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Photoelectron spectroscopy measurements and theoretical calculations of the lowest doubly hollow lithium state

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We have measured, using electron spectroscopy, the lowest-energy doubly hollow lithium triply excited $(3l3l'3l'')\ ^2P$ state. Energies, widths, and partial cross sections have been measured and calculated using the saddle-point technique and the R-matrix approximation. Our results show good agreement between experimental and theoretical data for the energy and the width of the doubly hollow state. [S1050-2947(97)50408-2]

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In a hollow atomic or ionic state, the first inner shell (the K shell) is empty. Correlation effects can produce simultaneous excitation of all three electrons in lithium atoms and create hollow lithium states of the type $(nln'l'n''l'')$ with $n \geqslant 2$. After the first observation of the lowest-energy triply excited state [1], several experiments involving the use of photoion [2–4] and photoelectron [5–8] spectrometries have contributed to provide the energies of a number of $(nln'l'n''l'')$ states with at least one of n, n', or n'' equal to 2, as well as the partial cross sections for photoionization of atomic lithium into various $(nln'l')$ final states of the Li^+ ion ($n=1$ or 2, $n' \geqslant 2$). Several Rydberg series have been measured and identified in the many observed hollow lithium states [8,9]. Theoretical calculations using the R-matrix approximation have provided results for the partial photoionization cross sections [5–9] that are generally in very good agreement with the experimental data, whereas the saddle-point technique [10–12] has given very accurate calculations of the energies of a number of hollow lithium states, sometimes within one or two hundredths of an eV of the measured values.

The demands on theoretical and experimental techniques increase at higher photon energies, for which triply excited states with all three electrons having principal quantum numbers equal to 3 or above can be created. We propose the name *doubly hollow* state for a triply excited state in which both K and L shells are empty. All n, n', and n'' have values that are higher than 2 for such a triply excited $(nln'l'n''l'')$ state. An earlier report on an experiment with ion detection in the Li^{2+} channel [4] mentioned some analogous features, but no data were shown at that time. Following submission of the present work, we received an article [13] in which one figure shows a profile of the first $(3l,3l',3l'')$ state recorded in the Li^{2+} ionic channel.

At excitation energies higher than the lowest doubly excited $2s^2\ ^1S$ Li^+ limit (151.66 eV), triply excited states can decay to either singly or doubly excited states of the Li^+ ion. Decay path into $(1snl)$ Li^+ ionic states causes interferences with the direct photoionization route as reported earlier [5,6]. Decay to doubly excited $(2l2l')$ Li^+ ionic states produces emission of a low-energy electron. This Li^+ state subsequently decays to the ground state of the doubly charged Li^{2+} ion, with emission of a high-energy electron. By measuring the photon-energy dependence of the intensity of these high-energy electrons, one determines a partial cross section in this channel that is essentially the cross section for photoionization into the doubly excited $(2l,2l')$ Li^+ final ionic states, since the radiative decay of a light element like Li is very weak compared to autoionization.

We present here photoelectron spectroscopy measurements of a doubly hollow atomic state produced by single-photon three-electron photoexcitation of neutral lithium atoms. In comparison with ion detection, the present electron spectrometry experiments provide *channel-selective* detection of the decay of the doubly hollow state. We have measured the energy of this state and the resonantly enhanced cross sections in several decay channels using synchrotron radiation at the Advanced Light Source at the University of California in Berkeley. We have also calculated the energy of several doubly hollow states with three different theoretical approximations, i.e., the multiconfigurational Dirac-Fock theory (MCDF), the saddle-point technique, and the R-matrix approximation. In addition, we have used R-matrix theory to calculate partial cross sections for photoionization of neutral lithium in various Li^+ final ionic states over the energy range of this doubly hollow state.

These electron spectrometry measurements were carried out on the undulator beamline 9.0.1 at the Advanced Light Source (ALS) with the same experimental setup as was previously used to measure photoionization cross sections and to detect Rydberg series [5,6]. A spectral resolution of 56

meV and an electron resolution $\Delta E/E$ of 0.4% were used. The relative partial cross sections were put on an absolute scale by normalization to the measured photoabsorption cross section [14].

Earlier calculations of Lipsky *et al.* [15] using a truncated diagonalization method predicted the first $(3l3l')$ doubly excited states of the Li^+ ion to lie close to 180 eV. To set a lower bound on the energy range to be explored, we used a multiconfigurational Dirac Fock [16] and the SUPERSTRUCTURE [17] programs to calculate an approximate energy of the $3s^2 3p\ ^2P$ state. Both calculations gave the same energy of 174.11 eV. We therefore decided to measure the intensity of the high-energy electrons emitted in the second step of the autoionization process (we call them Auger electrons) starting from 174 eV.

