Triple Photoionization of Lithium

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(Received 23 February 1998)

Triple photoionization of an atomic three-electron system has been observed for the first time. Triply charged lithium ("bare lithium") was found in the photoion spectrum following synchrotron irradiation of neutral Li vapor. Sequential decay processes, which must result in at least one remaining bound electron, cannot account for such triple ionization. We have measured the triple-to-single photoionization ratio between 187 and 424 eV and made the first, rough estimate for this ratio. The measured triple-photoionization cross section never exceeds 6 b. [S0031-9007(98)07006-9]

PACS numbers: 32.80.Fb

The investigation of multiple-ionization processes of atoms and molecules is of fundamental importance for understanding the interactions among charged particles in a Coulomb field, e.g., electrons and ions in a plasma. Not only the interaction itself but also the relative strength of multiple-ionization processes provide valuable information for, e.g., modeling conditions in astronomical objects [1]. Although multiple ionization appears to be a simple process, even the interaction of *three* charged particles cannot be described analytically. In order to find a model that is able to describe the multiple-ionization process, recent investigations have been focused on a simple case, namely, the double photoionization of helium. Numerous studies, theoretically as well as experimentally [2], of this three-body Coulomb system have advanced our understanding of the electron–electron interaction in a Coulomb field. A variety of experimental techniques such as photoion spectroscopy [3,4], photoelectron spectroscopy [5], and electron–electron coincidence measurements [6,7] have been used to elucidate the double-ionization process of He at various photon energies. In the past few years, satisfactory agreement between experiment and theory could finally be achieved in many aspects of the double-ionization process.

The established relationship between double ionization by photons and by charged particles [8] has been useful for relating the results from both experimental techniques [9]. However, in contrast to charged particles, ionization by a single photon (except for Compton scattering) has a well-defined energy and angular momentum transfer from the projectile to the target, and provides a simpler testing ground for theoretical models. Since the photoelectric operator is a one-electron operator, only single electron excitation or ionization is possible within the framework of the independent particle model. Therefore, multielectron processes are due entirely to correlation effects among the electrons.

The experiment presented in this Letter is an important step forward in the ongoing investigations of multiple-photoionization processes since it is a triple electron–electron correlation effect which is isolated. We report the observation of bare lithium ions (Li^{3+}) in the photoion time-of-flight spectrum and the measurement of the triple-to-single photoionization ratio from threshold to 424 eV. The complete breakup of the Li atom into four particles can occur only by *simultaneous* ejection of all three electrons; i.e., Auger decay processes (or autoionization), which leave behind at least one bound electron, cannot contribute to the triple-ionization cross section. Moreover, in contrast to other atoms, Li has only *one* triple-ionization threshold, which makes it well suited as a unique source of information on pure three-electron correlations, and corresponding theoretical calculations—when they become available—can be compared directly with our experimental results. Although direct, one-step, triple photoionization has been observed in other atoms, e.g., neon [10], the lithium case is unique since it is the simplest atom with the possibility of triple photoionization and lacks the contribution from relaxation (rearrangement) effects due to other electrons which are significant in heavier atoms. In addition, for such atoms (e.g., Ne), triple ionization originates partly from Auger decays, which may take place even in the valence shell [11] and generally complicate theoretical predictions. However, a consequence of the fact that we have a pure, unambigous direct triple-photoionization process in Li is having to deal with a particularly low triple-ionization cross section.

So far, to our knowledge, experimental data regarding the triple photoionization of Li, or other three-electron systems, are not available. Theoretical interest has been focused on the angular distribution pattern of the electrons [12].

The experiment was performed at the 2.5-GeV storage ring of the KEK Photon Factory. The photons coming

from the extreme ultraviolet (XUV) undulator beam line BL16B were monochromatized by a 24-m spherical grating monochromator [13]. Additional cylindrical mirrors focused the photon beam and provided a high flux. Because this experiment did not require a high energy resolution but did require high photon flux, the monochromator entrance and exit slits could be opened to 1000 μm each. The undulator gap was adjusted for each photon energy in order to maximize the photon flux. The photon energy was tunable in the range from 40 to about 600 eV, utilizing three laminar gratings with different line spacings for corresponding photon energy regions. The photon energy resolution was about 1.0 eV; the absolute value of the photon energy in this experiment had an uncertainty of ± 0.5 eV.

