

remainder of the discrepancy, and so (d) would seem to have little validity. If the mass of deuterium is taken as 2.01423 and the other masses as before, the reduced mass ratio is

0.51849. Again this is considerably higher than the B_e ratio when the corrections (a), (b) and (c) have all been made to the observed B_e^* values.

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Mass Ratio of the Lithium Isotopes from the Spectrum of Li_2

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It is shown from a study of the ${}^1\Sigma \rightarrow {}^1\Sigma$ Li_2 band system that the relative masses of the two isotopes of Li as calculated from the observed isotope effect in each of the two lowest states of Li_2 is in excellent agreement with the mass ratio obtained by other precise methods. Various methods of treating the data lead consistently to the conclusion that the mass-coefficient ρ is 1.04077 ± 0.00004 and that the mass ratio is 1.16640 ± 0.00016 . This result disagrees with

that of McKellar and Jenkins who, from a less extensive study of the ${}^1\Pi \rightarrow {}^1\Sigma$ system of Li_2 , concluded that the mass ratio was 1.1678 ± 0.0008 , a result which cast suspicion upon the band spectrum method of determining relative atomic masses. There has also been found a small but definite electronic isotope shift: $\nu_e^i - \nu_e = -0.064 \pm 0.010 \text{ cm}^{-1}$.

THE accuracy of the band spectrum method of determining the mass ratio of isotopes has been called in question by two series of investigations. First, a consistent ratio of the masses of H^2 and H^1 has not been obtained when the simple theory of the isotope shift has been applied to measurements on various hydrogen and hydride band systems. On account of the large change of reduced mass in these instances, they form a rather special case. Although this problem is not yet completely solved, sufficient reasons for the discrepancies have been advanced from various quarters, by Kronig,¹ by Dieke² and by Holst and Hulthén.³ Second, McKellar and Jenkins⁴ have found from measurements on the blue-green system of Li_2 bands (${}^1\Pi \rightarrow {}^1\Sigma$) that the mass coefficient $\rho (= (\mu/\mu^i)^{\frac{1}{2}}$, where μ is the reduced mass of $\text{Li}^7 \text{Li}^7$ and μ^i that of $\text{Li}^7 \text{Li}^6$) and, therefore, the mass ratio of Li^7 to Li^6 are greater by several times the estimated probable errors than the corresponding quantities as determined by Bainbridge⁵ who used the mass

spectrograph. The latter have been corroborated by the recent extremely precise determinations of Oliphant, Kempton and Rutherford⁶ who used the data from certain nuclear transformations. The comparison is given in Table IV. Since in some cases, notably that of oxygen, the mass ratio of the isotopes has been determined only from the band spectrum, it is worth while to examine the apparent discrepancy in the case of lithium, by determining spectroscopically the mass ratio of Li^7 to Li^6 under the more favorable conditions existing in the red band system of Li_2 . This system has been analyzed by Wurm,⁷ but the constants of $\text{Li}^7 \text{Li}^7$ were not determined with great precision, and the constants of $\text{Li}^7 \text{Li}^6$ not at all.

In a recent Letter to the Editor of this journal⁸ we showed that the mass ratio of the Li isotopes calculated from the molecular constants obtained from a study of the $(v',0)$ progression of the red ${}^1\Sigma \rightarrow {}^1\Sigma$ system of Li_2 was in good agreement with the mass ratio obtained by other methods. Since the most accurate value of ρ came from the vibrational constant ω_e of the

¹ R. de L. Kronig, *Physica* **1**, 617 (1934).

² G. H. Dieke, *Phys. Rev.* **47**, 661 (1935).

³ Holst and Hulthén, *Zeits. f. Physik* **90**, 712 (1934).

⁴ F. A. Jenkins and A. McKellar, *Phys. Rev.* **44**, 325 (1933); A. McKellar, *Phys. Rev.* **44**, 155 (1933).

⁵ K. T. Bainbridge, *Phys. Rev.* **44**, 56 (1933).

