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Optical second-harmonic electroreflectance from Ag(111)

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We have used an electrochemical sample chamber to modulate the surface charge of Ag(111) in spectral measurements (over a range of the incident photon energy from 1.4 to 2.23 eV) of the isotropic contribution to the second-harmonic reflectance. When the charge modulation was positive, and the harmonic energy was below the onset for interband transitions, the results compared favorably with a previously published prediction of the same phenomenon which was based upon time-dependent local-density-functional theory for jellium having the same bulk electron density as Ag. The correlation between this theory and our experiment was poor for negative charge modulation. However, this was not unexpected, since the jellium model makes no allowance for the influence of the *d* bands. We have tentatively assigned a localized feature in the spectrum for negative charge modulation, which appears at a harmonic energy of 3.4 eV, as a two-photon resonance involving crystal-potential and image-potential surface states.

INTRODUCTION

Optical second-harmonic generation (SHG) has emerged as a promising interfacial diagnostic technique.[1] However, progress has been delayed by inadequate understanding of the mechanisms, particularly those governing SHG at metal surfaces. Theoretical efforts have concentrated on the isotropic, free-electron character of metals.[2-5] In that case, the problem separates into two parts. The first involves local mixing of optical fields, in the electric dipole approximation, through a surface susceptibility, as well as higher-order multipole contributions driven by local fields in the bulk. The second, also dipole allowed, is intrinsically nonlocal. It is related to the field and electron-density variations in a direction along the surface normal. The local-field part is adequately described by electron hydrodynamics applied to a jellium model, with an abrupt termination at the surface. By contrast, the nonlocal part (whose magnitude depends upon a parameter a_{RS}) has been the object of controversy.[6]

Rudnick and Stern,[2] as well as others,[6,7] originally concluded that $|a_{\mathrm{RS}}|\approx 1$. This seemed to be confirmed by an early experiment which sampled the Ag-glass interface.[8] However, more recent models,[5] which involve time-dependent local-density-functional (LDF) concepts, have suggested that metal surfaces are more polarizable. They predict $a_{\mathrm{RS}}=-36-9i$ for Al with an incident photon energy of $\hbar\omega=1.17$ eV. This was confirmed in experiments on Al(100) and Al(111).[9] This test was conducted at one value of $\hbar\omega$, a common characteristic of SHG studies. Most of the fundamental data which relate to the suitability of the models have been obtained with one or only a few incident photon energies.[8-15] It is fully expected from the LDF prediction that there should be some significant ω dependence.[5,14] Features should appear at $2\omega\equiv\Omega\approx 0.8\omega_p$ and $\Omega=\Phi/\hbar$ (where ω_p is the bulk-plasmon frequency and Φ is the work function). The first effect is associated with the character of the nonlocal fields below, yet near to, the bulk-plasmon frequency. The second effect is related to the anticipated high second-order polarization of the surface electrons near the threshold for photoemission. In addition to these purely free-electron properties, real metals should demonstrate SHG phenomena related to the lattice potential.[10,16] These are indirectly present in the free-electron contributions. In a material like Ag, for example, the *d* bands hybridize with the *sp* bands, leading to a less polarizable system than would otherwise be the case for a metal with the same *sp*-electron density.[17] Beyond this, interband and inter-surface-state transitions should lead to resonant SHG when either $\hbar\omega$ or $\hbar\Omega$ coincides with the transition energy.[18] In the case of the surface states, the strength of the second-harmonic resonance is governed by a dipole-allowed susceptibility whose symmetry is directly related to matrix elements involving the participating states. Both of these effects were identified in a recent investigation of Al(100) and Al(110).[19] In that experiment, the spectral variation of the isotropic contribution to the second-harmonic reflectance was measured in a set of four bands centered about $\hbar\omega=1.48$, 1.68, 1.94, and 2.14 eV. The data were compared to the time-dependent LDF theory for a jellium simulation of Al.[5] This demonstrated that, even for Al, which is generally regarded as a good example of a free-electron metal, the model (which ignored the effects of the lattice potential) overestimated the nonlinear polarization. On the (100) surface, additional deviations were attributed to transitions between a filled surface state at Γ and empty bulk states near the Fermi energy.

