2000

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Rao, B. K., Jena, P. Alkalization of aluminum clusters. The Journal of Chemical Physics 113, 1508 (2000).

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(Received 8 February 2000; accepted 27 April 2000)

Equilibrium geometries, binding energies, ionization potentials, and electron affinities of neutral and charged Al_n clusters ($n \leqslant 8$) decorated with alkali atoms such as Li and K have been calculated using molecular orbital theory based on density functional formalism and generalized gradient approximation. While the electron affinities and the ionization potentials depend on size, no clear signatures of shell closings are found in this size range. Similar studies on Al_5X_m (X=Li, K, $1 \leqslant m \leqslant 4$) also fail to provide any indication consistent with shell closings. On the other hand, the ionization potentials and electron affinities of aluminum clusters decrease with the addition of alkali atoms. The results are in good agreement with available experimental data. © *2000 American Institute of Physics.* [S0021-9606(00)30728-0]

While a considerable amount of work has been published on the structure and properties of clusters consisting of only one kind of atom, not much attention has been paid to the study of properties of heteroatomic clusters. This is particularly surprising as even dilute impurities are known to change the properties of bulk materials significantly. In small clusters, a single impurity atom amounts to a large concentration and thus the properties of heteroatomic clusters are expected to be substantially influenced due to the presence of impurities. Consider, for example, the adsorption of alkali metals on transition metal surfaces. It is known to lower the work function of transition metals and hence alkali metals are used as promoters in catalysts.[1] This lowering is caused by the fact that the ionization potentials of alkali atoms are lower than those of transition metal atoms. The ionization potentials of alkali atoms vary from 5.39 eV in Li to 3.89 eV in Cs while in the early part of the $3d$ series, namely from Sc to Cr, these vary from 6.56 to 6.76 eV. Thus, alkali atoms lose their outermost s electron to the transition metal hosts which, in turn, lowers the work function of the host surfaces.

In this context, study of the interaction of alkali atoms with small aluminum clusters containing less than 15 atoms is interesting as the ionization potentials (IPs) of these clusters are around 6.3 ± 0.2 eV and are comparable to the IPs of the early transition metal atoms. Thus, one would expect the IPs of aluminum clusters to be lowered upon adsorption of alkali atoms. Second, the electronic shell structure of aluminum clusters may be more readily studied with the addition of alkali atoms. Since the electronic shell closings[2] occur for free-electron clusters containing 2, 8, 20, 40, ..., electrons and Al is trivalent, pure Al clusters cannot satisfy electronic shell closing, except for those shell closings in which the number of valence electrons are divisible by a common multiple of three. The smallest cluster in which this can happen is Al_{46}.

Recently the electronic structure of aluminum clusters has been studied systematically by photodetachment spectroscopy[3] and by *ab initio* theory.[4] The electronic structure of small aluminum clusters containing less than seven atoms is found to be consistent with aluminum being monovalent, while for larger clusters it behaves as a trivalent species. This behavior is rooted in the electronic structure of the aluminum atom itself. It has a $3s^2 3p^1$ configuration with an energy gap of approximately 5 eV separating the $3s^2$ and $3p^1$ shell. Thus, in small clusters where the hybridization of s and p shells is expected to be small, aluminum would behave as a monovalent atom, while in larger clusters the increased s-p hybridization would allow aluminum to assume its normal valence of three. The question then is: Do small aluminum clusters behave like free-electron systems as alkalies do? If so, then $Al_{8-n}X_n$ clusters would contain eight-valence electrons—sufficient for $1s^2 1p^6$ shell closure. These clusters should not only be energetically more stable than their neighbors, but also should exhibit high ionization potential and low electron affinity—consistent with electronic shell closure.

