

## Adsorbate-induced nonlocal corrections to Fresnel optics: Optical reflectivity of Cs overlayers on Ag

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The electronic excitation spectra of Cs overlayers on Ag are calculated with use of the time-dependent density-functional approach. These spectra are found to undergo characteristic changes as the coverage increases from 0.5 to 2.0 monolayers. The nonlocal corrections to the Fresnel optics obtained from these spectra are in qualitative agreement with reflectivity measurements for *p*- and *s*-polarized light.

### I. INTRODUCTION

Recent photoelectric yield measurements from cesiated Ag surfaces<sup>1</sup> gave strong indications of an enhancement of the normal component of the local electromagnetic field at the adsorbate-vacuum interface. The spectra show a broad feature at about 0.8 of the measured bulk plasma frequency of Cs. The energy position of this peak suggests that the mechanism for the observed enhancement might be closely related to that at clean simple metal surfaces which show an absorption peak near 0.8 of the bulk plasma frequency almost independently of the bulk electronic density.<sup>2-4</sup> Previous photoemission intensity measurements for Na overlayers on Cu were also interpreted in terms of a local-field enhancement at the adsorbate-vacuum interface.<sup>5</sup> Moreover, it has recently been shown<sup>6</sup> that the enormous increase of the second-harmonic intensity observed for alkali-metal adsorbates<sup>7,8</sup> might be partly caused by enhanced local fields at the overlayer-vacuum interface.

These data raise several interesting questions concerning the dynamic response properties of adsorbed alkali-metal layers. At which coverage does the excitation spectrum of an alkali-metal overlayer begin to resemble that of a semi-infinite alkali metal? What are the excitation mechanisms at smaller coverages? When do alkali-metal bulk plasmons begin to form well-defined excitations in the overlayer? In order to study the electronic excitations of adsorbed alkali-metal layers more systematically, we have performed reflectivity measurements for Cs overlayers on Ag at various coverages. We have also carried out microscopic density-functional calculations in order to analyze these spectra and to determine the dependency of the excitation processes on the overlayer coverage.

Our theoretical results suggest three distinct mechanisms for enhanced absorption of light as a result of Cs adsorption on Ag: At half-monolayer coverage, the excitation spectrum shows a single feature near the threshold for emission; at a full monolayer, the spectrum is dominated by a peak near 0.8 of the Cs bulk plasma frequency which is caused by the local-field enhancement at the adsorbate-vacuum interface; finally, at two monolayers, two features are seen which correspond to the local-field enhancement at the adsorbate-vacuum interface and to the excitation of a bulk plasmon in the Cs double layer. The experimental reflectivity data at these three Cs coverages are in qualitative agreement with these results. Thus, the adsorbate electronic excitations are found to be strongly coverage dependent and to be considerably more complex than the simple local-optics model would predict. In this model, adsorbate-induced absorption of light occurs only near the plasma frequency of the overlayer.<sup>9</sup>

### II. EXPERIMENT

The experiments have been performed in ultrahigh vacuum (pressure  $< 5 \times 10^{-11}$  Torr) with polycrystalline Ag surfaces made of an ensemble of microcrystals each presenting a well-defined (111) surface. These surfaces were prepared by depositing Ag films (about  $10^3$  Å thick) on fused silica substrates. The Cs coverages were determined by measuring the photoemission yield assuming that the minimum value of the work function occurs at a coverage of one-half monolayer. In order to adsorb several monolayers of Cs, the sample holder was cooled to 77 K. Cs was deposited at a rate of about one monolayer every 20 min. The reflectivity of the sample at an angle of incidence of  $\theta = 45^\circ$  was measured before and after Cs adsorption with a double-beam spectrophotome-

ter. The photoemission yield measurements, which were performed simultaneously with the reflectivity measurements, gave the following photoemission thresholds: 1.8, 2.03, and 2.15 eV at  $c=0.5$ , 1, and 2, respectively.

