In the case of CaCl and of SrCl, no definite assignments may be made, while for BaCl this has been discussed previously[7] with the conclusion that the ground state of BaCl does not dissociate into a Ba atom in its ground state and that the probable products of the X and A states of BaCl are, respectively, $(6s)(5d)\,{}^1D$ and $(6s)(6d)\,{}^1D$ states of Ba.

For both MgCl and BaCl it seems likely that the ground state gives rise upon dissociation to an excited Mg and Ba atom, respectively. From the spectra of CaH, SrH and BaH, we know that the dissociation of these molecules gives rise to an excited atom. And by analogy we may assume that the same is true for CaCl and SrCl. Finally we may arrive at the conclusion that an atom in a ground $(ns)^2\,{}^1S$ state will not in general form a stable molecule. This fact has been previously discussed by Lessheim and Samuels[9] and others.

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[9] H. Lessheim and R. Samuels, Zeits. f. Physik **84**, 637 (1933).

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The Band Spectra of the Hydrides of Lithium

Part I: Li$^{(7)}$D

F. H. Crawford and T. Jorgensen, Jr., *Physics Research Laboratory, Harvard University*

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The ${}^1\Sigma\rightarrow{}^1\Sigma$ spectrum of LiD has been photographed in absorption in the second order of a 21-foot grating giving a dispersion of 1A/mm. The spectrum is a headless concourse of lines stretching from λ3200 to λ4300A. About 80 percent of the lines (over 1400 in all) have been measured and assigned to 35 two-branch bands. The initial and final double differences, Δ_2F_v' and Δ_2F_v'', for Li$^{(7)}$D have been represented as functions of J by a semigraphical method; these represent the observed data on the average to within ± 0.023 cm^{-1} for the upper state and ± 0.019 cm^{-1} for the ground state. This gives $B_e'=1.6060$, $D_e'=4.8\times10^{-4}$, $B_e''=4.2338$ and $D_e''=2.756\times10^{-4}$. By using the rotational constants so determined the origins of the bands involved were computed and the values of $\Delta G'(v+\frac{1}{2})$ and $\Delta G''(v+\frac{1}{2})$ represented by least-square expressions in $(v+\frac{1}{2})$. The $\Delta G'$-values require a fifth degree polynomial while the $\Delta G''$ values are represented closely by a cubic. The corresponding expression for the origins of the whole system represents the data with an average deviation of ± 0.04 cm^{-1}. Here $\omega_e'=183.12$, $\omega_e'x_e'=-12.741$, $\omega_e''=1055.12$, and $x_e''\omega_e''=13.228$, with the electronic origin at $\nu_e=26{,}512.05$. The corresponding vibrational constants for Li$^{(7)}$H are computed from the simple isotope theory and although they differ considerably from the results of Nakamura, represent the isotope shifts within the rather large uncertainty involved. The question of possible l-uncoupling is examined and no *conclusive evidence is found for an appreciable l-uncoupling in either state of Li$^{(7)}$D.* This is contrary to the accepted interpretation of the anomalies of the spectrum.

Introduction

The spectra of the hydrides of the alkali metals are of unique interest among diatomic spectra because of the presence of certain anomalies. If we represent the total energy, E/hc (in inverse cm), of a rotating vibrator in the usual notation[1]

$$E/h_c=\nu_e+G(v)+F_v(J), \tag{1}$$

where

$$G(v)=\omega_v(v+\tfrac{1}{2})=\{\omega_e-x_e\omega_e(v+\tfrac{1}{2})+y_e\omega_e(v+\tfrac{1}{2})^2+z_e\omega_e(v+\tfrac{1}{2})^3+\cdots\}(v+\tfrac{1}{2}) \tag{2}$$

and

$$F_v(J)=B_vJ(J+1)+D_vJ^2(J+1)^2+H_vJ^3(J+1)^3+\cdots. \tag{3}$$

Then in a normal band spectrum certain general-

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[1] Jevons, *Report on Band Spectra*, Cambridge, 1932. Here, to avoid confusion the coefficient of $J^3(J+1)^3$ in Eq. (3) has been written H_v instead of F_v.

izations can be made regarding certain of the coefficients involved. Thus the coefficients x_e, y_e, $z_e \cdots$ in Eq. (2) decrease in magnitude in this order and x_e is normally positive and of such value that as more and more vibrational energy is added the vibrational rate decreases steadily from its value for small vibrations to the necessary limit of zero at dissociation. If likewise we represent B_v, D_v and H_v as functions of $(v+\frac{1}{2})$ we have

$$B_v = B_e + \alpha_1(v+\tfrac{1}{2}) + \alpha_2(v+\tfrac{1}{2})^2 + \cdots, \quad (4)$$

$$D_v = D_e + \beta_1(v+\tfrac{1}{2}) + \beta_2(v+\tfrac{1}{2})^2 + \cdots, \quad (5)$$

$$H_v = H_e + \gamma_1(v+\tfrac{1}{2}) + \gamma_2(v+\tfrac{1}{2})^2 + \cdots, \quad (6)$$

where $|\alpha_1| \gg |\alpha_2|$, etc., and in general α_1 is negative causing B_v to *decrease* monotonically with v. Since $B_e = h/8\pi c I_e$ this implies that the asymmetry of the vibrations together with the centrifugal effect of rotation causes the average of $h/8\pi c\mu r^2$, where μ is the reduced mass of the molecule and r the distance between nuclei, to decrease steadily with v.

