Mechanism for optical second-harmonic generation induced by an electric field at a metal-electrolyte boundary

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(Submitted 28 March 1994)
Zh. Eksp. Teor. Fiz. **106**, 1618–1627 (December 1994)

We investigated the generation of a reflected second-harmonic optical wave from the smooth surface of a polycrystalline silver electrode over a wide range of applied voltages and angles of incidence of the pump light. We found that the dependence of the second-harmonic intensity on the electrode potential φ measured at various angles of incidence is close to parabolic over a wide range of φ. The experimental data are described using the phenomenological theory of Rudnick and Stern. The dependence of the parameter a on φ is close to linear over the range of φ in which the second harmonic intensity is parabolic. This dependence is interpreted to be the result of modulation of the nonlinear optical properties of the gas of conduction electrons by the electrostatic field. For $\varphi \approx -0.4$ V, we observed a kink in the dependence of the second harmonic intensity on φ, which may be related to structure in the nonlinear susceptibility of the boundary caused by adsorption processes. We discuss the possibility of a threshold in the influence of adsorption on the electronic nonlinear response of the metal surface. © *1994 American Institute of Physics.*

INTRODUCTION

Second-harmonic generation at the surface of metals has long been the subject of intense experimental investigations. It is well known[1] that second-harmonic generation is forbidden in the electric-dipole approximation within the bulk of a centrosymmetric material. Since practically all metals and alloys are centrosymmetric, metallic nonlinear second-harmonic sources are due primarily to disruption of the centrosymmetric character of the material in the surface layer, and to the presence of a jump in the electric field component of the probe radiation normal to the surface. Hence, these sources are localized in a thin layer of metal (on the order of a few angstroms) near the surface. This implies that the process of second-harmonic generation is highly sensitive[2] to surface properties such as structure, charge state, roughness, surface concentration composition of adsorbates, etc.[3]

In this paper we describe our investigation of nonlinear electroreflectance at metal surfaces, in which an electrostatic field applied to the surface modulates the intensity of a reflected second-harmonic wave. There has been increased interest in this phenomenon among scientists, since its mechanism remains unclear at present. Nonlinear electroreflectance was observed for the first time by Bloembergen *et al.*[4] In their paper, as in all subsequent papers, the electrostatic field was applied to the surface of the metal by electrochemical methods;[3] therefore, the parameter controlled by the experimenter was the potential φ of the metal relative to the electrolyte. The shape of the dependence of the second-harmonic intensity $I_{2\omega}(\varphi)$ on the potential of the metal turns out to be close to parabolic (Fig. 1a).

However, the results of Bloembergen *et al.*[4] remained practically unnoticed in the course of the next fifteen years. The problems these authors addressed attracted interest once more in the mid-80's, when researchers noticed for the first time[5] that the metal potential had no observable effect on the intensity of giant second-harmonic generation (the so-called surface-enhanced second-harmonic generation). The authors of Ref. 5 measured the intensity $I_{2\omega}(\varphi)$ (shown here in Fig. 1b) for a roughened silver surface obtained by anodization in an electrochemical cell, and found that it had no sharply expressed features. Apparently, the electrochemical conditions for the experiment must be fulfilled more rigorously in order for the nonlinear electroreflectance to be observed and for a giant second-harmonic signal to be generated.[6] The corresponding dependence of the giant second-harmonic intensity on potential φ is shown in Fig. 1c. The results of Bloembergen *et al.* were also confirmed in investigations of nonlinear electroreflectance from the surface of a metal with controllable roughness.[7,8] The dependence of the intensity of reflected second harmonic had the form $I_{2\omega}(\varphi) \propto (\varphi - \varphi_0)^2$, where φ is the potential difference between the metal and electrolyte, and the quantity φ_0 corresponds to the minimum of the curve $I_{2\omega}(\varphi)$ and is close to the zero-charge potential, i.e., the value of φ that corresponds to an uncharged metal surface. The studies of Refs. 4–8 suggest that it is possible to use nonlinear electroreflectance as a method for investigating a metal-electrolyte boundary.

