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The Band Spectra of the Hydrides of Lithium

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About 1000 lines, comprising 26 bands, of Li^{7}H have been remeasured and given quantum assignments. The experimental arrangements are similar to those given in Part I on Li^{7}D. The corresponding $\Delta_2F_v(J)$ values have been represented as polynomials of the usual form in $J(J+1)$, where the ground state data are represented to within ±0.018 and the upper state data to within ±0.021 cm^{-1} (i.e., to within roughly ±0.0024A for the whole spectrum). **Constants.** Important constants for the ground state are $B_e''=7.5131$, $D_e''=-8.617\times10^{-4}$, $H_e''=11.4\times10^{-8}$, $\omega_e''=1405.65$, $x_e''\omega_e''=+23.20$ and $y_e''\omega_e''=+0.1633$; corresponding constants for the upper state although less certain because of the errors of extrapolation (which are greater than for LiD) are in order 2.8186, 15.8×10^{-4}, $100(\pm30)\times10^{-8}$, 234.41, -28.95 and -4.185. The constants for the ground state show a small discrepancy between ρ and ω_e^i/ω_e, and ρ^2 and B_e^i/B_e. In fact from these two ratios we find $\Delta\rho=+0.000143$ (±0.00003) and $\Delta\rho=+0.00020$ (±0.00006), where the plus sign indicates the fact that the observed ρ's are these amounts *greater* than the atomic mass ρ values. Consideration of Dunham's higher order calculation of the interaction of vibration and rotation accounts for about 1/3 of the discrepancy in the ρ from the ratio of the B_e's. The vibrational numbering adopted here agrees with Nakamura's and is such that the maxima in the B_v' and $\Delta G'(v+1)$ curves occur at energies which are approximately the same for the LiH and the LiD molecule. We find *no evidence* of *l*-uncoupling and feel that the anomaly of the upper state is to be ascribed to an anomalous potential curve. The *electronic origin isotope shift* of this ($^1\Sigma\rightarrow{}^1\Sigma$) system of LiH is 0.0($\pm0.5$) cm^{-1}.

INTRODUCTION

In a previous paper of the same title as the present (Part I[1]) the authors have presented the results of observations on the absorption spectrum of Li^{7}D. The corresponding spectrum of Li^{7}H having been reexamined in similar detail, the numerical results and intercomparisons will form the subject matter of the present paper. A more detailed examination of the potential curves of the two molecules is reserved for Part III.

The *absorption* photographs were made with the same apparatus as previously employed and under similar conditions, where, however, because of the more open nature of both the vibrational and rotational structure of the Li^{7}H bands a somewhat greater range of temperatures was employed. The higher temperatures and the lighter mass of the molecule both rendered the lines somewhat broader and therefore increased the difficulty of precise measurement. This was in part compensated for by measuring each lower state progression of bands on plates taken at temperatures just adequate for developing the lines in question. In any event the maximum J, v' and v'' values observed for Li^{7}H were in order, 18, 14 and 3 as against 25, 18 and 4 for Li^{7}D. The smaller number of rotational lines observable in a branch of course renders the higher coefficients in the rotational energy expression more uncertain in the present than the former case. On the other hand it was possible to obtain several well developed bands involving the $v'=1$ state and one rather faint band involving the $v'=0$ state. Furthermore, since the upper $^1\Sigma$ state involves a larger molecular radius than the lower $^1\Sigma$ state it is apparent that $(0,v'')$ bands should be more strongly developed in *emission* than absorption. Accordingly several emission photographs were made with a metallic lithium arc burning in hydrogen. These were quite difficult to obtain because of the general faintness and the frequent delays for replenishing the evaporated lithium. One 24-hour and one 6-hour exposure, however, gave the (0,5) and (0,6) bands with satisfactory intensity. Comparison of measurements on the two plates showed unfortunately a shift of about 0.10 cm^{-1}. Since this shift was quite small and fairly uniform

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[1] Crawford and Jorgensen, Phys. Rev. **47**, 358 (1935). In this connection the following corrections should be made in Part I (as the result of subsequent remeasurement). In Table IV for $v''=3$, $H_v''\times10^{+8}$ should be 1.6 instead of 1.85 and the average deviation ±0.20 instead of ±0.027. This then requires that Eq. (14) now read:

$$H_v''\times10^8=2.006-0.090(v''+\tfrac{1}{2})-0.005(v''+\tfrac{1}{2})^2(\pm0.01).$$

Also the horizontal scale readings for the insert in Fig. 3, except for the value $v''=-\tfrac{1}{2}$, should be *lowered* by unity.

TABLE I. *Vacuum frequencies of* $^1\Sigma-{}^1\Sigma$ *bands of* Li^7H.

