



A QUANTUM CHEMICAL STUDY OF INTERACTIONS BETWEEN Au_3^- ANION AND AMINO ACIDS

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ABSTRACT

Quantum chemical calculations are employed to examine the interactions of the Au_3^- cluster in its negatively charged states with several small amino acids. Thermodynamic parameters, electronic structures, bonding characteristics and spectroscopic properties of the resulting complexes are investigated in the framework of density functional theory (M06-2X functional) along with correlation consistent basis sets, namely aug-cc-pVTZ-PP for Au and aug-cc-pVTZ for nonmetals. Computed results show that these interactions are characterized by the nonconventional H-bonds $N-H\cdots Au$ and $O-H\cdots Au$. In addition, the forming of the nonconventional H-bonds is likely to accompany with a charge transfer from Au_3^- to the bimolecular species.

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1 INTRODUCTION

The interaction of coinage metal clusters with biomolecules such as amino acids and DNA bases has attracted much interest in recent times since these nanoparticles pose potential applications in sensors, biosensors, and biomedical diagnostics (Elghanian *et al.*, 1997). Various studies have been performed to elucidate the nature of the interaction between these species (Javan *et al.*, 2012). Most of the previous investigations are devoted to the small gold clusters in their neutral states. It was in general found that the binding mechanism is governed by two key bonding factors, namely the anchoring $N-Au$ and $O-Au$ bonds and the nonconventional $N-H\cdots Au$ and $O-H\cdots Au$ hydrogen bonds.

Contrary to the particular inertness of its bulk, gold becomes quite active either in the nanoscale form or when finely dispersed on metal oxide surfaces (Haruta, 1997). In the past decades, the reactivity of gold clusters toward small molecules in gas phase has extensively been investigated, in terms of both experimental and theoretical aspects (Nhat

et al., 2012). An interesting finding is that the reactions of gold cluster with these species are facile in nature, i.e. either molecular or dissociative chemisorptions are involved, rather than breaking molecular bonds and making again stronger bonds between the resulting fragments and the metals. This also holds true for the adsorption of several amino acids and DNA bases on small gold clusters (Kryachko *et al.*, 2005). The property to retain the original form of adsorbed molecules makes such clusters of great interest for the use in biochemical sensing and detection.

An early study on the interaction of glycine and cysteine with Au_3 by Pakiari *et al.* (2007) revealed that the bonding between these amino acids and gold clusters has partially electrostatic and partially covalent character. Of two major bonding factors, i.e. anchoring bonds and nonconventional H-bonds, the former is stabilized owing to the flow of an amount of electron density from lone pair electrons of sulfur, oxygen, and nitrogen to the antibonding orbitals of the metal, while the latter is character-

ized by the electron transfer from metal to the hydrogen atom of N-H and O-H bonds. Subsequent examinations by Xie *et al.* (2012) and Rai *et al.* (2012) for the absorption of cysteine, glycine and proline on Au₃ and Au₄ species support these findings, and in addition show that the Au-NH₂ anchoring bond could play as the dominant element determining the stability of these complexes.

One of the striking observations for small gold clusters is that their geometries and many related properties are significantly modified upon the electron attachment or detachment. Indeed, while the lowest-energy structure found for the neutral Au₃ is triangular, that of the anion Au₃⁻ is linear (Furche *et al.*, 2002). For Au₃⁻, the energetically closest isomer with D_{3h} symmetry is computed to stay ~1.2 eV above the linear form (Furche *et al.*, 2002). Consequently, the binding mechanism of amino acids on the anion Au₃⁻ can be tuned, and it is necessary to extend investigations of the absorption on anionic gold clusters. In this context, we thoroughly investigate the nature of the interaction of the anionic species Au₃⁻ with some small neutral amino acids, namely glycine and alanine. The main purpose is to probe the adsorption behavior of amino acids on the anionic gold cluster, including the binding sites, energies and mechanism. In addition, a comparison of the previous results obtained for the neutral Au₃ allows us to evaluate how the interaction is perturbed due to the presence of an extra electron.

2 COMPUTATIONAL METHODS

All calculations are performed using the Gaussian 09 suite of program (Frisch *et al.*, 2009). Optimal structures of complexes with Au₃⁻ anion are located using the hybrid meta-GGA approach M06-2X. This functional has been strongly recommended to examine noncovalent complexes as it surprisingly provides accurate binding energies for weak interactions (Hobza, 2011) which are poorly described by most of currently used functionals (Harvey, 2006).

