Absolute Transition Frequencies and Quantum Interference in a Frequency Comb Based Measurement of the ^{6,7}Li D Lines

Craig J. Sansonetti,[1] C. E. Simien,[1,*] J. D. Gillaspy,[1] Joseph N. Tan,[1] Samuel M. Brewer,[2,1] Roger C. Brown,[2,1] Saijun Wu,[1] and J. V. Porto[1]

[1]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
[2]*University of Maryland, College Park, Maryland 20742, USA*
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Optical frequencies of the D lines of ^{6,7}Li were measured with a relative accuracy of 5×10^{-11} using an optical comb synthesizer. Quantum interference in the laser induced fluorescence for the partially resolved $D2$ lines was found to produce polarization dependent shifts as large as 1 MHz. Our results resolve large discrepancies among previous experiments and between all experiments and theory. The fine-structure splittings for ^{6}Li and ^{7}Li are 10052.837(22) MHz and 10053.435(21) MHz. The splitting isotope shift is 0.599(30) MHz, in reasonable agreement with recent theoretical calculations.

In recent years lithium has been the subject of intense theoretical and experimental interest (see [1] and references therein). As the most complex atom for which *ab initio* atomic structure calculations approach spectroscopic accuracy, it is a benchmark system for validation of theory. In 2000 Yan and Drake [2] proposed that measured isotope shifts for the lithium $2s$-$2p$ (D lines) and $2s$-$3s$ transitions could be combined with precise theoretical calculations to determine relative nuclear charge radii of lithium isotopes. This provided additional impetus for advances in theory and experiment. The technique described in [2] has since been used to determine nuclear charge radii for the short-lived isotopes ^{8}Li, ^{9}Li, and ^{11}Li [3,4], providing a new tool for probing exotic nuclei.

In their paper Yan and Drake noted that observations of isotope shifts for the D lines of ^{6,7}Li disagreed with each other and with theory. Despite four recent experiments, large discrepancies persist [5–10]. Drake and his co-workers emphasize the isotopic difference in the $2p$ ^2P fine-structure interval, the splitting isotope shift (SIS), as a consistency check for experiment [11]. Since both quantum electrodynamic (QED) and nuclear size corrections largely cancel in calculating the SIS, it is the most reliable result of theory. In Fig. 1 we compare recent experimental and theoretical values. The more precise values disagree with each other and with theory by more than 6 times their uncertainties.

In this Letter we report new observations of the D lines for ^{6}Li and ^{7}Li. An optical comb synthesizer is used to measure the 19 hyperfine components in 12 resolvable features that are spread over a span of 20 GHz, providing absolute transition frequencies for determination of fine- and hyperfine-structure intervals and isotope shifts. We find clear evidence that quantum interference of transition amplitudes in the unresolved $D2$ lines can produce frequency shifts that were not considered in earlier work.

In our apparatus [12] light from a single-frequency diode laser crosses a beam of lithium atoms at a right angle. A magnetic shield surrounding the interaction region reduces the field to less than 1 μT. A corner cube retroreflector provides a reverse beam antiparallel to better than 1.45×10^{-6} radians, which is chopped at 500 Hz by a mechanical chopper. The laser is stabilized to a Fabry-Perot cavity [13] and scanned by varying the cavity length. To minimize optical pumping and multiple excitation recoil shifts, the laser beam is attenuated to 3 μW and expanded to 3.5 mm diameter. Lithium atoms effuse from a 450 °C oven filled with a mixture of natural lithium and isotopically enriched ^{6}Li to produce a beam in which the two isotopes can be detected with approximately equal signal strengths. We observe the spectrum by varying the laser frequency and recording the fluorescence viewed along an approximately vertical axis nominally perpendicular to the laser and atomic beams.

The signal is detected in two channels by a gated photon counter. One channel observes the fluorescence when both forward and reverse laser beams interact with the lithium beam. For the other channel the reverse beam is blocked by the chopper. By differencing the photon counts in the two channels, we recover the signal due to the reverse beam. In this way we obtain a correction of first order Doppler
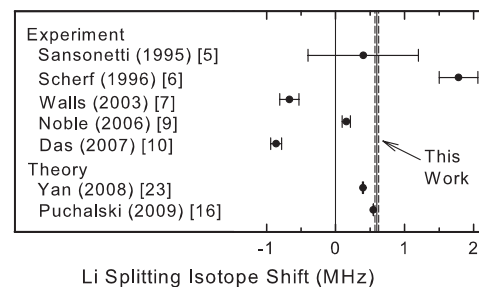

FIG. 1. Reported values of the ^{6,7}Li SIS.

shift from a single scan with accuracy limited only by the precision of the retroreflector.

