

*Aided by research grants to the Johns Hopkins University from the U. S. Army Research Office-Durham (Grant No. DA-ARO-D-31-124-G1065) and the National Science Foundation (Grant No. GP-6315X).

†Harkness Fellow of the Commonwealth Fund of New York.

‡National Institutes of Health Predoctoral Fellow.

¹A definite statement that the Hartree-Fock potential goes like $(-1/r)$ at large r may be found in D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961), p. 18. There are, moreover, many papers which note this " $(-1/r)$ asymptotic behavior" while discussing approxi-

mate ways of treating exchange. See, e.g., F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood, New Jersey, 1963), p. 1-8.

²We use atomic units. The unit of length is the Bohr radius, $a_0 \sim 0.53 \text{ \AA}$, and the unit of energy is $e^2/a_0 \sim 27.2 \text{ eV}$.

³C. Froese, *Can. J. Phys.* **41**, 1895 (1963). The choice of slope of the wave function at the outermost point in Froese's "tail procedure" seems to involve the neglect of exchange. See especially her Eq. (6).

⁴J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

⁵M. T. Marron, N. C. Handy, R. G. Parr, and H. J. Silverstone, to be published.

Multiplet Pattern and Assignments of $\text{Li } 1^b$ Transitions*

M. Levitt

Columbia Radiation Laboratory, Department of Physics, Columbia University, New York, New York 10027

and

P. D. Feldman

Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218

(Received 23 December 1968)

The experimental values of the fine and hyperfine energies of the metastable autoionizing $(1s2s2p)^4P^o$ states of Li are used to definitively identify the transitions responsible for the multiplets at 2934 and 3714 \AA in the optical spectrum of Li. It is found that the optical lines are due to the radiative decay to the $^4P^o$ state of the lowest-lying states with symmetries $^4S^e$ and $^4P^e$. The intervals between the quartet states and the fine and hyperfine splittings of these states are derived from an analysis of the multiplet structures.

I. INTRODUCTION

On the basis of our recent determination¹ of the fine and hyperfine structure of the metastable autoionizing $(1s2s2p)^4P^o$ state of Li, we have identified as 1^b lines² the 2934 and 3714 \AA multiplets observed in the course of studies³⁻⁵ on the $\text{Li}^7 \text{ II}$ spectrum. These lines cannot be classified in the spectrum of the singly excited atom or ion. Our work confirms the tentative assignments⁶ of these lines which are based solely on calculations of the energies of the quartet levels of Li. In the present paper we discuss the calculations of the multiplet structures and intensity profiles for these lines and the effect of hfs in markedly altering the relative line intensities in the case of Li^7 . The fine structure of the $(1s2p^2)^4P^e$ state is determined from an analysis of the 3714 \AA multiplet.

II. METASTABLE LEVELS AND THE Li QUARTET SPECTRUM

The first direct observation of doubly excited states in lithium, which are metastable against

both autoionization and radiative decay, was made by Feldman and Novick in 1963.⁷ The metastability results from the spin selection rule $\Delta S = 0$ for Coulomb autoionization since there are no quartet states in the continuum adjacent to the lowest-lying discrete quartet states. The lowest excitation threshold observed was at $57.3 \pm 0.3 \text{ eV}$, which was identified as corresponding to the $(1s2s2p)^4P_{5/2}$ level. Several secondary thresholds were also observed and were assumed to result from the radiative cascade to the $^4P^o$ state from other quartet states which are metastable against autoionization.

The configuration $(1s2s2p)$ has the lowest energy of those odd-parity quartet states which do not couple via the Coulomb interaction to adjacent continuum states. Holgøien and Geltman⁸ have shown that the lowest lying of such $^4P^o$ states can be classified as

$$|1s, 2n \pm\rangle = 2^{-1/2}(|1s, 2snp\rangle \pm |1s, 2pns\rangle),$$

since the configurations $(1s2snp)$ and $(1s2pns)$ are nearly degenerate (for small n) when the interaction between configurations is neglected. This

classification is similar to that introduced earlier for two-electron atoms.⁸ The $(1s2s2p)$ configuration belongs to the group of "+" levels, which converge as a Rydberg series to the $(1s2s)^3S^e$ series limit of Li^+ at 64.44 eV.

Among other metastable quartet states which have been treated theoretically are those having the symmetries $4S^e$ and $4P^e$. The first of these is associated with the configurations of the form $(1s2sns)$, $n \geq 3$, which also converge to the $(1s2s)^3S^e$ limit of Li^+ . The second can be specified as $(1s2mp)$, $n \geq 2$, converging to the $(1s2p)^3P^o$ limit of Li^+ at 66.50 eV. The $4S^e$ states cannot undergo Coulomb autoionization to the singlet ground state of Li^+ because of the spin selection rule $\Delta S=0$. The $(1s2p^2)^4P^e$ state is calculated to lie about 4 eV below the $(1s2s)$ triplet level of the ion and is similarly metastable. The higher lying $4P^e$ states are calculated to be above the $(1s2s)$ triplet level but are also metastable. This is because decay to a continuum $(1s2skl)$ state, with orbital angular momentum equal to $[l(l+1)]^{1/2}\hbar$ and parity equal to $(-1)^l$, would violate parity conservation for a kp final state and orbital angular momentum conservation for ks or kd final states.

