



SURFACE PLASMON EFFECTS ON THE OPTICAL REFLECTIVITY OF ADSORBED MOLECULAR MULTILAYERS

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We calculate the change in optical reflectivity due to the presence of thin films formed by a few layers adsorbed in a metal using a discrete point-dipole model, and we compare our results with those of the usual Fresnel theory. We find a considerable enhancement of the differential reflectance near the surface-plasmon resonance frequency of the vacuum-metal interface. In the case of *p*-polarization, the contributions coming from the images of molecules lying closer to the metal can be singled out if the angle of incidence is chosen to be the Brewster angle of the vacuum overlayer interface.

In recent years the study of the behavior of adsorbed species on metallic substrates has been stimulated by a vast amount of new experimental results using different kinds of spectroscopies such as Raman scattering, fluorescence, inelastic electron scattering and reflectance in the infrared and optical regions.¹ The main advantage of the optical techniques is that they are non-destructive and do not require a high-vacuum environment. In particular reflectometry and ellipsometry² can provide valuable information on the electronic structure and the geometrical arrangement³ of adsorbed species. A simple model frequently employed, first proposed by Drude,⁴ represents a physisorbed material by a continuous thin film with bulk optical constants. From here on we shall refer to this simple model as the continuous model. More sophisticated models which take into consideration the discrete nature of the adsorbates show that the contributions of the dipolar local fields are particularly important at electronic^{5,6} or vibrational⁷ resonances of the adsorbates. Also dipolar fields have been proved to be significant in the determination of the nonlinear response of adsorbates⁸ and of adsorption sites and molecular orientation of monolayers through reflectance³ and second harmonic generation.⁹

In this article we investigate the influence of the image fields on the optical properties and in particular the reflectivity of surfaces covered by adsorbed multilayers. This problem has been already repeatedly examined;^{8,10-13} however, here we show that the contribution of the image fields can be singled out by choosing angles of incidence near the Brewster angle of the vacuum film

interface, which suggests a way to study optically the first few adsorbed layers of the film.

We proceed first by extending the microscopic calculations of Ref. 5 from one to *N* layers in a similar way to that of Ref. 10. For simplicity, we choose square-lattice layers one on top of each other and in registry. In this case, the polarization of each layer can be obtained through the solution of the following set of linear equations

$$E_0^\gamma = \sum_{J=1}^N \left[\Gamma^{-1} \delta_{IJ} + \frac{1}{2a} (\xi_{IJ} - A \eta_{IJ}) d_J \right] P_J^\gamma, \quad (1)$$

$$E_0^z = \sum_{J=1}^N \left[\Gamma^{-1} \delta_{IJ} - \frac{1}{a} (\xi_{IJ} + A \eta_{IJ}) d_J \right] P_J^z, \quad (2)$$

where *I* and *J* label the layers, *P_J* is the dipole moment per unit volume and *d_J* the width of the *J*-th layer, *a* is the lattice parameter of the square lattice, $\gamma = x, y$, $\Gamma \equiv \alpha/a^3$, α is the isotropic polarizability of each adsorbate, $A = (\epsilon_s - 1)/(\epsilon_s + 1)$ is the strength of the image of a unit point charge, ϵ_s is the local dielectric function of the substrate and \mathbf{E}_0 is the external electric field. Here $\xi_{IJ} = F(z_I - z_J)$ and $\eta_{IJ} = F(z_I + z_J)$ represent the dipolar interaction between the *I*-th and *J*-th layers and between the *I*-th image layer and the *J*-th layer, respectively, where *z_I* is the distance of the *I*-th layer to the metal surface (see inset of Fig. 1) and *F* is a planewise dipolar sum that can be written as the following rapidly convergent series for $z \neq 0$,^{6,14}

$$F(z) = \sum_{i=0}^{\infty} \sum_{j=1}^{\infty} (i^2 + j^2)^{1/2} \times \exp[-(2\pi z/a)(i^2 + j^2)^{1/2}]. \tag{3}$$

The self-interaction of each layer is given by ${}^6\xi_{I,I} = -9.0336$.