⁶ M. L. E. Oliphant, A. E. Kempton and Lord Rutherford, *Proc. Roy. Soc.* **A149**, 406 (1935).

⁷ K. Wurm, *Zeits. f. Physik* **59**, 35 (1929).

⁸ G. M. Almy and G. R. Irwin, *Phys. Rev.* **48**, 104 (1935).

upper ${}^1\Sigma$ state, a state not involved in the ${}^1\Pi \rightarrow {}^1\Sigma$ system, our result did not conflict directly with that obtained by McKellar and Jenkins. We have since measured the $(0, v'')$ progression of the same system and made the calculations of ρ from the constants of the lower state, common to the ${}^1\Pi \rightarrow {}^1\Sigma$ and ${}^1\Sigma \rightarrow {}^1\Sigma$ systems. Again we have found agreement with the value of ρ obtained by other methods; there seems to be no question but that, in the case of Li_2 , the band spectrum method leads to the same mass ratio as other methods and that the probable error in the determination is not much larger than in the other methods.

An accurate calculation of the lower state constants has led to the determination, with considerable accuracy, of a small but definite electronic isotope shift. This point was in doubt in our letter.

ROTATIONAL AND VIBRATIONAL ANALYSIS

The plates used were photographed in absorption in the first order of a 21-foot, 30,000-lines per inch, concave grating. The dispersion is about 1.3A per mm. The standard lines were iron arc, second order. As in the case of the $(v', 0)$ progression measurements, all comparator settings were made by each of two observers, except for the (0,4) band which was carefully re-measured by the only observer. Since the work on the $(v', 0)$ progression showed consistent values of wave number among the various exposures, the $(0, v'')$ progression was measured on only one set of plates.

The method followed in the analysis was the same as that outlined in our previous letter. The first ten or twelve lines in each branch of each band were measured, $\Delta_2 F$'s were computed and corrected for a small D term, and the rotational B_v 's calculated. By using the relation $B_v = B_e - \alpha_e(v + \frac{1}{2})$ the best values of B_e and α_e were obtained by least squares. Due weight was given to the fact that there were five determinations (six in $\text{Li}^7 \text{Li}^7$) of B_0'' made in the analysis of the $(v', 0)$ progression.

The band origins (ν_0) were calculated with reference to each measured line (ν), with the relation,

$$\nu = \nu_0 + (B_v' + B_v'')M + (B_v' - B_v'')M^2 + 2(D' + D'')M^3, \quad (1)$$

where $M = -K''$ for P lines, $M = K'' + 1$ for R lines. Smoothed values of B_v were used, obtained from $B_v = B_e - \alpha_e(v + \frac{1}{2})$. Only rough values of the D 's were necessary on account of the smallness of the term in M^3 for small M ; McKellar gives D_v'' accurately and we estimated D' with sufficient precision from measurements to large quantum numbers on the (3,0) band. In both the $(v', 0)$ and $(0, v'')$ progressions ten to twenty lines free from serious blending were used in calculating the origin of each band, with the exceptions of the (0,0) $\text{Li}^7 \text{Li}^6$ band where only four good lines were available, and the (3,0) bands, where almost exact coincidence of the P and R branches occurs near the origin.

The average deviation from the mean of the calculated origins was in the case of each band, with the exceptions mentioned, less than $\pm 0.025 \text{ cm}^{-1}$. The probable error of a mean origin, then, is less than $\pm 0.01 \text{ cm}^{-1}$. This is, however, a statement only of the consistency of the relative measurements of wave number within a band, or, at most, for one setting of the plate on the comparator. Since only one isotopic pair of bands were measured at one setting of the plate, and since small discrepancies occasionally appeared in the calculation of iron lines between standards we believe the probable error of an origin to be in the neighborhood of $\pm 0.02 \text{ cm}^{-1}$. This belief is supported by the fact that the fluctuations in the very small third differences ($\sim 0.05 \text{ cm}^{-1}$) formed on the origins can be smoothed by

