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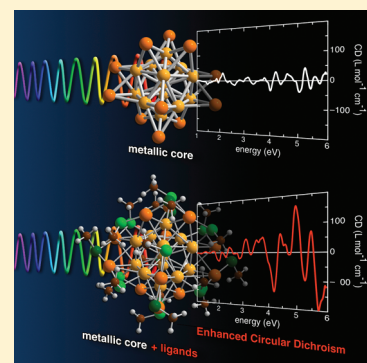
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Role of Morphology in the Enhanced Optical Activity of Ligand-Protected Metal Nanoparticles

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ABSTRACT: In recent years, much research has been dedicated to understand and predict the interaction of light with nanostructures, which exhibit a wide variety of interesting physical properties that can be tailored by altering their size, morphology, composition, and environment. One emerging area in nanoscience is the phenomenon where the optical activity can be influenced and enhanced due to the presence of metal nanoparticles, with possible technological implications in sensing and labeling chiral molecules, asymmetric catalysis, pharmacology, toxicology, among other applications. In this Perspective article, we talk about the theoretical aspects of this phenomenon and the relationship between morphology and the optical activity enhancement in ligand-protected metal nanoparticles.



The interest in the optical properties of nanoparticles (NPs) arises from the large morphology-dependent physical properties of these systems. These properties have technological implications in photonics, as nanoengineered substrates on Raman scattering and fluorescence, in chemical and biosensing applications, in drug delivery, and in photothermal destruction of cancer cells and pathogenic bacteria, among other applications.^{1–5} Additionally, the optical signature of NPs is widely used as a characterization tool.^{6,7} The latter is also interesting because optical spectroscopies offer nondestructive characterization, which is employed to perform in situ and real time measurements, providing statistical properties of the whole sample during and after preparation.

It has been observed that ligand-protected metal nanoparticles (LPNPs) have exceptional optical activity that contrasts those of the components.

One interesting spectroscopic technique that measures the optical activity of chiral systems, as well as their interaction, is circular dichroism (CD). Optical activity is the physical phenomenon associated with the rotation of linearly polarized light when it propagates through chiral systems.⁸ CD measures slight differences in extinction between left and right circularly polarized light existing in chiral molecules. Because most molecules

relevant for life are chiral, chirality plays a major role in biochemistry and pharmacology, and today, it is important in nanoscience and nanotechnology.^{9,10} For instance, chiral nanoscale materials are used for asymmetric catalysis, chiral recognition, enantiomeric analysis, enantioselective separation, and also as molecular devices,^{11–13} besides the fact that chiral nanoparticles like fullerenes and carbon nanotubes are common in nature.¹⁴ However, CD has a moderate sensitivity, which hampers the analysis of chiral molecules at low concentrations. On the other hand, it has been observed that ligand-protected metal nanoparticles (LPNPs) have exceptional optical activity that contrasts those of the components, ligands and nanoparticles.^{15,16} Therefore, it has been suggested that chiral NP complexes could offer the possibility to create strong optical activity in the visible region, where the geometry and composition of the LPNPs are crucial to enhance and understand CD signals.^{17–19}

Optical activity has been observed in a new class of metallic materials at the nanometric scale. Specifically, CD signals have been measured in LPNPs when chiral ligands were used.¹⁶ LPNPs are composed of a metallic cluster or NP core surrounded by organic molecules or organometallic compounds. Figure 1 shows a schematic atomic model of these compounds. During the last 15 years, considerable progress has been achieved to synthesize and characterize these novel nanomaterials. Additionally, there have been published several reports confirming the observation of optical activity using distinct chiral adsorbates as protecting ligands of Au, Ag, Pd, and FePd NPs, where the behavior depends on the composition of the NP.^{13–24} A key

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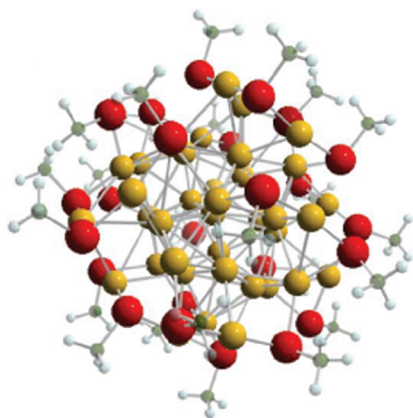


