PHYSICAL REVIEW A VOLUME 33, NUMBER 5 MAY 1986

Absolute wavelength measurement and fine-structure determination in ^{7}Li II

E. Riis,* H. G. Berry,† and O. Poulsen
Institute of Physics, University of Aarhus, DK-8000 Aarhus, Denmark

S. A. Lee and S. Y. Tang
Department of Physics, Colorado State University, Fort Collins, Colorado 80523

(Received 10 October 1985; revised manuscript received 4 February 1986)

We have used collinear fast-beam—laser fluorescence spectroscopy to obtain precise measurements of the fine structures and absolute wavelengths of the $1s2s\,^3S-1s2p\,^3P$ transitions in ^{7}Li II. Our results are about 50 times more accurate than the best nonrelativistic calculations for these energy differences, and they have a precision equivalent to 150 ppm of the QED corrections for the $2s$-$2p$ transitions.

I. INTRODUCTION

The energy levels of two-electron atoms continue to provide rigorous tests both of relativistic quantum theory, including quantum electrodynamics (QED), and of correlations within a multiparticle system. The transitions between the different levels of the same principal quantum number, $n=2$, $\Delta n=0$, have traditionally given the most precise tests of many of these effects. The near degeneracies of these levels are due to cancellation of most of the effects of the electrostatic force between the nucleus and each electron. For atoms of low nuclear charge, the nonrelativistic correlation effects dominate the energy differences, and thus can be tested precisely for elements such as helium and lithium. Relativistic and QED effects increase strongly with nuclear charge Z because of the consequently stronger electromagnetic fields involved. Many tests of these effects have been made in recent years mostly using beam-foil spectroscopy techniques for ions with Z in the range of 12—27. Many of the results are summarized and compared with theory by Goldman and Drake.[1] The most accurate measurements test QED theory to a precision of a few parts per thousand, with absolute wavelength measurements of a few parts in 10^5.

Since absolute wavelengths can be measured much more accurately using laser techniques, it is of interest to pursue tests of these relativistic parts of many-body relativistic quantum theory for the lower-Z elements, even though the relativistic effects are much smaller.

Several workers have recently combined high resolution, precision measurements to obtain values for the $2s$-$2p$ transitions in He I.[2] A summary for the helium system is given by Martin.[2] The results show good agreement with theory, particularly for the dominant nonrelativistic calculations of Accad *et al.*[3] The measurements test the QED corrections in helium to a precision of about five parts per thousand. In addition, the fine structure in the $2p\,^3P$ state of He I has been measured and calculated to very high precision.[4] The results are in good agreement.

For the $1s2s\,^3S-1s2p\,^3P$ transition in Li II, neither the theory[1,3] nor the experimental values[5,6] are as accurate. In addition, the fine structure is complicated by a strong hyperfine interaction which mixes the fine-structure components of the $1s2p\,^3P$ state. However, very accurate calculations of the hyperfine constants have been completed by two groups,[7,8] and these effects can be effectively removed from the experimental data. Hence, our experimental objective is to provide accurate values of the two fine-structure intervals of this state to compare with perturbation calculations of the Breit interaction. A second objective is to obtain an absolute wavelength measurement of the $2s$-$2p$ transition to compare with the most accurate calculations including the relativistic and QED calculations, recently completed by several authors.[1,9] Even though QED and relativistic corrections are much smaller in lithium than in the heavier high-Z ions whose transition energies have been measured by beam-foil techniques, our laser precision can be expected to lead to more accurate measurements of several of these energy corrections. This will become truer for similar measurements in the neighboring elements Be III and B IV. The experiments presented here for Li II should be feasible for these ions using the same techniques.

In this paper we describe precision wavelength measurements of three fine-structure components of the $1s2s\,^3S-1s2p\,^3P$ transition in Li II, using collinear laser excitation of a fast-ion beam of metastable Li$^+$ ions. The excitation of the lithium ions is followed by detection of the induced fluorescence, and comparison of the laser wavelength with standard iodine-saturated absorption lines. In a subsequent experiment, we have measured the absolute wavelengths of the iodine lines.

Our measurements lead to transition energies in Li II which are accurate to better than ±6 MHz (systematic and three standard deviations statistical errors). Thus the fine-structure intervals are measured to a precision of 50 ppm, and the QED corrections are accurate to 150 ppm. These results are a factor of 10 better than previous measurements, and a factor of about 50 better than the best available theoretical values for the transition wavelengths. The principal lack of precision in the theoretical wavelengths lies in the nonrelativistic correlation corrections.

