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Submillimeter-Wave Spectra and Equilibrium Structures of the Hydrogen Halides*

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Rotational transitions of a number of isotopic species of the hydrogen halides have been measured in the 1.0- to 0.38-mm wavelength region of the spectrum. These transitions have been measured with a submillimeter-wave spectrometer which employs a klystron-driven crystal harmonic generator and a 1.6 °K InSb photoconducting detector. The following results have been obtained: for $H\,^{35}Cl$, $B_0 = 312\,989.297 \pm 0.020$ Mc/sec, $D_0 = 15.836$ Mc/sec, $r_e = 1.274\,5991$ Å; for $H\,^{37}Cl$, $B_0 = 312\,519.121 \pm 0.020$ Mc/sec, $D_0 = 15.788$ Mc/sec, $r_e = 1.274\,5990$ Å; for $D\,^{35}Cl$, $B_0 = 161\,656.238 \pm 0.014$ Mc/sec, $D_0 = 4.196 \pm 0.003$ Mc/sec, $r_e = 1.274\,5990$ Å; for $D^{37}Cl$, $B_0 = 161\,183.122 \pm 0.016$ Mc/sec, $D_0 = 4.162 \pm 0.003$ Mc/sec, $r_e = 1.274\,5988$ Å; for $H\,^{127}I$, $B_0 = 192\,657.577 \pm 0.019$ Mc/sec, $D_0 = 6.203 \pm 0.003$ Mc/sec, $r_e = 1.609\,018$ Å; for $D\,^{127}I$, $B_0 = 97\,537.092 \pm 0.009$ Mc/sec, $D_0 = 1.578 \pm 0.001$ Mc/sec, $r_e = 1.609\,018$ Å; for $D\,^{79}Br$, $B_0 = 127\,357.639 \pm 0.012$ Mc/sec, $D_0 = 2.6529 \pm 0.0014$ Mc/sec, $r_e = 1.414\,4698$ Å; for $D\,^{81}Br$, $B_0 = 127\,279.757 \pm 0.017$ Mc/sec, $D_0 = 2.6479 \pm 0.0020$ Mc/sec, $r_e = 1.414\,4698$ Å; for $D\,^{19}F$, $B_0 = 325\,584.98 \pm 0.300$ Mc/sec, $D_0 = 17.64$ Mc/sec, $r_e = 0.916\,914$ Å.

I. INTRODUCTION

Extension of the high resolution of microwave spectroscopy to 0.37-mm wavelength has been reported by the authors in a previous paper.[1] This extension was made with a klystron-driven crystal harmonic generator as a tunable source and an indium antimonide photoconducting detector operated at low temperature. In addition to this extension, a significant improvement was made in the sensitivity and ease of operation of the microwave sweep-spectrometer in the region 1.0- to 0.4-mm wavelength. These advances have made possible the measurements reported here.

The $J = 0 \rightarrow 1$ transition of $H\,^{35}Cl$ was measured previously in this laboratory with signal strength barely above the noise level.[2] With the improved sensitivity obtained in the present experiments the accuracy of measurement of this transition has been increased by an order of magnitude; the $J = 0 \rightarrow 1$ transitions of $H\,^{37}Cl$ and of DF, which could not be detected in previous experiments, have likewise been measured with high precision. The previously unobserved $J = 1 \rightarrow 2$ rotational transitions of $D\,^{35}Cl$ and $D\,^{37}Cl$ have been measured for the first time. Likewise, rotational transitions of various isotopic species of hydrogen iodide and hydrogen bromide have been measured in the region between 1- and 0.38-mm wavelength. These measurements provide the first microwave values of the centrifugal distortion constants of the hydrogen halides and have also allowed the calculation of B_e and r_e to a high degree of accuracy.

II. EXPERIMENTAL METHODS

Tunable coherent submillimeter radiation necessary for this work was produced by methods similar to those originally described by King and Gordy.[3] Microwave energy from an OKI 55V11 klystron was coupled into a crystal multiplier to produce 6th–14th harmonic energy in the 0.38- to 1.0-mm wavelength region. The resulting submillimeter radiation was directed through the sample cell by a tapered horn and dielectric lens system. A bombarded silicon crystal, kindly supplied by C. A. Burrus of the Bell Telephone Laboratories, was used in the harmonic generator. A copper tube, $\frac{3}{4}$ in. diam. and 1 ft. long, with Teflon windows and O-ring flange vacuum seals, was used for the sample cell. In place of the usual point-contact crystal diode detector, a 1.6 °K InSb photoconducting far-infrared detector obtained from Mullard Ltd. was used. The input light pipe of this detector matched the output of the cell. In practice, it was found that in the region below 1 mm this detector was at least an order of magnitude more sensitive than the best point-contact crystal detectors.

III. SUMMARY OF THEORETICAL METHODS EMPLOYED

The theory of the spectra of diatomic molecules has been treated with varying degrees of sophistication and accuracy in the literature.[4–7] Dunham assumes the Born-Oppenheimer approximation and a potential of the form

$$U(\xi) = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + \cdots) , \tag{1}$$

where $\xi = (r - r_e)/r_e$ and r_e is the equilibrium distance between the nuclei. His treatment leads to the energy expression

$$W(v, J) = h \sum_{l,m} Y_{l,m} (v + \tfrac{1}{2})^l J^m (J + 1)^m , \tag{2}$$

which combined with the selection rules for pure rotational spectra leads to the rotational frequencies

$$\nu = 2Y_{01}(J+1) + 2Y_{11}(v+\tfrac{1}{2})(J+1) + 2Y_{21}(v+\tfrac{1}{2})^2(J+1) + 4Y_{02}(J+1)^3 + 4Y_{12}(v+\tfrac{1}{2})(J+1)^3 + \cdots \quad . \tag{3}$$