Figure 1. Schematic atomic model of a metallic nanoparticle of Au_{38} surrounded by methyl thiols. Au atoms are in yellow; S, red; C, green; and H white.

piece of information to look into the origin of the optical activity displayed by LPNPs is the CD spectrum of the isolated ligand adsorbates. As most of this type of molecules, they only absorb light and, therefore, have nonzero CD values in the ultraviolet region. Then, according to the experimental observations, the location and strength of the optical activity suggests that the electronic structure of the metallic core would be highly sensitive to the chiral environment imposed by the ligands or, even more, an inherently chiral metallic NP, or probably both mechanisms would be responsible for the nonzero values measured for the CD spectra.¹⁵ Within this context, CD enhancements that are not due to changes in the molecular absorption coefficient have been observed, but they could be assigned to a kind of metal NP-assisted phenomenon.¹⁸ The mechanisms that correspond to such CD signals are still unknown but depend on the size, morphology, and composition of the metallic NP, as well as on the chirality, location, and orientation of the ligands and on the specific assembly of the metal NPs.^{25,26}

Besides the significance of these observations, only few theoretical studies have been performed using state of the art quantum mechanical calculations to understand the origin of the optical activity of LPNPs and the possible CD signal enhancement mechanisms. In this Perspective, we discuss recent theoretical/computational work aimed to elucidate the origin of this exceptional optical activity shown by LPNPs, considering the relationship between morphology and CD. In particular, we discuss recent results proposed to distinguished among the two different mechanisms that have been formulated to explain the optical activity in chiral ligand-protected metal nanoparticles. The first one assumes a chiral metallic core, whereas the second one proposes an achiral core, with chirality induced by a dissymmetric field.

It is well-known that the electronic and optical properties of clusters and nanoparticles depend on the symmetry of the geometric structure of the system, as well as its morphology, and on the surface structure and bonding. Before the observation of the intense optical activity in L-glutathione-protected gold cluster compounds,¹⁶ it was found or assumed that the structures of metallic clusters and nanoparticles were based on fragments of the bulk crystal lattice or symmetrically adjoined or twinned combinations of them (e.g., fcc-derived octahedral or truncated pentagonal decahedra). In particular, for thiol-protected Au nanocrystals with sizes in the range of 20–200 atoms, there

was strong evidence favoring truncated decahedral structures, with symmetrically compact metal cores, slightly dilated by the weakly binding adsorbate groups. These considerations ruled out the possibility of topologically interesting structures, such as those having a helical or chiral character. To investigate the existence of chiral or helical structures in small gold clusters and provide support for the intrinsically chiral cluster core mechanism as being responsible for the optical activity observed in the glutathione-protected gold cluster compounds, reliable theoretical calculations, using state of the art methodologies, were required. Garzón and co-workers gave the first steps in that direction by combining genetic algorithms and many-body potentials (to perform global cluster structural optimizations) and density functional theory (DFT) calculations (to confirm the energy ordering of cluster isomers).²⁷ After a systematic search of energetically stable gold cluster structures of different sizes, chiral configurations were obtained as the lowest-energy isomers of bare, unprotected (Au_{28} and Au_{55}) and methylthiol-protected [$\text{Au}_{28}(\text{SCH}_3)_{16}$ and $\text{Au}_{38}(\text{SCH}_3)_{24}$] gold nanoclusters.^{27,28} Those results indicated that the largest CD responses could be expected to arise from more distorted chiral clusters.²⁹

Within the possible mechanisms that could explain the optical activity observed in chiral ligand-protected gold nanoclusters, one has also been mentioned that assumes a nonchiral or achiral core with chirality induced by chiral adsorption patterns or with chiral ligands in achiral adsorption patterns.^{20,30} A theoretical study that describes the so-called dissymmetrical field model demonstrates that the induced optical activity in chiral monolayer-protected clusters could arise from symmetric (achiral) metal cores perturbed by a dissymmetric or chiral field originating from the adsorbates.³⁰ This model implies that the electronic states of the nanocluster core are chiral, yet the lattice geometries of these cores need not be geometrically distorted by the chiral adsorbates. In other words, chiral adsorbates or dissymmetrically placed achiral adsorbates induce a chiral perturbation on the core, making it optically active, whereas symmetric achiral adsorbates or symmetric arrangements result in symmetric perturbations and are thus optically inactive.³⁰ Thus, the nature of the distance-dependent dissymmetric electrostatic perturbation, influenced by both the dissymmetry of the adsorption pattern and the centers of point asymmetry on the ligands (chiral ligands), is effective in inducing chirality even in a symmetric metal core. The dissymmetric field model predicts that the largest chiral image charges and CD responses are expected to arise from chiral adsorbates with the largest surface coverage and charge magnitude, smallest distance to the surface, and maximally dissymmetric adsorption pattern.³⁰

