

Electron attachment and dynamics of alkali atoms in Al_{13}X ($X=\text{Li}-\text{Cs}$) clusters

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(Received 22 January 2002; revised manuscript received 8 July 2002; published 27 November 2002)

Theoretical electronic structure studies on the anionic and neutral Al_{13}X ($X=\text{Li}-\text{Cs}$) clusters have been carried out using a gradient corrected density-functional approach. The alkali atoms occupy the hollow sites on the Al_{13} icosahedron surface and the calculated vertical transition energies from the ground state of the anions to various neutral states are found to be close to the recent preliminary experimental data. A detailed investigation of the Born-Oppenheimer surface of Al_{13}K shows that the minimum energy path for the motion of K atoms to the neighboring hollow sites passes through a bridge site and has a barrier of 0.13 eV. If energy could be imparted that will enable the K atoms to overcome the barrier and slide freely on the surface, the cluster will exhibit a small orbital magnetic moment that could be observed at low temperatures.

DOI: 10.1103/PhysRevB.66.193408

PACS number(s): 73.22.-f, 71.15.Nc, 31.15.Ar

One of the most fascinating developments in the field of atomic clusters has been the discovery of magic numbers and their subsequent explanation in terms of the shell model. About fifteen years ago, Knight and co-workers¹ found that the mass spectra of Na_n clusters generated in molecular beams exhibit marked peaks at clusters containing 2, 8, 18, 20, 40,... atoms. They also showed that these numbers could be understood within a simple shell model in almost the same way as the stable nuclei in the nuclear shell model. Assuming that the electrons move in a spherical jellium potential that is attractive and constant within a given radius and zero outside, it was shown¹⁻⁴ that the magic sizes correspond to the filled electronic shells and that several of the observed electronic properties can be understood within such a picture. Later experiments⁵ indicated that in addition to the electronic shells, the stability of the clusters is governed by their geometrical shell closure. This led to an interesting proposition for Al_{13} clusters. Its ground-state geometry is an icosahedron that has a closed geometric shell. Al is a trivalent atom and an Al_{13} cluster has 39 valence electrons, one short of filling the electronic shell containing 40 electrons.⁶ In a jellium picture, it corresponds to an electronic configuration of $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^5$ resembling the electronic shell structure of a halogen atom and it was suggested that it should exhibit electronic behaviors reminiscent of a halogen atom. The experimental^{7,8} studies indeed confirmed that the bare cluster has a high electron affinity of 3.62 eV, which is comparable to that of halogen atoms and that the anionic cluster is chemically inert like a closed shell system. This has led to two lines of enquiry. First, it was suggested that by replacing an Al atom by tetravalent atoms such as C or Si, one could stabilize an Al_{13} cage and this has led to investigations about the stability of extended structures built out of such units.^{6,9} Second, one could form ionic molecules by combining Al_{13} units with alkali atoms. Over the past few years, numerous theoretical investigations have suggested the ionic character of Al_{13}X ($X=\text{Li}-\text{Cs}$) (Refs. 10-12) clusters. They suggest that the clusters consist of an anionic core of an icosahedral Al_{13}^- and a X^+ located on the outer surface

and could form the basis for making cluster-based materials. The realization of this feature to form actual materials now seems probable, as Bowen and co-workers¹³ have recently succeeded in forming some of these clusters in molecular beams. They have also carried out negative ion photodetachment spectroscopy to examine their electronic structure and these can provide support to the theoretical calculations. In recent papers,^{12,14} we had compared the calculated vertical transitions from the doublet ground state of the Al_{13}X ($X=\text{Li}-\text{K}$) anions to the singlet and triplet neutral states and found them close to the preliminary data from anion-photodetachment spectroscopy. As the photodetachment spectra are a fingerprint of the atomic structure, these comparisons provided the first solid support to the theoretical predicted geometrical structures?

