

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

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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.

### 1. Introduction

Electric-dipole-allowed second-harmonic generation (SHG) requires a non-centrosymmetric 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 Lee et al. [3] showed that the potential dependence of the SHG at a silver electrode in a 0.1 M KCl solution exhibited a strong minimum. 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 non-linear 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 non-specifically adsorbing electrolyte ( $\text{NaClO}_4$ ), 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 dc 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].

## 2. Theory

### 2.1. Angular dependence of the SHG signal

Fig. 1B shows schematically how the Kretschmann 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 [14]:

$$(1 + \nu_1 \epsilon_2 / \nu_2 \epsilon_1)(1 + \nu_2 \epsilon_3 / \nu_3 \epsilon_2) + \exp(-2\nu_2 d) \\ \times (1 - \nu_1 \epsilon_2 / \nu_2 \epsilon_1)(1 - \nu_2 \epsilon_3 / \nu_3 \epsilon_2) = 0, \quad (1)$$

where

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

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

$$k_x = n_1(\omega)(\omega/c) \sin \theta_\omega. \quad (2)$$

Using the tabulated complex dielectric constant values [15] for silver, we calculated  $\theta_\omega$  to be  $54.9^\circ$  for our system (Schott glass SF5:  $n = 1.65$  at 1060 nm, silver, water:  $n = 1.33$ ) and measured the plasmon angle at  $55.2 \pm 0.5^\circ$ . 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

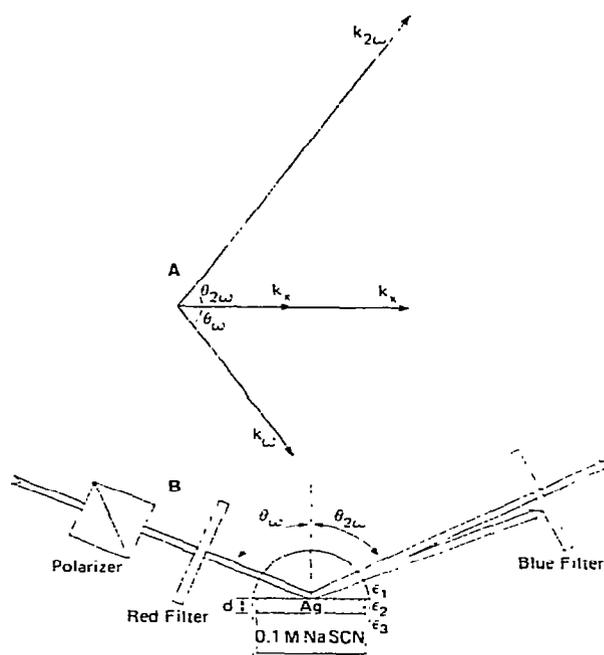


Fig. 1. (A) (top) Wave vector diagram for surface plasmon-enhanced SHG. The incident wave vector  $k_\omega$  excites a PSP with wave vector  $k_x$  on the surface. The second-harmonic beam is reflected with a wave vector  $k_{2\omega}$  such that the component along the surface is matched at  $2k_x$ . (B) (bottom) Schematic of the experiment. The incoming light is p-polarized.  $d$  is the thickness of the silver film,  $\epsilon_1 - \epsilon_3$  are the dielectric constants for the prism, silver, and solution respectively.

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:

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

which is just the usual phase matching relation for non-linear optical processes. From this expression we calculate (and also observe) an output angle  $\theta_{2\omega}$  of  $54^\circ$ . A pictorial representation of the phase/surface plasmon-matching of the wave vectors is shown in fig. 1A. 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  $58.6^\circ$ . 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  $2\omega$  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.

## 2.2. SHG from an electrified interface

The second-harmonic signal from the interface between two centrosymmetric media can be expressed in terms of a non-linear polarization  $P_0^{nls}(2\omega)$  [1,4]:

$$P_0^{nls}(2\omega) = \alpha E(\omega) \times H(\omega) + \beta E(\omega) [\nabla \cdot E(\omega)] \quad (4)$$

This non-linear 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]:

$$P_1^{nls}(2\omega) = \gamma E_{dc} |E(\omega)|^2 + \gamma' E(\omega) [E_{dc} \cdot E(\omega)] \quad (5)$$

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 non-linear polarization:

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

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  $\gamma$ ,  $\gamma'$  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  $\sigma$ . Thus the SHG signal can be expressed as a function of the excess charge on the electrode:

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

Eq. (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.

