Hyperfine Splitting, Isotope Shift, and Level Energy of the 3S States of ^{6,7}Li

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We study the $2S-3S$ transition of ^{6,7}Li by high-precision laser spectroscopy using two-photon Doppler-free excitation and photoionization detection. Interferometric cross referencing to metrologic Rb $3S-5D$ two-photon transitions allowed measurement of the transition isotope shift and hyperfine splitting in the 3S state with precision at the 30 kHz level. The results are IS = 11 453.734(30) MHz, $A_{3S}(^6\mathrm{Li}) = 35.263(15)$ MHz, and $A_{3S}(^7\mathrm{Li}) = 93.106(11)$ MHz. Combined with recent theoretical work, the isotope shift yields a new value for the change in squared nuclear charge radii $\Delta R^2 = 0.47(5)\ \mathrm{fm}^2$. This is compared with other work and some existing discrepancies are resolved.

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High-precision laser spectroscopy on lithium isotopes is of fundamental interest, experimentally as well as theoretically. The Li atom has long served as a test system for the calculation of various atomic properties in few-electron atoms and significant advances have been made in the past decade [1–3]. Recent calculations of $2S-2P$ and $2S-3S$ transition energies and their mass-dependent isotope shifts (IS) reported a relative accuracy of better than 1×10^{-7} and 5×10^{-6}, respectively [4,5]. These calculations are the foundation for experimental efforts at GSI Darmstadt, Germany, to determine the charge radii of the unstable Li isotopes [6,7]. The principle is that, if all mass-dependent contributions to the IS can be calculated with sufficient accuracy, the residual discrepancy between experiment and computation is caused by differences in nuclear charge radii [8]. This approach was used to determine the ^{6,7}Li charge radii difference from isotope shift measurements in heliumlike Li$^+$ [9] and the rms charge radius of ^{3}He [10]. In both cases, results were in agreement with nuclear scattering data but with substantially improved accuracy. Data on nuclear charge radii is of fundamental importance for nuclear physics, but electron scattering data is available only for stable ^{6,7}Li. Among the unstable isotopes, ^{11}Li is of particular interest since it consists of a ^{9}Li core surrounded by a halo of two loosely bound neutrons [11]. The mass radius of ^{11}Li has been determined from nuclear cross section measurements [12], but this does not allow a nuclear-model independent determination of charge radius. Thus, the question of whether the halo neutrons affect proton distribution in the ^{9}Li core is still unresolved. Comparison of experimental results with predictions from nuclear structure calculations will lead to better understanding of nuclear structure near the neutron drip line.

The $2S-3S$ transition will be used for studies on the unstable Li isotopes because of the high-resolution achievable with Doppler-free two-photon excitation. Therefore, a precise IS measurement for this transition is needed to verify that all mass contributions have been calculated correctly and to sufficient accuracy. While high-precision spectroscopy has been used for IS measurements in the $2S-2P$ D_1 and D_2 transitions of Li [13–15], the only published result for the $2S-3S$ two-photon transition has uncertainty of 20 MHz [16], 2 orders of magnitude larger than the accuracy of the latest calculations [5]. Thus, we have performed new measurements on the ^{6,7}Li $2S-3S$ transition IS with precision improved nearly 3 orders of magnitude to the 30 kHz level and derive a new value for ΔR^2. Also, because previously reported IS in the D_1 and D_2 lines are inconsistent with theory and with each other [4], we have made a new measurement of the D_1 IS, which resolves some inconsistencies and yields a ΔR^2 consistent with the $2S-3S$ result.

