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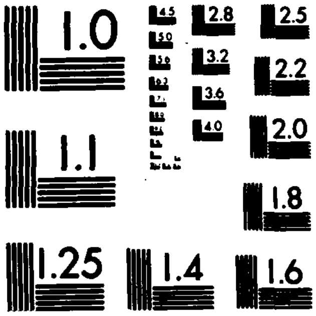

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Technical Report No. 3

THE POTENTIAL DEPENDENCE OF SURFACE PLASMON-ENHANCED SECOND HARMONIC GENERATION AT THIN FILM SILVER ELECTRODES

by

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Chemistry

Research Report

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ABSTRACT: The intensity of second harmonic light generated from plasmon surface polaritons at thin film silver electrodes in contact with an aqueous electrolyte exhibits a strong dependence on electrode potential for a variety of electrochemical systems. The surface plasmons enhance the electromagnetic field at the surface, thereby greatly increasing the second harmonic intensity at the interface. We have measured the potential dependence of surface plasmon-enhanced second harmonic generation at a silver electrode for aqueous solutions of sodium perchlorate, sodium thiocyanate, urea (a strong adsorbate), and for a buffered solution of lead acetate in the underpotential deposition region where a monolayer of lead is deposited onto the silver. The results can be interpreted by a simple theory relating the second harmonic signal to the static electric field at the surface; to first order this field is proportional to the excess charge density on the metal.

I. INTRODUCTION

Electric dipole allowed second harmonic generation (SHG) requires a noncentrosymmetric system. It was recognized early on by Bloembergen *et al.*[1] that this symmetry breaking occurred at the interface of two centrosymmetric media, such as silver and air. They measured the polarization and angular characteristics of the SHG from a variety of materials, including silver. In a subsequent study, Wang[2] noted that the SHG from a metal-liquid interface showed an enhancement which was dependent upon the liquid, and he concluded that the double layer of charge at the interface gave an additional, if not overwhelming, contribution to the second harmonic signal. Indeed, an earlier study of Bloembergen *et al.* showed that the potential dependence of the SHG at a silver electrode in a 0.1M KCl solution exhibited a strong minimum.[3] More recently, Shen *et al.*[4] repeated Bloembergen's experiment on a flat surface, and employed the sensitivity of the SHG signal to surfaces to examine the electromagnetic field enhancement at a number of rough surfaces, including some electrochemical systems. However, several complications arise when surface roughness is employed to enhance the fields at an electrode. In particular, recent underpotential deposition experiments[5] indicate that the surface-enhanced Raman scattering (SERS) which occurs at electrochemically roughened surfaces is due only to a small fraction (circa 0.3%) of the molecules on the surface. One would like a technique which samples the entire surface of the electrode. In addition, Murphy *et al.*[6] noted that even moderate optical energy densities during SHG can modify the surface topology of electrochemically roughened surfaces.

By using plasmon surface polaritons (PSPs) at optically flat surfaces we can obtain controlled field enhancements over the entire surface without the complications of surface roughness. The PSPs are the localized electromagnetic waves propagating along the surface which can be created on a thin silver film by the technique of attenuated total reflection (ATR).[7] Since the PSP is localized at the silver-solution interface, we are assured that we are only measuring surface effects. The PSPs on a silver surface increase the field intensity roughly by a factor of 100, greatly enhancing the signal from nonlinear processes such as second harmonic generation. In fact, surface plasmons have been used previously by several groups to enhance the SHG from thin silver films.[8-11]

Using this ATR technique, we have measured the potential dependence of the SHG from silver electrodes in a number of electrochemical environments: in the presence of a nonspecifically adsorbing electrolyte ($NaClO_4$), in the presence of an adsorbed organic material (urea), in the presence of a monolayer of underpotential deposited lead, and in the presence of specifically adsorbed ions (thiocyanate). The experiments can be interpreted by relating the SHG intensity to the square of the d.c. electric field at the silver surface which is due to the excess charge on the electrode. The direct measurement of the electric field provides heretofore unobtainable information about the electrified metal-solution interface; this paper details one in a number of experiments which we are evaluating as methods of probing the electrochemical systems.[12]