TABLE I. Rotational constants and origins of bands.

v', v''	B_v''	$B_v''^{\frac{1}{2}}$	B_v'	$B_v'^{\frac{1}{2}}$	ν_0	$\nu_0^{\frac{1}{2}}$
0,0	0.6690	—	0.4949	0.5360	14,020.616	14,018.602
0,1	0.6622	0.7166	0.4949	0.53535	13,674.416	13,658.536
0,2	0.6552	0.7083	0.4945	0.5365	13,333.403	13,304.049
0,3	0.64785	0.7003	0.4953	0.5368	12,997.697	12,955.341
0,4	0.6404	0.6918	0.49505	0.5362	12,667.253	12,612.345
1,0	0.6696	0.7252	0.4898	0.5305	14,272.950	14,281.113
2,0	0.6691	0.7248	0.4837	0.5232	14,522.107	14,540.160
3,0	(0.6681)	0.7248	(0.4767)	0.5179	14,768.148	14,795.822
4,0	0.6692	0.7240	0.4744	0.5113	15,011.073	15,048.180
5,0	0.6693	0.7248	0.4687	0.5050	15,250.906	15,297.170
$B_e'' = 0.67293$ ± 0.00017		$B_e''^{\frac{1}{2}} = 0.72892$ ± 0.00012	$B_e' = 0.49754$ ± 0.00025	$B_e'^{\frac{1}{2}} = 0.53933$ ± 0.00025		
$\alpha_e'' = 0.00719$ ± 0.00007		$\alpha_e''^{\frac{1}{2}} = 0.00823$ ± 0.00005	$\alpha_e' = 0.00522$ ± 0.00008	$\alpha_e'^{\frac{1}{2}} = 0.00623$ ± 0.00008		
$\rho = [B_e''/B_e']^{\frac{1}{2}} = 1.04077$ ± 0.00015			$\rho = [B_e^{\frac{1}{2}}/B_e']^{\frac{1}{2}} = 1.04114$ ± 0.0003			
$\rho = [\alpha_e''/\alpha_e']^{\frac{1}{2}} = 1.043$ ± 0.005			$\rho = [\alpha_e^{\frac{1}{2}}/\alpha_e']^{\frac{1}{2}} = 1.058$ ± 0.008			
McKellar: $\rho = \left[\frac{B_e''^{\frac{1}{2}}}{B_e''} \right]^{\frac{1}{2}} = \frac{0.7302 \pm 0.0007}{0.6721 \pm 0.0003} = 1.0422 \pm 0.0006$						

TABLE IIa. Lower state vibrational constants.
Column (2) contains the best values.

	(1)	(2)	(3)	(4)
	$y_e''\omega_e'' = -0.0063$	$y_e''\omega_e'' = -0.0097$	$y_e''\omega_e'' = 0$	
	$y_e''^2\omega_e''^2 = -0.0111$	$y_e''^2\omega_e''^2 = -0.0111$	$y_e''^2\omega_e''^2 = 0$	McKELLAR
ω_e''	351.398	351.346±0.017	351.494	351.374
$\omega_e''^2$	365.658	365.658±0.021	365.828	365.993
$x_e''\omega_e''$	2.583	2.557±0.004	2.630	2.590
$x_e''^2\omega_e''^2$	2.768	2.768±0.004	2.851	2.844
E_v	±0.010	±0.012	±0.014	
E_v^2	±0.015	±0.015	±0.020	
$\rho = \omega_e''^2/\omega_e''$	1.04058	1.040735	1.04078	1.0416±0.0002
		±0.00008		
$\rho = [x_e''\omega_e''/x_e''\omega_e'']^{1/2}$	1.0352	1.0404±0.0011	1.0412	1.048±0.01
ν_e	14068.316	14068.291±0.020	14068.408	
ν_e^2	14068.195	14068.215±0.032	14068.287	
$\nu_e^2 - \nu_e$	-0.121	-0.076±0.038	-0.121	

TABLE IIb. Upper state vibrational constants.

