

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 (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 potentials⁵⁻⁷ 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 semiempirical¹³ 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.*, $^{107}\text{Ag}_2$ (26.85%), $^{107}\text{Ag}^{109}\text{Ag}$ (49.93%) and $^{109}\text{Ag}_2$ (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 $[\text{Kr}]4d^{10}5s^1$, and the focus of their work was to use RECP properly. The potential which explicitly considers only the 4d and 5s 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 5s 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 1×10^{-5} hartrees/bohr.

The bond parameters (β) used in calculating resonance integrals are characteristics of an atom, so they are chosen according to formulas that take into account of different elec-

tronegativities.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 β 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 β parameters in the range of $\beta(s) = -1.0 \sim -10.0$ eV and $\beta(d) = -10.0 \sim -99.0$ 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 β parameters. Of these values, however, it is not easy to select one β parameter set only from Ag_2 calculations.

From the above comparisational study we find that our calculated bond length is not significantly dependent on the choice of β parameters when the β parameters are within the range of $\beta(s) = -2.0 \sim -5.0$ eV and $\beta(d) = -50.0 \sim -80.0$ eV. Therefore we chose four additional sets of β 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 β parameters influence on the bond length of geometry and sometimes convert one geometry into more stable geometry with different symmetry. However, the change of β 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 β parameters are changed within the range we considered.

Using the above five sets of β 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

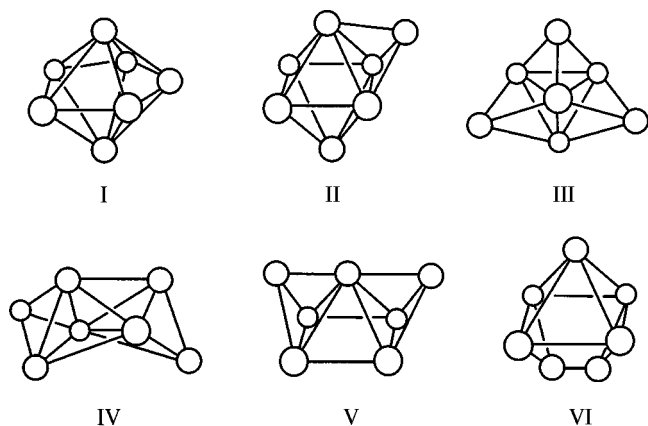


Figure 1. SCF optimized geometries for Ag₇ heptamers.

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

For neutral Ag₇ clusters, the original parameter set does not distinguish one geometry from the other effectively. The pentagonal bipyramid, Ag₇(I), is the most stable structure for all parameter sets, which is in good agreement with *ab initio* calculation by Bonačić-Koutecký *et al.*²³ The second most stable structure is Ag₇(II) for all parameter sets except the original set, in which Ag₇(III) is found to be slightly more stable than Ag₇(II) by ~ 0.002 eV. In the case of β parameters with $\beta(s) = -2.0$ eV, Ag₇(IV) is more stable than Ag₇(III), but Ag₇(III) is stabilized more than Ag₇(IV) with the increase of $\beta(s)$ parameter. Both of Ag₇(V) and Ag₇(VI) geometries have higher energies than the others. In the parameter set of $\beta(s) = -5.0$ and $\beta(d) = -80.0$ eV, the Ag₇(VI) geometry is stabilized considerably, which means that this geometry is converted into more stable geometry of Ag₇(II) form.

The pentagonal bipyramidal geometry of Ag₇⁺(I) is the most stable structure for all β parameter sets except the original set, in which Ag₇⁺(III) is the most stable structure. As Bonačić-Koutecký *et al.* reported, Ag₇⁺(I) is more likely to be in the global minimum rather than Ag₇⁺(III). Unlike the neutral heptamers, the Ag₇⁺(II) geometry has very high energy. The second most stable structure is the Ag₇⁺(III) geometry for all β parameters. The Ag₇⁺(IV) geometry is no more stable than Ag₇⁺(III) for the parameter sets of $\beta(s) = -2.0$ eV, which is less stabilized as the negative $\beta(d)$ parameter increases. The Ag₇⁺(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 Ag₇⁻ 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, Ag₇⁻(I) and the Ag₇⁻(II) geometry is the second most stable structure for all β parameter sets except for the original set. Like the neutral heptamers, Ag₇⁻(IV) is destabilized more than Ag₇(III) with the increase of $\beta(s)$ parameter. To the contrary, the Ag₇⁻(VI) geometry is stabilized more than Ag₇⁻(V) with the increase of $\beta(s)$ parameter, which means that the Ag₇⁻(VI) form may exist even

