Geometric, stable and electronic properties of $Au_{n-2}Y_2$ ($n = 3 - 8$) clusters*

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(Received 6 July 2009; revised manuscript received 9 September 2009)

Employing first-principles methods, based on the density function theory, and using the LANL2DZ basis sets, the ground-state geometric, the stable and the electronic properties of $Au_{n-2}Y_2$ clusters are investigated in this paper. Meanwhile, the differences in property among pure gold clusters, pure yttrium clusters, gold clusters doped with one yttrium atom, and gold clusters doped with two yttrium atoms are studied. We find that when gold clusters are doped by two yttrium atoms, the odd–even oscillatory behaviours of $Au_{n-1}Y$ and Au_n disappear. The properties of $Au_{n-2}Y_2$ clusters are close to those of pure yttrium clusters.

Keywords: $Au_{n-2}Y_2$ clusters, density function theory, geometric property, electronic property
PACC: 3640, 3640B, 3120A, 3130J

1. Introduction

Recently, noble-metal has become a hot topic in research due to its industrial applications and interesting optical properties. In particular, gold clusters are extensively used in catalytic reactions, adsorbing material[1−3] and photoabsorption.[4,5]

In addition, the gold clusters also show electronic shell structures due to the valence s electrons, in which each atom contributes essentially one binding electron while the completely filled 5d shell represents a small perturbation, which is similar to the alkali-metal clusters.[6,7] Meanwhile, bimetallic clusters have become materials of increasing interest in cluster research because of their adjustability in property by changing their composition and size. For noble-metal clusters, the introduction of the dopant atom in a coinage metal cluster can change their structural and electromagnetic properties and improve their stability significantly.[8−12] In particular, in contrast to other elements, transition metal clusters have enormous complexity and do not exhibit the electron shell effect because of the unfilled d shell. So it is interesting to examine the result of basic interaction between d electrons of transition metal with the nearly free s electrons of the host.

As is well known, many studies have been performed on impurity-doped or mixed gold clusters.[13−19] Bouwen *et al.*[18] and Heinebrodt *et al.*[19] investigated the bimetallic Au_nX_m (X= Cu, Al, Y, In) clusters by time-of-flight mass abundance spectrometry, and found the magic numbers of the electronic shell model for clusters. Yuan *et al.* investigated the geometric and electronic structures of gold clusters doped with platinum atom, Au_NM ($N = 1 - 7$, M=Ni, Pd, Pt) clusters,[20] which indicated the ground-states based on the density function theory. Koyasu *et al.* determined the electron affinities (EAs) and vertical detachment energies (VDEs) by photoelectron spectroscopy of Au_nPd^-.[21] Wang *et al.*[22] investigated the equilibrium geometries and electronic structural properties of mixed Au_nX_m ($n + m = 4$, X=Cu, Al, Y) clusters. Subsequently, Wang *et al.*[23] also researched the difference in structural and electronic properties between $Au_{n-1}Cu$ and Au_n clusters. Recently, the equilibrium geometries and electronic structural properties of Au_nAl ($n = 2 - 13$) were studied by Zhao *et al.*[24] Meanwhile, Mao *et al.*[25] investigated the structural and the electronic properties of $Au_{n-1}Y$($n\leq9$) clusters. The results showed that the vertical ionisation potential and the electron affinities of $Au_{n-1}Y$ clusters

*Project supported by the National Natural Science Foundation of China (Grant No. 10276028), and the Education Committee of Chongqing, China (Grant No. KJ051105).
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as a function of the cluster size each have an odd–even oscillatory behaviour, which resembles those of pure gold clusters.

In the present paper, using the first-principles methods, based on the density function theory, we investigate the geometrical and the electronic properties of the gold clusters doped with two Y atoms. In addition, a comparison among the pure gold clusters, pure yttrium clusters, and gold clusters doped with one Y atom and $Au_{n-2}Y_2$ ($n = 3-8$) clusters, separately, is made and viewed.

