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Structures and charge distributions of cationic and neutral $Cu_{n-1}Ag$ clusters ($n=2-8$)

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Geometries, electronic states, charge distributions, and stability of $Cu_{n-1}Ag$ ($n=2-8$) neutral and cationic clusters have been investigated using density functional theory. Structural optimization and frequency analyses were performed with the basis set of Lanl2dz. Our results reveal that all neutral and charged $Cu_{n-1}Ag$ ($n=2-8$) clusters can be derived from a substitution of the peripheral position occupied by Cu atom with an Ag atom in the corresponding Cu_n ($n=2-8$). The atoms at peripheral positions have a preference for bearing the most negative or least positive charges in the smaller clusters ($n<8$). All atomic charges depend on their atomic positions and ability to obtain or lose electrons in the cluster. In various copper-silver species, $Cu_{n-1}Ag$ (n=even number) and $Cu_{n-1}Ag^+$ (n=odd number) clusters are predicted to be more stable, which can be attributed to difficultly removing an electron from the doubly occupied HOMO of a closed-shell system.

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I. INTRODUCTION

The discovery of fullerenes and metcars has inspired theorists to consider other unusually stable aggregates (magic clusters) that might serve as building blocks for cluster-assembled materials. If such exotic materials could be formed, they might well exhibit unique electronic, magnetic, optical, mechanical, and catalytic properties, and these could potentially lead to technological uses. While several types of magic clusters have now been considered by theory and experiment,[1–3] noble metal clusters recur repeatedly because they offer a wide range of characteristic properties and their usages in industrial applications.

The electronic configurations of the noble metals Cu, Ag, and Au are characterized by possessing a closed *d* shell and a single valence electron. In view of this prominent characteristic, clusters of noble metals are expected to exhibit certain similarities to simple alkali-metal clusters. Most studies were focused on the either pure silver or pure gold clusters,[4–18] nevertheless much less is known for the mixed Cu-Ag clusters. Until now some copper-silver clusters[2,19–21] have been observed in the laser vaporization course of various copper targets in high vacuum as well as in an amorphous Al_2O_3 or silica matrix. However the laboratory observations have not yet been well understood due to the lack of the reliable information of their geometrical and electronic structures. Despite the geometrical arrangements of pure copper or silver clusters[22–49] and Cu_nAg_m ($n+m<4$, or $n+m>32$) clusters[50–54] have been studied, the electronic charge distributions of the mixed Cu-Ag clusters have not been reported. Up to now no systematic study of geometrical structures and relative stability has been reported for charged and neutral mixed copper-silver clusters. Hence it is of interest to carry on an investigation to reveal the geometries, stability, and electronic charge distributions of doped copper clusters and then improve our comprehension of the laboratory observations for the mixed copper-silver clusters.

The rest of the paper is organized as follows. In Sec. II, we give a brief description of the computational method used in this work. Results, discussion, and stability will be presented in Sec. III for copper-silver species. Finally, our conclusions will be summarized in Sec. IV.

II. COMPUTATIONAL METHODS

Electronic calculations and geometrical optimizations for metals require the treatment of electron correlation. In this context density functional methods provide a good alternative to post-Hartree-Fock method. The functional that we use is the Slater for exchange and Vosko, Wilk, as well as Nusair for correlation (SVWN, also called LSDA).[55,56] The basis set used for copper and silver atoms is Los Alamos ECP plus double ζ basis (Lanl2dz).[57–59] Partial charges were obtained from Natural Population Analysis (NPA).[60,61] The NPA solves most of the problems of the Mulliken scheme by construction of a more appropriate set of atomic basis functions, and so the atomic charges from NPA are usually more reliable than those from the Mulliken scheme. Frequency analyses were also performed at the same theoretical level to check whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding cluster. The most stable charged and neutral $Cu_{n-1}Ag$ clusters were all characterized as energy minima without imaginary frequencies. The first electron ionization potentials (IPs) of various clusters were calculated with adiabatic approximation. All calculations were carried out using the GAUSSIAN03 program.[62]

In the geometry optimizations of $Cu_{n-1}Ag$, we started mainly with three structures; (1) the same structure as Cu_n determined by Refs. 31, 3, 38, 39, and 47, where one Cu atom is substituted by one Ag atom, (2) the structure where one Cu atom was added to the $Cu_{n-2}Ag$ cluster, and (3) the structure where one Ag atom was added to the Cu_{n-1} molecule.