	(1)	(2)	(3)
	$y_e'\omega_e' = 0.0039$	$y_e'\omega_e' = 0.0039$	$y_e'\omega_e' = 0$
	$y_e'^2\omega_e'^2 = 0.0067$	$y_e'^2\omega_e'^2 = 0.0044$	$y_e'^2\omega_e'^2 = 0$
ω_e'	255.507	255.507±0.004	255.421
$\omega_e'^2$	265.963	265.914±0.015	265.816
$x_e'\omega_e'$	1.597	1.597±0.001	1.561
$x_e'^2\omega_e'^2$	1.745	1.725±0.003	1.685
E_v	±0.003	±0.003	±0.013
E_v^2	±0.010	±0.013	±0.024
$\rho = \omega_e'^2/\omega_e'$	1.04092	1.04073	1.04070
		±0.00006	
$\rho = [x_e'\omega_e'/x_e'\omega_e']^{1/2}$	1.0455	1.0394±0.0008	1.0387
ν_e	14068.295	14068.295±0.006	14068.344
ν_e^2	14068.196	14068.222±0.023	14068.279
$\nu_e^2 - \nu_e$	-0.099	-0.073±0.024	-0.065

shifting origins by 0.02 cm⁻¹ or less. There may still be a small systematic shift throughout the spectrum due to the use of second order lines for standards. Since differences of wave number are used in determining the molecular constants and ρ such a shift could not affect the results.

The results of the rotational analysis are given in Table I. For completeness, some of the results of our previous letter are included. The B_e 's and the origins of each of the twenty bands are listed, and the values of B_e and α_e given below. As mentioned above, due weight was given, in the calculation of the B_e 's and α_e 's, to the fact that several determinations were made of B_0' and B_0'' . The table also contains the values of ρ obtained from the ratios of rotational constants, and, on this point, a comparison with McKellar's results for the ground state.

From the band origins the vibrational constants may be computed, since,

$$\begin{aligned} \nu_0(v', v'') &= \nu_e + [\omega_e'(v' + \frac{1}{2}) \\ &\quad - x_e'\omega_e'(v' + \frac{1}{2})^2 + y_e'\omega_e'(v' + \frac{1}{2})^3] \\ &\quad - [\omega_e''(v'' + \frac{1}{2}) - x_e''\omega_e''(v'' + \frac{1}{2})^2 \\ &\quad + y_e''\omega_e''(v'' + \frac{1}{2})^3]. \quad (2) \end{aligned}$$

The general method for obtaining the vibrational constants of the lower state was to take the primed constants from our previous work on the $(v', 0)$ progression, insert the origins $(\nu_0(v', v''))$ from Table I and to compute ν_e , ω_e'' , $x_e''\omega_e''$ and $y_e''\omega_e''$ by least squares. Several variations of

this method were tried, the results of which are given in Table IIa.

(1) The constants obtained by straight least squares with the third degree Eq. (2) are given in column (1). This gives values of $y_e''\omega_e''$ and $y_e''\omega_e''$ which have a much larger ratio than the theoretically correct ratio, $\rho^3 \sim 1.13$. One may, however, expect these small constants to be correct only as to order of magnitude since the small third differences ($= 6y_e''\omega_e''$) formed on the origins, though showing a trend, fluctuate even in sign. The constants have been tested by computing the origins with them; the calculated probable error E_v of a single observed origin for each type of molecule is given. E_v is equal to $0.674([rr]/n - q)^{1/2}$ where $[rr]$ is the sum of the squares of the residuals, n the number of observations, and q the number of constants being determined.

