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Density functional study of the cysteine adsorption on Au nanoclusters

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Abstract. The adsorption of the cysteine amino acid (H–SC$_\beta$H$_2$–C$_\alpha$H–NH$_2$–COOH) on the Au$_{55}$ cluster is investigated through density functional theory calculations. Two isomers, with icosahedral (I$_h$) and chiral (C$_1$) geometries, of the Au$_{55}$ cluster are used to calculate the adsorption energy of the cysteine on different facets of these isomers. Results, only involving the S(thiolate)-Au bonding show that the higher adsorption energies are obtained when the sulfur atom is bonded to an asymmetrical bridge site at the facet containing Au atoms with the lowest coordination of the C$_1$ cluster isomer.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Jn Reactivity of clusters – 68.43.Bc Ab initio calculations of adsorbate structure and reactions

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, when cysteine and cystine molecules are deposited on different gold surfaces [5,6], including chiral ones [7], chiral recognition of cysteine enantiomers has been demonstrated when they are adsorbed on chiral gold surfaces like Au(17 11 9)^S [7]. On the other hand, adsorption studies of this type of molecules on metallic clusters and nanoparticles have not yet received much attention, despite the importance of these materials in nanotechnology [4].

In this paper, we report a theoretical study based on density functional theory (DFT) of the adsorption of a chiral organic molecule (cysteine) on a gold nanocluster with two different structures. One of them corresponds to the icosahedral (I$_h$) isomer, and the other one, to the most-stable (C$_1$) isomer of the Au$_{55}$ cluster [8]. The cysteine chiral molecule (H–SC$_\beta$H$_2$–C$_\alpha$H–NH$_2$–COOH) is formed by three functional groups: thiol, amino, and carboxyl. For this reason, it is a complex problem to determine its adsorption modes on a gold nanocluster. Recently, we have investigated the simultaneous adsorption of the three cysteine groups on the (C$_1$) Au$_{55}$ cluster, theoretically demonstrating the existence of enantiospecific adsorption on this system [9]. In this work, we perform an exhaustive search of the most stable adsorption conformation of cysteine on the I$_h$ and C$_1$ isomers of the Au$_{55}$ cluster, 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 4 contains a summary and the main trends obtained on the thiol adsorption modes of cysteine on the gold nanoclusters.

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 [10]. Standard norm-conserving scalar relativistic pseudopotentials for all the atomic species [11], and the Perdew, Burke and Ernzerhof parametrization for the GGA exchange-correlation functional [12] are used. Flexible linear combinations of numerical (pseudo)atomic orbitals are used as the basis set for the electron wave functions [10]. All the atoms of both the gold cluster and cysteine are let free to relax until the Hellmann-Feynman forces are less than 10 meV/Å. This methodology has been broadly used by our group to study the structural distortion of gold clusters upon thiol passivation [13] and the electron states in a lattice of Au nanoparticles [14]. The adsorption energies reported in this work are obtained from:

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

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.

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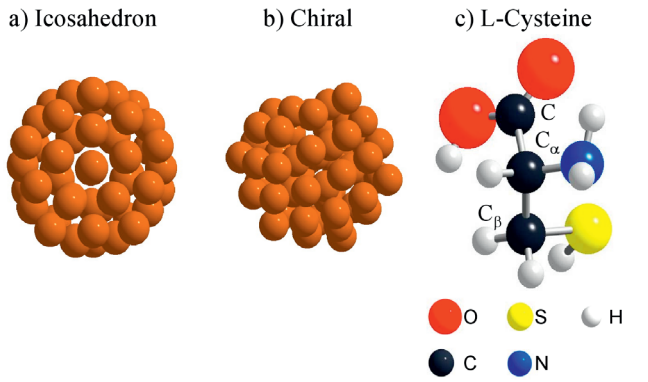

Fig. 1. (Color online) Geometric structure of the icosahedral (I_h) and C_1 Au_{55} clusters and the L-cysteine molecule.

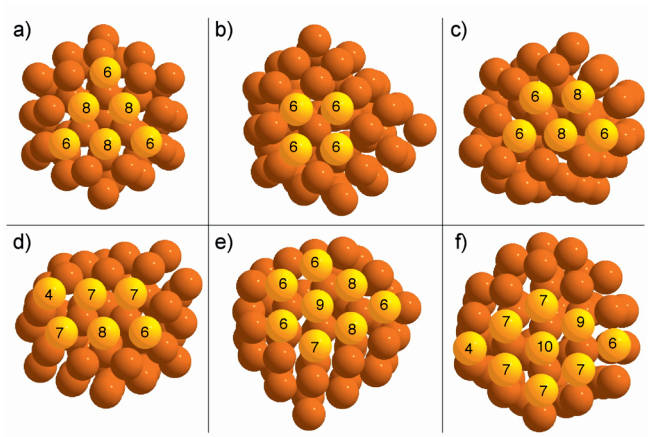

Fig. 2. (Color online) Top views of different facets of the lowest energy structures of the Au_{55} clusters. (a) Icosahedral and (b)–(f) C_1. The numbers on the Au atoms indicate the corresponding coordination number.