The model calculations show that a_{RS} is localized in the outer tail of the surface electron-density distribution, $n(z)$ ($+z$ being along the outward surface normal).[4] Likewise, any surface states would be localized beyond the outer layer of ion cores. Both of these important influences on SHG should be sensitive to static perturbation of the ground-state distribution, $n_0(z)$. The perturbation can be characterized by the integrated surface charge, $Q=-|e|\int[n(z)-n_0(z)]dz$. Changes in Q can be accomplished in an electrochemical sample chamber through manipulation of the applied interfacial potential difference, V_a.[20] Early experiments of this type were interpreted in terms of a phenomenological third-order susceptibility, which allowed mixing of the incident optical field in second order with the static electric field associated with surface charging.[21,22] A more recent study[14] [henceforth referred to as (GTL) (Guyot-Sionnest, Tadjeddine, and Liebsch)] was designed to measure the dependence of a_{RS} on Q. In that experiment (which was performed on Ag with only one value of $\hbar\omega$, 1.17 eV) a_{RS} for a variety of values of Q was extracted from an analysis of the second-harmonic reflectance versus the incident angle. Through a correct[23] analysis of their data, one finds $a_{\mathrm{RS}}=-13.18-1.6i$, $-7.0-0.4i$, and $-3.63+0.0i$ for $Q=-13$, 0, and $+13$ μC/cm^2, respectively. As part of the GTL report, predictions for a_{RS} versus Q were presented. These were extensions of the time-dependent LDF model for a jellium simulation of Ag, which involved charge-induced modifications of $n_0(z)$. At $Q=0$, the theoretical a_{RS} was $-17.7-4.03i$. The difference between theory and experiment in GTL was attributed to the effect of the d bands, and was accounted for through a scale factor μ (which should be about 0.3 based upon comparison to calculations for the static surface in which d bands were included[24]). If μ is set equal to 0.43, the data of GTL correspond very well to the theory, particularly near the zero charge condition. The success of the model is quite remarkable in this case.

Although it was not tested in their experiment, GTL presented calculations for the expected ω dependence of $a_{\mathrm{RS}}(Q)$. These show that the general influence of increasing Q is to shift the spectral features along the ω axis. This is particularly apparent in the vicinity of the work-function resonance. This feature is predicted to move from $\hbar\Omega\approx3$ eV to $\hbar\Omega\approx5$ eV as Q varies from -13 to $+13$ μC/cm^2.

It was our objective to exploit the surface charge perturbation method together with spectral variation to produce additional data that could be used in tests of the mechanism of SHG on Ag. The time-dependent LDF theory with a jellium model was shown to be fairly successful to GTL at 1.17 eV ($\hbar\Omega=2.34$ eV). It is an important question to establish the limits of this correlation. For higher energies (specifically, for $\hbar\Omega$ beyond the threshold for interband transitions), we certainly expect to observe resonances which are not built into the jellium model. These have been implicated in the results of previous workers (where one or two excitation energies were sampled).[13,15] However, the jellium-LDF theory predicts its own spectral variations, which can be emphasized through charge perturbation induced by the static electric field found at the electrochemical interface—in a second-harmonic electroreflectance experiment.

In our design, $\hbar\Omega$ was changed between the limits of 2.8 and 4.46 eV in 29 distributed increments, using a pulsed dye laser as the excitation source. We used an electrochemical sample chamber to modify Q at the surface of Ag(111). We referenced the SH reflectance to the $Q=0$ surface, thus providing a built-in normalization which eliminated many of the complications introduced in a spectral measurement. We used the published theory in GTL as a contact to the jellium-LDF model. We found that the model is correct within an order of magnitude; however, the predicted strong variations in $a_{\mathrm{RS}}(Q)$ with ω were not observed. The experiment demonstrates a much weaker spectral dependence, marked by features which are more naturally assigned to surface-state transitions than to structure in the free-electron response. Although this was not entirely unexpected, our data represent a direct test of these issues as they relate to Ag.

BACKGROUND

For a surface with C_{3v} symmetry [as has been shown to be appropriate for the (111) face of cubic materials], the power density of the p-polarized reflected light at the second-harmonic frequency can be expressed in a quite general, model-independent, form:[25,26]

$$S_\Omega=|E_\omega^2F[a+c\cos(3\varphi)]|^2\ . \tag{1}$$

In this expression, the p-polarized incident-field amplitude is E_ω. The sample is oriented with $\hat{\mathbf{z}}\|[111]$, the outward surface normal, $\hat{\mathbf{x}}\|[2\bar{1}\bar{1}]$, and $\hat{\mathbf{y}}\|[01\bar{1}]$. The angle between $\hat{\mathbf{x}}$ and the projection of the wave vector of the incident light on the surface plane is φ.

