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Ionization energy of $^{6,7}\text{Li}$ determined by triple-resonance laser spectroscopy

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Rydberg level energies for $^{7}\text{Li}$ were measured using triple-resonance laser excitation, followed by drifted field ionization. In addition to the principal $n\,2\,P$ series, weak Stark mixing from residual electric fields allowed observation of $n\,2\,S$ and hydrogenic Stark manifold series at higher $n$. Limit analyses for the series yield the spectroscopic ionization energy $E(\text{Li})=43\,707.25\,018$ cm$^{-1}$. The $^{6,7}\text{Li}$ isotope shift (IS) was measured in selected $n\,2\,P$ Rydberg levels and extrapolation to the series limit yields $\text{IS}(E) = 18\,067.54(21)$ MHz. Results are compared with recent theoretical calculations: $E$ values from experiment and theory agree to within 0.0011 cm$^{-1}$, with the remaining discrepancy comparable to uncertainty in QED corrections of order $\alpha^2$Ry. The difference between experiment and calculated mass-based IS($E_i$) yields a change in nuclear charge radii between the two isotopes $\delta(r^2)_{7,6} = -0.60(10)$ fm$^2$.

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I. INTRODUCTION

Precise measurement of the lithium ionization energy is important for testing recent advances in calculations on few-particle systems [1–3]. In addition to their intrinsic interest, these calculations are an essential underpinning for optical measurements that investigate changes in nuclear charge distribution for the short-lived radioisotopes $^{8,9,11}\text{Li}$ [4,5]. These measurements focus on how the two halo neutrons of $^{11}\text{Li}$ affect the charge distribution of the $^{7}\text{Li}$-like nuclear core, a subject of considerable current interest in nuclear physics [6]. Recent atomic physics calculations that include complete accounting for QED shifts up to order $\alpha^2$Ry have yielded refined values for both the ionization energy and the $2s\,2S-3s\,2S$ transition energy of $^{7}\text{Li}$ with estimated accuracy better than 0.001 cm$^{-1}$ [7]. Results for both are in good agreement with existing experimental data, but theoretical uncertainties are now smaller than experimental. Thus, improved experimental values are desirable for further refining and testing of theory, and consequently insuring that mass and nuclear volume effects can be accurately separated in the online radioisotope studies.

Recent measurement of the $2\,2S-3\,2S$ energy [8] decreased experimental uncertainty about 10-fold over previous discharge lamp Fourier transform measurements [9] and showed a closer agreement (+0.0016 cm$^{-1}$) with the calculated value. The $2\,2S-3\,2S$ energy in Ref. [8] has been independently confirmed by beat frequency methods referenced to an $I_2$ hyperfine stabilized diode laser [10].

The accepted value for the $^{7}\text{Li}$ ionization energy of $43\,707.25\,018$ cm$^{-1}$ [11] is derived from classic atomic emission measurements [12] that were combined with newer measurements and reanalyzed by Johansson in 1959 [13], with the resulting value “thought to be correct within 0.005 cm$^{-1}$.” However, remeasurement of a few transitions with laser-wavemeter methods suggested uncertainty more on the order of 0.030 cm$^{-1}$ [14]. More recently, pulsed laser studies have examined the $nf\,2F$ [15], and $np\,2P$ [16] Rydberg series, but precision in the derived $E\gamma$ values do not seem to improve on the accepted value. The most recent theoretical value $E(\text{Li}) = 43\,707.25\,183(6)$ cm$^{-1}$ [7] is in reasonable agreement with the accepted value, but has estimated precision that is better by more than an order of magnitude.

