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ALTERNATING INTENSITIES AND ISOTOPE EFFECT IN THE BLUE-GREEN ABSORPTION BANDS OF Li_2

By A. Harvey* and F. A. Jenkins
Department of Physics, University of California

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Abstract

Term analysis. The analysis of the blue-green Li_2 bands previously given by Wurm is extended by new data obtained with second order plates from the 15-ft. concave grating. The band heads are given by $\nu_h = 20{,}398.40 + 267.3v' - 3.1v'^2 - 347.4v'' + 2.5v''^2$. Wave-numbers of the rotational structure lines of the (0, 1) band are tabulated, and the evaluation of the rotational term-differences in the lower state completely confirms the assignment of this system to the electronic transition $^1\Pi \leftarrow {}^1\Sigma$. The molecular constants, as completely re-determined from our data, using a more accurate procedure than that of Wurm, agree closely with his values. The new constants resulting from our work are $F_e' = 1.337 \times 10^{-10}$ cm^{-1}, $F_e'' = 1.535 \times 10^{-10}$, $\alpha'' = 0.00744$, and $\beta'' = 0.765 \times 10^{-8}$. By means of the final constants and the theoretical equations, an accurate representation of the wave-numbers of the lines of the (0, 0) band is obtained. The origin of this band is found to be 20,395.96 cm^{-1}.

Isotope effect. The vibrational isotope effect is established by the identification of three band heads (1, 0), (2, 0), and (3, 0), due to the less abundant isotopic molecule, Li^6Li^7, which were found in their calculated positions within the error of measurement. The rotational isotope effect in the (0, 0) band is shown by the detection of two faint line series fitting closely the theoretical equations for the Q and P branches due to Li^6Li^7.

Alternating intensities The alternation ratio of the intensities of successive lines in the $Li_2{}^7$ bands is determined by a new method, depending partly on the theory of intensity distribution in this type of bands given by Mulliken. The best value is found from the Q branches of the (0, 0) and (1, 0) band to be 1.78 ± 0.2. A less reliable determination from the (0, 1) band gives 1.50. Evidence is given pointing to the true value as 1.67, which corresponds to a nuclear spin of the Li atom of $3/2(h/2\pi)$. This disagrees with the value $\frac{1}{2}(h/2\pi)$ found from hyperfine structure investigations by Schüler and Brück. As required theoretically, the isotope lines due to the unsymmetrical molecule Li^6Li^7 show no alternation.

CERTAIN interesting features of the absorption bands of lithium vapor have recently been discussed by the writers in two preliminary communications.[1,2] Spectrograms taken with both low and high dispersion showed that with a suitable adjustment of the density of the absorbing vapor, the vibrational and rotational structures of the blue-green system are simple enough to permit the quantum analysis. The close analogy of these bands with the corresponding Na_2 system[3] led us to ascribe them to a transition from a $^1\Sigma$ normal state to a $^1\Pi$ excited state. This is in harmony with the observed simple PQR

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* Commonwealth Fund Fellow.

[1] A. Harvey and F. A. Jenkins, Phys. Rev. **34,** 1286 (1929) (Quantum structure, alternating intensities).

[2] A. Harvey and F. A. Jenkins, Phys. Rev. **35,** 132 (1930), Abstract, (Vibrational isotope effect).

[3] F. W. Loomis and R. W. Wood, Phys. Rev. **32,** 223 (1928).

structure of the individual bands, which was verified by applying the combination principle. As was to be expected for a symmetrical molecule, the

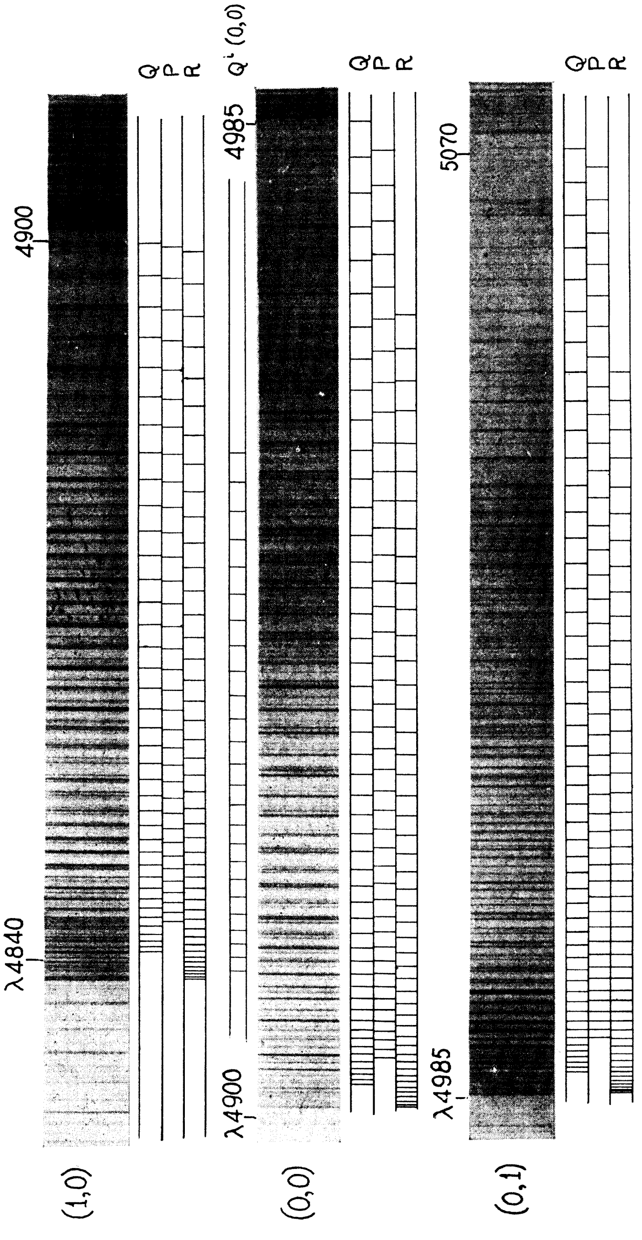

Fig. 1. Three bands of the blue-green system. Length of absorbing column 45 cm, $T=630°\text{C}$. Second order of the 15 ft. grating.

