# Equilibrium Geometries of the Neutral and Ionic Clusters of $Ag_7$, $Ag_8$, and $Ag_9$ Studied by Intermediate Neglect of Differential Overlap Method

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The equilibrium geometrical structures of silver atom clusters at their electronic ground states have been theoretically determined by using the nonrelativistic semiempirical INDO/1 method. The clusters investigated are $Ag_n$, $Ag_n^+$, and $Ag_n^-$ ($n$ = 7, 8, 9). In order to find the most stable structure, *i.e.*, the global minimum in energy hypersurface, geometry optimization and energy calculation processes have been repeatedly performed for all the possible graphical models by changing the bond parameters (resonance integral values). The heptamers are pentagonal bipyramidal-$Ag_7(D_{5h})$, $Ag_7^+(D_{5h})$, $Ag_7^-(D_{5h})$; the octamers are pentagonal bipyramidal with one atom capped-$Ag_8(D_{2d})$, $Ag_8^+(C_s)$, $Ag_8^-(D_{2d})$; the nonamers are pentagonal bipyramidal with two atoms capped -$Ag_9(C_{2v})$, $Ag_9^+(C_{2v})$, $Ag_9^-(C_{2v})$. Our structures are in good agreement with those by *ab initio* calculations except for the anionic $Ag_9^-$ cluster. And it is noted that the INDO/1 method can accurately predict the Ag cluster geometries when a proper set of bond parameters is used.

## Introduction

Perhaps the most fundamental problem in metal cluster research is to determine the cluster structures, but despite a considerable research effort, only in rare instances a progress in this direction has been made. For example, for the alkali metals, only the trimer and heptamer structures are known with any certainty.[1-4] For the Group IA elements, most experiments have been concerned with properties such as ionization potentials[5-7] and dissociation energies,[8,9] which only indirectly probes the structure of clusters themselves. Therefore the task of determining cluster structures has fallen largely to the theoreticians.[10] Even in theoretical studies, the available information is relatively sparse, except for the case of alkali trimers,[11,12] Recently semiempirical[13] and *ab initio*[14-17] calculations on alkali metal clusters have been reported. Notably the cluster size and geometries of large clusters consisting of 8 alkali atoms are investigated. These theoretical studies show a tendency that smaller alkali metal clusters have a planar geometry while larger (more than 7 atoms) clusters have three dimensional nonplanar structure.

Silver atom clusters are of particular interest because of their role in the formation of latent photographic images, of which electronic and structural properties have been studied at various theoretical or experimental levels. Previous works on the spectroscopy of silver dimers have suffered from serious limitations due to the presence of three isotopomers, *i.e.*, $^{107}Ag_2$ (26.85%), $^{107}Ag^{109}Ag$ (49.93%) and $^{109}Ag_2$ (23.32%). It causes the blending of spectral lines which makes the analysis of spectra very complicated. Recently, gas phase spectra of neutral silver dimers and trimers obtained from laser-induced fluorescence spectra have been reported. In addition, photoelectron spectra of $Ag_n^-$ clusters have been reported.[18-22]

While there are not many experimental studies on silver atom clusters, applications of various theoretical methods to silver clusters have increased the interests in this system explosively. Most of calculations up to now have been performed using *ab initio* methods such as relativistic effective core potential (RECP) method or pseudopotential method. Hay and Martin[23,24] made a comparison between all-electron and valence-electron calculations on the Ag atom and Ag diatomics. Silver is a Group IB metal, with ground state configuration of $[Kr]4d^{10}5s^1$, and the focus of their work was to use RECP properly. The potential which explicitly considers only the 4*d* and 5*s* electrons in the valence space [(36/11) RECP] adequately reproduces the results of all-electron calculations as far as the spectroscopic parameters, *e.g.*, $r_e$, $w_e$, and $D_e$ are concerned. On the other hand, Bonačić-Koutecký *et al.*[25,26] have determined the ground state geometries of small silver clusters within the framework of the Hartree-Fock and complete active space self-consistent field (CASSCF) employing the (46/1) RECP, where it includes only the 5*s* electron in the valence space. Even though the RECP faithfully reproduces the all-electron SCF and correlated wave functions, it does not always accurately reproduce the experimental bond lengths.

Baetzold[27,28] has previously investigated isolated silver clusters of up to 55 atoms using the extended Hückel (EH) and the complete neglect of differential overlap (CNDO) molecular orbital theories, in which he determined electronic properties such as electron affinity, binding energy, and *d*-orbital occupancy. However, these studies could not reproduce the geometries of Ag clusters found from *ab initio* calculations.