Most of the alkali metals have had their ionization energies precisely determined by Rydberg series spectroscopy [14,17–20], but studies on Li are lacking because of interference from one-photon absorption by $\text{Li}_2$ dimers in the same 460–470 nm region as the two-photon-excited atom Rydberg series [21,22]. We use stepwise excitation with three (red) high-resolution single-mode lasers, followed by drifted rf-field ionization and mass analysis, to detect the Rydberg series. In this work, Rydberg structure observed out to $n \approx 300$ is dominated by the principal $np\,2P$ series, but weak residual electric fields also allow observation of the $ns\,2S$ series and series of hydrogenic Stark manifolds (HSM) at higher $n$. For determination of the ionization energy, convergence analyses on the predominant $np\,2P$ series ($n = 28$ to 175) yields the value $E(\text{Li}) = 43\,707.25\,180(18)$ cm$^{-1}$, while the other series and measurements at higher electric field confirm the value, as well as the correction used for residual Stark shifts. Uncertainty in the relative series con-

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II. EXPERIMENT

The experimental apparatus and general methodology have been described in previous papers [23,24] and are only briefly summarized here. Within a field-free interaction region, $^7$Li in a collimated atomic beam ($\approx 1$ mrad, natural isotopic abundances) is excited to high-lying Rydberg levels by three single-mode cw lasers (diode, Ti:sapphire, dye) via

$$
2s\,^2S_{1/2}(F=2) \quad 2p\,^2P_{1/2}(F=2) \quad 3s\,^2S_{1/2}(F=2) \quad np\,^2P.
$$

(1)

The long-lived Rydberg atoms then drift out of the interaction region into a quadrupole mass filter (QMF) where they are ionized by rf fields. Continued passage through the QMF provides mass selection and transmitted ions are detected with an off-axis continuous dynode multiplier. Similar excitation schemes have been used for selective analytical measurements [25] and for measuring hyperfine structure (hfs) in the $^2S$ level using Stark spectroscopy [26], but neither reported Rydberg level energies.

Relative laser frequencies are controlled by interferometric offset locking to a stabilized single-frequency He:Ne laser [27] with a confocal Fabry-Perot interferometer (CFI) where FSR = 148.629 65 (6) MHz and are known with an accuracy of $\approx 5 \times 10^{-5}$ cm$^{-1}$ (1.5 MHz) over the $\approx 120$ cm$^{-1}$ range below $E_I$ studied here. Absolute laser frequencies are determined with an accuracy of $\approx 2$ MHz using a carefully aligned wavemeter that is calibrated against known frequency standards. Relevant calibrations used for these experiments are the $^7$Li $2\,^2S_{1/2}\rightarrow 2\,^2P_{1/2}(F=1 \rightarrow 2)$ transition at 671 nm [28], the $^{40}$Ca 657-nm $4s\,^1S_{1/2}\rightarrow 4s4p\,^3P_{1}$ intercombination line [29,30], the $^{85}$Rb $5\,^2S_{1/2}\rightarrow 5\,^2D_{5/2}(F=3 \rightarrow 5)$ two-photon transition at 778 nm [31], and the $^{133}$Cs $D_2(F=4 \rightarrow 5)$ transition at 852 nm [32]. After calibration on the 852 nm Cs line, our determinations for the other three wavelengths agree with the accepted values to within 1.7 MHz (average: $-0.76$ MHz from reference values).

Because of large Doppler shifts for lithium, atomic beam–laser beam perpendicularity is critical for accurate measurement of absolute energies. This was tested and adjusted with $1+1'$ ionization: the 671 nm resonance laser populated the $2P$ levels, which were then directly photoionized with the 345 nm line from an argon ion laser. The 671 nm beam was retroreflected and carefully aligned through translatable apertures separated by 1.2 m on either side of the atomic beam.

If there is significant deviation from perpendicularity between laser and atomic beams, the result is a bimodal peak (Fig. 1) corresponding to equal but opposite Doppler-shifted distributions for the two directions. The difference in intensity between the peaks is caused by four additional Fresnel reflection losses experienced by the retroreflected beam exiting and reentering through the vacuum chamber window. Changing the intersection angle by countermoving the apertures and realigning allows determination of the crossing point for the two Doppler-shifted peaks, corresponding to true perpendicularity. From the 0.25 mrad uncertainty in the crossing point, the corresponding residual Doppler shift uncertainty is $\approx 1$ MHz.

