Structural and electronic properties of Al_7I_n ($n = 1, 2, 3$)

Shi-Hao Wei, Li Huang, M. Ji, X.G. Gong *

Surface Physics Laboratory, Department of Physics, Fudan University, Shanghai 200433, PR China

Abstract

Based on the density functional theory with gradient corrected exchange–correlation potential, we have studied the atomic structures and electronic properties of Al_7I_N ($N = 1, 2, 3$) and $Al_{13}I$ clusters. The atomic structure of Al_7 is not significantly changed by doping three iodine atoms. However, the adsorption positions of iodine atoms are dependent on the charge state of Al_7I_n cluster. Analyzes of the electronic structure of $Al_7I_n^-$ cluster shows that some of the electrons are transferred to iodine atom, although most electrons in the highest occupied molecular orbits distribute around the aluminum atoms.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

The stability of atomic cluster has been one of the most important subjects in the cluster science. The geometric packing and the electronic shell closing are two key ingredients for the stability of the cluster [1–11]. For small clusters, icosahedral cluster with thirteen atoms, is the most closely packed, which should be very stable from the geometrical point of view [8,12,13]. In fact, many metal clusters [8] and inert gas clusters [14,15] adopt such a structure. The jellium model, proposed about twenty years ago [2,3], can correctly predict electronic shells closing at the number of valence electrons $N = 8, 10, 20, 34, 40, \ldots$ This model has been confirmed by various experiments in alkali-metal and other simple clusters [3,4,16].

The ground state structure of Al_7 is a capped octahedron with C_{3v} symmetry, while the ground state structure of Al_{13} cluster is an icosahedron. Both of the two structures should be geometrically stable. Coincidentally, the electronic shell of both clusters are close to closed [7]. Al_7 with 21 valence electrons is one-electron more to 2s shell, and Al_{13} with 39 valence electrons is one-electron deficiency to 1d shell. Therefore, the charged Al_7^+ and Al_{13}^- clusters are both geometrically and electronically sta-

ble. Both clusters show significant energy gap between the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO), which is ~1.6 eV for Al_7^+ [17], and ~1.8 eV for Al_{13}^- [18], respectively. The high stability of these two clusters had been confirmed by experiments. Theoretically, much attention has been paid to Al_{13}, partially due to its high symmetry and spherical-like shape. Since Al_{13} had been proposed as a building block for cluster assembled materials, many studies have tried to make the electronic shell of Al_{13} cluster closed by doping with other atoms [18–21], such as C or Si.

Very recently, density functional calculation, combined with experiment, was performed on the $Al_{13}I^-$ cluster [22]. It was found that Al_{13} shows the superhalogen behavior with HOMO electrons distributed around the aluminum opposite to the iodine atom. In this Letter, in order to understand more details of the electronic structure in aluminum clusters doped with iodine atoms, the structural and electronic properties of Al_7I_n ($n = 1, 2, 3$) clusters are calculated in comparison with that of $Al_{13}I$ cluster.

2. Calculation details

Present calculations are based on the spin polarized density functional theory. The Perdew and Wang (PW91) [23] gradient corrected functional is adopted for the

---

* Corresponding author.
  E-mail address: xggong@fudan.edu.cn (X.G. Gong).

exchange–correlation potential. The linear combinations of atomic-like orbitals are used as the basis functions, which are implemented in **DMOL**[3] [24,25]. All the atomic orbitals, including all the core orbitals and valence orbitals (3s3p3d for Al and 5s5p5d for I), are used as the basis functions.

In the optimization of the total energy, the electrons are kept on the lowest orbitals, while the occupation numbers in each of the orbitals are integers. The geometry optimization is performed by moving atoms along the direction of forces, with the accuracy of 1.5×10^{-4} eV/a.u. In order to check the accuracy of the present method, we have calculated the aluminum and iodine dimer, the obtained bond lengths are 2.49 and 2.75 Å, respectively, which are in agreement with the experimental data, 2.56 Å [21] and 2.67 Å [26].

