

First-Principles Study of Small Oxidized Silver Clusters

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The structure and stability of clusters Ag_nO_m^+ , Ag_nO_m , and Ag_nO_m^- ($n = 1\sim 6$, $m = 1\sim 2$) are studied by using the first-principles method. Calculated results show that the properties studied are strongly dependent on the size and charge state of the clusters, some of which show the odd-even alteration. Generally, the oxidation drives the transition of silver clusters from two-dimensional (2D) to three-dimensional (3D) structures. It is found that the structure with dissociated O_2 is more stable if the silver cluster can provide oxygen with enough electrons.

Keywords: Oxidized Silver Clusters, First Principles, Ground-State Structure.

1. INTRODUCTION

The reaction of transition metal clusters with small molecules has been an active field of experimental and theoretical research.^{1,2} Silver particles are known as a kind of very important heterogeneous catalysts for various oxidations, such as partial oxidation of methanol to form formaldehyde.^{3,4}

For neutral silver clusters, an earlier experimental study reported that neutral Ag_2 was inert against O_2 in a fast flow reactor at room temperature,⁵ however, hydroxide formation was observed in the reactive nucleation of neutral Ag_n with oxygen in the presence of water traces.⁶ Meanwhile the structural and optical properties of small oxygen-doped silver clusters have been theoretically studied by Bonačić-Koutecký et al.⁷ Chen et al. have studied the reaction of Ag^+ with O_2 molecule by using guided ion beam mass spectrometry and found the ground state of Ag^+ reacts with O_2 ineffectively via an impulsive pairwise mechanism, while the excited states react efficiently.⁸ Socaciu et al. have studied the reaction kinetics of the cationic silver cluster Ag_2^+ with O_2 at various temperatures and found the product is Ag_2O^+ with Ag_2O_2^+ as an intermediate of the reaction.⁹ Recently, Schmidt et al. have studied the stability of cationic oxidized silver clusters both experimentally and theoretically. The dissociation of the oxygen molecule and the loss of one oxygen atom have been found when the chemisorption transformed into oxidation. In addition, the small silver clusters undergo a 2D-to-3D structural transition during the oxidation.^{10,11} Besides such kind of kinetics study, equilibrium methods have been carried out to study the bonding

interactions of clusters $\text{Ag}^+(\text{O}_2)_n$ and $\text{Ag}_2^+(\text{O}_2)_n$ experimentally and theoretically.¹² For anionic silver clusters, an earlier report treating the reaction of anionic silver clusters with oxygen showed that clusters with odd Ag atoms exhibit an order of magnitude lower reaction rates than their even counterparts, and anionic silver clusters are inert against CO.¹³ A recent study also reported that oxygen selectively adsorbs on even-numbered Ag_n^- , whereas the odd-numbered Ag_n^- are not chemically active.¹⁴ However, Hagen et al. reported that the anions with even silver atoms adsorbed one O_2 molecule, while the odd ones adsorb up to two O_2 molecules, and silver anions are reactive toward the mixture of O_2 and CO.^{15–18}

In this paper the first principles calculations on the structures and related properties of Ag_nO_m , Ag_nO_m^+ , and Ag_nO_m^- ($n = 1\sim 6$, $m = 1\sim 2$) are carried out to get detailed information about oxidized silver clusters. The results show that the structures and relative properties of the oxidized silver clusters are strongly dependent on the size and charge state of the clusters.

2. CALCULATION DETAILS

Present calculations are based on the density functional theory with Local Spin Density Approximation (LSDA),^{19–21} which are implemented in the VASP code.^{22,23} The interaction between core and valence electrons is described with the projector augmented-wave (PAW) potential.^{24,25} The wave functions are expanded in a plane wave basis set with energy cutoff 282.6 eV. A supercell with a lattice constant of 15 Å is used, which is large enough so that the interaction between the cluster and its periodic images can be neglected. Only the Γ point is used

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for the summation in Brillouin zone. The calculated lattice constants of bulk Ag and Ag_2O are 4.02 Å and 4.67 Å respectively, in good agreement with the experimental values of 4.09 Å and 4.72 Å. In order to get the ground state structure of the oxidized silver clusters, the structures of pure silver clusters are firstly optimized by the conjugate gradient method,²⁶ then oxygen atoms or O_2 molecule are added to the pure silver clusters and the resultant structures are optimized again. Finally, various structures of the oxidized silver clusters are obtained and the structure with the lowest total energy is taken as the ground-state structure.