2. Computational method

All our calculations are carried out by using the Gaussian 03 program package.[26] The computational method is based on the density functional theory (DFT) calculation by combining the Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP),[27,28] which is widespread and has proved to be valuable to the study of transition metal clusters. A relativistic effective core potential (RECP) with corresponding valence basis sets, LANL2DZ[29] is used to treat the atoms. The core electrons are replaced by RECP and the outer 19-electrons ($5s^25p^65d^{10}6s^1$) of Au atom and 11-electrons ($4s^24p^64d^15s^2$) of Y atom are treated by Gaussian basis sets. All geometries have been fully optimized and frequency has been researched. We choose a structure with a lowest energy and without imaginary frequency as a ground state structure. The convergence criterions of energy, force and displacement are 1×10^{-6} a.u., 1×10^{-4} a.u./Bohr and 1×10^{-3} Bohr, respectively.

3. Results and discussion

In order to discuss the effects of doped impurity on gold clusters, we performed some calculations on pure gold clusters, pure yttrium clusters and $Au_{n-1}Y$ clusters. The lowest energy equilibrium structures of the Y_n ($n = 4-8$), Au_n (4–8) and $Au_{n-1}Y$ ($n = 4-8$) clusters and the equilibrium geometric structures of $Au_{n-2}Y_2$ ($n = 3-8$) are shown in Fig. 1. Obviously, AuY_2 has an isosceles triangle structure, which is similar to the structures of homoatomic Au_n, Y_n and $Au_{n-1}Y$ clusters. For Au_2Y_2, the ground state is of a distorted tetrahedron. While for Au_3Y, an equilateral triangle has been proved to be the stablest structure. Au_4 is of a planar rhombus. In Au_3Y_2, the ground state structure is of a trigonal bipyramid with D_{3h} symmetry. But for Y_5 and Au_5, the ground state is of a planar structure with 'W' shape. Compared with other homoatomic clusters, Au_3Y_2 has a more compact geometry. Au_4Y_2 can be made by adding one Au atom to the apical Y atom of Au_3Y_2 cluster. Its symmetry is C_{3V}. For other homoatomic clusters of Au_4Y_2, only the Y_6 is three-dimensional. For Au_5Y_2, the geometry is a trigonal bipyramid with each apical Y atom linked by an Au atom respectively. It can also be obtained by adding one Au atom to the other apical Y atom of Au_4Y_2 cluster. The geometry of Au_6Y_2 is an octahedron capped by an Au atom at the position of each apical Y atom. Its symmetry is C_{2V}. Because the cluster size is bigger, the Au_6Y_2 and its homoatomic clusters are three-dimensional.

From those clusters, we can know that the geometry of AuY_2 can be viewed as the basic structure of $Au_{n-2}Y_2$ ($n = 4-8$). And except AuY_2, the two Y atoms constitute a symmetry axis of other clusters. In this case, the coordinate number of Y atom increase with cluster size increasing.

In addition, comparing $Au_{n-2}Y_2$, Y_n with $Au_{n-1}Y$ and Au_n clusters, we find that with the increase of Y atom, the geometries of clusters tend to be three-dimensional. The reason is that in our calculated level, the valence shell of Y atom is $4d^15s^2$, and the d orbital is not completely filled. Thus, there is more sites for Y atom to be bound with other atoms. For the stability of cluster, the coordinate number of Y atom in ground-state structure tends to be largest. Therefore, the cluster will form a three-dimensional structure.

From Fig. 2 and Table 1, we can see that the average bond length of $Au_{n-2}Y_2$ is longer than those of $Au_{n-1}Y$ and Au_n but shorter than that of Y_n generally. The reason is that the atomic radius of Y is larger than that of Au atom. And the change of bond length does not show any odd–even oscillatory behaviour. We also studied the binding energies of those clusters. The particular feature of binding energy per atom in $Au_{n-2}Y_2$ is that the binding energy increases with cluster size increasing, which is different from the scenarios in other clusters. From $n = 5$ to 8, the $Au_{n-2}Y_2$ clusters become stablest compared with other homoatomic clusters. The reason is that Au–Y bond is stronger than Au–Au bond and Y–Y bond, and with the Y atom in clusters increasing the number of Au–Y bonds rises.