II. EXPERIMENT

In our experiment we observed laser-induced fluorescence from excited lithium ions. The apparatus is shown

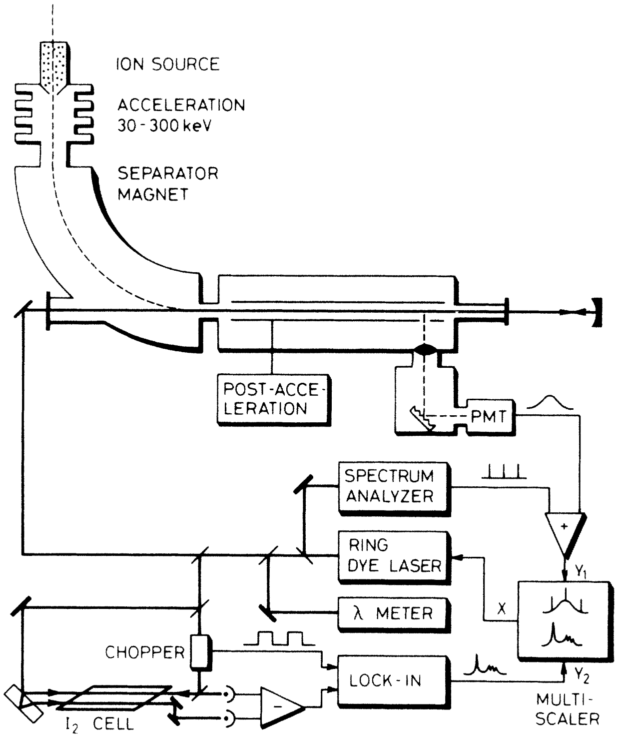

FIG. 1. Experimental arrangement.

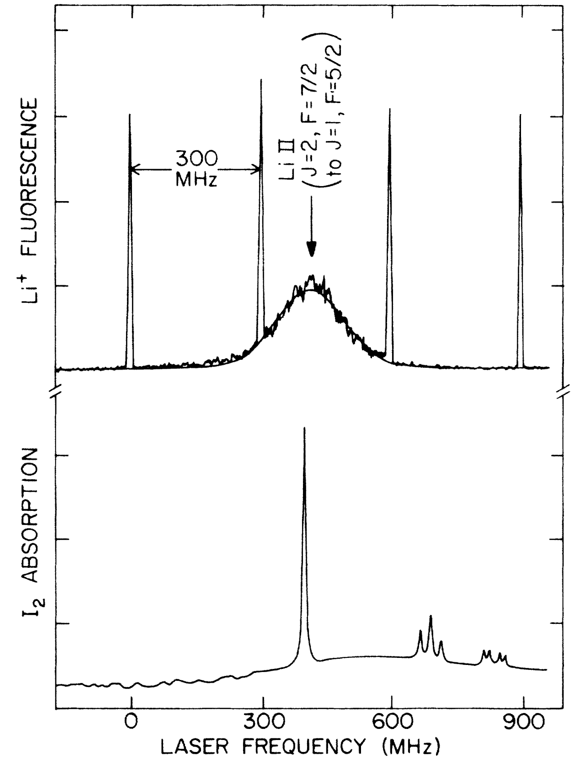

FIG. 2. Li II fluorescence spectrum for the $2s\,^3S_1$ ($F=\frac{5}{2}$) to $2p\,^3P_2$ ($F=\frac{7}{2}$) resonance excited by parallel laser light. The superposed spectrum analyzer markers are at 300 MHz intervals, and the simultaneously produced iodine-saturated absorption spectrum is shown below.

schematically in Fig. 1. Lithium ions in the metastable $1s2s\,^3S$ level ($\sim$64 eV above the ion ground state) were produced in the discharge of a universal ion source, at a potential of about 50 kV. The accelerated-ion beam was passed through a 90 degree separator magnet, and directed through a post-acceleration region held at a small fixed voltage (0–100 V) below ground potential. In this region the ion beam traveled collinearly with co- and counter-propagating laser beams of equal frequencies. The ion beam was excited by the laser when tuned to the Doppler-shifted [blue (red) shifted for parallel (antiparallel) excitation] resonance frequency of one of the transitions from the metastable levels. The fluorescence from a short length of the excited beam was collected with an optical-lens system as shown in Fig. 1. The light passed through a $\frac{1}{3}$-m monochromator and was detected with a photomultiplier. At the same time a part of the laser light was used to induce saturated absorption in an iodine cell as shown in Fig. 1.