The $4S^e$ and $4P^e$ states can cascade by radiative decay to the $(1s2s2p)$ level, the only one which is metastable against radiation as well as autoionization. This fact has prompted efforts to identify these doubly excited energy levels with those responsible for the lines observed by Herzberg and Moore⁵ and attributed to the spectrum of Li^+ , since high-excitation energy is required. These lines cannot be assigned to the normal spectrum of the atom or ion and are much narrower than lines associated with levels which can decay by Coulomb autoionization. The unassigned multiplets which are of special interest are those corresponding to transitions for which the $(1s2s2p)$ level is the presumed final state. These observed multiplets lie at 3714.2 Å (3.34 eV), 2934.2 Å (4.22 eV), and 2337.0 Å (5.31 eV), respectively. The first two groups of lines were observed previously by Schüler³ and Werner,⁴ and the last one was also seen by Werner. Shown in Fig. 1(a) are photographs of Herzberg and Moore's plates of the 2934 Å line. In Fig. 1(b) are shown typical microdensitometer line profiles which indicate that the 2934 Å multiplet of Li^+ contains four lines.

A variational calculation by Holøien and Geltman⁶ using linear combinations of Slater determinants with correlated trial functions gives for the transition energies of interest

$$(1s2s3s)^4S^e \rightarrow (1s2s2p)^4P^o: 4.22 \text{ eV,}$$

$$\text{and } (1s2p^2)^4P^e \rightarrow (1s2s2p)^4P^o: 3.27 \text{ eV.}$$

These results agree well with the optical data and, in addition, yield fairly good agreement between

calculated configuration energies and electron excitation thresholds observed by Feldman and Novick. The work of Weiss⁹ also tends to confirm the assignment for the 3714 Å and 2934 Å lines, since he obtains calculated values of

$$(1s2s3s)^4S^e \rightarrow (1s2s2p)^4P^o: 4.21 \text{ eV,}$$

$$(1s2p^2)^4P^e \rightarrow (1s2s2p)^4P^o: 3.32 \text{ eV.}$$

Weiss's results also indicate that the 2337 Å multiplet corresponds to the transition $(1s2s3d)^4D^e \rightarrow (1s2s2p)^4P^o$.

III. THEORY OF THE 2934 Å LINE PROFILE

In this section we apply our knowledge¹ of the $(1s2s2p)$ level scheme and wave functions to the question of the correctness of the assignments of the transitions discussed in Sec. II. First we consider $4S^e \rightarrow 4P^o$ transitions. In Table I we give our results for the zero-field energies and eigenfunctions of the $4P^o$ states. The eigenfunctions, which are needed for the line-profile calculation, are given as expansions in terms of the appropriate Russell-Saunders basis states in a representation in which J , I , and F are good quantum numbers. The numerical wave functions are obtained by diagonalizing the $4P^o$ energy matrix, also expressed in this representation. The states are designated in Table I by the quantum numbers of the dominant basis state at zero field.

There is no fine-structure splitting in the $(1s2s3s)^4S_{3/2}$ state, but there is hyperfine splitting due to the Fermi-contact interactions of the three s electrons at the nucleus. Since L - S coupling holds for this atomic system, the total contact interaction may be expressed as a single term:

$$\mathcal{H}_{\text{Fermi}} = a_c \vec{I} \cdot \vec{S}, \quad (1)$$

where I , the nuclear spin, is $\frac{3}{2}$ for Li^7 and 1 for Li^6 . The contact constant a_c scales as the sum of the squares of the (ns) radial wave functions at the nucleus (or more generally, as the total spin density at the nucleus). If we use the $1s$ and $2s$ hydrogenic Li orbitals of Wu and Shen¹⁰ and extrapolate the results for the $3s$ orbital from the case of H , we obtain

$$|R_{10}(r=0)|^2 : |R_{20}(0)|^2 : |R_{30}(0)|^2 \\ \approx 108 : 2.9 : 0.2. \quad (2)$$

These results lead to a theoretical value for a_c , which differs from the experimental value by less than 1%, and indicate that the contact energy for the $(1s2s3s)$ state should be the same as that for the $(1s2s2p)$ state to within several parts in a thousand if the sum of the $(1s)$ and $(2s)$ contact terms is the same for these two states. Strong evidence for the fact that the $[(1s), (2s)]$ contact energy is insensitive to the nature of the orbital of the outermost electron is provided by the re-