Now in the case of the ${}^1\Sigma \rightarrow {}^1\Sigma$ bands of the alkali hydrides, x_e' is *negative* and α_1' is *positive* so that both ω_v' and B_v' at *first* increase with v', attain maximum values (at different values of v') and thereafter decrease in regular fashion. This anomalous behavior is observed only in excited states and decreases rapidly in importance from LiH to KH. Furthermore in molecules in which the rotation does not affect the quantization of the l-vector the coefficient D_v in Eq. (3) is determined by the centrifugal stretching of the molecule. Hence as Kratzer[2] has shown for the vibrationless state it depends only on the curvature of the potential curve at the minimum, i.e.,

$$D_e = -4(B_e)^3/\omega_e^2, \quad (7)$$

a relation fairly closely verified by observation.

In the case of LiH Nakamura[3] has photographed the spectrum both in emission and absorption and carried out the analysis of the $\mathrm{Li^{(6)}H}$ and $\mathrm{Li^{(7)}H}$ bands. As Weizel[4] has pointed out Nakamura's results seemed to indicate that the empirically determined coefficients of $J^2(J+1)^2$ in Eq. (3) were numerically much too small compared with the coefficients of $J(J+1)$ and hence that Kratzer's relation, Eq. (7), was not even approximately true [i.e., observed values of D_e' were only half of those computed from Eq. (7)]. If this is true it would suggest that the coefficients in Eq. (2) had lost their normal mechanical significance. But as Hill and Van Vleck[5] and Dieke[6] have shown in the presence of the rotational uncoupling of the l-vector of a single p-electron in a $p-{}^1\Sigma$ state—when the uncoupling effect of rotation is *small*—we may write the rotational energy of Eq. (3) (to a constant) as

$$F(J) = XJ(J+1) + ZJ^2(J+1)^2 + \cdots, \quad (8)$$

where now X and Z have lost their purely mechanical significance. In fact

$$X = B(1-1/(Y-2)) \quad \text{and} \quad Z = D + 16B/(Y-2)^3,$$

etc., where YB gives the separation in $\mathrm{cm^{-1}}$ between the Π and Σ states formed from the same p-electron. Here Y is positive or negative according as the Π state is *above* the Σ state or below it. If Y is positive (and large) this causes X to be smaller than B and $|Z|$ to be smaller than $|D|$. Although of course Eq. (8) holds rigorously only for the vibrationless molecule, presumably a somewhat similar relation exists in the presence of vibration. If then as in the case of helium[6] increasing vibration increases the binding energy between the nuclear axis and l, Y should increase. Hence a Y_v might be defined which would be proportional to the separation in energy between Π and Σ levels of the same v-value. In effect therefore we should expect the empirical coefficients X_v to be of the form $(B_e + \alpha_1'(v+\frac{1}{2}) + \cdots)\,[1-1/(Y_v-2)]$ where α_1' has the negative value determined by the slowly expanding molecule. If then Y_v increases sufficiently rapidly with v the second factor predominates at first causing an initial rise in X_v. Ultimately the first factor predominates and causes the ultimate fall of X_v. Using the data of Nakamura for LiH and estimating the values of

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[2] Kratzer, Ann. d. Physik **67**, 127 (1922).

[3] G. Nakamura, Zeits. f. physik. Chemie **B80** (1929); Zeits. f. Physik **59**, 218 (1930). G. Nakamura and T. Shidei, Proc. Imp. Acad. Japan **7**, 303 (1930); Jap. J. Phys. **7**, 33 (1931).

[4] Weizel, Zeits. f. Physik **60**, 599 (1930).

[5] Hill and Van Vleck, Phys. Rev. **32**, 269 (1928).

[6] Dieke, Zeits. f. Physik **57**, 71 (1929).

$\alpha_1\cdots\beta_1\cdots$ in Eqs. (4) and (5), the authors[7] calculated the succession of Y_v values which must obtain if uncoupling were the *sole* cause of the anomalous behavior. Although the original data were taken at rather low dispersion and rather uncertain below $v'=2$ there seemed to be evidence for such a set of $^1\Pi$ levels lying only a few hundred cm^{-1} above the corresponding upper $^1\Sigma$ levels. Hence transitions from those levels should give a $^1\Pi\rightarrow{}^1\Sigma$ system overlying the known $^1\Sigma\rightarrow{}^1\Sigma$ bands.

Furthermore since the bands of LiD should give the same[8] progression of Y_v values (to within a constant of proportionality) but quite different B_v' and D_v' values, measurements on its spectrum should be of the greatest value in conjunction with more precise data on LiH.

Accordingly the present work was undertaken, the results of which will be reported in this and subsequent parts. Part I contains a summary of the data for Li$^{(7)}$D.

EXPERIMENTAL PROCEDURE

For the study of the hydrides in absorption an electric furnace was constructed through which passed a steel tube whose ends were attached to short Pyrex cylinders. Several grams of pure metallic lithium were placed at the center of the tube, quartz windows attached and the system exhausted, with the metal just molten, for several hours. Then pure tank H_2 or D_2 (produced by the action of metallic calcium on samples of heavy water of 99.5 percent purity) was introduced and allowed to combine with the lithium with a sufficient excess of gas to prevent too rapid diffusion of the hydride. The same tube was never used for both gases. A parallel beam of light from a 500-watt tungsten lamp* was then passed through the heated tube and focused on the slit of a 21-foot grating (dispersion 1A/mm in the second order). A series of exposures were then made at temperatures varying from a dull red heat to about 900°C. Eastman plates of fine grained type (Type IV–0) were employed and iron arc exposures were made before and after the hydride exposure. The iron arc exposures were of quite different intensity so that once the absence of any shift during the exposure was established, the standard lines could be measured on that exposure which gave the optimum density for precise settings. In all cases the narrowest slit widths feasible (around 0.015 mm) and the lowest temperatures sufficient to bring out the lines desired were employed. This was quite necessary because of the large Doppler broadening for such light molecules.

