

Strongly correlated states in the Li^- ion

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A collinear laser-ion beam apparatus has been used to investigate resonance structure in the $\text{Li}(3s) + e^-(kp)$ partial photodetachment cross section below the $\text{Li}(6p)$ threshold. A complex rotation calculation was used to identify the strongly correlated, doubly excited states of the quasi-two-electron ion Li^- that are responsible for the observed resonances. These represent the most highly excited states of Li^- observed thus far. Several members of a strong “+” type series were observed as well as at least one resonance with “-” type character. In particular, we report on an observation of a resonance that violates the $\Delta\nu=0$ propensity rule.

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Two electron atomic systems are excellent “laboratories” for investigating the interplay of the electron-nucleus and electron-electron interactions. This is particularly true if both electrons in the system are excited. Electron correlation effects are more enhanced in negative ions than in isoelectronic atoms and positive ions, since the negative ion is the lowest member of the sequence and the electron-nucleus interaction is weakest relative to the electron-electron interaction. Pioneering experiments on the study of doubly excited states in H^- were performed by Bryant *et al.* [1–4] using a fast ion beam from an accelerator and more recently by Balling *et al.* using a storage ring [5]. Theoretical interpretation of the resonance structure observed in the photodetachment experiments was quickly forthcoming. Energies and widths of the doubly excited states associated with the resonances have been calculated using several techniques including the hyperspherical method [6–10], the molecular orbital method [11], the complex coordinate rotation method [12–14], and the R -matrix method [15].

Resonances in two-electron systems can usually be labeled by a set of approximate correlation quantum numbers. Angular correlation can be described by the quantum numbers K and T , which were first introduced by Herrick and Sinanoglu [16] in a group theoretical study of double excitation in He. Radial correlation is commonly classified by the approximate quantum number A , which was suggested by Lin [17]. The value of $A = +1$ (-1) is often referred to as an in-phase (out-of-phase) radial oscillation of the two electrons about the nucleus. More precisely, the wave functions describing states with $A = +1$ (-1) have an antinode (node) at $r_1 = r_2$. Members of a series of doubly excited resonances

can be labeled as ${}_n(K, T)_m^A$, where n is the threshold to which the state is bound and m is a label to count the states. In the case of H^- , the motion of the electrons in a highly correlated state were shown to be similar to those in a floppy three-body rotor; a proton situated between the two excited electrons. In this “molecular” model, the angular and radial correlations of the two electrons were represented by vibrational motions labeled by $\nu = \frac{1}{2}(n - K - T - 1)$.

In the H^- spectrum Harris *et al.* [3,4] observed that only states with $A = +1$ (“+” type states) and maximum $K = n - 2$ were visible in the photodetachment spectra. The non-existence of states of “-” character is associated with the fact that the ground state has “+” character and that the probability of photoexcitation to the other type of radial correlation is weak. The observed spectrum led to the following propensity rules for the production of the doubly excited states [9,18]: $\Delta A = 0$ and $\Delta\nu = 0$.

In the present paper we report on an experimental observation of a state that violates the H^- propensity rule, $\Delta\nu = 0$. This resonance was not detected in the photodetachment spectrum of H^- but rather in that of the quasi-two-electron ion Li^- . The major differences between the resonance spectra of Li^- , which in the frozen core approximation is described as a two-electron system, and H^- are expected to arise from the presence of the finite core in Li^- that serves to lift the degeneracies of the excited state thresholds. This fundamental difference determines the form of the potential field that binds the outermost electron. In the case of H^- , it moves in an essentially permanent dipole field due to the degenerate $\text{H}(n)$ thresholds. In contrast, in a non-hydrogenic negative ion such as Li^- , the outermost electron moves in the shorter range field of an induced dipole.

H^- doubly excited states of “-” character are predicted by calculations to be several orders of magnitude narrower than corresponding states of “+” character. Such extreme differences are not found in Li^- [13]. Mixing of “-” and