The $Y_{l,m}$'s are to be determined by fitting the experimental data to Eq. (3). Dunham has shown that in the context of his theory

$$Y_{01} = B_e[1 + (B_e^2/\omega_e^2)\beta_{01}] \ , \tag{4}$$

where

$$\beta_{01} = Y_{10}^2 Y_{21}/4Y_{01}^3 + 16a_1(Y_{20}/3Y_{01}) - 8a_1 - 6a_1^2 + 4a_1^3 \ ,$$

$$a_1 = Y_{11}Y_{10}/6Y_{01}^2 - 1 \ .$$

Here $B_e = h/(8\pi^2\mu r_e^2)$, where r_e is the "equilibrium" value of the internuclear distance and μ is the reduced mass of the molecule. The Dunham value for B_e is therefore

$$B_e = Y_{01} - \delta \ , \tag{5}$$

where $\delta \ll B_e$ represents the Dunham correction.

For precise evaluation of B_e and r_e two higher-order corrections must also be included. If the mass of the electrons were spherically distributed about each of the nuclei, μ would simply be the reduced atomic mass μ^a of the two atoms. Although adequate for the electrons in closed shells about their respective nuclei, this model is not valid for the valence electrons. However, it has been shown that ΔB, a correction of the effects of the nonspherical distribution of the electrons on B, can be estimated by the relation[8,9]

$$B_e = B_e^a - \Delta B \ , \tag{6}$$

where

$$\Delta B = -(m_e/m_p)g_J B_e \ , \quad B_e^a = h/8\pi^2\mu^a r_e^2 \ .$$

Here m_e is the mass of the electron, m_p the mass of the proton, g_J the rotational g factor, and μ^a the atomic reduced mass. The second perturbation to B is that arising from the so-called wobble-stretch (ws) effect. Interactions between the molecular rotation and the electronic motions give rise to a centrifugallike stretching force which in diatomic molecules is along the internuclear axis. A correction for this effect was originally given by Van Vleck[10] and further developed and applied to CO by Rosenblum, Nethercot, and Townes.[8] For most molecules, the required details of the electronic states are not well known, but the ws correction to B can often be determined from the inverse proportionality of this correction with the square of the reduced masses. If rotational transitions of different isotopic species of a molecule can be measured and if accurate atomic masses are available, the constant of proportionality can be obtained by a least-squares procedure among the various isotopic species. Since the Dunham correction and the correction for the nonspherical distribution of electrons also have a $1/\mu^2$ dependence, it is no longer necessary to explicitly include these corrections to find B_e^a if the ws correction is made. If they are not included explicitly, they then appear implicitly in the ws correction.

Since we have for the ground vibrational state

$$\nu = 2B_0(J+1) - 4D_0(J+1)^3 \ , \tag{7}$$

$$D_0 \approx -Y_{02} - \tfrac{1}{2}Y_{12} \ , \tag{8}$$

we find, including the above corrections,

$$B_e^a = B_0 - \tfrac{1}{2}Y_{11} - \tfrac{1}{4}Y_{21} + \Delta B - \delta + \mathrm{ws} \ . \tag{9}$$

Other approaches have been developed which do not assume the Born-Oppenheimer approximation and hence do not require the two previous corrections. In particular, Bunker[7] has shown that

$$\mu^a Y_{01} = \mu^n B_e^n + (1/\mu^n)\{(\mu^{n^2} B_e^{n^2}/8a_0) \times [15 + 14a_1 - 9a_2 + 15a_3 - 23a_1a_2 + \tfrac{21}{2}(a_1^2 + a_1^3) + 8k_1] + (\mu^n B_e^n)(m_e/m_p)(\mu^n g_J)\} \ . \tag{10}$$

Here μ^a and μ^n are, respectively, the reduced atomic and reduced nuclear masses of the molecule. The factor in the braces is isotopically independent. This relation takes advantage of the fact that g_J is inversely proportional to reduced mass under isotopic substitution. If the Y_{01} for two or more isotopic species can be determined by means of Eq. (3), Eq. (10) yields the values of B_e and r_e if μ^n and μ^a are known.

IV. HYDROGEN CHLORIDE

The two isotopes of chlorine and the three isotopes of hydrogen give rise to six isotopic species of hydrogen chloride. During the course of this experiment, the $J = 0 \rightarrow 1$ transitions of $H^{35}Cl$ and $H^{37}Cl$ at 625 Gc/sec and of $D^{35}Cl$ and $D^{37}Cl$ at 325 Gc/sec, as well as the $J = 1 \rightarrow 2$ transition of $D^{35}Cl$ and $D^{37}Cl$ at 650 Gc/sec, were measured. Results from a previous experiment in this laboratory on $T^{35}Cl$ and $T^{37}Cl$,[11] the $J = 0 \rightarrow 1$ transitions of which fall at longer wavelengths, are included in the analysis. Figure 1 shows an oscilloscope tracing of the $J = 0 \rightarrow 1$ hyperfine triplet of $H^{35}Cl$ at 625 Gc/sec. This was obtained with the 11th harmonic of an OKI 55V11 klystron oscillator. Figure 2 shows a chart recorder tracing of the hyperfine structure of the $J = 1 \rightarrow 2$ transition of $D^{35}Cl$ at 650 Gc/sec. This tracing was obtained with the 12th harmonic of an OKI 55V11 klystron. Resolution and signal-to-noise ratio were similar for $H^{37}Cl$ and $D^{37}Cl$. The results of the measurements of these lines are

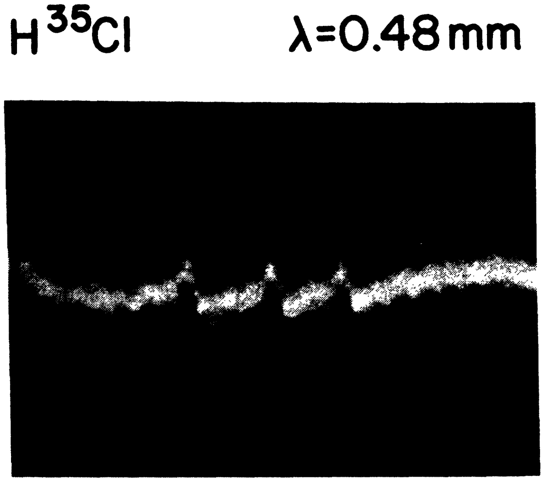

FIG. 1. Oscilloscope tracing of the $J=0\rightarrow 1$ hyperfine triplet of H ^{35}Cl at 625 Gc/sec.