3. Results and discussion

We have first optimized the structure of $Al_{13}I$ and $Al_{13}I^-$ cluster. The iodine atom is found to be capped on the bridge site of the icosahedral Al_{13}, with a distance of 2.83 Å between the iodine and aluminum atom. Although the main frame of the Al_{13} cluster remains, a significant distortion is observed. The largest change of the bond lengths can be as large as 0.4 Å. In the negatively charged clusters, we find that the top position of the iodine atom becomes the most stable, as shown in Fig. 1. We also notice that the distortion of the Al_{13} in $Al_{13}I^-$ is smaller than that in its neutral counterpart. The overall structural properties, are in agreement with Bergeron's results [22].

The obtained structures of the ground state and the first isomer for Al_7I, Al_7I_2 and Al_7I_3 clusters are shown in
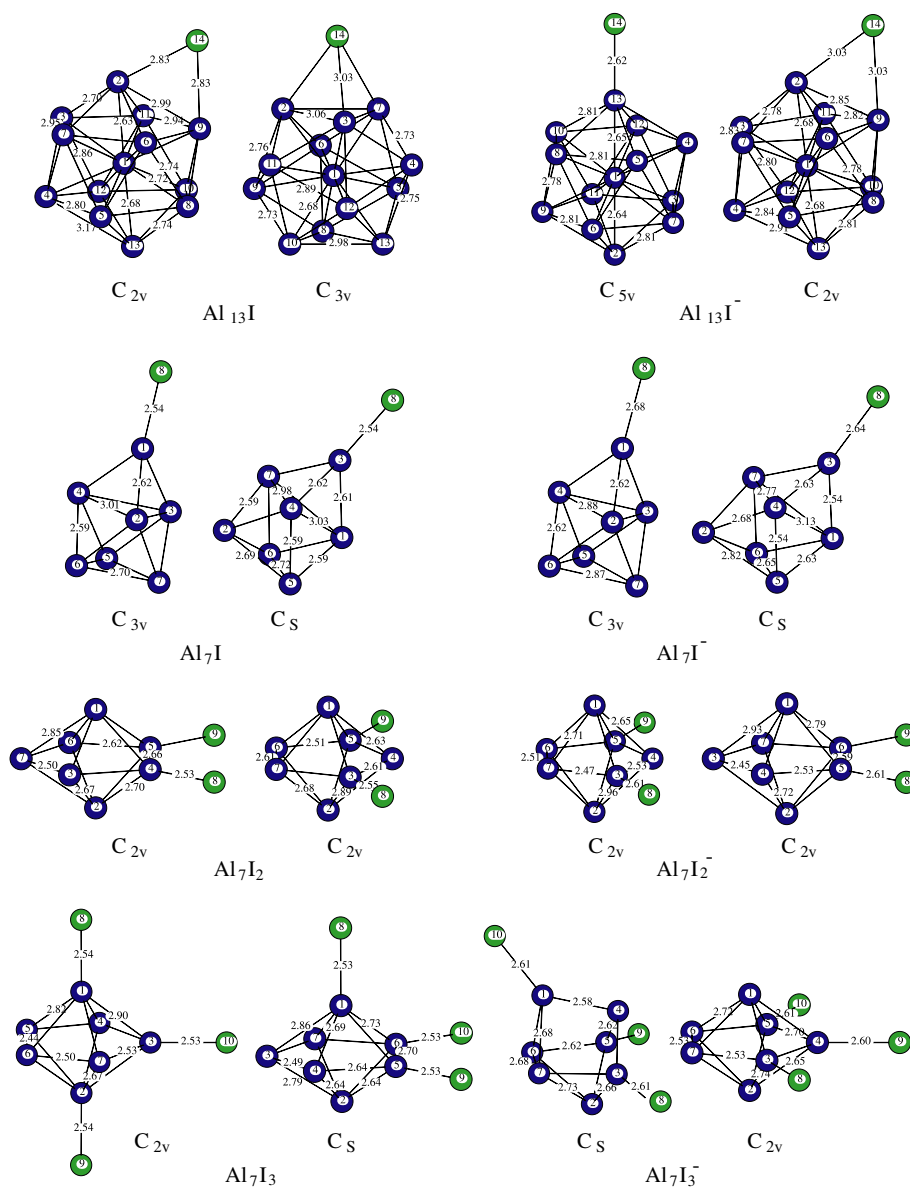

Fig. 1. Ground state structures (left) and their lowest energy isomers (right) for neutral and negatively charged aluminum cluster doped with iodine atoms. The bond lengths (in Å) are shown along the bond.