intensities of successive lines showed a definite alternation. The alternation factor was estimated as between 1.20:1 and 1.33:1, but for reasons given below the estimate was low. The vibrational isotope effect was also detected.[2] Li has isotopes of masses 6 and 7 in the proportion of about 1:16 (atomic weight 6.94). Besides the strong bands due to Li^7Li^7, two weaker systems should be present, due to Li^6Li^7 and Li^6Li^6, having respectively intensities 1/7.8 and 1/245 that of the strong system. The three most favorably placed band heads of the Li^6Li^7 system were observed. Measurements of heads are difficult in this case, especially at high temperatures, because the head occurs at a very low rotational quantum number. More satisfactory evidence of the isotope effect comes from a study of the rotational effect in the (0, 0) band the results of which will be given in the following section.

Near the completion of our work, two articles by Wurm[4,5] appeared, dealing with the blue-green and red systems of Li_2. The agreement of his analysis of the blue-green system with our unpublished results is excellent, not only in the wave-length data, but also in the quantum interpretation and in the resulting molecular constants. In point of self-consistency, our data seem nearly as accurate as those of Wurm, although obtained with somewhat lower dispersion (second order of a 15-ft. grating). This circumstance may be partly due to somewhat more favorable experimental conditions in our case, such as accurate control of the temperature of the electrically heated absorption tube. The spectra obtained in the present work, part of which are shown in Fig. 1, are undoubtedly less confused by the structure of faint underlying bands, since Wurm was only able to analyse the (0, 0) and (1,0) bands. We have been able to identify the branches of the (0, 1) band without difficulty, thus permitting a check on the combination differences in the lower, as well as in the upper state. Agreements in both states are required to be absolutely certain of a correct analysis.

ISOTOPE EFFECT

Vibrational terms. From measurements of the heads of the blue-green bands an equation for the vibrational structure was derived,[1] which agreed well with that previously given by Wurm.[4] By suitably weighting the two sets of data, we have adopted the following equation for heads:

$$\nu_h = 20,398.40 + 267.3v' - 3.1v'^2 - 347.4v'' + 2.5v''^2, \qquad (1)$$

where v is the true vibrational quantum number, $v = 0, 1, 2 \cdots$, formerly called n. In seeking evidence for the vibrational isotope effect, it was apparent that the faintest (Li^6Li^6) system could not be detected, due to the complexity of the spectrum, and to the fact that few of the heads are pronounced. On a low-dispersion spectrogram, taken with a carefully adjusted vapor density, it was, however, possible to find the Li^6Li^7 heads of the (2, 0) and (3, 0) bands, the measured isotope shifts being 4.5 and 6.4A toward the

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[4] K. Wurm, Zeits. f. Physik **58**, 562 (1929). We had unfortunately overlooked the preliminary notice of this work, (Naturwissenschaften **48**, 1028 (1928)), in which a vibrational analysis of the blue-green system is given, and an equation for heads which is in close agreement with that independently derived by us (Ref. 1). Alternation of intensities is also mentioned, but the rotational analysis had not been done.

[5] K. Wurm, Zeits. f. Physik **59**, 35 (1929).

violet, with a possible error of several tenths of a cm^{-1}. The theoretical shifts are most easily found by the following formula.[6] Denoting by a superscript i quantities appropriate to the $\mathrm{Li}^6\mathrm{Li}^7$ bands, this may be written

$$\nu_0{}^i - \nu_0 = (\rho - 1)(v' + \tfrac{1}{2})\omega_v' - (\rho - 1)(v'' + \tfrac{1}{2})\omega_v'' \tag{2}$$

where $\rho = (\mu/\mu^i)^{1/2} = 1.040833$. From Eq. (1) we have

$$\omega_v' = \omega_e' - 2x_e'\omega_e'(v' + \tfrac{1}{2}) = 270.4 - 2 \times 3.1(v' + \tfrac{1}{2});\ \omega_v'' = 349.9 - 2 \times 2.5(v'' + \tfrac{1}{2}),$$

assuming that the coefficients apply equally well to band origins. This is justified here because the heads are at a small and nearly constant distance from the origins. The computed shifts in the above two cases are 4.3 and 6.3A, respectively. The (1, 0) isotope head is too close to the main band to be resolved with the prism spectrograph, but on a first order grating plate the attendant (1, 0) head could be measured with difficulty. The observed and calculated shifts in this case were 2.06 and 2.08A. On the red side of the system-origin, the fainter bands are entirely concealed by the $\mathrm{Li}^7\mathrm{Li}^7$ bands.

Rotational terms. In identifying the individual lines of the (0, 0) isotope band, more accurate and complete rotational constants of the strong system than those given by Wurm were required. We have therefore made an independent evaluation of these from our data. The wave-numbers of the rotational lines of the (0, 0) and (1, 0) band agree very well with Wurm's published data, although there is a small, nearly constant, discrepancy amounting to about 0.1 cm^{-1} on the average, our values being higher. Measurements of these bands are therefore omitted here, although the constants obtained from them are tabulated below. Table I gives wave-numbers in vacuum for the (0, 1) band, which was not analysed by Wurm, and also shows the agreement of the resulting term-differences, $\Delta_2 F_0'$, with his values from the (0, 0) band.