The diffuse basis set aug-cc-pVTZ-PP with an effective core potential (ECP) is applied for gold, while the all electrons aug-cc-pVTZ basis set is used for non-metals. Harmonic vibrational frequencies are invariably calculated to confirm the character of optimized geometries as local minima on the potential energy surface. In order to calibrate the performance of the computational methods employed, we first make some benchmarks for the [Au₃NH₃]⁻ complex, using several functionals,

namely B3P86, B3LYP, PBE, PBE0, MPW1K, and M06-2X. Due to the lack of experimental data, the coupled-cluster CCSD(T) energy is employed as the reference.

In [Au₃NH₃]⁻ anion, the gold metals likely prefer to interact with the hydrogen atoms, forming the complex [M₃NH₃-I] as displayed in Figure 1. The ammoniac molecule can also anchor on the cluster via nitrogen atom, but the resulting complex [M₃NH₃-II] is around 4.0 kcal/mol less stable than [M₃NH₃-I]. Noticeably, of the functionals considered, the B3LYP predicts the latter complex unbound as its energy is ~1.5 kcal/mol higher than the total energies of Au₃⁻ and NH₃ constituents from infinite distance.

Table 1: Complexation energy (kcal/mol) of [Au₃NH₃]⁻ anion computed at different levels

Method	M ₃ NH ₃ -II	M ₃ NH ₃ -I
B3P86	0.7	3.8
B3LYP	-1.5	3.2
PBE	2.0	4.7
PBE0	0.9	4.7
MPW1K	0.9	3.9
M062X	1.0	5.5
MP2	4.0	7.4
CCSD(T)	2.4	6.2

In this paper, the complexation energy E_c of the complex [Au₃L]⁻ is computed as the absolute value of the energy difference, $E_c = E(L) + E(\text{Au}_3^-) - E([\text{Au}_3\text{L}]^-)$. Here $E(L)$, $E(\text{Au}_3^-)$, $E([\text{Au}_3\text{L}]^-)$ are the total energies of L, Au₃⁻ and [Au₃L]⁻, respectively. Hence, as for a convention, a positive value of E_c corresponds to a favorable complexation. In addition, this parameter can be used to evaluate the relative stability of a specific complex. As can be seen in Table 1, the E_c values of [M₃NH₃-I] and [M₃NH₃-II] at M06-2X level are 5.5 and 1.0 kcal/mol, which are more consistent with CCSD(T) results (6.2 and 2.4 kcal/mol) than any functional tested. Therefore, this functional is selected for most calculations carried out in this study.

3 RESULTS AND DISCUSSION

3.1 Interactions of Au₃⁻ with NH₃ and HCOOH

Owing to its lone pair of electrons, the interaction of NH₃ molecule with Au₃⁻ is a facile association reaction. Similar characteristic is also observed for the adsorption of formic acid on Au₃⁻. Indeed, we find the geometries of Au₃⁻, NH₃ and HCOOH almost unchangeable after the complexation.

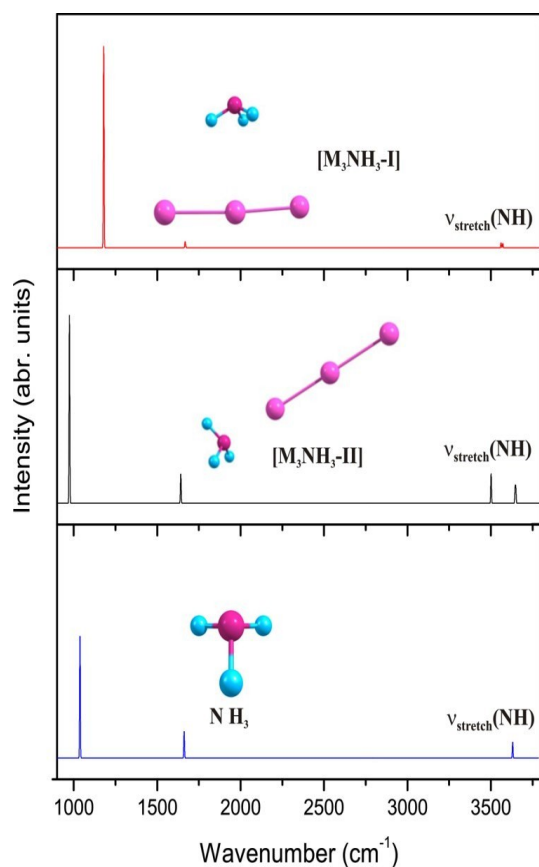


Fig. 1: Optimal structures and vibrational signatures of $[\text{Au}_3\text{NH}_3]^-$ complex

Previous study (Pakiari *et al.*, 2007) on molecular interaction between amino acids with Au_3 and Au_4 confirmed the existence of both anchoring bonds through electron-rich atoms nitrogen, oxygen, and sulfur of amine, carboxylic, and sulfur groups with gold atoms and the nonconventional hydrogen bonds $\text{N}-\text{H}\cdots\text{Au}$ and $\text{O}-\text{H}\cdots\text{Au}$, in which the former are more significant. Thus, gold can play the role as either an electron acceptor or a proton acceptor. In current text, the latter is likely to be the dominant mechanism of the interaction. The complexes with such kind of hydrogen bonds are found to be consistently more energetically favored than ones with anchoring bonds.

