Angular momentum dependence of photoionization cross section from the excited states of lithium isotopes

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We present measurements of the photoionization cross sections from the 3*s*, 3*d*, 4*s*, 4*p*, and 4*d* excited states of lithium isotopes near the first ionization threshold using two dye lasers pumped by a common Nd:YAG (yttrium aluminum garnet) laser in conjunction with an atomic beam–time-of-flight mass spectrometer system. It is observed that the photoionization cross section from the 3*d* and 4*d* excited state is maximum near the ionization threshold and decreases smoothly for the excess energies above the threshold. However, for the 3*s* and 4*s* excited states, the photoionization cross section is lower at the threshold, increases to a maximum value, and then decreases monotonically for the excess energies. It is also observed that a drop off in the cross section of the *nd* states is more hydrogenic than that of the *np* and *ns* excited states.

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I. INTRODUCTION

Lithium possesses two isotopes ^{6}Li and ^{7}Li with 7.5% and 92.5% natural abundances, and the utility of ^{6}Li in thermonuclear reactions has made this isotope particularly important. For a high isotopic purity, the atomic vapor laser isotope separation is very attractive [1–7]. This technique utilizes two-step or multistep photoionization that requires accurate knowledge of photoionization cross sections of the excited states of the pertinent isotope involved in the process.

Because of the importance of lithium, the photoionization cross section from the first excited state 2*p* has been calculated and measured by a number of groups [8–16]. Rothe [13] reported the first experimental value at threshold using radiative electron-ion recombination of the emission spectrum of lithium plasma into the 2*p*-excited state, whereas Karlov *et al.* [14] and Arisawa *et al.* [2] used the saturation technique for the measurement of a photoionization cross section from the 2*p* state of lithium. The saturation technique was initiated by Ambartzumian *et al.* [17] and exploited by numerous researchers [18–21]. Saleem *et al.* [16] employed an alternate technique for the simultaneous measurement of a photoionization cross section of the 2*p* states of lithium isotopes even if they have not been selectively excited by combining the saturation technique with a time-of-flight (TOF) mass spectrometer. Wippel *et al.* [15] trapped the sodium and lithium atoms in a magneto-optical-trap (MOT) and measured the photoionization cross section from the first excited state of sodium and lithium isotopes.

The motives of the present paper are to present experimental data on the photoionization cross sections from the excited states of lithium isotopes possessing different angular momentum quantum numbers: 3*s*, 3*d*, 4*s*, 4*p*, and 4*d*. The photoionization at and above the first ionization threshold have been measured at various ionizing laser wavelengths. The photoionization cross sections from the 3*p* state of lithium have already been reported [22], and, along with the present measurements, they have been used to explore the dependence of photoionization cross sections on the principal ($n=3-4$) and angular momentum ($\ell=0-2$) quantum numbers.

II. EXPERIMENTAL DETAILS

The experimental setup and other details are the same as described in our earlier papers [16,22]. Briefly, we have employed the two-step excitation and ionization technique. In the first step, the lithium atoms were promoted to different excited states and in the second step the excited atoms were transferred to the Li^+ $1s^2$ $\varepsilon\ell$ continuum. The photoions were subsequently separated and collected by a TOF mass spectrometer, which leads to the determination of the photoionization cross sections from the excited state of both lithium isotopes.

The 3*s*, 3*d*, 4*s*, and 4*d* excited states were populated via two-photon excitation from the ground state by tuning the dye laser at 735.13, 639.32, 571.23, and 546.1 nm whereas the 4*p* excited state was populated via single-photon absorption at 274.2 nm, which was achieved by frequency doubling the 548.4 nm dye laser. The photoionization from the 3*s* excited state was measured at 614, 532, 350, and 266 nm, from the 3*d* state at 614, 532, 690, 765, and 266 nm, and from the 4*s*, 4*p*, and 4*d* excited states at 1064, 690, 532, and 317 nm, respectively. The first step dye laser was TDL-90 (Quantel, France), the second step ionizing dye laser was a locally made Hanna type dye laser [23], and both dye lasers were pumped by a common Nd:YAG (yttrium aluminum garnet) laser (Brilliant, Quantel). The ionizing wavelengths 532 and 266 nm were the second and fourth harmonics of the Nd:YAG laser.

