300 °K were calculated in the quantum-mechanical formulation. To compare the two methods of calculation, we have evaluated the classical-path expression for NaHe at 300 °K at several frequencies. The results are included in Fig. 1. The classical approximation is very accurate at low frequencies, but at high frequencies it overestimates the absorption. At high frequencies the classical turning points R_i and R_f in the initial and final states are considerably different and in the quantum-mechanical treatment the region $R_i < R < R_f$ contributes little to the matrix elements of $D(R)$.

The dependence of the absorption coefficient on the interaction potential is similar to that of the elastic scattering cross section, but the thermal averaging tends to suppress detailed information of the kind that can be obtained from cross-section measurements.

---

*Permanent address: Schuster Laboratory, University of Manchester, England.

[1] L. M. Trafton, Astrophys. J. 147, 765 (1967).

[2] J. Linsky, Astrophys. J. **156**, 989 (1969).

[3] R. P. Futrelle, Phys. Rev. Lett. **19**, 479 (1967).

[4] J. Van Kranendork and Z. J. Kiss, Can. J. Phys. **37**, 1187 (1959).

[5] H. B. Levine and G. Birnbaum, Phys. Rev. **154**, 86 (1967).

[6] R. L. Matcha and R. K. Nesbet, Phys. Rev. **160**, 86 (1967).

[7] W. E. Baylis, J. Chem. Phys. **51**, 2665 (1969).

[8] S. B. Schneiderman and H. H. Michel, J. Chem. Phys. **43**, 3706 (1965).

[9] M. Krauss, P. Maldonado, and A. C. Wahl, J. Chem. Phys. **54**, 4944 (1971).

[10] C. Bottcher, J. Phys. B **4**, 1140 (1971).

[11] E. Clementi, IBM J. Res. Dev. **9**, 2 (1965).

[12] A. Dalgarno, C. Bottcher, and G. A. Victor, Chem. Phys. Lett. **7**, 263 (1970).

[13] C. Bottcher and A. Dalgarno (unpublished).

[14] W. Byers Brown and D. M. Wisnant, Chem. Phys. Lett. **7**, 329 (1970).

[15] G. Das and A. C. Wahl, Phys. Rev. A **4**. 825 (1971).

PHYSICAL REVIEW A VOLUME 7, NUMBER 5 MAY 1973

Hyperfine Structure of 1*snp* ^3P Terms of ^{6,7}Li II

H. G. Berry,* J. L. Subtil, and E. H. Pinnington†
Laboratoire de Spectrométrie Ionique et Moléculaire (associé au CNRS), Université de Lyon I, 43 bd du 11 Nov. 1918, 69-Villeurbanne, France

H. J. Andrä, W. Wittmann, and A. Gaupp
I. Phys. Inst. d. Freien Universität Berlin, Berlin 33, Boltzmannstrasse 20, W. Germany

(Received 3 November 1972)

Using the beam-foil technique, we have observed zero-field quantum beats in the intensity decays of transitions from the 1*snp* ^3P terms ($n = 2, 3, 4, 5$) in ^{6,7}Li II, and deduced the magnetic hyperfine coupling constant for each isotope for the 2*p* ^3P terms. Preliminary values for these coupling constants are $A(1s2p\,^3P, {}^6\text{Li II}) = 0.091 \pm 0.001$ cm^{-1} (2.73 GHz), $A(1s2p\,^3P, {}^7\text{Li II}) = 0.239 \pm 0.002$ cm^{-1} (7.17 GHz). The measured fine structures agree with recent calculations within a few percent.

I. INTRODUCTION

The fine-structure splittings of the *np* ^3P states ($n = 2-5$) of the He isoelectronic sequence have recently been calculated quite accurately up to $Z = 10$,[1] but experimental values exist only for the ^{4}He splittings.[2,3] We have therefore begun a series of experiments for the determination of some *np* ^3P fine-structure splittings of Li II using the technique of zero-field quantum beats subsequent to beam-foil excitation.[4,5] However, in both isotopes of Li the hyperfine interaction plays an important role in such a task. In particular, the strong Fermi contact term of the 1*s* electron in the hyperfine-interaction operator produces hyperfine-structure splittings comparable to the fine-structure splittings for all *np* ^3P states ($n = 2-5$) of the two natural isotopes ^{6}Li and ^{7}Li except for the 2*p* ^3P state of ^{6}Li. This was shown experimentally by Schüler[6] and by Herzberg and Moore,[7] and was calculated by Güttinger and Pauli.[8] The resolution in these earlier experiments was quite unsatisfactory, however, and the first step of our program is the determination of the magnetic hyperfine coupling constants for the *np* ^3P terms of both isotopes, which we present here.

