Single and double photoionization of lithium

M.-T. Huang,[1,*] R. Wehlitz,[1] Y. Azuma,[1] L. Pibida,[2] I. A. Sellin,[2] J. W. Cooper,[3] M. Koide,[4] H. Ishijima,[5] and T. Nagata[5]

[1]*Photon Factory, Institute of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, Ibaraki, 305-0801, Japan*

[2]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200*

[3]*Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742-2431*

[4]*University of Electro-communications, Chofu, Tokyo 182-8585, Japan*

[5]*Meisei University, Hodokubo, Hino, Tokyo 191-8605, Japan*

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The photoion Li^{2+}/Li^{+} production cross section ratio of ground-state atomic lithium has been measured for photon energies ranging from 80 to 424 eV. The absolute cross sections for the Li^{2+} and Li^{+} yield are also derived. In this energy region, the Li^{2+}/Li^{+} ratio reaches a plateau of about 1.0% before reaching a maximum of about 4.5%, then decreases slowly. Good agreement is found between the measured total photoionization cross sections of lithium and theoretical calculations. The Li^{2+}/Li^{+} ratio is also compared to the He^{2+}/He^{+} ratio from excited He$(1s2s)$ for photon energies up to 70 eV above threshold. The branching ratio of Li^{2+} to total Li ion production is also compared to the single-ionization cross section of electron impact on Li^{+} ions. [S1050-2947(99)03605-7]

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I. INTRODUCTION

During the past decade, double photoionization (or, the ratio of double to single photoionization) of helium has been under intensive investigation, both experimentally and theoretically [1–10]. The reason is that, since the photoelectric operator is a single-particle operator, the simultaneous detachment of two electrons by a single photon stems purely from electron correlation effects, which cannot be accounted for by the independent electron approximation. This makes double photoionization an ideal test case for our understanding of electron correlation effects. Although discrepancies between experiments and theories still exist, agreement has greatly improved over the years.

Lithium is the simplest open-shell atom, and the simplest atom that exhibits intershell electron correlation. In this three-electron system, there are fundamentally different processes involved in photoionization which do not find any analogue in a closed-shell two-electron system like helium. Examples for such processes are the intershell electron correlation, the overlap with resonant-photoexcitation of hollow lithium [12,13], two step processes for double ionization, and direct triple photoionization [14]. Moreover, lithium has an optically active electron that can be excited easily by laser light. This allows investigations on the electron correlation for different initial state configurations. Hence, the system provides a still richer testing ground for the understanding of electron-correlation effects.

The main purpose of this paper is to present the photoion Li^{2+}/Li^{+} production cross section ratio of ground-state atomic lithium, as well as the absolute production cross sections for Li^{2+} and Li^{+} yields, for photoionization as a function of photon energy.

*Electronic address: mth@mail.kek.jp

II. EXPERIMENTAL METHOD

The data presented in this paper were acquired with the same lithium oven and ion-time-of-flight (TOF) apparatus described previously [11–13]. So, the experimental methods used will be described only briefly.

The experiments were done at the 2.5-GeV electron storage ring of the Photon Factory, KEK, utilizing the extreme-ultraviolet (XUV) bending-magnet beam-line BL3B [15], and for some of the higher energy data points, the undulator beam-line BL16B. A photoion TOF analyzer viewed perpendicularly the Li atomic beam target effusing from an oven source. The interaction region was defined by the intersection of the incident monochromatized XUV radiation beam from the third orthogonal direction and the lithium vapor. Partial charge-state ion-yield spectra were acquired in the pulsed-field-TOF-extraction-mode with gated data acquisition. Background corrections derived from equal TOF-spectrum regions adjacent to and in-between the peaks corresponding to the singly and doubly charged states of ^{6}Li and ^{7}Li were made by subtraction, with error propagation being carried forward by standard statistical methods. Silicon and carbon foils were used upstream from the target region to filter out the contributions from higher-order light and stray zeroth order light. The voltages across the cheveroned double MCP stack were set to be -4 kV for entrance and -2 kV for exit, and the CFD threshold was set very low at about 35 mV to ensure that there was no discrimination between ''1+'' and ''2+'' ions. This was confirmed by measuring the Li^{2+} to Li^{+} ratio as a function of MCP voltages and CFD threshold settings. In the interest of achieving high count rates and thereby good statistics, a modest resolution of 0.5 eV was used.