The laser light was from a cw single-mode ring dye laser. The frequency of this laser was checked several different ways during the experiment. A lambda meter provided a reasonably accurate wave number measurement. It was calibrated with respect to a HeNe laser, and was accurate to a precision of about 1 part in 10^7. This was sufficient to identify the saturated absorption spectrum of iodine. The iodine lines were used as reference markers for the lithium resonance spectrum, the two spectra being recorded simultaneously. In addition, a Fabry-Perot spectrum analyzer provided markers at 300 MHz intervals, to give a relative frequency calibration of the spectra. This was obtained by fitting the separation of the markers to a low-order polynomial.

The fast ion velocity provided both a large Doppler shift and a kinematic line narrowing of the spectrum. The Li II line shapes for parallel and antiparallel excitation are shown in Figs. 2 and 3. The wave-number shift between the two spectra is $\sim$150 cm^{-1}. The lithium linewidths of about 100 MHz are due mainly to voltage fluctuations of the ion source relative to the observation region. These voltage variations are about ±2 V. Linewidths due to the ion source temperature are negligible due to the kinematic compression for these ion-beam velocities. The stability of the accelerator voltage supply (50 kV) could be measured over long time scales by the successive measurements of the resonance frequency in the red-shifted or blue-shifted direction. Figure 4 shows that the stability is of the order of 2 V/h, and this drift can be eliminated from the data to a precision of about 0.2 V. Similarly the data were corrected for variations of less than 0.5 V in the anode voltage (the beam energy being the sum of the anode, the acceleration, and the postacceleration voltages).

The experiment consisted of several series of measurements of the resonance fluorescence signals for three different hyperfine components of the Li II $1s2s\,^3S \rightarrow 1s2p\,^3P$ transition. These were chosen in order to obtain measurements from all three fine-structure levels, and they are in-

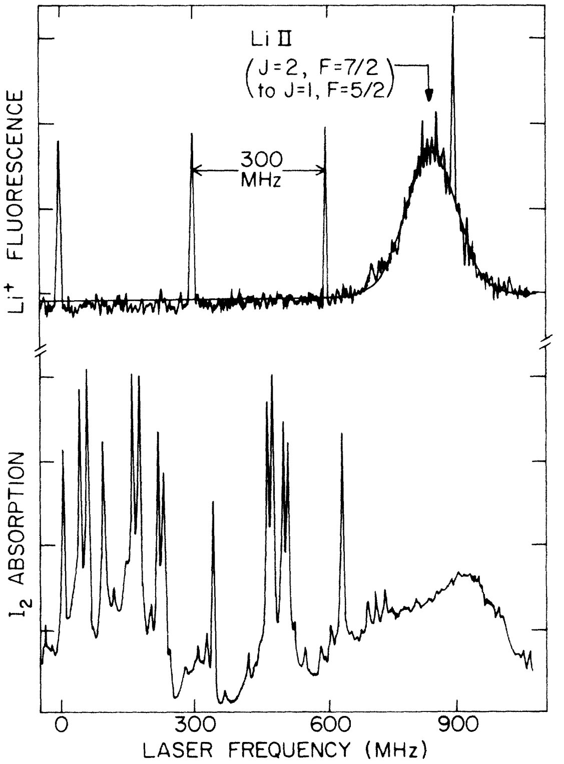

FIG. 3. The same Li II, $F=\frac{5}{2}$ to $F=\frac{7}{2}$ resonance excited in antiparallel laser light, under the same conditions as in Fig. 2.

dicated in Fig. 5. In each series of measurements, all parts of the system were held steady, in particular the acceleration voltage, while the laser was tuned back and forth between the red-shifted and blue-shifted resonance several times.

