[6]T. W. Donnelly and G. E. Walker, Ann. Phys. (N.Y.) 60, 209 (1970).
[7]S. M. Austin, in *The Two-Body Force in Nuclei*, edited by S. M. Austin and G. M. Crawley (Plenum, New York-London, 1972), p. 285.
[8]G. E. Walker, in *Dynamic Structure of Nuclear States*, edited by D. J. Rowe *et al.* (Univ. of Toronto Press, Toronto, 1972), p. 509.
[9]A. Picklesimer and G. E. Walker, private communication.
[10]V. C. Officer, R. S. Henderson, and I. D. Svalbe, Bull. Am. Phys. Soc. 20, 1169 (1975).
[11]O. Sundberg *et al.*, Nucl. Phys. A101, 481 (1967).
[12]Y. S. Horowitz, N. K. Sherman, and R. E. Bell, Nucl. Phys. A134, 577 (1969).
[13]A. Johnston and T. E. Drake, J. Phys. A 7, 898 (1974).
[14]S. Dahlgren *et al.*, Nucl. Phys. A90, 673 (1967).
[15]We thank F. E. Bertrand for sharing the silicon target, and W. Lozowski for preparation of the ^{24}Mg target.
[16]P. M. Endt and C. Van der Leun, Nucl. Phys. A214, 1 (1973).
[17]H. Zarek *et al.*, Phys. Rev. Lett. 38, 750 (1977).
[18]B. Zwieglinski *et al.*, Bull. Am. Phys. Soc. 22, 28 (1977).
[19]P. J. Moffa and G. E. Walker, Nucl. Phys. A222, 140 (1974).
[20]We thank A. Nadasen, P. Schwandt, P. T. Debevec, J. Meek, P. Pile, and P. P. Singh for their cooperation in these measurements.
[21]In an investigation of the reactions ^{12}C(p,p') and ^{16}O(p,p') it was found that predicted cross sections for scattering to some states required similar renormalizations: H. K. Lee and H. McManus, Phys. Rev. 161, 1087 (1967).
[22]G. E. Walker, Phys. Rev. C 5, 1540 (1972).
[23]S. Maripuu, private communication.

Laser Excitation and Ionization in a Dense Li Vapor: Observation of the Even-Parity, Core-Excited Autoionizing States

T. J. McIlrath
Optical Physics Division, National Bureau of Standards, Washington, D. C. 20234 and Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

and

T. B. Lucatorto
Optical Physics Division, National Bureau of Standards, Washington, D. C. 20234

(Received 13 April 1977)

The first optical absorption from excited states to autoionizing core-excited levels has been observed in lithium. A 1-MW dye laser tuned to the $1s^2 2s \rightarrow 1s^2 2p$ resonance produced ~10^{16} excited atoms/cm^2 in a heat-pipe oven. Far-uv absorption spectra of Li*($2p$) and Li^+ were obtained. A curve of the evolution from excited neutrals to ~95% ions is presented, and the significance of the Li observations for understanding the ionization mechanism is discussed.

The autoionizing levels of an atom play a significant role in several diverse physical phenomena. Among these are the important and sometimes dominant influence of dielectronic recombination (involving the inverse of autoionization) on the conditions in an astrophysical plasma,[1] the strong effect of autoionizing levels on the generation of tunable vacuum-uv radiation by four-wave parametric interactions in atomic vapors,[2] and the large gains associated with these levels in photoionization efficiency encountered in several laser isotope-separation schemes. This Letter reports the first observation of the photoabsorption spectrum of core-excited autoionizing states having the same parity as the ground state (the so-called "optically inaccessible" states).

In order to obtain photographic absorption spectra of autoionizing features, which generally have peak cross sections in the range $\sigma \leq 10^{-17}$ cm^2, a relatively high column density of absorbing atoms ($\geq 10^{16}$ cm^{-2}) is required. A previous Letter[3] reported studies of the absorption spectrum of laser-pumped Na in the 15–30-nm region which used a long-duration (500 ns), high-power (1 MW) laser for excitation. In that work we found strong ionization to Na^+ and observed the Na^+ absorption spectrum. We have now obtained absorption to core-excited levels from the first excited state of neutral Li. We were also able to attain nearly 100% ionization of Li to Li^+ and to show that the absorption spectra of the various species, from ground state Li($1s^2 2s$), to excited state Li*($1s^2 2p$),

to ionized $Li^+(1s^2)$, can be observed by varying the time of observation relative to the laser pulse.