The experimental results for the  $p$ - and  $s$ -polarized reflectivity changes caused by the adsorption of Cs,  $\Delta R_p$ , and  $\Delta R_s$ , are shown in Fig. 1. [ $\Delta R_{p,s} \equiv R_{p,s}^0 - R_{p,s}^1$ , where  $R_{p,s}^0$  ( $R_{p,s}^1$ ) is the reflectivity of the clean (cesiated) Ag

surface.]  $\Delta R_s$  is seen to give a small featureless background that is independent of the Cs coverage. Thus, this contribution seems to be caused by imperfections of the clean Ag surface (note the weak excitation of Ag surface plasmons at  $\omega=3.65$  eV) and by bulk absorption processes. A similar contribution is presumably also present for  $p$ -polarized light.

In contrast to  $R_s$ , the  $p$ -polarized reflectivity is found

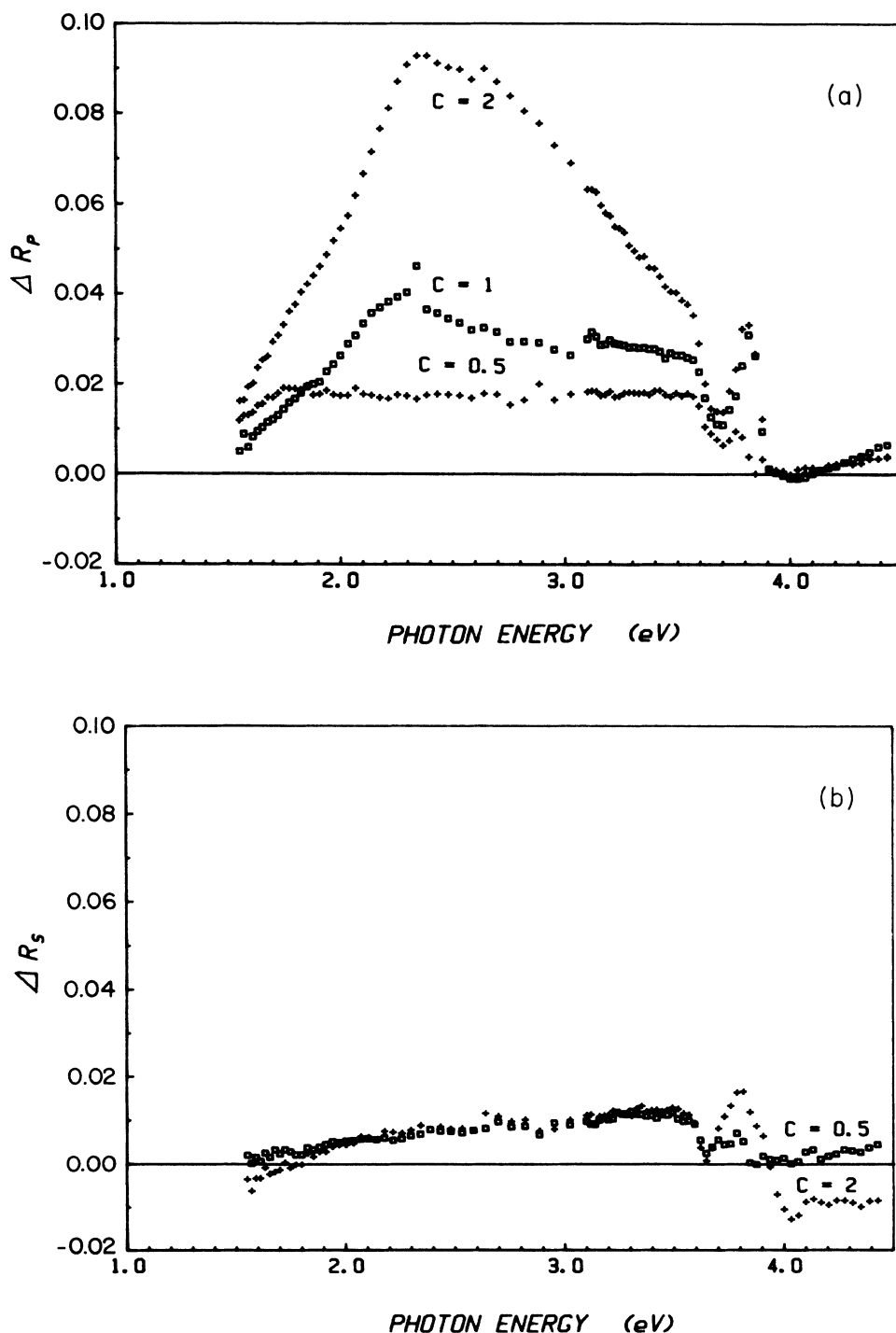


FIG. 1. Measured adsorbate-induced change of reflectivity of (a)  $p$ -polarized and (b)  $s$ -polarized light for three Cs coverages on Ag.

to be strongly coverage dependent. At  $c=0.5$ , a smooth background is observed. If a distribution similar to  $\Delta R_s$  were to be subtracted from this spectrum, the remaining part of  $\Delta R_p$  would show a weak maximum at about 1.8 eV, i.e., close to the work function of the system. At  $c=1$ ,  $\Delta R_p$  is larger and the maximum is shifted to about 2.3 eV, which agrees well with 0.8 of the experimental bulk plasma frequency of Cs (2.9 eV).<sup>10</sup> Finally, at  $c=2$ ,  $\Delta R_p$  becomes even larger and broader. In fact, this spectrum seems to consist of two features: one at about 2.3 eV and a second one in the range from 2.6 to 3.0 eV. Because of deviations from the perfect doublelayer geometry, the upper peak most likely consists of a series of plasmonlike excitations at slightly different frequencies. Like  $\Delta R_s$ , all three spectra of  $\Delta R_p$  show a structure related to the excitation of Ag surface plasmons at 3.65 eV, indicating that the Ag surface is not perfectly smooth.

