PHYSICAL REVIEW B VOLUME 45, NUMBER 16 15 APRIL 1992-II

Theory of second-harmonic generation at the metal-electrolyte interface

P. G. Dzhavakhidze
Department of General and Theoretical Physics, The Georgian Technical University, 380075 Tbilisi, Georgia

A. A. Kornyshev
The A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the U.S.S.R., 117071 Moscow, U.S.S.R.

A. Liebsch
Institute für Festkörperforschung, Kernforschungsanlage, 517 Jülich, Federal Republic of Germany

M. Urbakh*
School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

(Received 21 December 1990; revised manuscript received 26 December 1991)

A model for second-harmonic (SH) generation at the metal-electrolyte interface is proposed and treated by means of an electronic density-functional calculation. The dependence of the SH signal on the electrode charge σ is studied for different values of system parameters which represent different aspects of the metal-medium interaction. Characteristic differences between the SH signal at a free metal surface and for the same metal in contact with electrolyte are predicted in the range of negative surface charges and near the zero charge point. At large positive charges (when the surface electronic profile is almost entirely "hidden" within the metal positive ionic background) the solvent effect is small and the σ dependence of the SH signal approaches the corresponding curve for the free metal surface. General trends in the signal dependence upon ionic adsorption are established.

I. INTRODUCTION

A number of the theoretical and experimental studies of the second-harmonic generation (SHG) from smooth metallic surfaces[1,2] have been recently performed. The SH signal was shown[3-5] to be very sensitive to surface electronic properties, thus capable of yielding more detailed information about the electronic distribution near the surface and its polarizability than any method of linear optical spectroscopy.

However, the possibility of varying the parameters of surface electronic distribution is very limited for free metal surfaces. In practice, only the bulk electronic density can be varied by measuring the signal from different metals. The net charge on the metal surface σ is an efficient governing parameter, which modifies the surface electronic profile. At the metal-vacuum interface, however, it is impossible to reach values of σ which might influence appreciably the surface electronic profile. Such values of σ are available at the metal-electrolyte interface due to the high capacitance of the system. This is a well-known fact, widely employed in the linear optical studies where the immersion of the metal surface into electrolyte is used for studying electromodulated signals.[6,7] This trick lies in the heart of such methods as *in situ* electroreflectance and modulation ellipsometry. On the other hand, electronic properties of the metal-electrolyte interface are important per se in fundamental and applied electrochemistry.[6]

In situ measurements allow one to overcome the usual difficulty of SHG spectroscopy: the resolution of the bulk and surface contributions. Studying the charge dependence of the signal gives information about the surface properties because the charge, localized near the surface, does not affect bulk properties. The bulk and the surface contributions also differ in their angular dependences. Thus, valuable additional information can be obtained by studying this dependence.

In this paper a model of the electrochemical interface used previously for a description of the electrical[8,9] and linear optical[10,11] characteristics will be used to describe the electronic properties, which determine the SH signal. In doing so, we shall study the effect of various physical parameters of the system (which determine the medium effect on the surface electronic profile) on the variation of SH signal with the electrode charge σ.

As we shall see, the presence of the medium (electrolyte) leads to the dramatic changes in the σ dependence of the SH signal. The effect is sensitive to ionic adsorption. Consequently SHG can be a promising method for the *in situ* studies of electrode surfaces.

II. STRUCTURE OF THE SH SIGNAL

The generation efficiently of the p-polarized SH reflected radiation may be expressed as follows:[12]

$$\frac{I_{2\omega}}{I_{\omega}^{2}}=\frac{8\pi e^{2}}{m^{2}\omega^{2}c^{3}}\left|\frac{\epsilon_s(\omega)\epsilon_s(\Omega)\epsilon(\omega)[\epsilon(\omega)-\epsilon_s(\omega)]}{\epsilon(\Omega)+s(\Omega)}(P\cos^{2}\psi+S\sin^{2}\psi)\tan\theta\right|^{2}, \qquad (1)$$

where

$$P=\frac{a(\omega)\dfrac{\epsilon(\Omega)\epsilon_s(\omega)}{\epsilon(\omega)}\sin^2\theta-b(\omega)\dfrac{2s(\omega)s(\Omega)}{\epsilon(\omega)\epsilon_s(\omega)}\cos^2\theta+\tfrac{1}{2}d(\omega)}{[\epsilon(\omega)+s(\omega)]^2} \tag{2}$$

$$S=\frac{d(\omega)}{2\epsilon(\omega)[\epsilon_s(\omega)+s(\omega)]^2}\ , \tag{3}$$

and

$$s(\omega)=\frac{[\epsilon(\omega)-\epsilon_s(\omega)\sin^2\theta]^{1/2}}{\cos\theta}\epsilon_s^{1/2}(\omega)\ . \tag{4}$$

Here e, m, and c are the fundamental constants, $\Omega=2\omega$; furthermore $\epsilon(\omega)$ and $\epsilon_s(\omega)$ are the bulk optical dielectric constants of the metal and the electrolyte, respectively. The polar angle of incidence with respect to the surface normal is denoted by θ; ψ is the angle of polarization vector with respect to the plane of incidence ($\psi=0°$ corresponds to p polarization, while $\psi=90°$ to s polarization). We shall not specify here the parameters $b(\omega)$ and $d(\omega)$ which were shown to be practically independent of the nature of the metal; $b(\omega)\simeq-1$, $d(\omega)\simeq 1$.[13] The only quantity in Eq. (1) which depends on the surface properties is the parameter $a(\omega)$. This parameter is proportional to the integrated normal component of the nonlinear surface polarization. Microscopic calculation of $a(\omega)$, and particularly its dependence on the electrode charge σ, is the subject of this paper.

