

Optical Characterization of a Spheroidal Nanoparticle on a Substrate

Carlos E. Román-Velázquez, Cecilia Noguez and Rubén G. Barrera

Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, México, D. F. 01000 MEXICO

ABSTRACT

With the help of a spectral formalism recently formulated, we study the effects in the optical response of the material properties of a nanoparticle lying over a substrate. A spectral representation was formulated to calculate the optical response of spheroidal nanoparticles including multipolar effects. We present our results in terms of Differential Reflectance spectra that can be compared directly with measurements. We have found that multipolar contributions depend in the shape of the particle and type of substrate.

INTRODUCTION

In recent times, the study of supported nanoparticle systems has attracted the attention of many researchers due to some of their very interesting physical properties as well as the possibilities of promising technological applications [1]. In particular, the knowledge of the optical properties of a particle located above a substrate can be used as a tool to interpret optical spectra for the characterization of supported nanoparticle systems [2]. The fabrication of nanostructured systems and the growing process of thin films requires a precise characterization of the shape and size of the supported particles or islands. For this purpose the optical spectroscopies become an invaluable tool due to their non destructive character and in-situ capabilities of measurement.

The optical spectra of metallic nanoparticles deposited on an insulating substrate is characterized by the presence of resonances. The location and broadening of these resonances depend on the morphological and physical properties of the system. For example, they depend on the properties of the substrate because the particle interacts with the charges induced on the substrate. The interaction between different supported particles is also important, specially in the case of a high concentration of particles. However, the study of an isolated supported particle can be also performed in the dilute regime [3].

The optical properties of a particle on a substrate are determined by its response to the local field. In the first attempts to describe the optical properties of these systems the interaction of the particle with the substrate was neglected [4]. Later, the presence of the substrate was included by taking a dipolar interaction between the particle and its image [5-8]. However, the calculation of the interaction between a particle of finite size and its image requires the inclusion of multipolar interactions. This is because the field produced by the image, rather than being homogeneous over the size of the particle, as required by the dipolar approximation, it is strongly inhomogeneous, specially when the particle is close to the substrate. Different authors have included these multipolar interactions considering particles of different shapes [9-11]. However, the numerical complexity of the problem restricts tremendously the number of multipolar interactions taken to describe the system. This situation restricts the study to only a few specific systems.

The inclusion of multipolar interactions between the particle and its image gives rise to resonances additional to the dipolar one, which is the one that characterizes an isolated particle. It has been also shown that the location and strength of the multipolar resonances depend strongly on the properties of the substrate and the geometry of the system [3,12]. For example, when a particle is in close contact with the substrate smooth spectra are obtained. On the contrary, when the particle is located at a certain distance above the substrate, a well defined structure of resonances is obtained. The structure of these resonances is more evident when the contrast in the dielectric response of the ambient and the substrate increases [3,12].

Recently a powerful theoretical procedure has been developed to calculate the optical response of a particle-substrate system using a spectral representation [12]. The main advantage of

this representation is that the strength and localization of the resonances, when given in terms of the spectral variable, are independent of the dielectric properties of the particle, but depend only on its shape and the dielectric properties of the substrate. With this procedure one is also able to include a larger number of multipoles, allowing the treatment of substrates with a larger contrast in the dielectric constant and particles closer to the substrate. In this work we consider more asymmetric oblate particle than in previous treatments [12] and we also study the changes in differential-reflectance spectra for particles made of different materials.

FORMALISM

We consider an oblate particle located on a substrate. The particle is generated by the rotation around one of the axes of an ellipse with lengths $2a$ and $2b$, with $a > b$. The symmetry axis of the particle is perpendicular to the substrate, and its center is located at a distance d from the substrate which has a dielectric constant ϵ_s . The particle has a dielectric function ϵ_p and is embedded in an ambient of dielectric constant ϵ_a . We consider that the three media: particle, substrate and ambient are non-magnetic. The system is excited by light with frequency ω and a wavelength λ , such that $\lambda \gg a, b$ and d . Under this condition, a quasistatic approximation is valid to calculate the electromagnetic fields.

In the linear approximation, the dipolar moment of the particle, in the presence of a substrate, linearly depends with the components of the applied external field, throughout the so called effective polarizability tensor α_{eff} . Due to the symmetry of the system, α_{eff} has only two independent components corresponding to the polarizabilities in the direction normal and perpendicular to the substrate. When the particle is far from the substrate the effective polarizability becomes the polarizability of the isolated particle. But, when the particle is close to the substrate the multipolar interactions induced by the substrate modifies the optical response of the system.