III. THEORETICAL RESULTS

A. Geometry and charge distributions

The ground states of neutral and cationic $Cu_{n-1}X$ (X=Cu and Ag, $n=2-8$) clusters are shown in Fig. 1. The "bonds"

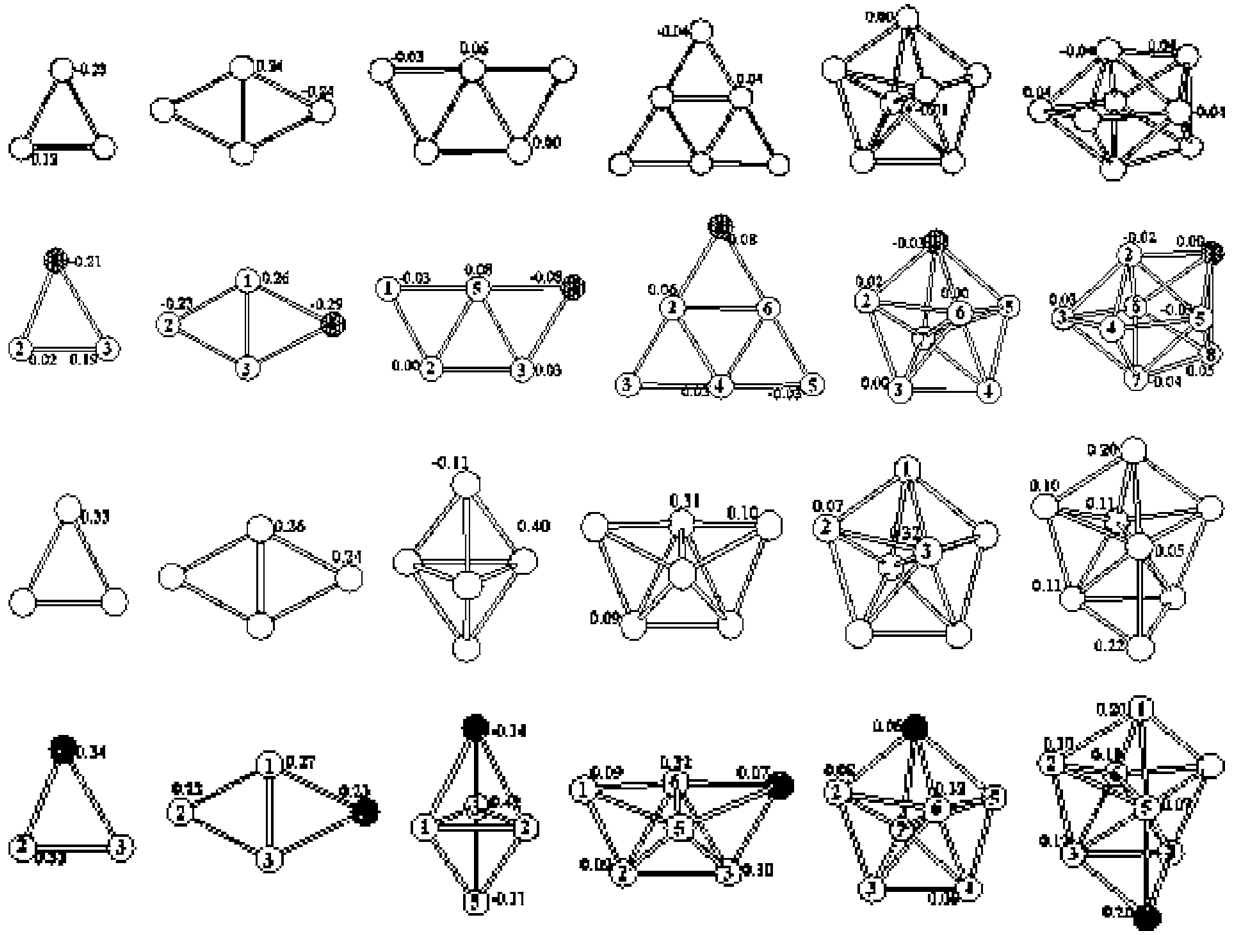

FIG. 1. Ground-state structures for neutral and cationic Cu_n and Cu_nAg. Cu and Ag atoms are shown by the white and gray ball, respectively. NPA charges ($/e$) are presented near the atoms