We chose to detect the autoionization of the triply excited state in three different ionic channels, which appear to be the most intense in the Auger electron spectra at these photon energies: the $2s^2\ ^1S$, the $2s2p\ ^3P$, and the lowest-lying $(2l3l')$ excited states [the latter must be described by a mixing of $2s3s\ ^3S$ and $(2s3p,2p3s)^1P$ doubly excited states]. The energies of the corresponding Auger electron lines are 70.63, 71.38, and 83.60 eV, respectively. We have observed a resonant structure in the variation of the partial photoionization cross section in these three channels, as shown in the upper panels of Figs. 1–3, respectively. In the $2s^2\ ^1S$ and $2s2p\ ^3P$ final ionic states, the partial-cross-section profiles appear to be mostly symmetric, while in the $(2l3l')$ ionic state the experimental curve presents a quite asymmetric Fano profile. Our measured value for the energy of the $3s^2 3p\ ^2P$ excited state is 175.165 ± 0.050 eV. Using the experimental spectral function to deconvolute the $2s^2\ ^1S$ channel profile, we also determined the width of this state to be 0.25 ± 0.05 eV.

We used two many-electron theoretical approximations to calculate the energy and wave function of the $3s^2 3p\ ^2P$ state: the saddle-point complex-rotation method [10–12] and the *R*-matrix approximation [5]. In the saddle-point method, the closed-channel part of the wave function is given by

$$\Psi_c(1,2,3) = \pi[1-P_{1s}(i)][1-P_{2s}(i)][1-P_{2p}(i)] \times \Psi(1,2,3),$$

where $\Psi(1,2,3)$ is a multiconfiguration wave function, P_{nl} is a projection operator given by

$$P_{nl} = |\Phi_{nl}(q_{nl})\rangle\langle\Phi_{nl}(q_{nl})|,$$

where Φ_{nl} represents the wave function of the vacancy orbitals. The Φ_{nl}'s are mutually orthogonal for different nl. In the variation calculation, the energy of $\Psi_c(1,2,3)$ is minimized with respect to the linear and nonlinear parameters in Ψ and maximized with respect to the nonlinear parameters q_{nl}. The energy converges well in the computation. For example, if we use a 357-term ten-angular-component wave function, we obtain an energy of $-1.042\,812$ a.u. If it is increased to a 570-term 25-angular-component wave function, the energy becomes $-1.043\,414$ a.u. The improvement is only 602 μa.u. (16 meV). The mass polarization and relativistic corrections are small; they amount to 88 μa.u.

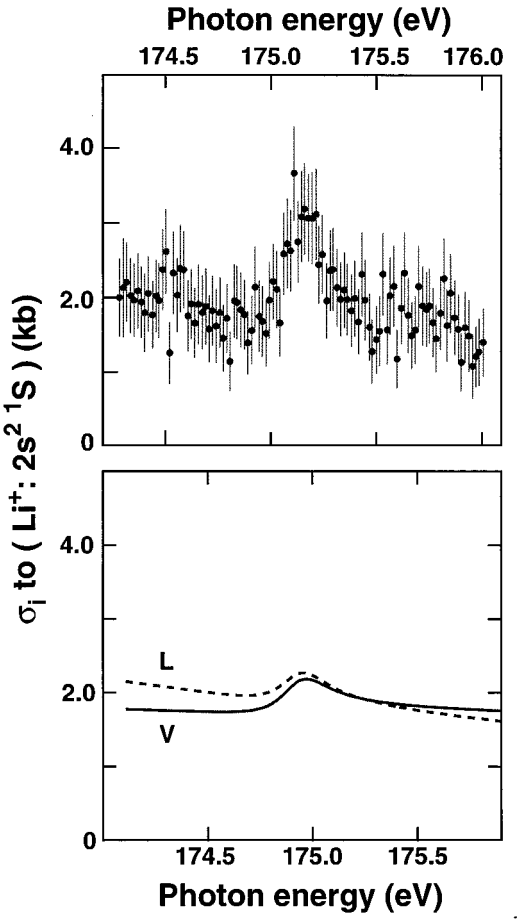

FIG. 1. Measured (upper panel) and *R*-matrix calculated (lower panel) partial cross sections for photoionization of Li atoms into the hollow $2s^2\ ^1S$ Li^+ ionic state in the energy range of the $3s^2 3p\ ^2P$ doubly hollow ionic state. In this figure and in Figs. 2 and 3, the theoretical calculations have been convoluted with the experimental spectral function.