(2) If one assumes a particular value of $y_e''\omega_e''$, or $y_e''\omega_e''$, to be correct and requires the other to bear approximately the proper ratio, ρ^3 , to it, appreciably different constants are obtained. Since Loomis and Nusbaum⁹ have made a vibrational analysis of the ground state extending to $v = 15$, their value of $y_e''\omega_e'' (= -0.0097)$ is probably more reliable than that given in column (1). Their value bears a sufficiently correct ratio to the least squares $y_e''\omega_e''$ to let the latter stand. When the observed origins of Li⁷Li⁷ are

⁹ F. W. Loomis and R. E. Nusbaum, Phys. Rev. **38**, 1447 (1931).

corrected by a term, $0.0097 (v'' + \frac{1}{2})^3$, and the corrected origins fitted by least squares to the second degree equation in $(v'' + \frac{1}{2})$, the constants in column (2) were obtained. The fit as indicated by E_ν , is almost as good as with the constants in column (1).

(3) As a special case of (2) one may assume $y_e''\omega_e''$ and $y_e''^i\omega_e''^i$ to be negligibly small. Column (3) shows the results obtained by fitting both the Li^7Li^7 and Li^7Li^6 to second degree equations.

Now the calculated probable errors, E_ν and E_ν^i , indicate that any of the three sets of constants will represent the observed origins rather more accurately than one could have expected from the estimate of experimental probable errors made above ($\pm 0.02 \text{ cm}^{-1}$ in an origin). A choice among them must therefore be made on the basis of considerations other than goodness of the fit. Since the $y_e\omega_e$'s of column (2) satisfy the theoretical condition on their ratio and since they agree with an independent determination of $y_e''\omega_e''$, the other vibrational constants of column (2) are presumably the best values in Table IIa.

Before discussing the value of ρ obtained from the vibrational constants, we will reconsider the data from the $(v', 0)$ progression according to the scheme outlined for the $(0, v'')$ progression. Table IIb gives in column (1) the results of a straight least-squares calculation. Since the fit of the Li^7Li^7 bands to the equation is so surprisingly good ($E_\nu = \pm 0.003 \text{ cm}^{-1}$), $y_e^i\omega_e^i$ was adjusted to $\rho^3 y_e'\omega_e'$ in column (2), and ω_e^i and $x_e^i\omega_e^i$ recomputed. Column (3) shows the constants obtained when the $y_e'\omega_e'$'s are assumed to be negligibly small. As in the case of the $(0, v'')$ progression the constants of column (2) represent the observed origins practically as well as those of column (1) and better than those of column (3). Moreover, they satisfy the condition that $y_e^i\omega_e^i/y_e'\omega_e' \sim (1.04)^3$ which the constants of column (1) do not, and they represent much better than column (3) the trend of the third differences. Column (2) is therefore the best choice. The constants therein do not differ significantly from those published in our previous report of the $(v', 0)$ progression. The errors given in column (2) are probable errors obtained by multiplying E_ν and E_ν^i by the weight factors

appropriate to each constant. In column (3) the errors would be somewhat larger, in column (1) some would be slightly smaller.

The values of ρ obtained from ratios of vibrational constants are also given in Table II. The most accurate values of ρ are obtained from the ratios of the ω_e 's in column (2) and in this column the agreement between $\omega_e''^i/\omega_e''$ and ω_e^i/ω_e' is seen to be excellent. A comparison with column (3), however, shows that the assumption of any pair of constants $y_e\omega_e$ and $y_e^i\omega_e^i$ (at least any pair between the limits set in these columns) which have approximately the correct ratio will lead, in the ratios of the other constants, to sensibly the same values of ρ . The values of ρ in column (1) obtained by using uncritically the constants obtained from a least-squares calculation with the third-degree equation lie somewhat outside the probable errors of column (2), one too high, one too low. We believe it may fairly be said, however, that the same mass coefficient ρ is obtained from the vibrational analysis of each of the two lowest states of Li_2 and that this coefficient is 1.04073 ± 0.00008 .

It should be remarked that if the more elaborate expression for the energy of a rotating vibrator, developed by Dunham,¹⁰ is used the values of the constants are not appreciably changed. The correction terms to B_e and ω_e are, however, large enough to be important if one attempts to evaluate ρ to seven significant figures, instead of six.