The atomic-transition frequency σ_0 can then be determined as

$$\sigma_0=(\sigma_R\sigma_B)^{1/2}\ , \tag{1}$$

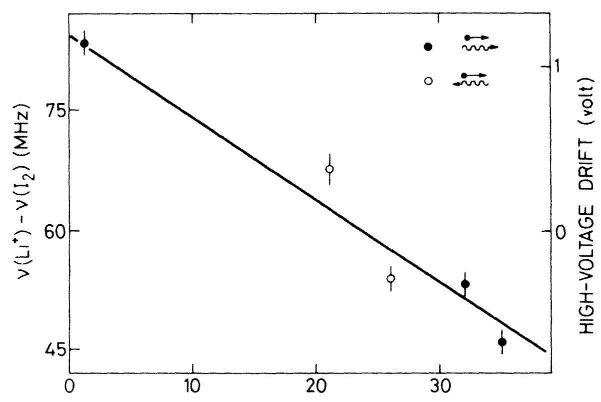

FIG. 4. Accelerator high-voltage drift, observed as a function of time during the experiment.

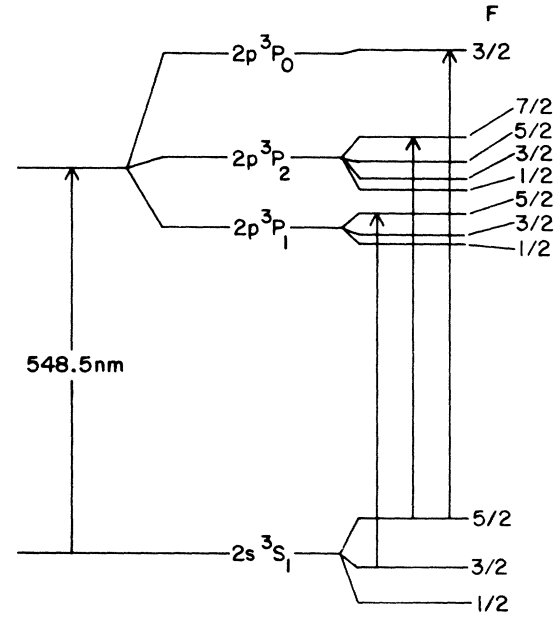

FIG. 5. Term level structures for the Li II $2s\ ^3S$—$2p\ ^3P$ transitions, at 5485 Å.

where σ_R and σ_B are the absolute wave numbers for the red- and blue-shifted transitions, respectively.

The experiment described above yields the wave-number differences between the Li transitions and a number of saturated absorption lines in the iodine spectrum. Table I shows the averages of these differences for all the series of measurements in this experiment. The iodine lines are identified in Table II. We do not attempt to assign the transitions of these lines as most of them are weak and may belong to weak bands which have not yet been analyzed.[10] Instead, in Table II, we identify lines in terms of the line numbers in the I_2 atlas.[11] Four of the references are not listed in the atlas, and we indicate their centroid position relative to known lines in the atlas. For each reference line, we list the type of transition: even J transitions have 15 hyperfine components, and odd J transitions have 21. The hyperfine components for each line are labeled a, b, c, . . . , starting from the blue side of the spectrum.

In the second part of the experiment, the absolute wavelengths of the I_2 reference lines were measured relative to wavelength standards in the visible spectrum using a 1-m confocal temperature-stabilized interferometer. A second confocal interferometer, 0.5 m in length, was used in the investigation of systematic errors, but its wavelength measurements were not included in the final results listed in Table II. Detailed information about the construction and the initial calibration procedure of the interferometers may be found in Ref. 12. In this experiment, five measurements were made for each hyperfine component, and the final calibration of the free spectral range was done with the iodine $R(47)9$-$2o$ and the $P(62)17$-$1o$ wavelength standards at 6118 and 5761 Å, respectively.[13] The

TABLE I. $^7Li^+$ resonance frequencies relative to I_2 saturated absorption lines (cf. Table II). Each series refers to a different energy, but it is corrected for drift in beam energy. Each series consists of a number N of measurements with parallel (upper line) and antiparallel (lower line) excitation. The fourth column shows the average frequency difference $\langle \Delta\nu(Li^+\text{-}I_2) \rangle$ between the Li^+ line and the I_2 line. By adding the absolute wave numbers for the I_2 lines (Table II), we obtain the absolute Doppler-shifted wave numbers σ_R or σ_B. Column six gives the absolute transition frequency σ_0. The averages $\langle \sigma_0 \rangle$ of these wave numbers weighted according to the number of measurements in each series are shown in the last column. The errors quoted in column four are three standard-deviation statistical errors. The systematic errors shown in Tables II and III are added in quadrature in column five.

