$2\ ^2S_{1/2}-4\ ^2S_{1/2}$ transition of atomic lithium by Doppler-free two-photon spectroscopy

W. DeGraffenreid* and Craig J. Sansonetti†
National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8422
(Received 23 September 2002; published 30 January 2003)

We have investigated the $2\ ^2S_{1/2}-4\ ^2S_{1/2}$ two-photon transition in atomic lithium by high resolution laser spectroscopy. The frequencies of the two-photon resonances have been measured with an accuracy of better than 1 MHz using a Fabry-Pérot wavemeter. The centers of gravity of the $4\ ^2S_{1/2}$ levels are 35 012.033 582 (26) cm^{-1} for ^{7}Li and 35 011.544 497 (30) cm^{-1} for ^{6}Li. The transition isotope shift is 14 662.4 (10) MHz. We have also determined the magnetic hyperfine splitting constant for the $4\ ^2S_{1/2}$ state for both isotopes.

DOI: 10.1103/PhysRevA.67.012509 PACS number(s): 32.80.Rm, 42.62.Fi

I. INTRODUCTION

In recent years there have been rapid advances in theoretical models and calculational techniques for few-electron systems. Atomic structure calculations for He and He-like ions now include not only the nonrelativistic energy but also relativistic and quantum electrodynamic (QED) contributions. The calculations are carried out with such high precision that they challenge the most accurate measurements.

Extension of these calculations to three-electron systems has become a field of intense activity. Recent review articles by King [1,2] summarize the development of the theory over the past decade. Rapid advances in the calculation of energy levels, ionization potentials, fine and hyperfine structure, and isotope shifts for Li and Li-like ions have created a need for improved experimental data to test theory.

Precise investigations using classical spectroscopic methods were reported in the middle of the twentieth century [3–5]. The introduction of tunable single frequency lasers led to investigations of the structure of the Li resonance lines [6–11] as well as two-photon studies of the fine- and hyperfine-structure and isotope shifts of the $3S$ [12,13], $3D$ [14–16], and $4S$ [14,15] levels. The energies of several low-lying levels, including $4S$, have been determined by two-photon spectroscopy of Li in a heat-pipe oven [17]. Recent measurements of the spectrum by Fourier transform spectroscopy (FTS) [18] have determined the excitation energies and isotope shifts of many low-lying levels.

In the present work, we use nonresonant two-photon laser spectroscopy to observe the $2\ ^2S_{1/2}-4\ ^2S_{1/2}$ transition in naturally occurring Li. A computer-controlled vacuum Fabry-Pérot wavemeter determines the laser wave number with respect to an I_2-stabilized helium-neon (He-Ne) laser with an uncertainty of a few parts in 10^9. From these measurements we obtain precise values for the energy of the $4S$ state, the transition isotope shift, and the $4S$ hyperfine splitting for both isotopes. In a companion experiment we have measured the collisional broadening and shift of the $2\ ^2S_{1/2}-4\ ^2S_{1/2}$ transition in the presence of neon and argon buffer gases [19].

*Present address: California State University, Sacramento, Sacramento, CA 95819-6041. Electronic address: degraff@csus.edu
†Electronic address: craig.sansonetti@nist.gov

II. EXPERIMENT

Our experimental apparatus for measuring two-photon transitions in Li is shown in Fig. 1. The Li source is a weakly collimated atom beam as shown in Fig. 2. It is similar to that used in our earlier study of the Li resonance lines [9], but has been modified to allow the detection of fluorescence from the laser/atom interaction region. Lithium metal is heated in a stainless-steel oven producing vapor which effuses through a stainless-steel chimney. The oven and chimney are connected with a Kovar seal to an envelope of low expansion borosilicate glass. The Li vapor condenses on the cold glass at the top of the envelope. Two pairs of small holes are drilled through the chimney along orthogonal diameters at the same height. One pair of holes is aligned with the long arms of the envelope which are terminated with optical windows for the laser beam. A shorter arm, aligned with the other pair of holes, supports a window through which fluorescence can be observed. This arrangement permits laser excitation of the Li vapor in a buffer gas-free environment while minimizing Li deposition on the windows.