III. DATA ANALYSIS

The Li^{2+} to Li^{+} ratios were obtained by directly taking the ratio of the integrated and background-corrected Li^{2+}

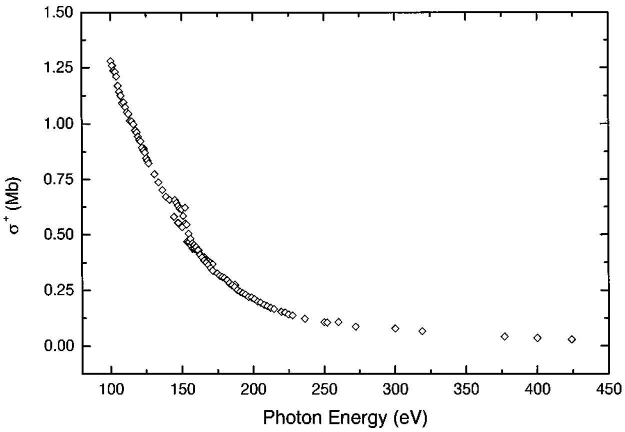

FIG. 1. Absolute cross section for the production of singly charged Li ions. Error bars for these data are discussed in the text. Some data (e.g., near 150 eV) show scattering beyond statistical errors, owing to hollow lithium resonances superimposed on the underlying continuum structure [12,13].

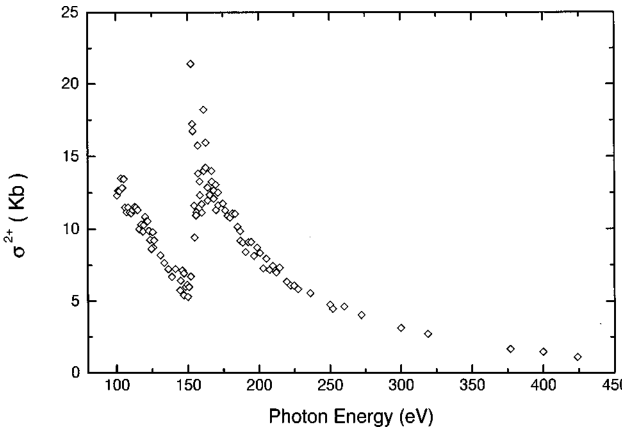

FIG. 2. Absolute cross section for the production of doubly charged Li ions. Error bars for these data are discussed in the text. Some data (e.g., near 150 eV) show scattering beyond statistical errors, owing to some hollow lithium resonances superimposed on the underlying continuum structure [12,13].

and Li^+ peak yields as a function of photon energy between the double ionization threshold (81.01 eV [16]) and the present upper limit of 424 eV. The absolute partial charge state cross sections could then be derived by the following two procedures.

(1) The relative partial (charge state) cross sections are obtained from the integrated and background-corrected Li^{2+} and Li^+ peak yields normalized to the photon flux, as a function of photon energy.

(2) The absolute total cross sections were then obtained by normalizing the relative total cross sections (namely, $Li^{2+}+Li^+$ only, since no appreciable Li^{3+} was observed) to the known absolute total photoabsorption cross section measurements obtained by Mehlman *et al.* [17] at 103.3 eV. The absolute partial charge-state cross sections could then be derived from the measured Li^{2+} to Li^+ ratios.

