First Experimental Determination and Theoretical Calculation of Partial Photoionization Cross Sections of Lithium over the Energy Region of Hollow Atomic States

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Photoelectron spectrometry has been used for the first time to study autoionization of photoexcited hollow lithium atoms into the various continua of the Li^+ ion. Absolute values of the partial photoionization cross sections have been determined. The *R*-matrix approximation has also been used to calculate the energies of the hollow states as well as all partial photoionization cross sections. Experimental and theoretical results are in very good agreement.

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In this Letter, we present the results of the first measurements of partial cross sections for resonant photoionization of lithium atoms at 142.3 eV, i.e., at the excitation energy of the two 1*s* inner electrons into the $2s^2 2p\ ^2P$ autoionizing state. Specifically both inner electrons are excited at this energy to form the lowest energy hollow state in lithium, i.e., an atomic state in which the *K* shell is empty and all electrons are in the *L* shell. In addition, we have used for the first time the *R*-matrix approximation to calculate *ab initio* the energy of many hollow lithium states between 142 and 165 eV, as well as the partial cross sections for photoionization into all continuum channels of the singly charged Li^+ ion. Over this energy region, direct photoionization of atomic lithium into the continuum is competing with autoionization of the resonantly excited states, producing interference effects in some of the continuum channels and strongly enhancing partial cross sections in other channels.

A hollow atomic system is an atom or an ion in which at least one inner shell is empty. Double excitation of helium, first studied by electron [1] or photon [2] impact and theoretically described by Fano [3] more than thirty years ago, was, in fact, the first observation of a hollow atomic state. Studies of these states were continuously improved over the years [4–6], providing new information on the correlated motion of a pair of electrons in the field of a nucleus. In a different field, collision experiments of highly charged ions with metallic surfaces [7] demonstrated the formation of highly excited hollow ions, with empty *K* and *L* shells.

Lithium, with one additional electron outside the $1s^2$ core, is the simplest open-shell many-electron system. Simultaneous excitation of all three electrons can create hollow atoms of the type $nln'l'n''l''$, with $n \geq 2$. With an empty *K* shell surrounded by three electrons in outer shells, this system offers an ideal case for investigating the four-body Coulombic problem and for testing theoretical approximations aiming to describe many-electron interactions.

The first observations of triply excited $2l^2 2l'$ states in lithium have been reported in beam foil [8,9] and collision experiments [10]. The first exploration of the lowest $2s^2 2p\ ^2P^o$ resonance at 142.3 eV energy was recently achieved in photoabsorption [11]. Soon after, two studies [12,13] using the photoion yield technique revealed the existence of numerous higher-lying resonances decaying into Li^+ and Li^{2+} final states. In these most recent works, energies of these states have been calculated, using multiconfiguration Hartree-Fock [12] and Dirac-Fock [13] approximations. However, neither photoabsorption nor ion yield measurements can discriminate against transitions into various continua of the Li^+ ion.

Photoelectron spectroscopy is the only method that allows us to determine when partial cross sections leave the singly charged ion into its different final states. When lithium atoms are photoionized in the 1*s* shell, according to $1s^2 2s\ ^2S_{1/2} + h\nu \rightarrow 1snl\ ^{1,3}L + \varepsilon l'$, the residual Li^+ ion can be left in any of the following ionic states: $1s2s\ ^3S$ and ^1S, with threshold energies of 64.42 and 66.32 eV, respectively (main lines in a photoelectron spectrum); $1s2p\ ^3P$ and ^1P (at 66.67 and 67.61 eV, respectively), $1s3l\ ^{1,3}L$, and $lsnl\ ^{1,3}L$, with $n > 3$ (corresponding to various correlation satellites).

Synchrotron radiation (SR) from bending magnet line SA23 of the Super ACO ring in Orsay was used between 140 and 152 eV photon energy to measure, with an

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electron cylindrical mirror analyzer (CMA), the relative intensities of the photoelectron lines corresponding to the different Li^+ final ionic states. Since the photon flux required for electron spectrometry experiments is 2 orders of magnitude higher than for total ion yield measurements and because of the low photon flux available, we had to open widely the exit slit of the monochromator to get enough photons, setting the bandpass of the monochromator at 0.5 eV. A resistively heated oven produced a beam of lithium atoms along the CMA axis. This axis was collinear to the photon beam and the emitted electrons were measured at the magic angle of 54° 44′. In this way, the integrated area under the electron lines is proportional to the absolute values of the partial cross sections. The $\Delta E/E$ resolution of our electron spectrometer was chosen to be equal to 0.7% of the pass energy. From the recorded electron spectra, we have determined relative cross sections for photoionization into various final states of Li^+. Absolute values of partial cross sections were obtained by normalizing our relative measurements at 110 eV to the measured photoabsorption cross section [14].

