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Millimeter-Wave Spectra and Molecular Constants of ^{6}LiD and ^{7}LiD[†]

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The $J=0\rightarrow 1$ rotational line of LiD has been measured in the ground vibrational state and in the first excited state. The measurements have provided values of the frequencies and the spectral constants.

	ν_0 (Mc/sec)	ν_1 (Mc/sec)	Y_{01} (Mc/sec)	Y_{11} (Mc/sec)	B_e(Mc/sec)
^{6}LiD	260 306.96 ± 0.05	254 596.63 ± 0.05	131 615.07 ± 0.04	−2898.90 ±0.04	131 673 ± 4
^{7}LiD	251 043.53 ± 0.05	245 635.62 ± 0.05	126 905.36 ± 0.04	−2744.61 ±0.04	126 961 ± 4

The value of r_e, which is independent of isotopic substitution, is found to be 1.594 90 ± 0.000 02 Å. From these constants the corresponding values for the LiH species are derived.

I. INTRODUCTION

Because the alkali hydrides have relatively simple electronic structures, precise physical measurements of these molecules are of particular interest. Probably because they have high vaporization temperatures and a tendency to dissociate, the microwave spectra of none of them have previously been observed. We report here successful measurements with microwave spectroscopy of the $J=0\rightarrow 1$ transitions of the isotopic species ^{6}LiD and ^{7}LiD in the ground state and in the first excited vibrational state. Their lowest rotational frequency falls in the 1.2-mm wave region, at 250 Gc/sec. The lowest rotational frequency of LiH falls in the submillimeter wave region, near $\lambda = 0.6$ mm. Although lines of LiF and LiCl have been measured with our hot-cell spectrometer in the region from 0.5 to 0.6 mm (see preceding paper), the sensitivity of the spectrometer in this region did not prove adequate for detection of the LiH lines because of the high degree of dissociation of the vaporized LiH molecules. We estimate that about 99% of the LiD molecules dissociate in the vaporized state; the dissociation rate for the LiH is expected to be still higher. From measurements on the deuterated species, precise evaluation has been made of the equilibrium internuclear distance, r_e, which is independent of isotopic substitution. Accurate calculations of B_e, the constant for the moment of inertia, and of other spectral constants of the LiH species have been made from the results of LiD measurements.

Measurements of molecular-beam electric resonance have been made on LiD and LiH in strong electric fields by Wharton, Gold, and Klemperer.[1] From these measurements alone, no evaluation of the rotational constants could be made, but the value of the molecular dipole moment and of the ^{7}Li nuclear-quadrupole coupling was gained. Lawrence, Anderson, and Ramsey[2] have measured the rotational magnetic moment by the molecular-beam magnetic-resonance method.

More than thirty years ago a remarkably complete and accurate study of the optical spectra of ^{7}LiH and ^{7}LiD was made by Crawford and Jorgensen,[3–5] who used a 21-ft grating with a dispersion of 1 Å/mm. We have used their values of the centrifugal distortion and vibration-rotation constants with our accurate microwave measurement of the $J=0\rightarrow 1$ rotational transitions in the $v=0$ and the $v=1$ states to obtain more precise values of Dunham's constants Y_{01} and Y_{11}, also of B_e and r_e.

The millimeter-wave spectrometer and free-space hot cell were the same as those used in the study of LiF and LiCl reported in the preceding paper. Doppler broadening at the observation temperature, 980°K, and at a frequency of 250 Gc/sec was of the order of 2.0 Mc/sec and thus greater than the nuclear-quadrupole splitting[1] expected for Li, $eqQ = 349$ kc/sec. Thus only a single line was observed for each isotopic species in a given vibrational state.

II. LITHIUM DEUTERIDE

Figure 1 shows the $v=0$, $J=0\rightarrow 1$ line of ^{7}LiD observed with the conventional video-sweep method. Figure 2 shows a recording of the $v=1$, $J=0\rightarrow 1$ line. The deuterium concentration was 99%. For the observations on ^{6}LiD the concentration of ^{6}Li in the sample was 95%. The sample of ^{7}LiD contained ^{7}Li in its natural concentration of 93%. Despite the rather large dipole moment, 5.9 D,[1] the lines are weak because of the high dissociation of the molecules in the cell. The large amount of hydrogen gas resulting from their dissociation tends to broaden the lines and necessitates a rapid, continuous pumping of the cell. Lines in the first excited vibrational state, $v=1$, have only one-fifth the strength of the $v=0$ lines. They could be observed only with difficulty on the CRO scope but were recorded with a signal-to-noise ratio of about 8 to 1. Lines for the $v=2$ state could not be detected.

