Millimeter- and Submillimeter-Wave Spectra and Molecular Constants of LiF and LiCl[†]

Edwin F. Pearson and Walter Gordy

Department of Physics, Duke University, Durham, North Carolina

(Received 15 July 1968)

High-precision measurements of many millimeter- and submillimeter-wave rotational lines of different isotopic species of lithium fluoride and chloride in four different vibrational states have provided accurate evaluation of their rotational, vibrational, and potential constants. The resulting values are:

	Y_{01} (Mc/sec)	Y_{11} (Mc/sec)	Y_{02} (kc/sec)	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
$^6\text{Li}^{19}\text{F}$	45 230.848	722.417	442.95	1.563 857	964.24	9.136
$^7\text{Li}^{19}\text{F}$	40 329.808	608.182	352.36	1.563 857	910.25	8.104
$^6\text{Li}^{35}\text{Cl}$	24 116.578	291.760	132.56	2.020 671	686.23	5.096
$^6\text{Li}^{37}\text{Cl}$	23 925.383	288.305	130.42	2.020 671	683.64	5.084
$^7\text{Li}^{35}\text{Cl}$	21 181.004	240.122	102.19	2.020 671	643.31	4.501
$^7\text{Li}^{37}\text{Cl}$	20 989.825	236.894	100.41	2.020 671	640.22	4.490

$B_e = h/8\pi^2\mu r_e^2$ is shown to differ from the observed value Y_{01} because of small isotopic effects.

I. INTRODUCTION

Although pure rotational transitions of both lithium fluoride and lithium chloride have already been observed, additional measurements at higher frequencies are needed for accurate evaluation of their molecular constants, all of which depend on centrifugal distortion effects which can be evaluated accurately only by measurements of higher J transitions. Also measurements of isotopic species are needed for evaluation of second-order isotopic effects which are expected to be significant for these light molecules. Because these molecules have very small moments of inertia, even their lowest frequency, the $J = 0 \to 1$ transition, falls well into the millimeter-wave range, that for LiCl at $\lambda = 7.1$ mm, that for LiF at $\lambda = 3.7$ mm.

The $J = 0 \to 1$ transition of ^{6}LiF has been measured with high accuracy by Wharton, Klemperer, Gold, Strauch, Gallagher, and Derr,[1] who used the electric-beam resonance method; the $J = 0 \to 1$ and $J = 1 \to 2$ transitions of ^{7}LiF were measured in this laboratory[2] with somewhat less accuracy by molecular-beam absorption techniques. Using a Stark-modulation microwave spectrometer, Lide, Cahill, and Gold[3] measured the $J = 0 \to 1$ of the ^{7}LiCl species in vibrational states up to $v = 2$. From the $J = 0 \to 1$ transitions alone, no measurement of the centrifugal constants could be made, and hence no accurate evaluation of the molecular constants was possible.

Because of the incomplete state of the work it seemed desirable that further measurements be made on these relatively simple molecules for which theoretical treatments are most applicable. We have been successful in making measurements of high precision at submillimeter-wave frequencies up to 504 Gc/sec ($\lambda = 0.59$ mm, $J = 11 \to 12$) on isotopic species of LiCl and to 538 Gc/sec ($\lambda = 0.56$ mm, $J = 5 \to 6$) on species of LiF. Vibrational states up to $v = 3$ were observed. From these measurements complete re-evaluation of all the molecular constants has been made.

II. EXPERIMENTAL PROCEDURE

The hot cell employed in this work consists of stainless-steel pipe 2.5 in. in diameter and 5 ft in length, through which the millimeter waves were focused with teflon lenses. The salt to be investigated was placed in the central region and was heated with external heating elements. The vaporized salt quickly condensed on the end sections of the pipe which were cooled to prevent condensation on the cell windows. A sketch of the over-all microwave system is given in Fig. 1. Details of the design of the hot cell are given in a previous publication.[4]

The radiation source and detector, described in an earlier paper,[5] have been used for a number of years in this laboratory. The multiplier crystal of bombarded silicon was kindly supplied us by C. A. Burrus, of the Bell Telephone Laboratories. Ample submillimeter-wave power was generated for measurements with the heated cell to wave
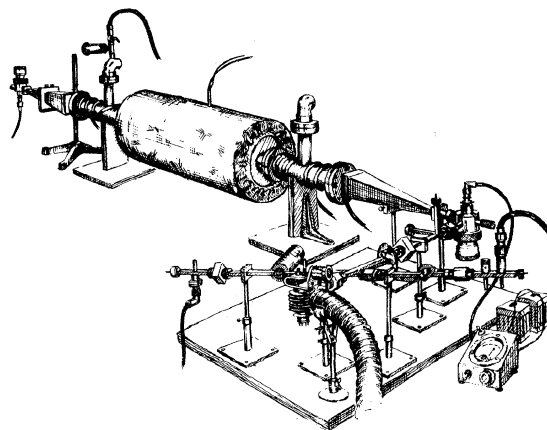