Table 1
The binding energy E_b (eV) and the HOMO–LUMO gap E_g (eV) for the neutral and charged Al_7, Al_{13} clusters

Al_7^{2+}			Al_7^+			Al_7			Al_7^-		
Symmetry	E_b	E_g	Symmetry	E_b	E_g	Symmetry	E_b	E_g	Symmetry	E_b	E_g
C_s	0.497	0.347	C_s	−10.530	1.972	C_{3v}	−16.311	0.800	C_s	−18.326	0.738
C_{3v}	0.496	0.348	C_{3v}	−10.527	1.971	C_s	−16.309	0.800	C_{3v}	−18.300	0.000
D_{5h}	0.911	0.651	D_{5h}	−9.728	1.180	C_{2v}	−15.734	0.415	C_{2v}	−17.862	0.548

Al_{13}^+			Al_{13}			Al_{13}^-		
Symmetry	E_b	E_g	Symmetry	E_b	E_g	Symmetry	E_b	E_g
C_s^1	−28.753	1.262	D_{3h}	−34.451	0.000	I_h	−38.005	1.833
C_s^2	−28.339	0.975	C_s^1	−34.439	0.644	D_{5h}	−37.580	1.498
O_h	−28.269	0.000	I_h	−34.396	0.000	D_{3h}	−37.269	1.472

Fig. 1. It is re-confirmed that the structure of bare Al_7 cluster is a capped octahedron [27]. The first isomer has similar structure of the ground state, but with a lower symmetry, as shown in Table 1. One iodine atom adsorbed on Al_7 cluster does not change the main frame structure of Al_7. With addition of the second and the third iodine atom, the structure of Al_7 becomes a bi-pyramid. In Al_7I_2, two iodine atoms are adsorbed on the aluminum atoms of the five-member ring. While in Al_7I_3, two iodine atoms are capped on the top of two apex atoms in bi-pyramid-like structure, another I atom is still capped on one aluminum atom in the five-member ring. To understand why the structure of Al_7 changes with I atoms added, we have calculated the binding energies of Al_7 of different charged states. The results show that, the energy difference between the ground state and bi-pyramid structure decreases when Al_7 is more positively charged. As more I atoms are capped on Al_7 cluster, more and more electrons in the Al_7 are transferred to I atoms, which leads to the structural transitions from capped octahedron to bi-pyramid.

As one can see from Fig. 1, the negative charge on Al_7I^- does not change the adsorption site of iodine atom. However, there are some changes for $Al_7I_2^-$ and $Al_7I_3^-$ cluster (see Fig. 1). For $Al_7I_2^-$, charging only reverses the relative stability for the ground state structure and the isomer structure. However, for $Al_7I_3^-$, the adsorption of iodine atoms results in a structure much different from that of its neutral cluster. Generally, due to the repulsive interaction, the charging will expand the cluster. In fact, the bond length between iodine atom and the closest aluminum atom is increased by ∼0.1 Å.

Table 2 shows the binding energies, electron affinities and ionization potentials of the calculated clusters. For Al_7 and Al_{13}, the calculated ionization potentials are 5.78 and 5.69 eV, the electron affinities are 2.01 and 3.56 eV, respectively, which are comparable to the experimental data of 6.3 and 6.5 eV for the ionization potential [5], 2.55 and 3.75 eV for electron affinities [28]. These results are in agreement with previous theoretical prediction [17]. The binding energies for the first, second and third iodine atom on Al_7 are about 3.41, 2.00 and 3.00 eV, respectively. Correspondingly, the electron affinity for Al_7I, Al_7I_2 and

Table 2
The binding energies E_b and electron affinity E_A for the neutral clusters

