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# Optical Properties of a Spheroid–Substrate System

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We developed a spectral representation (SR) to study the effective polarizability of a spheroidal particle lying over a substrate, where multipolar effects are included. This SR permits to do a complete general analysis of the optical properties of the system. With the help of the spectral representation, we present results that can be compared directly with differential reflectance measurements.

## 1. Introduction

In the last decades, the study of optical properties of inhomogeneous thin films has been stimulated by promising applications. The actual and potential applications cover a wide spectrum of systems and tools ranging from solar energy cells, and surface enhanced Raman spectroscopy (SERS) to the characterization of self-assembled quantum dots. To attain this description optical spectroscopies have become extremely useful tools, due to their non-destructive character and in situ potentiality.

The optical properties of a system of a particle lying on a substrate can be determined through its response to the local field. This local field comes from the charge distribution induced at the particle due to the presence of the substrate, which modifies the response of the particle. This modification can be incorporated by assigning, to the particle, an effective polarizability. In the early studies [1], an effective or renormalized polarizability was assigned to each particle, in which the interaction between the particle and its own image dipole is taken into account. However, this image-dipole model fails for particles of nanometric dimensions lying very close to the substrate, and extensions of this model had to include higher order multipolar interactions [2]. An alternative approach to the optical signature of inhomogeneous thin films is to look at the optical response in terms of the strength of coupling to the applied field of the optically active electromagnetic surface modes of the system [3]. Unfortunately, in the existing theories the location of the resonant frequencies of the proper modes of the system, and the calculation of their coupling strength to the applied field, is not immediate.

In this paper we present a theory which yields both, the frequencies of the proper modes as well as the size of their coupling strength to the applied field. We do this by building a spectral representation of the effective polarizability of a spheroidal particle,

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located at an arbitrary distance above any substrate. Finally, we show that the formalism constructed here can be used to generate results which can be compared with experiments.

## 2. Formalism

We consider spheroidal particles generated by the rotation of an ellipse around its major or minor axes, they correspond to prolate (PS) or oblate (OS) spheroids, respectively. The length of the major and minor axes of the ellipse is denoted, correspondingly, by $2a$ and $2b$. The particle has a local dielectric function $\varepsilon_{\mathrm{p}}$, and is embedded within a semiinfinite homogeneous matrix with dielectric constant $\varepsilon_{\mathrm{a}}$. The particle is placed at a distance $d$ above a semiinfinite substrate with dielectric constant $\varepsilon_{\mathrm{s}}$. The symmetry axis of the particle lies normal to the interface between substrate and matrix. We also consider that the three media: matrix, particle and substrate are non-magnetic. Let us consider that the system described above is in the presence of an applied external electric field propagating with wavelength $\lambda$ and oscillating with frequency $\omega$, such that $a$, $b$, and $d \ll \lambda$. Then, we will work in the quasi-static (non-retarded) approximation. We now define the *effective* polarizability $\overleftrightarrow{\alpha}$ of the spheroid–substrate system as the relation between the dipole moment $\mathbf{p}$ of the charge distribution induced in the spheroid in the presence of the substrate and the applied field $\mathbf{E}_0$.

The analysis of $\overleftrightarrow{\alpha}$ 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 was developed [4]. By identifying the dipole moment $\mathbf{p}$ induced in the particle, the components of the effective polarizability were obtained. Here, 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. [5].

Within SR the effective polarizability of the particle can be written in the following form:

$$\alpha_m = -\frac{v}{4\pi} \sum_s \frac{G_s^m}{u - n_s^m} \,, \tag{1}$$

where $v$ is the volume of the spheroidal particle, $m$ denotes the diagonal components of $\overleftrightarrow{\alpha}$, and $u = [1 - \varepsilon_{\mathrm{p}}/\varepsilon_{\mathrm{a}}]^{-1}$ is the spectral variable; $G_s^m \equiv [U_{1s}^m|^2$ are the so-called spectral functions. $U_{ls}^m$ is an orthogonal matrix which satisfies $(U^{-1})_{sl}^m \, H_{ll'}^m U_{l's'}^m = n_s^m \, \delta_{ss'}$. The matrix $H_{ll'}^m$ depends only on the geometrical properties of the model and on the dielectric properties of the substrate and the host matrix through the parameter $f_{\mathrm{c}} = (\varepsilon_{\mathrm{a}} - \varepsilon_{\mathrm{s}})/(\varepsilon_{\mathrm{a}} + \varepsilon_{\mathrm{s}})$. It is given by