It should be noted that Eq. (1) is valid under an assumption that the solution has a negligible nonlinear polarizability. With $\epsilon_s=1$ Eq. (1) describes the signal from the metal-vacuum interface; $a(\omega)$ is then related to the properties of the free metal surface.

III. $a(\omega)$ AND THE SURFACE ELECTRONIC PROFILE

A. Free metal surfaces

Following Refs. 3 and 4 we shall adopt the adiabatic approximation which assumes that s-p electrons of the metal follow the alternation of the incident electromagnetic field. In the case of simple metals with sufficiently high plasma frequency, this assumption has proved to reproduce fairly well the time-dependent local-density approximation calculations for standard 1.17-eV frequency of the Nd:YAG laser[5] (where YAG denotes yttrium aluminum garnet).

The normal component of the external field in the system is composed of two parts:

$$E(t)=4\pi\sigma+E_{em}(t)\equiv 4\pi[\sigma+\sigma_\omega(t)]\ , \tag{5}$$

where $4\pi\sigma$ represents the static charge contribution while $E_{em}=4\pi\sigma_\omega(t)$ is the field of electromagnetic wave with a frequency ω. Within the adiabatic approximation the density distribution of the metallic electrons near the surface can be expanded in a series:

$$n(z,t)=n_0(z)+\frac{E_{em}(t)}{4\pi}n_1(z)+\left[\frac{E_{em}(t)}{4\pi}\right]^2 n_2(z)+\cdots\ , \tag{6}$$

where

$$n_1=\left.\frac{dn}{d\sigma_\omega}\right|_{\sigma_\omega=0}=\frac{dn_0(z,\sigma)}{d\sigma}\ ,$$
$$n_2=\left.\frac{1}{2}\frac{d^2n}{d\sigma_\omega^2}\right|_{\sigma_\omega=0}=\frac{1}{2}\frac{d^2n_0(z,\sigma)}{d\sigma^2}\ . \tag{7}$$

Here $n_0(z,\sigma)$ is the ground-state electron density as a function of the coordinate z, normal to the surface, for a given surface charge density σ. The parameter $a(\omega)$ has been expressed in terms of $n_2(z)$ as[3,4]

$$a(\omega)\simeq a=4n_+\int_{-\infty}^{\infty}dz\int_{-\infty}^{z}dz'n_2(z',\sigma)\ , \tag{8}$$

where n_+ is the bulk electron density of the metal.

Using the definition of the center of mass of the excess charge distribution,

$$z_\sigma=-\frac{1}{\sigma}\int_{-\infty}^{\infty}dz[n(z;\sigma)-n(z;\sigma=0)]z\ , \tag{9}$$

it is easy to show that the formula (8) is equivalent to a more transparent expression of the form

$$a=2n_+\left[2\frac{dz_\sigma}{d\sigma}+\sigma\frac{d^2z_\sigma}{d\sigma^2}\right]\ . \tag{10}$$

The density $n(z;\sigma)$ has to be found from a variational calculation subject to an adopted form of the energy functional $E[n(z;\sigma)]$; thereby one can calculate z_σ and $a(\sigma)$. Unlike Refs. 3 and 4 we shall apply the trail function version of the variational procedure. We shall use a simple one-parameter trial function which is known to provide a very reasonable description of the system response to the charging of the surface:[6]

$$n(z;\sigma)=n_+\begin{cases}1-\frac{1}{2}e^{\beta(z-\bar{z})}\ , & z\le\bar{z}\\ \frac{1}{2}e^{-\beta(z-\bar{z})}\ , & z>\bar{z}\ ,\end{cases} \tag{11}$$

$$\bar{z}=-(\sigma+\sigma_\omega)/n_+\ . \tag{12}$$

The metal ionic background occupies here, by definition , the half-space $z<0$. Substitution of this expression into the given electron density functional allows us, after the energy minimization, to determine the true value of the variational parameter β as a function of $(\sigma+\sigma_{\omega})$.

Once we adopt the trial function Eq. (11), then

$$z_{\sigma}=\bar{z}/2+n_{+}[\beta^{-2}(\sigma=0)-\beta^{-2}]/\sigma$$

and Eq. (10) reduces to

$$a=-4n_{+}^{2}\left[3\frac{\beta'^{2}}{\beta^{4}}-\frac{\beta''}{\beta^{3}}\right]-2\ , \tag{13}$$

where $\beta'\equiv d\beta/d\sigma$, $\beta''=d\beta^{2}/d\sigma^{2}$. Thus the problem of the SH signal is reduced to an evaluation of $\beta(\sigma)$ and its first two derivatives. The constant -2 appears due to the condition of net charge conservation implied by the form of the trial function (11) and (12).

In a broad interval of charge values the expansion

$$z_{\sigma}\simeq z_{0}+p\sigma+r\sigma^{2} \tag{14}$$

reproduced fairly well the form of z_{σ} as obtained from the variational values of $\beta(\sigma)$.[14] Here $p\,(<0)$ and $r\,(>0)$ are functions of n_{+} only. Analytical expressions for $p(n_{+})$ and $r(n_{+})$ were obtained in Ref. 14 subject to a standard form of the kinetic-exchange-correlation-energy functional. These expressions were used to tabulate p and r for all "free-electron" metals.