Transition	I_2 line	N	$\langle \nu\ (Li^+\text{-}I_2) \rangle$ (10^{-3} cm^{-1})	σ_R or σ_B (cm^{-1})	$\sigma_0=(\sigma_R\sigma_B)^{1/2}$ (cm^{-1})	$\langle \sigma_0 \rangle$ (cm^{-1})
$\frac{3}{2}\rightarrow\frac{5}{2}$	H	5	4.50±0.30	18 301.768 51(35)	18 226.520 78(29)	18 226.520 75(13)
	C	4	−9.08±0.41	18 151.582 43(45)		
	G	4	−7.00±0.20	18 302.014 85(26)	18 226.520 91(25)	
	A	2	−1.01±0.38	18 151.338 37(42)		
	F	4	9.00±0.16	18 302.013 21(23)	18 226.520 50(15)	
	A	2	−0.20±0.02	18 151.339 19(18)		
	F	3	2.00±0.12	18 302.006 21(21)	18 226.520 82(19)	
	A	2	7.38±0.26	18 151.346 76(32)		
$\frac{5}{2}\rightarrow\frac{7}{2}$	E	3	0.00±0.32	18 299.928 31(37)	18 228.174 38(27)	18 228.174 37(17)
	B	2	7.09±0.34	18 156.701 80(38)		
	E	7	0.00±0.12	18 299.928 31(22)	18 228.174 36(21)	
	B	6	7.05±0.31	18 156.701 76(35)		
$\frac{5}{2}\rightarrow\frac{3}{2}$	E	6	−1.00±0.20	18 299.927 31(27)	18 230.932 51(29)	18 230.932 31(19)
	D	5	−19.46±0.47	18 162.197 82(50)		
	E	5	−28.40±0.38	18 299.899 91(42)	18 230.932 15(25)	
	D	7	7.01±0.19	18 162.114 30(26)		

stability of the interferometer was monitored in hourly intervals by these standard lines.

The saturated absorption spectra of the I_2 reference lines were obtained with conventional saturation spectroscopy, using counter-propagating laser beams. The I_2 saturation spectrum and the transmission fringes of the interferometer were recorded simultaneously while the laser was scanned. Absolute wavelengths of the I_2 lines were determined from the measured fringe separations. The accuracy of the absolute wavelength determination is better than ±3 MHz, where the statistical uncertainty is taken for three standard deviations.

By adding the relevant absolute iodine wave numbers to the frequency differences listed in Table I, we obtain the absolute red- and blue-shifted wave numbers for the measured Li II lines. Equation (1) then yields the atomic-transition frequencies. All the values are listed in Table I.

The systematic errors in the experiment are summarized in Table III. In addition to a 2 and 4 MHz uncertainty in correcting for drift in anode and acceleration voltages, respectively, we have a 1 MHz systematic error in determining the center of a Li II resonance relative to an I_2 line by fitting Gaussian and Lorentzian lines to the two sets of data, respectively. These systematic errors, together with the uncertainty in determining the wave numbers of the I_2 lines (quoted in Table II), are added in quad-

TABLE II. Indentification and measured wave numbers for I_2 saturated absorption lines used as reference markers in this experiment (see text). I_2 absorption-line numbers refer to the iodine atlas (Ref. 11).

I_2 line	Number in I_2 atlas	Transition even or odd J	hfs comp.	Wave number (cm^{-1})
A	3337 + 0.07 cm^{-1}	odd	c	18 151.339 384(85)
B	3384 + 0.07 cm^{-1}	even	a	18 156.694 710(60)
C	3338	even	f	18 151.591 508(90)
D	3415−0.03 cm^{-1}	even	o	18 162.217 286(67)
E	4236−0.03 cm^{-1}	even	o	18 299.928 309(100)
F	4251	odd	r	18 302.004 213(50)
G	4251	odd	d	18 302.021 846(68)
H	4250	odd	i	18 301.764 005(93)

TABLE III. The experimental systematic uncertainties.

Determination of Li II line center	±1 MHz
Correction for drift in anode voltage	±2 MHz
Correction for drift in acceleration voltage	±4 MHz
Absolute determination of I_2 wave numbers (see Table II)	±2–3 MHz

rature to the three standard-deviation statistical errors and shown in column five of Table I.