In the calculation of rotational constants, we have assumed the following expressions for the rotational energy:

$$\begin{aligned} {}^1\Sigma&: F(K) = B''K(K+1) + D''\,[K(K+1)]^2 + F''[K(K+1)]^3 \\ {}^1\Pi&: F(K) = B'[K(K+1) - 1] + D'[K(K+1) - 1]^2 + F'[K(K+1) - 1]^3. \end{aligned} \tag{3}$$

The observed rotational term-differences definitely require the F term, as is evident from Fig. 3 of Wurm,[4] where it was not taken into account. With the above term formulation, the $R - P$ differences should be given by

$$\Delta_2 F(K) = 4BK + 8DK^3 + 12FK^5, \tag{4}$$

in which some negligible terms have been omitted. By means of the relations

$$D_e = -\frac{4B_e{}^3}{\omega_e{}^2}; \quad F_e = \frac{D_e{}^3}{B_e}\left(2 - \frac{\alpha\omega_e}{6B_e}\right);$$

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[6] The general equation for the vibrational isotope effect has recently been considered by Birge (unpublished work). A sufficiently accurate approximation, in the present case, is given by the formula quoted, a form already used by Patkowski and Curtis, Trans. Farad. Soc. **25,** 725 (1929).

TABLE I. *Absorption lines and combination differences of the (0, 1) band.*

K	$R(K)$	$Q(K)$	$P(K)$	$\Delta_2F_1''(K)$	$\Delta_2F_0'(K)$	$\Delta_2F_0'(K)$*
6	20052.59	20044.63	20037.12		15.47	
7	051.81	042.90	034.78	20.42	17.03	
8	051.14	041.35	032.17	22.29	18.97	
9	050.36	039.37	029.52	24.83	20.84	
10	049.27	037.12	026.31	27.41	22.96	23.046
11	047.95	034.78	022.95	29.79	25.00	25.222
12	046.60	032.17	019.48	32.73	27.12	27.414
13	044.63	029.52	015.22	35.51	29.41	29.733
14	042.90	026.31	011.09	37.92	31.81	31.735
15	040.61	022.95	006.71	40.74	33.90	33.924
16	038.19	019.48	002.16	43.24	36.03	36.148
17	035.68	015.91	19997.37	45.83	38.31	38.350
18	032.73	012.00	992.36	48.54	40.37	40.431
19	029.52	007.81	987.14	51.02	42.38	42.570
20	026.31	003.47	981.71	53.54	44.60	44.649
21	022.95	19998.90	975.98	56.04	46.97	46.792
22	019.17	994.17	970.27	58.66	48.90	48.893
23	015.22	989.16	964.29	61.05	50.93	50.980
24	011.09	984.00	958.12	63.60	52.97	53.055
25	006.71	978.53	951.62	66.21	55.09	55.153
26	002.16	972.96	944.88	68.60	57.28	57.191
27	19997.37	967.17	938.11	71.26	59.26	59.245
28	992.36	961.06	930.90	73.65	61.46	61.310
29	987.14	954.71	923.72	76.06	63.42	63.394
30	981.71	948.27	916.30	78.52	65.41	65.369
31	975.98	941.61	908.62	80.97	67.36	67.338
32	970.27	934.63	900.74	83.40	69.53	69.348
33	963.95	927.52	892.58	86.08	71.37	71.277
34	957.75	920.17	884.19	88.27	73.56	73.315
35	950.98	912.64	875.68	90.75	75.30	75.238
36	944.19	904.90	867.00	92.90	77.19	77.053
37	937.14	896.92	858.08	95.06	79.06	79.119
38	929.97	888.71	849.13	97.49	80.84	81.010
39	922.46	880.30	839.65	99.87	82.81	82.872
40	914.80	871.62	830.10	102.11	84.70	
41	906.86	862.83	820.35	104.45	86.51	
42	898.84	853.86	810.35	106.74	88.49	
43	890.52	844.54	800.12	108.96	90.40	
44	881.88	835.03	789.88	111.15	92.00	
45	873.06	825.47	779.37	113.24	93.69	
46	863.61	815.53	768.64	115.54	94.97	
47	854.87	805.38	757.52	117.03	97.35	
48	845.52	795.02	946.58	119.88	98.94	
49	835.70	784.61	734.99	121.93	100.71	
50	825.47	773.07	723.59		101.88	
51	815.53	762.81				
52	805.38	751.79				
53	795.02	740.31				
54		728.84				

* (0, 0) band, Wurm.

TABLE II. *Rotational constants of Li_2^7 molecule.**

	Normal State $(^1\Sigma)$		Excited State $(^1\Pi)$	
	(H. & J.)	(Wurm)	(H. & J.)	(Wurm)
B_0	0.66914 cm^{-1}	0.6694	0.55321	0.5532
D_0	-0.9952×10^{-5}	-0.9865×10^{-5}	-0.9531×10^{-5}	-0.9407×10^{-5}
F_e	1.535×10^{-10}	—	1.337×10^{-10}	—
α	0.00744	—	0.00804	0.0084
β	0.765×10^{-8}	—	-14.48×10^{-8}	-11.7×10^{-8}
I_e	41.12×10^{-40} g cm^2	—	49.66×10^{-40}	—
r_e	2.67×10^{-8} cm	—	2.93×10^{-8}	—

* The values of B apply only to P and R branches (cf. text).

$$\beta=\frac{\alpha^2}{6\omega_e}+\frac{20\alpha B_e^2-32x_eB_e^3}{\omega_e^2};$$

$$B_v=B_0-\alpha v=B_e-\alpha(v+\tfrac{1}{2})\ ;\ D_v=D_e+\beta(v+\tfrac{1}{2})\ ;\ F_v\cong F_e,$$

we have solved Eqs. (4) for the four states $v'=0, 1$; $v''=0, 1$, by a well-known procedure[7] involving a number of successive approximations. In this calculation, the vibrational constants from Eq. (1) were used; $\omega_e'=270.4$, $\omega_e''=349.9$, $x_e'=1.146\times10^{-2}$, $x_e''=0.7145\times10^{-2}$. Table II gives the final constants and a comparison with their values as found by Wurm.

