

On the Origin of the Optical Activity Displayed by Chiral-Ligand-Protected Metallic Nanoclusters

Ariadna Sánchez-Castillo, Cecilia Noguez, and Ignacio L. Garzón*

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

Received August 31, 2009; E-mail: garzon@fisica.unam.mx

The optical activity displayed by chiral-ligand-protected metallic clusters (CLPMCs) is an enigmatic property occurring in these novel nanoscale materials with potential applications in chiral-related nanotechnology.¹ It was discovered by Schaaff and Whetten² for size-separated L-glutathione-protected Au clusters and later confirmed by other groups for CLPMCs covered with different ligands.³ Although various mechanisms,¹ including the *inherently chiral metallic core*, the *dissymmetric field effect*, and the *chiral footprint model*, have been proposed, to date it has not been possible to give a plausible explanation of the physicochemical origin of this phenomenon. This is mainly due to the lack of precise structural information on CLPMCs and the difficulty in quantifying their chiroptical response using quantum-mechanical approaches.^{1a} In this communication, we present a first-principles study, based on a recently developed methodology,⁴ of the circular dichroism (CD) spectrum of the thio group (RS)-protected Au₂₅(RS)₁₈ anionic cluster, for which reliable geometric and electronic structure information has been reported.^{5–7} By analyzing the calculated CD spectrum of the peculiar two-shell-structured metallic cluster core and the two chemically distinct thiolate–Au binding modes,⁷ we have obtained useful insights regarding the origin of the optical activity measured in glutathione-capped Au₂₅(GS)₁₈ clusters.^{2,7,8} We have found that the weak CD spectrum due to a slight structural distortion in the two-shell metallic core is enhanced by the dissymmetric location of the ligands participating in the two thiolate binding modes⁷ of the [Au₂₅(RS)₁₈][–] cluster. Thus, the mechanisms previously proposed¹ cannot be differentiated but act concurrently.

First-principles calculations using time-dependent density functional theory (TD-DFT) have been successful in explaining the optical absorption spectra measured in protected Au₂₅(RS)₁₈ clusters.^{5,6c,9} Although TD-DFT has previously been used in calculations of CD for relatively small molecules,¹⁰ this methodology has not been applied to explore the chiroptical properties of CLPMCs because of the huge computational effort involved. An alternative approach for calculating the CD of nanoscale materials is to use DFT time-dependent perturbation theory to evaluate rotational strengths.⁴ A test of the reliability of this theoretical procedure has shown excellent agreement with TD-DFT and experimental results for CD of small chiral molecules, fullerenes, and carbon nanotubes.^{4a} Further details of this methodology for thiolate-covered Au clusters have been reported previously^{4b} and are also given in SI-A in the Supporting Information.

To theoretically investigate the chiroptical properties of CLPMCs, we first used DFT to optimize the structure of the anionic cluster [Au₂₅(SR)₁₈][–] starting with the geometry of the isomer **1** from ref 5. Next, the structure optimization was done with two types of ligands: the chiral amino acid cysteine [R_{cys} = C_βH₂–C_αH(NH₂)–COOH] and the achiral methylthiolate group (R_{meth} = CH₃). While the [Au₂₅(SR_{cys})₁₈][–] cluster is an appropriate theoretical model of the glutathione-protected gold anionic cluster [Au₂₅(SG)₁₈][–], whose CD spectrum has been measured,^{2,7,8} the [Au₂₅(SR_{meth})₁₈][–] cluster is a useful reference for comparing the chiroptical properties of clusters protected by chiral and achiral ligands. The simplification in the ligands

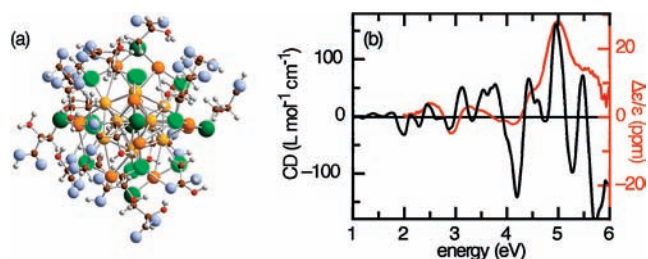


Figure 1. (a) Atomic structure and (b) CD spectrum of [Au₂₅(SR_{cys})₁₈][–]. The spectrum is compared with the experimental data⁸ for the [Au₂₅(SG)₁₈][–] cluster (red line). The calculated spectrum was blue-shifted by 0.3 eV, and a Gaussian broadening of 0.6 eV was used (see SI-A).

