Anomalous Spectroscopy of $Li_4{}^-$ Clusters

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(Received 3 October 1994; revised manuscript received 24 October 1995)

The photoelectron spectra of $Li_4{}^-$, in sharp contrast to that of other alkali tetramers, consist of two very narrow peaks separated by an energy gap that is about a factor of 5 smaller than those in $Na_4{}^-$ and $K_4{}^-$. Self-consistent field calculations based on both quantum chemical and density functional techniques reveal that the ground state of $Li_4{}^-$ consists of two nearly degenerate isomeric states with different spin multiplicities. The anomalous spectroscopy results from an intricate interplay among the geometry, electronic structure, and spin multiplicity of these two structures.

PACS numbers: 33.60.–q, 36.40.Mr

Although alkali metals are the flagships of the free-electron model, Li metal seems to be an exception to the rule. The electronic properties that characterize the non-free-electron behavior of Li metal include (i) the asphericity of the Fermi surface [1], (ii) anomalous pressure dependence of the Knight shift [2], and (iii) the broadening of the soft x-ray emission and absorption edges [3]. What is not clear is whether these discrepancies are manifestations of the electronic structure of the Li crystal or if they are rooted in the electronic structure of the atom itself. In this context, studies of Li clusters are relevant.

It is now well established that small atomic clusters constitute a new class of matter with structural and electronic properties quite unlike their bulk counterparts. For example, the geometries of all neutral alkali metal clusters consisting of less than six atoms tend to be planar [4,5]. Their relative stabilities and ionization potentials exhibit odd-even alternation with size, and clusters with 2, 8, 20, 40, ... atoms are unusually stable [6]. Thus, it may be concluded that Li clusters would not exhibit properties that differ from other alkali metal clusters such as Na and K.

A recent experiment on the photoelectron spectra of $Li_4{}^-$ by Sarkas *et al.* [7] suggests that Li clusters, after all, may not behave the same way as other alkali clusters do. These authors had earlier observed [8] that the photoelectron spectra of $Na_4{}^-$ and $K_4{}^-$ were similar and were both characterized by two broad peaks separated in energy by about 0.5 eV. In contrast, the photodetachment spectra of $Li_4{}^-$ are characterized by two very sharp peaks separated by an energy gap of about 0.1 eV. To understand the origin of this anomalous behavior, it is instructive to review the experimental procedure.

In the negative ion photoelectron experiment, a mass selected beam of cluster anions is crossed with a fixed-frequency photon beam and the resultant photodetached electrons are energy analyzed. Note that the anionic cluster has an equilibrium geometry that may be different from its neutral counterpart. Since this process is extremely fast, the geometry of the neutral cluster probed by this experiment is the same as that of its corresponding anions. Thus, experimentally, one measures the difference between the energy of the anionic cluster in its ground state and the energies of the excited states of the neutral cluster having the same geometry as that of its anionic parent. These energies can be compared with theoretical calculations and a quantitative agreement provides indirect evidence for the geometry obtained from theory by energy optimization.

Ab initio quantum mechanical calculations [9] have confirmed that the ground states of $Na_4{}^-$ and $K_4{}^-$ clusters have linear geometry while the corresponding neutral clusters have planar rhombus geometry. The peaks in the photoelectron spectra result from transitions between the spin doublet ground state of the anionic cluster and spin singlet and triplet excited states of the neutral cluster, all having the same linear geometry as the anionic cluster. The broadening arises due to the large geometry change between the anion and the neutral, resulting in a long vibrational progression, where the underlying modes are not resolvable in the experiment.

