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# Multipolar plasma resonances in supported alkali-metal nanoparticles

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## Abstract

Multipolar effects in the polarizability of metallic potassium particles on a silicon substrate were studied using differential reflectance spectroscopy. The experimental spectra were compared with calculations of the effective polarizability of particles of different shapes leading to the conclusion that the resonances in the spectra correspond to excitations of substrate-induced multipolar modes in the particle–substrate system. © 2000 Elsevier Science B.V. All rights reserved.

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In the last decade there has been a renewed attraction for the study of the optical response of metallic discontinuous films in different areas of surface and material science. The main reasons might be the variety of applications of this field in the development of surface-sensitive optical spectroscopies as well as the richness of physical phenomena involved in the optical response of these kind of systems. For example, at extremely low coverages one can model the film as a collection of atoms or molecules responding to an applied electromagnetic field in the presence of a substrate. As the coverage increases particle formation usually appears and the film becomes a collection of isolated nano-particles of different shapes, and if the coverage is further increased, coalescence phenomena develop leading to the formation of a rough surface. Besides this rich variety of morphologies there is also different types of information about these

systems which are required to understand a different kind of physical phenomenon. For example, the calculation of the scattered field at the surface of metallic nanometric particles or surfaces with roughness in the nanometric scale, is required for a full understanding of the electromagnetic effect in surface-enhanced Raman spectroscopy.

In this paper we deal with a metallic discontinuous potassium film over a silicon substrate in the stage of supported isolated nanoparticles and we study, both experimentally and theoretically, the effects of the substrate in the effective polarizability of the supported particles, in particular, on the Mie resonances. The difference between the polarizability of an isolated and a supported particle is the effect on the particle coming from the field induced in the substrate. Since this field might not be homogeneous over the nanometric volume of the sphere, even if the substrate is flat, multipolar modes higher than the dipole can also be excited. In the simplest model this multipolar coupling (MC) is neglected and the field induced by the substrate is regarded as the one coming from the mirror-image dipole leading to a red-shift of the dipolar resonance. The main effect of the MC in the effective polarizability is the appearance, as a function of

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frequency, of additional resonances which correspond to the resonant coupling of the applied field with modes with high multipolar character. However, despite the numerous experimental investigations on the optical response of supported particles, such additional resonances had not been observed. Here we report the first optical observation of these resonances in a differential-reflectance (DR) spectrum.

The silicon substrates were prepared by chemical etching and oxidation, following the procedure of Ishizaka and Shiraki [1], and this resulted in the formation of a silicon dioxide layer, whose thickness was  $2.2 \pm 0.2$  nm, as measured by ellipsometry. Potassium was evaporated from a SAES getter source, with a base pressure in the chamber of  $1 \times 10^{-10}$  mbar. The flux  $\Phi_K$  of K atoms arriving at the surface was estimated to be  $\sim 10^{-2}$  atom/nm<sup>2</sup>/s. This estimate was reached by determining the time needed to get a saturation layer of K on a Si(111)  $7 \times 7$  surface under the same experimental conditions [2,3]. The optical measurements were performed during the K deposition by use of an in situ DR spectrometer [4], which delivers the relative change of reflectivity of the substrate upon deposition of K, that is:

$$\frac{\Delta R_p}{R_p} = \frac{R_p[\text{K/Si}] - R_p[\text{Si}]}{R_p[\text{Si}]}, \quad (1)$$