Our primary interest is in a_{RS}, which is found in a, the isotropic term in Eq. (1). This can be written as

$$a=g[a_{\mathrm{RS}}a_1+b_{\mathrm{RS}}a_2+fa_3+(da_4)/2]+\zeta a_5\ . \tag{2}$$

Here, a_n and g, as well as F in Eq. (1), depend only on the linear optical properties of the bulk media at ω and Ω, not on Q. Electron hydrodynamic models have shown that $b_{\mathrm{RS}}=-1$ and $d=1$.[7] In this development, we will also follow conventional assumptions which set $f=0$.[3,14] The last term in Eq. (2) depends upon ζ, which is proportional to the previously mentioned higher multipole contributions from the bulk. In an isotropic sample, $\zeta=0$. Since we used a single crystal in our experiment we cannot, in general, discard this term. However, we will later show that, under the conditions of our experiment, ζ can be neglected by comparison to the other contributions to a.

By setting $\varphi=30°$ in Eq. (1), the SHG power becomes $S_\Omega(\Omega)=|E_\omega^2Fa(Q)|^2$. In our experiment, we have extracted this quantity for each value of ω. Our data are reported as

$$\Delta|a|/|a|\equiv[S_\Omega(\Omega)/S_\Omega(0)]^{1/2}-1\ . \tag{3}$$

This removes the strong ω dependence of F and eliminates the need for normalization with respect to $|E_\omega|$.

EXPERIMENTAL PROCEDURE

The Ag(111) sample was oriented to within 1° using x-ray diffraction, mounted in a Teflon shroud to expose only the 11-mm-diam face, polished through 0.05-μm alumina abrasive, chemically polished using a cyanide procedure,[27] and thoroughly rinsed with triple-distilled water. The sample chamber, with an uv-grade silica window, contained nitrogen-saturated triple-distilled water and "reagent grade" K_2SO_4 (0.1 M). Standard electrochemical methods were followed [saturated calomel reference electrode (SCE); Pd-wire counter electrode]. We used a potentiostat to control the applied interfacial potential $V_a = V_{Ag} - V_{SCE}$. On this scale, $V_a = -0.75$ V corresponds to $Q = 0$. Published capacitance data for this system[28] were used to identify a $Q(V_a)$ relationship.

The p-polarized incident light (at an incident angle of 45°) came from a dye laser pumped by the frequency-doubled output from a yttrium-aluminum-garnet (YAG) laser (20 nsec pulses at 10 Hz). At the sample, the pulse energy density was restricted to less than 5 mJ/cm². Suitable colored glass and dichroic filters helped purify the spectral content of the incident and detected light at ω and Ω, respectively. The latter was improved with a $\frac{1}{4}$-meter grating monochromator in front of the Hamamatsu R212 photomultiplier. The reflected light also passed through a quartz lens and a Glan-Thompson prism to select p polarization. Conventional gated integrating electronics were used. For each value of ω, the φ dependence of Eq. (1) was verified prior to acquisition of the $S_\Omega(Q)$ data.

RESULTS

Representative results are shown in Fig. 1 for the vicinity of $Q=0$ and three values of $\hbar\Omega$. For clarity only, one raw data set is displayed. The SHG signal was recorded as a function of time with $dV_a/dt = 10$ mV/sec. To determine $S_\Omega(Q)$, we averaged scans of V_a in the positive and negative directions. The result was approximated by a third-order polynomial. We used this fit to calculate $\Delta|a|/|a|$. The uncertainty which we report for each Ω is related to the average deviation between the actual data and the third-order polynomial for that value of Ω.

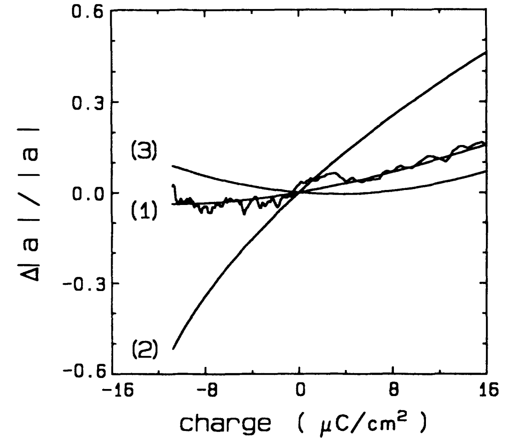

FIG. 1. Normalized change in $|a|$ vs the integrated surface charge Q. The zero charge condition corresponds to $V_a = -0.75$ V (vs the SCE). (1) $\hbar\Omega = 2.88$ eV, (2) $\hbar\Omega = 3.35$ eV, (3) $\hbar\Omega = 4.20$ eV. Raw data are shown only for (1) to improve clarity in the figure. Smooth curves are third-order polynomial fits to the corresponding data.