3. RESULTS AND DISCUSSION

3.1. Ag_nO , Ag_nO^+ , Ag_nO^- for $n = 1\sim6$

First, we optimized the structures of clusters Ag_nO , Ag_nO^+ and Ag_nO^- for $n = 2\sim6$. Figure 1 shows the

ground state structures and corresponding first isomers, of which the total energy is the second lowest. All the ground states of Ag_2O , Ag_2O^+ and Ag_2O^- show a triangle-like structure with O atom located at the side-bridge position. In Ag_2O and Ag_2O^- , two Ag atoms are bound together with bond length of 2.7 Å, while in Ag_2O^+ , two Ag atoms are well separated from each other with a distance of 3.7 Å.

The most stable structures of Ag_3O and Ag_3O^+ are tetrahedron-like with C_{3v} symmetry, in which the O atom occupies the vertex position, in agreement with that reported by both Bonačić-Koutecký and Schmidt.^{7,10} However, the ground state of Ag_3O^- shows planar structure of C_{2v} symmetry with O atom located at the side-bridge site of the silver triangle.

The ground state structures of Ag_4O and Ag_4O^+ can be considered as Ag_4 tetrahedron capped with an oxygen atom, also in agreement with the theoretical results

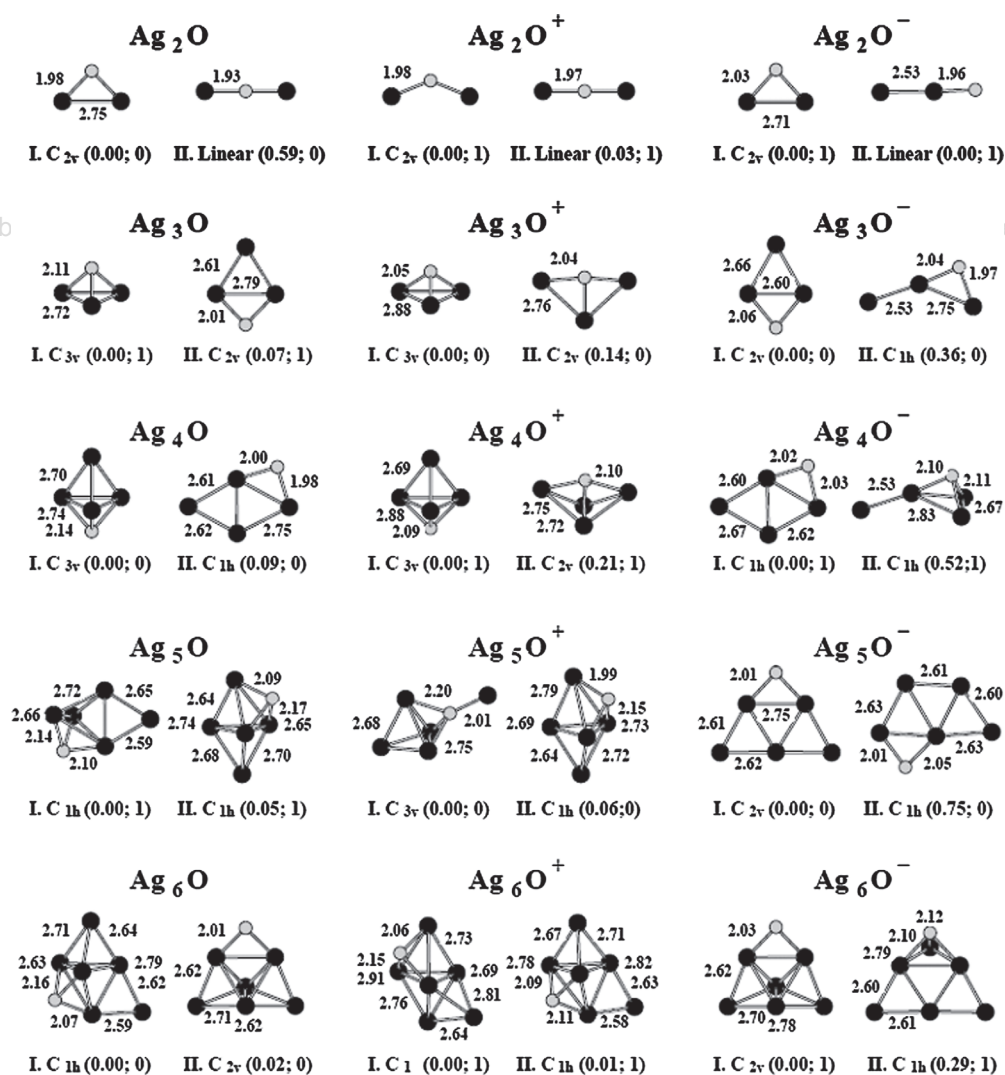


Fig. 1. The optimized structures of Ag_nO , Ag_nO^+ and Ag_nO^- ($n = 2\sim6$). What shown in the bracket are relative energy ΔE (eV) and magnetic moment (μ_B) respectively.

reported by Bonačić-Koutecký and Schmidt.^{7,10} Our calculation shows that Ag_4^+ is also of rhombi structure, while the Ag_4^{2+} and Ag_4^{3+} have tetrahedron structures. Due to the charge transferring, adding an oxygen atom to Ag_4 and Ag_4^+ changes their structures, while the ground state structure of Ag_4O^- can be considered as an oxygen atom capped on the ground state structure of Ag_4^- . The structure difference between Ag_4O^- and Ag_4O^+ (Ag_4O) can be attributed to the charge transfer from metal clusters to the oxygen atom. The ground state structure of Ag_5O can be obtained by capping one Ag atom on one side of the ground state Ag_4O structure. If one more Ag atom is added on the face of the Ag_4O ground state structure, the first isomer of Ag_5O can be obtained. The ground state structure of Ag_5O^+ , which has a C_{3v} symmetry, can be obtained by adding one Ag atom on the top