The vibrational analysis also leads to the determination of the origin of the two isotopic systems and hence to the electronic isotope shift. In Table II the origins are given as obtained from the least-squares calculation outlined above for each of the columns. The difference $\nu_e^i - \nu_e$ is defined as the electronic shift. Added indication of the superiority of the constants of column (2) lies in the fact that with these constants both progressions extrapolate to practically identical values of ν_e and ν_e^i . The mean electronic isotope shift is $-0.074 \pm 0.025 \text{ cm}^{-1}$.¹¹

¹⁰ J. L. Dunham, Phys. Rev. **41**, 721 (1932).

¹¹ In our previous account we found $\nu_e^i > \nu_e$. Improved constants for the lower state have made possible better values of the origins and it is found that $\nu_e^i < \nu_e$. The contradiction then existing between the values of the electronic shift as obtained by two methods has thus disappeared.

ALTERNATIVE CALCULATION OF ρ AND
ELECTRONIC SHIFT

There is an alternative method of determining ρ and the electronic shift which appears to be superior to the methods which have been discussed. It consists of taking as observed data the total isotope shifts of the band origins and calculating by least squares the values of ρ and $\Delta\nu_e$ which best fit the data. On the experimental side, the advantage of this method is that only isotope *shifts* are involved. The two bands concerned in one observed datum are measured without moving the plate and under nearly identical conditions so that an observed shift, though a difference of two measured origins, is probably correct to ± 0.02 cm^{-1} . The (0,0) and probably the (3,0) bands are exceptions. The former was omitted but the latter was used in this calculation.

The isotope shift of the origin of the (v',v'') band may be written,

$$\begin{aligned} \Delta\nu_0(v', v'') = & \Delta\nu_e + (\rho - 1) \\ & \times \{ [\omega_e'(v' + \frac{1}{2}) - \omega_e''(v'' + \frac{1}{2})] \\ & - (\rho + 1)[x_e'\omega_e'(v' + \frac{1}{2})^2 - x_e''\omega_e''(v'' + \frac{1}{2})^2] \\ & + (\rho^2 + \rho + 1)[y_e'\omega_e'(v' + \frac{1}{2})^3 - y_e''\omega_e''(v'' + \frac{1}{2})^3] \}, \quad (3) \end{aligned}$$

where $\Delta\nu_e = \nu_e^i - \nu_e$ and all of the constants are those of $\text{Li}^7 \text{Li}^7$. Writing the quantity in braces $\{V\}$ we have,

$$\Delta\nu_0(v', v'')/\{V\} = \Delta\nu_e/\{V\} + (\rho - 1). \quad (4)$$

We wish to obtain $\Delta\nu_e$ and $\rho - 1$ by least squares. This requires that we know $\{V\}$. Since it is $(\rho - 1)$, rather than ρ which is the last term in Eq. (4), relatively high accuracy in ρ will be obtained without accurate knowledge of the ρ or the constants appearing in $\{V\}$. It does not matter, for example, which column of constants from Table II is used. Actually the constants of column (2) were used and $\{V\}$ rounded to the nearest integer ($\{V\}$ varies from 200 to 1300). In $\{V\}$, ρ was put at 1.04075; 1.041 would have done as well.

The chief assumption made in this calculation is the usual one in the theory of the isotope effect, that the ratio of each pair of vibrational constants is a power of ρ or, more specifically, that,

TABLE III. $\Delta\nu_e$ and $(\rho - 1)$ from Eq. (3).