are shown for internuclear separations less than 3.0 Å (Cu-Cu and Cu-Ag). The internuclear separations of ground states are given in Table I. SCF energies and the zero point energies (ZPE) of neutral and cationic clusters are given in Table II.

1. CuAg

The Cu and Ag atoms bear $0.05e$ and $-0.05e$ in CuAg ($^1\Sigma^+$, $C_{\infty v}$) molecule, respectively, whereas the respective Cu and Ag atoms possess $0.52e$ and $0.48e$ in the $CuAg^+$ ($^2\Sigma^+$, $C_{\infty v}$) cationic ion. The cationic ion has a longer bond length relative to its neutral molecule. The bonding in the cationic dimer is reduced because a bonding orbital is only singly occupied.

The neutral bond length (2.3255 Å) obtained with the SVWN level of computation is smaller than its experimental value of 2.4682 Å.[50] One can rationalize the trends by invoking the well-known effect of overbinding in the local spin density approximation.

Cu-Ag diatom can be viewed as a substitution of a Cu atom by one Ag atom in the Cu_2 dimer. For neutral and cationic CuAg dimer, their bonding lengths are longer than those of neutral and cationic Cu_2 diatom due to larger atomic radius of a silver atom.

2. Cu_2Ag

The energetically lowest minimum of Cu_2Ag is a triangle configuration ($^2A'$, C_s) 1(b), which can be viewed as a substitution of the peripheral Cu atom with the most negative charges by an Ag atom in the triangle Cu_3 ($^2B_2$, C_{2v}) molecule[24,29–33,38,39,47] 1(a).

The symmetries of Cu_3^+ ($^1A_1'$, D_{3h}) (Refs. 31, 34, and 47) 1(c) and Cu_2Ag^+ ($^1A_1$, C_{2v}) 1(d) boost upon charging. This is expected from the electronic structure of the neutral trimer because the Jahn-Teller distortion is avoided if one electron is removed.

3. Cu_3Ag

The energetically most favorable isomer is the planar rhombus ($^1A_1$, C_{2v}) 1(f). It can be described as a substitution of the most negatively charged Cu atom, located long diagonal position, by an Ag atom in the rhombus Cu_4 (^1A_g, D_{2h}) structure[26,29,31,35,38,39,47] 1(e). The silver atom prefers to occupy an outer position due to its larger atomic radius so as to easily reduce geometrical relaxation. This replacement will keep the most stable geometrical structure in the course of substitution from pure copper to the mixed copper-silver cluster. Three copper atoms have different charges due to their different positions. This reveals atomic charges depend

TABLE I. Distances between two atoms (L/Å) in $Cu_{n-1}Ag$ and $Cu_{n-1}Ag^+$ clusters.

	Type	L		Type	L		Type	
Cu_2Ag	1–2	2.615		6–7	2.567		5–6	2.286
	2–3	2.216	Cu_7Ag	1–2	2.508		3–5	2.449
	3–1	2.437		2–5	2.403		2–3	2.409
Cu_3Ag	1–2	2.331		1–5	2.557		3–4	2.518
	1–3	2.234		5–6	3.068		4–5	2.556
	1–4	2.491		2–4	2.378	Cu_6Ag^+	1–2	2.620
Cu_4Ag	1–2	2.308		3–4	2.479		2–3	2.433
	1–5	2.287		4–5	2.340		3–4	2.457
	2–5	2.355		4–7	2.388		1–3	4.168
	2–3	2.336		5–7	2.397		1–6	2.563
	3–5	2.359		1–8	2.655		6–7	2.337
	3–4	2.476		5–8	2.382	Cu_7Ag^+	5–6	2.512
	4–5	2.450	Cu_2Ag^+	1–2	2.450		1–5	2.337
Cu_5Ag	1–2	2.453		2–3	2.288		1–6	2.428
	2–6	2.394	Cu_3Ag^+	1–2	2.332		3–5	2.429
	2–3	2.292		1–3	2.296		3–6	2.406
	2–4	2.373		1–4	2.503		3–4	2.487
	3–4	2.290	Cu_4Ag^+	1–2	2.323		2–5	2.440
Cu_6Ag	1–2	2.543		1–4	2.565		2–6	2.413
	2–3	2.361		1–5	2.423		1–2	2.427
	3–4	2.380	Cu_5Ag^+	1–2	2.360		5–7	2.498
	1–3	4.058		1–5	2.401		3–7	2.553
	1–6	2.578		2–5	2.450			