TABLE I. Observed and calculated frequencies of hydrogen chloride transitions.

Transition $J\rightarrow J'$	$F\rightarrow F'$	Frequency (Mc/sec) Calculated[a]	Observed	Difference
H ^{35}Cl				
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{3}{2}$	625 901.614	625 901.603	−0.011
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{5}{2}$	625 918.733	625 918.756	0.023
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{1}{2}$	625 932.023	625 932.007	−0.016
H ^{37}Cl				
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{3}{2}$	624 964.353	624 964.374	0.021
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{5}{2}$	624 977.852	624 977.821	−0.031
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{1}{2}$	624 988.315	624 988.334	0.019
D ^{35}Cl				
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{3}{2}$	323 282.181	323 282.174	−0.007
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{5}{2}$	323 299.099	323 299.109	0.010
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{1}{2}$	323 312.480	323 312.481	0.001
$1\rightarrow 2$	$\frac{5}{2}\rightarrow\frac{5}{2}$[b]	646 475.204	646 475.310	0.106
$1\rightarrow 2$	$\frac{5}{2}\rightarrow\frac{7}{2}$[b]	646 492.148	646 492.055	−0.093
$1\rightarrow 2$	$\frac{3}{2}\rightarrow\frac{3}{2}$	646 504.097	646 504.084	−0.013
D ^{37}Cl				
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{3}{2}$	322 338.958	322 338.946	−0.012
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{5}{2}$	322 352.287	322 352.301	0.014
$0\rightarrow 1$	$\frac{3}{2}\rightarrow\frac{1}{2}$	322 362.805	322 362.797	−0.008
$1\rightarrow 2$	$\frac{5}{2}\rightarrow\frac{5}{2}$[b]	644 587.137	644 587.224	0.087
$1\rightarrow 2$	$\frac{5}{2}\rightarrow\frac{7}{2}$[b]	644 600.490	644 600.362	−0.128
$1\rightarrow 2$	$\frac{3}{2}\rightarrow\frac{3}{2}$	644 609.883	644 609.927	0.044

[a] Calculated from values of B_0, D_0, eQq, and C in Table VII.

[b] Value listed here is hypothetical frequency of completely resolved line. Experimentally observed line is overlap of several hyperfine components.

presented in Table I; the spectral constants obtained by a least-squares procedure are shown in Table VII. In order to gain redundancy for the least-squares procedure for H ^{35}Cl and H ^{37}Cl, the six lines of the two isotopes were fitted to four independent constants: ν_0 (H ^{35}Cl), ν_0 (H ^{37}Cl), eQq (H ^{35}Cl), and C (H ^{35}Cl). The eQq and the C for the two isotopic species were constrained by the relations

$$(eQq)_{\mathrm{H}\,^{37}\mathrm{Cl}} = (Q_{^{37}\mathrm{Cl}}/Q_{^{35}\mathrm{Cl}})(eQq)_{\mathrm{H}\,^{35}\mathrm{Cl}}\,, \tag{11}$$

$$C_{\mathrm{H}\,^{37}\mathrm{Cl}} = (\mu_{\mathrm{H}\,^{37}\mathrm{Cl}}B_{\mathrm{H}\,^{37}\mathrm{Cl}}/\mu_{\mathrm{H}\,^{35}\mathrm{Cl}}B_{\mathrm{H}\,^{35}\mathrm{Cl}})C_{\mathrm{H}\,^{35}\mathrm{Cl}}\,. \tag{12}$$

These relations were found to be valid when applied to the independently determined eQq and C of D ^{35}Cl and D ^{37}Cl. The fine-structure constants and their probable errors for both H ^{35}Cl and D ^{35}Cl are consistent with the precise fine-structure spectra obtained in a molecular beam electric resonance experiment by Kaiser.[12]

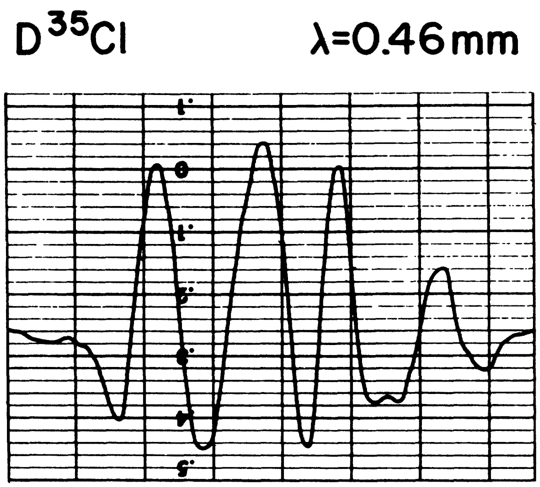

FIG. 2. Chart recorder tracing of the hyperfine components of the $J=1\rightarrow 2$ transition of D^{35}Cl at 646 Gc/sec.