Cluster	Symmetry	E_b (eV)	E_g (eV)	E_A (eV)	E_{IP} (eV)
Al_7	$C_{3v}(C_s)$	0.000 (0.000)	0.800 (0.738)	2.016	5.781
	$C_s(C_{3v})$	0.002 (0.026)	0.800 (0.000)	1.991	5.782
Al_7I	$C_{3v}^1(C_{3v}^1)$	−3.413 (−3.469)	1.760 (0.000)	2.071	6.994
	$C_{3v}^3(C_s^1)$	−3.411 (−3.411)	1.748 (0.674)	2.015	7.058
Al_7I_2	$C_{2v}^3(C_{2v}^2)$	−5.420 (−6.626)	0.486 (1.440)	3.221	6.841
	$C_{2v}^2(C_{2v}^3)$	−5.364 (−6.573)	0.284 (1.142)	3.224	6.855
Al_7I_3	$C_{2v}^1(C_s^2)$	−8.417 (−9.384)	0.973 (0.480)	2.983	6.798
	$C_s^1(C_{2v}^3)$	−8.160 (−9.275)	0.922 (0.449)	3.130	6.589
Al_{13}	$D_{3h}(I_h)$	0.000 (0.000)	0.000 (1.833)	3.554	5.697
	$C_s^1(D_{5h})$	0.012 (0.424)	0.644 (1.498)	3.142	6.100
$Al_{13}I$	$C_{2v}(C_{5v})$	−2.975 (−2.409)	1.201 (0.715)	2.988	6.148
	$C_{3v}(C_{2v})$	−2.925 (−1.895)	1.371 (0.329)	2.523	6.363

The values in the parenthesis are those of their corresponding anion counterparts. The E_b of Al_7 is set to zero.

Al_7I_3 are 2.10, 3.22 and 2.98 eV, respectively, i.e., the cluster with larger binding energy has a smaller electron affinity. The relatively large binding energies and small electron affinities suggest that, the Al_7I and Al_7I_3 cluster should be very stable. This is further confirmed by the large HOMO–LUMO gap of these two clusters.

In fact, the stability of Al_7 cluster doped with iodine atoms can be qualitatively understood by the electronic shell structure. Al_7 has 21 valence electrons and iodine atom is of one-electron deficiency in respect to a closed shell, therefore Al_7I has 20 electrons with a closed electron shell predicted by the jellium model, with a large HOMO–LUMO gap of 1.76 eV. In this sense, Al_7I_2 cluster with 19 electrons must be energetically less stable, and has a largest E_A among all the studied clusters. While Al_7I_3 cluster has 18 electrons just filling the sub-electron shells to 1d, so it should also be energetically stable with a large HOMO–LUMO gap up to 0.97 eV which is about half of the energy gap of Al_7I. The above discussion indicates that the bond between Al_7 cluster and iodine atom is ionic.

If one just concerns the number of valence electrons, $Al_{13}I$ and Al_7I_3 are similar, in the sense that both of them

have two electron deficiency in respect to a close electronic shell. In order to see if Al_7I_3 cluster has similar behavior, we have calculated the density distribution of HOMO for $Al_{13}I^-$ and $Al_7I_3^-$, as shown in Fig. 2A,C. We do find that most of HOMO electrons of $Al_{13}I^-$ are distributed around the aluminum atoms farthest from the iodine atom, which is in close agreement with recent theoretical results [22]. In $Al_7I_3^-$ cluster (Fig. 2C), the HOMO electrons are also mostly distributed around the Al atoms away from iodine atoms. This is qualitatively confirmed by the Mulliken
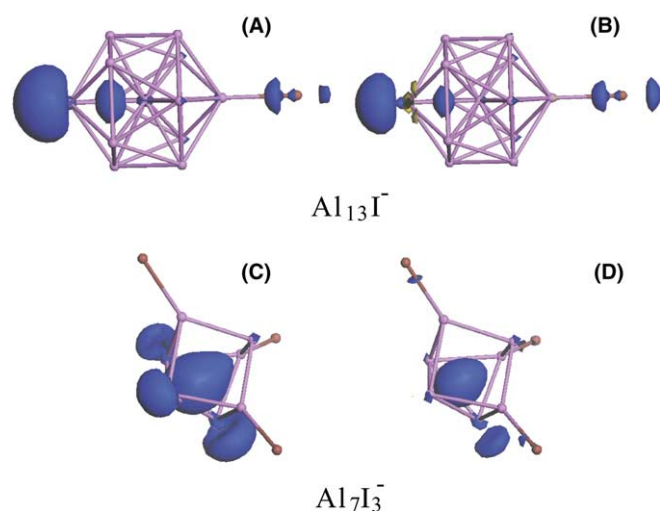
Isosurface=0.015