While some earlier works on alkali–aluminum clusters are available,[5–7] to our knowledge, no systematic theoretical studies have been carried out to address the above-mentioned issue. In a recent experiment, Nakajima *et al.*[8] measured the ionization potentials of Al_nNa_m ($n=2-26$, $m=1-3$). They found that the ionization potentials of Al_nNa are lowered compared to those of Al_n with the exception of $Al_{13}Na$ and $Al_{23}Na$, whose IPs are higher than or equal to that of Al_{13} and Al_{23} respectively. Note that the number of valence electrons in $Al_{13}Na$ and $Al_{23}Na$ (assuming Al to behave as a trivalent atom) are 40 and 70, respectively, and these correspond to closing of electronic shells. As more Na atoms are added, the IPs decrease monotonically. The ionization potentials of $Al_{8-n}Na_n$ clusters do not show any anomalous behavior characteristic of electron shell closure.

In this paper, we present a systematic theoretical study of the equilibrium geometries, adsorption energies, ionization potentials, and electron affinities of Al_nLi, Al_nK ($n \leqslant 8$) and Al_5Li_m ($m=1-4$) and Al_5K_m ($m=1-4$) clusters. The calculations were carried out from first principles using the molecular orbital theory. The cluster wave function was constructed from a linear combination of atomic orbitals centered at respective atomic sites. We have used the Gaussian basis sets and frozen-core approximation and the GAUSSIAN

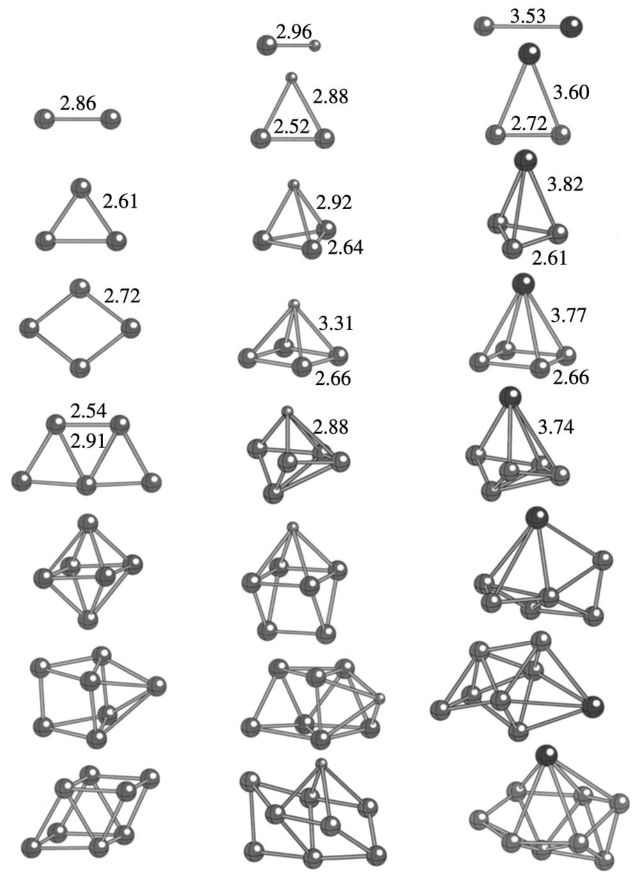

FIG. 1. Equilibrium geometries of neutral Al_n (column 1), Al_nLi (column 2), and Al_nK (column 3) ($n=1-8$) clusters.