Our purpose is to obtain the electronic ground state geometries of $Ag_n$ ($n$ = 7, 8, 9) neutral and ionic clusters through other technique beyond such limits as the complexity of *ab initio* methods and the inaccuracy of EH method. Therefore another semiempirical theory is considered to be in better agreement with the results from *ab initio* calculations or experiments than EH or CNDO theory. We have chosen the INDO/1 method provided in the ZINDO program package.[29,30] But due to the lack of parameters for Ag transition metal atom some new parameters must have been predetermined. Furthermore a search for the better bond parameter set has been performed to produce the reasonable geometries in agreement with those found in accurate *ab initio* results.

## Computations

To find the most stable geometrical structure of the electronic ground state of Ag clusters we performed two-step calculations. In the first step, we constructed all the possible locally stable geometries of small $Ag_n$ ($n$ = 2-6) clusters by using graph theory, and in the second step, carried out energy and/or geometry optimization calculations for each geometry (local minimum) found in the first step to find the most stable geometry (global minimum). The second step calculations were performed by using the intermediate neglect of differential overlap method in the ZINDO program package. For large $Ag_n$ ($n$ = 7, 8, 9) clusters the first step calculations were not performed. Instead the locally stable geometries for the large clusters were obtained from the analyses of the first step results for the small clusters, $Ag_n$ ($n$ = 2-6). These studies on small Ag clusters are not presented in the present article.

In the second step, that is, energy or geometry optimization calculations, we adopted the semiempirical intermediate neglect of differential overlap (INDO/1) method[29,30] at the self-consistent field (SCF) level. The ZINDO program has two kinds of parameter sets, *i.e*., spectroscopic gammas for energy and theoretical gammas for geometry. There exist no spectroscopic gammas reported for Ag atom, which means that CI calculations of single point energy are not possible using ZINDO. Hence we have performed the SCF level INDO calculations for Ag clusters.

The details of calculations are as follows. The Ag atom has the ground state configuration of $4d^{10}5s^1(^2S_{1/2})$, therefore open-shell (odd number of Ag atoms in cluster) and closed-shell (even number of Ag atoms) electronic configurations are compatible. The stability of the different spin multiplicities for a given cluster size has been investigated by comparing various searches (starting from different initial geometries which are associated with the different symmetries) with the number of atoms that define the cluster. The 11 electrons in both of $4d$ and $5s$ orbitals are considered to be the valence electrons. The optimization of the interatomic distances and angles was performed without any constraints on their variation. For the numerical method of optimization the Newton-Raphson algorithm was used. Convergence to a stationary point on the energy hypersurface is assumed when the maximum component of the gradient is less than $1 \times 10^{-5}$ hartrees/bohr.

The bond parameters ($\beta$) used in calculating resonance integrals are characteristics of an atom, so they are chosen according to formulas that take into account of different electronegativities.[31-33] Zerner used $\beta(d)$ = -27.94 eV to obtain the geometry for silver hydride by setting the resonance integral $\beta(s) = \beta(p)$ = -1.0 eV (the default value in the package) for the INDO/1 version of the ZINDO. However these values do not produce good geometries for Ag clusters.

To find the optimal $\beta$ parameters we have calculated the equilibrium bond length of the ground state ($X^1\Sigma^+$) of $Ag_2$ molecule which is in the range of 2.47-2.75 Å.[18,19,23-26,34-36] We carried out the INDO calculations by changing the only $\beta$ parameters in the range of $\beta(s)$ = -1.0 ~ -10.0 eV and $\beta(d)$ = -10.0 ~ -99.0 eV. The calculated bond length varies from 2.43 to 3.43 Å, which covers almost all the values found from *ab initio* calculations or experiments. Hence it means that we can approach any value of interest by changing only $\beta$ parameters. Of these values, however, it is not easy to select one $\beta$ parameter set only from $Ag_2$ calculations.

From the above comparisonal study we find that our calculated bond length is not significantly dependent on the choice of $\beta$ parameters when the $\beta$ parameters are within the range of $\beta(s)$ = -2.0 ~ -5.0 eV and $\beta(d)$ = -50.0 ~ -80.0 eV. Therefore we chose four additional sets of $\beta$ parameters besides the Zerner's parameters, i) $\beta(s)$ = -1.0 and $\beta(d)$ = -27.94 eV, and performed five different calculations for each silver cluster. The additional sets are ii) $\beta(s)$ = -2.0 and $\beta(d)$ = -60.0 eV, iii) $\beta(s)$ = -2.0 and $\beta(d)$ = -80.0 eV, iv) $\beta(s)$ = -5.0 and $\beta(d)$ = -60.0 eV, and v) $\beta(s)$ = -5.0 and $\beta(d)$ = -80.0 eV.