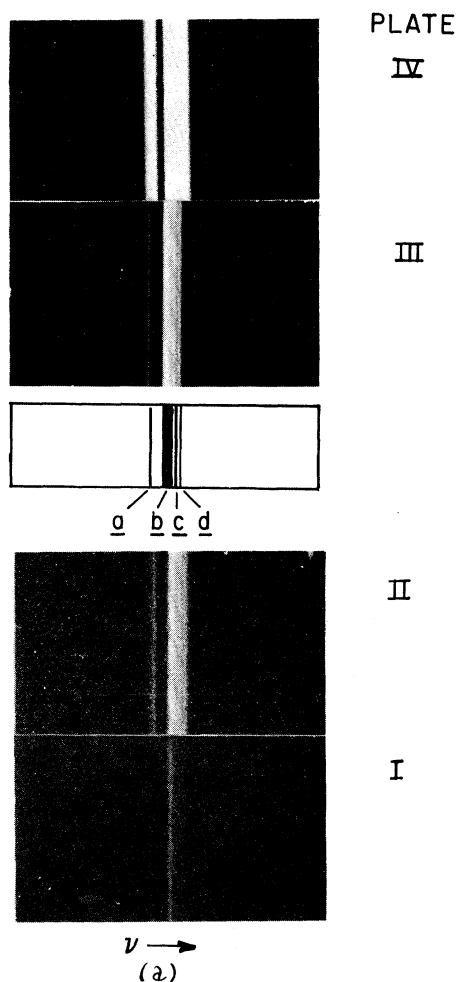


FIG. 1. (a) The 2934 Å multiplet of Li^7 (from the plates of Herzberg and Moore). The plates are numbered in order of increasing exposure time. (b) Typical microdensitometer line intensity profiles of the 2934 Å multiplet for plates I and II. The intensity ordinate of plate II is scaled down by a factor of about 2 relative to that of plate I.

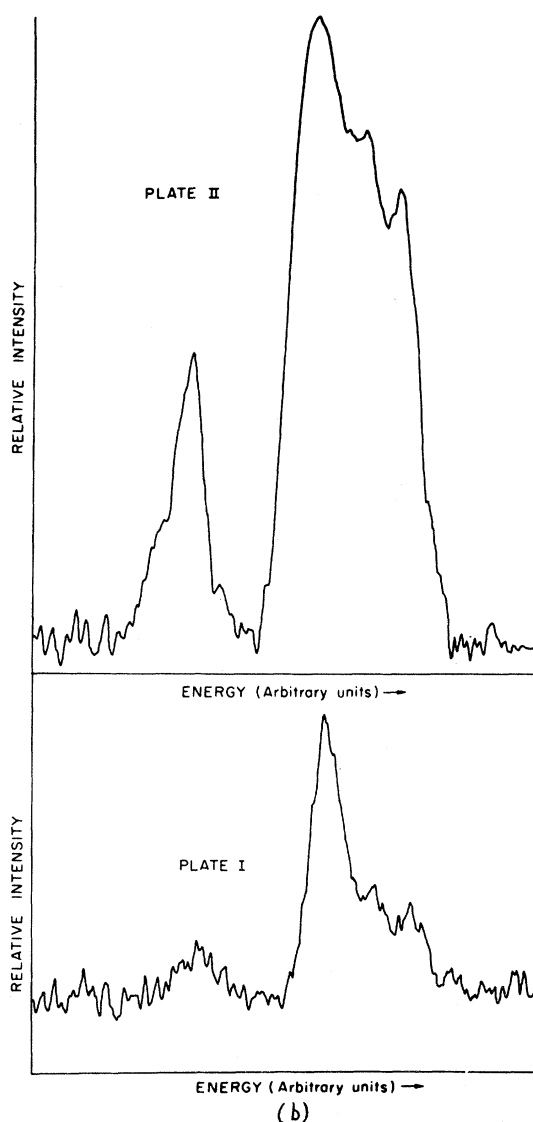
sult that the contact constant for the $(1s2s)^3S$ state⁵ of Li^+ is the same as that for the $4P^0$ state¹ to within 0.5%.

We therefore make the assumption that

$$a_c(^4S^e) = a_c(^4P^0) = 0.172 \text{ cm}^{-1} \quad (3)$$

and calculate the energies of the $4S$ hyperfine levels from the expression

$$\begin{aligned} E_F(^4S_{3/2}^e) &= a_c \langle (^4S^e)_{J=\frac{3}{2}, I=\frac{3}{2}, F} | \vec{I} \cdot \vec{S} | (^4S^e)_{\frac{3}{2}, \frac{3}{2}, F} \rangle \\ &= \frac{1}{4} a_c [2F(F+1) - 15]. \end{aligned} \quad (4)$$



The calculated $4S^e$ level scheme is illustrated in Fig. 2.

If we take as the final state for a given transition a particular basis vector $| (SL)J', I, F' \rangle$ (case I), the total intensity of the line, obtained by summing over magnetic sublevels and polarizations, is given by¹¹

$$S = | \langle (^4S^e)_{J, I, F} | \vec{P} | (^4P^0)_{J', I, F'} \rangle |^2 \quad (5)$$

where \vec{P} is the electric dipole moment operator. For $4S^e$ to $4P^0$ transitions, this expression reduces to

$$\begin{aligned} S &= 4(2F+1)(2F'+1)(2J'+1) \\ &\quad \times | \langle (^4S^e) | \vec{P} | (^4P^0) \rangle |^2 \end{aligned}$$

TABLE I. $(1s2s2p)^4P^o$ energies and eigenfunctions.