In later work, Richmond[9–11] obtained results that were similar on the whole. However, in Ref. 11 he observed a different kind of dependence for a smooth surface of silver, which was noticeably asymmetric around φ_0 and did not have a well-defined minimum (Fig. 1d). At the same time, he observed that for roughened metal surfaces the dependence of the second-harmonic intensity on φ is close in form to that obtained in Ref. 4. Therefore, he asserted that an asymmetric dependence of $I_{2\omega}(\varphi)$ was characteristic for a smooth surface and that the parabolic dependence arises from the presence of roughness.

The two different types of function $I_{2\omega}(\varphi)$ for a smooth surface can only be explained by invoking fundamentally different theoretical descriptions of the nature of the surface

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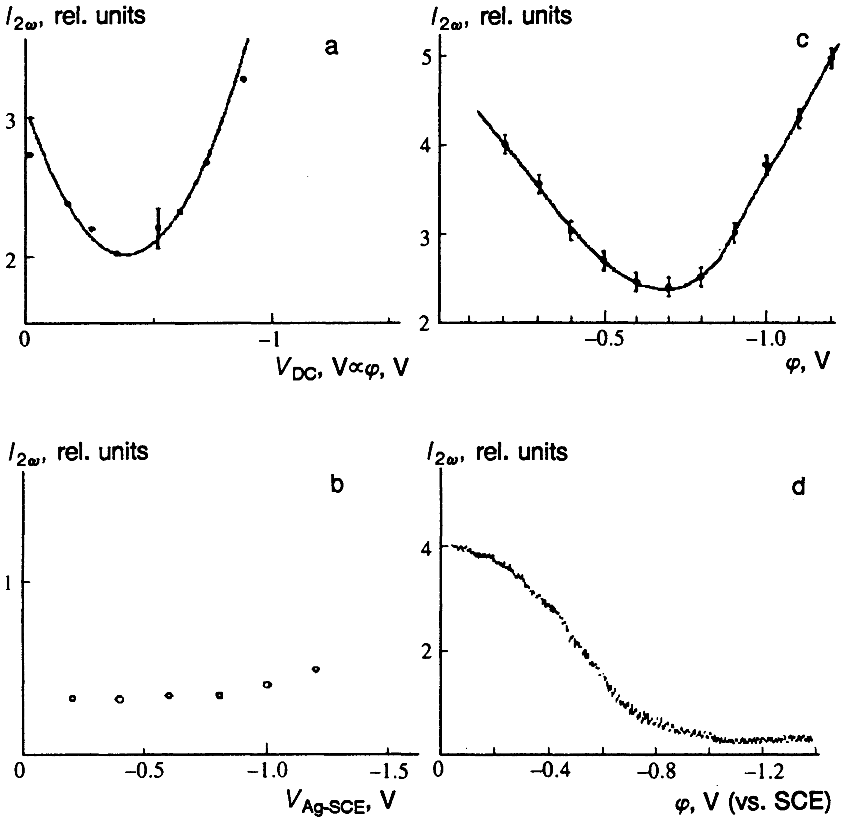

FIG. 1. Dependence of the intensity of reflected second harmonic on the potential φ for polycrystalline silver given in Ref. 4 (a), Ref. 5 (b), Ref. 6 (c), and Ref. 11 (d).

nonlinearity. In Ref. 12, Richmond associated the asymmetric dependence with the existence of adsorbed surface states whose response had a resonant character. However, the parabolic dependence can be explained without assuming that there is a resonant contribution in the quadratic response of the surface: this dependence can be explained within the framework of a model of the electron-induced surface nonlinearity of a spatially bounded gas of conduction electrons.[13,14]

In Ref. 13, Richmond et al. obtained the angular dependence for the second-harmonic intensity reflected from a smooth surface (for fixed values of the surface charge). From this data, they also concluded that the dependence of the intensity of reflected second harmonic on the metal potential was symmetric (parabolic), i.e., close in character to the function $I_{2\omega}(\varphi)$ for a rough surface.[8]

