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Structures and electronic properties of $Au_{n-1}Cu$ and Au_n $(n \leq 9)$ clusters*

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A systematic study on the structure and electronic properties of gold clusters doped each with one copper atom has been performed using the density functional theory. The average bond lengths in the $Au_{n-1}Cu$ $(n \leq 9)$ bimetallic clusters are shorter than those in the corresponding pure gold clusters. The ionization potentials of the bimetallic clusters $Au_{n-1}Cu$ $(n \leq 9)$ are larger than those of the corresponding homoatomic gold clusters except for Au_5. The energy gaps of the Au–Cu binary clusters are narrower than those of the Au_n clusters except AuCu and Au_3Cu. No obvious even–odd effect exists in the variations of the electron affinities and ionization potentials for the $Au_{n-1}Cu$ $(n \leq 9)$ clusters, which is in contrast to the case of gold clusters Au_n.

Keywords: Au-Cu bimetallic cluster, equilibrium geometry, bond energy, HOMO–LUMO gap
PACC: 3640, 3640B, 3120A, 3130J

1. Introduction

During the last decade, noble-metal clusters such as Cu, Ag and Au have been extensively studied both experimentally and theoretically.[1−3] There have been a number of papers devoted to the study of the structures of both neutral and ionic gold clusters.[4−24] Ion mobility experiments and photoelectron spectroscopy (PES) with the assistance of the density functional theory (DFT) have confirmed that planar structures are energetically preferred up to $N = 12$ for anion gold clusters, while the transition from two-dimensional (2D) to three-dimensional (3D) configurations occurs around $N = 8$ for cationic gold clusters.[11,15] There have been no direct experiments on neutral clusters. However, recently the CCSD(T) approach has predicted that the lowest structure for Au_8 is 3D configuration,[25] although most relativistic DFTs have shown planar structures for gold clusters with more than ten atoms.[26,27] Our previous DFT study has predicted that the turnover point is at Au_7.[28]

However, only a few reports of bimetallic clusters are available. Bimetallic clusters doped each with a single impurity atom produce an exciting field. The functions of bonding and valence are still unknown. Their structures and properties differ from those of the homogeneous clusters greatly. As has been extensively demonstrated, the structural and electronic properties of small clusters vary with the cluster size in a discontinuous manner. The properties of the heterogeneous clusters cannot be obtained, in general, by interpolating (as a function of concentration) the behaviour of the corresponding pure clusters. Bimetallic clusters combine the characteristics of the finite size systems with those of the alloys. One can expect to find new and interesting properties as a function of the cluster size and concentration for the microalloy.

Recently, some studies have been carried out on impurity-doped gold clusters in order to enhance the stability of gold clusters and improve their chemical activities. These studies include, for instance, the effects of alloying on the structural and thermal properties of $Cu_{n-x}Au_x$ $(n = 13, 14)$ clusters, which were investigated by constant energy molecular dynamics simulations, [29] geometric and electronic properties of planar configurations of Cu–Ni clusters containing up to five atoms, which were studied by using the density functional theory (DFT).[30] A general tight-binding total energy scheme has been used to calculate the structural properties of the bimetallic com-

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pounds: Cu_3Au, CuAu, $CuAu_2$, $CuAu_3$, and Cu_6Au_8 clusters.[31] Bonacic *et al*[32] studied the structural and electronic properties of bimetallic Ag_mAu_n ($3 \leq (m+n) \leq 5$) clusters using the DFT. Bouwen *et al*[33] and Heinebrodt *el al*[34] investigated the bimetallic Au_nX_m(X = Cu, Al, Y, In, Cs) clusters, and found the electronic shell effects separately. Koszinowski *el al*[35] have found that the reactions of bimetallic $Pt_mAu_n^+(m+n<5)$ cluster ions with O_2 and CH_4 exhibit the great dependence on cluster composition, and their reactions with O_2 are consistently diminished as a function of gold content. Yuan *et al*[36] studied the geometric and electronic structures of gold clusters doped with platinum atoms, $Au_nM(n=1-7$, M = Ni, Pd, Pt), which are in a ground state, by employing the first-principles method.

