Triple photoionization of lithium up to 650 eV photon energy

P. N. Juranić* and R. Wehlitz†
Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin 53589, USA
(Received 2 July 2008; published 2 September 2008)

We have investigated the relative triple-photoionization cross section of lithium from near threshold to 650 eV photon energy using monochromatized synchrotron radiation. Specifically, we reduced the statistical error bars in the 300 to 420 eV region and significantly extended the energy range compared to previous measurements. From the measured triple-to-double photoionization ratio, we determine the triple-to-single photoionization ratio and derive the triple-photoionization cross section. We make an estimate for the high-energy limit of that ratio and compare it to theoretical predictions. We also compare the Li^{3+} cross section with theoretical calculations.

DOI: 10.1103/PhysRevA.78.033401 PACS number(s): 32.80.Fb

I. INTRODUCTION

The double- and triple-photoionization process in which two or three electrons are simultaneously emitted from an atom is of fundamental importance for the understanding of electron correlation. The triple-to-single photoionization ratio is a convenient way to quantify this correlation and to investigate its photon energy dependence. Many experimental and theoretical investigations have dealt with double photoionization (see, e.g., [1,2]) with a strong emphasis on helium, while the study of triple photoionization (i.e., simultaneous emission of three electrons) has been lagging behind mainly due to its small cross section and the possible presence of sequential processes. Early investigations of the triple-ionization process concentrated on the threshold region of oxygen and neon [3] as well as of neon and argon [4]. However, the prime candidate for studying triple photoionization is lithium, which becomes a bare ion after triple ionization takes place. Since it has only three electrons, sequential processes (autoionization) cannot contribute to the triple-ionization cross section. The first (and only) triple-photoionization experiments with lithium have been performed in the late 1990s [5,6] and theoretical investigations followed. Noteworthy here is that so far the only other experimental triple-ionization study of Li was done by electron impact using a 1000-eV impact energy [7].

Previous photoionization measurements were performed below a photon energy of 424 eV with rather large error bars above 300 eV. In order to investigate the high-energy behavior of the triple-photoionization process we have taken data with greatly reduced statistical errors in the 300 to 420 eV range and extended the energy range up to 650 eV. We compare our data to recent theoretical calculations and predicted high-energy limits.

II. EXPERIMENT

The experiment was performed on the varied-line-spacing plane grating monochromator (VLS-PGM) [8] with an undulator photon source at the Synchrotron Radiation Center (SRC) in Stoughton, WI (U.S.A.). The beamline has no entrance slit and is equipped with three gratings providing a high photon flux at a moderate energy resolution. The low-energy grating used below 300 eV has 200 lines/mm while the medium-energy grating used at higher energies has 500 lines/mm. Since this experiment did not require a high energy resolution but rather high flux, we used a wide exit slit of 500 μm that yielded a resolution of about 1.2 eV at 244 eV. Second-order light and stray light were suppressed using carbon, titanium, and iron filters for energies below 280 eV, 430 eV, and 700 eV, respectively.

The photon beam entered the interaction region in the vacuum chamber where it crossed a beam of Li atoms produced by a resistively heated oven. The Li was heated to a temperature of about 480 °C. The crucible was biased to +10 V in order to keep thermal electrons inside the oven, thus avoiding electron-impact ionization of Li.

The ion time-of-flight (TOF) spectrometer consists of a pusher plate, extractor plate, drift tube, and a Z stack of microchannel plates (MCP) to detect the ions [9]. A pulsed electric field of 25 V/cm (period=16 μs, width=1.5 μs), that was applied to the pusher plate, accelerated the photoions towards the grounded extractor plate equipped with a high-transmission copper mesh. From there, the ions got further accelerated towards the drift tube by a permanent 250 V/cm electric field. After flying through the 15.4-cm-long drift tube, which is terminated on either side by a copper mesh, the ions were accelerated onto a commercial (Hamamatsu) MCP detector that has an active diameter of 20 mm and a potential of 3400 V on its front plate. Each pulse created by the MCP detector was discriminated against noise by a constant-fraction discriminator set at its lowest threshold of 28 mV. While this pulse was the start signal for the TOF measurement, the following electric pulse applied to the pusher plate provided the stop signal. The flight-time measurement was performed by a time-to-amplitude converter that provided the input for a computer interface and its multichannel-analyzer software. A sketch of the experimental setup and information on the experimental parameters that are important for ion TOF measurements can be found in Ref. [10].