Using the beam-foil technique, we have observed zero-field quantum beats in intensity decays of *ns* $^3S - n'p\,^3P$ lines of ^{6,7}Li II. These quantum beats, superimposed on the exponential decay curves, arise from interference between coherently and nonisotropically excited fine and hyperfine levels in the upper terms of the radiating transitions. A number of measurements of fine[4] and hyperfine[5] structures in H I, ^{4}He I, and Li II have already been made using this technique, and the theory is also well developed[9] and in complete agreement with the measurements.

II. EXPERIMENT

Intensity decay curves of the transitions were recorded for times up to 10 nsec after excitation by a thin carbon foil. The light was collected within a small solid angle at 90° to the beam axis, and focused on the entrance slit of a 60-cm Czerny–Turner monochromator. Photons polarized parallel to the beam axis were selected with a polarizer placed in parallel light between two quartz lenses. Photons collected in repeated scans over the decay curve were accumulated in a 4000-channel analyzer with the channel numbers synchronized to the position of the foil as it moved at constant speed along the beam.

Figures 1 and 2 show the decay curves obtained for the transition $2s\,^3S$-$2p\,^3P$ of ^{6}Li II and ^{7}Li II, respectively, at 5485 Å. A fast growing-in cascade produces the slight rise of the curves at times

