Eur. Phys. J. D **34**, 19–22 (2005)
DOI: 10.1140/epjd/e2005-00103-0

THE EUROPEAN
PHYSICAL JOURNAL D

First-principles study of neutral and charged silver clusters

Yao Wang[1] and X.G. Gong[1,2,a]

[1] Institute of Solid State Physics, Chinese Academy of Sciences, Hefei-230031, P.R. China
[2] Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai 200433, P.R. China

Received 6 September 2004

Abstract. The structures of neutral and charged Ag_n ($n = 3{\sim}6$) clusters are comparably studied by the first principles methods. We find that the neutral silver clusters sustain two dimensional structures up to $n = 6$ and the charged ones undergo a transition from two dimensional structures to three dimensional structures at $n = 6$. The ionization potential, electron affinity and the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital for all these clusters show an oscillating behavior with odd-even valence electron alteration. By calculating the dissociation energy, we have studied the possible dissociation channel of the silver clusters, the results are in agreement with the experiment.

PACS. 61.48.+c Fullerenes and fullerene-related materials – 61.50.Ks Crystallographic aspects of phase transformations; pressure effects – 71.15.Pd Molecular dynamics calculations (Car-Parrinello) and other numerical simulations – 73.63.Fg Nanotubes

1 Introduction

Metal clusters have been extensively studied by both theoretical calculations and experimental measurements for many years [1,2]. It has been found that coinage metal (Cu, Ag and Au) clusters show intriguing physical and chemical properties due to their $d^{10}s^1$ electronic configuration.

Various experiments were performed to understand the structures and stability of the silver clusters. By analyzing the frequencies and intensities of seven vibrational modes, Haslett et al. suggested that the structure of Ag_5 is a planar trapezoidal structure [3]. However, an earlier ESR study [4] indicated that Ag_5 has a three-dimensional (3D) structure, a trigonal-bipyramid, with Jahn-Teller distortion. Kruckeberg et al. studied the low energy dissociation channels of Ag_n^+ ($2 \leq n \leq 22$) using collision-induced dissociation (CID) [5], and found that the main dissociation channel is to lose one atom for Ag_n^+ ($n =$ even) or a dimmer for Ag_n^+ ($n =$ odd). However, by using the similar method, Spasov et al. found that the negatively charged Ag_n^- ($n = 2{\sim}11$) cluster is more favorable to lose one atom for Ag_n^- ($n =$ even) or a dimmer for Ag_n^- ($n =$ odd) [6].

Most of the theoretical work were devoted to the structures of the neutral clusters. Only a few calculations were performed for the charged clusters, where some obvious discrepancies exist. For instances, the structure of Ag_5^+ was found to be a 3D trigonal-bipyramid by Bonačić-Koutecký et al. [7], while recently Huda et al. [8] predicted that it is still a 2D structure with a planar structure. Theoretically, Ag_3^+ was predicted to dissociate into Ag and Ag_2^+, however, the experimental measurements [5] showed Ag_3^+ likes to decompose into Ag^+ and Ag_2. To address these differences observed in the experiments and in the theoretical calculations, in this paper, we perform the first principles calculations on both neutral and charged silver clusters.

2 Calculation details

Our calculations are based on the density functional theory with the spin-polarized Local Density Approximation (LSDA) [9], which are implemented in the VASP code [10]. The interaction between the core and valence electrons is described with the projector augmented-wave (PAW) potential. The wave functions are expanded in a plane wave base with an energy cutoff of 249.8 eV. We use a supercell with a lattice constant of 15 Å, which is large enough so that the interaction between a cluster and its periodic images can be neglected. Due to the large supercell, only the Γ point is used in the summation of the Brillouin zone.

