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# Optical Absorbance of Colloidal Suspensions of Silver Polyhedral Nanoparticles

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The optical absorption of colloidal suspensions made of silver nanoparticles with polyhedral shapes is studied experimentally and theoretically. The influence of the shape on the optical response is investigated by comparing the measured absorbance with theoretical results for icosahedral, decahedral, and cuboctahedral silver nanoparticles. The theoretical spectra are obtained within the discrete dipole approximation. We find that colloidal suspensions of silver nanoparticles with a small dispersion of size distribution show very few structural shapes.

## I. Introduction

It has been shown that shape, size, and ambient conditions are fundamental ingredients to find out the optical response of metal nanoparticles.<sup>1–4</sup> Therefore, to develop new technological devices, it is crucial to determine as exactly as possible the influence of these parameters to control the fabrication of nanoparticles designed for a particular application. In addition to the technological implications, the right knowledge and correct physical interpretation of the optical properties of nanoparticles can be also used as tools of characterization of themselves. The correct physical interpretation of optical properties is noteworthy because optical techniques are nondestructive, and with proper implementation, they can be used to perform in situ and real-time measurements, which provide statistical properties of the whole sample. These attributes of optical techniques are important because the properties of nanoparticles depend on the environment,<sup>2,3</sup> and when growth and characterization are made in different ambient conditions, this might be an additional uncontrollable variable during fabrication.

Since a long time ago, the estimation of the shape and size of nanoparticles has been achieved using techniques to resolve their structure, such as high-resolution transmission electron microscopy (HRTEM),<sup>5–8</sup> atomic force microscopy (AFM),<sup>9</sup> scanning tunneling microscopy (STM),<sup>10</sup> etc. These structural techniques provide information in real space with atomic resolution of the local properties of the sample, characterizing a few nanoparticles at a time. Nanoparticles of different polyhedral shapes, such as icosahedra, cuboctahedra, decahedra, etc., have been observed with the use of these structural techniques.<sup>6–10</sup> It is known that metal nanoparticles of a few nanometers show different structural motifs depending on their size, composition, and energetic conditions.<sup>11,12</sup> Therefore, one might suppose that if one is able to control the size of nanoparticles under some experimental conditions, it would also be possible to manipulate their shape and vice versa.

In this work, we show that it is possible to elucidate among different polyhedral shapes of silver nanoparticles of less than

10 nm by studying their optical response. When a particle is excited by an electromagnetic (EM) field, the electrons start to oscillate with the same frequency as that of the incident EM. The excited charges can transform energy from the incident EM wave into, for example, thermal energy in a so-called absorption process. However, the charges can also be accelerated and they can radiate energy in any direction in a so-called scattering process. The sum of both effects is called the light extinction. For nanoparticles of less than 10 nm, radiation processes are negligible, so the particle only absorbs energy.<sup>2</sup> There are mainly three different absorption mechanisms related to the size of the particles: (i) surface plasma resonances, (ii) surface dispersion, and (iii) radiation damping. Radiation damping becomes important when the size of the particle is larger than 20 nm, and for nanoparticles of less than 10 nm, the surface resonances are independent of the size. Therefore, for small particles (<10 nm), the surface dispersion effect is the only one that depends on the size; as the particle gets smaller, the surface dispersion is more important.<sup>2</sup> Notice that these absorption mechanisms also depend on the shape of the nanoparticle.<sup>1–4</sup>

The surface plasma resonances of small particles can be studied in terms of the strength of the coupling to the applied field of the optically active EM surface modes of the system. The location of the resonant frequencies of the proper modes of the system and the calculation of their coupling strengths to the applied field are not immediate because they usually require taking the nondissipation limit, a procedure that might call for a vast amount of numerical effort. However, using a spectral representation of the polarizability of the particle, we could construct, in principle, a theory that yields both the frequencies of the proper modes and the sizes of their coupling strengths to the applied field. In the spectral representation of the particle, the polarizability is expressed as a sum of terms with single poles.<sup>13–15</sup> The location of the poles is associated with the frequencies of the normal modes of the particle, and their strengths are associated with the coupling of these modes to the applied field. The main advantage of this type of representation is that the location of the poles and their strengths are independent of the size and dielectric properties of the particle and depend only on its shape. However, explicit expression of the single poles is difficult to obtain, and up to now, it has been found only for spherical,<sup>16</sup> spheroidal,<sup>17</sup> and cubic particles.<sup>13</sup>

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Notice that surface dispersion effects do not change the location of the proper modes, but they affect the coupling of the proper modes with the applied field.

