Hyperfine and fine-structure measurements of $^{6,7}Li^+$ $1s2s\ ^3S$ and $1s2p\ ^3P$ states

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The $1s2s\ ^3S_1 \rightarrow 1s2p\ ^3P_{1,2}$ transition in $^{6,7}Li^+$ was investigated by exciting a 5–6-keV ion beam with a nearly copropagating ring-dye laser beam. The laser scan was calibrated using an electro-optic modulator to generate frequency sidebands. Results for the $^6Li^+$ hyperfine splittings are an order of magnitude more precise than existing data in the literature and the $^7Li^+$ results resolve an 11-MHz (17σ) discrepancy for the $^3P_{1-2}$ fine-structure interval as determined by two previous experiments. The results for 12 (all 13) measured hyperfine intervals in $^{6,7}Li^+$ are within 2σ (3σ) of the latest Hylleraas variational calculations.

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Significant recent advances in theory for two-electron atomic systems have been made using variational techniques [1,2]. It is therefore important for precision measurements to test these predictions. Unfortunately, different experimental groups have published sharply disagreeing results for Li^+ transition frequencies as well as fine-structure intervals [1,3–5]. It is particularly troubling that these disagreements have persisted over the past ten years. High-precision measurements of lithium are also of interest for a number of diverse applications. They have permitted the determination of relative nuclear sizes of the $^{6,7}Li$ isotopes to nearly an order of magnitude better than electron scattering experiments [1,6]. Work is ongoing at two accelerators to trap unstable $^{8,9,11}Li$ nuclei to measure isotope shifts and thereby examine exotic properties such as halo neutrons [7]. Precision measurements of absolute $^7Li^+$ transition frequencies are ongoing to test special relativity [8] and may improve the determination of the fine-structure constant [9,10].

The Li^+ $1s2s\ ^3S_1 \rightarrow 1s2p\ ^3P_{0,1,2}$ transition at 548.5 nm, shown in Fig. 1, has been studied using a variety of techniques including spectrometers [11–13], rf magnetic resonance [14], quantum beats [15], Doppler tuning [16–18], saturation spectroscopy [19], and microwave techniques [20]. For the $^7Li^+$ $1s2p\ ^3P_{1,2}$ fine-structure interval, the two experiments claiming the smallest uncertainties use the so-called laser heterodyne method [3] or precisely measure a number of absolute transition frequencies [1,4,5,21]. Each group quotes a 1σ uncertainty of less than 1 MHz but their results differ by 11 MHz [1,3].

This experiment investigated the hyperfine and fine-structure splittings of the $^{6,7}Li^+$ $1s2s\ ^3S_1 \rightarrow 1s2p\ ^3P_{1,2}$ transition using a different experimental technique. A ring-dye laser beam that was electro-optically modulated probed a 5–6-keV ion beam in a near-collinear arrangement. Fluorescence from the ions was recorded as the laser frequency was scanned. Each transition was excited by the various laser frequency sidebands allowing each scan to be independently calibrated.

An overview of the apparatus is shown in Fig. 2. The Li^+ beam was generated using an ion source that is described in detail elsewhere [22]. A sample of either natural (92.58% ^7Li, 7.42% ^6Li) or isotopically purified (99% ^6Li) lithium was first distilled in a separate vacuum chamber. A neutral lithium atomic beam was produced by an oven heated to 650 °C and collimated by a 3.8-mm-diam aperture. Ions were produced by intersecting the atomic beam with an 80-mA beam of 500-eV electrons. The ions were extracted and accelerated using a 6-kV power supply (Fluke 408b) that had a ripple of less than 1 mV rms. The high voltage was monitored using a 1:5000 voltage divider (Julie Research Labs KV-50) having an accuracy of 0.02% and a precision voltmeter (HP 34401A). A voltage stability of better than 0.5 parts in 10^5 was observed throughout the experiment. Approximately 1% of the Li^+ ions emerged from the source in the $1s2s\ ^3S_1$ state [22], which has a lifetime of 59 ± 13 s [23]. The ions propagating in the $\hat{z}$ direction were focused with an Einzel lens and then directed by $\hat{x}$ and $\hat{y}$ deflection plates into a Wien velocity filter. A Faraday cup located 1.3 m from the Wien filter measured a Li^+ ion current of 250 nA. The ion beam propagated in a vacuum chamber maintained at a pressure of 1×10^{-7} torr using two diffusion pumps and liquid-nitrogen traps.

