Chirality in bare and passivated gold nanoclusters

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Chiral structures have been found as the lowest-energy isomers of bare (Au_{28} and Au_{55}) and thiol-passivated $[Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}]$ gold nanoclusters. The degree of chirality existing in the chiral clusters was calculated using the Hausdorff chirality measure. We found that the index of chirality is higher in the passivated clusters and decreases with the cluster size. These results are consistent with the observed chiroptical activity recently reported for glutathione-passivated gold nanoclusters, and provide theoretical support for the existence of chirality in these compounds.

Detailed knowledge of the lattice structure, shape, morphology, surface structure, and bonding of bare and passivated gold clusters is fundamental to predict and understand their electronic, optical, and other physical and chemical properties. This information is essential to optimizing their utilization as novel nanocatalysts,[1] and as building-blocks of new molecular nanostructured materials,[2] with potential applications in nanoelectronics[3] and biological diagnostics.[4] An effective theoretical approach to determine gold cluster structures is to combine genetic algorithms and many-body potentials (to perform global structural optimizations), and first-principles density functional theory (to confirm the energy ordering of the local minima). Using this procedure we recently found many topologically interesting *disordered* gold nanoclusters with energy near or below the lowest-energy ordered isomer.[5–8] The structures of these clusters showed low spatial symmetry or no symmetry at all, opening the possibility of having distinct electronic and optical properties in such systems. In other studies on passivated gold nanoclusters,[9,10] we also found that the effect of a methylthiol monolayer (24 SCH_3 molecules) on a truncated-octahedron (with fcc geometry) Au_{38} cluster is strong enough to produce a dramatic distortion on the gold cluster, resulting in a *disordered* geometry for the most stable $Au_{38}(SCH_3)_{24}$ passivated cluster.

Although the calculated structure factors of the disordered gold clusters were in qualitative agreement with the data obtained from x-ray powder diffraction on experimental samples,[6,7] the direct confirmation of the existence of bare and thiol-passivated gold nanoclusters with low or no spatial symmetry had not been possible due to the lack of enough experimental resolution for clusters in the size range of 1–2 nm.[11–13] Nevertheless, in a recent study using circular dichroism, Shaaff and Whetten (SW)[14] found a strong optical activity in the metal-based electronic transitions (across the near-infrared, visible and near ultraviolet regions) of size-separated glutathione-passivated gold clusters in the size range of 20–40 Au atoms. SW pointed out that the most plausible interpretation of these results is that the structure of the metal-cluster core of the gold-glutathione cluster compounds would be inherently chiral. Moreover, since the most abundant cluster in the experimental samples corresponds to

the passivated cluster $Au_{28}(SG)_{16}$, where SG denote the gluthatione adsorbate, SW proposed a chiral structure, with T point group, for the Au_{28} cluster.[14]

In earlier studies,[5–10] we have reported several structural, vibrational and electronic properties of the disordered gold nanoclusters. However, although an initial quantification of the amount and type of local disorder present in amorphouslike structures of Au_{55} was obtained,[15] to our knowledge, no attempt to theoretically investigate the existence of chirality in gold nanoclusters has been done before. In the light of the results obtained by SW regarding the intense chiroptical activity of size-separated glutathione-passivated gold nanoclusters, it is of interest to determine if the most-stable disordered structures we have found for bare and passivated gold nanoclusters are chiral, and to quantify their degree of chirality. In this paper, we present a structural analysis that shows the existence of chirality in these nanostructures. This is done by implementing a method, based on the Hausdorff chirality measure,[16,17] to quantify the index of chirality of clusters. Our results show that the metal cores of the passivated clusters are more chiral than the bare clusters and that the degree of chirality decreases with the cluster size. These results provide new insights on the effect of passivating agents on the bare metal cluster as a mechanism to generate chiral nanostructures with novel and perhaps unexpected properties.