of the oxygen atom of Ag_4O^+ . The ground state structure of Ag_6O can be deduced from the ground state structure of Ag_5O by adding one Ag atom on its triangle face. For Ag_6O^+ , the structure of the ground state can be derived by capping one Ag atom on a triangle face of the first isomer of Ag_5O^+ . Since the bi-capped tetrahedron represents the ground state structure of Ag_6^+ ,²⁶ the ground state structure of Ag_6O^+ can also be considered as an O atom capped on one face of ground state Ag_6^+ . In fact, the ground state structure of Ag_6O^- is very similar to the structure of the first isomer of Ag_6O .

It is interesting to compare the general growth modes of pure silver clusters with oxidized silver clusters. It is well known that pure silver clusters keep the two dimensional growth mode (triangle lattice), for Ag_n up to $n = 6$, for Ag_n^- up to $n = 5$ and for Ag_n^+ up to $n = 4$ or $n = 5$.^{26–30} However, only Ag_nO^- keeps the two dimensional growth mode as Ag_n^- , i.e., the structure transition of Ag_nO^- cluster takes place at $n = 6$. Meanwhile for the neutral and cationic silver clusters, an additional oxygen atom causes the structure to translate a little bit earlier, in which the planar structures of Ag clusters change at $n = 4$. For $n \geq 4$ all the silver atoms in Ag_nO or Ag_nO^+ form a tetrahedron-like structure. Furthermore, all the structures of the neutral and charged Ag_nO clusters can be obtained by capping one more Ag atom on the Ag_{n-1}O cluster.

Some oxidized silver clusters are found to have net magnetic moment, as shown in the brackets of Figure 1. Generally, if the number of the valence electrons of a cluster is even, the total magnetic moment is zero, while if it is odd, the total magnetic moment is $1 \mu_B$. Similar results have been found for the pure silver clusters.²⁶

It is well-known that the ionization potential (IP) and electron affinity (EA) for noble metal cluster show an even-odd alteration.^{26,27,30–33} Figure 2 shows IP and EA of clusters Ag_nO , in which the even-odd alteration is not remarkable but still observable except for AgO cluster. The clusters with even valence electrons have higher IP and lower EA than those with odd valence electrons. In AgO ,