In addition to optimal structures, Figures 1 and 2 display the computed harmonic frequencies for $[\text{Au}_3\text{NH}_3]^-$ and $[\text{Au}_3\text{HCOOH}]^-$ complexes. In principle, analysis based on the vibrational signatures is an effective way to get deeper insights into both bonding sites and strengths because the molecular vibrations map the forces between the atoms and thereby reflects the internal interactions. In $[\text{M}_3\text{NH}_3\text{-I}]$, the asymmetric stretching mode $\nu(\text{N}-\text{H})$ is predicted to be shifted from 3630 cm^{-1} of free

NH_3 to 3560 cm^{-1} . Concerning $[\text{Au}_3\text{HCOOH}]^-$, the more significant red-shifts are observed for the stretching mode $\nu(\text{O}-\text{H})$, around 331 and 493 cm^{-1} in $[\text{M}_3\text{FA-I}]$ and $[\text{M}_3\text{FA-II}]$, respectively. Previously, the vibrational frequency analysis has also been performed to reveal the adsorption of methanol molecule on Au_3^+ cation (Li *et al.*, 2009).

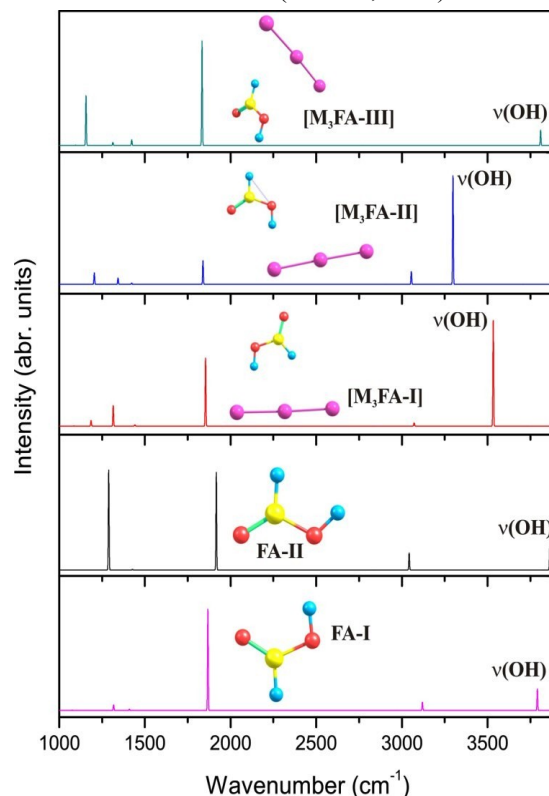


Fig. 2: Optimal structures and vibrational signatures of $[\text{Au}_3\text{HCOOH}]^-$ complex

As stated above, two possible structures are located for the $[\text{Au}_3\text{NH}_3]^-$ complex. For $[\text{Au}_3\text{HCOOH}]^-$, it becomes more complicated since formic acid can appear as either the *cis* or *trans* conformation, in which the former is computed to lie $\sim 4.2\text{ kcal/mol}$ above the latter. However, the adduct $[\text{M}_3\text{FA-I}]$ coming from the *cis*- HCOOH form is more stable than the isomer $[\text{M}_3\text{FA-II}]$ containing the *trans*- HCOOH as $[\text{M}_3\text{FA-I}]$ possesses two hydrogen bonds with $\text{O}-\text{H}$ and $\text{C}-\text{H}$ groups (Figure 2), while $[\text{M}_3\text{FA-II}]$ has only one hydrogen bond with $\text{O}-\text{H}$ group. At the applied level of theory, their complexation energies are 17.4 and 9.8 kcal/mol , respectively. Formic acid is also able to form a single hydrogen bond with Au_3^- through its CH group, but the resulting complex $[\text{M}_3\text{FA-III}]$ is much less stable than $[\text{M}_3\text{FA-I}]$, being separated by 8.1 kcal/mol .