A single frequency ring dye laser with rhodamine-6G dye produces approximately 600 mW at 571 nm to excite the $2S$-$4S$ transition. The laser beam passes through an optical isolator to prevent feedback to the laser cavity and is steered through the lithium beam. A plane mirror reflects the laser beam back onto itself. The beam is focused to a waist in the interaction region with a pair of lenses ($f=250$ mm).

Excited atoms are detected by fluorescent decay. The most probable decay path is

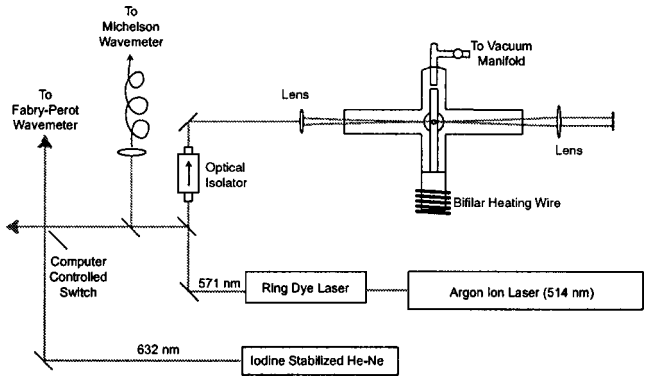

FIG. 1. Schematic diagram of the experimental layout.

 ©2003 The American Physical Society

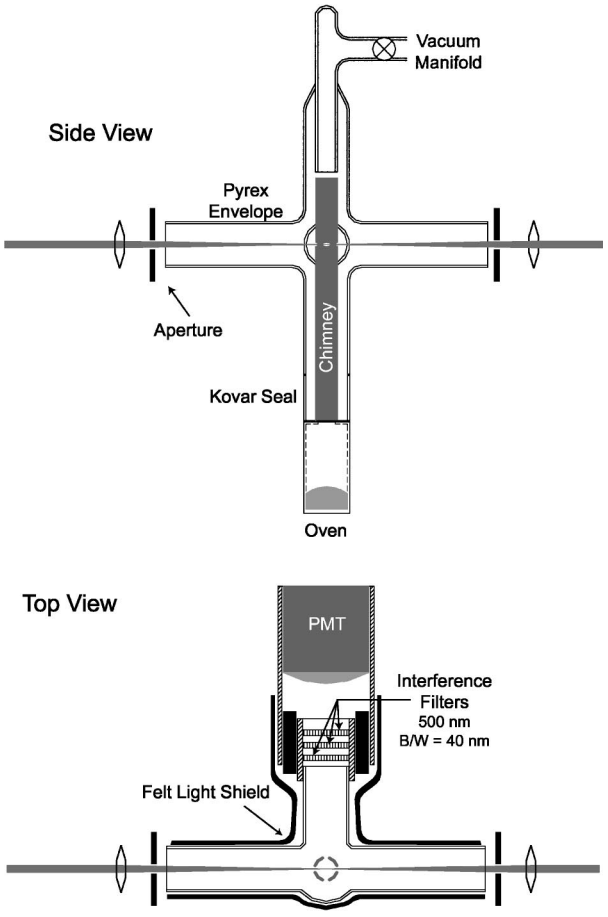

FIG. 2. Schematic diagram of the lithium beam source.

$$4S \xrightarrow{497\ \text{nm}} 2P \xrightarrow{671\ \text{nm}} 2S.$$

We observe the fluorescence at 497 nm with a photomultiplier tube (PMT) optimized for photon counting. To limit spurious counts from scattered laser light and background radiation, three 500-nm interference filters are placed in front of the PMT as shown in Fig. 2. Each filter has a bandwidth of 40 nm full width at half maximum (FWHM). Several layers of black felt surrounding the Pyrex envelope and apertures at the laser windows further reduce background light.