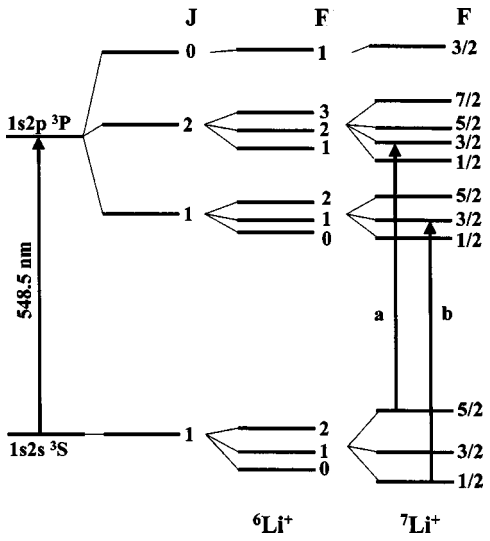

FIG. 1. Energy levels of $^{6,7}Li^+$ relevant to the experiment. The vertical energy axis is not drawn to scale. The labels a and b indicate the transitions studied to determine the $^7Li^+$ fine-structure splitting.

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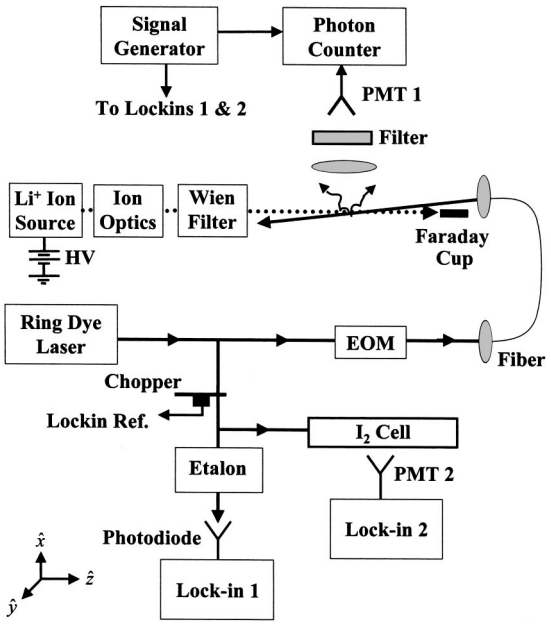

FIG. 2. Apparatus. See text for description.

Laser radiation was supplied by a cw ring-dye laser (Coherent 669) that generated in excess of 600 mW at 548 nm using pyromethene 556 laser dye. The dye laser had a linewidth of less than 1 MHz and could be tuned 30 GHz without mode hops. The frequency was monitored by passing part of the laser beam through an iodine cell and observing the fluorescence with a photomultiplier tube (PMT2) [24]. The signal was analyzed by a lock-in amplifier (Lock-in 2).

The dye laser beam passed through one of two electro-optic modulators (EOM, ν focus 4851) operating at either 6.8 or 9.2 GHz. The modulation frequency was specified to better than one part in 10^7 using a frequency synthesizer (Agilent E8241A). The modulation frequency was amplified (Quinstar QPN-08403534) to a power of up to 3 W. The laser beam emerging from the EOM was focused into a single-mode polarization-maintaining fiber (Thorlabs FS-PM-2021) with a coupling efficiency of 70%. The fiber ensured that the 15 mrad angle of intersection of the laser and ion beams remained constant. The laser beam was retroreflected by a mirror. Data were taken using calibrated neutral-density filters to vary the laser power from 1 to 10 mW.

The laser light excited the $1s2s\ ^3S_1 \rightarrow 1s2p\ ^3P$ transition. Fluorescence produced by the radiative decay of the upper state, which has a natural lifetime of 43 ns [20], was detected using an $f/1.5$ optical system. Laser scatter was reduced using an interference filter (Omega 550BP10) with a bandwidth of 10 nm centered at 550 nm as well as a spatial filter. A liquid-nitrogen-cooled photomultiplier tube (PMT1, Hamamatsu R943-02) detected the fluorescence. The PMT1 signal was first processed by a preamplifier (SRS 445) and then sent to a photon counter (SRS SR430) that recorded data at a rate of 40 Hz. A data file containing 25 000 data points was recorded for each 30 GHz scan.