FIG. 1. Sketch of microwave components of the high-temperature submillimeter-wave spectrometer.
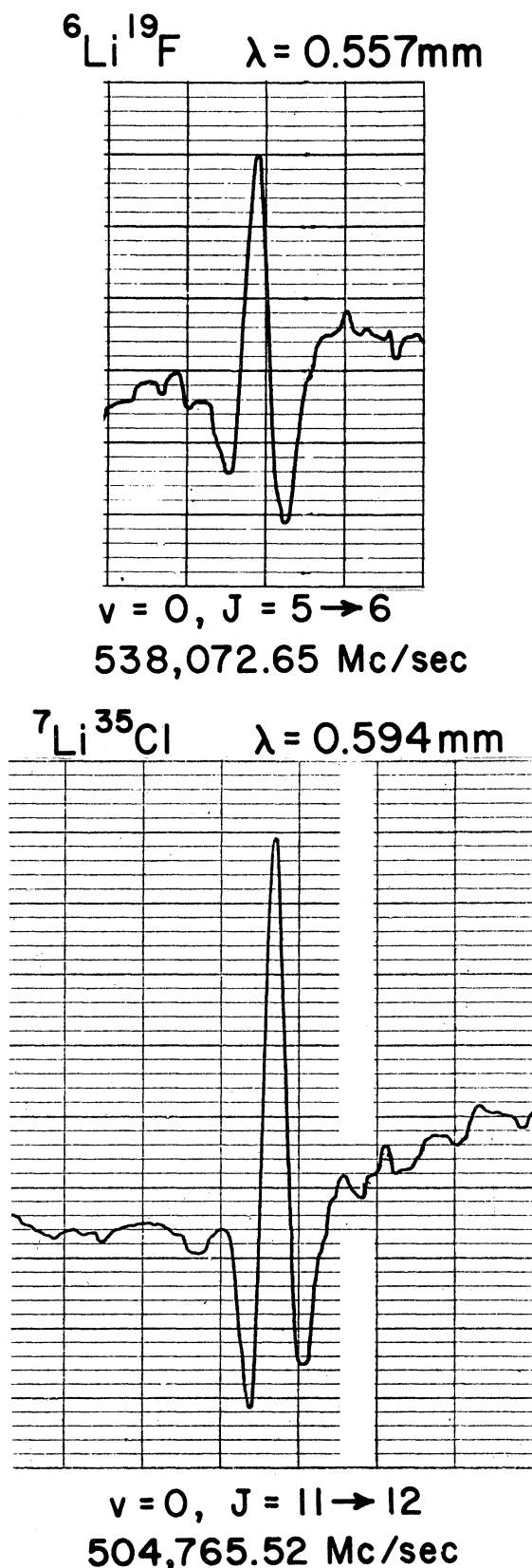
^{6}Li^{19}F $\lambda = 0.557$mm

v = 0, J = 5→6

538,072.65 Mc/sec

^{7}Li^{35}Cl $\lambda = 0.594$mm

v = 0, J = 11→12

504,765.52 Mc/sec

FIG. 2. Rotational lines of LiF and LiCl in the 0.5—0.6 millimeter-wave region. Separations of vertical scale markers 3 Mc/sec.

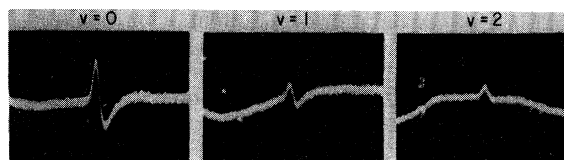FIG. 3. Oscilloscope display of the $J = 3 \to 4$ transition of ^{6}Li^{19}F in different vibrational states ($\lambda = 0.85$ mm). Linewidth approximately 1.6 Mc/sec.

lengths of approximately a half-millimeter. Figure 2 shows lines of LiF and LiCl observed in the 0.5- to 0.6-mm wave region. Figures 3 and 4 illustrate the signal-to-noise ratio obtained on submillimeter rotational lines of molecules in excited vibrational states, displayed on the oscilloscope and on the pen-and-ink recorder. Frequency measurements were made at the fundamental klystron frequency with standard frequency markers monitored by standard frequencies broadcast by station WWV of the National Bureau of Standards.