II. THEORY

A. Angular Dependence of the SHG Signal

Figure 1 shows schematically how the Kretchmann configuration[13] of the ATR method is used to excite a PSP wave along the metal-solution interface. The wave vector of the PSP, k_x, is given for a particular frequency by the "upper branch" of the dispersion curves for a three layer dielectric/metal/dielectric system represented by Eq. (1):[14]

$$\left(1 + \frac{\nu_1\epsilon_2}{\nu_2\epsilon_1}\right)\left(1 + \frac{\nu_2\epsilon_3}{\nu_3\epsilon_2}\right) + \exp(-2\nu_2 d)\left(1 - \frac{\nu_1\epsilon_2}{\nu_2\epsilon_1}\right)\left(1 - \frac{\nu_2\epsilon_3}{\nu_3\epsilon_2}\right) = 0 \qquad (1)$$

where

$$\nu_i^2 = k_x^2 - \epsilon_i\omega^2/c^2 \qquad i = 1, 2, 3$$

and d is the thickness of the silver film. This wave vector, k_x, in turn corresponds to a particular incident angle, θ_ω

$$k_x = n_1(\omega)\ \frac{\omega}{c}\ \sin\theta_\omega\ . \qquad (2)$$

Using the tabulated complex dielectric constant values[15] for silver, we calculated θ_ω to be 54.9° for our system (Schott glass SF5: n=1.65 at 1060 nm, silver, water: n=1.33) and measured the plasmon angle at 55.2±0.5°. At the low laser powers used here, the second harmonic generation was observed only when the incident laser light excited a plasmon surface polariton at 1060 nm.

Since the second harmonic generation is a coherent process involving three waves it requires the conservation of the momenta; in this particular case of surface interaction the condition is promptly satisfied by equating the x-components of the two incoming wave vectors with that of the outgoing second harmonic. Mathematically, this is expressed as:

$$n_1(\omega) = n_1(2\omega)\ \sin\theta_{2\omega}/\sin\theta_\omega \qquad (3)$$

which is just the usual phase matching relation for nonlinear optical processes. From this expression we calculate (and also observe) an output angle $\theta_{2\omega}$ of 54°. A pictorial representation of the phase/surface plasmon-matching of the wave vectors is shown in Fig. 2. Note that the second harmonic wave vector is different than that required by the dispersion formula of Eq. (1), from which we calculate a surface plasmon angle of 58.6°. Thus, the outgoing second harmonic beam cannot avail itself of the enhancement from the plasmon at 532 nm. The wave vector mismatch of the SHG and the plasmon at 2ω can be rectified by depositing the silver film onto a grating rather than a flat surface. By choosing a grating spacing $q=k_x(2\omega)-2k_x(\omega)$, one should be able to match the plasmon dispersion curve, creating a surface plasmon at the second harmonic frequency as well as the fundamental.

B. SHG from an Electrified Interface

The second harmonic signal from the interface between two centrosymmetric media can be expressed in terms of a nonlinear polarization $\underset{\sim}{P}_0^{\text{nls}}(2\omega)$:[1,4]

$$\underset{\sim}{P}_0^{\text{nls}}(2\omega) = \alpha\underset{\sim}{E}(\omega) \times \underset{\sim}{H}(\omega) + \beta\underset{\sim}{E}(\omega)(\underset{\sim}{\nabla}\cdot\underset{\sim}{E}(\omega)) . \tag{4}$$

This nonlinear polarization leads to an effective $\chi^{(2)}$ for the surface. For an absorbing medium, $\chi^{(2)}$ can be complex. At an electrode, there is an additional signal due to the third order hyperpolarizability:[3]

$$\underset{\sim}{P}_1^{\text{nls}}(2\omega) = \gamma\underset{\sim}{E}_{dc}\,|\underset{\sim}{E}(\omega)|^2 + \gamma'\underset{\sim}{E}(\omega)(\underset{\sim}{E}_{dc}\cdot\underset{\sim}{E}(\omega)) \tag{5}$$

where E_{dc} is the static electric field at the surface. Similar electric field effects have been observed in crystals of calcite.[16] The SHG signal, $I_{2\omega}(E_{dc})$, is proportional to the square of the total nonlinear polarization:

$$I_{2\omega}(E_{dc}) \propto a + b^2(E_{dc} - c)^2 \tag{6}$$

where the constants a, b, and c are given by $|\text{Im}P_0|^2$, $(\gamma+\gamma')|E(\omega)|^2$, and $\text{Re}\,P_0/b$ respectively (we have assumed γ, γ' real). At the surface of a perfect conductor, Gauss' law requires that the electric field (which must be normal to the surface) is proportional to the surface charge density σ. Thus the SHG signal can be expressed as a function of the excess charge on the electrode:

$$I_{2\omega}(\sigma) = a + b^2(4\pi\sigma - c)^2 . \tag{7}$$

Equation (7) suggests that the SHG signal should be related to the square of the charge density, and reaching a minimum at a charge density of $c/4\pi$. As a first approximation we will assume that the constants a, b, and c are independent of electrode potential and solution composition.