To gain some insight into the optical activity shown by LPNP, time-perturbed DFT for the electronic, optical, and chiroptical properties of the optical activity in thiolated ($-\text{SR}$)-protected neutral $\text{Au}_{38}(\text{SR})_{24}$ and the anionic $[\text{Au}_{25}(\text{SR})_{18}]^-$ nanoclusters was performed.^{17,31,32} Here, we analyze the main conclusions of these results to discuss the role of the metallic core and ligands in the optical activity by considering different parameters, such as the size of the metallic NP, as well as different morphologies, the chirality of the ligands, and their orientations. Then, at the end of the paper, we discuss future issues of this emerging area and challenges for theory and simulations.

In the case of $\text{Au}_{38}(\text{SR})_{24}$, two completely different metallic structures were analyzed to gain insights into the relevance of the metallic cluster morphology in the optical activity.³¹ The first compound had a metallic cluster with low symmetry and, thus,

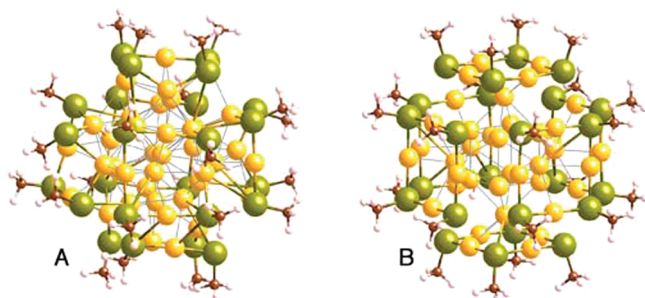


Figure 2. Atomic structure of gold LPNPs **A** and **B** according to refs 28, 33, and 27. Au, yellow; S, olive green; C, brown; H white. Adapted from ref 31.

chiral morphology, and the second one came from a high-symmetry metallic cluster. These structures were surrounded by 24 thiol units, where methylthiols ($R_{\text{meth}} = \text{CH}_3$) were used, which are nonchiral molecules. It was found that the distortion of the metallic cluster is directly related to the intensity of the spectra, such that lower distortion (or high symmetry) shows a less intense CD, as we explain below. To arrive at such a conclusion, the contributions to the total CD spectra from the isolated building parts of the nanoparticle, namely, the core atoms, shell atoms, and ligand molecules, were analyzed separately.³¹ The results support the proposal of an intrinsically or ligand-induced chiral metallic core as mainly responsible for the optical activity.²⁹

The two different structures for the $\text{Au}_{38}(\text{SCH}_3)_{24}$ compound **A** of lowest symmetry and thus chiral and compound **B**

The distortion of the metallic cluster is directly related to the intensity of the spectra, such that lower distortion (or high symmetry) shows a less intense CD.

coming from a high-symmetry cluster, with sizes similar to those of experimental compounds (1–1.5 nm), are shown in Figure 2. Compound **A** was obtained by Garzón and collaborators²⁸ by relaxing the nonchiral Au_{38} cluster with O_h symmetry, which interacted with 24 molecules of SCH_3 on the three-atom hollow sites of the faces of the bare NP. They found that the most stable thiol-passivated NP was chiral. Compound **B** was obtained by Häkkinen and collaborators³³ and consists of a core of 14 gold atoms with cubic structure with one Au atom in each corner plus six other Au atoms, each one sitting atop of the center of each cubic face. The core is protected with a shell formed by 24 gold-thiolated molecules, which are arranged in six tetramers of $(\text{AuSCH}_3)_4$.³³ Both structural models were found using the DFT generalized-gradient approximation (GGA) within the same level of approximation, where they were found to be very close in energy, with the chiral structure **A** favored by 0.5 eV.³³