The $\beta$ parameters influence on the bond length of geometry and sometimes convert one geometry into more stable geometry with different symmetry. However, the change of $\beta$ parameters does not alter the relative stabilities among various geometries, in general. We have not found any instance such that an unstable geometry has lower energy than the stable structures when the $\beta$ parameters are changed within the range we considered.

Using the above five sets of $\beta$ parameters along with the Zerner's original set, we performed the geometry optimization for starting geometries obtained from the graph theory. From these initial calculations we obtain several structures which lie in local minima of energy hypersurface. For each structure the INDO energy calculations are performed to find the structure having the lowest energy. After finding the lowest energy structure, the INDO geometry optimization is again performed to determine the accurate structural geometry that lies in the global minimum, *i.e*., the equilibrium structure of $Ag_n$, $Ag_n^+$ and $Ag_n^-$ ($n$ = 7, 8, 9). We focused only on the electronic ground state of each cluster.

## Results

For $Ag_7$, the selection of starting geometries is based on our previous unpublished studies on $Ag_n$ ($n$ = 2-6) clusters as well as the studies of Bonačić-Koutecký *et al.*[25,26] Bonačić-Koutecký *et al.* have considered several possible structures-pentagonal bipyramids ($D_{5h}$), capped trigonal antiprism ($C_{3v}$), and other structures. In addition to their choices, we consider more similar structures. Our calculations indicate that planar

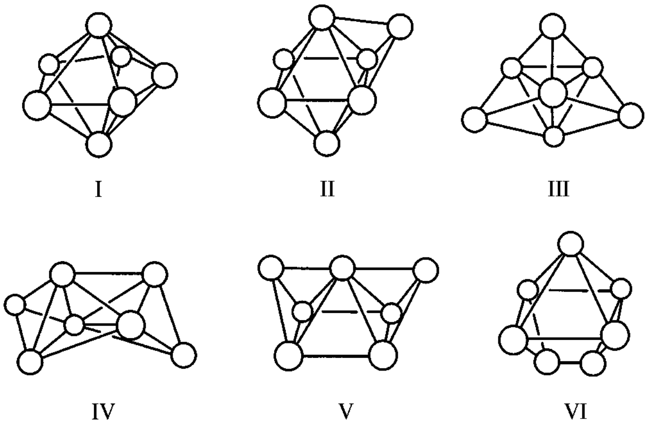


**Figure 1**. SCF optimized geometries for $Ag_7$ heptamers.

or linear geometries are unstable. The six choices of our starting geometries are drawn in Figure 1.

For neutral $Ag_7$ clusters, the original parameter set does not distinguish one geometry from the other effectively. The pentagonal bipyramid, $Ag_7$(I), is the most stable structure for all parameter sets, which is in good agreement with *ab initio* calculation by Bonačić-Koutecký *et al.*[25] The second most stable structure is $Ag_7$(II) for all parameter sets except the original set, in which $Ag_7$(III) is found to be slightly more stable than $Ag_7$(II) by ~0.002 eV. In the case of $\beta$ parameters with $\beta(s)$ = -2.0 eV, $Ag_7$(IV) is more stable than $Ag_7$(III), but $Ag_7$(III) is stabilized more than $Ag_7$(IV) with the increase of $\beta(s)$ parameter. Both of $Ag_7$(V) and $Ag_7$(VI) geometries have higher energies than the others. In the parameter set of $\beta(s)$ = -5.0 and $\beta(d)$ = -80.0 eV, the $Ag_7$(VI) geometry is stabilized considerably, which means that this geometry is converted into more stable geometry of $Ag_7$(II) form.