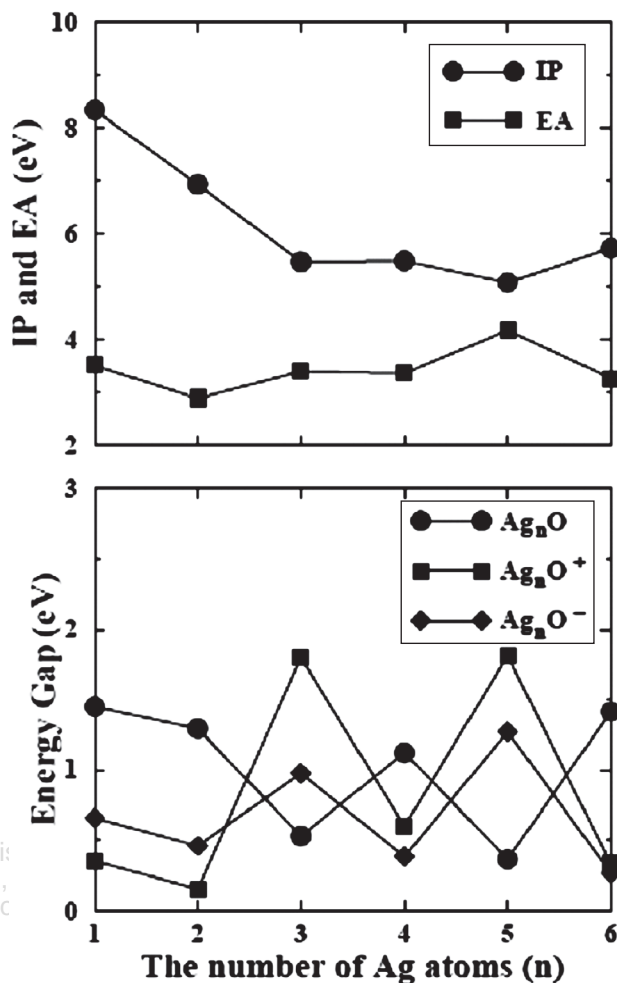


Fig. 2. Top panel: Calculated ionization potential and electron affinity of clusters Ag_nO ($n = 1 \geq 6$). Bottom panel: the calculated HOMO–LUMO gap of clusters Ag_nO , Ag_nO^+ and Ag_nO^- ($n = 1 \geq 6$).

the valence electron of Ag is transferred to oxygen, the ionization of the electrons from the inner shell costs high energy. In the clusters with even valence electrons, the highest occupied molecular orbital (HOMO) is completely filled, resulting in higher IP.

In order to investigate the relative stability and possible dissociation channels of the oxidized silver clusters, we have calculated the dissociation energy (DE) which is defined as $DE = E(A) + E(B) - E(AB)$ for dissociative reaction $AB \rightarrow A + B$, where $E(A)$, $E(B)$ and $E(AB)$ are the total energy of A, B, and AB respectively. DE represents the energy barrier of the dissociation channel, and the most possible channel should have the lowest DE. The DE for various channels is listed in Table I. The most possible dissociation channels are:

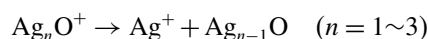
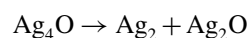
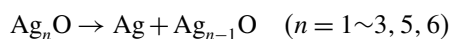
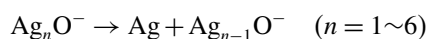
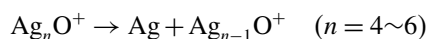


Table 1. Dissociation energy (eV) of Ag_nO^q ($q = 0, +, -$; $n = 1\sim6$) clusters. For the two final products of the dissociation process $AB \rightarrow A + B$, only the smaller one is listed.

Initial cluster	Final product						
	Ag	Ag_2	O	AgO	Ag_2O	Ag^+	Ag^-
AgO	3.17		3.17				
Ag_2O	3.05	3.93	3.93	3.05			
Ag_3O	2.07	2.83	4.63	2.83	2.07		
Ag_4O	2.55	2.33	4.49	4.01	2.33		
Ag_5O	2.30	2.56	4.51	3.62	3.27		
Ag_6O	3.02	3.04	4.56	4.37	3.60		
AgO^+			1.68			1.68	
Ag_2O^+	4.45		3.98	2.96		2.96	
Ag_3O^+	3.54	5.70	3.88	4.35	3.45	3.45	
Ag_4O^+	2.53	3.78	4.59	3.23	3.82	3.91	
Ag_5O^+	2.72	2.95	4.56	4.13	2.90	4.08	
Ag_6O^+	2.38	2.80	4.36	3.76	3.46	4.15	
AgO^-	3.13		3.81				3.81
Ag_2O^-	2.43	3.26	4.41	3.06			3.06
Ag_3O^-	2.59	2.72	4.39	3.83	2.60		2.60
Ag_4O^-	2.52	2.81	4.87	3.74	3.30		3.04
Ag_5O^-	3.12	3.34	5.29	4.82	3.81		3.61
Ag_6O^-	2.12	2.94	4.95	4.23	3.89		3.42