## 3. Experimental considerations

The experimental arrangement is shown in fig. 1B.

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 ns pulses of approximately 2 mJ in energy. Since the beam is not focused on the sample, this gives an energy density of approximately 2 mJ/cm<sup>2</sup> (this in comparison to the 470 mJ/cm<sup>2</sup> 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. 2, 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 deionized water. The solutions were bubbled with dry nitrogen prior to injection into the sealed electro-

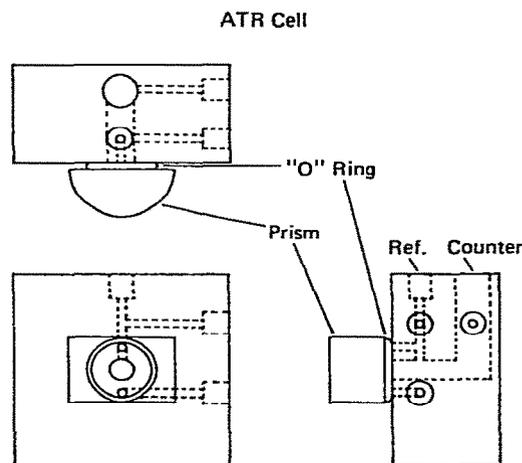


Fig. 2. Electrochemical cell. The prism is pressed onto the O-ring which confines the electrolyte; electrical contact is made with the silver film by a piece of copper tape. The silver film is the working electrode in a three-electrode system with a Ag/AgCl reference electrode and a platinum wire.

chemical cell. The entire sample cell was then mounted on a double staged, ganged rotary table which allowed independent selection of the incident laser angle ( $\theta_{\omega}$ ) 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.

#### 4. Results and discussion

The potential dependence of the second harmonic signal at a thin silver film in contact with a 0.1 M  $\text{NaClO}_4$  solution is plotted in fig. 3. A similar curve was obtained from a 0.01 M  $\text{NaClO}_4$  solution. In both cases, the second-harmonic signal reaches a minimum at  $-750$  mV. Eq. (7) predicts that the second-harmonic signal should reach a minimum at a potential slightly shifted from the potential of zero charge

(pzc). For silver electrodes, the pzc depends on the particular crystal face employed [17]. Although our thin films are polycrystalline, X-ray diffraction measurements indicate that the crystallites are  $\approx 90\%$  oriented with their (111) surface parallel to the prism. This finding is in agreement with the literature on the vacuum deposition of thin silver films onto amorphous substrates [18]. As a first approximation, we will therefore assume that our silver films will behave electrochemically in a manner similar to that of single crystal silver (111) electrodes. Differential capacitance studies of the latter in  $\text{NaClO}_4$  solutions have determined the pzc to be  $-735$  mV [17]. We therefore observe a shift of approximately  $-15$  mV from the pzc for the minimum in 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 surface.

