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ENERGIES AND LIFETIMES OF THE METASTABLE AUTOIONIZING $(1s2s2p)^4P_J$ STATES OF Li^6 AND Li^7; ASSIGNMENT OF Li-I[b] QUARTET LINES*

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A Zeeman-quenching atomic-beam method has been developed and used for the determinations of the energies and lifetimes of the metastable autoionizing $(1s2s2p)^4P$ states of Li^6 and Li^7. The values obtained for certain of these parameters are in serious disagreement with existing theoretical estimates. The energy values have been used for the definitive identification of previously unassigned lines in the Li spectrum.

A sensitive test of electron correlation and other dynamical effects in a three-electron atom is provided by the fine-structure energies and autoionization rates of the metastable $(1s2s2p)^4P^\circ$ atomic states of Li. We report here preliminary experimental values for these parameters as determined by an atomic-beam Zeeman quenching experiment. The results provide for the first time definitive verification of the assignments[1] of the levels associated with the 2934- and 3714-Å multiplets observed in the course of studies on the Li II spectrum.[2] Since the ratio of natural linewidth to fine-structure splitting for the $^4P^\circ$ level is smaller by a factor of $\approx 5\times 10^3$ than the corresponding ratio for the P states of H, future high-precision measurements of the intervals may serve as a new critical test of the theory of the fine structure of simple atomic systems. It is hoped that the present results will stimulate the development of precise numerical three-electron wave functions and the calculations of the radiative, relativistic, and related corrections. We have also used our results to evaluate a proposal[3] to use metastable autoionizing states to obtain polarized Li nuclei.

The application of a magnetic field to a beam of metastable autoionizing atoms modifies the atomic lifetimes[4] and decreases the beam intensity. These results arise from the mixing caused by the Zeeman interaction of shorter-lived fine-structure states with the long-lived $^4P_{5/2}$ state. The $J=\frac{5}{2}$ state, which autoionizes through the spin-spin interaction, has a smaller decay rate than either the $^4P_{3/2}$ or $^4P_{1/2}$ levels. These levels are directly coupled to the continuum through the spin-spin, spin-orbit, and spin–other-orbit interactions and indirectly coupled through these operators to the continuum as a result of mixing with the rapidly ionizing $^2P_{3/2,1/2}$ states. In addition to the gradual decrease of beam intensity with increasing magnetic field, pronounced sharp dips are observed at certain magnetic fields. This effect is due to anticrossings between sublevels having the same magnetic quantum number but different values of J and, hence, different autoionization lifetimes.

The strong state mixing of the interacting levels which causes the anticrossing dips does not require coherent excitation of the states. From the field positions and line shapes of the structure in the quenching curve, the energies and lifetimes of the various states were determined. These results are at variance with theoretical estimates.

The experimental apparatus is similar to that described previously[5] except that the vacuum chamber containing the oven, electron bombarder, and detector for metastable decay products is entirely located in a uniform magnetic field provided by a Harvey-Wells 12-in. magnet. To discriminate against background signals and to maximize the signal-to-noise ratio, the excitation voltage was modulated about the ^4P threshold, and the modulated ionization signal was detected with a narrow-band phase-sensitive amplifier used in conjunction with a digital signal averager.

The Zeeman quenching curve for a natural sample of lithium (92.5% Li^7, 7.5% Li^6), showing three anticrossing features, appears in Fig. 1(a). For a sample enriched to 95% Li^6, three dips are also observed but at quite different field values, and the overall curve differs conspicuously from the Li^7 case. Differences in the quenching for the two isotopes are clearly related to their respective nuclear spin interactions. A typical Li^6 anticrossing line appears in Fig. 1(b). The experimental magnetic fields and half-widths of all observed lines are given in Part A of Table I, with the anticrossing level identifications and the theoretical anticrossing fields determined from the analysis discussed below. Also included in the table are calculated high-field anticrossings,

