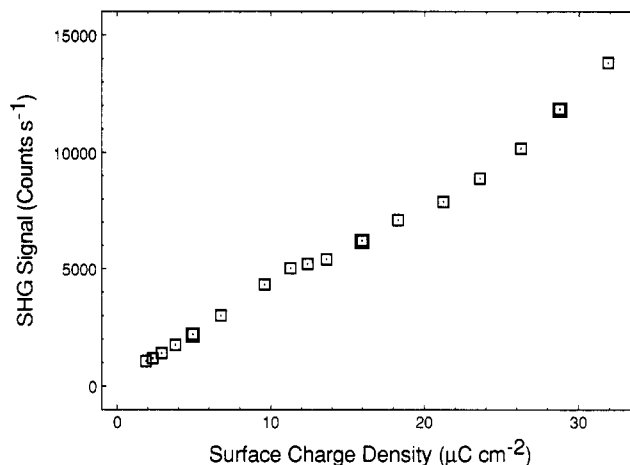

Figure 6. SHG signal from chemisorbed methylene blue at a sulfur-modified platinum electrode as a function of surface charge density. A surface charge density of 32 $\mu C/cm^2$ corresponded to the maximum surface coverage observed.

decreases as the surface coverage decreases. However, it is evident in the figure that the SHG signal decreases nonmonotonically. If the molecular orientation distribution function of the chemisorbed dye molecules were independent of surface coverage, the SHG signal should have decreased quadratically with surface charge density. The nonquadratic behavior of the SHG signal, especially at lower surface concentrations, suggests that the molecular orientation of the chemisorbed dye molecules varies with surface concentration. The polarization measurements described in the next two sections confirm this conclusion.

D. Polarization Dependence of the Molecular SHG Signal. The in situ resonant SHG signal from a full chemisorbed methylene blue monolayer at an electrode potential of –0.100 V is listed for four different input and output polarization combinations in Table I. Following the notation of Dick et al.,[26] a polarization angle γ is defined such that 0° corresponds to p-polarized input light and 90° corresponds to s-polarized input light. The four measured SHG intensities are I_1 [45° in, 90° out], I_2 [0° in, 0° out], I_3 [90° in, 0° out], and I_4 [45° in, 0° out]. The nonresonant SHG signal from the metal substrate in the absence of methylene

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TABLE II: Constants Employed in the Fresnel Coefficients for the Molecular Orientation Calculations

Z^a	real (Z)	imag (Z)	Z^a	real (Z)	imag (Z)
$n_{Pt}(\omega)$	2.22	3.88	$r_\parallel(2\omega)$	0.2165	0.4769
$n_{Pt}(2\omega)$	1.45	2.12	$e_x(\omega)$	0.3488	−0.3314
$n_{H_2O}(\omega)$	1.33	0	$e_y(\omega)$	0.2501	−0.3098
$n_{H_2O}(2\omega)$	1.36	0	$e_z(\omega)$	1.0010	0.2830
$r_\perp(\omega)$	−0.7499	−0.3098	$e_x(2\omega)$	−0.6046	0.3680
$r_\parallel(\omega)$	0.5412	0.4358	$e_y(2\omega)$	0.4669	−0.4321
$r_\perp(2\omega)$	−0.5331	−0.4321	$e_z(2\omega)$	0.7738	0.3033

$^a n(\omega)$ and $n(2\omega)$ are the complex indexes of refraction at 585.0 and 292.5 nm, and the other symbols are defined in the text.

blue is small enough to be neglected. (Subtraction of the background nonresonant SHG does not change the SHG intensities within experimental error.) However, the metal electrode does affect the polarization dependence of the SHG signal through its modification of the local electromagnetic field at the surface; this modification must be taken into account by the use of Fresnel factors for the interface.