Figure 3a shows the CD of compounds **A** and **B** in the left and right top panels, respectively. The calculated CD spectra show features that allowed us to distinguish between these two different compounds. The optical activity of compound **A** is

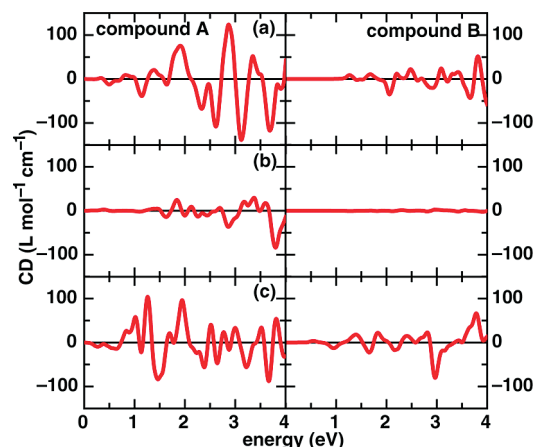


Figure 3. CD spectra of compounds **A** and **B** in the top panels (a), left and right, respectively. Panels (b) and (c) show the corresponding CD spectra of both compounds for their different building parts, gold core (Au_{14}) and metallic cluster (Au_{38}), both without ligands. A Gaussian broadening of 0.15 eV was employed in all curves. Adapted from ref 31.

more evident than that for **B**, possibly due to the strong structural distortion in the LPNP upon thiol passivation that induces chirality in an achiral bare cluster.^{27,28} CD of compound **A** shows more negative and positive peaks in the range of interest than the one of compound **B**, which is also less intense. While for **A** the more intense peaks are between 2.0 and 3.2 eV, for **B**, they are above 3.5 eV. To understand the difference of both spectra, the CD for their different isolated metallic building parts are shown separately. As we mentioned, both compounds consist of a core of 14 gold atoms surrounded by a shell of 24 gold atoms. In Figure 3b, the CD from the 14 Au atoms in the core of both LPNPs is shown. The core of compound **B**, with cubic symmetry, does not show any optical activity, while the core of compound **A** shows CD from 1.5 eV, and its intensity increases as the photon energy does. The CD intensity coming just from the disorder core in **A** is smaller as compared with the total signal of the whole LPNP observed in Figure 3a. In Figure 3c, the CD from all Au atoms, the 14 Au atoms in the core, plus the outer shell with 24 Au atoms is shown. Now, both compounds show optical activity, with the one for the disorder LPNP, compound **A**, being more intense and richer in peak structure. By comparing panels (a) and (c), we can observe the influence of the ligands, which open the optical gap and modify the CD line shape but do not modify the overall intensity.

The results described above for $\text{Au}_{38}(\text{SCH}_3)_{24}$ show that the distortion of the geometry in the metallic cluster is directly related to the intensity of the CD signal as the signal is increased with higher distortion. The intensity of the CD signal of just the metallic cluster is similar to the total CD signal of the LPNP, $\text{Au}_{38}(\text{SCH}_3)_{24}$. On the other hand, significant optical activity has been observed experimentally in protected clusters where the metallic core possess higher symmetry than the intense signal observed in the CD spectra of the anionic $[\text{Au}_{25}(\text{SG})_{18}]^-$ particle.³⁴ Because the metallic part of $[\text{Au}_{25}(\text{SR})_{18}]^-$ is highly symmetrical, it was thought that in this case, the ligands could play a crucial role in the displayed optical activity.

In the case of the $[\text{Au}_{25}(\text{SR})_{18}]^-$ anionic protected cluster, the atomic structure of the metallic core and S atoms was determined experimentally,^{35–37} and an accurate comparison with theoretical results has been done.^{17,38} As shown in Figure 4, this LPNP

