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Examination of the Surface Second Harmonic Response from Noble Metal Surfaces at Infrared Wavelengths

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Abstract:

Contributing factors to the second harmonic response from Ag(111) and Au(111) surfaces have been examined in the long wavelength limit where nonresonant conditions prevail. The rotational anisotropy in the nonlinear response is found to persist for both metals in the absence of surface resonances and to show convergent behavior in both the relative phase and intensity as the incident energy is lowered from resonant to nonresonant conditions. The phase difference between the in-plane and out-of-plane response in the long wavelength limit can be described by linear Fresnel theory. Whereas the tensor elements corresponding to the out-of-plane response are found to dominate, the in-plane contributions are found to be non-negligible.

I. INTRODUCTION

The rotational anisotropy in the reflected second harmonic (SH) response from crystalline metal surfaces has been the focus of an increasing number of surface science and electrochemistry studies in recent years.[1-5] This rotational anisotropy has been

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exploited as a means of determining the structural symmetry and electronic properties of buried interfacial regions. Although a number of applications to surface problems have been realized, fundamental questions remain regarding the factors that contribute to the anisotropic response. In previous experimental studies of the observed anisotropy from Al(111)[6] and Cu(111)[7], surface resonances have been invoked as the source of the anisotropy. For the former it was presumed that, in the absence of surface resonances, the SH response from this "free electron-like" metal would be isotropic. For Ag(111), recent studies have shown that even in the absence of surface resonances, rotational anisotropy can be observed on Ag(111).[8] Nearly all theoretical studies of a microscopic nature have ignored the experimentally observed anisotropic behavior from metals. Most of these studies employ a hydrodynamic approach based on a jellium model that does not take into account a structural background (such as lattice potential) which would give rise to the observed anisotropy in the electron motion.

This study examines the source of the anisotropy from noble metal (111) surfaces at the long wavelength limit using the 1530-nm output from an optical parametric oscillator (OPO). The term "long wavelength limit" is defined here to be a frequency region far away from any possible surface or bulk resonances. In previous studies of the SH response primarily from noble metals, the typical excitation wavelengths employed were between 1064 nm (1.17 eV) and 532 nm (2.23 eV) where resonances between the incident and SH fields and surface electronic transitions are likely to occur. Although this is less a factor for Ag(111), since the threshold for interband transitions is relatively high (3.8 eV [9]), for Au(111) and Cu(111) the interband threshold is lower, 2.25 eV[10] and 2.3 eV[9], respectively. Both Ag(111) and Au(111) surfaces are examined in this study and provide an interesting comparison because of the difference in the interband threshold relative to the excitation wavelengths employed. The anisotropy in the SH response at nonresonant frequencies is studied in detail and is compared with similar measurements at resonant frequencies. The magnitude of the perpendicular and parallel contributions to the response are compared with recent calculated values of the related Rudnick and Stern[11, 12] parameters. Absolute intensity SH measurements for several wavelengths are compared with the dielectric properties of the metals and the wavelength dependence of the relative phase of the perpendicular and parallel response is discussed with regard to linear Fresnel theory.

The experiments are conducted in an electrochemical cell where the dc field at the surface can readily be varied to monitor the surface sensitivity of the SH response and any possible trace contaminants in the system. In the electrochemical environment, the SH response from these two metals in solution biased at the potential of zero charge (PZC) is found to be identical to the response for these metals in UHV.[13, 14] In contrast, copper electrodes show a very different response in solution relative to vacuum[15] due to surface oxide and are thus not examined here.

II. THEORETICAL CONSIDERATIONS

Several theoretical models to be used in the discussion are described below. When an electromagnetic field of light interacts with a medium, a polarization in the metal is induced by motion of the electrons. This interaction between the fields and the medium and the subsequent optical properties are governed by Maxwell's equations.[16] Under the electric dipole approximation, an SH response will result where the medium is noncentrosymmetric. Consequently, the SH response vanishes in the bulk of the centrosymmetric media and is allowed only at the interface. The surface second harmonic polarization is expressed as

$$P_i(2\omega) = \chi^{(2)}_{ijk} E_j(\omega)\, E_k(\omega) \qquad (1)$$

where $\chi^{(2)}$ is the second order susceptibility tensor. Several models describing the surface SH response from a metal surface have been proposed. When the driving fields are evaluated inside the metal and the SH field is calculated from an infinitesimal nonlinear polarization sheet which lies just above the metal surface, the reflected SH intensity is then expressed as [17]

$$I(2\omega) = \frac{32\pi^3\omega^2 \sec^2(\theta_{2\omega})}{c^3\varepsilon(\omega)\sqrt{\varepsilon(2\omega)}} \left| e^{2\omega} \cdot \chi^{(2)}_{s,eff} : e^{\omega} e^{\omega} \right|^2 I^2(\omega) \tag{2}$$

where the $\theta_{2\omega}$ is the reflected angle at the 2ω and ε is the linear dielectric constant of the medium through which the incident and reflected beams propagate. The e^{ω} and $e^{2\omega}$ are the Fresnel vectors for the field at the fundamental and SH frequencies, respectively. These Fresnel vectors play an important role in the SH radiation efficiency from a metal. They contain the local correction factor for the input and SH fields as well as the change in phase of the fields that occurs in passing from one medium to another medium.