The experimental setup is similar to the one used to observe the Na^+ absorption spectrum which is described in Ref. 3. It consists of a 15-cm-long lithium heat-pipe oven with a vapor density of $\sim 6\times10^{15}$ cm^{-3} placed several centimeters from the entrance slit of a 3-m grazing-incidence spectrograph, and a triggered vacuum spark which provides a 100-nsec continuum probe pulse in the region 10–30 nm.[4] The laser is a flash-lamp-pumped dye (cresyl violet) laser tuned to the 670.8-nm $2s \rightarrow 2p$ resonance line of Li with an output of 1 MW in 0.1 nm bandwidth for 800 ns. The delay time between the initiation of the laser pulse and the peak of the uv probe pulse was controlled to within ± 50 nsec, and the uv probe pulse was sequentially stepped to sample the laser-excited vapor at various times after the initiation of laser pulse.

Densitometer traces of four spectrograms taken on Kodak 101.05 plates of the region 16–22 nm under the same operating conditions of the heat-pipe oven and laser are shown in Fig. 1. The first, designated (a), represents the conventional ground-state absorption spectrum taken with the laser off. A partial analysis of this spectrum has been published previously.[5] Trace (b) represents the spectrum obtained when the peak of the probe pulse occurs 200 nsec after the initiation of the laser pulse. Over twenty lines representing absorption resonances from the excited $1s^22p\ ^2P$ levels are observed. (See Table I.) At 400 nsec after laser initiation [Fig. 1c)], it is obvious that considerable ionization has already occurred by observing the jump in cross section at the onset on the Li^+ continuum (16.391 nm). At 600 nsec after laser initiation [Fig. 1d)], the ionization is practically complete as evidenced by the disappearance of the very broad neutral absorption features. Several absorption lines of the neutral species remain, but these are associated with saturated narrow features having large cross sections. The $1snp$ levels of Li^+ can be observed to $n = 12$.

Table I summarizes the spectroscopic data on the absorption lines observed in the laser-excited vapor. The lowest possible autoionizing absorption line out of a $1s^22p\ ^2P$ state, associated with the $1s2s^2\ ^2S_{1/2}$ level, is too weak to be observed with the column densities used in the present experiment. The energies for the terms associated with the configuration $1s2s^2$, $1s2p^2$, $(1s2s\ ^3S)\,ns$ and nd $(n = 3,4)$, $(1s2s\ ^1S)$ $3s$ and $3d$, and $(1s2p\ ^{3,1}P)$ $3p$ were calculated by Weiss using a multiconfigurational Hartree-Fock technique.[6] These energy values were used to assign unambiguously ten of the observed lines. Other, higher-series members were then assigned using quantum-defect comparisons and relative intensities.

