

Angle-Resolved Photoelectron Spectrometry Studies of the Autoionization of the $2s^2 2p^2 P$ Triply Excited State of Atomic Lithium: Experimental Results and R -Matrix Calculations

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We have measured the angle-resolved energy dependence of the electrons emitted over the energy range of the triply excited $2s^2 2p^2 P$ lithium resonance using synchrotron radiation. We have also calculated the behavior of the angular distribution parameter β using the R -matrix approximation. Experimental and theoretical results are in good agreement and show deep minima in the $1s2p^1,^3P$ ionic channels. The energy at which the minima occur does not coincide with the resonance energy, but is shifted towards higher energy.

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In this Letter, we present the results of a new experiment investigating the angular distribution of electrons emitted in autoionization of the lowest-energy triply excited state of atomic lithium. We made a critical comparison of the data with the results of advanced R -matrix calculations performed in order to interpret the energy behavior of the angular distribution parameter β . Photons from the Advanced Light Source (ALS) photoexcited the $2s^2 2p^2 P$ hollow lithium state both on and off resonance. The electrons emitted were angularly analyzed with a cylindrical mirror analyzer (CMA) electron spectrometer. The experimental results reveal a pronounced energy dependence of the angular distribution parameter β in the $\text{Li}^+ 1s2p^1,^3P\epsilon l$ satellite channels, in good agreement with theoretical prediction. Both experiment and theory show that the minima in the β profiles occur on the high energy side of the resonance.

From the early 1960s [1], doubly excited states of helium have provided the ideal case for studying the three-body system of two correlated electrons interacting with the nucleus. Recent investigation on this system achieved very high resolution photoabsorption [2] and photoelectron [3] measurements. Experimental studies of helium helped to establish the theory of autoionization [4] and to introduce a new set of quantum numbers [5] describing doubly excited states in two-electron systems. The challenge to extend these investigations to triply excited states in neutral lithium started with their observation in collision experiments [6]. Subsequently, photoexcitation experiments [7–10] allowed accurate measurements of the excitation energies, identification of many of the resonances, and the determination of some partial photoioniza-

tion cross sections for autoionization into the lowest continua of the Li^+ ion. Most recently, the investigation of this system received strong impetus from the use of a third generation storage ring delivering high-brightness photon beams in the photon energy range (140–200 eV). High-resolution partial cross sections were determined for triple excitation of lithium atoms [11,12] including a classification of many of the states into Rydberg series. The lowest-energy triply excited state in which all three electrons have the same principal quantum number ($n = 3$) was also measured [13,14]. Theoretical calculations involving various approximations (R matrix [10–13], saddle point [15]) were carried out providing good agreement with the measured excitation energies as well as with the partial cross sections. More recently, a new approach using hyperspherical coordinates was developed [16] in an attempt to establish a systematic classification of the triply excited states and to visualize the correlated electron motions in the case of the intrashell states for $n = 2$. States with all three electrons sharing the same principal quantum number, termed intrashell, are particularly interesting for study as they are expected to show strong correlation effects.

All results to date on triply excited states produced by photon impact have been angle integrated. More challenging angle-resolved experiments provide the potential for greater insight into the symmetries, dynamics, and classification of the resonances. They can help to disentangle overlapping resonances and offer a more stringent test of theory. By combining the high brightness of the ALS with an electron spectrometer capable of *simultaneously* counting the electron emission at several different angles with respect to the polarization vector

of the photon beam, we were able to carry out the first angle-resolved measurements. Six identical electron multipliers were placed in the focal plane of a CMA electron spectrometer. The counting rate was reduced by roughly a factor of 20 compared to previous angle-integrated experiments. Working at the magic angle $\theta = 54^\circ 44'$ between the photon beam axis and the direction of the photoelectrons, the differential cross section [17] is proportional to $\sigma[1 + 0.495\beta P \cos 2(\varphi + \varphi_0)]$ where σ is the cross section, P is the degree of linear polarization of the photon beam, φ_0 is the rotation angle of the polarization ellipse after the refocusing mirror, and φ is the polar angle of the photoelectrons measured in a plane perpendicular to their propagation direction. Details of the experimental procedure have been described earlier [18]. We measured $P = 0.95(4)$ and $\varphi_0 = 2.0(5)^\circ$. The efficiency of electron detection at each angle φ was determined *in situ* by measuring the electrons emitted in the process $1s^2 2s^2 S + h\nu \rightarrow 1s 2s^3 S + \varepsilon p$, for which the angular distribution parameter is rigorously 2 in the nonrelativistic approximation (see Fig. 1). Angle-resolved spectra were recorded primarily in the constant ionic state mode in which a $\text{Li}^+(1s2l)$ state is scanned