III. ANALYSIS

Evaluation of the spectral constants was done by the usual least-squares method.[6,7,2] The rotational line frequencies are expressed in a series involving the Dunham Y constants:

$$\nu_{J,v} = 2Y_{01}(J+1) + 2Y_{11}(J+1)(v + \tfrac{1}{2})$$
$$+ 2Y_{21}(J+1)(v + \tfrac{1}{2})^2 + 2Y_{31}(J+1)(v + \tfrac{1}{2})^3$$
$$+ 4Y_{02}(J+1)^3 + 4Y_{12}(J+1)^3(v + \tfrac{1}{2})$$
$$+ Y_{03}(J+1)^3[(J+2)^3 - J^3] + \cdots . \tag{1}$$

In practice, the fundamental klystron frequency rather than the line frequency was used in the above expression, and the right side of this equation was divided by the integer representing the harmonic of the klystron at which the transition was observed. This procedure gave a uniform

^{6}Li^{35}Cl $J = 9 \to 10$, $\lambda = 0.63$mm

v = 0   v = 1   v = 2

478,893.22   473,123.40   467,415.12
(Mc/sec)
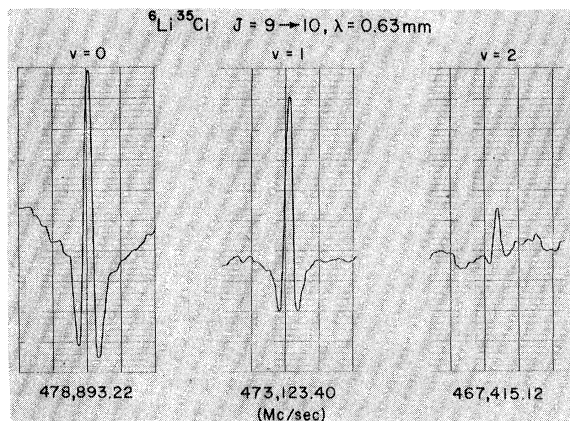
FIG. 4. Recording of submillimeter-wave lines of LiCl in different vibrational states. Separations of vertical scale markers 3 Mc/sec.

E. F. PEARSON AND W. GORDY

weighting of the data since all measurements of the klystron frequency were of nearly equal precision. The n equations corresponding to n different observed frequencies were then reduced to m least-squares normal equations in m unknowns, and this set of simultaneous equations was then solved for the spectral constants and their rms errors. All calculations were programmed in FORTRAN IV language for machine computation. They were processed on the IBM system 360/75 at the Triangle Universities Computation Center.

Most of the previous data on the alkali halides[5-7] have been fitted adequately with five Dunham constants Y_{01}, Y_{11}, Y_{21}, Y_{02}, and Y_{12}. In the present work the additional constants Y_{03} and Y_{31} were required for LiF and Y_{03} for LiCl so there would be consistent fitting of the measured frequencies within the estimated limits of error.

Table I gives the measured and calculated frequencies for different transitions of ⁶LiF and ⁷LiF. The expected hyperfine structure in the Li quadrupole coupling is too small for resolution. The accuracy of measurement of the $J = 0 \rightarrow 1$ transition, previously measured by Wharton et al.[1] with the molecular-beam electric resonance method could not be improved. Hence, in our analysis we have used their value for this frequency. The calculated frequencies are those obtained from Eq. (1) with the optimum choice of seven Dunham constants. Since there are many more measured frequencies than adjustable parameters, the agreement of the observed and calculated fre-

quencies gives an indication of the accuracy and internal consistency of the measurements. Because the term involving Y_{03} has only slight effects on the frequencies, this constant is not measured with significant accuracy. However, its effects are definitely outside the limits of error for the highest observed values of v and J. It was therefore computed from the other spectral constants and its effect subtracted from the high J lines. So far as we are aware, the effects of the cubic term involving Y_{31} have not been detected previously. Because of its poor signal-to-noise ratio, Wharton et al. did not include the $v = 3$, $J = 0 \rightarrow 1$ line in their analysis and could not have detected effects of the Y_{31} term. The omission of this term has reduced the accuracy of their analysis. Our measurements, which include three rotational transitions in the $v = 3$ state, permit a reliable evaluation of Y_{31} and show that the term must be included for best evaluation of the other parameters.

