

Radiation from the Negative Lithium Ion

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It is confirmed that the 3489-Å transition observed in beam-foil excited lithium spectra originates from the negative lithium ion. It is most probably the transition $1s2s2p^2\ ^5P - 1s2p^3\ ^5S^o$, as suggested by Bunge. A new electric field acceleration technique provides identification of the charge state of the emitting ion. The decay curve is a cascade-free single exponential. The polarization and beam energy dependence of the light yield have also been measured. The transition has been identified in heavier isoelectronic ions.

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We have verified the recent suggestion by Bunge¹ of a radiative transition between core-excited bound states in the Li^- ion. This is the first time that observed line radiation has been ascribed to a negative ion.

Since negative ions have only a finite number of bound states, in contrast to neutrals and positive ions, the possibilities for radiative transitions are limited. Additionally, most of their multiply excited states (Feshbach resonances) decay rapidly through autoionization processes. Thus, in H^-

and He^- a number of electron resonances² have been observed, notably the recent H^- photodetachment work of Bryant *et al.*³ H^- continuum absorption does not involve bound final states, but consists of bound-free transitions.⁴ However, some states in Li^- with all four electron spins aligned are metastable (in the Coulomb approximation) against autoionization. Similar long-lived states might also exist in heavier negative ions such as the alkalis. However, to our knowledge, no radiative emission has ever been identified from

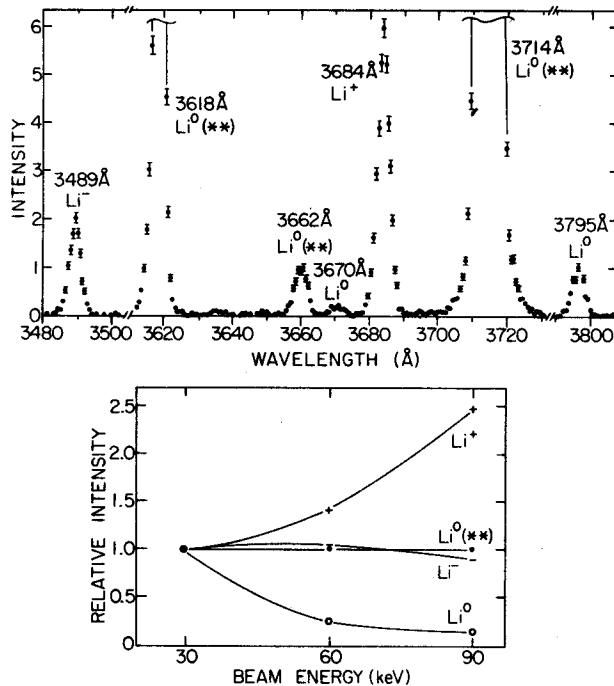


FIG. 1. Lithium spectrum (upper half), 90-keV beam energy, 1.90 mm from foil, used to obtain relative light yields from Li^- , Li^0 , Li^{0**} , and Li^+ excited states as a function of beam energy (lower half). The yields of Li^{0**} have been normalized to 1.0 at each energy.

such negative ions.

Bunge¹ suggested that the 3489-Å line observed in many lithium beam-foil spectra⁵ is the transition $1s2s2p^2\ ^5P-1s2p^3\ ^5S^0$ of Li^- . Even though the theoretical precision claimed by Bunge appears to identify the transition, the lithium spectrum in this region is complicated. Other identifications of both this line and nearby transitions (see Fig. 1) have been made in the doubly excited neutral-lithium quartet system, and a number of these identifications remain uncertain.⁶ Hence a conclusive identification needs to be made.

We made several preliminary test measurements of the 3489-Å transition. As the charge state of this transition is different from all of the other identified transitions, it might be expected that its excitation function with projectile velocity might also be different. Hence, we obtained spectra as in Fig. 1 for three different beam energies (30, 60, and 90 keV) at three separate decay lengths (1.90, 3.48, and 5.06 mm) after foil excitation. The intensities extrapolated to the time of excitation (Fig. 1) show that each of the three transitions of doubly excited neutral lithium (Li^{0**}) and the 3489-Å line have the same projectile velocity dependence, and are distinctly dif-

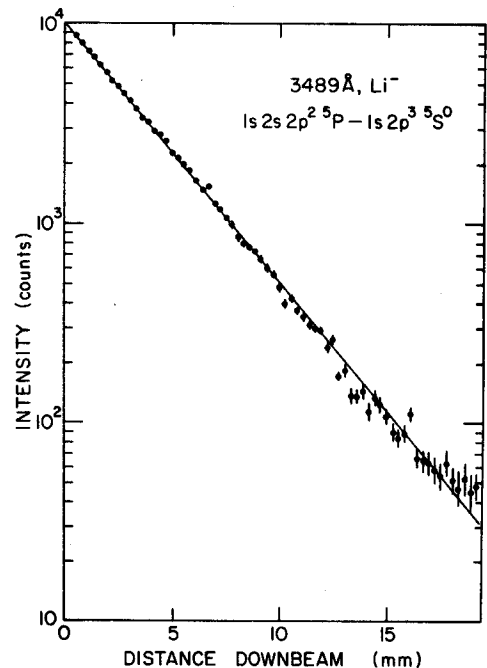


FIG. 2. Experimental decay curve of the 3489-Å decay.

ferent from the Li^+ and singly excited Li^0 transitions. From these results alone it is not surprising that previous work⁶ had identified the 3489-Å transition as a Li^{0**} transition. However, Bunge expects similar excitation functions for Li^- quintets as for Li^0 quartets.