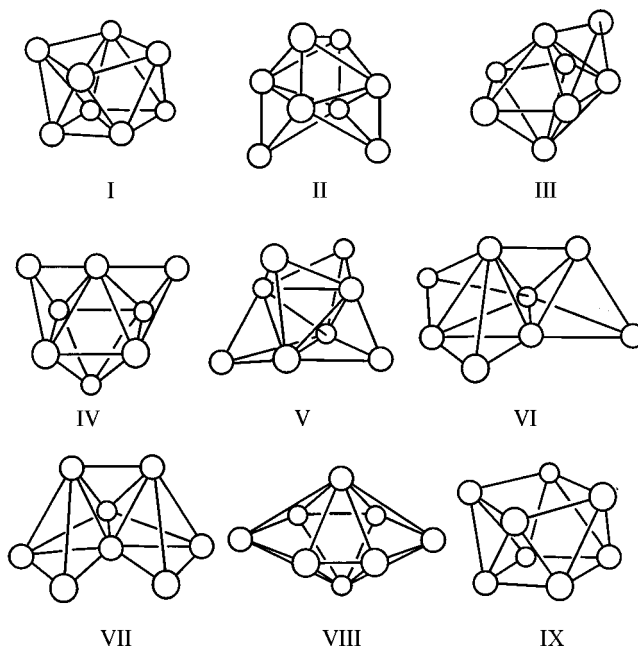


Figure 2. SCF optimized geometries for Ag₈ octamers.

though it has higher energy.

For Ag₈, 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 Ag₈(V) geometry is the most stable structure in the original parameter set, but in other β parameter sets the Ag₈(II) geometry is the most stable structure, where this structure is converted into the similar form of Ag₈(I). The Ag₈(I) geometry is the D_{2d} structure which is a deformed section of *fcc* lattice. In case of $\beta(s) = -2.0$ eV, Ag₈(II) has the same structure as Ag₈(I), but its C_{2v} structure is slightly distorted from Ag₈(I) as increasing the negative $\beta(s)$ value. Therefore the most stable structure for the neutral octamers is the Ag₈(I) geometry. The square antiprism of Ag₈(IX) has considerably higher energy than the Ag₈(I) or Ag₈(V) geometries. The second most stable structure is the pentagonal bipyramid of Ag₈(III) with a face capped atom. Among the geometries of Ag₈(V), Ag₈(VI), and Ag₈(VII), the Ag₈(V) form is the most stable.

For the cationic Ag₈⁺ clusters, the most stable structure is the pentagonal bipyramid of Ag₈⁺(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 Ag₈⁺(II) geometry is converted into Ag₈⁺(I) as increasing the negative $\beta(s)$ value. Unlike the neutral case, the T_d structure of Ag₈⁺(V) has higher energy than the Ag₈⁺(VI) geometry.

For the anionic Ag₈⁻ clusters, the lowest energy structure changes as the parameters change. In the cases of $\beta(s) = -2.0$ eV, the capped pentagonal bipyramid of Ag₈⁻(III) is the most stable structure, but this structure is destabilized more than Ag₈⁻(I) as the $\beta(s)$ value increases. The Ag₈⁻(VII) geometry is more stable than Ag₈⁻(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 β 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 β parameters of $\beta(s) = -5.0$ and $\beta(d) = -60.0$ 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