III. EXPERIMENTAL CONSIDERATIONS

The experimental arrangement is shown in Fig. 1. The fundamental (1060 nm) of a Nd:YAG laser is directed onto the sample, and the second harmonic (532 nm) is detected with an RCA C31034 photomultiplier tube. The laser is Q-switched at a repetition rate of 2 Hz yielding 15 nsec pulses of approximately 2 millijoules in energy. Since the beam is not focussed on the sample, this gives an energy density of approximately 2 mJ/cm^2 (this in comparison to the 470 mJ/cm^2 pulses of Murphy *et al.*). The SHG signal from the photomultiplier tube is accumulated by a Princeton Applied Research (PAR) Model 162 boxcar equipped with a Model 165 averaging unit.

The sample cell, depicted in Fig. 3, consists of a hemicylindrical prism of Schott SF5 glass in contact with a small volume of electrolyte. A thin film (45 nm as measured by a quartz microbalance) of silver is vapor-deposited onto the back side of the prism and serves as the working electrode in a three electrode electrochemical cell controlled by a PAR 173 potentiostat. A platinum wire counter electrode and a Ag/AgCl reference electrode were employed. All potentials noted here are relative to Ag/AgCl. All solutions were made from reagent grade chemicals and de-ionized water. The solutions were bubbled with dry nitrogen prior to injection into the sealed electrochemical cell. The entire sample cell was then mounted on a double staged, ganged rotary table which allowed independent selection of the incident laser angle (θ_ω) and the monitored output angle ($\theta_{2\omega}$). This arrangement facilitated the measurement of the angular dependence of the second harmonic signal. However, for the determination of the second harmonic-potential curves all slits were removed to insure that the variation of the signal with potential was not due to surface plasmon shifts.

IV. RESULTS AND DISCUSSION

The potential dependence of the second harmonic signal at a thin silver film in contact with a 0.1M $NaClO_4$ solution is plotted in Fig. 4. A similar curve was obtained from a 0.01M $NaClO_4$ solution. In both cases, the second harmonic signal reaches a minimum at -750 mV. Equation (7) predicts that the second harmonic signal should reach a minimum at a potential slightly shifted from the potential of zero charge (pzc). Differential capacitance studies of polycrystalline silver electrodes in $NaClO_4$ solutions have measured an average pzc value of -1020 mV.[17] We therefore observe a shift of ca. +250 mV from the pzc for the second harmonic signal. Not all of this shift is due to the constant c in Eq. (7): the orientation of the water dipoles at the electrode surface should make some contribution to the electric field at the metal, which would lead to an apparent discrepancy between the differential capacitance studies and the SHG results.

What part of the interface is contributing to the signal? The charge at the electrode can be formally divided into three parts: q_m, the excess charge on the metal, and the balancing charges q_i and q_d from the solution layer directly on the electrode (*i.e.*, at the inner Hemoltz plane), and from the diffuse double layer respectively. Miller's rule[18] suggests that the nonlinear coefficients of the silver should dominate those of the solution. In addition, the silver is the only absorbing media present (at this wavelength) so that the shift in the minimum of the second harmonic signal should be due solely to the metal. Sodium perchlorate exhibits virtually no specific ion adsorption, so that q_i is very small. The independence of the signal on solution concentration also suggests that q_d is unimportant for the second harmonic intensity. Thus we conclude that the surface of the metal is where the majority of the second harmonic signal is generated. This was actually tacitly assumed in part II when we stated that a, b, and c in Eq. (7) were independent of solution composition.

To check this hypothesis we added 50 mM of urea to the 0.1M $NaClO_4$ solution. The SHG-potential curve is plotted in Fig. 5. Urea will adsorb to the electrode in the potential region around the pzc, changing the dielectric constant and nonlinear coefficients of the solution layer immediately adjacent to the metal. In addition, the pzc is shifted slightly due to the adsorption of the organic molecules.[19] The SHG-potential curve shows a slight shift in the minimum to more negative potentials, but we observe no dramatic changes in the second harmonic signal due to the presence of the urea. This supports the claim above that the silver is the main agent of the SHG.