The Li^- transition is predicted to be from a $^5S_2^0$ state, which has spherical symmetry and hence should have zero orbital alignment or orientation. This was verified by measuring the circular polarization fraction S to be zero for the 3489-Å line when excited by a carbon foil tilted at 50° to the beam axis. We found $S = (0.1 \pm 0.5)\%$, whereas for the two Li^{0**} transitions, 3714 and 3618 Å, we found $S = (2.8 \pm 0.1)\%$ and $(1.2 \pm 0.3)\%$, respectively.

As the $1s2p^3\ ^5S^0$ state is the most energetic predicted bound state¹ of Li^- , this transition should be rigorously cascade-free—a case unique in beam-foil excitation. This has been observed, and Fig. 2 shows a single exponential decay. (Approximately twelve counts of photomultiplier dark current have been subtracted from each point.) From just the observation of a single exponential one cannot unambiguously conclude that the decay is cascade-free. However, had the decay not been a single exponential (and most beam-foil decay curves appear multiexponential) the proposed assignment would have been proven incorrect.

While some of the above tests agree with the prediction of Bunge,¹ definitive evidence has been obtained by applying an accelerating (and retarding) electric field parallel (and antiparallel) to the beam after foil excitation. Bunge¹ suggested the use of a perpendicular field, but this is a difficult technique for such a short decay time.

For an uncascaded decay curve of lifetime τ , the intensity of light I , detected along a uniformly viewed segment Δx of beam of instantaneous velocity v , at time t since excitation, is given by

$$I = Ce^{-t/\tau} \sinh(\Delta x/2v\tau). \tag{1}$$

A uniform electric field is applied parallel to the beam just downstream from the foil, by use of field plates with a potential difference V_F and

a spacing s_F . In this case, t and v are given in terms of the foil emergent velocity v_0 and the downbeam distance x from the foil by

$$t = [(1 + x/x_F)^{-1/2} - 1](2x_F/v_0), \tag{2}$$

$$v = v_0(1 + x/x_F)^{1/2}. \tag{3}$$

Here, x_F is the distance which would be required for this field to accelerate the ion from rest to v_0 , and characterizes the field strength. For a foil emergent ion of charge state Z which has an energy corresponding to an accelerator terminal voltage V_0 , x_F is given by

$$x_F = V_0 s_F / Z V_F. \tag{4}$$

In terms of these quantities, the ratio of the field-on to field-off intensities becomes

$$I(V_F)/I(0) = \exp\{-[(1 + x/x_F)^{1/2} - 1 - x/2x_F](2x_F/v_0\tau)\} \sinh[\Delta x/2v_0\tau(1 + x/x_F)^{1/2}] / \sinh(\Delta x/2v_0\tau). \tag{5}$$

For $\Delta x \ll 2v_0\tau$ and $x < 6v_0\tau \ll x_F$, Eq. (5) can be very accurately represented by a low-order power expansion, in terms of which the difference between field-reversed measurements is given by

$$[I(V_F) - I(-V_F)]/I(0) = (x/2v_0\tau - 1)x/x_F. \tag{6}$$

(For the Li^- measurement reported here $x \approx 1$ mm, $v_0\tau \approx 3.9$ mm, and $x_F \approx 182$ mm.) Notice that this expression passes through an optimum at the distance $x = v_0\tau$ downbeam and changes signs at the distance $x = 2v_0\tau$ downbeam. This occurs because two competing factors are distorting the exponential decay curve: The acceleration causes a given distance downbeam to correspond to an earlier position on the decay curve [cf. Eq. (2)], but the increased velocity [cf. Eq. (3)] decreases the dwell time of the ion in the viewed region. Since the former depends on τ and the latter does not, their contributions vary along the decay curve.

In the top part of Fig. 3, we show three curves of 3489-Å light using accelerating voltages of ± 4000 and 0 V which show clearly the changes caused by the field. These changes correspond to light emission from negative lithium ions. Each of the three decay curves have been normalized for equal intensity at the foil. The photon counts at each point were collected for a fixed time to avoid stray-field effects associated with beam-charge integration at the Faraday cup. To eliminate spurious results due to long-term foil and beam-current variation, measurements were made at each point with the three field conditions.