The pentagonal bipyramidal geometry of $Ag_7^+$(I) is the most stable structure for all $\beta$ parameter sets except the original set, in which $Ag_7^+$(III) is the most stable structure. As Bonačić-Koutecký *et al.* reported, $Ag_7^+$(I) is more likely to be in the global minimum rather than $Ag_7^+$(III). Unlike the neutral heptamers, the $Ag_7^+$(II) geometry has very high energy. The second most stable structure is the $Ag_7^+$(III) geometry for all $\beta$ parameters. The $Ag_7^+$(IV) geometry is no more stable than $Ag_7^+$(III) for the parameter sets of $\beta(s)$ = -2.0 eV, which is less stabilized as the negative $\beta(d)$ parameter increases. The $Ag_7^+$(VI) geometry which is considerably unstable in the other sets is stabilized greatly in the beta parameter set of $\beta(s)$ = -5.0 and ($d$) = -60.0 eV.

The anionic $Ag_7^-$ cluster shows a tendency similar to the neutral heptamers. Especially, the ordering of relative stabilities is in good agreement with *ab initio* calculation by Bonačić-Koutecký *et al.* The most stable structure is the pentagonal bipyramid, $Ag_7^-$(I) and the $Ag_7^-$(II) geometry is the second most stable structure for all $\beta$ parameter sets except for the original set. Like the neutral heptamers, $Ag_7^-$(IV) is destabilized more than $Ag_7$(III) with the increase of $\beta(s)$ parameter. To the contrary, the $Ag_7^-$(VI) geometry is stabilized more than $Ag_7^-$(V) with the increase of $\beta(s)$ parameter, which means that the $Ag_7^-$(VI) form may exist even though it has higher energy.

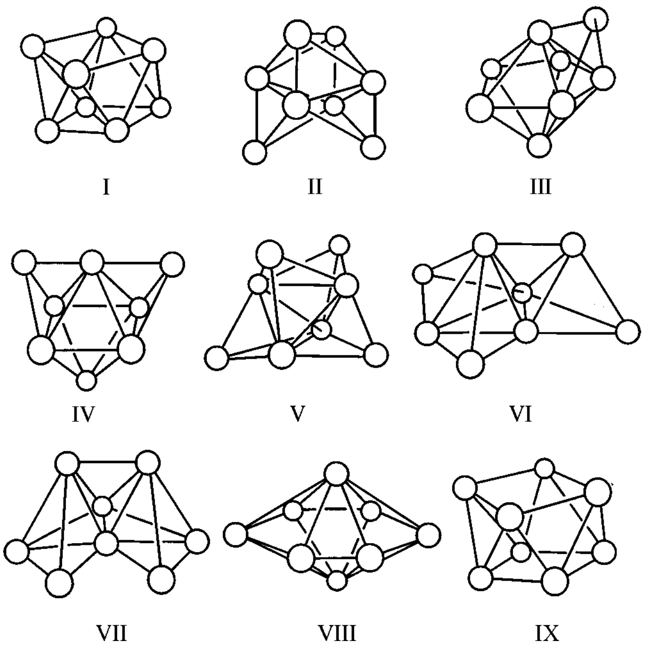


**Figure 2**. SCF optimized geometries for $Ag_8$ octamers.

For $Ag_8$, the starting geometries for the octamers were selected based on the studies by Bonačić-Koutecký *et al.*[25,26] and our current optimization results for the $Ag_n$ ($n$ = 2-7) clusters. The stable geometries we selected are shown in Figure 2.

The $Ag_8$(V) geometry is the most stable structure in the original parameter set, but in other $\beta$ parameter sets the $Ag_8$(II) geometry is the most stable structure, where this structure is converted into the similar form of $Ag_8$(I). The $Ag_8$(I) geometry is the $D_{2d}$ structure which is a deformed section of *fcc* lattice. In case of $\beta(s)$ = -2.0 eV, $Ag_8$(II) has the same structure as $Ag_8$(I), but its $C_{2v}$ structure is slightly distorted from $Ag_8$(I) as increasing the negative $\beta(s)$ value. Therefore the most stable structure for the neutral octamers is the $Ag_8$(I) geometry. The square antiprism of $Ag_8$(IX) has considerably higher energy than the $Ag_8$(I) or $Ag_8$(V) geometries. The second most stable structure is the pentagonal bipyramid of $Ag_8$(III) with a face capped atom. Among the geometries of $Ag_8$(V), $Ag_8$(VI), and $Ag_8$(VII), the $Ag_8$(V) form is the most stable.

For the cationic $Ag_8^+$ clusters, the most stable structure is the pentagonal bipyramid of $Ag_8^+$(III) with a face capped atom in most of parameter sets, which is in good agreement with *ab initio* calculation by Bonačić-Koutecký *et al.*[25] The $Ag_8^+$(II) geometry is converted into $Ag_8^+$(I) as increasing the negative $\beta(s)$ value. Unlike the neutral case, the $T_d$ structure of $Ag_8^+$(V) has higher energy than the $Ag_8^+$(VI) geometry.

