

# A comparative study on geometries, stabilities, and electronic properties between bimetallic $\text{Ag}_n\text{X}$ ( $\text{X}=\text{Au}, \text{Cu}$ ; $n=1-8$ ) and pure silver clusters\*

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Using the meta-generalized gradient approximation (meta-GGA) exchange correlation TPSS functional, the geometric structures, the relative stabilities, and the electronic properties of bimetallic  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters are systematically investigated and compared with those of pure silver clusters. The optimized structures show that the transition point from preferentially planar to three-dimensional structure occurs at  $n=6$  for the  $\text{Ag}_n\text{Au}$  clusters, and at  $n=5$  for  $\text{Ag}_n\text{Cu}$  clusters. For different-sized  $\text{Ag}_n\text{X}$  clusters, one  $\text{X}$  ( $\text{X}=\text{Au}$  or  $\text{Cu}$ ) atom substituted  $\text{Ag}_{n+1}$  structure is a dominant growth pattern. The calculated fragmentation energies, second-order differences in energies, and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps show interesting odd–even oscillation behaviours, indicating that  $\text{Ag}_{2,4,6,8}$  and  $\text{Ag}_{1,3,5,7}\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ) clusters keep high stabilities in comparison with their neighbouring clusters. The natural population analysis reveals that the charges transfer from the  $\text{Ag}_n$  host to the impurity atom except for the  $\text{Ag}_2\text{Cu}$  cluster. Moreover, vertical ionization potential (VIP), vertical electronic affinity (VEA), and chemical hardness ( $\eta$ ) are discussed and compared in depth. The same odd–even oscillations are found for the VIP and  $\eta$  of the  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters.

**Keywords:**  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ) clusters, geometric structure, meta-GGA exchange correlation functional

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## 1. Introduction

Noble metal ( $\text{Au}, \text{Ag}, \text{Cu}$ ) clusters have aroused considerable interest because they possess unique electronic, magnetic, optical, and mechanical properties, which have extensive applications in a great number of fields.<sup>[1–7]</sup> In view of previous literature, pure silver, gold, and copper clusters have been widely investigated experimentally and theoretically.<sup>[8–12]</sup> Especially it is well known that the noble metal atoms possess similar valence electron configurations, which are a closed d shell and a single s shell valence electron. Due to a single s shell valence electron similar to that of an alkali metal atom, the prominent characteristic properties of noble metal clusters are expected to exhibit certain similarities to simple alkali-metal clusters. Therefore, similar to bimetallic alkali metal clusters,<sup>[13–17]</sup> the exploration of physical and chemical properties of bimetallic noble metal clusters is of remarkable interest, which gives us a broad insight into the essence of atomic bonding in solid. For exam-

ple,  $\text{AgAu}$  dimer has been studied by Fabbi *et al.*<sup>[18]</sup> using dispersed fluorescence spectroscopy. Bishea *et al.*<sup>[19]</sup> have established the equilibrium bond length and binding energy for the  $\text{AgCu}$  dimer using resonant two-photo ionization spectroscopy. Negishi *et al.*<sup>[20]</sup> have carried out an investigation on photodetachment of anionic  $\text{Ag}_m\text{Au}_n$  ( $m+n \leq 4$ ) clusters. In the laser vaporization course of various copper targets in high vacuum as well as in an amorphous  $\text{Al}_2\text{O}_3$  or silica matrix, some copper-silver clusters<sup>[21,22]</sup> have been observed. By Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, the ionization potential (IP) for the mixed  $\text{AgCu}$  dimer has been reported by James *et al.*<sup>[23]</sup> and that for the trimers calculated by Cheeseman and Eyler.<sup>[24]</sup>

Theoretically, the geometries and the electronic properties for the neutral  $\text{Ag}_m\text{Au}_n$  ( $m+n \leq 7$ ) clusters have been systematically investigated by Lee *et al.*<sup>[25]</sup> Weis *et al.*<sup>[26]</sup> performed the density functional theory (DFT) calculations for structures of  $\text{Ag}_m\text{Au}_n^+$  ( $m+n < 6$ ) clusters. Bonačić-Koutecký<sup>[27]</sup> has deter-

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mined the structures, the ionization potentials, and the vertical detachment energies (VDEs) of neutral and charged bimetallic  $\text{Ag}_m\text{Au}_n$  [ $3 \leq (m+n) \leq 5$ ] clusters. Killmis and Papageorgiou<sup>[28]</sup> have reported on the determination of the structures of  $\text{Ag}_n\text{Cu}_m$  (the number of atoms up to five) clusters using spin-polarized DFT. Partridge *et al.*<sup>[29]</sup> and Bauslicher *et al.*<sup>[30]</sup> have systematically studied the structures, the energies, and the ionization potentials of the mixed Ag–Cu dimer and trimers. Jiang *et al.*<sup>[31]</sup> have performed the investigation of the geometries and the charge distributions of the CuAg dimer by DFT of the Slater for exchange and Vosko, WILK, as well as Nusair for correlation (SVWN, also called LSDA).<sup>[32,33]</sup> They obtained the bond length of a neutral AgCu dimer to be 2.3255 Å (1 Å=0.1 nm) at the SVWN level, compared with the experimental value 2.37 Å.<sup>[19]</sup>

In the present work, we perform a systematic study of the geometries, the relative stabilities, the electronic properties of the bimetallic  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters compared with those of corresponding pure silver clusters. The motivation of our work is threefold. Our first intention is to give a comprehensive study of the geometric structures and the growth patterns for  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters. The second intention is to probe the different electronic properties of the bimetallic clusters which are affected by doped atoms; furthermore, some regular changes are compared in serial alloy and bare clusters. We are motivated, thirdly, by the hope that such

a study might obtain some further understanding of the structures and stability properties of the bimetallic clusters, and other metallic clusters.