Values of B_e^a and r_e were calculated by both procedures described in Sec. III. To obtain the Y_{01}'s for the various isotopic species from the low-J rotational transition described here, infrared values[13] of the higher order $Y_{l,m}$'s were used. Although these values are considerably less accurate than the microwave B values, their contribution to the total energy is small, and they therefore introduce relatively little inaccuracy into the analysis. Since the most abundant species, H ^{35}Cl, has been studied more extensively than any of the other isotopic species of hydrogen chloride,[13] the higher order $Y_{l,m}$'s of the other species calculated from H ^{35}Cl data by the relation

$$Y_{l,m} \propto (1/\mu)^{l/2+m} \tag{13}$$

are regarded as more accurate, in most cases, than those provided by the direct infrared measurements available at the present time for the other species. The results from the Dunham solution (which assumes the Born-Oppenheimer approximation) with corrections for the nonspherical distribution of electrons and ws are shown under method I in Table II. Comparison of the r_e's obtained for

TABLE II. Equilibrium structure of hydrogen chloride.

	H ^{35}Cl	H ^{37}Cl	D ^{35}Cl	D ^{37}Cl	T ^{35}Cl	T ^{37}Cl
			Method I			
B_0 (Mc/sec)	312 989.297	312 519.121	161 656.238	161 183.122	111 075.843	110 601.620
Correction for vibration-rotation interaction: $-\frac{1}{2}Y_{11}-\frac{1}{4}Y_{21}$ (Mc/sec)	4 590.906	4580.498	1695.011	1687.541	963.169	956.981
Correction for nonspherical electron distribution: ΔB(Mc/sec)^2	−81.294	−81.048	−21.509	−21.383	−10.119	−10.032
Dunham correction: $-\delta$(Mc/sec)	5.285	5.269	1.398	1.390	0.658	0.652
Wobble-stretch correction: ws(Mc/sec)	52.921	52.761	14.002	13.920	6.587	6.531
B_e^a(Mc/sec) $= B_0-\frac{1}{2}Y_{11}-\frac{1}{4}Y_{21}+\Delta B-\delta+$ws	317 557.115	317 076.601	163 345.140	162 864.590	112 036.139	111 555.752
r_e (Å)^b	1.274 5991	1.274 5990	1.274 5990	1.274 5988	1.274 5997	1.274 5985
			Method II			
B_e^a (Mc/sec)	317 557.115	317 076.601	163 345.140	112 036.139	111 555.752	162 864.590
r_e (Å)^b	1.274 5991	1.274 5990	1.274 5998	1.274 5997	1.274.5985	1.274 5988

[a] Calculated by use of g_J of Ref. 12.

[b] Calculated by use of B(Mc/sec) $= (5.053\,76\times10^5)/I_b$(amu Å^2). See W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley-Interscience, New York, 1970).

the six isotopic species show that they all lie well within 10^{-6} Å of 1.274 5990 Å. The absolute accuracy is limited to considerably less than this because of the uncertainty in Planck's constant. The r_e's shown under method II in the second part of Table II were calculated according to the procedure of Bunker outlined above. Inspection of the r_e's resulting from this treatment shows that they are identical with those calculated by method I.

Comparison of the two methods shows that although their theoretical origins are different, they are, in fact, virtually identical in final mathematical form. This results from the functional dependence of the Dunham correction, the ws correction, and the correction for the nonspherical electron distribution all of which vary as $(1/\mu)^2$ under isotopic substitution. Thus the relation between B_e^a and Y_{01} in method I can be written

$$B_e^a = Y_{01} + C(1/\mu^a)^2 , \tag{14}$$

where C is a constant which will include contributions from all three corrections. Since $B_e^a = B_e^n \times(\mu^n/\mu^a)$ and $(\mu^n/\mu^a) \approx$ const, multiplication of Eq. (14) by μ^a results in Eq. (10) where C of Eq. (14) is identified with the term in the braces in Eq. (10). Thus the final values of B_e^a and r_e are independent of the method employed.

Whether the consistency among the r_e for the various isotopes can be considered as a measure of the absolute accuracy of r_e (to within Plank's constant) depends upon several factors. Within the limits of the theory, these factors are (i) the measured $J=0\to1$ microwave line frequency, (ii) the perturbation due to centrifugal distortion which is proportional to $D_0 \approx -Y_{02} - \frac{1}{2}Y_{12}$, and (iii) the vibration-rotation terms Y_{11} and Y_{21}. Measurement of each of the line frequencies is independent of the others, and errors in them should contribute to the scatter in r_e. For three of the six isotopic species, the perturbation due to centrifugal distor-

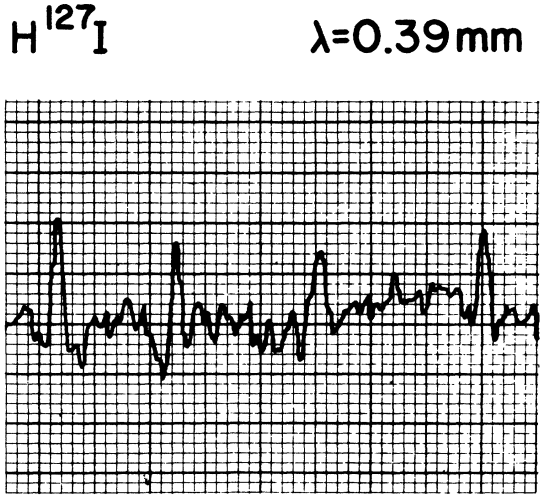

FIG. 3. Recorder tracing of four of the hyperfine components of the $J=1\to2$ transition of $H\,^{127}I$ at 770 Gc/sec. From left to right the components are $F=\frac{7}{2}\to\frac{9}{2}$, $F=\frac{5}{2}\to\frac{7}{2}$, $F=\frac{3}{2}\to\frac{1}{2}$, and $F=\frac{5}{2}\to\frac{5}{2}$.