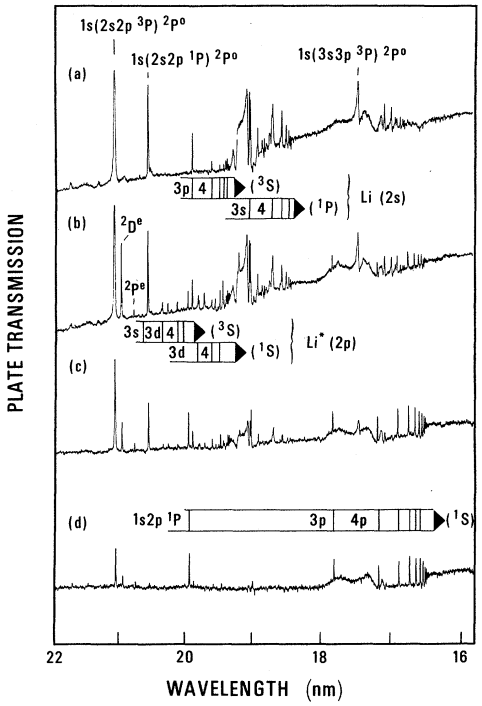

FIG. 1. Densitometer tracings of spectra taken (a) before laser initiation; (b) 200 nsec after laser initiation; (c) 400 nsec after laser initation; (d) 600 nsec after laser initiation. Broad persistent structure from 17 to 18 nm is a source feature. Bar graph below (a) designates several series members of the type $1s2s(^3S)np$ and $1s2p(^1P)ns$ going to the Li^+: $1s2s(^3S)$ and $1s2p(^1P)$ limits. The solid triangles mark the positions of these limits relative to the Li: $1s^22s(^2S)$ level. Graph below (b) designates series members of the type $1s2s(^3S)ns$, $(^3S)nd$ and $1s2s(^1S)nd$ going to the Li^+: $1s2s(^3S)$ and (^1S) limits. The positions of these limits relative to the Li: $1s^2p(^2P)$ levels are indicated by the triangles. Note disappearance of slope in transmitted continuum as neutrals are removed.

Some of the levels listed in Table I recently have been observed by other techniques. Two of the levels have been observed optically: The $1s2p^2\ ^2P$, which autoionizes at a rate much less than the optical decay rate has been observed in optical emission with beam-foil excitation by Buchet *et al.*[7]; the $1s2p^2\ ^2D$, which is associated with the strongest autioionizing absorption line out of a $1s^22p\ ^2P$ state, was observed in a Li plasma created in a flash pyrolysis by Cantu *et*

TABLE I. Even-parity, core-excited levels in Li.

Observed λ(nm)±0.002	Tentative Assignment	Energy from 2s State(eV)	Calculated[a] Value(eV)	Other Measurements(eV)
--	$1s(2s^2)^2S$	--	56.54	56.35±0.01[d,e,f]
20.939	$1s(2p^2)^2D$	61.062	61.11	61.07±0.01[d,f,g]
20.773[b]	$1s^24s\ ^2S \rightarrow 1s2p(^3P)3s$?			
20.744	$1s(2p^2)^2P$	61.617	61.66	61.60±0.1[h]
20.615	$1s2s(^3S)3s^2S$	61.992	62.03	62.00±0.01[d]
20.309	$(^3S)3d^2D$	62.899	62.98	62.98±0.03[d]
20.230	$1s2s(^1S)3s^2S$	63.135	63.23	63.17±0.03[d]
20.172	$(^3S)4s^2S$	63.313	63.26	
20.123	$1s(2p^2)^2S$	63.462	63.50	
20.089	$(^3S)4d^2D$	63.565	63.62	63.58±0.03[d]
20.034	$(^3S)5s^2S$	63.735		
19.992	$(^3S)5d^2D$	63.865		
19.970	c	63.935		
19.775	$(^1S)3d^2D$	64.545	64.40	
19.762	$1s2p(^3P)3p^2P$	64.586	64.66	
19.684	$(^3P)3p^2D$	63.834	64.94	
19.629	c	65.012		
19.520	$(^1S)4d^2D$	65.366		
19.474	$1s2p(^1P)3p^2P$	65.514	65.69	
19.448	$(^1P)3p^2D$	65.599		
19.405	$(^1S)5d^2D$	65.743		
19.355	$(^1S)6d^2D$	65.907		
19.336	c	65.971		
19.291	c	66.118		
19.158	$(^1P)4p^2D$	66.566		
18.944	c	67.297		
17.714		71.841		

[a]Ref. 6.

[b]An extremely weak line, $\Delta\lambda \approx \pm 0.005$ nm.

[c]Weak lines of questionable origin.

[d]Ref. 9.

[e]Ref. 10 in which the $1s2s^2\,^2S$ was observed at 55.9 ±0.5 eV.

[f]Ref. 11; the $1s2s^2\,^2S$ was observed at 56.31±0.03 eV and the $1s2p^2\,^2D$ at 61.04±0.03 eV.