The substitution of the "parabolic" approximation (14) into Eq. (10) gives

$$a\simeq 4n_{+}(p+3r\sigma)\ . \tag{15}$$

It is interesting to compare the values of a predicted by Eq. (15) with the results of the Khon-Sham calculation.[3,5] The latter are available only for $\sigma=0$. Thus, we have to limit this comparison to the value of $a(\sigma=0)$ for which we come to an exact relation

$$a(\sigma=0)=4n_{+}p\ . \tag{16}$$

In Table I we compare the results of calculation of Weber and Liebsch[3] using the local-density approximation (LDA) and the values of p parameter obtained by Dzhavakhidze, Kornyshev, and Tsitsuashvili.[14] We, thus, see that an extremely simple Eq. (15), viz., the trial function approach, gives the results for $a(\sigma=0)$ which are in qualitative agreement with more involved Kohn-Sham calculations, particularly in the range of intermediate densities. A somewhat larger difference for large and small r_s values is not unexpected. For large r_s it is due to the usual inefficiency of the one-parameter trail functions which neglect the Friedel oscillation. At small r_s the discrepancy can be attributed to the asymmetry of the electronic profile which is not taken into account in this paper. Results obtained at $r_s=2$ using three-parameter jellium trial functions[15] (which simulate the asymmetry of profile) almost coincide with the Kohn-Sham LDA results for the parameter p.

TABLE I. $-a(\sigma=0)$ for different metals (all quantities in a.u.).

$r_s=(\frac{4}{3}\pi n_{+})^{-1/3}$	2	3	4	5
LDA[a]	28.4	12.9	8.6	6.6
Eq. (16) (with p from Ref. 14)	17.7	14.1	8.35	4.4

[a] M. Weber and A. Liebsch, Phys. Rev. B **35**, 7411 (1987).

It should also be noted that three-parameter trial function calculations are in good agreement with the Kohn-Sham results for large negative charges.[15] They demonstrate a very steep rise of z_{σ}, a sign of approaching the field emission regime. This is not observed within the one-parameter approximation. Actually, in the case of three-parameter function the form of the energy surface as a function of these parameters reflects the system instability at large negative charges. We do not have it for one-parameter functions. Thus the use of a one-parameter trial function can lead to inaccuracies for large negative values of charge σ, while at moderate and positive σ it works fairly well.

B. Metal-electrolyte interface

In the case of SHG from the metal-electrolyte interface we usually deal with metals of intermediate densities. So, the estimates of the preceding section encourage us to treat $a(\sigma)$ for the electrochemical interface in the same manner, i.e., using the simple one-parameter trial function approach.

How does the parameter a change when the metal is immersed into solution? As long as the nonlinear optical polarizabilities of the solvent and ions are neglected,[2] the influence of the medium is manifested through its effect on the surface electronic profile.

It should be stressed that the characteristic frequencies of the motions of the medium particles are much slower than the optical frequencies. Therefore, the field $E_{\omega}(t)$ cannot affect the positions and orientations of the medium particles which depend only on the static charge of the electrode σ.

The parameter a can then be described by the same Eq. (10) [or (13)] as in the vacuum case. However, the parameter of the surface electronic profile $\beta(\sigma)$ (or z_{σ}) should now be calculated accounting for the metal-medium interaction. Furthermore, there is another very important difference. By definition of n_1 and n_2 we deal with the derivatives over $d\sigma_{\omega}$. We thus must keep in mind that at the metal-medium interface the derivatives over $d\sigma_{\omega}$ and $d\sigma$ in the calculation of β' and β'' (or z'_{σ} and z''_{σ}) may be different. Indeed, the medium degrees of freedom can respond only to $d\sigma$ but they are too slow to rate on $d\sigma_{\omega}$.

In order to calculate $\beta(\sigma+\sigma_{\omega})$ we shall apply a jellium model of the interface (Fig. 1). In this model, the metal is represented by a half-space with homogeneous charge density n_{+}. The medium is described by a half-space $z>l$, characterized by its static dielectric constant ϵ and the repulsive pseudopotential which contributes to the system energy:

$$E_{\rm rep}=D\int_{l}^{\infty}dz\,n(z)\ , \tag{17}$$

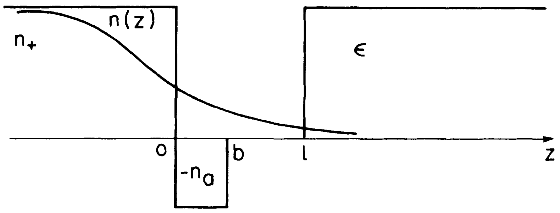

FIG. 1. The "profile" of the metal-electrolyte interface. $z < 0$, metal ionic background with the bulk charge density n_+; $n(z)$, the distribution of the s-p electrons of the metal; $z > l$, solvent with the effective dielectric constant ϵ; $0 < z < b$, adsorption layer with charge density $-n_a$.