A small portion of the laser power is diverted by a beam splitter for measurement of the wave number. Approximately

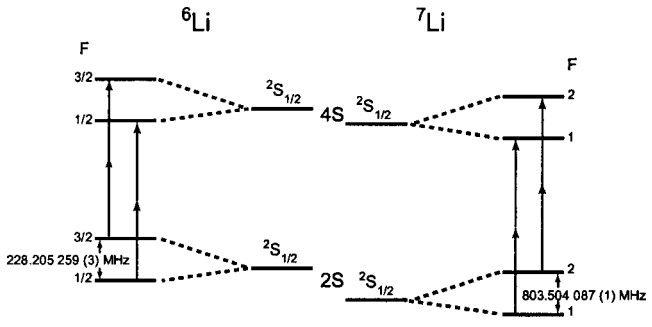

FIG. 3. Hyperfine structure for the $2s$ and $4s$ states of lithium. The ground-state hyperfine splittings are from Ref. [25].

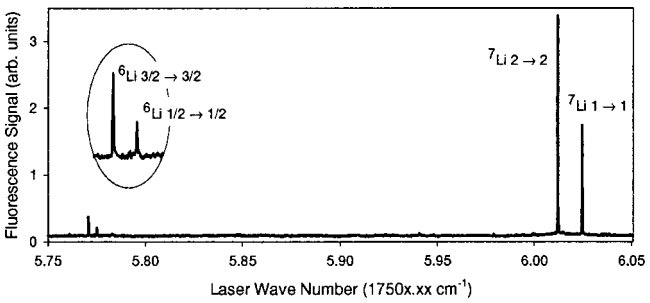

FIG. 4. Two-photon spectrum near 571 nm. The inset magnifies the ^{6}Li transitions.

half of the diverted power is sent through an optical fiber to a fringe-counting Michelson wavemeter. This wavemeter is referenced to a stabilized He-Ne laser and has an uncertainty of about 0.002 cm^{-1}. The Michelson wavemeter is used to tune the dye laser to the desired transition and to obtain an initial measurement of the wave number.

The remaining portion of the diverted beam is directed to the Fabry-Pérot wavemeter which has been described in several earlier papers [20–22]. Briefly, it consists of a plane-plate Fabry-Pérot interferometer illuminated alternately by the dye laser and a reference laser that is frequency-offset locked to an I_2-stabilized He-Ne laser [23]. The reference laser frequency is known to a few parts in 10^{10} [24]. Circular interference fringes from the interferometer are projected onto a linear array detector and read by a computer that determines the fractional order of interference for both lasers by analyzing the fringe patterns. The integer orders of interference are determined from an initial measured value of the Fabry-Pérot spacer length, the known wave number of the reference laser, and an approximate value for the wave number of the dye laser from the Michelson wavemeter. The computer then calculates the wave number of the dye laser and resamples the fringes, producing a new measurement every 0.5 s. With an interferometer spacer 218.2 mm long the uncertainty of the measurement is a few parts in 10^9. A systematic correction is required due to the wavelength-dependent phase change on reflection from the aluminized surfaces of the interferometer plates. For this work the correction was determined by measuring a series of well-known I_2 lines [22] that span the region of the Li transitions.

The $^2S_{1/2}$ states of ^{6}Li and ^{7}Li each split into two hyperfine substates as shown in Fig. 3. The ground-state hyperfine intervals are known to extremely high accuracy from magnetic resonance measurements [25]. Since selection rules limit two-photon transitions from an S state to $\Delta F = 0$, there are four observable transitions between the $2\ ^2S_{1/2}$ and $4\ ^2S_{1/2}$ levels as shown in Fig. 3. The two ^{7}Li lines are much stronger than the two ^{6}Li lines because ^{6}Li accounts for only 7% of natural Li. Figure 4 shows a typical two-photon spectrum.

Because the transitions were observed to be quite narrow (FWHM$\approx$12 MHz), we were able to make the measurements by manually setting the laser to the peak of each line. The observed linewidth can be attributed primarily to transit

TABLE I. Measured laser wave number and transition energies for the four transitions in the $2S$-$4S$ manifold.