PLATE MEASUREMENTS AND ANALYSIS OF DATA

Since these spectra present no obvious heads, but rather an irregular concourse of lines, often 3 or 4 in the space of an Angstrom, the recognition of individual bands presents some difficulty. It was finally found that the lines could more quickly and certainly be arranged into branches by first making densitometer records of the plates, beginning with those taken at the lowest temperatures. Then with a millimeter scale and the line shapes and relative blackenings as a guide practice soon enabled a single branch to be picked out in a few minutes. In this way some 5000 lines belonging to Li$^{(6)}$H, Li$^{(7)}$H, Li$^{(6)}$D and Li$^{(7)}$D were provisionally assigned to bands. The lines due to the Li$^{(6)}$ isotope were of course found on only the higher temperature plates, where the Li$^{(7)}$ spectra were very much richer and superposition was more bothersome. This assignment included probably 80 percent of the measurable lines and when an attempt was made to assign *all* of the visible lines on the LiD plates most of the faintest lines were found to be due to Li$^{(7)}$H present as an impurity. In no *single* case was a band discovered having more than a single P or R branch. If such are present they must be very faint indeed. It is more likely that the feeble lines remaining unidentified were simply the few central members of branches of higher initial vibrational progressions.

The plates were measured on a tested comparator and to render the wavelength estimates more precise correction curves were drawn for each 50 or 75A section of a plate from the large

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[7] F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **45**, 737 (1934).

[8] Except for the small difference between the potential energy curves of hydrides and deuterides observed by Holst and Hulthén (Nature **133**, 496 (1934) and discussed theoretically by Kronig (Physica, p. 617, May, 1934)). See also F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **46**, 746 (1934).

* A carbon arc was used for the lower wavelength region.

TABLE I. *Vacuum frequencies of* $^1\Sigma\rightarrow{}^1\Sigma$ *bands of* $Li^{(7)}D$.

	(4 −2) Band 23,000 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 27,000 cm^{-1}		(13 −0) Band 27,000 cm^{-1}		(15 −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	—		—		—		1674.58		1966.13?		2552.95		2140.22	
1	1974.23	—	—	—	1509.83	1499.98	672.64	1662.95	964.17	1954.25	550.85	2541.44	137.90	2128.55
2	968.02	1951.64	2233.16	2216.77	503.22*	486.87	665.49	649.46	956.97	941.03	543.42?	527.86	130.34	114.89
3	957.06	934.21	221.61	198.78	491.68	468.88	653.20	630.77	944.58	922.31	530.91	508.87	117.50	096.06
4	941.39	912.00	205.18*	175.83	475.26	445.93	635.79	606.67?	927.05	898.43	513.14	484.96	099.34	071.82
5	920.91	885.13	183.89	148.06	453.89	418.13	613.20	578.08	904.32	869.41	490.07	455.75	075.97	042.34
6	895.77	853.56	157.67	115.46	427.66	385.48	585.51	544.03	876.45	835.30	461.85	421.37	047.27*	007.60
7	—	817.24*	126.52	—	396.51	347.96	—	504.93	843.48	796.04	428.44	381.86*	2013.33	1967.66
8	831.24	776.37	090.53	2035.65	360.49	305.66	514.75	460.84	805.31	751.76	389.84	337.15	1974.21	922.55
9	791.90	730.86	049.66	1988.48*	319.57	258.53	471.74	411.65	762.11	702.41	346.08	287.35	929.80	872.28
10	747.86	680.73	2003.95	936.71*	273.90	206.60	423.69	357.47	713.84	648.04	297.25	232.55	880.24	816.89
11	—	625.98	1953.47	880.04	223.33	149.96	370.61	298.39	—	588.74	243.26	172.69	825.54	756.35
12	645.94	566.78	898.11	818.70	168.04	088.61	312.51	234.34	602.14	524.44	184.28	107.93*	765.64*	690.86
13	587.99	502.93	837.92	752.71	107.93	1022.58	249.51	165.44	538.85	455.31	120.26	2038.11	700.82	620.28
14	525.44	434.61	773.09	681.97	1043.08	0951.92	181.58	091.70	470.58	381.31	2051.27	1963.39	630.85	544.86?
15	458.30	361.81	703.51	606.64*	0973.54	876.64	108.77	1013.15	397.48	302.45	1977.29	883.82	555.92*	464.38
16	386.59	284.57	629.22	526.83	899.40*	796.87	1031.09	0929.85?	319.45	218.87	898.43*	799.46	476.01	379.10
17	310.35	202.92	550.27	442.47	820.51	712.47	0948.61	841.86	236.65	130.59	814.77	710.39*	391.25	289.05*
18	229.60	116.91	467.62	353.56	737.00	623.60	861.40	749.21	149.06	1037.63	726.26	616.58	301.63	194.19
19	144.39	1026.60	378.62	260.20	649.03	530.29	769.49	—	1056.79	0940.04	633.02	518.18	207.14	1094.69
20	1054.76	0931.97	285.88	162.39	556.51	432.72	—	550.20	0959.78	837.89	535.11	415.17	107.93*	0990.40
21	0960.72?	833.07	188.71	1060.20	459.50	330.71	571.68	443.98	858.25	731.31	432.53	307.56	1004.04	881.63
22	862.58	730.00	1087.02	0953.75	358.17	224.49	465.94	333.29	752.12	—	325.33	195.52	0895.51	768.31
23	759.64	622.75	0980.92	0843.05	252.39	113.92	355.79	218.26			213.70	1091.70?	782.41	650.63
24			0870.50	728.08			241.18	098.95			1097.42*	0959.30?	664.84	528.49
25													542.78	402.05