III. RESULTS AND DISCUSSION

For the simultaneous measurement of the photoionization cross section, the exciting laser is tuned at the central frequency of both the isotopes ^{6}Li or ^{7}Li. The TOF detector is

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adjusted to operate in the linear mode so that the ion signals of the isotopes appear in accordance with their natural abundance. The ionization signal is connected with the photoionization cross section through the relation [22]

$$Q = eN_0V_{\mathrm{vol}}\left[1 - \exp\left(-\frac{\sigma U}{2\hbar\omega A}\right)\right]. \quad (1)$$

Here e is the electronic charge, N_0 is the density of the excited atoms, A is the cross-sectional area of the ionizing laser beam, U is the total energy per pulse of the ionizing laser, V_{vol} is the interaction volume, and σ is the absolute cross section for photoionization. Thus, a measurement of Q as a function of U provides data that, when fitted to Eq. (1), yield the quantities N_0 and σ. It is, however, important to have accurate measurements of U and A. The uncertainty in the energy determination is owing to the energy fluctuations in the Nd:YAG laser ($\pm 5\%$) and in the energy measuring instrument ($\pm 3\%$). The actual distribution of photons in our laser pulse is Gaussian and the area of the overlap region in the confocal limit is calculated using the following relation [24]:

$$A = \pi\omega_0^2\left[1 + \left(\frac{\lambda_{\mathrm{io}}z}{\pi\omega_0^2}\right)^2\right].$$

Here $\omega_0 = f\lambda_{\mathrm{io}}/\pi\omega_s$ is the beam waist at $z=0$, ω_s is half the spot size of the ionizing laser beam on the focusing lens, f is the focal length, and λ_{io} is the wavelength of the ionizing laser. The spot size of the Gaussian laser beam is determined as ≈ 4 mm at which the irradiance (intensity) falls to $1/e^2$ of their axial values. The parameter A might introduce about 10% error incorporating the Gaussian width instead of the top hat beam profile. In addition, the detection efficiency of the detector ($\sim 5\%$), ion transmission through the acceleration grids ($\pm 5\%$ from each grid), and the statistical measurement error ($\sim \pm 5\%$) also contribute in the overall uncertainty in the measurement of cross section that is estimated as $\approx 15\%$ [25].

The exciting dye laser is passed through the atomic beam without focusing, whereas the ionizing laser is focused on the atomic beam with a plano convex lens of focal length 250 mm. An aperture of diameter 4 mm is placed before the focusing lens to minimize the effect of the wings of the Gaussian laser pulse, since laser wings limit the complete saturation in the photoion signal [20]. However, this effect can be reduced further by enhancing the energy density of the ionizing laser. The long focal length lens serves two purposes: first, it provides high photon flux to saturate the transition from the excited state, and secondly, it enables a uniform focal volume over the size of the atomic beam (≈ 4.5 mm), the interaction length. Due to focusing, the diameter of the ionizing laser beam on the atomic beam is smaller than that of the exciting laser to ensure the spatial overlap of the laser beams.

The temporal overlap is also essential for an accurate determination of photoionization cross section. The lifetimes of the excited states $3s$ ($\tau \approx 27.9$ ns), $3d$ ($\tau \approx 14.9$ ns), $4s$ ($\tau \approx 57.24$ ns), $4p$ ($\tau \approx 424.85$ ns), and $4d$ ($\tau = 33.5$ ns) [26] are much larger than the pulse duration of both the exciting and the ionizing lasers (≈ 5 ns). Therefore, in order to separate the excitation and the ionization steps to ensure a pure two-step photoion signal, the ionizing laser is delayed by ≈ 5 ns.

