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The Band Spectra of the Hydrides of Lithium

Part III. Potential Curves and Isotope Relations

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The empirical band spectrum rho-values, ρ^*, as computed from the constants of LiH and LiD depart markedly from the ratio of the reduced masses, $\rho=(\mu/\mu^i)^{\frac{1}{2}}$. The isotope discrepancy, $(\rho^*-\rho)$ is *positive* for the 11 band constants measured for the ground state and *negative* for 10 of the 13 in the upper state. By using Dunham's equations, the *anharmonicity* constants a_1, $a_2\cdots a_6$ are computed for the ground state and the effect of anharmonicity on the isotope ratio calculated. In only 2 cases out of 5 does this reduce the isotope discrepancy and then by amounts from 6 to 22 percent. In the *upper state* the anharmonicity constants must be got by a laborious approximation process. It is shown that the resulting set of a values accounts quite satisfactorily for both the *sign* and *value* of the 9 band constants, which have been previously reported as *abnormal*. This well-known abnormality can therefore not be ascribed in any significant measure to L uncoupling. The Dunham corrections further *reduce* the isotope discrepancy in 4 out of 5 cases by an average of about 25 percent. The dissociation energies (Morse) are found to be for LiD, $\mathbf{D}_0''=2.53$, $\mathbf{D}_0'=1.15$ volts and for LiH $\mathbf{D}_0''=2.54$ and $\mathbf{D}_0'=1.18$ volts (all ±0.2 volt and measured from the $v=0$ level).

INTRODUCTION

THE $^1\Sigma\rightarrow{}^1\Sigma$ band spectra of LiH and LiD are of particular interest for testing the finer points of the theory of molecular spectra for two reasons. In the first place the molecules are relatively light and therefore the isotope shifts to be expected are larger than for any known molecules except H_2 and HD. In the second place the upper electronic state is quite abnormal in that the molecules appear to *shrink* in size as well as to vibrate more rapidly as the amount of vibrational energy increases. Similar effects are present in the case of the hydrides of Na and K though they are there less pronounced in magnitude than in the present case. In addition the simplicity of the structure of $^1\Sigma\rightarrow{}^1\Sigma$ bands is of great assistance in the measurement of those molecular constants on the precise determination of which the present discussion so largely depends.

Preliminary accounts of results and the data on which the present paper depends have been given earlier.[1]

It is now well known experimentally that the molecular constants of hydrides and deuterides (MH and MD) are not in general related precisely by powers of the reduced mass ratio $\rho\equiv(\mu/\mu^i)^{\frac{1}{2}}$, where $\mu=MH/(M+H)$ and $\mu^i=MD/(M+D)$, of the simple isotope theory. As here defined $\rho=0.750486$ and is therefore <1 and we find in the *ground state* that the eleven constants which can be measured with reasonable certainty all give ratios (say ρ^*) which are slightly *nearer* unity.

Thus $(\rho^*-\rho)$ which we may call the *isotope discrepancy* is in every case *positive*. In the *first excited* state, on the other hand, we find $(\rho^*-\rho)$ is positive for only three of the constants and *negative* for the other ten. It seems probable—although sufficient data are not at hand for certainty—that the first result, i.e., $(\rho^*-\rho)>0$, is the normal behavior for the ground states of most molecules.

As in Part II we shall write the complete energy expression (in cm^{-1}) for a rotating-vibrating diatomic molecule in a singlet state as

$$\frac{W}{hc}=\frac{W_0}{hc}+\sum_{l=0,\,1\cdots}\ \sum_{j=0,\,1\cdots}\times Y_{lj}^*(v+\tfrac{1}{2})^l[J(J+1)]^j. \quad (1)$$

The empirically determined "rho-value," ρ_{lj}^* referred to in the paragraph above, is then given by $(Y_{lj}^{i*}/Y_{lj}^*)^{(1/l+2j)}$ and in general varies with *both* l and j. Since the elementary isotope theory[2]

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[1] Crawford and Jorgensen, Phys. Rev. **45**, 737 (1934); Part I, Phys. Rev. **47**, 358 (1935); Part II, Phys. Rev. **47**, 932 (1935); Phys. Rev. **48**, 475 (1935). In Parts I and II complete references to the earlier literature are given.

[2] See, for example, Jevons, *Report on the Spectra of Diatomic Molecules*, p. 212.

predicts that $(\rho_{lj}{}^*-\rho)=0$ the departure of this difference from zero may be taken as an indication that the empirical molecular band constants $Y_{lj}{}^{i*}$ and $Y_{lj}{}^*$ have lost their (assumed) precise mechanical significance. This implies for example that $Y_{10}{}^*$ (identical with the vibration constant $\omega_e{}^*$, where the asterisk is used to emphasize its empirical nature) does not give *exactly* the rate of vibration for small amplitude motions about the equilibrium position. This latter mechanically simple constant we shall designate by ω_e. Likewise $Y_{01}{}^*\equiv B_e{}^*\neq B_e$, where $B_e=h/8\pi^2cI_e$, and therefore the actual moment of inertia at the equilibrium position, I_e, cannot be computed directly from $h/8\pi^2cB_e{}^*$.