Here, we study the optical response of different polyhedral shapes of silver nanoparticles of less than 10 nm. Then, we show that colloidal suspensions made under well-controlled synthesis conditions not only exhibit narrow-size distributions but also exhibit very few structural shapes. This paper is organized as follows. In section II, we describe the discrete dipole approximation used to model the interaction of light with the nanoparticles. In section III, we present the main characteristics of the experimental results of the silver colloidal suspension studied here. The theoretical results are compared and discussed in section IV, and conclusions are made in section V.

## II. Discrete Dipole Approximation

To study the optical properties of metal particles with nanometric sizes, we employ the discrete dipole approximation or DDA, developed by Purcell and Pennypacker to model the interaction of light with dust particles in space.<sup>18</sup> The main idea behind DDA is to approach the particle with a finite number of polarizable entities to mimic its optical response to an applied electromagnetic field. DDA is also known as the Purcell–Pennypacker method and, along the years, has suffered several modifications and improvements to study solid targets with nonspherical shapes. These improvements have been done mainly by Draine and co-workers,<sup>19–21</sup> who have made available the so-called DDSCAT computational code.<sup>22</sup> In this work, we employ DDSCAT to study the optical response of nanoparticles.

DDSCAT builds up a solid object using an array of  $N$  polarizable entities located in a periodic lattice which resembles the shape and size of the particle under study. These polarizable entities are located at the positions  $\vec{r}_i$ , with  $i = 1, 2, \dots, N$ . DDSCAT assigns to each entity a dipole moment given as

$$\vec{p}_i = \vec{\alpha}_i \cdot \vec{E}_{i,\text{loc}} \quad (1)$$

where  $\vec{\alpha}_i$  is the dipolar polarizability of the entity at  $\vec{r}_i$  and  $\vec{E}_{i,\text{loc}}$  is the total electric field acting on the  $i$ th dipole, also called the local field. The discretization of the particle is a good approximation when the distance  $d$  between adjacent polarizable entities is much smaller than the wavelength  $\lambda$  of the incident electromagnetic field. Once  $\vec{r}_i$  and  $\vec{\alpha}_i$  are given and the condition  $d/\lambda \ll 1$  is fulfilled, it is possible to predict the light absorption and scattering by free and embedded particles. In our case, the silver nanoparticles of interest are suspended in a solvent in such a way that both the solvent and the particles constitute a dilute colloidal suspension.

The local field due to an array of point dipoles under an applied electromagnetic field is given as

$$\vec{E}_{i,\text{loc}} = \vec{E}_{i,\text{app}} + \vec{E}_{i,\text{ind}} \quad (2)$$

where  $\vec{E}_{i,\text{app}}$  is the applied field and  $\vec{E}_{i,\text{ind}}$  is the induced field acting on the  $i$ th entity because of the radiation of all the other  $N - 1$  dipoles that compose the nanoparticle.

Let us consider the applied field as a monochromatic plane wave

$$\vec{E}_{i,\text{app}} = \vec{E}_0 \exp(i\vec{k} \cdot \vec{r} - \omega t)$$

where  $\vec{E}_0$  denotes the magnitude of the incident electric field,  $\vec{k}$  is the wave vector,  $\omega$  is the frequency, and  $t$  means time. On

the other hand, the induced field is given by

$$\vec{E}_{i,\text{ind}} = \sum_{j=1}^N \vec{\mathbf{A}}_{ij} \cdot \vec{p}_j \quad (3)$$

where the symbol  $(\cdot)$  means  $i \neq j$  and  $\vec{\mathbf{A}}_{ij}$  is the matrix that couples the electromagnetic interaction among dipoles. This interaction matrix is expressed as

$$\vec{\mathbf{A}}_{ij} \cdot \vec{p}_j = \frac{e^{ikr_{ij}}}{r_{ij}^3} \left\{ k^2 \vec{r}_{ij} \times (\vec{r}_{ij} \times \vec{p}_j) + \frac{(1 - ikr_{ij})}{r_{ij}^2} [r_{ij}^2 \vec{p}_j - 3\vec{r}_{ij}(\vec{r}_{ij} \cdot \vec{p}_j)] \right\} \quad (4)$$

where  $\vec{r}_{ij}$  is a vector from the position of dipole  $i$  to dipole  $j$ ,  $r_{ij}$  denotes its magnitude, and  $k = |\vec{k}|$ .