3.2 Interactions of Au_3^- with carbamic acid

Technically, carbamic acid, which is designated in the literature as NH_2COOH , is the simplest amino acid, but its instability under normal circumstances allows glycine this title. Although its structural aspects have been predicted theoretically by *ab-initio* calculations (Nanpeng *et al.*, 1995), to our best knowledge, the experimental data are still not available so far. In an attempt to characterize the molecule, Khanna and Moore (1999) were able to locate the zwitter-ion $\text{NH}_3^+\text{COO}^-$, rather than NH_2COOH . At the M06-2X/aug-cc-pVTZ level, we identify two possible structures CA-I and CA-II (Figure 3) in that the former is ~ 7.3 kcal/mol more stable than the latter.

The computed results for $[\text{Au}_3\text{NH}_2\text{COOH}]^-$ adduct are presented graphically in Figure 3. As for NH_3 and HCOOH , NH_2COOH also prefer to attack Au_3^- through the hydrogen atoms of its amine and carboxylic groups, giving rise to $[\text{M}_3\text{CA-I}]$, $[\text{M}_3\text{CA-II}]$, and $[\text{M}_3\text{CA-III}]$ complexes as shown in Figure 3. Amongst these, the lowest-energy isomer $[\text{M}_3\text{CA-I}]$ is relatively stable and has a particularly high E_c value (20.4 kcal/mol) as the acid molecule can form two hydrogen bonds with the metals through both $-\text{NH}_2$ and $-\text{OH}$ groups. There also exist two hydrogen bonds in $[\text{M}_3\text{CA-II}]$ via two hydrogen atoms of amine, but it has a much smaller complexation energy (10.6 kcal/mol). This indicates that the bonding with amine ($\text{N-H}\cdots\text{Au}$) is less effective than that via hydroxide ($\text{O-H}\cdots\text{Au}$). The complex $[\text{M}_3\text{CA-III}]$ with one hydrogen bond *via* $-\text{OH}$ group is located to be 5.6 kcal/mol above $[\text{M}_3\text{CA-I}]$ and has the E_c value of 7.5 kcal/mol. We could not locate the complex with gold atoms directly bound to electron-rich atoms nitrogen and oxygen. This indicates that the proton transfer is likely to outweigh the electron transfer during the complexation.

In $[\text{M}_3\text{CA-I}]$, the distances of the hydrogen bonds $\text{N-H}\cdots\text{Au}$ and $\text{O-H}\cdots\text{Au}$ correspond to 2.58 and 2.46 Å, as compared to 3.08 and 2.53 Å in $[\text{M}_3\text{NH}_3\text{-I}]$ and $[\text{M}_3\text{FA-I}]$, respectively. In addition, after the complexation, the bond lengths of N-H and O-H in $[\text{M}_3\text{CA-I}]$ are increased by 0.005 and 0.015 Å. These observations are clearly manifested in the frequency red-shift of the stretching modes $\nu(\text{N-H})$ and $\nu(\text{O-H})$. Such vibrations undergo the red-shifts by 193 and 297 cm^{-1} when forming the complex $[\text{M}_3\text{CA-I}]$. Concerning $[\text{M}_3\text{CA-II}]$, a red-shift of 104 cm^{-1} is also observed for $\nu(\text{N-H})$, but the $\nu(\text{O-H})$ undergoes a blue-shift by 24 cm^{-1} (Figure 3). On the contrary, in $[\text{M}_3\text{CA-III}]$, while the vibration of $\nu(\text{O-H})$ occurs at a much lower

energy than that of free molecule, the $\nu(\text{N-H})$ nearly stretches at the same level. Thus, additional information from measured spectra will be more reliable for the structural assignments. Then the complexation energy can be evaluated more accurately.