BAND	OBSERVED SHIFT $\nu_0^i - \nu_0$	CALCULATED SHIFT Eq. (3)	O - C
($v', 0$) progression: $\rho - 1 = 0.040810 \pm 0.000010$ $\Delta\nu_e = 0.0683 \pm 0.0001 \text{ cm}^{-1}$			
0,0*	-2.014	-2.002	-0.012
1,0	+8.163	8.159	+ .004
2,0	18.053	18.060	-.007
3,0	27.674	27.703	-.029
4,0	37.107	37.093	+ .014
5,0	46.264	46.231	+ .031
(0, v'') progression: $\rho - 1 = 0.040773 \pm 0.000007$ $\Delta\nu_e = 0.0542 \pm 0.0001 \text{ cm}^{-1}$			
0,0*	- 2.014	- 1.987	-0.027
0,1	-15.880	-15.882	+ .002
0,2	-29.354	-29.341	- .013
0,3	-42.356	-42.356	.000
0,4	-54.908	-54.922	+ .014

* Not used in calculation of constants.

in Eq. (3), the factor $(\rho - 1)$ has the same value for each term within the braces that it is to be multiplied into.

The results of the calculations are given in Table III. $(\rho - 1)$ and $\Delta\nu_e$ as obtained from each progression are given as well as the detailed comparison of the observed and calculated shifts. Alternative calculations were made in one of which the observations were weighted approximately according to the magnitude of the shift. In still another calculation of the $(v', 0)$ progression, the observations were thus weighted and the (3,0) band omitted. In each case the changes in $(\rho - 1)$ and $\Delta\nu_e$ were of the order of magnitude of the formally calculated probable errors in Table III.

This method of calculation leads to somewhat higher values of ρ (though within the probable errors) than the earlier methods of comparing constants individually. The probable errors, as judged by internal consistency, of the two values of ρ obtained by the second method are so small as to indicate disagreement between these two values. This discrepancy can be traced to the chief assumption, that in Eq. (3) $(\rho - 1)$ is the same factor for all terms in the braces. Actually $[x_e'^i \omega_e'^i / x_e' \omega_e']^{\frac{1}{2}}$ was found in Table II to differ from $\omega_e'^i / \omega_e'$ by more than the probable errors; if this is actually the case Eq. (3) with a common $(\rho - 1)$ factor is not strictly applicable. The difference of $[x_e'^i \omega_e'^i / x_e' \omega_e']^{\frac{1}{2}}$ and $\omega_e'^i / \omega_e'$ is not definite enough to give the argument much weight but it may signify that there is a slight difference in the potential energy curves of the

TABLE IV. Comparison of determinations of mass ratio.

	ρ	m_7/m_6
McKellar-Jenkins: $\omega_e''/\omega_e'(^1\Pi)$	1.0411 ± 0.0002	1.1678 ± 0.0008
Li ₂ spectrum $^1\Sigma \rightarrow ^1\Sigma$: $\omega_e'^3/\omega_e'$	1.04073 ± 0.00006	
$\omega_e'^3/\omega_e''$	1.040735 ± 0.00008	
$[B_e'^3/B_e']^{\frac{1}{2}}$	1.04114 ± 0.0003	
$[B_e''^3/B_e'']^{\frac{1}{2}}$	1.04077 ± 0.00015	
From isotope shift: $(v', 0)$	1.040810 ± 0.000010	
$(0, v'')$	1.040773 ± 0.000007	
Band spectrum value:	1.04077 ± 0.00004	1.16640 ± 0.00016
Bainbridge (mass spectrograph)		1.16628 ± 0.00010
Olyphant, Kempton and Rutherford (nuclear transformation)		1.16635 ± 0.00005

upper state for the two isotopic molecules. Such considerations would reduce the weight of the calculation of ρ from data on the upper state, especially by the use of Eq. (3). Since the constants of the lower state may be similarly but less affected one cannot claim to have determined ρ to the accuracy indicated by the consistency of the calculations based on Eq. (3). Considering the various determinations of ρ , reviewed in Table IV, one may, however, conservatively conclude that the band spectrum value of ρ is 1.04077 ± 0.00004 .