on their positions even though the same atoms occupy different positions in the molecule. There exists another ($^1A_1$, C_{2v}) rhombus isomer, lying 0.26 eV higher in energy, which can be viewed as interchanging positions between 1 and 4 atoms in Fig. 1(f). Its silver atom bears 0.22e electronic charges at this position. Apparently the silver atom cannot occupy the central positions due to its larger atomic radius in this series clusters.

In order to further understand the influence of Pauling's electronegativity on the atomic charges, the geometry and charge distribution of Cu_3Au is reported here for comparison with Cu_3Ag. Cu_3Au also has the rhombus topology similar to Fig. 1(f). The gold atom still occupies the peripheral position analogical to Ag atom in the Cu_3Ag. The Au atom possesses $-0.49e$, and the copper atoms at 1, 2, and 3 positions bear $0.31e$, $-0.15e$, and $0.31e$, respectively. The gold atom bears more negative charges than silver atom in Cu_3Ag due to its larger electronegativity. After substitution all charges will redistribute depending on the atomic positions and atomic ability to obtain or lose electron in the cluster. The atomic positions are key factor in determining atomic charges in the cluster.

The Cu_3Ag^+ ($^1A_1$, C_{2v}) 1(h) and $Cu_4{}^+$ ($^1A_1$, C_{2v}) 1(g) species have the similar structures to their corresponding mol-

TABLE II. SVWN SCF energies (−a.u.) and ZPEs (a.u.) values at Lanl2dz level for mixed copper-silver clusters.

	$Cu_{n-1}Ag$			$Cu_{n-1}Ag^+$		
n	Symm	Energy	ZPE	Symm	Energy	ZPE
2	$C_{\infty v}$	342.0636	0.0006	$C_{\infty v}$	341.7387	0.0005
3	C_s	538.2600	0.0012	C_{2v}	538.0189	0.0014
4	C_{2v}	734.5104	0.0024	C_{2v}	734.2322	0.0022
5	C_s	930.7409	0.0032	C_{3v}	930.4824	0.0032
6	C_{2v}	1127.0001	0.0042	C_s	1126.7298	0.0042
7	C_{2v}	1323.2609	0.0055	C_{2v}	1323.0109	0.0053
8	C_s	1519.5266	0.0069	C_s	1519.2570	0.0063

ecules. A remarkable change is all atoms bear positive charges.

4. $\mathbf{Cu_4Ag}$

Present calculation predicts that the Cu_4Ag has a planar trapezoidal structure ($^2A'$, C_s) 1(j). This can be regarded as a substitution of a peripheral Cu atom by an Ag atom in the planar trapezoidal Cu_5 ($^2A_1$, C_{2v}) molecule[26,29,31,35,38,39,47] 1(i). The electronic charges of the Ag atom are practically small due to the existence of many atoms to compete for charges in the cluster and smaller IP difference between Cu and Ag atoms. The silver atom actually always substitute a peripheral copper atom in this series cluster, this is an unambiguous trend in Fig. 1. Larger silver atoms favor occupancy in outer sites so as to lead to a slight geometrical reconstruction.