From various initial configurations, the structures of the clusters are optimized by the conjugate gradient method, and the structure with the lowest total energy is taken as the ground-state structure. In order to testify the accuracy of our method, we have calculated the bond lengths of Ag_2, Ag_2^+ and Ag_2^-. The obtained results are 2.49 Å, 2.61 Å and 2.59 Å, which are in a close agreement

---

[a] e-mail: `xggong@fudan.edu.cn`

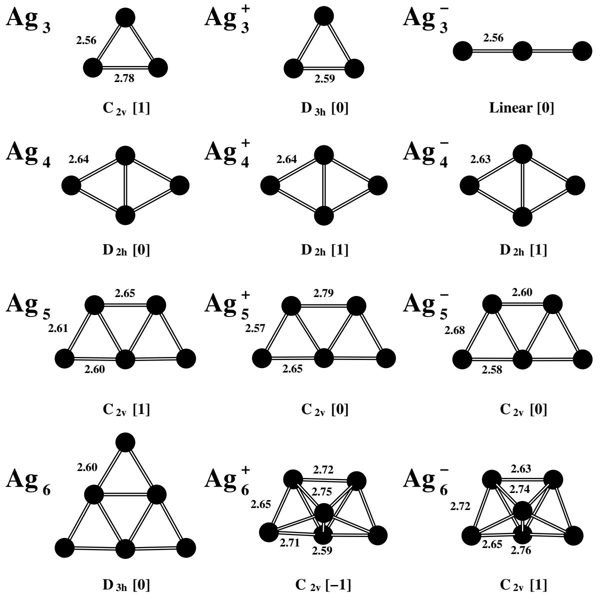

Fig. 1. The optimized ground state structures of neutral and charged Ag_n ($n = 3{\sim}6$) clusters. What shown in the brackets are the magnetic moments (μ_B).

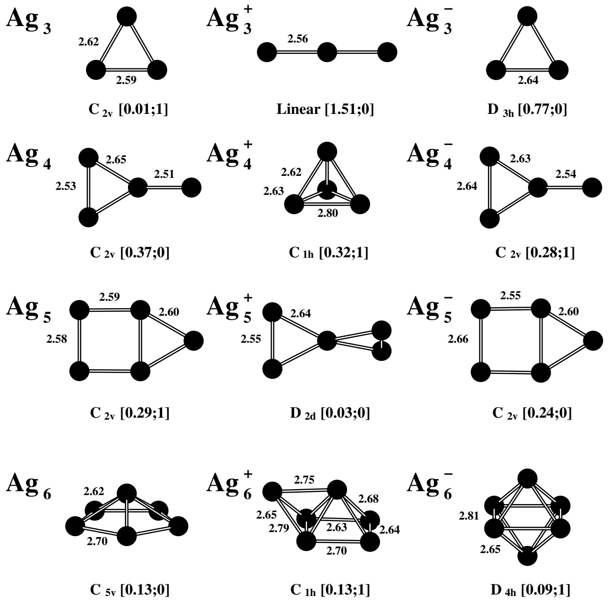

Fig. 2. The structures of the first isomer for the neutral and charged Ag_n ($n = 3{\sim}6$) clusters. What shown in the bracket are the energy (eV) relative to the ground state, and the magnetic moment (μ_B).

with the experimental data, 2.53 Å, 2.63 Å and 2.66 Å, respectively. So these results suggest that the present theoretical method should be appropriate to study Ag clusters.

3 Results and discussions

3.1 The atomic structures

We have studied the structures of Ag_n, Ag_n^+ and Ag_n^- ($n = 3{\sim}6$) clusters. For each cluster, we find several isomers whose binding energies are close to that of the ground state structure, Figure 1 shows the ground state structures for neutral and charged clusters. For Ag_3, the isoceles triangle is the most stable structure, and energy of the obtuse triangle is only slightly lower, 0.008 eV, than that of the acute one. Although the equilateral triangle is highly symmetrical, it is not the ground-state structure due to Jahn-Teller effect, which was strongly suggested by experimental evidences [11–14]. However, the charge on the Ag_3 changes the structure of the cluster. We find that, as shown in Figure 1, the equilateral triangle and the linear structure, which are the isomers of the neutral Ag_3 cluster, becomes the most stable structure for Ag_3^+ and Ag_3^- clusters, respectively. All these results are in agreement with experimental observation and other theoretical calculations [7,8,11,15]. The obtained structure of Ag_4 is a rhombi. Our calculation finds that the energy difference between the ground state structure and its first isomer is about 0.37 eV, the largest difference found in all the studied clusters. Therefore, Ag_4^+ and Ag_4^- clusters still shows the rhombi structure, the charge on the cluster does not change the ground state structure significantly. We find that the structure of Ag_5 is a planar trapezoid, in agreement with most of the other reports [7,8,15]. While a recent theoretical studies by Zhao et al. claimed the ground state should be a deformed trigonal bipyramid [16]. However, in our calculation the energy difference between the planar structure and trigonal bipyramid is as large as 0.4 eV. Our calculations predict that the ground state structure of the charged Ag_5^+ is very similar to that of Ag_5. However, a 3D structure with D_{2d} symmetry, a planar structure with D_{2h} symmetry and a trigonal-bipyramid were found to be the ground state structure of Ag_5^+, respectively [7,8,17]. Contradictorily, these structures are the second, forth, and fifth isomer in our calculations.