| Isotope | State J, F | Energy (cm ⁻¹) | Eigenfunction, $\psi_i = \sum_{J', F'} a_{J', F'}^i ({}^4P^o); J, F\rangle$ |
|-----------------|----------------------------|----------------------------|--|
| Li ⁷ | $\frac{5}{2}, 4$ | 0.4347 | $ \frac{5}{2}, 4\rangle$ |
| | 3 | 0.0757 | $(0.9639) \frac{5}{2}, 3\rangle - (0.2664) \frac{3}{2}, 3\rangle$ |
| | 2 | -0.2485 | $(0.9741) \frac{5}{2}, 2\rangle - (0.2246) \frac{3}{2}, 2\rangle - (0.0269) \frac{1}{2}, 2\rangle$ |
| | 1 | -0.4818 | $(0.9889) \frac{5}{2}, 1\rangle - (0.1475) \frac{3}{2}, 1\rangle - (0.0155) \frac{1}{2}, 1\rangle$ |
| | $\frac{3}{2}, 3$ | -0.7224 | $(0.2664) \frac{5}{2}, 3\rangle + (0.9639) \frac{3}{2}, 3\rangle$ |
| | 2 | -1.1156 | $(0.2261) \frac{5}{2}, 2\rangle + (0.9705) \frac{3}{2}, 2\rangle + (0.0838) \frac{1}{2}, 2\rangle$ |
| | 1 | -1.3359 | $(0.1482) \frac{5}{2}, 1\rangle + (0.9864) \frac{3}{2}, 1\rangle + (0.0715) \frac{1}{2}, 1\rangle$ |
| | 0 | -1.4300 | $ \frac{3}{2}, 0\rangle$ |
| | $\frac{1}{2}, 2$ | 2.0070 | $(0.0073) \frac{5}{2}, 2\rangle - (0.0877) \frac{3}{2}, 2\rangle + (0.9961) \frac{1}{2}, 2\rangle$ |
| | 1 | 1.4281 | $(0.0048) \frac{5}{2}, 1\rangle - (0.0730) \frac{3}{2}, 1\rangle + (0.9973) \frac{1}{2}, 1\rangle$ |
| Li ⁶ | $\frac{5}{2}, \frac{7}{2}$ | 0.1434 | $ \frac{5}{2}, \frac{7}{2}\rangle$ |
| | $\frac{5}{2}, \frac{5}{2}$ | 0.0096 | $(0.9978) \frac{5}{2}, \frac{5}{2}\rangle - (0.0665) \frac{3}{2}, \frac{5}{2}\rangle$ |
| | $\frac{3}{2}, \frac{3}{2}$ | -0.0902 | $(0.9986) \frac{5}{2}, \frac{3}{2}\rangle - (0.0519) \frac{3}{2}, \frac{3}{2}\rangle - (0.0020) \frac{1}{2}, \frac{3}{2}\rangle$ |
| | $\frac{3}{2}, \frac{1}{2}$ | -0.8840 | $(0.0665) \frac{5}{2}, \frac{1}{2}\rangle + (0.9978) \frac{3}{2}, \frac{1}{2}\rangle$ |
| | $\frac{1}{2}, \frac{3}{2}$ | -1.0051 | $(0.0520) \frac{5}{2}, \frac{3}{2}\rangle + (0.9983) \frac{3}{2}, \frac{3}{2}\rangle + (0.0266) \frac{1}{2}, \frac{3}{2}\rangle$ |
| | $\frac{1}{2}, \frac{1}{2}$ | -1.0737 | $(0.9998) \frac{5}{2}, \frac{1}{2}\rangle + (0.0174) \frac{3}{2}, \frac{1}{2}\rangle$ |
| | $\frac{1}{2}, \frac{3}{2}$ | 1.8257 | $(0.0007) \frac{5}{2}, \frac{3}{2}\rangle - (0.0267) \frac{3}{2}, \frac{3}{2}\rangle + (0.9996) \frac{1}{2}, \frac{3}{2}\rangle$ |
| | $\frac{1}{2}, \frac{1}{2}$ | 1.6626 | $(0.0174) \frac{5}{2}, \frac{1}{2}\rangle - (0.9998) \frac{3}{2}, \frac{1}{2}\rangle$ |

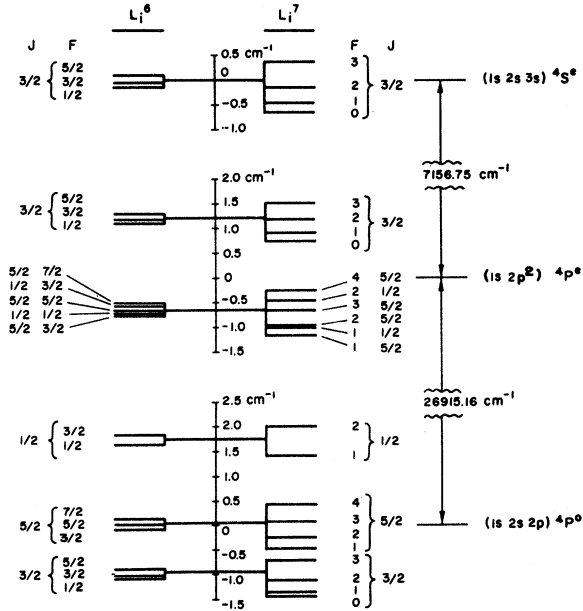


FIG. 2. Energy-level diagrams for the $(1s2s2p)^4P^o$, $(1s2p^2)^4P^e$, and $(1s2s3s)^4S^e$ states of Li⁶ and Li⁷. Since the ordering of the $J = \frac{5}{2}$ and $J = \frac{1}{2}$ fine-structure energies of the ${}^4P^e$ state is uncertain, the levels are shown as degenerate in the figure.

