Triple Ionization of Lithium by Electron Impact

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Ejection of the three electrons from lithium in a single electron collision has been observed for the first time. Triply charged lithium was observed in an ion time-of-flight spectrum following electron impact on a sample of ultracold, trapped lithium. The higher signal/background afforded by the trap environment made the observation of Li^{3+} possible. We measured the ratios of triple-to-double and double-to-single ionization at an impact energy of 1000 eV. The $3+/2+$ ratio is ≈ 0.001, a value 2 orders of magnitude lower than semiempirical predictions. We present a simple method that uses photoionization data combined with sum-rule analysis to predict the asymptotic charge-state ratios. The sum-rule predictions compare reasonably with experiment and shake calculations, but disagree sharply with the semiempirical estimates.

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Multiple ionization of atoms has both practical and fundamental interest. The practical interest stems from the desire to model plasmas, astrophysical environments, strong-field laser ionization, and new laser schemes. Semiempirical methods [1] are typically used to predict electron-impact ionization. From the fundamental viewpoint, multiple ionization of atoms is an excellent testbed for developing methods to handle complex problems by building up from prototypical systems [2]. Theoretical challenges are great as even the simplest three-body breakup problem, e.g., electron-impact of hydrogen [3], has no analytical quantum mechanical solution. Significant progress has been made in understanding theoretically the intricacies of electron-impact ionization [4] and the related problem of double photoionization [5]. This active field remains largely concentrated on double ionization phenomena [6].

Triple photoionization of a three-electron atom has only recently been observed [7]. A single photon liberating the three electrons in lithium is unusual; the incoming photon interacts predominantly with a single electron and the ejection of the other two is a manifestation of the correlated motion of the three electrons. After the experimental observation, theoreticians adapted formalism originally developed for the double photoionization of helium at high energy to estimate the asymptotic limits ($E_{\text{photon}} \rightarrow \infty$) of the charge-state ratios $Li^{3+}/Li^{2+}/Li^{1+}$ [8]. Subsequent theoretical work on asymptotic limits studied the accuracy of modeling triple ionization as a shakeoff of the $2s$ electron following sudden removal of the two $1s$ electrons [9]. The intermediate energy range was later tackled with impressive success using a half-collision model to calculate absolute cross sections [10]. The half-collision model was an extension of Samson's original idea that double photoionization could be viewed as electron-impact ionization following absorption of the photon by the primary electron [11]. A related area of activity for triple ejection processes has been the study of the energy dependence of the cross section near threshold. Theoretical work [12–14] has alternated with experiment on oxygen and neon [15] and on lithium [16] to probe the validity of the Wannier threshold law. Finally, the angular correlation patterns for three-electron ejection from lithium [17] were calculated in anticipation of experiments.

To our knowledge, there has been no previous observation of triple ionization of a three-electron atom by charged-particle impact, although there have been previous attempts [18], as well as detailed studies of double ionization and hollow lithium production [18–20]. In contrast, for many-electron systems ($n \geq 10$), there have been numerous studies of multiple ionization by electron impact [21–23]. The salient difference between a three-electron and a many-electron system is that, for the latter, triple ionization can occur through indirect processes, e.g., the Auger effect, which significantly enhance the triple ionization yield. In these atoms, the experimental $3+/2+$ ratios range from $\approx 5\%$ to 30%. The indirect pathways are absent for triple ionization of lithium, where, anticipating our result, the $3+/2+$ ratio is $\approx 0.1\%$. The only published guidance for triple ionization by electron impact is an extension [23] of the "universal" semiempirical method developed by Lotz [1] based upon a Born-Bethe formalism.

In this Letter, we report the first observation of triple ionization of a three-electron system by electron impact under single-collision conditions. For triple ejection studies, lithium is the obvious choice with one triple ionization threshold (203.4 eV), accurate ground-state wave functions [24], and high-quality photoabsorption data [25]. It is possible to exploit the established relationship between ionization by photons and by charged particles [26] to develop estimates for triple ionization. Earlier work on the double ionization of helium showed that the asymptotic ratio $2+/1+$ for charged-particle impact could be predicted with reliable photoionization data near the double ionization threshold [27].