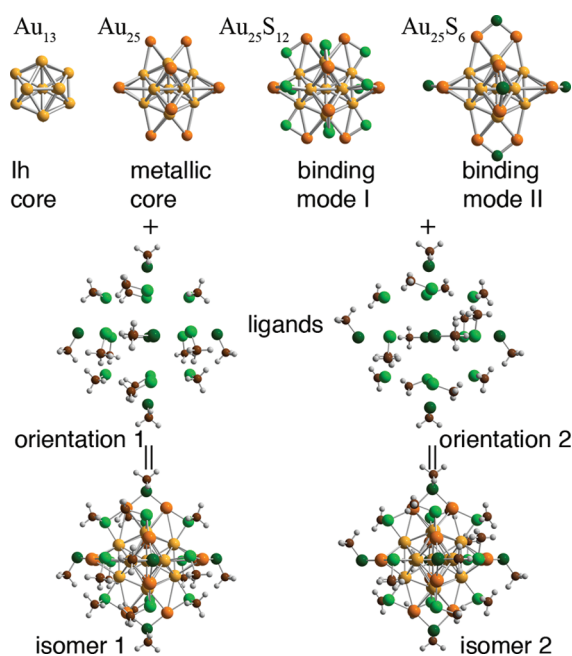


Figure 4. Atomic model of the $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ cluster composed of an icosahedral Au_{13} core (Au atoms in yellow), plus 12 external Au atoms (in orange), plus six staple motifs formed by $-\text{S}-\text{Au}-\text{S}-\text{Au}-\text{S}-$ structures, which give rise to two distinct binding modes I and II. The S atoms forming binding mode I are in dark green, while S atoms in mode II are in light green. Finally, we show two different orientations of the protecting ligands, which give rise to different isomers. S atoms (light and dark green) are displayed twice, in the upper and middle atomic structures, to facilitate the description. However, only one set of S atoms should be taken into account. Adapted from ref 17.

is composed of an icosahedral (Ih) core Au_{13} capped with 12 external gold atoms to form the metallic core of 25 Au atoms and the ligands, which adopt a bridging bonding mode forming six “staple” motifs ($-\text{S}-\text{Au}-\text{S}-\text{Au}-\text{S}-$).³⁸ Twelve of the $-\text{SR}$ ligands are connected with one external Au atom and one Au atom that belongs to the icosahedral core forming what is called the Au–S–Au binding mode I.³⁷ On the other hand, the six V-shaped Au–S–Au binding modes II are composed each one by a pair of external Au atoms bridged by one $-\text{SR}$ ligand, as shown in Figure 4.

Exploiting the fact that the morphology of the metallic core of this NP is well known, the optical activity of the $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ was studied theoretically by considering two different kind of thiols to protect the Au_{25} metallic cluster, the chiral ligand cysteine ($\text{R}_{\text{cys}} = \text{C}_\beta\text{H}-\text{C}_\alpha\text{H}(\text{NH})_2-\text{COOH}$) and the nonchiral methylthiolated ligand ($\text{R}_{\text{meth}} = \text{CH}_3$).¹⁷ Also, different ligand orientations were analyzed to understand the influence of the ligand motif on the optical activity. In this case, it was found that the optical activity is mainly due to the overall chiral geometry of the relaxed cluster structures and independent of whether the ligands are chiral or not. However, the incorporation of the ligands creates a dissymmetric field that induces chiral character in the electronic transitions, which results in an enhancement in the intensity of the optical activity signal from the metallic core. In addition, it was found that the CD intensity depends on the orientation of the thiolate ligands forming the cluster protecting layer, but the line shape is quite independent.

The calculated CD spectra of the complete LPNPs with either ligand R_{cys} or R_{meth} are shown in the left and right panels of

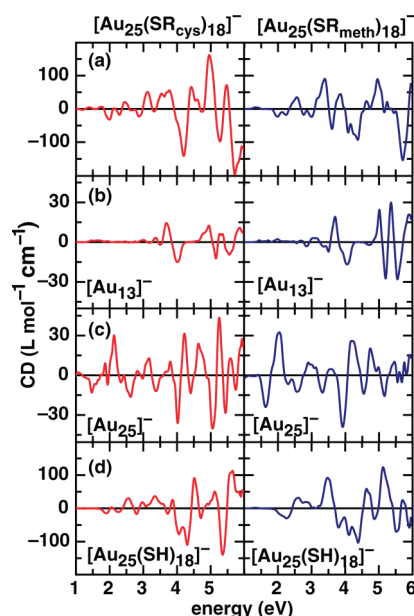


Figure 5. Circular dichroism of (a) $[\text{Au}_{25}(\text{SR})_{18}]^{-}$, (b) the icosahedral core of the Au_{13} cluster, (c) two capped Au_{25} clusters, and (d) $[\text{Au}_{25}(\text{SH})_{18}]^{-}$. The left panels correspond to LPNP protected with $\text{R} = \text{R}_{\text{cys}}$, and the right panel is for LPNP protected with $\text{R} = \text{R}_{\text{meth}}$. Adapted from ref 17.