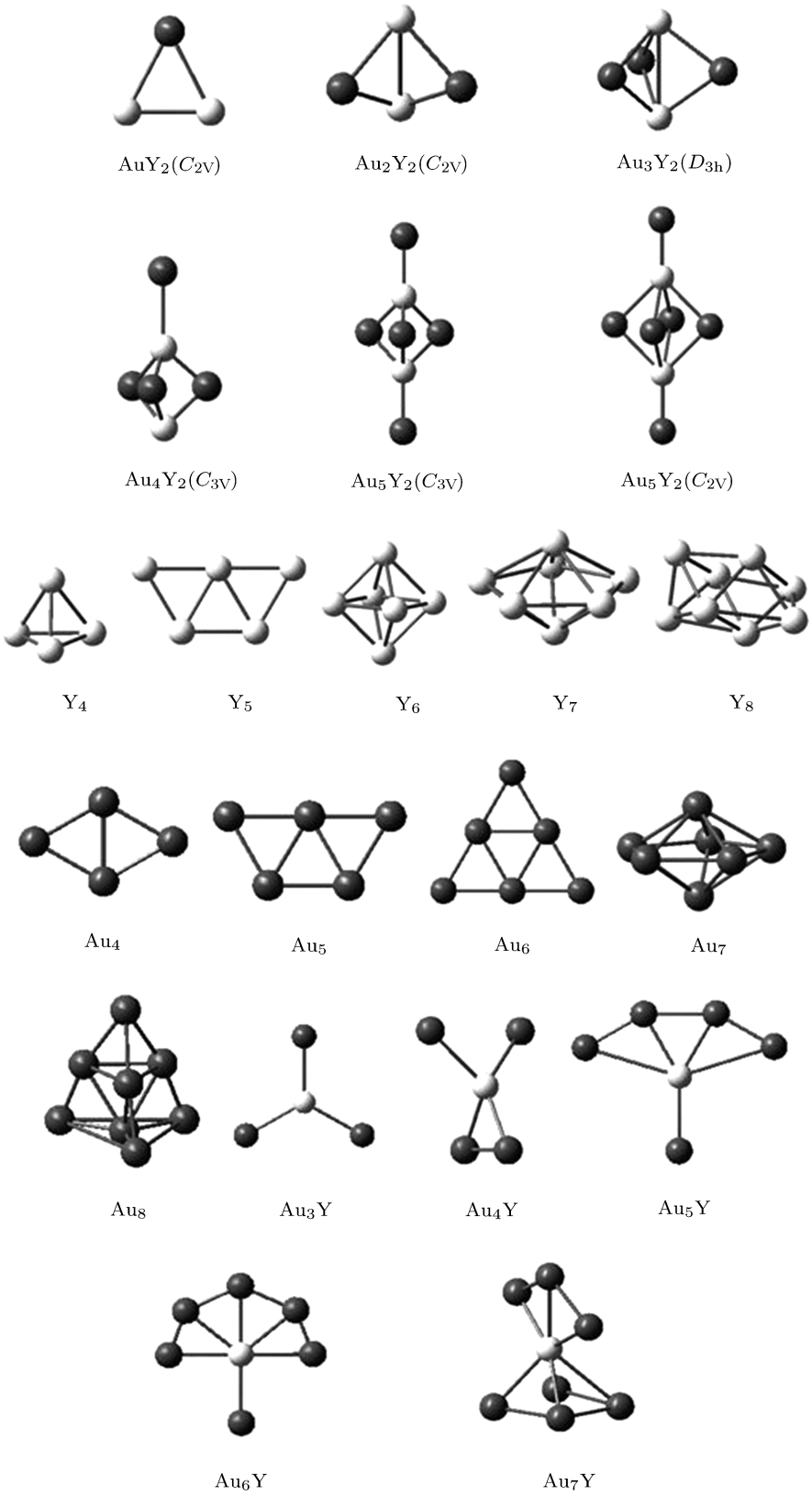


Fig. 1. Equilibrium geometric structures of $Au_{n-2}Y_2$ $(n = 3-8)$, Y_n $(n = 4-8)$, Au_n $(n = 4-8)$ and Au_nY $(n = 3-8)$ clusters.