For Ag_6, the planar structure (shown in Fig. 1) has the lowest energy and the pentagonal pyramid is the first isomer, which is in agreement with the recent theoretical results [7,8,15]. However, Zhao et al. reported that a bicapped tetrahedron should be the most stable structure [16], which is the ground state structure for both Ag_6^+ and Ag_6^- in the present study. From our calculation, one can conclude that the neutral clusters prefer to the planar structure up to $n = 6$, while both the positively and negatively charged clusters keep the planar structure only up to $n = 5$. In Figure 2, we show the structures of the first isomer for all the calculated clusters. One can see, except for neutral Ag_3, the energy difference between the ground state structure and its isomer decreases as the size of the cluster increasing. In fact, the first isomer of Ag_6 is a three dimensional structure. Meanwhile, in the positively charged cluster, the three dimensional structure of the isomers appeared even in Ag_4^+.

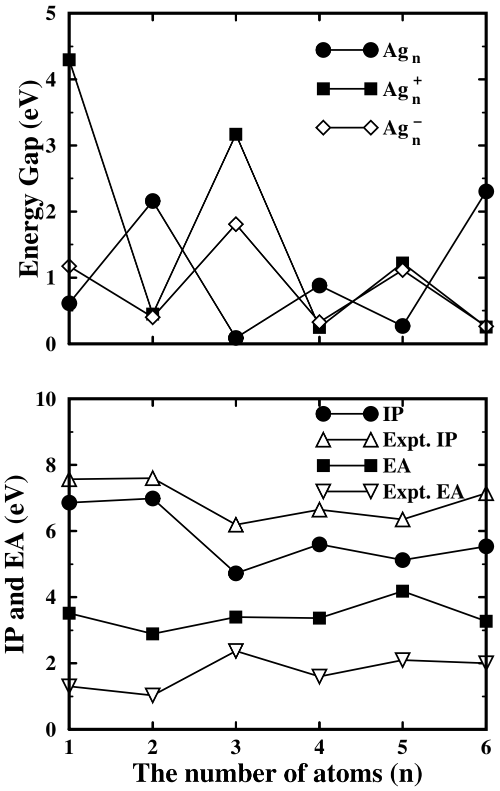

Fig. 3. Upper panel: the calculated HOMO-LUMO gaps of the neutral and charged Ag_n ($n = 1{\sim}6$) clusters. The clusters with even number of electrons show a large HOMO-LUMO gap. Lower panel: the calculated ionization potential and electronic affinity of the neutral and charged Ag_n ($n = 1{\sim}6$) clusters, the experimental data [6,18] are shown for comparison. The general trend of the theoretical results is in agreement with experiment observation.

Table 1. Dissociation energy (eV) of $\mathrm{Ag}_n^{(\pm)}$($n = 3{\sim}6$) clusters. For the final product, we only show the neutral Ag_m in the dissociation process $\mathrm{Ag}_n^{(\pm)} \to \mathrm{Ag}_{n-m}^{(\pm)} + \mathrm{Ag}_m$ ($n > m \geq 1$).

