Submillimeter-Wave Spectra of HCl and HBr†

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The $J=0 \to 1$ transitions of HCl and HBr have been measured in the wavelength regions of 0.59 and 0.48 mm, respectively. These measurements led to the following values of molecular constants: for HCl³⁵, $\nu_0 = 625\,919.24 \pm 0.52$ Mc/sec, $eQq = 63.0 \pm 2.8$ Mc/sec, $C_I \approx 0$, $B_0 = 312\,991.30 \pm 0.26$ Mc/sec, $B_e = 317\,587$ Mc/sec, $r_0 = 1.2838_7$ Å, $r_e = 1.2745_5$ Å; for HBr⁷⁹, $\nu_0 = 500\,675.24 \pm 0.52$ Mc/sec, $eQq = 535.4 \pm 1.4$ Mc/sec, $C_I = 0.29 \pm 0.20$ Mc/sec, $B_0 = 250\,360.78 \pm 0.13$ Mc/sec, $B_e = 253\,790$ Mc/sec, $r_0 = 1.4243_9$ Å, $r_e = 1.4146_0$ Å; and for HBr⁸¹, $\nu_0 = 500\,519.41 \pm 0.26$ Mc/sec, $eQq = 447.9 \pm 1.4$ Mc/sec, $C_I = 0.31 \pm 0.20$ Mc/sec, $B_0 = 250\,282.88 \pm 0.13$ Mc/sec, $B_e = 253\,710$ Mc/sec, $r_0 = 1.4140_2$ Å, $r_e = 1.4146_0$ Å.

R ECENTLY it has become possible to extend the high-resolution methods of microwave spectroscopy to wavelengths below a half-millimeter.[1] A rotational line of $C^{12}O^{16}$ was measured at the frequency $691\,472.60 \pm 0.60$ Mc/sec$(\lambda = 0.43$ mm). Also rotational transitions of HCl³⁵ were measured in the 0.48-mm wave region. The present paper is a report of measurements on HBr transitions in the region of 0.60 mm wavelength, together with an analysis of the results for HCl and HBr.

EXPERIMENTAL METHODS

Basically, the methods for generation and detection of the submillimeter-wave radiation are those originally described by King and Gordy[2] and used for measurements[3,4] in the first octave of the submillimeter-wave region ($\frac{1}{2}$ to 1 mm). The essential elements of this system are a klystron-driven crystal harmonic generator and a crystal detector. For the present study a bombarded silicon crystal,[5] supplied by C. A. Burrus, of Bell Telephone Laboratories, was used in the multiplier unit. The klystron which reached wavelengths below a half-millimeter had a higher frequency than the klystrons used in the earlier work. This necessitated a scaling down of the waveguide section of the multiplier unit and the employment of a modified frequency-measuring system. The driving klystron was an OKI one, No. 55 V 10, which operates in the 5- to 6-mm region with a power output of 100 to 200 mW.

The techniques for measurement of the frequencies in the 5- to 6-mm region are similar to those of earlier measurements in this laboratory with the following exceptions. The secondary frequency standard normally used would not give markers as high as those of the fundamental of the driving klystron (55 kMc/sec). For this reason a tertiary frequency standard was used to give markers in this region. The tertiary standard consisted of an X-band klystron, frequency stabilized through electronic coupling to a standard marker signal, and monitored by a secondary frequency standard[6] which provided strong markers in the X-band region (9 kMc/sec). The output of the X-band klystron (201B Varian tube) was then fed into a crystal harmonic multiplier unit which generated harmonics in the 55-kMc/sec region.

THEORY APPLIED

The assumption of the Morse potential function[7] leads to the characteristic rotation-vibration energies.[8]

$$W_{J,v} = h[w_e(v+\tfrac{1}{2}) - w_e x_e(v+\tfrac{1}{2})^2 + \cdots + B_v J(J+1) - D_v J^2(J+1)^2 \cdots]. \quad (1)$$

With the selection rules $\Delta v = 0$, $\Delta J = 1$ for rotational transitions, this gives

$$\nu = 2B_v(J+1) - 4D_v(J+1)^3, \quad (2)$$

for the pure rotational frequencies of a diatomic molecule. In this expression J represents the rotational quantum number, and

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2, \quad (3)$$

$$D_v = D_e + \beta_e(v+\tfrac{1}{2}) \cdots, \quad (4)$$

in which

$$B_e = h/8\pi^2 \mu r_e^2, \quad (5)$$

and

$$D_e = 4B_e^3/w_e^2, \quad (6)$$

where v is the vibrational quantum number, α_e and γ_e are small constants which measure the interaction between vibration and rotation, r_e is the "equilibrium" internuclear distance, μ is the reduced mass of the molecule, and D_v and β_e are centrifugal stretching constants. The constant w_e represents the fundamental vibrational frequency and $w_e x_e$ is a small constant which depends on the anharmonicity of the potential function.