Since the single crystal surfaces used in these experiments are cubic media, the symmetry of the crystals also needs to be considered. In the phenomenological treatment of the SH intensity as a function of an azimuthal angle, a crystalline (111) surface of C_{3v} symmetry gives the following angular dependence for the combinations of incident and SH polarizations used in these studies. [18]

$$\begin{aligned} I_{p/p}(2\omega) \ \alpha \ \omega^2 \,|\, (F_z f_z f_z \chi_{zzz} + F_z f_x f_x \chi_{zxx} + F_x f_z f_x \chi_{xzx}) \\ + F_x f_x f_x \chi_{xxx} \cos(3\phi) \,|^2\, I^2(\omega) \end{aligned} \tag{3}$$

$$I_{s/p}(2\omega) \ \alpha \ \omega^2 \,|\, F_z f_y f_y \chi_{zyy} + F_x f_y f_y \chi_{xyy} \cos(3\phi) \,|^2\, I^2(\omega) \tag{4}$$

$$I_{m/s}(2\omega) \ \alpha \ \omega^2 \,|\, F_y f_z f_y \chi_{yzy} + F_y f_x f_y \chi_{yxy} \cos(3\phi) \,|^2\, I^2(\omega) \tag{5}$$

The input/output polarizations are indicated by p, s, and m (mixed) where m denotes equal s- and p-polarized fields. The subscript z is the direction of normal to the surface in the (x,y,z) coordinate system where the x direction lies along the $[2\bar{1}\bar{1}]$ crystallographic direction. For C_{3v} symmetry, the second order susceptibility tensor elements are related as $\chi_{xxx}=-\chi_{xyy}=-\chi_{yxy}$, $\chi_{zxx}=\chi_{zyy}$, and $\chi_{xzx}=\chi_{yzy}$. The input (f_i) and SH output (F_i) Fresnel coefficients are derived based on the linear Fresnel theory and the model of Mizrahi and Sipe,[17] which calculates the surface SH intensity. The Fresnel transmission coefficients are used alone for the fundamental fields to describe the fields at the interface. However, two contributions to the SH output field are considered, a modified Fresnel coefficient is used for the SH fields. The detail of the description can be referred to somewhere else.[17] Previous experiments for these metals have shown that the higher order bulk susceptibility is negligible under nonresonant conditions[19] and is not considered here.

Many of the experiments to be discussed pertain to p-input and p-output polarizations (Eq. 3) and will be discussed in terms of a more simplified equation

$$I_{p/p}(2\omega)\ \alpha\ |\, a^{(\infty)} + c^{(3)} \cos 3\phi\, |^2\, I^2(\omega) \qquad (6)$$

where $a^{(\infty)}$ and $c^{(3)}$ are referred to as the isotropic and anisotropic coefficients, respectively. The observed rotational anisotropy, described by the $c^{(3)}$ arises from the in-plane polarization alone, whereas $a^{(\infty)}$ contains the isotropic surface tensor elements responsible for either the in-plane or out-of-plane polarization. The best fits of the data to Eq. (6) yield the ratio of $a^{(\infty)}/c^{(3)}$. Since both susceptibility and Fresnel factors for metal can be complex, this ratio has magnitude as well as phase. The measured phase angle in the ratio represents the phase difference between the $a^{(\infty)}$ and $c^{(3)}$.

In addition to this phenomenological treatment of the SH intensity of a macroscopic nature, theoretical calculations of the SH intensity from a metal based on the jellium model have been reported. In this microscopic approach, the hydrodynamic model has been most frequently used.[11, 20-23] This approach treats the conduction electrons at the surface as being free electron-like with a background of positive ionic charge. The positively charged ion background is considered uniform and thus the ground state electron density profile is translationally invariant in the x-y plane. The electron density varies spatially in the direction perpendicular to the surface and extends into the vacuum region. In these calculations, the source of the induced nonlinear polarization of a metal is the motion of the conduction electrons of the metal when the metal reacts to the incident field. The induced SH current at the surface is then calculated. Rudnick and Stern[11, 12] were the first to use such an approach and they set the stage for the future studies in this area by introducing two parameters to characterize the SH response, a(ω) and b(ω), which represent the integrated normal and parallel SH currents, respectively. Since then, much effort has gone into obtaining an accurate value of a(ω) via different approaches. The term a(ω) is taken as frequency dependent and very sensitive to the surface potential and the electron density profile whereas the b(ω) has been assumed dispersionless. Liebsch has performed the most thorough calculation of a(ω) and has also derived expressions for the SH efficiency from a metal with the time-dependent local density function approach under two different polarization combinations.[24]