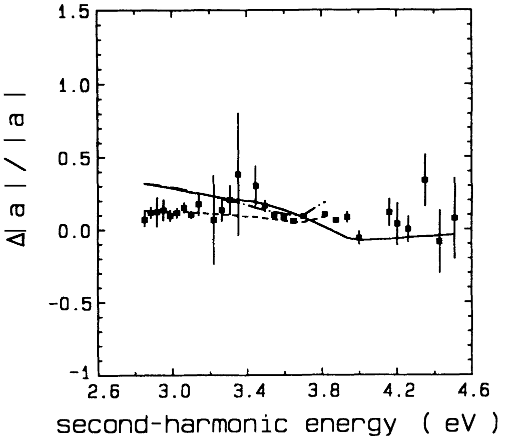

FIG. 2. Normalized change in $|a|$ vs $\hbar\Omega$ for $\Delta Q = +13$ μC/cm² (■). Predicted results from Eq. (4) using $a_{RS}(\omega,Q)$ from GTL, with $\mu=0.43$ (–·–·–), $\mu=0.23$ (— — —); $a_{RS}(Q)$ is independent of ω and set to 6.99 for $Q=0$ and -3.63 for $Q=+13$ μC/cm² (——).

The spectral presentation of our experiments are shown as the squares in Figs. 2 and 3. Each of the measured points is derived from $\Delta|a|/|a|$ at one of two discrete values of Q (as determined by the smooth curves such as are exemplified in Fig. 1). Figure 2 uses $Q=+13$ μC/cm², while Fig. 3 represents $Q=-10.8$ μC/cm². Our most negative Q did not reach -13 μC/cm², which was the value used in the predictions of GTL. The more positive extreme was set in our conservative avoidance of conditions under which cathodic decomposition of water might have otherwise occurred.

For a comparison between our data and the jellium-LDF theory, we need information about ζ, the bulk anisotropic, higher-order susceptibility. This can be obtained through a consideration of c in Eq. (1). On Ag(111), $c = \chi_{xxx}c_1 + \zeta c_2$.[25,26] Like the a_n, the c_n depend only on the linear optical properties of the system. χ_{xxx}

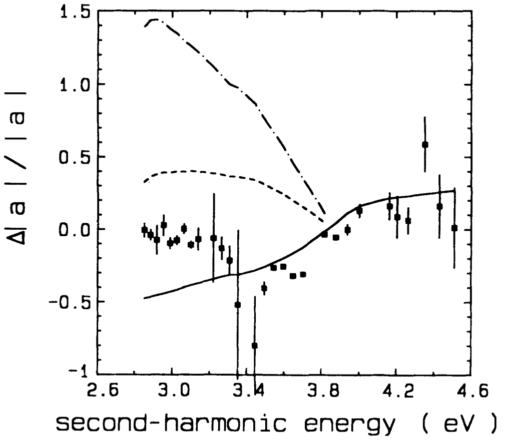

FIG. 3. Normalized change in $|a|$ vs $\hbar\Omega$ for $\Delta Q = -10.8$ μC/cm² (■). Predicted results from Eq. (4) using $a_{RS}(\omega,Q)$ from GTL (where $\Delta Q = -13$ μC/cm²), with $\mu=0.43$ (–·–·–), $\mu=0.23$ (— — —); $a_{RS}(Q)$ is independent of ω and set to -6.99 for $Q=0$ and -11.84 for $Q=-10.8$ μC/cm² (——).

is a second-order surface susceptibility which should be sensitive to interband transitions. On Ag(100), the general form of S_Ω is very similar to that which applies to Ag(111). However $\cos(3\varphi)$ in Eq. (1) must, on the (100) surface, be replaced by $\cos(4\varphi)$. The a_n are similar to, or identical with, those which refer to Ag(111). The biggest difference between these two orientations is that, on Ag(100), the inversion symmetry in the surface plane forces χ_{xxx} to be zero. This leaves c directly proportional to ζ. Therefore, should any anisotropy be observed on Ag(100), it must originate in the bulk portion of the sample. This provides an estimate of the relative strength of ζ.