### III. THEORY

Corrections to the standard Fresnel reflection amplitudes may arise due to the diffuseness of the electron density near the surface and the nonlocal nature of the electronic response to the electromagnetic fields.<sup>2,11-13</sup> These corrections are conveniently described within the so-called  $d$ -parameter formalism.<sup>2</sup> For example, the reflection amplitudes for  $p$ - and  $s$ -polarized light incident from the vacuum are given by the expressions

$$r_p = \frac{\epsilon(\omega) - q'_\perp/q_\perp + i[\epsilon(\omega) - 1][d_\perp(\omega)q_\parallel^2/q_\perp - d_\parallel(\omega)q'_\perp]}{\epsilon(\omega) + q'_\perp/q_\perp - i[\epsilon(\omega) - 1][d_\perp(\omega)q_\parallel^2/q_\perp + d_\parallel(\omega)q'_\perp]}, \quad (1)$$

$$r_s = \frac{1 - q'_\perp/q_\perp + i[\epsilon(\omega) - 1]d_\parallel(\omega)(\omega/c)^2/q_\perp}{1 + q'_\perp/q_\perp + i[\epsilon(\omega) - 1]d_\parallel(\omega)(\omega/c)^2/q_\perp}, \quad (2)$$

where  $\epsilon(\omega)$  is the bulk dielectric function,  $q_\parallel = (\omega/c)\sin\theta$ ,  $q_\perp = (\omega/c)\cos\theta$ , and  $q'_\perp = (\omega/c)[\epsilon(\omega) - \sin^2\theta]^{1/2}$  with  $\theta$  the angle of incidence and  $c$  the speed of light. In the case of a semi-infinite system with translational invariance parallel to the surface,  $d_\perp(\omega)$  is given by the centroid of the surface charge induced by a uniform electric field normal to the surface:<sup>2</sup>

$$d_\perp(\omega) = \int dz z \delta n(z, \omega) / \int dz \delta n(z, \omega). \quad (3)$$

The other  $d$  function,  $d_\parallel(\omega)$ , will be specified below.