	(2–2) BAND 22,000 cm^{-1}		(4–2) BAND 22,000 cm^{-1}		(5–1) BAND 24,000 cm^{-1}		(6–1) BAND 25,000 cm^{-1}		(10–0) BAND 27,000 cm^{-1}		(11–0) BAND 28,000 cm^{-1}		(13–0) BAND 28,000 cm^{-1}	
J	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
0	1868.26	—	2556.74	—	—	—	1612.99	—	2524.75	—	1915.76	—	2690.73	—
1	—	1848.52	554.43	—	2234.62	2217.31	610.12	—	521.02	2504.44*	911.86	1895.48	686.51	2670.60
2	855.33	826.38	543.83	2514.92	223.15	194.32	598.57	1569.85	508.02	480.35	898.61	871.34	672.66	646.27
3	836.56	796.12	525.16	484.66	—	162.83	578.52	538.28	485.70	447.07	876.00	837.94	649.35	612.48
4	809.61	757.81	498.28	446.36	174.56	122.71	549.69	498.20	454.18	404.60	844.06	795.26	616.54	569.25
5	774.47	711.46	465.21	400.03	137.37	074.35	512.25	449.62	413.41	352.98	802.85	743.30	574.26	516.69
6	—	657.07	420.38	345.70	091.69	2017.43	466.48	392.56	363.56	292.39	752.40	682.29	522.57	454.75
7	679.70	594.71	368.91	283.44*	2037.46	1952.17	412.05	327.16	304.43	222.72	692.77	612.20	461.50	384.07?
8	620.08	524.40	309.65	213.43*	1974.83	878.64	349.20	253.49	236.34	144.14	624.04	533.21	391.14	303.30
9	552.32	446.20	242.42	135.44	903.76?	796.97	277.93	171.59	159.24	2056.74	546.20	445.12	311.58	213.83
10	476.48	360.19	167.24	2049.80	824.43	707.12	198.41	1081.51	2073.27	1960.72	459.39	348.26	222.83	—
11	392.56	266.41	2084.19	1956.76	736.83	609.61	110.53*	0983.53	1978.52	855.93	363.56*	242.95	125.02	2008.21
12	300.67	164.93	1993.34	855.72	641.05	503.50	1014.59	877.39	876.39	742.87*	259.30	128.83	2018.36	1892.27
13		1055.80	894.74	747.42	537.22	389.86	0910.43	763.58	762.97	621.19	146.15	1006.38	1902.82	767.74
14	1093.05	0939.11	788.46	631.78	425.38	268.57	798.48	642.03	642.39	—	1024.52	0874.99?	778.56	634.71
15	0977.42	815.00	674.67	508.87	305.68	140.05	—	513.29	513.47	353.05	0894.44	—	645.75	493.27
16	854.04	683.40*	552.82	378.81	178.15	1003.26	551.00	376.33	376.34	207.59	756.02	—	504.44*	343.67
17	722.98	544.50	424.68	—	1042.90	0859.45	415.65		231.06	1053.84			354.81	186.02
18	584.34		288.71	1097.64	0900.22	708.48			1077.87	0892.44			197.03	1020.56
19			1145.59	0946.50*	750.03	550.42			0916.94	723.59			1031.23	0847.28
20			0995.44	789.33	592.54	385.41			747.87*				0858.90*	666.54
21			838.42	625.24	427.64*	213.43*							676.27	
22			674.59		256.26									

it was not thought that it could affect the accuracy of the $\Delta_2F(J)$ values appreciably. Accordingly the $\Delta_2F(J)$ values accepted for final computation of the rotational constants of the $v'=0$ state were averages of the absorption and emission results. The emission spectra being less sharp and involving much more superposition (both due to the higher temperatures involved), the emission data were not employed elsewhere.

All told the vacuum frequencies of about 1000 lines were determined including 13 bands of the $(v',0)$, 6 of the $(v',1)$, 5 of the $(v',2)$, 2 of the $(v',3)$ progressions and one faint band each of the $(v',5)$ and $(v',6)$ progressions. In general the results agree with those of Nakamura[2] made at a much lower dispersion, but individual assignments of lines differ considerably and vacuum frequencies often by several cm^{-1}. In some cases indeed we have been forced to conclude that certain of Nakamura's bands (notably the (0,2) band) were merely accidental sequences of lines, many being unresolved superpositions, which on our plates are resolved and obviously members of entirely different bands. The result of course is to involve considerable differences in the molecular constants and computed origins (see Table VIII. Also compare column 2 of Table XI with Tables VII and VIII of Part I). In general, however, the differences are only such as the higher dispersion and the constant use of densitometer results would cause. Actually the densitometer records made on plates taken at a series of temperatures were, as in the case of LiD, of the very greatest aid in the analysis of the plates, enabling correct rotational assignments in a majority of cases to be made *de novo* from the records before any actual vacuum frequencies had been determined.

In Table I are recorded vacuum frequencies of some of the stronger bands of Li^{7}H (corresponding to the data in Table I, Part I for Li^{7}D), where as before the number at the head

TABLE II. *Values of* $\Delta_2F_0''(J)$.

J	(10,0) BAND	(13,0) BAND	AVERAGE OF ALL $(v',0)$ BANDS	AVE. OBS.
1	44.40	44.46	44.43	−0.022
2	73.93	—	73.94	+ .005
3	103.42	103.41	103.39	− .008
4	132.72	132.66	132.66	− .014
5	161.78	161.79	161.78	+ .004
6	190.69	—	190.68	− .004
7	—	219.27	219.27	+ .039
8	247.69	247.67	247.65	− .009
9	275.62	—	275.64	+ .005
10	303.31	303.37	303.28	± .000
11	—	330.56	330.56	− .043
12	357.30	357.28	357.34	− .014
13	—	383.65	383.67	+ .001
14	—	409.55	409.54	− .010
15	434.80	434.89	434.86	+ .011
16	459.63	459.73	459.69	− .005
17	483.90	—	483.91	+ .029
			Ave.	±0.013

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[2] Nakamura, Zeits. f. Physik **59**, 218 (1930).

of each pair of columns is to be *added* to the figures below to give the vacuum frequencies of the desired branch lines. This includes about one-fourth of the measured lines.

ROTATIONAL CONSTANTS

As in Part I the corresponding $\Delta_2F_v(J)$ values were computed and expressed as

$$\Delta_2F_v(J)=[B_v-3/2D_v+\cdots]4(J+\tfrac{1}{2})$$
$$-[2D_v-17/2H_v]4(J+\tfrac{1}{2})^3+12H_v(J+\tfrac{1}{2})^5+\cdots \quad (1)$$

or more simply

$$\frac{\Delta_2F_v(J)}{4(J+\frac{1}{2})}=a_v^0-a_v^1(J+\tfrac{1}{2})^2+a_v^2(J+\tfrac{1}{2})^4, \quad (2)$$

where the intercept of the curve of experimental $\Delta_2F/4(J+\frac{1}{2})$ values against $(J+\frac{1}{2})^2$ with the $(J+\frac{1}{2})^2=0$ axis gave a_v^0. Here, however, because of the larger numerical values obtained for LiH it was not feasible to determine a_v^1 and a_v^2 from the same graph. Actually it was just as rapid and rather easier to plot a second curve with

$$[\Delta_2F_v(J)/4(J+\tfrac{1}{2})-a_v^0]/(J+\tfrac{1}{2})^2$$

as ordinates and $(J+\frac{1}{2})^2$ as abscissae. The intercept of this second curve at $(J+\frac{1}{2})^2=0$ then of course gave a_v^1 and its slope a_v^2. When the coefficient a_v^2 was large it was then often desirable to replot