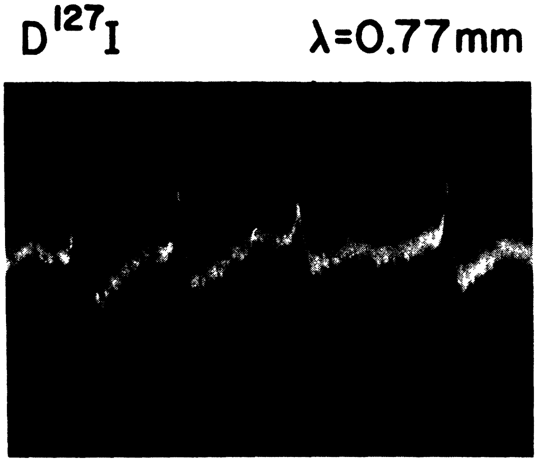

FIG. 4. Oscilloscope display of four of the hyperfine components of the $J=1\to2$ transition of $D\,^{127}I$ at 390 Gc/sec. These lines correspond to the same transitions as those shown in Fig. 3 for $H\,^{127}I$.

TABLE III. Observed and calculated frequencies of hydrogen iodide transitions.

Transition $J\to J'$	$F\to F'$	Frequency (Mc/sec) Calculated[a]	Observed	Difference
$H\,^{127}I$				
$0\to1$	$\frac{5}{2}\to\frac{7}{2}$	385 382.688	385 382.693	0.005
$0\to1$	$\frac{5}{2}\to\frac{5}{2}$	384 997.512	384 997.523	0.011
$0\to1$	$\frac{5}{2}\to\frac{3}{2}$	385 545.191	385 545.176	−0.015
$1\to2$	$\frac{7}{2}\to\frac{9}{2}$	770 471.891	770 471.867	−0.024
$1\to2$	$\frac{7}{2}\to\frac{7}{2}$	770 117.696	770 117.606	−0.090
$1\to2$	$\frac{5}{2}\to\frac{7}{2}$	770 502.872	770 502.790	−0.082
$1\to2$	$\frac{5}{2}\to\frac{5}{2}$	770 593.187	770 593.316	0.129
$1\to2$	$\frac{3}{2}\to\frac{5}{2}$	770 045.509	770 045.563	0.054
$1\to2$	$\frac{3}{2}\to\frac{3}{2}$	770 305.749	770 305.529	−0.220
$1\to2$	$\frac{3}{2}\to\frac{1}{2}$	770 540.310	770 540.543	0.233
$D\,^{127}I$[b]				
$0\to1$	$\frac{5}{2}\to\frac{7}{2}$	195 159.551	195 159.554	0.003
$0\to1$	$\frac{5}{2}\to\frac{5}{2}$	194 776.095	194 776.100	0.005
$0\to1$	$\frac{5}{2}\to\frac{3}{2}$	195 322.747	195 322.706	−0.041
$1\to2$	$\frac{7}{2}\to\frac{9}{2}$	390 137.387	390 137.417	0.030
$1\to2$	$\frac{7}{2}\to\frac{7}{2}$	389 784.995	389 784.989	−0.006
$1\to2$	$\frac{5}{2}\to\frac{7}{2}$	390 168.453	390 168.462	0.009
$1\to2$	$\frac{5}{2}\to\frac{5}{2}$	390 259.276	390 259.212	−0.064
$1\to2$	$\frac{5}{2}\to\frac{3}{2}$	390 519.170	390 519.204	0.034
$1\to2$	$\frac{3}{2}\to\frac{5}{2}$	389 712.622	389 712.610	−0.012
$1\to2$	$\frac{3}{2}\to\frac{3}{2}$	389 972.518	389 972.523	0.005
$1\to2$	$\frac{3}{2}\to\frac{1}{2}$	390 206.711	390 206.741	0.030
$2\to3$	$\frac{9}{2}\to\frac{11}{2}$	585 074.245	585 074.148	−0.097
$2\to3$	$\frac{5}{2}\to\frac{7}{2}$	584 999.994	585 000.078	0.084

[a] Calculated from values of B_0, D_0, eQq, and C in Table VII.

[b] The $J=0\to1$ line frequencies are from M. Cowan and W. Gordy, Phys. Rev. 111, 209 (1958).

tion is determined independently. The $H^{35}Cl$ constants are derived from infrared measurements; those for $D^{35}Cl$ and $D^{37}Cl$, from independent microwave measurements. For $H^{37}Cl$, $T^{35}Cl$, and $T^{37}Cl$, Y_{02} and Y_{12} are calculated by Eq. (13) from the $H^{35}Cl$ data. Thus inaccuracies in centrifugal distortion data should also result in a scatter in the values of r_e among the three independent determinations. While the values of Y_{11} and Y_{21} for the various isotopic species depend entirely upon the $H^{35}Cl$ data and upon Eq. (13), and while error limits on the infrared $Y_{l,m}$ are not quoted, a shift 100 times larger than the last quoted digit in Y_{11} and Y_{21} does not produce a significant change in the calculated r_e values. An independent measurement of Y_{11} for $D^{35}Cl$ agrees well with the value calculated from the Y_{11} of $H^{35}Cl$ by means of Eq. (13).[13]

The line frequencies reported here for $H^{35}Cl$ differ by 4 Mc/sec from the earlier measurement in this laboratory.[2] Despite the fact that the earlier microwave value of B_0 combined with the infrared data of Rank *et al.*[13] on $H^{35}Cl$ yields a value for the speed of light in agreement with the accepted value, whereas the B_0 value obtained in the present work does not, we believe the present value to be the more accurate one. The earlier microwave measurements were made with difficulty from signals barely above the noise level, whereas the present measurements were made from signals so strong that they could be displayed on a cathode-ray oscilloscope (see Fig. 1). Because of this discrepancy, however, we have taken considerable precautions: The measurements were repeated with good signal strength under varying conditions—12th harmonic of tube frequency, 11th harmonic of tube frequency, video-sweep measurement, chart measurement—and all measurements gave values well within our quoted error limits. In addition, the older value of B_0 for $H^{35}Cl$ leads to inconsistencies in the analysis of r_e. These results seem to indicate a consistent error in both the microwave and infrared measurements reported earlier.