For triple-resonance excitation to Rydberg levels, the 813 nm and 614 nm lasers are carefully overlapped with the aligned 671 nm laser (angular deviation $<0.1$ mrad), and with counterpropagation of successive excitation steps. Frequencies of the first two lasers are centered by tuning the third step slightly above the ionization limit (611 nm) and observing direct photoionization. While centering of the individual steps is within 3 MHz, the sum frequency can be set with an accuracy of $\approx 0.5$ MHz to selectively populate the $3\,^2S_{1/2}(F=2)$ intermediate excited state. The third step laser is then tuned near a high Rydberg level ($n \approx 150$), and electric fields within the interaction region are minimized by adjusting correction electrodes in three dimensions to minimize the Stark redshift in the observed resonance position [24].

The overall approach is to carefully measure the energy of a reference Rydberg level (we use $n=76$) and then use relative frequencies to calculate the energies of other levels. For high $n$ ($>70$), where levels are closely spaced, resonances were observed using continuous scanning with fringe-offset-locking, as previously described in Ref. [23]. Transitions could also be investigated in individual short scans that were still linked to the reference level by fringe-offset-locking, using the wavemeter to confirm CFI order number, as shown in Fig. 2.
For determination of the reference level absolute energy, the energy of the third-step laser was added to the known energy of the 3 2 S second excited level [8,10]. With several measurement sets over the course of these experiments, we find the 7Li 3 2 S/H20849 F=2/H20850 =2/H20850 transition energy to be 16 262.04 190/H20849 7/H20850 cm−1, and the corresponding energy of 76 2 P above the center of gravity (c.g.) of the ground level hyperfine structure is 43 468.138 43/H20849 17/H20850 cm−1.

III. RESULTS AND DISCUSSION

A. Rydberg spectra

Figure 3 shows the Rydberg spectrum observed for 7Li over the last ≈20 cm−1 below El, obtained with minimized electric field. Below n≈80, only members of the np 2 P series are observed, and with better than five orders of signal to background. A weak substructure grows at higher n, as shown in the vicinity of n=131–132 in Fig. 4. In the minimized field case (=0.3 mV/cm) the n 2 P series is the dominant feature and is still well resolved, but because of Stark mixing from the residual field, the 2 S series appears weakly (3×10−4 relative intensity) at quantum defect δ=0.4. Broader peaks appear at energies slightly higher than the 2 P levels (centered around δ=0), and are attributed to manifolds of Stark states, corresponding to the zero-field ℓ=2 to n−1 higher orbital angular momentum states. The effect of increased electric field (=20 mV/cm) is shown in the bottom of Fig. 4: the Stark manifold broadens and subsumes the 2 P levels as the manifold width becomes >2δ; while the 2 S

FIG. 3. Rydberg spectrum of 7Li obtained by triple-resonance excitation and drifted field ionization, minimized electric field in the excitation region. Principal structure is the n 2 P series. Unresolved weak structure above n=100 are detailed in Fig. 4.
levels remain distinct, become much stronger, and are only slightly shifted. This structure is completely analogous to the \( n=15 \) behavior examined in the seminal work of Kleppner et al. [33]; however, our electric field is in the mV/cm range instead of kV/cm, and we do not resolve the (many more) individual Stark states. For determination of the ionization energy, it is important to note that, as long as the electric field perturbations are small, the induced shifts in the \( ^2S \) and \( ^2P \) series scale proportional to \( F^2(n^*)^7 \) [34].