where  $R_p[\text{K/Si}]$  and  $R_p[\text{Si}]$  are the reflectivities of the oxidized silicon substrate with and without potassium, respectively. The experiments were performed in p-polarization, at an angle of incidence  $\theta = 60^\circ$ . Several experiments have been performed for different substrate temperatures between  $-120^\circ\text{C}$  and  $45^\circ\text{C}$ , and all of them gave qualitatively the same results. In Fig. 1 we show a series of experimental spectra of  $\Delta R_p/R_p$  as a function of photon energy  $\hbar\omega$ , on a substrate maintained at  $-80^\circ\text{C}$ , for times of deposition running from 30 to 210 s. After this time the evaporation was stopped and no additional change in the spectrum was observed. The spectra displayed a well-defined peak around 1.8–1.9 eV, whose size increase with the K deposition time and its location shifts slightly to 2 eV for longer times. A very distinctive feature around  $\sim 2.3$  eV is seen for the spectra corresponding from 30 to 150 s, and is progressively “washed out” in the high-energy tail of the spectra taken at larger times. In Fig. 2 the DR spectrum obtained after 60 s of deposition time has been enlarged, and to make the 2.3 eV feature more evident to the eye, we have drawn a continuous curve fitted to the data by assuming a single Lorentzian resonance in the dielectric response of the film.

For times between 30 and 120 s the system was modelled as a collection of supported isolated particles. Although a direct observation of the size and shape of the particles was not possible due, essentially, to their instability, a couple of facts suggest that the particles might be

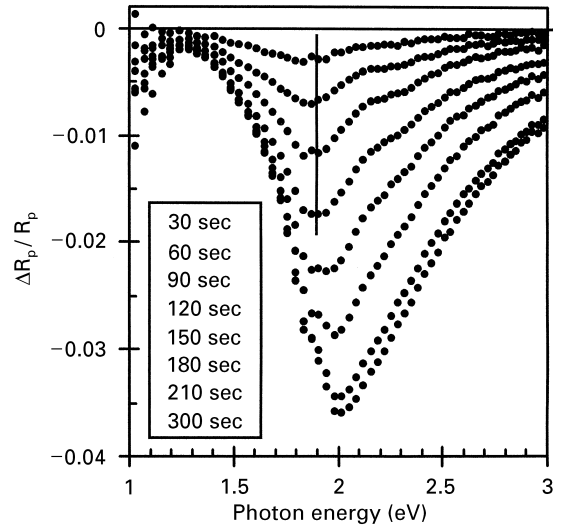


Fig. 1. Experimental DR spectra for increasing times of K deposition on an oxidized Si surface, maintained at  $-80^\circ\text{C}$ . The times of deposition are indicated in the figure. The evaporation was stopped just after 210 s.

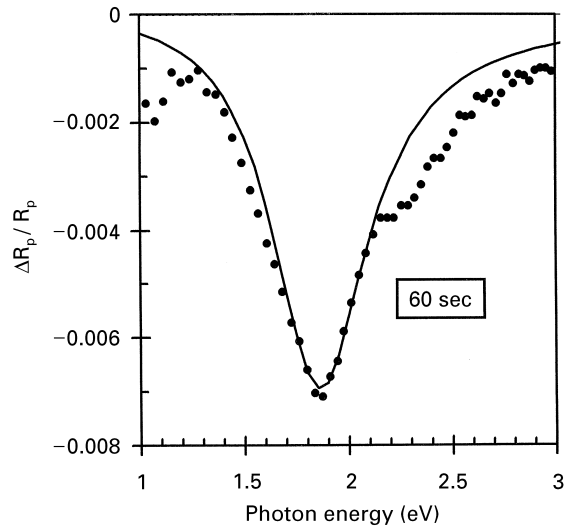


Fig. 2. Experimental DR spectrum obtained after 60 s of K deposition. The continuous line is a guide to the eye.

close to be spherical: (i) The particles are not stable at room temperature and they re-evaporate, as it has been determined previously by the decrease of the DR signal after stopping the deposition [5], thus one might expect that they are close to their free equilibrium spherical shape. The shape of DR spectra at low temperatures does not change, therefore one might expect that the shape of the particles does not change either. (ii) Taking oblate

spheroids as the simplest possible model for a supported flat island, calculations of the DR spectra showed a main negative peak at frequencies which are too high relative to the frequency of the main peak in the experimental spectra [6]. Thus we will assume that the particles have a spherical shape.