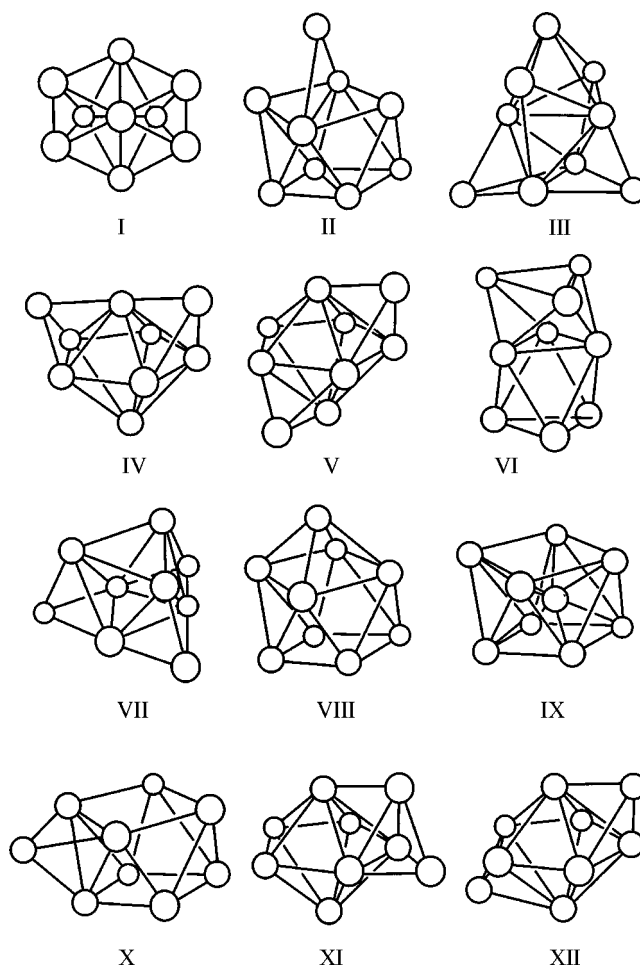


Figure 3. SCF optimized geometries for Ag_9 nonamers.

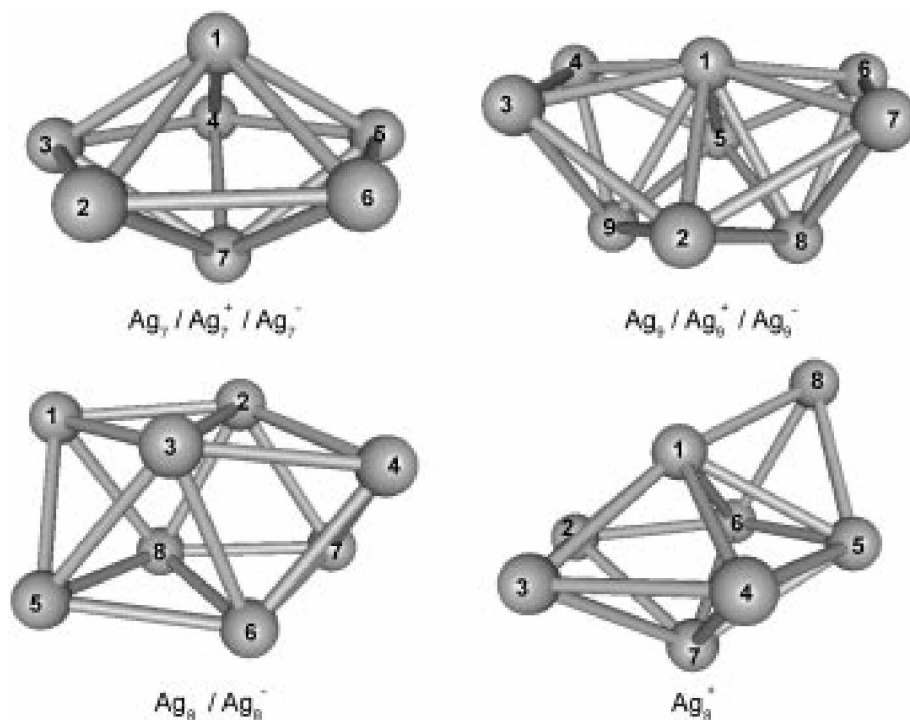


Figure 4. The most stable geometries for the neutral and ionic Ag_7 , Ag_8 and Ag_9 clusters.