The photon beam entered the experimental chamber, intersecting a beam of Li atoms emerging from an effusive metal vapor oven [14]. The lithium photoions, which were produced in the interaction region, were detected with an ion time-of-flight spectrometer operating in the pulsed extraction mode, as described previously [15]. The background pressure in the experimental chamber during the experiment was lower than 1×10^{-7} mbar. The threshold of our constant-fraction discriminator (CFD) was set to a very low level ($\leq$31 mV) to ensure that there was no detection efficiency difference between the Li^+ and Li^{3+} ions; this was established experimentally by measuring the triple-to-single photoionization ratio as a function of the CFD threshold. A spectrum taken below the triple-ionization threshold of Li (203.4 eV [16]) at 187 eV did not reveal any triply charged Li ions. From that, we conclude that the monochromatized photon beam did not contain appreciable higher-order photon energy contributions. Also low-energy stray light was known to be negligible in this experiment because of the characteristics of this undulator. This was experimentally verified by measuring the double-to-single photoionization ratio, which confirmed a previous experiment [17] at a different beam line where filters were used to eliminate the stray light. The contribution of Li dimer (Li_2) in the lithium vapor was negligible in our experiment because of its much lower vapor pressure [18]. Moreover, no triply charged ions were detected at 187 eV; this is lower than the triple-ionization threshold of atomic Li but presumably higher than the one for Li_2 since the latter has two lightly bound valence electrons.

In order to determine the triple-to-single photoionization ratio we took ion time-of-flight spectra at several photon energies. As an example, Fig. 1 shows an ion spectrum taken at $h\nu = 260.5$ eV. The area of the Li^+ peak was numerically integrated, whereas the area of the Li^{3+} peak was determined by a least-squares fit using a Gaussian profile. A numerical integration of the Li^{3+} peak yielded the same area as the fitting program within the error bars. The statistical error provided by the fitting program corresponds to a 1σ error bar. Figure 2 shows the measured triple-to-single photoionization ratios which

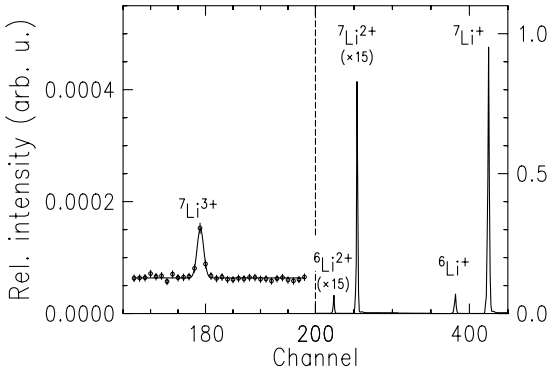

FIG. 1. Li ion time-of-flight spectrum at a photon energy of 260.5 eV. Peaks corresponding to the main isotope ^{7}Li as well as to the less abundant ^{6}Li isotope. The Li^{3+} peak is shown together with a corresponding least-squares fit. Note the different scales to the left and right of the dashed line.

are observed to rise approximately linearly from threshold (203.4 eV) to about $h\nu = 300$ eV, and reach a plateau with a value of approximately 0.0066%. This behavior is similar to the one observed for Ne [19], where the triple-to-single photoionization ratio remains almost flat for energies above 300 eV before reaching other thresholds. However, the triple-to-single ionization ratio of Ne rises much more steeply over a larger energy region (up to $\approx$1.5% at 300 eV) probably due to a multiplicity of different triple-ionization thresholds.

