

## First Observation of a Photon-Induced Triply Excited State in Atomic Lithium

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Using a dual laser plasma technique we have measured for the first time the photoabsorption spectrum of atomic lithium at energies corresponding to the simultaneous excitation of both  $1s$  electrons. We have observed the main triply excited  $1s^2 2s(^2S) \rightarrow 2s^2 2p(^2P)$  transition with Fano parameters  $E_0 = 142.32 \pm 0.05$  eV,  $\Gamma = 0.20 \pm 0.04$  eV, and  $q = -2.2 \pm 0.6$ . Our experiment represents the first step in photoionization studies of this fundamental atomic system in which the motion of the three electrons in the field of the nucleus is so highly correlated.

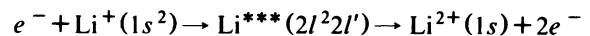
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Helium and He-like ions have represented the archetypal system in which the effects of electron-electron correlation may be studied. Such effects are most readily observed in multiply excited species and hence the study of doubly excited states in He provides important information on the correlated motion of a pair of electrons in the field of a nucleus (the fundamental Coulombic three body problem). Although the first definitive observation of the doubly excited  $2s2p(^1P)$  state was in inelastic scattering of electrons by He [1] the advent of extreme-UV (EUV) synchrotron light sources at about the same period made possible the production of high quality photoabsorption data on this atomic system [2] for direct comparison with theory [3]. This first photoabsorption experiment provided the stimulus for many subsequent theoretical and experimental studies of photoexcitation of doubly excited states in He. Indeed this atomic system continues to attract considerable theoretical [4] and experimental attention [5]. Extension of the  $1s^2 \rightarrow 2snp(^1P)$  series to isoelectronic  $\text{Li}^+$  by Carroll and Kennedy [6] was realized only after the development of laser produced plasmas both as EUV light sources and also as high density sources of ions for photoabsorption studies. The series was later extended to  $\text{Be}^{2+}$  using the same technique [7].

On moving from He to Li the addition of a single electron makes possible the formation of triply excited states [8] in which all three electrons reside in the  $n=2$  subshell leaving the  $K$  shell unoccupied. Such a multiply excited species can be considered an ideal planetary or hollow atom and represents a model system for the study of electron correlation in a three electron atom (the Coulombic four body problem). Further, while helium exhibits only direct double photoionization [9],  $\text{He} + h\nu \rightarrow \text{He}^{2+} + 2e$ , lithium offers the potential for the study of both direct and resonant ( $\text{Li} + h\nu \rightarrow \text{Li}^{***} \rightarrow \text{Li}^{2+} + 2e$ ) double photoionization where  $\text{Li}^{***}$  corresponds to a triply excited (or double  $K$ -shell vacancy) state. Hence a strong case exists for the initiation of studies into the photoabsorption

spectrum of atomic lithium at energies corresponding to the simultaneous photoexcitation of both  $K$ -shell electrons.

As in the early studies of doubly excited resonances in He, first experiments on three electron systems were exclusively collisional in nature. The first observation of triply excited states in three electron systems was in  $e^- + \text{He}$  scattering [10]. A gap of ten years elapsed before the observation of triply excited states in atomic lithium was reported using a beam-foil technique [11,12]. More recently, fluorescence from triply excited states in lithium has been measured [13,14] while the cross section for the process



has been reported by Muller *et al.* [15].

The primary advantage of the photoabsorption technique is that it is selective and probes the fundamental photon-atom interaction. It produces spectra of less complexity as it accesses only those states which are optically connected to a known ground state; it can also provide sufficient resolution to measure resonance widths and  $q$  values. It is therefore a very attractive technique for the investigation of complex multiply excited atomic systems such as  $\text{Li}^{***}(nl, n'l', n''l'')$  where  $n, n'$ , and  $n'' \geq 2$ . In this Letter we present the first measurement of the photoabsorption spectrum of atomic lithium in the energy range corresponding to the simultaneous excitation of both  $1s$  electrons.