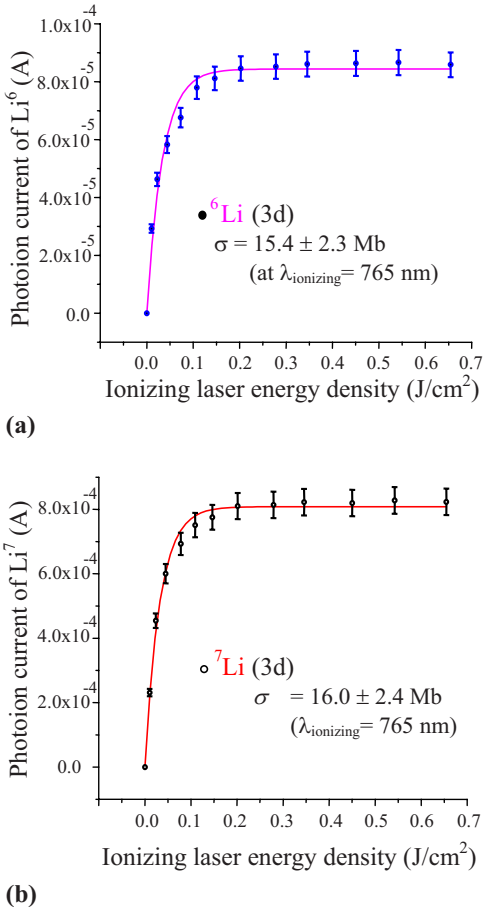

FIG. 1. (Color online) Photoion current of (a) ^{6}Li and (b) ^{7}Li isotopes measured simultaneously as a function of ionizing laser energy density from the $3d$ excited state. The error bars (5%) result from fluctuations in the photoion signal due to the laser energy.

The measurement of the photoionization cross section of the excited states also depends on the polarization of the exciting as well as the ionizing lasers [27] because their polarizations determine the populated M_J levels in a given transition and J and M_J final states in the continuum. In these experiments, the ground-state lithium atoms $2s_{1/2}$ ($m_j = \pm\frac{1}{2}$) are excited by the linearly polarized dye laser to the $ns_{1/2}$ ($m_j = \pm\frac{1}{2}$), $np_{1/2}$ ($m_j = \pm\frac{1}{2}$), or $np_{3/2}$ ($m_j = \pm\frac{1}{2}$) and $nd_{3/2}$ ($m_j = \pm\frac{1}{2}$) or $nd_{5/2}$ ($m_j = \pm\frac{1}{2}$) excited states. The ionizing dye laser is also linearly polarized with the polarization vector parallel to that of the exciting dye laser. Due to the selection rule that the m_j values of the exited state and that of the continuum remain the same, the ns states with $m_j = \pm\frac{1}{2}$ dissociate into the εp ($m_j = \pm\frac{1}{2}$) channels. The photoionization from the $np_{1/2,3/2}$ ($m_j = \pm\frac{1}{2}$) excited states dissociates to the εs ($m_j = \pm\frac{1}{2}$) and εd ($m_j = \pm\frac{1}{2}$) channels, whereas photoionization of the $nd_{3/2,5/2}$ ($m_j = \pm\frac{1}{2}$) excited states dissociates into the εp ($m_j = \pm\frac{1}{2}$) and εf ($m_j = \pm\frac{1}{2}$) channels.

Figure 1 shows a plot of the photoion current versus the ionizing laser energy density originated from the $3d$ excited states of both the lithium isotopes. The photoion data points

are recorded by varying the intensity of the ionizing laser with neutral density filters while the intensity of the exciting laser is kept fixed. The solid lines that pass through the experimental data points are the least-squares fit to Eq. (1). The fitting procedure yields the photoionization cross section from the $3d$ excited state as 15.4 ± 2.3 for ^{6}Li and 16.0 ± 2.4 for ^{7}Li at 765 nm ionizing laser wavelength. Similarly, the photoionization cross sections from the $3s$, $4s$, $4p$, and $4d$ excited states of the lithium isotopes have been determined by employing the procedure described above. In Table I, we tabulate the photoionization cross sections from different excited states at different ionization wavelengths along with the literature values for comparison.

Figure 2 shows a collective presentation of the measured photoionization cross sections from the $3s,3p,3d$ and $4s,4p,4d$ excited states of the ^{7}Li isotope. A similar trend has been found for the same excited states of the ^{6}Li isotope. The experimental curve for the $3p$-excited state is taken from our previous work [22]. The cross-section values from the $3s$ and $4s$ excited states are multiplied by 25 just to compare the trends of the photoionization cross sections with other states on a single graph. The dotted lines passing through the measured data points of the $3s$ and $4s$ excited states at different ionizing wavelengths are the hand-drawn curves to guide the trends of the energy dependence of photoionization cross sections from the excited states corresponding to the same principal quantum number but different orbital angular momentum quantum number states.