$$\begin{aligned} & \times |W(\frac{3}{2}, J', F, 1; F', \frac{3}{2})|^2 \\ & \times |W(\frac{3}{2}, 0, J', 1; \frac{3}{2}, 1)|^2, \end{aligned} \quad (6)$$

where W is the Racah coefficient. To calculate

the theoretical line profile, the line shapes are taken to be Gaussian functions of the form

$$I = I_0 e^{-b(E - E_0)^2}, \quad (7)$$

and the contributions from the overlapping lines are added. We first choose b so that for two lines separated by 0.2 cm^{-1} , which is equal to the quoted resolution of the optical experiments of Herzberg and Moore, we obtain a result satisfying the Rayleigh criterion. The results, which appear in Fig. 3, are approximate because we have used only the dominant components $|SLJ, I, F\rangle$ of each of the 4P states, thereby neglecting the hyperfine mixing of basis states differing in J quantum number by one.

If we use the numerical wave functions of Table I (case II), the expression for the relative strength of a transition from a state with total angular momentum quantum number F to the i th ${}^4P^o$ state becomes

$$\begin{aligned} S_i^F &= \left| \sum_{J', F'} a_{J', F'}^i (1s2s3s)(LS) \right. \\ & \quad \left. J, I, F \| \vec{P} \| (1s2s2p)(L'S) J', I, F \right|^2 \\ &= 4(2F+1) |({}^4S^e \| \vec{P} \| {}^4P^o)|^2 \\ & \times \left| \sum_{J', F'} a_{J', F'}^i (2F'+1)^{1/2} \right. \\ & \quad \left. \times (2J'+1)^{1/2} W(\frac{3}{2}, J', F, 1; F', \frac{3}{2}) \right. \\ & \quad \left. \times W(\frac{3}{2}, 0, J', 1; \frac{3}{2}, 1) \right|^2. \end{aligned} \quad (8)$$

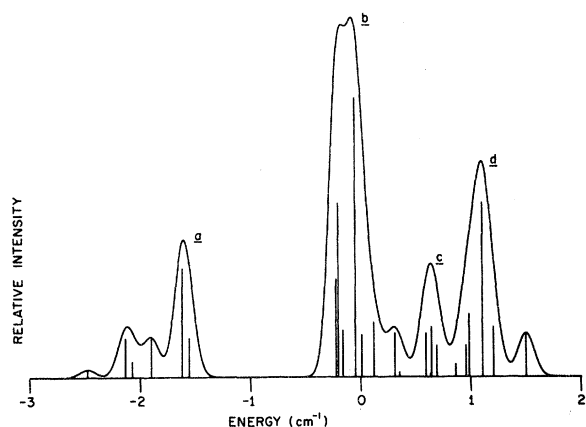


FIG. 3. Theoretical line profile of the 2934 Å multiplet of Li^7 for the case where J is a good quantum number. The resolution is taken to be 0.2 cm^{-1} . The ${}^4S^e - {}^4P^o$ energy interval has been subtracted from the energies of the lines as shown in Figs. 3 to 6.

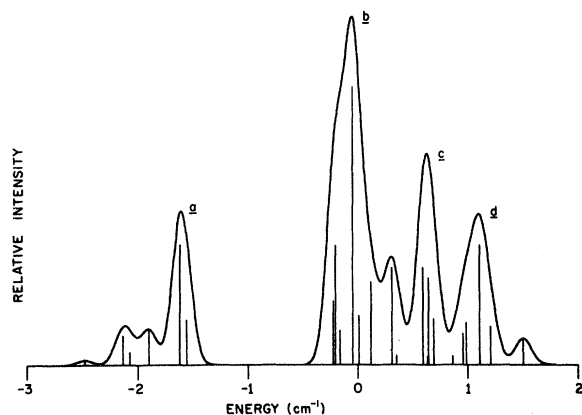


FIG. 4. Theoretical line profile of the 2934 Å multiplet of Li^7 . The resolution is taken to be 0.2 cm^{-1} .

The results for case II appear in Fig. 4. In both Figs. 3 and 4, the major contributions to line a come from transitions of the form

$${}^4S_{\frac{3}{2}, I, F} \rightarrow {}^4P_{\frac{1}{2}, I, F-1},$$

where we denote states by their dominant components. Line b corresponds to

$${}^4S_{\frac{3}{2}, I, F} \rightarrow {}^4P_{\frac{5}{2}, I, F},$$

and

$${}^4S_{\frac{3}{2}, I, F} \rightarrow {}^4P_{\frac{5}{2}, I, F+1},$$

and line d to ${}^4S_{\frac{3}{2}, I, F} \rightarrow {}^4P_{\frac{3}{2}, I, F}$.