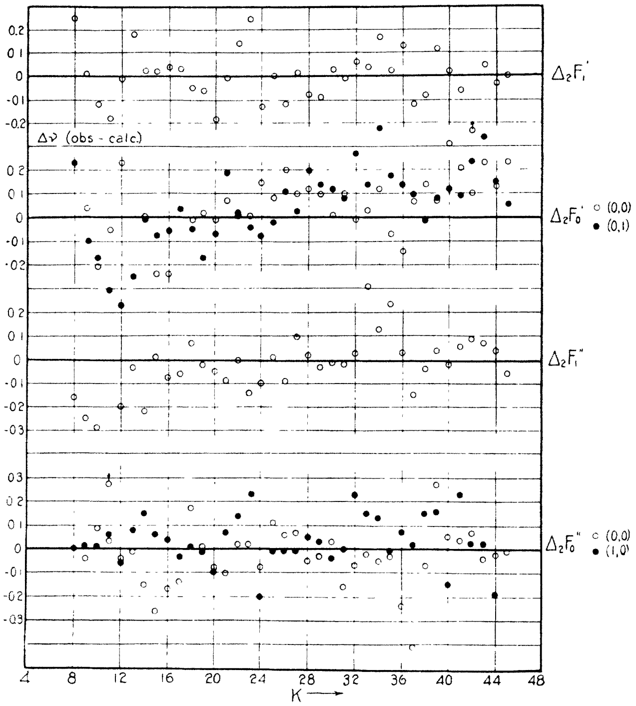

Fig. 2. Deviations (obs-calc) of all rotational term-differences from their values as given by Eq. (4).

Fig. 2 gives the residuals of the available term-differences from those calculated by Eqs. (4) using the above constants. The small linear trend which appears in the Δ_2F_0' residuals indicates the necessity for a small constant term in the true expression for Δ_2F. Such a "secondary ρ" term is justified theoretically, but was not used here since the error is small.

As is expected in a $^1\Pi$ state, the Λ-type doubling of rotational terms causes a small combination defect to appear when an attempt is made to obtain Δ_1F values by combinations with the Q branch. This doubling is proportional[4] to $(K+\frac{1}{2})^2$ and hence the initial terms of the Q branch may also be represented by Eq. (3), using a slightly smaller value of B. Wurm has found

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[7] Method 3 of Birge, "Molecular Spectra in Gases," pp. 173–5.

this difference for the (0, 0) band to be $B_B' - B_A' = 0.00018$, and since our data on the combination defect are in essential agreement with his, we have adopted $B_0' = 0.55303$ for the Q branch.

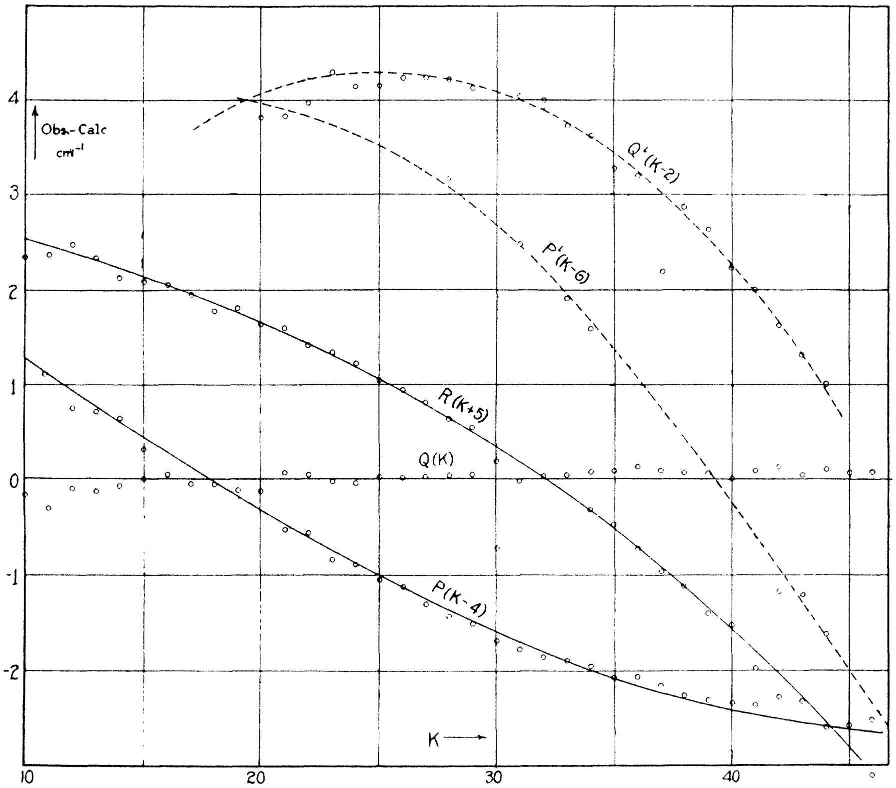

Fig. 3. Differences in wave-numbers of all lines of the (0, 0) band from the calculated Q lines. Solid lines, theoretical values from Eqs. (5); dotted lines, Q and P branches of the (0, 0) isotope band, from Eqs. (6).