## 2. Computational details

The structure optimization, together with the frequency analyses of  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters, have been performed by using the GAUSSIAN03 program.<sup>[34]</sup> Because the meta-generalized gradient approximation (meta-GGA) functional includes the kinetic energy density in the functional expression, the more accurate results both for the atomization energy and for the relative stability of computing isomers are produced. So in our calculations, the meta-GGA Tao–Perdew–Staroverov–Scuseria (TPSS) functional<sup>[35]</sup> is used instead of the traditional GGA functional. Taking time-consumption into account, we introduce the RECP to describe the inner-core electrons of the noble metal Au, Ag, Cu atoms. Under this approximation, the outmost valance electrons  $5s^25p^65d^{10}6s^1$  for the Au atom,  $4s^24p^64d^{10}5s^1$  for the Ag atom, and  $3s^23p^63d^{10}4s^1$  for the Cu atom are described through the corresponding labeled GENECP of LANL2TZ(f)<sup>[36–38]</sup> basis set. We check our computational method by calculating bond lengths, vibration frequencies, dissociation energies, and VIPs for  $\text{Ag}_2$ ,  $\text{Au}_2$ ,  $\text{Cu}_2$ , AgCu, and AgAu dimers, which are compared with the available experimental values<sup>[18,19,23,24,39–45]</sup> listed in Table 1.

**Table 1.** The calculated values of bond length ( $r$ ), dissociation energy ( $D_e$ ), frequency ( $\omega_e$ ), and vertical ionization potential (VIP) for the  $\text{Ag}_2$ ,  $\text{Au}_2$ ,  $\text{Cu}_2$ , AgAu, and AgCu Molecules.

| Methods                  | PW91PW91        | PW91P86 | B3LYP | TPSSTPSS | Experimental |                           |
|--------------------------|-----------------|---------|-------|----------|--------------|---------------------------|
| $r/\text{\AA}$           | Ag <sub>2</sub> | 2.58    | 2.57  | 2.74     | 2.57         | 2.53 <sup>[39]</sup>      |
|                          | Au <sub>2</sub> | 2.86    | 2.52  | 2.52     | 2.52         | 2.47 <sup>[42]</sup>      |
|                          | Cu <sub>2</sub> | 2.23    | 2.23  | 2.93     | 2.23         | 2.22 <sup>[40]</sup>      |
|                          | AgAu            | 2.56    | 2.55  | 2.58     | 2.55         | 2.50 <sup>[18]</sup>      |
|                          | AgCu            | 2.40    | 2.39  | 2.43     | 2.39         | 2.37 <sup>[19]</sup>      |
| $D_{\text{e}}/\text{eV}$ | Ag <sub>2</sub> | 1.78    | 1.91  | 1.54     | 1.74         | 1.66±0.03 <sup>[39]</sup> |
|                          | Au <sub>2</sub> | 2.32    | 2.43  | 1.98     | 2.31         | 2.29 <sup>[42]</sup>      |
|                          | Cu <sub>2</sub> | 2.43    | 2.57  | 2.05     | 2.33         | 2.08 <sup>[41]</sup>      |
|                          | AgAu            | 2.22    | 2.34  | 1.93     | 2.19         | 2.08±0.10 <sup>[30]</sup> |
|                          | AgCu            | 2.11    | 2.24  | 1.79     | 2.02         |                           |
| $\omega/\text{cm}^{-1}$  | Ag <sub>2</sub> | 185     | 188   | 176      | 189          | 192 <sup>[42]</sup>       |
|                          | Au <sub>2</sub> | 177     | 178   | 169      | 181          | 191 <sup>[42]</sup>       |
|                          | Cu <sub>2</sub> | 282     | 287   | 264      | 285          | 265 <sup>[42]</sup>       |
|                          | AgAu            | 183     | 185   | 177      | 186          |                           |
|                          | AgCu            | 228     | 231   | 220      | 230          | 232 <sup>[42]</sup>       |
| VIP/eV                   | Ag <sub>2</sub> | 7.88    | 8.16  | 7.75     | 7.73         | 7.60 <sup>[43,44]</sup>   |
|                          | Au <sub>2</sub> | 9.70    | 9.79  | 9.50     | 9.36         | 9.20 <sup>[45]</sup>      |
|                          | Cu <sub>2</sub> | 8.53    | 8.74  | 8.26     | 7.90         | 7.78 <sup>[24]</sup>      |
|                          | AgAu            | 8.79    | 8.99  | 8.61     | 8.62         |                           |
|                          | AgCu            | 8.22    | 8.44  | 7.99     | 7.81         | 7.78 <sup>[23]</sup>      |

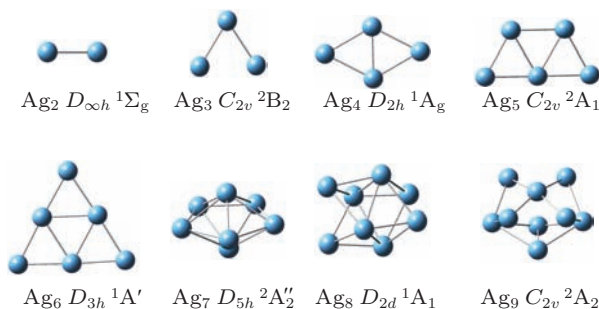
In a series of trials, we find that the results based on the TPSS method are in better agreement with experimental values than others. This indicates the suitability of current computational method to describe small  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters. A large number of possible initial isomers for  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters have been considered in optimized procedure. All clusters are relaxed fully without any symmetry constraints. The previous investigations on silver clusters are also extensively referenced.<sup>[23,39-42]</sup> In the present article, we list only a few of the low-energy isomers in Figs. 1–3. Considering the spin polarization, different spin multiplicities are also taken into account for each initial configuration, and we find that all optimized structures prefer to stay in the lowest spin state.

### 3. Results and discussion

#### 3.1. Geometries

##### 3.1.1. Bare silver clusters $\text{Ag}_{n+1}$ ( $n=1-8$ )

To discuss the effects of dopant atoms on the silver clusters, we first optimize the pure silver clusters by using the same method and basis set. In the present work, the possible isomers of bare neutral silver clusters for each cluster size are extensively referenced from the previous literature,<sup>[8-9]</sup> but the most stable geometric structures are only selected and shown in Fig. 1. As displayed in Fig. 1, we can see that the geometric structures and the electronic states are in line with the previous results.<sup>[9]</sup>



**Fig. 1.** (colour online) The lowest energy structures of pure silver clusters for each size. The corresponding point-group symmetries and the electronic states are also given by the TPSS functional.