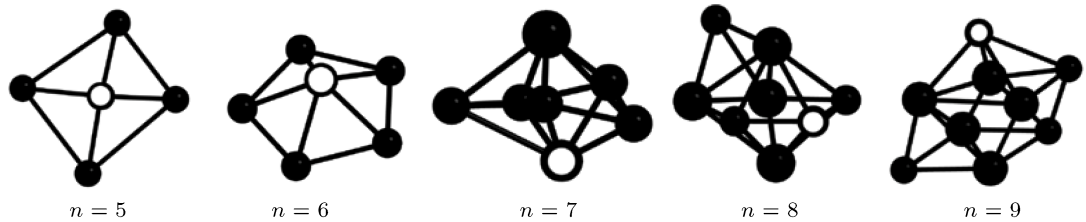
In the present work, we report a systematic investigation of $Au_{n-1}Cu$ ($n \leq 9$) clusters, in which a monovalent impurity is doped in a monovalent host. This preliminary study suggests that atoms in the same group can mix with each other at any ratio.[37] We focus here on small Au-Cu clusters containing up to nine atoms in order to understand the dependence of their electronic characteristics on cluster size. In addition, we calculate the energy gaps and Fermi energies for a series of $Au_{n-1}Cu$ clusters in order to compare the energy gaps and Fermi energies of both $Au_{n-1}Cu$ and Au_n clusters ($n \leq 9$). These results can be used to predict the experimental properties of bimetallic clusters.

2. Computational details

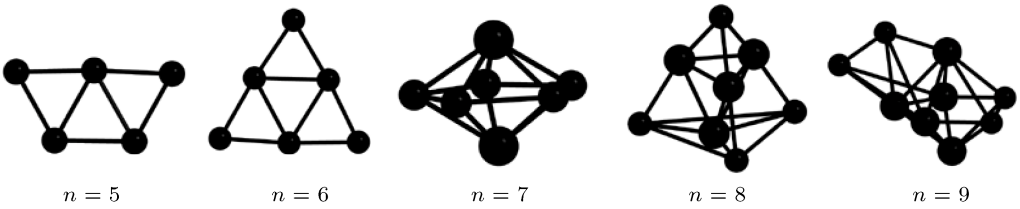
A DFT treatment combined with effective core potentials (ECPs) was used to optimize the geometries of several clusters $Au_{n-1}Cu$ ($n \leq 9$). The relativistic ECPs developed by Hay and Wadt[38] to represent the inner-core electrons. The outermost core orbitals, 3s (5s) and 3p (5p), were explicitly included in the Cu or Au valence shells. The structures of Au clusters doped each with one Cu atom into one of their different sites were used as starting geometries for optimization, of which, the structure with the lowest energy was chosen as the most stable configuration. The B3LYP method with the Los Alamos National Laboratory double ζ (LANL2DZ) ECP was used. All computations were performed using the Gaussian 98 program.

3. Results and discussion

The equilibrium structures of the $Au_{n-1}Cu$ ($n \leq 9$) clusters along with the geometries of the original host Au_n ($n \leq 9$) clusters are shown in Fig.1, where the impurity atoms are indicated as the open circles. The $Au_{n-1}Cu$ clusters with $n = 2, 3, 4$ are found to be very similar to the pure Au_n clusters in geometry. Therefore the equilibrium geometries of clusters with $n \leq 3$ are not included in Fig.1.



(a) $Au_{n-1}Cu$ ($n \leq 9$) (the Cu atom is denoted by the open circle).



(b) Au_n ($n \leq 9$).

Fig.1. Ground state geometries of $Au_{n-1}Cu$ (a) and Au_n (b).

After one Cu atom is doped into the Au_4 cluster with a planar trapezoid structure, the Au_4Cu cluster becomes a Cu-centred Au_4 rhombus. The $Au_{n-1}Cu$ structures show an early appearance of three-dimensional (3D) geometries starting at $n = 6$ (Au_5Cu). The addition of a single Cu atom to Au_5 generates a pentagonal pyramid with an Au base and a Cu apex. For Au_6Cu, the pentagonal ring remains intact after the addition of an Au atom to Au_6Cu, leading to a pentagonal bipyramid with an axial Cu atom. The substitution of a Cu atom with Au distorts the original structure of Au_8, but the structures of the larger clusters are similar to those for pure Au_n with one of the surface Au atoms replaced by Cu. The binding energies of the diatomic systems Au-Au and Cu-Au are found to be 1.87 eV and 2.29 eV, respectively, indicating that the Au-Cu bond is stronger than the Au-Au bond. The tendency of Cu to remain on the surface can therefore be attributed to the larger ionic radius of Au (1.79 Å) relative to Cu (1.57 Å).