Fig. 2. Charge density distribution of the HOMO (A,C), the total charge density difference between $Al_{13}I^-$ and $Al_{13}I$ (B), and between $Al_7I_3^-$ and Al_7I_3 (D). Most of HOMO electrons are distributed on the Al atom which is far from I atom.

occupation number as shown in Table 3. In $Al_{13}I^-$, about half of the HOMO electrons are at the aluminum atom labelled with number 2 in Fig. 1. In $Al_7I_3^-$ cluster, less than 7% of HOMO electrons sit on iodine atoms.

It is well known, charging on the cluster could lead to redistribution of charge density, and sometimes even structural transformations [29]. The distribution of HOMO density of $Al_{13}I^-$ and $Al_7I_3^-$, which is mainly around the aluminum atoms, does not necessarily mean that the distribution of net charge on the clusters is also around the aluminum atoms. To make this issue more clear, the difference of the charge density between the neutral and charged clusters, $\Delta\rho$, is calculated, and shown in Fig. 2B,D. The obvious difference can be observed. By examining the HOMO density which is mainly distributed on the aluminum atom farthest from iodine atom, one can see that $\Delta\rho$ is distributed on both aluminum atoms and iodine atom. For $Al_7I_3^-$ cluster, the very similar results can be observed. This can be confirmed by the partition of $\Delta\rho$ to each atom (see Table 3), and the occupation number relative to the free atoms. One can easily find that there is significant charge transfer from aluminum cluster to iodine atom. The non-negligible $\Delta\rho$ on iodine atom suggests that, some negative charge has been transferred to the iodine atom. The very small amount of HOMO electrons on the iodine atom does not indicate that the whole negative charge goes to the aluminum atoms. These results suggest that the charge transfer between the aluminum cluster and iodine atom can not simply determined by the electron affinities (ionization potentials) of the isolated aluminum cluster and iodine atom. Due to strong hybridization interaction between aluminum cluster and iodine atom, the charge transfer can occur from neutral aluminum cluster to the iodine atom in the iodine doped aluminum clusters.

Table 3
The occupation numbers on each atom partitioned from HOMO (n), the difference of the charge density ($\Delta\rho$) between the negatively charged cluster and the neutral cluster

$Al_{13}I^-$	I(14)	Al(1)	Al(2)	Al(3) × 5	Al(4) × 5	Al(13)	
	0.077	0.091	0.470	0.014	0.035	0.118	
	0.149	−0.028	0.149	0.070	0.075	0.003	
	−0.417	0.159	−0.076	−0.088	−0.089	0.220	
$Al_7I_3^-$	I(8) × 2	I(10)	Al(1)	Al(2)	Al(3) × 2	Al(4)	Al(6) × 2
	0.020	0.028	0.058	0.287	0.050	0.058	0.215
	0.123	0.126	0.037	0.141	0.040	0.105	0.132
	−0.427	−0.426	0.260	−0.099	0.244	−0.141	−0.113
$Al_7I_2^-$	I(8) × 2	Al(1) × 2	Al(3) × 2	Al(4)	Al(6) × 2		
	0.026	0.200	0.166	0.017	0.101		
	0.123	0.151	0.037	0.122	0.129		
	−0.443	−0.096	0.252	−0.139	−0.147		
Al_7I^-	I(8)	Al(1)	Al(2) × 3	Al(5) × 3			
	0.012	0.105	0.113	0.181			
	0.181	0.142	0.153	0.073			
	−0.519	0.110	−0.146	−0.052			

The number N is the electrons on the atoms in the negatively charged cluster relative to the free atoms. The values in the parenthesis are the atom numbers shown in Fig. 1.

4. Summary

We have performed the density functional calculation on Al_7 and Al_{13} clusters doped with the iodine atoms. The obtained ground state structures of $Al_{13}I$ and $Al_{13}I^-$ are in close agreement with recent theoretical data [22]. It is found that in Al_7I cluster, iodine atom is capped on the ground state structure of Al_7 cluster. The capping of the second and third I atoms drives the structure of Al_7 from capped octahedron-like to bi-pyramid-like, indicating that some electrons have been transferred to I atoms.