Now although various approximations in the solution of the wave equation for a rotating-vibrating diatomic molecule have been pointed out as partly responsible for these differences, it seems desirable to call attention to the classification of neglected effects given by Van Vleck[3] in a recent careful reexamination of the whole problem. The neglected energy terms, although not all capable of specific evaluation in forms suitable for immediate comparison with experiment can be considered as due to four effects:

1. *Anharmonicity* terms due to the interaction of *rotation* and *vibration*. This question has been considered in great detail by Dunham[4] who, writing the molecular potential energy function in the general form:

$$V=a_0\xi^2[1+a_1\xi+a_2\xi^2+a_3\xi^4+a_4\xi^5+\cdots] \quad (2)$$

obtained small correction terms to the usual energy expression. These correction terms (actually only five were evaluated, see Eqs. (7) to (11) below) involve the potential coefficients a_1, a_2, etc., and a factor $p^2=(B_e/\omega_e)^2$ and in general may be positive or negative depending on the precise form of Eq. (2). Since their values depend on p^2, these terms will be very small for heavy molecules and of importance only for hydrides. Here p^2 varies from $\approx 10^{-4}$ for certain states of H_2, LiH, etc., to 10^{-5} and 10^{-6} for a large number of the electronic states of molecules formed from the first two rows of the periodic table.

2. Terms due to the *interaction* of *electronic* and *nuclear* motions (neglecting the interaction of neighboring electronic levels). The use of a potential function of the type of Eq. (2) is equivalent to considering the frequencies of electronic motions so high that the nuclei in a nonvibrating molecule are essentially fixed. To this approximation, terms in the original complete wave equation for a diatomic molecule[5] which vanish when averaged over the frequencies connected with the electronic motions, are neglected. In higher order approximations of the energy of the system these neglected terms do, however, make contributions. The form of these contributions has been considered by Kronig,[6] Dieke[7] and Van Vleck[3] where simple approximations for a few of these terms are given, suitable for electronic states of symmetrical molecules with $L=0$ or for those states (with $L\neq 0$) which can be satisfactorily approximated by considering the nuclei coalesced. The precise evaluation of these terms in the general case requires more detailed knowledge of the molecular wave-functions concerned. They do, however, contain p^2 as a factor and probably tend to *increase* both $(\rho_{10}{}^*-\rho)$ and $(\rho_{01}{}^*-\rho)$. The remaining corrections arise from the interaction of other electronic states with the one under consideration and are of two sorts.

3. L uncoupling terms.[8] These are due to the interaction of electronic states whose Λ values differ by ± 1, are zero for $\sigma^1\Sigma$ states and have no appreciable effect on vibrational constants, i.e., the coefficients $Y_{l0}{}^*$. Their sign is $+$ or $-$ according as the perturbing state is *above* or *below* the one in question. They vary as b_e/ν, where $\nu\approx$ the electronic separation of the states involved.

4. Terms arising from the interaction of states of the *same* Λ *value*.[3] These terms are of a distinctly *new* type and do not affect the rotational constants $Y_{0j}{}^*$. They also are of the order of B_e/ν and may be $+$ or $-$.

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[3] Van Vleck, Phys. Rev. **49**, 417A (1936); J. Chem. Phys. (in press). Note that the energy expressions used by Van Vleck are in absolute energy units while ours are in cm^{-1}.

[4] Dunham, Phys. Rev. **41**, 721 (1932).

[5] Van Vleck, Phys. Rev. **33**, 467 (1929), Eq. (11).

[6] Kronig, Physica **1**, 618 (1934).

[7] Dieke, Phys. Rev. **47**, 661 (1935).

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

A detailed evaluation of the effects (3) and (4) requires of course a fairly complete knowledge of the electronic states of the molecule in question. Since the corrections of these four types (unless an actual large scale "perturbation" is present) are usually small, we can treat them as independently additive. Consequently we can write:

$$Y_{lj}^* = Y_{lj}[1+(\Delta_1)_{lj}+(\Delta_2)_{lj}+(\Delta_2)_{lj}+(\Delta_4)_{lj}] \quad (3)$$

where Y_l is the mechanically significant value Y_{lj}^* would assume if the contributions $(\Delta_1)_{lj}$, etc., of the above effects were zero or experimentally undetectable. Here then

$$Y_{lj}^{i*}/Y_{lj}^* = (\rho^*)^{l+2j}, \quad (4)$$

and since ρ is usually near unity we may write to the same degree of approximation:

$$(\rho_{lj}^* - \rho) = \Delta_1\rho_{lj}+\Delta_2\rho_{lj}+\Delta_3\rho_{lj}+\Delta_4\rho_{lj}, \quad (5)$$

where in general $\Delta_4\rho_{l0}$ and $\Delta_4\rho_{0j}$ will be zero.

From the above it is apparent that only the corrections due to anharmonicity $[(\Delta_1)_{lj}$ and $\Delta_1\rho_{lj}]$ can be computed in a detailed manner at the present time. We therefore propose in this paper to deal primarily with these.