Transition	Laser wave number (cm^{-1})	Transition energy (cm^{-1})
^{7}Li $1\rightarrow 1$	17 506.024 440 (15)	35 012.048 880 (29)
^{7}Li $2\rightarrow 2$	17 506.012 202 (14)	35 012.024 403 (28)
^{6}Li $\frac{1}{2}\rightarrow\frac{1}{2}$	17 505.774 560 (17)	35 011.549 120 (34)
^{6}Li $\frac{3}{2}\rightarrow\frac{3}{2}$	17 505.771 093 (18)	35 011.542 185 (35)

time broadening ($\approx$8 MHz), but the natural linewidth (2.8 MHz) and twice the laser linewidth ($\approx$2 MHz) also contribute.

We collected data during seven sessions over a period of several weeks. Each transition was measured two to five times in each session with different values for the reference laser frequency offset. A measurement consisted of the average of 16 manual settings on the line. Before every setting the laser was tuned well off the feature and reset to the peak. To minimize bias in setting the laser, we approached the peak alternately from the high energy and low energy sides. Our results are therefore based on about 340 settings for each of the four lithium lines.

III. RESULTS AND DISCUSSION

The measured laser wave numbers and the transition energies for the four two-photon lines are summarized in Table I. The reported wave numbers include a phase dispersion correction of $-0.000\,055\,(11)$ cm^{-1}. During a single measuring session the primary sources of scatter in the data were random variations due to the manual setting of the laser frequency, laser drift during the time it took to make a measurement, and small systematic variations correlated with the reference laser offset frequency. The variation of results from session to session was somewhat larger. We therefore report in Table I the unweighted mean of the seven session averages for each line as our best determination of the wave number.

The uncertainty reported in Table I is the quadrature sum of the measurement uncertainty and the uncertainty of the phase dispersion correction. The measurement uncertainty is taken to be the standard deviation of the mean of the seven session averages increased by a factor of 1.09 so that it represents a 68% confidence interval [26]. Uncertainty in the wave number of the I_2-stabilized He-Ne reference laser contributes negligibly to the overall uncertainty of our results. Recoil shifts can be significant for a light atom like lithium [9], but there is no net recoil correction for Doppler-free two-photon transitions. No other quantifiable random or systematic contributions to the uncertainty have been identified.

Uncertainties for the derived values of the hyperfine splittings, center of gravity energies, and isotope shift are obtained by propagating the measurement uncertainty using the usual root-sum-of-squares method. The uncertainty of the phase correction is added in quadrature for the center of gravity energies, but makes no contribution to the uncertainties in the hyperfine splittings and isotope shift. All uncertainties are reported at the 68% confidence level.

TABLE II. Experimental and theoretical magnetic hyperfine splitting constants for the $4\,^2S_{1/2}$ level in both stable isotopes of Li.

	^{7}Li $A_{1/2}$ (MHz)	^{6}Li $A_{1/2}$ (MHz)
Experimental work		
This work	34.9 (4)	13.5 (8)
Lorenzen and Niemax [15]	38 (3)	15 (3)
Kowalski *et al.* [14]	36.4 (40)	13.1 (13)
Theoretical work		
Godefroid *et al.* [27]	35.09 (2)	
Guan and Wang [28]	35.068	
Jönsson *et al.* [29]	35.026	
King [30]	35.0	13

A. Hyperfine splitting

The hyperfine splitting of the $2\,^2S_{1/2}$ level in atomic lithium is known to extremely high accuracy [25]. The interval between the $F=1$ and 2 states for ^{7}Li $2\,^2S_{1/2}$ is 803.504 086 6 (10) MHz. The splitting between the $F=1/2$ and 3/2 states for the $2\,^2S_{1/2}$ level in ^{6}Li is 228.205 259 0 (30) MHz. Combining these values with our measured transition energies, we determine the $4\,^2S_{1/2}$ hy-

TABLE III. Center of gravity energies for the $4\,^2S_{1/2}$ levels in atomic lithium.