How this theoretical approach can be correlated to our experimental results is described below. According to the Rudnick and Stern model,[11, 12] a simple expression of the SH polarization with p-polarized incident light can be written as

$$P(2\omega) \;\alpha\; [\; a(\omega)E_{\perp}E_{\perp}F_{a} + b(\omega)E_{\parallel}E_{\perp}F_{b} + F_{d}d(\omega)\,(\mathbf{E}\cdot\mathbf{E}) \;] \tag{7}$$

where the first two terms are surface contributions and the last term of the equation originates from the bulk. The first two terms of the equation correspond to the respective

χ_{zzz} and χ_{xzx} tensors in the phenomenological expression shown in Eq. (3). The relationship between the a(ω) and the SH polarization is defined as[25]

$$\int dzP_2(z,\omega)=\frac{a(\omega)n_b e^3}{4\omega^4 m_e^2}E_iE_i \qquad (8)$$

where n_b is bulk electronic density of the metal, and m_e is the free electron mass. By comparing Eq. (5) for the SH integrated polarization with the Eq. (1), the relation between χ_{zzz} and a(ω) can be extracted where

$$\chi_{zzz}=\frac{a(\omega)n_b e^3}{4\omega^4 m_e^2} \qquad (9)$$

Following the same procedure, χ_{xzx} and b(ω) are related by

$$\chi_{xzx}=\frac{b(\omega)n_b e^3}{2\omega^4 m_e^2} \qquad (10)$$

III. PROCEDURE

The fundamental and harmonic light from the Nd:YAG laser operating at 10 Hz and with 13 nsec pulses has been employed directly for the SH experiments as well as to pump an optical parametric oscillator that generates the 1530 nm laser light used in the long wavelength SHG measurements. The laser light impinges on the working electrode in the electrochemical cell at 31° from the normal of the electrode surface. A Fresnel rhomb is used to rotate the polarization of the laser light. The beam is collimated and reduced to a beam size ~ 2-mm in diameter. The typical power used in the experiment is about 3 mJ/pulse. The reflected SH signal is separated from the fundamental light with a set of infrared filters before the SH signal passes through a collection lens and a Glan-Taylor polarized analyzer that selects the desired output polarization. A further separation of the SH signal from the remaining fundamental light is achieved with a single-pass monochromator.

Both 99.999% pure Ag(111) and Au(111) crystals are aligned to within 1° of the (111) plane by Laue X-ray back diffraction. Subsequently, the crystals are electrochemically polished. For the Ag(111), the surface is electrochemically polished and is transferred into an electrochemical cell, all procedures conducted under an inert atmosphere to minimize surface oxide formation.[26] For Au electrodes, an additional procedure, bulk cleaning in a UHV chamber, follows the electrochemical polish in order to minimize the diffusion of impurities from the bulk to the surface while the metal is under study. For the long wavelength studies, D_2O is used since H_2O strongly absorbs 1530 nm light. The SH signal from the metal electrode surface in 0.01 M $HClO_4$ at the (PZC) is monitored as the surface is rotated azimuthally by 360° as has been described previously. The PZC for Ag(111) and Au(111) used here are -0.73 V [27] and 0.25 V[28] vs Ag/AgCl, respectively. In addition, Cyclic voltammetry (CV) is used to monitor the cleanness of the surface and the solution. For these studies, the applied potential is always restricted to an ideally polarizable region to avoid disruption of the surface by any faradaic processes.

The surface SH response at each wavelength is calibrated with the SH intensity from a y-cut quartz single crystal.[29] The magnitude of $\chi^{(2)}$ for the quartz crystal is given as 1.9×10^{-9} esu[30] at the excitation wavelength of 1064 nm. In order to calibrate SH intensity from the sample throughout a wide range of excitation wavelengths, Miller's rule is applied to estimate $\chi^{(2)}$. Miller's rule is a reasonable approximation of $\chi^{(2)}$ over the wavelength range of this study since the optical resonances for quartz occur near 6 eV.[9] The modulation of SH intensity from the quartz crystal is collected as the quartz crystal is rotated about the z-axis, which is perpendicular to both the wavevector and polarization vector. These Maker fringes are fitted with a theoretical envelope function and the maximum intensity of the theoretical envelope function is used for the intensity calibration.