In the dilute limit, and in cgs units,  $\Delta R_p/R_p$  for a collection of spheres on a substrate is given by [7,8]

$$\frac{\Delta R_p}{R_p} = 16 \frac{\omega a}{c} f_2 \cos \theta \times \text{Im} \left[ \frac{(\epsilon_B - \sin^2 \theta) \tilde{\alpha}_{\parallel} - \epsilon_B^2 \sin^2 \theta \tilde{\alpha}_{\perp}}{(1 - \epsilon_B)(\sin^2 \theta - \epsilon_B \cos^2 \theta)} \right], \quad (2)$$

where  $f_2 = N\pi a^2/A$  is the two-dimensional filling fraction of the spheres of radius  $a$  and by dilute limit we mean  $f_2 \ll 1$ . Here  $\epsilon_B$  is the dielectric function of the substrate,  $\tilde{\alpha}_j \equiv \alpha_j/a^3$  ( $j = \perp, \parallel$ ),  $\alpha_{\perp}$  and  $\alpha_{\parallel}$  are the effective polarizabilities of the supported K particles for an applied field perpendicular ( $\perp$ ) and parallel ( $\parallel$ ) to the interface, and  $c$  is the speed of light. The main ingredient in this calculation is the effective polarizability of the spheres including multipolar coupling. This effective polarizability was determined following the procedure of Wind et al. [9–11] which consists in the solution of Laplace’s equation through expansions of the potential in spheroidal coordinates. The coefficients of the expansion are then determined through the fulfillment of the boundary conditions. Since in our case the Si substrate is coated by a thin layer of  $\text{SiO}_2$ , which decreases the Si interaction with the K sphere, we will assume, for simplicity, that the main effect of this layer is to keep the particle a certain effective distance  $D$  above the Si substrate, where  $D$  is close to the actual thickness  $d$  of the oxide layer. In relation with the value of the dielectric functions which also appear in Eq. (2), we took for Si the optically determined values given in Ref. [12], for  $\text{SiO}_2$  we took  $\epsilon_B = 2.25$ , and for potassium we adopted a Drude model  $\epsilon(\omega) = 1 - \omega_p^2/(\omega^2 + i\omega/\tau)$  with  $\hbar\omega_p = 3.8 \text{ eV}$  [13] and  $\Gamma \equiv \hbar\tau^{-1} = 0.4 \text{ eV}$ . Our choice of  $\Gamma = 0.4 \text{ eV}$ , is supported by recent photo-absorption experiments on beams of ionized K clusters [14].

A plot of the calculated DR spectrum for a potassium sphere located at a distance  $D/R = 0.12$  above the silicon substrate is shown in Fig. 3. This value corresponds to spheres of radius around 18 nm. The shape of the DR spectrum resembles now quite closely the experimental one. With the chosen parameter ( $af_2 = 0.0023 \text{ nm}$ ) the profile of the main minimum and the distinctive shoulder agree fairly well with the data of the 60s spectrum, differing only in the wider low- and high-energy tails of the experimental spectrum. In order to show that the distinctive shoulder in the DR spectrum is actually a remnant of well-defined multipolar resonances which have been broadened by dissipative effects, in Fig. 3 we also show the DR spectrum calculated with the same

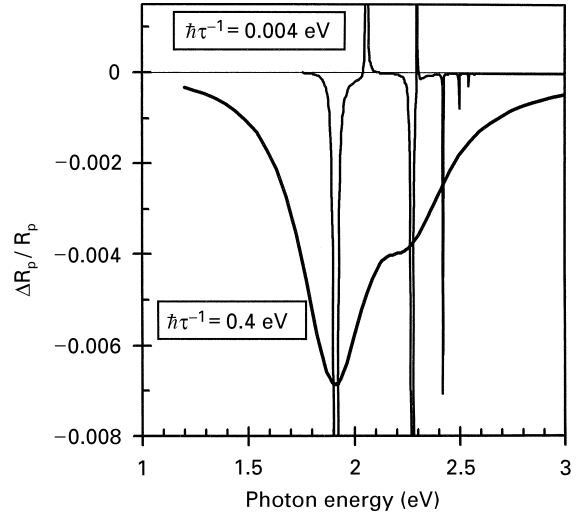


Fig. 3. Calculated DR spectra for K spheres above Si ( $D/R = 0.12$ ). Thick line : damping parameter  $\Gamma = 0.4 \text{ eV}$ ; thin line:  $\Gamma = 0.0004 \text{ eV}$ .