Although the addition of urea did not significantly alter the SHG-potential curve, we did observe a dramatic loss of signal upon the deposition of a monolayer of lead onto the surface. The SHG-potential curve for a solution of 0.1M sodium acetate and 5 mM lead acetate is plotted along with the urea data in Fig. 5. No data was taken below -400 mV, the potential at which bulk lead deposition occurs. The underpotential deposition (upd) of a monolayer of lead at ca. -350 mV changes the charge q_m on the electrode,[20] and also changes the nonlinear coefficients involved in Eqs. (4)-(5). The upd experiment strongly supports the idea that the signal arises from the metal surface and not the solution. In addition to the SHG-potential curve, we measured the cyclic voltammogram for the lead upd.

We observed a series of broad overlapping peaks centered at -350 mV. This voltammogram is indicative of a polycrystalline silver surface.[21]

As a final test of the dependence of the SHG on the excess charge q_m, we measured the SHG from a 0.1M sodium thiocyanate solution. Thiocyanate adsorbs tenaciously onto silver electrodes.[22] This specific ion adsorption is thought to strongly shift the pzc towards more negative potentials. Indeed, the SHG-potential curve in Fig. 5 is shifted by -400 mV. Care must be taken in the interpretation of the shift, however. The presence of thiocyanate ions on the electrode even at $q_m = 0$ (superequivalent adsorption) can produce a static electric field at the silver surface, thereby generating second harmonic intensity from the nonlinear polarization in Eq. (5).

V. CONCLUDING REMARKS

We have measured the potential dependence of second harmonic signal generated at thin silver films via surface polaritons in a number of widely varying electrochemical environments. The use of surface plasmons to enhance the electromagnetic field at the surface greatly facilitates the measurement of the second harmonic signal from the interface. The potential dependence of this signal in each electrochemical system can be explained in terms of a straightforward theory relating the SHG to the square of the excess surface charge on the metal. This technique greatly extends our ability to measure the charge at an electrochemical interface, removing all of the limitations and assumptions which arise from the differential capacitance techniques. It should be remembered, however, that the excess charge is being probed only through the associated large static fields. As seen in the case of specific ionic adsorption, the measurement of the electric fields at the metal and within the inner Hemholtz plane can provide new information on the structure of the metal-electrolyte interface. A final point worth mentioning is that the present experiments were carried out at a fixed wavelength, 1060 nm. SHG at wavelengths in resonance with a molecular transition of a component in the solution could provide additional information on electrochemical processes.

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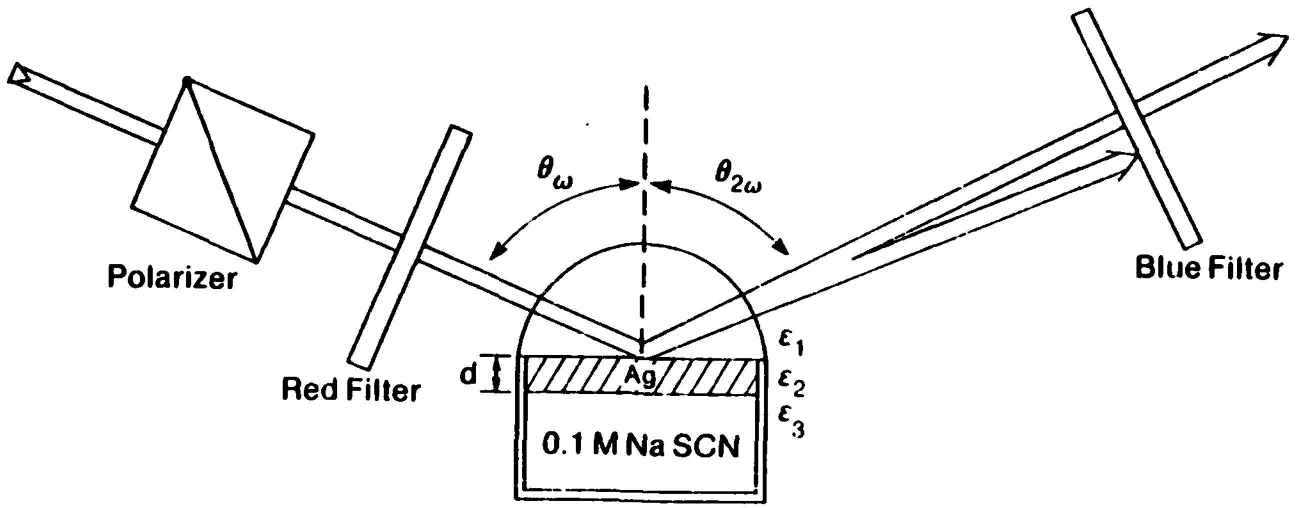

Figure 1. Schematic of the experiment. The incoming light is p-polarized. d is the thickness of the silver film, ε_1-ε_3 are the dielectric constants for the prism, silver, and solution respectively.