EFFECTS OF VIBRATION AND ROTATION INTERACTION

Dunham's calculations of the explicit form of the Y_{lj}'s in terms of the anharmonicity constants a_1 to a_6 of Eq. (2) indicate that each coefficient of Eq. (1) is of the form:

$$Y_{lj}^* = f_{lj}(\omega_e, B_e)[A_{lj}(a_1, a_2\cdots) + p^2 C_{lj}(a_1, a_2\cdots)] \quad (6)$$

and that therefore by neglecting the last three terms of Eq. (3), $Y_{lj} = f_{lj}/A_{lj}$ and $(\Delta_1)_{lj} = p^2 C_{lj}/A_{lj}$. Here A_{lj} and C_{lj} are functions of the anharmonicity constants $a_1, a_2\cdots$ and are therefore the same for each isotope, while f_{lj} and p both contain factors dependent on mass and are different in the two cases. In general f_{lj} decreases rapidly with both l and j. Dunham's calculations were carried far enough to obtain five of the C_{lj} terms. Since it will be necessary to refer repeatedly to these equations we shall give them here in a form slightly more suitable for numerical reckoning.[8a]

$$Y_{10}^* = \omega_e^* = \omega_e[1+p^2C_{10}], \quad (7)$$

$$Y_{01}^* = B_e^* = B_e[1+p^2C_{01}], \quad (8)$$

$$Y_{02}^* = D_e^* = -4B_e p^2[1+p^2C_{02}], \quad (9)$$

$$Y_{11}^* = \alpha_1^* = B_e p[6(1+a_1)+p^2C_{11}], \quad (10)$$

$$Y_{20}^* = x_1^* = B_e/2[3(a_2-1.25a_1^2)+p^2C_{20}], \quad (11)$$

$$Y_{00}^* = B_e/8[3a_2-1.75a_1^2], \quad (12)$$

$$\begin{aligned} Y_{30}^* = x_2 = B_e p/2[&10a_4-35a_1a_2 \\ &+(56.25a_1^2-8.5a_2)a_2-22.0313a_1^4], \end{aligned} \quad (13)$$

$$\begin{aligned} Y_{40}^* = x_3 = 5B_e p^2[&3.5a_6-15.75a_1a_2 \\ &+(33.9375a_1^2-8.125a_2)a_4 \\ &-(61.0313a_1^3-60.375a_1a_2+7.875a_3)a_3 \\ &+(90.8791a_1^4-77.9531a_1^2a_2 \\ &\quad +4.6875a_2^2)a_2-22.6084a_1^6], \end{aligned} \quad (14)$$

$$\begin{aligned} Y_{21}^* = \alpha_2 = 6B_e p^2[&5a_3-(3+13a_1)a_2 \\ &+(10+7.5a_1+7.5a_1^2)a_1+5], \end{aligned} \quad (15)$$

$$\begin{aligned} Y_{31}^* = \alpha_3 = 20B_e p^2[&7a_5-(4.5+25.5a_1)a_4 \\ &+(14+26.25a_1-22.5a_2+54.375a_1^2)a_3 \\ &-(8.5+45a_1-6.375a_2+59.0625a_1^2 \\ &-51.375a_1a_2+94.3125a_1^3)a_2 \\ &+(21+28.125a_1+35.25a_1^2 \\ &\quad +29.7422a_1^3+29.7422a_1^4)a_1+7], \end{aligned} \quad (16)$$

$$Y_{12}^* = \beta_1 = 12B_e p^3[4a_2-(9+4.5a_1)a_1-9.5], \quad (17)$$

$$\begin{aligned} Y_{22} = \beta_2 = 24B_e p^4[&15a_4-(30+47.5a_1)a_3 \\ &+(61+117a_1+103.5a_1^2-26a_2)a_2 \\ &-(125+123.75a_1+90a_1^2+45a_1^3)a_1-65], \end{aligned} \quad (18)$$

$$Y_{03}^* = H_e^* = 16B_e p^4(a_1+3), \quad (19)$$

$$\begin{aligned} Y_{13}^* = \gamma_1 = 12B_e p^5[&26.6667a_3-(120+88a_1)a_2 \\ &+(279+189a_1+63a_1^2)a_1+233], \end{aligned} \quad (20)$$

$$Y_{04}^* = 64B_e p^6[a_2-(9+2.25a_1)a_1-13], \quad (21)$$

where the C_{lj}'s are given by

$$\begin{aligned} C_{10} = \tfrac{1}{4}[&25a_4-47.5a_1a_3+(57.375a_1^2 \\ &-16.75a_2)a_2-18.0469a_1^4], \end{aligned} \quad (22)$$

$$\begin{aligned} C_{01} = \tfrac{1}{2}[&15a_3-(9+23a_1)a_2 \\ &+(14+10.5a_1+10.5a_1^2)a_1+15], \end{aligned} \quad (23)$$

$$\begin{aligned} C_{02} = \tfrac{1}{2}[&-45a_4+(90+102.5a_1)a_3 \\ &-(119+207a_1+166.5a_1^2-46a_2)a_2 \\ &+(199+173.25a_1+126a_1^2 \\ &\quad +62a_1^3)a_1+163], \end{aligned} \quad (24)$$