The *R*-matrix code requires the *same* configuration interaction (CI) expansion to describe *both* initial and final states [15]. To obtain a complete description of the processes using the code developed for inner-shell photoionization [15], it was necessary to employ a sufficiently large close coupling (CC) expansion. The *ab initio* CC method automatically yields complete series of resonance states converging on excited terms. The accuracy of the calculations depends crucially on two criteria. First, the model ion must be such that the calculated energies of all target states included in the CC expansion match the experimental energies very closely. In the case of Li^+, this meant that all terms lying between $1s^2$ and $2s3p\ ^3P$, spanning 11.8 Ry, had to be accurately represented using the same orbitals and configurations throughout. Second, the selected CC channels and the complementary expansion over $(N+1)$-electron bound states must be consistent. This requires a rigorous selection in the CI expansion of the $(N+1)$-electron system [15].

In order to investigate triply excited $(n\ell n'\ell' n''\ell'')$ states of Li, the CC expansion of the Li^+ was represented by 29 states: 19 states obtained from $1s^2$, $1snl$ with $n = 2,3,4$; $1 = s,p,d,f$; 6 states obtained from $2s^2$, $2s2p$, $2p^2$; 4 additional states obtained from $2s3s$; and the lowest $^1P^o, ^3P^o$ combinations of $2s3p$ and $2p3s$. The CI expansion includes 151 "basic" configurations, giving 369 configuration couplings to construct the 29 target states. The radial functions for the orbitals in these configurations were evaluated using the code CIV3 [16]. For the Li^+ target state energies, our calculated values are in excess of the experimental energies by at most 0.2 eV, indicating that the ground state energy is too high by this amount.

Initial bound states and final continuum states of the $(N+1)$-electron system were calculated on the same footing with the following parameters: *R*-matrix radius $a = 30.2a_0$, 38 continuum basis functions for each orbital angular momentum, range of orbital angular momenta of scattered electron $\ell \leq 3$. For the two $LS\pi$ states $^2S^e$ and $^2P^o$ of the $(N+1)$-electron system considered in this work, the number of channels and bound terms retained in the CC expansion are, respectively, 28 channels and 486 bound terms for the $^2S^e$ state and 44 channels and 921 bound terms for the $^2P^o$ state.

We show, in Fig. 1, how the partial sections we have determined vary for photoionization of lithium into $1s2s\ ^1S + \varepsilon p$ (further noted $n = 2\ ^1S$, upper part) and $1s2p\ ^3P + \varepsilon s$ ($n = 2\ ^3P$, lower part) continuum channels around 142.3 eV. The two profiles show quite different behavior: In the ($n = 2\ ^1S$) channel the shape of the cross section has a Fano-type profile, while in the ($n = 2\ ^3P$) channel one observes a symmetric profile. This was expected, since the direct photoionization cross section to the $1s2s\ ^1S$ state has a significant value, allowing interferences to occur over the energy range of the resonance, while the cross section to the $1s2p\ ^3P$ state is weak at these photon energies. In Fig. 1, the dashed line was obtained from a fitting of the experimental data to a Fano-Starace profile valid in the case of one resonance interfering with many continua. We show also as solid lines the results of our *ab initio* theoretical calculations after convolution with our instrumental function. Agreement between theory and experiments is excellent, especially since there is no normalization of the experimental results to any theoretical parameter, and since the total photoabsorption cross section has been measured with only 25% accuracy [14]. In the ($n = 2$, ^3S, and ^1P) channels, the conclusion is the same as for the ^1S and ^3P channels, respectively. For photoionization into the $n = 3$ channels,