The sharp peaks in the case of the $Li_4{}^-$ cluster clearly suggest that the anionic geometry cannot be a linear chain as in $Na_4{}^-$ and $K_4{}^-$. Why the geometry of $Li_4{}^-$ should be different from other alkali atom tetramer anions is another matter and will be discussed later. The sharpness of the peaks can be easily explained in terms of lack of relaxation after photodetachment if the geometry of the $Li_4{}^-$ is a rhombus (i.e., close to the geometry of its neutral counterpart) instead of being linear. This can also explain the narrow gap between the peaks by noting that the gap between the two sharp peaks should correspond to the gap between the singlet and triplet energies of neutral Li_4 having identical rhombus configuration as $Li_4{}^-$. An earlier calculation [10] of the gaps in the energies between spin singlet and triplet states of neutral Li_4 suggests that, for this situation, the ideal apex angle of the $Li_4{}^-$ rhombus that would account for the narrow gap in the photodetachment spectra should be about 75°. To verify if this conclusion is correct we calculated the equilibrium geometry of the Li_4^- using an extensive basis set and quantum chemical method (Hartree-Fock + Möller-Plesset perturbation theory for correlation) [11]. Although the ground state of the Li_4^- geometry was found to be a rhombus, its apex angle was found to be 60°. The energy gap between the singlet and triplet states of the neutral Li_4, with the above geometry, is unfortunately 1.1 eV which does not match with the experimental value of 0.1 eV. The origin of the anomalous photoelectron spectra of Li_4^- has thus to be found elsewhere.

In this Letter, we provide the answer to this puzzling problem. We show that the ground state of the Li_4^- consists of two nearly degenerate isomeric structures—a spin doublet rhombus and a spin quartet tetrahedron. The sharpness as well as the narrow gap between the photoelectron peaks can be explained from the transitions between the spin doublet rhombic (spin quartet tetrahedral) Li_4^- to spin singlet rhombic (spin triplet tetrahedral) neutral Li_4. These transitions originate from an intricate interplay between geometry, electronic structure, and spin multiplicities of alkali clusters. This Letter establishes for the first time that photoelectron spectroscopy can identify the existence of metal cluster isomers. The existence of isomers in carbon clusters and the $(N_2O_2)^-$ ion molecule complex has been known before [12]. In the following, we outline the details of our theoretical approach and elaborate on the mechanisms that underlie the anomalous spectroscopy of Li_4^-.

Using the GAUSSIAN 92 software [13], self-consistent field calculations were performed for the Li and Na clusters using the unrestricted Hartree-Fock approximation. The correlation effect due to all the (valence + core) electrons was included through Möller-Plesset perturbation theory up to fourth order (MP4). A global search was made for the ground state geometry of the Li_4^- at the MP4 level by minimizing the force using the gradient technique. Then the MP4 energies were calculated for the neutral tetramers having the same geometry as its anionic counterpart for various spin multiplicities. Choice of a basis set for anions is notoriously difficult as diffuse functions are needed to represent the situation correctly. After exhaustive tests a $(11s5p/4s3p)$ basis was chosen for the calculations. The calculated value of electron affinity with this basis is 0.49 eV which compares well with the experimental value of 0.62 eV. All the results for Li systems presented in this Letter were obtained using this basis set. The calculations were repeated using the density functional technique and the physics of the results remained identical.

The equilibrium geometries of Li_4^- with doublet and quartet spin configurations are, respectively, rhombus and tetrahedron. The interatomic distance in the rhombus structure is 3.13 Å and the apex angle is 60°. The tetrahedron in nearly perfect with an interatomic distance of 3.05 Å. The corresponding energies are given in Table I. Note that the two structures differ in energy by only about 0.1 eV and are nearly degenerate. As the added electron is photodetached, the spin doublet rhombic Li_4^- can undergo transitions to spin singlet or triplet neutral Li_4, while the spin quartet tetrahedral Li_4^- can undergo transitions to spin triplet neutral Li_4 only. The transition from spin quartet Li_4^- to spin singlet neutral Li_4 is forbidden by the spin selection rule. The energies of the neutral clusters for various spin states and geometries are also given in Table I. The energies for transitions between the anionic and neutral clusters are given in Fig. 1. Note that the present theory predicts three transitions at electron binding energies of 0.70, 0.94, and 1.80 eV. Experimentally, two major peaks are seen at 0.76 and 0.85 eV. Another peak clearly exists at an energy of approximately 2 eV, but it is partially truncated by the transmission function of the electron energy analyzer. We consider the above agreement between theory and experiment to be good.

We next discuss the sharpness of the peaks observed in the experiment on Li_4^-. The transition at 0.70 eV is from a rhombic Li_4^- with an apex angle of 60°. Since the ground state of the neutral Li_4 is a rhombus with an apex angle of 52°, the structure of the excited neutral is not too different in comparison. Consequently, almost no Frank-Condon broadening can be expected in this peak. The transition at 0.94 eV, on the other hand, is from quartet tetrahedral Li_4^- to triplet neutral Li_4. Since the equilibrium geometry of spin triplet neutral Li_4 is also tetrahedral [14], one may not expect any Frank-Condon broadening of this peak either.