##### 3.1.2. Bimetallic gold-doped silver clusters $\text{Ag}_n\text{Au}$ ( $n=1-8$ )

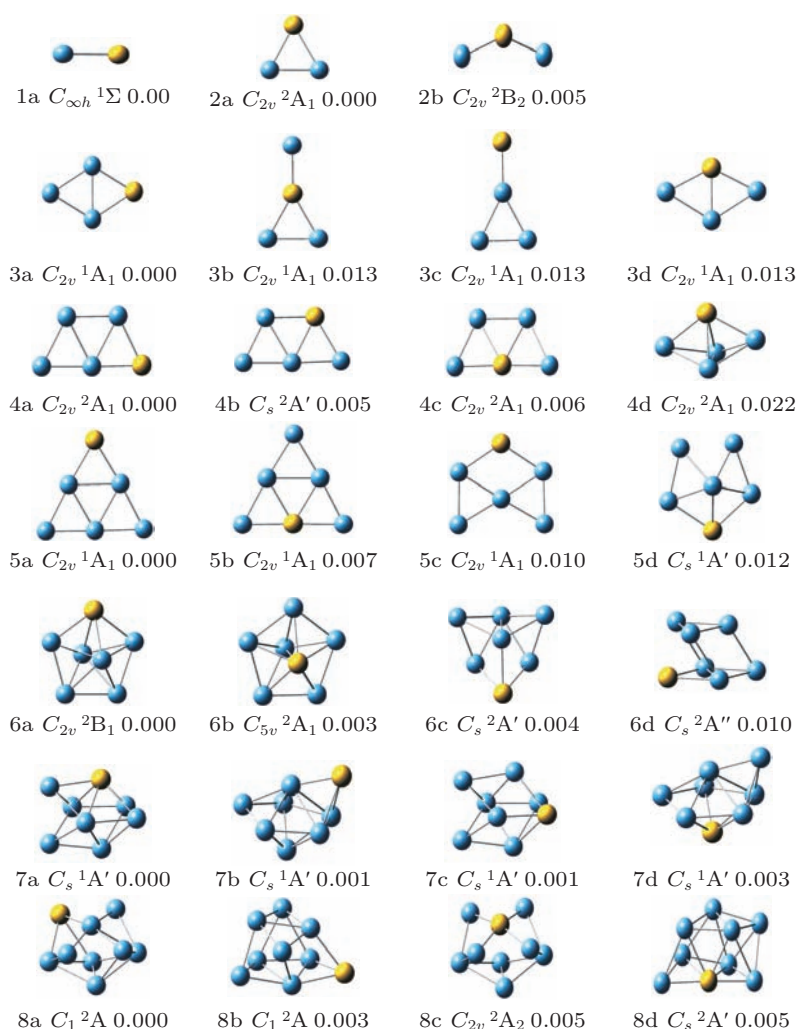
In this subsection, we discuss the structural details of  $\text{Ag}_n\text{Au}$  ( $n=1-8$ ) clusters. In order to

search for the lowest-energy structures, lots of possible initial structures, which include one-, two-, and three-dimensional configurations, are considered, starting from the previous optimized  $\text{Ag}_n$  and  $\text{Ag}_n\text{X}$  geometries.<sup>[8-9,25,28,46-47]</sup> As a result, many stable isomers are obtained. Here, for each size, these structural isomers are displayed in Fig. 2. In the order of total energies from low to high, the isomers are denoted by  $na$ ,  $nb$ ,  $nc$ , and  $nd$ , respectively (“ $n$ ” is the number of Ag atoms). Meanwhile, the corresponding point-group symmetries, electronic states, and relative energies are also given in the isomers.

The  $\text{AgAu}$  dimer has a bond length of 2.55 Å and dissociation energy of 2.19 eV, which are slightly higher than the experimental data (2.50 Å and  $2.08 \pm 0.10$  eV).<sup>[18,23]</sup> For  $\text{Ag}_2\text{Au}$  clusters, the linear structures  $C_{\infty v}$  (Ag–Ag–Au),  $D_{\infty h}$  (Ag–Au–Ag), and triangular structures (acute angle or obtuse angle) are optimized as initial stable structures. According to the calculated results, it is found that the lowest-energy structure is an acute angle isosceles triangular structure with two Ag–Au (2.73 Å) and Ag–Ag (2.64 Å) distances, respectively. In the case of  $\text{Ag}_3\text{Au}$ , a planar rhombus (3a) with the lowest energy and a planar quadrilateral (3d) are optimized, in which the dopant Au atoms substitute different sited Ag atoms of the  $\text{Ag}_4$  clusters. Therefore, a relative energy (0.023 eV), and different VIP values (7.11 eV and 6.49 eV) exist between them. The low-lying Y-shaped structure isomers 3b with Au atom in the centre and 3c with Au at the top site are, respectively, 0.0127 eV and 0.0129 eV above the lowest-energy structure. Three planar trapezoidal structures of  $\text{Ag}_4\text{Au}$  clusters are optimized when different sites of Ag atom are substituted in the ground state  $\text{Ag}_5$  cluster by one Au atom. The calculated total energy reveals that the lowest-energy structure (4a) of  $\text{Ag}_4\text{Au}$  clusters has  $C_s$  symmetry and the doped Au atom occupies the foot of trapezoidal structure. Similar to the case of  $\text{Ag}_3\text{Au}$  clusters, there are two low-lying substituted structures of ground-state  $\text{Ag}_6$  cluster for  $\text{Ag}_5\text{Au}$ . Two planar triangular structures (5a, 5b) have identical symmetry ( $C_{2v}$  point group) and electronic state ( $^1A_1$ ). The incomplete pentagonal pyramid isomer 5d is 0.012 eV higher in total energy than the 5a isomer. As shown in Fig. 1, one can see that the transition point of pure silver clusters from planar geometry to 3D structure appears at  $n = 7$ . It is earlier than that ( $n = 15$ ) of pure gold clusters because the s-d hybridization of silver differs from gold. For bimetallic  $\text{Ag}_n\text{Au}$  clusters, we find that the cluster containing

seven atoms also has a transition point. In addition, the lowest-energy isomer (6a) can be viewed as a substituted version of the structure of ground-state  $\text{Ag}_7$  clusters, which has  $C_{2v}$  point group. Another substituted structure (6b) of  $\text{Ag}_7$  clusters keeps higher symmetry ( $C_{5v}$ ) but its total energy is 0.003 eV higher than that of the 6a structure. For  $\text{Ag}_7\text{Au}$  clusters, the 7a and 7c isomers are obtained by the dominant growth pattern of one Au atom substituted  $\text{Ag}_{n+1}$

structure. Isomer 7b is generated by the other growth pattern of one Au atom capped on  $\text{Ag}_n$  isomer, and 7d isomer is optimized by that of one Ag atom capped on  $\text{Ag}_{n-1}\text{Au}$  structure. The nonamer 8a and 8c isomers are two different derivatives of the ground-state  $\text{Ag}_9$  cluster. 8c isomer, with  $C_{2v}$  symmetry and the doped Au atom occupying high coordinated site, is 0.005 eV higher in energy than the lowest-energy 8a isomer.