number of good iron standards available in the region (λ3200 to λ4300). The results are consequently probably dependable to ±0.004A, or about ±0.025 cm^{-1}, in the most favorable regions. This is in agreement with the fact that the data on the double differences could in all cases be represented by empirical expressions to about this uncertainty. The vacuum frequencies of the lines, of which about 1400 of $Li^{(7)}D$ have been measured, were then arranged in bands and the first double differences $\Delta_2F_v'(J)$ and $\Delta_2F_v''(J)$ determined. The measurement of so many lines was necessitated by the fact that with no head formation whatever as a guide and the early lines in a branch usually faint—the origins could only be computed subsequent to the complete rotational analysis. The 35 bands obtained included 17 bands of the $(v',0)$, 7 of the $(v',1)$, 6 of the $(v',2)$, 4 of the $(v',3)$ and a single faint band of the $(v',4)$ progression. For obvious reasons of space actual vacuum frequencies of only 7 bands are given here. These are recorded in Table I and include about one-fifth of the lines measured. To save space at the head of each pair of columns is given a number which is to be *added* to the number opposite any J-value to give the appropriate vacuum frequency for the branch of the band in question. Since in the more intense parts of the LiD plates there are over twenty branches of $Li^{(7)}D$, 6 or 8 of $Li^{(7)}H$ and probably 8 or 10 of $Li^{(6)}D$ overlapping, the number of accidental superpositions, unresolved blendings, etc., is necessarily rather large. When the densitometer records indicated that a measurement is of questionable value for any of these reasons the line is marked by an asterisk. Question marks indicate the fact that a number of lines occur (usually weak and of similar intensity) so close together as to render identification doubtful. Blanks occur where lines were too near the end of a plate for trustworthy measure-

TABLE II. *Values of* $\Delta_2F_v''(J)$.

J	(11 −0) Band	(15 −0) Band	Ave. of all $(v',0)$ bands	Ave. −Calc.
1	25.10	25.33	25.14_2	−0.022
2	41.86	41.84	41.86_6	− .022
3	58.54	58.52	58.51_6	+ .020
4	75.17	75.16	75.17_9	+ .003
5	91.75	91.74	91.78_5	− .016
6	108.28	108.31	108.29_1	− .004
7	124.69	124.72	124.70_9	+ .011
8	141.07	141.05	141.05_4	+ .004
9	157.27	157.32	157.25_6	+ .030
10	173.37	173.45	173.39_0	− .005
11	189.40	189.38	189.36_1	+ .010
12	—	205.26	205.19_9	+ .006
13	220.83	220.78	220.87_1	+ .013
14	236.40	236.44	236.39_6	+ .007
15	251.71	251.75	251.75_6	− .016
16	266.89	266.87	266.91_5	− .022
17	281.82	281.82	281.83_6	− .009
18	296.61	296.55	296.61_0	− .009
19	311.17	311.23	311.17_5	+ .014
20	325.48	325.51	325.49_3	− .016
21	—	339.62	339.58_5	− .023
22	—	353.41	353.36_8	+ .053
23	—	367.02	367.00_3	+ .036
24	—	380.36	380.38_5	+ .023
		Av. deviation		± .016 cm^{-1}

TABLE III. *Values of* $\Delta_2 F_{11}'(J)$.

J	Obs. (11,0) Band	(Obs. −Calc.)	J	Obs. (11,0) Band	(Obs. −Calc.)
1	(9.57)	+0.002	13	83.54	+0.002
2	15.94	− .004	14	89.27	+ .039
3	22.27	+ .018	15	95.03	− .041
4	28.62	− .003	16	100.58	− .005
5	34.91	+ .008	17	106.06	+ .003
6	41.15	+ .034	18	111.43	− .019
7	47.44	− .033	19	116.75	− .022
8	53.55	+ .033	20	121.89	+ .006
9	59.70	+ .005	21	126.94	− .013
10	65.80	− .031	22	(131.87)	+ .038
11	(71.74)	+ .023	23	(136.68)	+ .008
12	77.70	− .007		Ave. dev.	± 0.017 cm^{-1}

ment or were obscured by the occultor supports or where the wrong line was measured. (With such a wealth of data a few missing lines caused very little trouble.)

From the data so arranged the upper state and lower state double differences $\Delta_2 F_v'(J)$ and $\Delta_2 F_v''(J)$ were computed. Since so many bands involved common lower states very trustworthy averages could be obtained by using only those differences which were above suspicion. A typical pair of these sets for $v''=0$ is given in Table II together with the final averages of the values from the 15 strongest bands. The last column of this table gives the differences (average—calculated) obtained from equations of the form of Eq. (10) with the constants given in Table V.

In the case of $\Delta_2 F_v'(J)$-values, those from two or three and often only one band were available. In order to obtain the most likely values for use in determining rotational constants all the $\Delta_2 F_v'(J)$-values for a constant J were plotted to scale against v. Almost without exception when a point was noticeably (say more than ± 0.06 cm^{-1}) off the smooth curve through the points it was found to involve a line (or lines) whose $\Delta_2 F_v''(J)$-value departed from the average in the appropriate direction. Careful reexamination of the plates in several dozen test-cases showed without exception that one or both of the frequencies were in doubt because of incomplete resolution, misidentification or a blunder in measuring. It therefore seemed legitimate thereafter to smooth such values by interpolation. Extrapolation was not resorted to. Values interpolated in this way are in parentheses in Table III which gives $\Delta_2 F_{11}'(J)$ as observed together with those computed from the constants of Table V (below).