The purpose of this paper is twofold. First, we want to supplement our earlier studies on Li-K with those on Rb and Cs, thus providing a comparison of the electronic structure of the entire alkali Al_{13}X series with the experiments on negative ion photodetachment spectroscopy. Second, we closely examine the energetics of the Al_{13}K . In particular, we investigate the energy needed for moving K ions on the Al_{13} surface. This is motivated by the fact that in an atom, the moving electrons lead to orbital magnetic moments. It is then of interest if such orbital moments could be generated in this ionic superatom and what would be the magnitude of such moments under ordinary conditions. Note that the motion of K atoms would also affect the observed electric dipole moments but here we focus only on the magnetic part. We would like to add that an investigation of energetics of K on the Al_{13} surface requires one to examine the Born-Oppenheimer surface for a possible sliding motion of K on the Al_{13} surface. It is important to underscore that this requires optimization of the geometry of the Al_{13}K cluster for defined paths of K on the Al_{13} surface. This is far more complex than a mere determination of the ground state as it requires freezing of the angular parameters while optimizing the remaining degrees of freedom. The key parameter is the energy required for a free motion of the K on the surface. For

Al_{13}K , we show that the potential barrier separating the various hollow sites is less than 0.13 eV.

Our theoretical investigations are based on a linear combination of atomic orbitals molecular-orbital approach within a density-functional formalism.¹⁵ The cluster wave functions are constructed from atomic orbitals centered at the atomic sites. The atomic orbitals are further expanded as a sum of Gaussian functions. The exchange-correlation effects are incorporated through a gradient corrected density functional.¹⁶ The Hamiltonian matrix elements entering the solution of the Kohn-Sham equations are calculated by numerically integrating over a carefully chosen mesh. The actual calculations were carried out using the NRLMOL set of codes developed by Pederson and co-workers.¹⁷⁻¹⁸ The basis sets consisted of $6s$, $5p$, and $3d$ functions with an auxiliary d function for Al; $5s$, $3p$, and $1d$ with 1 auxiliary p and 1 auxiliary d functions for Li; $6s$, $4p$, and $3d$ functions with an auxiliary d function for Na; $7s$, $5p$, and $3d$ functions with an auxiliary d function for K; $8s$, $6p$, and $4d$ functions with an auxiliary d function for Rb; and $8s$, $6p$, and $8d$ functions for Cs. These were built by contracting a set of 16 primitive Gaussians in the case of Al, 10 for Li, 16 for Na, 17 for K, 22 for Rb, and 25 for Cs. For further details of the basis sets, the reader is referred to earlier papers.¹⁹ Note that an alkali atom can occupy an on-top, bridge, or a hollow site. For each alkali atom, we optimized the geometry of the anionic and neutral cluster starting from the icosahedron and decahedron geometries. The symmetries were then broken to get lowest-energy structures. The final geometries therefore include possible Jahn-Teller distortions.

We first start by comparing the present results with the recent experiments involving photodetachment spectroscopy on Al_{13}X ($X=\text{Li}-\text{Cs}$) clusters. In these experiments, the mass selected anions are crossed with a laser of fixed frequency and the energy of the photodetached electrons is measured.²⁰ The energy difference between the photon energy and the energy of the ejected electrons is then a measure of the transition energy from the anion to the various states of the neutral. To be more specific, consider an anionic cluster with N unpaired spins or a spin multiplicity of $N+1$. As an electron is detached, the resulting neutral cluster will have a spin of $N+1$ or $N-1$. Further, for each spin, one can go to the lowest or the excited electronic states of the same multiplicity if the excitations occur from inner states. Since the photodetachment process occurs on a femtosecond scale, the transition to neutrals is almost vertical. In addition to providing information on the electronic structure, the photodetachment spectroscopy has emerged as a valuable tool to probe the geometry of clusters. This is because the electronic structure is sensitive to the geometry, and by comparing the calculated vertical transitions from the anion with the experimental spectra one can infer the geometry. This is particularly important in view of the fact that the clusters are generally too large for conventional spectroscopy and too small for microscopic techniques.

