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Density functional study on structural and electronic properties of bimetallic gold–yttrium clusters: comparison with pure gold and yttrium clusters*

Mao Hua-Ping(毛华平)[a)b)], Wang Hong-Yan(王红艳)[b)c)], and Sheng Yong(盛 勇)[d)†]

[a)] *Department of Chemistry and Environment Engineering, Chongqing Three-Gorge College, Chongqing* 404000, *China*
[b)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*
[c)] *Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens Georgia* 30602, *USA*
[d)] *Material Science and Engineering College, Sichuan University, Chengdu* 610065, *China*

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Employing first-principles methods, based on the density functional theory, this paper investigates the ground state geometric and electronic properties of pure gold clusters, pure yttrium clusters and gold clusters doped each with one yttrium atom. It is shown that the average bond lengths in the $Au_{n-1}Y(n \leq 9)$ bimetallic clusters are shorter than those in the corresponding pure gold and yttrium clusters. The most stable isomers of the yttrium-doped gold clusters tend to equally delocalize valence s, p and d electrons of the constituent atoms over the entire structure. The Y atom has maximum number of neighbouring Au atom, which tends to be energetically favourable in the lowest-energy equilibrium structures, because the Au–Y bond is stronger than the Au-Au bond. The three-dimensional isomers of $Au_{n-1}Y$ structures are found in an early appearance starting at n=5 (Au_4Y). Calculated vertical ionization potential and electron affinities as a function of the cluster size show odd-even oscillatory behaviour, and resemble pure gold clusters. However, one of the most striking feature of pure yttrium clusters is the absence of odd-even alternation, in agreement with mass spectrometric observations. The HOMO–LUMO gap of Au_3Y is the biggest in all the doped $Au_{n-1}Y(n \leq 9)$ bimetallic clusters.

Keywords: gold–yttrium bimetallic cluster, density functional theory, HOMO–LUMO gap, equilibrium structure
PACC: 3640, 3640B, 3120A, 3130J

1. Introduction

Atomic metal clusters continue to be an important object of investigation due to their wide range of application. Their physical and chemical properties, greatly determined by the cluster size and constituent, represent great advantages compared to other molecular systems as far as nanostructured materials technology is concerned. During the past two decades, noble-metal (Cu, Ag and Au) clusters have been extensively studied both experimentally and theoretically.[1−3] The experimental values of electron affinities, vertical detachment energies and ionization potentials of pure gold clusters as function of their size are known from early investigation.[4−6] Structural properties of small anionic and neutral Au_n (n=3–8) clusters have been theoretically investigated.[7−9] Coinage metal (Cu, Ag and Au) clusters are treated as simple metal clusters in the same manner as alkali metal clusters, for coinage metals have a completely filled d-shell and one valence s electron in the electronic ground state. However, this simple electronic shell model cannot be applied for transition metal clusters (e.g. yttrium) with an open d-shell, because transition metal clusters are intriguing as a result of the large number of electronic states of different spin multiplicities and the complexity of the metal-metal bond involving the metal s, p and d orbitals. Experimental studies on yttrium clusters are limited in that earlier studies which were focused mainly on Y_2 and Y_3.[10,11]

Recently bimetallic clusters have become a matter of increasing interest in cluster research. This is not only because of their intrinsic scientific importance, as small scale precursors of bulk alloys, but also because of the anticipated possibility for the production of new types of nanostructured materials with unique

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†Corresponding author. E-mail: shengyong69@163.com

mechanical, optical, thermal, electrical and /or magnetic properties. Moreover, several elemental systems which are supposed to be non-miscible in bulk alloys readily mix in clusters or nanoparticles. This enlarges the variety of binary systems, in comparison with bulk alloys. In order to enhance the stability of gold clusters and improve their chemical activities, or examine the electronic shell structures in doped gold clusters, many studies have been performed on impurity gold clusters. For instance, Bouwen *et al* investigated the stability effects of 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.[12] 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,[13] which are in a ground-state, by employing the first-principles method. Koyasu *et al* determined the electron affinities(EAs) and vertical detachment energies (VDEs) by photoelectron spectroscopy of palladium-doped gold cluster anions, Au_nPd^-.[14]