[8a] For convenience fractions have been divided out and given uniformly to four decimals. This is quite accurate enough for any experimental data.

$$\begin{aligned}C_{11}=[&175a_5-(112.5+397.5)a_4\\&+(190+356.25a_1-357.5a_2\\&+643.125a_1^2)a_3-(167.5+459a_1\\&-125.625a_2+602.4375a_1^2-584.625a_1a_2\\&+891.1875a_1^3)a_2+(285+286.875a_1\\&+288.75a_1^2+243.6328a_1^3\\&\qquad+243.6328a_1^4)a_1+175],\end{aligned}\tag{25}$$

$$\begin{aligned}C_{20}=\tfrac{1}{2}[&256a_6-682.5a_1a_5+(1066.875a_1^2\\&-442.5a_2)a_4-(1491.5625a_1^3\\&-1833.75a_1a_2+271.25a_3)a_3\\&+(1873.3203a_1^4-1940.1563a_1^2a_2\\&\qquad+213.375a_2^2)a_2-408.3106a_1^6].\end{aligned}\tag{26}$$

From the equations it is at once apparent that if all of the Y^*'s could be determined with comparable precision most of the a's could be determined in two or more ways. Actually Y_{00}^* is not measurable directly, Y_{04}^* is seldom obtained and only an extremely complete and careful analysis gives the α's, β's or γ's with enough accuracy to be of much value. The detailed procedure to be employed therefore depends on the data available and in any event the uncertainty in a given a increases with its subscript.

GROUND STATE

In the ground state of both LiH and LiD the quantities ω_v, B_v, D_v and H_v change so regularly with v that relatively good values of most of the smaller constants are obtainable. It is desirable therefore to compute the a's from the smaller constants and to use these for determining independently the correction factors C_{lj} of Eqs. (22) to (26). This is open to the objection that the corresponding correction terms are not known for Eqs. (13) to (21) and may be relatively important. Since their contributions to the total energy expression will be small if not experimentally undetectable this means merely that to represent data of a given precision we need the a's very much less accurately.

A glance at Eqs. (13) to (21) shows that a_1 can be obtained from (19) and thence a_2 from (17). Then a_3 can be obtained from either (15) or (20) and a_4 from (13) or (18). Finally a_5 and a_6 can be obtained from (16) and (14), respectively. The results of these calculations are given in Table I for both LiH and LiD where because of the larger number of bands observed in the latter case the results for LiD are more trustworthy. When a given a is obtained in two ways, one usually can be recognized as the more reliable. Thus x_2 contributes 26 percent of the final value 5.79 of a_4 in Eq. (13) while β_2 contributes 23 percent towards 6.53 in Eq. (18). Since x_2 is probably more certain than the very small β_2 the first value is the more dependable. Such values are indicated by a dagger. It should be further remarked that since $\alpha_3(\equiv Y_{31}^*)$ was too small to be measured for either isotope, theoretically a_5 could not be determined. Actually, however, solution of Eq. (16) for a_5 shows that unless $|\alpha_3|$ exceeds considerably its rough theoretical value of 1.3 percent $|\alpha_2|$, a reasonably good value should result from setting $\alpha_3=0$. Likewise in the case of a_6 determined from Eq. (14) we require $x_3(\equiv Y_{40}^*)$ which could be measured only for LiD. Since this occurs only in the practically dimensionless ratio $x_3/5B_ep^2$ in the solution for a_6, the LiD value of this term was employed in finding a_6 for LiH. The coefficients are seen to alternate regularly in sign and to increase almost *linearly* in absolute value with the subscript. This as Dr. H. M. James, in this laboratory, has found, is apparently a characteristic of normal electronic levels.

TABLE I. *Potential coefficients for ground state.*

Eq.	a_n	$\mathrm{Li^7H}$	$\mathrm{Li^7D}$
(19)	a_1	-1.84	-1.858
(17)	a_2	$+2.33$	$+2.580$
(15)	a_3	-2.69	-3.446
(20)		-2.98†	-3.456
(13)	a_4	$+5.51$†	$+5.79$†
(18)		$+4.35$	$+6.53$
(16)	a_5	-14.0	-12.2
(14)	a_6	$\approx+33$	$+20.7$

† Values so marked are the more reliable of a pair.

With a reasonably good set of a values we are now in a position to do several things. We may first determine from Eqs. (7) and (8) better approximations to the mechanically significant constants ω_e and B_e. These then enable us to determine what we might call the Dunham approximation to D_e^*, x_1^* and α_1^*, and finally to determine $\Delta_1\rho_{lj}$ the Dunham contributions to the isotope discrepancy. The first step gives us

$$Y_{10}^{i*}=\omega_e^i[1+1/10{,}042],\quad Y_{10}^*=\omega_e[1+1/5660],$$

$$Y_{01}^{i*}=B_e^i[1-1/7376],\quad Y_{01}^*=B_e[1-1/4157].$$

TABLE II.