It is also important to point out that the intensity of the low energy peak (at 0.76 eV) is larger than that of the high energy peak (at 0.85 eV) for Li_4^- while the *reverse* is true for Na_4^- and K_4^-. The present calculation also offers a qualitative understanding of this anomalous result. The intensity of the peak is governed not only by the probability of transition but also by the preponderance of the anionic isomers from which transitions take place. In the case of Li_4^-, there are two nearly degenerate isomeric states—the rhombus and tetrahedral configurations from which transitions occur, but the transitions are to the lowest excited states of the corresponding neutrals. We expect the rhombic Li_4^- clusters to be larger in number than that of tetrahedral Li_4^- as the ground state of neutral Li_4 is rhombic. Consequently, the peak at 0.76 eV would be more intense than the peak at 0.85 eV, as seen experimentally. In the case of Na_4^- and K_4^-, there is only one anionic ground state geometry. In this case, the transition probability to the higher excited state is larger than to the lower excited state and, hence, the intensity of the high energy peak is higher than that of the low energy peak.

While the above results completely explain the experiment, one wonders if Li_4^- could still exist in the form

TABLE I. Total energies of Li_4^- and the corresponding singlet and triplet states of Li_4 with different optimized geometries. The energy gaps for the spectra are given by $\Delta E = -[E(Li_4^-) - E(Li_4)]$ for the neutral singlet and triplet states.

Geometries	$E(Li_4^-)$ (hartree)	$E(Li_4)$ singlet (hartree)	$E(Li_4)$ triplet (hartree)	Singlet ΔE (eV)	Triplet ΔE (eV)
Tetrahedron	−29.82417	−29.77548	−29.78963	1.32	0.94
Rhombus	−29.82908	−29.80334	−29.76321	0.70	1.80

of a linear chain and if the closely spaced peaks in the spectrum could result from a linear-linear transition with a short vibrational progression in a bending mode. To answer this, we have optimized the geometry of the Li_4^- in the linear form. It is found to lie 0.3 eV above the Li_4^- rhombus configuration. Based on this small energy difference alone, it is difficult to rule out the possibility that Li_4^- could exist in the linear form, especially if it is protected by a large energy barrier. However, the transitions from Li_4^- linear doublet to the corresponding neutral linear structures with spin singlet and triplet configurations are calculated to lie at 1.07 and 1.34 eV, respectively. These do not coincide with the experimental peaks which are at 0.76 and 0.85 eV as mentioned earlier. Thus, we can conclude that the existence of Li_4^- in the linear form is not supported by the experimental photoelectron spectra.

It is now important to ask how a Li_4^- cluster can assume a tetrahedral configuration while the starting neutral cluster is a planar rhombus. To answer this, we have examined the vibrational frequencies of the ground state of Li_4 neutral cluster calculated by Shillady, Rao, and Jena [15]. These authors had analyzed all the normal modes of vibration of the Li_4 cluster and found that the easiest mode to excite (100 cm^{-1}) coupled the planar rhombus structure to the tetrahedral structure. Therefore, the electronic singlet-triplet transition may arise due to a vibronic mechanism. The triplet tetrahedral state of neutral Li_4 is unstable. However, the tetrahedral state is stabilized by attaching an electron, as the quartet tetrahedral Li_4^- is nearly degenerate with the doublet planar structure. To calculate the energy barrier needed for the Li_4^- quartet structure to transform to the Li_4^- rhombus structure, we computed the total energies of Li_4^- as a function of the dihedral angle θ. For $\theta = \pi$, the structure is a rhombus and for $\theta = 70.6°$, it is an almost perfect tetrahedron. For each value of θ in this calculation, we optimized the Li_4^- bond lengths and angles. The energy barrier for this process is approximately 0.3 eV. Thus, once Li_4^- is formed in the high spin state, it is unlikely that it will convert to a low spin structure. It is necessary to carry out similar vibrational analysis of Na_4 and K_4 clusters to see if the vibronic mechanism can lead to a singlet-triplet transition.