**Fig. 2.** (colour online) Lowest energy and low-lying structures of the  $\text{Ag}_n\text{Au}$  ( $n=1-8$ ) clusters. The corresponding point-group symmetries, electronic states, and relative energies (eV) are presented by the TPSS functional. The yellow and blue balls represent Au and Ag atoms, respectively.

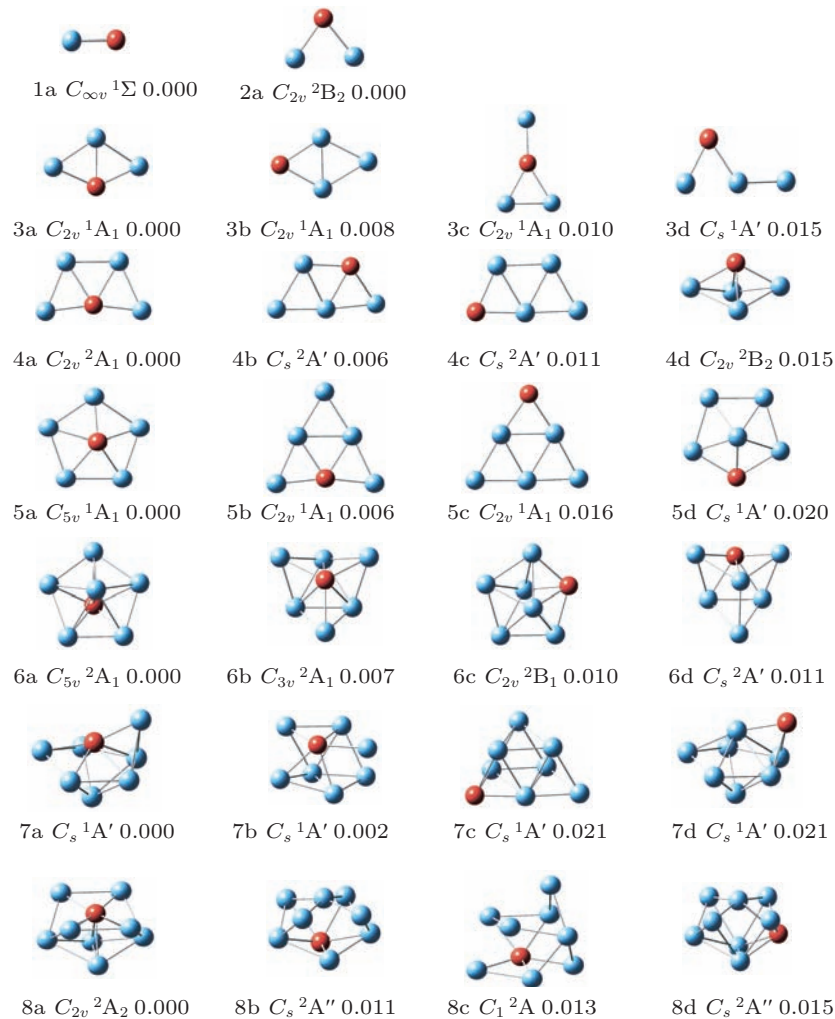
According to Figs. 1 and 2, it is found that all of the lowest-energy isomers of  $\text{Ag}_n\text{Au}$  ( $n=1-8$ ) are of the Au-substituted structures of the corresponding ground-state  $\text{Ag}_{n+1}$  clusters. The transition point from planar geometry to 3D structure appears at  $n=6$  for  $\text{Ag}_n\text{Au}$  cluster.

### 3.1.3. Bimetallic copper-doped silver clusters $\text{Ag}_n\text{Cu}$ ( $n=1-8$ )

The equilibrium geometries of the most stable structures and the optimized low-lying isomers of  $\text{Ag}_n\text{Cu}$  ( $n=1-8$ ) clusters are shown in Fig. 3. As seen from Table 1, for the  $\text{AgCu}$  dimer, the calculated dis-

sociation energy is 2.02 eV, which is lower than that of AgAu (2.19 eV) but higher than that of Ag<sub>2</sub> molecular (1.74 eV). Namely, the stabilities of mixed clusters exhibit a sequence of AgAu > AgCu > Ag<sub>2</sub>, indicating that the dopant Au and Cu atoms can enhance the stabilities of the pure silver clusters. As for Ag<sub>2</sub>Cu clusters, no low-lying isomer with Ag–Cu–Ag obtuse angle is found. When  $n = 3$ , the lowest energy isomer (3a) is also a substituted structure of the rhombic Ag<sub>4</sub> cluster. However, the doped Cu atom occupies the short diagonal of the quadrilateral structure which is different from the case of the Ag<sub>3</sub>Au isomer (3a). When the central Ag atom at the bottom of trapezoid Ag<sub>5</sub> cluster is substituted by one Cu atom, the lowest-energy structure 4a is generated. In comparison with the lowest-energy structure of the Ag<sub>5</sub>Au isomer, different results can be obtained. We find

that the transition point from planar geometry to 3D structure changes at  $n = 6$ . The lowest-energy 3D isomer 5a, with  $C_{5v}$  symmetry and equal Ag–Cu bonds (2.50 Å), can be derived from a low-lying pentagonal pyramid Ag<sub>6</sub> cluster. In Ag<sub>6</sub>Cu isomers, it can be seen that the impurity atom Cu is located inside and almost at the central position. The lowest-energy isomer 7a is formed by an Ag atom capping on 6a isomer, which is generated by another growth pattern of the clusters. The substituted isomer (7b) of the ground state Ag<sub>7</sub> cluster is 0.002 eV higher in total energy than 7a. When  $n = 8$ , the lowest-energy isomer 8a is still a substituted structure. However, compared with Ag atom in the Ag<sub>8</sub>Au species, the Cu atom in the lowest-energy of the Ag<sub>8</sub>Cu isomer occupies the central site. Hence, the 8a isomer keeps the same high  $C_{2v}$  symmetry as the pure Ag<sub>9</sub> cluster keeps.