Unfortunately, no calculations or even estimates for the triple-to-single photoionization ratio of ground state Li are currently published. Therefore, we made a first preliminary estimate for the high-energy limit of this ratio employing a simple shakeoff model. We consider the *double*-to-single photoionization ratio. At moderately high energies of 300–400 eV above threshold, the dominant single-photoionization process is K-shell ionization. Also, correlation within the K shell is expected to be much stronger than between the $1s$ and $2s$ electrons. Therefore, we are completely ignoring the $2s$ electron in

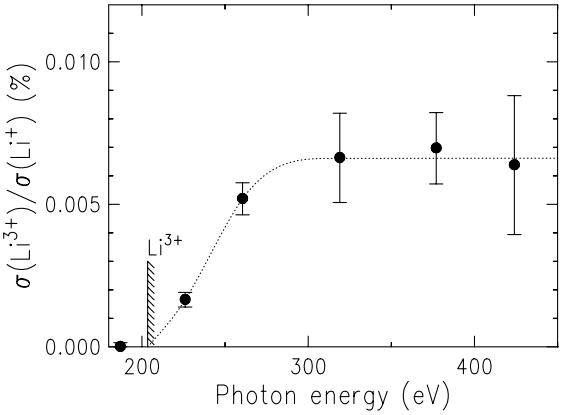

FIG. 2. The triple-to-single photoionization ratio of Li as a function of photon energy. The dotted line serves to guide the eye.

the double-photoionization process of Li and assume that the double ionization of Li($1s^2$) is similar to the one of the Li^+ ion. The double-to-single photoionization ratio for Li^+ is reported to be 0.89% [20].

In order to estimate the high-energy limit of the ratio of *triple*-to-single photoionization, one has to estimate the probability of removing the $2s$ electron when both $1s$ electrons are suddenly ejected. Physically this would be much less likely when *two* electrons are removed than for single ionization since the valence electron is exposed to higher nuclear charge and thus is more likely to collapse rather than be shaken off. The probability of this happening can be roughly estimated as follows. The overlaps of a $2s$ Hartree-Fock orbital with hydrogenic orbitals corresponding to a Li^{2+} ion are calculated. The squares of these overlaps represent the probability of the $2s$ electron being shaken down to $1s$, remaining, or being shaken up to an ns orbital, as shown in Table I, which reveals two interesting results. First, although the probability of the $2s$ electron not being changed is ≈ 0.5, the shakeup to $3s$ is nearly as high. Second, shakeup to higher ns orbitals is very low, which means that shakeoff, when two electrons are removed, is very unlikely.

Assuming the same double-to-single photoionization ratio for Li as for Li^+ (0.89% [20]), the ratio of triple-to-single photoionization will be this value multiplied by the probability of shakeoff of the valence electron, $1 - 0.998256 = 0.001744$ (see Table I), yielding 0.0015%. Although this is only a rough estimate for the high energy limit, it is only a factor of 4 lower than the observed ratio. This discrepancy might be due to electron correlations not taken into account by this simple model. Obviously, more sophisticated calculations are needed for a serious comparison with our experimental data.

In order to derive the absolute partial cross section for the triple photoionization we employed a calibrated photodiode [21] to measure the number of incident photons assuming a constant Li vapor pressure while acquiring the spectra. Since the absolute photoabsorption cross section of Li at 103.3 eV is known [22], we have calculated the total cross section at those photon energies where we have measured triply charged ions. After fitting a smooth curve through the calculated total cross sections $\sigma_{\text{tot}}(h\nu)$, we have used those values to determine the triple-photoionization cross section $\sigma(Li^{3+})$ using the formula:

$$\sigma(Li^{3+}) = \frac{\sigma_{\text{tot}}(h\nu) R^{3+}}{1 + R^{2+} + R^{3+}}. \quad (1)$$

Here, R^{2+} and R^{3+} denote our measured double-to-single and triple-to-single photoionization ratio, respectively. As shown in Fig. 3, the partial cross section of Li^{3+} rises from threshold to about 260 eV and then slowly decreases with increasing photon energy.

According to a theoretical model [23,24], the shape of the photon energy dependence of the *double*-ionization cross section depends only on the effective charge Z_{eff}. If we regard the triple photoionization of Li as mimicking the double photoionization of Li^+, we can tentatively compare the photon energy dependence of the triple photoionization of Li with that of the double photoionization of He. The energy axis for the measured double-photoionization cross section of He [25] was multiplied by the factor $Z^2_{\text{eff}}(\text{He})/Z^2_{\text{eff}}(\text{Li}) = 4/9$ and shifted according to the energy difference of the thresholds. The resulting curve is displayed as a solid line in Fig. 3 along with our data points. Included in the figure is the theoretical double-photoionization cross section of Li^+ [23] as a dotted line. The absolute values of both lines are scaled in magnitude to fit our data. The energy dependence for higher photon energies agrees surprisingly well, particularly for the scaled He data.