IV. RESULTS AND DISCUSSION

Figure 1(a) displays the p-polarized SH response from the Ag(111) electrode surface biased at -0.73 V (PZC) using p-polarized incident light of 1530 nm. A strong anisotropic response is observed and can be fit with Eq. (3) to give $(0.6\pm0.1)e^{i85^\circ\pm4^\circ}$ for the ratio of $a^{(\infty)}/c^{(3)}$. This data can be compared with the 1064-nm results shown in Figure 1(b) where a ratio of $a^{(\infty)}/c^{(3)}$ equal to $0.8\ e^{i86^\circ}$ is obtained as in previous work.[13] The data for the two wavelengths are quite similar although the anisotropic response at the longer wavelength is somewhat stronger. This contradicts any expectation that the rotational anisotropy from Ag metal would disappear, or at least diminish, at this longer wavelength where Ag metal has theoretically been treated as a free electron metal. To be addressed in more detail later, the phase angle of the ratio of $a^{(\infty)}/c^{(3)}$ for both sets of data is approximately $\pi/2$.

The response under resonant conditions where 532-nm excitation wavelength is used is very different from the longer wavelength data as has been published previously[14, 31] and as is shown in Figure 1(c). For this experiment, the SH photon energy of 4.66 eV using 532-nm excitation wavelength is well above the threshold of the interband transition, which for Ag is near 3.8 eV. With 532-nm excitation, the SH rotational anisotropy is also strong but the phase angle is 0 degrees compared to $\pi/2$ in the nonresonant case. This change in phase angle of 0 to $\pi/2$ as the optical resonances are respectively accessed and avoided is a clear indication of the important role that this phase angle measurement can play in identifying electronic resonances and their absence. This change of the phase angle of $a^{(\infty)}/c^{(3)}$ from 0 to $\pi/2$ will be described later in terms of the linear optical properties of the metal.

Figure 2 displays the experimentally measured isotropic and anisotropic SH intensity from the Ag(111) electrode as a function of SH photon energy where the surface is biased at the PZC. The isotropic and anisotropic intensities are represented by the filled circles and open triangles, respectively. A relatively small increase in the SH intensity occurs between 1530 nm (0.81 eV) and 1064 nm (1.17 eV). A much greater increase is observed at 532 nm. This large increase in intensity at shorter wavelengths is expected as the optical fields couple to interband transitions. For illustrative purposes the imaginary part of the linear dielectric constant (Im(ε)), which was determined for Ag from linear reflectance measurements,[32] is superimposed on the SH data in Figure 2. Below the onset of the interband transition near 3.8 eV, the Im(ε) shows a $1/\omega^3$ dependence, which is characteristic of a free electron behavior in the Drude model.[32] The Im(ε) decreases with ω^3 until the onset of the interband transition occurs. The relatively small and nearly constant SH intensities measured at the two infrared wavelengths are consistent with the linear reflectance measurements which indicate that resonance is not a factor here. The enhancement in the SH response from Ag with excitation energy of 2.33 eV (4.66 eV SH photon energy) is consistent with the higher Im(ε).

Figure 3 displays the p-polarized SH rotational anisotropic response from the Au(111) electrode surface biased at the PZC. The same wavelengths and polarization conditions used in the Ag work were used here. Although Au has a similar electronic density to Ag, the band structure is quite different. The onset of the interband transition of Au is about 2 eV, which is much lower than Ag. For all excitation wavelengths, the SH response from the Au(111) surface exhibits strong rotational anisotropy, but the phase angles of $a^{(\infty)}/c^{(3)}$ are distinctly different for all three excitation wavelengths. As with Ag(111) a progressive convergence of the phase angle from 0 to near $\pi/2$ is observed as the excitation energy is decreased from 2.33 eV (532 nm) to 0.81 eV (1530 nm). No evidence of Au(111) reconstruction[33] was observed for these samples nor was it expected since they were not flame annealed.

Figure 4 shows the intensity measurements for the isotropic and anisotropic response from Au(111) at three wavelengths and a plot of the imaginary part of the linear dielectric function for this metal[32] as a function of photon energy. The Im(ε) of Au also exhibits a $1/\omega^3$ dependence in the free electron regime. For 1064-nm excitation wavelength, a sharp increase in the imaginary part of the dielectric function is present. This accounts for the phase angle of 70° rather than $\pi/2$ which was observed for Ag at this wavelength. The intensity measurements (Figure 4) also suggest that optical resonances play a role in the Au(111) response at 1064-nm since the intensity continues to decline with lower excitation energy. With the 1064 nm excitation wavelength, the response from Au is five times that from Ag(111).

The relative contributions from each of the tensor elements at the long wavelength limit have also been studied. For the p-in and p-out experiment, the measured isotropic term contains three surface tensor elements, χ_{zzz}, χ_{zxx}, and χ_{xzx}. Whereas χ_{zxx} and χ_{xzx} involve both perpendicular and parallel fields, the χ_{zzz} only involves the perpendicular field and cannot be independently measured. Using a select combination of input and output polarization corresponding to Eqs. 3-5, the relative importance of these three terms can be determined. The Ag(111) surface will be examined first. The s-in and p-out SH response from Ag(111) in solution for an incident wavelength of 1530 nm is displayed in Figure 5(a) and is fit with Eq. 4. The isotropic response can be extracted by measuring the SHG at $\phi = 30°$. However, for our incident laser power density at this wavelength the signal was too small to detect, leaving the small contribution from the χ_{zyy} (χ_{zxx}) undetermined. The same was true for the mixed-in and s-out experiment where the isotropic response corresponding to χ_{yzy} ($=\chi_{xzx}$) was too small to determine. Since there is clearly an isotropic response from Ag(111) in the p-in and p-out experiment (Figure 1(a)), and the contributions from both χ_{zxx} and χ_{xzx} appear negligible, this might suggest that the primary contributor to the isotropic response is χ_{zzz}.