**Fig. 3.** (colour online) Lowest energy and low-lying structures of the Ag<sub>n</sub>Cu ( $n=1-8$ ) clusters. The corresponding point-group symmetries, the electronic states, and the relative energies (eV) are shown by TPSS functional. The red and blue balls represent Cu and Ag atoms, respectively.

Although the structures of  $\text{Ag}_n\text{Cu}$  and  $\text{Ag}_n\text{Au}$  are similar for most of the sizes, we find that the copper atoms in corresponding  $\text{Ag}_n\text{Cu}$  clusters tend to occupy the central site. Furthermore, the transition from 2D to 3D structure occurs at  $n = 5$  for  $\text{Ag}_n\text{Cu}$ .

### 3.2. Relative stabilities

It is imperative to calculate the values of averaged atomic binding energy  $E_b(n)$ , fragmentation energy  $D(n, n-1)$ , and second-order difference in energy  $\Delta_2 E(n)$  for  $\text{Ag}_n X$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters for studying the relative stability. In order to compare the degree of relative stability of silver clusters effected by  $X$  atom, we also calculate  $E_b(n+1)$ ,  $D(n+1, n)$ , and  $\Delta_2 E(n+1)$  of the pure silver clusters by the following formula:

$$E_b(n+1) = [(n+1)E(\text{Ag}) - E(\text{Ag}_{n+1})] / n+1, \quad (1)$$

$$D(n+1, n) = E(\text{Ag}_n) + E(\text{Ag}) - E(\text{Ag}_{n+1}), \quad (2)$$

$$\Delta_2 E(n+1) = E(\text{Ag}_n) + E(\text{Ag}_{n+2}) - 2E(\text{Ag}_{n+1}), \quad (3)$$

where  $E(\text{Ag})$ ,  $E(\text{Ag}_{n+1})$ ,  $E(\text{Ag}_n)$ , and  $E(\text{Ag}_{n+2})$  are the total energies of the most stable  $\text{Ag}$ ,  $\text{Ag}_{n+1}$ ,  $\text{Ag}_n$ , and  $\text{Ag}_{n+2}$  clusters, respectively.

For the bimetallic  $\text{Ag}_n X$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters,  $E_b(n)$ ,  $D(n, n-1)$ ,  $\Delta_2 E(n)$  can be expressed as

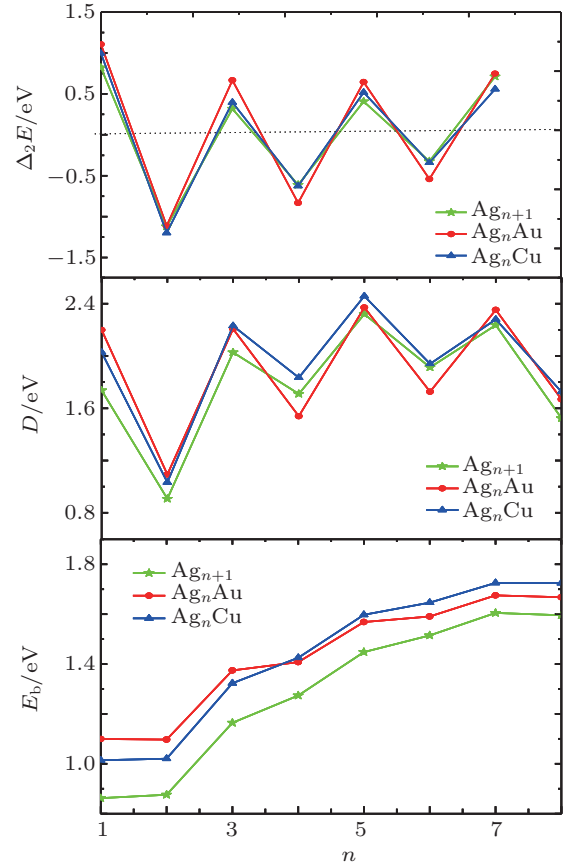
$$E_b(n) = [E(X) + nE(\text{Ag}) - E(\text{Ag}_n X)] / n+1, \quad (4)$$

$$D(n, n-1) = E(\text{Ag}_{n-1} X) + E(\text{Ag}) - E(\text{Ag}_n X), \quad (5)$$

$$\Delta_2 E(n) = E(\text{Ag}_{n-1} X) + E(\text{Ag}_{n+1} X) - 2E(\text{Ag}_n X), \quad (6)$$

where  $E(X)$ ,  $E(\text{Ag})$ ,  $E(\text{Ag}_n X)$ ,  $E(\text{Ag}_{n-1} X)$ , and  $E(\text{Ag}_{n+1} X)$  represent the total energies of atomic and cluster systems  $X$ ,  $\text{Ag}$ ,  $\text{Ag}_n X$ ,  $\text{Ag}_{n-1} X$ , and  $\text{Ag}_{n+1} X$ , respectively. In this case, the  $E_b(n)$ ,  $D(n, n-1)$ , and  $\Delta_2 E(n)$  values of the most stable  $\text{Ag}_{n+1}$  ( $n=1-8$ ) and  $\text{Ag}_n X$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters against the corresponding number of the  $\text{Ag}$  atoms are plotted as curves in Fig. 4. From Fig. 4, one can see that the averaged binding energies of the lowest-energy  $\text{Ag}_n X$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters are larger than those in the corresponding  $\text{Ag}_{n+1}$  ( $n=1-8$ ) clusters. It hints that the impurity  $X$  ( $X=\text{Au}, \text{Cu}$ ) atom may enhance the stability of pure silver clusters. In addition, the  $\text{Ag}_n\text{Au}$  clusters generally have the larger binding energies with sizes from  $n = 1$  to  $n = 4$  than  $\text{Ag}_n\text{Cu}$  clusters, whereas, for up to four atoms the phenomenon is

reverse, which may be related to the shell structures of the  $\text{Au}$  and  $\text{Cu}$  atoms. Besides, further detailed features of both functions are very similar: they increase very steeply in the interval between  $n = 2$  and  $n = 3$ . There are two visible peaks at  $n = 3$  and  $n = 5$  for  $\text{Ag}_n X$  clusters.