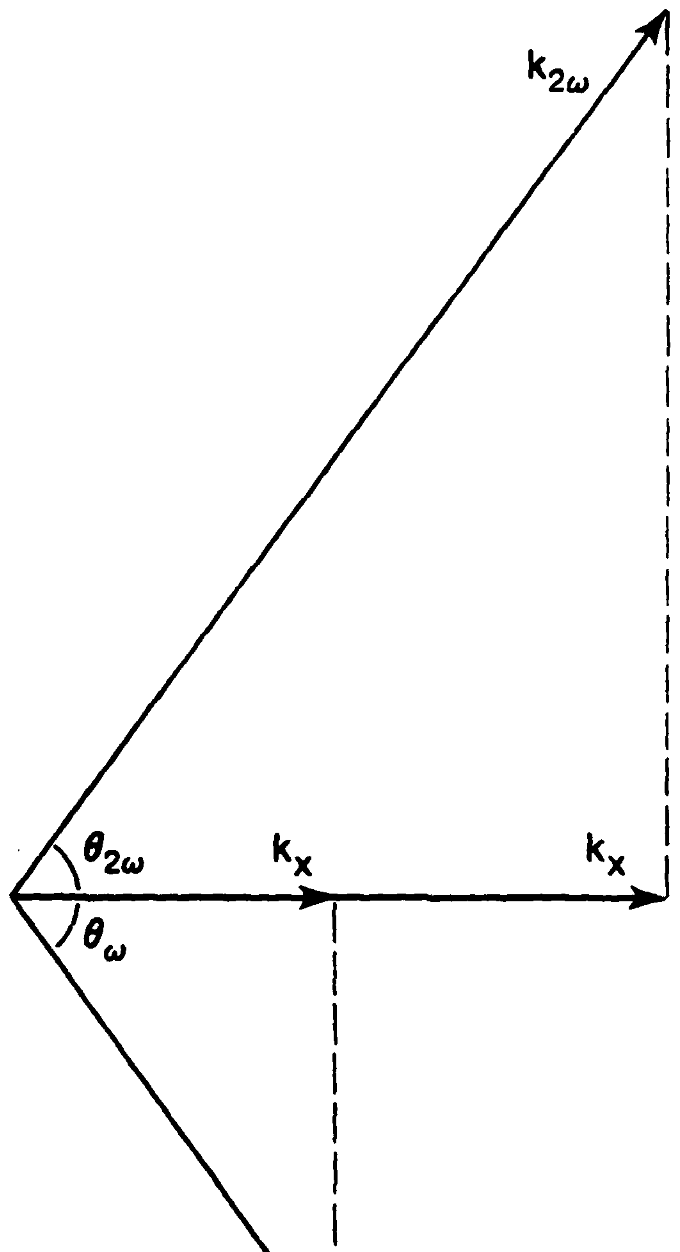

Figure 2. Wave vector diagram for surface plasmon-enhanced SHG. The incident wave vector k_ω excites a PSP with wave vector k_x on the surface. The second harmonic beam is reflected with a wave vector $k_{2\omega}$ such that the component along the surface is matched at $2k_x$.