The SHG response for a monolayer of molecules (or atoms), $I(2\omega)$, is related to the intensity of input light $I(\omega)$ by the equation[10,27]

$$I(2\omega) = \frac{32\pi^3\omega^2 \sec^2\theta_{2\omega}}{c^3 A} \left| e(2\omega)\cdot\chi^{(2)}:e(\omega)\ e(\omega) \right|^2 I(\omega)^2 \quad (1)$$

where $\theta_{2\omega}$ is the angle at which the SHG signal occurs, χ is the surface second-order nonlinear susceptibility tensor, the vectors $e(\omega)$ and $e(2\omega)$ describe the fundamental and second harmonic light fields at the surface, A is the illuminated surface area, and all other symbols have their usual meaning. The two light field vectors depend upon both the polarization of the light and the Fresnel factors for the surface. For an s-polarized input light vector, e_y is the only nonzero component of $e(\omega)$, and for a p-polarized input light vector, e_x and e_z are the only nonzero components. These components are given by

$$e_x(\omega) = (\cos\theta_\omega)[1 + r_\parallel(\omega)]$$

$$e_y(\omega) = 1 + r_\perp(\omega)$$

$$e_z(\omega) = (\sin\theta_\omega)[1 + r_\parallel(\omega)] \quad (2)$$

where θ_ω is the angle of incidence and $r_\perp(\omega)$ and $r_\parallel(\omega)$ are the complex Fresnel coefficients[28] for light perpendicular and parallel to the plane of incidence at the fundamental wavelength. Formulas similar to those in eq 2 hold for the output light vector $e(2\omega)$:

$$e_x(2\omega) = (\cos\theta_{2\omega})[r_\parallel(2\omega) - 1]$$

$$e_y(2\omega) = [1 + r_\perp(2\omega)]$$

$$e_z(2\omega) = (\sin\theta_{2\omega})[1 + r_\parallel(2\omega)] \quad (3)$$

The use of complex Fresnel coefficients described here is similar to that employed in the phenomenological treatment of surface SHG by Sipe,[27] 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. This choice is more appropriate for the case of molecular SHG from a chemisorbed monolayer above the platinum surface. These equations also assume that the linear indexes of refraction for the methylene blue monolayer at ω and 2ω are the same as the bulk solution and that any local field corrections can be neglected.[29] With these assumptions, the Fresnel coefficients calculated from the tabulated optical constants for platinum and water at 585.0 and 292.5 nm[30] can be employed. The Fresnel coefficients differ substantially for s-polarized and p-polarized light (as expected from a metal surface[31]) and are a major contribution to the polarization de-

pendence of the SHG signal level. Table II lists the optical constants employed in the calculation as well as the reflection coefficients and components of $e(\omega)$ and $e(2\omega)$ for the geometry ($\theta_\omega = 40.5°$, $\theta_{2\omega} = 39.9°$) used in the molecular SHG experiments.

The polarization dependence of the SHG signal is related to the light field vectors and the components of the surface nonlinear susceptibility tensor χ. For SHG from a monolayer of molecules that (i) have an orientational distribution function which is invariant upon rotation about the surface normal (defined as the Z axis) and (ii) have a plane of symmetry, the only nonzero tensor elements are χ_{ZZZ}, $\chi_{ZXX} = \chi_{ZYY}$ and $\chi_{XXZ} = \chi_{XZX}$.[26] The p-polarized SHG signal $I_p(2\omega)$ and the s-polarized SHG signal $I_s(2\omega)$ can be written as a function of the input polarization angle γ

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

$$I_p(2\omega) \propto |(\cos^2\gamma)(a_2\chi_{XXZ} + a_3\chi_{ZXX} + a_4\chi_{ZZZ}) + (\sin^2\gamma)a_5\chi_{ZXX}|^2 \quad (5)$$

where we have followed the notation of Dick et al.[26] and defined the constants a_i for a given angle of incidence:

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

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

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

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

$$a_5 = |e_y(\omega)|^2 e_z(2\omega) \quad (6)$$

The calculated a_i constants relate the measured SHG intensities I_1-I_4 to the macroscopic nonlinear susceptibility tensor elements χ_{ZZZ}, χ_{ZXX}, and χ_{XXZ} of the chemisorbed methylene blue monolayer. These tensor elements are in turn related to the *molecular* nonlinear polarizability tensor β when averaged over the orientational distribution function for the molecules on the electrode surface. In the next section the molecular nonlinear polarizability tensor elements are calculated, and the experimental SHG intensities are related to the average molecular orientation of the chemisorbed methylene blue.