The average bond length between atoms in the cluster may be defined as

$$\bar{R} = \frac{1}{N_b} \sum_i R_{ij}. \tag{1}$$

In Eq.(1) R_{ij} is the nearest-neighbour distance, which is 15% less or more than the equilibrium distance. The average coordination number is the average number of nearest neighbours within a given cut-off distance, namely,

$$\mathrm{CN} = \frac{1}{n} \sum_i \mathrm{i} n_i. \tag{2}$$

In Eq.(2) i is the number of nearest-neighbour atoms. The geometrical parameters and electronic properties of the $Au_{n-1}Cu$ and Au_n clusters containing up to nine atoms are summarized in Table 1.

Table 1. The average bond length (R), average coordination number (CN), binding energy per atom (E_b), ionization potential (IP) and electron affinity (EA) for $Au_{n-1}Cu$ and Au_n ($n \leq 9$).

	R/Å		CN		E_b/eV		IP/eV		EA/eV	
	$Au_{n-1}Cu$	Au_n	$Au_{n-1}Cu$	Au_n	$Au_{n-1}Cu$	Au_n	$Au_{n-1}Cu$	Au_n	$Au_{n-1}Cu$	Au_n
2	2.405	2.573	1.0	1.0	1.15	0.94	8.80	9.43	1.18	2.03
3	2.642	3.418	2.0	2.0	1.15	0.92	7.19	7.26	1.89	3.68
4	2.662	2.751	2.5	2.5	1.41	1.17	7.94	7.94	2.04	2.62
5	2.956	2.814	1.6	2.8	1.16	1.28	8.41	7.16	3.79	3.18
6	2.707	2.769	3.3	2.7	1.57	1.50	8.16	8.46	2.03	2.15
7	2.845	2.876	4.0	4.3	1.49	1.34	6.95	6.42	2.75	3.32
8	2.861	2.837	3.9	4.5	1.52	1.50	7.51	7.33	2.17	2.40
9	2.893	2.893	4.6	4.7	1.50	1.41	7.12	5.66	3.20	4.03

Table 1 indicates that the average bond lengths in the $Au_{n-1}Cu$ bimetallic clusters are shorter than those in the homoatomic Au_n clusters. For diatomic molecules the Au-Cu bond length is 1.68 Å shorter than Au-Au bond length. Furthermore, the electron binding energy per atom in the $Au_{n-1}Cu$ clusters is larger than that in the corresponding Au_n clusters except for the case of Au_4Cu versus Au_5 clusters. This suggests that the Au- Cu bond is stronger than the AuAu bond. The most interesting characteristic of the pure Au_n clusters is that their electron affinities (EAs) and ionization potentials (IPs) show a non-monotonic variation with cluster size, namely the even-odd effect. In contrast, the variations in EA and IP for the $Au_{n-1}Cu$ bimetallic clusters are irregular. For $n \leq 5$, a monotonic increase of the electron affinity is observed when a Cu atom replaces an Au atom. For $n > 5$ an even-odd effect is observed. The Au_4Cu cluster has the largest ionization potential and exhibits an anomalously high stability.

The Cu atom has a valence shell isoelectronic to that of the Au atom, with a single s electron located beyond the filled d^{10} shell. However, the bonding in a heteroatomic Au-Cu binary cluster is expected to have some degree of ionic character, since the Pauling's electronegativities of Au and Cu are significantly different. As a result, the energy level distributions in the heteroatomic $Au_{n-1}Cu$ clusters differ from those in the pure Au_n clusters. The highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO), HOMO–LUMO gaps (HLG), and Fermi energies for the $Au_{n-1}Cu$ and $Au_n (n \leq 9)$ clusters are studied by optimizing the structures of negative and positive ions for these clusters using the same method and basis set. The optimized structures of the negative and positive ions are similar to those of the

neutrals.