$$[\Delta_2F_v(J)-4a_v^2(J+\tfrac{1}{2})^5]/4(J+\tfrac{1}{2})$$

and obtain a more trustworthy value of a_v^0 and hence better a_v^1 and a_v^2 values by the second step. From these constants "theoretical" Δ_2F_v values were computed and the differences between these and the observed Δ_2F_v values determined. Occasionally where small systematic deviations seemed to be present a better representation was then obtained by slight empirical adjustments of the constants. This at times indicated that too much graphical "weight" had been given to values of $\Delta_2F(J)$ (for low J values usually) which were computed from very faint and uncertain lines. In any case the amount of adjustment possible without perceptible alteration of the accuracy of representation of the data, gave a rough indication of the reliability of the constants themselves. Here again as an illustration of the accuracy of the representations two typical sets of measured Δ_2F values are given in Tables II and III with deviations from the computed values in the last column. The values of B_v, D_v and H_v for the ground $^1\Sigma$ state and the upper $^1\Sigma$ state of Li^{7}H are given in Tables IV and V. Here the average deviations of observed and calculated Δ_2F values are recorded in the last column of each table. The average deviations are for the ground state ±0.018 cm^{-1}

TABLE III. *Values of* $\Delta_2F_8'(J)$.

J	OBS. $\Delta_2F_8'(J)$	OBS. −CALC.
1	(16.95)	+0.036
2	28.26	+ .015
3	39.52	− .003
4	50.71	− .025
5	61.80	+ .018
6	72.75	− .008
7	83.57	+ .007
8	—	—
9	104.80	+ .018
10	115.20	− .030
11	125.36	− .033
12	135.28	− .014
13	145.03	− .003
14	—	—
15	—	—
16	172.50	+ .030
		Ave. ±0.019

TABLE IV. *Rotational constants for lower* $^1\Sigma$ *state of Li*^{7}*H.*

v''	B_v''	$-D_v''\times10^4$	$H_v''\times10^8$	(AVE. Δ_2F_v'' CALC. $-\Delta_2F_v''$ OBS.)
$(-\frac{1}{2})$	(7.5131)	(8.617)	(11.4)	
0	7.4067	8.537	11.08	±0.012
1	7.1950	8.377	10.25	± .015
2	6.9848	8.216	9.17	± .014
3	6.7782	7.95	7.8	± .029
			Ave.	±0.018

TABLE V.

v'	B_v'	$-D_v'\times10^{-4}$	$H_v'\times10^8$	AVE. Δ_2F' CALC. $-\Delta_2F'$ OBS.
$(-\frac{1}{2})$	(2.8186)	(15.8)*	(100±30)	
0	2.8536	11.87	93.	±0.019
1	2.8897	7.837	23.6	.012
2	2.9044	6.295	10.9	.017
3	2.9083	5.477	7.47	.012
4	2.9057	5.039	6.23	.017
5	2.8959	4.73	5.42	.020
6	2.8804	4.51_3	5.05	.026
7	2.8589	4.30_6	4.04	.015
8	2.8333	4.19	4.08	.019
9	2.8022	4.05	3.4	.032
10	2.7707	4.10	4.87	.027
11	2.7322	4.07	5.2	.022
12	2.6895	4.07	6.3	.016
13	2.6442	4.17	7.2	.031
14	2.5942	4.12	6.67	.023
			Ave.	±0.021

* or 16.3×10^{-4} (see text).

and for the excited state ±0.021 cm^{-1}, indicating an uncertainty substantially that of the data in Part I.

The rotational constants of Table IV are represented by the following expressions (where $u=v+\frac{1}{2}$):

$$B_v''=7.5131-0.2132u+0.00075u^2, \tag{3}$$

$$-10^4\times D_v''=+8.617-0.1590u-0.0005u^2, \tag{4}$$

$$10^8\times H_v''=11.40-0.58u-0.125u^2. \tag{5}$$

The uncertainties in the values of B_v'', D_v'' and H_v'' are estimated as roughly ± 0.0003, $\pm 0.01 \times 10^{-4}$ and $\pm 0.1\times 10^{-8}$, respectively.

To test Kratzer's relation,

$$-D_e=4(B_e)^3/\omega_e^2 \tag{6}$$

values of $4B_v^3/\omega_v^2$ were plotted against v and extrapolated to $v=-\frac{1}{2}$, and a similar procedure was used for testing Birge's approximate relation,[3]

$$H_e=(D_e/B_e)(2-\alpha\omega_e/6B_e^2). \tag{7}$$

TABLE VI. *Theoretical relations among ground state constants of Li⁷H and Li⁷D.*

THEOR. EQ.	CONST.	Li⁷H OBS.	Li⁷H COMP.	Li⁷D OBS.	Li⁷D COMP.
(6)	$-D_e''\times 10^4$	8.617	8.586	2.756	2.728
(7)	$H_e''\times 10^8$	11.4	11.0	2.07	1.97
(8)	$-\alpha_1$	0.2132	0.2478	0.09198	0.1062
(9)	$-\alpha_1$	0.2132	0.1823	0.09198	0.0782
(10)	$\beta_1\times 10^4$	0.159	0.139	0.066	0.034

The results are given in Table VI (where similar results for $\mathrm{Li^7D}$ are included). In Table VI are also included computed values of α_1 (the coefficient of u in Eq. (3)), from Kratzer's approximate relation[4]

$$\alpha_1=2B_ex_e \tag{8}$$

as well as from a more recent expression given by Pekeris,[5]

$$\alpha_1=2x_eB_e[3(B_e/x_e\omega_e)^{\frac{1}{2}}-3(B_e/x_e\omega_e)] \tag{9}$$

and in addition values of β_1 (the coefficient of u in Eq. (4)) from the approximate relation given by Birge.[3]