Substituting the local field from eqs 2 and 3 into the expression for the dipolar moment in eq 1, we obtain a system of  $3N$  complex coupled equations:

$$\vec{p}_i = \vec{\alpha}_i \cdot (\vec{E}_{i,\text{inc}} + \sum_{j=1}^N \vec{\mathbf{A}}_{ij} \cdot \vec{p}_j) \quad (5)$$

From the above expression, we can calculate the set of dipole moments that mimics the optical response of the particle, and once we know each  $\vec{p}_i$ , it is possible to obtain the light extinction and absorption cross sections using the following expressions:<sup>18</sup>

$$C_{\text{ext}} = \frac{4\pi k}{|\vec{E}_0|^2} \sum_{j=1}^N \text{Im}\{\vec{E}_{j,\text{inc}} \cdot \vec{p}_j^*\} \quad (6)$$

$$C_{\text{abs}} = \frac{4\pi k}{|\vec{E}_0|^2} \sum_{j=1}^N \left\{ \text{Im}[\vec{p}_j \cdot (\alpha_j^{-1})^* \vec{p}_j^*] - \frac{2}{3} k^3 |\vec{p}_j|^2 \right\} \quad (7)$$

where  $*$  means complex conjugate. The scattering cross section  $C_{\text{sca}}$  is defined as the difference between extinction and absorption cross sections,  $C_{\text{sca}} = C_{\text{ext}} - C_{\text{abs}}$ .

DDSCAT<sup>22</sup> creates a cubic lattice array of dipoles and assigns to each one a polarizability given by the lattice dispersion relation (LDR):<sup>20</sup>

$$\alpha^{\text{LDR}} = \frac{\alpha^{\text{CM}}}{1 + \alpha^{\text{CM}}[b_1 + b_2\epsilon + b_3S\epsilon](k^2/d)} \quad (8)$$

where  $\epsilon$  is the macroscopic dielectric function of the particle;  $S$ ,  $b_1$ ,  $b_2$ , and  $b_3$  are the coefficients of the expansion to a third-order in  $k$  to incorporate radiation effects, and  $\alpha^{\text{CM}}$  is the polarizability given by the well-known Clausius–Mossotti relation,<sup>23</sup>

$$\epsilon - 1 = \frac{4\pi n \alpha^{\text{CM}}}{1 - 4\pi n \alpha^{\text{CM}}/3} \quad (9)$$

Here, we have assumed that the polarizability is isotropic and that all the entities are isotropic as well,  $\vec{\alpha}_i = \alpha^{\text{LDR}}$ . A key factor in determining the level of accuracy that can be reached for a given number of dipoles is the prescription for assigning dipole polarizabilities.<sup>20</sup> Besides the finite wavelength, it is also important to include the influence of the geometry of the particle in the dipole polarizabilities.<sup>24</sup>

In this work, we use the dielectric function measured for bulk silver,  $\epsilon_{\text{bulk}}$ , by Johnson and Christy.<sup>25</sup> The experimental data of the macroscopic dielectric function have contributions due to interband (inter) and intraband (intra) electron transitions, such that

$$\epsilon = \epsilon_{\text{inter}} + \epsilon_{\text{intra}} \quad (10)$$

The intraband electron transitions can be described by the Drude model of free electrons:<sup>23</sup>

$$\epsilon_{\text{intra}} = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \quad (11)$$

where  $\omega_p$  is the plasma frequency and  $1/\tau$  is a damping constant due to dispersion of the electrons by the ions of the system.

We are interested in nanoparticles whose sizes are smaller than 10 nm, such that physical phenomena associated with radiation effects, such as scattering and radiation damping, are negligible ( $C_{\text{sca}} \approx 0$ ).<sup>2</sup> However, we have to consider that conduction electrons suffer an additional damping effect due to surface dispersion or finite size effects. The surface dispersion effects depend on the particle size and shape.<sup>4</sup> Here, we consider the surface dispersion of a sphere of radius  $a$ , such that dielectric function also depends on  $a$  as<sup>26</sup>

