

# Density functional study of the cysteine adsorption on Au nanoparticles

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## ABSTRACT

The adsorption of the cysteine amino acid ( $\text{H-SC}_\beta\text{H}_2\text{-C}_\alpha\text{H-NH}_2\text{-COOH}$ ) on the  $\text{Au}_{55}$  nanocluster is investigated through density functional theory calculations. Two isomers, with icosahedral and chiral geometries, of the  $\text{Au}_{55}$  nanocluster are used to calculate the adsorption energy of the cysteine on different facets of these isomers. Results involving the S(thiolate)-Au bonding show that the higher adsorption energies are obtained when the cysteine adsorbs on bridge sites of the facets containing Au atoms with the lowest coordination of the chiral  $\text{Au}_{55}$  cluster. These results are relevant to show the existence of enantiospecific adsorption on chiral gold clusters.

**Keywords:** gold nanoparticles, chiral clusters, cysteine adsorption, enantiospecific adsorption, enantioselectivity

## 1 INTRODUCTION

The study of the adsorption of organic molecules and biomolecules, with a sulfur headgroup, on metallic surfaces is a very active research subject [1] because of their importance in nanotechnology-related fields, like surface patterning and functionalization [2,3], and molecular electronics [4]. For example, cysteine and cystine molecules have been deposited on different gold surfaces [5], including chiral ones [6]. In particular, chiral recognition of cysteine enantiomers has been demonstrated when they are adsorbed on chiral gold surfaces like  $\text{Au}(111)$  [6]. On the other hand, adsorption studies of this type of molecules on metallic nanoparticles have not yet received much attention, despite the importance of these materials in nanotechnology [4].

In this work, we report a theoretical study based on density functional theory (DFT) of the adsorption of a chiral organic molecule (cysteine) on gold nanoparticles with two different structures. One of them corresponds to the icosahedral isomer, and the other one, to the most stable (lowest energy structure) isomer of the  $\text{Au}_{55}$  cluster. The latter cluster isomer has been classified as a chiral cluster [7]. The cysteine molecule ( $\text{H-SC}_\beta\text{H}_2\text{-C}_\alpha\text{H-NH}_2\text{-COOH}$ ) is formed by three functional groups: thiol, amino, and carboxil. For this reason, it is a complex problem to determine its adsorption modes on a gold nanoparticle. To initiate the investigation of these adsorption modes, the present study is realized only considering the S(thiolate)-

Au bonding. Section 2 includes a brief description of the theoretical methodology, whereas in Section 3 results of the analysis of the structural properties and energetics of the different adsorption geometries are presented. Section 3 contains a summary and the main trends obtained of the thiol adsorption mode of cysteine on a gold nanoparticle.

## 2 THEORETICAL METHODOLOGY

First principles calculations are performed in the frame of DFT, within the generalized gradient approximation (GGA), as implemented in the SIESTA code [8]. Standard norm-conserving scalar relativistic pseudopotentials for all the atomic species [9], and the Perdew, Burke and Ernzerhof parametrization for the GGA exchange-correlation functional [10] are used. Flexible linear combinations of numerical (pseudo)atomic orbitals are used as the basis set for the electron wave functions, allowing for multiple  $\zeta$  and polarization orbitals. All the atoms of both the gold cluster ( $\text{Au}_{55}$ ) and the molecular adsorbate (cysteine) are let free to relax until the Hellmann-Feynman forces are less than  $10 \text{ meV}/\text{\AA}$ .

This methodology has been broadly used by our group to study, for instance, the structural distortion of gold clusters upon thiol passivation [11] and more recently, the electron states in a lattice of Au nanoparticles [12].

