Precise measurement of hyperfine structure in the $2P_{1/2}$ state of $^7$Li using saturated-absorption spectroscopy

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We report a precise measurement of the hyperfine interval in the $2P_{1/2}$ state of $^7$Li. The transition from the ground state ($D_1$ line) is accessed using a diode laser and the technique of saturated-absorption spectroscopy in hot Li vapor. The interval is measured by locking an acousto-optic modulator to the frequency difference between the two hyperfine peaks. The measured interval of 92.040(6) MHz is consistent with an earlier measurement reported by us using an atomic-beam spectrometer [Das and Natarajan, J. Phys. B 41, 035001 (2008)]. The interval yields the magnetic dipole constant in the $P_{1/2}$ state as $A = 46.047(3)$, which is discrepant from theoretical calculations by $> 80$ kHz.

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I. INTRODUCTION

Measurement of hyperfine structure in the low-lying states of Li is motivated by the fact that its simple three-electron structure makes it amenable to accurate calculations. We have recently reported the most-precise measurements to date of hyperfine intervals (with accuracy of 6 kHz) in the $2P_{1/2}$ state of $^6$Li [1]. Around the same time, there have been high-accuracy calculations of the hyperfine constants in this state using both the configuration-interaction method [2] and the coupled-cluster method [3]. Furthermore, Beloy and Derevianko [4] have pointed out the importance of taking second-order effects into account when calculating the hyperfine constants from the measured intervals. The largest corrections are for Li, and in the case of $^7$Li, the corrections are much larger than the experimental error.

The measured interval in $^6$Li reported by us in the earlier work was 26.091(6) MHz. From this, we obtained an uncorrected constant of $A = 17.394(4)$ MHz [1]. However, taking the $+4.01$ kHz second-order correction given in Ref. [4], the measured interval yields a constant of 17.398(4) MHz, which is in good agreement with the calculated value of 17.4058(8) MHz reported in Ref. [2]. However, the situation in $^7$Li is quite unsatisfactory. Our measured interval of 92.047(6) MHz yields an uncorrected constant of $A = 46.045(3)$ MHz. The second-order correction from Ref. [4] is $+27.0$ kHz, almost an order-of-magnitude larger than the experimental error. More importantly, there are two independent calculations of the hyperfine constant, one reporting a value of 45.966(1) MHz [2] and the other a value of 45.958 MHz [3]. Thus, the uncorrected constant from our measurement differs from both calculations by $\sim$ 60 kHz (20 $\sigma$), while the correction increases the difference still further. Indeed, the agreement in $^6$Li and the discrepancy in $^7$Li is surprising because one would expect larger errors in $^6$Li due to its 13$\times$ smaller natural abundance, resulting in correspondingly lower signal-to-noise ratio.

Though theoretically Li is the simplest alkali-metal atom to deal with, experimentally it is the most challenging. This is because of its high reactivity with all kinds of glasses, which precludes the use of vapor cells. Vapor cells exist for all the other alkali-metal atoms, and the standard technique of saturated-absorption spectroscopy (SAS) [5] in a vapor cell gives spectra with linewidths close to the natural linewidth. This problem can be partly addressed by using a buffer gas in the cell, but that causes collisional broadening of the line and large shifts of the line center [6], making it useless for precision measurements. As a result, most high-precision spectroscopy experiments in Li have been done using laser-induced fluorescence from a collimated atomic beam. In such experiments, it is crucial that the laser beam be perpendicular to the atomic beam. Any misalignment angle would cause a systematic Doppler shift of line center. Since our earlier experiments on Li [1] were done with an atomic beam, and because of the discrepancy with theoretical calculations of the hyperfine constant in $^7$Li, we decided to repeat these measurements using the SAS technique in a new non-atomic-beam spectrometer. Most important for precision measurements is that the SAS technique does not cause a systematic shift of line center even if there is a small misalignment angle between the pump and probe beams.