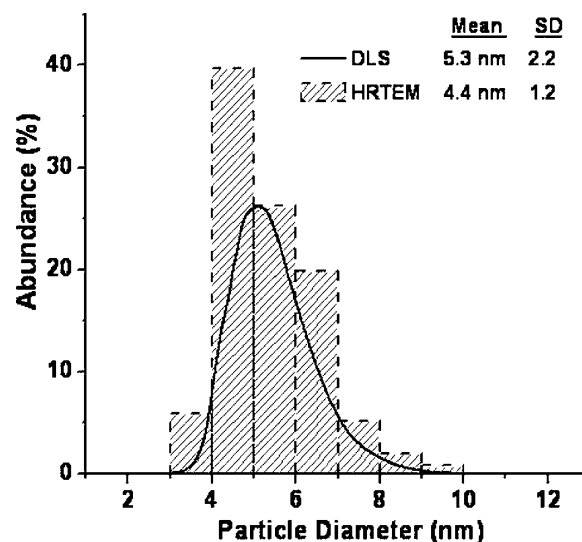
$$\epsilon(\omega, a) = \epsilon_{\text{bulk}} - \epsilon_{\text{intra}} + \left\{ 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau + i/\tau_a)} \right\} \quad (12)$$

where  $1/\tau_a$  is the surface-damping term given by  $1/\tau_a = v_f/a$ , and  $v_f$  is the Fermi velocity of the electron cloud. In this work, we use the parameters for  $\omega_p$  and  $v_f$  found by Kreibitz, for silver nanoparticles of less than 10 nm.<sup>26</sup> As the particle gets smaller, the surface dispersion becomes more important. However, the surface dispersion does not change the location of the surface plasmons, but as the particle gets smaller, the resonance is less pronounced and broadens.

### III. Silver Colloidal Suspension

Rodríguez-Gattorno et al. reported a novel process for the synthesis of silver nanoparticles with a small distribution of sizes.<sup>28</sup> The synthesis is produced by reduction of silver 2-ethylhexanoate [Ag(ethex)] in dimethyl sulfoxide (DMSO) at room temperature. The colloidal system was stabilized with sodium citrate. It was found that the surface-modified silver nanoparticles were stable for more than six months. The colloidal suspension has a concentration of about  $8 \times 10^{11}$  particles/mL.<sup>29</sup>

**A. Experimental Details. 1. Materials and Equipment.** Silver 2-ethylhexanoate [Ag(ethex)] (Stream Chem., 99%), dihydrated trisodium citrate [ $\text{Na}_3\text{Cit} \cdot 2\text{H}_2\text{O}$ ] (Aldrich, 99%), and argon (Praxair Inc., 99.998%) were used as starting materials. These chemical reagents were used without further purification. The employed DMSO was from Sigma (ACS reagent). The electronic absorption spectra were collected in an Ocean Optics CHEM2000 UV-vis spectrophotometer. The HRTEM study was carried out in a JEOL 2000F at 200 kV by depositing a drop of the sample over a carbon/collodion coated copper grid, and no special care was taken to avoid aggregation. The size distribution was obtained from a digitalized amplified micrograph by averaging the larger and smaller axis diameters measured for each particle. Also the solvo-dynamic diameter distributions of the colloidal dispersions were collected using



**Figure 1.** Comparison of the particle size distributions of a silver colloidal suspension obtained from HRTEM and DLS.

dynamic light scattering (DLS) equipment (HPPS nanoparticle sizer from Malvern).