In this paper, using the first-principles methods based on a density functional theory (DFT), we systematically investigated the geometric and electronic structures of pure gold clusters, pure yttrium clusters, and gold clusters doped each with one yttrium atom. In addition, we calculated the ionization potential, electron affinities, energy gaps and Fermi energies as a function of the cluster size for a series of $Au_{n-1}Y$ ($n \leq 9$) clusters in order to compare the energy gaps and Fermi energies of Y_n ($n \leq 8$) and Au_n ($n \leq 9$) clusters. These results can be used to predict the experimental properties of gold–yttrium bimetallic clusters.

2. Method of computations

All our calculations were carried out by using the GAUSSIAN 98 program packages.[15] The computational method is based on a DFT calculation with the Becke's three-parameter hybrid functional incorporating the Lee–Yang–Parr correlation functional (B3LYP).[15,16] 19-electron ($5s^25p^65d^{10}6s^1$) and 11-electron ($4s^24p^64d^15s^2$) relativistic effective core potentials[17] with the corresponding valence basis set LanL2DZ were taken into account for Au and Y atoms, respectively. A DFT treatment combined with effective core potentials was used to optimize the geometries of clusters $Au_{n-1}Y$, Au_n and Y_n, and those with the lowest energy were chosen as the most stable configurations. All geometries have been fully optimized and vibrational analysis (without imaginary frequency) has been carried out for the ground state structures . All reported structures are converged to 1×10^{-6}a.u..

3. Results and discussions

In order to discuss the effects of doped impurity atom on gold clusters, we first performed some calculations on pure gold clusters and pure yttrium clusters. The lowest energy equilibrium structures of the $Au_{n-1}Y$ ($n \leq 9$) clusters along with the geometries of the original host Au_n ($n \leq 9$) and Y_n ($n \leq 8$) clusters are presented in Fig.1, where the impurity atoms are indicated with majuscule Y. The calculations revealed that all the lowest-energy equilibrium structures of the smaller bimetallic $Au_{n-1}Y$ ($n \leq 3$) clusters have resembling structure with those of the homoatomic gold clusters and yttrium clusters. Therefore the equilibrium geometries of clusters with $n \leq 3$ are not included in Fig.1. Y_4 cluster has distorted tetrahedron structure, Au_4 is a parallelogram structure, and for Au_3Y, a Y-centred Au_3 equilateral triangle with C_{3v} symmetry is more stable than the isosceles triangle with C_{2v}. For Au_5 and Y_5, the lowest-energy structures are planar trapezoid (W-form), Au_4Y is a Y-centred Au_4 distorted tetrahedron structure. In the case of Au_6, we obtain a planar triangle with D_{3h} symmetry, Y_6 is a distorted octahedron structure, Au_5Y is a relaxed shovel shape structure. For n equals 7, the lowest-energy structures of Y_7 and Au_7 with the pentagonal bipyramid are most stable in their isomers Au_6Y which has also shovel shape structure resembled Au_5Y. When $n \geq 8$, Y_n, Au_n and $Au_{n-1}Y$ are flat and compact three-dimensional (3D) structure.

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

$$\bar{R} = \frac{1}{N_\mathrm{b}} \sum_i R_{ij}. \tag{1}$$

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

$$CN = \frac{1}{n} \sum_i \mathrm{in}_i. \tag{2}$$

In Eq.(2) i is the number of the nearest-neighbour atoms. The geometrical parameters of Au_n, Y_n and $Au_{n-1}Y$ clusters are summarized in Table 1.