The adsorption energies reported in this work are obtained from:

$$E_{\text{ad}} = E_{\text{tot}}(\text{Cluster} + \text{cysteine}) - E_{\text{tot}}(\text{Cluster}) - \{E_{\text{tot}}(\text{cysteine}) - 1/2 E_{\text{tot}}(\text{H}_2)\} \quad (1)$$

where the terms on the right-hand side are the total energies of the fully relaxed system of cysteine adsorbed on the cluster, the fully relaxed bare cluster, the cysteine in gas phase, and one half of the hydrogen molecule total energy, respectively.

## 3 RESULTS AND DISCUSSION

To investigate the adsorption of the cysteine amino acid on gold clusters, two isomers of  $\text{Au}_{55}$  are utilized: one with icosahedral symmetry, and the other corresponds to the lowest energy isomer with low-symmetry (chiral) [7]. The total energy difference between these isomers is of  $0.56 \text{ eV}$ , in favor of the low-symmetry chiral cluster. Figures 1(a) and 1 (b) show both cluster structures. The icosahedral cluster is composed by 20 triangular flat facets. The six Au

atoms that constitute each of these facets have been highlighted with a different color in Fig. 2(a). The facets of the low symmetry chiral cluster are geometrically diverse and quasi-planar, most of them reminiscent of (111) planes. Figure 2(b)-2(f) shows five of the most relevant facets, where the cysteine adsorption is favored. The largest facet has a 9-atom rhombic shape. The coordination numbers  $N_c$  of the Au atoms forming these facets are indicated with black labels.

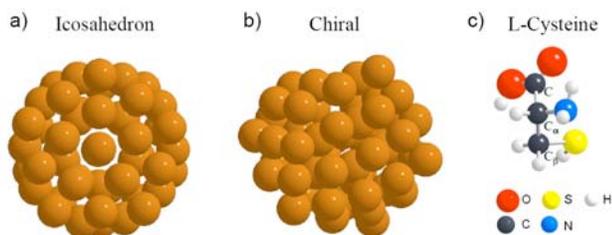


Figure 1: Geometric structure of the icosahedral (achiral) and chiral  $Au_{55}$  clusters and the cysteine molecule.

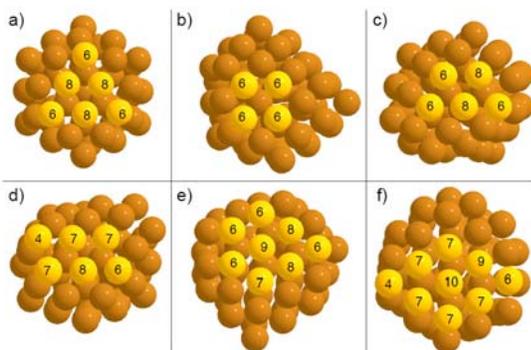


Figure 2: Top views of different facets of the lowest energy structures of the  $Au_{55}$  clusters. (a) Icosahedral and (b)-(f) chiral. The numbers on the Au atoms indicate the corresponding coordination number.

Cysteine, one of the twenty amino acids that constitute the most common proteins, is a chiral organic molecule interesting enough to study its adsorption on Au clusters. Figure 1(c) shows the geometry of the cysteine enantiomer used in these calculations. Previous investigations of cysteine-metal bonding have revealed a complex scenario where, depending of the experimental conditions, it may vary substantially and even exhibit different configurations [1]. Therefore, it is expected that the three functional groups, thiol (SH), amino ( $NH_2$ ), and carboxil (COOH), of the cysteine molecule can also induce different adsorption modes with the metal cluster. In this work, it is assumed that the cysteine molecule is in its neutral configuration (unprotonated form). Also, the exploration of possible adsorption structures is limited only to configurations where the molecule is bonded to the gold cluster, via the SH thiol group. Such adsorption mode is of particular

relevance. For instance, organic molecules with a sulfur headgroup have attracted significant interest due to their broad use in nanotechnology-related fields [3, 4]. In particular, the S containing cysteine amino acid is very important for often being at the border of large proteins. If the carboxyl and the amino groups of the cysteine molecule are engaged in other functions, like polymerizations and adhesion [14], as well as forming peptide bonds in proteins [5, 15, 16], then only the thiol group remains available for molecule-metal coupling. Therefore cysteine molecule could provide the link between proteins and inorganic supports.