The analysis of α_{eff} for the system described above was done as follows. First, the electric potential induced in the system at any point in space was calculated to all multipolar orders. To find the solution for the induced potential a spectral representation (SR) of the Bergman-Fuchs-Milton type [13] was developed [12]. By identifying the dipole moment p induced in the particle, the components of α_{eff} were obtained. The behavior of the spectral function for different shapes and locations of the particles is analyzed. For a detailed description of the method see Ref. [12].

Within SR, we can write the components of α_{eff} in the following form:

$$\alpha_{eff}^m = -\frac{\nu}{4\pi} \sum_s \frac{G_s^m}{u(\omega) - n_s^m}, \quad (1)$$

where ν is the volume of the particle, m denotes the diagonal components of α_{eff} , and $u(\omega) = [1 - \epsilon_p(\omega)/\epsilon_a]^{-1}$ is the spectral variable; $G_s^m = (U_{1s}^m)^2$ are the so-called spectral functions where U_{1s}^m is an orthogonal matrix that satisfies the relation,

$$\sum_{ll'} U_{ls}^m H_{ll'}^m U_{l's}^m = n_s^m \delta_{ss'}. \quad (2)$$

The matrix $H_{ll'}^m$ depends only on the geometrical properties of the model and on the dielectric properties of substrate and ambient, through the contrast parameter $f_c = (\epsilon_a - \epsilon_s)/(\epsilon_a + \epsilon_s)$. $H_{ll'}^m$ is a symmetric matrix and can be written in the following form [12]

$$H_{ll'}^m = n_{lm}^0 \delta_{ll'} + f_c D_{ll'}^m(d), \quad (3)$$

here n_{lm}^0 are the depolarization factors of an isolated spheroid, and $D_{ll'}^m$ is a matrix given by the multipolar coupling due to the presence of the substrate, this later vanishes when $d \rightarrow \infty$. Note that $H_{ll'}^m$ contains all the information on the geometry of the system and the dielectric constant of the substrate, and is independent of the material properties of the particle. From Eq. (1), α_{eff} is given as the sum of terms which show resonances at frequencies ω given by the poles of the equation, when $u(\omega) = n_s^m$. As a consequence, an explicit procedure to obtain the strengths G_s^m and the position of the resonances is obtained.

With this SR a systematic study of the spectral function in term of the parameters a , b , d and f_c , has been reported in Ref. [12]. In this paper, we present a systematic study of the spectral function of oblate particles with different asymmetries and considering two different kinds of substrates. We present our results in terms of Differential Reflectance spectra, where different material properties of the particle are also considered.

RESULTS AND DISCUSSION

In order to determine the effective polarizability of spheroidal particles located at a distance d above a flat substrate, first we construct the interaction matrix $H_{ll'}^m$ choosing the value of m equal to 0 or 1, depending on whether the applied external field lies perpendicular or parallel to the substrate. A maximum value of multipolar excitations L_{max} is chosen in order to assure multipolar convergence in the spectral function G_s^m , which gives the strength of the coupling of the optical active modes labeled by n_s^m , to the applied field. Its actual value will depend on the values of a/b , f_c and d . A numerical procedure to calculate $D_{ll'}^m$ is given in [11]. However, that method has convergence problems in the case of oblate particles with a large asymmetry ($a/b > 1.7$), where only a reduced number of multipolar interactions ($L_{max} \sim 25$) can be taken. Here we devised an alternative method starting from expressions given by Lam [14], which are valid for the case of particles with $c/d < 1$, where c is the semidistance between the foci of the ellipse. We then calculate the spectral function G_s^m , the effective polarizability and the spectrum of differential-reflectance (DR) for specific systems of supported spheroidal particles. Some recent DR measurements on metallic supported particles have shown the presence of multipolar effects [3, 12], and the shape of the particles has been determined through a detailed analysis of these spectra [12]. In DR spectroscopy one compares the reflectance of the substrate-film system with the reflectance of the clean substrate, that is,

$$\Delta R_p / R_p = \frac{R_p[\text{film} + \text{substrate}] - R_p[\text{substrate}]}{R_p[\text{substrate}]}. \quad (4)$$