$$H_{ll'}^m = n_l^m \, \delta_{ll'} + f_{\mathrm{c}} D_{ll'}^m \,, \tag{2}$$

where $n_l^m$ are the depolarization factors of the isolated spheroid, and $D_{ll'}^m$ is a matrix given by the multipolar coupling due to the presence of the substrate. The spectral functions are positive real quantities which represent the strength of the coupling to the applied field of the normal modes of the system whose eigenfrequencies $\omega_{\mathrm{s}}$ are determined by the poles, $u(\omega_{\mathrm{s}}) = n_{\mathrm{s}}^m$, in Eq. (1). The eigenvalues $0 \le n_{\mathrm{s}}^m \le 1$ are known as depolarization factors and can be used to label the modes.

The main advantage of this type of representation is, that for a given substrate, the location of the poles as well as their strength are independent of the dielectric properties of the particle, depending only on its shape. It is important to notice that the information about the dielectric properties of the spheroidal particle are contained only in the spectral variable $u$. On the other hand, the information about the geometry of the model, as well as the dielectric properties of the host and substrate are contained in $n_s^m$ and $G_s^m$. Therefore, it is now possible to carry out an analysis of the optically active modes for *any* spheroidal particle.

## 3. Results and Discussion

We present results for the SR of the effective polarizability of spheroidal particles located at a distance $d$ from a flat substrate. First, we construct the matrix $H_{ll'}^m$ depending on whether the particle is PS or OS, or a sphere, and one also chooses the value of $m$ as $m = 0$ or 1, depending on whether the applied external field lies perpendicular or parallel to the substrate. Then, a maximum value of multipolar excitations $L_{\max}$ is chosen in order to assure multipolar convergence in the eigenvalues and eigenvectors of $H$. Its actual value will depend on the values of $a/b$, $f_c$, and $d$. One then calculates the spectral functions $G_s^m$ that, for a particular system, give the strength of the coupling to the applied field of the optically active modes labeled by $n_s^m$. Finally, the effective polarizabilities for a given spheroidal particle characterized by a dielectric function $\varepsilon_p$ are found.

In Fig. 1, we present the spectral function of OS (upper panels) and PS (lower panels) with $\{a/b, d, f_c\}$ shown in the figure. The external field in this case is perpendicu-