where D is the pseudopotential constant.[9] The "gap" l corresponds to the distance of closest approach of the solvent to the edge of the metal ionic background which is generally nonzero due to a repulsion of the closed shells of solvent molecules from the electronic tail of the metal. Of course, the value of l is determined by the overall metal-medium interaction which includes the electrostatic attraction, pseudopotential repulsion, van der Waals attraction, etc. The dependence of l on σ was a subject of a number of theoretical and experimental evaluations.[8-10,16-18] In the earlier papers the distance of closest approach was denoted by a (Refs. 8-10) (an "occupied" symbol in the SHG context) or d.[18]

A brief comment about the value of ϵ follows. Near the boundary with the metal the effective values of ϵ may be considerably smaller than the bulk value. This may happen either due to spatial dispersion effects, local inhomogeneity, or dielectric saturation.[6] Note that just a short range of distances is of relevance for self-consistent solution of the surface electronic profile problem. Therefore, in our numerical calculations we shall vary this parameter in order to study the sensitivity of the SH signal to the local dielectric properties of the solvent.

In this paper we shall make no attempts to calculate $l(\sigma)$ self-consistently. Using all the preceding experience[8-10,16-18] we shall approximate $l(\sigma)$ in order to represent its main features by a minimum number of parameters. Varying these parameters later, we shall be able to explore the role of interfacial relaxation in SH signals.

The approximation to be used is

$$l = (A_0 - A_1\sigma - A_2\sigma^2)\Theta(A_0 - A_1\sigma - A_2\sigma^2) \ . \tag{18}$$

The parabolic form with $A_0 > 0$, $A_1 > 0$, and $A_2 > 0$ simulates the two main effects determining the interfacial relaxation.[6]

(i) Due to repulsion between the hard cores of solvent molecules and the surface electronic profile, the distance of the closest approach is established at a plane which corresponds to a certain value of the electron density. With negative charging the profile is spread out from the metal, and thus l moves from the skeleton edge; by the same reason with positive charging l relaxes towards the electrode.

(ii) An overall contraction of a "flexible capacitor" with charging occurs.

The first of these effects is asymmetric ($\sim\sigma$) with charge while the second one is symmetric ($\sim\sigma^2$). A typical $l(\sigma)$ curve is plotted in Fig. 2.

Figure 1 also accounts for the possibility of adsorption of ions, say anions. In this case we shall assume that when $l > b$, the gap thickness $l(\sigma)$ follows the adsorption-free behavior [Eq. (18)]; when $l(\sigma)$ reaches $b(\sigma)$ it then follows $b(\sigma)$, i.e., the solvent immediately contacts the adsorption layer.

We shall consider the adsorption of anions induced by the electrode polarization:[11]

$$n_a(\sigma) = -\gamma \frac{\sigma - \sigma_0}{\bar{b}} \Theta(\sigma - \sigma_0) \ , \tag{19}$$

$$b = \bar{b} \frac{|n_a(\sigma)|}{\bar{n}_a} \ . \tag{20}$$

Here σ_0 is the value of the charge at which the adsorption of anions starts; $\bar{b}$ and $-\bar{n}_a$ stand for the "thickness" and electron density of the full adsorbate monolayer; γ is the parameter which characterizes the "magnitude" of the "field-induced" adsorption. One may, of course, consider more complicated dependences of adsorption isotherms on the charge of the electrode. However, at sufficiently small $(\sigma - \sigma_0)$, they all can be reduced to such a linear expansion. We consider it as a reasonable start for the simulation of the effect of the field-induced adsorption in SHG.

Substitution of the trial function (11) into the electron density functional with standard kinetic-exchange-correlation terms gives an equation on the variational parameter β:

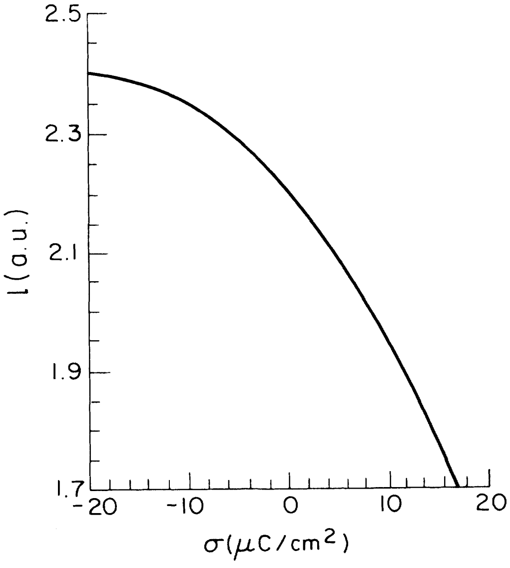

FIG. 2. The plot of $l(\sigma)$ [Eq. (18)] ($A_0 = 2.2$, $A_1 = 114$, $A_2 = 16\,345$ a.u.).

$$\frac{n_+\ln 2}{72}\beta^4-Q\beta^2+\pi n_+\left[\left(\frac{1}{\epsilon}-1\right)[4\bar{z}\beta-\tfrac{1}{2}(l-\bar{z})\beta e^{-\beta(l-\bar{z})}+2(l-\bar{z})\bar{z}\beta^2-\tfrac{3}{4}e^{-\beta(l-\bar{z})}]e^{-\beta(l-\bar{z})}\right.$$
$$+\Theta(-\sigma)[6e^{-\beta\bar{z}}-7.5+2\bar{z}\beta(e^{-\beta\bar{z}}+4)]+\Theta(\sigma)(6e^{\beta\bar{z}}-7.5-2\bar{z}\beta e^{\beta\bar{z}})$$
$$\left.+\Theta(\sigma-\sigma_0)2\frac{n_a}{n_+}\{e^{-\beta(b-\bar{z})}[3+(b-\bar{z})\beta]+e^{\beta\bar{z}}(\beta\bar{z}-3)\}\right]$$
$$-\tfrac{1}{2}\beta^2 Dn_+[\beta(l-\bar{z})+1]e^{-\beta(l-\bar{z})}=0\ . \qquad (21)$$