Our initial step was to determine the lowest-energy structures of the bare and passivated gold nanoclusters. To this end we first performed global optimizations using the Gupta *n*-body potential and a genetic-symbiotic algorithm for bare gold nanoclusters of different sizes (Ref. 7 provides details on this methodology) . Through this procedure we obtained the distribution in energy of the most stable isomers for each cluster size. From this distribution, we selected representative isomers like those with the lowest energy, and those isomers that were considered good candidates to be the lowest-energy minima based on the existence of well known symmetric structures for certain cluster sizes such as the truncated octahedron, icosahedron, decahedron, etc. The representative isomers were then locally reoptimized through unconstrained relaxations using forces calculated from density functional theory (DFT) in the local-density (LDA) and
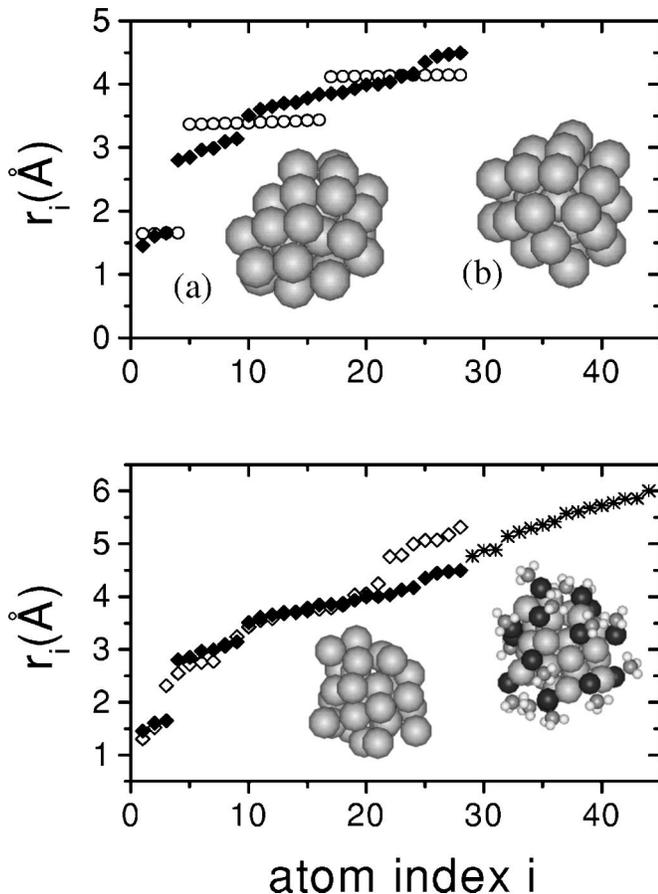
FIG. 1. Top panel: Distances of the gold atoms from the center of mass and cluster geometry for the lowest-energy disordered [closed diamonds and inset (a)] and the T [open circles and inset (b)] isomers of the bare Au_{28} cluster. Bottom panel: Distances of the gold (open diamonds) and sulphur (stars) atoms from the center of mass for the lowest-energy structure of the thiol-passivated $Au_{28}(SCH_3)_{16}$ cluster. The closed diamonds denote the same gold atom distances as in the top panel. They are included to show at the same scale, the degree of distortion and expansion of the gold metal cluster core upon passivation. The insets show the geometries of the metal core and the passivated cluster. Sulphur atoms are depicted as darker spheres.

generalized-gradient (GGA) approximations. The DFT calculations were done using the SIESTA code[18] with scalar-relativistic norm-conserving pseudopotentials[19] and a double-ζ basis set of numerical atomic orbitals[18] (see Refs. 8,10 for additional details on these calculations).

Here, we report results for the Au_{28} cluster since the lowest-energy structures for the Au_n, $n=38,55,75$, clusters have been published elsewhere.[5–8] Our results for the Au_{28} cluster show a similar pattern as was found for the larger sizes: the distribution of low-energy isomers shows a set of nearly degenerate in energy disordered structures, where the lowest-energy one corresponds to a highly distorted geometry. The T structure proposed by SW[14] was obtained as a local minimum of the potential energy surface with higher energy. The top panel of Fig. 1 shows both cluster geometries and the distribution of distances from the cluster center of mass. These structures mainly differ in the presence of a three-atom core in the lowest-energy disordered isomer whereas the T geometry contains a tetrahedral core. The DFT-LDA-GGA results confirm the higher stability of our disordered structure as compared with the T structure: we obtained an energy difference of -0.885 eV (LDA) and -0.638 eV (GGA) between both isomers. A similar trend, showing the higher stability of disordered isomers with respect to ordered ones, has been obtained for larger cluster sizes Au_n, $n=38,55,75$.[5,8] The physical origin of the higher stability of amorphouslike structures in bare gold nanoclusters has been studied by analyzing the metallic bonding and its effect on the local stress of the clusters. It results that the amorphization is a mechanism for strain relief that lowers the cluster energy, being more prominent in the case of gold due to the short-range of the n-body metallic interaction.[7,8,20]