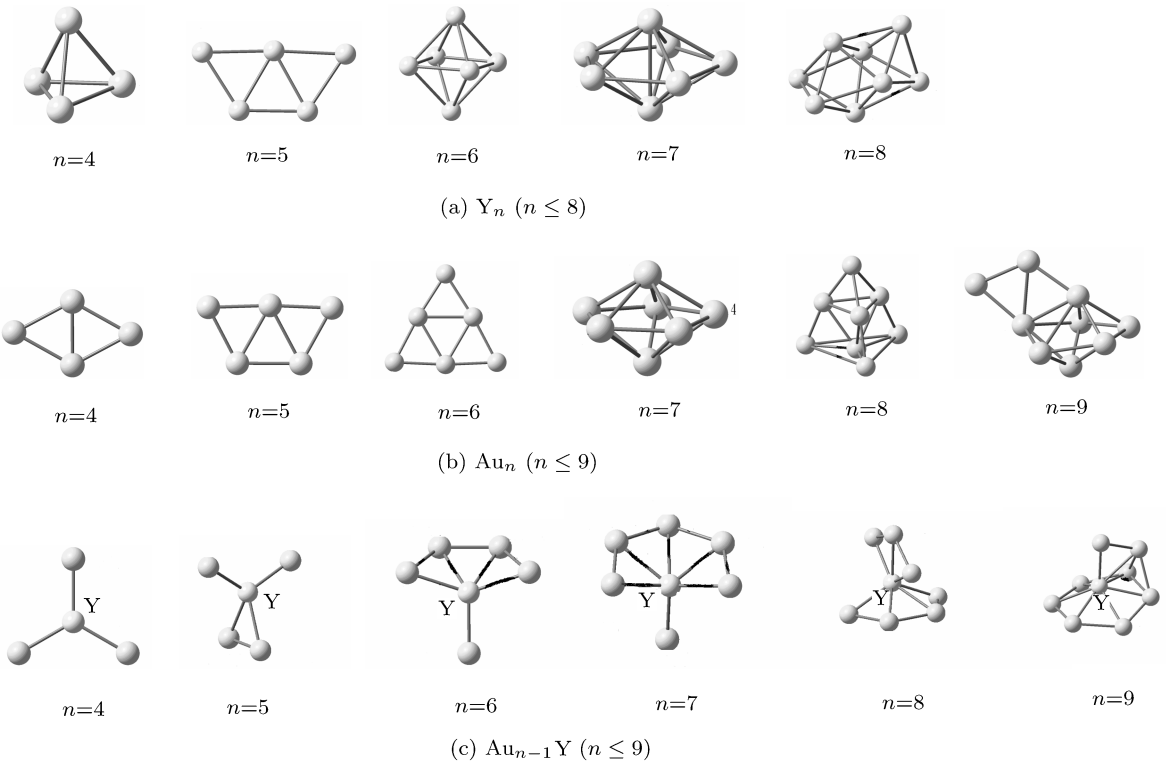


Fig.1. The equilibrium geometric structure of Y_n(a), Au_n(b) and $Au_{n-1}Y$(c) clusters.

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 $Au_{n-1}Y$ ($n \leq 9$), Au_n ($n \leq 9$) and Y_n ($n \leq 8$) clusters.

n	R/nm			CN			E_b/eV			IP/eV			EA/eV		
	$Au_{n-1}Y$	Au_n	Y_n	$Au_{n-1}Y$	Au_n	Y_n	$Au_{n-1}Y$	Au_n	Y_n	$Au_{n-1}Y$	Au_n	Y_n	$Au_{n-1}Y$	Au_n	Y_n
2	0.2662	0.2573	0.2775	1	1	1	1.375	0.936	0.304	6.18	9.43	4.77	1.091	2.028	0.137
3	0.2699	0.3418	0.3188	1.33	1.33	2	1.947	0.918	1.065	5.58	7.26	4.93	1.353	3.680	1.205
4	0.2691	0.2751	0.3254	1.5	2.	3	2.286	1.166	1.441	8.48	7.94	4.75	1.142	2.621	0.165
5	0.2784	0.2814	0.3287	2	2.8	2.8	2.104	1.281	1.279	6.89	7.16	4.67	3.662	3.179	0.402
6	0.2578	0.2769	0.3336	2.67	3	4	2.133	1.504	1.725	7.59	8.46	4.78	2.641	2.151	0.404
7	0.2850	0.2876	0.3372	2.86	4.28	4.29	2.062	1.339	1.849	6.58	6.42	4.23	3.390	3.317	0.084
8	0.2878	0.2837	0.3358	3.5	4.5	4.5	2.079	1.496	1.904	7.13	7.33	4.17	3.096	2.396	0.864
9	0.2724	0.2893		3.67	4.67		2.046	1.412		6.46	5.66		3.780	4.027	