We have performed this test by measuring $S_\Omega(Q,\varphi)$ on Ag(100). The procedure was similar to what we have already described. The details of that experiment will be presented elsewhere. The important point, central to our current discussion, is as follows: On Ag(100), $S_\Omega(Q,\varphi)$ is independent of φ (there is no anisotropy) for $Q<20$ μC/cm^2 at all values of Ω. This can only mean that, relative to the isotropic contributions in a, the size of ζ is quite small. On these grounds, we will neglect the ζ term in Eq. (2) as we present our analysis of the second-harmonic response of Ag(111).

DISCUSSION

The isotropic second-harmonic electroreflectance spectra in Figs. 2 and 3 are, for the most part, featureless. This is true even for the region above $\hbar\Omega=3.86$ eV, the interband transition threshold. There is more variation in Fig. 3, where the charge perturbation produces an electron excess on the surface. The most prominent structure occurs under these conditions near $\hbar\Omega=3.4$ eV. The potential origin of this phenomenon will be commented upon later. First, we wish to compare our results to the jellium-LDF theory as it was presented in GTL through $a_{\mathrm{RS}}(\omega,Q)$.

Under the conditions of this experiment the full form for $|a|$ is

$$|a|\propto|\mu a_{\mathrm{RS}}(\omega,Q)+(4/\epsilon_\Omega)[\epsilon_\Omega-(\epsilon_0/2)]^{1/2}\times[\epsilon_\omega-(\epsilon_0/2)]^{1/2}+(\epsilon_\omega/\epsilon_\Omega)|\ . \tag{4}$$

This expression is based upon an incident angle of 45°, and the approximation that water has the same dielectric function for both ω and Ω, $\epsilon_0=1.77$. The complex dielectric functions for Ag are ϵ_ω and ϵ_Ω.^{29} The only adjustable parameter in our adaptation of this model was μ. We have restricted our comparison to the harmonic photon energy range below the interband transition threshold. Since the jellium-LDF model does not allow for the influence of d bands, it cannot be expected to apply above that energy.

Using Eq. (4), we obtain the dash-dotted lines in both Figs. 2 and 3 for $\mu=0.43$. This scale factor is the same as that derived from the data in GTL for $\hbar\Omega=2.34$ eV. By adjusting μ to achieve the best fit to the data in Fig. 2 (dashed line), we arrive at $\mu=0.23$. This confirms that, in this range where Ag is less like a free-electron metal than at 2.34 eV, the d bands are playing a more prominent role in reducing the nonlinear polarizability of the surface. We show the $\mu=0.23$ prediction in Fig. 3 as well. Here the correlation is not so good. We were not able to achieve fits to the data in Fig. 3 that were acceptable, using values of μ between 0.1 and 2.0. The origin of the larger magnitude effect in the theoretical prediction for $\Delta|a|/|a|$ in Fig. 3 is the charge dependence of the two-photon resonance associated with the threshold for photoemission. One explanation of the lack of correlation between the theory and experiment under these circumstances may be the different surface energies between jellium and Ag. Also, because our experiment was performed in an electrolyte consisting mostly of water molecules, the *effective* work function becomes 3.0 eV.^{30} Although these are counteracting influences, we have no method of quantitatively estimating their relative, if any, importance.

In Eq. (4), there are spectral dependencies contained in ϵ_ω and ϵ_Ω. We recognized that some of the variations which our data show must come from these factors. As a rough estimate of these effects, we have developed a very simple static model for $\Delta|a|/|a|$. We treated a_{RS} as a constant with respect to ω, but retained its Q dependence as was experimentally determined at $\hbar\omega=1.17$ eV in GTL. Our rendition of that dependence is represented in the following empirical expression (with Q in μC/cm^2):

$$a_{\mathrm{RS}}(Q)=-6.99+0.399Q-8.34\times10^{-3}Q^2+1.7\times10^{-4}Q^3\ . \tag{5}$$

With this approach, using values of Q which are consistent with our experiment and $\mu=1$, we have calculated $\Delta|a|/|a|$, which is shown as the solid lines in Figs. 2 and 3. All of the Ω dependence in this simple model is provided by the linear optical properties of Ag. The correlations between the solid lines and the data are striking. This tells us that the nonlinear source terms have a weaker spectral variation than what would have been expected—certainly weaker than the jellium-LDF model in GTL.

