K-Shell Photodetachment of Li^-: Experiment and Theory

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An experimental *K*-shell photodetachment study of Li^- giving rise to doubly photoionized Li^+ ions has been carried out at the Advanced Light Source, using a collinear photon-ion beam apparatus. The experiment reveals dramatic structure, differing substantially both qualitatively and quantitatively from the corresponding processes above the $1s$ ionization threshold in Li and Li^+, as predicted by our enhanced *R*-matrix calculation. The experimental/theoretical comparison shows good agreement over some of the photon energy range, and also reveals some puzzling discrepancies.

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Investigation of the dynamics in negative ions provides valuable insights into the general problem of the correlated motion of electrons in many-particle systems such as heavy atoms, molecules, clusters, and solids. Photoexcitation and photodetachment processes of negative ions stand out as an extremely sensitive probe and theoretical test bed for the important effects of electron-electron interactions because of the weak coupling between the photons and the target electrons. In addition, negative ions present a severe theoretical challenge since the independent-electron model is inadequate for even a qualitative description of their properties. But while it has long been known that negative ions exist only because of electron correlation, it has usually been thought that it is correlation of the valence shell electrons. In contrast, the present work shows that the correlation involves all four of the electrons of Li^-. The demonstration is unambiguous because inner-shell photoionization of Li or Li^+ in this energy range is structureless, while the Li^- spectrum is clearly structured by a variety of negative ion resonances. Therefore, the investigation of inner-shell photoexcitation processes in negative ions offers a new persective for a fundamental understanding of strongly correlated systems such as nanostructures and superconducting materials.

In addition, studies of the properties of ions are needed since the production and destruction of negative ions in systems such as dilute plasmas appearing in the outer atmospheres of stars are strongly affected by the characteristics of these ions [1]. Therefore, the benefits of understanding the general underlying dynamical processes occurring in photoexcitation have applications in several other fields including atmospheric and plasma physics allowing these underpinning studies to be an enabling science for other disciplines. Previously, many calculations took only the electron-correlation contributions from the valence shell into account. However, new theoretical work including core-valence and core-core effects has led to much better agreement with experiments than just a few years ago [2].

Numerous theoretical and experimental studies of outer-shell photodetachment have been conducted using lasers [2–10]. Although negative ions usually exist only in a single bound configuration, it is known that numerous resonances exist in the detachment cross section originating from short-lived excited states above the first detachment limit [3,5,11,12]. Shape and Feshbach resonances have been observed for a number of negative ions at low photon energies [3,13]. An example is the sophisticated study of resonances in H^- [14], in which a series of resonances was revealed by angle tuning a fixed-frequency laser beam to a relativistic H^- beam. Also, it has been shown [15] that the presence of a resonance, close to the threshold for detachment to an excited state of the neutral atom, will strongly affect the usual Wigner dependence [16] of the photodetachment cross section.

Li^- [ground state $1s^2 2s^2$ (^1S)] is one of the simplest negative ions. Its extended nuclear core compared to H^- has, however, a profound effect on the resonance structure. The lifting of the degeneracy of different l states with the same quantum number n, opens up new decay channels. Outer-shell resonance structures in the photodetachment cross section of Li^- have been investigated both experimentally [9,17] and theoretically [7,18]. The energy region studied was between the Li($3s$) and Li($3p$) thresholds and the observed resonances were shown to be well explained by calculations [7,18]. However, up until a very recent calculation [19] on the *K*-shell photodetachment in Li^- (resulting in neutral Li), no published work in inner-shell photodetachment of negative ions was available [20] other than the inner-shell theoretical work in He^- [11,21]. With the advent of 3rd generation synchrotron light sources with higher flux, brightness, and resolution, it is now possible to investigate experimentally inner-shell processes in tenuous negative ion targets.

In this Letter, we report dramatic structure measured and calculated for the photodetachment of the Li^- K-shell, unlike the structureless decreasing $1s$ photoionization cross section of Li and Li^+. This process leads to a core-excited state of Li which decays predominantly to the Li^+ ion. The agreement between measured and calculated Li^+ ion spectra is good in some energy regions but only fair in others, indicating the complex dynamics even in a simple four electron system.