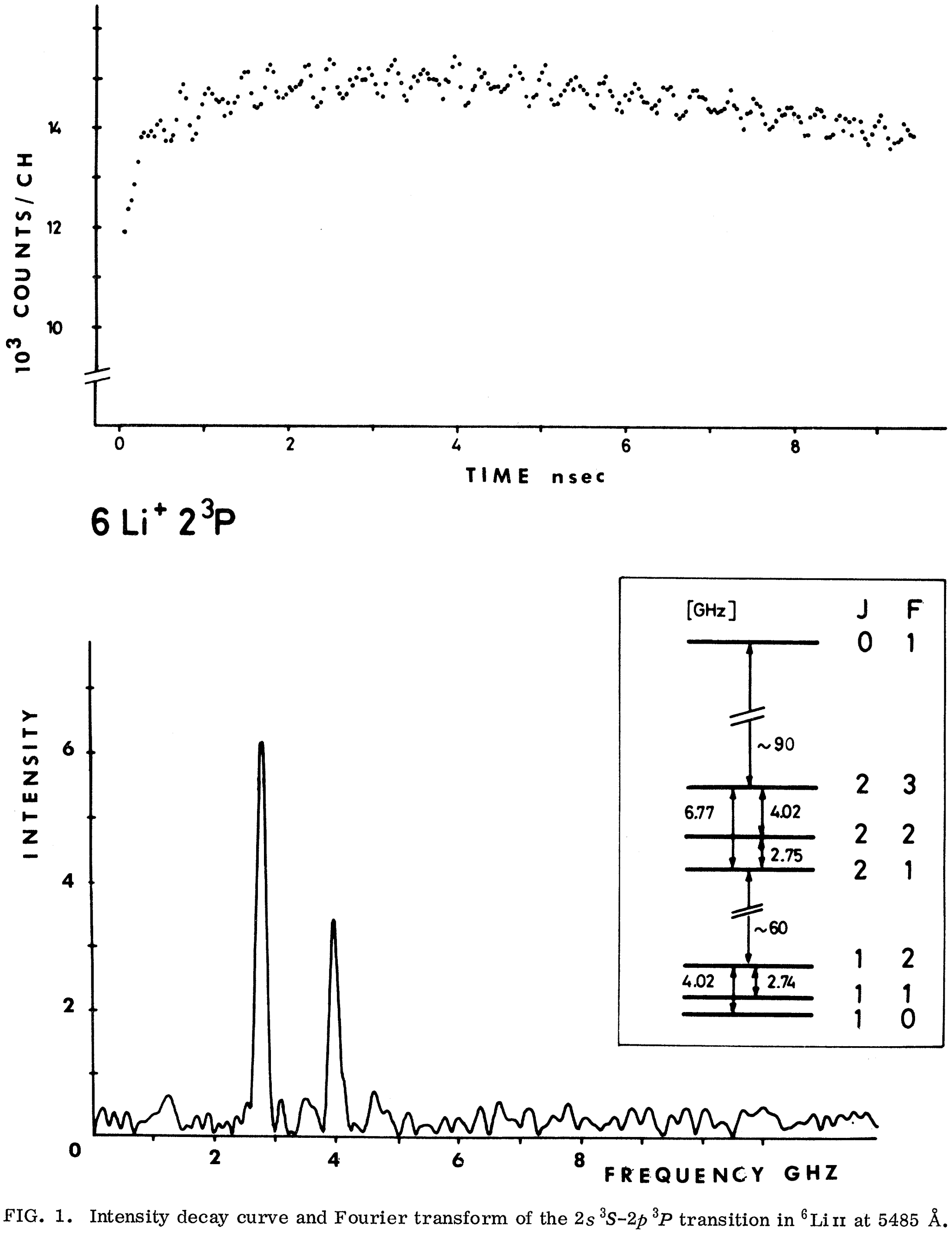

FIG. 1. Intensity decay curve and Fourier transform of the $2s\,^3S$-$2p\,^3P$ transition in ^{6}Li II at 5485 Å.

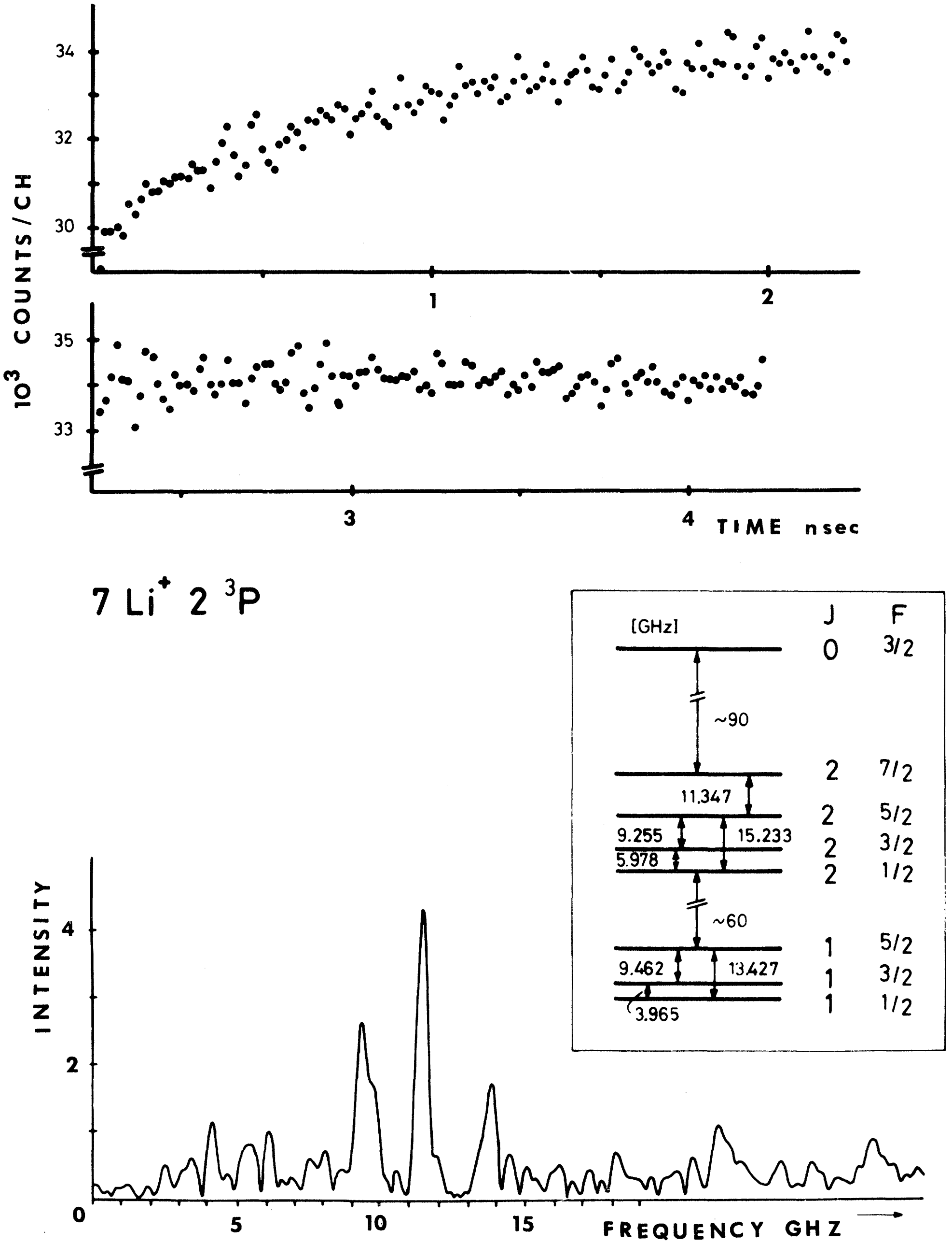

FIG. 2. Intensity decay curve and Fourier transform of the $2s\ ^3S$-$2p\ ^3P$ transition in ^{7}Li II at 5485 Å.

