

## Identification of Bound States of Core-Excited Negative Lithium Atoms in Beam-Foil Experiments

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Configuration-interaction calculations show the existence of bound  $\text{Li}^-(1s2s2p^2)^5P$  and  $\text{Li}^-(1s2p^3)^5S^\circ$  states lying 56.910 and 60.460 eV above the Li ground state, respectively. The  $^5S^\circ$  state decays into the  $^5P$  state with  $\lambda = 3489.5 \pm 1.1 \text{ \AA}$  and  $\tau = 2.86 \pm 0.10 \text{ nsec}$ . Experimental and theoretical evidence about an unclassified, cascade-free, medium-intensity line with  $\lambda = 3489.7 \pm 0.2 \text{ \AA}$  and  $\tau = 2.9 \pm 0.2 \text{ nsec}$  in the beam-foil spectra of doubly excited lithium strongly suggests the presence of core-excited  $\text{Li}^-$  ions in the beam-foil source.

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This Letter reports for the first time (i) the existence of two bound states of core-excited negative lithium, (ii) an electric dipole transition between bound states of a negative ion, and (iii) its occurrence in the beam-foil source.

The bound states of core-excited negative ions are metastable against autoionization. Therefore, they should occur below the onset of the continuum with the same  $L-S$  symmetry and parity.<sup>1</sup> Neutral Li has a system of bound quartet states whose first two members are  $\text{Li}(1s2s2p)^4P^\circ$ , lying<sup>2</sup> 57.410 eV above the Li  $1s^22s$  ground state, and  $\text{Li}(1s2p^2)^4P$ , lying at 60.747 eV.<sup>2</sup> We have found  $\text{Li}^-(1s2s2p^2)^5P$  about 500 meV below  $\text{Li}(1s2s2p)^4P^\circ$  and  $\text{Li}^-(1s2p^3)^5S^\circ$  about 287 meV below  $\text{Li}(1s2p^2)^4P$ .

The calculations announced here will be pre-

sented in detail elsewhere<sup>3</sup> in a paper which discusses all possible long-lived<sup>4</sup> negative lithium ions and their binding energies. I find accurate approximations to the eigenvalues of Schrödinger's nonrelativistic equation for bound states by means of configuration-interaction (CI) expansions<sup>5</sup> based on (i) energy-optimized Slater-type orbitals (STO's), (ii) four-electron  $L-S$  eigenfunctions, and (iii) the consideration of STO truncation errors  $\Delta E_{\text{STO}}$  and CI truncation errors  $\Delta E_{\text{CI}}$ . Relativistic, radiative, and mass-polarization corrections to transition energies are small but not negligible.<sup>2</sup> I assume that they are equal to those in  $\text{Li}^+(1s2s)^3S$  and  $\text{Li}^+(1s2p)^3P$  for  $\text{Li}^-(1s2s2p)^5P$  and  $\text{Li}^-(1s2p^3)^5S^\circ$ , respectively.

In Table I, I collect the calculated nonrelativistic energies for the  $^5P$  and  $^5S^\circ$  bound states of  $\text{Li}^-$ .

TABLE I. Nonrelativistic energies for the bound core-excited states of negative lithium, in atomic units for Li; approximate relativistic, radiative, and mass polarization corrections,  $E_{\text{rrmp}}$ ; wavelength, oscillator strength, and mean lifetime for the  $^5S^\circ \rightarrow ^5P$  decay. 1 a.u. ( $^7\text{Li}$ ) = 219 457.48  $\text{cm}^{-1}$ .

	$\text{Li}^-(1s2s2p^2)^5P^a$	$\text{Li}^-(1s2p^3)^5S^\circ{}^b$
$E_u$	-5.386 346	-5.255 890
$\Delta E_{\text{CI}}$	-0.000 040(5)	-0.000 009(1)
$\Delta E_{\text{STO}}$	-0.000 093(36) <sup>c</sup>	-0.000 081(39) <sup>c</sup>
$E_{\text{nr}}$	-5.386 479(41)	-5.255 980(40)
$E_{\text{rrmp}}$	-0.000 538 <sup>d</sup>	-0.000 493 <sup>e</sup>
$E$	-5.387 017(41)	-5.256 473(40)
$\Delta E_{\text{nr}} = 0.130 499 = 28 639.0 \text{ cm}^{-1}$	$\lambda_{\text{vac}} = 3491.7 \pm 1.1 \text{ \AA}$	$\lambda_{\text{air}} = 3490.7 \pm 1.1 \text{ \AA}$
$\Delta E = 0.130 544 = 28 649.2 \text{ cm}^{-1}$	$\lambda_{\text{vac}} = 3490.5 \pm 1.1 \text{ \AA}$	$\lambda_{\text{air}} = 3489.5 \pm 1.1 \text{ \AA}$
	$f = 0.212 \pm 0.006$	$\tau = 2.86 \pm 0.10 \text{ nsec}$

<sup>a</sup>An energy-optimized  $7s7p5d4f2g1h$  STO basis is used.

