

First-principles calculation of the second harmonic response of Ag(111) and Ag(100) surfaces

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In this Brief Report we show first-principles results on the nonlinear optical response of silver surfaces as a function of surface charge. The results are compared with existing ones obtained from the jellium model and experiment.

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Second harmonic generation (SHG) is a useful method for the study of the nonlinear optical properties of matter. For materials with inversion symmetry, such as ordinary liquids and most metals, SHG is forbidden in the bulk in the dipole approximation; so in these systems the observed signal must come from the surface or from an interfacial region. This inherent surface sensitivity makes SHG particularly useful for electrochemical interfaces, for which there are few other *in situ* methods that give information about their electronic properties.

Electrochemical interfaces resulting from the contact between a metal and an electrolyte show a charge distribution consisting of two narrow regions of equal and opposite charges—the electrical double layer. This can be viewed as a capacitor with an extremely small effective plate separation. The magnitude of the surface-charge density σ on the metal can be controlled through the electrode potential ϕ ; these two quantities are related through the differential capacity C per unit area:

$$\sigma = \int_{\phi_{pzc}}^{\phi} C(\phi') d\phi' \quad (1)$$

where ϕ_{pzc} is the potential of zero charge. Therefore, electrochemical interfaces are of special interest for the application of SHG since an additional observable, the surface charge density or, equivalently, the electrode potential, can be varied.

The interpretation of SHG data is not straightforward; this is especially true for the dependence of the signal on the surface-charge density. Therefore, reliable theoretical calculations of the surface properties that govern SHG are of great importance. However, so far there have been very few first-principles calculations of the nonlinear polarizability of metal surfaces, and these have been restricted to uncharged metals in the vacuum (see, e.g., Ref. 1). Therefore, the interpretation of electrochemical SHG experiments has mostly relied on the jellium model, both in its simple form with

a constant positive background charge,²⁻⁴ and in the version with pseudopotentials.⁵ Obviously, it is desirable to have first-principles results for charged surfaces that can validate the results of the simple models.

The SHG signal is composed of several contributions. The most interesting one is the electronic response perpendicular to the metal surface, which depends strongly on the state of the surface, in particular on its surface-charge density. This response can be characterized by the so-called Rudnick and Stern parameter a (Ref. 6). In the long-wavelength limit, in which the surface electrons follow the incident radiation adiabatically, this can be expressed through the variation of the electronic density $n(z, \sigma)$, averaged parallel to the surface:²

$$a = -2\bar{n} \int_{-\infty}^{\infty} z \frac{\partial^2 n(z, \sigma)}{\partial \sigma^2} dz. \quad (2)$$

Here z is the direction perpendicular to the surface, \bar{n} is the average bulk electron density, and σ is the surface-charge density.

In a number of papers^{3,7-9} experimental values for this parameter a have been obtained for Ag(111) and Ag(100) surfaces in contact with aqueous solutions using a standard neodymium-doped yttrium aluminum garnet (Nd:YAG) laser at a frequency of 1.17 eV. This frequency is far below the plasma frequency of silver, so that the long-wavelength approximation holds. In this work we have calculated the dependence of a on the surface-charge density for these two surfaces.

The experimental data for the real part of the coefficient a shown in the present paper have been obtained from relative measurements of the intensity of the SHG signal. The latter contains both an isotropic and an anisotropic contribution, which can be separated by a mathematical analysis. The coefficient a can be obtained from the isotropic part by assuming an appropriate reference value; details of this procedure can be found in the literature.^{7,10}

To model the electronic structure of the surfaces and obtain the electronic density as a function of the surface charge we have used the local density approximation^{11,12} (LDA) to density functional theory.^{13,14} The implementation we have used is based in the iterative minimization of a free energy functional¹⁵ that has the same stationary point as the finite temperature functional of Mermin.¹⁶ The method was used as implemented in the CPMD code.¹⁷ The electron-ion interaction was represented by relativistic Troullier-Martins pseudopotentials.^{18,19} A plane wave basis set with a 60 Ry cutoff was used, which ensures convergence of total energies down to 10^{-3} hartrees. In order to check for the accuracy provided by the basis and the pseudopotential, calculations for bulk silver were performed obtaining a bulk modulus of 1.29 Mbar and a lattice parameter of 4.053 Å, to be compared with the experimental values of 1.04 Mbar and 4.086 Å, respectively.^{20,21} The LDA calculated lattice parameter was used in all further calculations. The agreement with experiment is the usual for the local density approximation giving a slightly smaller lattice constant than experiment and a bulk modulus that is 20–30% higher. For the sake of comparison, using the Perdew-Burke-Ernzerhof generalized gradient approximation,²² we obtain a lattice parameter of 4.196 Å and a bulk modulus of 0.822 Mbar. For the work function, we obtain values of 4.78 and 4.81 eV for the (100) and (111) surfaces, respectively. These are in good agreement with existing theoretical results^{23–25} and the experimental values of 4.64 eV (100) and 4.74 eV (111).²⁰