In the following, we discuss the electronic response of a homogeneous overlayer on a semi-infinite metal. For simplicity, we treat both adsorbate and substrate within the jellium model, i.e., the positive ions of the adsorbate are represented by a thin slab of uniform density corresponding to the average density  $n_a$  of the bulk alkali metal. The width  $a$  of the slab for a full monolayer is taken to be the spacing of the most densely packed atomic planes of the bulk material. Thus, the ionic density is assumed to have the profile

$$n_+(z) = \begin{cases} n_b, & z \leq 0 \\ n_a, & 0 < z \leq a \\ 0, & a < z, \end{cases} \quad (4)$$

where  $n_b$  is the bulk density. This model neglects possible interband transitions between the two-dimensional adsorbate bands but emphasizes the metallic character of the overlayer. Despite its simplicity, this model has been used successfully to explain the dependence of the work function on alkali-metal coverage.<sup>14</sup>

Since the surface excitation spectra are known to depend rather sensitively on the details of the electron distribution, we use the time-dependent density-functional approach<sup>15</sup> to calculate the function  $d_\perp(\omega)$ . This scheme treats the ground-state electronic properties in a realistic fashion. In particular, the detailed shape of the electron distribution at the adsorbate-vacuum interface and the hybridization between substrate and adsorbate states are computed self-consistently. This approach also take into account the self-consistently screened, nonlocal response to the perturbing time-dependent fields. For clean Al, the closely related random-phase-approximation (RPA) response approach<sup>2</sup> gave an excellent description of the local field enhancement observed in Al surface photoemission spectra.<sup>16</sup> Within the model outlined above, the second  $d$  function appearing in Eqs. (1) and (2) is given by the constant<sup>17</sup>

$$d_\parallel(\omega) = a n_a / n_b. \quad (5)$$

Figure 2 shows the ground-state electron densities for three Cs overlayers on a semi-infinite substrate ( $r_s=3$ ) whose average density corresponds to the free-electron density of Ag. The shape of the density is seen to depend rather strongly on the adsorbate coverage  $c$ : at one-half monolayer, the Cs electrons essentially amplify the tail of the substrate density. At  $c=1$ , two separate substrate-adsorbate and adsorbate-vacuum interfaces can be

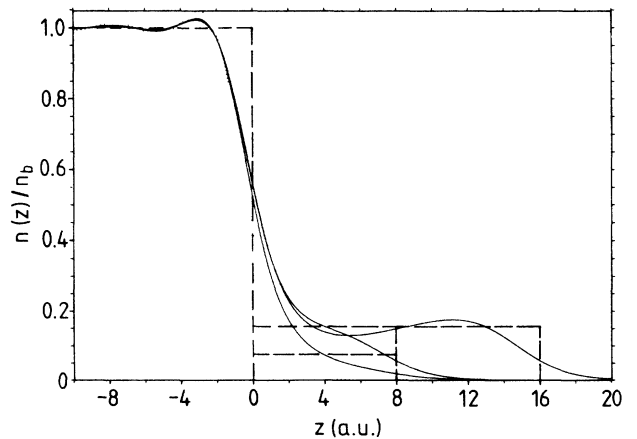


FIG. 2. Ground-state electron distributions for Cs overlayers on Ag at coverages  $c=\frac{1}{2}$ ,  $c=1$ , and  $c=2$ . The density of the clean Ag surface is shown by the dotted line. The profiles of the positive ionic charge distributions are indicated by the dashed lines.

identified; this monolayer, however, is too thin to give a region of constant Cs density. At  $c=2$ , finally, the adsorbate-vacuum interface is almost identical to the clean Cs surface and the overlayer is sufficiently thick to give a region of approximately constant Cs density.

