New Photon-Induced Triply Excited Hollow Atom States of Lithium

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(Received 29 December 1994)

Numerous new resonances of triply photoexcited hollow Li atoms have been found above the $2s^2 2p\ ^2P^o$ resonance at 142.3 eV. The main features are reproduced by multiconfiguration Dirac-Fock calculations. The spectrum lacks regular series structure and the pattern is found to manifest the effect of the hollow atomic nature of triply excited states. Fano parameters for the $2s^2 2p\ ^2P^o$ resonance were obtained. One-step double autoionization was observed for the first time in the decay from this resonance.

PACS numbers: 32.80.Dz

Triple photoexcitation of a three-electron system, i.e., one-step resonant photoproduction of a "hollow atom," is an unusual, little explored manifestation of electron correlation, requiring joint coherent excitation of all three electrons despite the single-particle nature of the electron-photon dipole operator. Recently, Kiernan *et al.* [1] reported the first observation of the photoexcitation of the lowest $2s^2 2p\ ^2P^o$ resonance "A" at 142.3 eV utilizing the dual laser plasma technique, and subsequently a preliminary report was made on the observation of some higher-lying resonances [2]. Here we report the exploration and analysis of numerous new higher-lying resonances measured by the total photoion yield method, and also study the $2s^2 2p$ A resonance by the photoion time-of-flight (TOF) method.

Brief summaries of prior studies of doubly and triply excited states in $H^-, He, Li^+; H^{2-}, He^-, Li, \ldots$, are given in Ref. [1], and in a paper on electron-impact ionization of Li^+ which reports resonant capture of the incident electron accompanied by double core excitation [3]. We note that in Refs. [1,3], and others quoted therein, the term "triply excited" came into general usage, though in fact the states so far observed are doubly core excited, with at least one electron still present in an $n = 2$ orbital (one profoundly altered, however, by the extreme change in shielding). Triply excited refers to a hollow atom in which three electrons occupy excited states, to distinguish it from a doubly excited two-electron atom.

Our experiments were done at the 2.5 GeV positron storage ring of the Photon Factory. We use the bending magnet beamline BL3B, employing a 24 m spherical grating monochromator [4] with a 1800 lines/mm laminar grating. Symmetric slit widths of 200 μm provided a resolution of $\approx$0.1 eV over the $h\nu$ region of interest. A TOF analyzer combined with an effusive metal vapor oven described previously [5] was used. Photoions were extracted in a dc field and detected with the microchannel plate at the end of the drift tube as the monochromator was scanned. The $h\nu$ scale was calibrated with Ar, Kr, and Xe resonances and the estimated accuracy is $\pm$0.1 eV absolute ($\pm$0.03 eV relative).

In the photoion yield spectrum in Fig. 1, a particularly conspicuous feature is the "F" resonance at 152.32 eV whose strength is comparable to that of the $2s^2 2p$ A resonance. Several weaker peaks are clustered in the vicinity of F. At higher energies, a few small peaks are found around the "M" resonance at 161.59 eV. The most striking aspect of the spectrum is the *complete absence of any identifiable Rydberg series structure,* since even He double photoexcitation [6] as well as Li double photoexcitation [7] still retain recognizable Rydberg character.

We performed multiconfiguration Dirac-Fock (MCDF) calculations utilizing the general purpose atomic structure program [8] (GRASP). The following procedure was devised for this system. (1) Hollow atom configurations, 198 in total with three electrons occupying three among the $2s$, $3s$, $4s$, $5s$, $2p$, $3p$, $4p$, $5p$, and $3d$ orbitals, were optimized by the MCDF procedure with the average level (AL) option. (2) Next, the ground state was optimized with an additional 24 configurations including core filled $1s^2 2s$, $1s^2 3s$, etc. and singly core excited $1s2s^2$, $1s2s3s$, etc., while keeping the higher-lying orbitals frozen to maintain their hollow atom character. (3) All configurations, 222 in total, were optimized with the AL option while keeping the $1s$ orbitals frozen. (4) The second and third steps were iterated a few times until good stabilization of the results was obtained. By this procedure, we obtained a unique set of orthonormal atomic orbital wave functions common to both the ground state and the hollow atomic states, maintaining the hollow atomic character in the excited atomic orbital functions.

