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Near-threshold triple-photoionization cross section of lithium

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The triple-photoionization cross section of atomic Li was measured near its threshold. Our results can be described by a threshold power law up to ≈ 5 eV with an exponent of 2.05(25) which is consistent with a previous experiment and theoretical predictions. At higher energies, we find that the cross section is well described by the threshold law for *double* ionization. The present analysis is based on the notion that for sufficient excess energy, triple photoionization of Li is reasonably well described by a double ionization of the inner electrons followed by a shakeoff of the outer electron.

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The probability for multiple ionization of atoms and molecules is a sensitive probe for the interaction among the outgoing electrons (see, e.g., [1]). This fundamental process, the correlated motion of two or more electrons in the Coulomb field of the residual ion, is usually referred to as the ''three-body problem'' in the continuum and is highly complex. Of particular importance is the threshold region where the electrons leave the ion slowly and electron correlations are most pronounced. A first successful attempt to derive a threshold law for this process was made by Wannier for the case of the double escape of electrons after single ionization by electron impact [2]. He predicted a threshold law that has the form of a power law, namely $\sigma \propto E^{\alpha}$ with σ as the cross section, E the excess energy above threshold, and α ($=1.127$ for neutral-atom targets) the Wannier exponent. This threshold law was qualitatively extended to multiple ionization later [3] where it was argued that the exponent α should be slightly larger than the number of outgoing electrons n minus one. The difference $\Delta = \alpha - n + 1$ is a measure for the mutual dynamical screening (''final-state correlation'') among the outgoing electrons and vanishes in the limit of ionization of independent particles in the Coulomb field of the core. However, measurements at that time did not support the predicted exponent [4].

Several investigations have focused on the two-electron escape near threshold using photon impact [5–9] and electron impact [10–12] in order to test the Wannier threshold law, particularly the value of the exponent and its energy range of validity. Most experiments as well as most theoretical studies using different approaches [13–16] confirmed Wannier's threshold law for this case. Other theoretical models [17,18], such as the Coulomb-dipole theory of Temkin cannot be ruled out and find support in photodetachment experiments of negative ions [5,6,19,20]. Regarding the energy range of validity for the Wannier threshold law, there is no agreement among the different values reported. While one theory [21] claims its applicability for the double-electron escape to be restricted to well below 1 eV excess energy, different ranges of validity from 2 eV [7] to 50 eV [12] have been reported.

A threshold law for the *triple*-ionization cross section was introduced by Klar and Schlecht [22] yielding a power law that an exponent of 2.162 for triple photoionization in accordance with Wannier's estimate [3], which was confirmed by another calculation [23]. Both papers predicted a single power law that was tested by Samson and Angel [24] for the case of neon and atomic oxygen. Their experiment confirmed the predicted exponent of 2.16 up to 5.5 eV above the triple-photoionization threshold, but in addition also found a secondary power law for higher energies. This secondary power law had an exponent of 1.84 and 1.88 for oxygen and neon, respectively. Since their highest energy was only 10 eV

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above threshold, the range of validity of such a secondary power law could not be tested. A theoretical model developed by Feagin and Filipczyk [25] introduced a secondary power law which was based on a second unstable normal mode in the breakup configuration. They calculated an exponent of 1.821 in agreement with the previous experiment [24]. Nevertheless, in a recent paper [26] the possibility for the appearance of a secondary power law was questioned. Moreover, it was found by Pattard and Rost [27] that in certain cases the Wannier power law needs to be modified by a logarithmic term but not by an additional (secondary) power law. The logarithmic correction does not apply to the case of triple photoionization and they conclude that there still is a discrepancy between theory and experiment. Except for the region *very* near threshold, the energy dependence of the triple-photoionization cross section is far from being understood.

Here we present a study of the triple-photoionization process of Li in the threshold region. Lithium is a well suited target since the complete breakup of the 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, and rearrangement effects involving other electrons cannot contribute to the triple-photoionization cross section. First results for triple photoionization of Li were reported recently [28].