V. HYDROGEN BROMIDE AND HYDROGEN IODIDE

Both the $J=0\rightarrow1$ and $J=1\rightarrow2$ transitions of $H^{127}I$ at 385 and 770 Gc/sec, respectively, have been measured in the present work. Figure 3 shows a chart recorder tracing of four of the hyperfine components of the $J=1\rightarrow2$ transition. These lines fall at a wavelength of less than 0.39 mm. The $J=0\rightarrow1$ transition was measured previously in this laboratory.[14] These early values differ from our present precise values by approximately 3 Mc/sec. The previously unmeasured $J=1\rightarrow2$ and $J=2\rightarrow3$ transitions of $D^{127}I$ were also measured in the present experiment. Figure 4 shows an oscilloscope tracing of four of the hyperfine components of the $J=1\rightarrow2$ transition of $D^{127}I$. These lines correspond to the same transitions as those shown in Fig. 3 for $H^{127}I$. Results of a previous experiment on $T^{127}I$, the $J=0\rightarrow1$ transition of which falls at a longer wavelength, are included in the analysis.[15] Table III shows the observed and calculated line frequencies for both $H^{127}I$ and $D^{127}I$, and Table VII lists the resulting spectral constants.

The hyperfine components of the $J=1\rightarrow2$ and $J=2\rightarrow3$ transitions for both $D^{79}Br$ and $D^{81}Br$ were observed during the course of these experiments, thereby providing the first microwave determination of the centrifugal distortion constant of hydrogen bromide. These transitions fall at wavelengths of 0.59 and 0.39 mm, respectively. The results are shown in Table IV. Also included in the analysis is earlier work on HBr [2,16] and TBr.[11]

Neither the infrared spectrum of hydrogen iodide nor that of hydrogen bromide has been studied as extensively as that of hydrogen chloride. Consequently, Y_{11} and Y_{21} for these molecules are not known to a sufficient degree of accuracy to ensure that they do not make a significant contribution to the error in the calculated values of B_e^a and r_e. This is particularly true for hydrogen iodide. If, however, a sufficient number of isotopic species of these molecules is observed, the effect of Y_{11} and Y_{21} on B_e^a may be accounted for in a manner anal-

TABLE IV. Observed and calculated frequencies of hydrogen bromide transitions.

Transition		Frequency (Mc/sec)		
$J\rightarrow J'$	$F\rightarrow F'$	Calculated[a]	Observed	Difference
$D^{79}Br$[b]				
$0\rightarrow1$	$\frac{3}{2}\rightarrow\frac{5}{2}$	254 678.366	254 678.380	0.014
$0\rightarrow1$	$\frac{3}{2}\rightarrow\frac{3}{2}$	254 810.665	254 810.634	−0.031
$0\rightarrow1$	$\frac{3}{2}\rightarrow\frac{1}{2}$	254 571.656	254 571.661	0.005
$1\rightarrow2$	$\frac{5}{2}\rightarrow\frac{7}{2}$[c]	509 334.514	509 334.512	−0.002
$1\rightarrow2$	$\frac{5}{2}\rightarrow\frac{5}{2}$	509 466.664	509 466.718	0.054
$1\rightarrow2$	$\frac{3}{2}\rightarrow\frac{3}{2}$	509 239.265	509 239.277	0.012
$1\rightarrow2$	$\frac{1}{2}\rightarrow\frac{3}{2}$	509 478.273	509 478.266	−0.007
$1\rightarrow2$	$\frac{1}{2}\rightarrow\frac{1}{2}$	509 345.366	509 345.318	−0.048
$2\rightarrow3$	$\frac{7}{2}\rightarrow\frac{9}{2}$[c]	763 853.227	763 853.201	−0.026
$D^{81}Br$[b]				
$0\rightarrow1$	$\frac{3}{2}\rightarrow\frac{5}{2}$	254 526.998	254 526.984	−0.014
$0\rightarrow1$	$\frac{3}{2}\rightarrow\frac{3}{2}$	254 637.450	254 637.448	−0.002
$0\rightarrow1$	$\frac{3}{2}\rightarrow\frac{1}{2}$	254 437.703	254 437.641	−0.062
$1\rightarrow2$	$\frac{5}{2}\rightarrow\frac{7}{2}$[c]	509 025.034	509 025.040	0.006
$1\rightarrow2$	$\frac{5}{2}\rightarrow\frac{5}{2}$	509 135.327	509 135.334	0.007
$1\rightarrow2$	$\frac{3}{2}\rightarrow\frac{3}{2}$	508 945.328	508 945.406	0.078
$1\rightarrow2$	$\frac{1}{2}\rightarrow\frac{3}{2}$	509 145.074	509 145.066	−0.008
$1\rightarrow2$	$\frac{1}{2}\rightarrow\frac{1}{2}$	509 033.958	509 033.958	−0.022
$2\rightarrow3$	$\frac{7}{2}\rightarrow\frac{9}{2}$[c]	763 387.530	763 387.356	−0.174

[a] Calculated from values of B_0, D_0, eQq, and C in Table VII.

[b] The $J=0\rightarrow1$ line frequencies are from M. Cowan and W. Gordy, Phys. Rev. 111, 209 (1958).

[c] Value listed here is hypothetical frequency of completely resolved line. Experimentally observed line is overlap of several hyperfine components.

TABLE V. Equilibrium structure of hydrogen iodide and hydrogen bromide.