[g]Ref. 8 in which the $1s2p^2\,^2D$ was observed at 20.942 ±0.001 nm.

[h]Ref. 7.

al.[8] The other previously observed levels were detected in the energy spectrum of electrons ejected from autoionizing states excited by H^+ and He^+ impact,[9] by beam-foil collisions,[10] and by beam–gas-target collisions.[11]

The observation of efficient ionization by a laser tuned to the lowest resonance line in both sodium and lithium under similar conditions of laser intensity, laser duration, and vapor density makes it reasonable to assume that the same mechanism is operating in both cases. Processes leading to ionization which are possible in sodium are (1) two-photon ionization out of the $3p$ levels; (2) laser-induced collisional transfer of energy in the form $Na^*(3p) + Na^*(3p) + h\nu_L \rightarrow Na(3s) + Na^+(2p^6) + e$; (3) superelastic collisional heating of an initially small number of free "seed" electrons by the excited-state atoms, followed by electron-impact ionization by the heated electrons; (4) direct collisional exchange of energy of the form $Na^*(3p) + Na^*(3p) \rightarrow Na^*(5s) + Na(3s)$ followed by photoionization out of the $5s$ level; (5) promotion of the atoms from the $3p$ to the $4p$ levels by stimulated Raman scattering and subsequent single-photon ionization out of the $4p$ or $4s$ levels; (6) associative ionization to Na_2^+ followed by photodissociation. Of these, only the first three are energetically possible in Li. The rates for processes (1) and (2) have been calculated for both the Na and Li experiments and shown to give comparable ionization rates which are $\sim 10^{17}$ ions cm^{-3} sec^{-1} for Na and $\sim 10^{18}$ ions cm^{-3} sec^{-1} for Li[12]; these values are four orders of magnitude too small to explain the present results. Hence, of the possibilities mentioned, only the one involving the superelastically heated electrons seems plausible.

The seed electrons which could initiate the ionization in this scheme are provided by both processes (1) and (2) above. After the start of the pulse the laser radiation provides the seed electrons and also creates a large population density in the excited ^2P level. The cross section for the superelastic de-excitation of the seed electrons created by processes (1) and (2) are quite large for both Na and Li. For example, in Na the value of this cross section at 1.17-eV seed electron energy [obtained by detailed balance from the measured value[13] of $\sigma(3s \rightarrow 3p)$] is $\sigma(3p \rightarrow 3s) \approx 8 \times 10^{-15}$ cm^2. The collision rate for a seed electron in a vapor of 3×10^{15} cm^{-3} excited states is 3×10^8 sec^{-1}. Thus, at an electron density of $\sim 10^9$ cm^{-3} (which is achieved in $\sim 10^{-8}$ sec) the superelastic collision rate begins to exceed the rate of production of cool electrons by processes (1) and (2), and the electron temperature will rise. The resultant hot electrons will then both further excite and ionize the atoms. It is possible that one (and, interestingly, only one) of the lines observed (the extremely weak line at 20.773 nm) originates from an excited state other than the $1s^22p$. An accurate model is needed to explain the process in detail; Measures has taken an initial step by proposing a simplified model for a related experiment.[14]

The neutral ground-state population in the column was obtained by using the broad absorption feature at 19.16 nm which has a known cross section of 8 Mb.[15] The Li^+ cross section at the photoionization step at 16.39 nm was obtained in the manner of Ref. 3 by comparing the strength of the neutral absorption in Fig. 1(a) with the strength