$$\beta_1=D_e[\omega_e\alpha_1^2/24B_e^3+5\alpha_1/B_e-8x_e]. \tag{10}$$

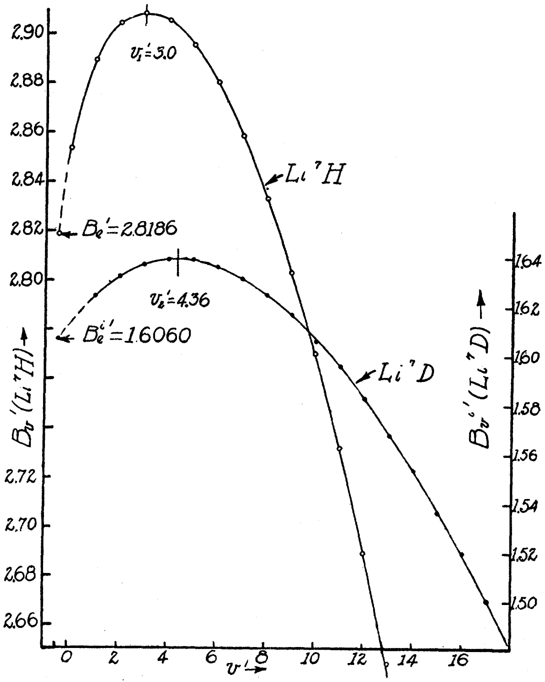

FIG. 1. Curves of B_v'' for $\mathrm{Li^7H}$ and $\mathrm{Li^7D}$. The extraordinarily rapid rise and fall of the first curve is particularly noteworthy. The maxima of the two curves occur at approximately the same energy as we should expect if the anomalous B_v behavior is to be ascribed entirely to peculiarities in the potential energy curve. Here $(v_1'+\frac{1}{2})\approx\rho(v_2'+\frac{1}{2})$.

It is to be noted that Eq. (6) is satisfied to within almost the experimental uncertainty and that the agreement of results with Eqs. (7) and (10) is probably as good as the approximations underlying their theoretical deduction and the experimental uncertainty would warrant. On the other hand Eq. (8) gives values as much above the observed ones as Eq. (9) does below. This fact will be considered later.

The rotational constants of the upper $^1\Sigma$ state of $\mathrm{Li^7H}$ vary even more radically with vibration than do those of $\mathrm{Li^7D}$, in fact so rapid is the change for low values of u that least-squares expressions computed for the observed range of vibration are of very little theoretical value. In order, however, to obtain approximate values for B_e', D_e' it was necessary to obtain such expressions for a small range of v' values near the origin. Actually the constant terms so determined depend rather strongly on the precise

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[3] Bull. Nat. Res. Counc. (Ed. by E. C. Kemble, 1926), p. 237; Birge, Nature **116**, 783 (1925).

[4] Kratzer, Zeits. f. Physik **3**, 289 (1920).

[5] Pekeris, Phys. Rev. **45**, 98 (1934).

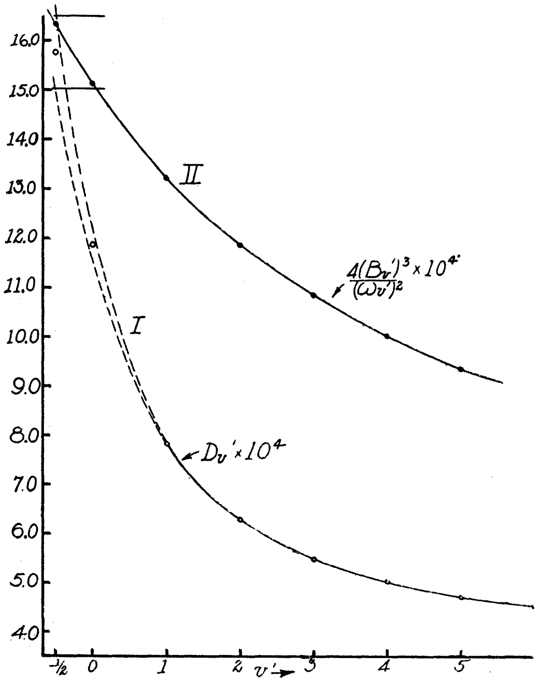

FIG. 2. Test of Kratzer's Eq. (6) for Li^{7}H. Here the dotted curves are drawn from least-squares curves computed from the first 7D_v' values with $D_0'=(11.87+0.3)\times 10^{-4}$ and $(11.87-0.3)10^{-4}$, respectively. Since the extrapolation is so uncertain we can only infer that Kratzer's relation is approximately true.

number of observations used and are in consequence much more in doubt than the general precision of the data would suggest.

The expression for B_v' for LiH (with the first 6 values) is

$$B_v'(\text{LiH})=2.8186+0.078305u-0.026271u^2+0.0041648u^3-0.000275u^4 \quad (11)$$

where the uncertainty in B_e' may be as high as ±0.005. (See Fig. 1 where B_v' for LiH and LiD are shown for comparison.)

The same difficulty arises in a more aggravated way in attempting to test Kratzer's Eq. (6). We have, however, proceeded as in the case of Li^{7}D, estimating the uncertainty of D_1' as $\pm 0.5\times 10^{-4}$ and drawing the dotted extrapolations in Fig. 2 curve I of the experimental results (with the first 7 points only). It is seen that at $v=-\frac{1}{2}$ curve II falls well within the dotted branches of I. Despite the irreducible uncertainty involved in such a process we feel justified in assuming that there is no experimental evidence of the failure of Eq. (6) and hence of the presence of l-uncoupling. We may therefore presume to take as the most likely value of D_e', the intercept of curve II, giving $D_e'=16.3\times 10^{-4}(\pm 0.1)$.[6]

The values of H_v' (for LiH) exhibit an even more marked variation with v' than do those of D_v', and because of the much greater uncertainty of H_1' (say $\pm 20\times 10^{-8}$) least-squares curves are meaningless. Here the actual numerical intercepts at $v'=-\frac{1}{2}$ (for LiD) of Eq. (7) with subscript v replacing e certainly agree to within the error of the extrapolation with the extrapolation of the H_v' values and fall within the same range for LiH. This may be taken as further evidence of the mechanical significance of H_e' and hence of the absence of l-uncoupling.