We used an ultracold atom target combined with an imaging time-of-flight ion detector. The use of ultracold

lithium offers some advantages, namely, elimination of contamination by dimers, reduction of the background due to the localized target image, and the possible use of multiparticle momentum-imaging techniques to elucidate dynamical electron correlation [17]. The reduction in background, a factor of ≈ 10 relative to the atomic beam [18], is essential for observation of Li^{3+}. (In photoionization the $3+/1+$ ratio is ≈ 15 times larger at 424 eV, easing the signal/background requirements.) The use of ultracold atom targets for electron scattering studies was pioneered for absolute ionization cross section measurements [28]. The basic strategy was to prepare a target of ultracold lithium atoms at the center of a time-of-flight (TOF) ion spectrometer. After switching off the trapping light and magnetic fields, the ground-state lithium was ionized by a pulse of electrons. The resulting ions were extracted onto a position sensitive detector and identified by their TOFs. The setup described below represents a 150-fold improvement in sensitivity relative to our earlier work on Li^{2+}/Li^{1+} [29], due to enhanced capture efficiency and an improved TOF spectrometer. The improvements enabled detection of Li^{3+}.

Lithium effused from a resistively heated stainless steel ampoule at 350 °C through a 1-mm nozzle to the magneto-optical trap (MOT) located 10 cm away. During transit to the trap location, the lithium atoms were slowed by a counterpropagating electro-optic-modulator-broadened and frequency-shifted (-200 MHz) laser beam of ≈ 200 mW. This slowing beam enhanced the capture rate by a factor of 20, and ≈ 100 million atoms were trapped in a volume of ≈ 3 mm diameter. A fast-acting shutter located between the oven nozzle and entrance to the trapping chamber was used to admit Li vapor during the MOT loading period (3 s) and to block the Li beam during the experimental period (2 s). The chamber pressure was typically 1.4×10^{-9} Torr. The circularly polarized trapping beams were ≈ 20 mW/cm^2 and detuned from resonance by -20 MHz ($\Delta \approx 3.4\Gamma$, natural linewidth, $\Gamma = 5.9$ MHz). A magnetic field gradient of 8 G/cm was used.

The timing sequence differed slightly from our earlier experiment [29]. After trap loading, the lithium beam, laser beams, and B-field were switched off for a 2-s period during which the ultracold lithium was alternately interrogated for 1 ms and retrapped for 2 ms. During the 1 ms interrogation period, 17 electron pulses of 300 ns duration and 1000 eV kinetic energy were incident onto the ultracold lithium once every 40 μs following a 315 μs delay to permit residual eddy currents to decay. A 50 V/cm pulsed extraction-field (rise time ≤ 25 ns) was applied between two 35 mm $\times$ 35 mm electrodes separated by 80 mm and centered on the MOT. A second acceleration region (43 mm) followed by a drift region of double the length (167 mm) allowed the TOF spectrometer to be operated under space focusing conditions. The simple, open architecture allowed free optical access for the trapping beams. The extraction fields were continually present except for a 3 μs window that allowed the electron pulses to pass unperturbed. The resolution for Li^+ (flight time of 3.5 μs) was $\Delta t/t = 0.49\%$ and the ion image on the detector was ≈ 2.6 mm FWHM.

For the observation of triple ionization, we collected data continuously over a period of 58 h, of which 37 h were used for observation of Li^{3+}. The remaining time was used for background (laser detuned) and Li^{2+}/Li^{1+} measurements. During the experiment, the number of trapped atoms was monitored by fluorescence and the electron flux was monitored with a Faraday cup located ≈ 50 cm from the MOT. The major peaks in the full TOF spectrum were Li^{1+}, H_2^+, and Li^{2+}, which appeared in the proportion of 1:0.04:0.004. The TOF window of 2.22 μs was adjusted to include only the H_2^+, Li^{3+}, and Li^{2+} peaks. In this window, the electron beam intensity was set to give an event rate of approximately 600 counts/5 s cycle and an event probability of 5.3% per pulse. The Li^{3+} ions were accumulated at a rate of ≈ 1 count/2 min. A 9 h background TOF spectrum showed neither the Li^{2+} or Li^{3+} peaks. The cumulative spectrum for Li^{3+}/Li^{2+} and a typical spectrum for Li^{2+}/Li^{1+} are shown in Fig. 1.

A number of auxiliary tests were made to assure that the measured ratios were indeed reliable. The position and FWHM of the Li^{2+} and Li^{1+} ion images were measured as a function of the extraction voltage to check for vignetting of the charge states. At extraction-field strengths of ≥ 50 V/cm, the $2+/1+$ ratio remained constant and movement/broadening of the ion images was <0.1 mm. However, at a field strength of 25 V/cm, the ion image moved 2.4 mm and the FWHM increased to 3.8 mm causing the outer edges of the ion image to scrape an