III. RESULTS

In order to compare the experimentally determined wave numbers listed in Table II with theoretical calculations, we have made several reductions of the data. The hyperfine-structure constants are well known for both the upper and lower levels of the transitions. First we have removed the effect of hyperfine structure in the lower ($^3S_1$) state using the values taken from Kotz *et al.*[14] The singlet-triplet hyperfine mixing between the ^1P and ^3P states is very small. We find that it decreases the energies of the $F=\frac{3}{2}$ and $F=\frac{5}{2}$ states by 0.000007 cm^{-1}.

The energies of the three hyperfine-structure-free levels (measured relative to the $1s\,2s\,^3S$, $F=\frac{1}{2}$ level) were deduced using the values of the hyperfine coupling constants given by Aashamar and Hambro.[8] The fine-structure energy E_2 of the $J=2$ level can be obtained from the measured energy of the $J=2$, $F=\frac{7}{2}$ level:

$$\begin{aligned} E_2 &= E^{\mathrm{meas}}_{2,7/2} - \langle 2,7/2\,|\,H_{\mathrm{hfs}}\,|\,2,7/2\rangle \\ &= 18\,228.860\,39\ \mathrm{cm}^{-1}\ , \end{aligned} \tag{2}$$

where H_{hfs} represents the hyperfine interaction.

Using this value and the fact that the measured wave number for the transition to the $J=1$, $F=\frac{5}{2}$ level is a solution to the secular equation for the $F=\frac{5}{2}$ part of the energy matrix we have

$$\begin{aligned} H_{5/2}\psi &= \left[\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + H_{\mathrm{hfs}5/2} \right] \psi \\ &= E^{\mathrm{meas}}_{1,5/2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \psi\ , \end{aligned} \tag{3}$$

from which the fine-structure energy E_1 is found:

$$E_1 = 18\,226.773\,10\ \mathrm{cm}^{-1}\ . \tag{4}$$

Similarly, fine-structure energy E_0 is obtained from the $F=\frac{3}{2}$ part of the energy matrix,

$$\begin{aligned} H_{3/2}\psi &= \left[\begin{bmatrix} E_0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{bmatrix} + H_{\mathrm{hfs}3/2} \right] \psi \\ &= E^{\mathrm{meas}}_{0,3/2} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \psi\ , \end{aligned} \tag{5}$$

yielding

$$E_0 = 18\,231.962\,92\ \mathrm{cm}^{-1}\ . \tag{6}$$

TABLE IV. $^7\mathrm{Li}^+\ 2^3S_1 - 2^3P_0$ transition wave numbers (cm^{-1}).

This work	18231.301 88(19)
Other measurements	
Holt *et al.* (Ref. 6)	18231.3030(12)
Englert *et al.* (Ref. 5)	18231.3028(8)
Theory	
Accad *et al.* (Ref. 3)	18232.5569(10)
Goldman and Drake (Ref. 1)	18231.313(10)

The results for the two fine-structure splittings and the hyperfine-structure-free wave number for the $^3S_1 \rightarrow {}^3P_0$ transition are shown in Tables IV and V.

Our results agree with the earlier measurements of Holt *et al.*[6] and of Englert *et al.*,[5] but with a considerably improved precision. Drake[1] has recently summarized the theoretical work and estimated the precisions for the relevant energy intervals. These are included in Tables IV and V.

IV. CONCLUSIONS

We have achieved improved precision measurements of both the absolute wavelengths of the $1s\,2s\,^3S - 1s\,2p\,^3P$ transitions and the $1s\,2p\,^3P$ fine structures. The measurements are accurate to within about 50 ppm of the fine-structure intervals and of the $2s$-$2p$ QED corrections to the absolute wavelengths (note that the QED corrections are of the same order as the fine structure: 1.2 cm^{-1} compared with 2–4 cm^{-1}).

The results agree, within experimental errors, with previous measurements. They also agree with theory. However, the theoretical values of both the fine structures and the total energy ($2s$-$2p$) are less accurate by 1–2 orders of magnitude. The discrepancies in the fine-structure intervals with the calculations of Accad, Pekeris, and Schiff[3] are somewhat surprising and not well understood. Much of the inaccuracy of the theoretical total-energy splitting, $2s$-$2p$, is due to the need for a more accurate nonrelativistic wave function.

Nonrelativistic calculations in Li II could be significant-

TABLE V. Fine-structure splittings of 2^3P in cm^{-1}.

