Second-harmonic generation from alkali-metal overlayers

A. Liebsch

Institut für Festkörperforschung, Kernforschungsanlage, 517 Jülich, West Germany

(Received 19 May 1989)

The frequency dependence of the linear and nonlinear electronic response of alkali-metal over-layers adsorbed on metal surfaces is calculated within the time-dependent density-functional approach. The nonlinear dipole moment which characterizes the perpendicular surface component of the second-harmonic polarization shows a pronounced resonance near $2\omega \approx 0.8\omega_p(\text{ads})$, where $\omega_p(\text{ads})$ is the bulk plasma frequency of the adsorbed alkali metal. This resonance can enhance the second-harmonic intensity by several orders of magnitude. This surface local-field effect might partly explain the huge enhancements that have been observed for optical second-harmonic generation from alkali-metal overlayers on Rh and Ag surfaces.

I. INTRODUCTION

One of the most striking examples of the extreme surface sensitivity of optical second-harmonic generation (SHG) is the adsorption of alkali-metal atoms on metal surfaces.[1,2] Even small amounts of these adsorbates can easily be detected. Full alkali-metal monolayers on Rh (Ref. 1) or Ag (Ref. 2) have been observed to enhance the clean-surface signal by several orders of magnitude. Alkali-metal atoms on transition- and noble-metal surfaces are particularly interesting chemisorption systems because of their great technological relevance. At low coverages, as long as direct overlap of alkali-metal atomiclike electron states is negligible, the observed changes of the SH signal can be qualitatively understood in terms of optical transitions between the hybridization-broadened adatom levels.[1,3] At higher coverages, however, the metallic character of the alkali-metal overlayers becomes important. The question then arises as to how the extended nature of the overlayer states contributes to the observed enhancements of the SH intensity. Using a simple model of an interface between two centrosymmetric systems, Tom *et al.*[1] argued that the SH signal will be enhanced when the effective dielectric function of the interfacial layer goes through a minimum, i.e., when the incident laser frequency corresponds to about one-half of the effective plasma frequency of the interface electrons. Since SHG depends very sensitively on the electronic properties in the surface region, it is clear, however, that a more detailed understanding of the excitation spectrum of adsorbed alkali-metal layers is needed.

In previous work[4,5] on the nonlinear electronic response at simple metal surfaces, we found characteristic spectral features near $2\omega \approx \Phi$ (work function) and $2\omega \approx 0.8\omega_p$ (ω_p is the bulk-plasma frequency). These calculations were carried out within the time-dependent density-functional theory[6–10] and by using the jellium model to represent the positive ions of the semi-infinite metal. The details of the ground-state electron distribution in the surface region, the nonlocality of the electronic response to the incident electromagnetic fields, and the self-consistent screening of the induced surface charges are fully taken into account in this approach. The second-harmonic di-

pole moment obtained from these calculations was recently found to be in excellent agreement with absolute intensity measurements of SHG from Al at 1.17-eV incident laser frequency.[11] The feature near $2\omega \approx 0.8\omega_p$, which becomes a very sharp resonance in the case of the low-density alkali surfaces, is closely related to the well-known local-field enhancement seen near $0.8\omega_p$ in linear response.[12–15] For example, the striking frequency dependence of the photoyield from Al can be quantitatively understood in terms of these linear dynamic surface response properties.[16]

In the present paper, we extend the above calculations in order to determine the linear and nonlinear excitation spectra of alkali-metal monolayers on a metal surface. For simplicity, we represent the positive charges in the overlayer by a homogeneous jellium slab. This model neglects possible interband transitions between the two-dimensional adsorbate states but emphasizes the metallic character of the overlayer. In particular, the electronic hybridization at the substrate-adsorbate interface and the detailed shape of the electron distribution at the adsorbate-vacuum interface are described adequately. Despite its simplicity, this model has been used quite successfully, for example, to explain the dependence of the work function on alkali coverage.[17]

We find that the *linear* excitation spectrum of various alkali-metal monolayers on an Al surface is dominated by a resonance approximately near $0.8\omega_p(\text{ads})$, where $\omega_p(\text{ads})$ is the bulk-plasma frequency of the alkali metal. This resonance has the same origin as the corresponding resonance obtained for the clean simple metal surfaces. The shapes of the density distributions on the clean surfaces and on the absorbate-vacuum surfaces are indeed very similar so that, at low frequencies, similar response properties are to be expected. A second spectral feature in the linear response is seen near $\omega_p(\text{ads})$. However, it is rather broad and tends to be much weaker than the resonance near $0.8\omega_p(\text{ads})$. Apparently, because of the small thickness of the alkali overlayers, alkali-metal bulk plasmons do not represent well-resolved excitations in these systems.