A sample spectrum of $^6Li^+$ is shown in Fig. 3(a). The background was dominated by scattered laser light (90%) and ion collisions with residual gas (10%). The

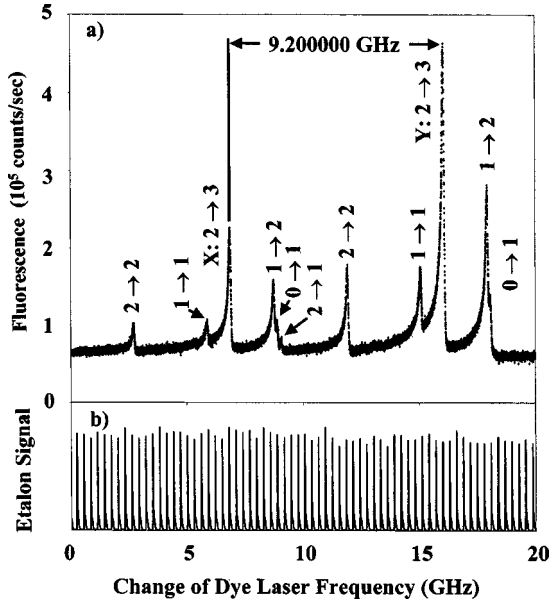

FIG. 3. Typical signal. (a) shows fluorescence produced when the laser frequency was scanned across the $^6Li^+ 1s2s\ ^3S_1 \rightarrow 1s2p\ ^3P_2$ resonance. The transitions are denoted by $F \rightarrow F'$ where F and F' denote the hyperfine levels of the $1s2s\ ^3S_1$ and $1s2p\ ^3P_2$ states, respectively. Several transitions are excited twice as the laser was frequency modulated at 9.200 000 GHz. (b) displays the transmission of part of the laser beam through an étalon.

$1s2s\ ^3S_1\ (F) \rightarrow 1s2p\ ^3P_2\ (F')$ transitions are indicated by the label $F \rightarrow F'$. Several transitions were excited first by a frequency sideband of the laser beam and subsequently by the frequency-unshifted laser beam. These data were taken

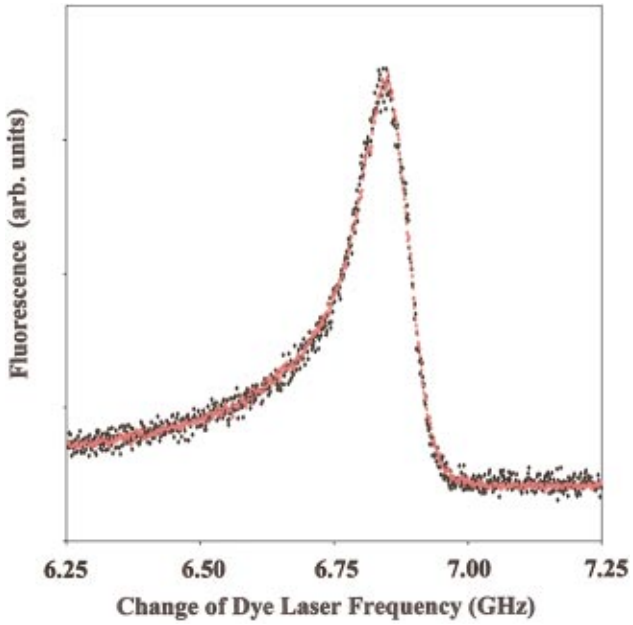

FIG. 4. (Color) Determination of frequency intervals. The black points correspond to peak X in Fig. 3(a) while the red points were generated by scaling the amplitude of peak Y and shifting its position to obtain the optimum overlap with peak X.

TABLE I. $^{6,7}Li^{+}$ hyperfine structure splittings.