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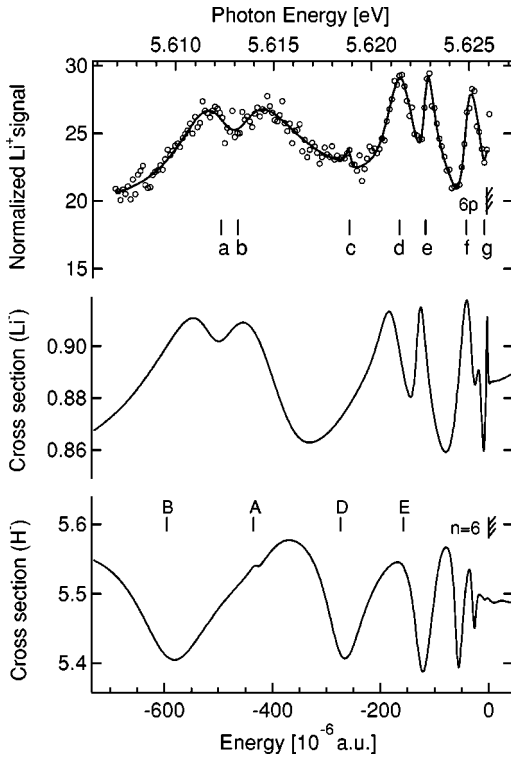


FIG. 1. Top: Experimental $\text{Li}(3s) + e^-(kp)$ partial photodetachment cross section for Li^- . The open circles represent the measurements and the solid line is a fit based on Shore parametrization. The measured energies of the resonances are indicated by the lines a – g . Resonance c is a very weak structure and its assignment is therefore only tentative (see text). Middle: Calculated total photodetachment cross section of Li^- . Bottom: Calculated total photodetachment cross section of H^- below the $\text{H}(n=6)$ threshold. Scales: The energy scale at the top is relative to the Li^- ground state and applies to the top and middle curves, whereas the energy scale at the bottom shows the energy relative to the $\text{Li}(6p)$ threshold (top and middle) and the $\text{H}(n=6)$ threshold (bottom).

“+” type states should lead to less pronounced differences in widths, a phenomenon discussed by Greene [19]. The situation in Li^- can be understood from the hyperspherical adiabatic approximation where autodetachment is described as a localized nonadiabatic transition between two hyperspherical potential curves. In Li^- a larger number of curves arise from the nondegeneracy of the excited states of Li leading to “avoided” level crossings and the possibility of enhanced mixing of “–” and “+” type states.

In the present experiment we have used an apparatus in which a laser beam is collinearly superimposed on a 3.1-keV beam of Li^- ions. The experimental procedure has been described in a previous publication [20,21]. With this collinear arrangement it is possible to attain, simultaneously, high sensitivity and resolution in the measurements. A two-color laser excitation-detection scheme was used to investigate the photodetachment of Li^- via the $\text{Li}(3s) + e^-(kp)$ channel. The first laser was used to induce the photodetachment process. Of particular interest was the resonant process in which Li^- ions were excited to doubly excited states of $^1P^o$ symmetry that were bound with respect to the excited $\text{Li}(6p)$

TABLE I. Energies E_r (eV, relative to the ground state) and widths Γ (eV) of doubly excited states in Li^- . Labels refer to the resonances shown in Fig. 1 (top). Note that the assignment of resonance c is only tentative since this is a very weak structure in the spectrum. The K quantum number is calculated as $-n\langle\cos\theta_{12}\rangle$ and $\langle r_{>} \rangle$ is the expectation value of the radial coordinate of the outermost electron (Bohr radii).

Label	$E_r(\text{Expt.})$	$\Gamma(\text{Expt.})$	E_r (Theor.)	Γ (Theor.)	K	$\langle r_{>} \rangle$
a	5.6123(14)	0.0022(11)	5.6120	0.003	3.4	154
b	5.6132(13)	0.0018(11)	5.6142	0.007	4.2	173
c	5.61888(12)	0.00013(10)	5.6163	0.004	2.3	139
d	5.62143(13)	0.00093(11)	5.6208	0.002	3.1	209
e	5.62277(5)	0.00030(5)	5.6223	0.001	3.2	229
f	5.62484(8)	0.00045(10)	5.6245	0.002	2.2	235
g	5.6258(3)	0.00026(19)	5.6255	0.0005	2.5	438

atom. The $\text{Li}(3s) + e^-(kp)$ channel was isolated from the many open decay channels by selectively ionizing the residual atoms left in the $\text{Li}(3s)$ state following photodetachment. This was accomplished by using a second laser to resonantly photoexcite the Li atoms from the $3s$ to the $24p$ state. Atoms in such high Rydberg states are very efficiently ionized in a weak electric field. The resulting Li^+ ion signal is proportional to the partial cross section for photodetachment of Li^- via the $\text{Li}(3s) + e^-(kp)$ channel. The relative partial cross section was obtained by recording the Li^+ signal as a function of the laser frequency. A small background was subtracted and the signal was normalized to the ion beam current and the photon flux. The frequency scale of the first laser was calibrated by use of reference spectral lines in Ar produced via the optogalvanic effect in a hollow cathode lamp. The internal scale of the laser was used to interpolate between these absolute calibration points. A small Doppler shift arising from the unidirectional motion of the ions was calculated from the known ion beam energy and taken into account in the calibration.