As mentioned above, Bowen and co-workers¹³ have recently conducted negative ion photodetachment spectroscopy of all Al_{13}X^- anions and we start by comparing our calculated results with the preliminary experimental spectra. In

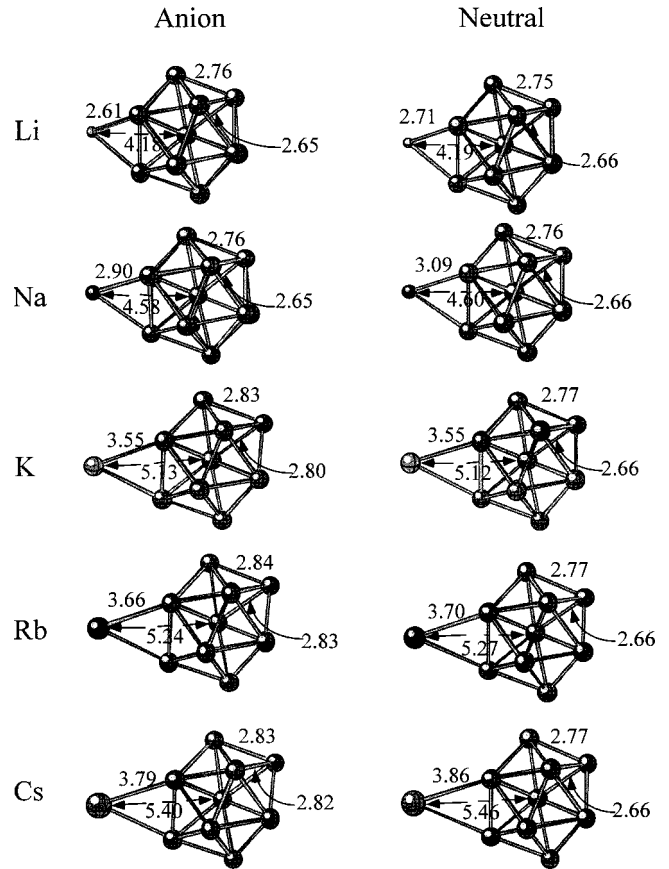


FIG. 1. Ground-state geometries of the anionic and neutral Al_{13}X ($X=\text{Li}-\text{Cs}$) clusters. The bond lengths are in Å.

Fig. 1 we show the ground-state geometries of anionic and neutral Al_{13}X clusters. To compare with the photoelectron spectra, note that the ground state of all Al_{13}X^- are spin doublets. One can therefore make transitions to neutral clusters with singlet or triplet multiplicity. In Table I we give the binding energy (BE) of the alkali atom to the neutral and anionic Al_{13} and the vertical detachment energy (VDE) from the anionic ground state to singlet and triplet neutral clusters at the anion geometries. These are defined as

$$\text{BE} = -E(\text{Al}_{13}\text{X}) + E(\text{Al}_{13}) + E(X) \quad (\text{neutral cluster}),$$

TABLE I. The binding energy of the various alkali atoms to the neutral and anionic Al_{13}X clusters. The vertical dissociation energy (VDE) from the doublet anion ground states to the singlet and triplet neutral states, and the adiabatic electron affinities (AEA) are also given.

| Cluster | Binding energy (eV) | | VDE (eV) | | AEA (eV) |
|-----------------------------|---------------------------|---------------------------|-------------------|-------------------|----------|
| | $\text{Al}_{13}+\text{X}$ | $\text{Al}_{13}+\text{X}$ | $2 \rightarrow 1$ | $2 \rightarrow 3$ | |
| $\text{Al}_{13}\text{Li}^-$ | 1.24 | 2.77 | 2.05 | 3.30 | 1.85 |
| $\text{Al}_{13}\text{Na}^-$ | 0.72 | 2.39 | 1.94 | 3.22 | 1.71 |
| Al_{13}K^- | 0.66 | 2.51 | 1.75 | 3.04 | 1.54 |
| $\text{Al}_{13}\text{Rb}^-$ | 0.70 | 2.57 | 1.72 | 3.00 | 1.51 |
| $\text{Al}_{13}\text{Cs}^-$ | 0.88 | 2.78 | 1.71 | 2.94 | 1.49 |

$$BE = -E(\text{Al}_{13}\text{X}^-) + E(\text{Al}_{13}^-) + E(\text{X}) \quad (\text{anionic cluster}),$$

$$VDE = -E(\text{Al}_{13}\text{X}^-) + E(\text{Al}_{13}\text{X}),$$

where E is the total energy of the system, and VDE is calculated from the energy of the neutral cluster at the ground-state geometry of the anion.