DETERMINATION OF ROTATIONAL CONSTANTS

Since the Fortrat diagrams for the bands are parabola-like curves of extreme narrowness it is not possible to determine the origins at all closely by any direct graphical method, particularly when the early lines are either very faint or altogether missing. It was therefore necessary to determine the rotational constants for each vibrational level with considerable precision and compute the origins from the lines themselves.

If we represent the double difference $\Delta_2 F_v(J) = F_v(J+1) - F_v(J-1)$ as a power series in J it is of course possible to evaluate the coefficients in the usual least-squares fashion. Besides being rather laborious this has the disadvantage of ignoring the theoretical relations which must exist between the coefficients (as for example those of J^3 and J^4). If again we write from Eq. (3),

$$\Delta_2 F_v(J) = (4J+2)[B_v + 2D_v(J^2+J+1) + \cdots] \quad (9)$$

and plot $\Delta_2 F_v(J)/(4J+2)$ against J we have a parabola-like curve with vertex at $J=-\frac{1}{2}$ and intersecting this line at $B_v + 3/2D_v$. This, however, involves the extrapolation of a curve which is rising rapidly when $|D_v|$ is large. It further does not permit a precise evaluation of D_v when the data are such as to require higher terms in the energy expression, Eq. (3). Our data very definitely do require at least one more term.

We have consequently employed a graphical method due to Knave[9] which is so satisfactory as to warrant much wider use than it has thus far received. A little algebraic reduction shows that from Eq. (3) we may most conveniently write Eq. (9) as a function not of $J(J+1)$ but of $(J+\frac{1}{2})$. The result is

$$\Delta_2 F_v(J) = 4(J+\tfrac{1}{2})[(B_v + 3/2D_v + 27/16H_v) + 2(D_v - 17/4H_v)(J+\tfrac{1}{2})^2 + 3H_v(J+\tfrac{1}{2})^4 + \cdots] \quad (10)$$

$$\text{or} \quad \Delta_2 F_v(J)/4(J+\tfrac{1}{2}) = a_0 + a_1 x + a_2 x^2 + \cdots, \quad (11)$$

where $x = (J+\frac{1}{2})^2$. Hence if $\Delta_2 F_v(J)/4(J+\frac{1}{2})$ is plotted against x we have a curve whose departure from a straight line gives a measure of a_2, whose initial slope is a_1 and whose intercept at

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[9] E. Bengtsson Knave, Nova Acta Reg. Soc. Sci. Uppsala, Series IV **8**, 1 (1932).

$x=0$ is a_0 (see Fig. 1). Further since a_0, a_1, a_2 are of the order of 1, 10^{-4} and 10^{-8}, respectively, in magnitude the procedure is rapid and certain. In practice the data were plotted to a generous scale (this was repeated using a different scale to avoid systematic errors) and the best straight line through the first 8 or 10 points determined by the criterion that the computed values of a_2 must not increase or decrease with x. The constants so determined were then used in Eq. (11) and the complete set of $\Delta_2F_v(J)$-values computed. In most cases the differences between calculated and observed values were satisfactorily small and irregular. In other cases it was possible to improve the fit somewhat by small trial and error variations of a_2 and a_3, particularly when the scale chosen was inadequate for the precision of the data. In the last columns of Tables II and III are given the values of Δ_2F(calculated) $-\Delta_2F$(observed) for typical cases. In Tables IV and V are recorded the values of B_v, D_v and H_v for the lower and upper $^1\Sigma$ states, respectively, together with the averages for each value of v of the departures of Δ_2F(calculated) from Δ_2F(observed). These average departures are seen in all but one case to be less than 0.03 cm^{-1}. It is believed accordingly that the data are rather more consistent than most published molecular data.

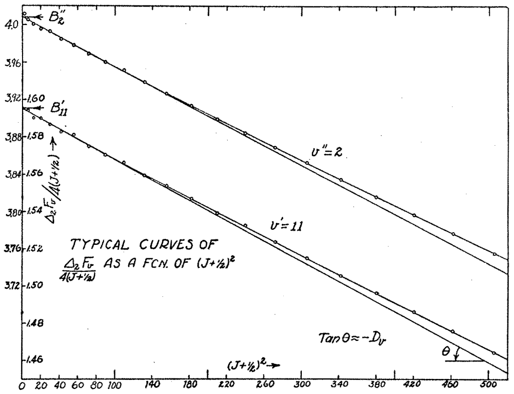

FIG. 1. Here are shown typical curves of $\Delta_2F_v(J)/4(J+\frac{1}{2})$ plotted against $(J+\frac{1}{2})^2$ for the upper and lower $^1\Sigma$ states of $\text{Li}^{(7)}\text{D}$. The curves are practically linear—the departure from linearity determining H_v in Eq. (3) and the slope, D_v. The regularity of the points enable these constants to be determined with rather greater than the usual precision. The departure from linearity in all cases was definite and marked though small.