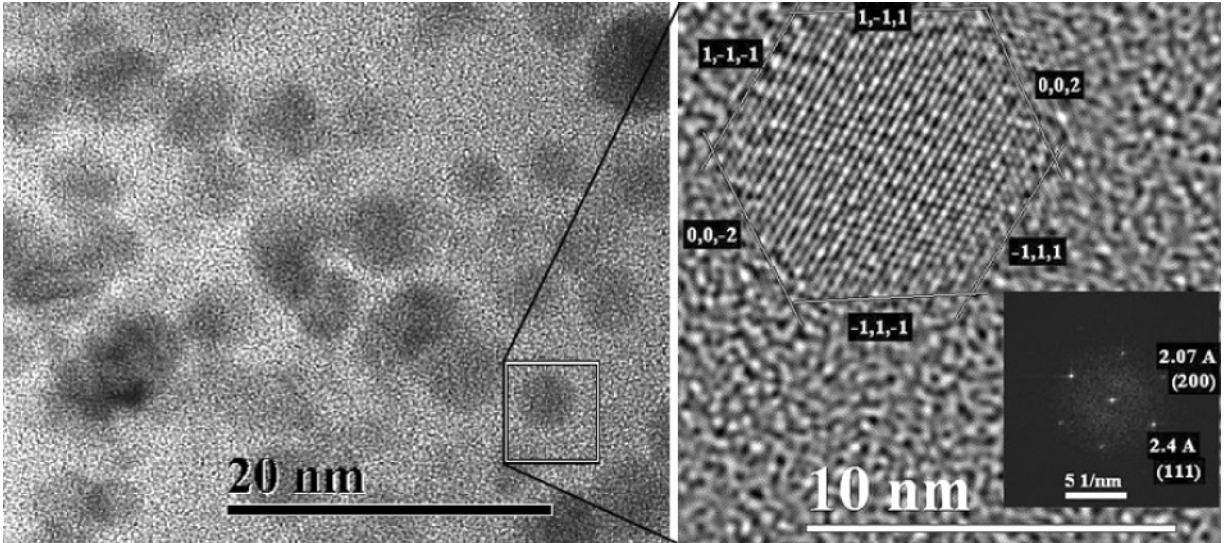
**2. Preparation.** The required quantity of [Ag(ethex)], to obtain a final concentration of  $1 \times 10^{-4}$  M, was added to 50 mL of DMSO (previously saturated with argon) in an Erlenmeyer flask with continuous stirring. Powdered sodium citrate ( $1 \times 10^{-4}$  M) was dissolved in DMSO before adding the silver salt. This solution was heated at 60 °C in a hot plate thermostat for 20 min. The stability of the colloidal dispersion is found by measuring the UV-vis absorption spectra at different times. A more detailed description of the synthesis procedure can be found elsewhere.<sup>28</sup>

**B. Properties of the Colloidal Suspension. 1. Structural Characterization.** We estimate the size of the nanoparticles by analyzing the HRTEM images. We perform a statistic over 250 particles, and we find that the distribution of the diameters of the nanoparticles is centered around 4.4 nm with a standard deviation of 1.2 nm, as shown in Figure 1. The diameter distribution is also collected using DLS, and the distribution is found to be centered at 5.3 nm with a standard deviation of 2.2 nm. For comparison, both measurements are shown in Figure 1. The similarity of the measurements is a good indication that the colloidal suspension mainly consists of well-dispersed nanoparticles at a low concentration.

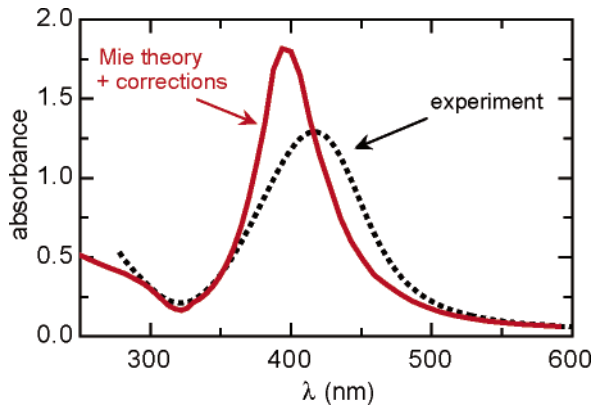
The HRTEM image at low resolution in Figure 2 (left) shows that the silver nanoparticles exhibit a “spherical-like” shape. When the resolution is increased, a considerable number of defects such as stacking faults and twinning are observed and some particles appear to have icosahedral and cuboctahedral shapes (see Figure 2, right). However, we note that the shape of nanoparticles could be substantially modified during the sample observation using HRTEM because this is an invasive technique that, sometimes, could literally destroy the sample.<sup>28</sup> Therefore, it is possible to not find a quantitative relationship between HRTEM images and in situ characterization using optical spectroscopies.

**2. Optical Characterization.** The light absorbance as a function of the wavelength of the incident light was measured for colloidal dispersions at different times using naked and stabilized nanoparticles with different capping agents.<sup>28</sup> More details about the optical characterization can also be found in ref 28. We observe that, for all the spectra, a large absorbance was found for  $\lambda < 310$  nm independently of the ligands and





**Figure 2.** HRTEM micrographs of silver colloidal nanoparticles. The micrograph on the right shows a cuboctahedral particle obtained from the magnification of the inset shown on the left micrograph.