Surfaces were represented by periodically repeated supercells consisting of a single surface unit cell of nine-layer slabs for (111) surfaces and 11-layer slabs for (100) surfaces. The SHG response is not very sensitive to the thickness of the slab and smaller numbers of layers than what we have used were found to be sufficient in previous studies.⁵ Periodic images on the direction perpendicular to the surface were separated by a vacuum space equivalent to seven metal layers for (111) surfaces and eight metal layers for (100) surfaces. For the sampling of the surface Brillouin zone 12 and 15 \mathbf{k} points in the irreducible wedge were used for (111) and (100) surfaces, respectively. Relaxations of surface atoms were neglected and surfaces were assumed to have the bulk terminated structure. This approximation is justified for the (111) and (100) surfaces of Ag since the relaxation of the outermost planes in this surfaces is known to be very small (less than 2%).^{23,24,26}

In order to deal with charged surfaces within a periodic supercell approach we have used the “charged plane” method developed and implemented in the CPMD code by Lozovoi *et al.*^{27,28} The method relies on the inclusion of a charged plane at the boundary of the cell parallel to the surface; bearing a charge equal in magnitude but of opposite sign to the charge on the slab. Since overall the system (metallic slab plus charged plane) is neutral, only dipole-dipole and higher multipole moment interactions can occur between periodic images in the z direction. The dipole-dipole interaction is avoided by using a symmetric slab with no net dipole moment.

The electron density was obtained for a total of 42 different charges ranging between -0.023 and 0.080 electrons per surface unit cell for each of the surfaces considered. The

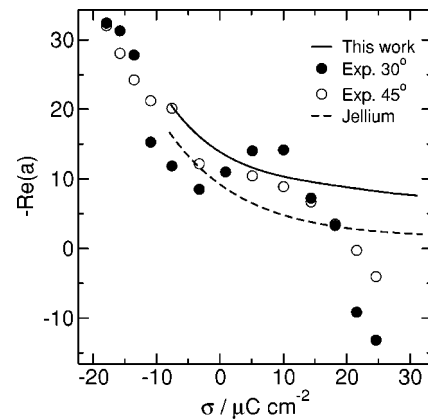


FIG. 1. Comparison of experimental and theoretical data of the real part of the a coefficient for Ag(100). The experimental data are for a 50 mM solution of KClO_4 and two different angles of incidence (Refs. 7 and 8).

range of negative charges that can be achieved is limited by the onset of field emission. For a sufficiently large negative charge the Fermi level of the metal goes above the value of the electrostatic potential at the cell boundary and electrons bind to the charged plane.²⁷ This condition was carefully excluded in the calculations shown here. The three-dimensional electron density was averaged over the surface unit cell in the direction parallel to obtain $n(z_i, \sigma)$ for every grid point z_i . The density at each point was then fitted to a linear combination of Chebyshev polynomials up to degree 6 on the charge density via a least square procedure. Further increasing the degree of the polynomial produced no significant change in the results obtained.³⁶ The derivative $\partial^2 n(z_i, \sigma) / \partial \sigma^2$ was obtained by analytical differentiation of the polynomial at each grid point. The use of orthogonal polynomials is essential to ensure stability of the procedure. The a parameter as a function of charge was then obtained by numerical quadrature of Eq. (2).³⁷

We have extended the results obtained by Leiva *et al.*⁵ using a jellium with pseudopotentials method^{30–32} to a larger charge range using the interpolation procedure described in the preceding paragraph. A comparison of our results using first-principles three-dimensional calculations, the jellium model, and experiment are shown in the figures.