At the excitation wavelength of 1064 nm, both the isotropic and anisotropic responses are observed in the s-in and p-out experiment, as shown in Figure 5(b). Since the isotropic response is also observed in the mixed-in and s-out experiment at 1064 nm, the contribution from χ_{xzx} can also be obtained at this wavelength. With the three different combinations of input and output polarizations, a_{zzz} can be extracted where a_{ijk} is defined as $|F_i\chi_{ijk}f_jf_k|$. The relative contribution to the SH isotropic response from a_{zzz}, a_{zxx} and a_{xzx} with the excitation wavelength of 1064 nm is determined to be 1.6:1.3:1 with the a_{zzz} term being the largest. When the incident wavelength is decreased to 532 nm, the relative contributions become more equal, as 1.1:1.2:1. When the wavelength dependence of the Fresnel factors are taken into account in the nonresonant region, the ratio of $\chi_{zzz} : \chi_{xzx} : \chi_{zxx}$ is 192:12:1. Thus without the enhancement due the Fresnel factors, the contributions from χ_{xzx} and χ_{zxx} are dwarfed by the contribution from χ_{zzz}. This analysis demonstrates the important role that Fresnel factors play in understanding the SH efficiency. The experimental determination that $|\chi_{zzz}|$ is the dominant contribution is important since most theoretical efforts have focused on calculation of this element. Since the Fresnel coefficients are not significantly different between the 1064-nm and 1530-nm experiments, we conclude that the χ_{zzz} term is also dominant in the isotropic response for the long wavelength experiment.

Table 1 shows the experimentally determined values for the susceptibilities for Ag(111) at the three wavelengths examined. The values for χ_{xxx} are determined from the anisotropic response and are shown to be small but non-negligible for all three wavelengths.

Even though we determine the SH response from Au to be at least 4 times larger than Ag, the isotropic intensities from the s-in and p-out, and mixed-in and s-out experiments with the excitation wavelength of 1530 nm are still too small to be detected. Only the anisotropic intensity is clearly observed, even though the isotropic response from Au(111) is observed under the conditions of p-in and p-out. Thus, the perpendicular component is still the dominant factor in the SH isotropic response from Au metal at longer wavelengths. The experimental ratios of a_{zzz} : a_{zxx} : a_{xzx} for Au are 2:1.4:1 and 0.9:1.6:1 for the incident wavelengths of 1064 nm and 532 nm, respectively. These results are consistent with those from Ag where a_{zzz} decreases as the wavelength decreases. When the Fresnel coefficients are taken into account, χ_{zzz} remains the dominant tensor element for all of the wavelengths examined. The magnitudes of the various tensor elements are shown in Table 2 for Au(111).

The persistence of anisotropy in the SH response from these metals in the long wavelength limit raises questions about the validity of using a hydrodynamic model to calculate the SH efficiency from a metal, since a uniform ionic background is used rather than a structural background (such as a lattice potential) which would give rise to the anisotropies reported here. Second, the hydrodynamic model cannot address the strong in-plane response. Based on symmetry arguments, the in-plane χ_{xxx} is responsible for the SH anisotropic response from metal, and this contribution is induced by the parallel incident field only. In the hydrodynamic model, the electron density varies spatially in the direction normal to the surface but it spreads out uniformly along the x-y plane, resulting in no spatial variation of the incident field parallel to the surface.

The hydrodynamic approach based on the jellium model is too simple to treat rotational anisotropy from a metal. Nevertheless, the model is a reasonable starting point for treating the isotropic response from a metal.[11] Therefore, we compare our results for the nonlinear perpendicular a(ω) and parallel b(ω) currents. Numerous theoretical efforts have been devoted to the calculation of a(ω), whereas b(ω) is always presumed to have a nearly constant value of -1. Only 1064-nm data is appropriate here, since resonances are not considered in the time-dependent local density function calculation. Using the calculated values[24] of a(ω) of -15-3i and b(ω) of -1, the values for χ_{zzz} and χ_{xzx} are estimated to be 3.3×10^{-12} and 0.4×10^{-12} esu, respectively. The experimental value of χ_{zzz} agrees quite well, whereas the theoretical value for χ_{xzx} is too large. The frequency dependence of the anisotropic response due to parallel field can be easily determined by the p-in and p-out experiment since χ_{xxx} is the only surface tensor element contributing to the SH anisotropic response. For Au(111) at 1064 nm, the experimentally determined χ_{zzz} value is much greater than the theoretical value ($3.3\text{x}10^{-12}$ esu) even though the theoretical value for Au is similar to that for Ag since the electronic density and radius r_s of the free electron sphere of both metals are almost the same. The primary difference and the likely reason for disagreement is that resonances are a factor at 1064 nm for Au(111) and such resonance effects are not taken into account in the Fresnel theory.