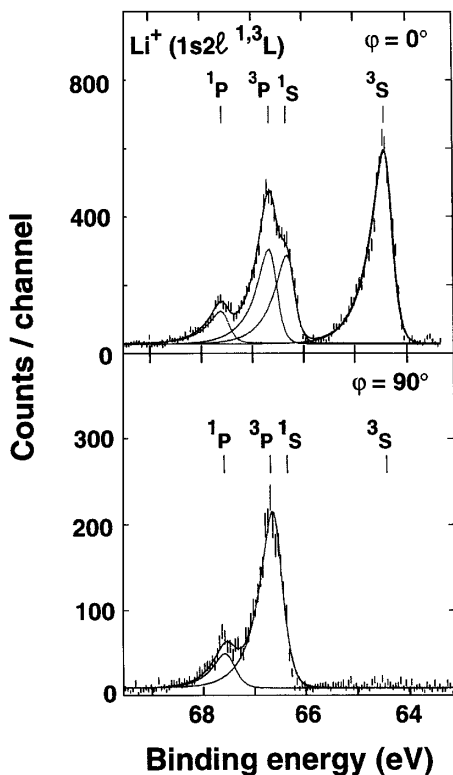


FIG. 1. Angle-resolved (at $\varphi = 0^\circ$, upper panel; and 90° , lower panel) photoelectron spectra measured in the photoionization of lithium atoms at the excitation energy (142.28 eV) of the $2s^2 2p^2 P$ triply excited state. The photolines shown result from photoionization of the lithium atoms in the $1s$ shell, and correspond to the main lines (final Li^+ states: $1s 2s^3 S$) and to the first correlation satellites ($1s 2p^3 P$).

synchronously with photon energy. Angle-resolved photoelectron spectra were also recorded at some fixed photon energies. The theoretical approach is based on the R -matrix method already described [10–13] and is here extended to provide differential cross sections and β parameters.

In Fig. 1, we show angle-resolved photoelectron spectra measured in the $\text{Li}^+(1s 2l^1,3L)\varepsilon l$ ionic continua at the measured energy of the $2s^2 2p^2 P$ resonance (142.28 eV photon energy) for $\varphi = 0^\circ$ and $\varphi = 90^\circ$. The residual Li^+ ion can be left either in the $1s 2s^3 S$ states (main lines), or in the $1s 2p^3 P$ states (correlation satellites). As already reported [11], the intensity of these satellites is strongly enhanced on resonance. At $\varphi = 0^\circ$, the direction of the emitted electrons is parallel to the electrical field vector of the photon beam, while at 90° it is perpendicular. Both spectra are deconvolved in Fig. 1 as the natural width of the $2s^2 2p^2 P$ state and the instrumental function of the electron spectrometer (fitted to a sigmoid form in the angle-resolved mode) are known. The two spectra have drastically differing angular behavior. The main lines vanish at $\varphi = 90^\circ$, while the correlation satellite lines still have significant intensities, almost as intense as in the 0° spectrum. The behavior of the main lines, with zero intensity at $\varphi = 90^\circ$, confirms that $\beta = 2$, as expected. The experimental spectra indicate that the angular distribution of the correlation satellites is almost isotropic and suggest a small positive value of the angular distribution parameter β on resonance. Off-resonance data show that all electron lines nearly vanish at $\varphi = 90^\circ$, indicating a β value close to 2.

The variation of the angular distribution parameter determined from our analysis is shown in Fig. 2 over the energy range of the $2s^2 2p^2 P$ resonance for $[(1s 2p^3 P)\varepsilon l]$ and $[(1s 2p^1 P)\varepsilon l]$ electrons. Both show a similar photon energy dependence, with β values near 2 outside of the resonance and deep minima of the order of 0.3–0.4 near the energy of the resonance. The full lines are the results of our convolved R -matrix calculations, in good agreement with the experimental results; the observed energy shift between theory and experiment was already noted and explained in the analysis of the partial cross sections [11].

To understand the observed β behavior, we first discuss the physical processes. Outside the resonance region, the correlation satellites produced with transfer of angular momentum can be viewed as resulting from electron-electron scattering, producing excitation of the $2s$ electron into a $2p$ orbital. Selection rules indicate that the εp photoelectron can be scattered into an εs or εd continuum state, which interfere to produce the observed angular distribution. Direct photoionization is very weak in comparison with the resonant pathway [10]. The process which is likely to be the most important for the decay of the $2s^2 2p^2 P$ excited state is when there is no change of angular momentum. Thus, the dominant relaxation route is likely to occur via an Auger transition in which one of the $2s$ electrons fills