shortly after excitation. The position of the maximum intensity varies with beam energy, showing that the amount of cascading varies as indicated previously.[10] It is important to note that the frequencies observed remain exactly the same with different cascade contributions. All other decay curves observed are single exponentials with little or no cascade components, and we show in Figs. 3 and 4 examples of the decay curve of the $3s\ ^3S$-$4p\ ^3P$ transition of ^{6}Li II and ^{7}Li II, respectively, at 3684 Å.

The experimental evidence that cascade effects do not disturb the frequency measurements is complemented by Macek's proof[11] that coherent cascade transfer of frequencies from higher terms is strongly reduced in our cases.

As can be seen from Figs. 1–4 a number of frequencies are present in each decay curve, and we have extracted these by two techniques: the background decay curve is first subtracted in the form of an exponential or a polynomial fit, and a Fourier transform is then made of the remaining modulations. Alternately, the decay curve is least-squares fitted to an exponentially decaying sum of cosines of variable amplitude, frequency, and phase. Where both techniques are applied, the results are the same. However, the Fourier transform involves much less computer time and appears to be at least as accurate.

The measured frequencies are linearly dependent on the beam velocity, which has been estimated to within ± 1% using the calculations of Lindhard and Scharff[12] for the energy loss with the carbon foil.

III. THEORY

The theory of zero-field quantum beats in decay curves[9] has previously been considered for systems described by $(LS)J\text{-}I\text{-}FM_F$ coupling. Thus we obtain for the amplitude of the frequency between two levels (J, F) and (J', F') of the upper term in the observed transition $(LS)\ J,\ I,\ F$, to $(L_0S_0)\ J_0,\ I,\ F_0$:

$$Q^0(JF, J'F') = N|\,q^{(0)}(JF, J'F')\,|^2\ , \qquad (1)$$

where N is a constant proportional to the fractional alignment, and

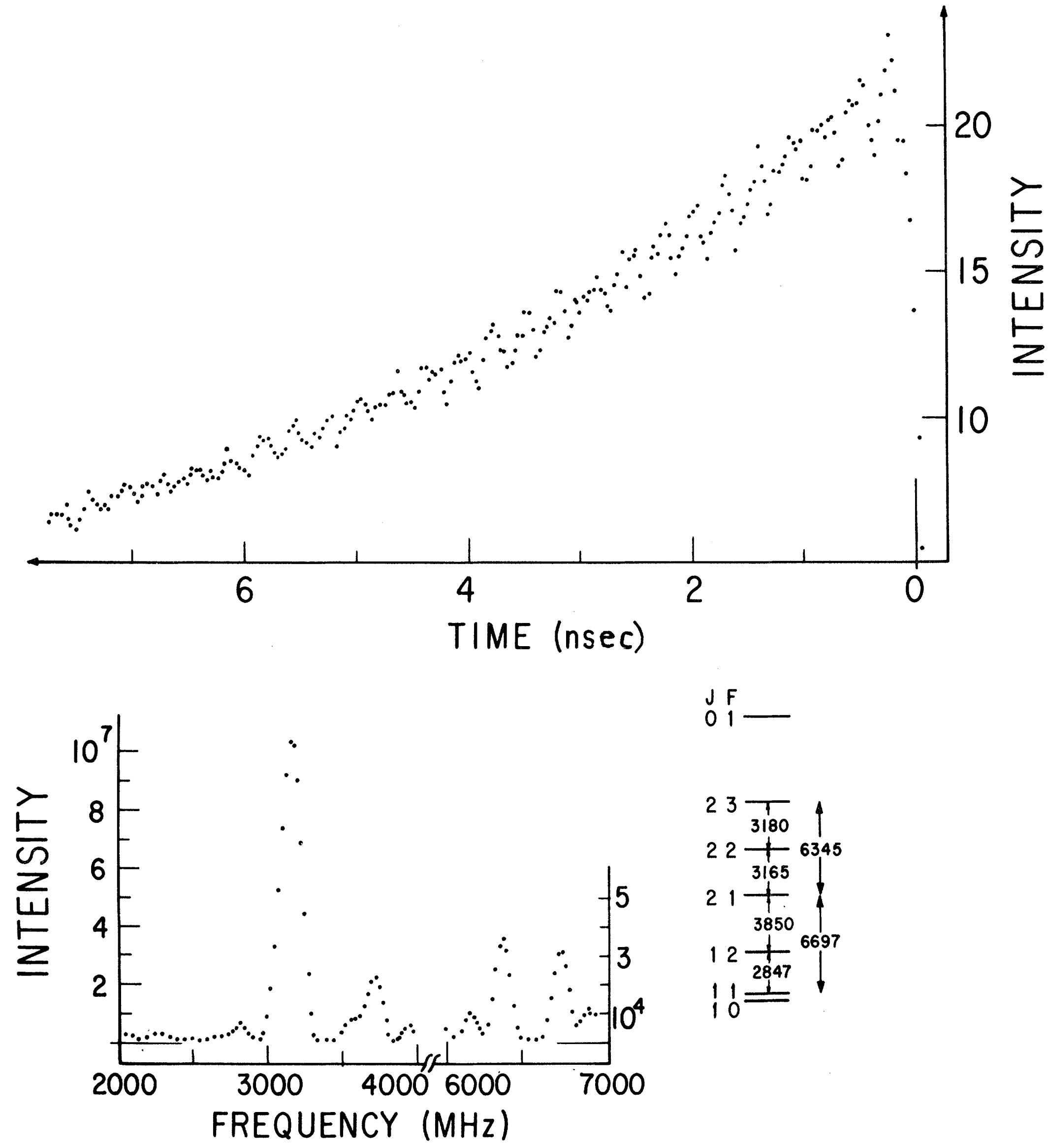

FIG. 3. Intensity decay curve and Fourier transform of the $3s\,^3S$-$4p\,^3P$ transition in ^{6}Li II at 3684 Å.

