High Resolution Measurements of Partial Photoionization Cross Sections in Hollow Lithium: A Critical Comparison with Advanced Many-Body Calculations

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Photoelectron data for hollow lithium states obtained with unprecedented high spectral resolution and sensitivity are presented. A critical comparison is made with the most recent theoretical results. Partial cross sections are measured providing the first definitive test of advanced \textit{ab initio} calculations for this highly excited four-body atomic system.

In this Letter, we present photoelectron data for hollow lithium states obtained with unprecedented spectral resolution (0.019 eV) and sensitivity which allows a critical comparison with the most advanced recent theoretical calculations. The partial cross sections are measured and resonance profile parameters are determined. In addition, we have used the $R$-matrix approximation to calculate \textit{ab initio} the partial photoionization cross sections into all continuum channels of the Li$^+$ ion over a wide photon energy range. The experimental results provide the first definitive test of such advanced calculations for this highly excited four-body atomic system.

The photoexcitation and decay dynamics of hollow lithium atoms, in which all three electrons are in excited states, have become the subject of intense recent experimental and theoretical interest. The single-photon three-electron excitations depend entirely on electron-electron correlation interactions and so hollow lithium atoms constitute an ideal four-body Coulomb system for testing the most advanced atomic theories. Following the first photon-excited observation [1] of the lowest hollow atom resonance ($1s^22s\,^2S \rightarrow 2s^22p\,^2P$), two total ion yield photoion experiments at high [2] and medium [3] spectral resolution measured the autoionization of several hollow states in both the Li$^+$ and Li$^{2+}$ decay channels. Photoelectron spectrometry [4] was also used with low resolution to study the decay of the hollow lithium $2s^22p$ state into the different continua of the Li$^+$ ion. The 0.5 eV spectral bandpass of the latest experiment however limited the critical nature of the comparison with theory.

Double K-shell excitations in atomic helium have culminated in recent ultrahigh resolution measurements [5]. The third electron makes the theoretical and experimental study of hollow lithium states an even greater challenge than that of helium. Although triply excited states of lithium were first observed in collision experiments [6–8], only photon-excitation experiments provide the selectivity, sensitivity, and resolution required to unravel the many hollow lithium resonances. The dipole selection rules ensure that only $^2P^o$ final states can be photoexcited from the ground state of the lithium atom. Photoelectron spectrometry combines the advantages of photon excitation with the unique capacity to measure separately the many decay channels and to provide insight into decay dynamics. The key role played by hollow atom states in ion-surface interactions has also been recognized [9].
The previous photoelectron spectroscopy measurements [4] were carried out at the SuperACO storage ring at Orsay with modest resolution (0.5 and 0.23 eV on the bending magnet and undulator beam, respectively). The present experiments were performed on beam line 9.0.1 at the Advanced Light Source in Berkeley, which provides the most intense source available of highly monochromatic light in this energy range. The very high photon beam brightness (>10^12/sec in 20 meV spectral width at 150 eV) allowed a number of very significant improvements to be made. The bandpass of the electron spectrometer was reduced by a factor of 2 (0.45% of the electron energy) allowing better discrimination of the decay channels. The maximum spectral resolution was improved by a factor of 10 (0.019 eV). Many of the measurements were carried out with a spectral resolution of 40 meV. Furthermore, the high photon flux allowed the use of lower atomic densities which resulted in very low background count levels in our experiments. The relative partial cross sections were measured by constant ionic state spectroscopy. The statistical error was about 3%. The total uncertainty on the relative values of the partial cross sections is usually less than 10%. They were put on an absolute scale by normalizing the data measured at 110 eV to the photoabsorption cross section [10], which introduces an additional uncertainty of 25%.

Several approximations have been exploited to compute the energies (and sometimes the widths) of a number of multiply excited states in lithium [11–15]. It is, however, only the most recent developments in R-matrix theory which have allowed a comprehensive photoionization calculation including resonances to be carried out. Application of the code to inner-shell photoionization involves specific difficulties, previously described [16]. Initial R-matrix results for lithium have already been reported [4]. Here, we present a comparison of our high-resolution results with the theoretical values of several partial cross sections over a wider range of photon energies. The recent experimental results on hollow lithium have also stimulated very detailed calculations with the saddle-point and saddle-point complex-rotation methods [13,17].

In Fig. 1, we show the measured variation of the partial cross section for photoionization into the 1s2p^1P + eS channel in the vicinity of the 2s^22p^2P resonance and compare it with the R-matrix results. The agreement in terms of the resonance width and profile and the relative amplitude of the cross section is impressive. With regard to the absolute value of the cross section, the theoretical result is about 50% higher than the measured value, while the total experimental uncertainty is close to 35%. The measured absolute energy of the resonance differs from the R-matrix value by 0.13 eV. Using the Fano-Starace formulation for deconvoluting the instrumental profile (0.019 eV), a FWHM of 0.118 ± 0.003 eV is obtained for the 2s^22p^2P resonance profile. In Table I, we show a comparison between the present and previous measurements together with recent theoretical results.

The present high spectral resolution experiment succeeds in determining the profile width with an uncertainty sufficiently small (the smallest to date) to test the most recent theoretical calculations. Our results agree extremely well for both the resonance energy and width, with the very recent high precision calculation using the saddle-point technique [17]. The partial cross-section behavior for decay of this state to 1s2s^3S + ep shows an asymmetric profile due to the strong interaction with the direct photoionization process in this channel. The deconvoluted width of 0.122(5) eV is consistent with that determined from the more symmetric 1s2p^1P channel.