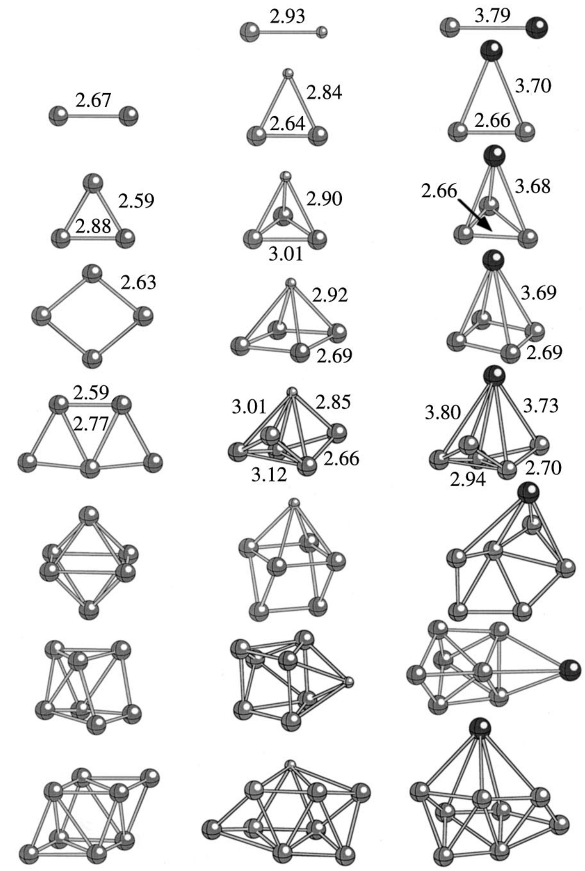

FIG. 2. Equilibrium geometries of anionic Al_n (column 1), Al_nLi (column 2), and Al_nK (column 3) ($n=1-8$) clusters.

94 software.[9] For all atoms except Li, we have used the frozen core basis sets due to Hay and Wadt (referred to as the LanL2DZ basis in GAUSSIAN 94 software). For Li atoms, we have used all-electron 6-311G** basis. The exchange–correlation potential was calculated using the generalized gradient approximation due to Becke, Perdew, and Wang (BPW91 in the GAUSSIAN 94 code). The coefficients of linear combination were calculated self-consistently by solving the Raleigh–Ritz variational equation. The geometries of Al_nX_m clusters for neutral and charged configurations were optimized by calculating the forces at atomic sites and moving the atoms along the path of steepest descent until the forces vanish. The threshold of the maximum force, root mean square force, the maximum displacement of the atoms, and the root mean square displacement of the atoms were set at 0.000 45 a.u./bohr, 0.0003 a.u./bohr, 0.0018 a.u., and 0.0012 a.u., respectively. Different initial starting configurations were used to avoid trapping in local minima of the potential energy hypersurface. Since these clusters contain *s-p* valence electrons, optimization of their preferred spin multiplicities was restricted to two lowest values. These correspond to $2S+1=1$, and 3 for even electron systems and $2S+1=2$, and 4 for odd electron systems.

First we discuss the equilibrium geometries of these clusters. In Fig. 1 we compare the ground state geometries of neutral Al_nLi (column 2) and Al_nK (column 3) ($1\leqslant n\leqslant 8$) clusters with those of the bare Al_n clusters (column 1). Figure 2 presents similar information on the anionic clusters. The corresponding total energies along with their preferred spin multiplicities are given in Table I. We note that the bond length of the AlK dimer is larger than that of AlLi as can be expected since K is a larger atom than Li. However, the bond length of the AlLi dimer is also larger than that of Al_2. This, at first, may be surprising, but it is consistent with the size of the Li and Al atoms. The standard radii of ions in inert gas (filled shell) configuration of Li and Al are 0.68 and 0.50 Å, respectively. As the cluster size increases, the nearest-neighbor distances between K–Al and Li–Al remain larger than those between Al–Al in Al_n clusters. The geometries also undergo significant changes. For example, Al_n clusters remain planar until $n=5$ while Al_nLi and Al_nK clusters become three dimensional for $n\geqslant 3$. While the structures of Al_nLi and Al_nK clusters differ significantly from both Al_n and Al_{n+1} clusters, the difference between Al_nLi and Al_nK cluster geometries is less marked. The geometries of the anion clusters (Fig. 2) remain very similar to those of the corresponding neutrals (see Fig. 1). This suggests that the peaks in the photodetachment spectra would be narrow except for those clusters where the geometry changes between the ground states of the neutral and anion clusters are significantly different.

To establish the suitability of the use of the frozen core basis set for aluminum, we have repeated our calculations on the equilibrium geometries of the neutral Al_nLi clusters using all-electron 6-311G** basis. The resulting geometries

TABLE I. Total energies and preferred spin multiplicities of neutral Al_nX (X=Li, K; $n=1-8$) clusters and their anions in atomic hartree units.