To obtain the resonance position and width, open channel effects need to be considered. In the case of $3s^2 3p\ ^2P$, there are an infinite number of open channels. Most of its Auger width comes from those Li^+ target states with a $3s$ or $3p$ electron. There are 24 such open channels associated with 16 Li^+ target states. We have calculated the partial widths associated with each of these Li^+ states and many others with an accurate target-state wave function, and found that four of the partial widths are much larger than others, as can be seen in Table I. We used the eight most important open channels to calculate the total widths, and made a coupled calculation. The coupled width, 271 meV, is remarkably close to the sum of the individual widths, 272 meV. We then added the sum of all other partial widths and obtained 282 meV for the total width. The energy shift from the coupled calculation is 830 μa.u. Including the relativistic effects, the predicted resonance position becomes 175.12 eV. The calculated values of both energy and width of the $3s^2 3p\ ^2P$ state are in excellent agreement with the experimental data. It is noticeable that our calculations predict the major decays to occur in $(2l3l')$ Li^+ states, while we observe that the levels of the resonant enhancement in the $2s^2\ ^1S$, $2s2p\ ^3P$, and $(2s3s\ ^2S + \cdots)$ final Li^+ states are about the same.

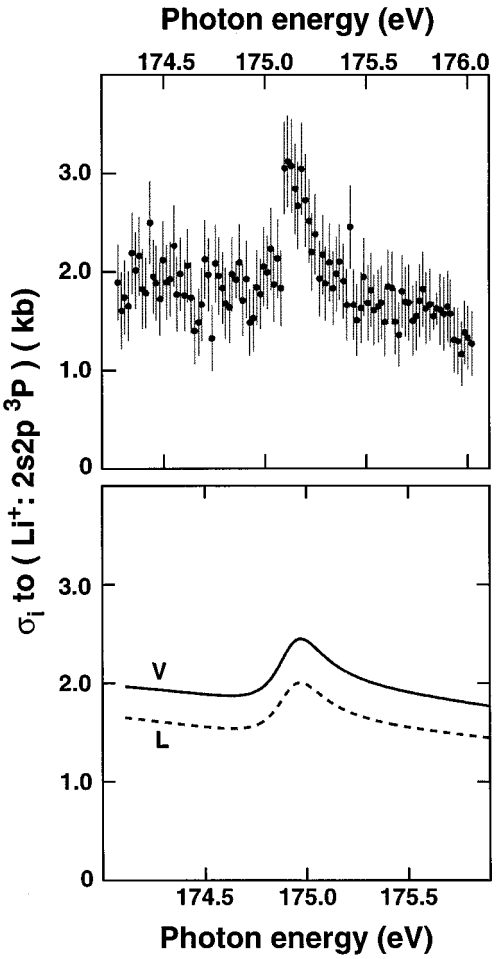

FIG. 2. Measured (upper panel) and R-matrix calculated (lower panel) partial cross sections for photoionization of Li atoms into the hollow $2s2p\ ^3P$ Li^+ ionic state in the energy range of the $3s^2 3p\ ^2P$ doubly hollow state.