As a result of the different electron distributions, these Cs overlayers have also rather different excitation properties. This is illustrated in Fig. 3 where the quantity  $\text{Im}d_{\perp}(\omega)$  is shown as a function of frequency. At  $c=\frac{1}{2}$ , the spectrum exhibits a peak near the threshold for emission (at this coverage the work function is reduced to  $\Phi=1.8$  eV; for the clean surface,  $\Phi=3.5$  eV in our model). This feature is reminiscent of the increased absorption at threshold that is also found in dynamical response calculations for clean simple-metal surfaces.<sup>3,4</sup> The origin of this enhancement is most likely related to the fact that the density of unoccupied states increases as the photon energy approaches the work function. An additional increase of the absorption due to the self-consistent screening response might also play a role. An analogous feature is obtained at full monolayer coverage as shown in Fig. 3(b). However, in this case, the computed value of the work function ( $\Phi=2.6$  eV) is very close to the local field enhancement expected near  $0.8\omega_p(\text{Cs})=2.85$  eV so that it is not possible to distinguish between these two mechanisms. At the plasma frequency of Cs (the theoretical value is 3.56 eV),  $d_{\perp}(\omega)$  shows only a weak shoulder. Apparently, a monolayer is not sufficiently thick to sustain a well-defined bulk plasma oscillation. This result is in accordance with the density shown in Fig. 2 which for  $c=1$  does not show a plateaulike region of Cs bulk density.

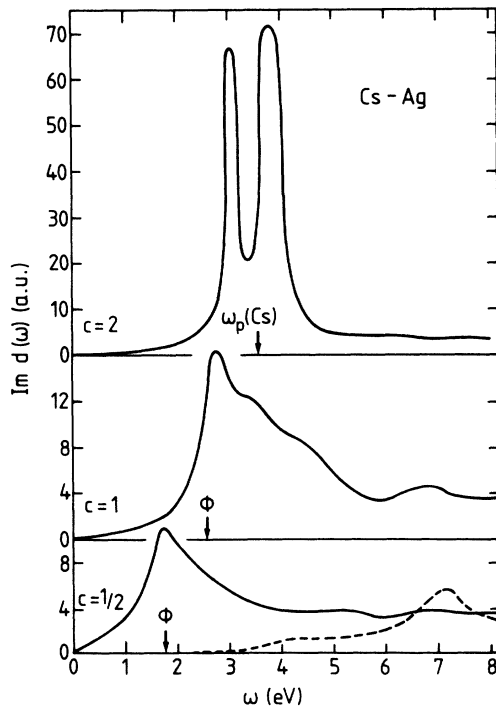


FIG. 3. Spectral distributions of  $\text{Im}d_{\perp}$  for the three Cs overlayers on Ag specified in Fig. 2. The dotted line denotes the corresponding function for the clean Ag surface (Ref. 3). The arrows indicate the work functions.

ty. For a Cs double layer, on the other hand, a strong peak is obtained near  $\omega_p(\text{Cs})$  in addition to the pronounced local-field enhancement near  $0.8\omega_p(\text{Cs})$ . For  $c \leq 1$ , a weak structure is also seen near  $0.8\omega_p(\text{Ag})$  as a result of the local-field enhancement at the overlayer-substrate interface.