Petukhov[34] has published a qualitative calculation of quadrupole-allowed (bulk) second-order nonlinear polarizability of noble metals. The calculations only consider the anisotropy of the electron plasma near the Fermi surface without any interband contribution. His calculations also predict a strong anisotropy in the SHG response from noble metals, but the model has its shortcomings. For example the model does not include the surface quadrupole or the surface dipole effect that has been shown in numerous studies to be very important and often dominant over the bulk response under nonresonant conditions. The bulk response is neglected in the long wavelength region, and the calculation cannot account for the anisotropy we observe under nonresonant conditions. We are currently involved in theoretical studies that investigate the source of the anisotropy using a tight-binding model.

Recent studies by Janz et al.[35, 36] of Al single crystal surfaces have suggested that the anisotropy from this crystal is from surface steps and defects and not from the intrinsic electronic structure as suggested in an earlier study.[6] A recent study of Ag(111) stepped surfaces[37] shows that whereas steps can enhance the anisotropic response, all observed features are compatible with the understanding of the anisotropy being due to a global interaction with the whole irradiated surface and not due to specific sites on the surface as postulated by Janz et al.[36] The convergence of the phase angle with wavelength is also difficult to explain solely in terms of surface defects as is the fact that we observe very little variation in the anisotropy for a fixed wavelength for several different Ag(111) samples studied.

The phase angle of $a^{(\infty)}/c^{(3)}$ has been monitored to determine the resonant and nonresonant conditions. In addition, a further examination on the source of this phase angle variation of $a^{(\infty)}/c^{(3)}$ and the measured convergence to $\pi/2$ in the phase angle at the longer wavelengths is explored. Using the Fresnel theory to interpret the change of the phase angle is examined. For the p-in and p-out experiment, the phase angle of $a^{(\infty)}/c^{(3)}$ can be written as

$$\mathrm{Arg}(a^{(\infty)}/c^{(3)}) = \mathrm{Arg}\{\, (F_z\chi_{zzz}f_zf_z + F_z\chi_{zxx}f_xf_x + F_x\chi_{xzx}f_zf_x) / F_x\chi_{xxx}f_xf_x \,\} \quad (11)$$

For the case where the SH isotropic response is dominated by χ_{zzz}, the phase angle of $a^{(\infty)}/c^{(3)}$ under p-in and p-out condition can be rewritten as

$$\mathrm{Arg}(a^{(\infty)}/c^{(3)}) = \mathrm{Arg}(\, F_z\,\chi_{zzz}\,f_zf_z / F_x\,\chi_{xxx}\,f_xf_x\,). \quad (12)$$

In our analysis of contributing factors in Eq. 12, based on the single particle excitation picture,[16] no phase shift would be expected between χ_{zzz} and χ_{xxx} under nonresonant conditions since both terms should be real. The remaining factors are the Fresnel coefficients in each term. The phase difference in (f_zf_z/f_xf_x) will be examined first. Performing the mixed-in and s-out experiment, the phase difference between the out-of-plane and in-plane Fresnel coefficients $(\mathrm{Arg}(f_z/f_x))$ can be determined by measuring the $a^{(\infty)}/c^{(3)}$ ratio. Figure 6 shows the SH anisotropy from the Ag(111) electrode surface at the PZC with an incident wavelength of 1064 nm under the mixed-in and s-out condition where $a^{(\infty)}/c^{(3)}$ is determined to be $0.5e^{i87^\circ \pm 4^\circ}$. The phase angle for Au(111) under the same condition is also found to be near $\pi/2$. Figure 7(a) compares these results with $|\mathrm{Arg}(f_Z/f_X)|$ based on Fresnel theory and shows that at longer wavelengths, the calculated angle is in good agreement with the experiments. With the overall phase shift for the pair of input Fresnel factors taken as π, the remaining factor in the left side of Eq. 12 is the ratio of the SH Fresnel coefficients. Figure 7(b) shows the experimental values for $\mathrm{Arg}(F_Z/F_X)$ as determined by p-in and p-out experiments, and the calculated curve for the wavelength dependence of $|\mathrm{Arg}(F_Z/F_X)|$. The triangles and circles represent the experimental values of the phase angle of Ag and Au, respectively, after the input Fresnel coefficients are taken into account in the p-in and p-out experiments. In the long-wavelength, nonresonant region, the experimental values approach $\pi/2$ and follow the calculated line closely for both Ag and Au suggesting that the Fresnel theory appears quite adequate in describing the variation of the phase angle of $a^{(\infty)}/c^{(3)}$ with wavelength under nonresonant conditions. However, there is a limitation of using the Fresnel theory to describe the change of the phase angle. When the SH photon energy is well above the onset of interband transition, as indicated by the steep rise in the calculated values, the experimental values no longer agree with the theoretical values. In this wavelength region both Fresnel coefficients and susceptibility tensors are complex, which makes quantitative comparison much more difficult. In addition, the dielectric functions used in the Fresnel theory are bulk in nature and, therefore, do not take into account any additional resonances due to surface electronic structure (i. e., eigenstates created by truncation of the bulk lattice). For both Ag(111) and Au(111) there are numerous surface resonances possible in the region near the threshold for interband transitions. For the infrared region studied here the surface electronic structure excludes the possibility of interband or state to band resonances. The nonlinear signal and the corresponding anisotropic response is a manifestation of the collective response of the electrons. Within the nonresonant conditions, the Fresnel theory alone is adequate in explaining the wavelength dependence of the phase angle.