<sup>b</sup>An energy-optimized  $4s7p6d4f2g1h$  STO basis is used.

<sup>c</sup>These estimates might still be somewhat lower, but that should not affect energy differences.

<sup>d</sup>For  $\text{Li}^+(1s2s)^3S$ , taken from Ref. 2.

<sup>e</sup>For  $\text{Li}^+(1s2p)^3P$ , taken from Ref. 2.

The energy upper bounds  $E_u$  are rigorous eigenvalues of truncated CI expansions of about 300 terms. The truncation errors  $\Delta E_{CI}$  are computed as usual<sup>5</sup> whereas the STO truncation errors are calculated as explained in Ref. 3. We see that relativistic, radiative, and mass-polarization corrections to the transition energies are within the uncertainties in the nonrelativistic calculations. Also in Table I, I give the oscillator strength for the corresponding  ${}^5S^\circ \rightarrow {}^5P$  decay. The estimated uncertainty in the  $f$  value and in  $\tau$  takes into account an error analysis<sup>6</sup> which makes use of the length, velocity, and acceleration forms of the  $f$  value. The calculations predict the  $E1$  decay of  $\text{Li}^-(1s2p^3) {}^5S^\circ$  into  $\text{Li}^-(1s2s2p^2) {}^5P$  with  $\lambda = 3489.5 \pm 1.1 \text{ \AA}$ . Since the negative ions have very extended charge distributions, one might expect unusually large oscillator strengths and consequently very short mean lifetimes. Surprisingly, this is not the case, the mean lifetime for the  $E1$  decay of  ${}^5S^\circ$  being  $\tau = 2.86 \pm 0.10$  nsec. Decay of  $\text{Li}^- {}^5S^\circ$  into the  ${}^5S^\circ$  and  ${}^5P^\circ$  continuum is also possible; see Fig. 1. This radiative autoionization is probably one order of magnitude less frequent than the  $E1$  decay.<sup>9</sup>

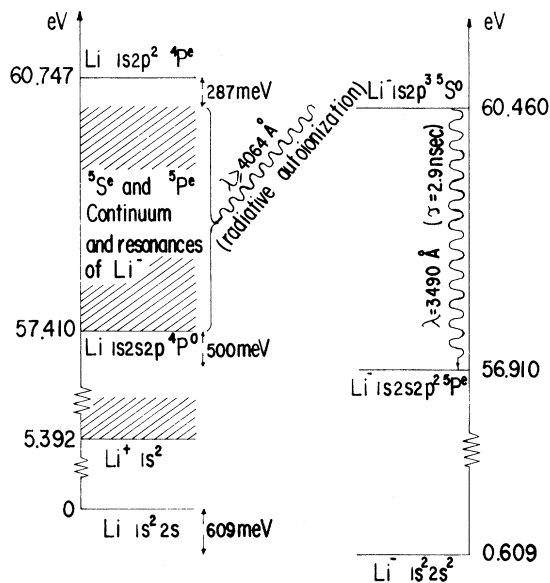
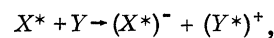
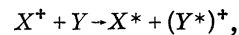


FIG. 1. Energy diagram of bound  $\text{Li}^-$  ions and photo-dissociation thresholds. The electron affinity of  $\text{Li } 1s^2 2s$  is from Sims *et al.* (Ref. 7); the ionization potential is from Moore (Ref. 8), slightly corrected in the light of the most recent values for the fundamental constants. The absolute term values of  $\text{Li}(1s2s2p)^4 P^0$  and  $\text{Li}(1s2p^3)^4 P$  are from Ref. 2 and the other ones are from Ref. 3.

It has been shown<sup>3</sup> that  $\text{Li}^-(1s2s2p^2) {}^5P$ ,  $\text{Li}^-(1s2p^3) {}^5S^\circ$ , and the ground state  $\text{Li}^- 1s^2 2s^2$  are the *only* bound states of negative lithium. This datum clearly sets constraints to the possibilities of occurrence of long-lived  $\text{Li}^-$  ions in various kinds of experiments.