Comparison of measurements and calculations is presented in Table I and Fig. 1. The calculated energies were found to have a systematic shift to lower energies com-

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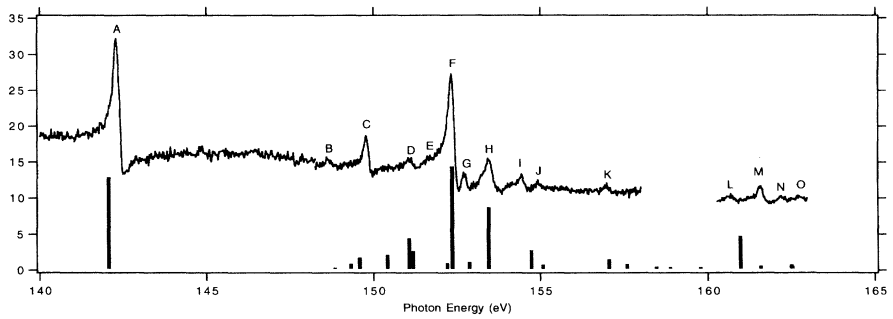

FIG. 1. Hollow Li resonances as a function of photon energy. The vertical scale represents total photoion yield normalized by photon flux, with the subtraction of a slope obtained by visual inspection. The bar diagram overlaid indicates energy positions and relative intensities obtained by MCDF calculations. Calculated energy positions in this figure have 0.4 eV added to compensate for the systematic shift mentioned in the text.

pared to experimental results. This is attributed mostly to a ground state energy shift, caused by the inclusion of $n > 1$ orbitals optimized exclusively to the hollow atomic states, in the ground state expansion. Dominant ground state configurations were found to be $1s^22s$ (41.76%), $1s^23s$ (56.35%), $1s^24s$ (0.37%), $1s^25s$ (0.17%), $1s2s^2$ (0.37%), and $1s2s3s$ (1.01%). The calculations reproduce most features of the experimental spectrum well, although agreements are not necessarily good in the details, with positions of some higher resonances off by as much as 1 eV. A simple interpretation of the spectrum can be made by the "intensity borrowing" model based on configuration mixing in both the ground state and excited states. Hollow atom states can be formed by single-electron $1s \rightarrow np$ transitions from the small components of single core excited configurations mixed in the ground state. For example, a $2s^22p$ hollow atom state can be formed by a single core-electron excitation from the $1s2s^2$ configuration mixed by 0.37% in the ground state, and $2s2p3s$ from $1s2s3s$ mixed by 1%. Note that the $1s2s3s$ population is considerably greater than the $1s2s^2$ population. This can be understood since the orbital wave functions with $n > 1$ were optimized to have a strong hollow atomic character and are severely shrunk by the significantly reduced shielding of the nuclear charge. This results in the hollow atomic $3s$ orbital having a greater overlap with the normal ground state $2s$ orbital than the hollow atomic $2s$ orbital. Our calculations show that the mean radius of the hollow atomic $2s$ orbital is only 2.21 a.u. compared to 5.32 a.u.

TABLE I. Measured resonances compared with MCDF calculations. The E_0 value for A resonance was obtained by a Fano profile fit, while peak maximum positions are presented for other resonances. The experimental $h\nu$ scale has absolute and relative accuracies of ± 0.1 and ± 0.03 eV, respectively.

Resonance	E_0 (eV) Expt.	E_0 (eV) MCDF	Oscillator strength MCDF	Dominant configuration admixtures (in %) in the excited states			
A	142.35	141.657	1.293 46	74 $2s^22p$,	12 $2p^3$,	8 $2s2p3s$	
B	148.7	148.439	0.032 299 8	30 $2p^3$,	15 $2s^23p$,	14 $2p^23p$,	14 $2s2p3s$
		148.92	0.085 023 6	40 $2s^24p$,	13 $2p^23p$,	12 $2p^24p$	
		149.187	0.178 457	36 $2s2p4s$,	20 $2s^24p$,	10 $2s^25p$	
C	149.79	150.008	0.213 238	65 $2s2p5s$,	20 $2s2p4s$		
$D1$	151.10	150.665	0.441 158	36 $2s2p3d$,	20 $2s2p5s$,	12 $2s2p3s$	
$D2$		150.789	0.264 139	50 $2s2p3d$,	16 $2p^23p$		
E	151.7	151.805	0.101 476	56 $2p^24p$,	28 $2p^23p$,	9 $2s2p3s$	
F	152.32	151.955	1.444 77	40 $2s2p3s$,	29 $2p^23p$,	25 $2p^24p$	
G	152.72	152.47	0.111 862	83 $2p^25p$,	9 $2p^24p$		
H	153.43	153.042	0.874 026	37 $2p^23p$,	29 $2s2p3s$,	13 $2p^24p$,	11 $2p^25p$
I	154.43	154.32	0.275 326	40 $2s2p3d$,	26 $2s2p4s$,	12 $2s2p5s$	
J	155.0	154.668	0.074 214 9	85 $2s2p5s$			
K	157.0	156.644	0.150 73	35 $2p^23p$,	21 $2p^3$,	12 $2s2p3s$	
		157.176	0.083 625 5	44 $2p^23p$,	16 $2p^24p$,	13 $2s^23p$	
L	160.6	159.367	0.041 475 7	40 $2s3s3p$,	31 $2p3s^2$,	19 $2p3p^2$	
M	161.59	160.567	0.477 756	35 $2p3p^2$,	33 $2p3s^2$,	23 $2s3s3p$	
N	162.2	161.171	0.056 383 5	44 $2p3p^2$,	22 $2p3s3d$,	12 $2s3s3p$,	12 $2s3p3d$
$O1$	162.7	162.091	0.073 798	25 $2s3p4s$,	23 $2p3s4s$,	16 $2p3s3d$,	12 $2p3p^2$
$O2$		162.132	0.053 637 2	25 $2p3s4s$,	22 $2s3p4s$,	17 $2p3d^2$,	13 $2p3p^2$