State	Interval ($F \rightarrow F'$)	Interval (MHz)	Reference
$^{6}Li^{+}$ $1s2p\ ^{3}P_{1}$	$2 \rightarrow 1$	2 880±5	[14]
		2 889±8	[15]
		2 878±6	[17]
		2 886±4	[19]
		2 888.98±0.63	This work
		2 888.327±0.029	Theory [1]
	$1 \rightarrow 0$	1 318±17	[15]
		1 310±6	[17]
		1 316±8	[19]
		1 316.06±0.59	This work
		1 317.649±0.046	Theory [1]
$^{6}Li^{+}$ $1s2p\ ^{3}P_{2}$	$3 \rightarrow 2$	4 128±9	[15]
		4 113±18	[17]
		4 125±14	[19]
		4 127.16±0.76	This work
		4 127.882±0.043	Theory [1]
	$2 \rightarrow 1$	2 856±8	[15]
		2 861±6	[19]
		2 857.00±0.72	This work
		2 858.002±0.060	Theory [1]
$^{6}Li^{+}$ $1s2s\ ^{3}S_{1}$	$2 \rightarrow 1$	5 993±6	[17]
		5 997±4	[19]
		6 003.600±0.050	[20]
		6 003.66±0.51	This work
		6 003.614±0.024	Theory [1]
	$1 \rightarrow 0$	2 998±6	[17]
		2 998±4	[19]
		3 001.780±0.050	[20]
		3 001.83±0.47	This work
		3 001.765±0.038	Theory [1]
$^{7}Li^{+}$ $1s2p\ ^{3}P_{1}$	$5/2 \rightarrow 3/2$	9 932±24	[16]
		9 953±9	[19]
		9 965.2±0.6	[20]
		9 966.30±0.69	This work
		9 966.14±0.13	Theory [1]
	$3/2 \rightarrow 1/2$	4 224±18	[16]
		4 246±20	[19]
		4 237.8±1.0	[20]
		4 239.11±0.54	This work
		4 238.86±0.20	Theory [1]
$^{7}Li^{+}$ $1s2p\ ^{3}P_{2}$	$7/2 \rightarrow 5/2$	11 761±12	[16]
		11 760±6	[19]
		11 775.8±0.5	[20]
		11 774.04±0.94	This work
		11 773.05±0.18	Theory [1]
	$5/2 \rightarrow 3/2$	9 602±12	[16]
		9 598±12	[19]
		9 608.7±2.0	[20]
		9 608.90±0.49	This work
		9 608.12±0.15	Theory [1]
	$3/2 \rightarrow 1/2$	6 182±18	[16]
		6 204±13	[19]
		6 203.6±0.5	[20]
		6 204.52±0.80	This work
		6 203.27±0.30	Theory [1]

TABLE I. (*Continued*).

State	Interval ($F \rightarrow F'$)	Interval (MHz)	Reference
$^7Li^+$ $1s2s\ ^3S_1$	5/2→3/2	19 798±24	[16]
		19 796±10	[19]
		19 817.673±0.040	[20]
		19 817.90±0.73	This work
		19 817.680±0.025	Theory [1]
	3/2→1/2	11 872±12	[16]
		11 879±9	[19]
		11 890.018±0.040	[20]
		11 891.22±0.60	This work
		11 890.013±0.038	Theory [1]

using copropagating ion and laser beams. The asymmetric line shape resulted from the distribution of ion velocities and was inverted for counterpropagating ion and laser beams.

The frequency intervals between the various peaks in Fig. 3(a) were found by scaling the intensity of the largest peak labeled *Y* and translating its position to optimize the overlap with the peak of interest. For example, the black data points in Fig. 4 correspond to peak *X* in Fig. 3(a), while the red points show peak *Y* scaled and translated to obtain the best overlap with peak *X*. This method of determining frequency intervals worked since all peaks observed during one day of data taking had the same asymmetric line shape. A double peak resulting from the closely spaced $1\rightarrow2$ and $0\rightarrow1$ transitions could be well modeled using two shifted and scaled *Y* peaks.

The linearity of the laser frequency scan was monitored by passing part of the laser beam through a confocal Fabry-Pérot étalon. The latter consisted of two dielectric mirrors having a reflectivity greater than 99.5% and a 25-cm radius of curvature mounted on an invar bar. The étalon was housed in a chamber maintained at a pressure of 1 torr to reduce effects of air pressure. The chamber's temperature varied by less than 0.1 °C during data acquisition. A photodiode detected the light transmitted through the étalon. This signal was processed by a lock-in amplifier (Lock-in 1, SRS SR850) where the reference signal was supplied by a chopper that modulated the laser beam at 2 kHz. Data acquisition by lock-in-1 and the photon counter was synchronized by a signal generator.