Table II gives the observed and calculated frequencies for the different isotopic species of lithium chloride. Dunham constants used with Eq. (1) in calculation of the frequencies for both LiF and LiCl are listed in Table III. Effects of the Y_{03} term, although small, were measureable; but effects of the Y_{31} term, measured in LiF, could not be detected for LiCl.

In terms of the more familiar spectral notation, the Dunham constants have the following significance:

TABLE I. Observed frequencies of lithium fluoride.

v	$J \rightarrow J'$	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)
		⁶Li¹⁹F		⁷Li¹⁹F	
0	0 → 1	89 740.46[1]	−0.01		
0	1 → 2	179 470.35	−0.02	160 096.33	0.01
0	2 → 3	269 179.18	0.05	240 123.47	0.02
0	3 → 4	358 856.19	0.03	320 125.36	0.01
0	4 → 5	448 491.07	0.15	400 095.62	0.01
0	5 → 6	538 072.65	−0.18	480 019.73	−0.09
1	0 → 1	88 319.18[1]	−0.01		
1	1 → 2	176 627.91	−0.01	157 700.92	−0.01
1	2 → 3	264 915.79	0.05	236 530.55	−0.05
1	3 → 4	353 172.23	0.04	315 335.27	−0.03
1	4 → 5	441 386.83	0.01	394 106.70	−0.01
1	5 → 6			472 836.69	0.16
2	0 → 1	86 921.20[1]	0.00		
2	1 → 2	173 832.04	−0.02	155 342.51	−0.02
2	2 → 3	260 722.24	0.02	232 993.30	0.07
2	3 → 4	347 581.39	0.01	310 619.23	0.02
2	4 → 5			388 212.19	−0.10
3	1 → 2	171 082.27	0.02	153 020.86	−0.01
3	2 → 3	256 597.84	0.01	229 510.98	0.02
3	3 → 4	342 082.66	−0.05	305 976.64	0.03
3	4 → 5			382 409.64	−0.06

TABLE II. Observed frequencies of lithium chloride.

ν	$J \to J'$	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)
		$^6\text{Li}^{35}\text{Cl}$		$^6\text{Li}^{37}\text{Cl}$	
0	$2 \to 3$	143 812.25	0.01	142 675.64	0.01
0	$3 \to 4$	191 734.87	0.02	190 219.61	0.00
0	$4 \to 5$	239 644.77	−0.01		
0	$5 \to 6$	287 538.84	−0.02	285 267.05	0.04
0	$6 \to 7$	335 413.85	−0.05	332 764.13	−0.06
0	$9 \to 10$	478 893.22	−0.02	475 112.22	−0.02
1	$2 \to 3$	142 080.39	0.05	140 964.20	0.00
1	$3 \to 4$	189 425.70	−0.04	187 937.80	0.01
1	$5 \to 6$	284 075.59	0.00	281 844.58	−0.07
1	$6 \to 7$	331 373.70	−0.03	328 771.68	−0.04
1	$9 \to 10$	473 123.40	0.15	469 410.42	0.13
2	$2 \to 3$	140 366.96	−0.03	139 271.10	0.01
2	$3 \to 4$			185 680.41	0.02
2	$5 \to 6$	280 649.43	−0.02		
2	$6 \to 7$	327 376.87	−0.01	324 821.92	−0.07
2	$9 \to 10$	467 415.12	−0.05		
3	$2 \to 3$	138 672.25	0.02		
0	$3 \to 4$	168 463.84	0.01	166 947.76	0.03
0	$4 \to 5$	210 561.50	0.04	208 666.65	0.01
0	$5 \to 6$	252 646.80	−0.05	250 373.49	−0.03
0	$6 \to 7$			292 066.02	0.02
0	$7 \to 8$	336 771.14	−0.03	333 741.59	−0.06
0	$10 \to 11$	462 804.95	0.08	458 643.70	0.02
0	$11 \to 12$	504 765.52	−0.08		
1	$3 \to 4$	166 562.04	0.01	165 071.41	−0.05
1	$4 \to 5$	208 184.31	0.01	206 321.40	0.00
1	$5 \to 6$	249 794.36	−0.04	247 559.38	0.01
1	$7 \to 8$	332 968.36	−0.07	329 989.98	0.06
1	$10 \to 11$	457 577.67	0.13		
2	$3 \to 4$	164 679.28	0.04	163 213.99	0.05
2	$4 \to 5$	205 830.92	0.00	203 999.55	−0.04
2	$5 \to 6$	246 970.49	−0.01	244 773.35	0.00
2	$7 \to 8$	329 203.68	−0.05	326 275.66	−0.02
3	$4 \to 5$	203 501.30	−0.01		
3	$5 \to 6$	244 175.15	0.02		

TABLE III. Rotational constants of lithium fluoride and lithium chloride.