A rigorous test of the accuracy of these constants is obtained by finding how well the observed *wave-numbers* of the P, Q and R branches are reproduced by the theoretical formulas:

$$\begin{aligned}
R(K) &= \nu_0 - \tfrac{1}{4}C_B + 2B_B'(K+\tfrac{1}{2}) + (C_B + 4D')(K+\tfrac{1}{2})^2 + 4D'(K+\tfrac{1}{2})^3 \\
&\quad + (E + 12F')(K+\tfrac{1}{2})^4 + 6F'(K+\tfrac{1}{2})^5 + G(K+\tfrac{1}{2})^6, \\
P(K) &= \nu_0 - \tfrac{1}{4}C_B - 2B_B'(K+\tfrac{1}{2}) + (C_B + 4D')(K+\tfrac{1}{2})^2 - 4D'(K+\tfrac{1}{2})^3 \\
&\quad + (E + 12F')(K+\tfrac{1}{2})^4 - 6F'(K+\tfrac{1}{2})^5 + G(K+\tfrac{1}{2})^6, \\
Q(K) &= \nu_0 - B_A' - \tfrac{1}{4}C_A + (C_A - 2D')(K+\tfrac{1}{2})^2 + E(K+\tfrac{1}{2})^4 + G(K+\tfrac{1}{2})^6,
\end{aligned} \tag{5}$$

where $C_A = B_A' - B''$, $C_B = B_B' - B''$, $E = D' - D''$ and $G = F' - F''$. Since the origin ν_0, is as yet undetermined, this amounts to testing the constancy of ν_0 as computed from the various lines. We find small trends of the order of 0.3

cm,$^{-1}$ and have taken 20,395.96 as the best average. To show the results of the calculation of wave-numbers of the lines by Eqs. (5), it is convenient to use a graphical method due to Loomis and Wood.[3] For this, a plot is made of the differences of every measured line in the band from the calculated values of the Q lines. Since the line series in bands of this kind run nearly parallel, the P and R branches also show on the diagram as series of points lying on a smooth curve. In Fig. 3 is given such a graph for the (0, 0) band. The two solid curves represent the differences of the *calculated* R and P lines from the adjacent Q lines. The agreement is as close as can be expected. This method of plotting was first used in identifying the branches of the (0, 0) band. It was then found that a number of lines were not accounted for as P, Q or R lines,

TABLE III. *Comparison of calculated and observed wave-numbers for the Q branches of the* Li^7Li^7 *and* Li^6Li^7 *(0, 0) bands.*

K	$Q(K)$ calc	$Q(K)$ obs	$Q^i(K)$ calc	$Q^i(K)$ obs
6	20390.53	20390.42		
7	388.91	388.80		
8	387.05	386.98		
9	384.96	384.96		
10	382.64	382.47		
11	380.09	379.78		
12	377.31	377.20		
13	374.29	374.15		
14	371.05	370.97		
15	367.57	367.56		
16	363.86	363.90		
17	359.92	359.86		
18	355.75	355.69	20350.76	20350.52
19	351.35	351.22	346.00	345.62
20	346.72	346.58	340.98	340.72
21	341.86	341.92	335.72	335.73
22	336.76	336.80	330.20	330.03
23	331.44	331.41	324.44	324.26
24	325.89	325.84	318.42	318.32
25	320.11	320.12	312.16	312.08
26	314.10	314.10	305.66	305.61
27	307.86	307.88	298.90	298.82
28	301.40	301.43	291.90	
29	294.70	294.74	284.64	284.66
30	287.78	287.96	277.15	277.25
31	280.62	280.60	269.40	269.35
32	273.25	273.28	261.41	261.41
33	265.64	265.68	253.18	253.01
34	257.80	257.87	244.69	244.67
35	249.74	249.82	235.96	
36	241.47	241.60	226.99	227.07
37	232.94	233.03	217.77	217.86
38	224.20	224.27	208.31	208.27
39	215.23	215.29	198.60	198.62
40	206.04	206.05	188.65	188.59
41	196.62	196.71	178.45	178.42
42	186.97	187.11	168.01	168.01
43	177.10	177.15		
44	167.01	167.12		
45	156.69	156.76		
46	146.15	146.24		
47	135.38	135.34		
48	124.39	124.36		
49	113.18	113.05		
50	101.74	101.65		

and, in fact, a number formed a distinct fourth series, with indications of a fifth. The explanation of these extra branches appears when the positions of the isotope lines of the (0, 0) band of Li^6Li^7 are determined by the theory of the isotope effect. The origin $\nu_0{}^i$, of this band is, from Eq. (2), 1.635 cm^{-1} lower in wave-number than that of the strong (0, 0) band. Assuming, as is usual, a negligible electronic isotope effect, we may now compute all the lines of the fainter band. It is only necessary to multiply the coefficients of Eqs. (5) by the appropriate powers of ρ, and to insert the new origin. There results:

$$\begin{aligned} R^i(K) &= \nu_0{}^i - \tfrac{1}{4}\rho^2 C_B + 2B_B'\rho^2(K+\tfrac{1}{2}) + (\rho^2 C_B + 4\rho^4 D')(K+\tfrac{1}{2})^2 + 4\rho^4 D'(K+\tfrac{1}{2})^3 \\ &\quad + (\rho^4 E + 12\rho^6 F')(K+\tfrac{1}{2})^4 + 6F'\rho^6(K+\tfrac{1}{2})^5 + \rho^6 G(K+\tfrac{1}{2})^6, \\ P^i(K) &= \nu_0{}^i - \tfrac{1}{4}\rho^2 C_B - 2B'_B\rho^2(K+\tfrac{1}{2}) + (\rho^2 C_B + 4\rho^4 D')(K+\tfrac{1}{2})^2 - 4\rho^4 D'(K+\tfrac{1}{2})^3 \qquad (5') \\ &\quad + (\rho^4 E + 12\rho^6 F')(K+\tfrac{1}{2})^4 - 6F'\rho^6(K+\tfrac{1}{2})^5 + \rho^6 G(K+\tfrac{1}{2})^6, \\ Q^i(K) &= \nu^i{}_0 - \rho^2 B_A' - \tfrac{1}{4}\rho^2 C_A + (\rho^2 C_A - 2\rho^4 D')(K+\tfrac{1}{2})^2 + \rho^4 E(K+\tfrac{1}{2})^4 + \rho^6 G(K+\tfrac{1}{2})^6. \end{aligned}$$

The calculated Q^i and P^i branches are shown in Fig. 3 to be in excellent agreement with the two anomalous series, although P^i is rather fragmentary, due to its faintness. With these isotope lines explained, only two measured lines in the (0, 0) band remain unaccounted for, and one perhaps belongs to the R^i branch. This constitutes probably the most exacting test of the theory of the isotope effect yet applied. The numerical accuracy of the agreement appears in Table III. This is within the error of the calculation, and hence discrepancies cannot be taken as indicating that the atomic weights of Li^6 and Li^7 do not differ by integers.

Further confirmation of the isotope character of these lines is found in their failure to show alternating intensities, as discussed below.

ALTERNATING INTENSITIES

The alternation of the intensities of successive lines in each branch already established by the writers,[1] and by Wurm,[4] is of special interest, since the alternation ratio gives a measure of the spin of the Li nucleus.[8] To determine the latter, a quantitative measure of the ratio is required. This is particularly difficult in the present case, due largely to the many erratic fluctuations resulting from superpositions with faint underlying structure. There is also the difficulty, at least with our experimental arrangements, that neither the density of vapor nor length of the absorbing column can be found accurately, so that calculations of the absorption coefficients cannot be made, even though the intensities of the absorption lines themselves be correctly evaluated. It was at first thought that the vapor density was low enough for the observed intensities of absorption to be proportional to absorption coefficients, and a preliminary estimate of the ratio was made with this assumption. Density curves were obtained with the Zeiss-Koch recording microphotometer. An example of these curves is given in Fig. 4. In each branch of the (0, 0) band, the average electrometer deflection (background to line center) for the stronger set of lines, those with odd K'', was compared with

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[8] For a review of this theory see R. S. Mulliken, Trans. Faraday Soc. **25,** 634 (1929).

the average deflection for the weaker set. The ratio of these gave 1.2:1. Using the usual law relating densities to intensities, the alternation ratio was estimated as lying between 1.2 and 1.33. Uncertainty in the estimated contrast factor, γ, allowed considerable latitude in this result. Upon repeating the microphotometer curves with a better spectrogram, it was found that, by plotting the electrometer throws for a given branch two fairly good curves were obtained, corresponding to the stronger and weaker sets, as shown in Fig. 5. A number of values lie definitely above the general run, and many of these lines are shown by the structure analysis to be blended with other lines of the band. Neglecting these, and giving the smaller values more weight in drawing the curves, satisfactory curves could be obtained for the Q branches of the three bands studied. The mean ratio of the deflections now becomes about 1.4:1. It will be seen that failure to take into account the evident superpositions tended to render our earlier estimate of the ratio too low.

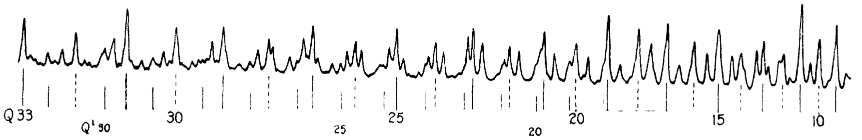

Fig. 4. Microphotometric trace (retouched) of part of the (0, 0) band, showing alternation of intensity in the Q branch of the stronger (Li^7Li^7) band. No alternation is apparent in the weaker branch, Q^i, due to Li^6Li^7.

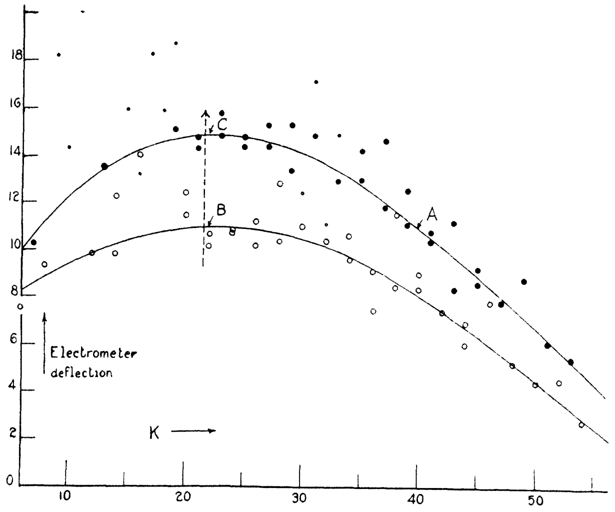

Fig. 5. Height of peaks on microphotometer curves for the Q branches of the (0, 0) and (1, 0) bands as a function of K. To render the two sets of data comparable, that for the (1, 0) band has been multiplied throughout by 0.84. Dots represent the stronger set of lines (K odd) and circles the weaker (K even). Lines known from the analysis to be blends are indicated by small dots or circles. The arrow indicates the theoretical intensity maximum, from Eq. (7). The significance of points A, B and C is discussed in the text.