For most of the Ag_nO and Ag_nO^- , the most possible dissociation channel is to eject Ag atom, except that Ag_4O prefers to dissociate into Ag_2 and Ag_2O since both Ag_2 and Ag_2O have the closed electronic shells and lower energy is needed for this dissociation. For Ag_nO^+ , when $n \leq 3$, dissociation tends to eject the Ag^+ ion, while the most probable channel for $n \geq 4$ is to eject one Ag atom, in agreement with Schmidt's experimental results that the stability of Ag_nO^+ dropped for $n \leq 3$.¹⁰ Among all the clusters studied here, AgO^+ possesses the lowest DE of 1.68 eV, and Ag_3O^+ possess the highest DE of 3.45 eV. The lowest DE of AgO^+ indicates that it is very unstable, since the oxygen atom can not get the valence electron from the Ag^+ ion, while Ag_3O^+ is the most stable structure with a closed electronic shell, resulting in a high dissociation energy.

3.2. Ag_nO_2 , Ag_nO_2^+ , Ag_nO_2^- for $n = 1\sim6$

The structures of the ground state and the first isomer of Ag_nO_2 , Ag_nO_2^+ and Ag_nO_2^- ($n = 1\sim6$) are shown in Figure 3. In AgO_2 and AgO_2^+ , the O_2 almost keeps its molecular state, with the O–O bond length of 1.33 Å in AgO_2 and 1.29 Å in AgO_2^+ , compared with the bond length 1.28 Å of an isolated oxygen molecule. The different O–O bond lengths indicate the different charge transfer from silver atom to O_2 molecule. In AgO_2 , one electron is transferred from the Ag atom to the anti-bonding π^* orbital of O_2 state, which increases the bond length of O_2 ,

while in AgO_2^+ , the valence electron of Ag atom is lost, no electron could be transferred to O_2 any more, thus O_2 in AgO_2^+ remains its free molecular state. Ag^+ is inert to O_2 adsorption, this result is in agreement with an experimental study.⁸ For AgO_2 , the two structures shown in Figure 3 have been found to be the ground state structure by previous experimental studies,^{17,18} while in our calculation the O_2 end-on adsorbed structure is more stable than the O_2 side-on adsorbed one. However in Ag_nO_2^- , O_2 is dissociated, much different from that in AgO_2 and AgO_2^+ . In fact, the ground state structure of AgO_2^- is very similar to that of AgO_2^- .³⁴

Ag_2O_2 and Ag_2O_2^- have very similar structures for both ground states and their first isomers. The bond length of O_2 in Ag_2O_2^- is slightly longer than that in Ag_2O_2 , as shown in Figure 3, suggesting that negative charge is mainly located on O_2 molecule. In Ag_2O_2^+ , one of the valence electrons of two Ag atoms is lost, resulting in a half-filled valence shell. Thus the electron left behind can be transferred to O_2 , leading to an increasing of bond length between O atoms, as what happened in AgO_2 . Since two Ag atoms are positively charged, the strong Coulomb repulsion makes them well-separated.

The ground state structure of Ag_3O_2 can be thought as an oxygen molecule capped on one side of Ag_3 triangle. The increase of O_2 bond length (1.37 Å) indicates that O_2 gets electron from Ag_3 , and two electrons are left behind to form a closed shell. Compared with Ag_3O_2 , the cationic silver cluster Ag_3O_2^+ itself has only two valence electrons, leading to the charge transfer from the Ag atoms to oxygen atoms negligible, which is confirmed by the bond length of the O_2 molecule (1.29 Å) in Ag_3O_2^+ . In Ag_3O_2^- , besides two electrons forming a closed electronic shell, two extra electrons can be transferred to O_2 . So in the two most stable structures of Ag_3O_2^- , O_2 is dissociatively adsorbed. In comparing with the experiments, in which the O_2 was found to be molecularly absorbed on the Ag_3^- at room temperature,^{13–16} the present results indicate that the dissociation of O_2 needs to overcome a significant barrier. In fact, we find some structures with O_2 molecularly absorbed, but their energies are higher.