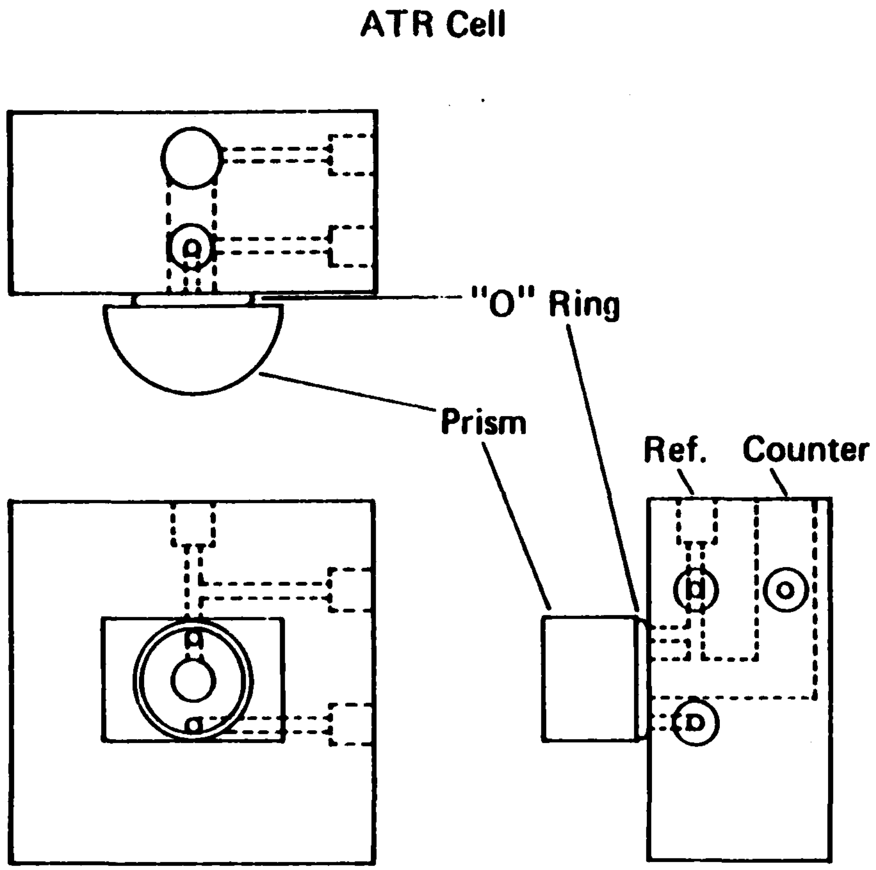

Figure 3. Electrochemical cell. The prism is pressed onto the o-ring which confines the electrolyte; electrical contact is made with the silver film by a piece of copper tape. The silver film is the working electrode in a three electrode system with a Ag/AgCl reference electrode and a platinum wire.