A new method has now been applied which renders unnecessary the evaluation of absorption coefficients, or determination of γ, since it rests purely on the *equality* of certain intensities. Thus, in Fig. 5, we first determine the value of K for the point A, at which the deflections for the stronger set have fallen to that of the maximum value, B, in the weaker set. Since the blackening is the same at A and B, the intensities are equal at these points. We may then calculate, using the well-established theoretical formulas for intensities in $^1\Sigma-{}^1\Pi$ bands,[9] the ratio of intensities of two lines having the K values of points A and B, which ratio is then the required one, becuase the intensity ratio of points C to A equals that of C to B.

The intensity distribution in the Q branch of a band with $\Lambda'-\Lambda''=+1$ is given, according to Mulliken's formulas,[9] by

$$I_Q=[2A(K+\tfrac{1}{2})(K+\Lambda')(K+1-\Lambda')/K(K+1)]e^{-E/kT}$$

or, when $\Lambda'=1$

$$I_Q=A(2K+1)e^{-E/kT}. \tag{6}$$

Since we are dealing with absorption, $E=F''(K)$. This formula has been shown[9] to be in agreement with experimental data in a number of cases. The corresponding equations for the P and R branches were not of use for the purpose in hand, since the data for these branches, which are roughly half as intense as the Q branch, are not as complete or as consistent. Appreciable deviations of experiment from theory have also been found,[9] particularly in the case of the P branch. It therefore seems best to restrict ourselves to the Q branches, and to evaluate the alternation ratio from the curves of Fig. 5.

First we may show that Eq. (6) is in agreement with the observed K value of the maximum intensity. Differentiating, and equating to zero:

$$\frac{dI_Q}{dK}=2Ae^{-E/kT}+A(2K+1)e^{-E/kT}\frac{d}{dK}\left(-\frac{E}{kT}\right)=0$$

whence we find, inserting for E its value $B''\ [K(K+1)]+D''[K(K+1)]$,[2] that, for the intensity maximum,

$$2B''(K+\tfrac{1}{2})^2+4D''(K+\tfrac{1}{2})^4=kT. \tag{7}$$

The temperature of the absorption tube was measured by a thermocouple in direct contact with the heavy Ni tube which was covered with asbestos and electrically heated from the outside. For the plate used in this work $T=630°\pm10°\text{C}=903°K$. Solving Eq. (7), using the B_0'' and D_0'' from Table II, it is found that, for the maximum of intensity, $K=21.5$. Fig. 5 shows that this is in good agreement with the observed value.

Such a check on the correctness of the theory lends more confidence to the application of the method for determining the alternation ratio outlined above. From Eq. (6) we obtain the ratio of any two lines of the Q branch,

$$I_{Q(K_1)}/I_{Q(K_2)}=\frac{K_1+\frac{1}{2}}{K_2+\frac{1}{2}}e^{(E_2-E_1)/kT}. \tag{9}$$

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[9] R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

The stronger lines of the Q branch become equal to the maximum of the weaker set at $K=40$ (point A, Fig. 5). The ratio of intensities at C and A then becomes, from Eq. (6),

$$I_{Q(22)}/I_{Q(40)}=\frac{22+\frac{1}{2}}{40+\frac{1}{2}}\exp\left[\frac{1070.62-336.04}{903\times 0.698}\right]=1.78.$$

A similar evaluation from the (0, 1) band with much less reliable data, and fewer points, gave 1.50. The limit of accuracy of these figures is determined principally by the accuracy with which the curves can be drawn. It is found, however, that the highest possible value for the ratio, corresponding to a reasonable fit with the observed points is 2.0, and the lowest 1.6. The result is also rather sensitive to the value of T assumed. A change of T by 10° changes the ratio by 0.02. We obtained consistent readings of the temperature with the Pt-Pt, Rh thermocouple in various positions along the length of the tube, and it was standardized at the melting point of antimony, 630.5° C. A certain portion of the vapor near the water-cooled ends of the tube must of course have been at a lower temperature, but the vapor density decreases rapidly at this temperature, the absorption with the tube at 580°C being negligible.[10] Hence the effects of the cooler ends should not be great.

According to the theory of alternating intensities in band spectra,[8] only certain definite values of the alternation ratio are possible. Denoting by i the angular momentum of the Li nucleus in units $h/2\pi$, the statistical weights of successive rational levels contain a factor alternating in the ratio $(i+1)/i$. The nuclear spin, i, may in general be integral or half-intergal. In the neighborhood of the observed value we have the following possibilities:

$i=1$	$3/2$	2
Ratio 2:1	1.67:1	1.50:1

The value 1.67 is within the limit of error of our measurement, but the others are not excluded. In view of relations discussed below, however, they must be regarded as improbable. From eye estimate of intensities by Wurm,[4] the average ratio of successive lines is 1.7:1, and in the red bands[5] he estimates the factor to be 2:1.

These results therefore indicate the spin of the Li nucleus to be 3/2 $h/2\pi$. This is in harmony with some recent generalizations[11] which have been drawn by considering all known values of i. For convenience the latter are collected in Table IV.

The conclusion of Heitler and Herzberg[12] that the spin of the electron is not effective in the nucleus, and that the addition of one proton adds or subtracts $\frac{1}{2}$ unit finds strong support in such a table. On this view, an integral value of i would not be expected for Li^7, nor for any atom with an odd number of protons. One is fairly sure that in Li^7 the α-particle configuration gives a resultant spin of zero; for the He nucleus it is proven by the absence of alter-

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[10] Wurm, Ref. 4, estimates absorption to begin at 400°C. We were unable to detect any molecular absorption below 580°C.