To show the accuracy of the methodology employed, the properties of cysteine in the gas phase before adsorption were examined. The conformation used is structurally similar to the one observed in molecular cysteine crystals, i.e, the L-Cysteine(A) enantiomer in its *gauche*<sup>+</sup> configuration characterized by Görbitz et al. [17], also named as L-Cysteine-II by Moggach et al. [18]. In particular, the calculated torsion angles are similar to the cysteine structure of X-ray data [17], indicating that the functional groups orientations are well-defined and allow to identify our configuration as the L-Cys(A). Figure 1(c) shows the optimized structure obtained for this conformation. The values of the calculated bond distances and angles are reported in Table 1 and are compared with the experimental data of cysteine in its crystallized monoclinic L-Cys(A) [17]. The theoretical results are in quite good agreement with the X-Ray data [17]. The bond lengths and angles have an average accuracy of 3%, the only exceptions being the  $C-O_H$  distance (5%), and the  $C_\alpha-C_\beta-S$  (8%). Such larger deviations can be attributed to the fact that the intermolecular interactions of the L-Cysteine crystal are mainly dominated by  $N-H \cdots O$  hydrogen bonding [18]. Also, the protons of the carboxyl groups are expected to be largely transferred to neighboring amino groups through intermolecular  $N-H \cdots O$  hydrogen bonds. An analogous situation occurs for the SH thiol group, which is also capable of forming weak hydrogen bonds [18]. The present results are also consistent with other DFT calculations [1], particularly the bond lengths and angles. Only the dihedral angles differ from those of Ref. [1] since in that work, a cysteine enantiomer similar to the L-Cys-(B), instead of L-Cys-(A), was considered. It is worth mentioning that not only the tail group geometry and its orientation, with respect to the cluster facet, will influence the lateral intermolecular interactions, but also the type of cysteine isomer. The calculated energy for the  $RS-H$  bond (with  $R=C_\beta H_2-C_\alpha H-NH_2-COOH$ ) is  $E_{S-H}=86.2$  kcal/mol, which is in excellent agreement with other theoretical calculations of  $E_{S-H} = 89.5$  kcal/mol [1], and comparable with experimental estimates of  $E_{S-H} = 86$  kcal/mol obtained for methanethiol adsorption on Au(111) surface [19]. To find the most stable conformations of the cysteine amino acid adsorbed on an icosahedral and chiral  $Au_{55}$  clusters, several adsorption configurations were systematically investigated.

	Cys	Ico(a)	(b)	(c)	(d)	(e)	(f)
N-C <sub>α</sub>	1.46 (1.47)	1.46	1.45	1.46	1.46	1.45	1.45
C-O	1.23 (1.25)	1.22	1.22	1.22	1.22	1.22	1.23
C-O <sub>H</sub>	1.38 (1.31)	1.39	1.38	1.39	1.39	1.39	1.38
C <sub>β</sub> -S	1.87 (1.82)	1.89	1.89	1.89	1.88	1.89	1.88
C-C <sub>α</sub> -N	106.9 (109.9)	112.2	108.9	112.1	110.8	111.8	112.9
C <sub>α</sub> -C-O	122.9 (118.0)	122.6	122.5	122.3	122.2	122.5	121.8
C <sub>α</sub> -C-O <sub>H</sub>	115.8 (116.7)	116.6	115.9	116.1	116.5	116.8	117.3
C <sub>α</sub> -C <sub>β</sub> -S	106.0 (115.1)	110.0	111.2	110.1	106.3	107.1	115.3
C <sub>β</sub> -C <sub>α</sub> -C-O <sub>H</sub>	52.9	79.4	55.4	70.9	58.9	79.1	53.8
S-C <sub>β</sub> -C <sub>α</sub> -N	52.5	54.2	39.8	57.7	42.5	65.3	66.3
N-C <sub>α</sub> -C-O	11.2	21.3	3.5	14.0	2.9	19.6	2.9
N-C <sub>α</sub> -C-O <sub>H</sub>	171.4	158.8	177.5	167.7	179.7	159.6	179.5
E <sub>ads</sub> (Cys/Au <sub>55</sub> )		-1.161	-0.941	-0.866	-1.285	-0.667	-1.313