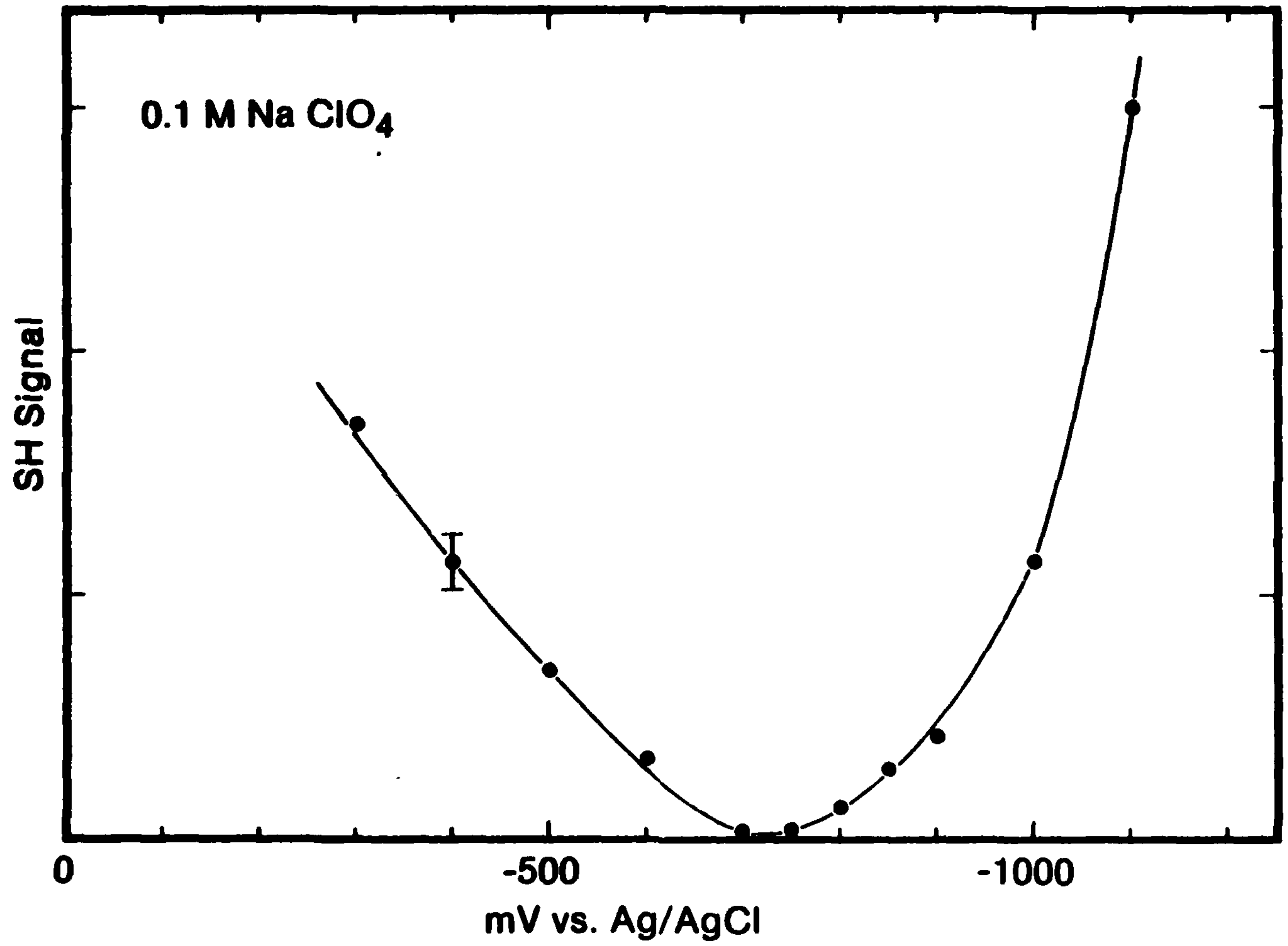

Figure 4. SHG from a polycrystalline silver film (45 nm) in contact with a solution of 0.1M NaClO$_4$ as a function of electrode potential (*versus* Ag/AgCl). The second harmonic intensity at the mininum (approximately -750 mV) is approximately 1/20th the signal at -300 mV.