VIBRATIONAL CONSTANTS

From the rotational constants the band origins were computed as before and the frequencies given in the usual square array. These origins are given in Table VII (and for comparison in Table VIII the differences between origins as observed by us and as reported by Nakamura) where the *vertical* and *horizontal* differences are in italics and are, respectively, $\Delta G''(v+\frac{1}{2})$ and $\Delta G'(v+\frac{1}{2})$. The former are given precisely by

$$\Delta G''(v+\tfrac{1}{2})=1405.649-2\times 23.200(u+\tfrac{1}{2})+3\times 0.1633(u^2-u+\tfrac{1}{3}), \quad (12)$$

where

$$\Delta G=\omega_e-2x_e\omega_e(u+\tfrac{1}{2})+3y_e\omega_e(u^2-u+\tfrac{1}{3}). \quad (13)$$

The values of $\Delta G'(v+\frac{1}{2})$ in contrast, increase very rapidly with v', attain a maximum at about $v'=10$ and thereafter decrease. Fig. 3 shows the curves for LiH and LiD, where maxima occur at approximately the same energy values. The fact that this curve rises so rapidly at the start (especially for LiH) makes the meaning of the constants of a polynomial representation in u even less significant than in the case of B_v curves. If we use the least-squares method for expressing the results in the form

$$\Delta G'(v+\tfrac{1}{2})=\omega_e-2x_1(u+\tfrac{1}{2})+3x_2(u^2-u+\tfrac{1}{3})+\cdots \quad (14)$$

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[6] The same procedure in Part I gives $D_e'(\text{LiD})=5.0\times 10^{-4}(\pm 0.1)$ as against the rougher value $4.8\times 10^{-4}(\pm 0.3)$ given there.

TABLE VII.

	V''				ORIGINS OF $^1\Sigma\rightarrow{}^1\Sigma$ BANDS OF Li^{7}H		
v'	0		1		2		3
0					23268.52		
					280.96		
1			24864.32	*1314.84*	23549.48		
			312.97		*312.96*		
2	26537.02	*1359.73*	25177.29	*1314.85*	23862.44	*1270.89*	22591.55
	335.76		*335.73*		*335.71*		*335.69*
3	26872.78	*1359.76*	25513.02	*1314.87*	24198.15	*1270.91*	22927.24
	352.80		*352.78*		*352.80*		
4	27225.58	*1359.78*	25865.80	*1314.85*	24550.95		
	365.83		*365.87*				
5	27591.41	*1359.74*	26231.67				
	375.64		*375.56*				
6	27967.05	*1359.82*	26607.23				
	382.68						
7	28349.73						
	387.55						
8	28737.28						
	390.37						
9	29127.65						
	391.59						
10	29519.24						
	391.05						
11	29910.29						
	389.19						
12	30299.48						
	385.94						
13	30685.42						
	381.32						
14	31066.74						

then the values of ω_e, x_1, x_2, etc., depend unfortunately very largely on how much data are used (and on the number of the terms in the expansion—which from practical consideration of labor is limited to the term in x_5). Below (Table IX) are given the results for LiH and LiD when the values of $\Delta G'$ for the first 5 and 7 available values are used[7] (and in the latter case when all the data are used). The differences indicate clearly to what extent the molecular constants for the upper state must remain in doubt—at least until some theoretical expression better suited to this state than a power series, is available. We have, therefore, provisionally taken the constants based on the first $7\Delta G'$ values as the most probable ones. On this basis the system origin for LiH is 26,516.24 cm^{-1} and for LiD 26,513.70 where, however, the values themselves are uncertain to several cm^{-1} and hence even the *sign* of the difference is in doubt. [It should be emphasized at this point that this

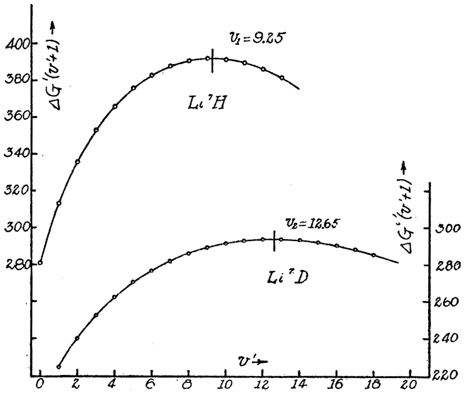

FIG. 3. $\Delta G'(v'+1)=G'(v+3/2)-G'(v+\frac{1}{2})$ for Li^{7}H and Li^{7}D. The large slope of the first curve near the origin renders the actual value of the upper state vibrational constants considerably in doubt. As in the case of the B_v' curves, the maxima occur at almost exactly the same energy values, i.e., $G'(v+\frac{1}{2})=G^{i\prime}[\rho(v+\frac{1}{2})]$ and approximately $\Delta G'(v+1)=(1/\rho)\Delta G^{i\prime}[\rho(v+1)]$. Hence we expect to find $(v_1+1)=\rho(v_2+1)$ and actually v_2 calculated is 12.7 compared with 12.65 from the curve. (The maximum is obtained in each case quite precisely by plotting the first-difference curve.)

TABLE VIII. *Comparison of band origin as measured by us (C and J) and as measured by Nakamura (N).*

BAND	$(C+J)-N$ cm^{-1}	BAND	$(C+J)-N$ cm^{-1}	BAND	$(C+J)-N$ cm^{-1}	BAND	$(C+J)-N$ cm^{-1}
(2–0)	−1.29	(1–1)	+0.02	(8–0)	−1.52	(0–2)*	+5.92
(3–0)	−2.02	(2–1)	−0.51	(9–0)	−0.15	(1–2)	+0.18
(4–0)	−0.22	(3–1)	−0.28	(10–0)	—	(2–2)	+0.18
(5–0)	−0.79	(4–1)	+1.00	(11–0)	+1.09	(3–2)	+0.35
(6–0)	−0.15	(5–1)	−1.13	(12–0)	+0.38	(4–2)	+1.05
(7–0)	−1.27	(6–1)	—	(13–0)	+0.32		
				(14–0)	+1.74		

* Reported as uncertain by Nakamura.

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[7] Fifth power least-squares calculations, in an attempt to represent the LiH data from $v'=0$ to $v'=14$, gave values differing in a regular oscillatory fashion from the observations—as they did when the same process was carried out for the *first differences* of the $\Delta G'$ values.