E. Orientation Calculation for the Chemisorbed Methylene Blue. As noted in the Introduction, the polarization dependence of the molecular SHG signal has been used at a variety of interfaces to estimate the average molecular orientation at the surface. Since the SHG signal from our electrode is dominated by the methylene blue contribution, we can use the polarization dependence of the SHG signal to monitor in situ the average molecular orientation at the electrochemical interface. Measurements of this type are very important for a detailed understanding of the electrochemical properties of the interface, since changes in orientation and packing density can often control the electrochemical reaction pathways at an electrode surface.

To calculate the average molecular orientation of the chemisorbed methylene blue, we must relate the nonlinear susceptibility tensor elements χ_{ZZZ}, χ_{ZXX}, and χ_{XXZ} to the second-order molecular polarizability tensor β of the methylene blue molecule. In general, this calculation requires two parts: first, we must determine which tensor elements dominate β as defined in an internal molecular coordinate system, and second, this internal molecular coordinate system must be related to the macroscopic coordinate system through a model of the orientational distribution function for the molecules. Both aspects of the calculation have been discussed by other authors, and the methodology applied here to the study of electrochemically adsorbed methylene blue is a combination of that employed in previous studies.[32,33]

1. Molecular Nonlinear Polarizability Calculation. To obtain the molecular orientation information, it is first necessary to determine which tensor elements are important in creating the polarization in the methylene blue molecule at the second harmonic

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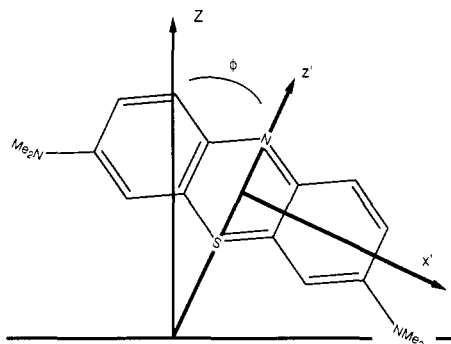(33) Dick, B. *Chem. Phys.* **1985,** *96,* 199.

Figure 7. Methylene blue molecule, the definition of the molecular axes z', x', and the definition of the angle ϕ relating the molecular coordinate z' to the normal of the electrode surface Z.

TABLE III: Excited-State Energies for Methylene Blue Obtained from a Pople–Pariser–Parr π-Electron Calculation and Used in the Nonlinear Polarizability Calculation

energy, eV	symmetry	oscillator strength	Δ(dipole moment)[a]
1.81	B_2	1.690	-3.133
2.73	A_1	0.024	-6.643
3.45	A_1	0.050	-1.925
3.86	B_2	0.023	-2.746
3.87	A_1	0.159	0.797
4.12	B_2	0.060	-0.331
4.30	A_1	0.324	-0.888
4.60	B_2	0.576	-3.038
5.01	B_2	0.133	-2.755
5.18	B_2	0.035	-2.477
5.43	A_1	0.002	-3.888
5.47	B_2	0.000	-0.816

[a] The change in the dipole moment with respect to the ground-state dipole moment, in debyes. The ground-state dipole moment is calculated to be -12.626 D.

wavelength. The molecular nonlinear polarizability tensor elements are defined with respect to the symmetry axes x', y', and z' of the methylene blue molecule as defined in Figure 7. It is reasonable to assume that the π-electronic structure in the dye molecule is the sole contributor to the nonlinear polarizability.[32] Since the π-electron structure of methylene blue has C_{2v} symmetry, the dominant tensor elements will be $\beta_{z'z'z'}$, $\beta_{z'x'x'}$, and $\beta_{x'x'z'} = \beta_{x'z'x'}$.