To obtain the ratios, as mentioned above, no knowledge of the photon flux is needed since the flux will cancel out at each datum point. However, to obtain the relative cross sections as a function of photon energy, relative photon flux measurements are essential. The photon flux was monitored by a factory calibrated far UV photodiode [18] downstream from the target region. Thus the relative cross sections above 120 eV were obtained by normalizing to the photon flux monitored by this diode. (Note that, for energies above 240 eV, the diode calibration was obtained by extrapolation from the calibrated curve [18].) However, because the calibration of the photodiode used shows some structures (i.e., peaks and dips) for photon energies below 120 eV, it was decided to use another set of measurements, which used a different way to monitor the photon flux, to obtain the cross sections for the energy region below 120 eV. The relative photon flux in that measurement was monitored by measuring the electron drain current created by monochromatized photons striking the final focussing mirror just upstream of the experiment. A photon energy dependence of the drain current production efficiency will give rise to a secular variation in the photon flux detection efficiency *versus* photon energy. This variation of detection efficiency can be monitored and corrected for by coetaneously making measurements of the photoionization of He, studied in this energy range over a period of many years, and reviewed carefully by Samson *et al.* [5]. By normalizing to the total photoabsorption cross section values recommended by Samson *et al.*, we were able to calibrate (relatively) this flux detection efficiency to an accuracy limited primarily by the accuracy of Samson *et al.*'s recommended photoabsorption measurements, which are believed by them to be no worse than 5% inaccurate in the energy range discussed here.

In the region of 120 eV to 180 eV these two relative cross section measurements overlap each other, indicating that these two ways of monitoring the photon flux are consistent with each other. Due to the worse statistics observed with the drain current method, only the cross sections for energies below 120 eV are reported from that measurement. In addition, since no reliable data below 100 eV were obtained in that measurement, the cross section data reported here will be only for photon energies from 100 eV to 424 eV.

IV. RESULTS AND DISCUSSION

Figures 1, 2, and 3 display the principal results of our absolute partial photoionization cross sections for the singly and doubly ionized charge states, and their ratio, respectively. The error bars of the measured Li^{2+} to Li^+ ratio are due to statistics. The error bars on the relative scale of partial photoionization cross sections (for clarity, they are not displayed) are estimated to be about 10–15 %. They arise from a combination of statistical errors and uncertainties of photon flux determination. The uncertainty on the absolute scale is about 20%, which is propagated from the measurement [17] to which our relative cross sections were normalized to obtain the absolute cross sections. Some data (e.g., near 150 eV) show scattering beyond statistical errors, owing to some hollow lithium resonances superimposed on the underlying continuum structure [12,13]. Here we will focus only on the continuum (nonresonant) structure. In order to understand the energy behavior of the curves shown in Figs. 1, 2, and 3, a number of important threshold energies are needed. Their values are listed in Table I.

The cross section curve of Li^+ (Fig. 1) is smooth, and monotonically declining with photon energy in this energy

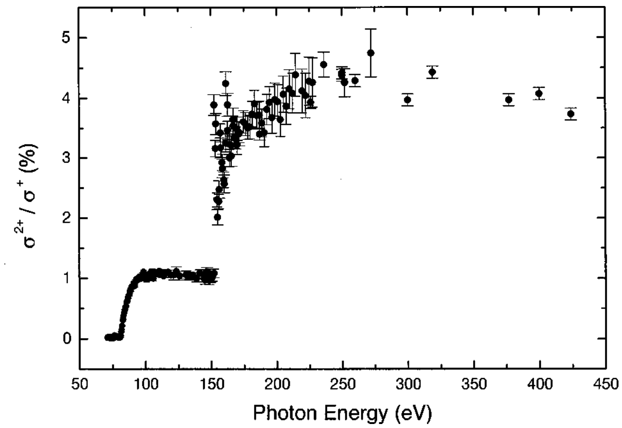

FIG. 3. Ratio of the Li^{2+} to Li^{+} yields. Some data (e.g., near 150 eV) show scattering beyond statistical errors, owing to some hollow lithium resonances superimposed on the underlying continuum structure [12,13].