The rotational constants of both states were then represented as power series in $(v+\frac{1}{2})$ by the least-square method of Birge and Shea.[10] The lower state constants are represented by the following expressions where the number in parenthesis is in each case the average departure of the observed constants from those calculated. The departures from linearity are small.

$$B_v''=4.23384-0.09198(v''+\tfrac{1}{2})+0.0006714(v''+\tfrac{1}{2})^2, \quad (\pm 0.0002), \tag{12}$$

$$-D_v''\times 10^4=2.756-0.0663(v''+\tfrac{1}{2})+0.00575(v''+\tfrac{1}{2})^2, \quad (\pm 0.001), \tag{13}$$

$$H_v''\times 10^8=2.1175-0.105(v''+\tfrac{1}{2}), \quad (\pm 0.05). \tag{14}$$

In the case of the upper state constants, however, fifth degree polynomials are required for adequate representation of the data. The results with the average departures from the observed values of Table V are:

$$\begin{aligned} B_v'=1.60602&+0.0145042(v'+\tfrac{1}{2})-0.00184351(v'+\tfrac{1}{2})^2+0.0000546903(v'+\tfrac{1}{2})^3\\ &-1.08582\times 10^{-6}(v'+\tfrac{1}{2})^4+8.43455\times 10^{-9}(v'+\tfrac{1}{2})^5, \quad (\pm 0.00035), \end{aligned} \tag{15}$$

$$\begin{aligned} -D_v'\times 10^4=4.0188&-1.12148(v'+\tfrac{1}{2})+0.20873(v'+\tfrac{1}{2})^2-0.019880(v'+\tfrac{1}{2})^3\\ &+9.2475\times 10^{-4}(v'+\tfrac{1}{2})^4-1.6576\times 10^{-5}(v'+\tfrac{1}{2})^5, \quad (\pm 0.010), \end{aligned} \tag{16}$$

$$\begin{aligned} H_v'\times 10^8=11.663&-6.4585(v'+\tfrac{1}{2})+1.50170(v'+\tfrac{1}{2})^2-0.16791(v'+\tfrac{1}{2})^3+0.00900623(v'+\tfrac{1}{2})^4\\ &-0.000185934(v'+\tfrac{1}{2})^5, \quad (\pm 0.08 \text{ to } v'=15). \end{aligned} \tag{17}$$

Values of B_v' and H_v' are plotted in Fig. 2.

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[10] Birge and Shea, Univ. of Cal. Publ. in Math. **2** (5), 67–118 (1927).

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

v''	B_v''	$-D_v''\times 10^4$	$H_v''\times 10^8$	(Ave. Δ_2F_v'' calc. $-\Delta_2F_v''$ obs.)
0	4.1882	2.726	1.96	±0.016
1	4.0970	2.670	1.86	± .017
2	4.0082	2.625	1.75	± .017
3	3.9204	2.593	1.8_5	± .027
4	3.833_4	$2._6$	—	
				Average = ±0.019

Constants for $v''=4$ are quite doubtful due to faintness of lines.

TABLE V. *Rotational constants for upper* $^1\Sigma$ *state of* $Li^{(7)}D$.

v'	B_v'	$-D_v'\times 10^4$	$H_v'\times 10^8$	(Ave. Δ_2F'calc. $-\Delta_2F'$obs.)
1	1.6238	2.775	4.9	±0.027
2	1.6316	2.206	2.25	.015
3	1.6365	1.939	1.7	.019
4	1.6383	1.746	1.2	.018
5	1.6382	1.626	0.92	.021
6	1.6358	1.557	0.93	.021
7	1.6310	1.495	0.91	.026
8	1.6243	1.432	0.83	.027
9	1.6162	1.399	0.89	.026
10	1.6057	1.357	0.88	.028
11	1.5955	1.345	0.81	.017
12	1.5824	1.317	0.74	.018
13	1.5678	1.293	0.78	.024
14	1.5534	1.289	0.75	.025
15	1.5361	1.290	0.59	.020
16	1.5197	1.304	1.1	.032
17	1.5002	1.302	0.9	.021
				Av. = ±0.023

VIBRATIONAL DATA

With reliable values of the rotational constants the origin of each band was then computed independently from the first 8 or 10 lines in each branch excluding questionable lines. These gave values whose consistency was a further check on the precision of the measurements and whose average was taken as the true origin. Thus for a typical set (from the $(6-1)$ band) as M the ordinal number of a line runs from $M=+10$ (R branch) to $M=-10$ (P branch) the origins computed are 26,508.18 cm^{-1} -0.03, ± 0.00, ± 0.00, ± 0.00, -0.02, ± 0.00, -0.01, $+0.01$, $+0.03$, -0.01, ± 0.00, $+0.03$, -0.01, -0.01, $+0.00$, -0.01, $+0.02$, $+0.03$ and -0.01 in order. (Here the line $M=+1$ is missing.) In Table VI are recorded the origins so determined where the *horizontal* and *vertical* differences, $\Delta G''(v+\frac{1}{2})$ and $\Delta G'(v+\frac{1}{2})$ are indicated in italics.

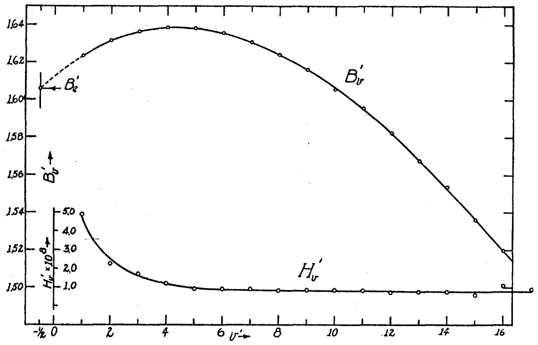

FIG. 2. The upper and lower curves show, respectively, the observed values of B_v' and H_v' [Eq. (10)]. The upper curve attains a maximum value between $v'=4$ and $v'=5$ and thereafter falls steadily. The observed B_v'' values fall steadily from the origin.