In order to eliminate dead-time problems of the electronics, we did not process the events generated by the Li^+ ions but recorded only the Li^{2+} and Li^{3+} ions. This also greatly

*Present address: HASYLAB at DESY, Notkestr. 85, 22607 Hamburg, Germany.
†wehlitz@src.wisc.edu

reduces the problem with stray light because the much lower Li^+ threshold—compared to the Li^{2+} threshold—makes the Li^+ ion yield very susceptible to stray light.

III. DATA ANALYSIS

We tested the energy calibration of the beamline by measuring the Ar^+ ion signal while scanning the monochromator across the Ar $2p_{3/2} \rightarrow 4s$ resonance at 244.39 eV. We found that a photon energy correction was not necessary because the beamline energy was off by less than 0.1 eV, which is well within its energy resolution.

We extracted the areas of the doubly and triply charged ion peaks in our time-of-flight spectra using direct numerical integration. At most energies, the spectra were repeated once or twice with acquisition times of 1 to 2 hours each. Here, only the averaged values of the measurements at each photon energy are presented.

Because we have measured the Li^{3+}-to-Li^{2+} ratio to avoid dead-time problems of the electronics caused by the much stronger Li^+ peak we used our previously presented values for the Li^{2+}-to-Li^+ ratio R^{2+} [10] to determine the Li^{3+}-to-Li^+ ratio R^{3+}. From that ratio we have then derived the triple-photoionization cross section σ^{3+} using the total photoionization cross section σ_t determined previously [11],

$$\sigma^{3+} = \frac{\sigma_t R^{3+}}{1 + R^{2+} + R^{3+}}. \tag{1}$$

These relative cross-section measurements [11] were normalized with the help of the absolute cross-section measurement at 103.3 eV of Mehlman *et al.* [12]. A smooth total cross-section curve was then fitted to the cross-section data taken between 100 and 424 eV and extrapolated to 650 eV.

IV. RESULTS AND DISCUSSION

Figure 1 shows our triple-to-single photoionization cross-section data along with those of Wehlitz *et al.* [5,6]. The two sets show qualitative agreement with our data being slightly but systematically higher above about 300 eV. The (blue) asterisks represent the calculated double-to-single photoionization ratios for Li^+ ions [13], using the convergent closed coupling method, and show a very similar photon energy dependence as our triple-to-single photoionization ratio. Note that the theoretical curve was shifted by 5.4 eV according to the $2s$ binding energy and the ordinate was scaled to fit the data. This similarity supports the previous finding that the primary mechanism of the triple-photoionization process is double photoionization of the two $1s$ electrons followed by the shake off of the outer $2s$ electron into the continuum [5]. Also included in Fig. 1 is the single-ionization cross section of Li^+ by electron impact [14] [(red) squares]. The cross section is scaled to fit the experimental data demonstrating an energy dependence very similar to the one for the Li^{3+}-to-Li^+ ratio.