The interesting presence of the fourth line c is due to transitions of the form

$${}^4S_{\frac{3}{2}, I, F} \rightarrow {}^4P_{\frac{3}{2}, I, F+1}.$$

Line c is displaced from the other ${}^4S_{3/2} \rightarrow {}^4P_{3/2}$ line because of the relatively large hyperfine splittings in the P state. The enhancement of line c in the more rigorous calculation of case II is related to the presence of small admixtures of $|{}^4P_{5/2}, I, F+1\rangle$ components in the final states (see Table I) because of the off-diagonal hyperfine contact terms. This gives rise to interference terms in the expression for the theoretical line intensity involving the ${}^4S_{3/2} \rightarrow {}^4P_{3/2}$ electric dipole matrix element and the larger ${}^4S_{3/2} \rightarrow {}^4P_{5/2}$ dipole matrix element. The relative phases are such that the interference is constructive.

For the case of Li^6 , the contact term is smaller by a factor of about 3, and the effect of the hfs on line intensities is less important. The theoretical $\text{Li}^6({}^4S^e - {}^4P^o)$ line profile appears in Fig. 5. It can be seen that only three lines are predicted for this case. Unfortunately, Li^6 spectral data are not presently available for comparison with theory.

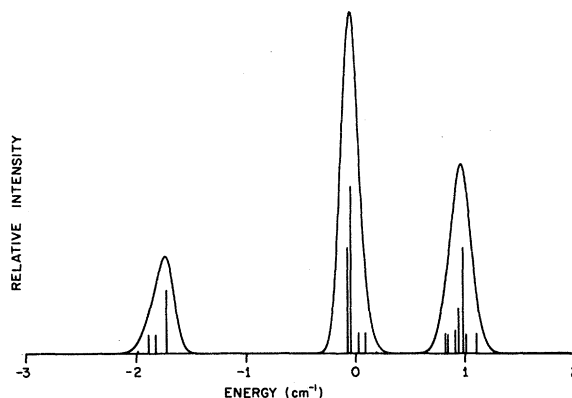


FIG. 5. Theoretical line profile of the 2934 Å multiplet of Li^6 . The resolution is taken to be 0.2 cm^{-1} .

A microdensitometer analysis of the original plates indicates that a best fit of theory to experiment is obtained when the resolution is taken to be 0.45 cm^{-1} . This value is also consistent with the widths of other lines measured on Herzberg's plates. The theoretical and experimental profiles for this case appear in Fig. 6. It can be seen that the predicted line profile agrees quite well with the experimental intervals and relative intensities. The results thus provide definitive confirmation of the assignment of the 2934 Å line. The ${}^4S^e - {}^4P^o$ interval, as obtained from the calculated ${}^4S^e$ splittings, the known ${}^4P^o$ splittings, and the observed optical wavelengths, is given by

$$E_{4S^e} - E_{4P^o} = 34\,071.91 \pm 0.05 \text{ cm}^{-1},$$

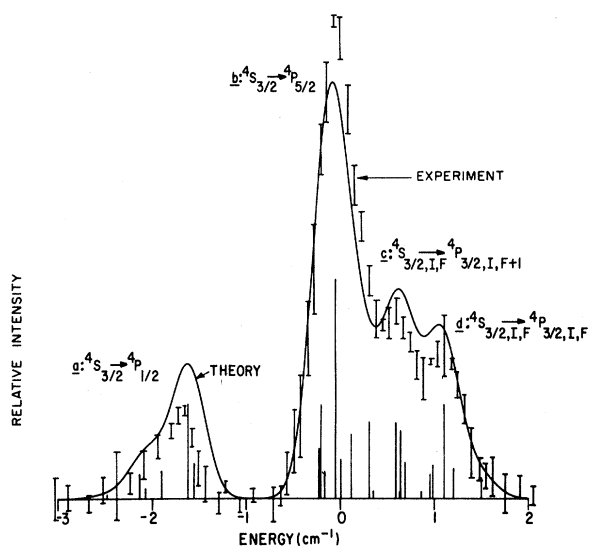


FIG. 6. Theoretical and experimental 2934 Å multiplet line intensity profiles of $\text{Li } 1^b$. The theoretical curve is calculated by taking the resolution to be 0.45 cm^{-1} . Since the least-exposed plate was used, the poor fit for line a may be due to the nonlinearity in transmission versus intensity. For more exposed plates, line b is saturated.

where the uncertainty reflects the precision of the optical measurements.

It should be noted that the 2337 Å multiplet consists of three lines whose splittings correspond to within 0.1 cm^{-1} of those for lines a, b, and c of the 2934 Å multiplet. A calculation of the 2337 Å line profile, which hopefully would account for the fact that there is no line corresponding to d (2934 Å), requires knowledge of the three fine-structure matrix elements (diagonal in J) for the D state.