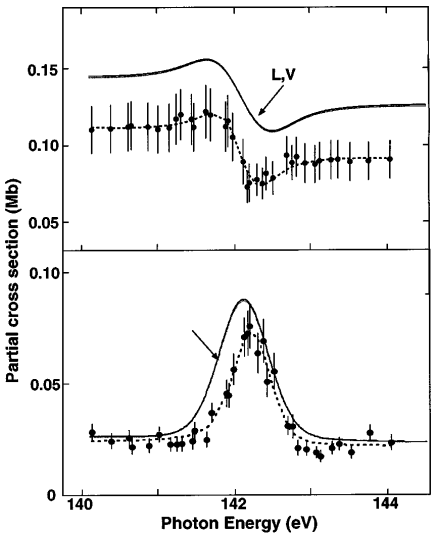

FIG. 1. Photoionization cross sections of lithium atoms to the $1s2s\ ^1S$ (upper part) and $1s2p\ ^3P$ (lower part) final Li^+ ionic states over the photon energy region of the first hollow state at 142.3 eV. The identical *L* and *V* curves are the results of the *ab initio* *R*-matrix calculations after convolution with the instrumental resolution.

we did not measure any variation of the cross section, within 5% accuracy.

Adding the partial cross sections, we reconstructed, on an absolute scale, the photoabsorption cross section. Thus we determined the following values for the Fano parameters: $E_0 = 142.30(5)$ eV, $\Gamma = 0.20(4)$ eV, and $q = -1.4(4)$, in agreement for E_0 and Γ with the first determination of Kiernan *et al.* [142.32(5) eV, 0.20(4) eV, and $-2.2(6)$] in photoabsorption [11]. Our theoretical values are 142.2 eV, 0.132 eV, and -1.86, respectively. In ion yield measurements carried out at higher resolution (20 meV [12] and 100 meV [13]), quite smaller values have been determined for Γ, 0.14(2), and 0.15(2) eV, and higher values for q, $-2.0(3)$, and $-2.2(1)$, respectively. These latest data are certainly more accurate than the photoabsorption data, as already discussed by Kiernan *et al.* [12], as well as our data, since they have been measured with a better resolution. They are in good agreement with our calculations. Among several previous calculations [11] of Γ, only one, carried out in the many-body perturbation theory approximation [17], gives a result (0.13 eV) which is also close to the lowest experimental value [12].

Our *R*-matrix calculations predict spectacular variations of the partial cross sections with photon energies. In Fig. 2, we show two examples for photoionization into the $(n = 2\ ^1S)$ and $(n = 2, ^3P)$ channels between 140 and 154 eV. Here the theoretical results are free of the influence of the experimental resolution. Figure 2 also shows the existence of many more hollow states. Our calculated values for the energies of these states are given in Table I, together with a proposed identification. They are compared to previous determinations [configuration interaction Hartree-Fock (CIHF) and multiconfiguration Dirac-Fock (MCDF)]. In the last column of the table, capital letters refer to the notation given by Azuma *et al.* [13]. Our calculated values of the various $2s^2$, $2s2p$, and $2p^2$ ionization thresholds of Li^+ are also given in bold characters. There is an overall agreement of our calculations, within 0.2 eV, with the experimental determinations, but the other calculations do not differ much either. However, our results in Fig. 2 show that the effect of the second most intense resonance measured with the total ion yield method, and calculated here at 152.41 eV, is very weak in the $n = 2$ channels. This is not true for the $n = 3$ channels, as it can be seen in Fig. 3, which shows calculated cross sections for photoionization into all $n = 2$ and $n = 3$ channels between 142 and 154 eV. The state(s) at 152.4 eV appear(s) to strongly autoionize into the $n = 3$ channels.

Our experimental result at 142.3 eV for the $n = 3$ channels is in good agreement with our calculations, since the convolution of the theoretical results with the instrumental function severely attenuates the calculated resonant enhancement. In spite of the strong decrease in the photon flux available in our experiments at 152 eV, we were able to measure that the $(n = 3)/(n = 2)$ branching ratio increased to a value of 32% at this energy (with a 0.7 eV resolution) as compared to 24% measured off resonance. Preliminary measurements using an undulator of Super ACO confirm this enhancement in the $n = 3$ channel (66% with a 0.23 eV resolution), and more specifically in the $(n = 3\ ^3P$ channel), as well as also in the $n = 4$ channel at 152.4 eV. These latest results strongly support the identification of the resonance at 152.4 eV as being mainly a $2p^2 3p$ excited state. This resonance is only a few tenths of an eV above the $2s^2\ ^1S^o$ threshold and can first decay to this state of Li^+, decreasing the lifetime of the excited state and