	AL_nLi				Al_nK			
	Neutral		Anionic		Neutral		Anionic	
n	Energy	Multiplicity	Energy	Multiplicity	Energy	Multiplicity	Energy	Multiplicity
1	−9.455 55	1	−9.481 33	2	−30.100 84	3	−30.127 65	2
2	−11.467 39	2	−11.516 14	3	−32.112 05	4	−32.155 83	3
3	−13.488 87	1	−13.537 40	2	−34.132 33	3	−34.170 80	2
4	−15.512 13	2	−15.582 42	1	−36.159 63	2	−36.217 77	3
5	−17.528 68	1	−17.593 47	2	−38.173 48	1	−38.225 84	2
6	−19.564 32	2	−19.654 80	1	−40.185 53	2	−40.252 68	1
7	−21.593 83	1	−21.664 55	2	−42.231 94	1	−42.295 58	2
8	−23.600 40	2	−23.681 69	1	−44.245 14	2	−44.317 20	1

(Fig. 3, column 2) are compared with those obtained from the frozen core calculations (Fig. 3, column 1). It is clear that the geometries remain almost unchanged except for very minor changes in some of the bond lengths. To study the relative stability of the Al_n (X=Li, K, $1 \leqslant n \leqslant 8$) clusters, we calculate the energy gain in adding an alkali atom to an Al_n cluster as a function of n. This can be computed from the results in Table I by using

$$\Delta E_n(\mathrm{X}) = -[E(\mathrm{Al}_n\mathrm{X}) - E(\mathrm{A1}_n) - E(\mathrm{X})], \quad (1)$$

where E is the total energy of a cluster or atom. The results are plotted in Fig. 4. We have given the results for the frozen core basis only because the results from the all-electron calculations for Al_nLi clusters are not even distinguishable from that obtained using the frozen core basis. We note that the energy gain, ΔE_n in adsorbing a Li atom steadily rises up to $n=4$ and shows an anomalous peak at $n=6$. If Al_n clusters in this size range were to behave like a free-electron system, as is the case with alkali metal clusters, and since in this size range aluminum behaves as monovalent according to the photodetachment studies,[3] we expect Al_7Li to be more stable than Al_6Li. From the results in Fig. 4 we see that the relative stability of Al_nX clusters is not consistent with the electronic shell structure effects. On the other hand, the large binding energy of Li to Al_6 compared to that of Al_5 or Al_7 can be understood on the basis of their electron affinities. The adiabatic electron affinities[3] of Al_5, Al_6, and Al_7 clusters are, respectively, 2.25, 2.63, and 2.43 eV. Since Li is electropositive, its tendency to bind strongly to a more electronegative cluster is understandable. In this context, the steady rise in the energy gain ΔE_n from $n=1$ to 4 is also consistent with increasing electron affinities of Al_n clusters in this size range. (The electron affinities of Al, Al_2, Al_3, and Al_4 are, respectively, 0.44, 1.46, 1.89, and 2.20 eV.)

The trend in the energy gain in adding a K atom to Al_n is also similar to that in Al_nLi with the only exception being