In this work, we present results of measurements of the hyperfine interval in the $2P_{1/2}$ state of $^7$Li using saturated-absorption spectroscopy in this new spectrometer. To the best of our knowledge, this is the first time such high-resolution SAS spectra have been obtained in Li. The interval is measured with our well-developed technique of locking an acousto-optic modulator (AOM) to the frequency difference between two hyperfine peaks [1, 6]. The results from the current set of measurements are consistent with the previous set, giving confidence that Doppler-shift errors were under control in the previous atomic-beam spectrometer.
II. EXPERIMENTAL DETAILS

The new Li spectrometer consisted of a 25-mm-diameter × 100-mm-long cylindrical pyrex cell. The cell was connected to a resistively-heated Li source and a turbo-molecular pump to maintain pressures below 10⁻⁷ torr. During the experiment, the cell was continuously loaded with Li vapor by heating the source. If the source was turned off, the pump would rapidly evacuate the remaining atoms. The 2S₁/₂ → 2F₁/₂ transition (D₁ line) in Li is at 670 nm. This was accessed with a home-built diode laser system [8], which was frequency stabilized using grating feedback to give an rms linewidth of 1 MHz. The two beams were elliptic with size of 4 mm × 1.5 mm. The probe beam had a power of 12 µW and the pump power was varied from 50 to 120 µW. Thus the highest pump intensity was less than the saturation intensity of 2.5 mW/cm².

A typical spectrum of the D₁ line in ⁷Li is shown in Fig. 1. The spectrum is Doppler corrected by subtracting the signal from a second probe beam without a counter-propagating pump beam. The entire spectrum, as shown in the inset of the figure, has three sets of peaks. The first and third set are easy to understand; they are for transitions starting from the F = 1 ground level and the F = 2 ground level respectively. It is well known that the use of counter-propagating pump-probe beams in SAS causes spurious crossover resonances, exactly in between two real peaks. The real peaks are caused when the pump saturates the transition for zero-velocity atoms, so that probe absorption is reduced. The crossover resonances are caused when a non-zero-velocity group is resonant with one transition for the probe beam and the other transition for the pump beam. Thus two velocity groups contribute to each crossover resonance, and these resonances are generally more prominent than the real peaks. As the figure inset shows, each set of transitions has three peaks corresponding to F' = 1, F' = (1, 2) (the prominent crossover resonance), and F' = 2.

The middle set of peaks is a further artifact of SAS, and is called a ground crossover resonance labeled as F = (1, 2) → F'. It appears because the ground hyperfine interval in ⁷Li is 803 MHz, which corresponds to a Doppler shift within the velocity profile of the Li vapor. Thus, for atoms moving with a velocity v = +269 m/s and when the laser frequency is exactly between transitions starting from the F = 1 and F = 2 levels, the pump induces transitions from the F = 1 level and optically pumps atoms into the F = 2 level. For the same velocity group, since the counter-propagating probe beam (with opposite Doppler shift) is exactly resonant with transitions starting from the F = 2 level, the probe beam shows enhanced absorption. The roles of the F = 1 and F = 2 levels are interchanged for atoms moving with v = −269 m/s. The ground crossover set is therefore inverted compared to the other two sets (see figure) and, as expected, more prominent. We have therefore used this peak for the measurements. A multipeak fit to this set of peaks with a Voigt profile fits the spectrum quite well and shows that there is no significant asymmetry of the line shape. The full-width-at-half-maximum of each peak is about 10 MHz. The Voigt profile and linewidth can be understood as arising from a combination of a Lorentzian contribution due to the natural linewidth of 6 MHz and a Gaussian contribution from a small angle between the counter-propagating beams.

The measurement of the hyperfine interval proceeds as follows. The laser is first locked to the F = (1, 2) → F' = 2 transition using SAS in the vapor cell. For locking, the diode current is modulated at f = 20 kHz with a depth of modulation of about 2 MHz, and the signal demodulated at 3f is fed back to the piezoelectric transducer controlling the angle of the diode-laser grating. Such third-harmonic locking makes the locking insensitive to the underlying Doppler profile in the probe spectrum [8]. The locked beam is sent through another part of the cell for a second SAS. Here, we use a counter-propagating pump beam whose frequency is shifted and scanned using an AOM, so that it is nearly resonant with the F = (1, 2) → F' = 1 transition. Scanning only the pump beam is a technique that we have developed to make the spectrum appear on a Doppler-free background [10]. In other words, the locked probe beam addresses only those atoms which are moving at v = ±269 m/s, so that it drives transitions to the F' = 2 level. This absorption remains flat until the pump beam also comes into resonance with the same v = ±269 m/s atoms, which drives transitions to the F' = 1 level and