In view of these contradictory experimental data and the significant differences in their interpretation, further study of the nonlinear electroreflectance of a smooth metal surface is called for, over a wider range of variation of the surface parameters [e.g., the charge state of the surface and angle of incidence of pump radiation, which can strongly affect the shape[13] of the curve $I_{2\omega}(\varphi)$] while monitoring the surface smoothness *in situ*. The latter procedure is especially valuable for a correct interpretation of the experimental data, since the contradictory results of Refs. 4, 6–8, and 11 could be due to the influence of weak surface roughness on the nonlinear-optics response. For this reason, we will attempt in this paper to elucidate the features of nonlinear electroreflectance at a smooth metal surface in order to determine the mechanism of the phenomenon and to resolve the contradictions obtained in previous work.

2. EXPERIMENT

In this work, our source of probe light was a single-mode pulsed YAG:Nd^{3+} laser with wavelength $\lambda_0 = 1.064$ μm, pulse duration $\sim$15 ns, and diameter 0.15 cm, with an energy per pulse of 2 mJ and a repetition frequency of 12.5 Hz. Light at the second harmonic frequency was separated out using a double monochrometer and recorded with an electronic stroboscopic system. An electrostatic field was applied to the sample surface using an electrochemical method.[3,15] The sample was placed in an electrochemical cell, whose working volume was bounded by a hemispherical quartz glass. This construction of the cell allowed us to measure the angle of incidence ϑ of the pump radiation with respect to the metal surface in the interval from 0° to 85° with respect to the normal. The potential difference φ between the working electrode (sample) and the electrolyte (0.1 M water solution of KCl) was measured with reference to a saturated silver chloride comparison electrode.

The object of our investigation was a smooth surface of polycrystalline silver. In order to obtain the smooth surface, the sample was mechanically polished using a powder of artificial diamond (with grain size on the order of 0.5 μm). Then a silver film of thickness 300 to 500 angstroms was thermally deposited on the sample surface, and the sample was maintained at a potential of -1.3 V for one to two hours (cathode polarization) in order to remove possible organic