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[2] W. C. King and W. Gordy, Phys. Rev. 93, 407 (1954).
[3] C. A. Burrus and W. Gordy, Phys. Rev. 93, 897 (1954).
[4] M. Cowan and W. Gordy, Phys. Rev. 104, 551 (1956).
[5] R. S. Ohl, P. P. Budenstein, and C. A. Burrus, Rev. Sci. Instr. 30, 765 (1959).
[6] R. R. Unterberger and W. V. Smith, Rev. Sci. Instr. 19, 580 (1948).
[7] P. M. Morse, Phys. Rev. 34, 57 (1929).
[8] G. Hertzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), pp. 107, 141, 144.

Because the convenient expression Eq. (2) is not entirely adequate for treating the precise microwave measurements for diatomic molecules, we used in part the more refined treatment of Dunham,[9] who expressed the potential function in terms of a power series. For the energy eigenvalue, Dunham's treatment leads to the expression

$$W(v,J) = h \sum_{m,n \neq 0} Y_{mn}(v+\tfrac{1}{2})^m J^n (J+1)^n. \quad (7)$$

With the above selection rules for rotational transitions, this expression gives the pure rotational absorption frequencies as

$$\nu = 2Y_{01}(J+1) + 2Y_{11}(v+\tfrac{1}{2})(J+1)$$
$$+ 2Y_{21}(v+\tfrac{1}{2})^2(J+1) + 4Y_{02}(J+1)^3$$
$$+ 4Y_{12}(v+\tfrac{1}{2})(J+1)^3 + \cdots, \quad (8)$$

in which the Y's are the Dunham constants to be evaluated from the experimental measurements. Generally, one needs to include only the first five or six constants in the series to obtain a consistent fit of the experimental data to the obtainable experimental accuracy. Except for Y_{01}, the Dunham constants can be equated within the present accuracy to the corresponding second-order constants in the frequency equation based on the Morse potential. The Y_{m0}'s are obtained from the infrared vibrational transitions. Thus one can here set

$$Y_{10} = w_e, \qquad Y_{02} = -D_e, \qquad Y_{11} = -\alpha_e,$$
$$Y_{20} = -w_e x_e, \qquad Y_{21} = \gamma_e, \qquad Y_{12} = -\beta_e. \quad (9)$$

The Y_{01}, which corresponds to B, is not equivalent to B_e within the experimental accuracy. For this reason, these constants are related by the Dunham expression:

$$Y_{01} = B_e[1 + (B_e^2/w_e^2)\beta_{01}], \quad (10)$$
where
$$\beta_{01} = \frac{Y_{10}^2 Y_{21}}{4Y_{01}^3} + 16a_1 \frac{Y_{20}}{3Y_{01}} - 8a_1 - 6a_1^2 + 4a_1^3$$
and
$$a_1 = \frac{Y_{11}Y_{10}}{6Y_{01}^2} - 1.$$

Since microwave measurements can at this time be made on only the $J=0 \to 1$ transitions of the ground vibrational states of HCl and HBr, the band spectra values must be used for all the second-order constants, D_e, α_e, γ_e, $-w_e x_e$, etc. Fortunately, these constants are known to the accuracy with which they alter the $0 \to 1$ rotational frequency. Thus our measurements can be combined with the band spectra data to give a more precise evaluation of the important constant B_e, and from it the equilibrium internuclear distance r_e. The quantity (B_e^2/w_e^2) in the above equation (10) for Y_{01}

is of the order of 10^{-4}, and thus the use of the w_e from optical measurements is justified. In the present treatment δ is designated thus:

$$\delta = Y_{01} - B_e = B_e(B_e/w_e)^2 \beta_{01} \approx Y_{01}(Y_{01}/w_e)^2 \beta_{01}. \quad (11)$$

The corrected value for B_e is therefore

$$B_e = Y_{01} - \delta, \quad (12)$$

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

The above theory assumes that the mass of the entire atom, nucleus plus electrons, is concentrated at a point. Such an approximation is good only because the electrons are very light as compared with the atomic nuclei, which are concentrated within a very small radius. Obviously, however, the electrons have an extension in space about the nuclei so that the contribution to the molecular moment of inertia caused by spatial distribution and motion of the electrons must be considered in a very precise treatment.