In this equation

$$\bar{z}=\frac{n_a(\sigma)}{n_+}b-\frac{\sigma+\sigma_\omega}{n_+} \qquad (22)$$

and

$$Q=-\tfrac{3}{10}(3\pi^2)^{2/3}0.572n_+^{5/3}+\tfrac{3}{4}(3/\pi)^{1/3}0.339n_+^{4/3}-0.056n_+\left[1.762k^2-0.39k+\frac{0.435k^2-0.205k}{1+k^2}\right.$$
$$\left.-3k^3\ln\left[\frac{k+0.794}{k}\right]-\frac{3k^6}{1+k^3}\ln\left[\frac{k+0.794}{k+1}\right]\right]\ , \qquad (23)$$
$$k=\frac{0.794}{n_+^{1/3}}\ .$$

Due to the adiabatic arguments given above, of all the parameters in Eq. (21), $(\bar{z},l,n_a,b)$, only $\bar{z}$ is a function of σ_ω while l, n_a, and b depend only on σ. Therefore when calculating the derivatives figuring in Eq. (13), $d\beta/d\sigma_\omega|_{\sigma_\omega=0}$ and $d^2\beta/d\sigma_\omega^2|_{\sigma_\omega=0}$, which we obtain by differentiation of Eq. (21) over $d\sigma_\omega$, one should keep in mind that only β and $\bar{z}$ are subject to such differentiation.

IV. RESULTS FOR $a(\sigma)$

A. Electrochemical interface with no specific adsorption of ions

Let us study the $a(\sigma)$ dependence for different values of system parameters ϵ, D, $l(\sigma)$, and n_+. The results will be compared with $a(\sigma)$ calculated for the metal-vacuum case ($\epsilon=1$, $D=0$). Note that drawing the "metal-vacuum" $a(\sigma)$ curve is a formal action: for a free metal surface it is experimentally impossible to reach such high values of σ at plane surfaces.

In the consideration of interfacial relaxation we will apply the parabolic approximation (18) with $A_0=2.2$ a.u., $A_1=114$ a.u., and $A_2=16\,345$ a.u. It is expected that the parabolic shape is typical for metals without solvent chemisorption (the case of strong chemisorption corresponds to $A_1=A_2=0$). However, the particular values of parameters vary with a system. The order of magnitude of the chosen values of A_0, A_1, and A_2 is typical for the self-consistent calculations[9,17] and evaluations based on linear optical reflection measurements[10] or capacitance data.[8] In no way would we insist on these values, but we need some values to demonstrate the role of interfacial relaxation in the formation of the SHG signal. These ones will be enough demonstrative.

Figure 3 shows the medium effect on the surface electronic profile decay length β^{-1}. We see that apart from the range of very large positive charges the presence of the medium strongly increases the steepness of the profile. The weak effect for large anodic polarizations is obvious: the profile is mostly hidden into the metal half-space and only a negligible portion of the tale is in contact with the solvent. Another very important feature seen from these curves: β increases remarkably, with the increase of ϵ in the range of $1<\epsilon<5$, but further changes

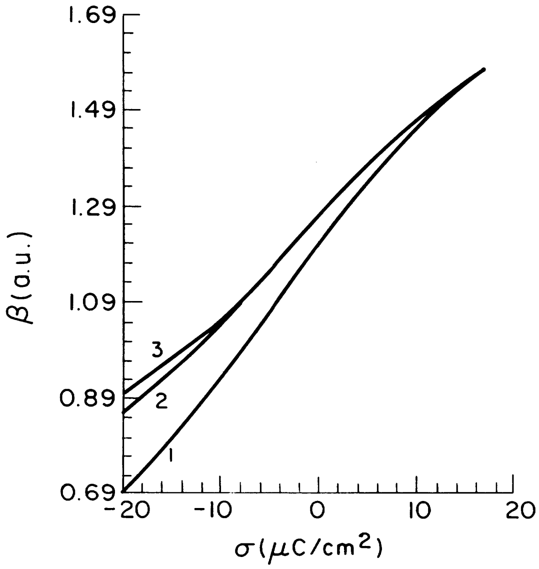

FIG. 3. The effect of solvent dielectric constant on $\beta(\sigma)$ in the presence of interfacial relaxation [$n_+=0.873\times10^{-2}$ a.u. ($r_s=3$)]. 1, Metal vacuum ($\epsilon=1$, $D=0$); 2,3, $D=0.03$ a.u., A_0, A_1, and A_2 as in Fig. 2. 2, $\epsilon=5$; 3, $\epsilon=80$.

of β at large ϵ are of minor importance. A number of alternative electric characteristics suggest that the effective values of ϵ near the interface lie in the range of 5–10,[19,6] but its precise value is poorly known. Thus, we are very lucky to conclude that $\beta(\sigma)$ is strongly affected by the presence of the medium ($\epsilon \geq 5$) but is not too sensitive to the particular local dielectric properties near the electrode. According to Eq. (13) these features will be revealed in $a(\sigma)$ as well.[20]

Figure 4 demonstrates the influence of the medium on $a(\sigma)$. We see that in the presence of the medium $a(\sigma)$ dependence becomes relatively weaker than in the metal-vacuum case; $|a(\sigma)|$ becomes much smaller. Again, this difference disappears in the range of large positive charges due to a negligible overlap between the electronic tail and the medium. The results of the numerical simulations also show that at negative charges the influence of the medium on $a(\sigma)$ is essential until the gap thickness $l = 5$ Å.