From the Table 1, we can see that the average bond lengths of the $Au_{n-1}Y$ bimetallic clusters are shorter than those of the homoatomic pure Au and Y clusters except for biatomic molecules. The electron binding energy per atom in the $Au_{n-1}Y$ clusters is larger than that in the corresponding Au_n and Y_n clusters. For Mulliken Charge populations of the equilibrium geometries of $Au_{n-1}Y$ clusters found in the past study,[18] the Y atom is always cationic, the Pauling electronegativity of Au(2.54) is larger than that of Y(1.22). The structure, in which the Y atom has maximum number of neighbouring Au atom, tends to be energetically favourable, because the Au–Y bond is stronger than the Au–Au bond.

Figure 2 indicates that the most striking feature of electronic properties of the $Au_{n-1}Y$ clusters is that their ionization potential and electron affinities as a function of the cluster size show odd-even oscillatory behaviour, and resemble pure gold clusters.[12] In contrast, the changes of pure yttrium clusters in EA and IP are irregular: absence odd–even alternations, in agreement with mass spectrometric observations.[19] The Au_3Y cluster has the largest ionization potentials, which shows high stability.

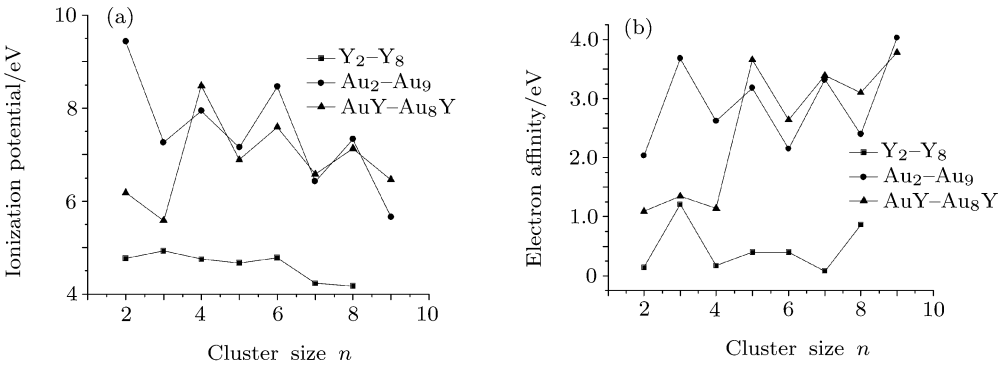


Fig.2. Ionization potential and electron affinity versus the cluster size.

The valence shell of the Au atom and the Y atom is $5d^{10}6s^1$ and $4d^15s^2$, respectively. The vertical ionization potential and electron affinities of $Au_{n-1}Y$ clusters as a function of the cluster size show odd–even oscillatory behaviour, and resemble pure gold clusters. The even-numbered $Au_{n-1}Y$ and Au_n clusters are more stable than the neighbouring odd-sized ones and have a larger IP, however, one of the most striking features of pure yttrium clusters is the absence odd-even alternation, which implies that the threshold for photoionization occurs mainly from a localized 4d orbital rather than from a 5s orbital of Y. The odd–even oscillation behaviours can be understood by electron pairing effect, odd-(even-) sized clusters have an odd (even) total number *s-sd* valence electrons. $4d^15s^2$ state is almost degenerate with that of $4d^25s^1$ in Y atom, therefore, one or three electrons can be contributed in Y-doped Au clusters according to the amount of gold atoms. The bonding in a heteroatomic Au–Y binary cluster is expected to have some degree of ionic character, since the Pauling's electronegativities are quite different. As a result, the energy level distribution may become different from that of the pure Au and Y cluster. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), HOMO–LUMO gap (HLG), and Fermi Energy for the $Au_{n-1}Y$, Au_n ($n \leq 9$) and Y_n ($n \leq 8$) clusters have been studied by optimizing the structures negative and positive ions for these clusters using the same method and basis set. The optimized structures of the negative and positive ions are very similar to those of the neutrals.