Since Ag_4O_2 and Ag_3O_2^- have the same number of valence electrons, the structure of Ag_4O_2 can be considered as one Ag atom capped on Ag_3O_2^- , as shown in Figure 3. Similarly, the Ag_4O_2^+ and Ag_3O_2 are isoelectronic counterparts, and their ground state structures are similar to each other, in which O_2 molecules are not dissociated. Since O_2 molecule in Ag_4O_2 is already dissociated, adding one more electron to the cluster would not significantly change the structure, the ground state structure of Ag_4O_2^- is therefore very similar to that of Ag_4O_2^+ . It is interesting to mention that, the ground state structures of clusters Ag_nO and Ag_nO^+ change to 3D for $n > 2$, while the structures of the ground state Ag_nO_2 and Ag_nO_2^- remain 2D up to $n = 4$. By comparison, the structure of cluster Au_nO_2 ^{35–38} remains 2D or quasi 2D up to $n = 8$.

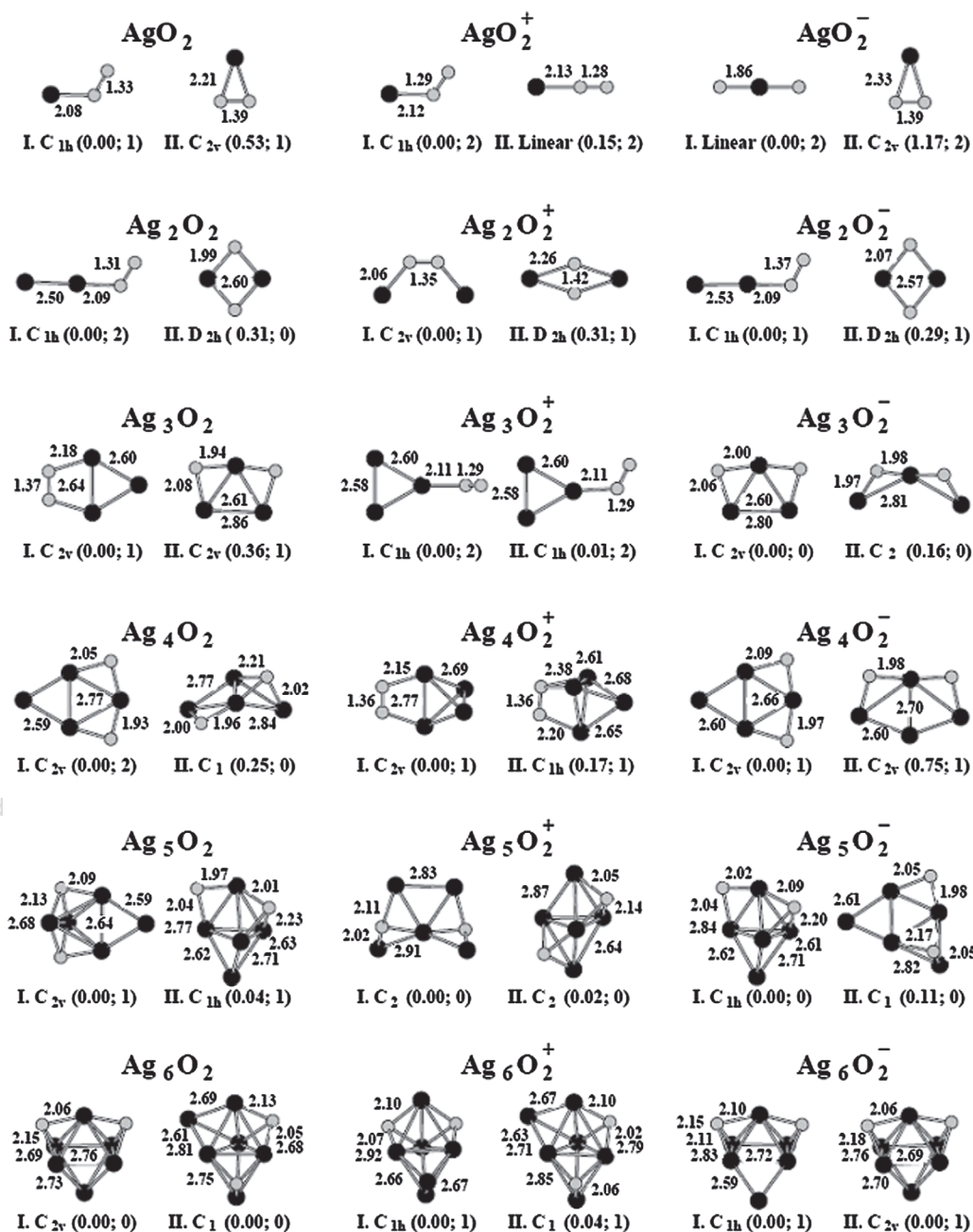


Fig. 3. The optimized structures of Ag_nO_2 , Ag_nO_2^+ and Ag_nO_2^- ($n = 1\sim 6$). What shown in the bracket are relative energy ΔE (eV) and magnetic moment (μ_B) respectively.

The ground state structure of Ag_5O_2 has a C_{2v} symmetry, which can be obtained by capping one oxygen atom on the face of Ag_5O , similarly one can get its first isomer structure from the first isomer of Ag_5O . The ground state structure of Ag_5O_2^- is very similar to the first isomer of Ag_5O_2 , except some differences in bond length. Since the structure of Ag_5O_2^- is 2D, adding one O atom to it drives the structure transition to 3D. We have found that the ground state structure of Ag_5O_2^+ is completely different from that of Ag_5O^+ . However, the first isomer structure of Ag_5O_2^+ can be deduced by capping one O atom on the first isomer of Ag_5O^+ .

For Ag_6O_2 , the present calculation results in two most stable structures essentially with the same energy. The ground state structure has a C_{2v} symmetry, in which O_2 is dissociated and two O atoms are capped on two opposite faces of the silver octahedron, respectively. In the ground state and the first isomer of Ag_6O_2^+ , two O atoms are separately capped on two faces of silver bi-capped tetrahedron Ag_6^+ . For Ag_6O_2^- , the total energy difference between ground state and first isomer is approximately zero. In the ground state structure, five silver atoms form a pyramid with the sixth Ag atom hanging on its side, and two O atoms are crossly capped on two opposite faces