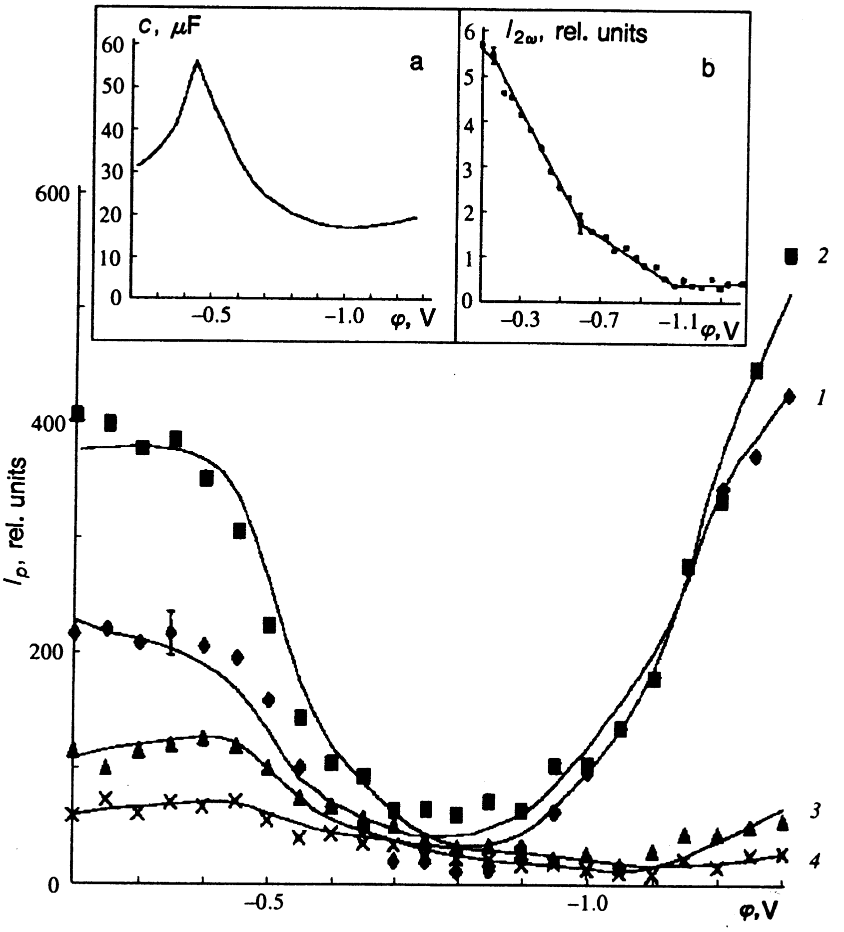

FIG. 2. Experimental intensity of p-polarized second-harmonic light reflected from a smooth polycrystalline silver surface in a solution of KCl with concentration 0.1 M versus the potential φ for various values of ϑ (points), along with curves plotted using the method described in this paper (solid curves): 1—$\vartheta=75°$, 2—$\vartheta=60°$, 3—$\vartheta=45°$, 4—$\vartheta=30°$; the function $I_{2\omega}(\varphi)$ is shown in inset (a) for a water solution of NaF with concentration 0.1 M ($\vartheta=30°$). The differential capacitance of the electric double-layer for a smooth polycrystalline silver surface in a water solution of KCl with concentration 0.1 M is shown in inset (b).

impurities. The surface smoothness was monitored *in situ* using a nonlinear-optics method based on the application of polarization selection rules for reflected second-harmonic generation.[16] The criterion for submicron smoothness of the surface was the absence of an s-polarized second-harmonic component, whose generation at a smooth isotropic centrosymmetric surface of a medium is forbidden.[16]

The second-harmonic intensity was measured as the potential across the sample under study was varied from -1.3 to -0.2 V within intervals of 0.05 V, at angles of incidence of the probe light of 30, 45, 60, or 75 degrees with respect to the normal. Each series of measurements was preceded by a half-hour cathode polarization and monitoring of the surface smoothness *in situ*.

In addition to the nonlinear optics measurements, we also monitored adsorption processes at the surface of the same silver sample by measuring the dependence of the differential capacitance $c(\varphi)$ of the electric double-layer at the metal-electrolyte boundary on the metal potential, using the method discussed, e.g., in Ref. 17. Results of these measurements are shown in inset (a) of Fig. 2.

The dependence of the intensity $I_{2\omega}^{p-p}(\vartheta,\varphi)$ of p-polarized second harmonic on φ for p-polarized pump radiation, which we obtained from our measurements for various angles of incidence, is shown in Fig. 2. Thus, the dependence of $I_{2\omega}^{p-p}(\vartheta,\varphi)$ on $\varphi-\varphi_0$ over the interval $-1.2\ \text{V}<\varphi<-0.5$ V is close to quadratic.

It is clear from Fig. 2 that as the angle of incidence ϑ of the probe radiation at the boundary of the metal electrolyte decreases, the minimum of the curve $I_{2\omega}^{p-p}(\vartheta,\varphi)$ shifts towards the cathode region. Therefore, when we made our measurements around $\vartheta\sim30°$, which is the region of ideal polarizability, only one branch of the parabola appeared and the observed dependence was close to that obtained in Ref. 11 for $\vartheta=45°$. Apparently, the authors of Ref. 11 used an optical electrochemical cell with a planar input window, and the value 45° probably refers to the angle of incidence of the pump radiation on the air-glass boundary of the input window to the cell, which corresponds to an angle of incidence at the metal-electrolyte boundary $\vartheta\sim30°$. Thus, the asymmetry of the curves shown in Ref. 11 is occasioned only by their accidental choice of angle of incidence. In the general case, our results show that the dependence of the intensity of reflected second harmonic on the metal potential is close to parabolic in the interval $-1.2\ \text{V}<\varphi<-0.5$ V.