The étalon transmission signal corresponding to the spectrum in Fig. 3(a) is shown in Fig. 3(b). A Gaussian function was fitted to each étalon peak to determine its position. The free spectral range was determined using the 9.200 000-GHz interval indicated in Fig. 3(a). This was done separately for each laser scan to take into account possible variation of the free spectral range from scan to scan. The effect of any nonlinearity of the laser scan was minimized by measuring the interval from each lithium peak to the nearest étalon peak.

The nonlinearity of the laser frequency scan was investigated by taking ten scans as shown in Fig. 3. The average time interval for each free spectral range was plotted versus the étalon peak number and the nonlinearity of the laser scan was found to be less than 0.1%. In this experiment, the free spectral range is slightly less than 300 MHz. Hence, the uncertainty in the largest frequency interval separating a Li^+ peak and the nearest étalon peak was 0.15 MHz. The total uncertainty due to scanning nonlinearity in a frequency interval separating two Li^+ fluorescence peaks was estimated to be 0.21 MHz by adding two uncertainties of 0.15 MHz in quadrature.

The results for the various hyperfine intervals are shown in Table I. These data represent a total of 92 scans for $^6Li^+$ and 86 scans for $^7Li^+$ accumulated on 20 different days. The listed uncertainties were determined by adding the statistical standard deviation to the scanning nonlinearity in quadrature. The tabulated frequencies have also been corrected for the first-order Doppler shift difference of the two peaks. The latter was computed from the acceleration voltage and matched that observed using copropagating and counterpropagating laser-atomic beams.

Results for the hyperfine splittings of the $^{6,7}Li^+$ $1s2s\ ^3S_1$ state are in very close agreement with previous measurements as well as theoretical predictions made using the Hylleraas variational technique. Microwave techniques [20] are well suited to studying this state due to its long lifetime, and the results therefore have smaller uncertainties than our measurements. The close agreement of our measurements with the microwave results is a stringent test of the validity of the experimental technique.

The $^6Li^+$ $1s2p\ ^3P_{1,2}$ hyperfine splittings have been investigated by Doppler-tuning an ion beam [16,17] and saturation spectroscopy [19]. Our results have about an order of magnitude smaller uncertainty than those found previously. The $^7Li^+$ $1s2p\ ^3P_{1,2}$ hyperfine intervals have also been investigated using the microwave technique [20]. The microwave results have a quoted 3σ error bar and agree well with those of the present experiment. However, our results appear to be somewhat closer to theory [1], most notably in the case of the $1s2p\ ^3P_2$ 7/2→5/2 interval. Indeed, all but one of our 13 measured hyperfine intervals lie within 2σ of the theoretical values.

The fine-structure interval separating the $^7Li^+$ $1s2p\ ^3P_{1-2}$ levels can be studied by measuring the frequency interval between transitions labeled *a* and *b* in Fig. 1 [25] and adding appropriate hyperfine intervals. The results,

TABLE II. Li^+ $1s2p\ ^3P_{1-2}$ fine-structure interval.

Interval (MHz)	Reference
62 658±28	[19]
62 678±14	[13]
62 682±6	[21]
62 667.4±2.0	[3]
62 678.41±0.65	[1]
62 679.46±0.98	This work
62 679.4±0.5	Theory [26]

given in Table II, represent 49 laser scans taken on seven days. These were compared to results obtained by other groups that studied transitions to various hyperfine levels of the $^7Li^+$ $1s2p\ ^3P_{1,2}$ manifolds. The experiments quoting the lowest uncertainties use the laser heterodyne technique [3] or measure absolute transition frequencies to various levels [1]. Our result strongly agrees with theory [26] as well as the measured result found by Ref. [1] and strongly disagrees with the result of the laser heterodyne experiment whose quoted uncertainty equals 3σ.

In conclusion, the measured hyperfine intervals are in excellent agreement with the latest Hylleraas variational theory. Moreover, the discrepancy for the $^7Li^+$ $1s2p\ ^3P_{1-2}$ fine-structure interval as measured by two experimental groups has been resolved. The technique used in this experiment is completely different from that used by the other groups. It is in principle simpler as absolute transition frequencies are not required. Each laser scan is individually calibrated and the experiment is therefore insensitive to any change in étalon calibration. This experimental approach therefore is a useful tool for precision laser spectroscopic measurements.

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