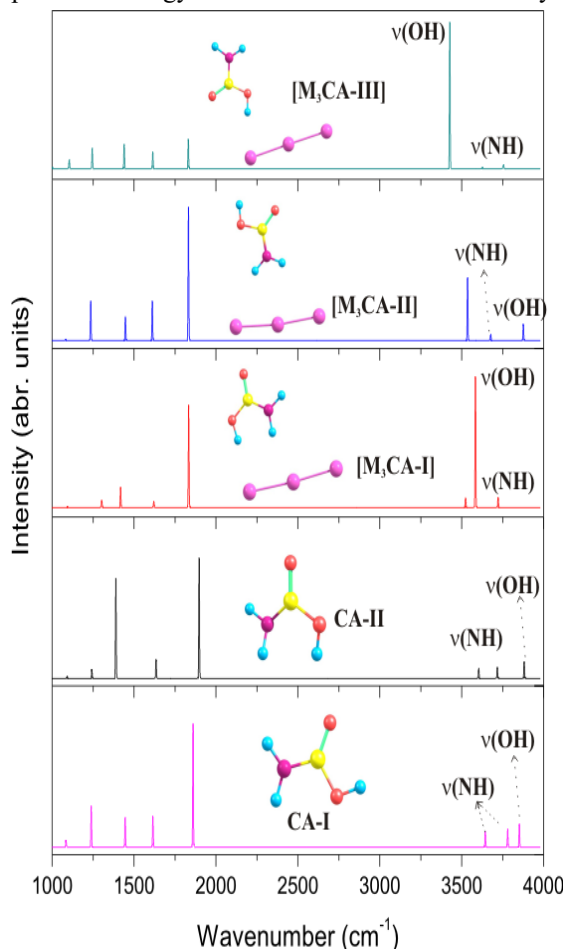


Fig. 3: Optimal structures and vibrational signatures of $[\text{Au}_3\text{H}_2\text{NCOOH}]^-$ complex

The nonconventional bonds $\text{N-H}\cdots\text{Au}$ and $\text{O-H}\cdots\text{Au}$ present in $[\text{Au}_3\text{NH}_2\text{COOH}]^-$ complex are thus naturally similar to conventional hydrogen bonds deriving from the interaction of a hydrogen atom and a non-metal atom, such as nitrogen, oxygen or fluorine. Indeed, both N-H and O-H bonds elongates relative to those in free NH_3 and HCOOH ; the hydrogen bond separation $r(\text{H}\cdots\text{Au})$ of 2.58 Å is shorter than the sum of van der Waals radii of H and Au (2.86 Å); and the stretching modes $\nu(\text{N-H})$ and $\nu(\text{O-H})$ experience a red-shift with respect to those of the monomers.

However, the magnitudes of $\text{O-H}\cdots\text{Au}$ nonconventional hydrogen bonds in complexes $[\text{Au}_3\text{NH}_2\text{COOH}]^-$ and $[\text{Au}_3\text{HCOOH}]^-$ ranging from 8 – 10 kcal/mol indicate that such bonding is rela-

tively stronger than the traditional hydrogen bonds O–H···O and O–H···N (5 – 7 kcal/mol, Emsley, 1980). Similarly, the strength of the hydrogen bond N–H···Au (5 – 8 kcal/mol) is also predicted to be larger than that of either N–H···O or N–H···N (2 – 3 kcal/mol, Emsley, 1980).

3.3 Interactions of Au₃[−] with glycine and alanine

In agreement with previous studies (Topol *et al.*, 1999), *trans*-molecular skeletons with two amino hydrogens pointing towards the oxygen atom of the C=O group, i.e. Gly-I and Ala-I in Figures 4 and 5 are located as the global minima for both glycine and alanine in gas phase. The *cis* skeletons with the presence of a hydrogen bond between the nitrogen lone pair and the carboxylic hydrogen, namely Gly-II and Ala-II in Figures 4 and 5, are computed to be around 1.5 and 0.75 kcal/mol higher in energy than Gly-I and Ala-I, respectively. They are thus energetically degenerate and each of them can emerge as the most stable isomer.

Like ammoniac, formic and carbamic acids, both glycine and alanine interact with Au₃[−] *via* the hydrogen atoms of amine and carboxylic groups, forming nonconventional hydrogen bonds Au···H–N or Au···H–O. Relevant structures located for [Au₃Glycine][−] and [Au₃Alanine][−] complexes are plotted in Figures 4 and 5.

A recent investigation (Xie *et al.*, 2012) on interactions of Au_{*n*} (*n* = 3–4) neutral clusters with cysteine and glycine revealed that the complexes possessing Au–NH₂ anchoring bond are found to be more energetically favored and have higher intermolecular interaction energies than those with nonconventional hydrogen bonds. It was in addition found that in these adducts gold atoms play a role of an electron acceptor, in which the negative charge is transferred from the lone pair electrons of sulfur, oxygen, and nitrogen elements. However, we are not able to locate the complexes possessing Au–N or Au–O anchoring bonds between the anion Au₃[−] and glycine and alanine molecules. All geometry optimizations invariably converge to the conformations with non-conventional N–H···Au and O–H···Au hydrogen bonds.