used in the present calculations is justified by experimental and theoretical results indicating that the structural and energetic properties as well as the optical absorption of Au₂₅(RS)₁₈ do not depend on the ligand R.^{5,9,11} Figure 1a shows the optimized structure of the cysteine-protected anionic gold cluster [Au₂₅(SR_{cys})₁₈][–]. Its geometrical properties, as well as those of the [Au₂₅(SR_{meth})₁₈][–] cluster, are in good agreement with the structural parameters obtained from the crystalline phase^{6a,c} using R = CH₂–CH₂Ph, including the slight distortion of the icosahedral Au₁₃ kernel, and the asymmetric positions of the sulfur atoms participating in binding mode I.⁷ Comparisons of the calculated and measured structural parameters are given in Table SI-1. The calculated optical absorption of the protected clusters for both the R_{cys} and R_{meth} ligands are also in good agreement with other theoretical⁵ and experimental results^{2,7,8} (see Figure SI-1), confirming the reliability of our methodology in predicting the optical properties of thiolate-protected gold clusters.

Figure 1b shows a significant result of the present study: an overall agreement between the line shapes of the calculated CD spectrum for the [Au₂₅(SR_{cys})₁₈][–] cluster and the measured⁸ spectrum for [Au₂₅(SG)₁₈][–]. Since our methodology has been shown to be reliable enough,⁴ the slight differences between theory and experiment might be due to cluster fluxionality¹² and to temperature and solvent effects¹⁰ not included in these calculations. To gain insight into the origin of the optical activity displayed by [Au₂₅(SR_{cys})₁₈][–], additional CD calculations were performed for its structural components and for [Au₂₅(SR_{meth})₁₈][–] (isomer **a**), which is protected with achiral ligands.

The left and right panels of Figure 2a display the calculated CD spectra of [Au₂₅(SR_{cys})₁₈][–] and [Au₂₅(SR_{meth})₁₈][–], respectively. The nonzero value and great similarity of the two line shapes indicate 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. This result was confirmed when our calculations gave a null CD spectrum (Figure SI-2) for a symmetric (achiral) [Au₂₅(SH)₁₈][–] model cluster constructed from the coordinates of the originally unrelaxed cluster. The close resemblance between the two CD spectra, particularly in the optical region, also implies that similar overall chiral geometries characterize the two clusters. In fact, a further analysis of

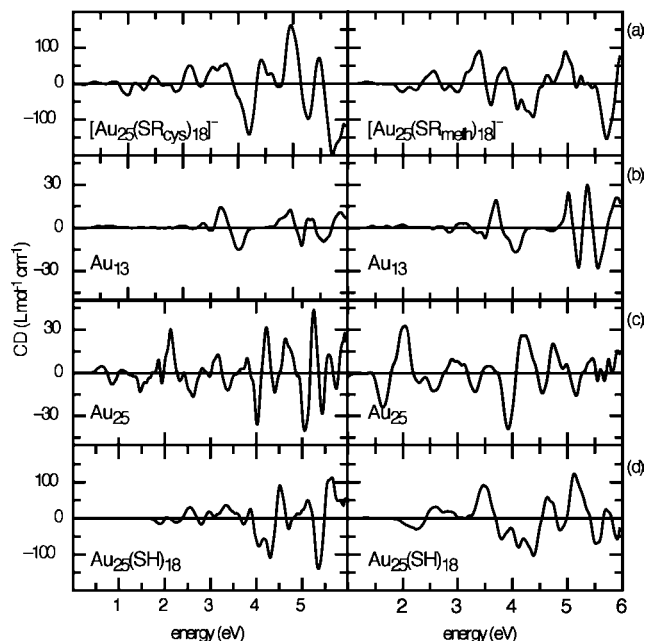


Figure 2. CD spectra of (left) $[\text{Au}_{25}(\text{SR}_{\text{cys}})_{18}]^{-}$ and (right) $[\text{Au}_{25}(\text{SR}_{\text{meth}})_{18}]^{-}$: total spectra (a) and spectra of (b) the distorted icosahedral Au_{13} core, (c) Au_{25} , and (d) $[\text{Au}_{25}(\text{SH})_{18}]^{-}$. A Gaussian broadening of 0.2 eV and a blue shift of 0.3 eV were used (see SI-A).