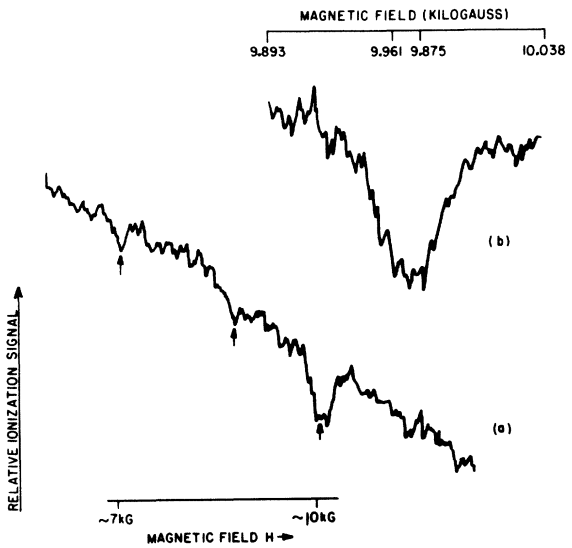

FIG. 1. (a) Experimental Zeeman-quenching curve for Li^7 with detector ≈2 cm from the source of metastables, as observed with a lock-in amplifier. (b) Experimental anticrossing signal in Li^6, obtained with the use of a lock-in amplifier and a signal averager.

which were previously observed qualitatively.[4]

Since the fine structure, magnetic hfs, and Zeeman energies of the $(1s2s2p)\,^4P$ level are all of comparable magnitude, as they are for the parent $(1s2p)\,^3P$ state of Li^+, the entire energy matrix, evaluated in the $[(LS)J, I, F, M_F]$ representation, is diagonalized for a number of field values to determine the level structure. To the precision of the present experiment it is sufficient to represent the matrix elements in terms of three unknown parameters, and we use a digital computer to determine the anticrossing fields as a function of these parameters. To be explicit, we represent the fine-structure splittings as $\Delta_{53} = E_{\frac{5}{2}} - E_{\frac{3}{2}} = \frac{5}{2}C_{SO} + (15/2)C_{SS}$, $\Delta_{51} = E_{\frac{5}{2}} - E_{\frac{1}{2}} = \frac{7}{2}C_{SO} - 6C_{SS}$, where C_{SO} and C_{SS} are the radial parts (appropriate to L-S coupling) of the spin-orbit and spin–other-orbit, and spin-spin matrix elements, respectively.[6] These matrix elements are diagonal in J, F, and M_F.

The hyperfine energy may be expressed in terms of the appropriate constants and angular matrix elements for the Fermi contact interaction and the nuclear magnetic dipole interaction. The Fermi constant a_C is taken as the third variable, and the dipole constant a_{MD}, which is two orders of magnitude smaller, has been calculated[7] to be $a_{MD} = 0.002\,047$ cm^{-1} (Li^7). Nonzero matrix elements for these hfs operators exist for $\Delta J = 0, \pm 1$; $\Delta F = 0$; $\Delta M_F = 0$.

The matrix elements of the Zeeman operator, $\mu_0 \vec{H} \cdot (g_L \vec{L} + g_S \vec{S} + g_I' \vec{I})$, are nonzero for $\Delta J = 0$, ± 1; $\Delta F = 0, \pm 1$; $\Delta M_F = 0$. In our calculations we use $g_S = 2.002\,32$ and $a_C(Li^6)/a_C(Li^7) = g_I'(Li^6)/g_I'(Li^7)$.

The fine-structure splittings and the contact constant were varied about the theoretically estimated values, and all predicted anticrossings involving a $J = \frac{5}{2}$ level were noted. Only a limited range of values for the constants gave agreement with the observations, and we used a least-squares method to obtain the best values. The results are given in Part B of Table I, with corresponding theoretical values, and the hfs is illustrated in Fig. 2(a). The errors quoted reflect the uncertainty in the experimental anticrossing fields and the estimated error in the theoretical value of a_{MD}. In the least-squares fit, the two very broad lines were not used, but the final results are in excellent agreement with these observations. It can be seen from Part B of Table I that there is good agreement between experiment and theory[7] for the values of C_{SS} and a_C, but there is a serious discrepancy in the case of C_{SO}. The

Table I. Results.