In accordance with the linear excitation near $0.8\omega_p(\text{ads})$, the frequency dependence of the *nonlinear* di-

pole moment which is of interest for SHG, shows a resonance near $0.4\omega_p$(ads). This frequency lies between 1.4 and 2.4 eV for various alkali metals. Since the real part of the nonlinear dipole moment gets large already below this peak in the imaginary part, this resonance can be detected with laser radiation at 1064 nm $= 1.17$ eV. Indeed, we find that at this frequency, the second-harmonic intensity can increase by several orders of magnitude. Thus, even in the absence of interband transitions, the nonlinear response properties of alkali overlayers can give rise to absorbate-induced changes of the SH signal similar to those observed experimentally.[1,2]

II. RESULTS AND DISCUSSION

Let us assume that p-polarized light of frequency ω is incident on a semi-infinite jellium system. The polar angle of incidence with respect to the surface normal is denoted as θ. The generation efficiency of p-polarized second-harmonic reflected output radiation may be expressed as follows:[5,18−21]

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

where

$$P = a(\omega)\frac{\epsilon(\Omega)}{\epsilon(\omega)}\sin^2\theta - b\frac{2s(\omega)s(\Omega)}{\epsilon(\omega)}\cos^2\theta + d/2 , \quad (2)$$

and

$$s(\omega) = [\epsilon(\omega)-\sin^2\theta]^{1/2}/\cos\theta . \quad (3)$$

Here e,m,c are fundamental constants, $\Omega = 2\omega$, and $\epsilon(\omega) = 1 - \omega_p^2/\omega^2$ is the bulk dielectric function with ω_p the bulk plasma frequency.

In a semi-infinite free-electron system, the parameters d and b which characterize the bulk and parallel surface contributions to the harmonic polarization, respectively, have the values $d = 1$ and $b = -1$, independent of frequency.[20] The dimensionless function $a(\omega)$, on the other hand, depends sensitively on the microscopic nonlinear screening properties in the surface region. It is defined in terms of the integrated weight of the normal component of the second-harmonic surface polarization[19−21] and can be expressed in terms of the dipole moment of the nonlinear surface screening charge induced by a uniform electric field normal to the surface and varying in time like $\exp(i\omega t)$:[4,5]

$$a(\omega) = -4\bar{n}\int_{-\infty}^{\infty}dz\, z\delta n_2(z,\omega)/\sigma(\omega)^2 , \quad (4)$$

where $\bar{n}$ is the bulk density and $\sigma(\omega)$ is the integrated first-harmonic–induced surface density:

$$\sigma(\omega) = \int_{-\infty}^{\infty}dz\,\delta n_1(z,\omega) . \quad (5)$$

In Refs. 4 and 5, $a(\omega)$ was calculated for various simple metal surfaces by applying the time-dependent density-functional approach.[6−10] Since the density profile at the surface is of primary interest in these systems, the positive ions are replaced by a semi-infinite homogeneous

background of density $\bar{n}$. In the present work, we extend these calculations to the case of adsorbed alkali-metal monolayers by placing a thin slab of constant positive charge density $\bar{n}$(ads) on top of the positive background of the substrate.[17] Here, $\bar{n}$(ads) is the average bulk density of the alkali metal and the thickness of the slab is taken to be the spacing between the densest lattice planes in the bulk of the alkali metal. Once the positive charges of this adsorbate-substrate system are specified, the electrons adjust themselves self-consistently to the ionic potential and to the applied electric fields.

In Fig. 1 the equilibrium density profile is shown for a Na monolayer $(r_s \approx 4)$ on an Al substrate $[r_s \approx 2$ with $\bar{n} = 3/(4\pi r_s^3)]$. Near the absorbate-vacuum interface the density is almost indistinguishable from the density at a clean Na metal surface. Also, the denser regions of the substrate electron profile (approximately $z < 0$) are very similar to those at the clean Al surface. As a result, the low-frequency electronic excitations of the Na-Al system [typically $\omega < \omega_p$(Na)] should be similar to those of the clean Na surface, while the excitations at higher frequencies will be similar to those at the clean Al surface.