The calculation of the molecular nonlinear polarizability tensor elements requires knowledge of the electronic structure of the molecule; in particular, it requires the dipole moment of each electronic state and the transition dipole moments from each state to all other electronic states.[32] Calculation of the nonlinear polarizability can range from a simple two- or three-state model of the dye molecule[34] to a complete SCF-CI calculation of the electronic structure.[35] With the assumption that the π-electronic structure controls the optical response of the molecule, an intermediate level of calculation used by DeQuan et al.[32] in which the Pople–Pariser–Parr (PPP) method[36] is used to calculate the π-electron wave functions can be employed. We have performed this π-electron calculation for methylene blue, and the calculated energies of the 12 lowest excited states are listed in Table III. The energies are in good agreement with previous π-electron calculations on methylene blue.[37] Also listed in Table III for each excited state is the state symmetry, the change in the dipole moment from the ground state, and the oscillator strength for a transition from the ground state. The ground- and excited-state dipole moments must lie along the z' axis, and transitions from the ground state will either be x'-polarized (for B_2 symmetry

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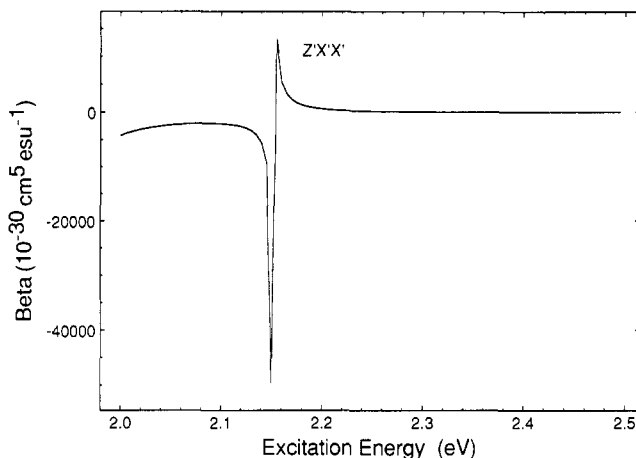

Figure 8. SHG nonlinear polarizability tensor element $z'x'x'$ for methylene blue as a function of fundamental photon energy, as calculated from the wave functions obtained by a PPP π-electron calculation.
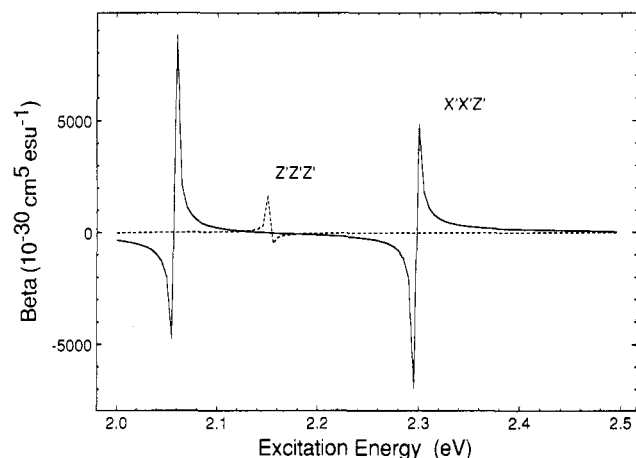

Figure 9. SHG nonlinear polarizability tensor elements $x'x'z'$ and $z'z'z'$ for methylene blue as a function of fundamental photon energy, as calculated from the wave functions obtained by a PPP π-electron calculation.

states) or z'-polarized (for A_1 symmetry states).