A. Experimental and Calculated Anticrossings for $^4P^o$ State of Lithium

Isotope	H_{AC}^{exp} (kG)	H_{AC}^{calc} (kG)	Anti-crossing "width" (G)	Zero field "good" quantum numbers of anti-crossing levels J, F	J', F'	M_F
Li^7	7.1098 ±0.001	7.1096	14.4±2.0	5/2, 4	1/2, 1	1
	8.977 ±0.010	8.9766	≈165	5/2, 3	1/2, 1	1
	10.279 ±0 005	10.2789	≈220	5/2, 4	1/2, 1	0
		17.891		5/2, 4	1/2, 2	2
Li^6	6.606 ±0.001	6.6062	28.6±2.0	5/2,3/2	3/2,5/2	-1/2
	6.900 ±0.001	6.8998	37.1±2.0	5/2,3/2	3/2,5/2	1/2
	9.968 ±0.002	9.9681	34.3±2.0	5/2,7/2	1/2,1/2	1/2
		15.985		5/2,7/2	1/2,3/2	3/2

B. Fine Structure Splitting and Fine and Hyperfine Constants for $^4P^o$ State of Li (in mK)

Constant	Experiment[a]	Theory[b]
$E_{5/2} - E_{1/2}$	-1724.70±0.27	+ 270.60
$E_{5/2} - E_{3/2}$	+ 997.34±0.33	+2248.92
C_{SO}	- 154.47±0.20[c]	+ 344.95
C_{SS}	+ 184.47±0.20[c]	+ 184.87
$a_c(Li^7)$	+ 172.09±0.56	+ 172.17
$a_c(Li^6)$	+ 65.16±0.21	+ 65.19

C. Experimental and Theoretical Data on $(1s2s2p)^4P$ Lifetimes (in μsec)

Atom	$\tau_{5/2}$	$\tau_{3/2}$	$\tau_{1/2}$	τ_J J not known	Ref.	Expt (E) or Theory (T)
Li	4.5±1.5	0.45±0.15[d]	0.14±0.07[d]		a	E
	5.1±1				e	E
	5.88	0.557	2.06		b	T
	7.20	0.85	2.40		f	T
	16				g	T
	7.60				h	T
He^-				> 10	i	E
				18.2±2.7	j	E
	1700				g	T
	1000	33	350		b	T
	550				h	T
Be^+	0.60±0.10			0.07±0.03	f	E
	1.20	0.04	0.1		f	T
B^{+2}	0.25±0.05				f	E
	0.40	5.7×10^{-3}	0.014		f	T
C^{+3}	0.11±0.01				f	E
	0.20	1.0×10^{-3}	2.8×10^{-3}		f	T
N^{+4}	0.055±0.020				k	E
	0.12	0.32×10^{-3}	0.86×10^{-3}		f	T
	0.058				b	T
O^{+5}	0.040±0.20				k	E
	0.075	0.13×10^{-3}	0.32×10^{-3}		f	T
	0.031				b	T

[a]This work.

[b]S. T. Manson, Phys. Rev. 145, 35 (1966), and Phys. Letters 23, 315 (1966), and private communication.

[c]Errors take into account uncertainty in ^4P-^2P mixing.

[d]Values obtained using $\tau_{5/2} = 5.1 \pm 1$ μsec.

[e]Ref. 5.

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fact that C_{SO} is negative indicates that the spin-orbit and spin–other-orbit terms arising from electron-electron interactions dominate over the spin-orbit energy which arises from the motion of the electrons in the electrostatic field of the nucleus. This is consistent with the results for the $(1s2p)\,^3P$ levels in He and Li^+. The calculations and experimental results[8] for He indicate that the effect of the inner electron overcompensates that of the nucleus so that C_{SO} is negative and that the ordering of the fine-structure levels is totally inverted. For Li^+, the experimental results[2] indicate that C_{SO} is only +0.009 cm^{-1} and the ordering of the levels is partially inverted. Our results, therefore, indicate that the addition of the 2*s* electron swings the balance back in favor of the interelectron spin-orbit terms for the ^4P level.