the two relaxed cluster structures indicates that the Au_{13} core shows a deviation from I_h symmetry. Additionally, the remaining 12 external Au atoms are also placed in nonsymmetric positions with respect to the slightly distorted icosahedral core. Figure 2b,c shows the relatively weak CD spectra for the Au_{13} and Au_{25} subunits, respectively, in the two protected clusters. They represent the relatively small contribution (with maximum and minimum intensities between -20 and $20 \text{ L mol}^{-1} \text{ cm}^{-1}$) of the two-shell metallic core to the CD spectrum of the CLPMC in comparison with the larger signal calculated for the more distorted metallic core of the $\text{Au}_{38}(\text{SCH}_3)_{24}$ cluster^{4b} and for the intrinsically chiral bare Au_{34}^{-} cluster.^{4c} When hydrogen-saturated sulfur atoms were attached to form binding modes I and II⁷ in each cluster, it was found that the calculated intensity of the CD spectrum increased by a factor of 4, with the first peak appearing with a positive sign at $\sim 2.25 \text{ eV}$ (Figure 2d). This increment is partially related to the additional cluster deformation caused by the bent-out positions of the 12 S atoms participating in binding mode I.⁷ A much higher enhancement in the CD spectrum was obtained when the whole R_{cys} and R_{meth} groups replaced the saturating H atoms to generate the total calculated CD signal shown in Figure 2a. This large enhancement in the CD intensity (varying from -180 to $180 \text{ L mol}^{-1} \text{ cm}^{-1}$) suggests that incorporation of the $\text{C}_\beta\text{H}_2\text{-C}_\alpha\text{H}(\text{NH}_2)\text{-COOH}$ and CH_3 groups creates a dissymmetric field that induces a chiral character in the electronic transitions involving the 24 Au atoms forming the two Au–S binding modes.⁷ In fact, the predominant states in the HOMO–LUMO region of the total and projected electron density of states of $[\text{Au}_{25}(\text{SR}_{\text{cys}})_{18}]^{-}$ correspond to the 24 external Au atoms ($\sim 75\%$) and the 12 S atoms involved in the binding mode I ($\sim 25\%$)⁷ (see Figure SI-3).

In the above discussion, it was established that our theoretical results predict a nonzero CD spectrum for $[\text{Au}_{25}(\text{SR}_{\text{meth}})_{18}]^{-}$. Since achiral ligands were used in that calculation, an immediate question is raised: why was a null CD spectrum measured when achiral protecting ligands were used?⁷ The answer is that only chiral ligands possess the enantioselectivity needed to break the symmetric environment in the racemic mixture of CLPMCs to generate an enantiomeric excess, which is responsible for the optical activity.

Additional calculations showed the strong influence of the thiolate groups on the CD signal of $[\text{Au}_{25}(\text{SCH}_3)_{18}]^{-}$. Optimization of a distinct isomer **b** that differs from the isomer **a** mentioned above just in the orientations of the methyl groups afforded a slightly more stable cluster (by 0.21 eV; see SI-B). A quite distinct CD spectrum for isomer **b** with similar overall intensity as for isomer **a** was found (see Figure SI-4).

In summary, our calculations show that the origin of the optical activity measured for the $[\text{Au}_{25}(\text{SG})_{18}]^{-}$ cluster is not unique but includes the slight structural distortion of the two-shell metallic core⁷ as well as the induction of a dissymmetric field generated by the R_{cys} and R_{meth} groups that also compose the protecting layers. These results are similar to those found in penicillamine-capped semiconductor nanocrystals,¹³ where the optical activity was assigned to a chiral interface. The chiral character of CLPMCs can be further studied to explore the enantiospecific interaction with chiral molecules of biological interest.¹⁴

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Supporting Information Available: Details of the theoretical procedure, description of isomer **b**, Table SI-1, and Figures SI-1–SI-4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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