Since the electrons are more or less spherically distributed about their respective nuclei, the moment of inertia might be expected to be greater than that calculated with the point-mass assumption, greater by an amount approximately equal to the moment of inertia of the electrons about their respective nuclei. Although this would be a large contribution, it is not actually present, because the orientation in space of a completely spherical shell of electrons remains fixed as the molecule rotates. There is, however, a small effect on the moment of inertia which is caused by a slight interaction of the electronic and molecular motions. This interaction also gives rise to a small molecular magnetic moment from which an estimate of the effects on the moment of inertia can be made with the formula[10,11]

$$\Delta B/B = -\mu_j/\beta_0 J, \quad (13)$$

where $\Delta B/B$ is the fractional change in B, μ_j is the molecular magnetic moment, β_0 is the Bohr magneton, and J is the angular momentum quantum number.

The chlorine and bromine nuclei have nuclear quadrupole moments which give rise to a triplet splitting of the $J=0 \to 1$ transition of the hydrogen halides considered here. This splitting can be calculated to sufficient accuracy from the first-order formula[12]:

$$W_Q = -\frac{eQq}{2I(2I-1)(2J-1)(2J+3)}$$
$$\times [\tfrac{3}{4}C(C+1) - I(I+1)J(J+1)], \quad (14)$$

where eQq is the nuclear quadrupole coupling constant and where C equals $F(F+1) - I(I+1) - J(J+1)$, and F equals $I+J$, $I+J-1$, $\cdots |I-J|$. This formula is

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

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[11] S. Geschwind, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 28, p. 44.
[12] W. Gordy, W. V. Smith, and R. F. Trambarulo, Microwave Spectroscopy (John Wiley & Sons, Inc., New York, 1953).

TABLE I. Observed and calculated frequencies of the $J=0 \to 1$ transition of hydrogen bromide.

Transition $F \to F'$	Quadrupole displacement (Mc/sec)	Magnetic displacement (Mc/sec)	Frequencies (Mc/sec) Calculated[a]	Observed
HBr^{79}				
$\frac{3}{2} \to \frac{1}{2}$	−133.85	−0.72	500 540.67	500 540.66±0.26
$\frac{3}{2} \to \frac{5}{2}$	− 26.77	0.44	500 648.90	500 648.90±0.26
$\frac{3}{2} \to \frac{3}{2}$	107.08	−0.29	500 782.03	500 782.04±0.26
HBr^{81}				
$\frac{3}{2} \to \frac{1}{2}$	−111.98	−0.78	500 406.65	500 406.68±0.26
$\frac{3}{2} \to \frac{5}{2}$	− 22.40	0.46	500 497.47	500 497.48±0.26
$\frac{3}{2} \to \frac{3}{2}$	89.58	−0.31	500 608.67	500 608.64±0.26

[a] Calculated with the values of ν_0 and eQq in Table II.

used with the known nuclear spin $I=\frac{3}{2}$ for Br^{79}, Br^{81}, and Cl^{35} for calculation of the nuclear couplings eQq from the experimental data.

For HBr, but not for HCl, it was possible to detect and measure a nuclear magnetic interaction with the molecular magnetic moment generated by the interaction of electron and molecular rotational motion mentioned above. The nuclear magnetic interaction is given by the equation[12]

$$W_{C_I} = \tfrac{1}{2}C_I[F(F+1)-J(J+1)-I(I+1)], \qquad (15)$$

where C_I is the nuclear magnetic coupling constant. From this experimentally observable constant and the known nuclear magnetic moment, the molecular magnetic moment can be readily obtained.

HYDROGEN BROMIDE

The two isotopes Br^{79} and Br^{81} have approximately equal natural abundance. The $J=0 \to 1$ transition of hydrogen bromide has an isotopic doublet splitting in addition to the triplet splitting arising from nuclear quadrupole interaction. Since the isotopic splitting is less than the nuclear quadrupole splitting, the hyperfine structures of HBr^{79} and HBr^{81} overlap. Figure 1 is a photograph of the cathode-ray oscilloscope (CRO) trace of four of the six components for the two isotopic species. The electronic tuning range of the klystron was not sufficient to include all six components on one sweep. The components omitted from the trace, the $F=\frac{3}{2} \to \frac{1}{2}$
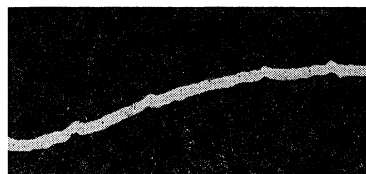