$\mathrm{Ag}_n^{(\pm)}$		Final	Product	Ag_m	
Cluster	Ag	Ag_2	Ag_3	Ag_4	Ag_5
Ag_2	2.29				
Ag_3	1.37	1.37			
Ag_4	2.69	1.77	2.69		
Ag_5	2.28	2.68	2.68	2.28	
Ag_6	2.98	2.96	4.28	2.96	2.98
Ag_2^+	2.16				
Ag_3^+	3.64	3.51			
Ag_4^+	1.81	3.16	3.95		
Ag_5^+	2.75	2.27	4.54	4.01	
Ag_6^+	2.57	3.03	3.47	4.42	4.30
Ag_2^-	1.82				
Ag_3^-	2.61	2.13			
Ag_4^-	2.04	2.35	2.80		
Ag_5^-	2.70	2.45	3.68	2.81	
Ag_6^-	2.46	2.87	3.53	3.45	2.99

3.2 Electronic properties and stability

We have calculated the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Figure 3 shows the HOMO-LUMO gaps for all of the calculated clusters at the ground state structures. Even-odd oscillation of the HOMO-LUMO gap versus the cluster size is observed. The clusters with even valence electrons have larger gap, while those with odd ones have smaller gap. This is because paired valence electrons filled the electron level and thus a large HOMO-LUMO gap opened. Ag_3^+ has the largest gap of 3.2 eV, while Ag_6, Ag_2 and Ag_3^- also have a gap as large as 2.0 eV. However, Huda et al. found this evident even-odd oscillation only occurred in the neutral and cationic clusters [8].

What shown in lower pannel of Figure 3 are the ionization potential (IP) and electron affinity (EA). Both IP and EA appear even-odd alternation. The clusters with even valence electrons have larger IP and smaller EA than those with odd valence electrons. One can attribute it to the electron pairing effect. In the clusters with even valence electrons, the HOMO is completely filled, resulting in a large IP. However, for the clusters with odd valence electrons, taking one electron away would lead to a closed HOMO, so IP is smaller. Comparing to Spasov's and Jackschath's experimental data [6,18], our results show the same trend, however, a systematic difference (~1.0 eV) between the experimental value and the theoretical data has been obtained.

To study the relative stability and the possible dissociation channels of the Ag clusters, we have calculated the dissociation energy (DE), which is defined as $DE = E_{n-m}^{(\pm)} + E_m - E_n^{(\pm)}$ for $\mathrm{Ag}_n^{(\pm)} \to \mathrm{Ag}_{n-m}^{(\pm)} + \mathrm{Ag}_m$ ($n > m \geq 1$), where E_n, E_n^+ and E_n^- are the total energy of Ag_n, Ag_n^+ and Ag_n^-, respectively. DE represents the energy barrier of the dissociation channel, and the most possible channel should have the smallest DE. Table 1 shows the calculated DE of all possible dissociation channels for Ag_n, Ag_n^+ and Ag_n^- clusters. In these cases, two most possible dissociation channels are observed: the clusters with even electrons would like to dissociate a silver dimmer, while the clusters with odd electrons would like to dissociate silver atom. In general, the dissociation of Ag_n, Ag_n^+ and Ag_n^- should follow these principles: $\mathrm{Ag}_n \to \mathrm{Ag}_{n-1} + \mathrm{Ag}$ ($n =$ odd) and $\mathrm{Ag}_n \to \mathrm{Ag}_{n-2} + \mathrm{Ag}_2$ ($n =$ even); $\mathrm{Ag}_n^+ \to \mathrm{Ag}_{n-1}^+ + \mathrm{Ag}$ ($n =$ even) and $\mathrm{Ag}_n^+ \to \mathrm{Ag}_{n-2}^+ + \mathrm{Ag}_2$ ($n =$ odd) $\mathrm{Ag}_n^- \to \mathrm{Ag}_{n-1}^- + \mathrm{Ag}$ ($n =$ even) and $\mathrm{Ag}_n^- \to \mathrm{Ag}_{n-2}^- + \mathrm{Ag}_2$ ($n =$ odd). This result is in good agreement with the experimental measurements of Kruckeberg and Spasov [5,6]. But it does not fully agree with Huda's theoretical study, in which Ag_6 and Ag_3^+ tend to decay silver atom and Ag_6^- tends to decay silver dimmer [8].