The present experiment was performed at the 2.5-GeV storage ring of the KEK Photon Factory. Photons coming from the undulator beam line BL16B were monochromatized by a 24-m spherical grating monochromator [29]. The undulator gap was adjusted for each photon energy in order to maximize the photon flux. The photon energy was tuned in the range from 205 to 240 eV, lying closely above the triple-photoionization threshold of Li at 203.48 eV [30].

The photon beam entered the experimental chamber, intersecting a beam of Li atoms emerging from an effusive metal vapor oven [31]. The Li photoions, which were produced in the interaction region, were detected with an ion time-of-flight (TOF) spectrometer operating in the pulsed extraction mode with a repetition time of 15 μs. The background pressure in the experimental chamber during the experiment was lower than 8×10^{-8} mbar. The threshold of our constant-fraction discriminator was set to a very low level ($\leqslant$25 mV) to ensure that there was no detection efficiency difference between the Li^+ and Li^{3+} ions. The triple-to-single photoionization ratio determined in our previous experiment [28] at 226 eV overlaps and agrees well with the current experimental data set. The contribution of Li dimer (Li_2) in the lithium vapor was negligible in our experiment because of its much lower vapor pressure [32]. Moreover, the triple-to-single photoionization ratio at our lowest photon energy (205.5 eV) is as low as expected and does not indicate any contribution from Li_2 or higher-order light.

Because of a greatly improved signal strength in comparison to our previous experiment [28] the large number of singly charged Li ions was able to cause dead time in our electronics. Therefore, we had to take two different ion TOF spectra at each photon energy: one with high photon flux and another one with reduced photon flux. The photoion spectra

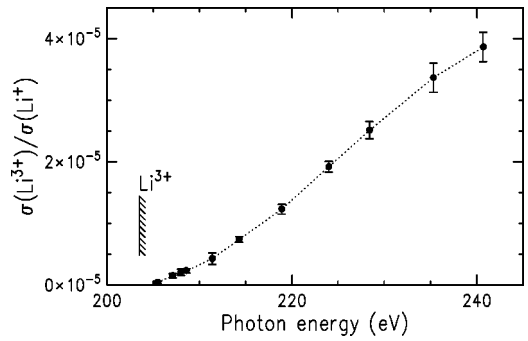

FIG. 1. The triple-to-single photoionization ratio of Li near threshold as a function of photon energy. The dotted line serves to guide the eye.

with reduced photon flux (by closing the entrance and exit slits to 30 μm each) show only the singly and doubly charged ions of ^{7}Li and its isotope ^{6}Li, while the Li^{3+} ions are indistinguishable from the background noise. The photoion spectra using high photon flux were taken with both slits opened to 1000 μm each, and the time window of our time-to-amplitude converter (TAC) was changed such that only the triply charged ions and the doubly charged ions of the ^{6}Li isotope were fast enough to be processed by the TAC, thus avoiding any dead-time indication on the analog-to-digital converter.

The energy of the monochromator was calibrated using the Li $2s^22p$ triply excited state (''*A*'' resonance), which is at 142.35 eV [33]. The energy calibration was performed at the beginning and at the end of our measurements yielding a photon energy accuracy of about 0.1 eV in the region of interest. The spectra were taken at several photon energies in random order to monitor possible time-dependent systematic changes.

In order to determine the triple-photoionization cross section near threshold we took several ion TOF spectra between 205 and 240 eV. The areas of the Li^+ and Li^{2+} peaks of both isotopes were numerically integrated. The area of the Li^{3+} peak was determined by a least-squares fit using a Gaussian profile. The statistical error provided by the fitting program corresponds to a 1σ error bar. After calculating the $^7Li^{3+}$ to $^6Li^{2+}$ ratio from the high photon-flux spectra, we determined the $^6Li^{2+}$ to $^7Li^+$ ratio from the low photon-flux spectra; from that we obtained the triple-to-single photoionization ratio. Since the isotope ratio does not change with photon energy and the double-to-single photoionization ratio varies only very little in the energy region of interest [34] a smooth curve was laid through the $^6Li^{2+}$ to $^7Li^+$ ratios. Figure 1 shows the triple-to-single photoionization ratios calculated as described above.

