Mass Ratio of the Lithium Isotopes from the Spectrum of Li,

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Wave-number data.—The blue-green absorption bands of lithium have been photographed in the second order of a 21-foot grating. In the main, $Li⁷Li⁷$, system the 2,0, 1,0, 0,0, 0,1 and 0,2 bands and in the isotopic, $Li⁶Li⁷$, system the $1,0$, $0,0$, $0,1$ bands and a somewhat incomplete $0,2$ band have been measured and analyzed. Wave numbers of the lines of all these bands are tabulated. An unsuccessful attempt was made to identify Li⁶Li⁶ band lines.

Vibrational constants. —Values of ΔG_v are calculated by least squares and from them are deduced the vibrational constants of the main and isotopic systems. The constants are given by the following equations: $\Delta G_v''=351.374-5.181$ $(v'' + \frac{1}{2})$, $\Delta G_v' = 270.941 - 6.266 \quad (v' + \frac{1}{2})$, $\Delta G_v'' = 365.923$ $-5.619(v''+\frac{1}{2}), \Delta {G_v}'^2 = 282.081-6.791(v'+\frac{1}{2}).$ The isotopic mass coefficient $\rho = (\mu/\mu^i)^{\frac{1}{2}} = \omega_e^i/\omega_v$ was calculated for the lower and upper states. The resulting values are, from the ¹2 state, $\rho = 1.04141 \pm 0.00008$ (considered the most trustworthy figure) and from the ¹II state, $\rho = 1.0411$ ± 0.0002 . These results are shown to correspond to a higher

INTRODUCTION

HE importance of accurate determinations of the mass defects of atoms has been recently emphasized in connection with atomic disintegration experiments and questions of the stability of nuclei. The mass defect of Li' is of special interest, for lithium has been disinte-'grated by bombardment both with protons^{1, 2, 3} and with α -particles.^{4, 5} From a consideration of the processes taking place certain deductions have been made, based on the Li⁷ mass defect; for example, it has been used to establish an upper limit for the mass of the neutron. The only existing determination of the atomic weights of the lithium isotopes by the mass-spectrograph is

isotopic mass ratio $Li⁷/Li⁶$ than that indicated by the massspectrograph results of Costa. By employing the Q branch of the 0,2 isotope band, $\Delta G_{1\frac{1}{2}}$ " was found and the relation $x_e^i/x_e = \rho$ was verified to within the probable error.

Rotational and electronic constants. —From rotational term differences, values of B_v were computed for the main and isotopic systems by least squares. The calculated constants are: $B_v''=0.6721-0.00708$ $(v''+\frac{1}{2})$, $B_v'=0.5577$ $-0.00888 \left(v' + \frac{1}{2}\right), \quad B_v'' = 0.7302 - 0.00830 \left(v'' + \frac{1}{2}\right), \quad B_v''$ =0.6046-0.00922 (v'+ $\frac{1}{2}$). From the relation $B_e^i/B_e = \rho^2$ are obtained values of ρ which agree to within their probable error (one part in 1500) with the more accurate results obtained from the vibrational constants. The A.-doubling for the two lowest vibrational levels of the 1 II state was investigated and found sensibly equal for the main and isotopic band systems. The origins of the two band systems were computed to be $v_e = 20436.25 \pm 0.02$ and $v_e^i = 20436.29$ ± 0.04 , indicating no measurable electronic isotope effect.

that of Costa,⁶ later modified by Aston.⁷ The masses given are $Li^6 = 6.012 \pm 0.002$ and Li^7 $= 7.012 \pm 0.002$. Thus it seems very desirable to obtain a completely independent check on the above results for lithium, using the band spectrum of the diatomic molecule Li2.

The most accurate determinations of the mass ratio of isotopes from molecular spectra are obtainable with light elements where the proportional difference in mass of the isotopes is large. Thus far the only results from optical methods comparable in accuracy with those from the mass-spectrograph have been obtained by Babcock and Birge⁸ on the ratio $O^{18}:O^{16}$ from the atmospheric oxygen bands, and by Jenkins and McKellar⁹ on B^{11} : B^{10} from the BO bands. In the case of oxygen, there are no mass- ¹ J. D. Cockcroft and E. T. S. Walton, Proc. Roy. Soc. spectrograph data with which to compare the

A137, 229 (1932).

² E. O. Lawrence, M. S. Livingston and M. G. White, Phys. Rev. 42, 150 (1932).
⁷ F. W. Aston, Proc. Roy. Soc. A115, 487 (1927).
⁸ H. D. Babcock and R. T. Birge, Phys. Rev. 31³

⁴ M. de Broglie and L. Leprince Ringuet, C. R. 194, 1616 (1931).
(1932).

⁵ I. Curie, F. Joliot and P. Savel, C. R. 194, 2208 (1932).

 6 J. Costa, Ann. de Physique 4, 425 (1925).

⁸ H. D. Babcock and R. T. Birge, Phys. Rev. 37, 233

⁹ F. A. Jenkins and A. McKellar, Phys. Rev. 42, 464 (1932).

band spectrum value. In the latter case the results by the two methods are in good agreement. The lithium molecular spectrum is, from some points of view, a favorable one with which to work. It yields a value of the isotopic mass coefficient $\rho = (\mu/\mu^i)^{\frac{1}{2}}$ differing by a greater amount from unity than either of those previously studied and is only exceeded in this respect by possible band systems from the hydrogen isotopic molecules, such as $HⁱH²$ or H^2H^2 with respect to H^1H^1 . The fact that the Li₂. bands are obtained in absorption partially compensates for the rather low abundance ratio of $Li^6: Li^7$, which is approximately 1:11. Furthermore, in the case of lithium, one can evaluate directly the mass ratio $Li⁷/Li⁶$ from the experimentally determined value of ρ . This is not so for diatomic molecules composed of two atoms of elements of different atomic number, such as Bo, where the absolute mass of one of the isotopes must be assumed to calculate the mass ratio $B^{11} : B^{10}$.