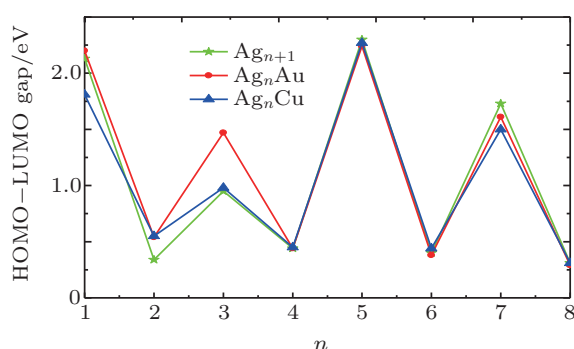


**Fig. 4.** (colour online) Size dependences of the averaged atomic binding energy  $E_b$ , the fragmentation energy  $D$ , and the second-order difference of energy  $\Delta_2 E$  for the most stable  $\text{Ag}_n X$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) and  $\text{Ag}_{n+1}$  ( $n=1-8$ ) clusters.

To further confirm the relative stabilities, we calculate  $D$  and  $\Delta_2 E$  for pure silver and doped clusters. As shown in Fig. 4, the  $D$  and  $\Delta_2 E$  values each exhibit a pronounced odd-even oscillation behaviour as a function of cluster size, suggesting that  $\text{Ag}_{2,4,6,8}$  and  $\text{Ag}_{1,3,5,7} X$  ( $X=\text{Au}, \text{Cu}$ ) clusters keep higher stabilities than their respective corresponding neighbours. For  $\text{AgAu}$  and  $\text{AgCu}$  clusters, they have the largest second-order differences in energy of 1.11 eV and 1.00 eV, respectively. It means that  $\text{AgAu}$  and  $\text{AgCu}$  isomers are more stable than other  $\text{Ag}_n X$  ( $X=\text{Au}, \text{Cu}; n=1-8$ ) clusters. This feature also occurs separately in chemical hardness and vertical ionization potential.

### 3.3. HOMO–LUMO energy gaps

The chemical stabilities of  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) and  $\text{Ag}_{n+1}$  ( $n=1-8$ ) clusters are discussed by examining the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It is found that a large HOMO–LUMO energy is associated with the enhanced chemical stability. The size dependences of the HOMO–LUMO energy gaps are plotted in Fig. 5. As seen from the figure, the HOMO–LUMO energy gaps for the  $\text{Ag}_nX$  and  $\text{Ag}_{n+1}$  ( $n=1-8$ ) clusters exhibit obvious odd–even oscillation: the even-numbered



**Fig. 5.** (colour online) Size dependences of the HOMO–LUMO energy gaps for the most stable  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) and  $\text{Ag}_{n+1}$  ( $n=1-8$ ) clusters.

clusters show larger HOMO–LUMO energy gaps than the odd-numbered ones as expected for closed/open

shell systems. Namely, the  $\text{Ag}_{1,3,5,7}X$  and  $\text{Ag}_{2,4,6,8}$  clusters keep higher chemical stability than their neighbours, which is in accordance with the behaviours of the fragmentation energy and second-order difference in energy. It indicates that these clusters possess dramatically enhanced chemical stability and may be selected as the building block of novel nano-materials.

### 3.4. Natural population analysis

In order to understand in depth the localization of the natural charge in  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters, the natural population analyses (NPAs) of the lowest energy clusters are summarized in Table 2. NPA clearly shows that the natural charges of Au and Cu atoms are negative in corresponding clusters except for  $\text{Ag}_2\text{Cu}$ , and in ranges of  $-0.3742e$ – $0.1199e$  and  $-1.3718e$ – $0.0019e$  charges, respectively, which suggests that the charges in corresponding clusters transfer from  $\text{Ag}_n$  frames to the  $X$  ( $X=\text{Au}, \text{Cu}$ ) atoms, contrarily, the Cu atom acts as electron donor in the  $\text{Ag}_2\text{Cu}$  cluster. In addition, one can find that there is a distinct valley and peak for  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) corresponding to  $\text{Ag}_7\text{Au}$  and  $\text{Ag}_6\text{Cu}$ , respectively.

**Table 2.** Natural charge populations for the most stable  $\text{Ag}_nX$  ( $X=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters.  $\text{Ag}(n)$  ( $n=1-8$ ) have different numbers of Ag atoms seen in Figs. 2 and 3 and the bold parts are dopant natural charges.

| Isomers            | X       | Ag(1)   | Ag(2)   | Ag(3)   | Ag(4)  | Ag(5)   | Ag(6)   | Ag(7)   | Ag(8)   |
|--------------------|---------|---------|---------|---------|--------|---------|---------|---------|---------|
| AgAu               | -0.2950 | 0.2950  |         |         |        |         |         |         |         |
| Ag <sub>2</sub> Au | -0.3742 | 0.1871  | 0.1871  |         |        |         |         |         |         |
| Ag <sub>3</sub> Au | -0.3332 | -0.0268 | 0.1800  | 0.1800  |        |         |         |         |         |
| Ag <sub>4</sub> Au | -0.1985 | 0.1135  | -0.1347 | 0.0619  | 0.1579 |         |         |         |         |
| Ag <sub>5</sub> Au | -0.1530 | 0.1351  | -0.0144 | -0.0883 | 0.1351 | -0.0144 |         |         |         |
| Ag <sub>6</sub> Au | -0.1559 | 0.2036  | 0.2036  | 0.1643  | 0.1643 | -0.2900 | -0.2900 |         |         |
| Ag <sub>7</sub> Au | -0.5848 | 0.2324  | -0.1731 | -0.0643 | 0.2382 | 0.1777  | -0.0643 | 0.2382  |         |
| Ag <sub>8</sub> Au | -0.1199 | 0.2901  | -0.1147 | -0.0235 | 0.2037 | 0.0941  | 0.2504  | 0.1619  | -0.7421 |
| AgCu               | -0.0019 | 0.0019  |         |         |        |         |         |         |         |
| Ag <sub>2</sub> Cu | 0.0426  | -0.0213 | -0.0213 |         |        |         |         |         |         |
| Ag <sub>3</sub> Cu | -0.0148 | -0.0722 | 0.1591  | -0.0722 |        |         |         |         |         |
| Ag <sub>4</sub> Cu | -0.3989 | 0.1219  | 0.0775  | 0.0775  | 0.1219 |         |         |         |         |
| Ag <sub>5</sub> Cu | -0.9646 | 0.1929  | 0.1929  | 0.1929  | 0.1929 | 0.1929  |         |         |         |
| Ag <sub>6</sub> Cu | -0.6804 | 0.1901  | 0.1907  | 0.1911  | 0.1911 | 0.1907  | -0.2734 |         |         |
| Ag <sub>7</sub> Cu | -1.2544 | 0.2616  | 0.2802  | 0.2616  | 0.1087 | 0.1087  | -0.0747 | -0.3084 |         |
| Ag <sub>8</sub> Cu | -1.3718 | 0.2613  | 0.0191  | 0.0191  | 0.2613 | 0.1442  | 0.2613  | 0.1442  | 0.2613  |