	$J=0-J=2$	$J=2-J=1$
This work	3.102 53(25)	2.087 29(21)
Other measurements		
Holt *et al.* (Ref. 6)	3.1051(17)	2.0897(17)
Bayer *et al.* (Ref. 5)	3.1029(3)	2.0906(7)
Theory		
Accad, Pekeris, and Schiff (Ref. 3)	3.104 55	2.089 88
Goldman and Drake (Ref. 1)	3.118(14)	2.086(14)

ly improved using more efficient basis sets than those of Accad, Pekeris, and Schiff[3] (as have been used in recent calculations in neutral helium[15,16]). Once these calculations have been completed, the relativistic and QED contributions can be tested at the few ppm level, not only in Li II, but also in similar laser resonance fluorescence measurements for $Z=4$ and 5. Very few other tests of many of these contributions are available at this level of accuracy. As cw laser techniques become available further into the ultraviolet spectrum (e.g., Ref. 17) tests of the relativistic and QED corrections will become possible for the higher-Z, few-electron systems at a level of a few MHz precision.

ACKNOWLEDGMENTS

This research was supported by the Carlsberg Foundation, Denmark, the NATO Science Fellowship Program, the U.S. National Science Foundation, Grant No. PHY-8508594, the NATO Exchange Grant No. 238/83, and the U.S. Department of Energy (Office of Basic Energy Sciences) under Contract No. W-31-109-Eng-38.

---

[*] Present address: Department of Physics, Colorado State University, Fort Collins, CO 80523.

[†] Permanent address: Physics Division, Argonne National Laboratory, Argonne, IL 60439.

[1] S. P. Goldman and G. W. F. Drake, J. Phys. B **17**, L197 (1984); and private communication.

[2] P. Juncar, H. G. Berry, R. Damaschini, and H. T. Duong, J. Phys. B **16**, 381 (1983); L. Hlousek, S. A. Lee, and W. M. Fairbank, Jr., Phys. Rev. Lett. **50**, 159 (1984); W. C. Martin, Phys. Rev. A **29**, 1883 (1984); **30**, 651(E) (1984).

[3] T. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

[4] On the experiment, see W. Frieze, E. A. Hinds, V. W. Hughes, and F. M. Pichanick, Phys. Rev. A **24**, 279 (1981); on the theory, see M. L. Lewis and P. H. Serafino, Phys. Rev. A **18**, 867 (1978).

[5] R. Bayer, J. Kowalski, R. Neumann, S. Noehte, H. Suhr, K. Winkler, and G. zu Putlitz, Z. Phys. A **292**, 329 (1979); M. Englert, J. Kowalski, F. Mayer, R. Neumann, S. Noehte, R. Schwarzwald, H. Suhr, K. Winkler, and G. zu Putlitz, Appl. Phys. B **28**, 81 (1982).

[6] R. A. Holt, S. D. Rosner, T. D. Gaily, and A. G. Adam, Phys. Rev. A **22**, 1563 (1980).

[7] A. N. Jette, T. Lee, and T. P. Das, Phys. Rev. A **9**, 2337 (1974).

[8] K. Aashamar and L. Hambro, J. Phys. B **10**, 553 (1977).

[9] J. Hata and I. P. Grant, J. Phys. B **16**, 523 (1983).

[10] P. Luc, J. Mol. Spectrosc. **80**, 41 (1980).

[11] S. Gerstenkorn and P. Luc, *Atlas du spectra d'absorption de la molecule de l'iode (14800—20000 cm*$^{-1}$*)* (CNRS, Paris, 1978).

[12] L. Hlousek, S. A. Lee, and W. M. Fairbank, Jr., Phys. Rev. Lett. **50**, 328 (1983).

[13] The vacuum wavelengths for these transitions as recommended by the CCDM (1983) are $R(47)9-2o=611\,970\,769.8(6)$ fm at $-5\,^{\circ}\text{C}$ and $P(62)17-1o=576\,294\,760.25(40)$ fm at $6\,^{\circ}\text{C}$.

[14] U. Kötz, J. Kowalski, R. Neumann, S. Noehte, H. Suhr, K. Winkler, and G. zu Putlitz, Z. Phys. A **200**, 25 (1981).

[15] K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).

[16] D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).

[17] C. J. Foot, B. Coillaud, R. G. Beausoleil, and T. W. Hänsch, Phys. Rev. Lett. **54**, 1913 (1985).