For \( n > 70 \), Rydberg spectra were recorded as continuous scans (Fig. 3), both with minimized and \( \approx 20 \) mV/cm electric fields. More detailed investigation examined the \( ^2P \) series for \( n=28–175 \) at minimized field using both continuous and localized, higher resolution scans (Fig. 2). Observed peaks were fit with Voigt profiles (statistical weighting) while positions within the CFI order were obtained by linear fitting of the simultaneously recorded CFI fringe position (bottom of Fig. 2). Typical statistical uncertainty for fitting peak centroids was \( \approx 200 \) kHz, and average standard deviation for repeated measurements taken on different days was 600 kHz (2 \( \times \) \( 10^{-5} \) cm\(^{-1} \)). We do not tabulate values for all of the individual levels here, but note that they are all reproduced within \( 6 \times 10^{-5} \) cm\(^{-1} \) by the simple Rydberg-Ritz formula discussed below.

### B. \(^7\)Li ionization energy

The energies of levels within a given Rydberg series for a one-valence-electron atom can be described by the Rydberg-Ritz equation:

\[
E_n = E_0 - \frac{R_M}{(n^*)^2},
\]

where \( R_M \) is the mass-reduced Rydberg constant for the particular isotope; \( R(\text{\(^7\)Li})=109 728.735 348 \) cm\(^{-1} \), based on CODATA 2002 values for \( R_\infty \) and electron mass [35], and \(^7\)Li mass from AME 2003 [36]. A new determination of the \(^7\)Li mass [37] has yielded a value \( 1.1 \times 10^{-9} a_u \) lower than the AME 2003 value, but this does not alter our results at the current level of precision. The effective principal quantum number \( n^* \) is expressed in terms of a state specific quantum defect, where the variation with \( n \) is generally expanded in inverse even powers of \( n^* \),

\[
\delta_n = \delta_0 + \frac{a_1}{(n^*)^2} + \frac{a_2}{(n^*)^4} + \cdots
\]

to account for small, slowly varying changes in quantum defect at low \( n \), which may be caused by core polarization, relativistic effects, and incomplete wave-function recapitulation. The formulation (3), generally requires an iterative solution, but, because of the compact \( 1s^2 \) core of lithium and because we study higher levels \( (n \geq 28) \), only the first expansion term is needed (indeed, for data sets with \( n > 70 \), the original Rydberg formula with constant quantum defect is sufficient). Also, the constant approximation \( n^*=n-\delta_0 \) has been used for calculation of the Ritz terms [19]; this may cause small shifts in determined Ritz coefficients \( a_n \), but has negligible effect on either \( E_f \) or the limit quantum defect \( \delta_0 \). Thus the measured level energies are fit according to

\[
E_n = E_0 - \frac{R_M}{n_0^2} + c_S n_0^7,
\]

where \( n_0=n-\delta-\delta_0/(n-\delta_0) \), and the final term is the Stark shift correction. Fitting was done by Levenberg-Marquardt nonlinear least squares with fit parameters \( E_f, \delta, a_1, \) and \( c_S \). For data sets taken from a single spectrum, the measured level energies were equally weighted with \( \sigma=6 \times 10^{-5} \) cm\(^{-1} \), the average day-to-day reproducibility. For the data sets with multiple determinations for each level, weights were the actual standard errors. Both \( a_1 \) and \( c_S \) could be fixed at zero to examine the effect of the Stark and Ritz terms. Results from a number of measurements are summarized in Table I.

The first two data sets, for the \(^2P \) and \(^2S \) series, are derived from the same experimental spectrum (Fig. 2). Agreement between the two series is relatively good, within \( 1.4 \times 10^{-4} \) cm\(^{-1} \), but greater than the combined uncertainty.

### Table I. Ionization energy and limit quantum defects determined from convergence analysis on Rydberg series of \(^7\)Li. Uncertainties in parentheses include only the statistical uncertainty (1\( \sigma \)) from the fitting procedure.