	^{7}Li energy level (cm^{-1})	^{6}Li energy level (cm^{-1})
Experimental work		
This work	35 012.033 582 (26)	35 011.544 497 (30)
Radziemski *et al.* [18]	35 012.032 6 (10)	35 011.543 2 (10)
Lorenzen and Niemax [17]	35 012.033 7 (7)	
Johansson [5]	35 012.044 (5)	
Theoretical work		
King [2]	35 012.05 (5)	
Wang *et al.* [31]	35 012.12	
Godefroid *et al.* [27]	35 009.78	

TABLE IV. Isotope shift for the $2\ ^2S_{1/2}$–$4\ ^2S_{1/2}$ transition in Li.

	Isotope shift (GHz)
Experimental work	
This work	14.6624(10)
Radziemski *et al.* [18]	14.670(30)
Lorenzen and Niemax [15]	14.656(6)
Kowalski *et al.* [14]	14.661(14)
Hughes [4]	14.73(13)
Theoretical work	
Godefroid *et al.* [27]	14.66
Lüchow and Kleindienst [32]	14.6558
King [33,30]	14.644

perfine splittings to be 69.7 (8) MHz for ^{7}Li and 20.3 (11) MHz for ^{6}Li. These values correspond to excited-state magnetic hyperfine constants $A_{1/2}$ of 34.9 (4) MHz and 13.5 (8) MHz.

The results are compared to other experimental and recent theoretical determinations in Table II. Our results are in good agreement with the previous experimental values, and we have reduced the uncertainties in the splitting constants by factors of 8 and 1.6 for the $4S$ levels in ^{7}Li and ^{6}Li, respectively. Agreement with the calculated values is also excellent.

B. Energy levels

We calculate the center of gravity (CG) energies for the $4\ ^2S_{1/2}$ levels of both Li isotopes using the ground-state hyperfine intervals from Ref. [25] and the transition energies from Table I. The results are presented in Table III and compared to other experimental and recent theoretical determinations. Our values are in agreement with previous experimental results and are more precise by a factor of approximately 35.

The theoretical calculations of the $4S$ levels vary significantly. The result obtained by King for ^{7}Li in a Hylleraas-type calculation with partial corrections for relativistic and QED effects [2] is in good agreement with our experimental value. Configuration-interaction (CI) [31] and multiconfiguration Hartree-Fock (MCHF) [27] methods are powerful tools for atoms with more than a few electrons, but are less precise than Hylleraas calculations in the case of lithium [1,2]. Our experimental results, which are about a factor of 1000 more accurate than the best available calculations, provide a precise benchmark to test improvements in the theory.

C. Isotope shift

Our observed transition isotope shift (TIS) for the $2\ ^2S_{1/2}$–$4\ ^2S_{1/2}$ transition is 14.6624 (10) GHz. This value is compared to other experimental and theoretical determinations in Table IV. We have reduced the uncertainty by a factor of 6. The calculated values are all slightly smaller than our current determination. None of these theoretical results include relativistic, quantum electrodynamic (QED), or finite nuclear size effects. In a recent study of the Li $2\ ^2S_{1/2}$–$3\ ^2S_{1/2}$ transition, Yan and Drake [34] included these contributions in their model and found that the TIS increased by 1.43 (39) MHz. It is not unreasonable to assume that the inclusion of these terms in the calculations for the $2S$-$4S$ transition would shift the results into better agreement with the experimentally determined value.

IV. CONCLUSIONS

We have made precise new measurements of the $2\ ^2S_{1/2}$–$4\ ^2S_{1/2}$ two-photon transitions in ^{6}Li and ^{7}Li. From these measurements and the well-known hyperfine structure intervals of the $2\ ^2S_{1/2}$ levels we determine the centers of gravity of the $4\ ^2S_{1/2}$ levels, their magnetic hyperfine splittings, and the $2S$-$4S$ transition isotope shift. These results provide precise benchmark data to test new developments in the theoretical calculations for lithium.