Figure 5a, respectively. In both cases, the orientation of the ligands corresponds to isomer 1 displayed on the left-hand side of

The incorporation of the ligands creates a dissymmetric field that induces a chiral character in the electronic transitions, which results in an enhancement in the intensity of the optical activity signal from the metallic core.

Figure 4. Good agreement between the line shape of the calculated CD spectrum of the $[\text{Au}_{25}(\text{SR}_{\text{cys}})_{18}]^{-}$ cluster with that one measured³⁴ for the glutathione-capped $[\text{Au}_{25}(\text{SG})_{18}]^{-}$ was recently reported.¹⁷ Although the nonchiral R_{meth} ligands were not reported in the experiments, useful information of the system was obtained by comparing the CD results for these and the chiral R_{cys} ligands. For instance, the CD signal of the LPNP using the chiral ligand is about 50% more intense at energies above 4 eV than the one where the nonchiral ligands are used. The main reason is because chiral ligands have nonzero CD at those energies and higher, while nonchiral ligands have zero CD at all energies. Also, both CD spectra are similar for energies smaller than 3 eV because the electronic transitions at those energies mostly belong to the metallic core, particularly to the Au atoms in the icosahedral core.¹⁷

Again, to better understand the difference of both spectra, the CDs for their different building parts were calculated separately;

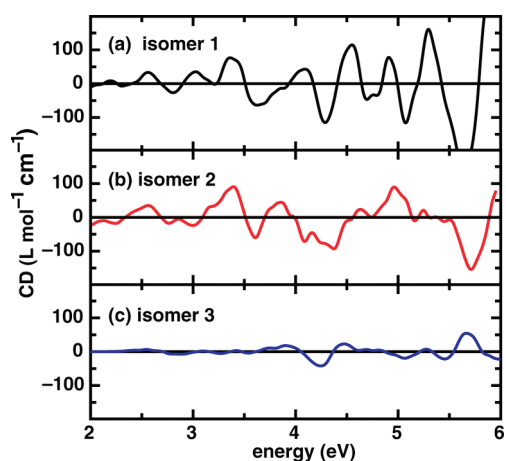


Figure 6. Calculated CD spectra of three isomers of $[\text{Au}_{25}(\text{SR}_{\text{meth}})_{18}]^{-}$, where the $-\text{CH}_3$ groups are oriented in different ways.

the isolated icosahedral core (Au_{13}) and the isolated metallic core (Au_{25}) are shown in Figure 5b and c, respectively. These CD signals of just the metallic parts have maximum and minimum intensities between -30 and $+30 \text{ L mol}^{-1} \text{ cm}^{-1}$ for both ligands. This represents a relatively small contribution to the total CD signal of the LPNP, in agreement with the fact that for smaller distortion, the CD signal is small. Compared with the calculated CD for both $\text{Au}_{38}(\text{SR})_{24}$ compounds A and B and their corresponding metallic cores, it is found that the Au_{13} and Au_{25} CD signals are also small, mainly due to the small structural distortion. Nevertheless, when hydrogen-saturated sulfur atoms (SH) are incorporated into the structure, the intensity of both CD spectra increases about four times with respect to the isolated metallic clusters (Au_{25}), as can be seen in Figure 5d. This enhancement in the CD intensity suggests that the incorporation of the thiols creates a dissymmetric field that induces a chiral character in the electronic transitions involving the 24 Au atoms. This observation is supported by the fact that a similar enhancement is obtained for both chiral and nonchiral ligands, R_{meth} and R_{cys} , as well as for SH groups, as shown in the left and right panels of Figure 5a and d. Therefore, it was concluded that the optical activity measured in $[\text{Au}_{25}(\text{SG})_{18}]^{-}$ includes the slight structural distortion of the two-shell metallic core, as well as the induction of a dissymmetric field generated by the ligand groups composing the protecting layers, independently of the chiral character of the molecules.