Using the wave functions obtained from the PPP π-electron calculation, one can calculate the nonlinear polarizability tensor elements using the formula[32]

$$\beta_{ijk} + \beta_{ikj} = -\frac{e^3}{4\hbar^2}\left[\sum_{\substack{n \neq n' \\ n \neq g \\ n' \neq g}} (r^j_{gn'}r^i_{n'n}r^k_{gn} + \right.$$

$$r^k_{gn'}r^i_{n'n}r^j_{gn})\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)} + \right.$$

$$\left.\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right) + (r^i_{gn'}r^j_{n'n}r^k_{gn} +$$

$$r^i_{gn'}r^k_{n'n}r^j_{gn})\left(\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}\right) +$$

$$(r^j_{gn'}r^k_{n'n}r^i_{gn} + r^k_{gn'}r^j_{n'n}r^i_{gn})\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)} + \right.$$

$$\left.\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right) + 4\sum_n (r^j_{gn}r^k_{gn}\Delta r^i_n(\omega_{ng}^2 - 4\omega^2) +$$

$$r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n)(\omega_{ng}^2 + 2\omega^2))\frac{1}{(\omega_{ng}^2-\omega^2)(\omega_{ng}^2 - 4\omega^2)}\right] \quad (7)$$

where $r^j_{n'n}$ is the dipole matrix element $\langle\phi_n|\mu_i|\phi_{n'}\rangle$, Δr^j_n is the difference in the dipole moment between the excited state n and the ground state g, $\hbar\omega_{ng}$ is the difference between the excited- and ground-state energies, and ω is the frequency of the applied electromagnetic field. The nonlinear polarizability tensor elements calculated from eq 7 are plotted in Figures 8 and 9 for the wavelength region of interest. Note that the nonlinear polariz-abilities in Figures 8 and 9 diverge when exactly on resonance. A more accurate calculation of the nonlinear polarizability should include lifetime broadening terms of the type $i\Gamma_{ng}$ in the energy denominators,[38] and an estimate of the actual width of the SHG resonance can be obtained from the optical absorption spectrum (Figure 4).[16] However, all that is required for the molecular orientation calculation is to determine the relative importance of the various nonlinear polarizability tensor elements in the wavelength region of interest; comparisons of the near-resonance calculations can provide us with this information for electronic states of rigid π-electron systems such as in the case of methylene blue. Figures 8 and 9 show that the tensor elements $\beta_{z'x'x'}$ and $\beta_{x'x'z'}$ are important in this wavelength region, whereas the $\beta_{z'z'z'}$ tensor element is small and can be neglected. For the wavelength of 585 nm, the calculation suggests that $\beta_{z'x'x'}$ will dominate. This is the same conclusion arrived at by Heinz et al. for the similar case of Rhodamine dye using a simple three-state model.[11] For methylene blue the fundamental wavelength is near resonance with the long-axis (x')-polarized transition at 1.8 eV, and the second harmonic wavelength is in resonance with a short-axis (z')-po-larized transition at 4.30 eV. This combination leads to a large $\beta_{z'x'x'}$ nonlinear polarizability tensor element. However, there are also x'-polarized states nearby at 4.12 and 4.60 eV. As the second harmonic wavelength comes into resonance with those states, the $\beta_{x'x'z'}$ tensor element also becomes significant. Unfortunately, the exact location of these states is difficult to ascertain; the π-electron calculations are good in energy to about 10%, and the energies will shift depending upon the molecular environment.[37] Thus, while it is reasonable to expect that $\beta_{z'x'x'}$ will dominate the nonlinear polarizability of the chemisorbed methylene blue, there may be a nonnegligible contribution from $\beta_{x'x'z'}$. We will first assume that the $\beta_{z'x'x'}$ tensor element dominates the molecular nonlinear polarizability and then see how an additional contribution from $\beta_{x'x'z'}$ will modify the orientation calculation results.

2. Orientational Distribution Calculation. The molecular orientation calculation assumes that the molecules are randomly oriented azimuthally about the Z (space-fixed) axis. In general, the z' molecular axis will make some average angle ϕ with respect to this surface normal (see Figure 7). The fact that the SHG signal was observed from the chemisorbed methylene blue means that ϕ and $\alpha \neq 90°$; in other words, the molecules are not all oriented flat on the surface. In addition to the angle ϕ, the chemisorbed molecules are oriented with some average direction for their x' and y' axes. Following Dick,[33] we define an angle α about the z' axis such that if $\alpha = 90°$ then the x' axes of all of the chemisorbed methylene blue are parallel to the surface and if $\alpha = 0°$ then the y' axes of all of the chemisorbed methylene blue are parallel to the surface. A third possibility that will be examined is the case where α is random.