TABLE IX. *Vibrational constants for LiH and LiD (upper state).*

ΔG Values used		ω_e	x_1	x_2	x_3	x_4	x_5
LiH	5	235.16	−28.0093	−3.64188	+0.347292	−0.01592	—
	7	234.413	−28.9474	−4.18486	+0.506467	−0.038833	+0.0012847
LiD	5	182.776	−12.6764	−0.782500	+0.20417	− .00033333	—
	7	180.711	−13.9871	−1.17839	+ .079316	− .0035303	+ .00006940
	16	183.1246	−12.74161	−0.8778501	+ .04261680	-1.332244×10^{-3}	$+1.808235\times10^{-5}$

The constants in the *second* and *fourth* row are taken as being the most likely values.

effect is not assignable to experimental uncertainties since curves of the 1st, 2nd, 3rd and 4th differences of the observed $\Delta G'$ values are quite smooth and regular. In addition the bands involving $\Delta G'(1)$ as well as those involving $\Delta G'(12)$, $\Delta G'(13)$ and $\Delta G'(14)$ were remeasured on new plates with results coincident to ±0.02 cm^{-1} with those obtained earlier.]

ISOTOPE EFFECT IN THE GROUND STATE

As Kemble and Van Vleck have shown,[8] as long as the potential curves of a molecule (LiH) and its isotope (LiD) can be regarded as identical, the general molecular constants in the complete energy expression in frequency units written as

$$E/hc=\sum_{l=0,\,1}\ \sum_{j=0,\,1\cdots} Y_{lj}(v+\tfrac{1}{2})^l[J(J+1)]^j \quad (15)$$

can be related for the two molecules, in the simple form:

$$Y_{lj}{}^i/Y_{lj}=(\mu/\mu^i)^{(l+2j)/2}=\rho^{(l+2j)}, \quad (16)$$

where μ and μ^i are the respective reduced masses of the normal molecule and the isotope and $\rho=(\mu/\mu^i)^{\frac{1}{2}}$ and where further l and j are simply the powers of $(v+\frac{1}{2})$ and $J(J+1)$ in the particular term of Eq. (15) which is under consideration.[9] Thus Y_{10} corresponds to ω_e, Y_{01} to B_e, Y_{20} to $x_e\omega_e$, Y_{02} to α_1, etc. Hence Eq. (16) expresses simply the powers of ρ required for, in our case, converting the constants of LiH to those of LiD. We shall say that any case for which Eq. (16) holds is covered by the "simple isotope theory."

On this basis Table X was constructed where column 1 gives the constant involved, column 2 the power of ρ and column 3 its numerical value, column 4 the observed constant for Li^7H, column 5 this multiplied by the number in the preceding column (3) and column 6 the observed constant for Li^7D. Finally column 7 gives the amount by which the theoretical value of ρ would have to be *increased* to cause coincidence of the numbers in columns 5 and 6. Since this quantity, say $\Delta\rho$, is small, it can only be ascertained with precision actually from the ω_e's and the B_e's. It is, however, to be noted that in all save three cases (H_e'', β_2'' and γ_2'', β_2'') the numbers in column 5 are *too small.* In the three exceptions the differences are well within the experimental error.

This failure in the simple isotope theory has been noted by a number of observers,[10–13] where the corresponding values (for the ground states) of $\Delta\rho$ as obtained from $B_e{}^i/B_e$ are: For AlH ($^1\Sigma$) $\Delta\rho=+0.00034$, for CaH ($^2\Sigma$) $\Delta\rho=0.00061$, for NaH ($^1\Sigma$) $\Delta\rho=+0.00023$ and for BeH ($^2\Sigma$) $\Delta\rho=+0.00025$. The corresponding values from the ratio $\omega_e{}^i/\omega_e$ are only available for AlH and NaH and are, respectively, +0.00041 and +0.00013. The values of +0.00020±0.00006 and +0.00014±0.00003 from the B_e and ω_e ratios, respectively, for LiH are thus of the same general order of magnitude.

Now in the first place it was thought that part of the discrepancy might be due to the use of an inaccurate value of the atomic mass of H, since according to a recent announcement of Oliphant and Kempton[14] this value should be raised from 1.0778 to 1.00810. This would cause the ρ computed from $(\mu/\mu^i)^{\frac{1}{2}}$ to increase by +0.00013 provided the accepted value of $D=2.01363$ were retained. Actually, however, this

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[8] E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).

[9] See Dunham, Phys. Rev. **41**, 721 (1932) for more details of this compact and useful notation.

[10] Hulthén and Holst, Zeits. f. Physik **90**, 712 (1934); (AlH).

[11] Watson, Phys. Rev. **46**, 319, 939 (1934); (CaH).

[12] E. Olsson, Zeits. f. Physik **93**, 206 (1934); (NaH).

[13] Koontz, Bull. Am. Phys. Soc. **10**, 14 (1935); (BeH).

[14] Oliphant and Kempton, Proc. Roy. Soc. (current issue) reported in Science **81**, No. 2099, Supplement p. 6.

TABLE X. *Molecular constants of ground state.*

MOLECULAR CONSTANT	CONVERSION FACTOR		LiH	LiH	LiD	$\Delta\rho$
	ρ^n	NUMERICAL VALUE	OBS.	$\times\rho^n$	OBS.	
ω_e''	ρ	0.750486	1405.649	1054.919	1055.12	0.00014 ±.00003
x_1''	ρ^2	.563227	+23.20	13.067	13.23	
x_2''	ρ^3	.422694	+0.16333	0.0690	0.13	
B_e''	ρ^2	.563227	7.5131	4.2316	4.23384	.00020 ±.00006
α_1''	ρ^3	.422694	−.2132	−.09012	−.09198	
α_2''	ρ^4	.317225	+.00075	.00024	.00067	
$D_e''\times10^4$	ρ^4	.317225	−8.617	−2.7335	−2.756	
$\beta_1''\times10^4$	ρ^5	.238073	+0.159	+.03785	.066	
$\beta_2''\times10^4$	ρ^6	.178670	+.0005	+.000089	−.006	
$H_e''\times10^8$	ρ^6	.178670	+11.4	+2.037	2.006	
$\gamma_1''\times10^8$	ρ^7	.134089	−.58	−.078	−.090	
$\gamma_2''\times10^8$	ρ^8	.100632	−.125	−.0126	−.005	