The blue-green lithium bands have been The blue-green lithium bands have been
studied by Wurm¹⁰ and by Harvey and Jenkins.¹¹ They were shown to arise from a ${}^{1}\Pi \leftarrow {}^{1}\Sigma$ electronic transition. Wurm analyzed the rotational structure of the $0,0$ and $1,0$ bands of the Li⁷Li⁷ system. Harvey and Jenkins extended the analysis to the 0,1 main band and succeeded in identifying a fairly complete Q branch and a fragmentary P branch in the 0,0 band due to the less abundant isotopic molecule, $Li⁶Li⁷$. They also measured the observed alternation of intensities in the Li⁷Li⁷ band lines, obtaining an intensity alternation ratio of 5/3 which assigns a nuclear spin of $(3/2)(h/2\pi)$ to the Li⁷ nucleus. This result was later verified by van Wijk and This result was later verified by van Wijk and
van Koeveringe.¹² Loomis and Nusbaum,¹³ fron an examination of the magnetic rotation spectrum under fairly low dispersion, considerably extended the vibrational analysis of this system and calculated a value for the heat of dissociation. In the present work additional ro-

tational analyses of bands of both the Li'Li', hereafter called the *main* system, and of the $Li⁶Li⁷$, hereafter called the *isotopic* system, have been carried out and most of the available data have been utilized in applying the theory of the isotope effect to obtain the best value of the mass coefficient.

EXPERIMENTAL DATA

The lithium vapor was enclosed in an electrically heated absorption tube giving an absorbing column about 50 cm long and 3.5 cm in diameter. The ends of the tube were watercooled to protect the plane glass windows, and the tube contained argon at about 20 mm pressure to retard diffusion of the lithium. Near the completion of the work a longer tube (80 cm) was used in order to identify some of the fainter isotope lines. Plates were taken with various vapor densities corresponding to temperatures of the absorption tube, measured by a thermocouple in contact with it, ranging from 570° C to 950° C. It was found that the bands were most free from underlying structure and exhibited most clearly their rotational structure when the temperature was 630'C. The spectrograms were taken in the second order of the 21-foot concave grating, which is mounted on the Paschen system and gives a dispersion of about 1.33A/mm. With a 500 c.p. Point-o-Lite lamp as a source, well exposed plates were obtained in an exposure time of about 3 hours.

The comparator used in measuring the plates was carefully calibrated for errors in the screw. These amounted at most to 0.002 mm. From independent measurement of the same band on different plates, it is estimated that the absolute accuracy of the measurements is about 0.05 cm^{-1} . Fortunately, with the present mounting, the region from 4800 to 5200A in the second order of the grating gives practically normal dispersion; thus corrections to linear interpolation of wave-lengths were small and never exceeded 0.01A. The 2,0, 1,0, 0,0, 0,1 and 0,2 bands of the main system were measured. No data have heretofore been given for the 2,0 and 0,2 bands. Also, in the $Li⁶Li⁷$ isotopic band system quite complete $1,0, 0,0$ and $0,1$ bands were identified. A somewhat less complete Q branch of the $0,2$ isotope band was found but only with con-

¹⁰ K. Wurm, Zeits. f. Physik 58, 562 (1929).

¹¹ A. Harvey and F. A. Jenkins, Phys. Rev. 35, 789 (1930).

¹² W. R. van Wijk and A. J. van Koeveringe, Proc. Roy. Soc. AL32, 98 (1931).

¹³ F. W. Loomis and R. E. Nusbaum, Phys. Rev. 38, 1447 (1931).

 $\frac{0}{2}$

 $K^{\prime\prime}$

 $\begin{array}{r}\n 20661.69 \ 662.38 \ 659.18\n \end{array}$

Q

3 662.S4 65S.85 4 662.S4 657.5S 5 662.S4 656.24

 \boldsymbol{R}

6 662.8S 654.6S 7 661.69 652.99 S 660.73 650.98 9 659.64 64S.?5 10 65S.35 646.26

siderable difficulty, due to the faintness of the lines and the complexity caused by superposition of the 1,3 and other weak bands. In this identification recourse was had to the graphical method devised by Loomis and Wood'4 and to an examination of microphotometer curves. In all cases the correctness of the analysis was checked by the upper and lower state combination differences. In Tables I to VIII will be found the wave numbers of the band lines obtained in our analysis; the wave-length given for each band being that of its head, formed by the R branch.

TABLE I. 2,0 Band, λ 4778.618.

In view of the differences discussed below between the results of the present work and those obtained from mass-spectrograph measurements, we consider it advisable to present all the wavenumber data used. Thus we include our measurenumber data used. Thus we include our measure-
ments of the three previously analy<mark>z</mark>ed bands.^{10, 11} Not only has the analysis of these been extended to higher and lower values of K , but the greater resolving power obtained in this investigation has given a considerable improvement in accuracy.

An unsuccessful attempt was made to identify lines due to the $Li⁶Li⁶$ molecule in the 0,0 and 1,0

 $\frac{25}{26}$

 $K^{\prime\prime}$

20606.S5 601.42 595.79 5S9.75 5S8.5S 577.13
570.39 570.89 568.47 55o.23 54S.S8 541.06

 \boldsymbol{R}

20579.10 572.61 565.98 55S.98 551.74 544.27
536.63 586.68 52S.6S 520.49 512.02 503.84

Q

20552.52 545.14 537.89 529.42 521.80 512.82 504.12 495.28 4S6.07 476.60 467.06

 \boldsymbol{p}

20656.9S 27 $\begin{array}{|c|c|c|} 655.18 & 28 \ \hline 652.99 & 29 \ \hline \end{array}$

 \overline{P}

 $\begin{array}{c} 650.93 & 30\ 648.14 & 31\ 645.38 & 32\ 642.32 & 33\ 638.97 & 34\ 635.38 & 35 \end{array}$