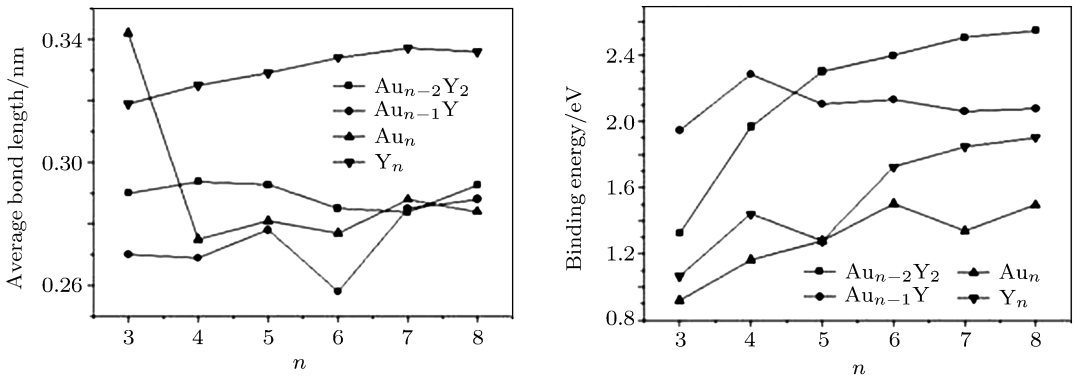


Fig. 2. Average bond length and binding energy as a function of cluster size.

Table 1. HOMO, LUMO, HLG, Fermi energy, IP, EA, Binding energy (E_b) and average bond length (R) of $Au_{n-2}Y_2$ ($n = 3 - 8$) clusters.

N	HOMO/a.u	LUMO/a.u.	HLG/eV	Fermi/eV	IP/eV	EA/eV	E_b/eV	R/nm
3	–0.1216	–0.08885	0.8917	–2.86359	4.9168	1.1783	1.3253	0.290
4	–0.1506	–0.09646	1.4735	–3.36156	5.4748	1.2550	1.9688	0.294
5	–0.1507	–0.09595	1.4890	–3.35544	5.4664	1.3225	2.3014	0.293
6	–0.1642	–0.10958	1.4849	–3.72429	5.8254	1.4599	2.3984	0.285
7	–0.1643	–0.11983	1.2098	–3.86565	5.8474	1.9404	2.5080	0.284
8	–0.2247	–0.11952	2.8624	–4.58052	7.5717	1.9568	2.5497	0.293

Figure 3 shows that the IP and the EA of $Au_{n-2}Y_2$ increase with cluster size increasing, which is different from those of $Au_{n-1}Y$ and Au_n. In other words, the odd–even oscillatory behaviour disappears in $Au_{n-2}Y_2$ cluster. This feature also occurs in Y_n cluster. It suggests that in the clusters the feature of Y_n cluster gradually appears. For $Au_{n-1}Y$ and Au_n, the odd–even behaviour can be explained by electron pairing effect.[22] But for $Au_{n-2}Y_2$ cluster, the situation is complex. Because there are more d orbitals and bonding electrons, and the d orbitals are not completely filled. Meanwhile, the IP and the EA of those clusters are closely related to d electrons of Y atom. Comparing $Au_{n-2}Y_2$ with homoatomic $Au_{n-1}Y$ and Y_n clusters, we find that the EA and the IP decrease when cluster size goes up. It indicates that the increase of Y atom can reduce the stability of clusters and make photoionisation easier.