The relations between the macroscopic nonlinear susceptibility tensor elements and the molecular nonlinear polarizability tensor elements can be described in terms of the first and third Legendre polynomials for cos ϕ: $P_1(\cos\phi) = \langle\cos\phi\rangle$ and $P_3(\cos\phi) = 0.5(5\langle\cos^3\phi\rangle - 3\langle\cos\phi\rangle)$.[33] The exact relations depend upon the choice of α, the angle about the z' axis. The proportionality constants between the molecular nonlinear polarizability tensor elements ($\beta_{z'x'x'}$, $\beta_{x'x'z'}$) and the macroscopic tensor elements (χ_{ZZZ}, χ_{ZXX}, χ_{XXZ}) are given for the various choices of α in Table IV. Using Table IV and eqs 4 and 5 (which relate the nonlinear susceptibility to the second harmonic intensity), one can calculate the SHG signal for a given ϕ and α.

In accordance with the molecular nonlinear polarizability tensor calculations, the molecular orientation calculation is first per-

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TABLE IV: Relations between the Macroscopic Nonlinear Susceptibility Tensor Elements and the Molecular Nonlinear Polarizability Tensor Element $\beta_{z'x'x'}$, $\beta_{x'x'z'}$, and $\beta_{x'z'x'}$

	α^a	χ_{ZZZ}	χ_{ZXX}	χ_{XXZ}
$\beta_{z'x'x'}$	90°	0	$0.5P_1{}^b$	0
	0°	$0.4(P_1 - P_3)$	$0.1(3P_1 + 2P_3)$	$-0.2(P_1 - P_3)$
	random	$0.2(P_1 - P_3)$	$0.1(4P_1 + P_3)$	$-0.1(P_1 - P_3)$
$\beta_{x'x'z'}$	90°	0	0	$0.5P_1$
	0°	$0.4(P_1 - P_3)$	$-0.2(P_1 - P_3)$	$0.1(3P_1 + 2P_3)$
	random	$0.2(P_1 - P_3)$	$-0.1(P_1 - P_3)$	$0.1(4P_1 + P_3)$
$\beta_{x'z'x'}$	90°	0	0	0
	0°	$0.4(P_1 - P_3)$	$-0.2(P_1 - P_3)$	$-0.2(P_1 - P_3)$
	random	$0.2(P_1 - P_3)$	$-0.1(P_1 - P_3)$	$-0.1(P_1 - P_3)$

$^a\alpha$ is the angle about the z' axis, with 90° defined such that x' is parallel to the surface. $^bP_1$ and P_3 are the first and third Legendre polynomial of cos ϕ, as described in the text.
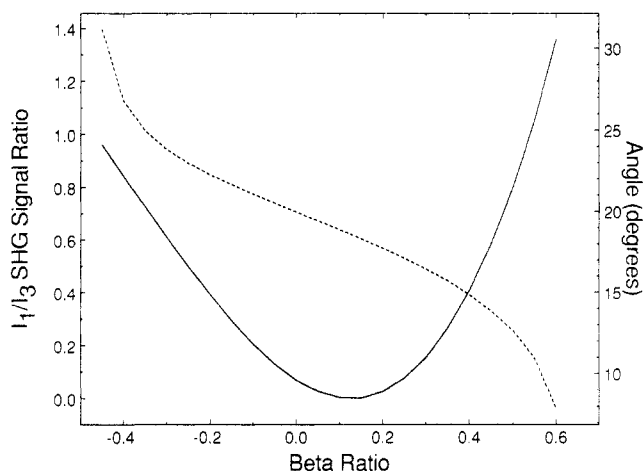