$K^{\prime\prime}$	R	Q	\boldsymbol{P}	$K^{\prime\prime}$	R	Q	P
	20920.03			24	20864.49	20838.23	20813.13
123456789	920.73	20917.51		25	858,78	831,49	805,51
	920.73	916.87		26	852.85	824.56	797.59
	920.73	915.61 914.33	20910.82	$\frac{27}{28}$	846.73 840.21	817,42	789.38
	920.73		908.84			809.95	780.83
	920.03	912.70	906.28	29 $\overline{30}$	833,34	802.16	772.21
	919.36 918.31	910.82	903.41 900.03	$31 -$	826.36 819.05	794.23	763.20 753.98
	916.87	908.84 906.28	896.62	$\overline{32}$	811.54	785,91 777,36	744.54
	915,33	903.41	892.86	33	803.61	768,56	734,81
$\frac{10}{11}$	913,41	900.74	888.82	34	795,37	759,55	724.82
$\frac{12}{13}$	911,41	897.43	884.54	$\frac{35}{36}$	787.14	750,07	714.53
	908,84	894.01	880.03		778,49	740.59	703.96
$\frac{14}{15}$	906.28	890.19	875.42	$\overline{37}$	769.54	730.83	693.22
	903.41	886,22 881,89	870.42	38	760.35	720.61	682,19
$\frac{16}{17}$	900.03		865.06 859.44	$\overline{39}$	750.82	710.11	670,89
	896.62	877.42		40 41	741.04 730.83	699.39	
19	892,86 888.82	872.68	853.60 847.54	42	720.61	688.35	
	884.54		841.12	43	710.11	677.32 665.87	
$\frac{20}{21}$	880.03	867.52 862.20 856.61	834.67	44	699.39		
22	875.03	850.73	827.67	45	688.01		
23	869,87	844,58	820.50	46	676.30		
				47	664.81		
				TABLE III. 0,0 Band, λ 4900.983.			
$K^{\prime\prime}$	\boldsymbol{R}	Q	\overline{P}	$K^{\prime\prime}$	\boldsymbol{R}	Q	\boldsymbol{P}
$\bf{0}$	20396.49			29	20327.09	20294.65	20263.71
		20395.12		30		287.84	
	397.28 397.91	394.55	20392.42	$\check{3}\check{1}$	321.17 315.03	280.65	255,78 247.66
	398.39	393.92	390.44	32	308,66	273.27	239.32
		392.96	388.49		302.05	265.62	230.77
	398.39 398.39 398.16	391.84					221.94 212.95
	397.67	390.44 388.79	386.34 383.77	$\frac{33}{34}$	295,20 288.14 280,65	257.91 249.78 241.53	203.65
	396.91	386.95	381.10 378.13	$\frac{36}{37}$	273.27	233.00	194.22
	395.92	384.96					
1234567890	394.55	382.49		$\frac{38}{39}$	$\frac{265.62}{257.45}$	224.26 215.30	184.53 174,62
11	393.21	379.81	$\frac{374.97}{371.53}$ $\frac{367.92}{300.00}$	40	249.15	206.08	164.38
$\overline{12}$	391.54	377.25	363,90	41	240.73	196.67	154.16
13		374.21					
$\overline{14}$	$\frac{389.69}{387.48}$ 384.96	370.96 367.52	359.88 355.68 351.19	$\frac{42}{43}$ 44	231.97 223.05 213.78	187.07 177.18	
$\frac{15}{16}$	382.49	363,90	346.29	45	204.47	167.07 156.74	143.58 132.72 121.76 110.58
	379.81	359.88	341.31				099.16
$\frac{17}{18}$	376.53	355.68	336.07		194.68	146.15 135.37	087.51
	373.19	351,19	330.62	$\frac{46}{47}$	174.62	124.35	075.62
$\frac{19}{20}$	369.60	346.70	324.92	49	164.38	113,00	063.60
		341.85 336.75 331.44			153.61 142.82	101.64	
		325,87	319.01 312.94 306.52 299.95	$\frac{50}{51}$ $5\overline{3}$	131.67 120.35		
$\begin{array}{c} 21 \\ 22 \\ 23 \\ 24 \\ 25 \end{array}$	365,85 365,85 361,82 357,58 353,07 348.35		293.19	54		078.05 053.49	
26		320.09 314.09	286.13	55	108.81		
27 28	343,36 338,16 332.74	307.86 301.42	278.87 271.39	56 57	084.83 072.65		

2 662.3S 659.1S $2893013233455678894041424344454748$ 11 656.46 648.52 12 654.6S 640.4S 18 652.58 687.29 $\begin{array}{|c|c|c|}\hline 631.64 & 36\ \hline 627.57 & 37\ \hline 623.14 & 38\ \hline \end{array}$ 588.19 524.7S 516.82 494.40 4S5.24 475.S1 457.1S 447.07 486.76 14 650.04 688.S1 15 647.42 630.15 16 644.50 626.0S 17 641.81 621.SQ 1S 687,S6 617.80 $\begin{array}{cccc} 650.04 & 633.81 \\ 647.42 & 630.15 \\ 644.50 & 626.08 \\ 641.31 & 621.80 \\ 637.86 & 617.30 \\ 334.19 & 612.63 \\ 630.15 & 607.65 \\ 626.08 & 602.44 \\ 621.80 & 596.97 \end{array}$ $\begin{array}{r|l} 618.70 & 39\ 613.87 & 40\ 608.84 & 41\ 603.59 & 42\ 598.05 & 43\ 592.25 & 44\ 586.27 & 45\ \end{array}$ 507.55 466.18 426.15 49S.59 415.30 456.22 446.05 485.61 424.95 414.0S 404.28 4S9.82 479.S6 470.00 459.9S 402.90 20 680.15 607.65 21 626.0S 602.44 22 621.SQ 596.97 28 617.02 591.24 449.78 489,12 42S.85 417.84 5S0.01 46 578.56 47 566.69 4S 559.S3 49 $\begin{array}{r} 617.02 \\ 611.91 \end{array}$ 591.24 405.9S TABLE IV. 0,1 Band, λ 4985.556. $K^{\prime\prime}$ \overline{R} \pmb{Q} \overline{P} $K^{\prime\prime}$ $\pmb R$ \pmb{Q} \boldsymbol{P} 19992.29 0 2S 19961.02 19930.98 20051.17 2004S.90 9S?.10 9S1.66 975.96 954.71 94S.28 923.74 916.26 1 29 30 2 8 051.S1 052.87 04S.4S 04?.S? 941.5S QQS.59 $20044.62\,53\,82\,932\,48\,935.26\,929.33\,87.90\,935.26\,932.46\,929.33\,926.24\,928.38\,926.24\,938.93\,937\,926.24\,938.93\,937\,937\,937\,937\,937\,937\,938\,938\,939\,938\,938\,938\,931\,938\,931\,931\,931\,941\,41$ 052.37 934.60 046.96
045.81
044.62
042.89
039.31
037.10
034.74
032.12 970.0S 963.S9 957.54 951.02 900.66 S92.54 SS4.22 5 6 7 S 9 052.87 052.87 051.S1 051.17 927.50 920.1S 912.60 S75.70 S66.99 944.17 987.13 929.97 922.46 904.89
896.89
888.71
880.30
871.68 050.88 049.28 047.S7 046.46 S5S.02 S4S.92 S39.5S 10 11 12 13 14 15 16 17 18 19 20 1 22 23 24 25 26 27 914.S1 S30.04 044.62 029.83 026.24 022.96 019.45 015.S5 011.95 007.S1 008.46 1999S.91 906.S2 862.85
853.80 S20.26 042.SQ SSS.7S S10.38 $\begin{array}{c|c} 011.03 & 42 \ 006.67 & 43 \ 002.12 & 44 \end{array}$ S58.80 S44.56 835.0S S25.42 040.57 08S.19 035,67 S90.41 SS1.91 S?8.12 S00.21 7SQ.S7 19997.33 779.28 76S,52 082.77 992.29 46 S64.14 S15.68 029.76 026.24 022.69 019.21 015.15 9S7.10 47 QS1.66 4S 975.96 49 970.88 50 S54.S7 S45.43 S85.74 S25.S9 S15.68 S05.41 705.01 ?84.57 778.S8 762.SS 757.51 746.3S 784.97 728.44 994.14 9S9.16 $\begin{array}{c} 964.28 \ 958.09 \ 951.60 \ 944.89 \ 938.11 \ 55 \end{array} \begin{array}{c} 51 \ 53 \ 54 \ 55 \end{array}$ $\substack{011.03 \ 006.67 \ 002.12} \ 19997.33$ 9S8.99 97S.54 9?2.98 S05.41 795.01 751.71 740.82 72S.?4 716.97