<table>
<thead>
<tr>
<th>Set</th>
<th>Series</th>
<th>( n ) range</th>
<th>Field(^a)</th>
<th>( E_0 ) (cm(^{-1} ))</th>
<th>( E_0 ) (cm(^{-1} )) (n.s.)(^b)</th>
<th>( \delta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( np^2P )</td>
<td>70–170</td>
<td>min</td>
<td>43487.15931(2)</td>
<td>43487.15915(2)</td>
<td>0.04709(5)</td>
</tr>
<tr>
<td>2</td>
<td>( ns^2S )</td>
<td>93–178</td>
<td>min</td>
<td>43487.15945(2)</td>
<td>43487.15929(1)</td>
<td>0.39977(13)</td>
</tr>
<tr>
<td>3</td>
<td>( ns^2S )</td>
<td>83–144</td>
<td>20</td>
<td>43487.15917(9)</td>
<td>43487.15856(6)</td>
<td>0.39744(32)</td>
</tr>
<tr>
<td>4</td>
<td>( np^2P )</td>
<td>76–110</td>
<td>20</td>
<td>43487.15949(9)</td>
<td>43487.1558(10)</td>
<td>0.051(7)</td>
</tr>
<tr>
<td>5</td>
<td>HSM</td>
<td>76–164</td>
<td>20</td>
<td>43487.15932(5)</td>
<td>=0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( np^2P )</td>
<td>28–93</td>
<td>min</td>
<td>43487.159347(11)</td>
<td>0.047180(11)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( np^2P )</td>
<td>28–153</td>
<td>min</td>
<td>43487.159416(6)</td>
<td>43487.159400(4)</td>
<td>0.047230(7)</td>
</tr>
<tr>
<td>8</td>
<td>( np^2P )</td>
<td>28–175</td>
<td>min</td>
<td>43487.159395(3)</td>
<td>43487.159287(9)</td>
<td>0.047192(5)</td>
</tr>
</tbody>
</table>

\(^{20}mV/cm\) estimated from Simion field calculations and applied correction potential. min: \( \approx 3 \) mV/cm estimated by comparing fit Stark coefficient with higher field case.

\(^{b}\)No Stark correction.

\(^{c}\)Fit level energies average of three to eight measurements on different days.
Because of the larger field effects, analysis for the beam axis. The effect on the spectra was shown in Fig. 4. The apparent $E_I$ values are slightly lowered if no Stark correction is applied. Including the first Ritz term was marginally significant, as expected, much more so for the $n$-series. The Stark coefficient is applied. Including the first Ritz expansion term as a free variable because the Stark shifts below $n=100$ are negligible. For sets 7 and 8, changes in $E_I$ from Stark correction are small but statistically significant. Inclusion of the first Ritz term was marginally significant; if not included, the derived $E_I$ values were $2 \times 10^{-5}$ cm$^{-1}$ higher.

The quality of the fit for the full data set (8) is illustrated in Fig. 5, which shows the deviations between the measured and fit energy levels: the maximum deviation is $6.2 \times 10^{-5}$ cm$^{-1}$ and the average is $1.9 \times 10^{-5}$ cm$^{-1}$. The figure also illustrates the nature and magnitude of the Ritz and Stark corrections. Statistical uncertainty for the convergence limit is $3 \times 10^{-6}$ cm$^{-1}$, but analysis on subsets ($n \leq 100$ and $n > 100$), where Stark and Ritz terms, respectively, become insignificant, as well as allowing higher-order Ritz terms, indicate that real uncertainty is on the order of $3 \times 10^{-5}$ cm$^{-1}$. This is primarily due to systematic errors from drift in the residual electric field, reflected by the fact that $\chi^2 = 1.0005$ for the low-$n$ subset while $\chi^2 = 2.87$ for the high-$n$ subset. Values for derived atomic parameters are given in Table II.