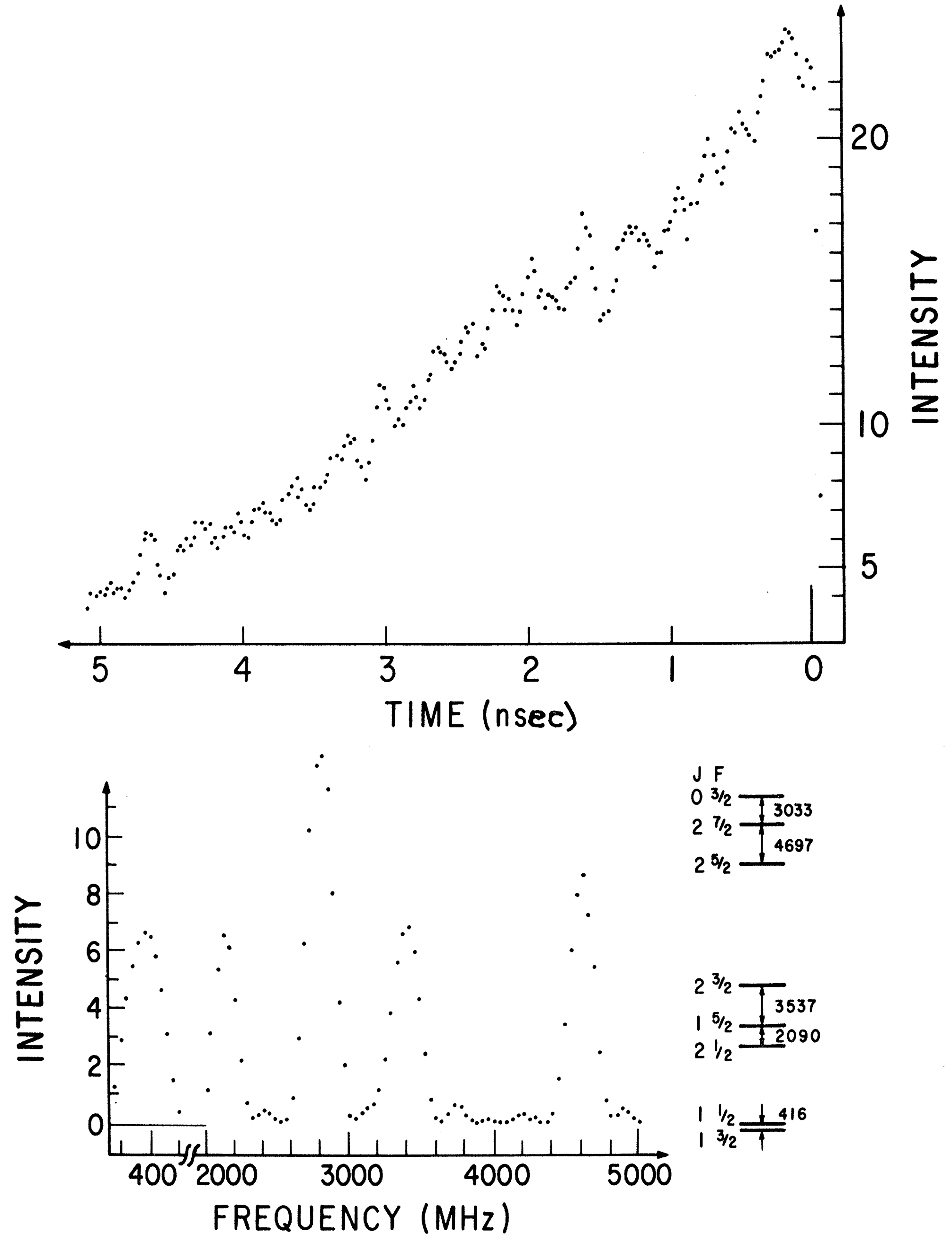

FIG. 4. Intensity decay curve and Fourier transform of the $3s\,^3S$-$4p\,^3P$ transition in ^{7}Li II at 3684 Å.

$$q^{(0)}(JF, J'F') = [(2J+1)(2J'+1)(2F+1)(2F'+1)]^{1/2} \times \begin{Bmatrix} 2 & L & L \\ S & J & J' \end{Bmatrix} \begin{Bmatrix} 2 & J' & J \\ I & F & F' \end{Bmatrix}\,, \qquad (2)$$

where the brackets { } denote 6-j symbols.

These amplitudes are obtained for the modulations observed from the $2p\,^3P$ term of ^{6}Li II. For all the other $np\,^3P$ terms of ^{6}Li and ^{7}Li observed the $(LS)J$-I-FM_F coupling does not hold any more owing to the nondiagonal matrix elements of the hyperfine operator $\vec{I}\cdot\vec{S}$, which mixes levels of different electronic angular momentum J, where $F=J+I$. Thus J is no longer a good quantum number and the new eigenstates $|\tilde{J}F\rangle\rangle$ of the atom are described by sums over the JFM_F states $|JF\rangle$:

$$|\tilde{J}F\rangle\rangle = \sum_J |JF\rangle\langle JF|\tilde{J}F\rangle\rangle = \sum_J |JF\rangle b^F_{\tilde{J}J}\,. \qquad (3)$$

The expansion coefficients $b^F_{\tilde{J}J}$ are calculated by diagonalization of the complete matrix of the hyperfine operator $\vec{\mathrm{I}} \cdot \vec{\mathrm{S}}$ as shown by Güttinger and Pauli[7] using the theoretical fine structure of Accad *et al.*[1] The beat amplitudes then become

$$Q(JF, J'F') = N\Big|\sum_{J_1 J_1'} b^{F}_{J J_1} b^{F'}_{J' J_1'} (-)^{J_1 - J_1'} q^{(0)}(J_1F, J_1', F')\Big|^2 \cdots . \tag{4}$$

In the following discussion, we use the hyperfine-coupling constant A as described in Eqs. (2.12) and (2.13) of Kopfermann.[13]

IV. RESULTS

A. ^{6}Li II

For the $1s2p\,^3P$ term, the hyperfine structure is small relative to the fine structure, but the energies were calculated including the nondiagonal hyperfine coupling. That is, we can use Eq. (1) with the frequencies calculated and expect only two low frequencies corresponding to the energy separations $\hbar\omega(JF, J'F') = \hbar\omega(12, 11) \approx \hbar\omega(22, 21)$ and $\hbar\omega(22, 10) \approx \hbar\omega(22, 10) \approx \hbar\omega(23, 22)$. These two frequencies are observed in the Fourier transform and give us directly a measurement of the A value, independent of the fine structure. Neglecting the quadrupole interaction, we obtain $A = 0.091 \pm 0.001$ cm^{-1}. Within this accuracy, A should remain the same for all higher $np\,^3P$ terms, since the hyperfine interaction is mainly due to the $1s$ electron and is therefore independent of the principal quantum number n of the p electron. To prove this we have made measurements on the $3p\,^3P$(at 1198 Å), $4p\,^3P$ (3684 Å), and $5p\,^3P$ (2674 Å) terms. The $3p\,^3P$ term was measured in the vacuum ultraviolet without a polarizing element, but by relying on the geometrical arrangement and the residual positive instrumental polarization of the monochromator. The

TABLE I. Comparison of measured and calculated frequencies in $np\,^3P$ of ^{6}Li II ($n = 2, 3, 4, 5,$). The calculations assume $A = 0.091$ cm^{-1} and the fine structures of Accad *et al.* (Ref. 1).