3. INTERPRETATION OF EXPERIMENTAL RESULTS

In order to interpret the experimental data it is necessary to relate the observed values to the nonlinear characteristics of the surface. Second-harmonic generation at a smooth surface of a macroscopically isotropic metal is normally described using the complex phenomenological coefficients a, b, and d introduced by Rudnick and Stern.[18] The effectiveness of excitation of normal and tangential components of the surface current at twice the frequency based on the dipole mechanism is determined by the parameters a and b respectively; the parameter d describes the quadrupole contribution to the generation of nonlinear current in the bulk of the metal.

In this approximation the efficiency with which p-polarized reflected second-harmonic light is generated at the surface of a metal for p-polarized pump radiation can be expressed in the following form:[14]

$$\frac{I_{2\omega}}{I_\omega^2}=\frac{8\pi e^2}{m^2\omega^2c^3}\left|\frac{\epsilon_s(\omega)\epsilon_s(\Omega)\epsilon(\omega)[\epsilon(\omega)-\epsilon_s(\omega)]}{\epsilon(\Omega)+S(\Omega)}P\mathrm{tg}\vartheta\right|^2, \tag{1}$$

where $S(\omega)=[\epsilon(\omega)-\epsilon_s(\omega)\sin^2\vartheta]^{1/2}\epsilon_s^{1/2}/\cos\vartheta$, and

$$P=\left\{a(\omega)\frac{\epsilon(\Omega)\epsilon_s(\omega)}{\epsilon(\omega)}\sin^2\vartheta-b(\omega)\frac{2S(\omega)S(\Omega)}{\epsilon(\omega)\epsilon_s(\omega)}\right.$$
$$\left.\times\cos^2\vartheta+\frac{1}{2}d(\omega)\right\}/[\epsilon(\omega)+S(\omega)]^2,$$

ω is the frequency of the pump radiation, $\Omega=2\omega$, $\epsilon(\omega)$ and $\epsilon_s(\omega)$ are the bulk optical dielectric constants of the metal and electrolyte, e and m are the charge and mass of an electron, and c is the velocity of light in vacuum.

According to Refs. 18 and 19, we may assume that the coefficients b and d are independent of the surface potential and pump frequency; here we set $b(\omega,\varphi)=-1$, $d(\omega,\varphi)=1$. The parameter a is a strong function of the state of the surface, especially of the metal potential φ with respect to the electrolyte, i.e., $a=a(\omega,\varphi)$.[14] In our experiments we used monochromatic pump radiation; therefore, in what follows, we will consider only the dependence $a(\varphi)$. Hence, in our model the nonlinear electroreflectance phenomenon is described by a single complex parameter a.

If we neglect the small imaginary parts of the dielectric constants ($\epsilon_{\mathrm{Ag}}(\omega)\approx-58+i0.6$, $\epsilon_{\mathrm{Ag}}(\Omega)\approx-11.8+i0.37$, $\epsilon_s(\omega)\approx2$, $\epsilon_s(\Omega)\approx1.8$) Eq. (1) reduces to the following expression for the second harmonic intensity:

$$I_{2\omega}=K(\vartheta)\left|a(\varphi)+\frac{4}{\sin^2\vartheta}\right|^2, \tag{2}$$

where the coefficient K depends only on the angle of incidence. This expression is the starting point for determining the unknowns a and K based on experimental data for $I_{2\omega}$. Here we are dealing with a problem of nonlinear curve fitting, for which there are no standard methods of solution. We used an algorithm, which, although simple, allowed us to obtain a solution to the problem with satisfactory errors.

Let us write $c(\vartheta)\equiv4/\sin^2\vartheta$, $a'(\varphi)\equiv\mathrm{Re}[a(\varphi)]$, $a''(\varphi)\equiv\mathrm{Im}[a(\varphi)]$, $|a(\varphi)|^2(\varphi)\equiv a'^2(\varphi)+a''^2(\varphi)$, $k(\vartheta)\equiv1/K(\vartheta)$; then Eq. (2) takes the form

$$|a(\varphi)|^2(\varphi)+2a'(\varphi)c(\vartheta)+c^2(\vartheta)-k(\vartheta)I_{2\omega}(\vartheta,\varphi)=0. \tag{3}$$

In our experiments we measured the function $I_{2\omega}(\varphi)$ for four angles of incidence: $\vartheta_1=75°$, $\vartheta_2=60°$, $\vartheta_3=45°$, and $\vartheta_4=30°$. These functions were interpolated graphically. We then introduced a grid with steps of 0.025 V in φ. In what follows we will omit the label 2ω to simplify the notation, and in place of the arguments ϑ and φ we will assign labels $i=1,\ldots,4$ and $f=0,\ldots,44$ to these variables respectively.