IV. THE 3714 Å MULTIPLET

We discuss next the identification of the various lines of the 3714 Å multiplet and the determination of the fine structure of the $(1s2p^2)$ state. In order to identify tentatively some of the 8 observed lines and to get a crude estimate of the fine structure of the $4P^e$ state, we first noted those pairs of lines which had spacings roughly equal to known splittings in the $4P^o$ state. It was assumed that each member of such pairs originated in $4P^e$ levels characterized by the same " J " value. A first-order calculation of the relative line intensities for the array of transitions also indicated that the strongest line should correspond to the transitions

$$4P_{\frac{5}{2}, F}^e \rightarrow 4P_{\frac{5}{2}, F}^o.$$

These two considerations enabled us to assign con-

sistently the dominant transitions corresponding to each of the observed lines and to specify the $4P^e$ fine-structure splittings to about 0.1 cm^{-1} . We also used the values previously cited for the s electron radial wave functions at the nucleus to estimate the value of the contact constant: $a_c(4P^e, \text{Li}^7) = 0.166 \pm 0.002 \text{ cm}^{-1}$. We then varied the fine-structure splittings about these approximate values. For each set of parameters, the corresponding $4P^e$ energy matrix, evaluated in the $[(LS)J, I, F]$ representation, was diagonalized with the use of a digital computer to determine the $(1s2p^2)$ level scheme and numerical wave functions. The associated theoretical line profile was obtained using the expression for the strength of a transition from state $\psi_j(4P^e)$ to state $\psi_i(4P^o)$ as given by

$$S_i^j = \left| \sum_{J, F} \sum_{J', F'} a_{J, F}^j a_{J', F'}^i \right. \\ \times \left. \left((4P^e)_{J, I, F} \parallel \tilde{\mathcal{P}} \parallel (4P^o)_{J', I, F'} \right)^2 \right. \\ = \left| (4P^e \parallel \tilde{\mathcal{P}} \parallel 4P^o) \right|^2 \left| \sum_{J, F} (-1)^F \right. \\ \times (a_{J, F}^j) (2F+1)^{\frac{1}{2}} (2J+1)^{\frac{1}{2}} \\ \times \sum_{J', F'} (-1)^{2J'} (a_{J', F'}^i) (2F'+1)^{\frac{1}{2}} \\ \times (2J'+1)^{\frac{1}{2}} W\left(\frac{3}{2}, J', F, 1; F', J\right) \\ \left. \times W\left(\frac{3}{2}, 1, J', 1; J, 1\right) \right|^2. \quad (9)$$

Implicit in the above expression is the assumption that none of the $4P^e$ states has an autoionization lifetime which is comparable with its radiative lifetime. [The radiative lifetime of the $(1s2p^2)$ level has been calculated¹² to be $1.7 \times 10^{-10} \text{ sec}$.] This assumption may not be altogether valid, since for the $4P^o$ case the $J = \frac{1}{2}$ fine-structure level has an autoionization lifetime of about 10^{-7} seconds, which is almost two magnitudes smaller than the $J = \frac{5}{2}$ lifetime.¹ In any case, this consideration is not expected to affect the values of the $4P^e$ energy parameters which give the best fit of the theoretical multiplet structure to the observed optical splittings. The numerical values obtained for these parameters are

$$E_{4P_{5/2}^e} - E_{4P_{1/2}^e} = +0.01 \pm 0.03 \text{ cm}^{-1}, \\ E_{4P_{5/2}^e} - E_{4P_{3/2}^e} = -1.83 \pm 0.03 \text{ cm}^{-1}.$$

The uncertainties reflect the range of parametric values for which the positions of seven theoretical

lines fit the optical data to within the experimental precision. The resultant calculated line profile and the relative positions of the observed lines appear in Fig. 7. The multiplet pattern for Li^6 is shown in Fig. 8. The level scheme of the $4P^e$ state is illustrated in Fig. 2, and the $4P^e-4P^o$ energy interval is found to be

$$E_{4P^e} - E_{4P^o} = 26\,915.16 \pm 0.06 \text{ cm}^{-1}.$$

The uncertainty in the interval is related to the accuracy of the $4P^e$ fine-structure determination and the precision of the optical data.

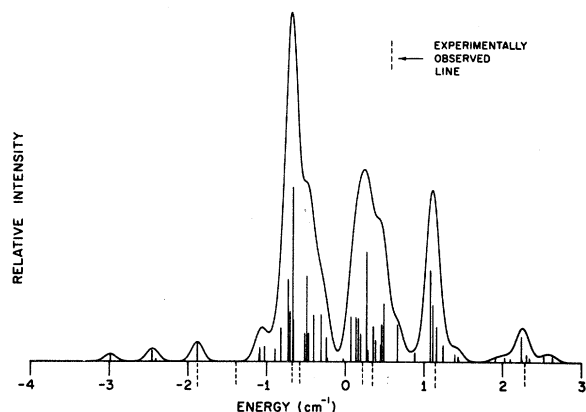


FIG. 7. Theoretical line profile of the 3714 Å multiplet of Li^7 . The resolution is taken to be 0.2 cm^{-1} . The energies of experimentally observed lines are indicated. The relative intensities, quoted by Herzberg and Moore (Ref. 5), are (from left to right) 0: 1: 10: 7sh: 8: 6sh: 5: 1 (sh indicates shoulder). The $4P^e-4P^o$ energy interval has been subtracted from the energies of the lines as shown in Figs. 7 and 8.