change produces no effect on the ratio H : D since the masses of H and D were both measured by comparison with He and hence raising H to 1.00810 raises D to 2.01423.[15] Thus the change introduced in ρ is a second order quantity. Quite recently and independently Bethe[16] has proposed a revision of the ratio of He^4 to O^{16}. He therefore determines a new set of atomic masses which includes H = 1.00807, D = 2.01423 and $Li^7 = 7.01694$. These values actually influence our ρ slightly since Li^7 was referred to O^{16}.[15] These new values give $\rho = 0.750481$ as against 0.750486, a difference which is almost inappreciable in this connection. We therefore conclude that the discrepancies in ρ of +0.00020 and +0.00014 are real. It should further be emphasized that although these values of the discrepancy, $\rho^* - \rho$, differ by no more than the experimental error involved (in the former, which is the less accurate of the two) they are not necessarily measures of the same thing.

In general for the simple isotope theory to hold (and hence for Eq. (16) to be rigorously valid) it is necessary that three classes of effects (which to a first order may be treated independently) shall be negligible. These are

(1) The perturbation of one electronic level by another, as in ordinary *l*-uncoupling, etc.[17]

(2) The interactions between nuclear and electronic motions (which are neglected when an average potential function of the usual Kratzer form is used).[18]

(3) The higher order terms in the interaction of rotation and vibration (which are neglected when the usual approximate form of Eq. (15) is derived).[9]

In the case of the ground state of most molecules the first effect will probably be insignificant. We may, therefore, attribute the failure of Eq. (16) to the presence of small modifications in the energy expression, Eq. (15), arising from interactions of the second and third types. Now consideration of these effects has the result of modifying the simple classical interpretation of all of the empirically determined molecular constants. The experimentally determined "ω_e," which we may write ω_e^* ($\equiv Y_{10}$), is not accurately the frequency of vibration for infinitesimal vibrations around the equilibrium position nor is the empirical "B_e," which we may similarly write B_e^* ($\equiv Y_{01}$), $h/8\pi^2\mu r_e^2 c$. We must rather write

$$\omega_e^* = \omega_e(1 + b_1 + b_2 + \cdots) \tag{17}$$

and

$$B_e^* = B_e(1 + c_1 + c_2 + \cdots), \tag{18}$$

where b_1, c_1, etc., are small terms of very complicated form (as yet not definitely evaluated). They depend, among other things, on ω_e and B_e, m/M, the ratio of electronic to protonic mass, and on the coefficients of the various powers in a Kratzer potential function of the form

$$\mu(\zeta) = (\omega_e^2/4B_e)\cdot\zeta^2[1 + a_1\zeta + a_2\zeta^2 + a_3\zeta^3 + a_4\zeta^4 + \cdots], \tag{19}$$

where $\zeta = (r - r_e)/r_e$, where μ is in frequency units and ω_e and B_e have their classical meanings.

Kronig[18] has given a qualitative account of the dependence of b_1 and c_1 on the second interaction mentioned above, while Dunham[9] has deter-

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[15] K. T. Bainbridge, Phys. Rev. **42**, 1 (1932); **43**, 103 (1933); **44**, 56 (1933).

[16] H. Bethe on *The Masses of Light Atoms from Disintegration*, which was made available to us in manuscript form as a letter to this Journal, through the kindness of Professor Bainbridge.

[17] R. de L. Kronig, Zeits. f. Physik **50**, 347 (1928); J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

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

mined approximately by the Wenzel-Brillouin-Kramer method their dependence on the third interaction, and incomplete papers which he left show that a detailed discussion of the second interaction was only interrupted by his untimely death.

Since both of the interactions considered here will usually be small we may consider them approximately additive and express ρ_{lj}^*, the empirically determined value of "rho" from band constants, as:

$$\rho_{lj}^* = (Y_{lj}^i/Y_{lj})^{1/(l+2j)} = \rho + \Delta_2\rho_{lj} + \Delta_3\rho_{lj}, \quad (20)$$

where the subscripts 2 and 3 refer to the theoretical interactions (2) and (3) and (lj) identifies the band constant involved.

Using the explicit equations which Dunham gives for the first 15 Y_{lj} coefficients in Eq. (15) and the data on $\mathrm{Li^7H}$ of Table X, we have evaluated approximately the first four a's of Eq. (19). The results are

$$a_1 = -1.86, \quad a_2 = +2.30, \quad a_3 \approx -4, \quad a_4 \approx 13,$$

from which we find for $\mathrm{Li^7H}$ $B_e^* = B_e(1-0.00035)$ and (assuming the same potential curve for each molecule) for $\mathrm{Li^7D}$

$$B_e^{i*} = B_e^i(1-0.00020).$$

Hence

$$B_e^{i*}/B_e^* = (B_e^i/B_e)[1+0.000157]$$
$$= \rho^2[1+0.000157] \approx (\rho+\Delta_2\rho_{01})^2,$$

where $\Delta_2\rho_{01} = +0.00006$ a value which though uncertain is about a third of the value $\rho_{01}^* - \rho = +0.00020$ which was observed. Unfortunately for computing the effect on ω_e we need very reliable values of a_4 since a small change in its value is enough to alter even the *sign* of the correction term. This is a rather laborious process and the value of a_4 depends largely on the accuracy of small constants like α_1, α_2, β_1, β_2, etc., of Table III. This calculation is in the process of being completed and will be considered again in Part III.[19]

In view of the above we may therefore say, (1) the discrepancy between the simple isotope theory and the band constant ratios, $\rho_{lj}^* - \rho$, will in general *vary* with (lj) and hence be different for ω_e^* and B_e^* ratios (the only ones which in practice are susceptible of very precise measurement) and (2) the failure of the simple isotope theory may be quite as much due to neglecting the higher interaction terms of rotation and vibration as to the effect of nuclear "wobbling." This latter possibility seems not to have been given due prominence in the literature.