Table 1: Structure of the gas-phase cysteine molecule (Cys) and the adsorbed cysteine on the icosahedral [Ico(a)] and chiral facets (b)-(f) of the Au<sub>55</sub> cluster. The values in parenthesis correspond to experimental X-Ray data [17]. Adsorption energies are in eV, bond distances in Å, and bond and torsion angles in (°).

In the case of the icosahedral Au<sub>55</sub> cluster, one of its 20 triangular facets was chosen and then several trial configurations were considered, particularly those configurations where the S headgroup was situated at bridge, hollow and top sites, while the NH<sub>2</sub> and COOH groups were located away from the cluster facet and with different tail group orientations for all the cases. The preferential adsorption site was found to be the bridge site, similar to the thiol adsorption on gold surfaces [20]. The bridge site is characterized for being located on the edges of a facet. Figure 3(a) displays top and side views of the most favorable configuration found, i.e., that one for which the adsorption energy is the highest one. The S atom forms bonds of length 2.55 Å with two neighboring Au atoms. The NH<sub>2</sub> and COOH groups remained away from the facet, free to react with other macromolecules like peptide chains [15]. It was found that it is energetically more favorable to keep the COOH group right above and closer to the cluster facet. The bond lengths and angles of cysteine radical remain basically unchanged, except for C-C<sub>α</sub>-N (5%) and C<sub>α</sub>-C<sub>β</sub>-S (4%) bond angles, see Table 1. Larger differences appear for C<sub>β</sub>-C<sub>α</sub>-C-OH and N-C<sub>α</sub>-C-O torsion angles due to the rearrangement of the functional groups to adjust to the cluster facet environment. In this case, the symmetric morphology of the cluster does not change after cysteine adsorption, but the atoms move slightly inward towards the cluster center (~0.04 Å).

Figures 2(b)-(f) show the five facets where several adsorption configurations were tested for the cysteine molecule on the chiral Au<sub>55</sub> cluster. Figures 3(b)-(f) show the top and side views of the lowest-energy structures found for each of the considered facets. Only the cysteine molecule and the Au atoms forming the corresponding facet have been displayed. For all the configurations the S atom is coordinated to two Au facet atoms with S-Au bond

lengths of 2.55 Å, typical of the thiol-Au bond. The data reported in Table 1 show that the bond lengths of the cysteine radical remain almost unaltered with respect to the free molecule values. The bond angles do not change significantly, except those characterizing the thiolate (C<sub>α</sub>-C<sub>β</sub>-S) and NH<sub>2</sub> (C-C<sub>α</sub>-N) groups orientation with respect to the backbone, where we observe changes up to 9%. All the dihedral angles are instead affected with respect to the free molecule. In particular those between the thioate group and the NH<sub>2</sub> (S-C<sub>β</sub>-C<sub>α</sub>-N), and between the NH<sub>2</sub> and COOH (N-C<sub>α</sub>-C-O<sub>H</sub>) group, up to 75%. The largest changes of the bond and torsion angles occur when the cysteine is adsorbed on the facet with largest area, see Fig.3 (f). In this case, such larger deviations are mainly due to the proximity of COOH group to the cluster facet and can be attributed to steric attractive interactions between the molecule and the surface facet. For the other cases, the NH<sub>2</sub> and COOH groups adopt different orientations, but they remain essentially away from the surface facet. The adsorption energies included on Table I clearly show that, from all the tested facets, the molecule prefers to be adsorbed to the largest facet with 9-atom rhombic shape. A careful inspection of Figs. 3(b)-(f) reveals that the most stable configurations obtained involve the thiolate group binding to the lowest coordinated edges of the Au<sub>55</sub> chiral cluster. A review of the first-neighbor coordination number N<sub>c</sub> of the atoms at the facet edges on Fig. 2(b)-(f) confirm this statement, especially for the facets (d), (e) and (f). The facets (d) and (f) share one edge and have in common the Au atom with the lowest coordination (N<sub>c</sub>=4) of the whole cluster. Indeed, this interesting trend leads to the fact that the S atom is situated mostly between a pair of Au atoms that have the lowest number of neighbors of the facet edge. This is the case for the configurations (b), (c), (d) and (e) on Fig. 3.