The density distribution of HOMO electrons for $Al_{13}I^-$ and $Al_7I_3^-$ are found to be mainly localized on the aluminum atom farthest from the iodine atom, in consistent with the qualitative analysis of occupation number of HOMO. However, we find that the charge on the cluster result in a significant redistribution of the charge density, the calculation of the total charge difference between the neutral and charged clusters suggests that the net charge can be located on iodine atoms and also on aluminum atoms. Therefore, one needs to pay much caution on the superhalogen on these two clusters.

Acknowledgements

References

[1] O. Echt, K. Sattler, E. Rechknagel, Phys. Rev. Lett. 47 (1981) 1121.
[2] W. Ekardt, Phys. Rev. B 29 (1984) 1558.
[3] W.D. Knight, K. Clemenger, W.A. de Heer, W.A. Saunders, M.Y. Chou, M.L. Cohen, Phys. Rev. Lett. 52 (1984) 2141.
[4] K. Clemenger, Phys. Rev. B 32 (1985) 1359.
[5] K.E. Schriver, J.L. Persson, E.C. Honea, R.L. Whetten, Phys. Rev. Lett. 64 (1990) 2539.
[6] T.P. Martin, T. Bergmann, H. Gohlich, T. Lange, Chem. Phys. Lett. 172 (1990) 209.
[7] X. Li, H. Wu, X.B. Wang, L.S. Wang, Phys. Rev. Lett. 81 (1998) 1909.
[8] M. Sakurai, K. Watanabe, K. Sumiyama, K. Suzuki, J. Chem. Phys. Lett. 111 (1999) 235.
[9] M. Calleja, C. Rey, M.M.G. Alemany, L.J. Gallego, P. Ordejón, D. Sánchez-Portal, E. Artacho, J.M. Soler, Phys Rev B 60 (1999) 2020.
[10] S.H. Wei, Zhi Zeng, J.Q. You, X.H. Yan, X.G. Gong, J. Chem. Phys. 113 (2000) 11127.
[11] O.C. Thomas, W.J. Zheng, K.H. Bowen Jr., J. Chem. Phys. 114 (2001) 5514.
[12] M. Castro, S.R. Liu, H.J. Zhai, L.S. Wang, J. Chem. Phys. 118 (2003) 2116.
[13] Z.Q. Li, B.L. Gu, Phys. Rev. B 47 (1993) 13611.
[14] D. Prekas, C. Lüder, M. Velegrakis, J. Chem. Phys. 108 (1998) 4450.
[15] D.C. Athanasopoulos, Surf. Sci. 462 (2000) 55.
[16] R. Fournier, J.B.Y. Cheng, A. Wong, J. Chem. Phys. 119 (2003) 9444.
[17] B.K. Rao, P. Jena, J. Chem. Phys. 111 (1999) 1890.
[18] X.G. Gong, Vijay Kumar, Phys. Rev. Lett. 70 (1993) 2078.
[19] J.J. Zhao, B.C. Liu, H.J. Zhai, R.F. Zhou, G.Q. Ni, Z.Z. Xu, Solid State Commun. 122 (2002) 543.
[20] V. Kumar, V. Sundararajan, Phys. Rev. B 57 (1998) 4939.
[21] S.N. Khanna, P. Jena, Phys. Rev. Lett. 69 (1992) 1664.
[22] Denis E. Bergeron, A. Welford Castleman Jr., Tsuguo Morisato, Shiv N. Khanna, Science 304 (2004) 84.
[23] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
[24] B. Delley, J. Chem. Phys. 92 (1990) 508.
[25] B. Delley, J. Chem. Phys. 94 (1991) 7245.
[26] K.P. Huber, G. Herzberg, Constants of Diatomic Molecules, Van Nostrand-Reinhold, New York, 1979.
[27] R.O. Jones, J. Chem. Phys. 99 (1993) 1194.
[28] K.J. Taylor, C.L. Pettiette, M.J. Graycraft, O. Chesnovsky, R.E. Smalley, Chem. Phys. Lett. 152 (1988) 347.
[29] S.F. Li, X.G. Gong, Phys. Rev. B 70 (2004) 75404.