The data for Ag(100) are shown in Fig. 1. The experimental data from Beltramo *et al.*⁸ are for two different angles of incidence; the difference between the two sets of values for a indicates the accuracy of the experiments, since the angle of incidence should affect only the Fresnel coefficients. The two theoretical curves are close and run almost parallel; our calculations give consistently somewhat higher values for $-a$ than jellium. However, within experimental accuracy both agree with the experimental results for surface charges σ less than about $15 \mu\text{C cm}^{-2}$.

The surface of silver becomes oxidized easily in contact with air. In an electrolyte solution the formation of an oxide occurs at sufficiently positive potentials; the onset depends on the pH and on the type of anions present in the solution. In contrast to gold or platinum, it is not possible to electrochemically reduce an oxide film on silver completely. A care-

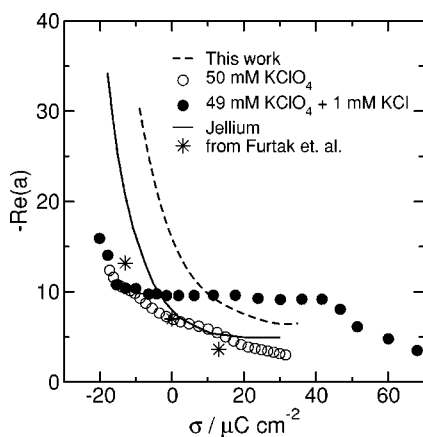


FIG. 2. Comparison of experimental and theoretical data of the real part of the a coefficient for Ag(111). Data from Furtak *et al.* from Ref. 29.

ful treatment before and during the measurements is important. For Ag(111) we have obtained data³³ from experiments where the single crystal was heated under an argon atmosphere in order to eliminate this oxide film. Subsequently, it was transferred to the cell under potential control at a value sufficiently negative to avoid oxidation of the surface. The results are shown in Fig. 2; they do not show the drop in $-a$ near $\sigma = 15 \mu\text{C cm}^{-2}$ found in older data.^{3,7,8} Within experimental accuracy, our data agree with the three values obtained by Furtak *et al.*²⁹ by a reevaluation of the data by Guyot-Sionnest *et al.*³—the latter work contains a small error in the Fresnel coefficients.²⁹ Chloride ions are known to inhibit oxide formation; therefore we have also included data by Beltramo *et al.*¹⁰ for Ag(111) in a Cl^- -containing solution. The authors of this work suggest that up to a charge density of about $42 \mu\text{C cm}^{-2}$ the Cl^- ions are only weakly adsorbed and do not affect the SHG signal, but keep the surface oxide-free. At higher charge densities a phase transition occurs in the adsorbate, and the coefficient $-a$ drops.

Again our first-principles calculations predict somewhat higher values for $-a$ than jellium does. Except for very negative charge densities, both sets of theoretical results agree with the experiments within experimental accuracy. Both our first-principles and the jellium calculations have disregarded the presence of water in the experimental system. The agreement between theory and experiment suggests, that at least in the range $\sigma > -10 \mu\text{C cm}^{-2}$ the presence of water has little effect on the SHG signal. For higher negative excess charges the electronic tail will extend further into the solvent, and may be more strongly affected by its presence. For reasons mentioned above, our calculations do not extend far into that region.

At a first glance, the good agreement between our results and the jellium values seems surprising. The jellium calculations were based on parameters for silver suggested by Amokrane and Badiali.³⁴ They suggested an effective valence of $z=1.5$ for Ag, and fitted the pseudopotential radius such that they obtained good work functions for the most important surface planes. They have thus been optimized to represent the surface properties. A simple application of jellium with a valency of $z=1$ and no pseudopotentials gives values for a that are too high by about a factor of three. Still, it remains a little surprising that a jellium model which has been designed to reflect the work function also gives good values for the second-order polarizability.

In conclusion, we think that a comparison of our calculations with the experimental data is quite encouraging. Our method can easily be extended to adsorbate-covered surfaces, for which simple models like jellium do not exist.

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- ³⁷The average bulk electron density \bar{n} used in Eq. (2) corresponds to 11 electrons per fcc unit cell at the equilibrium lattice parameter obtained from the calculation ($\bar{n}=0.09796$ a.u.). Note that only valence electrons are included explicitly in the calculations.