3 Results and discussion

To investigate the adsorption of the cysteine amino acid on gold clusters, two isomers of Au_{55} are utilized: one with I_h symmetry, whereas the other corresponds to the lowest energy isomer with C_1 symmetry [9]. The total energy difference between these bare cluster isomers is of 0.56 eV, in favor of the C_1 cluster. Figures 1a and 1b show both cluster structures. The icosahedral cluster is composed by 20 (111) planar facets. The six Au atoms that constitute each of these facets have been highlighted with a different color in Figure 2a. The facets of the C_1 cluster are geometrically diverse and quasi-planar, most of them reminiscent of (111) planes. Figures 2b–2f show 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. 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 1c 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, exhibiting different configurations [1]. Therefore, it is expected that the three functional groups, thiol (SH), amino (NH_2), and carboxyl (COOH), of the cysteine molecule can also induce complex adsorption modes in a 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 only limited to configurations where the molecule is bonded to the gold cluster, via the SH thiol group. Such adsorption mode is of great relevance, since organic molecules with a sulfur headgroup have attracted significant interest due to their broad use in nanotechnology-related fields [3,4]. In particular, the cysteine amino acid containing a thiol group, 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 [15], as well as forming peptide bonds in proteins [5,16,17], then only the thiol group remains available for molecule-metal coupling. Therefore, the cysteine molecule in the thiol adsorption mode could provide the link between proteins and inorganic surfaces.

To show the accuracy of the methodology employed, the properties of cysteine in 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+configuration characterized by Görbitz and Dalhaus [18], also named as L-Cysteine-II by Moggach et al. [19]. In particular, our calculated torsion angles are similar to the cysteine structure determined by X-ray data [18], indicating that the orientation of the functional groups are well-defined, allowing the identification of our configuration as the L-Cys(A). Figure 1c 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) [18]. The theoretical results are in quite good agreement with the X-ray data [18]. The bond lengths and angles have an average accuracy of 3%, the only exceptions being the C–O_H distance (5%), and the C_α–C_β–S angle (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 [19]. 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 [19]. The present results are also consistent with other DFT calculations [1], particularly the bond lengths and angles. Only the dihedral angles, calculated in this work, differ from those of reference [1] since in that calculation, 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

Table 1. Structure of the gas-phase cysteine molecule (Cys) and the adsorbed cysteine on the icosahedral (Ico(a)) and C_1 facets (b)–(f) of the Au_{55} cluster. The values in parenthesis correspond to experimental X-ray data [18]. Adsorption energies (E_{ads})) are in eV and bond distances in Å.

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

intermolecular interactions, but also the type of cysteine isomer. The calculated energy for the RS–H bond (with R=$C_\beta H_2$–C_αH–NH_2–COOH) is E_{S-H} = 86.2 kcal/mol (3.74 eV), which is in excellent agreement with other theoretical calculations of E_{S-H} = 89.5 kcal/mol (3.88 eV) [1], and comparable with experimental estimates of E_{S-H} = 86 kcal/mol (3.73 eV) obtained for methanethiol adsorption on Au(111) surface [20].

To find the most stable conformations of the cysteine amino acid adsorbed on an I_h and C_1 Au_{55} clusters, several adsorption configurations were systematically investigated. In the case of the I_h Au_{55} 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_2 and COOH groups were located away from the cluster facet and with different tail group orientations for all cases. The preferential adsorption site was found to be the bridge site, similar to the thiol adsorption on gold surfaces [21]. The bridge site is characterized for being located on the edges of a facet. Figure 3a 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 lengths 2.50 Å and 2.46 Å with two neighboring Au atoms. In this case, the Au−Au distance increases from 2.96 Å to 3.25 Å upon cysteine adsorption. The NH_2 and COOH groups remained away from the facet, free to react with other macromolecules like peptide chains [16], although it was found that it is energetically more favorable to keep the COOH group in an almost parallel configuration to the cluster facet than pointing outwards from it. The bond lengths and angles of cysteine radical remain basically unchanged, except for C–C_α–N (5%) and C_α–C_β–S (4%) bond angles, see Table 1. Larger differences appear for C_β–C_α–C–OH and N–C_α–C–O torsion angles due to the rearrangement of the functional groups to adjust to the cluster facet environment.

