

LETTERS TO THE EDITOR

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COMMUNICATIONS

Photoelectron spectroscopy of alkali metal tetramer anions: The anomalous spectrum of Li_4^-

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We present the photoelectron spectrum of Li_4^- . This spectrum displays a spectral pattern that is strikingly different from that of the other alkali tetramer anions. Using the photoelectron spectrum of Li_4^- along with our previously measured photoelectron spectra of Na_4^- , K_4^- , and Rb_4^- plus other existing evidence, we find that Li_4^- does not have a linear geometry, as do the tetramer anions of sodium, potassium, and rubidium. This observation indicates that for both anions and neutrals, lithium clusters appear to take on higher dimensional structures at smaller sizes than do sodium and probably other alkali clusters. By examining the clues found in its photoelectron spectrum, we then speculate as to what the structure of Li_4^- may be and also summarize the present state of theoretical progress on this problem. © 1995 American Institute of Physics.

In the condensed phase, lithium is significantly different from the other alkali metals, exhibiting electronic and optical properties that deviate noticeably from the trends seen among the other members of the group.¹⁻³ Here, we present the photoelectron spectrum of Li_4^- . This spectrum displays a spectral pattern that is strikingly different from that of the other alkali tetramer anions. Using the photoelectron spectrum of Li_4^- along with our previously measured photoelectron spectra of Na_4^- , K_4^- , and Rb_4^- plus other existing evidence, we find that Li_4^- does not have a linear geometry, as do the tetramer anions of sodium, potassium, and rubidium. By examining the clues found in its photoelectron spectrum, we then speculate as to what the structure of Li_4^- may be. Lastly, we summarize the present state of theoretical progress on this problem.

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. Our negative ion photoelectron spectrometer has been described previously.⁴ Briefly, anions are generated in a supersonic expansion ion source, skimmed, and transported through a series of ion optical components through an $\mathbf{E} \times \mathbf{B}$ Wien filter where they are mass selected. The mass-selected cluster anion beam is then crossed with the intracavity beam of an argon ion laser. A small solid angle of the resulting photodetached electrons is accepted into a hemispherical electron energy analyzer, where they are energy analyzed and counted. Photoelectron spectra of Li_4^- were recorded at an instrumental resolution of

30 meV using 110–120 circulating Watts of 2.540 eV photons.

Beams of Li_4^- were generated using a high temperature, supersonic expansion ion source.⁵ In this source lithium metal is heated to 1300 K, yielding ~ 50 torr of lithium vapor which is coexpanded with 50–150 torr of high purity argon into high vacuum through a 0.15 mm nozzle. A negatively biased hot filament injects low energy electrons directly into the expanding jet in the presence of a predominantly axial magnetic field, thereby generating negative ions. The resultant beam is skimmed by a high temperature skimmer and anions are extracted into the spectrometer.

The photoelectron spectrum of Li_4^- is presented in Fig. 1, along with our previously reported photoelectron spectra of Na_4^- and K_4^- .^{6,7} The features in all three spectra arise due to photodetachment transitions from a given alkali tetramer anion to energetically accessible states of its corresponding neutral. The Na_4^- and K_4^- photoelectron spectra show qualitatively similar spectral patterns for the three lowest electron binding energy (EBE) features in each spectrum. As an additional comparison, we also recorded a preliminary photoelectron spectrum of Rb_4^- , which displayed the same fingerprint pattern. This strongly suggests that these three systems (Na_4^- , K_4^- , and Rb_4^-) are similar to each other in a qualitative sense both in their initial (anion) states and in their final (neutral) states.⁸ The photoelectron spectrum of Li_4^- , on the other hand, displays a spectral pattern which is strikingly different from those of the Na_4^- , K_4^- , and Rb_4^- spectra, suggesting that lithium tetramer differs significantly from the other tetramers either in its anion state, in its neutral state, or in both.

The photoelectron spectra of Na_4^- and K_4^- have both been modeled theoretically by Bonacic-Koutecky and co-workers.⁹⁻¹² The two lowest energy forms of Na_4^- and of K_4^- were found from *ab initio* calculations to be linear and rhombic, with the linear (${}^2\Sigma_g^+$) form being slightly more