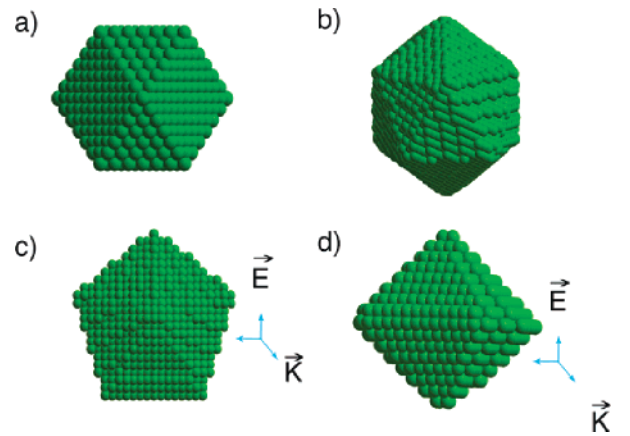


**Figure 3.** Light absorbance of silver colloidal nanoparticles: Mie theory vs experimental data.<sup>28</sup>

the concentration of the nanoparticles; we attribute this feature of the spectrum to the absorption of the DMSO solvent. For the stable colloidal dispersion, we measure a peak with a maximum at 420 nm and with a full width at half-maximum (fwhm) of about 90 nm.

In Figure 3, we show the experimental absorbance (dots) and the calculated spectrum (solid line) for a sphere of 4.4 nm diameter immersed in DMSO with a refractive index of  $n = 1.478$ . The theoretical curve is obtained using the theory of Mie<sup>27</sup> and includes corrections due to surface dispersion effects.<sup>26</sup> In the dilute limit, the interactions between particles are negligible, so we can model the absorbance as the optical response of one suspended particle times the concentration of particles.<sup>30</sup> The resonance peak maximum of the theoretical curve is at 390 nm, and the fwhm is about 55 nm. These values for the calculated resonance can vary with the choice of the input dielectric function; however, these variations are much smaller than those which are necessary to fit the experimental values. We also consider the size variation of the nanoparticles, so we calculate the weight average of the absorbance for the sphere of sizes given by the distribution of Figure 1. We do not find any difference between the absorbance calculated using the average size and the absorbance calculated using the weight average over different sizes, so we use, in this work, the average size for all our calculations.

We find differences between the calculated and measured spectra in both position and fwhm of the surface plasma

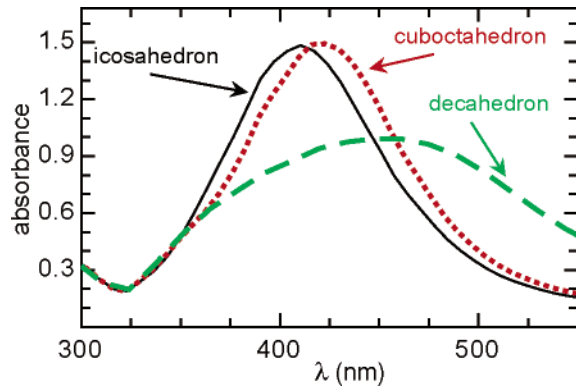


**Figure 4.** (a) Cuboctahedral, (b) icosahedral, and (c,d) regular decahedral nanoparticles. In (c), the light incidence is parallel to the pentagonal motif of the regular decahedral, and in (d), the light incidence is perpendicular to it.

resonance. Previously, these differences were attributed to molecular interactions between the surrounding medium and the surface of the particles.<sup>28</sup> The difference in fwhm was attributed to lattice imperfections which could increase the surface dispersion effects. However, the same differences have been reported for other silver colloidal dispersions that were stabilized with different capping agents and showed particles of different sizes.<sup>31,32</sup> Moreover, the passivation of dangling bonds at the nanoparticle surface does not change significantly the number of electrons which are involved in the collective plasma oscillations in the metallic particle. Indeed, we propose that both differences in the spectra are due to shape effects which substantially change the main characteristics of the surface plasmon resonances, as we will show in the next section.