The lowest-energy structures of the thiol-passivated $Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}$ clusters were obtained by performing local relaxations, using the forces calculated from the DFT-LDA-GGA first-principles method, and starting from different cluster-monolayer configurations. These include the lowest-energy ordered and disordered bare Au_{28} and Au_{38} cluster geometries obtained by the procedure described above, with the methylthiols molecules placed on different adsorption sites (top, bridge, hollow), as well as on random positions over the metal cluster surface. Figure 1 (bottom panel) shows a highly distorted passivated cluster that corresponds to the lowest-energy structure of the $Au_{28}(SCH_3)_{16}$ cluster, obtained by the relaxation of the disordered bare Au_{28} cluster with the thiols placed close to three-atom hollow sites. From the distribution of radial distances to the cluster center of mass shown in Fig. 1 (bottom panel), the degree of distortion and the ill-defined nature of the gold-thiol interface is evident. A similar strongly distorted geometry was found for the lowest-energy structure of the larger passivated $Au_{38}(SCH_3)_{24}$ cluster.[9,10] The main driving force producing the cluster distortion is the strong gold-sulphur interaction. An analysis of the metal-ligand interaction in the gold passivated clusters will be published elsewhere.[21] Meanwhile, recent calculations on smaller Au-thiolate compounds have confirmed that the strong covalent (directional) gold-sulphur interaction is mainly responsible for the metal cluster distortion.[22]

The principal objective of this work is to determine if the disordered lowest-energy structures of the bare Au_n, $n=28,38,55,75$, and passivated $Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}$ clusters are chiral, and to quantify the degree of chirality existing in them. This information is relevant for a proper interpretation of the circular dichroism measurements performed by SW on glutathione-passivated gold clusters.[14] Since chirality is a geometrical property of the system, independent of its chemical and physical manifestations, it is possible to quantify chirality without reference to experimental measurements, but using the inherent structural symmetry of the clusters. Although in recent years several approaches have been developed to measure chirality,[23,24] the Hausdorff chirality measure, proposed by Buda and Mislow (BM),[16] has emerged as the general method of choice for the quantification of chirality.[17] Within this approach, the degree of chirality is found by calculating the maximum overlap

between the actual molecular structure and its mirror image, using the Hausdorff distance[25] between their sets of atomic coordinates. By rotating and translating one structure with respect to the other, the optimal overlap can be calculated. This Hausdorff chirality measure (HCM) is a continuous and similarity invariant function of the molecular shape, and is zero only if the molecule is achiral. The advantage of this approach is that its numerical implementation for large clusters containing n atoms in a three-dimensional space is straightforward, as was discussed by BM.[16,17] Our numerical procedure was tested by calculating the degree of chirality of the three tetrahedra shapes considered by BM, obtaining the same values as reported by these authors.[16]

We calculate the HCM for the lowest-energy structures of the bare and thiol-passivated gold nanoclusters using their relaxed Cartesian coordinates measured with respect to the cluster center of mass. Through an inversion operation, the coordinates of the mirror image clusters were obtained. The HCM was obtained by calculating the maximum overlap between a given cluster and its mirror image. This corresponds to the minimum value of the Hausdorff distance between the sets of atomic coordinates of both structures. In order to obtain the minimum Hausdorff distance, the mirror cluster was translated and rotated around the original cluster in the three-dimensional space generating different configurations. For each of them, the Hausdorff distance with respect to the original cluster was calculated. The minimum of these values, normalized by the largest interatomic distance in the cluster, corresponds to the HCM. To check the reliablity of this methodology, the minimization of the Hausdorff distance was performed using the Broyden-Fletcher-Goldfarb-Shano method as suggested in Refs. 16,17, a conjugate gradient optimization, and a direct evaluation of the Hausdorff distance taking variations of $\pi/360$ for each rotational angle. The HCM values agree for the three methods up to the third significant digit.