Thus, in the lower part of Fig. 3, we compare

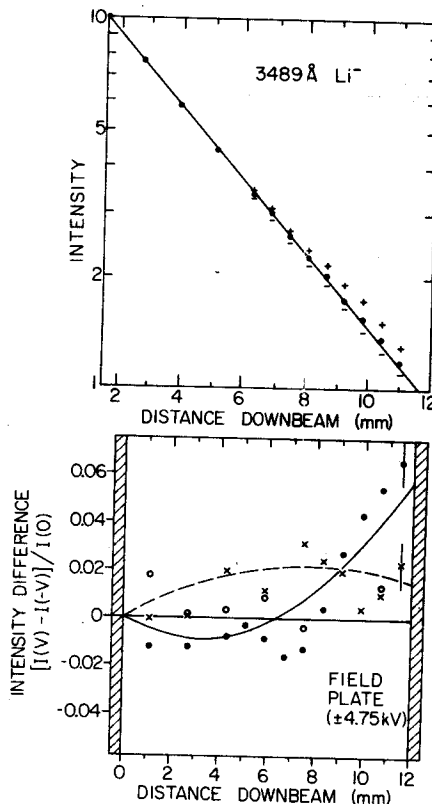


FIG. 3. Decay curves of the 3489-Å decay in zero field (open circles), in accelerating field (plusses), and in retarding field (dash). In the lower half are shown the differences of the field-affected decay curves of 3489 Å (closed circles), 3684 Å (plusses), and 3714 Å (open circles) at 70 keV. The theoretical curves discussed in the text are given by a solid line for Li^- (3489 Å) and a dashed line for Li^+ (3684 Å).

directly the differences in the relative light emission for oppositely applied voltages of ± 4750 V for 3489 (Li⁻), 3684 (Li⁺), and 3714 Å (Li⁰). The "fish-curve" represents the predictions of Eq. (6) [in the exact form of Eq. (5)] with use of measured values for V_0 , V_F , s_F , τ , and Δx for the intensity difference ratio $[I(+V) - I(-V)]/I(0)$. The figure shows clearly the two competing effects for the two charged components, while the neutral component remains unaffected. The dwell-time effect in the observing distance dominates at times less than two natural lifetimes. Thus, the 3684-Å decay from the longer-lived $4p^3P$ Li II state ($\tau = 5.6$ ns)⁷ does not reach the crossover point as does the 3489-Å decay ($\tau = 2.3$ ns) at a distance of about 7.5 mm from the exciter foil. The rapid increase in this ratio beyond the crossover point is very sensitive to the decay time of the transition.

Having verified that the 3489-Å line is a Li⁻ transition, it is interesting to note that we have found the excitation functions of levels in two different charge states to be the same (cf. Fig. 1). Hence, it appears that the excitation energy rather than electron-capture and -loss cross sections is most important in the excitation mechanisms of the beam-foil interaction. Clearly, in this case, an inner-shell 1s electron has been promoted for both the Li⁻ and the Li^{0**} states. The Li⁻ excited-state population is surprisingly high, being comparable to those of many neutral-lithium states (e.g., Fig. 1). However, we roughly estimate the Li⁻ emission to come from less than 10^{-6} of the beam ions. There being only three states of Li⁻, this suggests the negative-charge-state fraction is small. This fraction is unmeasured and thus the ground- to excited-state population ratio is also unknown.

We have made a preliminary search in the spectra along the isoelectronic sequence for the $1s2s2p^2\ ^5P - 1s2p^3\ ^5S^o$ transition. A multiconfiguration Dirac-Fock calculation, similar to one already published⁸ for the Li I-like $1s2s2p\ ^4P^o - 1s2p^2\ ^4P$ transition shows good agreement with the observed wavelengths—Table I. The 1909-Å line identification has been suggested independently by Andersen.⁹ The B II transition previously had an alternative classification,¹⁰ which subsequent work shows may be in error:¹¹ The higher- Z ions have partially resolved fine structure which help to confirm their identification; the F VI transition appears in a spectrum of Knystautas *et al.*¹²

Since submission of this manuscript, we have learned of two independent verifications of the Li⁻

TABLE I. Wavelengths of the $1s2s2p^2\ ^5P - 1s2p^3\ ^5S^o$ transition. The experimental precision is ± 1 Å.

Ion	Theory (Å)	Experiment (Å)
Li ⁻	3489 ^a	3489 ^c
Be I	1821 ^b	1909 ^c
B II	1279 ^b	1324.5 ^d
C III	989 ^b	1015.6 ^e
N IV	807 ^b	825 ^e
O V	682 ^b	695 ^e
F VI	589 ^b	597 ^f
Ne VII	519 ^b	...

^aRef. 1.

^bThis work.

^cH. G. Berry, J. Bromander, I. Martinson, and R. Buchta, *Phys. Scr.* **3**, 63 (1971).

^dRefs. 10 and 11.

^eUnpublished beam-foil spectra from this laboratory.
^fRef. 8.

identification: one by Mannervik, Astner, and Kisielinski¹³ using a similar electric-field technique, and another by Desesquelles¹⁴ using a Doppler-shift technique.

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