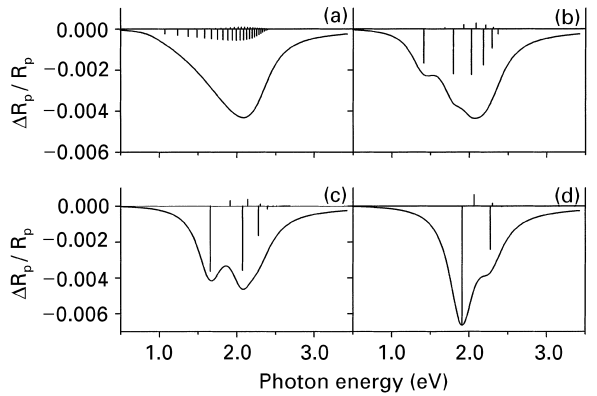


Fig. 4. DR spectra for a sphere on a substrate with a real dielectric function  $\epsilon = 15$ , for different distances  $D$  between the sphere and the surface. (a):  $D/R = 0.0005$ ; (b):  $D/R = 0.01$ ; (c):  $D/R = 0.035$ ; (d):  $D/R = 0.12$ .

parameters but with  $\Gamma = 0.0004 \text{ eV}$ . There is a series of very sharp positive and negative peaks, coming from the resonances of  $\tilde{\alpha}_{\parallel}$  and of  $\tilde{\alpha}_{\perp}$ , respectively. For each negative peak there is a blue-shifted positive one. This is seen in only two peaks in the figure due to resolution. The negative peaks have a greater strength than the corresponding positive ones, which simply means that the external field couples stronger with the perpendicular modes. This is the reason why when  $\Gamma$  increases the overall spectrum is negative. Also for large values of  $\Gamma$  the positive resonances appear either as negative minima, enhancing the distinctiveness of the negative maxima, or as inflection points in the profile. The larger width of the experimental spectra ( $\sim 0.6 \text{ eV}$ ) likely results, as

mentioned above, from a distribution of shapes of the particles around the spherical one.

Finally, we want to point out that the peaks in the resonance structure of the DR spectrum could be discriminated *only* because the particles were not touching the substrate due to the presence of the oxide layer. For this purpose, we calculated the DR spectra of potassium spheres on different substrates and at different distances from the substrate, following the procedure developed by some of us before [15]. We used a spectral representation of the DR spectra which yields directly the strength of the coupling to the applied field and the frequency of normal modes of the particle–substrate system. One of the limitations of this procedure is that the dielectric function of the substrate should be real. In Fig. 4 we show the DR spectra together with the frequency location and strength of the optically active modes of the system for four different locations of the spheres and a contrast parameter  $f_c = (1 - \epsilon_b)/(1 + \epsilon_b)$  equal to 0.875, corresponding approximately to the case of silicon. Spectrum (d) corresponds to the one shown in Fig. 3. One can see that for a sphere almost touching the substrate, the spectrum becomes broad due to the frequency span and density of the excited multipolar modes, something one could call multipolar broadening. But as the sphere is lifted from the surface this broadening effect transforms into a spectrum with well-defined peaks and/or shoulders. In this case the appearance of the shoulders is due, not only because the excited modes are more separated in energy, but also to the fact of having two neighboring modes, one with a positive and the other with a negative strength. In our case the oxide layer is the one which “lifts” the particles above the silicon substrate. If the particles would have been allowed to get in touch with the substrate, the distinct multipolar structure of the DR spectra would have been “washed out” giving rise to a broad peak, whose broadness would have been the result of an unraveled combination of dissipation and multipolar broadening.

We conclude by saying that in this work we have given a brief description of the DR experiments of potassium particles on silicon together with the model and the calculations that led us to conclude that the peculiar resonance structure found in the DR spectra correspond to the excitation of substrate-induced multipolar resonances.

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