The uncertainty for $E_I(7\text{Li})$ in Table II is only the statistical uncertainty derived from the various data sets given in Table I; additional systematic errors for the $E_I$ determination are discussed below. The limit quantum defects show good agreement with values determined by microwave measurement of $n-(n+1)$ level intervals [38]; however, those measurements did not yield a value for $E_I$. The Ritz coefficient for the $^2P$ series is relatively imprecise because only $n \geq 28$ are studied, and $\delta_0$ has already nearly converged to $\delta_0$ ($\delta_0 = 0.047$ 143). This could be improved by adding measurements at lower $n$, but was not the focus of this work and might require including higher-order Ritz terms. No Ritz coefficient was determined for the $^2S$ series, because it was observed only for $n > 80$ and $a_1(n^2S) = 0.029$ determined in Ref. [38] indicates that the effect is of similar magnitude (but opposite sign) as in the $^2P$ series.

In addition to the statistical uncertainty for $E_I(7\text{Li})$ given in Table II, there are other possible systematic errors, which are detailed in Table III. The first two entries are determined with the same instrumental method (wavemeter) and calibrations; thus, the uncertainties may be correlated and are added.

### Table II. Atomic parameters determined for $7\text{Li}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work</th>
<th>Microwave$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_I$ (cm$^{-1}$)</td>
<td>43487.159395(33)</td>
<td>399510(1)</td>
</tr>
<tr>
<td>$\delta_0(n^2S)$</td>
<td>0.3994(7)</td>
<td>0.04720(2)</td>
</tr>
<tr>
<td>$\delta_0(n^2P)$</td>
<td>0.04720(2)</td>
<td>0.047170(2)</td>
</tr>
<tr>
<td>$\delta_2(n^2P)$</td>
<td>$-0.040(13)$</td>
<td>$-0.024(1)$</td>
</tr>
</tbody>
</table>

$^a$From Ref. [38]; $\delta_0(n^2P)$ is an intensity weighted average for $n^2P_{1/2}$ and $n^2P_{3/2}$ values of 0.047 178 0(20) and 0.047 166 5(20), which are not resolved in our measurements.

<table>
<thead>
<tr>
<th>Source</th>
<th>Uncertainty (10$^{-5}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3S_{1/2}$ energy</td>
<td>10</td>
</tr>
<tr>
<td>$^3S_{3/2}$ energy</td>
<td>7</td>
</tr>
<tr>
<td>Beam perpendicularity</td>
<td>3</td>
</tr>
<tr>
<td>Interferometer scale</td>
<td>2</td>
</tr>
<tr>
<td>Convergence above $^76^2P$</td>
<td>3.3</td>
</tr>
<tr>
<td>Total</td>
<td>17.7</td>
</tr>
</tbody>
</table>

The uncertainty in the determination of the $^7\text{Li}$ ionization energy. Components and their addition are discussed in the text.
TABLE IV. Summary of experimental and theoretical values for bound transition energies and $E_I$ of $^7$Li, values in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Experiment</th>
<th>Reference</th>
<th>Theory</th>
<th>Reference</th>
<th>$\Delta$ (10$^{-4}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2S-\frac{3}{2}P_{1/2}$</td>
<td>14903.648130(14)</td>
<td>[28]</td>
<td>14903.6478(10)</td>
<td>a</td>
<td>−3.3 (10)</td>
</tr>
<tr>
<td>2S-3S</td>
<td>27206.09420(10)</td>
<td>[8]</td>
<td>27206.0926(9)</td>
<td>[7]</td>
<td>−16 (9)</td>
</tr>
<tr>
<td>2S-$E_I$</td>
<td>43487.15940(18)</td>
<td>This paper</td>
<td>43487.15830(60)</td>
<td>[7]</td>
<td>−11 (6)</td>
</tr>
</tbody>
</table>

$^14$ 903.647 7(39) cm$^{-1}$ from Ref. [39], revised after comparison with Bethe logarithms in Ref. [7].