Figures 2b–2f show the five facets where several adsorption configurations were tested for the cysteine molecule on the C_1 Au_{55} cluster. Figures 3b–3f 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 going from 2.44 Å to 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_α–C_β–S) and NH_2 (C–C_α–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 thiolate group and the

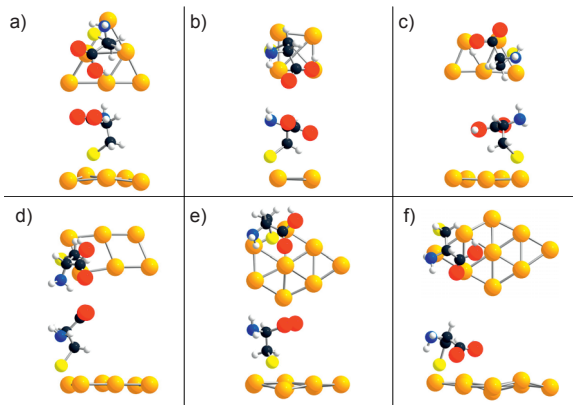

Fig. 3. (Color online) Top and side views of the lowest energy configurations of cysteine adsorbed on icosahedral and C_1 Au_{55} clusters. (Only the Au atoms forming a facet cluster are displayed.) (a) Cysteine at the icosahedral cluster, (b)–(f) Cysteine at the C_1 cluster.

NH_2 (S–C_β–C_α–N), and between the NH_2 and COOH (N–C_α–C–OH) 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 Figure 3f. In this case, such larger deviations are mainly due to the proximity of the COOH group to the cluster facet and can be attributed to steric attractive interactions between the molecule and the cluster facet. For the other cases, the NH_2 and COOH groups adopt different orientations, but they remain essentially away from the cluster facet. The adsorption energies included in Table 1 clearly show that, from all the tested facets, the molecule prefers to be adsorbed on the largest facet with 9-atom rhombic shape. A careful inspection of Figures 3b–3f reveals that the most stable configurations obtained involve the thiolate group binding to the lowest coordinated edges of the C_1 Au_{55} cluster. A review of the first-neighbor coordination number N_c of the atoms at the facet edges in Figures 2b–2f confirms 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 ($N_c = 4$) 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) in Figure 3. It is worth mentioning that 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 C_1 cluster. This characteristic can only be detected through the calculation of the second and third neighbors. On the other hand, the facet (f) of the C_1 cluster has two edges with the same number of first neighbors, namely $N_c = 4$, 7, and 7, but the bottom edge has the lowest number of second and third neighbors. However, the molecule prefers to be adsorbed on the upper edge since the COOH group is situated above and closer to the surface facet instead of pointing out from it. Moreover, in this case, the S atom forms bonds of lengths 2.50 Å and 2.54 Å with two neighboring Au atoms, which distance increases from 2.77 Å to 2.89 Å upon cysteine adsorption. This distortion in the bond lengths of the Au–Au bridge atoms is less than half of that observed for the cysteine adsorption on the I_h cluster. This analysis shows that, in general, the N_c value is helpful to determine the edge where cysteine is preferentially adsorbed to the C_1 Au_{55} cluster, however, in some particular cases, the COOH position and orientation should be considered.

4 Conclusions

In this paper the adsorption of the L-cysteine amino acid on I_h and C_1 Au_{55} clusters was investigated within the DFT-GGA framework. The structural properties of cysteine molecules as well as those of the clusters upon adsorption were discussed. The results show that the higher adsorption energies are obtained when the cysteine adsorbs on asymmetrical bridge sites of the facets containing Au atoms with the lowest coordination of the C_1 Au_{55} cluster. Moreover, the molecule is preferably adsorbed in the facets with largest area. When cysteine is adsorbed on an icosahedral cluster, the molecule maintains the same bond lengths and angles, but the cluster suffers a strong local distortion corresponding to an expansion of 0.29 Å of the bridge Au–Au distance. On the other hand, if cysteine is adsorbed on a low-symmetry gold cluster, a smaller distortion of 0.12 Å is found for the corresponding bridge Au–Au distance. This explains the greater binding energy found for the cysteine adsorbed on the C_1 cluster, where the Au atoms locally remain closer than in the I_h cluster. These results provide important insights about the structural and energetics properties of this system and could be useful in the study of molecular recognition involving the remaining cysteine functional groups.

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