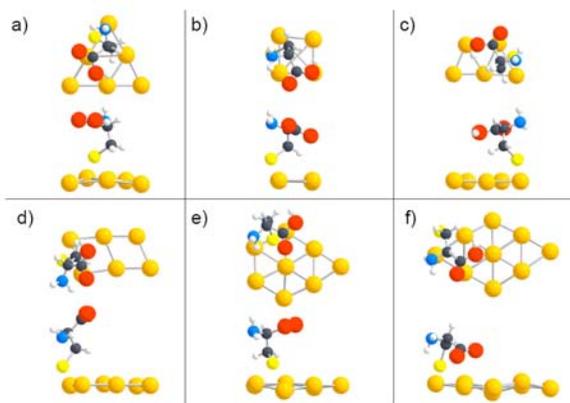


Figure 3: Top and side views of the lowest energy configurations of cysteine adsorbed on icosahedral and chiral  $Au_{55}$  cluster. (Only the Au atoms forming a facet cluster are displayed). (a) Cysteine at the icosahedral cluster, (b)-(f) Cysteine at the chiral cluster.

Although some of the edges on a given facet have the same  $N_c$ , they do not have the same environment due to the anisotropy of the chiral cluster. This characteristic can be detected only through the calculation of the second and third neighbors. The exception to this rule occurred for the cysteine adsorption at facet (f). This facet has two edges with the same number of first neighbors, namely  $N_c = 4$ , 7, and 7. From the two of them, the bottom edge has the lowest number of neighbors and the molecule prefers to be adsorbed on the upper edge. However, in this case other factors determining the lowest-energy structures like the COOH position and orientation should be considered. As in the achiral cluster, the COOH group prefers to be situated above and closer to the surface facet instead of pointing out of it. From this analysis it can be concluded that the  $N_c$  is very helpful to determine the edge where cysteine is preferentially adsorbed to the  $Au_{55}$  chiral cluster. Contrary to the achiral cluster case, in the chiral cluster, the atoms move away from the cluster center ( $\sim 0.15$  Å). Interestingly, the largest atom displacements correspond to the case with highest adsorption energy, i.e., when the cysteine is situated on the facet with largest area.

## 4 CONCLUSIONS

In this paper the adsorption of the cysteine amino acid on an achiral and chiral  $Au_{55}$  cluster was investigated within the DFT-GGA framework. The structural properties of cysteine molecules as well as those of the cluster upon adsorption were discussed. The results show that the higher adsorption energies are obtained when the cysteine adsorbs on bridge sites of the facets containing Au atoms with the lowest coordination of the chiral  $Au_{55}$  cluster. Moreover, the molecule is preferably adsorbed in the facets with largest area. When cysteine is adsorbed on a symmetric

icosahedral cluster, the molecule maintains the same bond lengths and angles, while the cluster becomes more compact but holding its symmetry. On the other hand, if cysteine is adsorbed on a low-symmetry gold cluster, a subtle additional distortion is found. These results provide important insights about the structural and energetics properties of this system and could be useful in the study of enantiospecific adsorption on chiral gold nanoclusters.

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