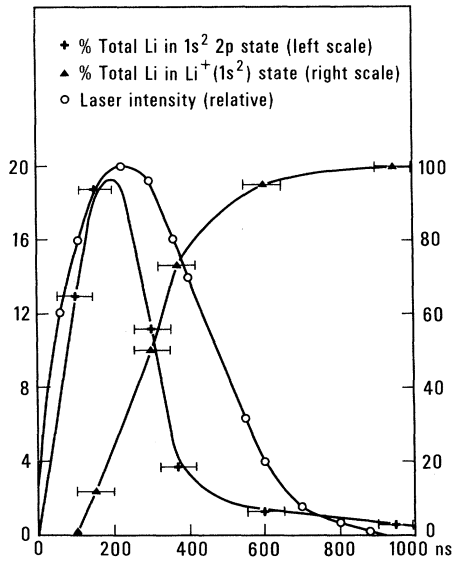

FIG. 2. Population of excited states and ions during the laser pulse. Population is an average over the 100 nsec width of the uv pulse. There is an experimental uncertainty of ±8% in the peak value of the Li*(2p) population.

of the absorption at 16.39 nm in Fig. 1(d) where there is complete ionization. The value obtained, $\sigma(Li^+ \rightarrow Li^{++}) = 2.0 \pm 1.0$ Mb, compares well to a calculated value of 2.7 Mb.[16]

The time dependences of the space-averaged population column densities of Li*(2p) and $Li^+(1s^2)$ obtained from seven plates taken at different times during the laser pulse are presented in Fig. 2. The Li*(2p) populations were obtained from a curve of growth for the equivalent widths for the absorption line associated with the $1s^2 2p\,{}^2P \rightarrow 1s2p^2\,{}^2D$ transition which has a calculated f value of 0.054[17] and a calculated width (autoionization) of 0.0027 nm.[18] The photoionization step at 16.39 nm was used to provide the Li^+ population. As a consistency check the Li* and Li^+ populations obtained by these methods were added to the Li(2s) population obtained by measurements on the 19.16-nm feature; agreement was within the experimental uncertainty.

It is surprising that the peak excited-state population is only 20%, in view of the fact that the laser is "burning through" the vapor which ordinarily would be an indication of saturation (i.e., 75% in the excited states). This may be a result of laser "filamenting," and, like the ionization process itself, will require further efforts to explain fully.

The authors gratefully acknowledge the help of G. Victor for suggesting the superelastic mechanism, the signficant contributions of J. W. Cooper and A. W. Weiss, the support and encouragement of R. P. Madden, and the helpful suggestions of M. M. Hessel and D. C. Morgan.

[1]A. Burgess, Astrophys. J. 139, 776 (1964).
[2]J. A. Armstrong and J. J. Wynne, Phys. Rev. Lett. 33, 1183 (1974).
[3]T. B. Lucatorto and T. J. McIlrath, Phys. Rev. Lett. 37, 428 (1976).
[4]T. B. Lucatorto, T. J. McIlrath, and G. Mehlman, to be published.
[5]D. L. Ederer, T. Lucatorto, and R. P. Madden, Phys. Rev. Lett. 25, 1537 (1970).
[6]A. Weiss, private communication.
[7]J. P. Buchet, M. C. Buchet-Poulizac, H. G. Berry, and W. F. Drake Phys. Rev. A 7, 922 (1973).
[8]A. M. Cantu, W. H. Parkinson, G. Tondello, and G. P. Tozzi, to be published.
[9]P. Ziem, R. Bruch, and N. Stolterfoht, J. Phys. B 8, L480 (1975).
[10]R. Bruch, G. Paul, J. Andra, and L. Lipsky, Phys. Rev. A 12, 1808 (1975).
[11]D. J. Pegg, H. H. Haselton, R. S. Thoe, P. M. Griffin, M. D. Brown, and I. A. Sellin, Phys. Rev. A 12, 1330 (1975).
[12]S. Geltman, to be published.
[13]E. A. Enemark and A. Gallagher, Phys. Rev. A 6, 192 (1972).
[14]R. M. Measures, J. Quant. Spectrosc. Radiat. Transfer 10, 107 (1970).
[15]D. L. Ederer, in *Proceedings of the Second International Conference on Inner Shell Ionization Phenomena, Freiburg, 1976*, edited by W. Mehlhorn and R. Bren (Univ. of Freiburg, Freiburg, Germany, 1976), p. 145.
[16]S. T. Manson, private communication.
[17]J. L. Fox and A. Dalgarno, Phys. Rev. A (to be published).
[18]A. Bhatia, private communication.