#### IV. Results and Discussion

To explore the influence of the shape on the optical response of the colloidal suspensions, we study the light absorption by silver icosahedral, cuboctahedral, and regular decahedral nanoparticles, shown in Figure 4. These nanoparticles are mainly related to the crystallographic surfaces  $\{111\}$  and  $\{100\}$  of face-centered cubic (fcc) structures and have different planar facets. HRTEM images of these polyhedral particles show very often



**Figure 5.** Light absorbances of silver icosahedral, cuboctahedral, and regular decahedral nanoparticles.

“spherical-like” shapes, depending on the particle orientation and focus of the electron beam.<sup>7</sup> Furthermore, fcc nanoparticles show defects such as stacking faults and twinning,<sup>5–7</sup> as do those observed here and reported previously.<sup>28</sup>

In Figure 4, we show (a) a cuboctahedron obtained from the symmetric truncation of a cube particle and composed of six planar squares and eight triangles, (b) an icosahedron composed of 20 planar triangular surfaces, and (c) a regular decahedron composed of 10 planar triangular surfaces which resemble two pentagons. In Figure 4d, we show the decahedral particle, such that the pentagon motif shown (c) has been rotated 90° around the axis, which is orthogonal to *E* and *k*. The decahedron is an asymmetric particle.

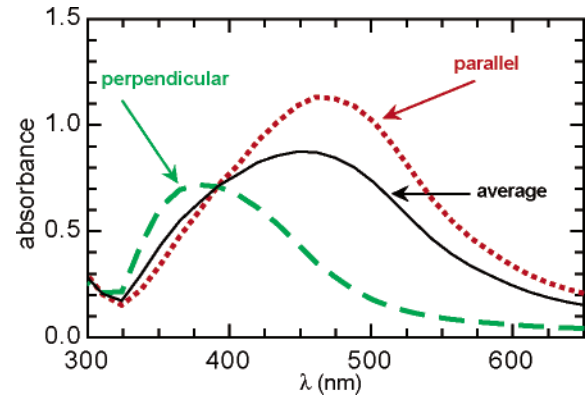
The absorption cross section,  $C_{\text{abs}}$ , for the icosahedron, cuboctahedron, and decahedron is calculated within DDA using  $N = 162\,000$ ,  $186\,663$ , and  $142\,971$  dipoles, respectively. The light absorbance is obtained as<sup>33</sup>

$$\text{absorbance} = \log(e^{-\phi C_{\text{abs}} D}) \quad (13)$$

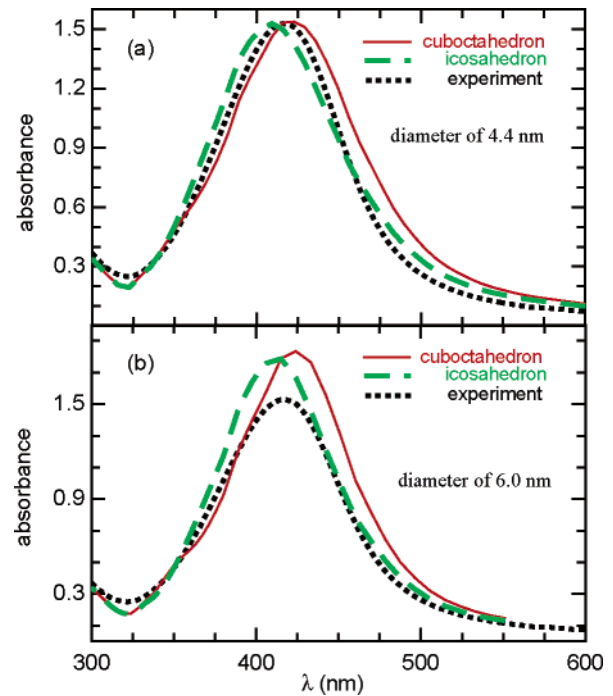
where  $D$  is the length of the colloidal sample and  $\phi$  is the concentration of particles. Here, we use the experimental values  $D = 1$  cm and  $\phi = 8 \times 10^{11}$  particles/mL. We find that the calculated and measured absorbances systematically differ by a factor of 4 at wavelengths between 300 and 350 nm, where only interband transitions are observed, i.e., where the absorption process is only due to material properties.

In Figure 5, we show the calculated light absorbance for icosahedral, cuboctahedral, and decahedral nanoparticles with a 4.4 nm diameter. We observe that the optical resonances of both icosahedral and cuboctahedral particles are very similar and have a fwhm of 100 nm. The resonance peak maxima for both kinds of particles show the same intensity and are located at 415 and 425 nm, respectively. The icosahedron and cuboctahedron are symmetric geometrical shapes, and this fact is manifested on their optical spectra. We find that, for both particles, the absorbance is independent of the direction of the incident light. On the other hand, the decahedral particle is asymmetric, as shown in Figure 4c,d, and we find that its optical response exhibits its asymmetry. In Figure 5, we show the average over different orientations of the absorbance for the decahedral particle, where the maxima of the spectrum is at 450 nm and the fwhm is about 200 nm.