TABLE VI. *Origins of* $^1\Sigma\rightarrow{}^1\Sigma$ *bands of* $Li^{(7)}D$. Values involving uncertainty in the tenth's place were not used in the least-square computation of the origins. These are indicated with the last digit in smaller type.

v'	v'' 0		1		2		3		4
1					24255.71	*978.₅*	23277.2		
					224.62		*224.₆*		
2			25483.94	*1003.61*	24480.33	*978.55*	23501.78		
			239.92		*239.92*		*239.91*		
3	26752.8	*1028.₉*	25723.86	*1003.61*	24720.25	*978.56*	23741.69	*953.84*	22787.85
	252.₃		*252.16*		*252.19*		*252.19*		
4	27005.08	*1029.06*	25976.02	*1003.58*	24972.44	*978.56*	23993.88		
	262.03		*262.03*		*262.03*				
5	27267.11	*1029.06*	26238.05	*1003.58*	25234.47				
	270.15		*270.13*		*270.15*				
6	27537.26	*1029.08*	26508.18	*1003.56*	25504.62				
	276.69		*276.69*						
7	27813.95	*1029.08*	26784.87						
	282.01		*281.98*						
8	28095.96	*1029.11*	27066.85						
	286.13								
9	28382.08								
	289.28								
10	28671.36								
	291.60								
11	28962.96								
	293.08								
12	29256.04								
	293.78								
13	29549.82								

v'	$v''=0$
13	29549.82
	293.90
14	29843.72
	293.34
15	30137.06
	292.11
16	30429.17
	290.41
17	30719.58
	288.₀
18	31007.6
	285.₂
19	31292.8

The extremely close agreement whenever two independent values have been found is gratifying. Least-square solutions for $\Delta G''$ and $\Delta G'$ were then obtained and vibrational constants determined. Because of the regular decrease of the $\Delta G''(v+\frac{1}{2})$ values a cubic expression in $(v''+\frac{1}{2})$ is adequate while for the $\Delta G'(v+\frac{1}{2})$ values the approximation afforded by even a fifth power expression in $(v'+\frac{1}{2})$ could probably be improved. We find the origins of the 36 measured bands are represented with an average deviation of ± 0.04 cm^{-1} by an expression of the usual form,

$$\nu \text{ origin} = 26{,}512.05 + u'[\omega_e' - x_1'u' + x_2'(u')^2 + x_3'(u')^3 + x_4'(u')^4 + x_5'(u')^5 + \cdots], \quad (18)$$

where $u = v+\frac{1}{2}$, $x_1 = x_e\omega_e$, $x_2 = y_e\omega_e$, etc.,

where the values of the constants ω_e, $x_e\omega_e$, etc., are those given in Table VII. The extreme size of the higher powers of $(v+\frac{1}{2})$ necessitates the number of decimals given. Inasmuch as $\Delta G'(v+\frac{1}{2})$ attains a maximum at about $v'=13.5$ and it is not possible to follow the system much beyond $v'=18$ or 19 the attempt to extrapolate Eq. (2) to dissociation leads to very uncertain results.

TABLE VII. *Vibrational constants for $Li^{(7)}D$.*

	Ground $^1\Sigma$ state	Upper $^1\Sigma$ state
ω_e	1055.12	183.1246
$x_e\omega_e = x_1$	+13.2282	−12.74161
$y_e\omega_e = x_2$	+0.1300	−0.8778501
x_3	−0.00667	+0.04261680
x_4		-1.332244×10^{-3}
x_5		$+1.808235\times10^{-5}$

COMPARISON WITH LiH

Assuming the simple isotope theory the vibrational and rotational constants of the ground $^1\Sigma$ state are in as good agreement with the published results of Nakamura as his lower dispersion would permit. See Table VIII.

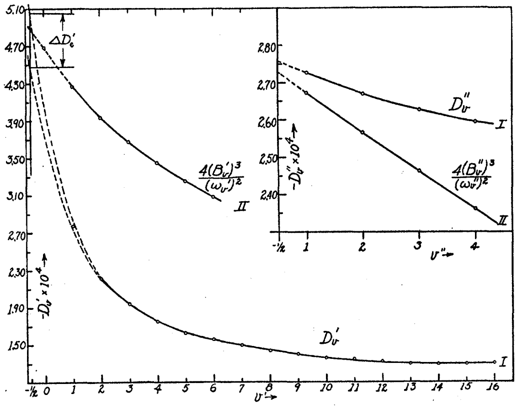

FIG. 3. The insert shows observed values of D_v'' (I) and $4(B_v'')^3/(\omega_v'')^2$ (II) plotted against v''. The difference between the intercepts at $v''=-\frac{1}{2}$ is small but probably real. In the other part of the figure are the corresponding curves for the upper state. Since the extrapolation of the lower curve to $v'=-\frac{1}{2}$ is rather uncertain the two dotted curves are drawn from the least-square representations of the data for $v'=1$ to 6 with D_1' taken, respectively, as 0.04×10^{-4} *above* and *below* the observed value. These are seen to extrapolate above and below the $v'=-\frac{1}{2}$ intercept of the upper curve (II) and hence indicate—if the present vibrational numbering is correct—no definite uncoupling in the upper state. The expression [Eq. (16)] which represents the actual observations from D_1 to D_{17}, due to the extreme flatness of the curve at the right end is not at all trustworthy for extrapolation outside of this range. Hence the initial constant in that equation is of little significance. The average of the dotted curves is taken as giving the most probable value, i.e., $D_e'=-4.8\times10^{-4}$ $(\pm0.3\times10^{-4})$.