The stable structure of cationic pentamer tends to deviate from planarity. The trigonal bipyramid ($^1A_1$, C_{3v}) 1(l) with a peripheral position occupied by an Ag atom competes in energy with the trapezoidal form, which can be viewed as a substitution of the peripheral Cu atom with the most negative charges by an Ag atom in the bipyramid ($^1A_1{}'$, D_{3h}) $Cu_5{}^+$ cluster[39,47] 1(k).

5. $\mathbf{Cu_5Ag}$

The Cu_5Ag molecule remains planar, and was found to be a planar triangle ($^1A_1$, C_{2v}) 1(n). This can be considered as a substitution of a peripheral Cu atom by an Ag atom in the triangle Cu_6 ($^1A_1{}'$, D_{3h}) molecule[38,39,47] 1(m). The electronic charges of the Ag and Cu atoms are actually small due to the same reasons as neutral Cu_4Ag molecule.

The geometry of Cu_5Ag^+ ($^2A'$, C_s) 1(p) significantly changes upon charging. Cu_5Ag^+ can be viewed as a substitution of a peripheral Cu atom by an Ag atom in the distorted octahedron $Cu_6{}^+$ ($^2A_1$, C_{2v}) 1(o).[39,47] The central atoms favor to bear the most positive charges and the silver atom occupies the peripheral position with the most negative charges in Cu_5Ag^+ cation.

6. $\mathbf{Cu_6Ag}$

The ground state of Cu_6Ag molecule is a pentagonal bipyramid ($^2B_1$, C_{2v}) 1(r). The three-dimensional structure occurs at this cluster size for neutral molecules. This can be described as a replacement of a peripheral Cu atom by an Ag atom in the pentagonal bipyramid Cu_7 ($^2A_2{}''$, D_{5h}) molecule[38,39,47] 1(q).

The Cu_6Ag^+ cationic ion 1(t) has the similar structure to its molecule. In fact, the central Cu atoms bear the most positive charges in Cu_4Ag^+, Cu_5Ag^+, and Cu_6Ag^+ cations. Their substitutions always occur at those peripheral positions.

7. $\mathbf{Cu_7Ag}$

The most stable state of Cu_7Ag molecule possesses a distorted bicapped octahedron ($^1A'$, C_s) 1(v). This can be treated as a substitution of an outer Cu atom by an Ag atom in the bicapped octahedron Cu_8 ($^1A_1$, C_{2v}) conformer[38,39] 1(u).

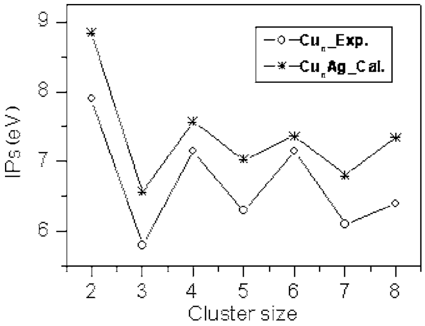

FIG. 2. Ionization potentials vs *n*.

The Cu_7Ag^+ cationic ion 1(x) is different from the Cu_7Ag 1(v), which can be viewed as a substitution of an outer Cu atom with most positive charge by an Ag atom in the $Cu_8{}^+$ ($^2A'$, C_s) conformer 1(w). There exists a nearly degenerate isomer ($^1A''$, C_s) very similar to the 1(v), lying only 0.04 eV higher relative to the cationic configuration 1(w). The Ag atom apparently prefers to occupy the peripheral positions rather than those with the most negative or least positive charges in this series when the electronic charges of all neutral and cationic clusters are taken into account.

Bonačić-Koutecký *et al.*[63] pointed out that Au atoms assume positions which favor the charge transfer from Ag atoms in the Ag_nAu_{n-m} ($2<n<6$, $m<n$) clusters based on the smaller cluster size, which is in agreement with our calculations on the smaller cations ($n<8$). Their conclusions seem to be reasonable because the most positively charged atoms always are located at the central positions in the smaller clusters ($n<8$). However, the charged distributions and geometrical structures cannot be understood in the Cu_7Ag^+ according to their views.