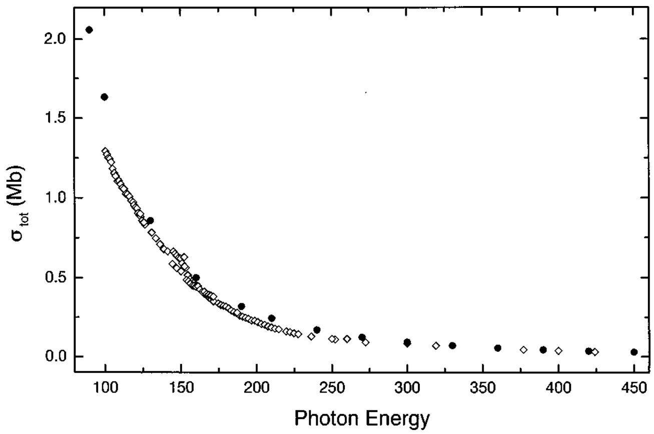

FIG. 4. The total photoionization cross sections of lithium. Diamonds: present work; closed circles: theoretical calculations done by Reilman and Manson [21].

region as expected. The Li^{2+} photoionization cross section curve (Fig. 2) is also decreasing smoothly until numerous additional continuum channels (beginning at about 152 eV) for double ionization set in, where it rises substantially, and then falls off fairly smoothly once again. Figure 4 shows the total photoionization cross sections, both experimental and theoretical, as a function of photon energy. The experimental data are the current results, which are the sums of Li^{+} and Li^{2+} production cross sections shown in Figs. 1 and 2. The theoretical calculations were done by Reilman and Manson [21]. It can be seen from Fig. 4 that the experimental and theoretical results agree very well with each other for photon energies above 120 eV. In the lower energy region, the calculations seem to rise faster than the experimental results.

It can be seen from Fig. 3 that the Li^{2+} to Li^{+} ratio rises for about 20 eV above threshold just as it does for helium and then levels off at about 1.0% until up to about 152 eV, where it rises again for the same reason just mentioned above. (Please see Table I for information on relevant threshold energies.) In this energy range (from 81 eV to about 152 eV), the only nonresonant process for double ionization is direct double photoionization of the $1s$ and $2s$ electrons of lithium leaving the other electron in $1s$ state. The only other measurements on direct double photoionization of two electrons from different shells, which is a result of intershell electron correlation, were done on sodium $2p3s$ double photoionization [22,23]. A similar plateau structure was seen in that study.

Since there is no calculation available to date on lithium double photoionization, we made an estimate of the $1s2s$ double photoionization ratio by considering a lithium atom with suddenly created K-vacancy and then calculating the shake off rate of the $2s$ electron while the third electron remains frozen. This was done using Hartree-Fock wave functions for both the Li ground state and the Li^{+*} excited states. This yielded a ratio of 1.91%, considerably larger than the 1.0% observed for the plateaulike region near 150 eV. Further sophisticated calculations are called for although it is not exactly certain from our data, whether the observed ratio of 1.0% is close to the asymptotic limit of $1s2s$ photoionization since at energies higher than about 152 eV additional continuum channels open up for double ionization as seen on Fig. 3.

TABLE I. Some relevant threshold energies for Li [19,20].

State	Threshold (eV)
$Li^{+}(1s^2)$	5.39
$Li^{+}(1s2s)$	64.4
$Li^{2+}(1s)$	81.01
$Li^{+}(2s^2)$	151.68
$Li^{2+}(2s)$	172.82
Li^{2++}	203.43

Moreover, since the second $1s$ electron of lithium does not take part in ionization or excitation for photon energies below 152 eV, it probably serves only to screen the nuclear potential from the other two electrons. So the system should resemble that of excited He$(1s2s)$. If it is assumed that this observed 1.0% ratio is the asymptotic limit for this process, then this ratio can be compared with the asymptotic limit of He^{2+} to He^{+} ratio of excited He$(1s2s)$. In a previous study by Forrey *et al.* [24], the asymptotic limits for He^{2+} to He^{+} ratio were calculated for excited ^1S and ^3S states of the helium isoelectronic sequence using the asymptotic formulation of Dalgarno and Stewart with highly correlated Frankowski-Pekeris-type wave functions as initial state wave functions. From their calculation, the asymptotic ratio is 0.9033% for He$(1s2s\,^1S)$ and 0.3118% for He$(1s2s\,^3S)$ compared to the current measurement of 1.0% for lithium at about 150 eV.