V. CONCLUSION

Our results clearly confirm that the multiplets having mean wavelengths of 2934 and 3714 Å arise from optical transitions involving the three low-

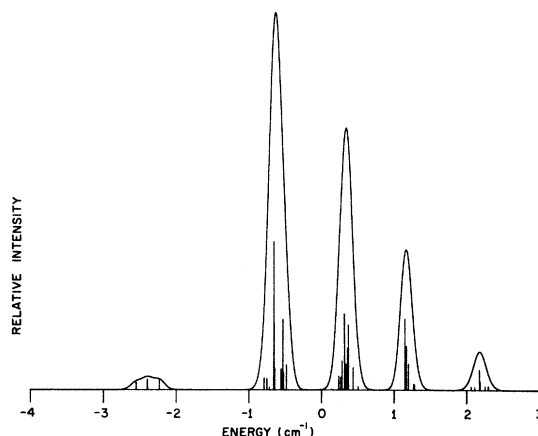


FIG. 8. Theoretical line profile of the 3714 Å multiplet of Li^6 . The resolution is taken to be 0.2 cm^{-1} .

est-lying quartet states of neutral lithium, which are metastable with respect to Coulomb autoionization. We have also determined from our studies the intervals between these doubly excited atomic states as well as their respective fine and hyperfine splittings. It is hoped that these quantities will prove useful for comparison with any future theoretical work on these three-electron configurations.

VI. ACKNOWLEDGMENT

It is a pleasure to acknowledge the continued support of Professor R. Novick. Professor G. Herzberg kindly lent us the original plates of the 2934 Å line. We are also grateful to the Upper Air Physics Branch of the Naval Research Laboratory for the use of its computer facility while one of us (P. D. F.) was a Research Associate in the E. O. Hulburt Center for Space Research.

* This work was supported wholly by the Joint Services Electronics Program (U.S. Army, U.S. Navy, and U.S. Air Force) under contract No. DA-28-043 AMC-00099(E).

¹P. Feldman, M. Levitt, and R. Novick, *Phys. Rev. Letters* **21**, 331 (1968).

²The notation l^b designates terms arising from the excitation of a single electron from the outermost closed shell of the neutral atom.

³H. Schüler, *Ann. Physik* **76**, 292 (1925).

⁴S. Werner, *Nature* **118**, 154 (1926).

⁵G. Herzberg and H. R. Moore, *Can. J. Phys.* **37**, 1293 (1959).

⁶E. Holþien and S. Geltman, *Phys. Rev.* **153**, 81

(1967).

⁷P. Feldman and R. Novick, *Phys. Rev. Letters* **11**, 278 (1963); *Phys. Rev.* **160**, 193 (1967).

⁸J. W. Cooper, U. Fano, and F. Prats, *Phys. Rev. Letters* **10**, 518 (1963); P. L. Altick and E. N. Moore, *ibid.* **15**, 100 (1965).

⁹A. Weiss, unpublished work cited in Ref. 6.

¹⁰T.-Y. Wu and S. T. Shen, *Chinese J. Phys.* **5**, 150 (1944).

¹¹A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), p. 76.

¹²J. D. Garcia and J. E. Mack, *Phys. Rev.* **138**, A987 (1965).

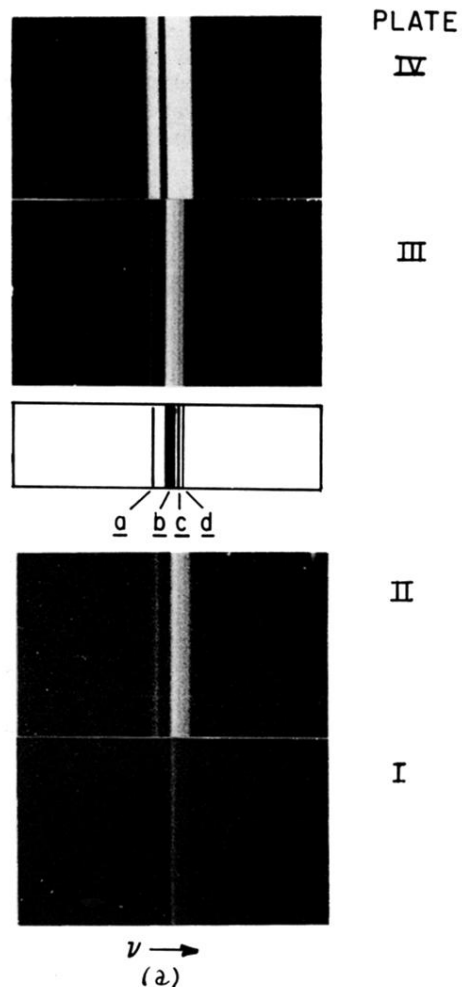


FIG. 1. (a) The 2934 Å multiplet of Li^I (from the plates of Herzberg and Moore). The plates are numbered in order of increasing exposure time. (b) Typical microdensitometer line intensity profiles of the 2934 Å multiplet for plates I and II. The intensity ordinate of plate II is scaled down by a factor of about 2 relative to that of plate I.