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Circular dichroism simulated spectra of chiral gold nanoclusters: A dipole approximation

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Circular dichroism (CD) spectra of chiral bare and thiol-passivated gold nanoclusters have been calculated within the dipole approximation. The calculated CD spectra show features that allow us to distinguish between clusters with different indexes of chirality. The main factor responsible of the differences in the CD lineshapes is the distribution of interatomic distances that characterize the chiral cluster geometry. These results provide theoretical support for the quantification of chirality and its measurement, using the CD lineshapes of chiral metal nanoclusters.

Recent theoretical studies on the structural properties of gold clusters have shown that the lowest-energy (most stable) isomers of bare Au_{28} and Au_{55}, and thiol-passivated $Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}$ clusters correspond to chiral nanostructures[1,2]. These results provided theoretical support for the existence of chirality in metal clusters, suggested by the intense optical activity measured in the metal-based electronic transitions of size-separated glutathione-passivated gold nanoclusters in the size range of 20-40 atoms[3].

Another theoretical prediction, based on quantifying chirality through the Hausdorff chirality measure (HCM)[1,2,4], indicates that the strong structural distortion in a gold cluster upon thiol passivation could induce chirality in an achiral bare cluster or increase the index of chirality in an already bare chiral cluster[1,2]. To confirm this prediction further experimental studies on chiral bare and passivated clusters are expected to be performed in the near future using, for example, circular dichroism (CD) spectroscopy[5].

To explore the capability of the CD technique to detect different indexes of chirality existing in bare and passivated gold nanoclusters it would be useful to have a theoretical estimation of their CD lineshapes. Quantum-mechanical calculations of CD spectra for small and moderately sized organic molecules had been performed[6], however, this type of approach is still inappropriate for passivated gold nanoclusters due to the huge computational effort that would be involved[6]. In this work, we present results on simulated CD spectra of chiral gold nanoclusters obtained through a dipole approximation[7,8]. This study allows to gain insights on the variations of the CD lineshape due to different indexes of chirality existing in gold clusters. It is expected that this information would be useful to motivate further experimental studies that confirm not only the existence of chirality in gold nanoclusters, but also to correlate distinct features of the CD spectra with the different indexes of chirality[1,2].

In this work the nanoclusters of interest are composed by N gold atoms. We suppose that each one of these atoms is represented by a polarizable point dipole located at the position of the atom. We assume that the dipole located at $\mathbf{r}_i$, $i = 1, 2, \ldots, N$, is characterized by a polarizability $\boldsymbol{\alpha}_i(\omega)$, where ω denotes the angular frequency. The cluster is excited by a circularly polarized incident wave $\mathbf{E}_{\text{inc}} = E_0(\hat{\mathbf{x}} \pm \imath\hat{\mathbf{y}})e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t}$, where t denotes time, $\mathbf{k}$ is the wave-vector, whose magnitude is given by $k = \omega/c = 2\pi/\lambda$, c is the speed of light, and λ is the wavelength of the incident light. Here $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ denotes the unitary vector along any of two orthogonal directions, and the sign $+$ $(-)$ corresponds to right- (left-) circularly polarized light.

Each dipole of the system is subject to a total electric field that can be divided into two contributions: (i) the incident radiation field, plus (ii) the radiation field resulting from all of the other induced dipoles. The sum of both fields is the so called local field and is given by

$$\mathbf{E}_{i,\text{loc}} = \mathbf{E}_{i,\text{inc}} + \mathbf{E}_{i,\text{dip}} = \mathbf{E}_{i,\text{inc}} - \sum_{i \neq j} \mathbb{T}_{ij} \cdot \mathbf{p}_j, \qquad (1)$$

where $\mathbf{p}_i$ is the dipole moment of the atom located at $\mathbf{r}_i$, and $\mathbb{T}_{ij}$ is an off-diagonal interaction matrix with 3×3 matrices as elements, such that

$$\begin{aligned} \mathbb{T}_{ij} \cdot \mathbf{p}_j = \frac{e^{ikr_{ij}}}{r_{ij}^3}\Bigg\{ &k^2\mathbf{r}_{ij} \times (\mathbf{r}_{ij} \times \mathbf{p}_j) \\ &+ \frac{(1 - ikr_{ij})}{r_{ij}^2}\left[r_{ij}^2\mathbf{p}_j - 3\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{p}_j)\right] \Bigg\}. \end{aligned} \qquad (2)$$

Here $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. On the other hand, the induced dipole moment at each atom is given by $\mathbf{p}_i = \boldsymbol{\alpha}_i \cdot \mathbf{E}_{i,\text{loc}}$, such that $3N$-coupled complex linear equations are obtained. These equations can be rewritten as

$$\sum_j \left[\frac{1}{\boldsymbol{\alpha}_j}\delta_{ij} + \mathbb{T}_{ij}(1 - \delta_{ij})\right] \cdot \mathbf{p}_j = \mathbb{M}_{ij} \cdot \mathbf{p}_j = \mathbf{E}_{i,\text{inc}}. \quad (3)$$

The matrix $\mathbb{M}$ is composed by a diagonal part given by $\frac{1}{\boldsymbol{\alpha}_j}\delta_{ij}$ and by an off-diagonal part given by $\mathbb{T}_{ij}$. The diagonal part is only related with the material properties

of each atom, while the off-diagonal part only depends on the geometrical properties of the system.