Doppler-free two-photon excitation is performed in a weakly collimated ($\simeq 5^\circ$ FWHM) atomic beam with a titanium-sapphire ring laser (TIS, CR 899-21), followed by ionization with a portion of the 514.5 nm light from its Ar ion pump laser. Resulting ions are separated and detected with a quadrupole mass spectrometer, operated at reduced resolution to transmit both ^{6}Li$^+$ and ^{7}Li$^+$. The TIS frequency is stabilized and scanned under computer control by offset locking to a single-mode HeNe laser [17], using an evacuated and temperature-stabilized scanning confocal interferometer (CFI, $\ell \simeq 50$ cm, finesse $\simeq 20$) as a transfer oscillator. The CFI is calibrated against known ^{87}Rb ground state hyperfine splitting [18] observed in $5S-5D$ two-photon excitation at 778 nm, similar to the Li excitation at 735 nm. The Rb hyperfine splitting calibrates the CFI to a relative accuracy of 2×10^{-5}. Then the TIS is set at several frequencies spread over ±5 THz that are fine-tuned to have mode coincidence in the CFI. The free-spectral-range (FSR) is refined by finding the minimum in $\sum \mathrm{mod}_1(f_i/\mathrm{FSR})$ over the range expected from initial hyperfine calibration. The f_i are measured with a commercial wave meter (Burleigh

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WA1500) calibrated against the ^{85}Rb($F = 3 \rightarrow 5$) hyperfine component of the same $5S - 5D$ transition, whose frequency is known to a relative accuracy of 1×10^{-11} [19]. This calibration, careful alignment, and signal averaging yield wave meter values with uncertainty of <5 MHz. Uncertainty in the f_i affects CFI calibration, but simulations show that a typical three-frequency mode coincidence results in an uncertainty of ± 2 modes in CFI length, and with $10 f_i$, exact mode numbers are determined with 95% confidence. Thus, if one f_i is the ^{85}Rb($F = 3 \rightarrow 5$) calibration line, the FSR is known with the same relative accuracy at or near the calibration wavelength. At other wavelengths, phase dispersion in interferometer mirror coatings can change the effective FSR and calibration accuracy is not maintained. However, the same fractional fringe method was used to track effective CFI length from the 778 nm Rb wavelength down to the 735 nm used for Li excitation, and effective CFI length did not change by more than 0.5 mode, yielding $\mathrm{FSR}_{735} = 148.628\,31(10)$ MHz. Accurate scanning also depends on linearity in piezoelectric sweeping the CFI length. This was tested by measuring the time between two successive modes as a function of the position of the first mode during the CFI sweep. After applying a small quadratic correction to the ramp voltage, the maximum nonlinearity over the 1 FSR used to lock the TIS laser corresponded to a frequency deviation of <8 kHz.

Figure 1 shows typical spectra recorded for the Li $2S - 3S$ transition. Figure 1(A) shows the overall structure with two hyperfine transitions ($\Delta F = 0$) for each isotope, $F = 1/2, 3/2$ for ^{6}Li and $F = 1, 2$ for ^{7}Li. The fitting function is a sum of two Gaussian pedestals corresponding to Doppler-broadened excitation in background gas and in the atomic beam, and a Voigt profile for the Doppler-free excitation. The pedestal Gaussian widths are as expected from normal Doppler width and atomic beam collimation. The Doppler-free peak has a width of 7 MHz (FWHM) with 4.5 MHz Lorentzian component, slightly less than the 5.3 MHz expected from the 29.8 ns lifetime of the $3S$ state [20]. To obtain better statistics for splitting determinations, skip-step scans were used as shown in Fig. 1(B): High-resolution scans were recorded near each resonance while interpeak regions were scanned in a single step without data acquisition. A single scan requires ~2 min and a typical measurement sums 5–10 scans to average out medium-term systematic fluctuations such as atomic beam flux and laser intensity. The solid line in Fig. 1(B) is the fit using the same line function as in Fig. 1(A) and determined centroids have typical uncertainty of 200 kHz. Precision is limited predominantly by the natural width of the resonances and counting statistics. Three intervals are taken from the spectra: The splitting between the two hyperfine components for each isotope, Δf_6 and Δf_7, and the ^{6}Li($F = 3/2$)–^{7}Li($F = 2$) interval, Δf_{76}. The variation in these intervals for 104 measurements performed over five days is shown in Fig. 2.