Two functions (a_f' and a_f'') and four normalization coefficients (k_i) make up the list of unknowns. In Eq. (3) the variables k_i, a_f', and $|a_f|^2$ enter linearly; therefore, in solving the inverse problem with respect to a_f' and a_f'' it is convenient to find a_f' and $|a_f|^2$ first. Then $a_f''=\sqrt{|a_f|^2-a_f'^2}$.

The unknown quantities are found by the method of least squares from the condition that the following functional be a minimum:

$$\sum_{i,f}[|a_f|^2+2a_f'c_i+c_i^2-k_iI_{i,f}]^2=\min, \tag{4}$$

the value of this function is treated as a criterion for the best approximation of the experimental functions by (2) using the fitting parameters k_i, a_f', and a_f^2, which satisfy the additional conditions:

$$k_i>0,\quad (a_f')^2<a_f^2 \tag{5}$$

(the second of these imposes significant limitations on the range of solutions).

Equation (4) leads to the following system of linear equations:

$$\begin{cases}\sum\limits_f[|a_f|^2I_{i,f}+2a_f'c_iI_{i,f}+c_i^2-k_iI_{i,f}^2]=0, & i=1,..,4,\\ \sum\limits_i[|a_f|^2+2a_f'c_i+c_i^2-k_iI_{i,f}]=0, & f=1,..,44,\\ \sum\limits_i[c_i|a_f|^2+2a_f'c_i^2+c_i^3-c_ik_iI_{i,f}]=0, & i=1,\ldots,44.\end{cases} \tag{6}$$

We solved the system (6) by the Gauss method, while monitoring fulfillment of condition (5).

The coefficients $I_{i,f}$ of the system (6) are the experimental data, which have finite errors. We will assume these errors are random variables normally distributed over the interval of experimental error, with fixed nonzero correlation lengths with respect to f that ensure the absence of rapid oscillations in the functions $I_{i,f}$. Furthermore, we will treat only those realizations $I_{i,f}$ that yield solutions of the system (6) that satisfy condition (5).

In accordance with these premises, we used the method of statistical trials; we chose an empirical correlation length for f equal to 0.6 V. The averages and dispersions of the unknown variables a_f' and $|a_f''|$ are determined by averaging the solutions to system (6) with respect to samples from an ensemble of realizations $I_{i,f}$ limited by condition (5). The final functions $\mathrm{Re}(a)$ and $|\mathrm{Im}(a)|$ with their mean-square deviations are shown in Fig. 3.

Note that the sign of $\mathrm{Im}\,a(\varphi)$ cannot be recovered from the available collection of experimental data, since the square of this quantity enters into Eq. (2). The character of the function $\mathrm{Im}\,a(\varphi)$ (the solid curve in Fig. 3) was identified by using $\mathrm{Im}\,a(\varphi)\sim0$ in the region of zero-charge potential. In our view, there are no physical factors in this voltage range that can disrupt the monotonic (linear) dependence of $\mathrm{Im}\,a(\varphi)$ or keep it from changing sign. In addition, in choosing the sign of $\mathrm{Im}\,a(\varphi)$ we were guided by the require-