Qualitatively, this behavior is indeed found for various alkali-metal adsorbates as illustrated in Fig. 2. Shown is the frequency dependence of the imaginary part of the normalized linear-induced dipole moment,

$$d(\omega) = \int_{-\infty}^{\infty}dz\, z\delta n_1(z,\omega)/\sigma(\omega) , \quad (6)$$

for three alkali-metal monolayers (Na, K, and Cs) on an Al substrate. Im$d(\omega)$ is proportional to the surface photoabsorption cross section.[12] All three systems exhibit an enhanced absorption near $0.8\omega_p \approx 13$ eV which is also present in the case of the clean surface. It corresponds to the well-known local-field enhancement observed in photoyield measurements on Al.[16]

A second, more pronounced spectral feature is found near $(0.7-0.8)\omega_p$(ads). While these peaks have about the same height as the resonances near $0.8\omega_p$ on the clean alkali-metal surfaces,[12−15] they are considerably broader.
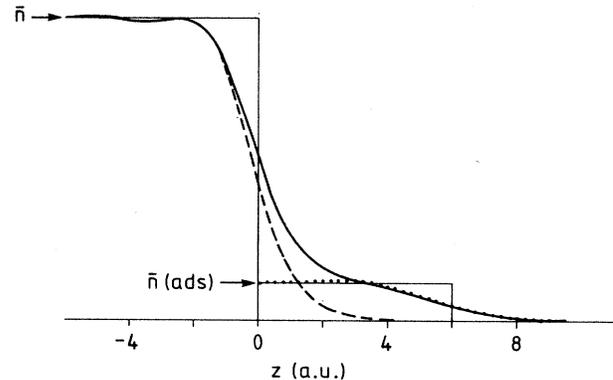

FIG. 1. Equilibrium electron density profile for the Na monolayer on the Al substrate (solid line). The positive ionic charges of the substrate and adsorbate are modeled by constant backgrounds of height $\bar{n}$ and $\bar{n}$(ads), respectively. The electronic density profiles of the clean Al and Na surfaces are indicated by the dashed and dotted lines, respectively.
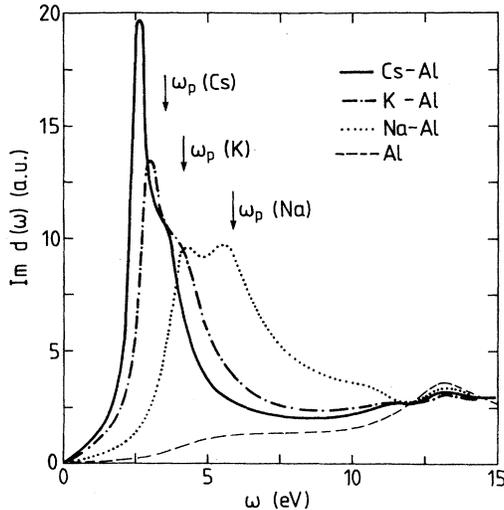
FIG. 2. Frequency dependence of the imaginary part of the normalized first-harmonic dipole moment $d(\omega)$, Eq. (6), for various alkali-metal monolayers on Al, calculated within the time-dependent density-functional approach. The spectrum of the clean Al surface is also shown (dashed line). The arrows denote the bulk-plasma frequencies of the alkali metals.

As in the case of the clean simple metal surfaces, the strength of these peaks gets larger with decreasing alkali-metal density because the surface density profile becomes more diffuse.

In addition, all three adsorption systems exhibit a spectral feature close to the bulk-plasma frequency of the alkali metal. Only in the case of the Na-Al system does this feature appear as a separate peak. For the lower-density alkali adsorbates, it merely forms a shoulder on the more prominent resonance near $(0.7-0.8)\omega_p(\text{ads})$. These results demonstrate that in the long-wavelength limit, bulk plasmons are not well-resolved electronic excitations in chemisorbed alkali-metal monolayers on Al. The excitation spectra of these systems are dominated by the local-field enhancement at the absorbate-vacuum interface.