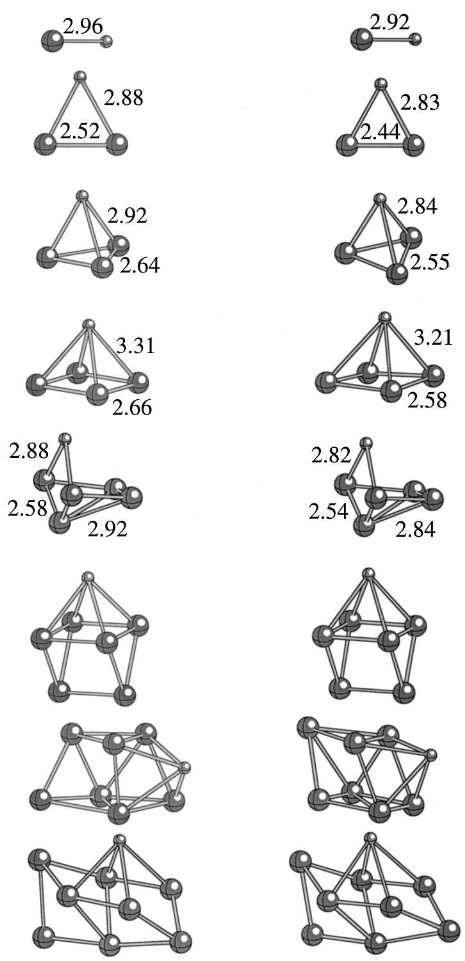

FIG. 3. Equilibrium geometries of neutral Al_nLi clusters obtained from LanL2DZ basis (column 1) and 6-311G** basis (column 2).

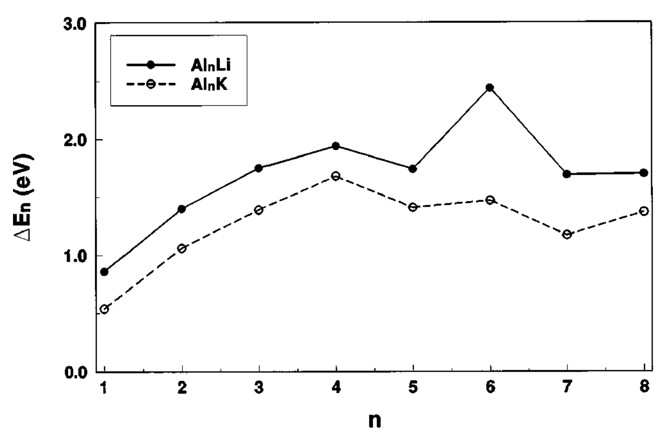

FIG. 4. Energy gain in adding an alkali atom (Li, K) to neutral Al_n ($n=1-8$) cluster.

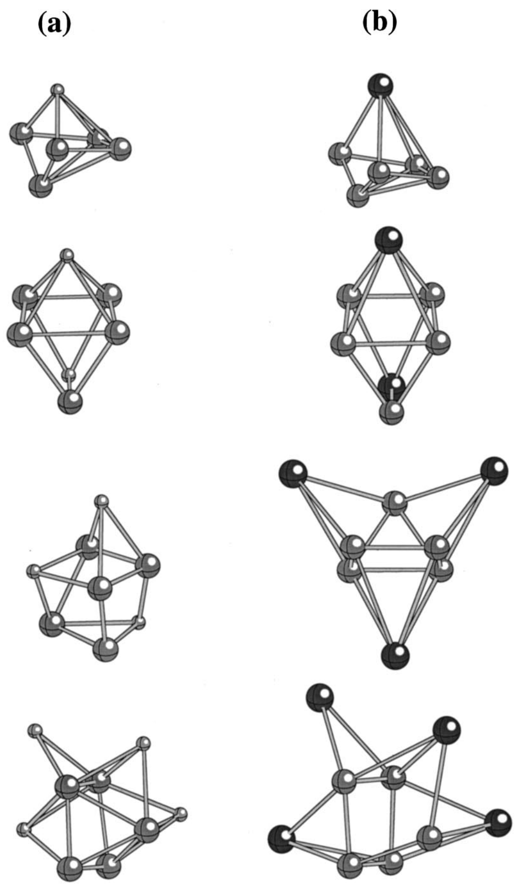

FIG. 5. Equilibrium geometries of neutral (a) Al_5Li_m and (b) Al_5K_m ($m=1-4$) clusters.