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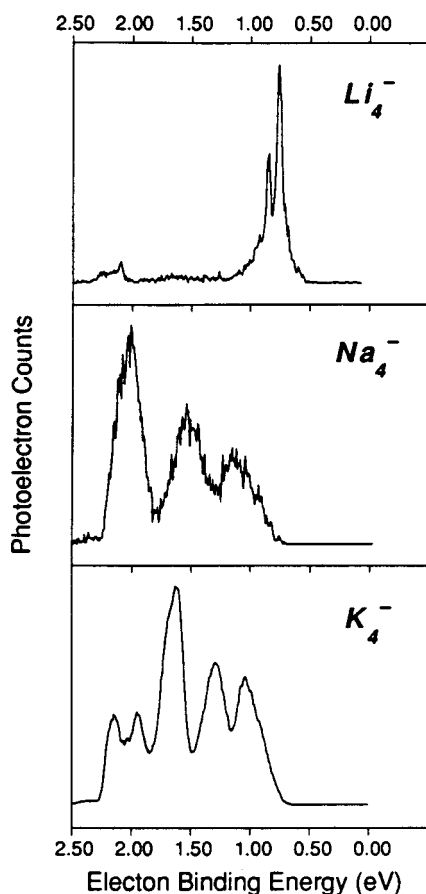


FIG. 1. The photoelectron spectra of Li_4^- , Na_4^- , and K_4^- recorded using 2.540 eV photons. The spectrum of Li_4^- was recorded with beam currents of 2–20 pA over approximately 4 h, and was calibrated using the spectrum of Li^- . The spectra of Na_4^- and K_4^- are taken from Refs. 6 and 7, respectively.

stable in both systems. A comparison of the computed vertical transition energies with the observed photoelectron spectra implied that both spectra were due to the photodetachment of linear anions. Based on the results of numerous theoretical studies, the potential energy surfaces for both sodium^{13–21} and potassium^{15,16,22} neutral tetramers are also expected to be qualitatively similar, both having 1A_g ground states with rhombic equilibrium geometries. Indeed, Bonačić-Koutecký's¹⁰ theoretical modeling of Kappes' ²³ photodepletion spectrum of Na_4 is consistent with theory's characterization of sodium tetramer. Thus, it is likely that the strong similarities seen in the photoelectron spectra of Na_4^- , K_4^- , and Rb_4^- arise due to the existence of linear geometries for each of these anions and the presence of qualitative similarities in the potential energy surfaces of their corresponding neutrals.

As in the cases of Na_4 and K_4 , numerous theoretical calculations also find Li_4 to have a 1A_g ground state with a rhombic equilibrium geometry,^{14,24–33} and Bonačić-Koutecký's³⁴ theoretical modeling of Broyer's^{34–36} photodepletion spectrum of Li_4 supports these findings. The fact that the neutral species Li_4 , Na_4 , and K_4 all exhibit the same ground state electronic symmetries with the same equilibrium geometrical symmetries suggests that their potential energy surfaces may share broad qualitative similarities. Of

course, the most pertinent portions of these neutral surfaces to consider in the present context are those corresponding to the anions' linear geometry, and these have been examined for Li_4 ^{25,29} and Na_4 ¹³ in several theoretical studies. In both cases, when the potential energy of the tetramer system was determined as a function of the distance between two dimers engaged in a collinear approach, no bond was formed, i.e., both systems acted similarly with no indication of differing behaviors in their linear configurations. This reassures us that the general similarities seen among the potential surfaces of neutral alkali tetramers at their equilibrium geometries are probably maintained at their linear geometries as well.

In summary, the photoelectron spectrum of Li_4^- displays a spectral pattern which is strikingly different from those of Na_4^- , K_4^- , and Rb_4^- , all three of which are qualitatively rather similar to each other. Existing evidence indicates that Na_4^- and K_4^- are both linear anions (likewise for Rb_4^-), that Li_4 , Na_4 , and K_4 all have rhombic equilibrium geometries, and that the potential surfaces of Li_4 , Na_4 , and presumably K_4 continue to display qualitatively similar topologies at their linear configurations. Taken together, this information implies that Li_4^- is qualitatively dissimilar to Na_4^- , K_4^- , and Rb_4^- . *Specifically, we conclude that Li_4^- is not a linear ($^2\Sigma_g^+$) anion, and thus possesses some higher dimensional structure than do Na_4^- , K_4^- , and Rb_4^- .*

Lithium cluster anions thus appear to undergo a transition from linear structures to structures of higher dimensionality at four atoms,³⁷ in contrast with cluster anions of sodium and potassium, where photoelectron data along with theoretical results imply a dimensionality transition at their pentamer anions, favoring planar trapezoidal geometries.^{6,7,9–12} Analogous behavior has also been observed for neutral clusters of lithium vs sodium. Photodepletion spectra³⁸ along with theoretical results³⁹ indicate a transition from planar to three-dimensional structures for neutral sodium clusters at seven atoms, in accord with matrix ESR results on Na_7 .⁴⁰ In the case of neutral lithium clusters, experiment and theory together indicate that such a transition has already occurred by six atoms.³⁴ Thus, for both anions and neutrals, lithium clusters appear to take on higher dimensional structures at smaller sizes than do sodium and probably other alkali clusters.