For the decahedral particle, we find a large anisotropy of the absorption when the light incidence is such that the electric field is parallel or perpendicular to the pentagonal motif of the particle; see part c or part d of Figure 4, respectively. In Figure 6, we show the parallel and perpendicular components of the light absorbance, as well as the average of the absorbance over



**Figure 6.** Light absorbances of silver decahedral nanoparticles for different light polarizations. The orientational average is also shown.



**Figure 7.** Light absorbances of silver icosahedral and cuboctahedral nanoparticles with (a) 4.4 nm and (b) 6.0 nm diameters. The spectra are compared with experimental data (dots).

different orientations. When the electric field is parallel to the pentagon (see Figure 4c), the spectrum is very wide with a fwhm of 200 nm and a maximum at about 475 nm. On the other hand, when the electric field is perpendicular to the pentagon (see Figure 4d), the spectrum shows a maximum at about 375 nm, is less intense, and is asymmetric; so a large fwhm of 140 nm is found. These features of the spectra are due to the geometrical asymmetry and to the 10 planar triangular facets that compose the particle and give rise to several resonances in a wide range of wavelengths.<sup>34</sup> The anisotropy of the optical response of decahedral particles does not correspond to the experimental observations. Therefore, we will only discuss the absorbance measurements in terms of the calculations for icosahedral and cuboctahedral nanoparticles.

In Figure 7, we show the experimental absorbance and the calculated spectra for icosahedral and cuboctahedral particles with diameters of (a) 4.4 and (b) 6.0 nm. We find an excellent agreement between the spectra for the particles with a 4.4 nm diameter, which corresponds to the experimental value obtained from the HRTEM images. The maximum of the experimental peak is found between the main optical resonances of both

icosahedral and cuboctahedral nanoparticles. The small differences on the positions of the main resonance of icosahedral and cuboctahedral particles at 415 and 425 nm, respectively, and the experimental peak at 420 nm could be attributed to small modifications of the charge density at the surface of the particles due to the ligands. This also suggests that the colloidal suspension could be made of a combination of both kinds of shapes of the silver nanoparticles.

We observe that the experimental absorbance is a smooth curve, whereas the calculated spectrum for cuboctahedral particles is not quite so smooth. In the experimental curve, we measure the optical properties of suspended nanoparticles, such that an averaging procedure over a distribution of sizes and shapes is done. This averaging procedure might smooth out the main relevant features of the spectra associated with the size and shape of the nanoparticles. However, our suspension does not show a large size distribution, and according to it, the features in the spectra should be more pronounced as the size of the particles increases. The plasmons for cuboctahedral particles become more pronounced as the size of the particle increases, as seen in Figure 7b where two small structures, besides the main resonance at 425 nm, can be found at 350 and 390 nm. These structures are related to additional surface plasmon resonances due to the planar facets of cuboctahedral particles.<sup>34</sup> These surface plasma resonances are attributed to different charge densities at the surface on the metallic particle. These kinds of resonances have been found for other geometries such as cubic particles, where several pronounced peaks have been identified.<sup>1,2,13</sup> On the other hand, the icosahedral particle has only one additional resonance at about 440 nm; however, this is less pronounced such that it slightly modifies the main resonance at 415 nm, as observed in Figure 7. Taking into account these features of both icosahedral and cuboctahedral nanoparticles, one might conclude that icosahedral particles resemble better the experimental absorbance spectrum. However, we cannot exclude the existence of cuboctahedral nanoparticles, as we found in the HRTEM study.

## V. Conclusions

We have studied the optical response of a colloid suspension made of silver nanoparticles with a small dispersion of sizes. The optical absorbance of the silver nanoparticles is calculated using the discrete dipole approximation. The shape of the nanoparticle is investigated by identifying the main optical resonances associated with the spectra. We find that a suspension with a small dispersion of size of the nanoparticles also shows very few structural shapes. We can conclude that colloidal suspensions with well-controlled synthesis conditions not only exhibit narrow-size distributions but also exhibit preferential structural shapes.

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