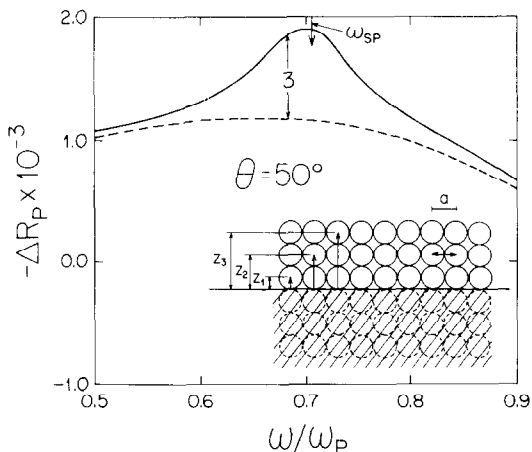
The continuous model appropriate to this system consists of a film of width $d = Na$ characterized by a bulk isotropic dielectric constant ϵ_f related to the normalized polarizability of the adsorbates by the simple Clausius-Mossotti relation

$$\frac{\epsilon_f - 1}{\epsilon_f + 2} = \frac{4}{3}\pi\Gamma \tag{4}$$

which is exact for an infinite cubic lattice.

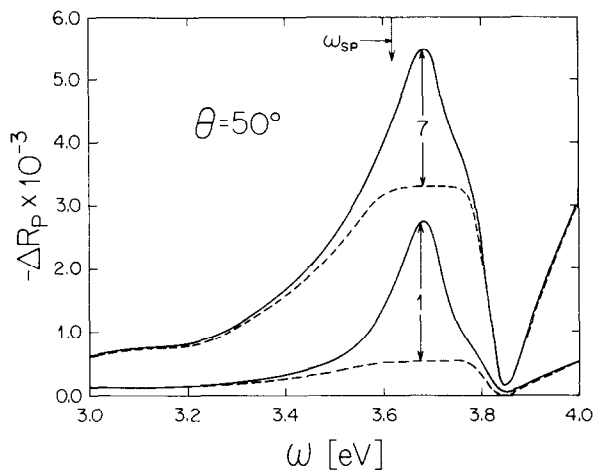
The discrete model can be cast into a continuous one consisting of a film of width- d with an anisotropic dielectric response $\epsilon_x = \epsilon_y = 1 + 4\pi \sum P_j^z / (NE_0^z)$ and $\epsilon_z^{-1} = 1 + 4\pi \sum P_j^z / (NE_0^z)$. Therefore the reflectance R can be obtained immediately using the classical formulae⁶ for a system composed of an anisotropic film on top of a homogeneous substrate. Here we ignore the molecular structure of the substrate. The results are most simply analyzed if we calculate the change in reflectance $\Delta R \equiv R - R_0$ with respect to the reflectance R_0 of the metal vacuum system.

In Fig. 1 we show the changes ΔR of reflectivity for p -polarized light at an angle of incidence $\Theta = 50^\circ$ produced by three layers of CCl_4 adsorbed on a substrate characterized by a Drude dielectric constant ($\omega_p = 10\text{eV}$, $\omega_p\tau = 10$). The density of the adsorbed layers $\rho = 1.59\text{gr/cm}^3$ was assumed to be equal to that of the bulk, yielding $a = 5.43\text{\AA}$ for a cubic array. The

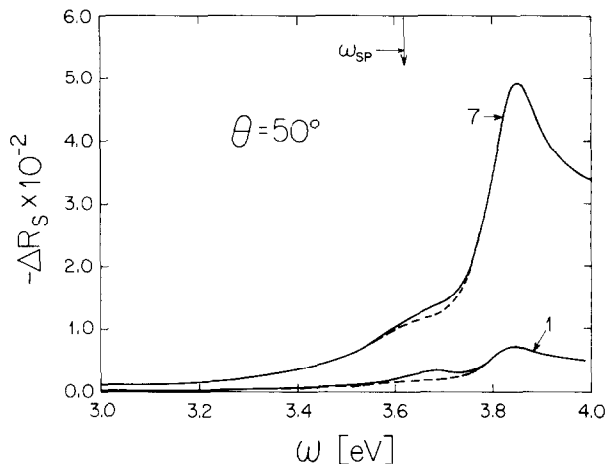


1. Change of reflectance $-\Delta R_p$ as a function of frequency ω for three layers of CCl_4 over a Drude metal as calculated with the continuous (dashed line) and the discrete (solid line) models. The surface plasma frequency ω_{sp} is indicated by a vertical arrow. The inset shows a cubic dipole arrangement of the molecules and their images.