[1] F.W. King, J. Mol. Struct.: THEOCHEM **400**, 7 (1997).
[2] F.W. King, Adv. At., Mol., Opt. Phys. **40**, 57 (1999).
[3] K.W. Meissner, L.G. Mundie, and P.H. Stelson, Phys. Rev. **74**, 932 (1948); **75**, 891(E) (1949).
[4] R.H. Hughes, Phys. Rev. **99**, 1837 (1955).
[5] I. Johansson, Ark. Fys. **15**, 169 (1959).
[6] M. Fuchs and H.-G. Rubahn, Z. Phys. D: At., Mol. Clusters **2**, 253 (1986).
[7] L. Windholz and C. Umfer, Z. Phys. D: At., Mol. Clusters **29**, 121 (1994).
[8] L. Windholz, Appl. Phys. B: Lasers Opt. **60**, 573 (1995).
[9] C.J. Sansonetti, B. Richou, R. Engleman, Jr., and L.J. Radziemski, Phys. Rev. A **52**, 2682 (1995).
[10] W. Scherf, O. Khait, H. Jäger, and L. Windholz, Z. Phys. D: At., Mol. Clusters **36**, 31 (1996).
[11] I.E. Olivares, A.E. Duarte, T. Lokajczyk, A. Dinklage, and F.J. Duarte, J. Opt. Soc. Am. B **15**, 1932 (1998).
[12] C. Vadla, A. Obrebski, and K. Niemax, Opt. Commun. **63**, 288 (1987).
[13] M.M. Kash, Ph.D. thesis, MIT, Cambridge, MA, 1988.
[14] J. Kowalski, R. Neumann, H. Suhr, K. Winkler, and G. zu Putlitz, Z. Phys. A **287**, 247 (1978).
[15] C.-J. Lorenzen and K. Niemax, J. Phys. B **15**, L139 (1982).
[16] I. Labazan and S. Milošević, Eur. Phys. J. D **8**, 41 (2000).
[17] C.-J. Lorenzen and K. Niemax, Phys. Scr. **27**, 300 (1983).
[18] L.J. Radziemski, R. Engleman, Jr., and J.W. Brault, Phys. Rev. A **52**, 4462 (1995).
[19] W. DeGraffenreid and C.J. Sansonetti (unpublished).
[20] C.J. Sansonetti, in *Advances in Laser Science–IV*, edited by J.L. Gole, D.F. Heller, M. Lapp, and W.C. Stwalley (AIP, New York, 1988), pp. 548–553.
[21] J.D. Gillaspy and C.J. Sansonetti, J. Opt. Soc. Am. B **8**, 2414 (1991).
[22] C.J. Sansonetti, J. Opt. Soc. Am. B **14**, 1913 (1997).

[23] H.P. Layer, IEEE Trans. Instrum. Meas. **IM-29**, 358 (1980).
[24] D.A. Jennings, C.R. Pollock, F.R. Petersen, R.E. Drullinger, K.M. Evenson, J.S. Wells, J.L. Hall, and H.P. Layer, Opt. Lett. **8**, 136 (1983).
[25] A. Beckmann, K.D. Böklen, and D. Elke, Z. Phys. **270**, 173 (1974).
[26] B.N. Taylor and C.E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Tech. Note 1297 (National Institute of Standards and Technology, Gaithersburg, MD, 1994).
[27] M. Godefroid, C. Froese Fischer, and P. Jönsson, J. Phys. B **34**, 1079 (2001).
[28] X.-X. Guan and Z.-W. Wang, Eur. Phys. J. D **2**, 21 (1998).
[29] P. Jönsson, C. Froese Fischer, and J. Bieroń, Phys. Rev. A **52**, 4262 (1995).
[30] F.W. King, Phys. Rev. A **43**, 3285 (1991).
[31] Z.-W. Wang, X.-W. Zhu, and K.T. Chung, Phys. Rev. A **46**, 6914 (1992).
[32] A. Lüchow and H. Kleindienst, Int. J. Quantum Chem. **51**, 211 (1994).
[33] F.W. King, Phys. Rev. A **40**, 1735 (1989).
[34] Z.-C. Yan and G.W.F. Drake, Phys. Rev. A **61**, 022504 (2000).