The previous discussion addressed the issue of what Li_4^- is not. The specific features in its photoelectron spectrum, however, provide clues as to what the structure of Li_4^- is. The Li_4^- spectrum is dominated by three features, two peaks at relatively low EBE and at least one feature at relatively high EBE, the latter of which is no doubt attenuated somewhat by the unavoidable electron transmission function cutoff at that end of the spectrum. All three features in the photoelectron spectrum of Li_4^- must be satisfactorily assigned before the structure of this anion can be determined, and such assignments must also be consistent with the observed spectral peak shapes. These features can all be attributed to separate electronic transitions. The two closely spaced peaks at low EBE cannot correspond to vibrational features within a single electronic transition. Given the harmonic frequencies of ground state Li_4 , calculated in several, closely agreeing theoretical studies,^{21,25,30,41} the 90 meV spacing between

them is inconsistent with such an explanation.

The shapes of the electronic bands in the Li_4^- spectrum provide additional information. The lowest EBE feature, in particular, is quite sharp, and this suggests rather similar structures for the anion (initial state) and neutral (final state). This naturally led us to speculate that the structure of Li_4^- is a rhombus, similar to the lowest energy structure found for Li_4 neutral.^{24–36} One difficulty with this explanation is that it implies an unexpectedly small singlet–triplet energy splitting for the neutral rhombus. Theoretical studies, however, had previously examined the variation of the singlet–triplet energy splitting in neutral Li_4 as a function of the rhombus apex angles.^{14,32} As the neutral rhombus was distorted toward a square geometry, singlet–triplet energy splittings were predicted that are comparable to the splitting observed here between the two low EBE peaks in the photoelectron spectrum of Li_4^- . While it is tantalizing to speculate on this basis that Li_4^- has a geometry tending toward a square, within this explanation one would expect the lower EBE feature to be somewhat broader (due to Franck–Condon overlap arguments). Even though this appears to be the case at the bases of the peaks, it is difficult to ascertain with confidence. In order to make a definitive assignment of the Li_4^- photoelectron spectrum, theoretical guidance is required.

In our initial efforts to explain the electronic features in the Li_4^- spectrum, the results of two early theoretical studies on small lithium cluster anions were considered. One study⁴² found Li_4^- to have a linear lowest energy structure with a T-shaped C_{2v} structure only slightly higher in energy, while the other study³¹ found the T-shaped C_{2v} form as the lowest energy structure. Unfortunately, neither structure considered in these pioneering calculations seems to be a likely candidate for explaining the observed spectrum. The above comparison of the Li_4^- spectrum with those of Na_4^- and K_4^- has already eliminated the linear form, and in addition, no features due to a linear isomer are apparent in the spectrum.⁴³ The T-shaped C_{2v} structure seems unlikely on the basis that it is thought to correspond to a saddle point on the neutral Li_4 surface,^{16,25} while the sharp spectral features in the Li_4^- spectrum suggest, on the other hand, a minimum in the neutral potential energy surface near the anion geometry.

The anomalous and intriguing nature of the photoelectron spectrum of Li_4^- has sparked a recent wave of theoretical interest in this anion. Currently, four theoretical studies are in progress regarding Li_4^- and its photoelectron spectrum.^{44–47} To date, Bonačić-Koutecký and co-workers⁴⁴ have considered a number of structures for Li_4^- and have computed vertical photodetachment transition energies for several of them. They find the ground electronic state of Li_4^- to be a rhombus having a doublet spin multiplicity, and their lowest computed transition energy for this form is consistent with the EBE of the lowest feature in our spectrum. They also predict the singlet–triplet energy splitting of neutral Li_4 at the optimized geometry of Li_4^- to be somewhat larger than that between the two lowest EBE features in the Li_4^- spectrum. In addition, they find a distorted D_{2d} form to be the best structure for Li_4^- having quartet spin multiplicity. Rao and Jena⁴⁵ have considered a range of geometries, also finding the ground state of Li_4^- to be a doublet rhombus and a distorted tetrahedron to be

the lowest energy form of quartet Li_4^- . They invoke the role of both of these isomeric forms to explain the Li_4^- spectrum, and their computed transition energies are consistent with the actual spectrum. Attempts to test this hypothesis experimentally via source condition studies have been inconclusive, however, due to the unusually narrow range of source conditions under which this anion can be generated in our ion source. Hamilton and Kawai⁴⁶ also find the ground electronic state of Li_4^- to be a doublet rhombus, while Hall and Kestner⁴⁷ are currently examining this problem using a combination of path integral simulations and quantum chemistry. Finally, three of these groups^{44–46} have also computed vertical transition energies for T-shaped Li_4^- , and have found them to be inconsistent with the observed spectral features. These continuing efforts should yield information enabling a complete assignment of the Li_4^- photoelectron spectrum, thereby elucidating the electronic and geometric structure of this anion.

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