In order to derive the absolute partial cross section for triple photoionization we used the same total cross-section curve that we employed for our previous measurements as described in [28,34]. In brief, we derived the total cross section with the help of a calibrated photodiode [35] that measured the number of incident photons. Assuming a constant Li vapor pressure while acquiring the spectra, we derived the total cross section in the energy region of interest by taking a photoion spectrum at 103.3 eV and using the known absolute

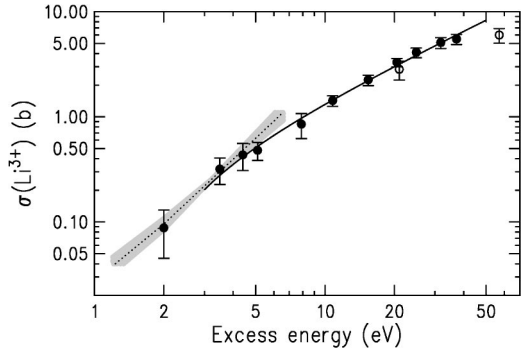

FIG. 2. The triple-photoionization cross section of Li as a function of excess energy on a log-log scale: full circles, this work; open circles, Ref. [28]. The error bars shown do not include the uncertainty of the total cross section at 103.3 eV, used for calibration, which is reported to be about 20% [36]. The solid line is a fit according to Eq. (2) with $\epsilon_0 = 6.95$ eV, while the dotted line corresponds to $\sigma \propto E^{2.05}$. The gray shaded area around the dotted line corresponds to exponents between 1.8 and 2.3.

photoabsorption cross section at this energy [36].

The partial cross section of Li^{3+}, shown in Fig. 2, is displayed on a log-log scale in order to determine the exponent α of the power law of the triple-photoionization cross section $\sigma \propto E^{\alpha}$ (if any). Because of the very low cross section only a few data points were taken below 5 eV. The dotted line in Fig. 2 was fitted to our data points below 5.5 eV taking into account that the cross section starts with zero at threshold. Its slope of 2.05(25) is consistent with previous results of Samson and Angel [24] and theoretical predictions [22,25–27]. Above about 5.5 eV, the experimental data bend over to a weaker energy dependence that could be parametrized by another, smaller exponent α'. This is a general feature for ionization cross sections. We note that such a ''secondary power law'' has already been found by McGowan and Clarke [37] 30 years ago for *single* ionization of hydrogen by electron impact, an experiment widely cited as one of the first significant tests of the original Wannier law. In that case, the Wannier exponent $\alpha = 1.127$ describes the data up to an excess energy of about 0.4 eV, while a secondary power law with $\alpha' = 0.99$ describes the cross section for higher energies up to almost 4 eV, i.e., over an energy range nearly ten times that of the true threshold law. Clearly, in this case no second unstable mode can contribute. In the present case, the exponent α' that can be fitted to the experimental data is in a range between $\alpha' \approx 1.2$ and $\alpha' \approx 1.5$ depending on exactly which data points are taken into account. An exponent of 1.8 as fitted by Samson and Angel and theoretically derived by Feagin and Filipczyk, however, can be clearly ruled out for the present data. We therefore conclude that our data present a case in which the secondary threshold law is inapplicable.