	$H^{127}I$	$D^{127}I$	$T^{127}I$	$H^{79}Br$	$H^{81}Br$	$D^{79}Br$	$D^{81}Br$	$T^{79}Br$	$T^{81}Br$
B_0(Mc/sec)	192 657.577	97 537.092	65 752.305	250 358.510	250 280.582	127 357.639	127 279.757	86 251.993	86 174.078
Correction for vibration-rotation interaction: $-\frac{1}{2}Y_{11}$(Mc/sec)	2569.948	920.417	508.151	3504.031	3502.394	1263.787	1262.622	702.512	701.555
Correction for nonspherical electron distribution: ΔB(Mc/sec)[a]	−20.537	−5.223	−2.366	−50.050	−50.019	−12.849	−12.834	−5.873	−5.862
Dunham correction: $-\delta$(Mc/sec)	2.576	0.655	0.297	11.032	11.025	2.832	2.829	1.295	1.292
Wobble-stretch correction: $ws-\frac{1}{4}Y_{21}$(Mc/sec)	18.785	4.778	2.164	12.662	12.654	3.251	3.247	1.486	1.483
B_e^a (Mc/sec) $=B_0-\frac{1}{2}Y_{11}+\Delta B-\delta+(ws-\frac{1}{4}Y_{21})$	195 228.349	98 457.719	66 260.551	253 836.185	253 756.636	128 614.660	128 535.621	86 951.413	86 872.546
r_e(Å)[b]	1.609 018	1.609 018	1.609 018	1.414 4691	1.414 4705	1.414 4698	1.414 4698	1.414 4705	1.414 4691
Microwave Y_{11} (Mc/sec)	−5139.896	−1840.834	−1016.302	−7008.061	−7004.788	−2527.574	−2525.245	−1405.024	−1403.109

[a] Calculated by use of the g_J of Ref. 19.

[b] Calculated by use of B(Mc/sec) = $(5.053\ 76\times10^5)/I_b$ (amu Å^2).

TABLE VI. Results of the DF spectroscopic measurements.

$J=0\rightarrow 1$ measured line frequency	
$\nu_0 = 651\,099.393$ Mc/sec[a]	
Equilibrium structure	
B_0 (Mc/sec)	325 584.980
Correction for vibration-rotation interaction: $-\frac{1}{2}Y_{11}-\frac{1}{4}Y_{21}$ (Mc/sec)	4520.719
Correction for nonspherical electron distribution: ΔB (Mc/sec)	...
Dunham correction: $-\delta$ (Mc/sec)	3.883
Wobble-stretch correction: ws (Mc/sec)	...
B_e^a (Mc/sec) $= B_0-\frac{1}{2}Y_{11}-\frac{1}{4}Y_{21}+\Delta B-\delta+\text{ws}$	330 109.58
r_e(Å)[b]	0.916 914

[a] See Ref. 1.

[b] Calculated by use of $B\,(\text{Mc/sec}) = (5.053\,76\times 10^5)/I_b$ (amu Å^2).

ogous to the ws effect. Since, under isotopic substitution, Y_{11} should have a $(1/\mu)^{3/2}$ dependence upon the reduced mass μ, and Y_{21} a $(1/\mu)^2$ dependence [see Eq. (13)], the requirement that the r_e's among at least three isotopic species have a minimum least-squares deviation results in the determination of the value of both the ws correction and the Y_{11} correction. Since Y_{21} has the same dependence on the reduced mass as the ws effect, contribution due to this term will appear as part of the ws correction. It was found that, in the case of hydrogen chloride when this procedure was applied to the microwave data, the value of r_e so determined differed by about 3 parts in 10^6 from that determined from use of the highly accurate infrared values of Y_{11} for this molecule.

The r_e's obtained for the isotopes of hydrogen bromide by use of the infrared value of Y_{11} differ by about 2×10^{-5} Å from those obtained by the fit in which Y_{11} is derived from the microwave data. Since this difference is considerably larger than that which occurred for the same comparison in hydrogen chloride where precise infrared values of Y_{11} are available, the r_e values obtained from the microwave analysis are considered to be more

TABLE VII. Spectral constants of the hydrogen halides.

	B_0 (Mc/sec)	D_0 (Mc/sec)	$(eQq)_{\text{hal}}$ (Mc/sec)	$(C)_{\text{hal}}$ (Mc/sec)
$D^{19}F$	325 584.98 ± 0.300	17.64[a]	...	...
$H^{35}Cl$	312 989.297 ± 0.020	15.836[b]	−67.800 ± 0.095	0.068 ± 0.010
$H^{37}Cl$	312 519.121 ± 0.020	15.788[b]	−53.436 ± 0.095	0.056 ± 0.010
$D^{35}Cl$	161 656.238 ± 0.014	4.196 ± 0.003	−67.417 ± 0.098	0.026 ± 0.011
$D^{37}Cl$	161 183.122 ± 0.016	4.162 ± 0.003	−53.073 ± 0.113	0.024 ± 0.013
$T^{35}Cl$	111 075.84[c]	1.977[b]	−67.0 ± 0.6[d]	0.018 ± 0.008[e]
$T^{37}Cl$	110 601.62[c]	1.960[b]	−53.0 ± 0.6[d]	0.016 ± 0.008[e]
$H^{79}Br$	250 358.51 ± 0.15[f]	10.44 ± 0.06[g]	535.4 ± 1.4[h]	0.29 ± 0.20[h]
$H^{81}Br$	250 280.58 ± 0.15[f]	10.44 ± 0.06[g]	447.9 ± 1.4[h]	0.31 ± 0.20[h]
$D^{79}Br$	127 357.639 ± 0.012	2.6529 ± 0.0014	530.648 ± 0.074	0.148 ± 0.009
$D^{81}Br$	127 279.757 ± 0.017	2.6479 ± 0.0020	443.363 ± 0.105	0.158 ± 0.012
$T^{79}Br$	86 251.993[c]	1.234[g]	530 ± 2[d]	0.100 ± 0.005[i]
$T^{81}Br$	86 174.078[c]	1.232[g]	443 ± 2[d]	0.106 ± 0.006[i]
$H^{127}I$	192 657.577 ± 0.019	6.203 ± 0.003	−1828.418 ± 0.200	0.349 ± 0.010
$D^{127}I$	97 537.092 ± 0.009	1.578 ± 0.001	−1823.374 ± 0.105	0.165 ± 0.006
$T^{127}I$	65 752.305[j]	0.7150[k]	−1823 ± 3[l]	0.115 ± 0.005[m]

[a] Calculated from data in Ref. 20.

