Laser Spectroscopy of Metastable Extreme-Ultraviolet Levels in Lithium Atoms and Ions

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An experiment is reported in which an intense laser is used to cause the intercombination transfer of metastable $1s2s2p\,^4P_{5/2}$ atoms to the $1s2p^2\,^2P_{3/2}$ level with subsequent radiation in the extreme ultraviolet, thereby providing the first direct tie between the quartet and doublet manifolds in neutral Li. Intercombination transfer between the triplet and singlet manifolds of Li^+ and tunable anti-Stokes radiation centered near 199 Å are also described.

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Core-excited levels of atomic Li which are metastable against autoionization have been studied for many years.[1-4] The longest lived of these is the quartet level $1s2s2p\,^4P_{5/2}$. Since the spins of the three electrons are aligned, in the absence of a spin-spin interaction, there is no lower configuration into which the atom may decay. This level lies 57.4 eV above the ground state and 52 eV above the $1s^2\,^1S$ ionization potential of the atom, and has a measured lifetime of 5.8 μs. Core-excited levels in the doublet series may also be stable against autoionization. An important example is $1s2p^2\,^2P$ which decays primarily to $1s^22p\,^2P^\circ$ by emission at 207 Å. The high radiative yield is due to the fact that there is no autoionizing decay from this state which conserves L, S, and parity.

Visible spectroscopy using beam-foil excitation has been used extensively to study and to compare with theory the energy levels within the quartet manifold and, to a limited extent, levels within the doublet manifold.[5] However, because of the very small intercombination oscillator strengths between manifolds ($\sim 10^{-8}$) and the rapid decay rates of the doublet states in the extreme ultraviolet (XUV), the relative position of the quartet and doublet manifolds has remained uncertain.

In this Letter we report an experiment in which an intense laser at 2952 Å is used to cause the intercombination transfer of metastable $1s2s2p\,^4P_{5/2}$ atoms to the $1s2p^2\,^2P_{3/2}$, with subsequent radiation in the XUV, thereby providing the first direct tie between the quartet and doublet manifolds.[6] We also report the use of the same apparatus to connect the triplet and singlet manifolds of Li^+ via the laser-induced transition $1s2s\,^3S \rightarrow 1s2p\,^1P$ at 3880.3 Å, with subsequent radiation at 199 Å. Tunable spontaneous anti-Stokes scattering from the $1s2s\,^1S$ ionic level into a 200-cm^{-1} range centered at 199.3 Å is also described. In each of these measurements, population was stored in a metastable level near 60 eV, then transferred by a laser to a level that radiates in the XUV. The intensity of the XUV emission as a function of laser wavelength was recorded.

A schematic of the apparatus is shown in Fig. 1. Metastable atoms were prepared by electron-impact excitation in a microwave-heated Li discharge. The discharge cell was made from a stainless-steel X-band waveguide by welding short tapered ridges to its upper and lower faces, with a gap between ridges of about 1 mm. Narrow longitudinal slots in the ridges allowed Li vapor to enter from a side-arm cell on one side, and allowed XUV radiation to be viewed from the other. At a typical side-arm operating temperature of 580 °C, the Li vapor density in the gap was about 10^{14} atoms/cm^3.

A 9-GHz pulsed magnetron with a peak power of 50 kW, a pulse width of 1 μs, and a repetition rate of 10/s provided rf power for the discharge. The laser light entered the cell through end windows and was brought to a focus of ~0.2 mm^2

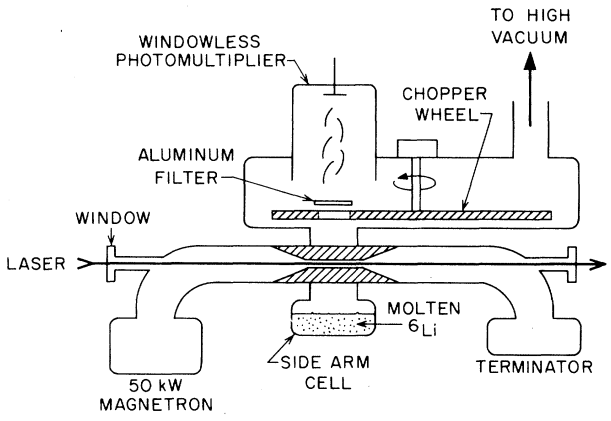


FIG. 1. Schematic of experimental apparatus.

under the ridge slots.

The laser-induced XUV radiation was detected by a windowless photomultiplier (EMI model D233B) located behind a 1000-Å-thick aluminum filter, and a chopper wheel. The aluminum filter prevented visible and near-UV radiation and ions from entering the detector. The chopper wheel, synchronized to the laser and magnetron pulses, reduced the accumulation of Li on the aluminum filter and significantly extended operating times.