Our results show that the HCM index of chirality for Au_{38} and Au_{75} is zero. These values are expected since the lowest-energy structures corresponding to these sizes have one plane of symmetry and therefore are achiral. In fact, these results constitute an additional test of our numerical implementation for calculating HCM in large clusters. The HCM index of chirality for the lowest-energy structure and the T isomer proposed by SW for Au_{28} are displayed in Table I, together with the value obtained for the lowest-energy structure of Au_{55} (see Fig. 1 in Ref. 15). These results show that the most stable structure of Au_{28}, obtained in this work, is less chiral than the one proposed by SW, and that the index of chirality varies slightly with the cluster size from 28 to 55 atoms. For the calculation of the HCM of the thiol-passivated gold nanoclusters, we only consider the coordinates of the Au atoms since we are interested in testing the suggestion of SW who proposed that the metal cluster core would be inherently chiral.[14] The HCM values for the metal core of the passivated $Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}$ clusters are also shown in Table I. These results show that both metal cluster cores are more chiral than the bare Au_{28} and Au_{38} clusters, and that the index of chirality for the passivated clusters decreases with the cluster size. It is noteworthy that the

TABLE I. Index of chirality of the lowest-energy structures of bare (first column) and thiol passivated (third column) gold nanoclusters. The second column shows that all the ordered isomers are achiral except the T isomer of Au_{28}. The index of chirality was calculated using the Hausdorff distance between the sets of atomic coordinates of the cluster and its mirror image. The cluster geometry was obtained through structural optimizations using a many-body potential, genetic algorithms and density functional theory.

Bare		Passivated
Au_{28} (disordered)	Au_{28} (T)	$Au_{28}(SCH_3)_{16}$ (disordered)
0.106	0.129	0.160
Au_{38} (C_s)	Au_{38} (O_h)	$Au_{38}(SCH_3)_{24}$ (disordered)
0.000	0.000	0.121
Au_{55} (disordered)	Au_{55} (I_h)	
0.117	0.000	
Au_{75} (C_s)	Au_{75} (D_{5h})	
0.000	0.000	

HCM values obtained for the bare and passivated chiral Au clusters are smaller than the values of the chiral tetrahedral shapes (HCM $= 0.221$, 0.252, 0.255 for D_2, C_2, and C_1 tetrahedra, respectively) obtained by BM.[16] In order to compare the HCM of Au clusters with a physical system, we calculated the index of chirality of the chiral D_2-C_{76} and D_2-C_{84}, and the achiral I_h-C_{60} fullerenes, obtaining the values 0.109, 0.102, and 0.000, respectively. These results support the reliability of our methodology since there is experimental evidence on the existence of chirality in the D_2-C_{76} fullerene.[26] This comparison also provides a useful reference to classify cluster and molecules in terms of their indexes of chirality, and indicates that the bare Au_{28} and Au_{55} clusters are as chiral as the D_2-C_{76}, but the passivated $Au_{28}(SCH_3)_{16}$ and $Au_{38}(SCH_3)_{24}$ clusters are slightly more chiral than such fullerene.

The above results on the existence of chirality in thiol-passivated Au nanoclusters are consistent with the chiroptical activity measured on size-separated glutathione-passivated gold nanoclusters in the size range 20–40 Au atoms since it was shown that the optical properties are insensitive to the tail of the adsorbate thiol.[14] Also, in the experimental samples it was found that the optical activity is weaker as the cluster size increases, and it is lost for larger clusters and for samples with mixed cluster sizes.[14] It remains to be verified if indeed there is a correlation between the value of the index of chirality and the strength of the intensity or other spectral features of the optical activity signal in the chiral samples. Another interesting prediction from the present calculations, to be confirmed experimentally, is related with the smaller index of chirality existing on bare clusters as compared to those for the metal core of passivated clusters. Our results imply that the effect of the passivating monolayer is strong enough to distort a bare cluster geometry, producing chiral metal cores that give rise to the intense chiroptical activity. This effect could change an achiral cluster into a chiral one, as in the Au_{38} case, or increase the index of chirality in an already chiral structure, as in the Au_{28} cluster.

The main contribution of this theoretical work has been to

show the existence of, and quantify chirality in the lowest-energy structures of gold nanoclusters using the Hausdorff chirality measure. These results provide useful insights for a proper interpretation of the experimental results that report optical activity on passivated gold nanoclusters.[14] Our results also establish that passivating with thiol monolayers provides a mechanism to induce or increase chirality in bare Au clusters in the size-range of 20–40 atoms. This information is relevant for the growth and sample preparation of different chiral metal nanoclusters. Theoretical precedents on metallic chiral nanostructures would include the Ni_{28} cluster,[27] and the Al and Pb helical nanowires,[28] however, the present results and those obtained by SW provide both theoretical and experimental evidence on the existence of chirality in gold nanoclusters. Electronic, optical, thermal, and other physical and chemical properties of chiral gold nanoclusters are currently being calculated and will be reported in forthcoming publications. At present, it is expected that novel and interesting properties emerge from the chiral character of metal clusters that could be useful for new nanotechnological applications.

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