	$Y_{01}(\approx B_e)$ (Mc/sec)	$Y_{11}(=-\alpha_e)$ (Mc/sec)	$Y_{21}(=\gamma_e)$ (Mc/sec)	$Y_{31}(=\delta_e)$ (Mc/sec)	$Y_{02}(=-D_e)$ (kc/sec)	$Y_{12}(=-\beta_e)$ (kc/sec)
$^6\text{Li}^{19}\text{F}$	45 230.848	−722.417	5.918	−0.0212	−442.95	4.81
	± 0.013	± 0.028	± 0.016	± 0.0028	± 0.16	± 0.12
$^7\text{Li}^{19}\text{F}$	40 329.808	−608.182	4.670	−0.0104	−352.36	3.73
	± 0.014	± 0.029	± 0.017	± 0.0028	± 0.17	± 0.09
$^6\text{Li}^{35}\text{Cl}$	24 116.578	−291.760	1.547		−132.56	0.80
	± 0.005	± 0.006	± 0.002		± 0.04	± 0.02
$^6\text{Li}^{37}\text{Cl}$	23 925.383	−288.305	1.526		−130.42	0.77
	± 0.006	± 0.009	± 0.003		± 0.04	± 0.03
$^7\text{Li}^{35}\text{Cl}$	21 181.004	−240.122	1.189		−102.19	0.57
	± 0.004	± 0.005	± 0.001		± 0.02	± 0.02
$^7\text{Li}^{37}\text{Cl}$	20 989.825	−236.894	1.172		−100.41	0.52
	± 0.006	± 0.008	± 0.002		± 0.03	± 0.03

E. F. PEARSON AND W. GORDY

$$Y_{01} \approx B_e \qquad Y_{10} = \omega_e \qquad Y_{20} = -\omega_e x_e$$
$$Y_{02} = -D_e \qquad Y_{11} = -\alpha_e \qquad Y_{21} = \gamma_e \qquad (2)$$
$$Y_{03} = H_e \qquad Y_{12} = -\beta_e \qquad Y_{31} = \delta_e \ .$$

The correspondence of these constants is close except that of Y_{01} and B_e, which is more correctly expressed by

$$Y_{01} = B_e \ [1 + (B_e/\omega_e)^2 \beta_{01}], \qquad (3)$$

where β_{01} is a small factor, which is a function of the potential constants.

IV. ISOTOPIC EFFECTS AND INTERNUCLEAR DISTANCES

The simple theory of a vibrating diatomic rotor gives the following relation between the spectral constants and reduced masses μ and μ' of two isotopic species of a molecule:

$$Y_{l,m}{}'/Y_{l,m} = (\mu/\mu')^{(l+2m)/2} . \qquad (4)$$

The only spectral term in this report for which the simple isotopic relation is not adequate is Y_{01} ($\approx B_e$). The isotopic corrections to Y_{01} are caused by three effects:

(1.) $\delta_1 =$ correction for uncertain electron distribution caused by ionic transfer of electrons and L uncoupling,

(2.) $\delta_2 =$ correction for interaction between nuclear and electronic motion not including perturbations of nearby electronic states,

(3.) $\delta_3 =$ correction for anharmonicity caused by the interaction of rotation and vibration (the Dunham correction).

All these corrections are sufficiently small for them to be taken additively. The term B_e can be expressed as

$$B_e = Y_{01} + \delta_1 + \delta_2 + \delta_3 . \qquad (5)$$

The correction δ_1, which is proportional to the molecular g factor, can be expressed[8] approximately by

$$\delta_1 = g_J Y_{01}/1838. \qquad (6)$$

Crawford and Jorgensen[9] suggested that the second isotopic effect, which manifests itself as a wob-

bling of the nuclei, should be appreciable in light molecules. Van Vleck[10] treated both the first and second effects. Later, Rosenbloom, Nethercot, and Townes[11] re-examined these effects for the terms which affect Y_{01} and from perturbation theory derived expressions for the corrections mentioned above. Although their expression for δ_2 cannot be evaluated explicitly, it shows that δ_2 varies inversely as the square of the reduced mass. Since B_e depends upon the first power of the inverse reduced mass, measurements on more than one isotopic species can be used for correction of the B_e values from the known mass ratios. One does this by writing