From Table I it is seen that the alkali atoms are more strongly bound in the neutral Al_{13}X than in case of anionic Al_{13}X^- . This is related to the fact that Al_{13}^- is a closed-shell system. For the neutral cluster, the alkali atom donates charge to Al_{13} icosahedron that forms a closed Al_{13} shell with 40 electrons. Consequently, Al_{13}X is bound by ionic forces. This has been discussed in several previous works.^{10,11} For the anionic clusters, Al_{13}^- is a closed shell and an extra electron from the alkali is not needed to fill the electronic shell. Consequently, the alkali atom is only weakly bound. The change in bonding between the anionic and neutral clusters is really transparent in the differences in the ground-state geometries of the anionic and neutral clusters shown in Fig. 1. All these features can be verified through the photodetachment spectra.

The preliminary experimental spectra¹³ of all the Al_{13}X clusters exhibit two peaks, one around 1.7–2.0 eV and the other around 3.0 eV. The position of the first peak decreases from around 2.0 eV for Li to around 1.7 eV for K, shifts towards higher energies and broadens significantly for Rb and Cs. The position of the second peak decreases from around 3.1 eV for Li to 3.0 eV for K, Rb, and Cs. From Table I it is seen that theoretical transitions from the doublet ground state to the singlet neutral are 2.05, 1.94, 1.73, 1.72, and 1.71 eV for Li, Na, K, Rb, and Cs, respectively. The peak positions for Li, Na, and K are close to the experimental values and we correctly reproduce the shift towards lower energies in going from Li to K. The transitions from the anion to the triplet neutral vary from 3.2–2.9 eV and these are within 0.1 eV of the experimental values. All these results indicate that the theoretical geometries as well as the calculated electronic structures are in reasonable agreement with the experiments.

We now focus on Al_{13}K and the possibility of K motion on the Al_{13} surface. As pointed out earlier, the K atom prefers to occupy a hollow site. To find the mobility, one has to calculate the potential-energy surface as the K moves from one hollow site to the next. For this calculation, the Al_{13}K cluster was initially allowed to relax to its minimum. Note that the Al_{13} subunit has approximate icosahedral symmetry. The K atom occupies a site above the equator whose position can be specified by \mathbf{R} , \mathbf{Z} , and θ (see Fig. 2). To find the barrier, one can rotate the icosahedron around a vertical axis (Z axis in Fig. 2) and allow K and Al atoms to relax as the cluster is rotated. This is equivalent to allowing the K atom to move cylindrically around a surface which mirrors itself on rotation through 18° and repeats on rotation past 72° . The total energy was calculated by displacing the K atom along θ at intervals of 3° from 0° to 18° while allowing it to relax in the \mathbf{R} and \mathbf{Z} directions. There are three nearest neighbor Al atoms to the K atom. The two Al atoms closest to the K atom in the direction of rotation were given three degrees of free-