4 Summary

In conclusion, we have comparably studied the structures of the neutral and charged Ag clusters. The important quantities, such as HOMO-LUMO gap, ionization potential (IP), electron affinity (EA), and dissociation energy (DE) are obtained. We have found that the neutral silver clusters remain 2D structures up to $n = 6$, while the charged silver clusters undergo a transition from 2D structures to 3D structures at $n = 6$. Our calculations show that, the most possible dissociation channel is: the cluster with odd number of electrons tends to dissociate a silver atom, while the cluster with even number of electrons prefers to dissociate a silver dimer. The obtained results are in close agreement with available experimental data.

YW thanks W. Fan, G. Chen and S.F. Li for the discussions. This work is supported by the National Science Foundation of China, the special funds for major state basic research and CAS projects. Most of the calculations were performed in CCS, HFCAS.

References

1. W.A. de Heer, Rev. Mod. Phys. **65**, 611 (1991)
2. M. Brack, Rev. Mod. Phys. **65**, 677 (1993)
3. T.L. Haslett, K.A. Bosnick, M. Moskovits, J. Chem. Phys. **108**, 3453 (1998)
4. J.A. Howard, R. Sutcliffe, B. Mile, Surf. Sci. **156**, 214 (1985)
5. S. Kruckeberg, G. Dietrich, K. Lutzenkirchen, L. Schweikhard, C. Walther, J. Ziegler, Int. J. Mass Spectrom. Ion Proc. **155**, 141 (1996); S. Kruckeberg, G. Dietrich, K. Lutzenkirchen, L. Schweikhard, C. Walther, J. Ziegler, J. Chem. Phys. **110**, 7216 (1999)
6. V.A. Spasov, T.H. Lee, J.P. Maberry, K.M. Ervin, J. Chem. Phys. **110**, 5208 (1999)
7. V. Bonačić-Koutecký, L. Cespiva, P. Fantucci, J. Koutecký, J. Chem. Phys. **98**, 7981 (1993); V. Bonačić-Koutecký, L. Cespiva, P. Fantucci, J. Pittner, J. Koutecký, J. Chem. Phys. **100**, 490 (1994); V. Bonačić-Koutecký, V. Veyret, R. Mitric, J. Chem. Phys. **115**, 10450 (2001)
8. M.N. Huda, A.K. Ray, Eur. Phys. J. D **22**, 217 (2003); M.N. Huda, A.K. Ray, Phys. Rev. A **67**, 013201 (2003)
9. J.P. Perdew, A. Zunger, Phys. Rev. B **23**, 5048 (1981)
10. G. Kresse, J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996); G. Kresse, J. Furthmuller, Phys. Rev. B **54**, 11169 (1996); G. Kresse, J. Joubert, Phys. Rev. B **59**, 1758 (1999); P.E. Blochl, Phys. Rev. B **50**, 17953 (1994)
11. T. Leisner, S. Vajda, S. Wolf, L. Woste, J. Chem. Phys. **111**, 1017 (1999)
12. D.W. Boo, Y. Ozaki, L.H. Andersen, W.C. Lineberger, J. Phys. Chem. A **101**, 6688 (1997)
13. F. Wallimann, H.-M. Frey, S. Leutwyler, M. Riley, Z. Phys. D **40**, 30 (1997)
14. E.E. Wedum, E.R. Grant, P.Y. Cheng, K.F. Willey, M.A. Duncan, J. Chem. Phys. **100**, 6312 (1994)
15. Z.F. Liu, W.L. Yim, J.S. Tse, J. Henfer, Eur. Phys. J. D **10**, 105 (2000)
16. J. Zhao, Y. Luo, G. Wang, Eur. Phys. J. D **14**, 309 (2001)
17. P. Weis, T. Bierweiler, S. Gilb, M.M. Kappes, Chem. Phys. Lett. **355**, 355 (2002)
18. C. Jackschath, I. Rabin, W. Schulze, Z. Phys. D **22**, 517 (1992)