The data point at 226 eV does not agree with the curve derived from the He double-photoionization cross section. In general, our low-energy data points agree only poorly with the theoretical curve for the Li^+ double ionization. This may indicate that either the triple ionization of Li

TABLE I. Relative probabilities for the Li $2s$ electron being shaken down or shaken up to a particular ionic state due to the ejection of both $1s$ electrons.

Ionic state	Relative probability
$1s$	0.001 799
$2s$	0.516 877
$3s$	0.476 079
$4s$	0.002 928
$5s$	0.000 150
$6s$	0.000 122
$7s$	0.000 081
$8s$	0.000 055
ns $(n \geq 9)$	0.000 165
$\sum_{n=1}^{\infty} ns$	0.998 256

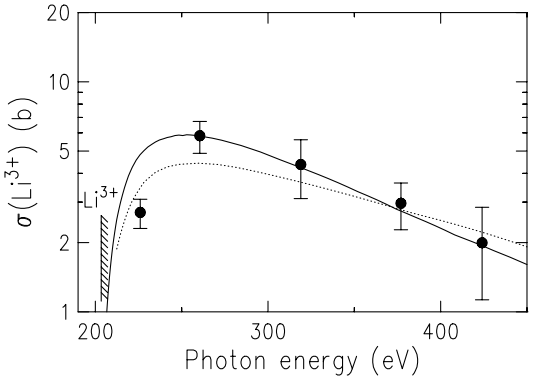

FIG. 3. The triple-photoionization cross section of Li as a function of photon energy derived from our data using the absolute photoabsorption cross-section data of Ref. [22]. The error bars shown do not include the uncertainty of the total cross section at 103.3 eV, used for calibration, which is reported to be about 20% [22]. The solid line represents the double photoionization of He [25] scaled using a simple model (see text for details). The dotted line shows the shape of the predicted photon energy dependence of the double-photoionization cross section of Li^+ [23].

cannot be compared with the double ionization of Li^+ or the energy scaling described above cannot be applied near threshold. This disagreement may be due to stronger electron correlations in the triple photoionization of Li not present in the double photoionization of He, or because of a more pronounced influence of the third electron near the triple-ionization threshold. It is also possible that threshold laws for the triple-photoionization cross section have a larger range of validity than for the double photoionization.

In conclusion, we have determined the triple-to-single photoionization ratio and the triple-photoionization cross section of lithium at several photon energies. The ratio rises from threshold to about 300 eV and then appears to level off for photon energies up to 430 eV at a value of $\approx 0.0066\%$. The first, simple estimate of the ratio at the high-energy limit, based on the shakeoff model, yields a value of 0.0015% which is about a factor of 4 lower than our experimental values. The triple-photoionization cross section is low, as expected, and at most 6 b in the region of interest. The shape of the photon energy dependence of the triple-ionization cross section can be described above 250 eV by a simple model based on the double-photoionization cross section of He. It also agrees with the theoretical double-photoionization cross section of Li^+ [23] at higher photon energies. Recently, in addition to the Wannier threshold law [26], different threshold laws for the triple-ionization process have been predicted [27,28]. The type of threshold law and its range of validity is now the subject of vigorous debate. While studies of the triple photoionization of other targets, such as Ne, are important, they are restricted to the near-threshold region due to overlapping processes as mentioned above. Therefore, these other targets may not promise as clean a test of these differing threshold laws and their range of validity as does Li, an ideal testing ground for such investigations. In addition to identifying and quantifying a case of pure triple photoionization, this Letter demonstrates the feasibility of such measurements. We hope that our results will stimulate further theoretical calculations on triple-photoionization processes.

We wish to thank T. Hayaishi for assistance with the data acquisition software. We also thank the Japanese Ministry of Education, Culture, and Science (Monbusho), the U.S. National Science Foundation for support through the Japan-U.S. Cooperative Science Program, and the NSF Division of Physics. R. W. gratefully acknowledges financial support from the Japan Society for the Promotion of Science. This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 96G137).