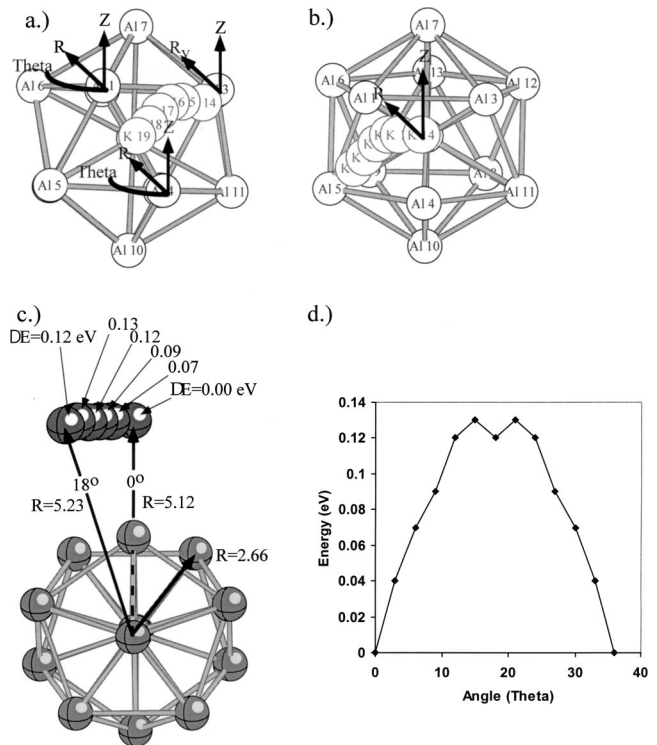


FIG. 2. The minimum energy path for the transition of a K atom from a hollow site to a neighboring hollow site in Al_{13}K . θ is the angle of rotation. (a) shows the relaxation of the neighboring Al atoms and (b) shows the relaxation of the K atom. (c) The change in energy, DE , relative to the ground state for various angles of rotation. (d) The energy as a function of angle of rotation.

dom to fully relax. The third Al was allowed to relax with two degrees of freedom. A final calculation was done after the K atom was rotated through 18° in which all constraints were removed and the cluster was allowed to fully relax. There was only minor relaxation and the barrier dropped by 0.02 eV, which shows that this is a reasonable approach to calculating the barrier. The variation of energy as a function of θ and the path for transition are shown in Fig. 2. It is interesting to note that the barrier for the motion of K is less than 0.13 eV. This corresponds to an energy of 0.01 eV/atom and indicates that the K atoms may be mobile provided energy could be imparted.

We now discuss the magnitude of orbital magnetic moments and their possible enhancement through the mobility of K. A Mulliken population analysis confirms that the K atom loses about an e^- to the Al_{13} core. The cluster is therefore characterized by an Al_{13} icosahedron with K^+ occupying the hollow sites. In general, in a rotating cluster, both the Al_{13}^- and K^+ will generate orbital currents and hence the orbital magnetic moments. Because of the difference in the radii, however, the net moment will be dominated by K^+ . Assuming a circular orbit of radius r_{K^+} and a speed of v_{K^+} , the magnetic moment due to K^+ alone can be expressed as

$$\mu_{\text{K}^+} = \frac{m_N r_{\text{K}^+} v_{\text{K}^+}}{1.91 \hbar} \mu_{N,Z},$$

where $\mu_{N,Z}$ is the magnitude of the moment of a neutron and m_N is the mass of the neutron. Using the equilibrium distance of the K atom from the center ($r_K^+ = 5.12 \text{ \AA}$) in Al_{13}K as the radius of the orbit, one finds that the K needs a velocity of 235 m/s to generate a moment of one $\mu_{N,Z}$ (note that the velocity of the electron in the first Bohr orbit in a H atom is around $2.2 \times 10^6 \text{ m/s}$). This shows that despite a large area for orbital motion, the magnetic moments are relatively small and would only be observable at ultralow temperatures. Thus, while the presence of orbital moments is interesting, one needs a mechanism to accelerate K atoms on surface to generate significant magnetic moments.

To summarize, we have carried out detailed electronic structure calculations to examine the electronic spectrum and

the dynamics of the alkali atoms in Al_{13}X clusters. The calculated vertical transitions from the anion clusters are close to the recent preliminary experiments. A detailed investigation of the potential-energy surface of Al_{13}K reveals that the barrier for the mobility of K atoms is only 0.13 eV and the atoms will be mobile at high temperatures or kinetic energies. The orbital magnetic moments associated with a possible orbital motion of K are, however, small. We hope that the present studies would generate interest in finding more ways to accelerate K through the small barrier of 0.13 eV.

This work was supported by a grant from the Department of Energy (Grant No. DEFG05-87E61316). We are grateful to Professor K. H. Bowen for sharing the experimental results.

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