the Ag_5^0 (V) in the parameter sets with $\beta(s) = -2.0$ eV. The C_{3v} structure of Ag_5^0 (VII) is more stable than the D_{3h} structure of Ag_5^0 (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_5^0 (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_5^- clusters is similar to that of the cationic nonamers. In the original parameter set, the $\text{Ag}_5^-(\text{III})$ geometry is the most stable structure. However in the other sets, the $\text{Ag}_5^-(\text{I})$ geometry is the most stable structure as the neutral and cationic nonamers. The $\text{Ag}_5^-(\text{III})$ geometry is more stable than $\text{Ag}_5^-(\text{II})$ in the β parameter set of $\beta(s) = -2.0$ and $\beta(d) = -60.0$ eV, but has higher energy with the increase of beta values. The $\text{Ag}_5^-(\text{VIII})$ geometry has lower energy than $\text{Ag}_5^-(\text{VII})$ 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 $\text{Ag}_5^-(\text{X})$ and $\text{Ag}_5^-(\text{XI})$ have relatively lower energies. In the case of $\beta(s) = -5.0$ and $\beta(d) = -80.0$ eV, the C_s structure of $\text{Ag}_5^-(\text{X})$ 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_5^0 D_{3h}	Ag_5^- D_{3h}	Ag_5^+ D_{3h}	Ag_8^0 D_{2d}	Ag_8^- D_{2d}	Ag_8^+ C_s	Ag_9^0 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	$r(1,2)$	2.82	2.82	2.82
$r(1,3)$	2.78	2.80	2.77	$r(4,7)$	2.82	2.75	$r(1,3)$	2.76	2.76	2.76
$r(1,4)$	2.78	2.80	2.77	$r(2,3)$	2.74	2.75	$r(1,8)$	2.93	2.91	2.95
$r(1,5)$	2.78	2.80	2.77	$r(3,6)$	2.74	2.75	$r(3,4)$	2.84	2.84	2.84
$r(1,6)$	2.78	2.80	2.77	$r(6,8)$	2.74	2.75	$r(6,8)$	2.78	2.81	2.76
$r(2,3)$	2.79	2.83	2.76	$r(8,2)$	2.74	2.75	$r(2,7)$	2.81	2.83	2.80
$r(7,2)$	2.78	2.80	2.77	$r(1,2)$	2.78	2.78	$r(5,9)$	2.80	2.81	2.80
$r(7,1)$	2.90	2.87	2.93	$r(5,6)$	2.78	2.78	$r(8,9)$	2.80	2.77	2.84
$a(3,1,2)$	60.2	60.6	59.8	$r(5,8)$	2.78	2.78	$a(3,1,4)$	61.9	61.8	62.0
$a(4,1,2)$	108.5	109.5	107.5	$a(1,2,3)$	60.5	60.5	$a(2,1,5)$	106.6	107.6	105.5
$a(5,1,2)$	108.5	109.5	107.5	$a(1,2,4)$	120.0	119.3	$a(8,1,9)$	57.1	56.8	57.5
$a(6,1,2)$	60.2	60.6	59.8	$a(2,3,5)$	99.3	98.2	$a(2,1,3)$	60.5	61.0	60.1
$a(7,2,1)$	62.6	61.7	64.0	$a(2,3,6)$	80.1	80.7	$a(5,1,6)$	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	$a(6,8,7)$	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	61.3	64.6
$d(1,2,3,7)$	74.1	72.9	75.4	$d(1,2,3,4)$	168.2	166.4	$d(2,3,1,4)$	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	$d(3,4,1,5)$	137.3	138.0	136.6
				$d(3,1,5,8)$	94.6	94.8	$d(3,9,4,1)$	68.0	68.3	67.6
				$d(3,2,1,8)$	95.4	96.1	$d(2,8,9,5)$	137.0	137.0	137.5
				$d(3,6,4,7)$	121.7	122.1	$d(6,5,8,9)$	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 β parameters the structures of the larger Ag clusters will be investigated in the future.

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