The signal from the electron multiplier was integrated over a 10-ns gate coincident with the laser, and then digitized and recorded by a microcomputer. The laser power was also recorded on each shot. During an experiment the laser wavelength was scanned many times through the region of interest, under computer control. The results from each scan were added to previous scans and averaged. This method of data collection greatly reduced the effect of slow drifts in the background ion fluorescence and laser intensity. The computer also controlled the phase-matching of the partially deuterated potassium dihydrogen phosphate crystals in those experiments which required mixing or doubling of the dye laser output.

The apparatus was designed to be able to detect transitions with very small oscillator strengths. For example, for the $1s2s2p\,^4P_{5/2}-1s2p\,^2P_{3/2}$ transition with an oscillator strength[7] of 2×10^{-8}, 36% of the population within the 0.2-mm^2 beam area could be transferred with about 10 mJ of laser energy.

Figure 2 shows experimental results for near resonant anti-Stokes scattering in $^6Li^+$. About 2 mJ of tunable radiation near 9584 Å was produced by Raman downshifting a Quanta-Ray dye laser in a 10-atm H_2 cell. About 100 XUV (199.3 Å) photons per pulse were incident on the detector at the peak of the curve (10 times above the background). This signal implies a $1s2s\,^1S$ population of about 10^8 atoms/cm^3. Due to the large oscillator strength ($f=0.21$) of the transition, an anti-Stokes signal was observable over a tuning range of about 200 cm^{-1}. The center wavelength of 9584 Å is in agreement with the value calculated by Pekeris.[8] Such an anti-Stokes radiation source could be used for very high-resolution XUV spectroscopy as recently described by Rothenberg *et al.*[9]

Figure 3 shows experimental results for transfer from the metastable $1s2s\,^3S$ to the radiating $1s2p\,^1P$ level in $^6Li^+$. The experiment was undertaken in order to verify the sensitivity of our apparatus for very weak transitions (calculated oscillator strength $=9.4\times10^{-8}$).[10] The pulsed dye-laser output was mixed with 1.06-μm radiation to produce about 10 mJ in a 3-cm^{-1} bandwidth near 3880 Å. The separation between the $1s2s\,^3S$ and $1s2p\,^1P$ levels was found to be $25\,771\pm2$ cm^{-1}. Allowing for an isotopic correction, this is in agreement with the Pekeris[8] value of 25 773.25 for $^7Li^+$. Although the intercombination oscillator strength in this experiment was about six orders of magnitude smaller than that of the singlet anti-Stokes experiment, the peak signal strength was only about 5 times smaller.

Figure 4 shows the results for the quartet-doublet experiment in neutral ^6Li. The Q-switched dye laser was frequency doubled to provide 10 mJ of tunable radiation in a 2-cm^{-1} bandwidth near 2952 Å. The amplitude of the observed XUV signal was about 100 times smaller than that of the singlet anti-Stokes experiment. A

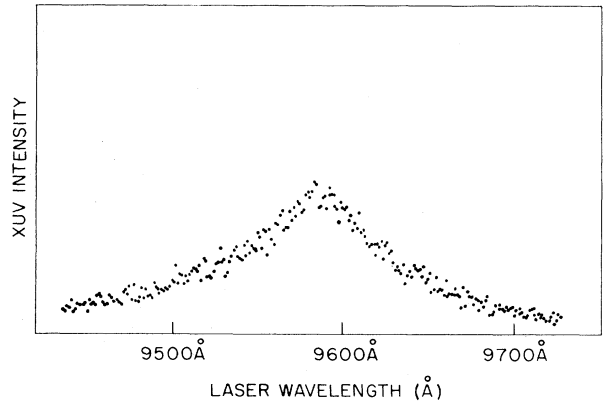
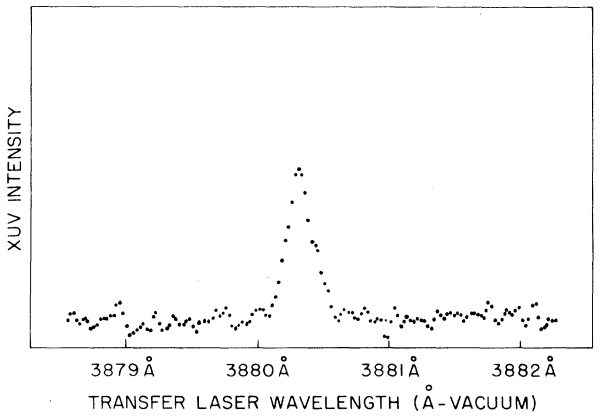


FIG. 2. XUV intensity vs laser wavelength for $1s2s\,^1S \rightarrow 1s2p\,^1P$ transfer in $^6Li^+$.