IV. CONCLUSIONS

The SH responses from Ag(111) and Au(111) surfaces have been examined in the long wavelength limit to understand the source of the rotational anisotropy in the nonlinear response and to compare the results under these nonresonant conditions with current theoretical models. A convergence in the phase angle between the in-plane and out-of-plane response is observed as nonresonant conditions are attained. The phase difference in the long wavelength limit can be described by linear Fresnel theory. As resonance factors contribute as a shorter excitation wavelength is employed, the experimental agreement with the Fresnel theory declines. SH intensity measurements correlate well with the linear dielectric functions for these materials with the largest response corresponding to resonance effects and a convergence to a relatively small value at the longer wavelengths where resonances are avoided. The persistence in the anisotropy in the absence of resonance calls into question the validity of viewing the SH response in terms of a jellium model. However the experimental results at the longer wavelengths do show that the out-of-plane response, the focus of most theoretical efforts, is dominant over the in-plane response. Although the in-plane susceptibility (χ_{xxx}) is smaller than the out-of-plane susceptibility (χ_{zzz}), the in-plane contribution is still significant due to the enhancement by the in-plane Fresnel coefficient where the in-plane Fresnel coefficient is greater than the out-of-plane one. The Fresnel coefficients play an important role in the SH radiation efficiency from the metals and the change of the phase angle. The contribution from the in-plane response is non-negligible and frequency dependent, two points that should not be ignored if an accurate theoretical model is desired.

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Figure Captions

Figure 1 SH intensity from Ag(111) electrode surface at the PZC as a function of angle of rotation, under p-polarized fundamental light and p-SH output light condition at the excitation wavelength of (a) 1530 nm, (b) 1064 nm, and (c) 532 nm. The fits of $a^{(\infty)}/c^{(3)}$ are $(0.6\pm0.1)e^{i85^\circ\pm4^\circ}$, $0.8e^{i86^\circ}$ and $1.5e^{i0^\circ}$ respectively.

Figure 2 SH intensity from Ag(111) electrode surface as a function of SH energy. The closed circles represent isotropic intensity and the open triangle represent anisotropic intensity under p-in and p-out condition. The solid line is the imaginary part of the dielectric function of Ag from the linear reflection experiment.[32]

Figure 3 SH intensity from Au(111) electrode surface at the PZC as a function of rotational angle, under p-in and p-out condition at the incident wavelength of (a) 1530 nm, (b) 1064 nm and (c) 532 nm. The fits are $-0.9e^{i82^\circ}$, $-1.1e^{i70^\circ}$ and $0.9e^{i0^\circ}$ respectively.

Figure 4 SH intensity from Au(111) electrode surface at the PZC as a function of SH energy; the closed circles represent isotropic intensity and the open triangle represent anisotropic intensity. The solid line represents the imaginary part of the dielectric function of Au.[32]

Figure 5 p-polarized SH anisotropy from Ag(111) electrode surface with s-polarized incident light of (a) 1530 nm, (b) 1064 nm.

Figure 6 s-polarized SH light from Ag(111) electrode surface with mixed-polarized incident light. of 1064 nm.

Figure 7 (a) the phase difference between the in-plane and out-of-plane for the fundamental fields as function of incident photon energy. (b) the phase difference between in-plane and out-of-plane Fresnel coefficients for the SH fields vs. SH photon energy. The triangles and circles represent the experimental values for the Ag and Au, respectively.