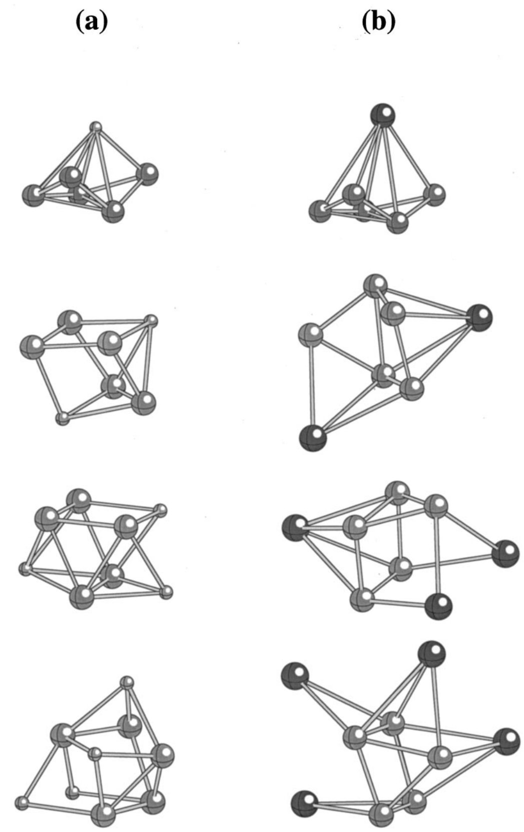

FIG. 6. Equilibrium geometries of (a) $Al_5Li_m^-$ and (b) $Al_5K_m^-$ ($m=1-4$) clusters.

that the peak in ΔE_n corresponding to Al_6K is not as well marked as it is in Al_6Li. We also note from Fig. 4 that the energy gains in adding a K atom are consistently smaller than those involving Li atoms. Part of this reason could be due to the size of the K atom, which necessarily makes the Al–K bond lengths much larger than the Al–Li bond lengths. (See Figs. 1 and 2.)

To further examine if alkali metal adsorption can illustrate shell closings in small aluminum clusters, we have calculated the total energies of the ground states of neutral and anionic Al_5X_m ($X=Li, K$, $1\leqslant m\leqslant 4$) clusters. In Fig. 5 we present the geometries of the neutral Al_5Li_m and Al_5K_m ($m=1-4$) clusters. The corresponding geometries for the anions are given in Fig. 6. We note that as alkali atoms are successively added to the Al_5 cluster, they prefer to stay as far away from each other as possible. This is due to the fact that the alkali–alkali bonds are much weaker than the alkali–aluminum bonds. This is also evident from the cohesive energies of bulk Li, K, and Al, which are, respectively, 1.63, 0.934, and 3.39 eV/atom. As in Al_nLi and Al_nK clusters, the neutral and anionic clusters of Al_5Li_m and Al_5K_m have very similar geometries.

The energy gain in adding an alkali atom to the Al_5X_{m-1} cluster is calculated using the total energies in Table II and

$$\Delta E_m=-[E(Al_5X_m)-E(A1_5X_{m-1})-E(X)]. \qquad (2)$$

The results are plotted in Fig. 7. We note that there is essentially no size dependence of ΔE_m in the Al_5Li_m cluster, but the energy gain oscillates as one adds K atoms to Al_5. What is particularly interesting is the lack of a pronounced peak corresponding to Al_5Li_3 or Al_5K_3, although Al_5K_3 is relatively more stable than Al_5K_2 or Al_5K_4. Since Al is monova-

TABLE II. Total energies and preferred spin multiplicities of neutral Al_5X_m ($X=Li$, K; $n=1-4$) clusters and their anions in atomic hartree units.

	AL_5Li_m				Al_5K_m			
	Neutral		Anionic		Neutral		Anionic	
m	Energy	Multiplicity	Energy	Multiplicity	Energy	Multiplicity	Energy	Multiplicity
1	−17.528 68	1	−17.593 47	2	−38.173 48	1	−38.225 84	2
2	−25.073 68	2	−25.143 62	1	−66.353 48	2	−66.396 71	1
3	−32.623 51	1	−32.687 22	2	−94.539 23	1	−94.571 25	2
4	−40.169 25	2	−40.235 00	1	−122.703 75	2	−122.739 04	1