[11] H. Schüler and H. Brück, Zeits. f. Physik **58,** 735 (1929).

[12] W. Heitler and G. Herzberg, Naturw. **17,** 673 (1929).

nate lines in the band spectrum that $i=0$. The probable value of 3/2 in our case may then be interpreted as due to the parallel orientation of the spins of the three remaining protons. It will be seen in Table IV that all atoms with an odd number of nuclear protons heretofore studied have yielded only values of $i=\frac{1}{2}$, 5/2, and 9/2, differing by 4/2. The possible significance of this has been mentioned by White,[13] but it may be that the absence of intermediate values is due to the scarceness of data for the lighter elements. In a preliminary announcement of their work on the hyperfine structure of the Li II line λ5485, Schüler and Brück[11] state that the pattern can be completely explained on the assumption that $i=\frac{1}{2}$ for the Li^7 nucleus. It will be readily seen even upon visual inspection of the bands in Fig. 1, that the alternation ratio of 3:1 required by this is out of the question.

TABLE IV.

Element	Number of nuclear		Nuclear spin $=i$	Determined from
	Protons	Electrons		
H	1	0	$\frac{1}{2}$	Band Spectra
He	4	2	0	" "
Li^7	7	4	3/2	" "
C^{12}	12	6	0	" "
N^{14}	14	7	1	" "
O^{16}	16	8	0	" "
F	19	10	$\frac{1}{2}$	" "
Na	23	12	$>5/2$	" "
Cl^{35}	35	18	5/2	" "
Mn	55	30	5/2	Hyperfine structure
Zn	64	34	0	Hyperfine structure Zeeman effect
	66	36		
	68	38		
	70	40		
Cd	110	62	0	Hyperfine structure
	111	63	$\frac{1}{2}$	
	112	64	0	
	113	65	$\frac{1}{2}$	
	114	66	0	
	116	68	0	
I	127	74	$>5/2$	Band spectra
La	139	82	5/2	Hyperfine structure
Pr	141	82	5/2	" "
Tl	205	124	$\frac{1}{2}$	" "
Bi	209	126	9/2	Hyperfine structure Zeeman effect

In conclusion, we may mention that a careful examination of the photometric curves has failed to reveal any consistent alternation in the intensities of the lines in the Q branch of the (0, 0) band due to the isotope molecule, Li^{6}Li^7. The ratio of the average height of the peaks for odd K to that of even K was 1.05:1, which means sensible equality when we are dealing with such faint lines. The absence of alternation is of course to be expected for a nonsymmetrical molecule, and our result is similar to that obtained by Elliott[14] from his study of the Cl$_2$ bands.

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[13] H. E. White, Phys. Rev. **34,** 1404 (1929).

[14] A. Elliott, Proc. Roy. Soc. **123A,** 629 (1929).

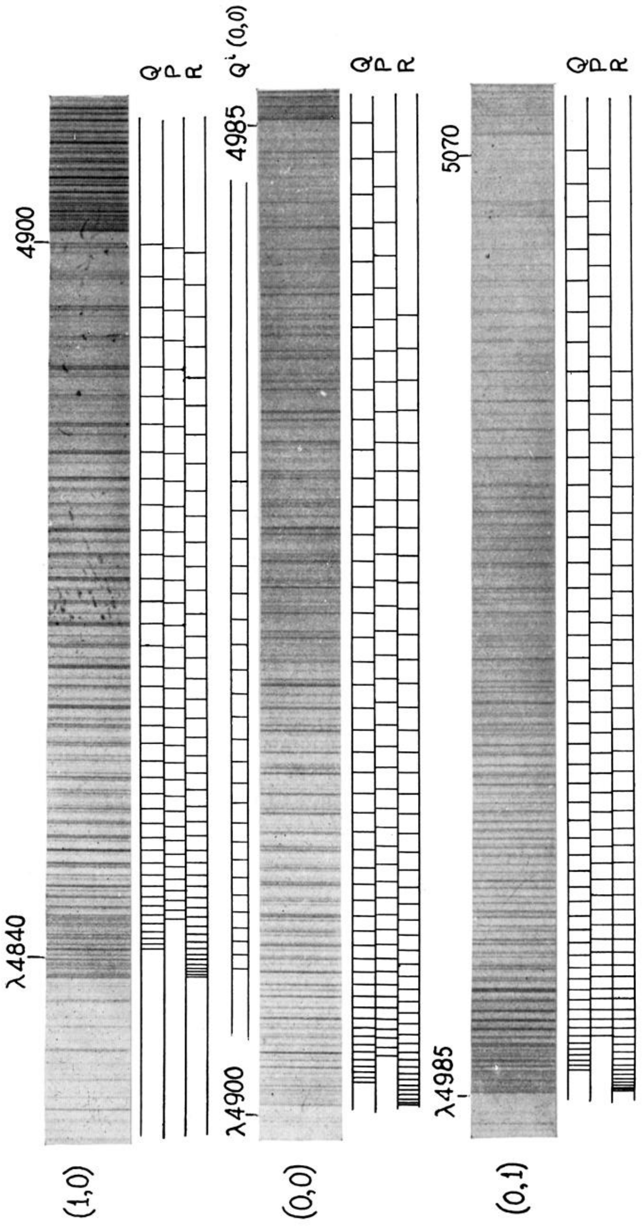

Fig. 1. Three bands of the blue-green system. Length of absorbing column 45 cm, $T = 630°C$. Second order of the 15 ft. grating.