The previous photoion experiments [2,3] demonstrated a rich spectrum of multiply excited states in the 145–165 eV energy region. Because of cancellation effects particular resonances may sometimes be very weak in such experiments but be large if observed in a specific decay channel as in a photoelectron experiment; application of photoelectron spectroscopy to these higher lying resonances is therefore particularly advantageous. In Fig. 2 we show, as examples, the decay into the 1s3s^3S and 1s2p^1P channels, for the energy range 140.4–154 eV which encompasses many of the hollow atom states previously observed in photoion experiments, together with the corresponding R-matrix theoretical partial cross-section results. Apart from an energy shift of 0.1 to 0.3 eV, the detailed agreement (on a relative cross-section basis) is a tribute to both the quality of the new experimental data and the R-matrix calculations.

FIG. 1. The experimental photoionization cross section of lithium to the 1s2p^1P ionic state (upper part) compared with the result of the ab initio R-matrix calculation (lower part), in the vicinity of the lowest hollow atom state (2s^2p^2P).

FIG. 2. A rich spectrum of multiply excited states in the 145–165 eV energy region. Because of cancellation effects particular resonances may sometimes be very weak in such experiments but be large if observed in a specific decay channel as in a photoelectron experiment; application of photoelectron spectroscopy to these higher lying resonances is therefore particularly advantageous.
TABLE I. A comparison between the present experimental results and previous photoexcitation measurements together with a selection of theoretical results for the \(1s^22s^2S \rightarrow 2s^22p^2P\) transition.

<table>
<thead>
<tr>
<th></th>
<th>(E_0) (eV)</th>
<th>(\Gamma) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>142.28(3)</td>
<td>0.118(3)</td>
</tr>
<tr>
<td>Photoabsorption [1]</td>
<td>142.32(3)</td>
<td>0.20(6)</td>
</tr>
<tr>
<td>Photoion [2]</td>
<td>142.32(3)</td>
<td>0.14(3)</td>
</tr>
<tr>
<td>Photoion [3]</td>
<td>142.35(10)</td>
<td>0.15(2), (a) 0.20(4) (b)</td>
</tr>
<tr>
<td>Photoelectron [4]</td>
<td>142.30(5)</td>
<td>0.20(4)</td>
</tr>
<tr>
<td>Theoretical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R)-matrix</td>
<td>142.12</td>
<td>0.13</td>
</tr>
<tr>
<td>Saddle point [17]</td>
<td>142.255</td>
<td>0.1175</td>
</tr>
<tr>
<td>Multiconfiguration Hartree-Fock [2]</td>
<td>141.90</td>
<td>0.21</td>
</tr>
<tr>
<td>Multiconfiguration Dirac-Fock [3]</td>
<td>141.657</td>
<td></td>
</tr>
<tr>
<td>Many-body perturbation theory [12]</td>
<td>142.661</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\(a\) Photoion yield measurement.

\(b\) \(Li^{++}\) (time of flight).

The asymmetry of the 150 eV resonance and the detailed structure in the neighborhood of the strong 152.4 resonance is accurately reflected in both experimental and theoretical curves, including the near zero minimum at 152.55 eV. The latter shows however additional weak and narrow resonances in the \(1s2p\) \(^{1,3}P\) channel, which are not fully reproduced in the experimental data due to resolution limitations. The absolute cross-section values calculated by the \(R\)-matrix method are again greater than the experimentally determined values. In Table II, we give our energy measurements for the main resonances observed in this energy range. They are usually in good agreement, within the error bars, with those previously determined in the high resolution [2] photoion yield experiment.

In order to make a comparison between our new result and the earlier photoion work, we have summed the different \(^1L\) decay spectra in the \(n=2,3,4\) channels, as shown in the three upper frames of Fig. 3. This provides a good estimate of the total photoabsorption cross section in this spectral region as decay to higher channels is very weak. The comparison of our results with the relative photoion yield data [2] confirms that the profiles of the resonances are very different in the different channels. For example, the 152.5 resonance predominantly decays to the \(n=3\) channels whereas the 150 eV feature shows up strongly in the \(n=3\) and \(n=4\) channels. This pattern provides valuable clues to

![FIG. 2. Upper part: a comparison, for the 149.4–154 eV energy range, of the experimental photoionization cross sections to the \(1s3s\) \(^3S\) with \(ab\) initio \(R\)-matrix calculation and (lower part) a similar comparison for photoionization to the \(1s2p\) \(^{1,3}P\) final \(Li^{++}\) ionic states (the individual \(^1P\) and \(^3P\) patterns are similar).](image-url)
the principal configurations in the decaying resonances. Care, however, needs to be taken in the analysis; the uniqueness of normal spectroscopic orbital labeling of the resonances (based on the independent-particle model) is questionable in view of the strongly correlated motions of the hollow atom resonances. In doubly excited helium it was found advantageous to introduce new quantum numbers which take into account the correlated motions of the two electrons directly [18]. In recent work on $H^-$ [19], it was shown that the autodetaching Feshbach resonances decay primarily into the nearest energetically accessible continuum channel, with similar angular and radial correlations, and the delay-time matrix [20] is very appropriate for study of the excitation and decay of such quasistable states. Here, we found that it is, indeed, the $n = 4$ channel in which the decay of the resonances is the strongest on a relative scale. A calculation of triply excited states of lithium in hyperspherical coordinates has been carried out recently [21]. It is expected that further theoretical efforts in these directions will provide additional physical insight into this strongly correlated four-body atomic system.

In summary, the present experimental results provide the most stringent test to date of calculations for hollow lithium states. The $R$-matrix code is seen to produce remarkable agreement with the relative values of the measured profile cross sections while the measured profile for the lowest lying resonance ($2$s$^2$ $p^2$P) is in good agreement with the saddle-point calculations.

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