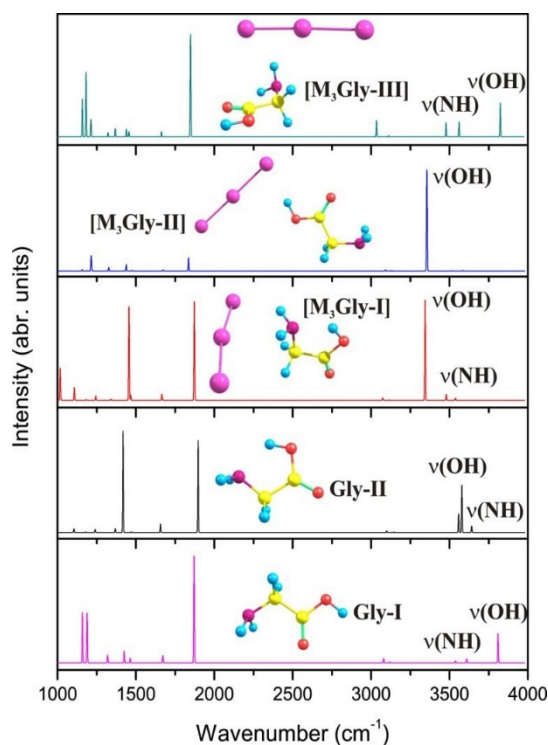


Fig. 4: Optimal structures and vibrational signatures of [Au₃Glycine][−] complex

In current text, the lowest-energy form of [Au₃Glycine][−], i.e. [M₃Gly-I] in Figure 4, is found to have a bidentate interaction through the –NH₂ group with gold cluster. This conformation is computed to be around 6 kcal/mol more stable than [M₃Gly-II], which contains a monodentate interaction through the –COOH end. The complexation energies in these two cases, namely 17 and 10 kcal/mol respectively, also differ significantly.

Forming the N–H···Au and O–H···Au bonds in addition leads to a substantial red-shift in the stretching mode of O–H bond vibration. At the applied level of theory, the frequencies of the O–H bond in [M₃Gly-I] and [M₃Gly-II] are red-shifted as compared to isolated fragments, Gly-II and Gly-I, by 234 and 454 cm^{−1}. On the contrary, the red-shifts in the stretching mode of N–H bond vibrations are much less considerable, namely 104 and 23 cm^{−1} for [M₃Gly-I] and [M₃Gly-II], respectively (see Figure 4).

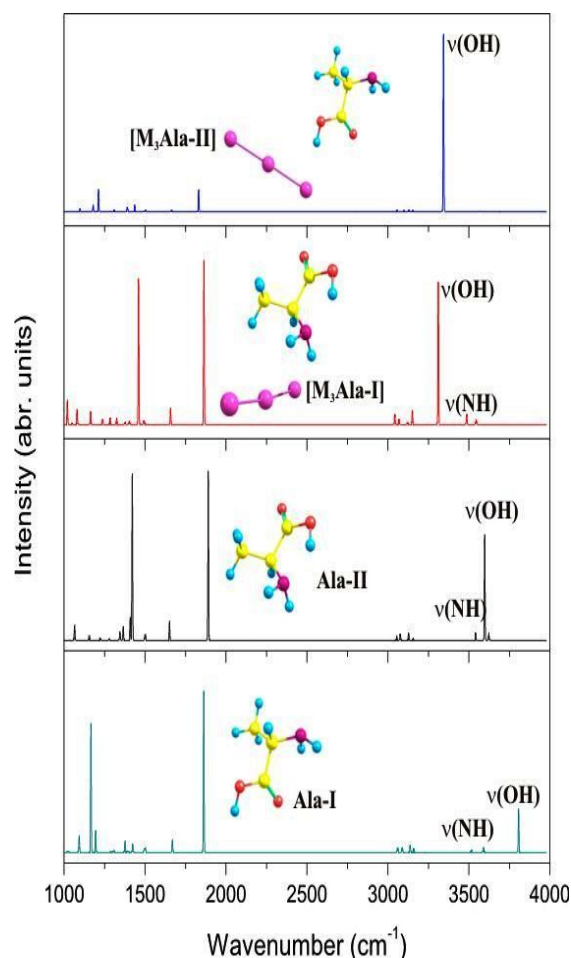


Fig. 5: Optimal structures and vibrational signatures of $[\text{Au}_3\text{Alanine}]^-$ complex

In agreement with the interaction between Au_3^- and glycine, the most stable form found for $[\text{Au}_3\text{Alanine}]^-$, namely $[\text{M}_3\text{Ala-I}]$ in Figure 5, also has a bidentate interaction through the $-\text{NH}_2$ group with Au_3^- moiety. Again, the one with a monodentate interaction via the $-\text{COOH}$ end, cf. structure $[\text{M}_3\text{Ala-II}]$ in Figure 5, is predicted to lie around 6 kcal/mol higher in energy than $[\text{M}_3\text{Ala-I}]$. In addition, the complexation energies of $[\text{M}_3\text{Ala-I}]$ and $[\text{M}_3\text{Ala-II}]$ amount to 17 and 10 kcal/mol, respectively, and thus are practically equal to those obtained for $[\text{M}_3\text{Gly-I}]$ and $[\text{M}_3\text{Gly-II}]$. The above results indicate that glycine and alanine have a comparable affinity to the anion Au_3^- .