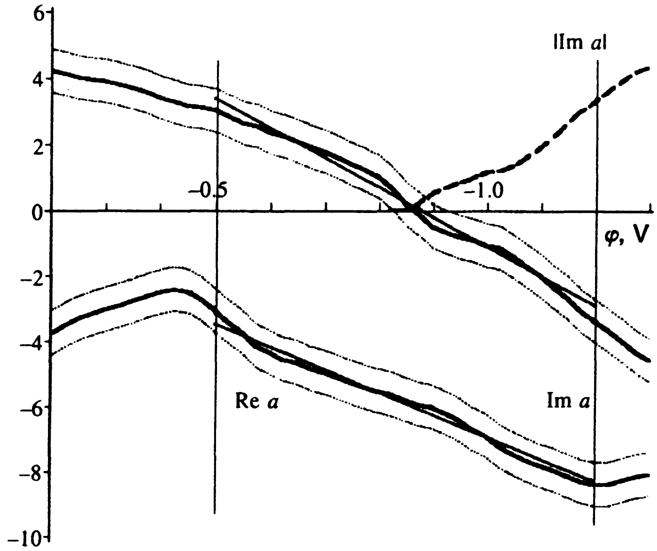

FIG. 3. Dependence on φ of the imaginary and real parts of the parameter a reconstructed from the experimental data. The points show the function $|\mathrm{Im}(a)|$. The dashed curves denote the confidence intervals for the results obtained. The vertical lines bound the intervals in which the functions $\mathrm{Re}(a)$ and $\mathrm{Im}\, a(\varphi)$ are linear within experimental error. The fine solid sloped lines are the result of linear approximation of the functions $\mathrm{Re}(a)$ and $\mathrm{Im}\, a(\varphi)$ in this interval.

ment that the results agree qualitatively with those of numerical ab initio calculations of the parameter a given in Fig. 2 of Ref. 13.

Using the behavior for $\mathrm{Re}(a)$ and $\mathrm{Im}\, a(\varphi)$ and the normalizing coefficients K_i obtained from Eq. (2), we constructed curves for the intensity of the p-polarized component of second-harmonic light and superimposed them on the corresponding experimental curves (Fig. 2, solid curves). Using these data we could evaluate the accuracy our approximations and our computational procedures.

4. DISCUSSION OF RESULTS

The data shown in Fig. 2 match the results of Refs. 4, 6–8, and 13, and show that the functions $I_{2\omega}^{p-p}(\vartheta,\varphi)$ have essentially the same shape for large and small ϑ, i.e., all of them are close to parabolic. As we have already noted, the data of Ref. 11 suggest that mechanisms involving the existence of adsorbed surface states play a decisive role in nonlinear electroreflectance.[12] However, in this case we should only observe a second-harmonic signal for values of φ that exceed the zero-charge potential. According to Ref. 17, this will happen when anions are adsorbed, including the OH^- group. The second-harmonic signal that we observe in the cathode portion of the dependence shows that, at least in this region, the dominant mechanisms for nonlinear electroreflectance are nonresonant ones connected only with changes in the charge state of the metal surface.[13,14]

From Fig. 3 it is clear that in the voltage range $-1.2\ \mathrm{V}<\varphi<-0.5\ \mathrm{V}$ the functions $\mathrm{Re}\,(a)$ and $\mathrm{Im}\, a(\varphi)$ are linear within the limits of error, which corresponds to a parabolic dependence of the second-harmonic intensity on potential. This allows us to describe nonlinear electroreflectance in silver (in the interval of potentials we studied) using a model of electron-induced surface nonlinearity[13,14] without additional considerations involving resonant response of surface states. We note that a theoretical calculation carried out in Ref. 14 based on this model gave a linear dependence for $\mathrm{Re}\, a(\varphi)$ in the quasistatic approximation.

It follows from the linearity of the function $a(\varphi)$ in the range $-1.2\ \mathrm{V}<\varphi<-0.5\ \mathrm{V}$ that, according to Eq. (2), the position of the minimum of the curve $I_{2\omega}^{p-p}(\vartheta,\varphi)$ depends on the parameter ϑ; this is confirmed by our experimental data (Fig. 2). Thus, this minimum is not rigidly tied to the value of the zero-charge potential. This fact contradicts the conclusions arrived at in Ref. 8. However, it should be noted that the zero in the function $\mathrm{Im}\, a(\varphi)$ appears at a value $\varphi\approx-0.9$ V that is close to the zero-charge potential for this combination of metal and electrolyte (Fig. 3). Further investigations would be interesting in order to clarify the question of how sensitive the position of the zero of $\mathrm{Im}\, a(\varphi)$ is to changes in the composition of the electrolyte, the type of metal, and the frequency of the pump radiation (over the range of frequencies much smaller than the plasma frequency of the metal, i.e., where the quasistatic approximation is applicable[13]).