967.09

¹⁴ F. W. Loomis and R. W. Wood, Phys. Rev. 32, 223 (1928).

TABLE V. 0,2 Band, λ 5071.727 and $(0,2)^i$ Band, λ 5079. TABLE VII. $(0,0)^i$ Band, λ 4901.296.

$K^{\prime\prime}$	\boldsymbol{R}	Q	Qi	P	$K^{\prime\prime}$	\boldsymbol{R}	Q	Qi	P
	0 19709.08				31			19642.19 19607.80 19570.90 19574.70	
1		710.01 19707.94			32	636.50	601.25	563.81	567.14
	710.76	707.42		19705.01	33	631.08	594.65	556.79	559.71
2345678	711.26	706.75		703.34	34	624.97	587.81	549.36	551.68
	711.67	706.11		701.32	35	619.06	580.76		543,77
	711.67	705.01		699.65	36	612.82	573.52		535.68
	711.67	703.88		696.83	37	606.38	566.08		527.25
	711.26	702.40		694.70	38	599.63	558.55		518,62
	710.76	700.76		692.23	39	592.78	550.62		509.97
9	710.01	699.02		688.95	40	585,63	542.58		500.94
10	709.08		696.83 19666.66	685.92	41	578.38	534.36		491.82
11	707.94	694.70	664.10	682.62	42	570.90	525.99		482.56
12	706.75	692.23	661.85	679.12	43	563.27	517.24		472.95
13	705.01	689.62	659.00	675.27	44	555.44	508.49		463.21
14	703.34	686.77	655.99	671.47	45	547.13	499.46		453.38
15	701.32	683.76	652.68	667.31	46	538,88	490.25		443.25
16	699.02	680.46	648.49	663.01	47	530.33	480.84		432.97
17	696.83	677.04	645.47	658.47	48	521,80	471.34		422.53
18	694.26	673.42		653.78	49	512.63	461,37		411.79
19	691.45	669.57		648.89	50	503.83	451.45		401.06
20	688.46	665.50	633.01	643.71	51	494.54	441.26		389.97
21	685.28	661.24	628.36	638.52	52	485.09	430.85		378.70
22	681.92	656.80	623.46	633.01	53		420.22		367.40
23	678.28	652.17	618.66	627.28	54	465.04	409.40		355.80
24	674.49	647.29	613.11	621.35	55	454.65	398.51		344,28
25	670.47	642.19	607.83	615.31	56		387.31		332,17
26	666.27	636.93	602.05	609.03	57		376.02		319.90
27	661.85	631.58	596.62	602.50	58		364.37		
28	657.26	625.85	590.39	596.00	59		352.63		
29	652.37	620.03		589.03	60		340.52		
30	647.29	614.01	577.53	581.98					

TABLE VI. (1,0)ⁱ Band, λ 4836.192.

bands. The low abundance of Li⁶, and the complexity of the spectrum prevented the observation of these lines, though a careful search was made by the methods mentioned above. The abundance ratio $Li^7: Li^6$ has been determined by various observers and the results have varied considerably. Mass-spectrographs have yielded ratios varying from 15 to 10 and the most recent and most consistent of these are the determinations of Bainbridge¹⁵ and Aston¹⁶ which give a ratio of 11. From band spectra the much lower abundance ratio of 7.2 has been found by van Wijk and van Koeveringe¹¹ from the Li₂

bands and by Nakamura¹⁷ from the LiH bands. Taking as the most favorable case the ratio 7.2 measured by the band spectrum methods, the intensity of the Li⁶Li⁶ lines relative to the Li⁷Li⁷ lines should be 1:40. One would expect to be able to observe lines of this intensity in absorption but unfortunately the vibrational structure of the band system interferes to such an extent that it makes the task almost impossible. As is evident from the Franck-Condon diagram given by from the Franck-Condon diagram given by
Loomis and Nusbaum,¹³the.intense.bands.of.low vibrational quantum number are complicated by the superposition of fainter lines due to bands of higher vibrational energy. Thus even though the absorption is increased at Iow temperature by

¹⁷ G. Nakamura, Nature 128, 759 (1931).

¹⁵ K. T. Bainbridge, J. Frank. Inst. 212, 317 (1931).