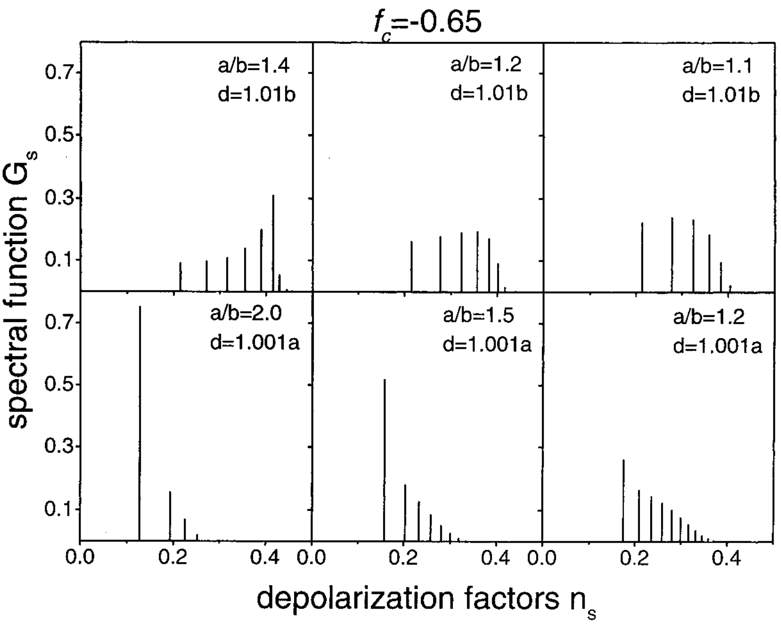


Fig. 1. Spectral function as a function of $n_s$ of OS (upper panels) and spheres (lower panels), for an external field perpendicular to the substrate. The parameters $a/b$, $d$, and $f_c$ are shown in the figure

lar to the substrate ($m = 0$). We observe that for both kinds of spheroids, there is a dominant mode as the asymmetry of the particle increases ($a/b > 1$). For OS the dominant mode is at the right ($n_s^m = 0.42$), while for PS this mode is at the left ($n_s^m = 0.13$). On the contrary, as $a/b \to 1$ the dominant mode merges down and the mode-strength distribution becomes broader and equal to that found for the sphere. In conclusion, we observe that multipolar effects become more important as the ratio $a/b$ of a spheroid tends to unity, that is, when the actual shape tends to be spherical (right-side panels). When the particle is closer to the substrate (lower panels), the coupling between multipolar modes with $l > 1$ becomes more important, thus more modes are excited and their single multipolar identity starts to get lost as $a/b \to 1$. As $a/b$ increases, the PS resembles a needle, and the particle can be polarized only along the minor axis. The PS has a dipolar character, and its interaction with the substrate is well described by the dipolar approximation. As $a/b$ increases, the OS becomes a plate such that when it is polarized perpendicular to the substrate the system resembles a capacitor, where the electric field will be constant inside.

In Figs. 2 and 3 we present calculations of the differential reflectance (DR) in p-polarization of a substrate with $R_p[K/S]$ and without $R_p[S]$ potassium particles given by $\Delta R_p/R = (R_p[K/S] - R_p[S])/R_p[S]$. The $\Delta R_p/R$ spectra were calculated for OS and spheres using the following expression:

$$\frac{\Delta R_p}{R} = 16\,\frac{\omega}{c}\,bf_2\cos\theta\,\mathrm{Im}\,\frac{(\varepsilon_s - \sin^2\theta)\,\alpha_\parallel - \varepsilon_s^2\sin^2\theta\alpha_\perp}{(1-\varepsilon_s)\,(\sin^2\theta - \varepsilon_s\cos^2\theta)}\,, \tag{3}$$

where $\theta$ is the angle of incidence and $f_2$ is the two-dimensional filling fraction of particles. We describe the potassium particle by the Drude model, $\varepsilon_p = 1 - \omega_p^2/(\omega^2 + i\omega\tau)$ with

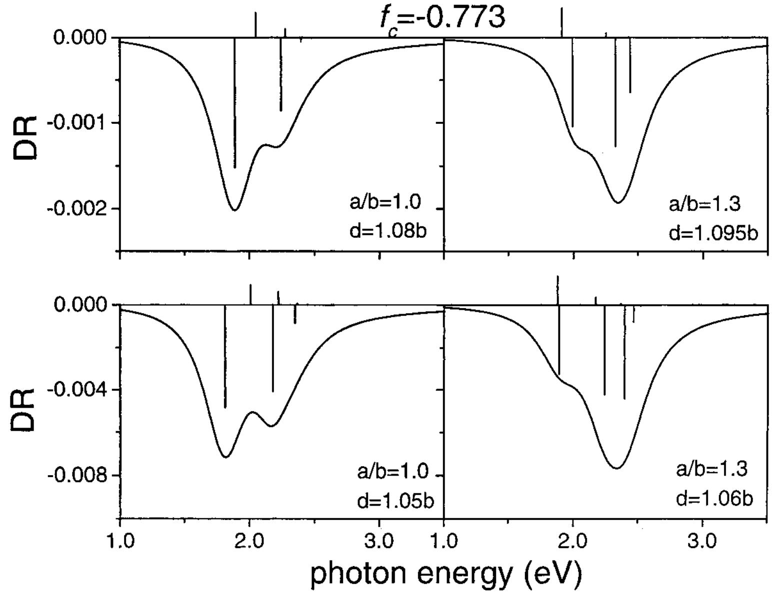


Fig. 2. DR for a potassium particle embedded in air and lying over a substrate of $TiO_2$. Left panels are spheres, while right panels are OS