The decay rate of the *i*th metastable state, $R_i(H)$, is given by a weighted sum of the decay

rates γ_J of the ^4P_J levels:

$$R_i(H) = \gamma_{\frac{5}{2}} \sum_{F=1}^{4} [a_{\frac{5}{2},F}{}^{i}(H)]^2 + \gamma_{\frac{3}{2}} \sum_{F=0}^{3} [a_{\frac{3}{2},F}{}^{i}(H)]^2 + \gamma_{\frac{1}{2}} \sum_{F=1}^{2} [a_{\frac{1}{2},F}{}^{i}(H)]^2. \quad (1)$$

The coefficients $a_{J,F}{}^{i}$ are the expansion coefficients of the wave functions determined from the transformation matrix used in diagonalizing the ^4P energy matrix. There are no cross terms of the form $[\pm a_{J,F}{}^{i} a_{J\pm1,F}{}^{i}(\gamma_J\gamma_{J\pm1})^{\frac{1}{2}}]$ in R_i because of negligibly small hyperfine coupling between quartet and doublet states.[7] By using expression (1) to obtain the theoretical metastable signal as a function of field, values for γ_J and associated errors were determined. The lifetime of the $J=\frac{5}{2}$ state was determined from data on ionization signal as a function of detector position. The errors reflect internal inconsistencies in the data which are attributed to geometrical factors appearing in the theory that are difficult to treat. Our analysis took into account the possibility of threshold polarization. The results appear in Part C of Table I along with theoretical values and data for $(1s2s2p)$ states in other members of the Li isoelectronic series.

It can be seen from Parts B and C of Table I that for quantities determined by the spin-spin interaction, such as $\gamma_{5/2}$ and C_{SS}, there is relatively good agreement between theory and experiment, while for quantities dependent on the spin-orbit and spin–other-orbit interactions, C_{SO}, $\gamma_{3/2}$, $\gamma_{1/2}$, there are marked discrepancies. A survey of calculations[8] on the $(1s2p)\,^3P$ state of He also indicates that theoretical values of C_{SS} are more accurate than those for C_{SO}, especially when correlation effects are neglected. It is suggested that this pattern is due to the fact that to first order the spin-spin energy depends on the electric fields in the atom only insofar as they determine the proper wave functions, while the interactions determining the spin-orbit and spin–other-orbit energies in addition exhibit explicit dependence on the atomic fields.

The present results provide for the first time definitive assignments of principal quartet lines of the Li I[b] spectrum. Term values for levels involved in these transitions are given by calculations[1,9] which indicate that the decay of the levels $(1s2s3d)\,^4D^e$, $(1s2s3s)\,^4S^e$, and $(1s2p^2)\,^4P^e$ to the $(1s2s2p)\,^4P^\circ$ level gives rise to the multiplets observed at 2337, 2934, and 3714 Å, respectively. We have applied our knowledge of the $^4P^\circ$ structure to verify these assignments. In the case of the 2934-Å multiplet, we made the assumption $a_C(^4S^e) = a_C(^4P^\circ)$, since calculated hydrogenic orbitals[10] for Li indicate that the spin densities at the nucleus of the $1s$, $2s$, and $3s$ electrons scale as $\rho_{1s}(0):\rho_{2s}(0):\rho_{3s}(0) \approx 108:2.9:0.2$. Using this result we calculated the hyperfine splittings of the $^4S^e$ state and the spacings between the lines involved in allowed transitions to the $^4P^\circ$ state. The former is shown in Fig. 2(a). We also calculated the relative oscillator strengths within the multiplet and a theoretical line-intensity profile. In the result shown in Fig. 2(b), the interesting presence of the fourth line c is due to transitions of the form $^4S_{\frac{3}{2}}, I, F \rightarrow {}^4P_{\frac{3}{2}}, I, F+1$. It is displaced from the other $^4S_{3/2} \rightarrow {}^4P_{3/2}$ line because of the relatively large hyperfine splitting in the P state. Figure 2(b) also shows the observed lines of the 2934-Å multiplet,[11] positioned with respect to the energy scale