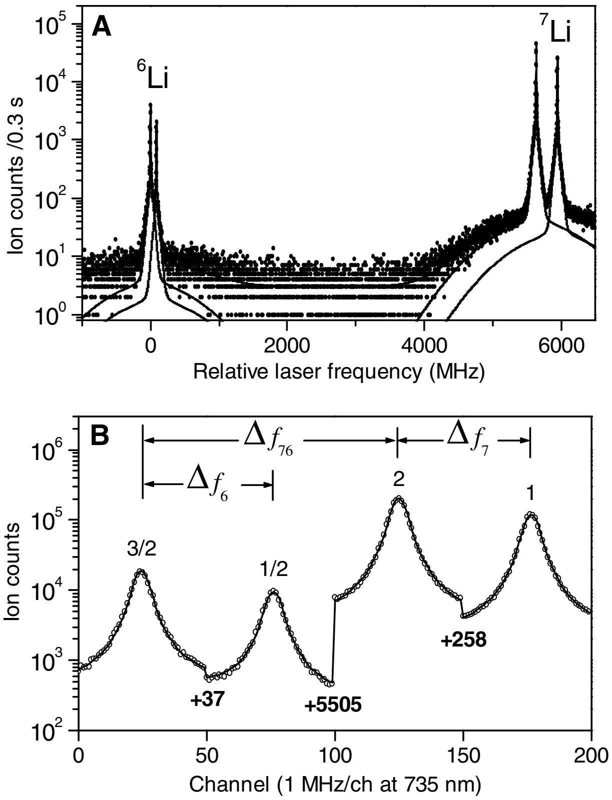

FIG. 1. Two-photon resonant, three-photon ionization spectra of ^{6,7}Li. (A) Overall spectrum and line shape. (B) Skip-step scan for splitting determination; peak labels are hyperfine $F(\Delta F = 0)$ and the size of the skip steps is indicated beneath the curve.

During the first four days, various operating conditions were altered to check for systematic errors. These included intensity and focusing of the resonance and ionization lasers, CFI scan speed and dynamic recalibration time constant, atomic beam flux and pointing, ion extraction field, and residual magnetic fields. None were found to have a significant effect on the observed splittings. Transit-time broadening of a few MHz could be observed when the resonance laser was sharply focused ($d \simeq 40\ \mu$m), but most measurements were made with softer focusing (200–300 μm). Absolute line positions (but not splittings) showed a weak dependence on the ionization laser intensity; a red shift of ~120 kHz at the highest intensity (250 W/mm^2, diffraction limited focusing), consistent with ac Stark shift calculations. Stray magnetic fields were observed as weak Zeeman splitting of a few MHz for some of the low-F ^{87}Rb reference lines. This was reduced by adding external mu-metal magnetic shielding. However, for Li no Zeeman structure was resolved and there was no apparent shift in centroids with or without the added shielding. On the fifth day, measurements were performed with no systematic changes, and it can be seen that the statistical fluctuations are not significantly different from days that included systematic alteration.

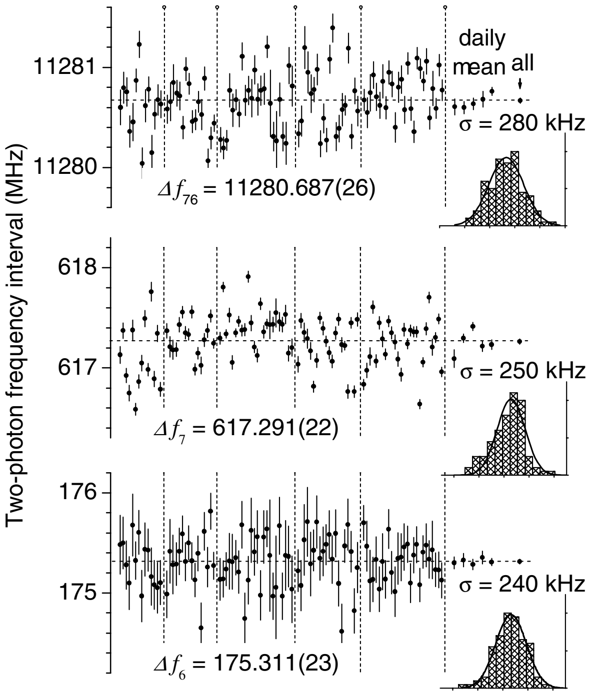

FIG. 2. Variation of measured intervals over five days of measurement. Error bars are 1σ estimates from nonlinear least squares fitting using statistical data weighting, while final values are weighted averages of the daily means.