The first-harmonic excitation spectra of the clean simple metal surfaces also show that $\text{Im}d(\omega)$ increases near the threshold for electron emission.[13-15] However, the bulk-plasma frequency of the low-density metals decreases relative to the work function. As a result, the rise at threshold becomes only a weak shoulder on the low-energy side of the resonance near $0.8\omega_p$. The work functions of the alkali-metal–Al systems are also too close to the resonance near $(0.7-0.8)\omega_p(\text{ads})$ so that the increase of $\text{Im}d(\omega)$ at threshold cannot be resolved.

We point out here that the spectra in Fig. 2 are in qualitative agreement with photoemission measurements from adsorbed Na layers on Cu.[22] Within the jellium model, partial coverages are equivalent to lower average densities in the overlayer. Thus, apart from slight differences in overlayer thickness, the K $(r_s \approx 5)$ and Cs $(r_s \approx 5.6)$ spectra in Fig. 2 correspond to Na $(r_s \approx 4)$ spectra at $(\frac{4}{5})^3 = 0.51$ and $(\frac{4}{5.6})^3 = 0.36$ coverage, respectively. As a consequence, upon Na evaporation on a surface, the absorption cross section at a fixed photon energy of about 5

eV rises monotonically until monolayer coverage is reached, whereas at about 4 eV it goes through a maximum as observed experimentally.[22]

The local-field enhancement shown in Fig. 2 for the linear-response properties of the alkali-metal adsorbates is of direct relevance for the second-harmonic response of these systems, as illustrated in Fig. 3. The imaginary part of $a(\omega)$ shows a pronounced resonance just below $0.4\omega_p(\text{ads})$, i.e., when two photons approach the resonance in linear response below $0.8\omega_p(\text{ads})$. This resonance is much stronger than on the clean simple metal surfaces for the following reason: The quantity $\bar{n}$ in the definition of $a(\omega)$, Eq. (4), refers to the average electron density deep inside the system which determines, via the bulk-plasma frequency, the asymptotic electric field in the interior. Thus, for the alkali-metal overlayers, this quantity is enhanced by the ratio $\bar{n}(\text{Al})/\bar{n}(\text{ads})$, as compared to the clean alkali-metal surfaces. For the adsorption systems shown in Fig. 3, this ratio has the values 8 (Na-Al), 16 (K-Al), and 22 (Cs-Al). The static values of $a(\omega)$ of these systems are also enhanced by about these ratios if compared to the clean surface values.[23]

At the laser frequency of 1.17 eV, $a(\omega)$ has the values (see dots in Fig. 3) $a = -132 - 24i$ (Na-Al), $a = -400 - 175i$ (K-Al), and $a = -800 - 715i$ (Cs-Al). For clean Al, the value at this frequency is $a = -36 - 9i$.[5] Since the parameters b and d in Eq. (2) remain unchanged upon adsorption of a monolayer, we can easily calculate that ratio of second-harmonic intensities with and without adsorbates. For example, for incident and reflected p-polarized light at $\theta = 60°$ we obtain from Eq. (1), and using experimental data[24] for the Al dielectric function $I_{2\omega}(\text{ads})/I_{2\omega}(\text{Al}) \approx 17$, 195, and 1200 for adsorbed Na, K, and Cs, respectively. Thus, the local-field enhancement at the adsorbate-vacuum interface can cause an increase of the SH signal by several orders of magnitude.
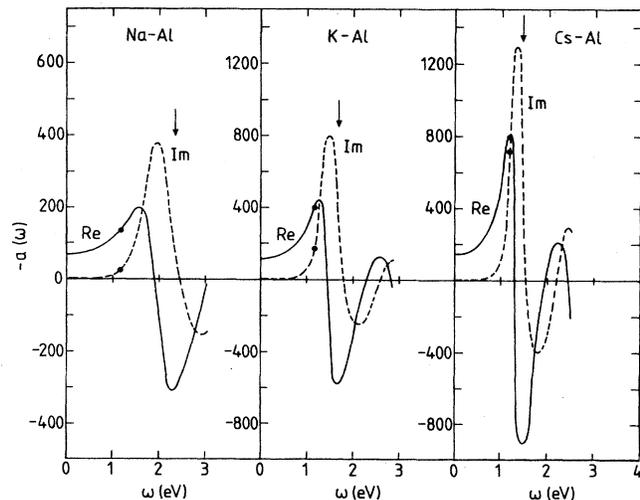

FIG. 3. Frequency dependence of the normalized second-harmonic dipole moment $a(\omega)$, Eq. (4), for various alkali-metal monolayers on Al. The arrows indicate the frequency $0.4\omega_p(\text{ads})$. The dots denote the values of $a(\omega)$ at the laser frequency 1.17 eV.