It was also predicted that the CD line shape of $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ can be highly sensitive to the orientation of the thiolate ligands forming the cluster-protecting layer and thus to the stability of the thiolate–Au binding modes.¹⁷ To explore the influence of ligand configuration on the CD spectra, three isomers with

are shown, and a third orientation with higher symmetry was considered for isomer 3 (not shown here). The energy difference between isomers is smaller than 0.20 eV. The CD spectra of these three isomers are plotted in Figure 6. Notice that the general behavior of the CD spectra is similar in all cases, but the intensity is very sensitive to the orientation of the $-\text{CH}_3$ groups. The latter shows that the orientation of the ligand could be more important than the chirality of the ligands themselves.

The study of ligand-protected NPs that shows the extraordinary optical activity described here provides important challenges for theory/simulation models and has repercussions in sensing chiral molecules and in applications in asymmetric catalysis. Here, we have examined some recent results where the CD of thiolated ($-\text{SR}$)-protected neutral $\text{Au}_{38}(\text{SR})_{24}$ and anionic $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ nanoparticles was calculated. It was shown that the distortion of the geometry in the metallic cluster is directly related to the intensity of the CD signal. It was also observed that a weak CD signal, due to the slight distortion of the cluster core, can be enhanced several times by the presence of the ligands, independently of the chirality of the ligands. Similar enhancements were obtained for ligands with different chirality, in particular, for the nonchiral R_{meth} , and the chiral R_{cys} ligands, as well as for SH groups. Additionally, the CD intensity is very sensitive to the orientation of the R groups. These results suggest that CD signals of given molecules can be substantially modified and intensified by using metallic NPs or that the CD signal coming from a small distorted metallic cluster can be enhanced by the presence of the ligands.

In this Perspective, we have discussed the role of morphology in the different mechanisms involved in the extraordinary optical activity displayed by ligand-protected metallic nanoparticles. These results show the possibility to enhance CD signals exhibited by chiral molecules by using metallic nanoparticles or those exhibited by chiral metallic nanoparticles by using ligands. Two different mechanisms were identified from first-principles calculations; the first one assumes a chiral metallic core, whereas the second one proposes an achiral core, with chirality induced by a dissymmetric field. Thus, the two mechanisms cannot be differentiated, but they act concurrently and seem to depend on the size and shape of the metallic nanoparticle, as well as on the location and orientation of the ligands. In this sense, further studies should be performed to clarify the specific contributions of all of the possible mechanisms that can enhance the optical activity to exploit potential applications in, for example, the characterization at low concentrations of chiral molecules and their interactions for sensing catalysis based on asymmetric processes and other exciting applications in chiral nanotechnology. Therefore, it is necessary to study the specific contributions of each mechanism, including the possibility to enhance CD signals by using surface plasmon resonances. It is expected that this information will motivate further experimental and theoretical studies using metallic nanoparticles in this emerging area. Whether the goal is to use nanostructures for new approaches to solving problems in chiral technology or to use molecular chirality to engineer useful properties in nanoscale materials, this area is fruitful and exciting and is certain to continue to attract interest for the years to come.

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Similar enhancement is obtained for both chiral and nonchiral ligands.

nonchiral ligands ($[\text{Au}_{25}(\text{SR}_{\text{meth}})_{18}]^{-}$), where the only difference among these isomers is the orientation of the ligands, were considered. In Figure 4, the ligand orientations of isomers 1 and 2

BIOGRAPHIES

Cecilia Noguez obtained her doctorate in Physics at the Universidad Nacional Autónoma de México (UNAM) in 1995, working on the physical properties of low-dimensional structures. She spent 1 year at the University of Rome Tor Vergata in Italy, studying the optical response of surfaces, and then was a postdoctoral researcher at the Department of Physics and Astronomy at Ohio University, working on silicon clusters. In 1996, she joined the Institute of Physics at UNAM, where she has been a Professor of Physics since 2005. Some of her current research focuses on the surface plasmon resonances of metal nanoparticles and the optical activity of chiral nanoparticles and their applications (see <http://www.fisica.unam.mx/cecilia>).

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