For the anionic $Ag_8^-$ clusters, the lowest energy structure changes as the parameters change. In the cases of $\beta(s)$ = -2.0 eV, the capped pentagonal bipyramid of $Ag_8^-$(III) is the most stable structure, but this structure is destabilized more than $Ag_8^-$(I) as the $\beta(s)$ value increases. The $Ag_8^-$(VII) geometry is more stable than $Ag_8^-$(VI) in the parameter sets of $\beta(s)$ =

-2.0 eV, but has higher energy than $Ag_8^-$(VI) in the parameter sets of $\beta(s)$ = -5.0 eV. Comparing with *ab initio* calculation,[26] the parameter set with $\beta(s)$ = -5.0 and $\beta(d)$ = -60.0 eV gives the best agreement in relative stability. Therefore the $Ag_8^-$(II) geometry is the most stable structure, and the $T_d$ structure of $Ag_8^-$(V) has lower energy than $Ag_8^-$(VI) or $Ag_8^-$ (VII).

For all the parameter sets used, the most stable structure is the $C_{2v}$ structure of $Ag_9$(I), which is a pentagonal bipyramid with two atoms capping two neighboring faces of the one pyramid, as found in *ab initio* calculation by Bonačić-Koutecký *et al.*[25] The $Ag_9$(II) geometry is also the second most stable structure for all the parameter sets. The $C_{2v}$ structure of $Ag_9$(III) is the most stable next to $Ag_9$(II) in all parameter sets except that of $\beta(s)$ = -2.0 and $\beta(d)$ = -80.0 eV, in which $Ag_9$(III) has higher energy than $Ag_9$(V). So each graph for the $\beta$ parameter sets does not have similar tendency to each other, which means that each structure is so weakly bonded as to be affected easily. Especially for the $Ag_9$(IX) structure, the $\beta$ parameters of $\beta(s)$ = -5.0 and $\beta(s)$ = -60.0 eV stabilize this geometry to convert into more stable geometry. The $C_{4v}$ structure of $Ag_9$(VIII) is less stable than the $Ag_9$(VII) geometry ($C_{3v}$), but is stabilized as the negative beta values increase. From the $Ag_9$(III), $Ag_9$(IV), $Ag_9$(V), $Ag_9$(XI), and $Ag_9$(XII) geometries having the pentagonal bipyramid, it is found that the $Ag_9$(III) structure is easily formed from the energy point of view.

From the relative stabilities of the optimized geometries (Figure 3) for the cationic $Ag_9^+$ clusters, the $C_{2v}$ geometry of $Ag_9^+$(I) is the most stable structure and the $C_2$ structure of $Ag_9^+$(II) is the second most stable as the neutral nonamers. The third most stable structure is the $Ag_9^+$(III) geometry, but