¹⁶ F. W. Aston, Proc. Roy. Soc. **A134**, 571 (1932).

increasing the length of the column of lithium vapor, numerous extraneous lines appear in the region where the Li⁶Li⁶ lines are expected. Also it was found that in order to predict the positions of these lines with sufficient certainty to definitely identify them in the maze of other lines, the rotational constants of the Li⁷Li⁷ and Li⁶Li⁷ molecules must be known more precisely than they are known at present. It appears that, with the exception of the possibility of separating $Li⁶$ from Li' in fairly large quantities, the most promising method of obtaining Li⁶Li⁶ band lines is by an examination of the simplified spectrum is by an examination of the sim
obtained by magnetic rotation.¹³

VIBRATIONAL ISOTOPE EFFECT

The procedure followed in the evaluation of the mass coefficient ρ from the vibrational constants was essentially that described in previous work on the BO spectrum.⁹ By the combination principle, the difference of two terms having the same rotational quantum number, K , and having vibrational quantum numbers, v , differing by unity,

$$
\Delta T_{v+1}(K) = T_{v+1}(K) - T_v(K), \tag{1}
$$

may be obtained as the wave-number difference of two corresponding lines in a pair of bands suitably chosen. In the present case, three sets of ΔT values can be obtained from each pair, using the lines of the R , Q , and P branches. Those from the R and P branches should be identical, while that from the Q branches may differ slightly if A-doubling is present. Thus for example, using two bands $(v', 0)$ and $(v', 1)$, we may obtain the differences

$$
\Delta T_{\mathbf{i}}^{\prime\prime}(K) = Q^{\mathbf{v}',\mathbf{0}}(K) - Q^{\mathbf{v}',\mathbf{1}}(K)
$$

= $R^{\mathbf{v}',\mathbf{0}}(K) - R^{\mathbf{v}',\mathbf{1}}(K)$
= $P^{\mathbf{v}',\mathbf{0}}(K) - P^{\mathbf{v}',\mathbf{1}}(K) \cdots$ (2)

The dependence of ΔT on K can be shown^{17a} from the equation for the rotational terms in ${}^{1}\Sigma$ and $\rm{^1II}$ states to be given by

$$
\Delta T_{v+1}(K) = \Delta G_{v+1} - (B_v - B_{v+1})(K + \frac{1}{2})^2 + \cdots
$$

= $\Delta G_{v+1} - \alpha_e (K + \frac{1}{2})^2 + \cdots$, (3)

where terms in higher powers of $(K+\frac{1}{2})$ are

negligible at values of K not too large. When the values of ΔT are fitted by least squares methods to a parabola having its vertex at $K = -\frac{1}{2}$, the constant term in the solution gives the best value of the vibrational term difference ΔG_v . For the ¹II state, in which A-doubling is observed, the quantities ΔT will not be exactly the same for the Q as for the P and R branches. The ΔG_v should, however, be identical for the two because the difference, which is proportional to the Λ doubling, is itself a function of $(K+\frac{1}{2})^2$. The vibrational term differences may be represented by the equation

$$
\Delta G_v = \omega_e - 2x_e \omega_e (v + \frac{1}{2}) + 3y_e \omega_e [(v + \frac{1}{2})^2 + 1/12] + \cdots (4)
$$

From Eq. (4) in conjunction with the values of ΔG_v so obtained, the mass coefficient ρ can be obtained independently from each constant, since

$$
\omega_e{}^i/\omega_e = \rho \, ; \quad x_e{}^i/x_e = \rho \, ; \quad y_e{}^i/y_e = \rho^2. \tag{5}
$$

Here the superscript i refers to quantities pertaining to the isotopic molecule Li⁶Li⁷. As in the case of the BO bands, it was first proved from the observed data that the vertex of the $\Delta T: K$ parabola actually occurs at $K=-\frac{1}{2}$ by making certain that the constant term, ΔG_v , in the solution was unaffected by the introduction of a linear term in $(K+\frac{1}{2})$.

Lower state

The \sum state is the simpler of the two involved in the production of the blue-green lithium bands and since it is the normal state it should be free from perturbations. It has the added advantage for the precise determination of ρ that the value for the precise determination of ρ
of ω_e '' is greater than that of ω_e' .

Table IX contains. the results of the various least squares solutions for ΔG_{v} " and ΔG_{v} ". In the solutions only values of $\Delta T(K)$ up to $K = 30$ were used. The probable errors of the resulting average values of ΔG_{v} " are calculated on the basis of their external consistency¹⁸ for all cases except that of $\Delta G_{14}^{\prime\prime\prime}$ where this was impossible. Although it is not evident in this particular case, a more conservative estimate of the probable error is obtained by this procedure than by using internal consistency. It will be noted that the

 $\overline{R_{178}}$ R. S. Mulliken, Rev. Mod. Phys. 2, 100 (1930), Eq. (29) on p. 100 with $\Lambda = 0$ for ¹ Σ state and =1 for ¹II state.

¹⁸ R. T. Birge, Phys. Rev. **40**, 207 (1932).

	Branch	Bands	ΔG_{v} "	$\alpha^{\prime\prime}$	Wt.
Li ⁷ Li ⁷	R	$0,0-0,1$	346.191	0.00703	
		$0,0-0,1$	346.194	0.00713	3 5 1
	O_P	$0,0-0,1$	346.173	0.00709	
			Av. 346.193		
			$+0.003$		
	$\begin{array}{c} R \ Q \ P \end{array}$	$0, 1 - 0, 2$	340.979	0.00728	
		$0, 1 - 0, 2$	341.022	0.00726	$\frac{3}{5}$
		$0,1-0,2$	341.061	0.00735	
			Av. 341.012		
			± 0.013		
Li ⁶ Li ⁷	R	$0, 0 - 0, 1$	360.335	0.00844	6
	$\frac{Q}{P}$	$0,0-0,1$	360.299	0.00830	10
		$0,0-0,1$	360.173	0.00814	1
			Av.360.304		
			± 0.018		
	Q	$0, 1 - 0, 2$	354.616	0.00828	
			±0.046		
			ω_e " = 351.374 \pm 0.014; ω_e " = 365.993 \pm 0.058;		
			$\rho = 1.0416 \pm 0.0002$		
			$x_e'' = 0.00737 \pm 0.00002$; $x_e'' = 0.00777 \pm 0.00007$; $\rho = 1.05 \pm 0.01$		
	$(Cf. text page 160)$,		By assuming that $x_e^{i}/x_e = \rho$ and not using the value of ΔG_{1i}^{i}		
			$\omega_e'' = 351.374 \pm 0.014$ and $\omega_e'' = 365.923 \pm 0.023$, giving		
			$\rho = 1.04141 \pm 0.00008.$		

TABLE IX. Vibrational constants of the ${}^{1}\Sigma$ state.

probable error of $\Delta G_{1}^{\'\prime}$ is large relative to the others, even though its error was computed by internal consistency, i.e., from the residuals of the least squares solution from which it was obtained. This results from the much smaller degree of accuracy with which the Q branch of the 0,2 isotope band could be measured, as previously explained. The items were weighted according to the estimated precision of the measurements for the branches involved. All solutions were carefully examined for any trend in the residuals; this was another determining factor in assigning weights in the one or two cases in which slight evidence of a trend was present. Fig. 1 represents graphically the residuals in the solution from the Q branches. Missing points on this figure do not indicate that the corresponding lines were not identified, but that their measurement was regarded as unreliable because of blending.