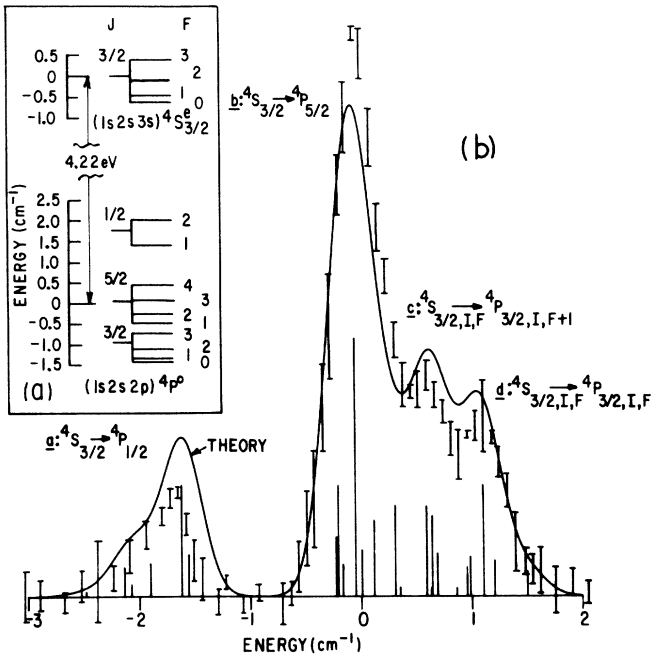

FIG. 2. (a) Energy-level diagrams for $(1s2s2p)\,^4P^\circ$ and $(1s2s3s)\,^4S^e$ states of Li^7. (b) Theoretical and experimental 2934-Å multiplet line-intensity profiles for Li^7. The theoretical curves are obtained by adding the contributions from overlapping transitions, taking the line shapes to be Gaussian, with a half-width determined by the assumed resolution, 0.45 cm^{-1}, of the optical experiments. Since the least-exposed plate was used, the poor fit for line a may be due to the nonlinearity in transmission versus intensity. For more exposed plates line b is saturated.

to give the best fit to the theory. It can be seen that the predicted line profile agrees quite well with the experimental intervals and relative intensities.

A similar analysis of the 3714-Å multiplet verifies the level assignments[1] and yields the results

$$\Delta_{53}(^4P^e) = -1.87 \pm 0.05 \text{ cm}^{-1},$$

$$\Delta_{51}(^4P^e) = -0.07 \pm 0.11 \text{ cm}^{-1}.$$

We also find that the splittings in the 2337-Å multiplet are consistent with the assignment[1,9] of the decaying level as $(1s2s3d)\,^4D^e$. The absence of a line in the 2337-Å group corresponding to line d in the 2934-Å multiplet is thought to be caused by the redistribution in line intensities due to the small fine-structure interaction in the D state.

Our knowledge of the $^4P^\circ$ level scheme can also be used to predict those magnetic fields at which long- and short-lived states of different M_F cross. By observing rf-induced transitions between these states, we hope to improve our precision by a factor of 200 and thus to measure the magnetic dipole and hyperfine quadrupole interactions. The small natural linewidths of the metastable states may permit the fine-structure splitting to be measured to one part in 10^7 if the magnetic field position of a resonance can be determined to an accuracy of 1/100 of its linewidth.

The preliminary determination of the $^4P^\circ$ lifetimes has also allowed us to evaluate better an earlier proposal[3] to exploit the differential metastability as a mechanism for producing polarized Li nuclei. An analysis indicates that vector and tensor polarizations for Li^6 at least comparable with existing deuterium sources can be obtained. A metastable Li source would have the convenient feature of not requiring electron-bombardment ionization, but it is not known yet whether adequate beam strengths can be obtained.

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