Interfacial relaxation [$l(\sigma)$ dependence] appears to be not too important: there is no drastic difference between the curves for $A_1 = A_2 = 0$ and $A_1, A_2 \neq 0$. This is understandable. Indeed, in the range of positive charges only a small portion of the electronic profile is in the medium. Thus, the variation of $l(\sigma)$ in this range has a small effect on $\beta(\sigma)$, and thereby on $a(\sigma)$. For negative charges, the profile is smeared out into the medium but the variation of $l(\sigma)$ here is centered around its maximum and, thereby, the $l(\sigma)$ dependence appears not be essential itself. Therefore, the resulting $\beta(\sigma)$ and $a(\sigma)$ do not show a strong dependence on interfacial relaxation. Consequently, SHG could be expected to be less sensitive to the interfacial relaxation than the phenomena directly concerned with $l(\sigma)$ dependence (like capacitance[8] or s-polarized electroreflectance[10]).

Figure 5 explores the influence of the intensity of the repulsive pseudopotential D. With an increase of D the $|a(\sigma)|$ is diminished. This is easy to understand. With D increasing, the electronic profile is pushed back toward the metal, it becomes more compact, and its polarizability decreases.

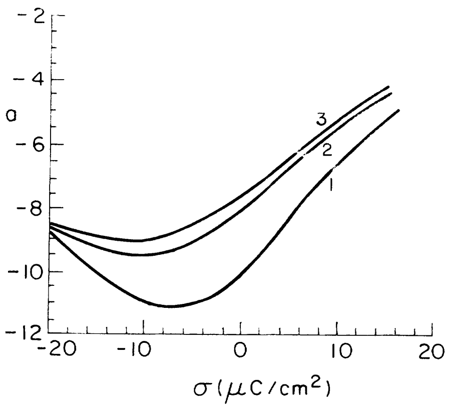

FIG. 5. The effect of pseudopotential repulsion on $a(\sigma)$. n_+ and A_0, A_1, and A_2 are the same as in Fig. 3; $\epsilon=5$. 1, $D=0$; 2, $D=0.03$ a.u.; 3, $D=0.04$ a.u.

The dependence $a(\sigma)$ on the bulk electron density of the metal is shown in Fig. 6. It is dominated not by changes of the profile polarizablity but by a trivial variation of the factor n_+^2 in Eq. (13) [or n_+ in Eqs. (10) or (15)]. The opposite variation of the profile liability coefficients [p,r, Eq. (15)], though incapable of changing the overall increase of $|a|$ with increase in n_+, still weakens this increase to some extent. The degree of the compensation depends on the value of the charge.

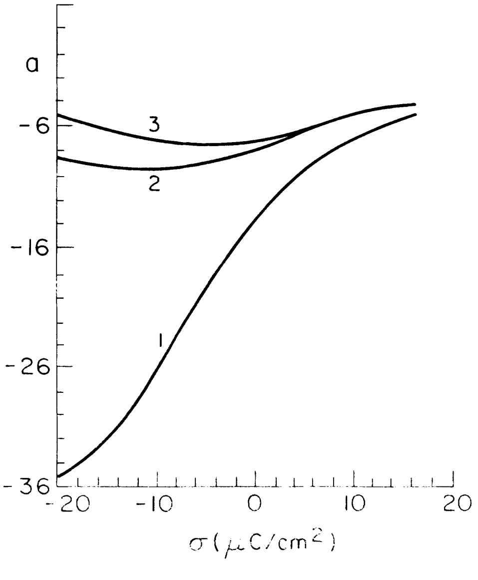

FIG. 4. The effect of solvent dielectric constant on $a(\sigma)$ (nomenclature of the curves is the same as in Fig. 3).

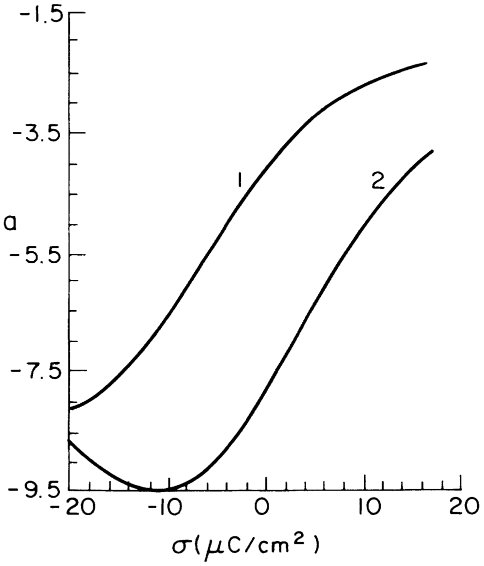

FIG. 6. $a(\sigma)$ and the bulk electron density of the metal. D, A_0, A_1, and A_2 are the same as in Fig. 3; $\epsilon=5$. 1, $r_s=4$; 2, $r_s=3$.