The A_{3S} magnetic-dipole hyperfine constants are derived from the observed splittings as

$$A_{3S}(^n\mathrm{Li}) = (\Delta f_{gs} - \Delta f_n)/(I + 1/2), \tag{1}$$

where the $2S$ ground state hfs splittings Δf_{gs} are precisely known from atomic beam magnetic resonance measurements [21]. Similarly, the isotope shift of the hfs center of gravity is

$$\mathrm{IS} = \Delta f_{76} + \tfrac{3}{4}(A_{2S} - A_{3S})_{^7\mathrm{Li}} - \tfrac{1}{2}(A_{2S} - A_{3S})_{^6\mathrm{Li}}. \tag{2}$$

Resulting values for A_{3S} and IS are given in Table I with uncertainties obtained from normal error propagation through Eqs. (1) and (2), using the Δf interval uncertainties with 8 kHz added to each for possible systematic error from local scan nonlinearity. Scale (CFI length) uncertainty, proportional to the final values, is insignificant for A_{3s} but adds $\simeq$ 7 kHz to the IS uncertainty.

The current result for $A_{3S}(^7\mathrm{Li})$ disagrees with the previous experimental determination by Stark spectroscopy [22], but is in excellent agreement with theoretical values, obtained by both Hylleraas variational [23] and multiconfiguration Hartree-Fock [20] methods. Also, the ratio $A_{3S}(^7\mathrm{Li})/A_{3S}(^6\mathrm{Li}) = 2.6403(12)$ is in good agreement with the $2S$ ground state ratio of 2.640 73 [21], indicating no hyperfine anomaly at the level of precision available in these experiments.

TABLE I. Hyperfine structure constants, Isotope shift, and transition energies for the ^{6,7}Li two-photon transition $2\,^2S_{1/2} \rightarrow 3\,^2S_{1/2}$. Theoretical calculations indicated by *.

	^{6}Li	^{7}Li	Ref.
A_{3S}, MHz	34(13)	95(10)	[16]
		94.68(22)	[22]
	35.263(15)	93.106(11)	This
		93.09	[23]*
		93.084	[20]*
IS, MHz		11 435(20)	[16]
		11 453.734(30)	This
		11 454.24(5)(39)[a]	[5]*
E, cm^{-1}	27 205.7129(10)	27 206.0952(10)	[24]
	27 205.712 14(10)	27 206.094 20(10)	This
		27 206.0924(39)	[5]*

[a] Second uncertainty from uncertainty in nuclear charge radii.

Another benchmark for comparison with theory is the $2S - 3S$ transition energy. This was measured with the wave meter and a mixed sample containing both Li and Rb. The TIS laser was switched between locking on the reference $^{85}\mathrm{Rb}\ 5S - 5D(F = 3 \rightarrow 5)$ and the $^7\mathrm{Li}(F = 2 \rightarrow 2)$ transitions. Five measurements averaging 100 readings were performed at each of the lock frequencies, and the collinear alignment of the test and reference HeNe lasers was readjusted for each measurement. This is needed because of small pointing changes when changing wavelengths, but also because collinearity is the limiting factor in wave meter accuracy, and realignment gives a good statistical assessment of this uncertainty. Thirteen measurement sets were performed over a period of ~1 month to yield $f(^7\mathrm{Li}{:}2S - 3S, F = 2) = 815\,617\,954(3)$ MHz. This is corrected to the hfs center of gravity and given in cm^{-1} in Table I for comparison with prior values. The cm^{-1} value given for ^{6}Li is the ^{7}Li value offset by the more accurately measured IS, rather than an independent measurement. The results are in good agreement with the theoretical value as well as the previous experimental value, but accuracy is improved by an order of magnitude.