This comparison is based on the following idea. In principle, triple ionization of Li can be viewed as double ionization of both $1s$ electrons resulting in the shake off of the $2s$ electron. This picture was already introduced in Ref. [5] and

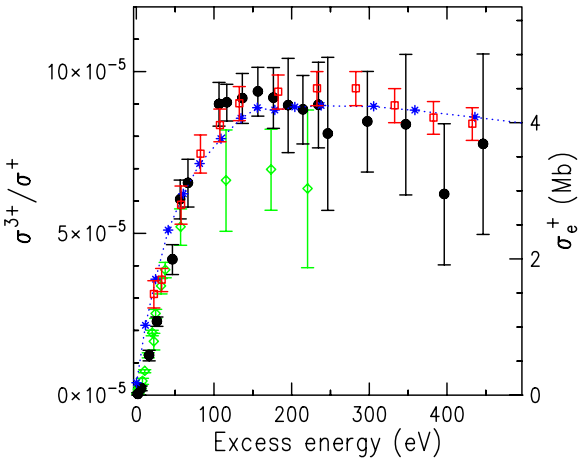

FIG. 1. (Color online) Triple-to-single photoionization cross-section ratio of Li. Black circles: This work. Green diamonds: Expt. [5,6]. Blue asterisks connected with a dotted line is the theoretical Li^{2+}-to-Li^+ ratio for Li^+ ions [13] scaled to fit our data. Red squares: Experimental single-ionization cross section of Li^+ by electron impact [14] (scale is on the right-hand side).

has been used by Kheifets and Bray [13]. For energies far above threshold, triple ionization appears like a double ionization multiplied by a shake factor. Because the $2s$ electron is only a weakly bound electron (in comparison to the $1s$ electron), one is rather quickly "far" above threshold. Thus, the triple-to-single photoionization ratio looks similar to the double-to-single photoionization ratio multiplied by a factor. This picture will most likely fail in a case where all three electrons originate from the same shell. According to Samson [15] the double-to-single photoionization ratio of an atom has a similar energy dependence as the electron-impact single-ionization cross section of the corresponding ion if the shake-off contribution is constant over the energy range considered. Because the single-ionization cross section of Li^+ by electron impact exhibits a similar energy dependence as the one for the Li^{3+}-to-Li^+ ratio, we conclude that the triple-photoionization process can indeed be treated as the double photoionization of the Li^+ ion. The small deviation at lower energies may indicate that our assumption that the shake-off contribution is constant is not fulfilled.

Similarly to Fig. 2 in Ref. [16], we show in our Fig. 2 the triple-to-double ionization ratio on an inverse photon energy scale. Our improved data allows us to apply a linear fit to ratios at high energies, thereby estimating the high-energy limit of that ratio. Note that the number of points included in the fit has been chosen such that as many points as possible are included ignoring low-energy points as they do not help in estimating the high-energy limit.

The error bar of the estimated high-energy limit is shown as a gray (green) bar on the left-hand side of the figure. Theoretical estimates of the high-energy limit are indicated as arrows in the figure. The half-collision model (HCM) of Pattard and Burgdörfer [16,19] decomposes the triple-photoionization process into a sequence of two-electron processes in which one ejected electron kicks out another electron by impact. This is a similar picture that was suggested by Samson for the double-photoionization process [15]. The

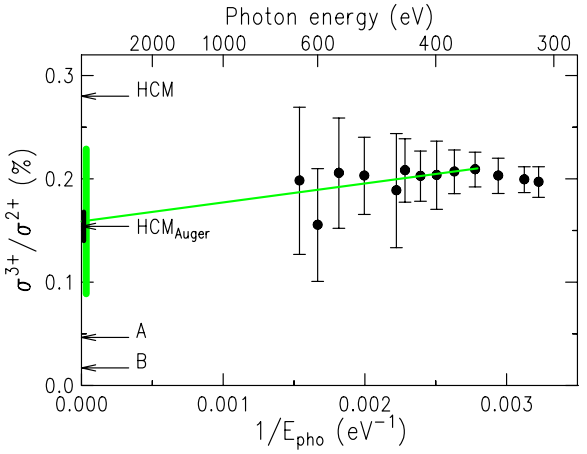

FIG. 2. (Color online) The high-energy region of the triple-to-double photoionization cross-section ratio of Li on an inverse energy scale. The solid line is a linear fit curve to our data pointing to the high-energy limit of that ratio. The corresponding error bar for the high-energy limit is depicted as a gray (green) bar on the left-hand side. Theoretical predictions are marked with an arrow; HCM calculations, Ref. [16]; arrow A, Ref. [17]; arrow B, Ref. [18].

half-collision model was the first approach to calculate the triple-photoionization cross section at finite photon energies. This model was later extended to the near threshold region [20].