At the bottom of Table IX are given the values of ρ calculated by Eqs. (4) and (5). Since the data only involve the states $v'' = 0.1$ and 2, they are insufficient for the determination of the $y_e\omega_e$ or higher terms. However, as shown below, this is of no consequence in the present case. The value of ρ

obtained from x_e^{i}/x_e is of course much less accurate than that from $\omega_e i/\omega_e$ but agrees with the latter to within its probable error. The second value of ρ given in the table from ω_e^i/ω_e is computed by using in the solution of Eq. (4) only $\Delta G_i''^i$ and assuming that $x_e''^i/x_e'' \equiv \rho$. This assumption was shown' to be justified in the case of BO so in view of the untrustworthiness of the measurements on the 0,2 isotope lines, it is considered that the figure $\rho = 1.04141 \pm 0.00008$, although not as purely experimental as the other, is the more reliable result.

This value of ρ corresponds, as shown below, to a mass ratio $Li⁷/Li⁶$ considerably greater than that found by Costa.⁶ Therefore the possible sources of error have all been carefully examined and it appears that none of them separately would change the result by more than the probable error. In their study of the lithium band spectrum, Loomis and Nusbaum¹³ were able to evaluate a $y_e\omega_e(v+\frac{1}{2})^3$ term in the expression for the vibrational terms of the lower state. Their value of $y_e\omega_e$ was -0.0097 . Introducing this into Eq. (4), and solving by means of our experimental ΔG 's, a value of ρ was found which differed by only one part in 40,000 from that calculated without this term. Recently Dunham¹⁹ has calculated the energy levels of a rotating vibrator by quantum mechanics, and compared the results with those of the old quantum theory. The correction to be applied to the ratio $\omega_e / \omega_e = \rho$ has been evaluated and found to be only one part in 200,000. Since the probable error of the most precise determination of ρ in the present work is one part in 12,000, it is quite evident that neither of the above corrections materially changes the result.

Upper state

The data for the 'Il state were obtained earlier than those for the Σ state, from a set of plates than those for the ¹2 state, from a set of plates
giving slightly less resolution.^{19a} They were treated in the same manner as for the normal state. As a consequence of the convention of designating a band line by its lower state value of Explaining a same line system state value of K , it follows that the vertex of the $\Delta T : K$ parabola occurs here at $K = -1\frac{1}{2}$, $-\frac{1}{2}$ and $+\frac{1}{2}$ for the parabolas from the R , Q , and P branches

¹⁹ J. L. Dunham, Phys. Rev. 41, 721 (1932).

¹⁹a A. McKellar, Phys. Rev. 43, 215 (1933).

FIG. 1. Residuals (observed-calculated) from adopted least squares solutions for $\Delta T : K$. The relativel large residuals in the single solution for ΔG_{1}^{3} , illustrate the unreliability of this determination.

respectively. The highest values of K used in these solutions varied from 30 to 40. The vibrational constants of the upper state calcu-

TABLE X. Vibrational constants of the 1 II state.

	Branch	Bands	ΔG_{p} '	α'	W_t .
Li ⁷ Li ⁷	R	$1,0-0,0$	264.709	0.00896	
	$^o_{\bar{P}}$	$1,0-0,0$	264.663	0.00888	$\frac{3}{5}$
		$1,0 - 0,0$	264.630	0.00882	
			Av. 264.675		
			± 0.013		
	R	$2.0 - 1.0$	258.450	0.00931	
	$\frac{Q}{P}$	$2,0-1,0$	258.394	0.00921	3 5 1
		$2,0-1,0$	258.364	0.00915	
			Av. 258.409		
			± 0.014		
Li ⁶ Li ⁷	R	$1.0 - 0.0$	275.255	0.00905	
	$\frac{Q}{P}$	$1,0-0,0$	275.399	0.00930	$\begin{smallmatrix}1\1\1\1\end{smallmatrix}$
		$1,0-0,0$	275.215	0.00926	
			$-Av. 275.290$		
			± 0.038		
			$\omega_e' = 270.941 \pm 0.029$; $\omega_e' = 282.081 \pm 0.044$; $\rho = 1.0411 \pm 0.0002$		

lated by least squares are given in Table X. The results of the three solutions for $\Delta G_{\rm A}^{\prime\prime\prime}$ were given equal weight in this case because, although there were a few more values of ΔT available from the Q branch than from the other two, the residuals in the computations involving the R and P branches appeared to be considerably smaller than those of the Q branch solution. No lines were identified in the 2,0 isotope band so a value of ΔG_{13} ["] could not be calculated. Therefore it was necessary to assume the theoretical fore it was necessary to assume the theoretical
equation $x_e'^i/x_e' = \rho$ in order to solve Eq. (4) for $\omega_e^{\prime\prime}$. Although the magnitude of ρ obtained from the upper state is slightly lower than those computed from the 12 state, the agreement constitutes a satisfactory check on the previous values. In view of the fact that the results from the upper state are less accurate and in general less trustworthy than those from the normal state they should carry much less weight than the latter.

RoTATIQNAL IsoToPE EFFEcT

It was considered of value to calculate the rotational constants of the main and isotopic molecules since for the latter they have not heretofore been found. They give entirely independent values of ρ for comparison with those from the vibrational constants. The rotational constants are also necessary if an attempt is to be made to detect a possible electronic isotope effect.