Figure 2 shows the Fermi energies for the $Au_{n-1}Cu$ and $Au_n(n \leq 9)$ clusters. The notable feature in the $Au_{n-1}Cu$ clusters is that their Fermi energies change irregularly once one Au atom is replaced by one Cu atom. Thus the Fermi energy of the $Au_{n-1}Cu$ binary clusters falls from $n = 3$ to $n = 5$ and then rises to $n = 7$ followed by a drop at $n = 8$. Meanwhile, the HOMO–LUMO gaps of the $Au_{n-1}Cu$ clusters exhibit a strict even-odd effect somewhat different from those of the Au_n clusters. Except the AuCu and the Au_3Cu clusters, the Au-Cu binary clusters have smaller HOMO–LUMO energy gaps than the pure Au clusters, suggesting that the bimetallic cluster is more reactive than the pure Au cluster. Because of this reason, the enhanced catalytic ability is anticipated when a copper atom is doped into the gold cluster, which is in accord with experimental results.[39]

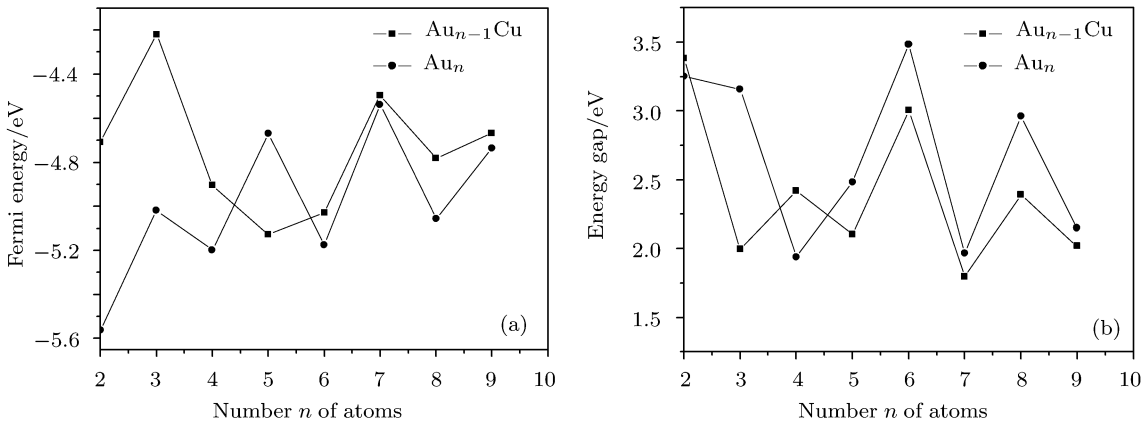


Fig.2. Fermi energy and energy gap versus the cluster size.

4. Conclusions

We have predicted the equilibrium geometries and electronic properties of $Au_{n-1}Cu$ ($n \leq 9$) clusters. The smaller bimetallic $Au_{n-1}Cu$ ($n \leq 4$) clusters have structures resembling those of the homoatomic gold clusters Au_n, whereas the structures of the large $Au_{n-1}Cu$ ($n = 5$–9) clusters are different from those with Cu located at the periphery. This research demonstrates that a gold cluster doped with a single Cu atom can reduce the energy gap (except Au_3Cu), even though the heteronuclear Au–Cu bond is stronger than the Au-Au homonuclear bond. The reactivity of the heteronuclear $Au_{n-1}Cu$ cluster is thus enhanced with respect to that of the homonuclear Au_n cluster. The variations of the electron affinities and ionization potentials of the $Au_{n-1}Cu$ ($n \leq 9$) clusters are irregular, showing no even–odd effect observed in the pure Au_n clusters.

The theoretical results in this study provide significant chemical information on $Au_{n-1}Cu$ binary clusters. The sensitivity of electronic structure to geometry is an interesting property, which can be examined both experimentally and theoretically. Though the studies of cluster anions by using photoelectron spectroscopy (PES) can give direct information on electronic energy levels, it is insufficient to determine the structures of clusters. With the electron affinities, the ionization potentials, and the HOMO–LUMO gaps together rather than only the calculated total energies taken into consideration, it is much more reliable to predict the experimental data.

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