When one considers that the film is constituted by a dilute distribution of particles, all located at the same distance from the substrate, one obtains, for p -polarized light, the following expression

$$\Delta R_p / R_p = 16 \frac{\omega}{c} b f_2 \cos \theta \operatorname{Im} \left[\frac{\alpha_{eff}^0 (\epsilon_s - \sin^2 \theta) - \alpha_{eff}^1 \epsilon_s^2 \sin^2 \theta}{(1 - \epsilon_s^2)(\sin^2 \theta - \epsilon_s \cos^2 \theta)} \right], \quad (5)$$

where $\theta (= 50^\circ)$ is the angle of incidence, f_2 is the two-dimensional filling fraction of particles and c is the speed of light. Note that the spectral representation of the effective polarizability α_{eff} leads to a spectral representation for the differential reflectance $\Delta R_p/R_p$. We consider here the case of particles of free-electrons metals whose dielectric function can be described by the Drude model $\epsilon_p(\omega) = 1 - \omega_p^2/(\omega(\omega+i\tau))$, where ω_p is the frequency of the bulk plasma resonance and τ is a phenomenological factor associated with the dissipation process. For potassium these parameters are $\hbar\omega_p = 3.8$ eV and $\tau/\omega_p = 0.105$, while for aluminium they are $\hbar\omega_p = 15.8$ eV and $\tau/\omega_p = 0.04$. We also consider silver particles, and in this case we use, in our calculations, the experimentally-determined dielectric function (see Fig. 3).

In Fig. 1 we show differential reflectance spectra and its associated spectral weights for two oblate particles of aluminium with $a/b = 2.5$ and $a/b = 4.0$, each one in two different substrates. In all cases $d = 1.05$, $\theta = 50^\circ$ and $f_2 = 0.0046 \text{ nm}^2/\text{b}$. The spectral function is plotted as a series of vertical lines whose location is given by the energy of the resonances and their length proportional to the strength of the coupling with the applied external field. Although a reduced number of resonances is observed, to obtain these spectra 25 multipoles have to be included in order to attain multipolar convergence in the calculation of the spectral functions. In the spectra of a particle with $a/b = 2.5$ over a substrate with $f_c = -0.773$ (titanium dioxide in air) one sees a structure of multipolar resonances. These resonances have different energies and the number of distinct resonances decreases with the magnitude of contrast factor; there are fewer for $f_c = -0.516$, (sapphire in air). In the case of the more asymmetric particle $a/b = 4.0$, the strength of the resonances decreases further. When we compare the full multipolar calculation with the dipolar approximation one sees that the dipolar approximation gives better results for more symmetric particles, and it becomes even better in the case of a substrate with a smaller contrast factor f_c .

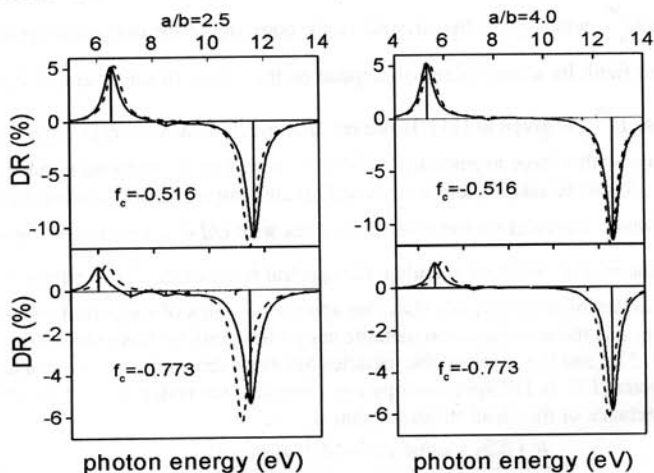


Figure 1. DR for aluminium particles embedded in air and lying over a substrate at a distance $d=1.05b$. Left panels are OS particles with $a/b=2.5$, while right panels are particles with $a/b=4.0$. Upper panels correspond to substrates of sapphire and lower panels to substrates of TiO_2 . The solid lines are the calculation with $L_{max}=25$, meantime the dashed lines correspond to dipolar approximation. The spectral function is represented by the solid vertical lines