Once we solve the complex-linear equations shown in Eq. (3), the dipole moment on each atom in the cluster can be determined. Then, we can find the extinction cross section of the whole nanoparticle, in terms of the dipole moments, as[7,8]

$$C_{\text{ext}} = \frac{4\pi k}{E_0^2} \sum_{i=1}^{N} \text{Im}(\mathbf{E}_{i,\text{inc}}^* \cdot \mathbf{p}_i), \qquad (4)$$

where $*$ means complex conjugate. The extinction efficiency is defined as $Q_{\text{ext}} = C_{\text{ext}}/A$, where $A = 4\pi d^2$, and d is the maximum distance between any two atoms in the nanocluster. Finally, the circular dichroism spectra is obtained by subtracting the averaged extinction efficiencies for left- and right-circularly polarized light,

$$CD = <Q_{\text{ext}}^R>_S - <Q_{\text{ext}}^L>_S, \qquad (5)$$

where $<\cdots>_S$ indicates an average of the extinction efficiency, calculated over S different angular incident directions of the electric field[9].

In this work, we assume that the polarizability for each atom α_i is the same for all the atoms in the cluster ($\alpha_i = \alpha$), and is given by the well-known Clausius-Mossotti relation

$$\alpha = \left(\frac{R}{3}\right)^3 \frac{(\epsilon - 1)}{(\epsilon + 2)}, \qquad (6)$$

where ϵ is the macroscopic dielectric function of the nanoparticle, and R is the ionic radii of the atom. The dielectric function is taken from the measurements by Johnson and Christy[10] for bulk gold. This approximation has been used before providing good qualitative agreement between calculated optical properties and experimental data on gold and silver nanoparticles[11]. On the other hand, since chirality is a geometrical property, the CD spectrum will be more sensitive to the second term inside the bracket in Eq. (3), which depends on the cluster geometry, than to the first one that is related with the atomic polarizability. Therefore, in the present calculations the simulated CD spectra will include the geometrical information about the chiral clusters, despite the polarizability is incorporated in an approximated form.

The lowest-energy structures of the bare Au_{28} and Au_{38}, and thiol passivated $Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}$ clusters had been obtained using density functional theory (DFT) within the generalized gradient approximation (GGA)[1,2]. Both, the bare and thiol passivated most stable 28-atom gold clusters were found to be chiral, but a higher index of chirality was obtained for the passivated cluster. This lowest-energy passivated cluster was found upon relaxation of the bare chiral cluster, interacting with 16 SCH_3 molecules placed close to the three-atom hollow sites on the metal cluster surface[1,2]. The most stable thiol-passivated $Au_{38}(SCH_3)_{24}$ cluster was also found chiral[1,2], but it was obtained from the

relaxation of the achiral Au_{38} cluster with O_h symmetry interacting with 24 SCH_3 molecules placed on the three-atom hollow sites of the (111) faces of the bare cluster[12]. The Au_{38} isomer with O_h symmetry corresponds to a local minimum of the bare cluster according to DFT-GGA calculations[13], while the lowest-energy structure of the bare Au_{38} was found with C_s symmetry[13], but upon passivation, it transforms into a higher-energy passivated isomer[12].

FIG. 1: Circular dichroism spectra of Au_{38} clusters. (a) Before, with O_h symmetry, (dotted line) and after, with C_1 symmetry, (full line) passivation with 24 methylthiol molecules. (b) Lowest-energy isomer, with C_s symmetry, (full line) and the same cluster geometry but taking out 10 atoms that are placed on the plane of symmetry (dotted line).

In this work, we use the relaxed Cartesian coordinates of the clusters mentioned above to calculate their CD spectra. Figure 1(a) shows the CD lineshape calculated using Eq. (5) for the Au_{38} cluster before (dotted line) and after (full line) relaxation with the 24 methylthiol molecules. The zero value of the CD spectra before relaxation indicates that the left- and right-circularly polarized light is equally absorbed by the gold cluster since its geometrical structure corresponds to a truncated octahedral structure with O_h symmetry. Since the geometry of this cluster is highly symmetric, its CD spectrum should be zero in agreement with our result. On the other hand, the CD spectrum of the passivated cluster shows a non-zero lineshape due to the different absorption of the circularly polarized light. This behavior is expected since the passivated Au_{38} has been found chiral using the geometrical approach described in Refs. 1,2.