The Li^{3+}-to-Li^{2+} ratio calculated in the original HCM is based only on the simultaneous emission of the electrons in the double-ionization process. In our experiment, however, some processes lead to a doubly charged ion via the sequential emission of electrons thereby increasing the probability for creating a doubly charged ion. This leads to a reduced Li^{3+}-to-Li^{2+} ratio as indicated in Fig. 2 by HCM_{Auger}. This ratio assumes a 40%–50% contribution of sequential processes to the total double-photoionization cross section. The estimate for the amount of sequential processes was first made by van der Hart and Greene [18], who used a *R*-matrix calculation with a *B*-spline basis set, and it is supported by the experimentally derived value of about 50% [10,21]. The agreement of our extrapolation with the estimated HCM_{Auger} value is very good albeit it has a large error bar. Other theoretical calculations by Cooper [17], using a shake model and Hartree-Fock wave functions, and by van der Hart and Greene [18], using the *R*-matrix method with a *B*-spline basis set, predict a much lower ratio and are clearly outside our error bar.

As described above, the triple-photoionization cross section has been derived from our ratios and is shown in Fig. 3 along with previously presented experimental values [5,6]. The error bars shown do not include the uncertainty of the measured total cross section [12] used to normalize the Li^{3+} cross section. Cross-section calculations by Pattard and Burgdörfer [16] using the half-collision model were performed for high photon energies and agree very well with our data in the 400 to 700 eV photon energy range. Colgan *et al.* [22] performed a time-dependent closed coupling calculation for medium photon energies. For the 260 to 420 eV (their highest point) energy region we find very good agreement with their calculation, but their data are lower than our data at lower energies. The brown triangles in Fig. 3 are theoretical values by Emmanouilidou and Rost [20] examining the four-body breakup semiclassically using a Monte Carlo method. Their ratio is slightly higher at energies below 270 eV but are in accord with our data above 260 eV.

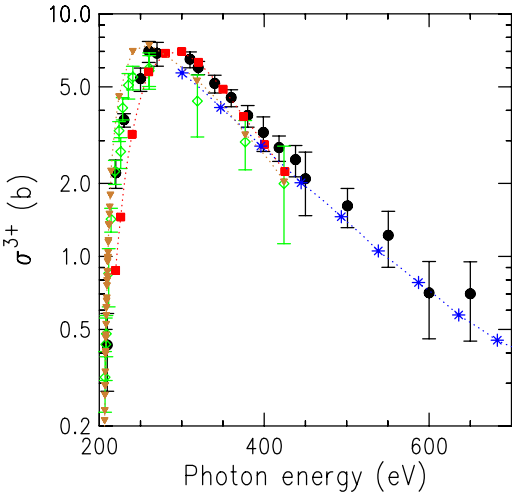

FIG. 3. (Color online) Triple-photoionization cross sections of Li. Black circles: This work. Green diamonds: Refs. [5,6]. Theoretical work is shown by red squares, Ref. [22]; blue asterisks, Ref. [16]; brown triangles, Ref. [20].

Figure 4 displays the triple-photoionization cross section on a logarithmic excess-energy scale putting more emphasis on the low-energy region. It is apparent that the shape function developed by Pattard [23] models the energy dependence of the triple-photoionization cross section very well. This shape function describes the transition between threshold behavior and high-energy behavior of the cross section and has two fit parameters, namely, the maximal cross section and the energy position of the maximum.