The behavior of the photoionization cross section from the ns-excited states at and above threshold is very interesting. There is only one channel εp through which the atoms from the ns excited states can be promoted to the ionization continuum. It has been shown [29] that if the phase difference between the initial discrete state and that of the final continuum state is about 0.5π, the Cooper minima may occur right at threshold. The difference between the ns quantum defect and the threshold εp phase shift is 0.37 (in units of π), which is less than 0.5π, therefore a minimum is expected in the discrete region near the ionization threshold. The presence of this minimum causes the ns cross section to be very small at threshold. Our measured values of cross section for the $3s$ and $4s$ excited states at threshold confirm the theoretical prediction of Lahiri and Manson [12]. Evidently, the decay of the photoionization cross section from the ns excited states is nonhydrogenic. In addition, the decreasing trend of the cross section from the $4s$ excited state is faster than that of the $3s$ excited state, which indicates that with an increase in the principal quantum number n, the effects of the inner nonhydrogenic region of the potential becomes less important.

The behavior of the photoionization cross section from the np-excited states is expected and indeed is different from that of the ns or nd excited states. The excited atoms from the p states can be promoted to the ionization continuum through two different channels $np \rightarrow \varepsilon s$ and εd. The contribution of the $np \rightarrow \varepsilon s$ channel toward photoionization cross section is very small while the most dominating channel is $np \rightarrow \varepsilon d$ according to the transition intensity selection rules. The threshold phase shift difference for $np \rightarrow \varepsilon d$ is 0.05π, which discards any possibility of the Cooper minima in the

TABLE I. Photoionization cross sections from different excited states at different ionization wavelengths.

Excited state	Lithium/ Lithium isotopes	Ionizing laser wavelength	Photoionization cross section (Mb)
$3s$	Li	614 nm (threshold)	1.48,[a] 1.27,[b] 1.42,[c] 1.17,[d] 1.42[e]
	^{7}Li	614 nm	1.31 ± 0.19
		532 nm	1.41 ± 0.21
		350 nm	1.32 ± 0.19
		266 nm	1.02 ± 0.15
	^{6}Li	614 nm	1.12 ± 0.17
		532 nm	1.20 ± 0.18
		350 nm	1.13 ± 0.17
		266 nm	0.80 ± 0.12
$3d$	Li	819.4 nm (threshold)	18.2,[a] 15.0,[c] 17.5[d]
	^{7}Li	765 nm	16.0 ± 2.4
		690 nm	9.0 ± 1.4
		614 nm	5.8 ± 0.9
		532 nm	3.8 ± 0.6
		266 nm	1.2 ± 0.2
	^{6}Li	765 nm	15.4 ± 2.3
		690 nm	8.5 ± 1.3
		614 nm	5.2 ± 0.8
		532 nm	3.5 ± 0.5
		266 nm	1.0 ± 0.2
$4s$	Li	1180 nm (threshold)	1.40,[a] 1.31[d]
		1064 nm	1.15 ± 0.21[f]
		690 nm	1.25 ± 0.23[f]
		532 nm	1.03 ± 0.18[f]
		317 nm	0.57 ± 0.10[f]
	^{7}Li	1064 nm	1.14 ± 0.17
		690 nm	1.25 ± 0.19
		532 nm	1.05 ± 0.16
		317 nm	0.54 ± 0.08
	^{6}Li	1064 nm	1.0 ± 0.15
		690 nm	1.07 ± 0.16
		532 nm	0.77 ± 0.12
		317 nm	0.45 ± 0.07
$4p$	Li	1425 nm (threshold)	41.70,[a] 34.20[d]
		1064 nm	23.9 ± 4.3[f]
		690 nm	8.8 ± 1.6[f]
		532 nm	3.9 ± 0.7[f]
		317 nm	2.0 ± 0.4[f]
	^{7}Li	1064 nm	24.5 ± 3.7
		690 nm	9.5 ± 1.4
		532 nm	5.2 ± 0.8
		317 nm	1.8 ± 0.3
	^{6}Li	1064 nm	22.0 ± 3.3
		690 nm	8.0 ± 1.2
		532 nm	4.5 ± 0.7
		317 nm	1.7 ± 0.3

TABLE I. (*Continued.*)

Excited state	Lithium/ Lithium isotopes	Ionizing laser wavelength	Photoionization cross section (Mb)
4*d*	Li	1456.9 nm (threshold)	36.20,[a] 30.60[d]
		1064 nm	18.7 ± 3.4[f]
		690 nm	4.0 ± 0.7[f]
		532 nm	1.8 ± 0.3[f]
		317 nm	0.5 ± 0.1[f]
	^{7}Li	1064 nm	15.9 ± 2.4
		690 nm	3.5 ± 0.6
		532 nm	2.2 ± 0.3
		317 nm	0.6 ± 0.1
	^{6}Li	1064 nm	14.6 ± 2.2
		690 nm	3.0 ± 0.5
		532 nm	1.7 ± 0.3
		317 nm	0.5 ± 0.1