In the analysis of our results we used the frequency equation

$$\begin{aligned}\nu_{Jv} = {} & 2Y_{01}(J+1) + 2Y_{11}(J+1)(v+\tfrac{1}{2}) \\ & + 2Y_{21}(J+1)(v+\tfrac{1}{2})^2 + 4Y_{02}(J+1)^3 \\ & + 4Y_{12}(J+1)^3(v+\tfrac{1}{2}) + \cdots , \end{aligned} \tag{1}$$

obtained from Dunham theory,[6] in which the Y's are the Dunham spectral constants described in the preceding paper. Since only two frequencies

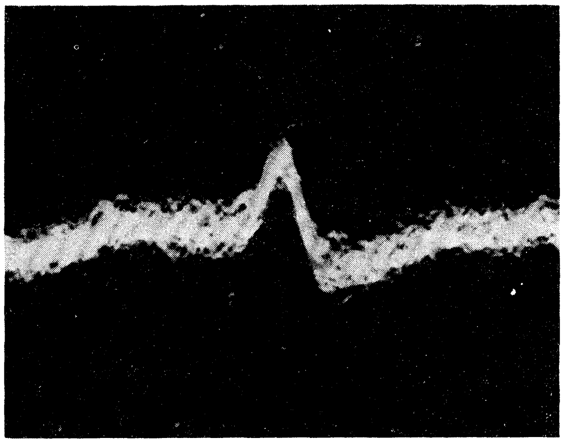

FIG. 1. Oscilloscope display of the $J = 0 \rightarrow 1$, $v = 0$ line of ^{7}LiD at 251 Gc/sec (linewidth approximately 1.6 Mc/sec).

were measured for each isotopic species, the second-order constants $Y_{21}(\approx \gamma_e)$, $Y_{02}(\approx D_e)$, and $Y_{12}(\approx \beta_e)$ were taken from the study by Crawford and Jorgensen[3] on optical spectra; the two constants Y_{01} and Y_{11} were evaluated from our measurements of ν_0 and ν_1 from the relations

$$Y_{01} = \tfrac{1}{4}(3\nu_0 - \nu_1) + \tfrac{3}{4}Y_{21} + 2Y_{02}, \tag{2}$$

$$Y_{11} = \tfrac{1}{2}(\nu_0 - \nu_1) + 2Y_{21} + 2Y_{12}, \tag{3}$$

which were obtained from Eq. (1). The terms of next-higher order, $2Y_{31}(J+1)(v+\frac{1}{2})^3$ and $Y_{03}(J+1)^3 \times [(J+2)^3 - J^3]$, do not influence the evaluation because of the low values of J and v employed. Table I gives the observed frequencies and the resulting Y values.

The errors stated for Y_{01} and Y_{11} in Table I are the result of our measurements only. However, the absolute errors in these terms are considerably larger because of the uncertainties in the terms Y_{21}, Y_{02}, and Y_{12} given by Crawford and Jorgensen.[3] The largest uncertainty comes from Y_{21}, which reduces the absolute accuracy of Y_{01} to ±1.0 Mc/sec and that of Y_{11} to ±2.4 Mc/sec. Because the values of Y_{21}, Y_{02}, and Y_{12} are small compared to Y_{01} and because these terms for the ^{6}LiD species could be calculated from simple isotopic relations, they do not significantly affect the ratio of $Y_{01}(^6\text{LiD})$ to $Y_{01}(^7\text{LiD})$. An accurate value for this ratio is needed for calculation of the isotopic effects discussed in the next paragraph.

The mechanically significant constant $B_e = h/(8\pi^2 I_e)$ is not exactly equivalent to the term Y_{01}, but can be obtained from Y_{01} by addition of some small corrections:

$$B_e = Y_{01} + \delta_1 + \delta_2 + \delta_3. \tag{4}$$

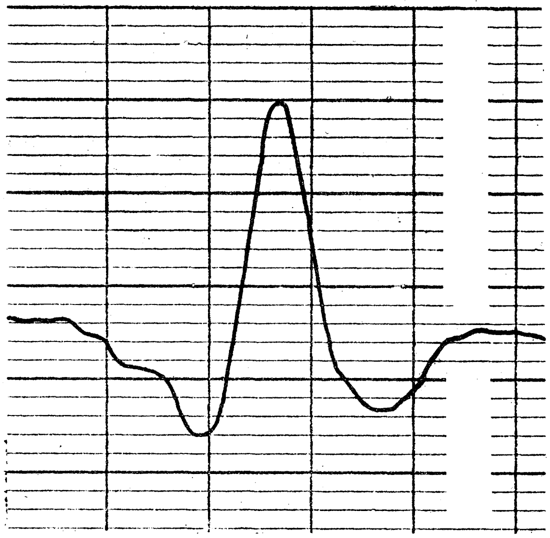

FIG. 2. Recording of the $J = 0 \rightarrow 1$, $v = 1$ line of ^{7}LiD at 245 Gc/sec (separation of vertical scale markers 1 Mc/sec).