B. The electrochemical interface with the field-induced adsorption of anions

The model of the field-induced adsorption discussed here allows us to obtain the family of $a(\sigma)$ curves for different parameters γ. Figure 7 demonstrates that adsorption of anions increases the rise of $a(\sigma)$ in positive charge range ($\sigma > \sigma_0 = 5\ \mu C/cm^2$) where it occurs. With the increase of the charge density of the adsorption layer $-n_a$, the electronic profile is pushed back toward the metal and its polarizability decreases. We see that the effect of adsorption on the profile polarizability is stronger than the effect of the double layer charging. If this prediction were experimentally approved, it could then be used as an indication of adsorption.

Using the $a(\sigma)$ dependencies obtained and Eq. (1), we can find experimentally measurable intensity of the reflected SH. In Fig. 8(a) we display the results of numerical calculations for the SH intensity as a function of electrode charge σ. Curve 1 in Fig. 8(a) corresponds to the bare metal surface without adsorption ($\gamma = 0$) and curve 2 corresponds to the case of field induced adsorption on the surface ($\gamma = 10$). Both curves are very unsymmetrical with respect to the point of zero charge. In the cathodic range SH intensity is small and practically independent of the charge but it grows sharply in the anodic range. In the case of the field-induced adsorption the position of the bending point is determined by the value of the critical charge σ_0 at which adsorption starts.

The predicted behavior of the SH intensity is in line with the one observed[21] for silver polycrystals and singlecrystals in contact with different electrolytes [see Fig. 8(b)]. The position of the bend points depends on the nature of the adsorbate qualitatively in the same way as one would obtain by variation of σ_0. The required direction of σ_0 variation is in accordance with the views of electrochemists[21,22] on the set of the potentials of adsorption of SO_4^-, Cl^-, and I^-. The important features of the experimental results seems to be well reproduced by this theory. The observable behavior of the SH signal is the result of the interference of the charge dependent and charge independent sources of the nonlinear polarization.

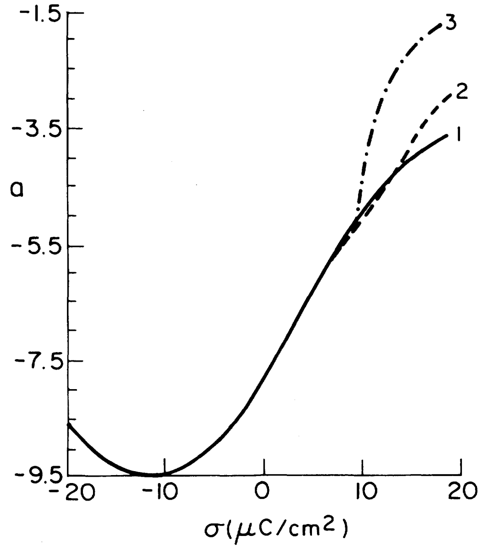

FIG. 7. The influence of the charge-induced adsorption of anions on $a(\sigma)$ ($n_+ = 0.873 \times 10^{-2}$ a.u., $\epsilon = 5$, $D = 0.03$, $\sigma_0 = 5\ \mu C/cm^2$). 1, $\gamma = 0$ (no adsorption); 2, $\gamma = 5$; 3, $\gamma = 10$.

V. CONCLUDING REMARKS

We suggested a theory of SHG at the metal-electrolyte interface, giving a number of predictions concerning the signal dependence on the nature of the metal and on the metal interaction with the bounding medium. The strong effect of the medium obtained shows a difference between the *ex situ* and *in situ* measurements.

In our theory we did not take into account explicitly the effect of reorientations in the first layer of solvent molecules with the variation of the charge σ. However, we made sure that any change of the effective dielectric constant of the medium in the range between 5 and 80 does not give rise to remarkable changes of the signal.