Figure 3 shows the Fermi energy for $Au_{n-1}Y$, Au_n ($n \leq 9$) and Y_n($n \leq 8$) clusters. The notable feature in $Au_{n-1}Y$ clusters is that their Fermi energies show odd-even oscillation behaviours and resemble pure gold clusters, however, pure yttrium clusters are different. The odd-numbered $Au_{n-1}Y$ clusters have a larger Fermi energies than the neighbouring even-sized ones, as the Fermi energies for Au_2Y, Au_4Y, Au_6Y Au_8Y are large. Meanwhile, the HOMO–LUMO gaps of pure yttrium clusters, pure gold clusters and yttrium-doped gold clusters change irregularly. Au_3Y binary cluster has a largest HOMO–LUMO gap in all yttrium-doped gold clusters, implying that the Au_3Y cluster is most stable, because s-d electron hybridization in yttrium atom forms three equal sd hybridizational orbitals, then three gold atoms and a yttrium atom form three equal Au–Y bonds, and the structure of Au_3Y cluster has a high C_{3v} symmetry. The most stable isomers of the yttrium-doped gold clusters tend to equally delocalize valence s, p and d electrons of the constituent atoms over the entire structure.

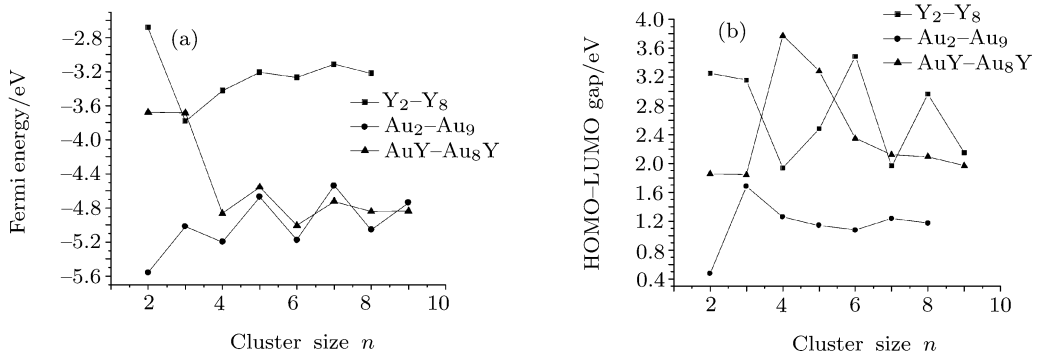


Fig.3. Fermi energy and HOMO-LUMO gap versus the cluster size.

4. Conclusions

We have investigated bimetallic yttrium-doped gold clusters, pure yttrium clusters and pure gold clusters by DFT calculations to elucidate their equilibrium structures and electronic properties, and effects of the doping.