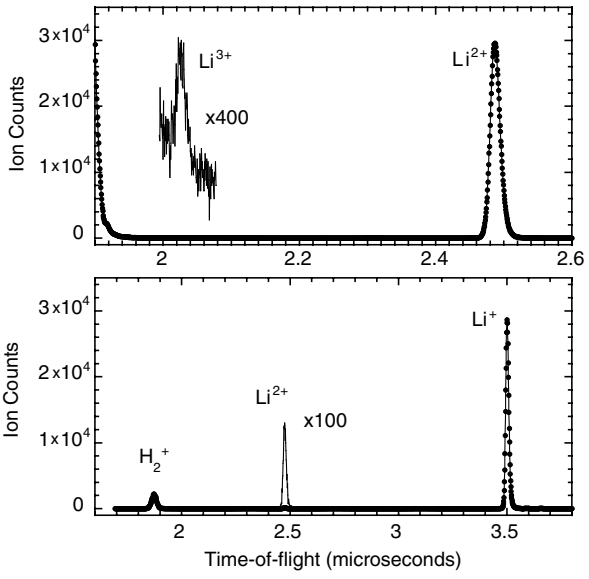

FIG. 1. Top panel shows the cumulative ion time-of-flight spectrum for Li^{3+} and Li^{2+}. Bottom panel shows a typical spectrum including the Li^{2+} and Li^{1+} peaks.

aperture and the $2+/1+$ ratio to change by 10%. Similar measurements were made as a function of the MOT size, which was varied by a factor of 8 by changing the intensity of the slowing beam. There was no measurable dependence of the $2+/1+$ ratio on the number of atoms in the trap at the higher extraction voltages and, hence, no evidence of charge exchange within the trap. We also increased the electron current/pulse by a factor of 7 to test for multiple collision effects and found no statistically significant effects on the measured $2+/1+$ ratio. Finally, we measured the charge-state ratio $3+/2+$ in neon at 1000 eV by flowing gas into the chamber and obtained $(6.32 \pm 0.21) \times 10^{-2}$, in agreement with the earlier measurement $(6.08 \pm 0.30) \times 10^{-2}$ [21].

The cumulative event-mode data were resorted to reduce background in the neighborhood of the Li^{3+} peak. Roughly circular regions of diameter 9.2 and 11 mm centered on the Li^{2+} ion position (representing 13% and 19% of the total detector area, detector $\phi = 25$ mm) were selected. Within these regions the background level was reduced by a factor of ≈ 5, whereas the Li ion counts remained constant. The Li^{2+} spot was approximately Gaussian when projected to either the x (transverse to e-beam) or y (along e-beam direction) axes with FWHM of ≈ 2.6 and 3.2 mm, respectively. The Li^{3+} and Li^{1+} spots were slightly shifted (<0.5 mm) and broadened or compressed (<0.5 mm) relative to the Li^{2+} spot. We estimated that the movement and broadening on the detector for the different charge states contributes an error of less than 1% to the charge-state ratios.

The yield of Li^{3+} was determined by fitting the resorted TOF data to a Gaussian plus background in the region of the peak. For the 11 and 9.2 mm cuts, the yields were 1070 ± 159 and 1063 ± 116, respectively. The yield for Li^{2+} was determined by summation and linear background subtraction. The results were corrected for multihit distortion [29], yielding a +5.0% correction for the Li^{2+} and a +4.0% correction for the Li^{3+} yields.

We carefully checked for inequivalent charge-state detection probabilities using the pulse-height distributions for the individual charge states. As the ion impact energy on the detector was varied from 2000 to 4000 eV, the centroid of the pulse-height distribution for Li^{1+} shifted dramatically, and the yield changed by about 10%, similar to our previous observations [29]. For the same impact energy variation, the centroid for Li^{2+} shifted much less and the yield changed by $<2\%$, a statistically insignificant amount. The centroid for the Li^{3+} ions detected during the long run fell within the region spanned by the Li^{2+} data. Therefore, we further corrected the $2+/1+$ ratio (-10.2%) but not the $3+/2+$ ratio for charge-state detection efficiency.

The final values for Li^{3+}/Li^{2+} and Li^{2+}/Li^{1+} for electron impact at 1000 eV are shown in Table I along with other pertinent data. Our ratios are reasonable in comparison with all except the semiempirical predictions.

TABLE I. Charge-state ratios for electron and photon impact ionization of lithium.

Process	σ^{3+}/σ^{2+} $\times 10^{-3}$	σ^{2+}/σ^{1+} $\times 10^{-2}$
Electron impact 1000 eV	1.08(0.15)	0.395(0.02)
Photon impact 424 eV[a]	1.8(0.6)	3.7(0.1)
Shake[b]	0.465	0.36
Asymptotic e^- impact (this work)	0.28	0.30
Semiempirical e^- impact[c]	112.0	0.56

[a][7] for $3+/2+$ and [30] for $2+/1+$.
[b]The σ^{3+}/σ^{2+} ratio [9] supercedes the values given in Ref. [7], which ignored some high-lying Li^{2+} states. The σ^{2+}/σ^{1+} ratio is specialized to electron-impact [18,19].
[c][1,31].