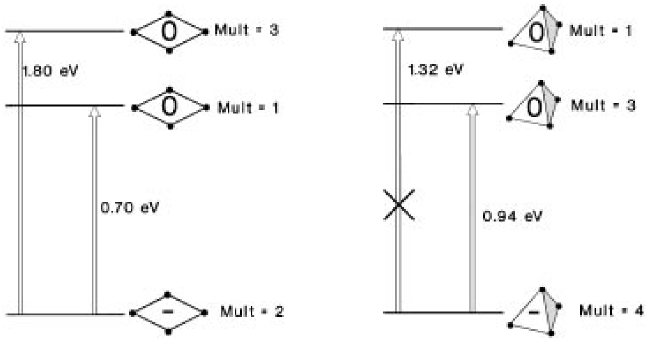

FIG. 1. Vertical photodetachment energies from the nearly degenerate Li_4^- isomers to the corresponding neutral clusters. The disallowed transition is marked by an ×.

We finally address the issue concerning the different geometries and electronic structures of Li_4^- and Na_4^-. It is quite clear that the equilibrium geometry is the one that minimizes the Coulomb repulsion caused by distribution of the extra charge. In a large cluster, the extra charge can be shared among many atoms, thus reducing the Coulomb repulsion. Consequently, the anionic geometry may not be very different from the neutral one. In a small cluster, however, this is not possible since there are not that many atoms to distribute the charge. Therefore, the only way the repulsion energy could be minimized is by separating the charges as far as possible. This dictates a linear chain configuration. Thus, small anionic clusters could start by becoming linear and transform to two-dimensional or three-dimensional structures as they grow. In the case of the Li_n cluster, this transition takes place with $n = 4$, while for Na_n clusters, the transition to planar structure occurs at $n \approx 6$.

To understand why the cluster sizes, where the transition occurs, are different for different alkali metal clusters, we need to look at their electronic structures. An analysis of Mulliken charges on various sites, and a comparison between the electron affinity and ionization potential of the constituent atom, can provide the needed answer. The Mulliken charges on the atoms of the tetrahedral Li_4^- are nearly the same (i.e., −0.21, −0.21, −0.29, and −0.29) while in the rhombus structure the farthest Li atoms carry most of the negative charge (i.e., −0.54 each). For the linear chain Na_4^-, the outer and inner atoms have −0.63 and +0.13 electron, respectively. Clearly, in Na_4^-, the Mulliken charge distribution is very different from that in Li_4^-. Na_4^- minimizes energy by introducing attractive interaction between the outer and inner atoms while coping with the repulsive interaction between the two inner and two outer atoms separately. There is no charge transfer from one atom to another in the case of Li_4^-. The different nature of charge distribution in the clusters of Li_4^- and Na_4^- is a consequence of their characteristic atomic ionization potentials and electron affinities. The electron affinity and the ionization potential for Li are 0.62 and 5.39 eV and for Na these are 0.55 and 5.14 eV, respectively. Thus, the difference between the ionization potential and the electron affinity for Li and Na are 4.77 and 4.59 eV, respectively. Consequently, the charge transfer between the Na atoms in an anionic cluster is more preferable than in a Li cluster.

In conclusion, we have carried out self-consistent field molecular orbital calculations of the equilibrium geometry, binding energy, and electronic structure of Li_4^- and Na_4^- clusters. We have demonstrated that, while the ground state of Na_4^- is a spin doublet linear chain, the ground state of Li_4^- consists of two nearly degenerate isomers having spin doublet rhombus and spin quartet tetrahedral configurations. The existence of these isomers is responsible for the anomalous photoelectron spectra of Li_4^-. It is argued that a comparison between theory and experiment of photoelectron spectroscopy cannot only give information regarding the cluster geometry but also about its isomers and spin multiplicities. We have also shown that unusual properties of Li_4^- are rooted in the electronic structure of the atom itself. We believe that independent experiments designed to detect the possible existence of a high spin Li_4^- state will be highly desirable.

The authors thank Dr. K. H. Bowen and Dr. H. Sarkas for sharing their experimental results prior to publication, for numerous stimulating discussions, and for a critical reading of the manuscript. Two of the authors (P. J. and B. K. R.) acknowledge partial support by the Department of Energy (Contract No. DEFG05–87ER45316). A. K. R. acknowledges support from the Welch Foundation, Houston, Texas (Grant No. Y-1092) and from the University of Texas System Center for High Performance Computing.

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