Spectra were obtained using the dual laser plasma (DLP) technique [16]. A Nd-YAG laser produced tungsten plasma acted as a backlighting source. The absorbing column was formed by focusing either the output of a flashlamp pumped dye laser (2.5 J, 0.5  $\mu$ s, R6G) or a ruby laser (1.5 J, 30 ns), in line focus geometry ( $l \sim 22$  mm and 15 mm, respectively), onto a spectroscopically pure Li metal target. Previous work [17] has shown that long pulse dye lasers favor the production of absorbing columns consisting almost exclusively of neutral species

while the short pulse ruby laser is more suited to the production of ions. Spectra were recorded on a 2.2 m grazing incidence spectrometer equipped with a 1200 groove/mm grating and an EUV optical multichannel analyzer. Data were acquired with ( $I$ ) and without ( $I_0$ ) the absorbing plasma present and the relative absorption determined from  $\ln(I_0/I)$ .

We first recorded the  $1s^2(^1S_0) \rightarrow 2s2p(^1P_1)$  resonance of  $\text{Li}^+$  to provide a benchmark for the measurement capability of the system. Using a slit width of  $10 \mu\text{m}$  the best resolution obtained was  $\sim 1500$  (prior to deconvolution)—limited by the spatial sampling period of the array detector. The dynamic range of the cooled detector used was  $\sim 2000$  counts with a dark noise of  $< 1$  count. In order to optimize the absorbing column density we

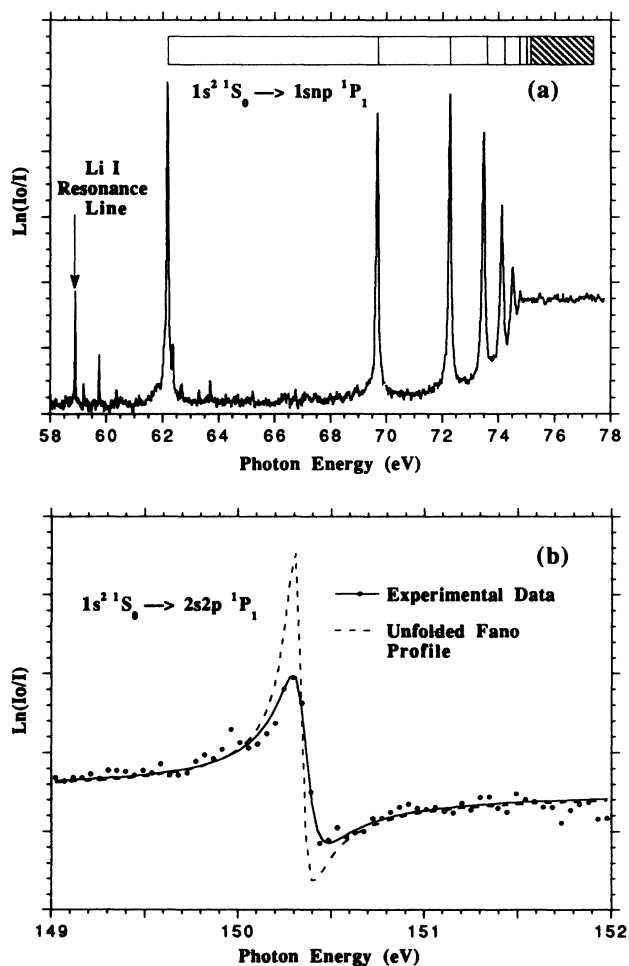


FIG. 1. (a) The photoabsorption spectrum of  $\text{Li}^+$  corresponding to single  $1s$  excitation,  $1s^2(^1S) \rightarrow 1snp(^1P)$ . The purity of the spectrum is demonstrated by the weakness of the main  $1s^2 2s(^2S) \rightarrow 1s[2s2p(^3P)](^2P)$  transition in neutral lithium. (b) Photoabsorption spectrum of  $\text{Li}^+$  in the vicinity of the  $1s^2(^1S) \rightarrow 2s2p(^1P)$  doubly excited transition. The broken curve represents a Fano profile fit to the restored data following removal of instrument broadening.

recorded the  $K$ -shell photoabsorption spectra of ruby laser produced lithium plasmas in the region of single  $1s$  electron excitation at various interplasma delays and optical paths through the plume of the absorbing plasma. In this way we constructed a space time map of  $\text{Li}^+$  absorption and were able to select the charge state of interest to a high degree of purity. We optimized the  $\text{Li}^+$  column density by maximizing the jump in photoabsorption in the vicinity of the  $K$  edge.