The calculations revealed that all the lowest-energy equilibrium structures of the smaller bimetallic $Au_{n-1}Y$ ($n \leq 3$) clusters have resembling structure with those of the homoatomic gold clusters and yttrium clusters. After one Y atom is doped into the Au_{n-1}, the Au_nY cluster become a Y-centred Au_{n-1} compact structure. The structures of $Au_{n-1}Y$ cluster show an early appearance of 3D geometries starting at n=5 (Au_4Y). The most stable equilibrium structures in which the Y atom has maximum number of neighbouring Au atoms to be energetically favourable, because the Au–Y bond is stronger than the Au–Au bond. Ground-state structures tend to equally delocalize valence s, p and d electrons of the constituent atoms over the entire structure. The average bond lengths of the $Au_{n-1}Y$ bimetallic clusters are shorter than that of the homoatomic pure Au and Y clusters except for biatomic molecules. The electron binding energy per atom in the $Au_{n-1}Y$ clusters is larger than that in the corresponding Au_n and Y_n clusters. The most striking feature of electronic properties of the $Au_{n-1}Y$ clusters is that their IP and EA as a function of the cluster size and show odd–even oscillatory behaviour, resemble pure gold clusters. In contrast, the changes of pure yttrium clusters in EA and IP are irregular: absence odd–even alternation, in agreement with mass spectrometric observations. The Au_3Y cluster has the largest IP, which shows high stability. Au_3Y binary cluster has a largest HOMO-LUMO energy gap in all yttrium-doped gold clusters, implying that the Au_3Y cluster is most stable.

The theoretical results in this study provide some physical and chemical information on the Au–Y binary clusters. From the viewpoint of the chemistry of cluster, characterization of the electronic properties of bimetallic doped gold clusters is an interesting subject for both computational and experimental investigations, because doping gold clusters with 3*d* transition metal clearly changes size-dependent features. Moreover, several elemental systems that are supposed to be non-miscible in bulk alloys readily mix in clusters or nanoparticles. This enlarges the variety of binary systems, compared with bulk alloys. The theoretical results can be considered as the predictions of experimental data according to our need.

References

[1] Fernández E M, Soler J L, GarzÓn I L and Balbás L C 2004 *Phys . Rev.* B **70** 165403

[2] Li X B, Wang H Y, Tang Y J, Xu G L, Mao H P, Li C Y and Zhu Z H 2004 *J. At. Mol. Phys.* **121** 388

[3] Wang H Y, Li C Y, Tang Y J and Zhu Z H 2004 *Chin. Phys.* **13** 677

[4] Taylor K J, Pettiette-Hall C L, Cheshnovsky O and Smalley R E 1992 *J. Chem. Phys.* **96** 3319

[5] Ho J, Ervin K M and Lineberger W C 1990 *J. Chem. Phys.* **93** 6987

[6] Handschuh H, Gantefor G, Bechthold P S and Eberhardt W 1994 *J. Chem. Phys.* **100** 7093

[7] Balasubramanian K and Liao M Z 1987 *J. Chem. Phys.* **86** 5587

[8] Brave-Pèrez G, GarzÓn I L and Novaro O 1999 *Chem. Phys. Lett.* **313** 655
[9] Häkkinen H and Landman U 2000 *Phys . Rev.* B **62** R2287
[10] Verhagen S, Smoes S and Drowart J 1966 *J. Chem. Phys.* **40** 239
[11] Knight L B, Woodward R W, Van Zee R J and Weltner W 1983 *J. Chem. Phys.* **79** 5820
[12] Bouwen W, Vanhoutte F, Despa F, Bouckaert S, Neukermans S, Kuhn L T, Weidele H, Lievens P and Silverans R E 1999 *Chem. Phys. Lett.* **314** 227
[13] Yuan D W, Wang Y and Zeng Z 2005 *J. Chem. Phys.* **122** 114310
[14] Koyasu K, Mitsui M, Nakajima A and Kaya K 2002 *Chem. Phys. Lett.* **358** 224
[15] Frisch M J, Trucks G W and Schlegel H B 1998 GAUSSIAN 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA 1998
[16] Becke A D 1993 *J. Chem. Phys.* **98** 5648
[17] Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 229
[18] Mao H P, Wang H Y, Zhu Z H and Tan Y J 2006 *Acta Phys. Sin.* **55** 4542 (in Chinese)
[19] Dai D and Balasubramanian 1995 *Chem. Phys. Lett.* **238** 203