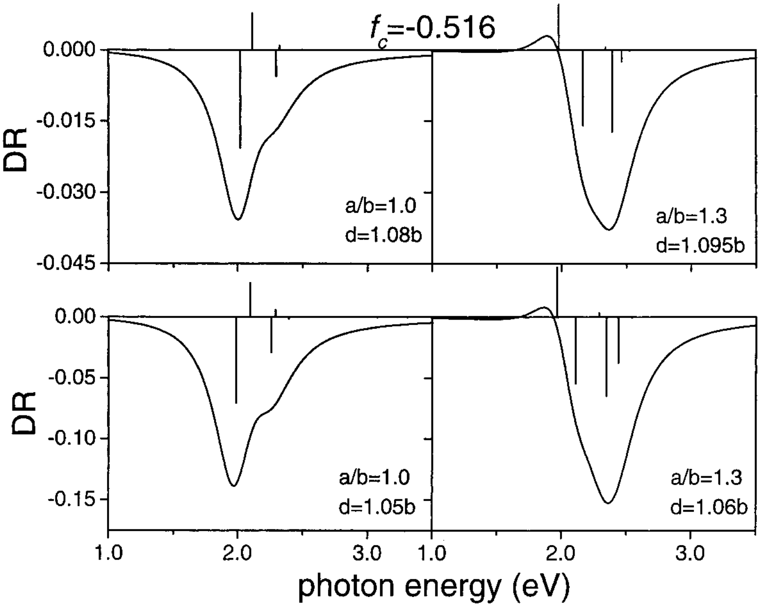


Fig. 3. DR for a potassium particle embedded in air and lying over a substrate of sapphire. Left panels are spheres, while right panels are OS

$\hbar\omega_p = 3.8$ eV and $\hbar/\tau = 0.4$ eV [6]. In both figures the corresponding spectral functions for $\alpha_\parallel$ and $\alpha_\perp$ are plotted with positive and negative vertical lines, respectively. The line shape of DR spectra is easily associated with the active modes of the respective spectral functions. The spectra in Fig. 2 (3) with $f_c = -0.773$ ($-0.516$) correspond to a potassium particle embedded in air over a substrate of $TiO_2$ (sapphire). In the left side we show DR for spheres with a radius $b = 20$ nm (lower panel) and 12.5 nm (upper panel), while the right side corresponds to OS with $b = 10.5$ nm (upper panel) and 16.8 nm (lower panel). In all cases $bf_2 = 0.0046$ nm. We observe that for a larger contrast ($f_c = -0.773$), the difference of DR with the particle shape is more pronounced. While for the sphere the larger negative peak is at 1.7 eV, for the OS this peak is at 2.4 eV. Both DR spectra show a shoulder at higher (lower) frequencies for spheres (OS). This shoulder is more pronounced when the particle is closer to the substrate, where multipolar effects are more important. The multipolar effects are also reflected in the DR intensity: while the particle is far away from the substrate the DR spectra is less intense, independently of the particle shape. Now, for a lower contrast ($f_c = -0.516$), the DR differences between spheres and OS are less pronounced; however, for OS we found a positive structure located at about 1.8 eV which corresponds to the positive mode from $\alpha_\parallel$, as shown in Fig. 3. On the other hand, this mode gives rise to the shoulder of DR of spheres.

In conclusion, we developed a spectral formalism which helps us to make a systematic identification of the main structures of DR spectra as a function of the particle shape, its distance to the substrate and the dielectric characteristics of surroundings and substrate.

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