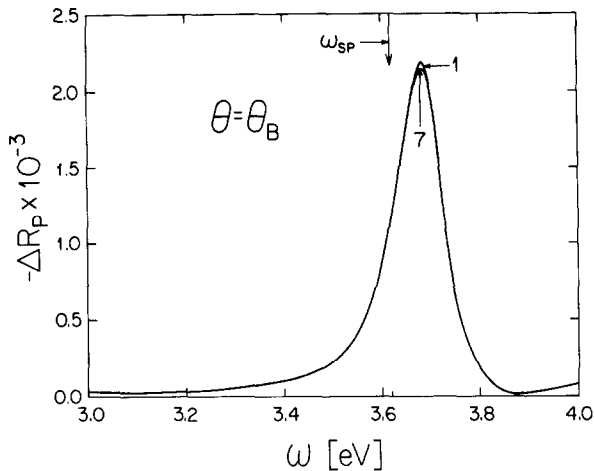
chosen molecular polarizability $\alpha = 10.475\text{\AA}^3$ is obtained from Eq. 4 taking $\epsilon_f = 2.141$ which corresponds to the bulk dielectric constant of CCl_4 in the visible. We chose the distance of the first layer to the surface to be $z_1 = a/2$ as indicated in the inset of Fig. 1. As expected, the discrete result shows a peak near the surface plasmon frequency $\omega_{sp} = \omega_p/\sqrt{2}$ corresponding to an enhancement of the image field. This peak is absent in the continuous model. However, for other frequencies the continuous model and the point-dipole model give similar results. In Figs. 2 and 3 we present the calculated ΔR for CCl_4 on Ag for p and s polarizations, with the same parameters for the adsorbates as in Fig. 1 but for one and seven layers. From these figures similar conclusions to those of Fig. 1 can be drawn, even though the reflectance of the Ag substrate has a richer structure than that described by the Drude model. Besides, we notice two facts; first, that even for one monolayer the macroscopic and microscopic calculation are similar



2. $-\Delta R_p$ vs. ω for one and seven layers of CCl_4 adsorbed over Ag within the continuous (dashed line) and the discrete (solid line) models.



3. Same as Fig. 2 but for s -polarization.



4. Same as in Fig. 3 but at the Brewster angle $\Theta_B = 55.6^\circ$. The continuous model would yield $\Delta R_p = 0$ for this angle.

away from the surface plasma frequency, and second, that the first monolayer is almost solely responsible for the peak near ω_{sp} since the absolute difference between the macroscopic and microscopic curves is almost independent of the number of layers. This is due to the fact that the self interaction η_{II} of the 2D square lattice is near to $8\pi/3$, the self interaction of the full 3D cubic lattice. Although this would not be the case for other 2D geometries, only the first few layers would contribute to the ω_{sp} peak.

Fig. 4 is like Fig. 3, but calculated at the Brewster angle of the vacuum-film interface $\Theta_B = \tan^{-1}(\sqrt{\epsilon_f}) =$

55.6° . From the optical point of view, at this angle the overlayer is nonexistent in the continuous model, and the changes of reflectivity are strictly zero independently of the thickness of the layer. However, the image interaction of the first monolayer with the substrate within the discrete model yields the large peak around the surface plasma frequency shown in Fig. 4. Notice that in contrast with Figs. 2 and 3, the height of this peak is now independent of the number of layers.

Although the classical dipole image calculations do not describe accurately the interaction of the adsorbed species with the substrate when they are very close to the surface,¹⁵ some important qualitative conclusions regarding the changes of reflectivity due to the presence of the adsorbates can be drawn. We conclude that near the Brewster angle of the vacuum-overlayer interface the differential reflectance signal originates from the overlayers closest to the surface. This signal can be enhanced if the substrate supports surface plasmons, permitting the optical study of the first adsorbed layers. The intensity of the peak that appears near the surface plasma frequency in the optical reflectivity depends strongly on the geometry of the first layer and its distance to the surface, allowing information of this layer to be obtained from optical reflectivity measurements.

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