We point out here that these results differ quite strongly from analogous random-phase approximation (RPA)-type response calculations for Na overlayers on Al which were modeled by a double-step surface barrier potential.<sup>18,19</sup> Neither the absorption near the threshold for emission nor the local-field enhancement at  $0.8\omega_p(\text{Na})$  are obtained in these models. Only an absorption peak just above the Na bulk plasmon is found. In fact, the predictions of this model are surprisingly similar to those of the local-optics model for which the  $d$  functions are determined by the simple formula<sup>9</sup>

$$d_{\perp}(\omega) - d_{\parallel}(\omega) = a \frac{\epsilon(\omega) - \epsilon_a(\omega)}{\epsilon(\omega) - 1} \frac{\epsilon_a(\omega) - 1}{\epsilon_a(\omega)}, \quad (6)$$

where  $\epsilon_a(\omega)$  is the local dielectric function of the overlayer. In this model, the only spectral feature is related to the vanishing of  $\epsilon_a(\omega)$ , i.e., to the "bulk" plasmon of the adsorbate regardless of the thickness  $a$ . It is clear, therefore, that for a detailed description of the excitation spectra of adsorbed overlayers, it is crucial to use self-consistently calculated electronic density profiles.

The magnitude of the nonlocal corrections to the Fresnel amplitudes introduced by the functions  $d_{\perp}(\omega)$  and  $d_{\parallel}(\omega)$  is roughly determined by the ratio between the effective surface thickness and the wavelength of the radiation, i.e., they are typically of the order of a few percent. Thus, in order to understand the effect of the Cs overlayers on the reflectivity, it is useful to expand  $r_p$  and  $r_s$  about the local-optics limit for the clean surface:<sup>20</sup>

$$r_p = r_p^F (1 + 2iq_{\perp} D_{\perp}), \quad (7)$$

$$r_s = r_s^F (1 - 2iq_{\perp} d_{\parallel}), \quad (8)$$

where  $r_p^F$  and  $r_s^F$  are obtained from Eqs. (1) and (2) by setting  $d_{\perp} = d_{\parallel} = 0$  and  $D_{\perp}$  is defined as

$$D_{\perp} \equiv (d_{\perp} - d_{\parallel}) \frac{\epsilon(\omega)}{\epsilon(\omega) \cot^2 \theta - 1} - d_{\parallel}. \quad (9)$$

Denoting the clean-surface quantities by the index 0 and those of the cesiated surface by the index 1, we obtain to lowest order the following expressions for the change of the reflectivity due to adsorption:

$$\Delta R_p = |r_p^0|^2 - |r_p^1|^2 = |r_p^F|^2 4q_{\perp} \text{Im}(D_{\perp}^1 - D_{\perp}^0), \quad (10)$$

$$\Delta R_s = |r_s^0|^2 - |r_s^1|^2 = |r_s^F|^2 4q_{\perp} \text{Im}(d_{\parallel}^0 - d_{\parallel}^1). \quad (11)$$

In the present model,  $d_{\parallel}$  is real, so that  $\Delta R_s = 0$ , i.e., the overlayer does not modify the reflectivity of  $s$ -polarized light. On the other hand, according to Eq. (9), the reflectivity of  $p$ -polarized light is essentially determined by the difference  $\text{Im}[d_{\perp}^1(\omega) - d_{\perp}^0(\omega)]$ . {At  $\theta=45^\circ$ , the factor  $\epsilon(\omega)/[\epsilon(\omega)-1]$  appearing in (9) is nearly real for Ag at frequencies below the interband onset.} Moreover, since the clean surface spectral function  $\text{Im}d_{\perp}^0(\omega)$  is small and featureless at low  $\omega$ ,<sup>3</sup> the frequency dependence of  $\Delta R_p$  is approximately proportional to the function

$\text{Im}d_{\perp}^1(\omega)$ , i.e., to the long-wavelength electronic excitation spectrum shown in Fig. 3.