The electronic shifts calculated from the two progressions by Eq. (3) do not agree within the probable errors suggested by internal consistency. This discrepancy is associated with the similar one found in $(\rho - 1)$. Giving the determinations in column (2), Table II some weight, one may conclude that $\Delta\nu_e = 0.064 \pm 0.010$ cm. This electronic shift, though definite, is probably too small to be discussed in terms of the incomplete theory of electronic shifts in molecular spectra at present available. Kronig has pointed out that even in the absence of rotation there is in the potential energy of Σ states a term $B_e L(L+1)$, which, with B_e , depends upon the reduced mass. For the ground $^1\Sigma$ state of Li₂, arising from $^2S + ^2S$ atomic states, L must be zero. The excited $^1\Sigma$ state, however, arises from $^2P + ^2S$ Li atoms and is presumably $\dots 2\rho\sigma 2p\sigma^1\Sigma$ for which $L=1$. Hence there should be a difference in the electronic energies of the two isotopic molecules equal to $2(B_e'^L - B_e^L)$ or about 0.08 cm⁻¹, and the

Li⁷ Li⁶ state should lie higher. Actually, if one assumes the observed shift to be entirely in the upper state, the Li⁷ Li⁶ state lies about 0.06 cm⁻¹ lower. But until other small effects (see Kronig) on the electronic energy can be calculated, significance can hardly be attached to this discrepancy with theory. One must, for example, consider the fact that there is an isotope shift of about 0.35 cm⁻¹ in the $^2P \rightarrow ^2S$ atomic lines of Li,¹² the Li⁷ lines being of greater frequency. That is to say, the products of dissociation of Li⁷ Li⁷ and Li⁷ Li⁶ have an isotope effect several times as large and in the same direction as the molecular electronic effect.

Note added to proof, December 6, 1935: Professor F. A. Jenkins has informed us of the results of recent measurements on the $^1\Sigma \rightarrow ^1\Sigma$ system of Li₂ bands made by him and Dr. McKellar for the purpose of testing our conclusion⁸ as to the value of ρ . Their results were reported at the Berkeley meeting of the Physical Society, December 20, 1935. Using the same bands but a different method of handling the data they secure values of ρ : $\omega_e'^3/\omega_e' = 1.04100$ and $\omega_e'^3/\omega_e'' = 1.04107$, lower than their previous estimates from the blue-green system but still higher than our present values. The remaining discrepancy is ascribed by them to the difference in the methods of handling the data. Their method has been described by McKellar.⁴ It consists in forming differences such as $\Delta T''_{v+\frac{1}{2}}(K) = R^{v', v''}(K'') - R^{v', v''+1}(K'') = P^{v', v''}(K'') - P^{v', v''+1}(K'')$ which are equal to $\Delta G''_{v+\frac{1}{2}} - \alpha_e''(K'' + \frac{1}{2})^2$ for not too large K'' . From the series of $\Delta G''$'s the vibrational constants are obtained.

To test our data by this method we have formed the differences $\Delta T''(K'')$ for the $(0, v'')$ progressions of the bands of both kinds of molecules, added the correction terms $\alpha_e''(K'' + \frac{1}{2})^2$, using our α_e'' 's from Table I, to get values of $\Delta G''_{v+\frac{1}{2}}$. The average $\Delta G''_{v+\frac{1}{2}}$ so obtained is, for each vibrational interval, exactly equal to the corresponding quantity obtained by taking the difference between origins in Table I; the greatest discrepancy is less than 0.02 cm⁻¹. Hence with our data, limited to low K , the two methods should give identical values of ρ , at least in the case of the $(0, v'')$ progression. The small remaining discrepancy in ρ then appears to be due to the fact that Jenkins and McKellar make use of lines of larger rotational quantum number while we use lines of $K < 13$, which provide ample data for exact analysis and which do not involve any complication which might arise from rapid rotation of the molecule.

¹² H. Schüler and E. Wurm, Naturwiss. **15**, 971 (1927); D. S. Hughes, Phys. Rev. **36**, 698 (1930); *ibid.* **38**, 857 (1931).