We should note that the preferred spin multiplicity of $Cu_{n-1}Ag$ (odd numbered n) is a doublet whereas that of $Cu_{n-1}Ag$ (even numbered n) is a singlet. The preferred spin multiplicities are always the lowest states for all members of this series, i.e., singlet for even-numbered electron systems and doublet for odd-numbered electron system. These revealed that clusters with even n are closed-shell systems whereas odd-numbered mixed copper clusters are open-shell systems. On the other hand, all ground state geometries of the neutral and cationic Cu_nAg clusters are similar to corresponding alkali-metal clusters[64,65] on the whole.

B. Relative stability

The experimental[9,66,67] IPs of Cu_n ($n=2-8$) and adiabatic theoretical IP of $Cu_{n-1}Ag$ ($n=2-8$) are shown in Fig. 2. Our calculations have the same trend with available experimental data. This strongly suggests that the topologies of $Cu_{n-1}Ag$ should be analogical to Cu_n. This can be expected from the[37,40,49] Ag_n and[31–33,38,39,47] Cu_n clusters have similar geometrical topologies. The IP value of CuAg has the largest maximum, which shows its special stability. The overall trend of the IPs shows a remarkable odd-even oscillation, which shows the alternation of cluster stability. The oscillat-

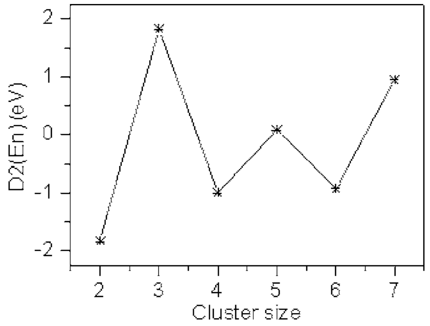

FIG. 3. Second difference in energy vs n.

ing behavior of the IPs reflects the change of spin multiplicity of the ground state of this series. Even-numbered clusters present the higher values of the IP with respect to their neighboring odd systems because it is more difficult to remove an electron from the doubly occupied HOMO of a closed-shell system than from a single occupied HOMO of an open-shell system.

To test the relative stabilities of cationic ions, the following energy variation of reactions is considered:

$$2(\mathrm{Cu}_{n-1}\mathrm{Ag}^{+}) \rightarrow (\mathrm{Cu}_{n-2}\mathrm{Ag}^{+}) + (\mathrm{Cu}_{n}\mathrm{Ag}^{+}).$$

We define the energy variation in the formula as $D2(E_n) = E_n + 1 + E_n - 1 - 2E_n$, which is the second difference in energy for cationic series with invariable number of total atoms. Hence, we obtain the curves shown in Fig. 3 corresponding to the energy variations in the formula as n. It is evident that the $D2(E_n)$ is larger as odd n and lower as even n in Fig. 3, which suggests that those $\mathrm{Cu}_{n-1}\mathrm{Ag}^{+}$ cationic species corresponding to odd n are more stable. This is because cationic clusters with an odd n present closed-shell states. The $D2(E_3)$ possesses the highest maximum in all peak values, which indicates a special stability of $\mathrm{Cu}_2\mathrm{Ag}^{+}$.

IV. SUMMARY

In this work, the geometries, charge distributions, and stability of the $\mathrm{Cu}_{n-1}\mathrm{Ag}$ $(n=2-8)$ neutral and cationic clusters were studied at SVWN/Lanl2dz level. Our results reveal that all $\mathrm{Cu}_{n-1}\mathrm{Ag}$ clusters can be derived from a substitution of a peripheral Cu atom with an Ag atom in the Cu_n $(n=2-8)$. Larger heteratoms favor to occupy outer positions in order to decrease geometrical reconstruction. The most negatively or least positively charged atoms are located at the peripheral positions in the smaller cations $(n<8)$. The neutral bimetallic clusters remain more planar for the larger sizes $(n<7)$ than their corresponding cations $(n<5)$. All ground state geometries of copper-silver clusters are similar to corresponding alkali metal on the whole. In this series clusters, $\mathrm{Cu}_{n-1}\mathrm{Ag}$ (n=even number) and $\mathrm{Cu}_{n-1}\mathrm{Ag}^{+}$ (n=odd number) clusters are predicted to be of high stability, which can be explained by the difficultly in removing an electron from the doubly occupied HOMO of a closed-shell system.

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