of the silver pyramid. However, the structure of its first isomer is similar to that of the ground state Ag_6O_2 , two O atoms crossly capped on two opposite faces of the silver octahedron.

The discussion above shows that two O atoms can be adsorbed on the clusters Ag_n^q ($q = 0, +, -$) either molecularly or dissociatively. For neutral, cationic and anionic silver clusters of n Ag atoms, one O_2 molecule adsorption is favorable when $n \leq 3$, $n \geq 4$ and $n = 2$, respectively, while two separated O atoms adsorption is favorable when

$n \geq 4$, $n \geq 5$, and $n \neq 2$, respectively. This can be easily understood by examining the charge transfer of the oxidation process. In the larger metal clusters, more electrons can be transferred to the anti-bonding state of O_2 , and O_2 prefers a dissociated state. Ag_n ($n \geq 4$), Ag_n^+ ($n \geq 5$), and Ag_n^- ($n \geq 3$) meet such requirement because they can provide O atoms with enough valence electrons for oxidation.

In the present work some electronic properties of Ag_nO_2^q ($q = 0, +, -$), such as magnetic moment, IP and EA, HOMO–LUMO energy gap and the binding energy of oxygen molecule are also calculated. These properties are very sensitive to the size and charge state of the cluster. The magnetic moment (see Fig. 3) shows the odd-even alteration, similar to that of mono-oxidized silver clusters. For the clusters with even electrons, their magnetic moment is $0 \mu_B$ or $2 \mu_B$, while the magnetic moment of the clusters with odd electrons is $1 \mu_B$. The IP and EA are plotted in the top panel of Figure 4. The EA shows somehow odd-even alteration, while IP decreases monotonically with increasing the cluster size. The middle panel of Figure 4 presents the HOMO–LUMO energy gaps. Like pure and mono-oxidized silver clusters, the energy gaps of ionic Ag_nO_2^+ and Ag_nO_2^- show odd-even alteration, while no significant odd-even oscillation appears for energy gap of neutral Ag_6O_2 . We also calculated the binding energy of O_2 molecule which is defined as $BE(\text{O}_2) = E(\text{Ag}_n^q) + E(\text{O}_2) - E(\text{Ag}_n\text{O}_2^q)$, where q is total charge of the cluster, and E is the ground state energy. As shown in the bottom panel of Figure 4, the binding energy of either neutral or charged cluster shows odd-even oscillation. The clusters with even electrons have relatively lower binding energy. Interestingly, Ag_nO_2^- clusters have higher binding energy than Ag_nO_2 and Ag_nO_2^+ clusters, except for $n = 3$.