Principal quantum number n	hyperfine transition J	F	J'	F'	separation frequency (MHz) obs.[a]	calc.
2	2	2	2	1		2769
					2795	
	1	2	1	1		2750
	2	3	2	2		3999
					4014	
	1	2	1	0		3999
3	2	2	2	1	2810	2811
	1	2	1	1	2924	2882
	1	2	1	0		3751
	2	3	2	2	3617	3751
4	1	2	1	1	2869	2847
	2	3	2	2		3177
					3212	
	2	2	2	1		3166
					3090	
	1	2	1	0		3177
	2	1	1	2	3780	3850
	2	3	2	1	6370	6343
	2	1	1	1	6740	6697
5	1	0	1	1	430	490
	2	1	1	2	1320	1256
	0	1	2	3		2302
					2310	
	2	3	2	2		2299
	1	2	1	0	2440	2299
	1	2	1	1	2950	2789
	2	1	1	0	3550	3555
	2	2	2	1	3810	3650
	2	1	1	1	4250	4045
	0	1	2	2	4600	4600
	2	2	1	2	5150	4906

[a] Frequencies are accurate to ± 1%.

TABLE II. Comparison of measured and calculated frequencies in $np\,^3P$ of ^{7}Li II ($n = 2, 4, 5$). The calculations assume $A = 0.239$ cm^{-1}, and the fine structures of Accad *et al.* (Ref. 1).

Principal quantum number n	hyperfine transition J	F	J'	F'	separation frequency (MHz) obs.[a]	calc.
2	1	$\frac{3}{2}$	1	$\frac{1}{2}$		3965
	2	$\frac{3}{2}$	2	$\frac{1}{2}$	6010	5984
	2	$\frac{5}{2}$	2	$\frac{3}{2}$		9255
					9250	
	1	$\frac{5}{2}$	1	$\frac{3}{2}$		9462
	2	$\frac{7}{2}$	2	$\frac{5}{2}$	11320	11347
	1	$\frac{5}{2}$	1	$\frac{1}{2}$	13700	13427
	2	$\frac{5}{2}$	2	$\frac{1}{2}$	15000	15233
4	1	$\frac{1}{2}$	1	$\frac{3}{2}$	375	416
	1	$\frac{5}{2}$	2	$\frac{1}{2}$	2130	2090
	0	$\frac{3}{2}$	2	$\frac{7}{2}$	2795	3033
	2	$\frac{3}{2}$	1	$\frac{5}{2}$	3385	3537
	2	$\frac{7}{2}$	2	$\frac{5}{2}$	4595	4697
5	1	$\frac{1}{2}$	1	$\frac{3}{2}$	360	440
	0	$\frac{3}{2}$	2	$\frac{7}{2}$	820	871
	2	$\frac{3}{2}$	1	$\frac{5}{2}$		1852
					1810	
	1	$\frac{5}{2}$	2	$\frac{1}{2}$		1677
	2	$\frac{7}{2}$	2	$\frac{5}{2}$	2665	2625
	0	$\frac{3}{2}$	2	$\frac{5}{2}$	3350	3495
	2	$\frac{3}{2}$	2	$\frac{1}{2}$	3640	3529

[a] Frequencies are accurate to ± 1%.

frequencies found are listed in Table I and are compared with calculations using the hyperfine constant found above and the fine-structure splittings calculated by Accad *et al.*[1]