for the normal ground state $2s$ orbital. Meanwhile, the hollow atomic $3s$ orbital with 5.94 a.u. mean radius almost coincides with the normal ground state $2s$ orbital. One might then expect a $2s2p3s$ resonance several times stronger than the $2s^22p$ A resonance. This proves not to be the case due to massive configuration mixing among the excited states. In fact, for many of the higher resonances, it is hard to assign any dominant configuration. Regular Rydberg series structures in the spectrum cannot possibly be formed, under this situation. The $2s2p3s$ configuration is found to be distributed among three excited states, constituting 40% of F, 29% of H, and 12% of K. For the A excited state, the $2s^22p$ configuration is dominant (74%). The transition rates can be described as the product of dipole transition probability of the one-electron $1s \rightarrow 2p$ transition, the population in the ground state $|GS\rangle$ and the population in the excited state. For resonances A and F,

$$|\langle A|r|GS\rangle|^2 = 0.0037 \times 0.74 \times |\langle 2s^2|2s^2\rangle\langle 2p|r|1s\rangle|^2 + 0.01 \times 0.08 \times |\langle 2s3s|2s3s\rangle\langle 2p|r|1s\rangle|^2,$$

$$|\langle F|r|GS\rangle|^2 = 0.01 \times 0.40 \times |\langle 2s3s|2s3s\rangle\langle 2p|r|1s\rangle|^2.$$

Since the overlap integrals are equal to unity, the relative intensities of peaks A and F become approximately 7 : 8. It is seen that strong contributions to the intensity of F as well as H and K come from the greater mixing of $1s2s3s$ in the ground state than $1s2s^2$. The calculated intensities in Table I are based on all combinations of configuration mixing and intensity borrowing within the configurations employed in the calculation. Apparently this greater distribution of oscillator strength to some resonances above the first in the series can be considered as a characteristic feature of hollow atom spectra.

Comparison of theory and experiment is not yet completely satisfactory. Larger scale R-matrix or close coupling calculations may have the potential of providing more accurate E_0 values. Still, providing transparent eigenstate descriptions might remain problematic. What may be needed is the formulation of new quantum numbers for these three-electron resonances analogous to those now used [9] to describe the doubly excited states of He.

We report the line shape fit only for the A resonance which is well isolated and decays mostly into a Li^+ final charge state (approximately 97%). We used the Fano formula for an isolated resonance interacting with a single continuum [1,10]

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

folding it with a triangular instrument function of base width 0.16 eV, which characterizes the setup employed [4]. The deconvoluted Fano profile is overlaid with the total photoion yield spectrum on Fig. 2(a). The energy position E_0, the width Γ, and the profile index q were in agreement within error limits to Kiernan *et al.* [1]. Also,