The upper state constants, however, present certain discrepancies. If $\rho=(\mu/\mu^i)^{\frac{1}{2}}$ where μ and μ^i are the reduced masses of Li$^{(7)}$D and Li$^{(7)}$H, respectively, and the atomic masses of Bainbridge[11] are used we have $\rho=1.33245$, $\rho^2=1.77542$, $\rho^3=2.36566$, etc. Hence by the usual isotope theory $B_e^i=B_e\rho^2$, etc., and the calculated B_e' values agree to within about 5 percent with Nakamura's results and much closer with our most recent remeasurements for Li$^{(7)}$H. The vibrational data, however, cannot be made to agree with Nakamura's constants though the vibrational numbering used in this paper seems the most nearly consistent. Now with the values of ρ, ρ^2, ρ^3, etc., given above and the data of Table VII we obtain the corresponding vibrational constants for Li$^{(7)}$H from the simple isotope theory. These are given in columns I and

TABLE VIII. *Vibrational constants for $Li^{(7)}H$.*

	Ground $^1\Sigma$ state		Upper $^1\Sigma$ state		
	Isotope theory	Nakamura	Isotope theory	Nakamura	Nakamura recalculated
ω_e	1405.895	1406.1	244.004	287.91	279.84
x_1	23.485	22.73	−22.622	−9.13	−9.5642
x_2	.307		−2.0766	+.318	+.06015
x_3			+0.13433		−.038719
x_4			−0.00556		+.0011546

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

III of Table VIII while columns II and IV give Nakamura's published values.[3] It is seen that while the lower state constants are in pretty good agreement, for the upper state the agreement is not at all satisfactory, the ω_e'-values differing by 16 percent and the $\omega_e'x_e'$-values by over 100 percent. We have made a recalculation by least squares of these constants from Nakamura's original data and obtain the results in the *last* column where ω_e' and $\omega_e'x_e'$ have changed slightly in the right direction. This gives as the system origin for $\text{Li}^{(7)}\text{H}$ 26,479.66 cm^{-1} as against 26,457.9 cm^{-1} obtained by Nakamura. Furthermore with the exception of one faint band the vibrational constants obtained from our $\text{Li}^{(7)}\text{D}$ data by the simple isotope theory reproduce the observed isotope shifts with no more systematic deviations than Nakamura's constants give (either as originally recorded or as recomputed). We therefore conclude that more precise observations are required before any inference can be drawn as to the actual electronic isotope shift or the failure of the simple isotope theory.

On the other hand, the following considerations lend independent support to the present vibrational numbering in the upper state. In Fig. 3 (insert) are drawn two curves, I being the observed values of $-D_v''$ and II, values of $+4(B_v'')^3/(\omega_v'')^2$. Each should extrapolate to the same value at $v''=-\frac{1}{2}$ if Kratzer's relation is true. The first actually gives $D_e''=-2.756\times10^{-4}$ while the other gives -2.728×10^{-4} a difference which is small but probably real and an indication perhaps of a *very* small amount of uncoupling in the ground state. In the other part of the same figure are drawn the corresponding curves for the upper state. Here unfortunately the most crucial point, the value of D_1' in curve I, is experimentally the least accurately known and therefore renders extrapolation to $v'=-\frac{1}{2}$ rather uncertain. We have, however, by trial and error found that D_1' cannot depart from the value -2.775×10^{-4} by more than ±0.04 and allow B_1' and H_1' in Eq. (10) to be changed in such a way as to represent the observed $\Delta_2F_1'(J)$-values. Consequently using the observed values of D_v' for the 6 lowest values of v', least-squares calculations were made with D_1' set equal to -2.810 and -2.730×10^{-4}, respectively.[12] The results are plotted as the dotted curves in the figure. It is seen that the intercept at $v'=-\frac{1}{2}$ of curve II is well within the range of uncertainty implied by the dotted curves. Since a shift of numbering of ±1 unit would cause a very large difference between D_e' and $-4(B_e')^3/(\omega_e')^2$ this would imply an uncoupling so marked as to influence markedly the linearity near the origins of the upper state curves of the type of that in Fig. 1. The present numbering seems therefore quite necessary. Thus within the range of experimental uncertainty there is *no evidence of appreciable uncoupling in either state of LiD.* This means therefore that the peculiar behavior of the observed B_v' and ω_v' values must be ascribed to peculiarities in the potential energy curve alone.

It becomes further apparent why attempts to calculate D_e' for LiH by extrapolation (of rather uncertain values) from say $v'=2$ to $v'=-\frac{1}{2}$ was bound to give results much below the true values and hence to suggest that both B_v' and D_v' had lost their mechanical significance. It is further apparent that although D_e' depends only on the curvature of the potential curve at the minimum, its rate of change with v is very sensitive to the precise way in which this curve alters as we leave the equilibrium position. A detailed examination of the empirical form of the potential curve will be possible when the remaining data on LiH have been adequately summarized.

We wish at this time to express our thanks for a generous grant from the Milton Fund of Harvard University which has defrayed part of the expenses of this investigation.

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[12] It must be borne in mind that when a curve changing as rapidly at one end and as nearly constant at the other as that of D_v' is represented by a power series by the method of least squares—the expression so obtained is not dependable for extrapolation. It is much more certain if a few points near one end or the other are used. For this reason the constant term in Eq. (16) is of no significance. The midpoint of the dotted curves of Fig. 3 is accordingly taken for D_e'. This gives $D_e'=-4.8\ (\pm0.3)\times10^{-4}$.