Our experiment differs from all previous work in that we measure the frequency of the laser directly using an optical frequency comb [14]. The comb is based on a femtosecond Er fiber laser at 1560 nm whose output is doubled and broadened with a photonic crystal fiber to produce a comb with broad spectral coverage in the red and near infrared. The nominal 250 MHz repetition rate and carrier offset frequency are referenced to an ultraclean quartz oscillator that is locked to a cesium clock. This frequency reference has an absolute accuracy of about 2 parts in 10^{13} and a stability (Allan deviation) of approximately 3×10^{-13} for integration times of 1 s to 100 s.

The spectroscopy laser is heterodyned with the comb, and the beat signal is filtered with a narrow band pass centered at 30 MHz. To record a calibrated scan, the comb repetition rate is adjusted so that the beat frequency between a selected comb mode and the laser is near 30 MHz. A computer generated voltage is used to scan both the laser frequency and comb repetition rate in steps of approximately 250 kHz so that the beat frequency remains fixed. Fluorescence data are accumulated alternately on the two gated photon counter channels for a total acquisition time of 72 ms per channel per data point. The heterodyne frequency is counted over the same time interval. For every data point the comb repetition rate and offset frequency, the heterodyne frequency and signal strength, the fluorescence signal on both photon counter channels, and the laser output power are recorded. A scan across components of the ^{7}Li $D1$ line that illustrates the typical quality of the data is shown in the leftmost panel of Fig. 2.

The data are analyzed by fitting a model profile composed of a sum of Voigt functions, one for each hyperfine component expected in the spectrum. For speed and stability in fitting, Kielkopf's analytic approximation to the Voigt function is used [15]. For the fully resolved components of the $D1$ lines, the position, intensity, half-width, Voigt parameter, and baseline offset are all fit as independent parameters. For the partially resolved features of the $D2$ lines, the relative intensities of the components are fixed at their theoretical values and the hyperfine-structure

splittings are fixed at values determined from the A and B hyperfine constants calculated by Puchalski and Pachucki [16]. These hyperfine constants are in good agreement with the best experimental values [17] but have much smaller uncertainties and are confirmed by other precise calculations [18].

For the $D1$ lines, the fitted profiles replicate the data with featureless residuals consistent with the shot noise limit (Fig. 2). The line width is 8.2 MHz, 40% greater than the natural width of 5.87 MHz. For the $D2$ lines, our initial data produced fits with structured residuals far larger than the random scatter. In investigating this problem, we found that the unresolved $D2$ profiles varied dramatically as a function of laser polarization, as shown in Fig. 2. Apparent line shifts as large as 1 MHz were observed when these data were fit as a simple sum of Voigt functions. A pronounced minimum in the residuals was noted for polarization angles near 51° from vertical (Fig. 2). Theoretical modeling showed that this effect is due to quantum interference in the fluorescence of coherently excited hyperfine components, whose separation is approximately equal to the natural line width. The calculations reproduce the features observed in the data and show that the interference vanishes when the angle between the laser polarization and the direction of fluorescence detection is the "magic angle" $\theta_m = 54.7°$. Similar effects appear in quantum beat spectroscopy [19], where the quantum interference vanishes when the fluorescence is detected with polarization at θ_m with respect to the excitation polarization. We have extended our data analysis to include the quantum interference effect on the line profiles. Work to obtain additional quantitative results by fitting data acquired at arbitrary laser polarization is in progress and will be reported elsewhere.

Because of the shielding surrounding our interaction region, we could not accurately survey the direction of fluorescence detection, which must be known to set θ_m directly. Instead, we measured θ_p, the laser polarization with respect to vertical, and determined its appropriate value by studying the residuals, the relative intensities of partially resolved components, and the lithium ground state intervals that result from fitting recorded data with
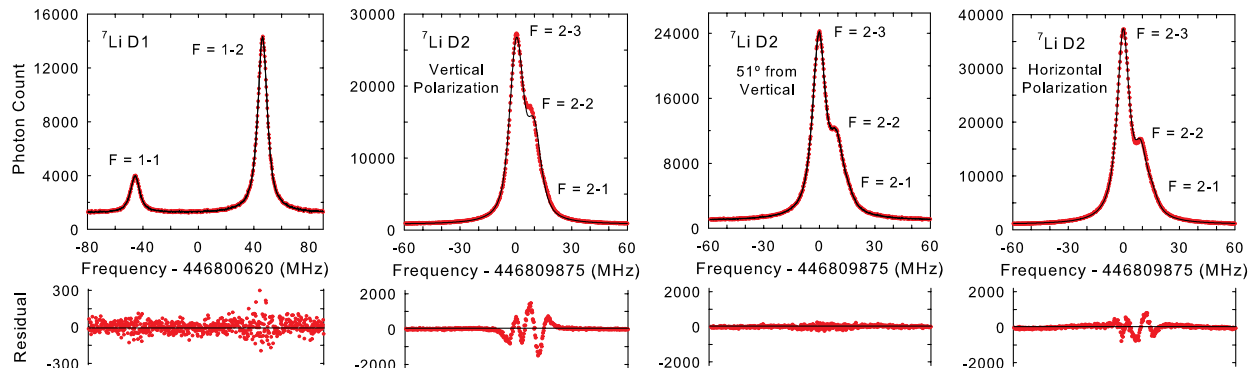