As pointed out above, within the jellium model partial coverages correspond to lower average densities in the overlayer. Thus, stronger enhancements could be obtained for the Na-Al system at less than a full monolayer. It should be kept in mind, however, that this model is not valid at too-small coverages and that the local density approximation breaks down at very low densities.

It is obvious from Fig. 3 that the SH signal depends sensitively on the wavelength of the incident radiation. For example, at 2.34 eV the nonlinear dipole moment has the values $a = +310 - 100i$ (Na-Al), $a = -30 + 200i$ (K-Al), $a = -200 - 180i$ (Cs-Al), and $a = -16 - 51i$ for clean Al.[5] At $\theta = 60°$, one therefore gets the intensity ratios $I_{2\omega}(\text{ads})/I_{2\omega}(\text{Al}) \approx 40$, 15, and 25 for adsorbed Na, K, and Cs, respectively. Thus, with the exception of Na-Al, the enhancement tends to be less pronounced than at 1.17 eV. A similar trend is observed on Rh (Ref. 1) and Ag (Ref. 2). However, at 2.34 eV the SH signal is much more substrate sensitive since 2ω lies close to or above the alkali-metal bulk-plasma frequency. Our results for alkali-metal adsorption on Al are therefore not applicable to these substrates.

In summary, optical second-harmonic generation is very sensitive to the response properties of the electron profile in the surface region. Even without considering interband transitions, the resonances in the surface excitation spectra of adsorbed alkali-metal monolayers can lead to enormous nonlinear dipole moments which determine the size and frequency dependence of the perpendicular surface contribution to the second-harmonic polarization. It would be of great interest to perform SHG measurements for alkali overlayers on Al in order to test the predictions of the calculations presented above.

[1] H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, Y. R. Shen, and G. A. Somorjai, Surf. Sci. **172**, 466 (1986).

[2] K. J. Song, D. Heskett, H. L. Dai, A. Liebsch, and E. W. Plummer, Phys. Rev. Lett. **61**, 1380 (1988).

[3] B. N. J. Persson and L. H. Dubois, Phys. Rev. B **39**, 8220 (1989).

[4] A. Liebsch, Phys. Rev. Lett. **61**, 1233 (1988); **61**, 1897(E) (1988).

[5] A. Liebsch and W. L. Schaich, Phys. Rev. B (to be published).

[6] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).

[7] M. J. Stott and E. Zaremba, Phys. Rev. A **21**, 12 (1980).

[8] G. D. Mahan, Phys. Rev. A **22**, 1780 (1980).

[9] A. Zangwill, J. Chem. Phys. **78**, 5926 (1983).

[10] G. Senatore and K. R. Subbaswamy, Phys. Rev. A **35**, 2440 (1987).

[11] R. Murphy, M. Yeganeh, K. J. Song, and E. W. Plummer, Bull. Am. Phys. Soc. **34**, 837 (1989); Phys. Rev. Lett. **63**, 318 (1989).

[12] P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).

[13] A. Liebsch, Phys. Rev. B **36**, 7378 (1987).

[14] K. Kempa and W. L. Schaich, Phys. Rev. B **37**, 6711 (1988).

[15] K. Kempa, A. Liebsch, and W. L. Schaich, Phys. Rev. B **38**, 12645 (1988).

[16] H. Levinson, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **43**, 952 (1979); H. Levinson and E. W. Plummer, Phys. Rev. B **24**, 628 (1981).

[17] N. D. Lang, Phys. Rev. B **4**, 4234 (1971).

[18] N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).

[19] J. Rudnick and E. A. Stern, Phys. Rev. B **4**, 4272 (1971).

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

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

[22] L. Walldén, Phys. Rev. Lett. **54**, 943 (1985).

[23] M. Weber and A. Liebsch, Phys. Rev. B **35**, 4711 (1987); **36**, 6411 (1987).

[24] E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, Phys. Rev. B **22**, 1612 (1980).