The rotational constants were calculated by the same method as that employed by Harvey the same method as that employed by Harve
and Jenkins.¹¹ The $R-P$ combination difference are given by

$$
\Delta_2 F(K) = 4B_v(K + \frac{1}{2}) + 8D_v(K + \frac{1}{2})^3 + 12F_v(K + \frac{1}{2})^5 \cdots
$$
 (6)

in which some negligible terms have been omitted, By means of the well-known relations connecting the vibrational and rotational constants preliminary values of D_v and F_v were calculated. With these, Eq. (6) was reduced to the linear form in $K+\frac{1}{2}$ and so could be solved by least squares for B_v . Such solutions were carried through for the $v' = 0,1$ and $v'' = 0,1$ states of both the main and isotopic systems. Extrapolating to the equilibrium state by means of the relation

$$
B_v = B_e - \alpha (v + \frac{1}{2}),\tag{7}
$$

one obtains the value of ρ by the requirement

$$
\rho^2 = B_e{}^i / B_e \cdots \tag{8}
$$

The results of such computations for the lower state are listed in Table XI. In obtaining

TABLE XI. Rotational constants of the ${}^{1}\Sigma$ state.

Li ⁷ Li ⁷		Li ⁶ Li ⁷	
Band	B_{ν} "	Band	$B_{n}^{\prime\prime i}$
$_{0,0}$	0.6685	$_{0.0}$	0.7276
1.0	0.6696	1.0	0.7269
2,0	0.6695		
0.1	0.6606	0.1	0.7166
B_{ϵ} " = 0.6721 \pm 0.0003		$B'_e{}'' = 0.7302 \pm 0.0007$	
	(using α_e " = 0.00708		(using $\alpha_e'' = 0.00830$
	from vibrational		from vibrational
analysis)		analysis)	
D_{e} " = -0.986 \times 10 ⁻⁵		$D_{e}^{\prime\prime i} = -1.16 \times 10^{-5}$	
F_{e} " = 2.00 \times 10 ⁻¹⁰		$F_e^{\prime\prime i} = 2.4 \times 10^{-10}$	
$\beta'' = -3.86 \times 10^{-8}$		$\beta'' = -2.1 \times 10^{-8}$	
		$\rho^2 = B_e^{\prime\prime i}/B_e^{\prime\prime} = 1.0863 \pm 0.0012; \quad \rho = 1.0422 \pm 0.0006$	

FIG. 2. A—doubling in the upper state $v' = 0$ for both main (solid points) and isotopic systems (circles). The points of the latter show a somewhat greater scatter due to the smaller degree of accuracy with which the fainter lines could be measured, but the two sets of data appear to fit the same curve. The curve given is the theoretical one

$$
\Delta(PQR) = 2\Delta v_{dc} = 2(B_d' - B_c')K(K+1),
$$

in which $B_d' - B_c' = 0.00018$, as given by Wurm.⁹

 $B_{e}^{\prime\prime i}$ the data from the 0,1 band were given double weight because the combination differences of the lines of low rotational quantum number in this band were more free from the inHuence of blends than were those of the other two bands. In calculating both B_{e} " and B_{e} " the two bands. In calculating both B_{e} " and B_{e} " the more exact values of α_{e} " and α_{e} " found from the vibrational analyses were used. The magnitude of ρ obtained from the data in Table XI is seen to be somewhat larger than those computed from the vibrational analysis but agrees with the latter to within its probable error.

Table XII gives the rotational constants calculated for the ¹II state. The data were treated in the same manner as for the normal state. Again the resulting ρ is in good agreement with the previous values. The A-doubling of the rotational levels of this state, although actually immaterial for the evaluation of ρ , was investigated for the main and isotopic molecules. The doubling in the lowest vibrational state is shown in Fig. 2, from which it appears to be sensibly the same for

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TABLE XII. Rotational constants of the 'II state.

Li ⁷ Li ⁷	Li ⁶ Li ⁷			
Band B_{\ast}	$B_{n}^{\prime i}$ Band			
0.5538 0.0	0.6001 0,0			
0.5520 0.1	0.5986 0.1			
0,2 0.5531				
0.5453 1.0	0.5933 1.0			
$B'_e = 0.5577 \pm 0.0003$ (using	$B_{e}^{\prime i}$ = 0.6046 ± 0.0007 (using			
α' = 0.00888 from	$\alpha'^{i} = 0.00922$ from			
vibrational analysis)	vibrational analysis)			
$D' = -0.945 \times 10^{-5}$	$D_{\epsilon}^{\prime i} = -1.11 \times 10^{-5}$			
$F_6 = 2.05 \times 10^{-10}$	$F_{e}^{\prime i} = 2.6 \times 10^{-10}$			
$\beta' = -7.68 \times 10^{-8}$	$\beta' = -7.5 \times 10^{-8}$			
$\rho^2 = B_e^{\prime i}/B_e^{\prime} = 1.0841 \pm 0.0014$; $\rho = 1.0412 \pm 0.0007$				

both molecules. Although a small difference is to be expected on theoretical grounds, no evidence for this can be found from our data.

ELECTRONIC ISOTOPE EFFECT

Since in BO the origins of the main and isotopic band systems were found to differ slightly²⁰ indicating an electronic isotope effect, and in view of the relatively large isotope shifts calculated and found²¹ in the atomic spectrum of lithium, it is of interest to examine the lithium molecular spectrum in this connection. The origins of the main and isotopic 0,0 bands were computed using the new rotational constants and the equations given by Harvey and Jenkins²² for the band line frequencies. The results are

$$
\nu_0^{(0,0)} = 20395.902 \pm 0.010;
$$

$$
\nu_0^{(0,0)} = 20394.201 \pm 0.010.
$$

Then, from the relation

$$
\nu_e = \nu_0^{(0,0)} - \left[\omega_e'(\frac{1}{2}) - x_e'\omega_e'(\frac{1}{2})^2\right] \\
+ \left[\omega_e''(\frac{1}{2}) - x_e''\omega_e''(\frac{1}{2})^2\right] \cdots \quad (9)
$$

the two system-origins may immediately be computed with the aid of the vibrational constants from Tables IX and X. The system origins found are

Li⁷Li⁷:
$$
\nu_e = 20436.25 \pm 0.02
$$
;
Li⁸Li⁷: $\nu_e{}^i = 20436.29 \pm 0.04$.

²⁰ Cf. reference 9, p. 483.

²¹ D. S. Hughes and C. Eckart, Phys. Rev. 36, 694 (1930); D. S. Hughes, Phys. Rev. 38, 857 (1931).

²² Cf. reference 11, p. 795.