FIG. 2 (color online).   Typical data and fitted profiles that show the polarization dependence of the unresolved ^{7}Li $D2$ line.

TABLE I. Measured frequencies of hyperfine components and centers of gravity (cog) of the Li D lines [a].

Line	F_L	F_U	Frequency (MHz)
^{6}Li $D1$	3/2	1/2	446 789 502.616(8)
	3/2	3/2	446 789 528.716(10)
	1/2	1/2	446 789 730.821(26)
	1/2	3/2	446 789 756.942(16)
^{6}Li $D1$ cog			446 789 596.091(7)
^{6}Li $D2$	3/2	5/2	446 799 571.082(26)
	3/2	3/2	446 799 573.977(26)
	3/2	1/2	446 799 575.689(26)
	1/2	3/2	446 799 802.200(33)
	1/2	1/2	446 799 803.912(33)
^{6}Li $D2$ cog			446 799 648.927(21)
^{7}Li $D1$	2	1	446 799 771.121(13)
	2	2	446 799 862.994(12)
	1	1	446 800 574.608(19)
	1	2	446 800 666.494(9)
^{7}Li $D1$ cog			446 800 129.853(6)
^{7}Li $D2$	2	3	446 809 874.988(27)
	2	2	446 809 884.450(27)
	2	1	446 809 890.263(27)
	1	2	446 810 687.944(29)
	1	1	446 810 693.757(29)
	1	0	446 810 696.516(29)
^{7}Li $D2$ cog			446 810 183.289(20)

[a]Unresolved component splittings for the $D2$ lines are fixed at values calculated from the hyperfine A and B constants of [16].

TABLE II. Representative uncertainty budgets (kHz).

Uncertainty component	^{7}Li $D1$ $F = 1 - 1$	^{6}Li $D2$ $F = 3/2 - 5/2$, 3/2, 1/2
Reference frequency	0.089	0.089
Statistical variation	19	15
First order Doppler effect	1.4	10
Estimate of θ_m	0	5
Laser power dependent shifts [a]	0.01	17
Magnetic field shift	<1	<1
Laser intensity variation	3	3
Hyperfine constant inaccuracy	0	2
Total	19	26

[a]Optical pumping, multiple excitation recoil, and ac Stark shift.

slightly over many hours of data taking. The largest contributors to the uncertainties of the $D2$ lines are the determination of the angle θ_p that corresponds to θ_m and the laser power dependent shifts. Optical pumping, multiple excitation photon recoil, and ac Stark effect are treated together as they all depend on laser power and may add or partially cancel. Our estimates for these uncertainties are

TABLE III. Hyperfine- and fine-structure intervals.

Interval	Splitting (MHz)	Reference
^{7}Li $2s$ ^2S hfs	803.493(14)	This Letter
	803.504 086 6(10)	Beckmann [20]
^{6}Li $2s$ ^2S hfs	228.215(17)	This Letter
	228.205 261(3)	Beckmann [20]
^{7}Li $2p$ $^2P_{1/2}$ hfs	91.877(9)	This Letter
	91.828(50)	Orth [17]
	92.020(50)	Walls [7]
	91.786(52)	Noble [9]
	92.047(6)	Das [10]
	92.040(6)	Singh [21]
	91.8784(22)	Puchalski (theory) [16]
^{6}Li $2p$ $^2P_{1/2}$ hfs	26.111(15)	This Letter
	26.079(46)	Walls [7]
	26.110(56)	Noble [9]
	26.091(6)	Das [10]
	26.1026(6)	Puchalski (theory) [16]
^{7}Li $2p$ ^2P fs	10 053.435(21)	This Letter
	10 053.184(58)	Orth [17]
	10 052.37(11)	Walls [7]
	10 053.119(58)	Noble [9]
	10 051.999(41)	Das [10]
	10 051.477(8)	Puchalski (theory) [16]
^{6}Li $2p$ ^2P fs	10 052.837(22)	This Letter
	10 052.76(22)	Brog [22]
	10 052.044(91)	Walls [7]
	10 052.964(50)	Noble [9]
	10 052.862(41)	Das [10]
	10 050.932(8)	Puchalski (theory) [16]

our simple model. Based on these criteria we find that $\theta_p = 51° \pm 1.5°$ from vertical corresponds to the angle $\theta_m = 54.7°$ between the polarization and direction of detection. All of the data for this Letter were taken at this empirical realization of θ_m.

