

Resonance Structure in the Li^- Photodetachment Cross Section

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We report on the first observation of resonance structure in the total cross section for the photodetachment of Li^- . The structure arises from the autodetaching decay of doubly excited $1P^o$ states of Li^- that are bound with respect to the $3p$ state of the Li atom. Calculations have been performed for both Li^- and H^- to assist in the identification of these resonances. The lowest lying resonance is a symmetrically excited intrashell resonance. Higher lying asymmetrically excited intershell states are observed which converge on the $\text{Li}(3p)$ limit.

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Processes such as double excitation and ionization of few-electron atomic systems provide valuable insights into the dynamics of electron-electron correlation [1]. Double excitation has been studied in experiments involving photon, electron, and heavy particle impact on atoms and ions. Photoexcitation, although restricted by the electric dipole selection rules, provides the potential for the highest energy resolution, which is of considerable importance in the investigation of narrow and closely spaced resonance structures. In such investigations the helium atom has been the most studied system [2,3]. Negative ions, however, are more sensitive to correlation effects than corresponding isoelectronic atoms or positive ions since for this member of a sequence the core field is weakest and therefore the masking of the subtler interelectronic interaction is reduced. The photodouble excitation of a negative ion involves the simultaneous promotion of a pair of electrons to relatively large distances from a singly charged core. Under this condition the interaction between the pair of electrons can become comparable in strength to the weakened interaction of each electron with the core. The motion of the excited electrons then becomes highly correlated and the independent electron model ceases to be a valid approximation.

Until recently, most investigations of photodouble excitation in negative ions involved the H^- ion. Experimental studies of photodetachment in this prototype anion have been reported by Bryant and co-workers [4,5], and several computational techniques [6–10] have been applied to account for the observed resonance structure. Negative ions of heavier alkali metals have also been studied [11].

In this paper we report on the first observation of resonance structure in the total cross section for the photodetachment of Li^- . The resonances are of $1P^o$ final state symmetry and are optically coupled to the ground state. They arise from the photoexcitation and subsequent autodetaching decay of doubly excited states of Li^- that are embedded in continua representing an excited Li atom and a free electron. The resonances were observed to lie in the energy region between the $\text{Li}(3s)$ and $\text{Li}(3p)$ thresholds. Recently Pan, Starace, and

Greene have used an eigenchannel R -matrix method to predict the shape of the photodetachment cross section in the vicinity of the Li ($n = 3$) threshold [12] and the Li ($n = 4, 5, 6$) thresholds [13]. The measurements reported here present us with an opportunity to compare experimental data on Li^- with corresponding data on H^- [4]. Differences in the spectra of Li^- and H^- associated with the lifting of the degeneracy characteristic of the H atom are apparent, as are certain similarities. We present also new calculations on Li^- and H^- which are used to explain the origin of the observed resonances. The method accounts for full correlation between the outer electrons, and the autodetaching decay of doubly excited states is treated using complex rotation.

Experimental investigations of narrow and relatively weak resonance structure in total photodetachment cross sections demand measurements of both high sensitivity and resolution. These conditions were achieved in the present experiment by the use of a collinear beam apparatus, described in detail elsewhere [14], in which a tenuous beam of Li^- is superposed with a laser beam over a common path of about 50 cm (see Fig. 1).

The energy resolution of our apparatus has been shown in a recent experiment [15] to be limited by the linewidth of the laser, which in the present experiment gives an energy resolution of $25 \mu\text{eV}$.

Li^- ions were generated in a hot-plasma-type ion source and accelerated to 4 keV. The tunable ultraviolet radiation used to transiently produce the doubly excited state by photoabsorption from the Li^- ground state was generated by frequency doubling of the fundamental output of

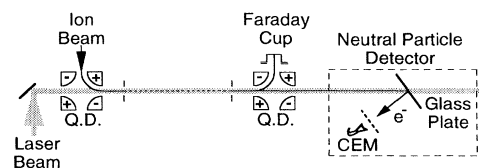


FIG. 1. Portion of the collinear laser ion beam apparatus showing the interaction and detection regions. Two quadrupole deflectors (QD) are used to merge the two beams.