(lj)	C_{lj}	VALUES OF Y_{lj}^{i*} (FOR LiD)				VALUES OF Y_{lj}^{*} (FOR LiH)			
		Observed	Dunham	Kratzer	Pekeris	Observed	Dunham	Kratzer	Pekeris
02	-35.69	$-2.856\cdot10^{-4}$	-2.72510^{-4}	-2.727	—	$-8.62\cdot10^{-4}$	-8.58510^{-4}	$-8.594\cdot10^{-4}$	—
11	-235.6	0.09198	-0.0875	-0.1060	-0.0780	-0.2132	-0.2070	-0.2480	-0.1823
20	-837	-13.23	-11.046	12.70	—	-23.20	-19.64	22.54	—

TABLE III. *Ground state isotope effects.*

BAND CONSTANT	(lj)	A_{lj}	C_{lj}	ρ_{lj}^*	$(\rho_{lj}^*-\rho)$	$\Delta_1\rho_{lj}$	$\Delta_1\rho_{lj}/(\rho_{lj}^*-\rho)$
ω_e^*	10	1	$+6.18$	0.750628	$+0.00014_2$	-0.00006	-42%
B_e^*	01	1	-8.42	.750685	$+$ .00020	$+$ .00004	$+22\%$
D_e^*	02	1	-35.69	.7520	$+$ .0015	$+$ .000084	$+$ 6%
α_1^*	11	$6(1+a_1)<1$	-235.6	.7556	$+$ .0051	$-$ .000143	-3%
x_1^*	20	$3(a_2-1.25a_1^2)<1$	-837	.7551	$+$ .0046	$-$ .000754	-16%

(+ sign in the last column indicates that the Dunham correction *decreases* the isotope discrepancy.)

TABLE IV. *Upper state isotope effects.*

BAND CONSTANT	(lj)	A_{lj}	ρ_{lj}	ρ_{lj}^*	$(\rho_{lj}^*-\rho)$	$\Delta_1\rho_{lj}$	$\Delta_1\rho_{lj}/(\rho_{lj}^*-\rho)$
ω_e^*	10	1	-53.25	0.770918	$+0.02043$	$+0.002618$	$+13\%$
B_e^*	01	1	-46.22	.754561	$+$ .004075	$+$ .001136	$+28\%$
D_e^*	02	1	$+214.4$	.7424	$-$ .008	$-$ .00264	$+30\%$
α_1^*	11	$+0.83538$	$+3550$	.2036	$-$ .1622	$-$ .06963	$+43\%$
x_1^*	20	$+18.064$	-8840	$.6951_2$	$-$ $.0553_7$	$+$ .01203	-22%

These results give $p^{i2}=2.859\times10^{-5}$ and $p^2=1.611\times10^{-5}$ and enable the observed values of $D_e^*x_1^*$ and α_1 to be compared with the Dunham approximations as well as those of Kratzer[9] and in the case of α_1^*, of Pekeris.[10] The numerical values are collected in Table II, where it appears that the difference between Kratzer's and Dunham's values for D_e^* are inappreciable and fairly close to the observations. In the case of α_1^* Dunham's values are the best, though differing by more than the experimental uncertainty, with Kratzer's too high and Pekeris' as much too low. The agreement in the case of x_1^* is not as good and Kratzer's expression in this case lies closer to the observations.

ISOTOPE RATIOS

Turning to the isotope relations a little manipulation of Eq. (6) shows that we can write

$$\Delta_1\rho_{lj}=-[\rho(p^2-p'^2)/(l+2j)A_{lj}]C_{lj}, \qquad (27)$$

where $\rho=0.750486$. We find also that $\rho_{10}^*=0.750628$ and $\rho_{01}^*=0.750685$. Hence $(\rho_{10}^*-\rho)=+0.00014_2$ and $(\rho_{01}^*-\rho)=+0.00020$. But from Eq. (27) we have $\Delta_1\rho_{10}=-0.00006$ and $\Delta_1\rho_{01}=+0.00004$. Therefore the residual discrepancy $(\rho_{lj}^*-\rho-\Delta_1\rho_{lj})$, in the first case is increased to $+0.00020$ and in the second decreased to $+0.00016$. Since L uncoupling is ruled out for the ground $\sigma^1\Sigma$ state the first discrepancy is presumably due to effects (2) and (4) while the second must be due to effect (2) (the Kronig effect) alone, since effect (4) does not influence rotational constants (and particularly B_e^*) appreciably. Similar calculations have been carried out for ρ_{02}^*, ρ_{11}^* and ρ_{20}^* and the results are collected in Table III where it is seen that the Dunham effect is inappreciable in the case of α_1^* and varies from 16 to 42 percent of the total discrepancy in the other cases. In only two cases does it decrease the discrepancy.