Our measured frequencies for all hyperfine components and resulting centers of gravity of each of the D lines are given in Table I. The results have been corrected for photon recoil and second order Doppler effect. For each spectral feature an uncertainty was determined considering all identified sources of error. Two examples of the uncertainty budgets are shown in Table II. The total uncertainty was determined by combining the individual elements in quadrature.

The dominant uncertainty for the resolved $D1$ lines is the random variation of multiple measurements. This includes the uncertainty in the correction of the first order Doppler effect from simultaneously recorded forward and reverse beam signals. The small Doppler contribution in the first column of Table II is the systematic uncertainty due to imperfections of the corner cube retroreflector. Because the retroreflector does not preserve the laser polarization, the Doppler correction for the polarization sensitive $D2$ lines is taken from a linear fit of correction versus time for resolved $D1$ components measured on the same day. This is necessary because the laser alignment drifts

TABLE IV. ^{6,7}Li isotope shifts.

Transition	Shift (MHz)	Reference
D1	10 533.763(9)	This Letter
	10 534.26(13)	Walls [7]
	10 534.039(70)	Noble [9]
	10 534.215(39)	Das [10]
D2	10 534.362(29)	This Letter
	10 533.59(14)	Walls [7]
	10 534.194(104)	Noble [9]
	10 533.352(68)	Das [10]
SIS	0.599(30)	This Letter
	−0.67(14)	Walls [7]
	0.155(60)	Noble [9]
	−0.863(79)	Das [10]
	0.396(9)	Yan (theory) [23]
	0.5447(1)	Puchalski (theory) [16]

based on a combination of empirical tests and modeling. The possible effect of inaccuracy in the hyperfine constants of [11] was assessed by holding the line shape parameters and component intensities fixed and letting the A and B constants vary.

The only previous precise measurements of absolute transition frequencies were reported by Das and Natarajan [10]. Our results in Table I disagree with their values by 18 to 83 times the combined uncertainties. None of the sources of error we have evaluated can account for discrepancies of this size.

Our results for hyperfine- and fine-structure intervals are compared with previous results in Table III. The ground state hyperfine splittings are in excellent agreement with atomic beam magnetic resonance results [20]. The hyperfine interval of the ^{6}Li $^2P_{1/2}$ state is also in good agreement with previous experiments and recent theory [16]. For the ^{7}Li $^2P_{1/2}$ hyperfine interval, experimental results are scattered. Our value is in disagreement with the most precise reported results [10,21] but in excellent agreement with theory [16]. For both isotopes our fine-structure intervals are more precise than previous results, which are scattered far outside their uncertainties. The best theoretical values are smaller by approximately 2 MHz. This is probably attributable to higher order relativistic and QED corrections not included in the calculation. The uncertainties shown for the fine-structure values of [16] represent only the numerical uncertainty and do not include any estimate of the size of corrections not included in the calculations.

Our isotope shift determinations are given in Table IV. Our new value for the SIS is in reasonable agreement with the recent result of [16], but in disagreement with an earlier value [23]. This confirms the importance of hyperfine-induced mixing of the $^2P_{1/2}$ and $^2P_{3/2}$ states that was treated for the first time in [16]. The discrepancy

between theory and experiment is reduced to 0.054 (30) MHz as compared to a discrepancy of 0.390 (60) MHz for the most precise previous experiment [9].

In conclusion, our measurements confirm recent calculations of the $2p\ ^2P$ hyperfine-structure splittings and resolve large disagreements between theory and experiment for the SIS. This supports the theoretical framework that underlies the use of isotope shifts of the D lines to determine nuclear charge radii for exotic lithium isotopes. Our new values for the $2p\ ^2P$ fine structure provide precise benchmark data that should stimulate extension of theory to include higher order relativistic and QED contributions to the energies of three electron systems. Such refinements of theory may eventually make possible the determination of absolute nuclear charge radii from atomic physics experiments.

*Current address: Department of Physics, West Virginia University, Morgantown, WV, USA.
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