The experiment was performed at the Advanced Light Source on the HRAMO undulator beam line 10.0.1. Li^- ions were produced using a cesium sputtering source (SNICS II) [22] and used in a photon-ion experimental apparatus described elsewhere [23]. The Li^- ion beam was accelerated to 11 keV, and a beam of 20–150 nA reached the interaction region. The ions were merged collinearly with the counterpropagating photon beam in a 30 cm long *energy-tagged* interaction region producing photodetached neutral Li atoms and Li^+ ions. Li^+ ions were detected as a function of photon energy, using a photon resolution of 75 meV. The resulting signal was normalized to the primary Li^- ion beam and the incident photon flux.

In the case of negative ions, merged experiments are a serious challenge since the signal is very easily swamped by background noise due to stripping of the negative ions with the residual gas (even though the background pressure in the interaction region was $\sim 10^{-10}$ Torr) or with apertures in the ion beam line. In order to reduce the effects of collisional noise, and correct for the background ionization, the photon beam was chopped at 1 Hz and the photodetachment signal intensity, corresponding to a relative cross section, was determined by subtracting the light-off signal from the light-on signal. The statistical error in the data was decreased by summing multiple sweeps of the photon energy of interest. The photon energies were calibrated separately using known resonance positions for neutral gases and corrected for the Doppler shift which amounts to about +108 meV for 60 eV photons.

Calculations of the photodetachment of Li^- were performed using the R-matrix methodology which was enhanced to handle negative ions [24] and inner shells [25]. The discrete state input was generated with CIV3 [26]. The $1s$ and $2p$ basis functions were obtained from a Hartree-Fock calculation of the Li $1s^2 2p$ state, and the $2s$, $3s$, $3p$, and $3d$ were optimized on the corresponding $1s^2 nl$ state, using the same $1s$ orbital for each. The $4s$ was optimized on the energy of $1s2s^2$, while $4p$, $4d$, and $4f$ were optimized on the energy of $1s2p^{2\,2}P$. The initial $1s^2 2s^2$ state of the Li^- ion and the final continuum states were calculated using the R-matrix code which employed the variable phase method in the outer region in the absence of a long-range coulomb field [25]. A total of 40 continuum basis functions were employed for each $l \leq 3$. A total of 29 target states were included in the close-coupling expansion: five $1s^2 nl$ states, $n \leq 3$ and $l \leq 2$, and 24 $1s2l3l'$, $l = 2, 3$, $l' = 0, 1, 2$ core-excited states of Li. Using this procedure, the electron affinity of Li^- was calculated to be 0.628 eV, in quite good agreement with the experimental value of 0.618 049 eV [27]. To obtain the cross section for Li^+ production from the Li^- photodetachment process, we summed the cross sections for all of the channels leading to core-excited Li since Li with a $1s$ vacancy decays via an Auger process virtually 100% of the time [28]. Because of this dominance of Auger decay, except for a small energy region near the first $1s$ threshold (below 58 eV) where theory predicts spectator Auger decay of a shape resonance [19], the calculated Li^+ production cross section and the calculated total photodetachment cross section [19] are about the same; i.e., virtually 100% of the photodetachment cross section leads to Li^+ production.

The measured relative intensity was normalized to the magnitude of the calculated cross section at 62 eV. The calculated spectrum required only a small shift, +0.2 eV, to align with the experimental data. This agreement was of significant value when performing the experiment in order to locate the resonance structure. It is interesting to note that this energy discrepancy between theory and experiment is the same as that found in the case of photoionization of neutral Li [29]. Our experimental and theoretical data are shown in Fig. 1 where the dramatic departure from the small, structureless, monotonically decreasing $1s$ photoionization cross section of Li and Li^+ [30] is clearly seen. The addition of a very loosely bound electron to neutral Li, which has only a negligible effect upon the $1s$ wave function, nevertheless dramatically affects the response of this $1s$ electron to ionizing radiation. The experimental data clearly show three structures: first, a step above the $1s2s^{2\,2}S$ threshold around 57.2 eV; second, a shape

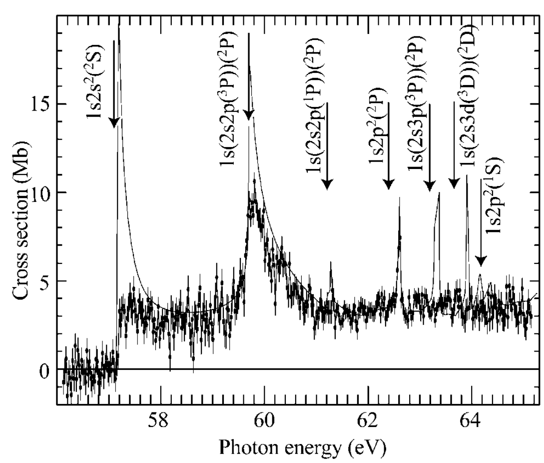

FIG. 1. Total double photodetachment cross section of Li^- giving rise to Li^+ in the vicinity of the $1s$ threshold. The solid curve is the R-matrix calculation and the dots with error bars are the experimental data normalized to the calculation at 62 eV. The arrows indicate neutral Li thresholds.