The spectrum corresponding to single  $1s$  electron excitation [ $1s^2(^1S_0) \rightarrow 1snp(^1P_1)$ ] is presented in Fig. 1(a). We flag the strongest line of neutral lithium in this energy region, the weakness of which is a good indicator of the high purity of the  $\text{Li}^+$  spectrum. In Fig. 1(b) the photoabsorption spectrum of  $\text{Li}^+$  in the vicinity of the  $1s^2(^1S) \rightarrow 2s2p(^1P)$  doubly excited transition is presented. Using a maximum likelihood procedure we removed the instrument broadening from the raw spectrum. We fitted the Fano profile formula to the restored data and obtained a resonance position  $E_0 = 150.28 \pm 0.05$  eV, a width  $\Gamma = 0.09 \pm 0.04$  eV, and a profile index  $q = -1.8 \pm 0.5$  which agree, within the limits of experimental error, with the values previously reported by Carroll and Kennedy [6] which were obtained from photographic plate data.

In order to optimize the atomic lithium column density it was necessary to use the long pulse duration dye laser for plasma production which yields a relatively cool absorbing plasma. As in the  $\text{Li}^+$  case we obtained a series of time and space resolved spectra of the dye laser produced plasmas to determine conditions for which neutral species dominated. We show the photoabsorption spectrum in the vicinity of the  $K$  edge in Fig. 2(a). The spectrum is in very good agreement with the original photoelectric data of Mehlman *et al.* [18] which were obtained using synchrotron radiation and a heat pipe. The agreement demonstrates both the purity of the neutral absorbing column and the reliability of the DLP technique for the measurement of relative cross sections.

Because of the inherent weakness of the triply excited resonances of atomic lithium we had, in a manner similar to  $\text{Li}^+$ , to optimize the column absorption by maximizing the absorption step at the  $K$  edge. In Fig. 2(b) we show the photoabsorption spectrum of atomic lithium in the vicinity of the main  $1s^2 2s(^2S) \rightarrow 2s^2 2p(^2P)$  transition. The spectrum was obtained by averaging eighteen independent spectra, each representing the accumulation of twenty  $I$  and twenty  $I_0$  scans. The feature is located at  $142.32 \pm 0.05$  eV in comparison to the computed value of 142.26 eV given by Chung [19]. In Table I we summarize the results of a number of other calculations of the resonance position [20–23].

The calculation of the autoionization width of the  $2s^2 2p(^2P)$  state has been reported by Safronova and Senashenko [22] who obtained a value of 0.24 eV using a  $1/Z$  expansion and Simons, Kelly, and Bruch [23] whose value of 0.14 eV resulted from many body perturbation

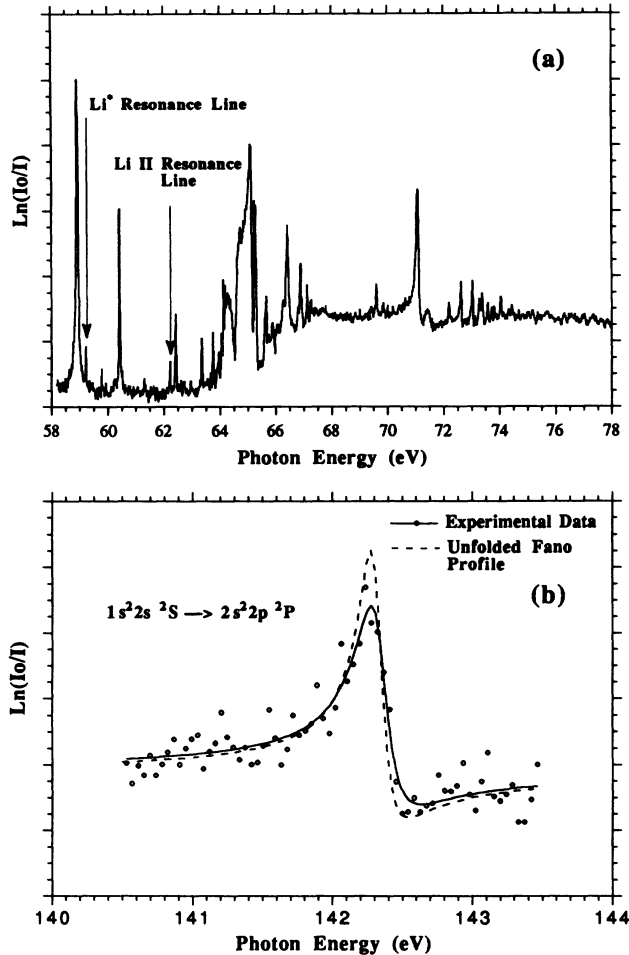


FIG. 2. (a)  $K$ -shell absorption spectrum of the dye laser produced lithium plasma at an interplasma delay of 750 ns corresponding to maximum ground state neutral lithium. Indicated on the plot are the strongest lines of valence excited Li and ground state  $\text{Li}^+$  in this energy region. The weakness of both lines is a good measure of the purity of the ground state neutral lithium in the absorbing sample. (b) Photoabsorption spectrum of atomic lithium in the energy window of the main  $1s^2 2s(^2S) \rightarrow 2s^2 2p(^2P)$  transition. The broken curve represents a Fano profile fit to the restored data following removal of instrument broadening.