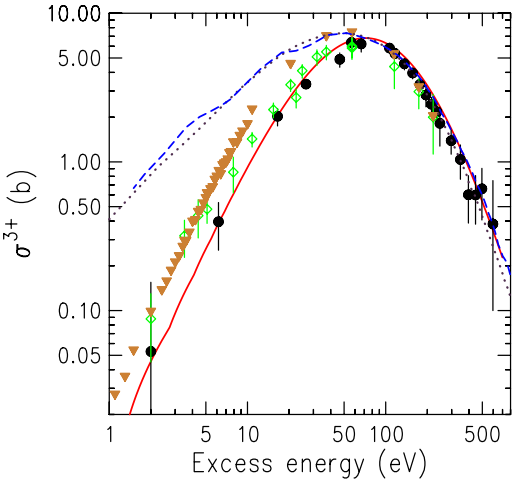

FIG. 4. (Color online) Triple-photoionization cross sections of Li. Black circles: This work. Green diamonds: Refs. [5,6]. Blue dashed line, calculated double-photoionization cross section of Li^+ [13] (scaled); gray dotted line, measured double-photoionization cross section of He [3] (scaled); brown triangles, theory [20]; red solid line, shape function [23].

As mentioned above, the semiclassical calculation by Emmanouilidou and Rost [20] seems to slightly overestimate the cross section at energies below 60 eV excess energy but agrees with our data at higher energies. Their calculation is in better accord with the previous measurements [5,6] at lower energies while our new and the previous measurements are still in agreement within their error bars. The double-photoionization cross section of Li^+ by Kheifets and Bray [13] has been scaled to fit our data at high energies and, indeed, above ca. 80 eV excess energy this cross section follows our cross section very nicely. At lower energies their $(Li^+)^{2+}$ cross section is clearly higher and follows the experimental He double-photoionization cross section of Samson *et al.* [24] rather than our triple-photoionization cross section. Note that the cross section of H^{2+} has been reduced by 20% to match the $(Li^+)^{2+}$ curve of Kheifets and Bray.

Overall, the cross-section data demonstrate that it seems to be easier to calculate the triple-photoionization cross section at higher energies [16,20,22] than at lower energies, perhaps because the process is rather double-ionization-like at high energies [13,24].

V. CONCLUSION

We have measured the triple-to-double photoionization cross-section ratio of Li from threshold to 650 eV photon energy. From that ratio we have determined the triple-to-single photoionization ratio and derived the triple-photoionization cross section. Below ca. 280 eV our data are in accord with previous measurements [5,6] but they are somewhat higher above that energy. Our measurements extend to higher energies and cover now 2 times the excess energy as before.

Furthermore, we find that the single-ionization cross section of Li^+ by electron impact [14] exhibits an energy dependence very similar to the one for the Li^{3+}-to-Li^+ ratio. For this comparison we made the assumption that the triple-photoionization process can be regarded as the double photoionization of both 1*s* electrons with the 2*s* electron being shaken off (see discussion above). The excellent agreement is a strong indication that this picture is indeed correct.

The high-energy behavior of the triple-to-double photoionization ratio points to a value that is close to the one predicted by the half-collision model [16] when the double-photoionization probability includes 40%–50% sequential processes. The two other predictions for the high-energy limit using Hartree-Fock wave functions and a shake model [17] or an *R*-matrix calculation with a *B*-spline basis set [18] are too low.

The triple-photoionization cross section calculated by Pattard and Burgdörfer [16] above 350 eV photon energy agrees very well with our data. Also the calculation by Colgan [22] is in good agreement with our data for energies above ca. 350 eV. Furthermore, we find that the energy dependence of the Li^{3+} cross section at high energies follows the energy dependence of the double-photoionization cross section of Li^+ [13]. This points to a similarity of the two processes at high energies, i.e., triple photoionization can be regarded as double photoionization with the third electron shaken off.