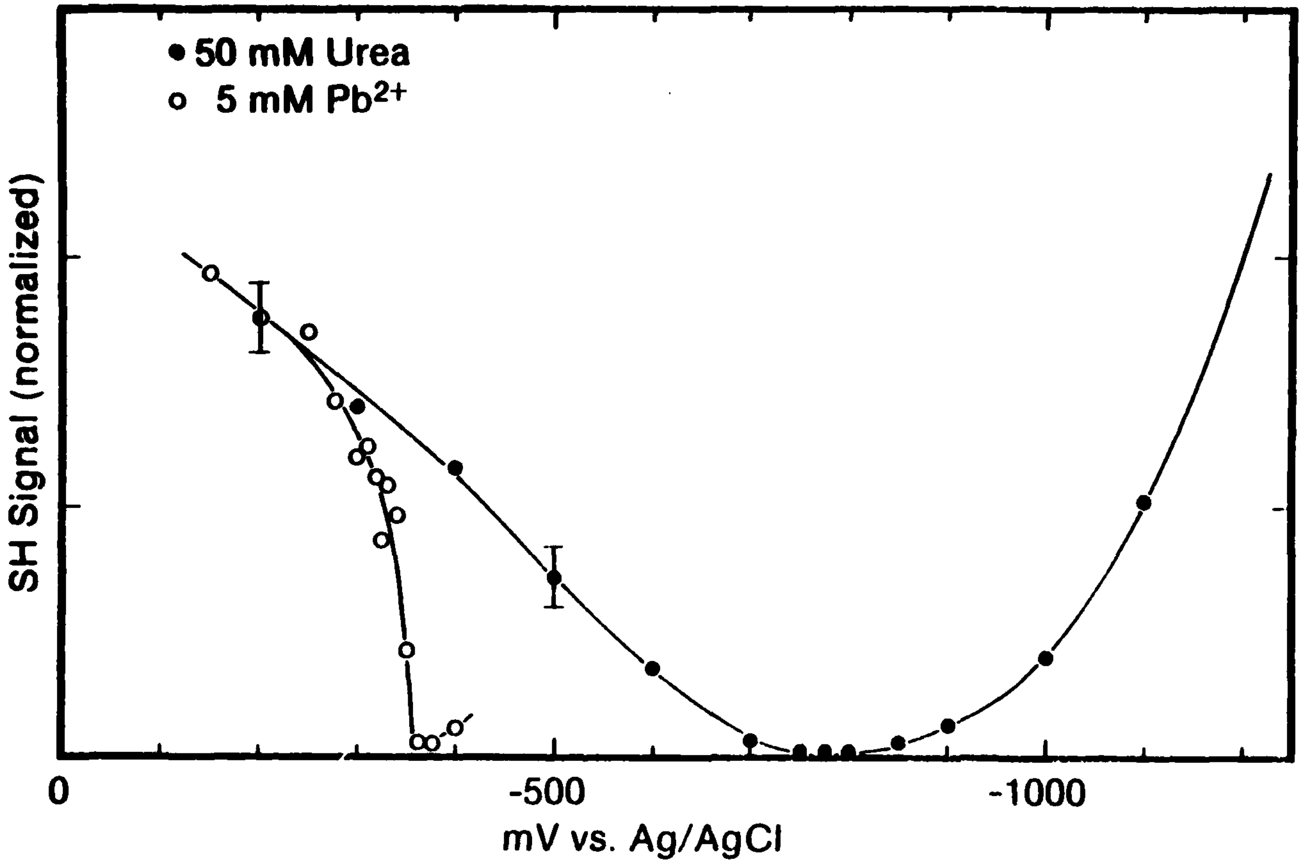

Figure 5. SHG-potential curves for a solution of 50 mM urea+0.1M $NaClO_4$ (solid circles), and for a solution of 0.1M sodium acetate+5 mM lead acetate (open circles) at a polycrystalline silver film.

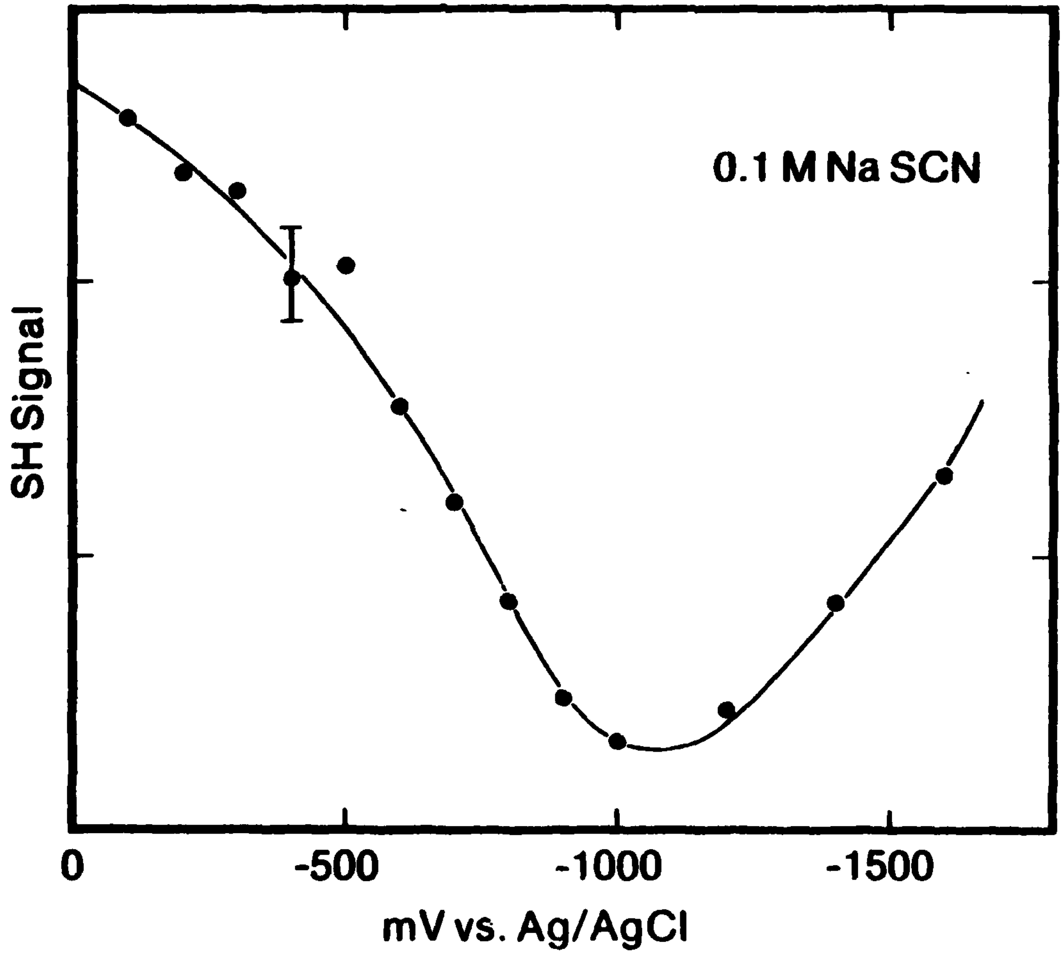

Figure 6. SHG-potential curve for a 0.1M NaSCN solution in contact with a polycrystalline silver film. Potentials are relative to Ag/AgCl.