resonance well defined by its sharp rise and decay tail above the second threshold $1s\ (2s2p\ ^3P)\,^2P$ around 59.65 eV; and third, a narrow resonance above the $1s2p^2\,^2P$ threshold around 62.6 eV which would not have been observed with lower photon resolution. As can be seen from Fig. 1, agreement between theory and experiment is quite good for the latter two structures; however, the measured spectrum does not show the theoretically predicted shape resonance structure in the region above the first $1s$ detachment threshold at 57.2 eV. Li^+ can be produced in this energy region by autodetachment of the $1s2s^2np$ Li^- shape resonances to the core-excited $1s2s^2\,^2S$ state of Li, which subsequently undergoes Auger decay to the ground state of Li^+, as shown in the energy level diagram of Fig. 2, labeled by process (a). A similar process leads to the observed resonance structure above the second $1s$ threshold at 59.65 eV, which shows strong production of Li^+. The different behavior above the first and second core-excited states of Li may be due to either differences in the nature of the negative ion resonances or to differences in the subsequent decay of the excited Li^-.

In order for photoexcitation of the $1s2s^2np$ Li^- resonances to produce Li^+, the resonances must lie above the first core-excited state of Li in energy. Negative ions are unlike atoms in the sense that there is not an infinite series of Rydberg states leading up to each threshold. In fact, for photodetachment from Li^- in the region of the $1s$ thresholds, there are no Feshbach (Rydberg) resonances below each threshold, leading to simpler spectra compared to photoionization of atoms (absence of the long-range Coulomb interaction) [19]. Thus, for example, the $1s2s^2np$ excitations are found to be slightly above the $1s2s^2\,^2S$ threshold, as illustrated in the energy level diagram shown in Fig. 2, which leads to the (above threshold) shape resonance predicted by the calculation but not observed directly in the measurements.

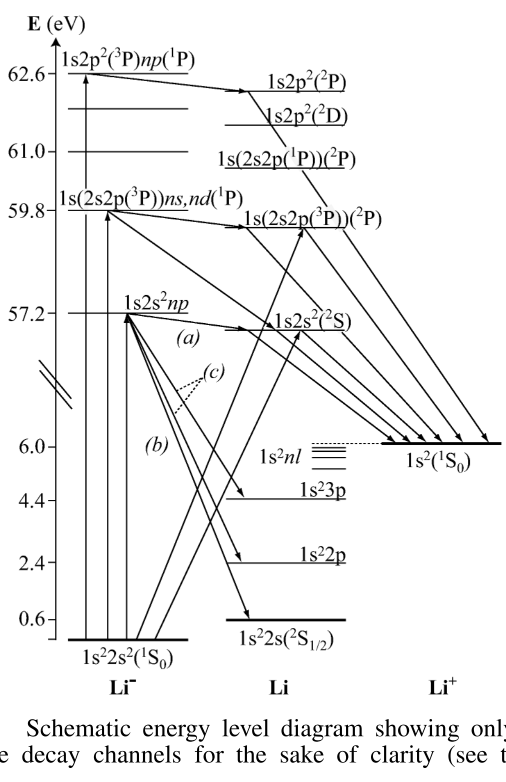

FIG. 2. Schematic energy level diagram showing only some possible decay channels for the sake of clarity (see text for details).