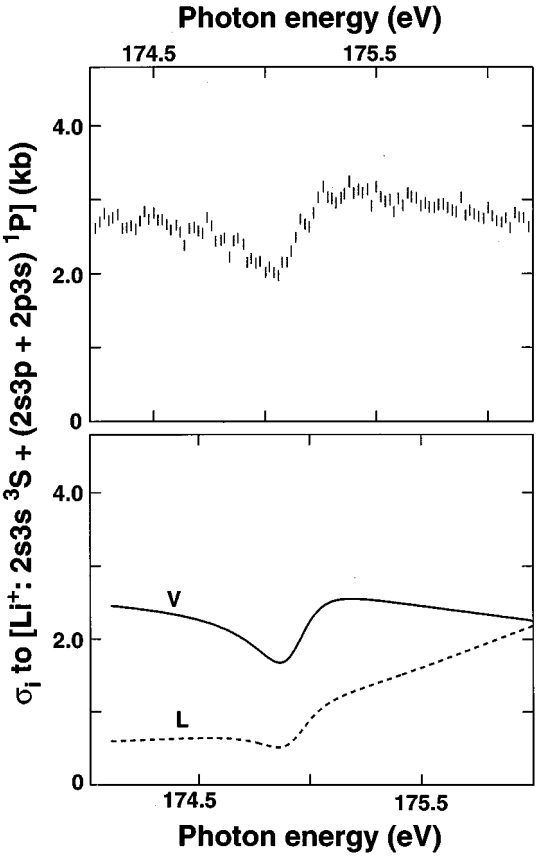

FIG. 3. Measured (upper panel) and R-matrix calculated (lower panel) partial cross sections for photoionization of Li atoms into the hollow $[2s3s\ ^3S+(2s3p\ ^1P, 2p3s\ ^1P)]$ Li^+ ionic state in the energy range of the $3s^2 3p\ ^2P$ doubly hollow state.

We also calculated the second and third lowest $(3l3l'3l'')$ states to be about 1.62 and 2.76 eV higher than the $3s^2 3p$ state, respectively. The spectral density of higher-energy doubly hollow atomic states must be quite high over such a narrow 5-eV energy range, suggesting there are strong overlaps between several nearby resonances interacting with many continua. This means that a more sophisticated theoretical approach should be used to calculate the characteristics of a high-lying doubly hollow atomic state.

In a further attempt to fully characterize the lowest doubly hollow state, we used the R-matrix approximation to calculate the partial cross sections for photoionization into each of the measured hollow ionic states. We have already described the application of the R-matrix approximation to calculate hollow lithium states [5,6]. As compared to these previous calculations using 29 Li^+ target states, we had to represent the close-coupling expansion of Li^+ by 86 states, including states obtained from $3s^2$, $3s3p$, $3p^2$, and the lower states of the other $3snl$ configurations for $n \leqslant 4$. However, the same set of orbital functions as for the 29-target-state expansion was used, assuming that the optimal orbitals representing the $(3l3l')$ states are close to the $3l$ orbitals of the $1s3l$ states. The results of our calculations for the $2s^2\ ^1S$ and $2s2p\ ^3P$ states are shown in the lower panels of Figs. 1 and 2, respectively. Whereas differences between our calculated results using either the length (L) or velocity (V) forms were not discernable for all ($n=2$) hollow states [5,6], here one notes a difference of 10% to 20% between them. The theoretical values of the cross sections in the $2s^2\ ^1S$ and $2s2p\ ^3P$ channels fit rather well the experimental data, but the calculated R-matrix enhancement of the cross sections is underestimated. One should keep in mind, however, that the accuracy of the photoabsorption measurements, is not better than 25%. The R-matrix predictions for the energy of the doubly hollow state is 174.90 eV, in reasonable agreement with the experimental value (a constant shift in the energy values predicted

TABLE I. The partial Γ widths of Li $3s^2 3p\ ^2P$ (the total width is 282 meV).

Li^+ target states	Γ_p (meV)
$2s3p-{}^3P$	122.8
$2s3p+{}^1P$	23.85
$2s3p-{}^1P$	6.64
$2p3p\ ^3P$	20.17
$2s3s\ ^1S$	86.48
$1s3p\ ^3P$	4.29
$2p3d\ ^1D$	6.12
others	11.7

5by the R-matrix method has also been recorded in our earlier works [5,6] on the $n=2$ states).

The results of our R-matrix calculations for the partial cross section into the third channel are shown in the lower panel of Fig. 3. Here, the results obtained using the length and velocity formulations are completely different and do not agree, even qualitatively, with each other. While the velocity cross section shows basically the same profile as the experimental cross section, the length result has a completely different shape. These results confirm, as might be expected, that the wave functions for the target states should be improved when all the electrons occupy $n>2$ orbitals.

Our R-matrix calculated values for the partial cross section into this third channel are comparable to the other cross sections for photoionization into the $2s^2\,{}^1S$ and $2s2p\,{}^3P$ channels. This result disagrees with the results of our saddle-point calculations, but it is confirmed, at least qualitatively, by our experiments.

To conclude, we have provided a photoelectron spectrometry measurement of the energy of the lowest-energy doubly hollow state in atomic lithium. We have found that its energy and width calculated with the saddle-point technique are in very good agreement with the experimental values. We have also shown that, even though our R-matrix results reproduce well the autoionization of this doubly hollow atomic state into the first hollow ionic states of Li^+, some improvement of the target orbitals should be made for the higher-energy doubly hollow ionic states.

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