Hence it appears that either the electronic terms of the two molecules are very nearly equal, or they differ by approximately the same amount for the ${}^{1}\Sigma$ and ${}^{1}\Pi$ states.

DISCUSSION OF RESULTS

A summary of the different determinations of the mass coefficient ρ , with their probable errors, is given in Table XIII. The values derived from

TABLE XIII. Summary of values of ρ and the corresponding mass-ratios $Li⁷/Li⁶$.

$Con-$ stants used	Bands used	ρ	Li^7/Li^6
	ω_e'' $(0,0)(0,1)(0,2)$ $(0.0)^{i}(0.1)^{i}$	$1.04141 + 0.00008$ $1.1690 + 0.0003$	
	ω_e'' (0,0)(0,1)(0,2) $(0,0)^{i}(0,1)^{i}(0,2)^{i}$	$1.0416 + 0.0002$	$1.1698 + 0.0008$
	ω_e' (0,0)(1,0)(2,0) (0,0) ⁱ (1,0) ⁱ	$1.0411 + 0.0002$	$1.1678 + 0.0008$
	B_{ϵ} " (0,0)(1,0)(2,0)(0,1) 1.0422 ± 0.0006 (0,0) ^{ι} (1,0) ^{ι} (0,1) ^{ι}		
	B_{e}' (0,0)(0,1)(0,2)(1,0) 1.0412 \pm 0.0007 $(0,0)^{i}(1,0)^{i}(0,1)^{i}$		

Li⁷ = 7.012 \pm 0.002 Li⁷/Li⁶ = 1.1663 \pm 0.0007 $\rho = 1.04075 \pm 0.00017$

the vibrational structure of the bands are somewhat more accurate than those found from the rotational structure. In the last column is included the mass ratio $Li⁷/Li⁶$ corresponding to the more exact mass coefficients. From the definition $\rho = (\mu/\mu^i)^{\frac{1}{2}}$, in which μ is the reduced mass of the diatomic molecule $= m_1 m_2/(m_1+m_2)$, it follows that

$$
Li^7/Li^6 = 2\rho^2 - 1.
$$
 (10)

The mass spectrograph results of Costa as modified by Aston⁷ are given for comparison at the bottom of the table. It is apparent that the band spectrum values of the mass ratio, although showing considerable variation, are all definitely higher than the mass-spectrograph determination.

There is some uncertainty as to the extent to which the masses of the electrons enter into the ratio determined by Eq. (10) . It is probably more nearly true to assume that the electrons of each atom vibrate with its nucleus than that the nuclei alone vibrate. On the former assumption, the result from Eq. (10) represents the actual mass ratio of the *atoms* (nuclei+electrons), whereas on the latter, it represents the ratio of the *nuclear* masses, and is to be corrected in obtaining the atomic ratio by the addition of three electrons to each mass. However, when this is done, the ratio is only decreased by one part in 25,000, which is well within the probable error of our most accurate result.

We now have independent evidence from disintegration experiments that the figure 7.012 is definitely low for the atomic weight of Li'. From experiments in which lithium is disintegrated by the impacts of protons, the mass of the $Li⁷$ atom may be found by considering it as the unknown quantity in the process represented by the equation.

Energy + proton + Li⁷ nucleus \rightarrow 2 α -particles +energy. Using the data of Cockcroft and +energy. Using the data of Cockcroft and
Walton,²³ who found 17.2 million volts as the total energy of the two α -particles produced by bombardment of lithium with 450,000 volt protons, the mass of the Li' atom is computed to be 7.015. In consequence of the precision with which the other factors are known, this figure should be accurate to better than ± 0.001 .

Taking this as the correct mass of Li⁷, and using the mass ratio $Li^7/Li^6 = 1.1690$, found from the vibrational constants of the normal state (considered the best value) the mass of $Li⁶$ is 6.001. From the upper state mass ratio $Li⁷/Li⁶$ = 1.1678, one obtains Li^6 = 6.007. On the packing raction-mass number diagram of Aston,²⁴ thes fraction-mass number diagram of Aston,²⁴ these figures place Li' directly upon the upper branch of the curve, occupied by the relatively easily disintegrated atoms. On the other hand, Li⁶ is shifted down to a position approximately on the lower branch of the curve upon which are He⁴,

 C^{12} and O^{16} , the more stable atoms. If the Li⁶ nucleus is composed of one α -particle, one proton and one neutron and the Li' nucleus is obtained by the addition of one neutron, it seems not at all unreasonable that the three entities outside the α -particle for Li⁷ should give a greater mass defect than the two for Li⁶. However, this does not appear to be so for the boron isotopes. An important difficulty appears if we consider the $Li⁶$ and $Li⁷$ nuclei to be so constituted, since one would expect the *lower* limit to the mass of Li⁶ to be the mass of Li' minus the mass of a neutron. The mass of $Li⁶$ computed from our best mass ratio is below this value by considerably more than its probable error. Therefore, in view of the unexpectedly high $Li⁷/Li⁶$ mass ratio obtained here it would appear very desirable to obtain new mass-spectrograph data on lithium.

In conclusion I wish to express my sincere appreciation of the invaluable assistance rendered by Professor F. A. Jenkins under whose guidance this work has been done. I am deeply indebted also to Professors R. T. Birge and R. H. Fowler for helpful discussions.

Note added in proof, July 17, 1933: K. T. Bainbridge has very recently²⁵ made accurate measurements of the masses of the lithium isotopes using his mass-spectrograph. His results are $Li^7 = 7.0146 \pm 0.0006$ and $Li^6 = 6.0145 \pm 0.0003$ corresponding to a mass ratio $Li⁷/Li⁶=1.16628$ ± 0.00016 . His value for Li⁷ is seen to be in very good agreement with that obtained from disintegration data. The mass ratio found is almost identical with the former mass-spectrograph determination of Costa and is thus considerably lower than that computed from band spectrum data as presented above. In view of the good agreement of the two methods in the cases of agreement of the two methods in the cases o
boron⁹ and hydrogen,²⁶ this result is very surprising. We are unable to account for the discrepancy at the present time.

²⁵ K. T. Bainbridge, Phys. Rev. 44, 56 (1933).

²⁶ J. D. Hardy, E. F. Barker and D. M. Dennison, Phys. Rev. 42, 279 (1932).

²³ Cf. reference 1, p. 236.

²⁴ Cf. reference 7, p. 511.