As in $[\text{M}_3\text{Gly-I}]$ and $[\text{M}_3\text{Gly-II}]$, there also exists a large red-shift of the O–H bond due to forming nonconventional H-bonds in $[\text{M}_3\text{Ala-I}]$ and $[\text{M}_3\text{Ala-II}]$. The frequencies of the $\nu(\text{O-H})$ stretch in these complexes are significantly reduced by 287 and 464 cm^{-1} , respectively, compared to the isolated alanine. These are thus comparable to the values obtained for $[\text{M}_3\text{Gly-I}]$ and $[\text{M}_3\text{Gly-II}]$.

Overall the results indicate that both glycine and alanine exhibit a favorable interaction with anion Au_3^- through the hydrogen atoms of amide end, resulting a large red-shift in the O–H stretching mode as the interaction reinforces the H-bonding $\text{N}\cdots\text{H}-\text{O}$.

3.4 Chemical bonding

As mentioned above, we find an insignificant geometrical modification of both gold cluster and amino acids after the complexation. The moiety Au_3 in all complexes considered is still linear as in the isolated monomer Au_3^- . This indicates that the extra electron is mainly localized on the gold cluster, since the neutral Au_3 prefers to stay as a triangular form. The main reason is due to the exceptionally high electron affinity (EA) of the triatomic gold cluster as compared to those of glycine and alanine molecules. In current text, the EA value of Au_3 is computed to be around 3.55 eV (Exptl value 3.67 ± 0.30 eV), while those of alanine and glycine are predicted to be -0.52 and -0.23 eV, respectively.

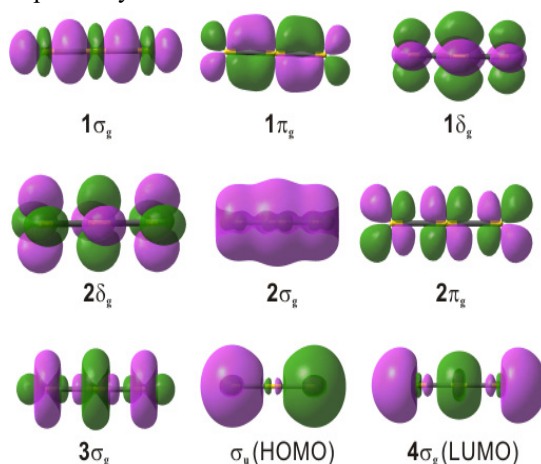


Fig. 6: Shapes and symmetries of frontier MOs derived from the interactions between valence orbitals of gold atoms in Au_3^-

In order to get deeper insights in to the nature of the interaction between glycine and alanine with anion Au_3^- , we further consider the characteristics of frontier orbitals in both individual systems and complexes. Let us take a closer look at $[\text{Au}_3\text{Glycine}]^-$ as a typical example. Figure 6 shows the shapes and symmetries of frontier MOs derived from the interactions between valence orbitals of gold atoms in Au_3^- , while Figure 7 plots the highest occupied and lowest unoccupied orbitals (HOMO and LUMO) of two isomers of glycine molecule. The shapes of orbitals generated from combinations between frontier MOs of glycine and Au_3^- are displayed in Figure 8.

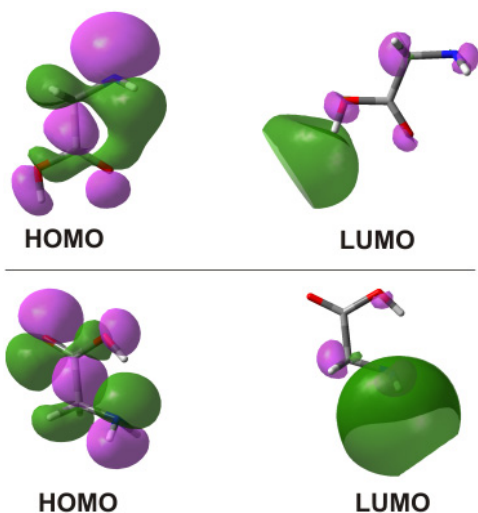


Fig. 7: The HOMO and LUMO of two isomers Gly-I (above) and Gly-II (below)