[b] Calculated from data in Ref. 13.

[c] Calculated from the line-frequency measurements in Ref. 11 and the D_0 listed here.

[d] From Ref. 11. A sign error has been corrected in the TCl values.

[e] Calculated from the microwave values of $(C)_{\text{hal}}$ for DCl.

[f] Calculated from the line-frequency measurements in Ref. 2 and the D_0 listed here.

[g] From Ref. 18.

[h] From Ref. 2.

[i] Calculated from the microwave values of $(C)_{\text{hal}}$ for DBr.

[j] Calculated from the line-frequency measurements in Ref. 15 and the D_0 listed here.

[k] Calculated from $H^{127}I$ and $D^{127}I$ microwave data.

[l] From Ref. 15.

[m] Calculated from the microwave values of $(C)_{\text{hal}}$ for HI and DI.

accurate. A consideration of the errors quoted for the infrared constants also indicates this to be the case. Since the infrared values of Y_{11} for hydrogen iodide are even less well determined than the Y_{11} of hydrogen bromide, the above procedure was also used. Table V gives the resulting values of the equilibrium structure. The Dunham corrections shown in this table are calculated from infrared values of $Y_{l,m}$[17,18] (except for Y_{11}); ΔB is calculated from the value of g_J reported by Burrus.[19] The corresponding microwave values of Y_{11}, which appear to be more accurate than the infrared values, are also given in Table V.

VI. DEUTERIUM FLUORIDE

For the preparation of deuterium fluoride, KDF_2 was produced by the exchange of KHF_2 with an excess of D_2O. Deuterium fluoride was subsequently generated by the thermal decomposition of KDF_2. Because of the reactive nature of DF with glass, it was necessary to construct the entire gas generation and handling system of copper. Gas pressures were monitored by a metal-encased thermocouple gauge, the glass base of which was coated with paraffin.

Since measurements of only one transition of DF could be made—the $J = 0 \rightarrow 1$ transition of the ground vibrational state—it was necessary to employ with our measurements infrared data on higher vibrational and rotational states[20] in order to evaluate the rotational constants and the values of B_e^a and r_e. The results for this molecule are shown in Table VI. Because fluorine has only one isotopic form and because g_J has not, to our knowledge, been measured for DF, neither the correction for the nonspherical distribution of bonding electrons nor the ws correction could be made by method I. The lack of these two corrections appears to be the limiting factor in the evaluation of B_e^a. It is reasonable to assume that the corrections would be on the order of those for HCl, ~50 Mc/sec. Method II requires observation of at least two isotopes and hence is not applicable.

VII. SPECTRAL CONSTANTS OF HYDROGEN HALIDES

With the measurements reported here all of the hydrogen halides have now been measured by means of high-resolution microwave spectroscopy. Table VII shows a collection of the spectral constants of these molecules.

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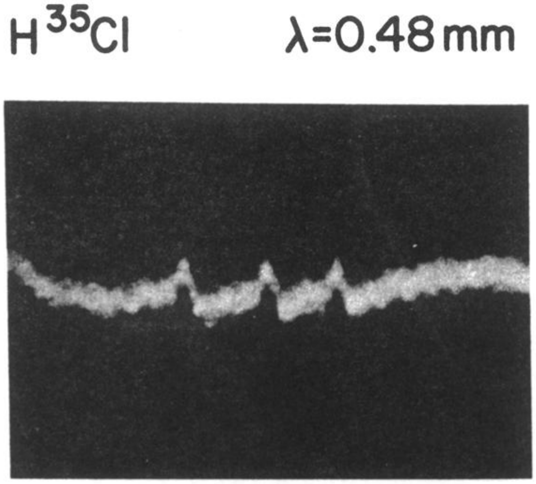

FIG. 1. Oscilloscope tracing of the $J=0\rightarrow 1$ hyperfine triplet of $H^{35}Cl$ at 625 Gc/sec.

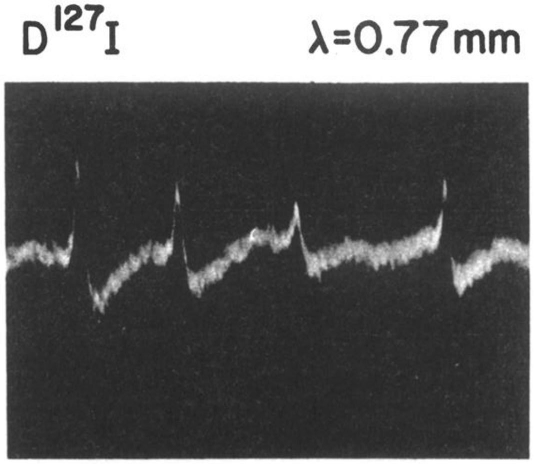

FIG. 4. Oscilloscope display of four of the hyperfine components of the $J = 1 \rightarrow 2$ transition of D ^{127}I at 390 Gc/sec. These lines correspond to the same transitions as those shown in Fig. 3 for H ^{127}I.