$$(B + \delta_2)/(B' + \delta_2') = \mu'/\mu \qquad (7)$$

and $\epsilon = (B/B') - (\mu'/\mu) . \qquad (8)$

Since $\delta_2 \sim 1/\mu^2$, these equations can be combined to give

$$\delta_2 = \epsilon \ BB'/(B' - B). \qquad (9)$$

In practice, the corrections δ_2 and δ_3 are usually calculated together. This can be done because δ_3, the anharmonic correction, also has an inverse-squared reduced-mass dependence. The anharmonic correction can, in principle, be calculated explicitly from the expression given by Dunham, Eq. (3), but this calculation usually does not give good accuracy. In the molecules studied here, the anharmonic effect makes a much smaller contribution than the wobbling effect.

Corrections to Y_{01} for the three isotopic effects described above are given in Table IV. The electron-distribution correction δ_1 was calculated by Eq. (6) from the g values given in the literature. The g values reported by Russell[12] were used for computation of the δ_1 values given in Table IV. Those for LiCl were those given by Mehran, Brooks, and Ramsey.[13] The Dunham correction δ_3 was calculated from the relations given by him. Because this effect was very much smaller than the other two and because the errors in the computed values were nearly as large as the values themselves, these terms were not explicitly used for correction of Y_{01}. Instead the Dunham effect was included in the mass-ratios adjustment of the B values.

Adjustment of the B values to yield correct reduced-mass ratios gives the correct for nuclear wobbling. The Y_{01} values were first corrected by

TABLE IV. Isotopic effects and molecular constants of lithium fluoride and lithium chloride (Mc/sec).

	$^6Li^{19}F$	$^7Li^{19}F$	$^6Li^{35}Cl$	$^6Li^{37}Cl$	$^7Li^{35}Cl$	$^7Li^{37}Cl$
Y_{01}	45 230.848	40 329.808	24 116.578	23 925.383	21 181.004	20 989.825
δ_1	− 2.015	− 1.410	− 1.369	− 1.372	− 0.978	− 0.982
δ_3	+ 0.046	+ 0.081	− 0.015	− 0.032	− 0.023	− 0.039
$\delta_2 + \delta_3$	+ 1.723	+ 1.370	+ 1.039	+ 1.023	+ 0.801	+ 0.787
B_e	45 230.5$_{56}$	40 329.7$_{68}$	24 116.2$_{48}$	23 925.0$_{34}$	21 180.8$_{27}$	20 989.6$_{30}$
r_e	1.563 857 Å				2.020 671 Å	
	± 0.000 021				± 0.000 027	

δ_1, and the resulting B values were used for computation of the isotopic discrepancies. Lithium fluoride, having only two isotopic species, provided only one determination of the effect and therefore gave no test of the consistency of the procedure. The four species of lithium chloride allow six independent determinations of the effect. Two of these determinations, however, come from the chlorine substitution only and are therefore not very accurate. The values of ϵ thus determined by the mass ratios with Eq. (8) were used with Eq. (9) for calculation of the $\delta_2 + \delta_3$ correction. The accuracy with which this calculation can be made depends upon the amount of change in reduced mass effected by exchange of isotopes. Even for ^{6}Li-^{7}Li exchange, the isotopic discrepancy ϵ had an estimated error about 15% as large as the value. Part of this problem came from the low accuracy of the g values. The resulting correction $\delta_2 + \delta_3$ is reliable to only two places. For this reason the last two places in the B_e values in Table IV are indicated as inaccurate. Nevertheless, the bond distances computed from the B_e values have a relative accuracy that is greater by an order of magnitude than the absolute accuracy, which is limited by Planck's constant.

Table V shows relative bond distances computed for different approximations. The r_e'' values were computed from Y_{01}. After Y_{01} was corrected for electron distribution, the apparent values r_e' were computed. The last column gives only one value of r_e for all isotopes because the correction with mass ratios forces the result that r_e is a constant for all species. If this correction is not made, the different species must be assumed to have different bond distances. It should be noted that the absolute change from r_e' to r_e is from 5 to 10 times the relative change in r_e' in a ^{6}Li-^{7}Li substitution. If the diameter of a chlorine nucleus is taken to be 5×10^{-13} cm, the effect of nuclear wobbling is a stretching of the molecule by slightly less than the nuclear dimension.