Plots of $\mathrm{Re}\, a(\varphi)$ and $I_{2\omega}^{p-p}(\varphi)$ are smooth curves that are almost linear functions in the first case and quadratic in the second, except for the region of anodic potentials $\varphi>-0.5$ V. For $\varphi\approx-0.5$ V the dependence is observed to deviate from linear and quadratic, respectively, in that both of them have a kink. Let us analyze possible reasons for this behavior.

The coefficient a can depend both on the field of the electric double-layer at the metal-electrolyte boundary and on the surface concentration of adsorbates. The plot shows that the differential capacitance $c(\varphi)$ of the working electrode as a function of potential φ [inset (a) of Fig. 2] has peaks for $\varphi\approx-0.5$ V associated with the presence of a specific adsorbate, here Cl^- ions.[17] On the other hand, the specific adsorption is small in fluoride solutions,[17] while measurements show that no peaks are observed in $I_{2\omega}^{p-p}(\varphi)$ for this case [inset (b) of Fig. 2]. Therefore, we may assume that the appearance of kinks is connected with the influence of an adsorbate.

From the width of the peak on the curve $c(\varphi)$, we can infer the range of the potential in which adsorption processes occur.[17] In our case this is the interval $-0.8\ \mathrm{V}<\varphi<-0.2$ V. Thus, the range over which an adsorbed layer forms is considerably wider than the interval in which a kink occurs in the curves $I_{2\omega}^{p-p}(\varphi)$ and $\mathrm{Re}\, a(\varphi)$ (Figs. 2 and 3). At any rate, the specific adsorption of Cl^- ions, which first begins for $\varphi\approx-0.8$ V, is not found to affect the behavior of $\mathrm{Re}\, a(\varphi)$, and accordingly $I_{2\omega}^{p-p}(\varphi)$, until $\varphi\approx-0.5$ V. Additional investigations are required to explain why the effect of adsorption on the nonlinear optics response of the boundary has this "threshold" character.

The distinctive features of the behavior of $I_{2\omega}^{p-p}(\varphi)$ described above, which are connected with the presence of adsorption, suggest that any description of nonlinear electroreflectance that is based on some mechanism of electron-induced surface nonlinearity to be determined in the future will by no means be unique. In this paper we have encountered one adsorption mechanisms that is related to the specifics of adsorption of chlorine ions.

5. CONCLUSION

Thus, we have established that for a smooth silver surface the dependence of the second harmonic optical intensity reflected by the metal on the potential applied to it is close to quadratic in the neighborhood of the zero-charge potential as the angles of incidence of the pump radiation at the boundary between metal and electrolyte vary over a wide range. In this case the position of the minimum of the function $I_{2\omega}(\varphi)$ depends significantly on the angle of incidence of the pump radiation.

We have calculated the coefficient a that describes the efficiency of excitation of the normal component of surface current at the double-layer versus the potential across the metal. This function is found to be close to linear in the neighborhood of the zero-charge potential.

We have arrived at certain conclusions regarding the possibility of describing nonlinear electroreflectance in silver using a model of electron-induced surface nonlinearity without invoking additional considerations regarding resonant response of surface states.

Based on the functions we have obtained, we have made inferences with regard to the threshold character of the effect of adsorption on the quadratic nonlinear optics response of the system.

We are grateful to O. A. Petrie, G. A. Zirlin, and T. Furtak for valuable consultations regarding questions of electrochemistry of metals and useful discussions of the result of this work, and also to Z. V. Kuz'minov and A. V. Ermushev for help in carrying out the experiments.

This work was carried out with the support of the Programs for "Physics of Nanostructures," and "Fundamental Metrology" INTAS-93 (grant 370) and ISF (grant M12000).

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Translated by Frank J. Crowne