The first correction δ_1 accounts for the unequal sharing of the electrons between the atoms and for effects of L uncoupling. Both these effects give rise to a molecular rotational magnetic moment. Consequently the correction δ_1 can be conveniently expressed as

$$\delta_1 = -g_J Y_{01}/1838, \tag{5}$$

where g_J is the molecular-rotational g factor. In evaluating δ_1, we have used the value of $g_J = -0.272 \pm 0.005 \mu_N$ for ^{7}LiD obtained by Lawrence *et al.*[2] The value $g_J = -0.254$ for ^{6}LiD was obtained by simple isotopic conversion based on an ion-pair model.[7] The correction δ_2 accounts for effects of a wobbling of the internuclear axis because of interaction between the electronic motions and the end-over-end rotation of the moleucle.[4,5,8] The third correction, δ_3, accounts for interaction between vibration and rotation arising from anharmonicity in the vibrational motions[6] (Dunham's correction). As was explained in the previous paper, δ_2 and δ_3 are both inversely proportional to the square of the reduced mass and can be calculated from the known reduced masses μ and μ' of the two isotopic species ^{6}LiD and ^{7}LiD from the relation

$$\delta_2 + \delta_3 = \epsilon B'B/(B' - B), \tag{6}$$

$$\text{where} \quad \epsilon = (B/B') - (\mu'/\mu), \tag{7}$$

$$\text{and} \quad B = Y_{01} + \delta_1. \tag{8}$$

The calculated values of δ_1 and $\delta_2 + \delta_3$ are listed in Table II with the resulting B_e and r_e values. Also

TABLE I. Measured frequencies and spectral constants of LiD (Mc/sec).

	^{6}LiD	^{7}LiD
ν ($v = 0$, $J = 0 \rightarrow 1$)	260 306.96 ± 0.05	251 043.53 ± 0.05
ν ($v = 1$, $J = 0 \rightarrow 1$)	254 596.63 ± 0.05	245 635.62 ± 0.05
Y_{01}	131 615.07 ± 0.04	126 905.36 ± 0.04
Y_{11}	−2 898.90 ± 0.04	−2 744.61 ± 0.04

TABLE II. Isotopic effects and internuclear distance of LiD (spectral constants in Mc/sec).

	^{6}LiD	^{7}LiD
Y_{01}	131 615.07	126 905.36
δ_1	$+18.21 \pm 0.34$	$+18.80 \pm 0.34$
δ_3	$+18.5$ (Ref. 5)	$+17.2$ (Ref. 5)
$\delta_2+\delta_3$	39 ± 4	37 ± 4
B_e	$131\,673 \pm 4$	$126\,961 \pm 4$
r_e	$1.594\,90 \pm 0.000\,02$ Å	

listed is the separate value of δ_3 obtained earlier from optical spectroscopic measurements. From comparison it is seen that δ_1, δ_2, and δ_3 for these molecules have the same sign and are approximaly of the same magnitude.

III. DERIVED CONSTANTS OF LiH

Certain of the spectral constants of LiH can be derived with good accuracy from those of LiD by use of their known, and highly accurate, mass ratios. Table III gives values of B_e, Y_{01}, and Y_{11} thus obtained. The mechanically significant constant B_e is calculated from the isotopic relation

$$\mu' B_e' = \mu B_e , \tag{9}$$

TABLE III. Calculated constants of LiH (Mc/sec).

	^{6}LiH	^{7}LiH
B_e	$230\,164 \pm 7$	$225\,452 \pm 7$
Y_{01}	$229\,964 \pm 5.5$	$225\,256 \pm 5.5$
Y_{11}	$6\,700 \pm 6$	$6\,495 \pm 6$

where μ is the reduced mass and where the primed values are those for the H isotope. The spectral constants Y_{01} for ^{6}LiH and ^{7}LiH were obtained by correction of the values of B_e' for the effects of electron displacement, wobbling, and anharmonicity, as described above, Eqs. (5) and (6). The values of Y_{11} given in Table III were obtained from the isotopic relation

$$Y_{11}' = (\mu/\mu')^{3/2} Y_{11} . \tag{10}$$

From optical spectra Crawford and Jorgensen[4] obtained an experimental value of 225 237 Mc/sec for Y_{01} of ^{7}LiH, in good agreement with our derived value. The difference of nearly 100 Mc/sec between their optional value for Y_{11}(^{7}LiH) 6393 Mc/sec and the value derived from our measurements in LiD indicates that there may be large isotopic effects on this term.

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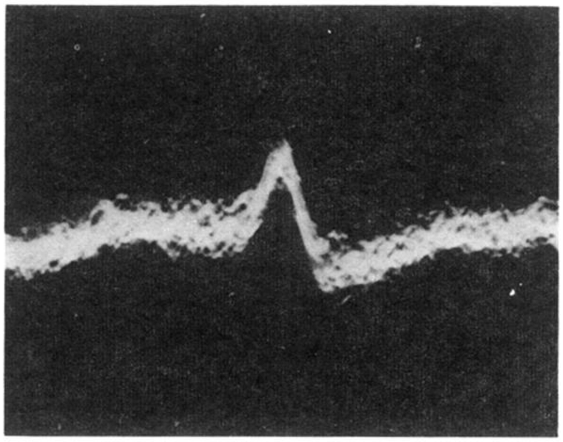

FIG. 1. Oscilloscope display of the $J=0\rightarrow 1$, $v=0$ line of ^{7}LiD at 251 Gc/sec (linewidth approximately 1.6 Mc/sec).