ISOTOPE EFFECT IN THE UPPER STATE

The first point to be considered in this connection is the choice of a proper vibrational assignment, which from the results of Table IX we should expect to be somewhat ambiguous. Actually three sets of quantum assignments were considered for both LiH and LiD. If the numbering used in this paper is called (a), that with an increase of $+1$ (b) and that with an increase of $+2$ (c) (with (a^i), (b^i) and (c^i) having the same significance for the LiD numbering of Part I) then the values of ω_e, x_1, x_2, etc., for LiH (observed), for LiD (computed from LiH by the simple isotope theory) with numberings (a), (b) and (c) and for LiD (observed) with numberings (a^i), (b^i) and (c^i) may be determined.

On carrying this out it was apparent that in no case was very close agreement obtained except in combinations (aa^i) and (bc^i).[20] Of these the second looks better than the first—though actually the *first* assignment alone is possible since on this assignment alone can one obtain satisfactory agreement between the $\Delta G'$ values observed for LiD and those computed from the constants for LiH. (See Table XI where the differences in the third column are probably significant only of the unsuitability of polynomials for representing the data.) There are fortunately three other facts reconcilable only

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[19] It is interesting to note in this connection that similar calculations for $D_e^*(\equiv Y_{02})$ show that Kratzer's relation for the ground state should be in error by roughly one percent, i.e., that $|D_e^*|$ should be about one percent *greater* than $|4(B_e)^3/\omega_e^2|$. As was indicated in Part I we found for the former 2.756×10^{-4} and for the latter 2.728×10^{-4}, a difference in the same direction of almost exactly one percent (±.3 of course). For the LiH molecule we found similarly $D_e'^* = 8.62$ whereas the extrapolation of Kratzer's relation gives 8.586, a difference of about 0.35 percent.

[20] These are, however, both seen to be very much more concordant than with Nakamura's observations. Thus the difference between the ω_e-values observed and calculated is about 12 percent and between the $x_e\omega_e$ values about 150 percent (see Part I Table VIII), and the remaining constants are of an entirely different order of magnitude.

TABLE XI. *$\Delta G'(v)$ values for LiD as observed and computed from LiH.*

$\Delta G'$ Obs.	$\Delta G'$ Calc. (aa^i)	Obs. −Calc.	$\Delta G'$ Calc. (bc^i)	Obs. −Calc.
—	203.518	—	—	—
224.62	224.153	+0.47	233.165	−8.54
239.92	239.791	.13	247.718	−7.79
252.18	252.058	.12	258.966	−6.78
262.03	261.965	.07	267.995	−5.96
270.14	270.08	.06		
276.69	276.68	.01		

with difficulty with any other numbering scheme. These are the approximate satisfaction of Kratzer's Eq. (6), which would be radically untrue with a change of numbering (especially for LiH), and the equality of the energy values in the two molecules at the maxima of their B_v' curves (see Fig. 1) and of their $\Delta G'$ curves (see Fig. 3). These three facts demand that the molecular constants have approximately their classical mechanical meaning and that any peculiarities of their variation with vibration shall be deducible from peculiarities in the potential curve. If now $B_v=B_e+\alpha_1u+\alpha_2u^2+\cdots$, then approximately $B_v{}^i=\rho^2B_e{}^i+\alpha_1\rho^3u+\alpha_2\rho^4\rho^2\cdots$ and hence $B_v{}^i/\rho^2=B_e+\alpha_1(\rho u)+\alpha_2(\rho u)^2+\cdots$, therefore if the B_v curve has its maximum at u_1, the $B_v{}^i$ curve should have its at u_2 where $\rho u_2=u_1$. We find $u_1=3.1$ and therefore $u_2=4.14$ whereas actually the isotope curve has its maximum at 4.36 (±0.2). But we know[8] also that if $G=f(v+\frac{1}{2})$, whatever the form of the function f, then $G^i=f[\rho(v+\frac{1}{2})]$. Consequently it can readily be shown that, provided the higher coefficients in the expansion of G in powers of $(v+\frac{1}{2})$ are small, we have $\Delta G(v+1)\approx\Delta G^i[\rho(v+1)]/\rho$. Hence, roughly, a maximum at v_1 in the ΔG curve should correspond to a maximum at v_2 in the isotope curve, where $(v_1+1)=\rho(v_2+1)$. Actually we find $v_1=10.25$ whence $v_2=12.7$, whereas 12.65 is found experimentally. The question of the relation of the maxima of the B_v curves to those of the ΔG curves will be considered in more detail in Part III.[21]

On the basis of the numbering thus arrived at we have computed where the LiD origins should be compared with their observed positions, i.e., determined $(\nu_0{}^i)$ obs. $-(\nu_0{}^i)$ calc. where any constant difference would be taken as giving the approximate electronic isotope shift. The result of this calculation is to give discrepancies which are always *positive* and vary from $+0.71$ cm^{-1} for the (1–3) band to $+1.84$ for the (7–3) band. It is, however, not legitimate to average these to obtain a value of the electronic isotope shift for the system origin since the differences vary smoothly in both *initial* and *final* progressions. Actually by extrapolating final progression curves to $v''=-\frac{1}{2}$ and this extrapolated curve to $v'=-\frac{1}{2}$ a value for this electronic origin shift is obtained. We have put it provisionally at 0.0 (±0.5) cm^{-1} which is of course more reliable than the value $+2.5$ obtained above by extrapolation of the $G'(v+\frac{1}{2})$ and $G^{i\prime}(v+\frac{1}{2})$ curves. This behavior will be considered in more detail in Part III.

We wish to take this opportunity of expressing our gratitude to the Milton Fund of Harvard University for a grant covering part of the expenses of this investigation and to the Monroe Calculating Machine Company, Inc. for the generous loan of a machine which has greatly facilitated the large amount of numerical reckoning involved.

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[21] Both Almy and Hause (Phys. Rev. **42**, 242 (1932)) and Olsson (reference 12) agree in attributing the anomalous behavior of the B_v and ΔG curves in the case of KH and NaH, respectively, to a common cause, i.e., the possession of a potential curve on the part of the excited $^1\Sigma$ state which is anomalous in particular in that the coefficient a_1 of Eq. (19) is abnormally *small* while a_2 is abnormally *large*.