The measured relative partial cross section for photodetachment of Li^- via the $\text{Li}(3s) + e^-(kp)$ channel is shown at the top of Fig. 1. The scatter in the data corresponds to shot noise in the counting of the Li^+ ions. Resonance structure is clearly present in the cross section below the $\text{Li}(6p)$ threshold. We have used a Shore parametrization [22] to extract the energies and widths of these resonances. It was found that a fit including seven Shore profiles best approximated the experimental data. The result of this fit is represented by the solid line in Fig. 1. The measured energies and widths of the resonances are listed in Table I, where the quoted errors represent the statistical uncertainties from the fit. The energies are also indicated by the labels a – g in Fig. 1.

In order to identify the observed resonances, we have calculated the expected spectrum of doubly excited states of Li^- in the energy range covered by the experiment. (An R -matrix cross section calculation has been made by Pan *et al.* [23], but no resonance parameters were quoted.) The theoretical results were obtained by employing the method of

complex rotation, to handle autodetaching states, combined with the use of B -splines, as described in [24]. First one-particle states in the potential arising from the nucleus and the $1s^2$ core are constructed. The interaction of each of the excited electrons with the core is described by a Hartree-Fock potential plus a polarization potential [13]. For each angular momenta we use 60 B splines defined in a spherical cavity of ~ 1600 Bohr radii. As a second step, the one-particle states are used to construct the Hamiltonian matrix of $^1P^o$ symmetry for the two outer electrons. Around 8000 configurations of angular symmetry up to $\ell_1\ell_2=6,7$ are used. The calculation thus includes all the $\text{Li}(n=6)$ thresholds. Diagonalization of the matrix yields a set of eigenstates, which comprise a discretized spectrum of the Li^- ion. Some eigenstates represent the doubly excited states with positions and half widths given by the complex eigenvalues. Other states give a (discretized) description of the continuum.

The calculated energies and widths of the doubly excited states in Li^- are compared to the measured values in Table I. The agreement is good in the case of energies, and to a lesser extent for the widths. The discrepancies in the widths are partly the result of our attempts to fit overlapping resonances. The separation between resonances a and b is, in particular, much smaller than their widths. The experimentally determined widths then become very sensitive to the fitting range. The sum of their widths is, however, relatively stable in the fitting procedure.

As a first step in the identification of these states we investigated if they belonged to one or several series. Here, we used the energy positions and widths, as well as the expectation value of $r_>$, the radial coordinate of the outermost electron. The relative spacings of the seven resonances in the Li^- spectrum, as shown by the labels $a-g$ in Fig. 1, clearly indicate that they do not all belong to a common series, in contrast to the case of H^- . In particular, resonances a and b cannot be members of a series since they are too closely spaced in energy (the separation of adjacent members of a series is largest for the lower members of a series). The results of our *ab initio* calculation allowed us to assign resonances b, d, f and g to a common series; the calculated values of E_r , Γ , and $\langle r_>$ shown in Table I follow the expected pattern of energy convergence, width reduction, and increase in the extension of the radial wave function for members of a series as the threshold is approached. This assignment was further supported by using the semiempirical expression derived by Kiyani [25] that can predict the number of resonances in a series bound in a short range potential and their relative binding energies. This expression was obtained by considering the semiclassical motion of the outermost electron of a negative ion in the induced-dipole field of the excited parent atom core. The Bohr-Sommerfeld quantization rule was used to determine the spectrum of bound states in the polarization potential arising from the induced dipole. Similarly, we have shown that resonances a and e belong to another series, whereas resonance c does not fit into either of these series and is possibly the sole observed member of a third series.