The structure at $\hbar\Omega=3.4$ eV in Fig. 3, where $Q=-10.8$ μC/cm^2, cannot be explained by any of the models which depend only on the free-electron properties of the sample. This harmonic photon energy and the conditions of surface charge are precisely the same as those under which Schneider, Franke, and Kolb^{31} have observed a feature in the linear electroreflectance of Ag(111). In that work, the structure was assigned to an excitation between a crystal-potential (CP) surface state and an image-potential (IP) surface state at Γ in the two-dimensional Brillouin zone. Both surface states are expected to shift as V_a changes. At the zero charge condition, the energy of the CP state is above the Fermi level. On the negatively charged surface, the energy of this state is lowered with respect to the bulk metal electron energies. If it moves below the Fermi level, it will become occupied and can therefore act as the initial state in a two-photon resonance with the IP state. In our experiment, this enhances χ_{zzz} for the negative charge modulation, as compared to the uncharged surface or the positively charged surface. The result is a feature in $\Delta|a|/|a|$, where $\hbar\Omega$ is equal to the energy separation between the two surface states on the negatively charged surface.[32] The *zzz* component of the surface susceptibility is the only allowed member under a consideration of the selection rules connecting the two resonant states.[33,34] (CP state symmetry $=\Lambda_1$, IP state is totally symmetric with respect to z.) It is also the same component which contains $a_{\rm RS}$. Therefore, our experiment is well suited to couple to this transition.

The IP surface state has already been identified as a resonant partner at $\hbar\omega=3.84$ eV in two-photon photoemission from Ag(111) in vacuum.[35] Although UHV conditions are most closely associated with $Q=0$ in our experiment, it is very possible that the electrochemical environment causes shifts in both the IP and the CP surface states. However, if we take the vacuum value for the IP state as our $Q=0$ condition, we can predict how much this state must shift in order for it to be participating in the proposed CP → IP resonance. First, we must look at the possible energies of the CP state. If we assume that when $Q=0$ the CP state is close to, yet above, the Fermi level, then it can be modulated by as much as -0.4 eV before becoming mixed with bulk states at the L_2' edge.[36] The IP state must be located 3.4 eV above the Fermi level on the negatively charged surface (since this is the two-photon energy at which the feature is observed). Assuming low dispersion in the IP state, transitions would be possible from the CP state at the Fermi level to the IP state, provided the latter shifts by $\Delta E_{\rm IP}/\Delta V_a=1.76$ eV/V. This is consistent with potential variation of the energies of surface states which have been reported through linear electroreflectance experiments.[31] It is also compatible with the expected large variation in the IP surface state, as the conditions at the surface are changed. The large magnitude of $\Delta E_{\rm IP}/\Delta V_a$ has been attributed to the discrete nature of the static screening in electrolyte solutions, which causes local amplification of the potential gradient at the surface.[37]

Although the conclusions regarding surface states are speculative, we regard them as the best interpretation for the feature at $\hbar\omega=3.84$ eV in Fig. 3. Other possible causes include surface-plasmon excitation[38] (not likely on a smooth single crystal) or surface states at steps[39] [exploiting a CP state 1.7 eV above the Fermi level on Ag(110) in UHV (Ref. 34)]. Additional spectral experiments involving more optical geometries and a variety of surface conditions are required to clarify these issues.

CONCLUSIONS

We have measured the second-harmonic electroreflectance on Ag(111) over a wide range of incident photon energies. We find that the isotropic component of this quantity does not vary a great deal as the excitation energy is changed. Most of the spectral variation can be accounted for by the linear optical properties of Ag at the incident and harmonic photon energies. The Rudnick-Stern factor, $a_{\rm RS}$, displays little or no frequency dependence under the conditions of our experiment. However, it must still depend upon the total surface charge to explain the observed electroreflectance signal. To help define the limits of models which simulate the second-order optical properties of Ag through jellium, we compared our results to a recent time-dependent local-density-functional theory. This comparison, for harmonic photon energies below the interband transition threshold, shows that the theory is quite accurate when the charge modulation is in the positive direction, but is less satisfactory for the negative direction. In addition to the free-electron characteristics of our data, we have identified a feature which is most likely caused by a two-photon resonance between surface states under conditions of negative charging. Work is now in progress, involving additional spectral measurements, to confirm these early conclusions.

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