ACKNOWLEDGMENTS

The authors wish to thank the staff of the Synchrotron Radiation Center for their excellent technical support. We also thank Dr. A. Emmanouilidou for sending her data in numerical form and Dr. S. Whitfield for a critical reading of the paper. This work is based upon research conducted at the Synchrotron Radiation Center, University of Wisconsin-Madison, which is supported by the NSF under Grant No. DMR-0537588.

[1] J. S. Briggs and V. Schmidt, J. Phys. B **33**, R1 (2000).
[2] I. Bray, D. V. Fursa, A. S. Kheifets, and A. T. Stelbovics, J. Phys. B **35**, R117 (2002), and references therein.
[3] J. A. R. Samson and G. C. Angel, Phys. Rev. Lett. **61**, 1584 (1988).
[4] J. B. Bluett, D. Lukić, and R. Wehlitz, Phys. Rev. A **69**, 042717 (2004).
[5] R. Wehlitz, M.-T. Huang, B. D. DePaola, J. C. Levin, I. A. Sellin, T. Nagata, J. W. Cooper, and Y. Azuma, Phys. Rev. Lett. **81**, 1813 (1998).
[6] R. Wehlitz, T. Pattard, M.-T. Huang, I. A. Sellin, J. Burgdörfer, and Y. Azuma, Phys. Rev. A **61**, 030704(R) (2000).
[7] M.-T. Huang, W. W. Wong, M. Inokuti, S. H. Southworth, and L. Young, Phys. Rev. Lett. **90**, 163201 (2003).
[8] R. Reininger and A. R. B. de Castro, Nucl. Instrum. Methods Phys. Res. A **538**, 760 (2005).
[9] R. Wehlitz, D. Lukić, C. Koncz, and I. A. Sellin, Rev. Sci. Instrum. **73**, 1671 (2002).
[10] R. Wehlitz, M. M. Martinez, J. B. Bluett, D. Lukić, and S. B. Whitfield, Phys. Rev. A **69**, 062709 (2004).
[11] M.-T. Huang, R. Wehlitz, Y. Azuma, L. Pibida, I. A. Sellin, J. W. Cooper, M. Koide, H. Ishijima, and T. Nagata, Phys. Rev. A **59**, 3397 (1999).
[12] G. Mehlman, J. W. Cooper, and E. B. Saloman, Phys. Rev. A **25**, 2113 (1982).
[13] A. S. Kheifets and I. Bray, Phys. Rev. A **58**, 4501 (1998).
[14] W. C. Lineberger, J. W. Hooper, and E. W. McDaniel, Phys. Rev. **141**, 151 (1966).
[15] J. A. R. Samson, Phys. Rev. Lett. **65**, 2861 (1990).
[16] T. Pattard and J. Burgdörfer, Phys. Rev. A **63**, 020701(R) (2001).
[17] J. W. Cooper, Phys. Rev. A **59**, 4825 (1999).
[18] H. W. van der Hart and C. H. Greene, Phys. Rev. Lett. **81**, 4333 (1998).
[19] T. Pattard and J. Burgdörfer, Phys. Rev. A **64**, 042720 (2001).
[20] A. Emmanouilidou and J. M. Rost, J. Phys. B **39**, 4037 (2006).
[21] R. Wehlitz, J. Colgan, M. M. Martinez, J. B. Bluett, D. Lukić, and S. B. Whitfield, J. Electron Spectrosc. Relat. Phenom. **144-147**, 59 (2005).
[22] J. Colgan, M. S. Pindzola, and F. Robicheaux, Phys. Rev. A **72**, 022727 (2005).
[23] T. Pattard, J. Phys. B **35**, L207 (2002).
[24] J. A. R. Samson, W. C. Stolte, Z. X. He, J. N. Cutler, Y. Lu, and R. J. Bartlett, Phys. Rev. A **57**, 1906 (1998).