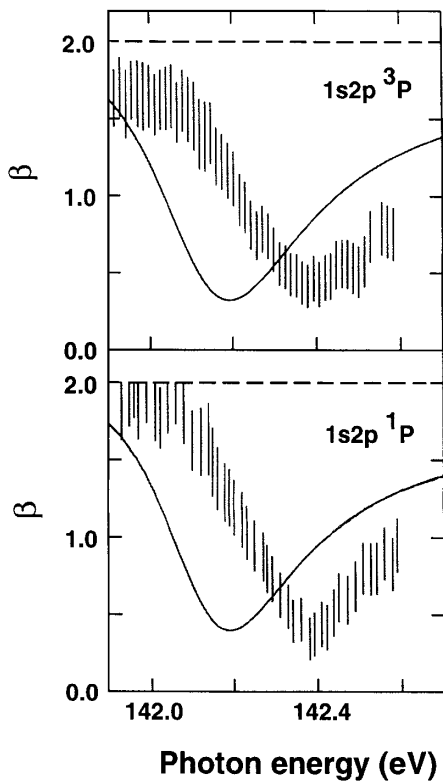


FIG. 2. Variation of the angular distribution parameter β of the electrons emitted in the $[(1s2p^3P)\epsilon l]$ (upper panel) and $[(1s2p^1P)\epsilon l]$ (lower panel) continua of the Li^+ ions in the energy range of the $2s^22p^2P$ triply excited state. The full lines are the L results of our R matrix calculations.

one of the empty $1s$ orbitals while the other $2s$ electron is emitted into the continuum without exchange of angular momentum. Thus, the continuum wave should be an ϵs wave. In the absence of higher-order contributions, the value of the angular distribution parameter would then be strictly equal to 0. The almost isotropic angular distribution of the satellite electrons which is experimentally observed confirm that this Auger transition is the dominant process.

Our R -matrix results, shown in Fig. 2, were calculated in the dipole formalism [19]. The angular momenta of the core L_c and of the initial state L_0 are 1 and 0, respectively, and the angular momentum transfer is $j_t = 1$, corresponding to a parity-favored transition for the photoionization process to the final state $[\text{Li}^+:1s2p^1,3P(\epsilon s \text{ or } \epsilon d)]^2P^0$. The expression for the angular distribution parameter β for either one of these transitions reduces to [20]

$$\beta = \{|S_d|^2 - \sqrt{2}[S_d S_s^* + S_d^* S_s]\} / \{|S_d|^2 + |S_s|^2\}, \quad (1)$$

where S_d and S_s are the scattering matrix amplitudes for the ϵd and ϵs waves, respectively. They are directly related to the dipole matrix elements and to the continuum wave phase shifts. For each wave ϵl , the phase shift

is equal to the sum of the Coulomb phase $\sigma_{\epsilon l}$ and the non-Coulomb short potential phase $\delta_{\epsilon l}$. In the LS coupling approximation, the expression for $\beta^3P(^1P)$ is [20]

$$\beta^3P(^1P) = [1 - 2\sqrt{2}(\rho \cos \Delta)] / (1 + \rho^2), \quad (2)$$

where $\Delta =$ is the difference between the ϵd and ϵs phase shifts and $\rho = |S_s|/|S_d|$. An examination of expression (2) confirms our qualitative conclusion for the behavior of $\beta^3P(^1P)$. If the number of electrons in the ϵ_d wave is negligible, i.e., $\rho \rightarrow \infty$, then $\beta = 0$ and the outgoing wave ϵ_s has an isotropic distribution. In the other extreme (number of electrons in the ϵ_s wave negligible), one would have $\beta = 1$. At high photon energy, assuming that the ϵs and ϵd waves are independent, $\Delta = \pi$, and the Racah algebra makes $\rho^2 = 1/2$ resulting in a β value of 2. At 140 eV photon energy, i.e., at about 2 eV below the resonance energy, the calculations indicate that $|S_d|^2$ is about twice $|S_s|^2$ and Δ is about π rad. The resulting values for $\beta(^3P)$ and (^1P) are 1.94 and 1.88, respectively, in good agreement with the experimental results. At the calculated resonance energy (142.119 eV), $|S_s|^2$ is about 20 times greater than $|S_d|^2$, giving the values $\beta(^3P) = 0.43$ and $\beta(^1P) = 0.62$. The corresponding experimental values, which have been directly measured from the angle-resolved spectra at the experimental value (142.28 eV) of the resonance energy, are 0.57 ± 0.16 for $\beta(^3P)$ and 0.80 ± 0.20 for $\beta(^1P)$ in reasonable agreement with theory.