V. POTENTIAL CONSTANTS

In his Wentzel-Kramers-Brillouin solution of the wave equation for the diatomic molecule Dunham[14] employed a series potential function of the form

$$U(r) = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^2 + \cdots)$$

$$+ B_e J(J + 1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots) , \quad (10)$$

where $\xi = (r - r_e)/r_e$ and where a_0, a_1, a_2, etc., are potential constants which can be evaluated

TABLE V. Relative bond distances (angstrom units).

	r_e'' a	r_e' b	r_e c
^{6}Li^{19}F	1.563 852 4	1.563 887 3	1.563 857 5
^{7}Li^{19}F	1.563 856 7	1.563 884 0	
^{6}Li^{35}Cl	2.020 657 6	2.020 715 0	2.020 671 4
^{6}Li^{37}Cl	2.020 656 6	2.020 714 5	
^{7}Li^{35}Cl	2.020 663 5	2.020 710 1	
^{7}Li^{37}Cl	2.020 661 6	2.020 708 9	

a r_e'' calculated from Y_{01}.
b r_e' calculated from $Y_{01} + \delta_1$.
c r_e calculated from $Y_{01} + \delta_1 + \delta_2 + \delta_3 = B_e$.

from observed Y values. From auxiliary relations given by Dunham, the following expressions for the first-four constants were obtained:

$$a_0 = B_e^2/D_e \approx Y_{01}^2/Y_{02} , \quad (11)$$

$$a_1 = Y_{11}/3(-Y_{02}Y_{01})^{1/2} - 1 , \quad (12)$$

$$a_2 = \tfrac{1}{6} Y_{12}(-Y_{01}/Y_{02}^3)^{1/2} + \tfrac{9}{8} a_1(2 + a_1) + \tfrac{19}{8} , \quad (13)$$

$$a_3 = \tfrac{-2}{15}(Y_{21}/Y_{02}) + \tfrac{1}{3} a_2(3 + 13a_1)$$

$$- \tfrac{1}{2} a_1 [4 + 3a(1 + a_1)] . \quad (14)$$

With these relations and the observed Y values of Table III we have evaluated the potential constants given in Table VI.

Approximate potential constants were obtained for the ^{7}LiF species from the previous measurements[2] on two rotational transitions in three vibrational states. These constants have errors about five times those of the present evaluations. From the $J = 0 \rightarrow 1$ transitions on the $v = 0$, 1 and 2 states and with the aid of infrared data, Lide et $al.$[3] obtained for LiCl the approximate values $a_0 = (4.36 \pm 0.04) \times 10^9$ Mc/sec, $a_1 = -2.75 \pm 0.01$, and $a_2 = 5.3 \pm 0.4$. The values of Table VI, so far as we know, represent the only complete and accurate set of potential constants available for these molecules.

VI. VIBRATIONAL CONSTANTS

The vibrational constants of lithium fluoride and lithium chloride are given in Table VII. The harmonic vibrational constant was calculated from Kratzer's relation,[15]

TABLE VI. Potential coefficients of LiCl and LiF.

	a_0 (cm^{-1})	a_1	a_2	a_3
^{6}Li^{19}F	154 063 ± 57	−2.701 27 ± 0.000 38	5.084 ± 0.017	−7.85 ± 0.14
^{7}Li^{19}F	153 976 ± 74	−2.700 62 ± 0.000 49	5.101 ± 0.018	−7.98 ± 0.15
^{6}Li^{35}Cl	146 349 ± 42	−2.720 03 ± 0.000 28	5.025 ± 0.014	−7.44 ± 0.11
^{6}Li^{37}Cl	146 407 ± 48	−2.720 42 ± 0.000 34	5.004 ± 0.020	−7.29 ± 0.16
^{7}Li^{35}Cl	146 437 ± 33	−2.720 40 ± 0.000 23	5.004 ± 0.017	−7.30 ± 0.13
^{7}Li^{37}Cl	146 356 ± 48	−2.720 04 ± 0.000 34	4.973 ± 0.024	−7.10 ± 0.19

TABLE VII. Vibrational constants of lithium fluoride and lithium chloride.