Figure 10. Variation of the SHG signal intensity ratio I_1/I_3 (—) and the molecular angle ϕ (- - -) as a function of the ratio of the molecular nonlinear polarizability tensor elements $\beta_{x'x'z'}/\beta_{z'x'x'}$ for a fixed I_2/I_3 ratio of 11.9.

formed assuming that $\beta_{z'x'x'}$ dominates the molecular nonlinear optical response. (Note: if it is assumed instead that the $\beta_{x'x'z'}$ or $\beta_{z'z'z'}$ tensor element dominates, no reasonable fit to the experimental data can be obtained.) If $\alpha = 90°$ (x' axes parallel to the surface), then $\chi_{ZZZ} = \chi_{XXZ} = 0$, there should be no s-po-larized SHG signal ($I_1 = 0$), and the ratio of I_2 and I_3 should be independent of ϕ and defined by the Fresnel coefficients. For the platinum–water interface at an incident angle of 40.5°, this ratio should be 2.1. Since the ratio of I_2 and I_3 was observed to be 17.5, and the s-polarized SHG signal was observed, this molecular orientation must be dismissed. A second possibility is if $\alpha = 0°$ (y' axes parallel to the surface). An angle ϕ of 20° will yield the appropriate ratio of I_2 and I_3; the calculated intensities I_1 through I_4 are listed in column A of Table I. (Of course, the four calculated intensities are relative and the value of I_2 has been fixed to match the experimental data.) This molecular orientation for the dye molecule is very similar to that determined by Heinz et al. for Rhodamine 6G and Rhodamine 110[11] and by DiLazzaro et al. for a variety of xanthene and pyronene dyes at silica surfaces.[17] A molecular orientation with the z'–x' plane perpendicular to the surface and $\phi \neq 0$ suggests that the methylene blue molecule is perhaps attached to the surface via one of the dimethylamino groups (see Figure 7). A third possibility for the molecular orientation calculation is if α is random. In this case an angle ϕ of 29° yields the appropriate ratio of I_2 and I_3. These two calculations imply that the SHG data can be described by a monolayer of chemisorbed methylene blue with their z' axes slightly tilted off the surface normal by 20–30°; however, the molecules are not necessarily oriented with *all* of their y' axes parallel to the surface.

An examination of the calculated intensities in Table I reveals that although the ratio of I_2 and I_3 can be fit by considering only the contribution of $\beta_{z'x'x'}$ to the nonlinear susceptibility of the

TABLE V: Average Molecular Angle of Methylene Blue as a Function of Surface Coverage

surface charge density, $\mu C/cm^2$	ϕ ($\alpha = 0°$)[b]	ϕ (α random)[b]
32 ± 3	24	35
28	26	38
24	28	41
18	32	48
16	34	52
11	37	58

[a] Determined electrochemically. 32 $\mu C/cm^2$ corresponded to the maximum surface concentration of methylene blue observed. [b] The molecular angle with respect to the surface normal calculated from the four SHG polarization measurements ($I_1 - I_4$) using a $\beta_{x'x'z'}/\beta_{z'x'x'}$ ratio of −0.3. Angles are accurate to approximately 10%.

surface; the calculated values of the SHG intensities I_1 and I_4 do not match the experimental data very well. A better fit to the set of four experimental data points can be obtained if the tensor element $\beta_{x'x'z'}$ is allowed to be nonzero. Figure 10 plots the SHG intensity ratio I_1/I_3 along with the average molecular angle ϕ as a function of the ratio of $\beta_{x'x'z'}$ to $\beta_{z'x'x'}$. At a ratio of −0.3 the calculated SHG intensities (listed in column B of Table I) provide a better match to the experimental data and the molecular angle ϕ changes to 24° (assuming $\alpha = 0°$). Figure 10 also shows that a better fit to the SHG intensities for the full monolayer can also be obtained if the ratio of $\beta_{x'x'z'}$ to $\beta_{z'x'x'}$ is set to 0.4; however, a ratio of −0.3 resulted in the better fit for all methylene blue surface coverages. Table V lists the molecular angle ϕ calculated at various methylene blue surface charge densities by using this ratio. For both the cases of $\alpha = 0°$ and α random the molecular angle ϕ increases as the surface coverage decreases. The true orientational distribution function for α probably lies between these two extreme cases. The changes in molecular orientation with methylene blue surface concentration agree with the nonquadratic behavior of the SHG signal as a function of surface charge density (Figure 6).