EXCITED STATE (CALCULATION OF a VALUES)

The attempt to determine the a values for the excited state in the same way as for the ground

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

[10] Pekeris, Phys. Rev. **45**, 98 (1934), also Jevons, reference 1, p. 27, and Birge, Bull. Nat. Res. Council (1926), p. 237.

state immediately leads to quite discrepant values. Thus Eq. (19) gives for a_1 roughly -2 whereas Eq. (10) (neglecting p^2C_{11}) gives -0.814. Now the discrepancy may be due to the uncertainty in H_e^* as measured, or to the neglect of p^2C_{03} in Eq. (19), of p^2C_{11} in Eq. (10) as well as of effects (2), (3) and (4) above. Whatever the difficulty, a reasonable value for a_1 cannot be obtained by averaging such divergent values—and since the value of a_2 depends to such an extent on the value of a_1, using Eqs. (11) and (17) we have four widely different values for a_2 with no basis for preferring any particular one of them. As a result, beyond a_2 even the sign of the higher a's is in doubt. After following down all the possibilities it soon became probable that the neglect of the Dunham correction terms was not the primary difficulty—but that the real trouble arose from the difficulty in extrapolating the measured values of D_v and H_v, respectively, to obtain D_e^* and H_e^*. This uncertainty was such as to produce even greater errors in β_1, γ_1, β_2, etc., and consequently to render the values of a_1, a_2, a_3 and a_4 as obtained respectively from Eqs. (19), (17), (15) and (13) quite untrustworthy. It seemed accordingly necessary to resort to a method of successive approximation, using only those experimental constants which could be determined fairly reliably from least squares representation of the remaining data, *viz.*, the values of ω_v and B_v. Since the variation with vibration of ω_v and B_v was much smaller for LiD than for LiH, the calculations were carried out for the LiD data (actually the LiH data gave comparable results—though the actual numerical values depended uncomfortably on the precise number of observations used in the least-square reckonings). The necessary expressions for LiD are:

$$\omega_v = 180.711 + 13.987u - 1.1784u^2 + 0.07932u^3 - 0.00353u^4 + 0.00006940u^5 \text{ (7 points)}$$

and

$$B_v = 1.6048_1 + 0.015940u - 0.0023732u^2 + 0.00012783u^3 - 0.00000417u^4 \text{ (6 points).}$$

An examination of the equations from (10) to (17) then shows that the a's of odd subscript can be obtained from the *rotational* constants α_1, α_2, and α_3 while the a's of even subscript can be obtained from the *vibrational* constants x_1, x_2 and x_3. The general procedure was to determine a first approximation to a_1, say a_{11}, from Eq. (10) by neglecting p^2C_{11}. With this a first approximation to a_2, say a_{21}, was then obtained from Eq. (11) neglecting p^2C_2O. Then by using Eqs. (15), (13), (16) and (17) in order, a_{31}, a_{41}, a_{51} and a_{61} were obtained. It was then possible to compute C_{11} and C_{20} approximately to get the second approximation of a_1 and a_2, say a_{12} and a_{22}, respectively. This led then to better values for the higher a's, to more reliable values for C_{11} and C_{20}, etc. The process is unfortunately very tedious and while not converging very rapidly soon gives results which do not oscillate very much in successive stages of the calculations.

The results are given in Table V for a_{n2} and a_{n5} together with the values of C_{lj} resulting.[11]

TABLE V. *Potential coefficients for upper state.*

Eq.	Band Constant	A_n	A_{n2}	A_{n5}		Value of C_{lj}
10	$Y_{11}^* = \alpha_1^*$	a_1	-0.8604	-0.8608	C_{10}	-53.45
11	$Y_{20}^* = x_1^*$	a_2	$+6.884$	$+6.948$	C_{01}	-46.22
15	$Y_{21}^* = \alpha_2$	a_3	-11.33	-11.44	C_{02}	$+214.40$
13	$Y_{30}^* = x_2$	a_4	$+30.40$	$+31.11$	C_{11}	$+3550$
16	$Y_{31}^* = \alpha_3$	a_5	-66.57	-67.77	C_{20}	-8840
17	$Y_{40}^* = x_3$	a_6	$+67.32$	$+68.48$		

The striking fact is the rapidity with which the coefficients increase in absolute magnitude as compared with the more normal ground state, and in particular the fact that a_2 is over 12 times as large as $|a_1|$. This will be discussed in more detail below.

The next step was to determine whether this set of a values was satisfactorily consistent with the predictions of the remaining equations. For this purpose Eq. (7) was used to determine from $Y_{10}^* = \omega_0^*$ the true value, ω_e, of the rate of oscillation for zero amplitude, and from Eq. (8), $Y_{01}^* = B_e^*$, the true value of $h/8\pi^2 I$. These then gave $p^2 = (B_e/\omega_e)^2$ and from Eqs. (9) and (19) theoretical values of $Y_{02}^* = D_e^*$ and $Y_{03}^* = H_e^*$, respectively, could be obtained. The results were $Y_{02}{}^{i*}(\text{calc.}) = -5.162 \times 10^{-4}$, $Y_{03}{}^{i*}(\text{calc.}) = +34.22 \times 10^{-8}$, $Y_{02}^*(\text{calc.}) = -16.88 \times 10^{-4}$ and $Y_{03}^*(\text{calc.}) = 202.18 \times 10^{-8}$. It was next necessary in each case to obtain least-square curves which