Although relatively intense beams of  $\text{Li}^-$  have been produced for a number of years<sup>10</sup> the possible presence of  $\text{Li}^-$  in states other than  $1s^2 2s^2$  has not been investigated. One would expect bound-state core-excited  $(X^*)^-$  ions to be formed from  $X^+$  ion beams by a two-step charge-exchange process,



analogous to the one established by Collins and Stroud<sup>11</sup> for the formation of metastable  $\text{He}^-$ . In support of the above, Nikolaev *et al.*<sup>12</sup> found that core-excited neutral Li is formed more readily in the passage of Li ions through a thin gas target when  $\text{Li}^{+2}$  rather than  $\text{Li}^+$  is used in the colliding beam. Unfortunately, neither the presence of  $\text{Li}^-$  nor the light emitted from the collision chamber was investigated<sup>10</sup> when  $\text{Li}^+$  beams were used. Double electron capture by positive ions seems to be a less efficient mechanism.<sup>13</sup>

The beam-foil source offers another possibility to search for bound states of  $\text{Li}^-$ . (Negative ions were never observed in beam-foil experiments, probably because it was not known that they could emit photons.) One would expect  $\text{Li}^-(1s2p^3) {}^5S^\circ$  to have an excitation function<sup>14</sup> similar to the one for the quartets of neutral Li, so that the  $\lambda = 3490 \text{ } {}^5S^\circ \rightarrow {}^5P$  transition should be observed together with the more profuse transitions in the doubly excited  $\text{Li}^{**}$  system. Fortunately, the  $\text{Li}^{**}$  spectra are among the most thoroughly studied both by theory and by experiment.

In the beam-foil spectra of  $\text{Li}^{**}$  there is a medium-intensity line<sup>15,16</sup> with  $\lambda = 3489.7 \pm 0.2 \text{ \AA}$  (Ref. 17) which has defied a conclusive explanation so far. The 3490 line was first attributed<sup>15</sup> to the transition  $\text{Li}(1s2p3p)^4 P \rightarrow \text{Li}(1s2s3p)^4 P^\circ$  in view of calculations<sup>18</sup> which in this particular instance proved to be wrong.<sup>19,20</sup> Recently<sup>21</sup> this line has been reassigned to the transition  $\text{Li}((1s2p)^3 P - 3d)^2 D^\circ \rightarrow \text{Li}(1s2p^2)^2 P$ . Very accurate calculations<sup>22</sup> of transitions between doubly excited doublets in neutral Li, however, show that the latter transition occurs at 3662  $\text{\AA}$ , in agreement

with an earlier<sup>23</sup> classification. Moreover, the calculations of the doublet Li\*\* system do not predict<sup>22</sup> a medium-intensity<sup>17</sup> line near 3490 Å. Similar conclusions may be drawn from an analysis of known transitions<sup>17</sup> and further calculations<sup>24</sup> on  $^4P^\circ$  and  $^4P^e$  excited states. Triply excited Li probably has a negligible excitation function in the 56–300-keV range of the Li<sup>+</sup> beams (used to produce Li\*\* spectra), since the prominent transition  $\text{Li}(2p^3)^4S^\circ \rightarrow \text{Li}(2s2p^2)^4P^e$ , which should occur<sup>24</sup> around  $\lambda = 3200$  Å and is expected to have an appreciable natural width, has not been observed in Li\*\* spectra. In other words, the observed 3490 line is too intense to escape classification within the present<sup>17,22,24</sup> knowledge of Li\*\* energy levels.

Ten years ago, Berry *et al.*<sup>25</sup> observed that the excitation function for the 3490 line was almost identical to the one for the 2934 line which corresponds to the decay of the lowest  $^4S$  state of Li\*\*. Shortly thereafter, Berry *et al.*<sup>26</sup> measured the mean lifetime of the level emitting the 3490 line. They found  $\tau = 2.9 \pm 0.2$  nsec, in good agreement with my  $\tau = 2.86 \pm 0.10$  nsec for the  $\text{Li}^-(^5S^\circ \rightarrow ^5P)$  transition. Moreover, they found a replenishment ratio of 0.00, which is an indication that no cascades from upper levels were present. This is precisely what one expects for the  $\text{Li}^-(^5S^\circ \rightarrow ^5P)$  transition, since there are no Li<sup>-</sup> upper states which can populate  $\text{Li}^-(^5S^\circ)$ , except through the highly improbable<sup>27</sup> free-bound transitions which are further minimized in the conditions of the beam foil experiments. I therefore conclude that the 3490 line observed in the beam foil source is due to the  $\text{Li}^-(^5S^\circ \rightarrow ^5P)$  transition. In this respect, direct experimental evidence could be obtained by placing an electric field after the foil<sup>28</sup> and recording spectra with and without field. It should then be possible to detect transitions between bound states of other negative ions, such as those occurring in other alkali and alkali-earth atoms,<sup>3</sup> and possibly in the chalcogens and in the halogens.