Also, in a recent paper by van der Hart *et al.* [25], the He^{2+} to He^{+} photoionization ratio of excited metastable He$(1s2s)\,^1S$ and ^3S states were calculated using a R-matrix approach as a function of photon energy up to 80 eV above threshold. An estimate made by van der Hart [26] using $1/z$ perturbation theory suggests that, to adequately compare these two cases, the energy axis of He data needs to be scaled by a factor of 1.19, which is the ratio of the ionization potentials of the $2s$ electron of Li$(1s^22s)$ and He$(1s2s)$. Since for lithium, the two ionized electrons can couple into either ^1S or ^3S states, the lithium data were compared with the calculated helium data for $\frac{1}{4}$He$(1s2s\,^1S)$

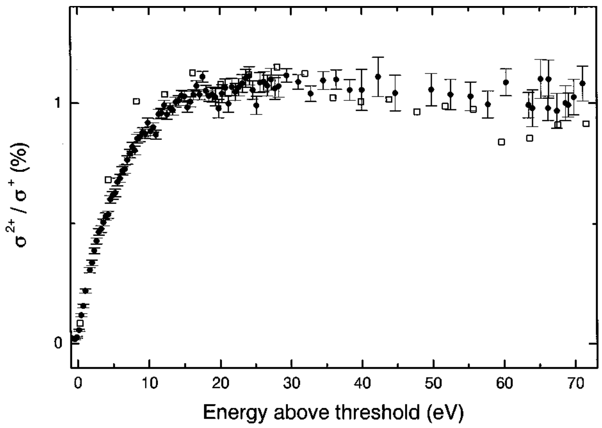

FIG. 5. Comparison between current experimental Li^{2+}/Li^{+} ratio and He^{2+}/He^{+} ratio of excited He$(1s2s)$ calculated by van der Hart *et al.* [25]. X axis is the energy above $1s2s$ double-ionization threshold. Closed circles: present work; open squares: calculated ratios of $\frac{1}{4}\mathrm{He}(1s2s\,^1S)+\frac{3}{4}\mathrm{He}(1s2s\,^3S)$. Note that the X axis of He data is scaled by a factor of 1.19. Please see text for details.

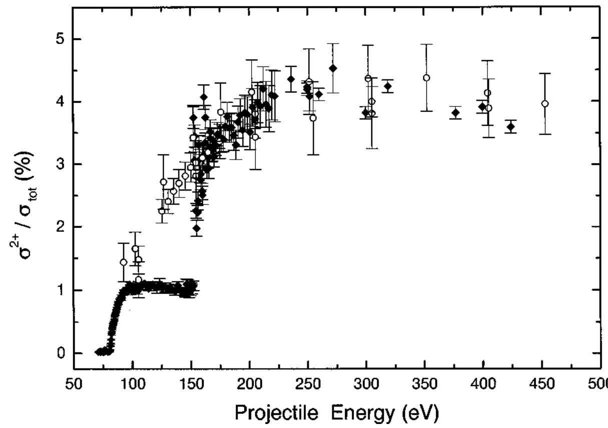

FIG. 6. Comparison between the branching ratio of Li^{2+} to total Li ion production and the single-ionization cross section of electron impact on Li^{+}. Closed diamonds: present work for lithium branching ratio; open circles: electron impact ionization data from [30]. Note that the energy axis for the electron impact data was shifted 5.39 eV upwards.