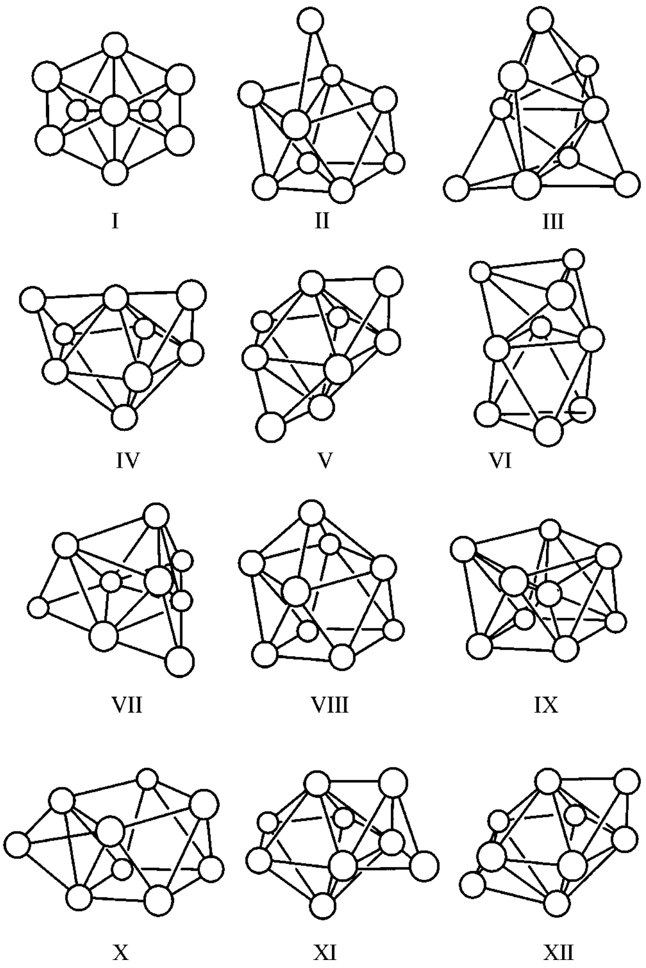
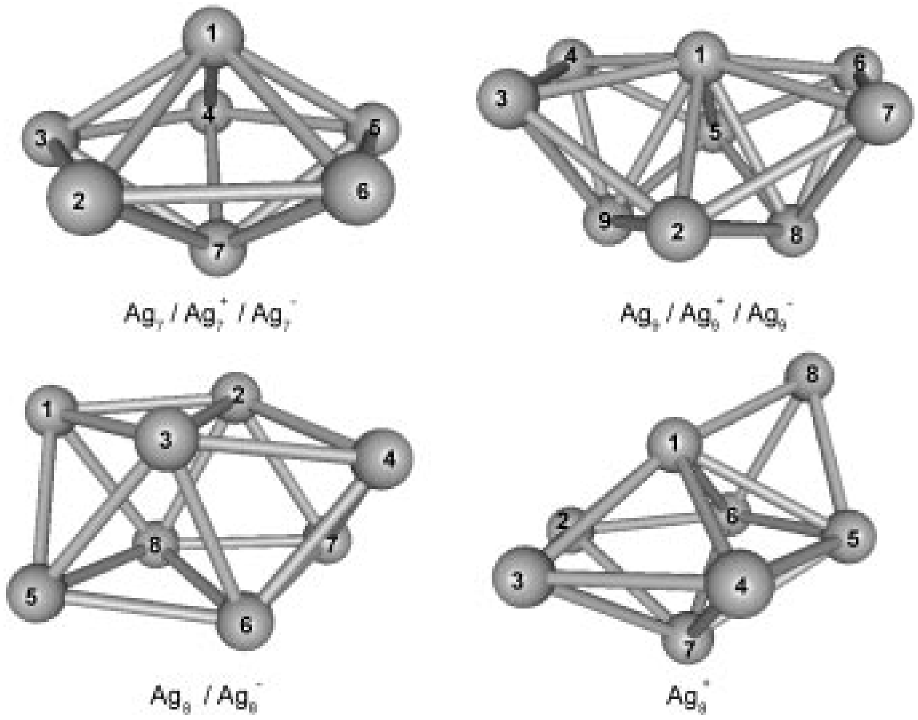


**Figure 3**. SCF optimized geometries for $Ag_9$ nonamers.



$Ag_7$ / $Ag_7^+$ / $Ag_7^-$

$Ag_9$ / $Ag_9^+$ / $Ag_9^-$

$Ag_8$ / $Ag_8^-$

$Ag_8^+$

**Figure 4**. The most stable geometries for the neutral and ionic $Ag_7$, $Ag_8$ and $Ag_9$ clusters.

the $Ag_9^+$(V) in the parameter sets with $\beta(s)$ = -2.0 eV. The $C_{3v}$ structure of $Ag_9^+$(VII) is more stable than the $D_{3h}$ structure of $Ag_9^+$(VI) in the case of $\beta(s)$ = -2.0 and $\beta(d)$ = -60.0 eV, but is destabilized more as the beta values increase. The $D_{4d}$ structure of $Ag_9^+$(IX) is highly unstable, but stabilized by being converted into the more stable structure with the same symmetry.

The tendency of the relative stabilities for the anionic $Ag_9^-$ clusters is similar to that of the cationic nonamers. In the original parameter set, the $Ag_9^-$(III) geometry is the most stable structure. However in the other sets, the $Ag_9^-$(I) geometry is the most stable structure as the neutral and cationic nonamers. The $Ag_9^-$(III) geometry is more stable than $Ag_9^-$(II) in the $\beta$ parameter set of $\beta(s)$ = -2.0 and $\beta(d)$ = -60.0 eV, but has higher energy with the increase of beta values. The $Ag_9^-$(VIII) geometry has lower energy than $Ag_9^-$(VII) in all the parameter sets except that of $\beta(s)$ = -2.0 and $\beta(d)$ = -60.0 eV. Unlike the neutral and cationic nonamers, the geometries of $Ag_9^-$(X) and $Ag_9^-$(XI) have relatively lower energies. In the case of $\beta(s)$ = -5.0 and $\beta(d)$ = -80.0 eV, the $C_s$ structure of $Ag_9^-$(X) is the fourth most stable structure.