If produced in good yield, metastable  $\text{Li}^-(1s-2s2p^2)^5P$  ions may provide an alternative to Harris's recent proposal<sup>29</sup> for an x-ray "laser." Instead of using  $\text{Li}(1s2s2p)^4P^\circ$  as an energy reservoir, one might use  $\text{Li}^-(^5P)$  ions, which live considerably longer<sup>3</sup> and can be stored in a ring, before undergoing photodissociation (by an impinging dye laser tuned to  $\lambda = 2636$  Å) into the  $\text{Li}(1s2p^2)^2P$  laser state.

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## Cooperative Relaxation in Coherently Pumped Three-Level Systems

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The behavior of a large number of coherently pumped three-level systems coupled to two resonant cavity modes at the two respective intermediate frequencies is shown to be qualitatively different from conventional laser-type behavior. The existence of three steady states and the dependence of their stability on the operating conditions allows the production of steady, modulated, or pulsed excitation of both modes.

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Coherent pumping of lasers (by other lasers) has become common practice, and pump lasers are available in a wide range of frequencies. The operation of a three-level laser depends both on induced emission at one intermediate frequency and on incoherent relaxation at the other. These two processes may be regarded as cooperative and noncooperative relaxation, respectively. It is the present purpose to analyze a novel and interesting type of possible behavior—qualitatively different from conventional laser-type behavior—in which the three-level atomic systems (hereafter referred to as “molecules”) undergo cooperative relaxation at *both* intermediate frequencies. This may be accomplished by letting molecules for which all three transitions couple to the electromagnetic field interact with two (lossy) cavity modes tuned to the two respective intermediate frequencies. Labeling the three molecular energy levels in ascending order by  $\hbar\omega_i$ ,  $i=1, 2, 3$ , we consider a model in which  $N$  identical molecules are coupled to two modes with respective frequencies  $\omega_{12}$ ,  $\omega_{23}$ , and pumped at frequency  $\omega_{13}$ , where  $\omega_{ij} = |\omega_i - \omega_j|$ . While such coupling, in accordance with well-known selection rules, may be too weak in most atomic systems to produce the present effects, there exist atoms and molecules for which forbidden lines or overtones are sufficiently strong (such as the OCS molecule<sup>1</sup>) or for which two-photon pumping may be possible. The present discussion is not necessarily restricted to optical or infrared frequencies but is also applicable to microwave frequencies.<sup>2</sup>

In order to exhibit most simply the new feature,

we introduce the idealizations that the coupling strength between molecule and mode depends only on the mode, and that transitions other than those due to induced emission are negligible. The former is used widely in analyses of cooperative phenomena,<sup>3</sup> and the latter will be discussed further. We use a formalism which is especially suitable for the analysis of cooperative phenomena and can be read directly both quantum mechanically and classically.<sup>4,5</sup> The atomic equations of motion, in the rotating-wave approximation, are given in this formalism by

$$\begin{aligned}\dot{A}_1 &= \omega A_3 - i\gamma_{12} B_{12}^\dagger A_2, \\ \dot{A}_2 &= -i\gamma_{23} B_{23}^\dagger A_3 - i\gamma_{12} A_1 B_{12}, \\ \dot{A}_3 &= -\omega A_1 - i\gamma_{23} A_2 B_{23}.\end{aligned}$$

Briefly, the  $A$ 's and  $B$ 's are the variables that describe the collection of molecules and the cavity fields, respectively, and are related to  $a_i$  ( $a_i^\dagger$ ), the annihilation (creation) operator of atoms in the  $i$ th level, and to  $b_{ij}$  ( $b_{ij}^\dagger$ ), annihilation (creation) operators of photons in the  $ij$  mode, respectively, by  $a_j = A_j \exp(-i\omega_j t)$ ,  $b_{jk} = B_{jk} \times \exp(-i\omega_{jk} t)$ ;  $\omega$  refers to the pump field,  $2\omega$  being the Rabi frequency of the (1, 3) pair of levels, and the  $\gamma$ 's are real coupling constants.<sup>6</sup> The equations are consistent with the normalization  $\sum A_i^\dagger A_i = N$ . Since our interest lies in macroscopic phenomena, with  $N$  large, the classical description is a good approximation under most conditions,<sup>4</sup> and will be used henceforth. We consider only the case of sufficiently damped cavity modes so that the fields follow the respective resonant polarizations adiabatically, as expressed