a XeCl excimer-pumped dye laser. Neutral Li atoms produced by photodetachment were separated from Li^- ions by means of an electrostatic quadrupole deflector (QD) and detected. The neutral atom detector consisted of a glass plate (coated with a thin layer of $\text{In}_2\text{O}_3 : \text{Sn}$ to prevent charge buildup) and a channel electron multiplier (CEM) that was employed to count the secondary electrons produced by the impact of the neutrals on the plate. A background signal from neutrals produced by the detachment in collisions with the residual gas in the experimental chamber was rendered essentially negligible by maintaining a vacuum of about 10^{-9} mbar. A potentially more serious background source, however, was associated with photoelectrons generated on the glass plate of the neutral atom detector by the pulsed uv radiation. This contribution was greatly reduced by modulating the bias on a grid placed between the glass plate and the CEM. For a short time after the arrival of the laser pulse, a grid voltage of -40 V was used to prevent the background photoelectrons from reaching the CEM. The grid voltage was reduced to zero about $0.5 \mu\text{s}$ after the laser pulse (the shortest flight time of the neutrals from the interaction region to the glass plate) in order to detect the neutrals constituting the signal. This gated detection procedure significantly enhanced the sensitivity of the measurement. The neutral atom signal, normalized to the intensities of the ion and photon beams, was used as a monitor of the relative total photodetachment cross section.

The experimentally determined total photodetachment cross section is shown as the dots in Fig. 2. All data

points have been normalized to the theoretically calculated value at the $3p$ threshold. The scatter in the data is primarily caused by the small but unavoidable change in the overlap of the ion and laser beams as the wavelength of the laser was scanned. The normalization procedure was unable to completely account for the beam overlap variation. We estimated, however, that this effect causes a maximum error in the relative cross section over the whole spectrum of less than 10%. The statistical scatter, mainly caused by the shot noise in counting of the neutral particles, is less than 3%. The experimental data exhibit three significant features. There is a small and narrow dip in the cross section just at the $3p$ threshold which we interpret as the Wigner cusp arising from the opening of a new photodetachment channel. Second, there is a narrow resonance structure just below the threshold and, finally, a very broad resonance occupies a large part of the region between the $\text{Li}(3s)$ and $\text{Li}(3p)$ thresholds.

In order to explain the origin of the resonances in the observed cross section, we have calculated the expected spectrum of resonances in the photodetachment cross section of Li^- . We have also made a calculation for H^- for the purpose of identifying differences associated with the presence or absence of a core. The calculated cross section for Li^- is shown in Fig. 2, and the parameters associated with the broad intrashell ($n = N$) resonance in each spectrum are listed in Table I. The calculation exploits a recently developed approach [16] which combines complex rotation, where the radial coordinates are scaled with a complex constant $r \rightarrow re^{i\theta}$, with the use of