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![Figure 1](image-url)  
**FIG. 1:** (Color online) Saturated-absorption spectrum in ⁷Li. The inset is the complete F → F' spectrum for the D₁ line showing respectively transitions starting from the F = 1 ground level, due to the F = (1, 2) ground crossover resonance, and transitions from the F = 2 ground level. Each set has three peaks corresponding to F' = 1, F' = (1, 2) crossover resonance, and F' = 2. The main spectrum is a close-up of the ground crossover resonance with peaks labeled with the value of F'. The solid curve is a multipeak fit to a Voigt profile.
increases probe absorption due to optical pumping (as explained earlier). The frequency shift that brings the pump beam into resonance is exactly the hyperfine interval between the $F' = 2$ and $F' = 1$ levels. Thus, by feeding back the demodulated signal at $f$ from the second SAS to the AOM driver, we can lock its frequency to the interval, which in turn can be read using a frequency counter.

III. ERROR ANALYSIS

The different sources of error in the technique have been discussed extensively in our earlier publications [1, 7], and are reviewed here for completeness.

A. Statistical errors

The primary sources of statistical error are the fluctuations in the lock point of the laser and the AOM. To minimize this, we integrate for 10 s for each reading of the frequency counter driving the AOM. We then take an average of about 10 independent measurements. The timebase in the frequency counter has a stability of better than $10^{-6}$, which translates to a negligible error of $< 0.1$ kHz in the frequency measurement.

B. Systematic errors

Systematic errors can occur if there are systematic shifts in the lock points of the laser and the AOM. This can arise due to one of the following reasons.

(i) Radiation-pressure effects. Radiation pressure causes velocity redistribution of the atoms in the vapor cell. In the SAS technique, the opposite Doppler shifts for the counter-propagating beams can result in asymmetry of the observed lineshape. We minimize these effects by using beam intensities that are smaller than the saturation intensity, and the spectrum in Fig. [1] shows that the observed line shape is symmetric.

(ii) Effect of stray magnetic fields. The primary effect of a magnetic field is to split the Zeeman sublevels and broaden the line without affecting the line center. However, line shifts can occur if there is asymmetric optical pumping into Zeeman sublevels. For a transition $|F, m_F⟩ → |F', m_{F'}⟩$, the systematic shift of the line center is $\mu_B (g_F m_F - g_{F'} m_{F'}) B$, where $\mu_B = 1.4$ MHz/G is the Bohr magneton, $g$’s denote the Landé $g$ factors of the two levels, and $B$ is the magnetic field. The selection rule for dipole transitions is $\Delta m = 0, \pm 1$, depending on the direction of the magnetic field and the polarization of the light. Thus, if the beams are linearly polarized, there will be no asymmetric driving and the line center will not be shifted. We therefore minimize this error by using polarizing beam-splitter cubes to ensure that the beams have near-perfect linear polarization.

(iii) Phase shifts in the feedback loop. We check for this error by replacing the AOM with two identical AOMs, and adjusting them so that they produce opposite frequency offsets. With the laser locked to a given hyperfine transition, the first AOM then produces a fixed frequency offset which is compensated by the second AOM. Thus the same hyperfine transition is used for locking in both spectrometers. Under these conditions, the second AOM should lock to the fixed frequency of the first AOM, with any error arising solely due to phase-shift errors. We find that the second AOM tracks the frequency of the first AOM to within 1 kHz.

(iv) Shifts due to collisions. To first order, collisional shifts are the same for different hyperfine levels, and hence do not affect the interval. Small differential shifts of the interval have been studied carefully in the ground state of Cs, due to its importance in atomic clocks. However, the size of the shift is in the mHz range. Collisional shifts are also important in buffer-gas filled cells.