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[11] The values of C_{11} and C_{20} are the fourth approximations since these were the values determining the corrections in Eqs. (10) and (11) for the fifth approximations to a_1 and a_2, respectively.

passed through the observed data and these calculated values for $v=-\frac{1}{2}$. Since measurements could not be made for $v=1$ on LiD (and were uncertain on LiH) it was necessary to assign a probable value to say D_1, compute a least-square expression for D_1 to D_5 and calculate a D_e^* by setting $v=-\frac{1}{2}$. After a few trials a value of D_1 could be chosen such that this extrapolated D_e^* coincided with the one calculated theoretically. This gave for LiD

$$\beta_1{}^i=+2.64\times10^{-4}, \qquad \beta_2{}^i=-0.8907\times10^{-5},$$

$$\beta_1=+11.23\times10^{-4} \quad\text{and}\quad \beta_2=-4.7353\times10^{-5}.$$

A similar procedure in the case of the H_v values gave for LiD $\gamma_1{}^i=-39.54\times10^{-8}$, $\gamma_2{}^i=+18.420$ and for LiH, $\gamma_1=-250.01\times10^{-8}$ and $\gamma_2=+122.44\times10^{-8}$. Now it is to be admitted at once that great reliance cannot be placed on the actual values obtained from such an attempt to represent by least squares functions changing as rapidly as are D_v and H_v. The results, however, do represent a considerable improvement over those obtained empirically in Parts I and II. Thus in the case of LiD using Eq. (17) and the old value of $\beta_1{}^i=1.32\times10^{-4}$ we find $a_2=+3.56$ which is about *half* the value given in Table V. If we use the *new* value of $\beta_1{}^i$ given above we find $a_2=+5.90$ a result differing by only 15 percent. Likewise for LiH from the *old* $\beta_1(=10.1\times10^{-4})$ we have $a_2=5.30$ while from the *new* β_1, $a_2=5.80$, likewise a shift in the right direction. Again using Eq. (20) and the values of $\gamma_1{}^i$ and γ_1 we have for LiD a_3 (old) $=+3.9$, a_3 (new) $=-5.9$ and for LiH, a_3 (old) $=+3.7$, a_3 (new) $=-3.0$. Here the new values are both too small but have been altered 200 percent in the right direction and actually changed in sign by our process. Finally, using Eq. (18) and the values of $\beta_2{}^i$ and β_2 we have for LiD: a_4 (old) $=+69.0$ and a_4 (new) $=+51.2$, while for LiH: a_4 (old) $=+56.5$ and a_4 (new) $=+53$, again a shift in each case in the right direction.

We therefore conclude that to the extent that (1) the undetermined Dunham corrections p^2C_{lj} and (2) the omitted Kronig and Van Vleck terms may be neglected—the anomalous behavior of the upper states of LiD and LiH can be accounted for semi-quantitatively in terms of a potential curve which departs in a characteristic way from the usual shape. It is thus apparent that the anomalies of the upper state involving some 9 small coefficients which differ in sign or magnitude from the usual case, are pictured in a very satisfactory way in terms of a single potential curve and that this same curve accounts for a sizable fraction of the observed isotope discrepancy.

UPPER STATE ISOTOPE RELATIONS

We are now in a position to compute the Dunham contributions, $\Delta_1\rho_{lj}$, to the isotope discrepancies just as in the case of the ground state. The results of this with $\rho(p^2-p^{i^2})$ of Eq. (27) $=0.4917\times10^{-4}$ are given in Table III where the striking fact is apparent that the isotope discrepancies are *reduced* in four out of five cases, the Dunham term varying from 13 to 43 percent of the total discrepancy $(\rho_{lj}{}^*-\rho)$.

POTENTIAL CURVES

With the a values determined we may now write approximations to the potential curves (convergent near the equilibrium positions only) of the ground $^1\Sigma$ and upper $^1\Sigma$ states of LiH and LiD. These are for the ground state:

$$V=a_0{}'\xi^2(1-1.858\xi+2.580\xi^2-3.45\xi^3 +5.79\xi^4-12.2\xi^5+20.7\xi^6+\cdots, \qquad (28)$$

where for LiH $a_0{}'=6.57078\times10^4$ and for LiD $a_0{}'=6.5715\times10^4$ and for the upper state:

$$V=a_0{}''\xi^2(1-0.8608\xi+6.948\xi^2-11.44\xi^3 +31.11\xi^4-67.77\xi^5+68.48\xi^6+\cdots, \qquad (29)$$

where for LiH $a_0{}''=4.91646\times10^3$ and for LiD $a_0{}''=5.11154\times10^3$.