[a]Aymar *et al.* [11].
[b]Moskvin [8].
[c]Ya'akobi [9].
[d]Gezalov and Ivanova [10].
[e]Caves and Dalgarno [28].
[f]Hussain *et al.* [21].

discrete region and it may occur above the threshold. We have explored the continuum region from near threshold up to 3 eV and found no evidence of the Cooper minima, and it might be of interest to extend these studies to higher photoelectron energies to locate it.

The cross sections from the *p*-states decrease monotonically with the decrease in the ionizing laser wavelength above the first ionization threshold, but this falloff of the cross section is not purely hydrogenic due to the smaller value of the quantum defects. The rapid decay of the cross section near threshold with increasing n indicates the decreasing contribution of the nonhydrogenic region of the potential.

For the photoionization of atoms from the *nd*-excited states, there are two possible ionization channels εp and εf through which the excited atoms can be uplifted to the ionization region. The $nd \rightarrow \varepsilon p$ cross section is slightly different from hydrogenic due to the smaller *p*-wave phase shift, but the $nd \rightarrow \varepsilon f$ is completely hydrogenic, as for $\ell \geq 2$ the quantum defects or phase shifts are effectively zero. In addition, the contribution of the $nd \rightarrow \varepsilon f$ channel toward the photoionization cross section dominates over the $nd \rightarrow \varepsilon p$ contribution. The fitted curves through the measured data points for the 3*d* and 4*d* excited states in Fig. 2 decrease more sharply with the increase in the ionizing laser photon energy. This decreasing behavior of the cross section from the *nd* excited states is more hydrogenic as compared to that of the *ns* or *np* excited states. In addition, the cross sections from the 4*d* excited state decay faster than the cross sections from the 3*d* state with the increase in the ionizing laser photon energy, which is in agreement with the theoretical prediction.

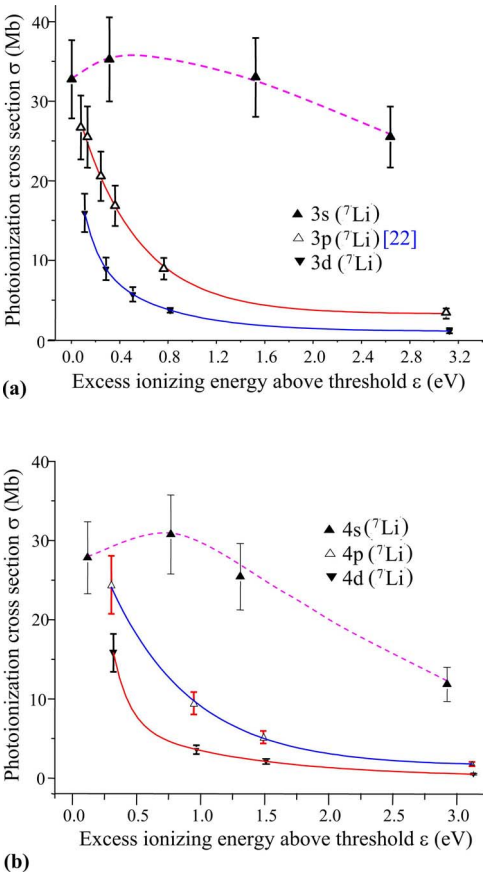

FIG. 2. (Color online) A comparison of the ionizing energy-dependent behavior of the measured values of the photoionization cross section from the (a) 3*s*,3*p*,3*d* and (b) 4*s*,4*p*,4*d* excited states of the ^{7}Li isotope.

In conclusion, the photoionization cross sections from the 3*p*, 3*d*, 4*p*, and 4*d* excited states of both the lithium isotopes are found to be maximum at the ionization threshold and decrease monotonically with the increase of the excess photon energy above the first ionization threshold except for the 3*s* and 4*s* excited states, where the cross section is lower at the ionization threshold, achieves a maximum value, and then decreases smoothly. Our measured values of the photoionization cross sections from the 3*s*, 3*d*, 4*s*, 4*p*, and 4*d* excited states at and above the threshold are in good agreement with the existing literature, where available.

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