We suggest an alternative description of the behavior above threshold, based on the electronic structure of Li consisting of a strongly asymmetric configuration in its ground state with a tightly bound, strongly correlated inner electron pair and the loosely bound, weakly correlated outer electron. It has been argued that correlation between the $2s$ electron and the $1s$ electrons should be weak and triple photoionization at energies not too low can be envisioned as a double photoionization of the inner electrons, accompanied by a (generalized) shake-off of the $2s$ electron. This decomposition of the three-electron breakup process into a two-electron emission plus shake-off should become meaningful when the excess energy $\Delta E = E_{ph} - E^{TI}$ relative to the triple-ionization threshold $E^{TI} = 203.48$ eV is of the order of or larger than the binding energy of the most weakly bound electron [$E_{ph} \geqslant E^{TI} + E_B(2s), E_B(2s) = 5.39$ eV]. This notion is supported by recent double-photodetachment calculations for H^- [38]. They show good agreement with the Wannier exponent up to about 1 eV excess energy that is comparable to the detachment energy of the loosely bound electron (0.75 eV). At excess energies of approximately the binding energy of the $2s$ electron, the pathway towards three-electron emission can substantially deviate from the symmetric Wannier configuration. Within this picture of a two-electron emission plus shake-off, the triple-ionization cross section of Li should be describable by the double-ionization cross section convoluted with an energy-dependent shake factor describing the ejection of the $2s$ electron due to the departing correlated electron pair whose initial binding energy [$E_B(1s^2) = 198.1$ eV] exceeds the binding energy of the outer electron by a factor of ≈ 40. Thus the removal of both $1s$ electrons causes a significant change in the potential resulting in a shake-off of the $2s$ electron. Since the cross section for the double ionization of the two $1s$ electrons peaks at about 260 eV photon energy, excess energies ΔE of the order of 10 eV still probe the threshold region for the ejection of the tightly bound electron pair [$\Delta E \ll E_B(1s^2)$] while deviations from the Wannier-configuration dominated three-electron breakup are to be expected [$\Delta E \gtrsim E_B(2s)$]. Therefore, the triple-ionization cross section σ^T is approximated for excess energies larger than $E_B(2s)$ by the double-ionization cross section σ^D and a shake-off factor P_S

$$\sigma^T(E_{ph}) = \int_{E_B(2s)}^{E_B(2s)+\Delta E} \sigma^D(E_{ph} - \epsilon) P_S(\epsilon) d\epsilon, \qquad (1)$$

where we expect $P_S(\epsilon)$ to peak at values $\epsilon = \epsilon_0 > E_B(2s)$ somewhat above $E_B(2s)$ due to the average nonzero ejection energy of the outer electron. Consequently, we find an above-threshold behavior

$$\sigma^T(E_{ph}) \propto [E_{ph} - E_B(1s^2) - \epsilon_0]^{1.056}, \qquad (2)$$

where we use the threshold exponent for the tightly bound electron pair and neglect the additional energy dependence of $P_S(\epsilon)$. Indeed, Eq. (2) permits an excellent fit to the data at excess energies from about 5 eV up to approximately 30 eV above the triple-ionization threshold as demonstrated in Fig. 2. At higher excess energies, from about 30 to 60 eV above threshold, the triple-photoionization cross section bends over to approach its maximal value. It is interesting to note that the change in the cross-section dependence takes place between 5 and 6 eV excess energy as was found in the case of Ne and O [24]. However, for the present case this value corresponds to excess energies of the order of the binding energy of the $2s$ electron, where we expect our model to become meaningful as argued above.

This simple physical picture suggests its applicability for other systems with strongly asymmetric electron configurations in its ground state, such as H^-, even though in that case the electron correlation is not negligible. As mentioned before, double photodetachment calculations [38] show good agreement with the Wannier exponent up to $\lesssim 1$ eV excess energy, which is comparable to the detachment energy of the loosely bound electron (0.75 eV). At higher energies, but still smaller than the binding energy of the inner electron (2 to 6 eV), the cross section is approximately constant (i.e., $\alpha' = 0$) as expected for the photoionization of the inner, hydrogenic electron. One further consequence of this proposed scenario should be a change of the angular distribution from the triangular Wannier configuration at the ''true'' threshold to a double-ionization Wannier configuration with back-to-back emission of the ''primary'' electrons accompanied by an approximately isotropic emission pattern for the ''third'' shake electron.

In conclusion, we have measured the triple-photoionization cross section of Li at several photon energies near its threshold. We found agreement with previous measurements on Ne and O [24] in the energy region from threshold to about 5 eV in accordance with the predicted exponent $\alpha = 2.16$. A secondary power law with an exponent of $\alpha' \approx 1.8$ as favored in [24,25] proved incompatible with the present data, providing significant experimental evidence against such a secondary threshold law. In contrast, we showed that the measured data can be interpreted with a model of triple photoionization in Li as a two-step process, namely the double ionization of the pair of highly correlated $1s$ electrons followed by electron-impact induced shake-off of the $2s$ electron. A more detailed theoretical analysis of the above-threshold behavior is currently underway [39].

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