$+\frac{3}{4}\mathrm{He}(1s2s\,^3S)$, with the energy axis of He data scaled by a factor of 1.19 as just mentioned above. The agreement is fairly good, as shown in Fig. 5.

It can also be seen from Fig. 3 that the cross section ratio rises rapidly at approximately 152 eV, the energy of the lowest doubly-excited state of $Li^{+}(2s^2)$. The reason for this enhancement is that above this energy, the two K electrons can be excited and decay via an Auger process leaving one electron in either the ground state or in an excited state of Li^{2+} [12,27], i.e., two-step processes open up for double ionization. However, no clear enhancement on the ratio is seen when the threshold for ionizing two K-shell electrons [i.e., $Li^{2+}(2s)$] is reached (also, no clear enhancements on other thresholds are observed). This is expected, since after reaching the $Li^{+}(2s^2)$ threshold, many continuum channels open up with threshold energies not very different from one another. Examples are $Li^{+}(2s^2)$ (about 152 eV), $2s3s$, $2s4s, \ldots$, all the way up to $Li^{2+}(2s)$ (about 172 eV) and other $nsn's$ series. So basically, these continuum channels with closely spaced thresholds superimposed on each other resulting in a general rise over a wide range of energy as shown in Fig. 3. After the rise at about 152 eV, the ratio peaks at about 4.5% at approximately 250 eV, it then appears to decrease slowly over the rest of the energy region. The asymptotic limit of this ratio was recently calculated to be 3.36% by van der Hart and Greene [28]. They found that an indirect mechanism through excitation of doubly excited states accounts for more than 40% of the double ionization providing an explanation why this calculated value of 3.36% is much bigger than that for He. If this calculation is correct, it means that the decrease of this ratio at high energies (from a maximum of 4.5% to the asymptotic limit of 3.36%) is much smaller than that of helium (from about 4% to 1.7%). To verify this, more measurements at higher energies are required.

In a previous study by Samson [29], it was found that the branching ratio of double photoionization of an atom was proportional to the single-ionization cross section of electron impact on the singly charged ion of the same atom over a range of energy immediately above the double-ionization threshold. The branching ratio of Li^{2+} is plotted in Fig. 6 and is compared with the published electron impact ionization data [30] scaled to give a good fit for the overall curve. The normalizing proportionality factor is 0.97×10^{16} cm^{-2}. In the same study [29], the He^{2+} branching ratio was also compared to the electron impact cross section, and the normalizing factor was found to be 1.02×10^{16} cm^{-2} for helium. It should be noted that the energy axis of the electron impact data shown is shifted by 5.39 eV due to the difference between the threshold energies. As is shown in Fig. 6, except for the region approximately between 100 and 150 eV, the two curves almost overlap with each other throughout the whole energy region displayed up to about 350 eV above threshold. The plateau that the lithium branching ratio reaches between 100 and 150 eV does not appear in the electron impact ionization cross section; the cross section still keeps rising in that region. So the proportionality seems to hold for the energy regions below and above the plateau region. (This is not very conclusive for the before-plateau region since the data for electron impact ionization do not go all the way down to the threshold energy, but the two curves do seem to meet before the plateau.)

V. CONCLUSIONS

In summary, the photoion Li^{2+}/Li^{+} production cross section ratio was measured for photon energies ranging from 80 eV to 424 eV. The absolute cross sections of the Li^{2+} and Li^{+} yields were also derived for photon energies ranging from 100 eV to 424 eV. The measured total photoionization cross sections were found to have good agreement with theoretical calculations. The ratio of Li and that of calculated He$(1s2s)$ were found very similar for photon energies up to 70 eV above thresholds. A good proportionality was also found over a wide energy region between the branching ratio of Li double photoionization and the single ionization cross section of electron impact on Li^{+}. In the future, it would be desirable to have more measurements at higher photon energies in order to estimate the asymptotic Li^{2+} to Li^{+} ratio, and also to test whether the similarities and proportionalities mentioned above hold at the higher photon energy regime.

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