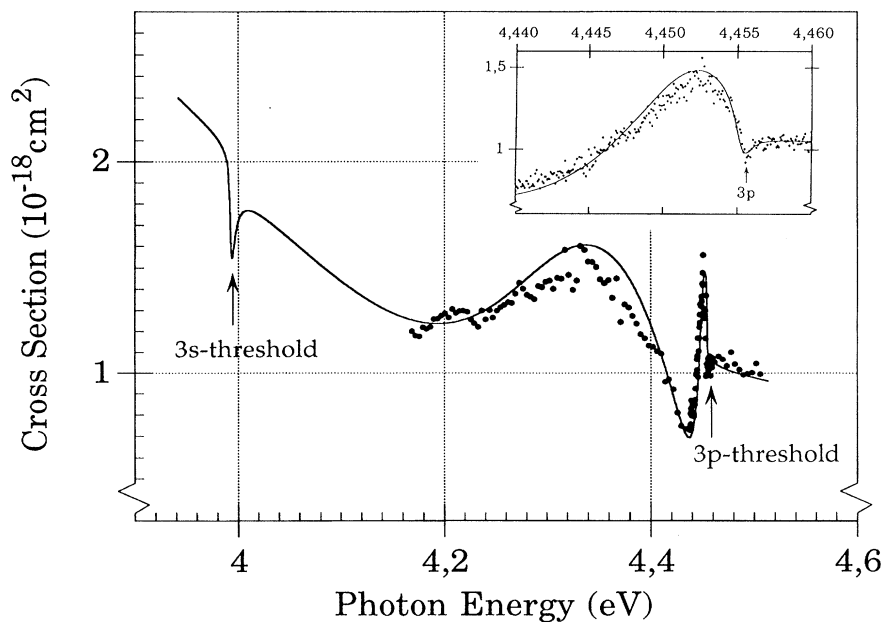


FIG. 2. Total photodetachment cross section for Li^- in the region between the $3s$ and $3p$ thresholds. The dots represent the experimental data, while the solid line represents the theoretical result. The inset shows an expansion of the region around the $3p$ threshold.

TABLE I. Comparison between experimental and theoretical results for intrashell $^1P^o$ states of H^- below the $H(n=3)$ threshold and of Li^- below the $Li(3p)$ threshold. Energies and widths for the doubly excited states are given in eV. Both transition energies (relative to the ground state) and binding energies (relative to the double detachment limit) are given.

	Ho ^a		Present ^b			Experiment ^c	
	E_{bind}	Γ	E_{bind}	Γ	E_{tran}	E_{tran}	Γ
H^-	-1.705689	0.03240	-1.706	0.033	12.647	12.650 ± 0.004	0.0275 ± 0.008
Li^-			-1.69	0.36	4.32		

^aHylleraas wave functions and complex rotation, Ref. [9].

^bPartial waves included up to $\ell_{max} = 3$.

^cHamm *et al.* [4].

a discrete numerical basis set [17]. The ground states of Li^- and H^- were calculated with the use of perturbation theory, while a representation of the spectrum of final states was obtained by diagonalization of the matrix for the interaction between the two outer electrons. This procedure yields a two-particle basis set which includes both doubly excited states, coupled to the continuum, and bound-continuum states. To construct the matrix we have typically used 1400 basis set combinations, including both continuum and bound orbitals, but the selection was limited to sp , pd , and df symmetries. The number of partial waves included is the only important approximation for H^- and determines the number of digits given in Table I. For Li^- , approximations are also made concerning the interaction between the core and the outer electrons. Our one-particle basis set consists of Hartree-Fock orbitals obtained in the potential arising from the $1s^2$ core plus a nonlocal polarization potential which accounts for the dominating correlation effects in neutral Li. Except for this correction the core is assumed to be inert. The eigenvectors of the matrix are denoted Ψ_n , and they constitute a discretized description of the correlated final states. Some of these states are rather localized doubly excited states, and the real and imaginary parts of their complex eigenvalues correspond to their energy, E_r , and half-width, $\Gamma/2$, respectively. The remaining eigenvectors constitute a discretized description of the bound-continuum channels.

The cross section for photodetachment in the complex rotation scheme has been discussed by Rescigno and McKoy [18] and is calculated as

$$\sigma(\omega) = \frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{3} \frac{\omega}{c} \Im \left(\sum_n \frac{\langle \Psi_0 | \sum_j \mathbf{r}_j e^{i\theta} | \Psi_n \rangle \langle \Psi_n | \sum_j \mathbf{r}_j e^{i\theta} | \Psi_0 \rangle}{E_n - E_0 - \hbar\omega} \right), \quad (1)$$

where each Ψ_n represents a correlated state with a complex energy, $E_n = E_r - i\Gamma/2$. The initial ground state is denoted by Ψ_0 . The usual expression which requires summation over discrete final states, Ψ_n , and integration over continuum states is replaced in this case by a summation over the discretized two electron

spectrum. The use of complex rotation allows us to carry out the sum directly without any special considerations close to the poles in the energy denominator.

The calculated cross section for Li^- obtained using Eq. (1) is shown as the solid line in Fig. 2. In general there is a good agreement with the experimental data. The major discrepancy is in the height of the broad resonance, but this difference is within the estimated experimental error. The theoretical resonance parameters, displayed in Table I, are obtained from the complex eigenvalues of the resonant states. A simple connection between the resonance parameters and the cross section can be established if the form of the latter was determined by the resonant state alone. The cross section could then be approximated by the Fano profile [19],

$$\sigma(\omega) = \sigma_0 \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}, \quad (2)$$

where $\varepsilon = [\hbar\omega - (E_r - E_0)]/(\Gamma/2)$, q is a shape parameter, and $\hbar\omega$ is the photon energy. This expression is obtainable from Eq. (1) if the sum over all states is replaced by one particular state. If the cross section is strongly influenced by more than one state, however, such a description will certainly not be adequate and as a consequence it will then no longer be possible to obtain the position and width of a particular doubly excited state from the total cross section. This is indeed the situation in the studied region of the Li^- spectrum.