B. ^{7}Li II

The hyperfine structure is as large as the fine structure for all the terms observed ($2p\ ^3P$, $4p\ ^3P$, $5p\ ^3P$). For the $2p\ ^3P$ term only very high frequencies are expected because of the large separations. The best spatially resolved decays have revealed all the structure with observed frequencies up to 15 GHz (Fig. 2). The results have been best interpreted using an A value of 0.239 ± 0.002 cm^{-1}. This value is in agreement with that value expected from the A value found for the $1s2p\ ^3P$ term of ^{6}Li II and the known ratio of nuclear magnetic moments of the two isotopes.[14] Thus, any hyperfine anomaly is less than 2%. However, the A value for ^{7}Li II disagrees by about 10% with the previous measurements of Schuler[6] and of Herzberg and Moore,[7] who found $A(2p\ ^3P) = 0.26$ cm^{-1}. This latter value was deduced from the incompletely resolved structure of the $2s\ ^3S$-$2p\ ^3P$ transition, whereas no hyperfine structure of any other transitions was resolved in the spectra. The new value of A is confirmed by measurements in ^{7}Li II on transitions from the $4p\ ^3P$ and $5p\ ^3P$ terms, as shown in Table II. Reasonable agreement with the calculations is obtained assuming $A = 0.239$ cm^{-1} and the fine-structure splittings of Accad *et al.*[1] It essentially settles the problem discussed by Herzberg and Moore that $A(1s2p\ ^3P)$ should be smaller by about 6% than $A(1s2s\ ^3S)$, which they measured to be 0.257 cm^{-1}, whereas they had to use this same number for the interpretation of their $2p\ ^3P$ data.

V. CONCLUSIONS

The method used in our experiments suffers most from the uncertainty of the beam velocity. It is this uncertainty which enters directly into the determination of absolute frequencies and is therefore responsible for the 1% error in our results. However, the relative accuracy of the frequencies is certainly better than 1%, thus indicating in Tables I and II that we have to expect slight changes in the fine-structure splittings calculated by Accad *et al.* for better fitting the experimental values obtained so far. Also the contribution of the $2p$ electron to the hyperfine interaction, especially its quadrupole interaction, has to be considered in a more thorough analysis for which better data are being collected. For the final improvement to our results, we expect to make a nonlinear least-squares-fitting analysis independent of the beam velocity successfully applied previously to the hyperfine-structure modulations of ^{3}He I.[5]

ACKNOWLEDGMENTS

We are greatly indebted to Dr. M. Lombardi of Grenoble for his help in deriving Eqs. (1)–(4) and are grateful to Professor M. Dufay for his continued encouragement and support.

---

*Present address: Dept. of Physics, University of Chicago, Chicago, Ill. 60637.

†On sabbatical leave from the University of Alberta, Edmonton, Canada.

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

[2] J. P. Descoubes, C.R. Acad. Sci. (Paris) **259**, 327 (1964); and in *Physics of the One- and Two-Electron Atoms* (North-Holland, Amsterdam, 1969), p. 341; R. D. Kaul, J. Opt. Soc. Am. 57, 1156 (1967).

[3] I. Wieder and W. E. Lamb, Jr., Phys. Rev. **107**, 125 (1957).

[4] J. Macek, Phys. Rev. Lett. **23**, 1 (1969); H. J. Andrä, Phys. Rev. Lett. **25**, 325 (1970); H. J. Andrä, Nucl. Instrum. Methods **90**, 343 (1970); D. J. Lynch, C. W. Drake, M. J. Alguard, and C. E. Fairchild, Phys. Rev. Lett. **26**, 1211 (1971); D. J. Burns and W. H. Hancock, Phys. Rev. Lett. **27**, 370 (1971); and H. G. Berry, J. L. Subtil, and M. Carré, J. Phys. 33, 950 (1972).

[5] H. G. Berry and J. L. Subtil, Phys. Rev. Lett. 27, 1103 (1971); K. Tillmann, H. J. Andrä, and W. Wittmann, Phys. Rev. Lett. **30**, 155 (1973).

[6] H. Schuler, Z. Phys. **37**, 568 (1926).

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

[8] P. Güttinger and W. Pauli, Z. Phys. **67**, 734 (1931).

[9] J. Macek, Phys. Rev. Lett. **23**, 1 (1969); J. Macek, Phys. Rev. A 1, 618 (1970); J. Macek and D. H. Jaecks, Phys. Rev. A 4, 2288 (1971); and H. G. Berry, J. L. Subtil, and M. Carré, J. Phys. 33, 950 (1972).

[10] F. Gaillard, thesis (University of Lyon, 1969) (unpublished).

[11] J. Macek, Phys. Rev. A **1**, 618 (1970).

[12] J. Lindhard and M. Scharff, Phys. Rev. **124**, 128 (1961).

[13] H. Kopfermann, *Nuclear Moments* (Academic, New York, 1958), p. 8.

[14] I. Lindgren, Ark. Fys. **29** (44), 553 (1965).