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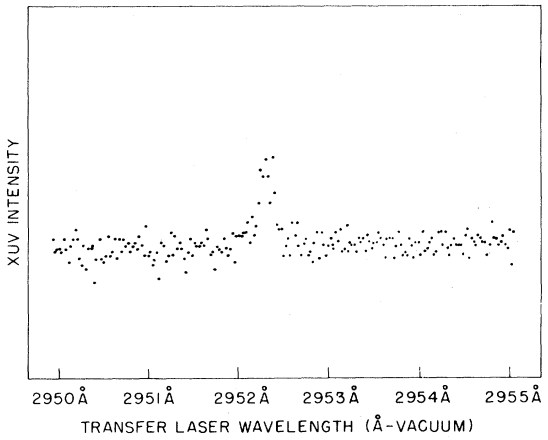

FIG. 4. XUV intensity vs laser wavelength for $1s2s2p\,^4P_{5/2} \rightarrow 1s2p^2\,^2P_{3/2}$ transfer in neutral ^{6}Li.

total scanning time of about 2 h, corresponding to 150 scans of the 2950–2955-Å wavelength region, was required to obtain the data shown. The measured separation between the levels is $33\,872 \pm 2$ cm^{-1}. On the basis of the longer metastability of the 5/2 component of the $1s2s2p\,^4P$ level, and the ratio of calculated oscillator strengths of the fine structure components,[7] it is likely that the largest component of our signal occurs on $^4P_{5/2}$-$^2P_{3/2}$. Our measured separation is about 5 cm^{-1} greater than that recently calculated by Jáuregui and Bunge[3] for ^{7}Li. The discrepancy probably is due to the uncertainty of experimental beam-foil results used in the calculation, and to the isotope shift between ^{6}Li and ^{7}Li.

In summary, we have described a new technique for connecting metastable and radiating manifolds which lie in the XUV spectral region. The method complements the high-resolution anti-Stokes absorption technique described by Rothenberg *et al.*[9]; both provide unprecedented resolution in the XUV. This work also bears on recent proposals for XUV lasers.[6,11,12]

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[1]P. Feldman and R. Novick, Phys. Rev. Lett. 11, 278 (1963), and Phys. Rev. 160, 143 (1967).

[2]H. G. Berry, E. H. Pinnington, and J. L. Subtil, J. Opt. Soc. Am. 62, 767 (1972).

[3]C. F. Bunge, Phys. Rev. A 23, 2060 (1981), and Phys. Rev. A 19, 936 (1979); R. Jáuregui and C. F. Bunge, Phys. Rev. A 23, 1618 (1981).

[4]J. R. Willison, R. W. Falcone, J. C. Wang, J. F. Young, and S. E. Harris, Phys. Rev. Lett. 44, 1125 (1980).

[5]S. Mannervik, Phys. Scr. 22, 575 (1980).

[6]S. E. Harris, Opt. Lett. 5, 1 (1980).

[7]H. Nussbaumer, Opt. Lett. 5, 222 (1980).

[8]C. L. Pekeris, Phys. Rev. 126, 143 (1962).

[9]J. E. Rothenberg, J. F. Young, and S. E. Harris, Opt. Lett. 6, 363 (1981).

[10]G. W. F. Drake and A. Dalgarno, Astrophys. J. 157, 459 (1969).

[11]J. E. Rothenberg and S. E. Harris, IEEE J. Quant. Elect. 17, 418 (1981).

[12]S. E. Harris, R. W. Falcone, M. Gross, R. Normandin, K. D. Pedrotti, J. E. Rothenberg, J. C. Wang, J. R. Willison, and J. F. Young, in "Laser Spectroscopy V" (Springer-Verlag, New York, to be published).

Rotational- and Spin-State Distributions: NO Thermally Desorbed from Ru(001)

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Rotational-state distributions have been measured for the first time in molecules thermally desorbed from a metal single crystal. Laser-excited fluorescence has been used to monitor, under ultrahigh-vacuum conditions, the desorption of NO from Ru(001). The population distribution for those states with less than 400 cm^{-1} of rotational energy (including spin) can be represented by a single Boltzmann factor, $T_{rot} = 235 \pm 35$ K, significantly lower than the surface temperature at the desorption maximum, $T_S = 455 \pm 20$ K.

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One of the severe obstacles in theoretically modeling the dynamics of reactive processes occurring at a gas-surface interface is the absence, until very recently, of experimental data on the details of the partitioning of energy within the incoming or exiting gas-phase species.[1] Such