Figure 4 shows the most stable geometries for the Ag clusters studied and the detailed geometrical parameters are listed in Table 1. Our INDO calculated structures are in good agreement with the *ab initio* results by Bonačić-Koutecký *et al.*[25,26] except for the $Ag_8^+$ ion. This work does not produce the more exact equilibrium structures for the silver clusters than *ab initio* studies. However, it strongly suggests that the computationally simple semiempirical theories like INDO might be helpful in investigating the transition metal systems when the parameters are carefully chosen.

All charged heptamers have the pentagonal bipyramidal structure with $D_{5h}$ symmetry as an equilibrium structure. The interatomic distance between atom 1 and atom 7 decreases in the order of anionic, neutral, and cationic heptamers. The silver atom octamers have the structure of $D_{2d}$ geometry for both neutral and anionic clusters and of $C_s$ geometry for cationic cluster, respectively, shown in Figure 4. All charged nonamers have the equilibrium structure with $C_{2v}$ symmetry, which is formed by a pentagonal bipyramid with two capped atoms.

Overall, the parameter set of $\beta(s)$ = -5.0 and $\beta(d)$ = -80.0 eV always gives the same geometry for the neutral and the anionic systems. The cationic system has also the same geometry except for the case of octamer. In all charged species, silver clusters of up to 9 atoms have the same geometry, but do not have the same symmetry all the time for all cluster sizes.

## Conclusions

The equilibrium geometries of $Ag_n$ ($n$ = 7, 8, 9) clusters have been determined using the intermediate neglect of differential overlap (INDO/1) method with the parameter sets determined from *ab initio* theoretical calculations for Ag atom and $Ag_2$ diatom. Since silver atom has many low-lying states, silver clusters have also many geometries (in local minima of energy). The number of locally stable geometries increases significantly as cluster size increases. Hence in order to find the most stable structure of global minimum, it is best to choose an initial geometry nearest to the global minimum structure. So it is needed to consider all possible

**Table 1**. Equilibrium geometrical structures of Ag clusters. *r* is the bond length in Å, a is the bond angle in degrees and *d* is the dihedral angle in degrees. The numbers in parenthesis indicate the atoms as shown in Figure 4