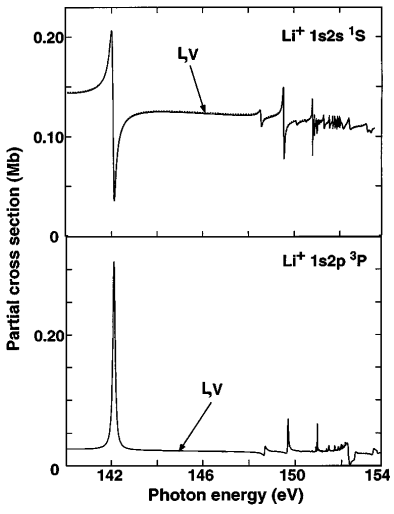

FIG. 2. *R*-matrix results showing the variation of the partial photoionization cross sections to the $1s2s\ ^1S$ (upper part) and to the $1s2p\ ^3P$ (lower part) final Li^+ ionic states between 140 and 154 eV. As for the first resonance at 142.3 eV, the behavior of the cross sections is quite different in both channels.

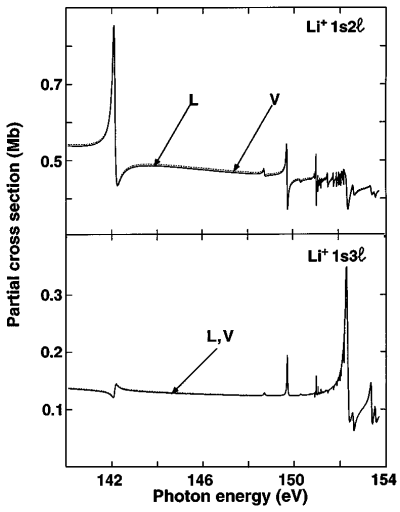

FIG. 3. *R*-matrix results showing the variation of the partial photoionization cross sections to the $1s2\ell$ (upper part) and to the $1s3\ell$ (lower part) final Li^+ ionic states between 140 and 154 eV.

TABLE I. Calculated energies and tentative assignment of $nln'l'n''l''\ ^2P$ hollow excited states in atomic lithium.

	Calculated energy			
Assignment	R matrix[a]	CIHF[c]	Mulitconfiguration Dirac-Fock method[d]	Experimental
$2s^2 2p$	142.20	141.8	142.06	142.25[a], 142.32[b], 142.34(A)[d]
$2s^2 3p$	148.68	148.85		
$(2p^2\ ^3P)2p$	149.01	148.48	148.84[d]	148.77[c], 148.7(B)[d]
$(2s2p\ ^3P)3s$	149.70	149.38		149.91[c], 149.79(C)[d]
$(2s2p\ ^3P)4s$	150.97	150.88		151.20[c]
$(2s2p\ ^1P)2s$	150.97			
$2s^2\ ^1S$ thres.	151.29			
$2s2p\ ^3P$ thres.	152.13			
$2p^2(^3P)3p$	152.408	152.15		152.46[c], 152.32(F)[d]
$2p^2(^3P)4p$	153.48	153.13		153.54[c], 153.43(H)[d]
$2s2p(^1P)3s$	153.68			
$2p^2\ ^3P$ thres.	154.39			
$2p^2\ ^1D$ thres.	155.16			
$2s2p\ ^1P$ thres.	155.46			
$2p^2\ ^1S$	159.12			

[a]This work.
[b]Kiernan *et al.,* Ref. [11].
[c]Kiernan *et al.,* Ref. [12].
[d]Azuma *et al.,* Ref. [13].

broadening the structure as seen in Fig. 3. In the direct decay of this $2p^2 3p$ excited state, the $3p$ electron can stay as a spectator, the autoionization process involving only the two $2p$ electrons in a decay to the $(n = 3\ ^3P)$ channel, or be shaken up to the $4p$ level. Among the other resonances, the highly correlated $2p^3$ state near 149 eV is particularly interesting. However, its observation in photoelectron spectroscopy will require photon beams with a much higher brightness.

In conclusion, we have successfully achieved this first study of hollow atomic lithium by electron spectroscopy and measured the partial photoionization cross sections at the excitation energy of the first of these states. We have also used the R-matrix approximation to calculate the energy, to identify the electronic configuration of several of these states, and to obtain theoretical values of the partial photoionization cross sections into all continuum channels of the Li^+ ion, which are in excellent agreement with the experimental data for the $2s^2 2p\ ^2P$ autoionizing state. These new results demonstrate the broad interest that more detailed studies with higher resolution will have for a better understanding of these exotic systems.

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