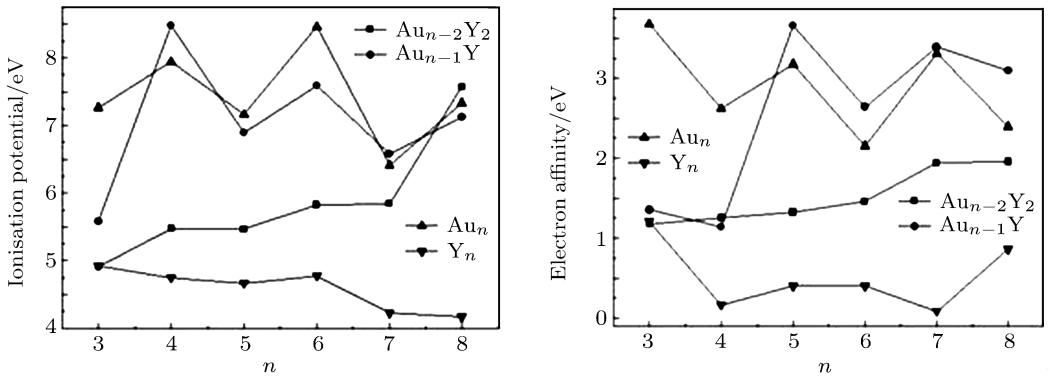


Fig. 3. Ionisation potential (IP) and electron affinity (EA) as a function of cluster size.

As shown in Table 1 and Fig. 4, the Fermi energy of $Au_{n-2}Y_2$ decreases when the cluster size increases. Just like the result shown in Fig. 3, there appears no odd–even oscillatory behaviour. And the Fermi energy increases as the number of Y atoms in the clusters increases when the cluster size is equal. For HOMO–LUMO gaps (HLGs) of $Au_{n-2}Y_2$, its change is irregular, which is similar to the scenarios of Au_n, Y_n and $Au_{n-1}Y$ clusters. From Table 1 and Fig. 4, we can know that the HOMO–LUMO gap of Au_3Y_2 is bigger, which suggests

that Au_3Y_2 is stabler than its neighbours. Similarly, a comparison of HLG among different homoatomic clusters obviously shows that the increase of Y atom number in the clusters leads to the decrease of HLG value. The reason is that the bonding electrons of Au atom origin from the 6s orbital, while the bonding electrons of Y atom origin from the 4d and 5s orbitals. With the increase of Y atom number, the total number of bonding electrons of clusters increases, which will provide more active electrons and enhance the delocalization of HOMO and HOMO orbitals and result in the decrease of HLGs.

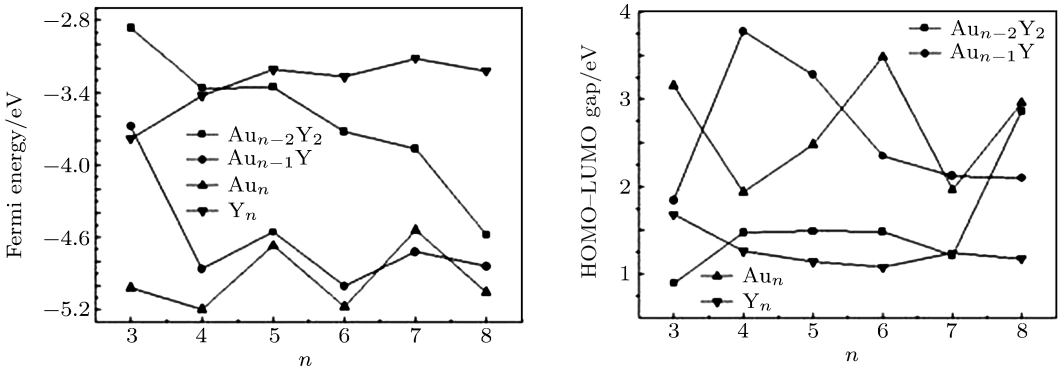


Fig. 4. Fermi energy and HOMO–LUMO energy as a function of cluster size.

4. Conclusion

The geometric, the stable and the electronic properties of $Au_{n-2}Y_2$ ($n = 3-8$) clusters are investigated. The results show that the two Y atoms constitute symmetry axis of clusters. The thermodynamic stability increases with the increase of cluster size based on the binding energy. For EA, IP and Fermi energy of $Au_{n-2}Y_2$, the odd–even oscillatory behaviour disappears. In particular, IP and EA of $Au_{n-2}Y_2$ increase with the rise of cluster size. In addition, comparing $Au_{n-2}Y_2$ with those of homoatomic $Au_{n-1}Y$, Au_n and Y_n clusters, we find that the average bond length and Fermi energy increase. Based on the same comparison, EA, IP and HOMO–LUMO gaps decrease, which suggests that the chemical stability is weakened. These results can provide theoretical reference for both the application and further study.

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