	This work	Infrared	This work	Infrared
	ω_e (cm^{-1})		$\omega_e x_e$ (cm^{-1})	
$^6\text{Li}^{19}\text{F}$	964.24 ± 0.18		9.136 ± 0.045	
$^7\text{Li}^{19}\text{F}$	910.25 ± 0.22	910.34[a]	8.104 ± 0.042	7.929[a]
$^6\text{Li}^{35}\text{Cl}$	686.23 ± 0.10		5.096 ± 0.019	
$^6\text{Li}^{37}\text{Cl}$	683.64 ± 0.11		5.084 ± 0.027	
$^7\text{Li}^{35}\text{Cl}$	643.31 ± 0.07		4.501 ± 0.019	
		641 ± 3[b]		4.2 ± 0.3[b]
$^7\text{Li}^{37}\text{Cl}$	640.22 ± 0.10		4.490 ± 0.027	

[a]See Ref. 16.   [b]See Ref. 17.

$$\omega_e \; (\approx Y_{10}) = 2(- Y_{01}{}^3 / Y_{02})^{1/2} \; . \tag{15}$$

Dunham[14] gives the expression

$$\omega_e x_e \; (\approx Y_{20}) = \tfrac{3}{2} Y_{01}(a_2 - \tfrac{5}{4} a_1{}^2) , \tag{16}$$

which was used for the calculation of the anharmonicity constant.

The agreement between the infrared and microwave values is very good. Vidale[16] gave three possible sets of vibrational quantum numbers in

his data. It has been pointed out[2] that his third, or least probable, set of values is, in fact, the correct set. For lithium fluoride the present determination of the vibrational constants is probably no more accurate than the infrared results. The infrared measurements on lithium chloride by Klemperer, Norris, and Buchler[17] did not resolve the isotopic shifts for chlorine. As a consequence, their values are an average value for two isotopic species. The present values for the lithium chloride vibrational constants show an improvement by more than an order of magnitude over previous values.

---

[1]L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38, 1203 (1963).

[2]S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).

[3]D. R. Lide, P. Cahill, and L. P. Gold, J. Chem. Phys. 40, 156 (1964).

[4]E. Pearson and W. Gordy, Phys. Rev. 152, 42 (1966).

[5]W. C. King and W. Gordy, Phys. Rev. 93, 407 (1954).

[6]J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).

[7]P. L. Clouser and W. Gordy, Phys. Rev. 134, A863 (1964).

[8]C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, Inc., New York, 1955).

[9]F. H. Crawford and T. Jorgensen, Phys. Rev. 49, 745 (1936).

[10]J. H. Van Vleck, J. Chem. Phys. 4, 327 (1936).

[11]B. Rosenblum, A. H. Nethercot, and C. H. Townes, Phys. Rev. 109, 400 (1957).

[12]A. M. Russell, Phys. Rev. 111, 1558 (1958).

[13]F. Mehran, R. A. Brooks, and N. F. Ramsey, Phys. Rev. 141, 93 (1966).

[14]J. L. Dunham, Phys. Rev. 41, 721 (1932).

[15]A. Kratzer, Ann. Physik 67, 127 (1922).

[16]G. L. Vidale, J. Phys. Chem. 64, 314 (1960).

[17]W. Klemperer, W. G. Norris, A. Buchler, and A. G. Emslie, J. Chem. Phys. 33, 1534 (1960).

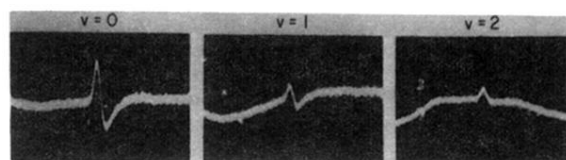FIG. 3. Oscilloscope display of the $J = 3 \rightarrow 4$ transition of $^6Li^{19}F$ in different vibrational states ($\lambda = 0.85$ mm). Linewidth approximately 1.6 Mc/sec.
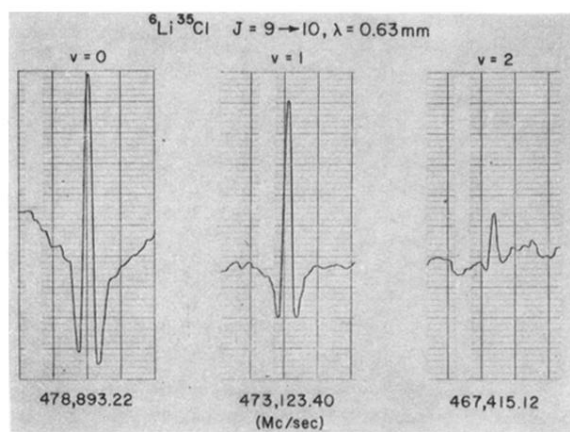
FIG. 4. Recording of submillimeter-wave lines of
LiCl in different vibrational states. Separations of
vertical scale markers 3 Mc/sec.