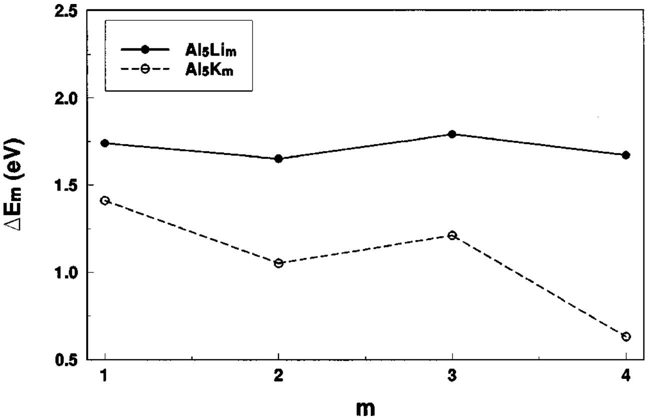

FIG. 7. Energy gain in adding an alkali atom (Li, K) to Al_5X_{m-1} ($m=1-5$) cluster.

lent in the Al_5 cluster, the Al_5X_3 clusters should contain eight valence electrons. The electronic shell closing which occurs at eight electrons should have clearly rendered these clusters enhanced stability. That it does not for Al_5Li_3 is consistent with our findings discussed earlier. We will see in the following that no signatures of shell closings are found in the analysis of the ionization potential and electron affinities either.

In Table III we list the vertical ionization potentials (IPs) of Al_nLi and Al_nK clusters and compare these with the IPs of bare Al_n clusters. The vertical ionization potentials were calculated by taking the difference between the total energy of the neutral ground state and that of the positively charged cluster having the neutral geometry. In this case, we have to emphasize that the spin multiplicity of the cation can differ from the neutral by $\Delta M=\pm 1$. We examined the total energies corresponding to both allowable spin multiplicities and that state with the lower energy entered into the computation of the vertical ionization potential. We see from Table III that with the exception of Al_2Li, the ionization potentials of $Al_n(n\geqslant 2)$ are lowered between 0.12 and 0.84 eV due to the addition of a Li atom. In $Al_nK(n\geqslant 2)$ clusters, the ionization potentials are also lower than those of Al_n clusters by 0.58–1.29 eV. These results are consistent with the experimental results of Nakajima *et al.*,[8] who found the ionization potentials of Al_nNa ($n\geqslant 2$) clusters to be lower than those of Al_n clusters by 0.2–0.6 eV.

TABLE III. Vertical ionization potentials (IPs) of Al_nLi and Al_nK clusters ($n\leqslant 8$) as compared to those of Al_n. $\Delta IP=IP(Al_nX)-IP(Al_n)$. The IPs are given in electron volts.

n	IP(Al_n)	IP(Al_nLi)	ΔIP(Al_nLi)	IP(Al_nK)	ΔIP(Al_nK)
1	6.27	5.24	−1.03	4.51	−1.76
2	5.87	5.99	+0.12	5.29	−0.58
3	6.55	5.71	−0.84	5.26	−1.29
4	6.58	6.15	−0.43	5.70	−0.88
5	6.69	6.11	−0.58	5.56	−1.13
6	6.74	6.39	−0.35	5.62	−1.12
7	6.19	6.07	−0.12	5.42	−0.77
8	6.35	6.00	−0.35	5.54	−0.81

TABLE IV. Vertical ionization potentials (IPs) and electron affinities of Al_5X_m (X=Li, K, $1\leqslant m\leqslant 4$) clusters.

m	Ionization potential (eV)		Electron affinity (eV)	
	Al_5Li_m	Al_5K_m	Al_5Li_m	Al_5K_m
1	6.11	5.56	1.76	1.42
2	5.96	4.82	1.91	1.18
3	5.69	4.11	1.73	0.87
4	5.47	4.11	1.79	0.96

In Table IV the vertical ionization potentials of Al_5X_m (X=Li, K, $1\leqslant m\leqslant 4$) are given. Note that the ionization potentials decrease with the increasing concentration of the alkali atoms. This is again consistent with the experimental findings of Nakajima *et al.*,[8] who observed a decrease in the ionization potential of Al_nNa_m with increasing Na content. Of particular interest here is again the case of Al_5X_3. If this cluster is magic because of its eight valence electrons, the IP should show a peak. The fact that it does not reinforces our argument made previously that aluminum clusters in this size range show no sign of electronic shell closure.