Moreover, we carry out some analyses for the natural electron configuration of impurity  $X$  ( $X=\text{Au}$ ,  $\text{Cu}$ ) atoms to understand the internal charge transfer. For free  $\text{Au}$  and  $\text{Cu}$  atoms, the configurations of valence electrons are  $5d^{10}6s^1$  and  $3d^{10}4s^1$  respectively. Namely, the electronic configurations of the noble metals  $\text{Au}$  and  $\text{Cu}$  are characterized by possessing a closed  $d$  shell and a single  $s$  valence electron. Here, the charges of  $6s$ ,  $5d$ ,  $6p$  states for the  $\text{Au}$  atom in  $\text{Ag}_n\text{Au}$  clusters and  $4s$ ,  $3d$ ,  $4p$  states for the  $\text{Cu}$  atom in  $\text{Ag}_n\text{Cu}$  clusters are listed in Table 3. Obviously, for the  $\text{Au}$  atom, the charges of  $s$  state exceed one electron except for the  $\text{Ag}_4\text{Au}$  isomer, whereas, they are less than one electron for  $\text{Ag}_n\text{Cu}$  clusters except for  $\text{AgCu}$ . It indicates that the  $s$  state for the  $\text{Au}$  atom obtains a small quantity of charges but it loses an electron for the  $\text{Cu}$  atom. This can be interpreted by different electronegativities among  $\text{Au}$  (2.54),  $\text{Ag}$  (1.93), and  $\text{Cu}$  (1.9). Nearly full electrons occupy the  $d$  orbital for  $\text{Au}$  and

$\text{Cu}$  atoms, indicating that  $d$  orbital is the dominant core orbital. Meanwhile, we find that the  $6p$  subshell of the  $\text{Au}$  atom in  $\text{Ag}_n\text{Au}$  clusters obtains 0.03–0.59 electrons and  $4p$  subshell of the  $\text{Cu}$  atoms in  $\text{Ag}_n\text{Cu}$  isomers gains 0.01–1.79 electrons.

### 3.5. Vertical ionization potential, vertical electron affinity, and hardness

Vertical ionization potential (VIP) and vertical electron affinity (VEA) are the most important characteristics reflecting the size-dependent relationship of electronic structure in cluster physics. Here, we calculate the VIP and VEA at the TPSS level by using the following formulas:

$$\text{VIP} = E_{(\text{cation at optimized neutral geometry})} - E_{(\text{optimized neutral})}, \quad (7)$$

$$\text{VEA} = E_{(\text{optimized neutral})} - E_{(\text{anion at optimized neutral geometry})}. \quad (8)$$

**Table 3.** Nature of electronic configurations of the  $X$  atoms in the most stable  $\text{Ag}_nX$  ( $X=\text{Au}$ ,  $\text{Cu}$ ;  $n=1-8$ ) systems.

| Isomers | Au   |      |      | Cu   |      |      |
|---------|------|------|------|------|------|------|
|         | 6s   | 5d   | 6p   | 4s   | 3d   | 4p   |
| $n=1$   | 1.32 | 9.95 | 0.03 | 1.02 | 9.95 | 0.01 |
| $n=2$   | 1.39 | 9.90 | 0.07 | 0.87 | 9.92 | 0.17 |
| $n=3$   | 1.40 | 9.90 | 0.03 | 0.74 | 9.90 | 0.37 |
| $n=4$   | 0.73 | 9.95 | 0.16 | 0.90 | 9.86 | 0.63 |
| $n=5$   | 1.23 | 9.91 | 0.02 | 0.87 | 9.85 | 1.24 |
| $n=6$   | 1.06 | 9.90 | 0.20 | 0.75 | 9.83 | 1.09 |
| $n=7$   | 1.09 | 9.90 | 0.59 | 0.79 | 9.84 | 1.62 |
| $n=8$   | 1.10 | 9.89 | 0.14 | 0.74 | 9.84 | 1.79 |

The calculated values of VIP and VEA for  $\text{Ag}_{n+1}$  and  $\text{Ag}_nX$  ( $X=\text{Au}$ ,  $\text{Cu}$ ;  $n=1-8$ ) clusters as well as the acquirable experimental data<sup>[24,43,44]</sup> are listed in Table 4. It is worthwhile noting that our calculated values of VIPs for doped and pure silver clusters are in good agreement with experimental values. Moreover, the values of VIP for doped  $\text{Ag}_nX$  ( $X=\text{Au}$ ,  $\text{Cu}$ ;  $n=1-8$ ) clusters are higher than those for the equivalent  $\text{Ag}_{n+1}$  clusters, suggesting that doped impurity atoms enhance the stability of host clusters.