Conclusions

In summary, this paper reports the extension of surface SHG–electrochemical studies to the observation of resonant molecular SHG from methylene blue molecules adsorbed onto sulfur-mod-ified polycrystalline platinum electrodes. At an incident angle of 40.5° the doubly resonant molecular SHG signal from the methylene blue monolayer dominates the nonlinear optical response of the interface, and the potential dependence of the doubly resonant SHG signal from both s-polarized and p-polarized light matches that expected during the electrochemical reduction and reoxidation of the chemisorbed methylene blue. The polarization dependence of the SHG signal yields an average molecular orientation for a full monolayer of chemisorbed methylene blue which has the z' axis tilted 24–35° relative to the surface normal and the x' axis out of the plane of the surface. The tilt of the z' axis increases as the surface coverage of methylene blue is decreased. This molecular orientation suggests that bonding to the sulfur-modified platinum surface via one or both of the dimethylamino groups of the methylene blue is as important as the sulfur–sulfur interaction. It is noted that a proper calculation of the average molecular orientation must include the complex Fresnel coefficients for the metal–electrolyte interface at the fundamental and second harmonic wavelengths and a full accounting of the various molecular nonlinear polarizability tensor elements.

In this paper we have shown that by using the resonant molecular SHG signal one can significantly enhance the specificity of SHG as a probe of electrochemical interfaces. For example, in the experiments reported here we are able to study methylene blue, which is in resonance with both the fundamental light at 585 nm and the second harmonic light at 292.5 nm, in the presence of a complete monolayer of chemisorbed sulfur. We also note that the use of SHG as an optical probe in these experiments eliminates the problem of separating the signal contribution from methylene blue molecules in solution, a problem with which any measurements utilizing linear spectroscopies (e.g., fluorescence) would have great difficulty. These experiments represent an initial, well-defined electrochemical system for which detailed molecular orientation information can be obtained in situ by the polarization dependence of the resonant SHG signal. Our future studies will be directed toward the demonstration of molecular orientation measurements at other well-defined electrochemical interfaces.

Registry No. S, 7704-34-9; Pt, 7440-06-4; methylene blue, 61-73-4.

Stabilities and Structures of $C_6F_6^-(C_6F_6)$ and $C_6F_6^+(C_6F_6)$

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The equilibria of clustering reactions $C_6F_6^+ + C_6F_6 = C_6F_6^+(C_6F_6)$ were studied with a pulsed electron beam high-pressure mass spectrometer. Thermochemical stabilities of the clusters $C_6F_6^-(C_6F_6)$ and $C_6F_6^+(C_6F_6)$ were determined. It was found that the bond energy of $C_6F_6^-(C_6F_6)$ is larger than that of $C_6F_6^+(C_6F_6)$. While $C_6F_6^+(C_6F_6)$ has the site-to-site type geometry, $C_6F_6^-(C_6F_6)$ has a stack form according to the ab initio MO calculation.

Introduction

Hexafluorobenzene (C_6F_6) is a characteristic multipolar molecule. It has large quadrupole moments[1] (Q_{xx}, Q_{yy}, and Q_{zz} are −8.6 × 10^{-26}–8.6 × 10^{-26} and 17.2 × 10^{-26} cgs esu, respectively)

and forms fairly strong bonds with ions. The fluoride ion was found to be captured as a substituent on the ring of C_6F_6 leading to the covalent tetrahedral structure.[2] Contrary to the covalent bond formation in the cluster $F^-\cdots C_6F_6$, the bonds of $X^-\cdots C_6F_6$ for X = Cl, Br, and I are found to be largely electrostatic.[3] Ab

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