In Table V we provide the results of our calculated electron affinities. Unlike the ionization potentials, the photodetachment spectra measure the binding energy of the ejected electron when a fixed frequency photon impinges on an anionic cluster. This provides information on vertical and adiabatic electron detachment energies. In the vertical detachment process, one measures the difference in the energy of the cluster anion in its ground state and the corresponding neutral cluster having the ground state geometry of the anion, but with spin multiplicities that differ from the anion by $\Delta M=\pm 1$. The adiabatic electron affinity, on the other hand, gives the energy difference between the ground states of the anion and the neutral. We see from Table V that the adiabatic electron affinities in Al_nX are lower than those of Al_n for both Li and K adsorption. Furthermore, the electron affinities of Al_nK are lower than those of Al_nLi for every value of n excepting $n=1$ where they are almost equal. The electron affinities of Al_7Li and Al_7K are lower than their neighboring clusters which would be consistent with a cluster with closed electronic shell. This is the only property that suggests that Al_7X could possibly correspond to an electronic closed shell structure, but the fact that similar characteristics are observed for Al_5Li, which does not have the number of electrons necessary for shell closure, casts doubt on this conclusion.

TABLE V. Adiabatic electron affinities (EAs) of Al_nLi and Al_nK clusters ($n\leqslant 8$) in electron volts. $\Delta EA=EA(Al_nX)-EA(Al_n)$.

n	EA(Al_n)	EA(Al_nLi)	ΔEA(Al_nLi)	EA(Al_nK)	ΔEA(Al_nK)
1	0.13	0.70	+0.57	0.73	+0.60
2	1.38	1.33	−0.05	1.19	−0.19
3	1.55	1.32	−0.23	1.05	−0.50
4	2.13	1.91	−0.22	1.58	−0.55
5	2.06	1.76	−0.30	1.42	−0.64
6	2.56	2.46	−0.10	1.83	−0.73
7	2.04	1.92	−0.12	1.73	−0.31
8	2.56	2.21	−0.35	1.96	−0.60

We also see a similar trend in the electron affinities of Al_5X_m ($X=Li, K$, $1 \leqslant m \leqslant 4$) in Table IV. The electron affinities of Al_5Li_3 and Al_5K_3 are lower than their neighboring clusters, but the differences are not large enough to conclude that these represent closed-shell systems, particularly when other indicators such as peaks in ionization potentials and energy gain point otherwise.

A summary of our results is as follows: (1) The addition of Li and K atoms lowers the ionization potentials of Al_n ($n \geqslant 2$) clusters by as much as 0.1–0.8 eV in Al_nLi and 0.6–1.3 eV in Al_nK. (2) The addition of subsequent Li and K atoms to an Al_5 cluster monotonically lowers the ionization potentials further. The IPs of Al_5Li_3 or Al_5K_3 do not show any anomalous behavior, as would be expected of clusters with electronic shell closure (note—Al behaves as a monovalent atom in Al_5 cluster). (3) The adiabatic electron affinities are also lowered by the addition of alkali atoms. This lowering ranges between 0.1 and 0.4 eV in Al_nLi and between 0.2 and 1.1 eV in Al_nK. (4) While the successive addition of K atoms to Al_5 cluster lowers the adiabatic electron affinity monotonically, it has no noticeable trend in Al_5Li_m. (5) No signature of Al_n clusters behaving as free-electron systems in the size range of $n<7$ is observed. We hope that this work will motivate experimentalists to study the ionization potentials and electron affinities of Al_nX_m ($X=Li, K$) clusters.

This work was motivated by discussions with Professor K. Bowen, who is measuring the electron affinities of these clusters. We thank Professor Bowen for many stimulating discussions. Discussions with Dr. V. Kumar during the early stages of this work are also acknowledged. This work is partly supported by a grant from the Department of Energy (No. DE-FG02-96ER45579).

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