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

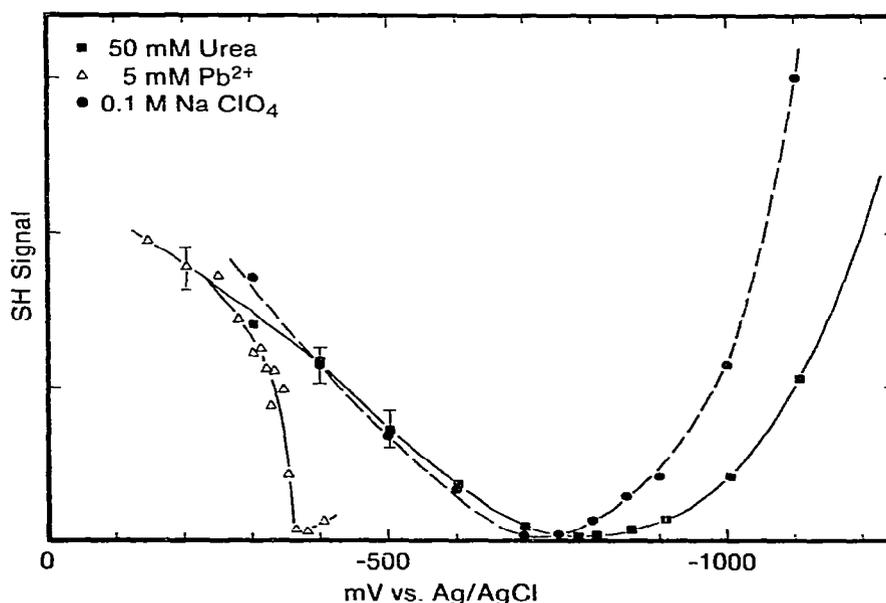


Fig. 3. SHG from a polycrystalline silver film (45 nm) in contact with a solution of 0.1 M  $\text{NaClO}_4$  (solid circles) as a function of electrode potential (versus Ag/AgCl). The second-harmonic intensity at the minimum (approximately  $-750$  mV) is approximately 1/20th the signal at  $-300$  mV. Also shown are SHG-potential curves for a solution of 50 mM urea + 0.1 M  $\text{NaClO}_4$  (solid squares), and for a solution of 0.1 M sodium acetate + 5 mM lead acetate (open triangles) at a polycrystalline silver film.

the metal, and the balancing charges  $q_i$  and  $q_d$  from the solution layer directly on the electrode (i.e. at the inner Helmholtz plane), and from the diffuse double layer respectively. Miller's rule [19] suggests that the non-linear 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 section 2 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 0.1 M NaClO<sub>4</sub> solution. The SHG-potential curve is also plotted in fig. 3. Urea will adsorb to the electrode in the potential region around the pzc, changing the dielectric constant and non-linear 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 [20]. 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 0.1 M sodium acetate and 5 mM lead acetate is plotted along with the urea and perchlorate data in fig. 3. No data were taken below -400 mV, the potential at which bulk lead deposition occurs. The underpotential deposition (upd) of a monolayer of lead at  $\approx -350$  mV changes the charge  $q_m$  on the electrode [21], and also changes the non-linear coefficients involved in eqs. (4) and (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 process. The observed peaks were broader than those measured at a silver

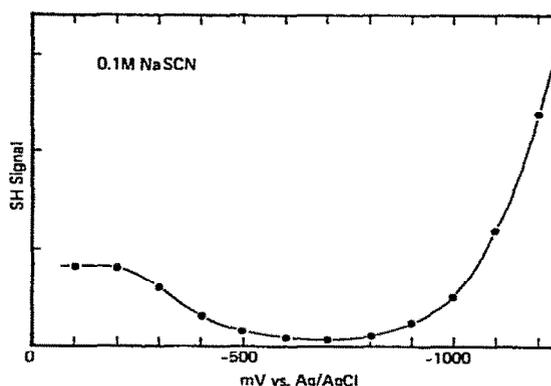


Fig. 4. SHG-potential curve for a 0.1 M NaSCN solution in contact with a polycrystalline silver film. Potentials are relative to Ag/AgCl.

(111) single crystal electrode [22], indicative of the polycrystallinity of our surface.

As a final test of the SHG from an electrified interface, we measured the second-harmonic intensity as a function of electrode potential in a solution of 0.1 M sodium thiocyanate. Thiocyanate adsorbs tenaciously onto silver electrodes [23]. This specific anion adsorption is thought to shift the pzc towards more negative potentials and, more importantly, strongly modify the electric fields at the surface. The SHG-potential curve is plotted in fig. 4; the overall intensity is less than that from the NaClO<sub>4</sub> solutions, and the qualitative shape of the curve is different. The case of specific anionic adsorption serves to remind us that care must be taken when interpreting the SHG in terms of the microscopic properties of the interface. Further studies on thiocyanate and other specifically adsorbed anions are planned.

## 5. 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. The measurement of these fields at the metal and within the inner Helmholtz plane will be to 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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