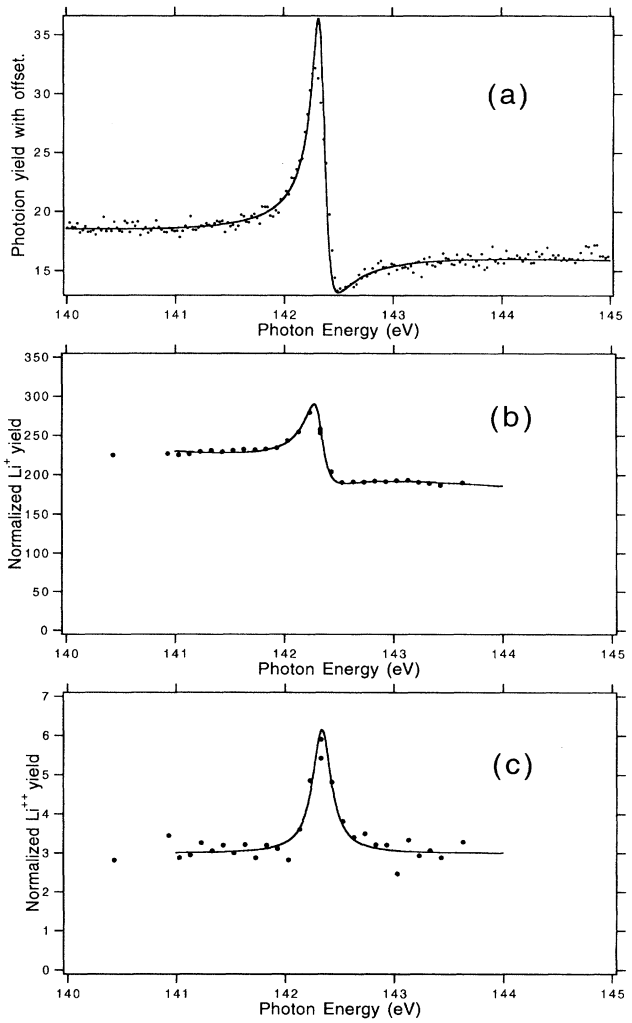

FIG. 2. (a) The $2s^22p$ A resonance in the total photoion yield spectrum with the unfolded Fano profile fit. The vertical scale is the same as in Fig. 1. (b) The A resonance in the Li^+ channel obtained by the TOF method, with the unfolded Fano profile fit. The vertical scale represents counts normalized with photon flux and the base-line level of the spectrum should represent direct single photoionization. (c) The A resonance in the Li^{2+} channel with the unfolded Lorentzian fit. The vertical scale unit is the same as that of the Li^+ channel in (b).

the E_0 agrees very well with the value of 142.261 eV determined by Chung [11], who used the saddle point technique to calculate triple L shell (222) excitations. Time-of-flight charge state resolved spectra over some of the resonances were taken with the TOF apparatus operated in the pulsed extraction mode. The Li^+ yield and Li^{2+} yield spectra over the A resonance are shown in Figs. 2(b) and 2(c), overlaid with unfolded Fano and Lorentzian profiles. The fit results are summarized in Table II. The ratio of peak heights in the Li^{2+} and Li^+ channels for higher resonances was found to rise by a factor of

TABLE II. Line-shape parameters for the $2s^2 2p$ A resonance in the total photoion yield channel, dual laser plasma (DLP) results by Kiernan *et al.* [1], Li^+ channel, and Li^{2+} channel.

Data type	Fit type	E_0 (eV)	Γ	q
Photoion yield	Fano	142.35	0.15 (2)	−2.2 (1)
Absorption (DLP)[a]	Fano	142.32	0.20 (4)	−2.2 (6)
Li^+ (TOF)/$h\nu$	Fano	142.33	0.20 (4)	−2.0 (5)
Li^{2+} (TOF)/$h\nu$	Lorentzian	142.34	0.20 (4)	N/A

[a]Reference [1].

≈40, starting from approximately 0.03 at A. This radical change is attributed to the sequential opening of channels for two-step autoionization to Li^{2+}, via a first-step decay to a growing succession of doubly excited Li^{+*} states which become progressively available as $h\nu$ is raised through various Li^{+*} thresholds, in a manner similar to cases previously found in Ba and other atoms [12]. The lowest doubly excited state $[(2,2a)\,^1S_0]$ has been placed theoretically at 151.72 eV [9] and 151.53 eV [13], and experimentally [14] at 151.6 eV. Ten more Li^{+*} limits [13,14] of the $(2,2a)$, $(2,2b)$, $(2,3a)$, and $(2,3b)$ types fall between 152.4 and 165.1 eV. However, for the lowest $2s^2 2p$ A resonance, the peak in the Li^{2+} channel must come solely from one-step double autoionization since it is below the lowest doubly excited Li^{+*} threshold. To our knowledge, this is the first observation of pure one-step double autoionization, free from interference with one-step double photoionization. The peak has a symmetric appearance within the noise and resolution limits, unlike the pronounced Fano-type asymmetry seen in the Li^+ channel or total photoion yield spectrum. This is attributed to the weakness of the direct double photoionization channel, insufficient to cause enough interference effect to manifest conspicuously in the line-shape asymmetry. The TOF spectra at 130 eV indicates that the direct double to direct single photoionization ratio is approximately (1.3 ± 0.3)%.

The present work suggests that studies of three-electron hollow atom resonances in a manner paralleling the rich development of predecessor studies of doubly excited heliumlike species is likely to provide fertile ground for future experimental and theoretical work.

We thank the Photon Factory staff for the stable operation of the storage ring. I. A. S. thanks MONBUSHO for visiting fellow support. We are indebted to J. W. Cooper for communicating his preliminary MCHF calculation [15] and for many helpful comments and advice. This work was supported in part by the U.S. National Science Foundation.

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