Figure 1(b) shows an interesting result on the relation between chirality and the lineshape of the CD spectrum. The full line corresponds to the calculated CD spectrum of the lowest-energy structure of the bare Au_{38}. The structure of this isomer has one plane of symmetry (C_s symmetry) and therefore is achiral[1,2]. However, as Fig. 1(b) shows, the CD spectrum is non-zero. The reason of such behavior is coming from the atomic array existing on the plane of symmetry. This plane contains 10 atoms that are not in symmetric positions but forming a chiral two-dimensional array. This subset of atoms generate the non-zero signal of the CD spectrum. To confirm this effect, the CD lineshape of the 38-atom cluster without including the atoms on the plane of symmetry was calculated (dashed line). Since in this case there is a complete reflection symmetry in the cluster, its CD spectrum is negligible.

FIG. 2: Circular dichroism spectra of Au_{28} clusters. (a) Before, with C_1 symmetry, and (b) after, with C_1 symmetry, passivation with 16 methylthiol molecules.

Figures 2(a) and 2(b) display the CD spectra of the

Au_{28} cluster before (bare) and after thiol relaxation (passivated), respectively. Both clusters are chiral according to the geometrical analysis, based on the HCM, described in Refs. 1,2. Therefore, it is expected that they have a non-zero signal in their CD spectra. However, Fig. 2 also shows that indeed there exist notorious differences between the CD lineshapes of these clusters. These differences could account for the distinct indexes of chirality existing in these clusters as was calculated before using the HCM[1,2]. In other words, Fig. 2 shows that clusters with different values of HCM can be distinguished through the lineshape of their CD spectra.

To understand the origin of the differences in the CD spectra of clusters with different values of their indexes of chirality, the extinction efficiencies, using right-circularly polarized light, are shown in Figs. 3 (a) and (b) for the bare and passivated Au_{28} clusters, respectively. Since the CD spectrum is calculated from the difference of this quantity with the one obtained using left-circularly polarized light, it is interesting to analyze the most important features of its lineshape. From Figs. 3 (a) and (b) it is evident that the clusters with different HCM values also generate distinguishable extinction efficiencies. By analyzing Eqs. (3 – 5), it is found that the cluster geometry, through the distribution of interatomic distances r_{ij}, is the main factor that generate the features (peaks and widths in the lineshape) of the extinction efficiency.

FIG. 3: Extinction efficiency using right-circularly polarized light of Au_{28} clusters. (a) Before, with C_1 symmetry, and (b) after, with C_1 symmetry, passivation with 16 methylthiol molecules. The insets show the geometry of the bare and passivated clusters.

The effect of the distribution of interatomic distances in the behavior of the extinction efficiency is more evident by comparing this quantity for the 38-atom cluster, before and after relaxation with the thiol molecules. Figure 4 shows the extinction efficiency using right-circularly polarized light for the bare Au_{38} isomer with O_h symmetry (upper panel) and for the passivated chiral cluster (bottom panel). The insets in Fig. 4 display the distribution of interatomic distances of the corresponding clusters. From these figures it can be noticed that the extinction efficiency of the chiral passivated cluster (bottom panel) has more structure and shows a broader

lineshape than the achiral cluster (top panel). This difference can be correlated with the different behavior of the distribution of interatomic distances that indicate a discrete variation of distribution for the achiral O_h cluster, whereas the chiral one shows a much broader and continuous distribution of interatomic distances.

The results presented in this work indicate that indeed chiral gold clusters with different indexes of chirality can be distinguished by the lineshape of their CD spectra. It was also found that within the dipole approximation, the origin of the distinct features of the CD lineshapes is related to the differences in the distribution of inter-

FIG. 4: Extinction efficiency using right-circularly polarized light of Au_{38} clusters. (a) Before, with O_h symmetry, and (b) after, with C_1 symmetry, passivation with 24 methylthiol molecules. The insets show the distribution of interatomic distances and the geometries of the bare and passivated clusters.

atomic distances. Therefore, CD spectra are able to detect the geometrical features that characterize clusters with different indexes of chirality. These geometrical differences will also be important in quantum mechanical calculations of the CD lineshapes. It is encouraging that despite the approximations included in the calculation of the simulated CD spectra, their lineshapes show similar features as those measured for glutathione-passivated gold nanoclusters[3]. In particular, there is a qualitative agreement between the calculated and experimental CD spectra in the energy range (2-4 eV), where the spectra shows the highest intensity .

In summary, CD simulated spectra are appropriate for the characterization of clusters with different chirality and provide useful information for further studies using a quantum mechanical approach, and for experimental studies on the quantification of chirality in metal nanoclusters.

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