The calculated photodetachment cross section of H^- is in close agreement with that of other calculations [8,10]. The lowest energy resonance is identified with a doubly excited state that has a calculated energy of 12.647 eV (relative to the H^- ground state) and a width of 0.033 eV. These values again agree well with other calculations, such as the accurate results obtained by Ho [9] using Hylleraas-type wave functions. It is also in agreement with the resonance parameters obtained by the analysis, in form of a fit by a Fano line shape, of the experimental data by Hamm *et al.* [4]. The comparison is displayed in Table I. This resonant state is dominated by a few hydrogenic configurations, $3s3p$ (35%), $3p3d$ (31%), and $3p4d$ (11%).

In Fig. 2 it is seen that for Li^- a broad resonance occupies essentially the whole region between the $Li(3s)$

and $\text{Li}(3p)$ thresholds. The calculated cross section is shown as a solid line and is in close agreement with a recent R -matrix calculation [12]. The present calculation predicts a resonant state of width 0.36 eV to lie 4.32 eV above the ground state of Li^- . This state appears to be analogous to the symmetrically excited intrashell state in H^- . It has a very similar binding energy relative to the double detachment limit, but is about 1 order of magnitude broader. The broadening of the resonance in Li^- arises from the strong coupling to the $3s\epsilon p$ continuum, which is not available below $\text{H}(n=3)$ in H^- . The resonant state in Li^- is dominated by the configurations $3p3d$ and $4s3p$, and there appears to be no significant contributions to the localized part of the wave function from configurations with one electron in the $3s$ orbital, which is also in contrast to the case of H^- .

While the H^- intrashell resonance is well described by a Fano profile, the width of the resonant state in Li^- is too broad for this to be possible. The calculated width of 0.36 eV is overlapping the $3p$ threshold as well as the narrow resonance seen just below it in Fig. 2. The latter resonance is due to asymmetrically excited Rydberg-like states. The presence of the threshold and the interference between the resonances affect the shape of the cross section curve significantly. The assumption necessary to obtain a Fano profile, that only one state determines the shape, is clearly not valid. The interference results in a narrowed structure in the spectrum, especially on the high energy side, compared to that which would arise from a hypothetically isolated doubly excited state of width 0.36 eV. Rydberg-like resonant states are also apparent in the calculated spectrum of H^- . These states are bound relative to $\text{H}(n=3)$ by the strong dipolar field between the two electrons arising due to the degeneracy of the $\text{H}(3\ell)$ states and resulting in nearly equal admixtures of $3snp$ and $3pns$ (or $3pns$ and $3dnp$) configurations in their composition. The Rydberg-like states in Li^- , however, do not have this character. They are completely dominated by $3pn\ell$ configurations, with $n \gg 3$, and the dipolar field is in this case insignificant. The explanation for the existence of the Rydberg states in Li^- is the inability of the monopole part of the electron-electron interaction to screen the singly charged core completely. The residual nuclear attraction binds the states below the $\text{Li}(3p)$ threshold.

To conclude, we have studied the total cross section for photodetaching an electron from the Li^- ion in the energy region between the $3s$ and $3p$ thresholds. This region is dominated by a broad resonance. A narrower resonance structure lies just below the $3p$ threshold. By comparing the data with calculated cross sections for Li^-

and H^- we have been able to identify the broad resonance in the Li^- spectrum as being associated with the presence of a symmetrically excited intrashell doubly excited state, analogous to, but much broader than, the intrashell state in H^- . The sharper resonance structure is identified with asymmetrically excited Rydberg-like resonant states. Our intention is to extend the measurements to higher lying resonances to further investigate the similarities and differences between the photodetachment spectra of Li^- and H^- .

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