The ground states for the two molecules are thus very closely alike and follow the usual type lying *above* the osculating parabola for $\xi<0$ and *below* for $\xi>0$. On the other hand, the curves for the upper states differ somewhat more from one another and are distinctly anomalous in that although they rise above the corresponding parabolas for $\xi<0$ they quickly cross over and pass *above* again for small positive values of ξ. This behavior is more readily seen in Fig. 1 where the dotted curve is given by $a_0{}''\xi^2$ and the heavy curve represents Eq. (28). It is this peculiar form of anharmonicity in the upper state which

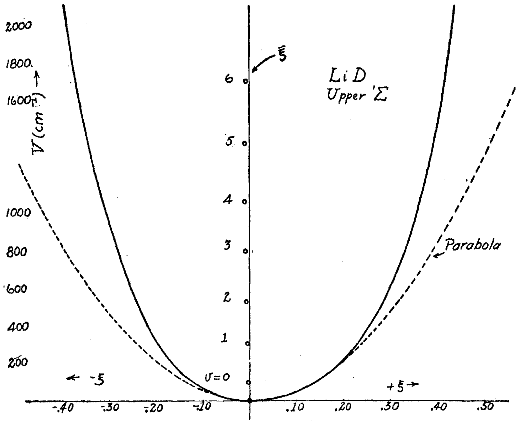

FIG. 1. The heavy line represents Eq. (29) while the parabola is $a_0\xi^2$. The rapid rise of the curve above the parabola on the right is to be noted. It is this which causes the molecule to travel more rapidly than usual along the right branch and hence to have an average ξ, $\bar{\xi}$, which is *less* than ξ_0. The corresponding average values for $v=0$, 1, etc., are indicated by circles at the appropriate height. It is this peculiar shape which likewise causes the observed vibrational rate ω_v to *increase* with v to a maximum value before decreasing thereafter in the normal way. The heavy curve of course must eventually fall away and cross the parabola as the molecule goes toward dissociation, though that point is far out of the range of validity of Eq. (29).

accounts in detail for the anomalies to which attention has been called so often in the literature. We therefore assume that although some L uncoupling may be present in this state it probably does not have much effect on the potential curve and is reflected only in the residual isotope discrepancies $(\rho_{lj}{}^*-\rho-\Delta_1\rho_{lj})$.

For purposes of reference the values of $B_e{}^*$ and $\omega_e{}^*$ as well as the values corrected for the Dunham effect for both states of the two molecules are given as follows:

$$\text{LiD}\left\{\begin{array}{lll} B_e{}^{i*\prime}=1.6048 & B_e{}^{i\prime}=1.6107 & r_e{}^{i\prime}=2.5795\text{A} \\ \omega_e{}^{i*\prime}=180.711 & \omega_e{}^{i\prime}=181.472 & \\ B_e{}^{i*\prime\prime}=4.2338 & B_e{}^{i\prime\prime}=4.2344 & r_e{}^{i\prime\prime}=1.5909_1\text{A} \\ \omega_e{}^{i*\prime\prime}=1055.12 & \omega_e{}^{i\prime\prime}=1055.015 & \end{array}\right.$$

$$\text{LiH}\left\{\begin{array}{lll} B_e{}^{*\prime}=2.8186 & B_e{}'=2.8375 & r_e{}'=2.5896\text{A} \\ \omega_e{}^{*\prime}=234.41 & \omega_e{}'=236.225 & \\ B_e{}^{*\prime\prime}=7.5131 & B_e{}''=7.5149 & r_e{}''=1.5915\text{A}. \\ \omega_e{}^{*\prime\prime}=1405.649 & \omega_e{}''=1405.401 & \end{array}\right.$$

From these the equilibrium separations are found where $(r_e{}'-r_e{}^{i\prime})=+0.0101\text{A}$ and $(r_e{}''-r_e{}^{i\prime\prime})=+0.00055\text{A}$.

Further from Eq. (12) we see that the *height* of the potential curves at the minima should be different for the two isotopes. Thus for the ground state $Y_{00}{}^*=15.93$ cm^{-1} and $Y_{00}{}^{i*}=8.98$, a difference of 6.95 cm^{-1}, while for the upper state $Y_{00}{}^*=7.39$ cm^{-1} and $Y_{00}{}^{i*}=0.26$ cm^{-1}, a difference of 7.13 cm^{-1}. Consequently we see that the electronic origin of the LiH bands should lie 0.18 cm^{-1} towards the violet of the LiD bands—an effect unfortunately too small to detect in this case.

These facts together with the data accompanying Eqs. (28) and (29) then enable us to draw three conclusions, *viz.*, (1) the *heavier* isotopic molecule is the *smaller*, its potential curve (2) has the greater convexity at the minimum and (3) lies below that of the lighter isotope. These differences it will be recalled are in the same direction as those predicted by Kronig[6] from the interaction of nuclear and electronic motions (effect (2) above).

By using Morse's expression for the dissociation energy, $D=\omega_e{}^2/4x$, we have after correcting for the zero-point vibrational energy $\mathbf{D}_0{}''=2.53$ volts for LiD and 2.54 volts for LiH where the difference is not significant. If then the upper state dissociates into a normal H atom and a 2^2P Li atom we have $\mathbf{D}_0{}'=1.15$ volts for LiD and $\mathbf{D}_0{}'=1.18$ volts for LiH. These results due to the small number of vibrational levels in the ground state can hardly be depended on to more than ±0.2 volt.