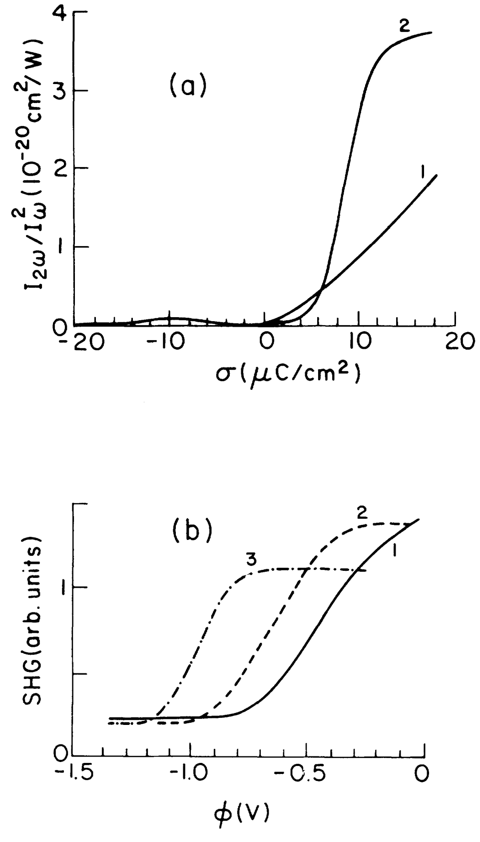

FIG. 8. (a) The dependence of $I_{2\omega}/I_\omega^2$ on the surface charge density σ for silver electrode ($n_+ = 0.873 \times 10^{-2}$ a.u., $\epsilon = 5$, $D = 0.03$ a.u., A_0, A_1, and A_2 are the same as in Fig. 2, $\sigma_0 = 0$, $\hbar\omega = 1.17$ eV), the incident angle of light θ is 45°. 1, $\gamma = 0$ (no adsorption); 2, $\gamma = 10$. (b) SH intensity plotted against the potential drop ϕ (vs saturated calomel electrode) for silver polycristalline electrodes in 0.1 *M* aqueous solutions of 1, K_2SO_4; 2, KCL; 3, KI; $\theta = 45°$. From Ref. 21.

Thus the nonlinear response of the solvent to the field of the charged electrode, which influences the effective values of ϵ near the electrode but cannot make them smaller than the intramolecular degrees of freedom value $\epsilon \simeq 5$ is likely to be unimportant in the SH signal.

In situ measurements of the SH normalized intensity [Eq. (1)] are still insufficient to extract data on $a(\sigma)$. Indeed, the overall intensity [Eq. (1)] is very sensitive to both the angle of incidence and the bulk optical constants. Thus, for unambiguous extraction of parameter $a(\sigma)$ from experimental data one needs accurate measurements of angular dependence of the SH signals which are now a subject of intensive investigations.[23] We hope that the predictions of the present paper will stimulate progress in this direction.

ACKNOWLEDGMENTS

The authors wish to thank Professor Abdus Salam, IAEA, and UNESCO for arranging our stay at the International Center for Theoretical Physics, where part of this joint work was performed. They also appreciate useful discussions with Professor Bill Schaich and Dr. M. B. Partenskii. One of us (A.L.) is thankful to Professor V. E. Kazarinov for arranging a visit to the Frumkin Institute, which helped advance this project.

---

[*] To whom correspondence should be addressed.

[1] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984); Nature **337**, 519 (1989).

[2] C. L. Richmond, I. M. Robinson, and V. L. Shannon, Prog. Surf. Sci. **28**, 1 (1988); Electrochim. Acta **34**, 1639 (1989).

[3] M. Weber and A. Liebsch, Phys. Rev. B **35**, 7411 (1987).

[4] A. Chizmeshya and E. Zaremba, Phys. Rev. B **37**, 2805 (1988).

[5] A. Liebsch and W. L. Schaich, Phys. Rev. B **40**, 5401 (1989).

[6] A. A. Kornyshev, in *The Chemical Physics of Solvation*, edited by R. R. Dogonadze, E. Kalman, A. A. Kornyshev, and J. Ulstrup (Elsevier, Amsterdam, 1988), Vol. C, p. 355; Electrochim. Acta **34**, 1829 (1989).

[7] A. M. Brodsky, L. I. Daikhin, and M. I. Urbakh, J. Electroanal. Chem. **171**, 1 (1984).

[8] A. A. Kornyshev and M. A. Vorotyntsev, J. Electroanal. Chem. **167**, 1 (1984).

[9] V. I. Feldman, A. A. Kornyshev, and M. B. Partenskii, Solid State Commun. **53**, 157 (1985).

[10] A. A. Kornyshev and M. I. Urbakh, J. Electroanal. Chem. **235**, 11 (1987); **257**, 305 (1988).

[11] P. G. Dzhavakhidze, A. A. Kornyshev, A. Tadjeddine, and M. I. Urbakh, Phys. Rev. B **39**, 13 106 (1989); Electrochim. Acta **34**, 1677 (1989).

[12] W. L. Schich and A. Liebsch, Phys. Rev. B **37**, 6187 (1988).

[13] M. Corvi and W. L. Schaich, Phys. Rev. B **33**, 3688 (1986).

[14] P. G. Dzhavakhidze, A. A. Kornyshev, and G. I. Tsituashvili, Solid State Commun. **52**, 401 (1984).

[15] M. Partenskii (private communication).

[16] J. W. Halley, B. Johnson, D. Price, and M. Schwalm, Phys. Rev. B **31**, 7695 (1985).

[17] D. L. Price and J. W. Halley, Phys. Rev. B **38**, 9357 (1988).

[18] S. Amokrane and J.-P. Badiali, Electrochim. Acta **34**, 39 (1989); J. Electroanal. Chem. **266**, 21 (1989).

[19] M. A. Vorotyntsev, in *Modern Aspects of Electrochemistry*, edted by B. E. Conway, R. E. White, and J. O'M. Bockris (Plenum, New York, 1986), Vol. 17, p. 131.

[20] The ϵ dependence of $\beta(\sigma)$ and $a(\sigma)$ in our calculation originates from the electrostatic energy term in the density functional. We made no attempts to account for the ϵ effect on the exchange-correlation energy [first steps in this direction have been recently discussed: M. B. Partenskii (private communication); V. Yu. Izotov, Elektrokhim. **24**, 1650 (1988)].

[21] G. L. Richmond, Langmuir **2**, 132 (1986).

[22] A. Frumkin and O. Petry, Electrochim. Acta **20**, 347 (1970).

[23] P. Guyot-Sionnest, A. Tadjeddine, and A. Liebsch, Phys. Rev. Lett. **64**, 1678 (1990).