References

1. Richmond, G.L. in *Advances in Electrochemical Science and Engineering* (eds. Gerischer, H. & Tobias, C.W.) (VCH Publishers, 1992).
2. Shen, Y.R. *Nature* **337**, 519 (1989).
3. Richmond, G.L., Robinson, J.M. & Shannon, V.L. *Prog. in Surf. Sci.* **28**, 1 (1988).
4. Hall, R.B., Russell, J.N., Miragliotta, J. & Rabinowitz, P.R. *Chemistry and Physics of Surfaces* (Springer-Verlag, 1990).
5. Heinz, T.F. in *Surface Nonlinear Electromagnetic Phenomena* (eds. Ponath, H. & Stegman, G.I.) (Elsevier, Amsterdam, 1992).
6. Murphy, R., Yeganeh, M., Song, K.J. & Plummer, E.W. *Phys. Rev. Lett.* **63**, 318 (1989).
7. Tom, H.W.K. & Aumiller, G.D. *Phys. Rev. B* **33**, 8818 (1986).
8. Wong, E.K.L., Friedrich, K.A. & Richmond, G.L. *Chem. Phys. Lett.* **195**, 628 (1992).
9. Palik, E.D. *Handbook of Optical Constants of Solids* (Academic Press, Inc., New York, 1985).
10. Chao, F., Costa, M., Lecoeur, J. & Bellier, J. *J. Chem. Phys.* **92**, 734 (1990).
11. Rudnick, J. & Stern, E.A. *Phys. Rev. B* **4**, 4274 (1971).
12. Rudnick, J. & Stern, E.A. in *Polaritons* (eds. Burstein, E. & deMartini, F.) 329 (Pergammon Press, Taormina, Italy, 1972).
13. Bradley, R.A., *et al. Chem. Phys. Lett.* **168**, 468 (1990).
14. Bradley, R.A., Georgiadis, R., Kevan, S.D. & Richmond, G.L. *J. Vac. Sci. Tech. A* **10**, 2996 (1992).
15. Bradley, R.A., Friedrich, K.A., Wong, E.K.L. & Richmond, G.L. *J. Electroanal. Chem.* **309(1-2)**, 319-24 (1991).
16. Shen, Y.R. *The Principles of Nonlinear Optics* (Wiley, New York, 1984).

17. Mizrahi, V. & Sipe, J.E. *J. Opt. Soc. Am. B* **5**, 660 (1988).

18. Tom, H.W.K. *Ph. D Thesis* (University of California, Berkeley, 1984).

19. Koos, D.A., Shannon, V.L. & Richmond, G.L. *Phys. Rev. B* (in press).

20. Corvi, M. & Schaich, W.L. *Phys. Rev. B* **33**, 3688 (1986).

21. Weber, M. & Liebsch, A. *Phys. Rev. B* **35**, 7411 (1987).

22. Liebsch, A. *Phys. Rev. Lett* **61**, 1233 (1988).

23. Chizmeshya, A. & Zaremba, E. *Phys. Rev. B* **37**, 2805 (1988).

24. Liebsch, A. & Schaich, W. *Phys. Rev. B* **40**, 5401 (1989).

25. Schaich, W.L. & Liebsch, A. *Phys. Rev. B* **37**, 6187 (1988).

26. Koos, D.A., Shannon, V.L. & Richmond, G.L. *J. Phys. Chem.* **94**, 2091 (1990).

27. Valette, G. & Hamelin, A. *45* 301 (1973).

28. Kolb, D.M. & Schneider, J. *Electrochim. Acta* **31**, 929 (1986).

29. Jerphagnon, J. & Kurz, S.K. *J. Appl. Phys.* **44**, 1667 (1970).

30. Pressley, R.J. *Handbook of Lasers, Chemical Rubber Co, Cleveland, Ohio* (1971).

31. Bradley, R.A., Georgiadis, R., Kevan, S.D. & Richmond, G.L. *J. Chem. Phys* submitted (1992).

32. Johnson, P.B. & Christy, R.W. *Phys. Rev. B* **6**. 4370 (1972).

33. Friedrich, A., *et al. Chem. Phys. Lett.* **63**, 123 (1989).

34. Petukhov, A.V. *Phys. Rev. B* **42**, 9387 (1990).

35. Janz, S., Bottomley, D.J., van Driel, H.M. & Timsit, R.S. *Phys. Rev. Lett.* **66**, 1201 (1991).

36. Janz, S., Pedersen, K. & Van Driel, H.M. *Phys. Rev. B* **44**, 3943-54 (1991).

37. Friedrich, A. & Richmond G. in preparation.

Table 1. Second Harmonic Nonlinear Susceptibilities for Ag(111)

$\lambda(\mu m)$	$\chi^{(2)}$ $(10^{-14}$ esu)			
	χ_{xxx}	χ_{zxx}	χ_{xzx}	χ_{zzz}
1.53	4.5	-	-	428
1.064	3.7	1.2	14.4	230
0.532	2	0.9	2.1	89

Table 2. Second Harmonic Nonlinear Susceptibilities for Au(111)

$\lambda(\mu m)$	$\chi^{(2)}$ $(10^{-14}$ esu)			
	χ_{xxx}	χ_{zxx}	χ_{xzx}	χ_{zzz}
1.53	9.4	-	-	1500
1.064	12.8	5.4	35	1253
0.532	5.0	1.1	10.3	37