First, our observed ratios are smaller than the photon impact ratios. This is expected because charged-particle impact averages over all energy transfers up to the impact energy of 1000 eV and lower energy transfers favor $1+$ formation. For photoionization, the energy transfer is fixed at the incident photon energy, in this case 424 eV. Next, the electron-impact ratio for $3+/2+$ is $\approx \times 2$ higher than the asymptotic "shake" limit, calculated assuming that both $1s$ electrons are suddenly removed from Li and the remaining $2s$ electron is shaken off [9]. As discussed by Cooper, this ratio depends critically on the accuracy of the ground-state wave function for lithium; the probability for triple ionization is 1 minus the sum of squared overlaps of the $2s$ orbital with hydrogenic $1s, 2s, 3s, 4s, \ldots$ wave functions. The shake limit for $3+/2+$ ranges from 0.0465% to 0.0853% for different $2s$ orbital wave functions [9]. Two related calculations for photoionization [8,10] are not shown in the table because the results are projectile dependent and reflective of the oscillator-strength distribution for Li^{1+}. However, the calculated ratios for $3+/2+$ for the asymptotic photoionization limit 0.0172% [8] and the half-collision model $\approx 0.16\%$ [10] are similar to the shake result and agree better with experimental observations than does the semiempirical prediction.

Next, we demonstrate the use of photoionization data and sum-rule analysis to predict the asymptotic limits for charged-particle ionization cross sections [25,32]. Asymptotically, the nonrelativistic Bethe formula for the ionization cross section, σ_i, as a function of electron energy, T, is

$$\sigma_i T/R = (4\pi a_0^2) M_i^2 \ln(4Tc_i/R), \tag{1}$$

where c_i is a constant which depends on the properties of the target, and R and a_0 are the Rydberg (energy unit) and the Bohr radius, respectively. Ratios of ionization cross sections at high T are determined roughly by the leading factor M_i^2, the squared dipole moment, which corresponds to the portion of $S(-1)$ leading to ionization, $S_i(-1)$.

[$S(n)$ corresponds to the oscillator-strength sum rule weighted by the nth power of the photon energy. See, for example [33].]:

$$M_i^2 = S_i(-1) = \int_{IP}^{\infty} (R/E)(df/dE)\, dE, \qquad (2)$$

where E is the energy transferred and f is the oscillator strength. We used the modeled Li^{3+} photoabsorption cross section given by Wehlitz *et al.* [7] to calculate the M_i^2 for Li^{3+}. The five experimental data points were modeled by scaling the double photoionization cross section of He; the energy axis was multiplied by $Z_{\rm eff}^2(He)/Z_{\rm eff}^2({\rm Li}) = 4/9$ and shifted by the energy difference of the thresholds. For Li^{2+} we used the measured photoabsorption cross section [30,34]. For Li^{1+} we used the $S(-1)$ sums in Berkowitz [25]. The resulting values of $M_i^2(Li^{3+})$, $M_i^2(Li^{2+})$, and $M_i^2(Li^{1+})$ are 4.26×10^{-7}, 1.52×10^{-3}, and 0.515 33 in atomic units, which yield the $3+/2+$ and $2+/1+$ asymptotic ratios shown in the fourth line of Table I. They are slightly lower than both the shake estimates and our experimental ratios as expected at $T = 1000$ eV, where $v_{\rm incident} = 8.3$ a.u. and the orbital speeds of Li $1s$ and $2s$ electrons are 3.0 and 1.5 a.u., respectively. (By analogy, with charged-particle double ionization of He, where asymptopia is observed for $v_{\rm incident}/Z_{\rm projectile} \geq 10 v_{\rm orbital}$ [26], $T \geq 12.3$ keV would be required for Li.)

In stark contrast is the semiempirical prediction for the $3+/2+$ ratio [1,23,31] shown in the last line of Table I. The semiempirical prediction for $3+/2+$ is more than *100 times* higher than the experimental observation, whereas that for $2+/1+$ is within a factor of 2. This can be rationalized; there are only direct paths to the $3+$ ion, in contrast to the $2+$ ion, and the semiempirical parameters are biased by data for many-electron systems.

In summary, the measured $3+/2+$ ratio for 1000 eV impact energy is in reasonable accord with expectations based upon photoionization results, shake estimates, and sum-rule analysis. However, the $3+/2+$ ratio is smaller by 2 orders of magnitude than the semiempirical prediction, which clearly does not apply to few-body systems. Few-body systems remain a challenge for theory, especially in the intermediate energy range.

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