**Table 4.** Vertical ionization potentials, vertical electron affinities, chemical hardnesses of most stable  $\text{Ag}_{n+1}$  ( $n=1-8$ ) and  $\text{Ag}_nX$  ( $X=\text{Au}$ ,  $\text{Cu}$ ;  $n=1-8$ ) clusters.

| Cluster size | $\text{Ag}_n\text{Au}$ |      | $\text{Ag}_n\text{Cu}$                       |      |      | $\text{Ag}_{n+1}$      |      |      |
|--------------|------------------------|------|----------------------------------------------|------|------|------------------------|------|------|
|              | VIP                    | VEA  | VIP <sup>[24,44]</sup>                       | VIP  | VEA  | VIP <sup>[43,44]</sup> | VIP  | VEA  |
| $n=1$        | 8.62                   | 1.22 | 7.61 <sup>[44]</sup><br>7.78 <sup>[24]</sup> | 7.81 | 1.21 | 7.60                   | 7.73 | 0.81 |
| $n=2$        | 6.33                   | 1.40 | 7.46 <sup>[44]</sup>                         | 5.89 | 1.06 | 5.66                   | 5.76 | 0.09 |
| $n=3$        | 7.11                   | 1.47 |                                              | 6.50 | 1.39 | 6.65                   | 6.43 | 1.43 |
| $n=4$        | 6.38                   | 2.06 |                                              | 6.17 | 1.84 | 6.35                   | 6.09 | 1.84 |
| $n=5$        | 7.20                   | 1.32 |                                              | 6.95 | 0.92 | 7.15                   | 7.24 | 1.16 |
| $n=6$        | 5.90                   | 1.79 |                                              | 5.79 | 1.57 | 5.69                   | 5.86 | 1.73 |
| $n=7$        | 6.56                   | 1.40 |                                              | 6.14 | 1.16 | 7.10                   | 6.63 | 1.30 |
| $n=8$        | 5.59                   | 1.89 |                                              | 5.18 | 1.51 | 5.15                   | 5.31 | 1.64 |

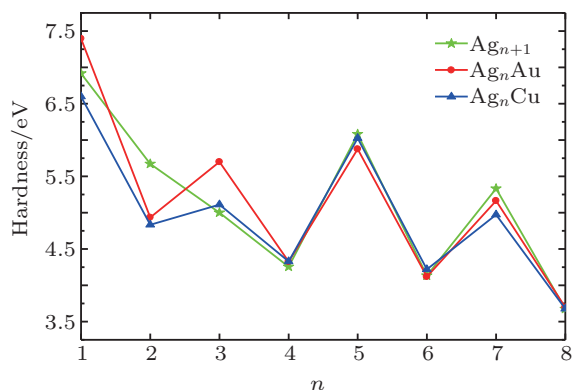
Chemical hardness has been established as an electronic quantity. In many cases, it may be used to characterize the relative stability of molecules and

aggregate through the principle of maximum hardness (PMH) proposed by Pearson.<sup>[48]</sup> So it is important to discuss the hardness of a cluster. In light of a finite-

difference approximation and the famous Koopmans theorem,<sup>[49]</sup> there is a rational definition for hardness as follows:

$$\eta = \text{VIP} - \text{VEA}. \quad (9)$$

According to Eq. (9), the values of chemical hardnesses ( $\eta$ ) of the most stable pure silver  $\text{Ag}_{n+1}$  and doped  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters are calculated, which are shown in Fig. 6. As seen from Fig. 6, the chemical hardness for doped systems also shows an interesting oscillating behaviour as the cluster size increases. But the values of  $\eta$  for pure  $\text{Ag}_{n+1}$  ( $n \leq 4$ ) clusters decrease with the increase of size. Through the PMH of chemical hardness, the oscillating behaviours indicate that the  $\text{Ag}_{6,8}$ ,  $\text{Ag}_{1,3,5,7}\text{Au}$ , and  $\text{Ag}_{1,3,5,7}\text{Cu}$  present higher values than their neighbouring  $\text{Ag}_{5,7}$ ,  $\text{Ag}_{2,4,6,8}\text{Au}$ , and  $\text{Ag}_{2,4,6,8}\text{Cu}$  isomers. That is to say, for pure silver clusters, even-numbered clusters keep a high stability in comparison with their neighbours at  $n \geq 4$ . Whereas, for doped impurity atom  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters, odd-numbered clusters are more stable than the even-numbered ones. It is worthwhile noting that the values of  $\eta$  are in accordance with the former analysis based on the fragmentation energy and second-order difference in energy for doped impurity atom  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) and  $\text{Ag}_{n+1}$  ( $n \geq 4$ ) clusters.



**Fig. 6.** (colour online) Size dependences of VIP, VEA, and chemical hardness (eV) for the lowest energy  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) and  $\text{Ag}_{n+1}$  ( $n=1-8$ ) clusters.

## 4. Conclusions

The geometrical structures, the relative stabilities, the electronic properties, the vertical ionization potentials, the vertical electronic affinities, and the chemical hardnesses are systematically investigated by using meta-GGA exchange correlation TPSS functional. All of the conclusions are summarized in the following:

(i) The optimized structures show that a transition point from 2D to 3D structure occurs at  $n = 6$  for the lowest energy isomer of  $\text{Ag}_n\text{Au}$  clusters, and at  $n=5$  for  $\text{Ag}_n\text{Cu}$  clusters. One X ( $\text{X}=\text{Au}$  and  $\text{Cu}$ ) atom substituted  $\text{Ag}_{n+1}$  structure is a dominant growth pattern for the stable alloyed  $\text{Ag}_n\text{X}$  clusters.

(ii) The fragmentation energies, second-order differences in energy, and the HOMO-LUMO energy gaps of the most stable pure silver and doped  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters exhibit an odd-even alternation. This indicates that  $\text{Ag}_{2,4,6,8}$ ,  $\text{Ag}_{1,3,5,7}\text{Au}$ , and  $\text{Ag}_{1,3,5,7}\text{Cu}$  clusters keep high stability compared with the clusters in their vicinity. In particular, we can conclude that  $\text{AgAu}$  and  $\text{AgCu}$  isomers have the most stable structures for  $\text{Ag}_n\text{X}$  clusters.

(iii) Based on the natural population analysis, it is revealed that the charges transfer from  $\text{Ag}_n$  host to the X ( $\text{Au}, \text{Cu}$ ) atom, while the  $\text{Ag}_2\text{Cu}$  cluster is the reverse. In addition, the internal charge transfers show that the 6s states attract electrons in the Au atom except for  $n = 4$ , while the 4s states lose electrons in the Cu atom except for  $n = 1$ . Meanwhile, d orbit is relatively stable.

(iv) The values of the vertical ionization potential, the vertical electron affinity, and the chemical hardness are calculated and compared with available experimental values. Our calculated results are in good agreement with experimental values. By comparison with HOMO-LUMO gaps, the same odd-even oscillations are found for the VIP and  $\eta$  of the  $\text{Ag}_n\text{X}$  ( $\text{X}=\text{Au}, \text{Cu}$ ;  $n=1-8$ ) clusters. The  $\text{AgAu}$ ,  $\text{AgCu}$ , and  $\text{Ag}_2$  clusters possess the largest VIP and  $\eta$  values.

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