theory (MBPT). Using the Cowan code [24] we have also carried out three separate autoionization rate calculations including three continuum configurations ( $1s2sep$ ,  $1s2pes$ , and  $1s2ped$ ) coupled with either one ( $2s^2 2p$ ), two

( $2s^2 2p + 2p^3$ ), or twenty-five discrete configurations. All orbitals were computed variationally. The results of these calculations yielded values of 0.18, 0.22, and 0.21 eV, respectively for the width of the  $2s^2 2p(^2P)$  state.

In order to estimate the experimental width of the  $2s^2 2p(^2P)$  state we used the Fano profile formula [3] for the interaction of a single discrete state with many continua. This formula is similar to the single-discrete-single-continuum channel case apart from the inclusion of a smoothly varying background,

$$\sigma = \sigma_b + \sigma_a [(q + \epsilon)^2 / (1 + \epsilon^2)],$$

where the symbols have their usual meanings.

The formula should be applicable as the autoionization rate calculations above show that the decay rate of  $2s^2 2p(^2P)$  is not strongly affected by discrete-discrete configuration interaction (CI) and to a good approximation the resonance can be considered as a single discrete state coupled to many continuum channels. As in the  $\text{Li}^+$  case we deconvolved the instrument broadening from the raw spectrum. The width obtained postdeconvolution is less than 25% narrower than that obtained from the raw experimental data and is to be contrasted with the  $\text{Li}^+$  case where the instrumental broadening approximately doubles the width of the  $2s 2p(^1P_1)$  state. The broken line represents the Fano fit to the deconvolved data and yielded the values of the  $E_0$ ,  $\Gamma$ , and  $q$  parameters given in Table I. Our experimental value of  $\Gamma$  ( $0.20 \pm 0.04$  eV) is in good agreement with both our computed value and that of Safronova and Senashenko [22] but not with that of Simons, Kelly, and Bruch [23]. To the best of our knowledge there is no published theoretical value for the profile index  $q$  for comparison with experiment.

In conclusion, we have observed for the first time the photoabsorption spectrum of triply excited atomic lithium and measured the position, width, and profile index of the main  $1s^2 2s(^2S) \rightarrow 2s^2 2p(^2P)$  resonance. Hartree-Fock (HF) calculations predict a substantial number of other weak triply excited resonances many of which have a width comparable to or less than that of our instrumental width. For example, we predict the width of the  $2p^3(^2P)$  state to be  $\sim 0.06$  eV. Hence further experiments on this fundamental atomic system will require high resolving power spectrometers coupled to high flux synchrotron sources with high dynamic range detection to resolve the supernumerary triply excited resonances which characterize the atomic lithium spectrum at excitation energies

TABLE I. Comparison of computed and measured Fano parameters for the  $1s^2 2s(^2S) \rightarrow 2s^2 2p(^2P)$  transition of atomic lithium.

$2s^2 2p(^2P)$	Experimental	HF-CI	Ref. [19]	Ref. [20]	Ref. [21]	Ref. [22]	Ref. [23]
$E_0$ (eV)	$142.32 \pm 0.05$	141.90	142.26	142.608	141.7	141.811	142.661
$\Gamma$ (eV)	$0.20 \pm 0.04$	0.21	...	...	...	0.24	0.13
$q$	$-2.2 \pm 0.60$	...	...	...	...	...	...

above 140 eV. Experiments on laser excited lithium to measure  $1s^2 2p(^2P) \rightarrow 2s 2p^2(^2L)$  transitions should be possible in the near future. In order to obtain detailed information on the dynamics of resonant double photoionization in three electron atomic systems angle resolved photoelectron spectroscopy on ground and laser excited and aligned lithium [25] at photon energies corresponding to triple excitation will be required. We also hope that this work will act as a stimulus for further theoretical work on resonant double photoionization of atomic lithium.

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