#### IV. COMPARISON WITH EXPERIMENT

The effect that the Cs overlayers have on the reflectivity of  $p$ -polarized light from a Ag surface is shown in Fig. 4. Plotted is the change  $\Delta R_p$  as calculated from Eq. (1) for  $\theta=45^\circ$ . The measured dielectric function of Ag (Ref. 21) is used and we take  $d_{\perp}^0(\omega)$  for the clean substrate from our previous response calculations for jellium surfaces.<sup>3</sup> In this case,  $d_{\parallel}^0=0$ . In accordance with the spectra shown in Fig. 3, we obtain for  $c=\frac{1}{2}$  a relatively flat distribution for  $\Delta R_p$  with a weak maximum near  $\omega \approx \Phi$ . For  $c=1$ , this maximum shifts to higher frequencies as a result of the local field enhancement at  $0.8\omega_p(\text{Cs})$  and because of the larger work function. Finally, for  $c=2$ , the maximum shifts even higher because of the excitation of Cs bulk plasmons in addition to the local field enhancement at the adsorbate-vacuum interface. We have phenomenologically broadened the spectrum for  $c=2$  in order to simulate the fact that the Ag surface as well as the Cs overlayers in the experiment are not perfectly smooth; the observed spectral features should therefore be much less sharp than the peaks shown in Fig. 3(c). At smaller coverages, this broadening has little effect. We also point out that, since the calculations do not include the effect of interband transitions and core polarization, the theoretical bulk plasma frequency of Cs (3.56 eV) is considerably higher than the measured value (2.9 eV).<sup>10</sup> For the purpose of comparing with experimental spectra, the frequencies of the calculated spectra should therefore be scaled down by about 20%.

Qualitatively, these spectra show a similar variation with Cs coverage as the experimental spectra for  $\Delta R_p$  shown in Fig. 1(a). The overall increase in weight and the gradual shift of the main feature to higher frequencies as the coverage is changed from 0.5 to 2.0 are well reproduced by the density-functional calculations. Thus, at half-monolayer coverage, the main excitation mechanism seems to be the enhanced absorption near threshold which, of course, is not observable in photoemission ex-

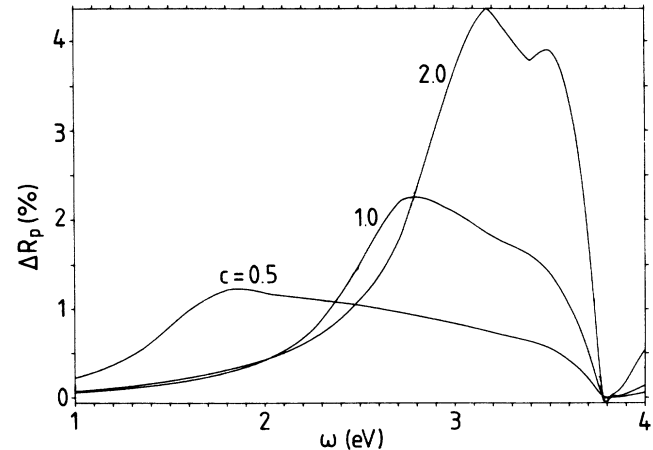


FIG. 4. Theoretical adsorbate-induced change of reflectivity of  $p$ -polarized light for the three Cs overlayers on Ag specified in Fig. 2.

periments. Neither the local-field enhancement at  $0.8\omega_p(\text{Cs})$  nor Cs bulk plasmon excitation play any role at this low coverage. At one monolayer, the enhancement at  $0.8\omega_p(\text{Cs})$  provides the dominant absorption mechanism. For a Cs doublelayer, on the other hand, the very broad spectrum seen in Fig. 1(a) appears to have two contributions: in the lower frequency range ( $\leq 2.5$  eV) the absorption is caused by the local-field enhancement at the Cs-vacuum interface, whereas at higher frequencies, Cs bulk plasmons provide an efficient excitation mechanism.

On the quantitative level, two main differences are found. First, as pointed out above, all the calculated frequencies are too high as a result of our use of the jellium model. Second, the magnitudes of the measured functions  $\Delta R_p$  are about twice as large as the calculated reflectivity changes. Since  $\Delta R_p$  is roughly proportional to the excitation spectrum of the overlayer, this discrepancy could imply that other processes such as damping via electron scattering and interband transitions, which are not included in our theory, also play an important role.

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