As the next step we tentatively identify these resonances using the classification scheme previously applied to H^- . This labeling is expected to be valid primarily for the lowest energy resonances, for which the $n=6$ thresholds appear to be approximately degenerate. For this classification we calculate the quantum number K , which is approximately equal to the quantity $-n\langle \cos \theta_{12} \rangle$. In Ref. [26] the direct projection of accurate two-electron wave functions onto pure (K, T) states was used to investigate both the validity of $K \approx -n\langle \cos \theta_{12} \rangle$ and to which extent a departure from an integer value indicates mixing of (K, T) states. It was shown that the expectation value of the interelectronic angle provides a simple way to identify a state and to determine the purity of it. In Table I the calculated values $K \approx -n\langle \cos \theta_{12} \rangle$ are listed. In particular, it can be seen that the lowest energy resonances of Li^- (a and b) can approximately be labeled with $K=3$ and $K=4$, respectively. It therefore appears that resonances b, d, f and g , which we previously attributed to one series, are members of a $^1P^o$ series corresponding to the ${}_n(K, T)^A = {}_6(4, 1)^+$ series in the H^- spectrum. This “+” type series, which is characterized by the maximum value of K and thus by the maximum value of $\langle \cos \theta_{12} \rangle$, dominates the Li^- spectrum as it did in the measured H^- spectrum. In a similar way we can label the a and e resonances to be members of the $(K, T)^A = (3, 0)^-$ series. Note that the identification of a state as $K=3$ below $n=6$ is enough to label it $(K, T)^A = (3, 0)^-$ since the quantum numbers are not independent of each other [8]. The wave function for resonance b clearly exhibits an antinode at $r_1=r_2$, confirming its “+” characterization. The wave function for resonance a should have a nodal structure at $r_1=r_2$ if it has a “-” character. The calculation shows a definite decrease in the probability density at $r_1=r_2$ but the nodal structure is not as sharp as the antinodal structure associated with resonance b . In the case of Li^- , the nodal and antinodal structures for resonances a and b , respectively, are not as well defined as for the corresponding resonances in H^- , due to the higher degree of mixing. Resonances with “-” character were not apparent in our measurements of Li^- photodetachment spectra at lower levels of excitation. Recently, however, Liu and Starace [27] theoretically predicted a “-” type resonance in the Li^- spectrum below the $\text{Li}(5p)$ threshold but it could not be conclusively identified in our previously measured spectrum covering this region [20].

The weakest resonance in the spectrum, labeled c in Fig. 1, has an energy which is in approximate agreement with the calculated energy of a member of the ${}_6(2, 1)^+$ series. Such a resonance corresponds to $K=n-4$.

This tentative assignment is based on the observation that the calculated interelectronic angle, and thus the value of the quantum number K , is smaller than for members of the $(4, 1)^+$ and $(3, 0)^-$ series. The presence of a resonance of this type would represent another violation of the H^- propensity rules. This assignment is only tentative, however, since the resonance is a relatively weak feature of the spectrum.

To further illustrate that we can label the states in Li^- according to the H^- classification scheme, we have made a comparison between the calculated total photodetachment

spectra of the two ions. For these calculations all the correlated states (both discretized and bound as described above) are used to span the available space for the Li^- and H^- ions after photoabsorption. In Fig. 1 (bottom) it can be seen how a prominent H^- window resonance, $(K,T)^A=(4,1)^+$ (labeled *B*), with a small and hardly visible companion, $(K,T)^A=(3,0)^-$ (labeled *A*), show up as a clear double peak structure in the Li^- spectrum (middle). In this case the ordering of the states has changed. Similarly, the unresolved resonances *D* and *E* in the H^- spectrum have been separated into the “+” type resonance *d* and the “-” type resonance *e* in the Li^- spectrum. Thus the pattern observed in H^- is broken. Photoexcitation of Li^- to $(K=n-2, T=1)^+$ states still dominate but the $(K=n-3, T=0)^-$ states are also weakly excited. The spectra of the two ions are shown with the same energy scale aligned at the $\text{H}(n=6)$ and the $\text{Li}(6p)$ thresholds. The calculated Li^- total photodetachment cross section is shown below the measured spectrum in order to allow an easy comparison. In this particular case the total and partial cross sections are similar in shape.

In conclusion, we have experimentally studied seven previously unobserved resonances in the Li^- spectrum situated below the $\text{Li}(6p)$ threshold. By investigating their relative

positions, widths, and the extent of their radial wave functions we have been able to show that they are members of at least two separate series. We have further shown that at least one of them is predominantly of “-” character. It is shown that at the present degree of excitation, sufficient mixing between “+” and “-” states exists in order to allow efficient excitation from the “+” character Li^- ground state to “-” type excited states. The mixing of the state, however, is at the same time sufficiently small to allow a positive identification of the states according to the H^- classification scheme. If the floppy-rotor model were to be extended to the observed correlated states in Li^- , the dominant “+” type series, starting with resonance *b*, would correspond to the ground state ($\nu=0$) of the bending vibrational motion. The resonance *a*, which we have identified as a member of the ${}_6(3,0)^-$ series, then corresponds to an excited state ($\nu=1$) of this motion. The excitation of this state violates the propensity rule $\Delta\nu=0$.

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