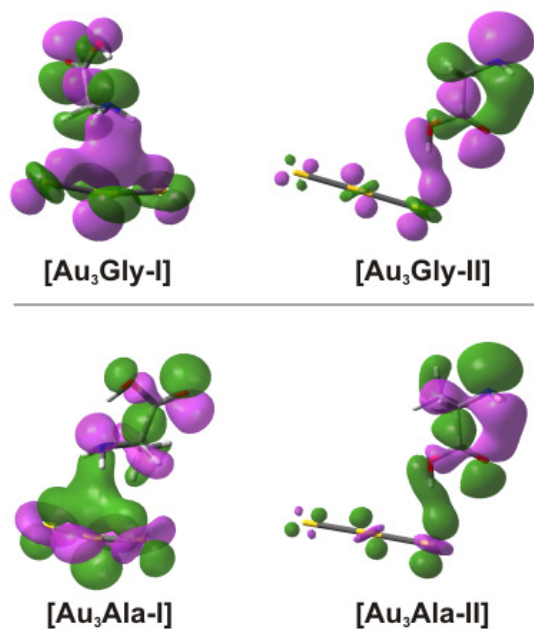


Fig. 8: The bonding orbitals in complexes of Au_3^- anion with glycine (above) and alanine (below)

Due to a difference in symmetry and energy, neither the LUMO nor the HOMO of Au_3^- does combine with any MOs of glycine. They become the LUMO and HOMO in $[Au_3Glycine]^-$ complex and both have a nonbonding character. When forming the complex $[M_3Gly-I]$, only the orbital $1\delta_g$ can interact with the HOMO of glycine, giving rise to a bonding orbital. On the contrary, in $[M_3Gly-II]$ complex, the bonding MO is largely contributed

from the HOMO of the glycine molecule (see Figure 8). Similar combinations are also observed for the interaction of alanine with Au_3^- .

As stated above, interactions between gold clusters and amino acids are basically characterized by donor and acceptor factors, in such a way that the charge transfer constitutes a key element for understanding their mechanism. The natural charges distributed on Au_3 moiety in $[Au_3Glycine]^-$ and $[Au_3Alanine]^-$ adducts are summarized in Figure 9. We here exploit natural bond orbital (NBO) charges for electron population analysis instead of Mulliken charges because the former are expected to be more reliable. The obtained results clearly show that the adsorbed glycine and alanine are negatively charged on every complex considered, indicating that an amount of electron has been transferred back from Au_3^- to these bimolecular species.

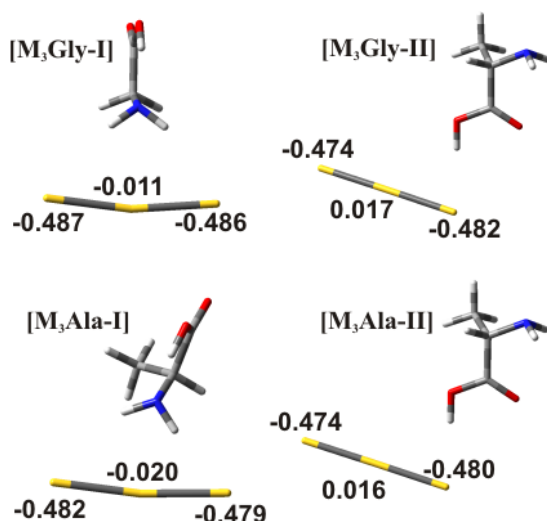


Fig. 9: Charges distributed on Au_3 moiety in complexes of Au_3^- with glycine and alanine

4 CONCLUDING REMARKS

A theoretical study of the adsorption of some small amino acids on the anionic cluster Au_3^- has been performed using the M062X functional in conjunction with the pseudo-potential aug-cc-pVTZ-PP basis set for metals and the full-electron aug-cc-pVTZ basis set for non-metals. A comparison with previous probes allows us to draw several interesting points as follows.

In general agreement with prior studies, the interaction of the amino acids with Au_3^- is facile in nature. We find the geometries not only of Au_3^- , but also of biomolecules almost unchangeable after the complexation. However, contrary to the dominance of the anchoring N–Au and O–Au bonds in complexes of amino acids with the neutral Au_3 , the

interaction of such biomolecular compounds with the anion Au_3^- is characterized by the nonconventional H-bonds $N-H\cdots Au$ and $O-H\cdots Au$. We are not able to locate the complexes possessing $Au-N$ or $Au-O$ anchoring bonds between the anion Au_3^- and glycine and alanine molecules.

The forming of the nonconventional H-bonds is likely to accompany with a minor charge transfer from Au_3^- to the bimolecular species. It in addition results in a significant red-shift of the $O-H$ bond in carbonyl group. Due to the higher electron affinity (EA) of Au_3 as compared to that of glycine and alanine, the extra electron is found to be mainly localized on the gold atoms.

The binding energies of Au_3^- with glycine and alanine through the hydrogen atoms of amine and carboxylic groups around 17 and 10 kcal/mol, respectively, are thus slightly smaller than the values of 20 and 12 kcal/mol reported in the literature for the absorption on Au_3 .

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