4. SUMMARY

In conclusion, we have theoretically studied the oxidized silver clusters containing one and two O atoms, respectively. The results show the structures and physical properties of the oxidized silver clusters are strongly dependent on the size and charge state of the clusters. Generally, compared with the pure silver clusters, oxidation facilitates the transition from 2D structure to 3D structure. Meanwhile, the transition occurs at larger size for the anionic clusters easier than that for the neutral and cationic clusters. For the clusters studied in the present work, it is found that O_2 can be absorbed on silver clusters either molecularly or dissociatively. If the silver cluster can provide enough electrons for oxidation, the dissociated O_2 adsorption is more favorable to the molecular adsorption. Ag atoms prefer to accumulate together, while O atom or O_2 molecule favors to stay at the outer sides or outer faces of the silver cluster. Similar to the pure silver clusters, the odd-even alteration is observed in some physical properties of the oxidized silver clusters. The clusters with even electrons often have higher stability than that with odd electrons.

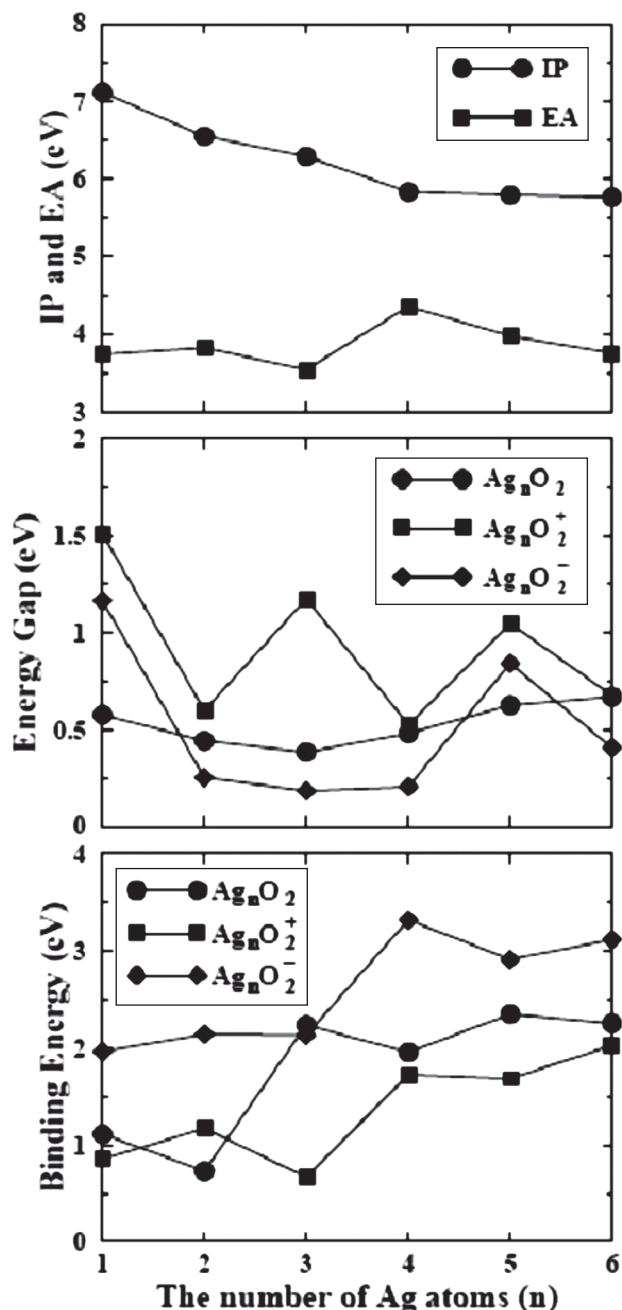


Fig. 4. Calculated ionization potential and electron affinity (top), HOMO–LUMO gap (middle), and binding energy of O_2 molecule (bottom) of clusters Ag_nO_2 , Ag_nO_2^+ and Ag_nO_2^- ($n = 1 \sim 6$).

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