(v) Peak pulling. Though the two peaks that we lock to are 94 MHz apart (compared to the linewidth of 10 MHz), we have to consider that the locations of the $3f$ peak points will be pulled by the central peak in Fig. [1]

The sizes of the various sources of error are listed in Table [1]. Since the laser and AOM are locked, the linearity of the laser-scan axis in Fig. [1] is not important. As mentioned in point (i) above, the peak center can be shifted due to radiation-pressure effects. Similarly, from point (ii), the center can be shifted if there is asymmetric pumping into the Zeeman sublevels in the presence of a residual magnetic field. Asymmetric optical pumping can occur if the beam polarizations are not perfectly linear, for example due to imperfections in the cubes or birefringence at the cell windows. From an experimental point of view, both these effects will change with laser power. Therefore, we can check for our estimate of these errors by repeating the measurements at different values of power and extrapolate to zero power.

| Source of error                        | Size (kHz) |
|---------------------------------------|------------|
| 1. Optical pumping into Zeeman sublevels | 5          |
| 2. Feedback loop phase shift           | 2          |
| 3. Collisional shifts                  | 2          |
| 4. Peak pulling                        | 2          |
FIG. 2: (Color online) Pump power dependence of the measured hyperfine interval. For simplicity, a fixed offset of 92 MHz has been removed. The error bars represent the standard deviation in each set. The solid line is a weighted linear fit extrapolated to zero power.

IV. RESULTS

The results of measurements at different pump powers is shown in Fig. 2. The vertical error bars give the standard deviation in each set. Although the power is increased by a factor of 2.5, the interval only changes by 2 kHz, which is less than the error bars. The straight-line fit yields a zero-power $y$ intercept of 40.1(1) kHz. By adding in quadrature the different sources of error in Table I, we estimate the total error in the average value to be 6 kHz. Thus our current value for the interval is

$^7$Li, $2P_{1/2}$: $\Delta \nu_{2-1} = 92.040(6)$ MHz.

This value can be compared to our previous measurement done with the atomic-beam spectrometer, 92.047(6) MHz. Within their error bars, both results are consistent with each other, though they have been done with completely different spectroscopy techniques. From the interval, we obtain the experimental value of the magnetic dipole constant $A$ as 46.047(3) MHz, taking into account the $+27.0$ kHz second-order correction from Ref. [1].

V. CONCLUSION

In conclusion, we have repeated the measurement of the hyperfine interval in the $2P_{1/2}$ state of Li using the SAS technique. As seen in Fig. 1, this technique produces spurious crossover resonances that are more prominent than the real peaks. Therefore, it can only be used in cases where the interval between hyperfine levels is at least 3 to 4 times the linewidth. Since the observed linewidth in Li is 10 MHz, the SAS technique does not give resolved peaks in the $D_1$ line of $^6$Li (where the interval in the $2P_{1/2}$ state is only 26 MHz). However, we have seen that the discrepancy with theory is only in the case of $^7$Li. Indeed, the large discrepancy in $^7$Li and the agreement in $^6$Li is surprising because the signal-to-noise ratio in $^6$Li is 13 times worse due to its smaller natural abundance (7.3% vs. 92.7%), and because velocity-dependent errors will be larger for the lighter isotope.

The current situation for the magnetic dipole constant $A$ in $^7$Li is summarized in Fig. 3. The present study yields a value of 46.047(3) MHz, which is consistent with a previous value from our laboratory [1] and with another experiment [11]. Both these previous experiments measured the hyperfine interval directly, and the hyperfine constant was extracted from the interval. The reported values have now been corrected for the second-order effects given in Ref. [4]. The figure clearly shows that all the three recent experimental values are discrepant with the two theoretical values. There is an older measurement by Orth et al. [12] from 1975, where a magnetic field was applied to resolve the transitions and a complex fitting routine was used to extract the hyperfine constants from the observed optical-double-resonance and level-crossing signals. That value is discrepant from the other experiments by more than 3.5 $\sigma$, and on the other side of theory at the 2 $\sigma$ level.

Recently, we have also completed measurements of the fine-structure splitting and isotope shifts in Li using the atomic-beam spectrometer [13]. Here again, there are fairly significant discrepancies with theory for the $D_2$ isotope shift and the splitting isotope shift (SIS) [14]. We plan to repeat these measurements with the new spectrometer. Though the peaks in the $D_2$ line are not resolved (because the intervals are smaller than the natural linewidth), we plan to use a magnetic field to separate them.
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