Of particular interest is the fact that both theory and experiment show that the β minima occur not at the energy of the resonance, but on the high energy side. The cross section σ varies as $|S_d|^2 + |S_s|^2$, and is most sensitive to the dominant channel (here the ϵs within the resonance), while β is sensitive to the ratio ρ and to the phase shift Δ [Eq. (2)]. These latter two quantities vary rapidly within the resonance and their energy behavior must be looked at in detail to gain understanding of the observed shift. We show in Fig. 3 the theoretical variation of σ , ρ , $\cos \Delta$, and β for the 3P channel around the resonance energy. The σ curve shows a Lorentzian profile with a lifetime broadened width of 0.120 eV, and an enhancement of the σ value by a factor of 10, in good agreement with previous experiments [11]. The maximum in the theoretical cross section occurs at the calculated resonance energy (142.119 eV), while the maximum of ρ (9.18) and the minimum of $\cos(\Delta)$ (-0.990) occur at 142.177 and 142.181 eV, respectively. The β curve [calculated from Eq. (2)] displays a broad and strongly asymmetric profile with an excursion of the β values from the off-resonance value extending over a much broader energy range on the high energy side of the resonance. $d\beta/dE$ is given by

$$\begin{aligned} d\beta/dE = & \{[2\sqrt{2} \cos(\Delta)\rho^2 - 2\rho - 2\sqrt{2} \cos \Delta] \\ & / (1 + \rho^2)^2\} d\rho/dE \\ & - \{(2\sqrt{2} \rho)/(1 + \rho^2)\} d \cos(\Delta)/dE. \end{aligned}$$

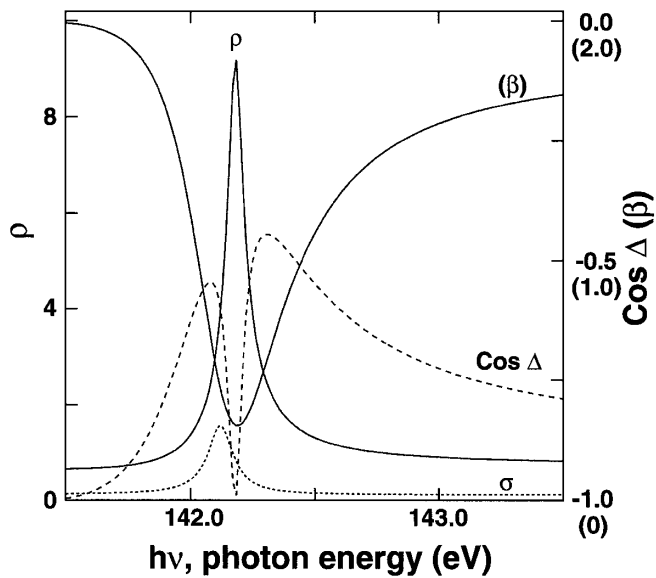


FIG. 3. Variation of the R matrix values of ρ , $\cos\Delta$, β , and σ over the energy range of the $2s^2 2p^2 P$ resonance. The β scale is shown in brackets on the right ordinate axis while the variation of σ is shown only on a relative scale.

Figure 3 shows that ρ^2 goes to a maximum value of about 80, driving the first term almost to zero at that energy; the second term then behaves like $2\sqrt{2}(\rho)^{-1}d(\cos\Delta)/dE$, i.e., becomes very small, and goes to 0 at the position of the minimum in $\cos(\Delta)$. The minimum in β therefore occurs almost at the energy of the maximum in ρ (the exact calculation shows the difference is only 0.004 eV). The theoretical shift (0.060 eV) between the calculated value of the resonance energy and the energy where the minimum of β occurs is about half the resonance width and is confirmed by our experiment. The same shift is also seen clearly in the $\beta(^1P)$ data.

The experimental observation of the energy shift of the β minimum relative to the resonance energy is not unique to date, since it has been measured and discussed earlier in the case of nitrogen and carbon dioxide molecules [21,22]. Also, one early measurement mentions the qualitative observation of such a shift for argon and xenon atoms [23]. The existence of a shift is not widely known, however, and has not been reported from more recent high-resolution experiments performed with undulator radiation. The probable reason is that most high-resolution β determinations in atoms do not measure the energy dependence over the energy range of autoionizing resonances, but only its value at the resonance energy. The present high-resolution observation of the energy shift of the β minimum relative to the resonance energy provides the most detailed analysis to date for inner-shell atomic photoionization. Furthermore, it is complemented by our theoretical calculations which are in full agreement with the measurements. As shown

in our analysis, β provides dynamical information which is unobtainable from integrated cross sections, e.g., phase information. It is clear that for high resolution β measurements, it is important to be aware that on-resonance determination of β does not necessarily provide a measurement of the minimum in β .

In conclusion, our first angle-resolved photoexcitation data provide additional insight for understanding the relaxation of the $2s^2 2p^2 P$ state of lithium. They confirm clearly the existence of a shift between the resonance energy and the energy where the minimum value of β is reached. For more highly excited states, which become less resolved as the orbital and principal quantum numbers increase, this method provides a way to disentangle the individual effects of the various resonances in the experimental spectra and possible interference effects between overlapping resonances.

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