| | $Ag_7$ $D_{5h}$ | $Ag_7^+$ $D_{5h}$ | $Ag_7^-$ $D_{5h}$ | | $Ag_8$ $D_{2d}$ | $Ag_8^-$ $D_{2d}$ | | $Ag_8^+$ $C_s$ | | $Ag_9$ $C_{2v}$ | $Ag_9^+$ $C_{2v}$ | $Ag_9^-$ $C_{2v}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| r(1,2) | 2.78 | 2.80 | 2.77 | r(1,5) | 2.82 | 2.75 | r(1,2) | 2.79 | r(1,2) | 2.82 | 2.82 | 2.82 |
| r(1,3) | 2.78 | 2.80 | 2.77 | r(4,7) | 2.82 | 2.75 | r(1,3) | 2.79 | r(1,3) | 2.76 | 2.76 | 2.76 |
| r(1,4) | 2.78 | 2.80 | 2.77 | r(2,3) | 2.74 | 2.75 | r(1,5) | 2.82 | r(1,8) | 2.93 | 2.91 | 2.95 |
| r(1,5) | 2.78 | 2.80 | 2.77 | r(3,6) | 2.74 | 2.75 | r(1,8) | 2.77 | r(3,4) | 2.84 | 2.84 | 2.84 |
| r(1,6) | 2.78 | 2.80 | 2.77 | r(6,8) | 2.74 | 2.75 | r(2,3) | 2.83 | r(6,8) | 2.78 | 2.81 | 2.76 |
| r(2,3) | 2.79 | 2.83 | 2.76 | r(8,2) | 2.74 | 2.75 | r(2,6) | 2.80 | r(2,7) | 2.81 | 2.83 | 2.80 |
| r(7,2) | 2.78 | 2.80 | 2.77 | r(1,2) | 2.78 | 2.78 | r(5,6) | 2.83 | r(5,9) | 2.80 | 2.81 | 2.80 |
| r(7,1) | 2.90 | 2.87 | 2.93 | r(5,6) | 2.78 | 2.78 | r(6,8) | 2.79 | r(8,9) | 2.80 | 2.77 | 2.84 |
| a(3,1,2) | 60.2 | 60.6 | 59.8 | r(5,8) | 2.78 | 2.78 | r(3,7) | 2.79 | a(3,1,4) | 61.9 | 61.8 | 62.0 |
| a(4,1,2) | 108.5 | 109.5 | 107.5 | a(1,2,3) | 60.5 | 60.5 | r(4,7) | 2.81 | a(2,1,5) | 106.6 | 107.6 | 105.5 |
| a(5,1,2) | 108.5 | 109.5 | 107.5 | a(1,2,4) | 120.0 | 119.3 | r(6,7) | 2.80 | a(8,1,9) | 57.1 | 56.8 | 57.5 |
| a(6,1,2) | 60.2 | 60.6 | 59.8 | a(2,3,5) | 99.3 | 98.2 | a(2,1,3) | 61.0 | a(2,1,3) | 60.5 | 61.0 | 60.1 |
| a(7,2,1) | 62.6 | 61.7 | 64.0 | a(2,3,6) | 80.1 | 80.7 | a(2,1,4) | 110.1 | a(5,1,6) | 60.5 | 61.0 | 60.1 |
| d(1,2,3,4) | 37.0 | 36.4 | 37.7 | a(3,6,7) | 99.3 | 98.2 | a(1,6,5) | 60.0 | a(6,8,7) | 61.3 | 60.6 | 62.1 |
| d(1,3,4,5) | 37.0 | 36.4 | 37.7 | a(1,2,8) | 60.5 | 60.5 | a(1,3,7) | 62.5 | a(1,3,9) | 63.8 | 62.92 | 64.6 |
| d(1,2,3,7) | 74.1 | 72.9 | 75.4 | d(1,2,3,4) | 168.2 | 166.4 | d(2,3,1,4) | 139.2 | d(2,3,1,4) | 137.3 | 138.0 | 136.6 |
| d(1,3,4,7) | 74.1 | 72.9 | 75.4 | d(2,1,3,5) | 121.7 | 122.2 | d(2,6,1,8) | 150.3 | d(3,4,1,5) | 137.3 | 138.0 | 136.6 |
| | | | | d(3,1,5,8) | 94.6 | 94.8 | d(3,4,1,5) | 138.1 | d(3,9,4,1) | 68.0 | 68.3 | 67.6 |
| | | | | d(3,2,1,8) | 95.4 | 96.1 | d(2,6,7,5) | 138.6 | d(2,8,9,5) | 137.0 | 137.0 | 137.5 |
| | | | | d(3,6,4,7) | 121.7 | 122.1 | d(7,6,5,8) | 142.8 | d(6,5,8,9) | 140.8 | 140.7 | 140.8 |
| | | | | | | | | | d(4,1,9,8) | 142.9 | 143.3 | 142.4 |

geometries as starting geometries for each size of cluster. We have simplified this problem to an extent by using the Hückel graphs from graph theory. We obtained and studied all simple graphs for Ag clusters of up to 6 atoms. For the $Ag_n$ ($n = 7$, 8, 9) clusters, initial geometries were chosen from the studies on smaller $Ag_n$ ($n = 2$-6) clusters as well as from the previous studies of *ab initio* calculations. SCF geometry optimization within INDO/1 was performed for each Hückel model of starting geometries. Through a series of semiempirical calculations, we obtained the most stable geometries for each cluster.

From the five tests (five parameter sets), generally we obtained the same global minimum structure, *i.e.*, the equilibrium geometry of a cluster. However, for some clusters different equilibrium geometries were obtained depending on the choice of parameter set. The parameter sets with the greater beta value, *i.e.*, $\beta(s) = -5.0$ and $\beta(d) = -80.0$ eV, gave the most stable structures in better agreement with *ab initio* calculations, which means that *d* orbitals play an important role in forming silver atom clusters. For ionic clusters, $Ag_n^+$ and $Ag_n^-$, the INDO/1 calculations also have been performed. It is found that $Ag_n^+$ and $Ag_n^-$ have a similar equilibrium structure as the neutral $Ag_n$ clusters.

From this work for $Ag_n$ clusters, we have found a way of extending and, consequently applying the semiempirical INDO method to the transition metal systems like silver whose parameters are rarely found in the literatures. With the new set of $\beta$ parameters the structures of the larger Ag clusters will be investigated in the future.

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