In Fig. 2 we show the DR spectra corresponding to particles of potassium and silver. In two of the panels, $a/b = 1$ (spheres) while in the other two $a/b = 2.5$. In all cases the substrate has a contrast factor $f_c = -0.516$. The spheres are located at $d/b = 1.0005$. Our procedure based in the spectral representation allows us to consider a number of multipolar contribution as large as $L_{max} = 2000$, which is the number required to obtain multipolar convergence in the calculation of the spectral function. In the left panels of Fig. 2 we observe how the final shape of the spectrum comes about by the superposition of resonances with strengths with different signs. In the right panels of Fig. 2 we also observe important differences in the shape of the spectra due to the difference in the dielectric response of the material the particles are made of, even when in both cases the resonance structure is the same. A more complex structure is observed in the case of particles of Ag. In potassium spheres the spectrum does not reflect such a rich resonance structure, and this is mainly because the particle lies too close to the substrate. From these differences in the spectra it is difficult to imagine how an invariant feature could be obtained from them. The spectral representation is that invariant. We can give a more detailed explanation of the spectra of Fig. 2 in the following way: In the Fig. 3 we show the imaginary part of $u(\omega)$ as function of frequency. We observe that in the region where the spheres have their resonances the imaginary part of $u(\omega)$ is smaller for silver than for potassium. This means that in the case of silver spheres the Lorentzian resonances associated to each resonant term of Eq. (1) are taller and sharper than for potassium. As a consequence the resonance structure is richer than in potassium where the broadening effects wash out the details of this resonance structure. From Fig. 3 we can also explain the differences between the shape of the spectra for the oblate particle. The peak at low frequencies is thinner and higher than that observed at higher frequencies, the opposite of what happens in the case of potassium, which arises from the specific combination of parameters in Eq. (2). As we can see in Fig. 3, for silver, at low frequencies, the imaginary part of $u(\omega)$ is smaller than at higher frequencies. Then, at low frequencies the Lorentzian resonances of each mode are taller and sharper than at high frequencies.

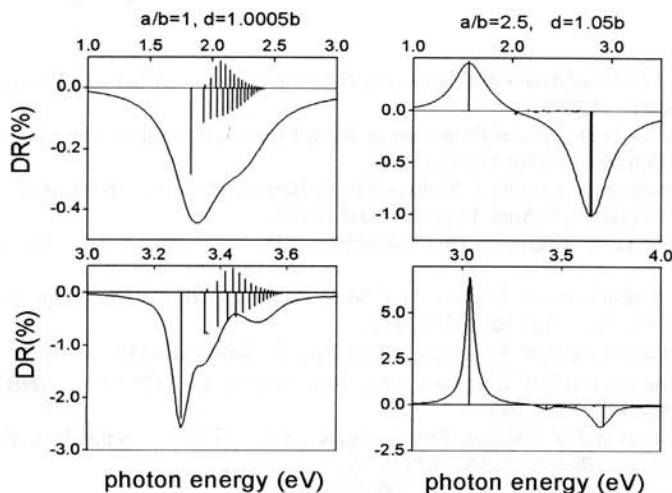


Figure 2. DR for particles embedded in air lying over a substrate of sapphire. Left panels correspond to spherical particles at a distance $d=1.0005b$ from the substrate, while right panels correspond to OS particles with $a/b=2.5$ at a distance $d=1.05b$. Upper panels correspond to particles of potassium and lower panels to particles of silver.

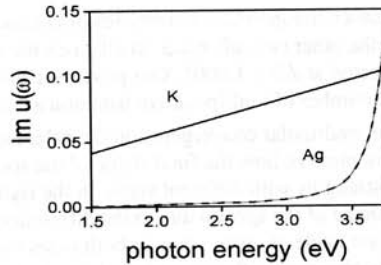


Figure 3. Imaginary part of the spectral variable $u(\omega)$ for potassium and silver as function of the photon energy

CONCLUSIONS

In conclusion, we have showed that the multipolar effects on the optical properties of a nanoparticle due to the presence of a substrate depend with the direction of the applied external field. We have found that for oblate particles with $a/b > 3$ the multipolar effects are reduced and the dipolar approximation gives a good description of the behavior of the system. Since multipolar effects become more important for systems where the substrate has a large dielectric constant, in this case the dipolar approximation is not good enough. We also have shown that very different spectra could be obtained considering particles of different material even if the geometry of the system is the same. Finally, we have demonstrated that the interpretation of the spectral representation could be helpful to elucidate the shape and size of the nanoparticles.

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