The IS can be compared with the most recent theoretical value [5] (Table I): The uncertainty in the experimental value and the calculated mass effects are comparable, 30 and 50 kHz, respectively, while the 0.51 MHz difference between experiment and theory is comparable to the uncertainty from nuclear charge radii. If the experiment is interpreted as a measurement of the difference in the squares of the nuclear charge radii, then from Eq. (25) of Ref. [5]

$$R^2_{\mathrm{rms}}(^6\mathrm{Li}) - R^2_{\mathrm{rms}}(^7\mathrm{Li}) = 0.47 \pm 0.05\ \mathrm{fm}^2. \tag{3}$$

This agrees with the value $0.79 \pm 0.25\ \mathrm{fm}^2$ obtained from nuclear scattering data [25], but there is a marked

TABLE II. Values for the squared difference in nuclear radii $\Delta R^2 = R^2(^6\mathrm{Li}) - R^2(^7\mathrm{Li})$ in units of fm^2.

Method	Ref.	IS (MHz)	ΔR^2
Electron scattering	[25]		0.79(25)
$\mathrm{Li}(2S-3S)$ IS	This work	11 453.734(30)	0.47(5)
$\mathrm{Li}(2S-2P_{1/2})$ IS	[13]	10 534.26(13)	0.84(8)
	[15]	10 533.13(15)	0.38(7)
	[14]	10 532.9(6)	0.29(25)
	This work	10 533.160(68)	0.39(4)
$\mathrm{Li}(2S-2P_{3/2})$ IS	[13]	10 533.59(19)	0.41(8)
	[15]	10 534.93(15)	0.96(7)
	[14]	10 533.3(5)	0.29(21)
$\mathrm{Li}^+(2\,^3S_1 - 2\,^3P_J)$ IS	[9]		0.73(5)

disagreement among the various spectroscopic determinations, as shown in Table II. For IS in the atomic Li resonance lines, D_2 is probably less reliable than D_1 because of unresolved hyperfine structure and electric quadrupole contributions to this structure. Also, optical pumping may alter relative intensities of the unresolved components. In contrast, the D_1 line is relatively simple with all components well resolved and only magnetic-dipole coupling. Thus, the discrepancy of 1.13 MHz in D_1 IS between [13] and [15] is rather disconcerting and leads to the large difference in ΔR^2 values given in Table II. These difficulties, as well as possible differential Doppler shifts from angular misalignment of atomic and laser beams ($\simeq$ 170 kHz/mr at 1000 K atomization temperature) may also contribute to disagreement of the splitting isotope shift for both [15] and [13] with the theoretical value of 0.393 MHz, which can be accurately calculated (see Ref. [5] for further discussion). Because of these discrepancies, we also reexamined the D_1 structure using one-photon excitation near 671 nm followed by photoionization at 345 nm (Ar ion laser). A well collimated ($\simeq$ 1 mr) atomic beam and line shape analysis with retroreflected resonance laser beam [26] were used to adjust perpendicularity error to <0.2 mr. With bidirectional excitation, the residual contribution to IS uncertainty is less than 10 kHz. The resulting $\mathrm{IS}(D_1) = 10\,533.160(68)$ MHz is in good agreement with [15] and the less precise results of [14], but in disagreement with the most recent result [13]. The ΔR^2 derived from our D_1 IS is 0.39(4) fm^2, substantially in agreement with the value we found from the $2S-3S$ IS. An average result of 0.43(6) fm^2 is still in marginal agreement with the less precise nuclear scattering result; however, there remains an unexplained discrepancy with the result from the $\mathrm{Li}^+(2\,^3S_1 - 2\,^3P_J)$ transitions [9].

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