C. $^6^7$Li isotope shift of ionization energy

While absolute energies may be the best overall test of theory, with relative accuracies for both experiment and theory approaching the 10$^{-8}$ level, isotope shifts are also of considerable interest. Many mass-independent terms in the theory, and their associated uncertainties, cancel for isotopic shift in transition energies, and theoretical uncertainties are on the order of 15 kHz ($5 \times 10^{-7}$ cm$^{-1}$). This is an order of magnitude smaller than uncertainty arising from imprecise knowledge of the nuclear charge distributions, and is indeed the basis for optical investigation of lithium nuclear charge radii [4,5]. The experimental situation is similar: the relatively small intervals of isotope shifts are more easily measured, and generally with greater accuracy, than absolute transition energies. Hence, for measurement of the isotope shift of the ionization energy between $^7$Li and $^6$Li, we do not perform an independent measurement of $E_I(^6$Li) as described for $^7$Li in the preceding section, but rather measure the isotope shift in a series of Rydberg levels and extrapolate to the ionization limit. The isotope shifts in the $^2S-\frac{3}{2}P_{1/2}$ and $^3S-\frac{3}{2}P_{1/2}$ transitions energies [40] may also contribute to understanding this problem, if corresponding theoretical calculations are performed.

\[ E_I(^7\text{Li})_{\text{exp}} = 43 487.159 40(18) \] (5)
given with respect to the hyperfine c.g. in the $^2S$ ground level. This may be compared with the most recent theoretical value [7],

\[ E_I(^7\text{Li})_{\text{theory}} = 43 487.158 30(60). \] (6)

Although the agreement is now quite good, at the $1 \times 10^{-7}$ cm$^{-1}$ level and nearly within the combined uncertainties, similar residual discrepancies are also observed for the $^2S-\frac{3}{2}S$ and $^2S-\frac{3}{2}P_{1/2}$ transitions energies, as summarized in Table IV.

The residual differences are of the same order as the uncertainty of $4 \times 10^{-4}$ cm$^{-1}$ for the higher-order QED corrections given in Ref. [7], and may give guidance to further development of these difficult to evaluate terms. Very accurate measurements of the $^6^7$Li $^2S-\frac{3}{2}S$ transition energies may also contribute to understanding this problem, if corresponding theoretical calculations are performed.

![Graph of isotope shift measurement for the 127 $^2p$ level.](image)

FIG. 6. Isotope shift measurement for the 127 $^2p$ level.
Doppler shifts, only partially resolved hyperfine structure, and the use of interferometric rather than frequency-based methods for determining the optical shifts. Further, only the 2S–3S transition has been used to study the radioactive isotopes $^8\text{Li}$, $^9\text{Li}$ [4, 5].

**IV. CONCLUSIONS**

While the current work has reduced the uncertainty in $E_P(\text{Li})$ by about two orders of magnitude, and to a level comparable to the theoretical uncertainty, dramatic improvements are still possible. The major source of uncertainty in the current measurements is the energy of the reference 76 $^2\text{P}$ level. This could be significantly improved using femtosecond frequency metrology (FFM) [44] for determination of transition energies defining the reference level energy, which would reduce the wavemeter uncertainty to negligible levels. Such a remeasurement of the 76 $^2\text{P}$ level energy, combined with the current convergence analysis, could reduce overall uncertainty to the $3 \times 10^{-5}$ cm$^{-1}$ level. Repeating the full set of measurements with FFM would remove the interferometer scale uncertainty, and it is likely that the convergence limit would also be improved. The major remaining source of uncertainty would be from atomic beam–laser beam perpendicularity, which could be addressed by reexamining Doppler-free two-photon excitation of the $ns^2\text{S}$ and $nd^2\text{D}$ Rydberg series. While this failed with pulsed lasers because of molecular Li$_i$ interference at the relatively high temperatures and vapor densities in the heat pipe used, it is unlikely to be a problem with a weak atomic beam, high resolution lasers (which can resolve atomic lines from molecular), and mass spectrometric detection. Further, excitation with the standing wave inside a resonant enhancement cavity, as has been demonstrated for the 2S–3S transition [4, 5], reduces retrobeam pointing error. Resonant intensity enhancement also increases the two-photon excitation $\approx P^2$, and if a third photon is used for direct photoionization, the overall efficiency improves $\approx P^3$.

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