The $1s2s^2np$ resonances are likely to exist above the core-excited neutral states; therefore, we must look to differences in the decay process leading to changes in the branching between the energetically allowed neutral Li or Li^+ final states. The lack of signal in the positive ion channel suggests that the new phenomenon of Auger decay of the shape resonance [19] may be occurring to neutral Li [processes (b) and (c) in Fig. 2]. This decay may leave the neutral atom in either the ground state $1s^22s$ state or in a valence-excited state, which is produced by a spectator Auger process in which one $2s$ electron drops down to $1s$ while the other $2s$ electron is ejected, leaving the np electron unchanged. This Auger mechanism has been predicted [19] to be significant for the $1s2s^2np$ Li^- shape resonance; in fact, the calculations show the cross sections for the formation of Li $1s^22p$ and $1s^23p$ to be of similar magnitude to the $1s2s^2$ autodetachment channel. However, what about $1s^24p$, $1s^25p$ final states, and so on? Nothing in the theoretical results indicates that the cross sections for these states are small, but they are omitted from the present calculation. Therefore the discrepancy between the observed and theoretical spectra may stem from an inadequacy in the calculation: the truncation of the close-coupling expansion omitting the higher $1s^2np$ final states of Li.

Nevertheless, these cross sections are not for core-excited states, but for normal-excited states of Li; thus, their omission cannot directly affect the Li^+ production cross section. However, they can indirectly through interchannel coupling (configuration interaction in the continuum) which recent work has shown to be ubiquitous in its effects on the photoionization process [31]. Therefore, our conjecture is that a number of the omitted higher $1s^2np$ final states have large cross sections, $\sim$10 Mb at their maximum, and these significantly modify the $1s2s^2$ cross section via interchannel coupling.

The Li^+ cross sections in the vicinity of the higher core-excited thresholds should not be affected substantially by this omission. This is because, although the phenomenon of Auger decay of a shape resonance occurs at each of the higher thresholds as well, the decay is primarily to other core-excited channels, so the omission of the higher $1s^2nl$ states has no significant effect; the cross sections for production of the ground state and singly excited states of Li is found to be quite small in the vicinity of the higher core-excited thresholds [19]. At the second threshold, $1s(2s2p\,^3P)\ ^2P$, around 59.65 eV, there are the $1s(2s2p\,^3P)ns\,^1P$ and $1s(2s2p\,^3P)nd\,^1P$ shape resonances just above threshold, but these decay primarily via either autodetachment to the $1s(2s2p\,^3P)$

state of Li^+ plus a photoelectron and via a spectator Auger process where the $2p$ electron drops down to $2s$ with the ejection of the ns or nd electron; i.e., the Auger decay results in the $1s2s^2$ core-excited state, not one of the valence-excited states. Thus, the omission of the higher $1s^2nl$ states will have no important effect upon the Li^+ production cross section in the vicinity of the higher core-excited states; for reasons explained above, the lowest core-excited threshold is special.

It is surprising to find that the experiment was able to resolve and measure the predicted narrow structure above the $1s2p^2\,{}^2P$ threshold around 62.6 eV due to the $(1s2p^2)\,{}^2P\; np\,{}^1P$ resonance in Li^-, but not the predicted structures above the $1s(2s3p\,{}^3P)\,{}^2P$ or $1s(2s3d\,{}^3D)\,{}^2D$ threshold above 63 eV or the weaker structure above the $1s(2s2p\,{}^1P)\,{}^2P$ around 61 eV as shown in Fig. 1. In the case of this last threshold, it may be that the signal to noise ratio is not sufficient to allow the observation of this weak structure. However, the structure around 62.6 eV has about the same predicted strength as the one around 63.2 eV and is narrower, which would have made it even more difficult to observe. It is therefore puzzling, since the experimental conditions were exactly the same, as to why one predicted resonance is observed and not the others. We currently have no explanation for the discrepancy between experiment and theory in this energy region.

As mentioned above, the experimental data have been normalized to the calculation, giving a maximum of 9.5 Mb at about 59.82 eV and a photodetachment background of about 3.2 Mb around 62 eV. It is interesting to find that the agreement for the resonance prediction of Li^+ just above the $1s2p^2\,{}^2P$ threshold is quite good, while the cross section is overestimated in the case of the $1s(2s2p\,{}^3P)\,{}^2P$ and the $1s2s^2\,{}^2S$ thresholds. Thus, it is evident that although much of the essential physics of the inner-shell photodetachment problem is embodied in the calculation, the discrepancies with experiment indicate that there is still more to be understood, even in this simplest multishell negative ion.

In summary, the first comparison between an experimental and theoretical K-shell study of the photodetachment of a simple negative ion, Li^-, has been carried out revealing dramatic structure qualitatively and quantitatively unlike K-shell photoabsorption of atoms and positive ions. These measurements and calculations lead the way to inner-shell studies of even more complex negative ion systems and suggest that further new physics will be uncovered.

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