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[1] P. L. Smith and W. L. Wiese, in *Atomic and Molecular Data for Space Astronomy*, edited by P. L. Smith and W. L. Wiese (Springer-Verlag, Berlin, 1992), Chap. 1.
[2] J. H. McGuire, N. Berrah, R. J. Bartlett, J. A. R. Samson, J. A. Tanis, C. L. Cocke, and A. S. Schlachter, J. Phys. B **28**, 913 (1995), and references therein.
[3] J. C. Levin, G. B. Armen, and I. A. Sellin, Phys. Rev. Lett. **76**, 1220 (1996).
[4] R. Dörner *et al.*, Phys. Rev. Lett. **76**, 2654 (1996).
[5] R. Wehlitz, F. Heiser, O. Hemmers, B. Langer, A. Menzel, and U. Becker, Phys. Rev. Lett. **67**, 3764 (1991).
[6] O. Schwarzkopf, B. Krässig, J. Elmiger, and V. Schmidt, Phys. Rev. Lett. **70**, 3008 (1993).
[7] J. Viefhaus, L. Avaldi, F. Heiser, R. Hentges, O. Gessner, A. Rüdel, M. Wiedenhöft, K. Wieliczek, and U. Becker, J. Phys. B **29**, L729 (1996), and references therein.
[8] J. H. McGuire, J. Phys. B **17**, L779 (1984).
[9] J. Wang, J. H. McGuire, J. Burgdörfer, and Y. Qiu, Phys. Rev. A **54**, 613 (1996).
[10] J. A. R. Samson and G. C. Angel, Phys. Rev. Lett. **61**, 1584 (1988).
[11] U. Becker, R. Wehlitz, O. Hemmers, B. Langer, and A. Menzel, Phys. Rev. Lett. **63**, 1054 (1989).
[12] A. W. Malcherek, J. M. Rost, and J. S. Briggs, Phys. Rev. A **55**, R3979 (1997); A. W. Malcherek and J. S. Briggs, J. Phys. B **30**, 4419 (1997).
[13] E. Shigemasa, Y. Yan, and A. Yagishita, KEK Report No. 95-2, 1995.
[14] Y. Sato *et al.*, J. Phys. B **18**, 225 (1985).
[15] Y. Azuma, S. Hasegawa, F. Koike, G. Kutluk, T. Nagata, E. Shigemasa, A. Yagishita, and I. A. Sellin, Phys. Rev. Lett. **74**, 3768 (1995).
[16] C. E. Moore, *Atomic Energy Levels*, U.S. National Bureau of Standards Spec. Publication 467 (GPO, Washington, D.C., 1949), Vol. 1.
[17] M.-T. Huang, R. Wehlitz, Y. Azuma, L. Pibida, I. A. Sellin, M. Koide, H. Ishijima, and T. Nagata (unpublished).
[18] T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. **77**, 2144 (1955).
[19] N. Saito and I. H. Suzuki, Int. J. Mass Spectrom. Ion Process. **115**, 157 (1992); Bull. Electrotech. Lab. **56**, 688 (1992).
[20] A. Dalgarno and H. R. Sadeghpour, Phys. Rev. A **46**, R3591 (1992).
[21] Far ultraviolet photodiode; manufacturer, NIST; serial No. 365.
[22] G. Mehlman, J. W. Cooper, and E. B. Saloman, Phys. Rev. A **25**, 2113 (1982).
[23] M. A. Kornberg and J. E. Miraglia, Phys. Rev. A **49**, 5120 (1994).
[24] M. Ya. Amusia, E. G. Drukarev, V. G. Gorschkov, and M. P. Kazachkov, J. Phys. B **8**, 1248 (1975).
[25] 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).
[26] G. H. Wannier, Phys. Rev. **90**, 817 (1953); **100**, 1180 (1954).
[27] J. M. Feagin and R. D. Filipczyk, Phys. Rev. Lett. **64**, 384 (1990).
[28] T. Pattard and J. M. Rost, Phys. Rev. Lett. **80**, 5081 (1998).