FIG. 1. Photograph of the oscilloscope display of part of the $J=0 \to 1$ transition of HBr. Only four of the six hyperfine components of HBr^{79} and HBr^{81} at 0.599 mm are shown. From left to right the components are $F=\frac{3}{2} \to \frac{5}{2}$ of HBr^{81}, $F=\frac{3}{2} \to \frac{1}{2}$ of HBr^{79}, $F=\frac{3}{2} \to \frac{3}{2}$ of HBr^{81} and $F=\frac{3}{2} \to \frac{5}{2}$ of HBr^{79}. The two outside components shown are separated by approximately 150 Mc/sec.

component of HBr^{81} and the $F=\frac{3}{2} \to \frac{3}{2}$ component of HBr^{79}, are off the scope at opposite ends of the trace. The HBr lines on a pen-and-ink recording have a signal-to-noise ratio much greater than that obtained for the CRO display. Such a recording is shown in Fig. 2. With optimum performance, we estimate that spectral lines can now be recorded with a signal strength at least 50 times noise level in the 0.60-mm region and about 25 times noise level in the 0.50-mm region. Thus high-resolution spectroscopy is proved to be not only possible but feasible in the half-millimeter wave region. For these recordings, a G-band waveguide cell 30 cm long was used. It was cooled by dry ice. The pressure of the gas was 10^{-3} mm of Hg.

All lines of HBr were measured by superposition of the markers from the tertiary frequency standard over the lines displayed on the cathode ray scope. Several measurements were made on each component. Mean values of these measurements are given in Table I, with error limits estimated from the spread in the values obtained from the measurements as well as from consideration of the possible errors inherent in the standard markers employed. In the same table calculated frequencies are given for comparison. These frequencies were calculated with the spectral constants given in Table II from the theory summarized above.

Table II gives the spectral constants and molecular dimensions of HBr derived from the measurements with the aid of the second-order constants D_0, α_e, γ_e, etc., derived from infrared spectroscopy by Thompson,
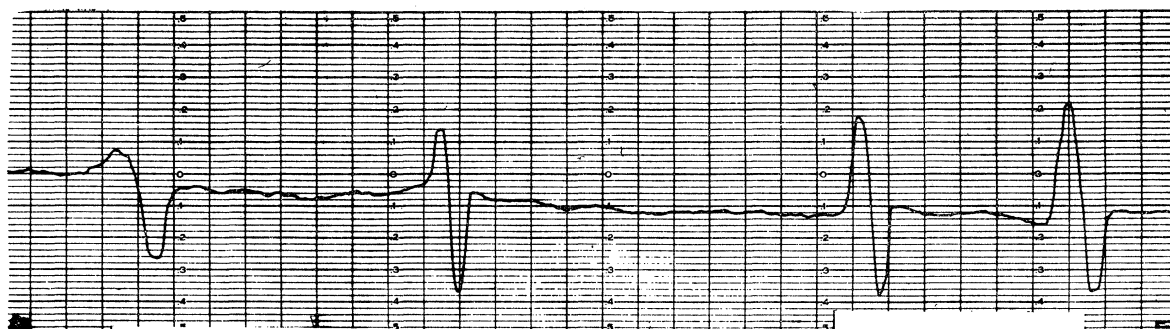

FIG. 2. Pen recording of the $J=0 \to 1$ transition of HBr. $\lambda_0=0.599$ mm. Components shown are the $F=\frac{3}{2} \to \frac{5}{2}$ of HBr^{81}, $F=\frac{3}{2} \to \frac{1}{2}$ of HBr^{79}, $F=\frac{3}{2} \to \frac{3}{2}$ of HBr^{81}, and $F=\frac{3}{2} \to \frac{5}{2}$ of HBr^{79}. The two outside components in the figure are separated by approximately 150 Mc/sec.

TABLE II. Derived molecular constants of the hydrogen halides.

	HCl^{35}	HBr^{79}	HBr^{81}	HI^{127}
ν_0 in Mc/sec	$625\,919.24 \pm 0.52$	$500\,675.24 \pm 0.26$	$500\,519.41 \pm 0.26$	$385\,293.27 \pm 0.70$
λ_0 in mm	0.48	0.599	0.599	0.778
eQq (hal.) in Mc/sec	68.0 ± 2.8	535.4 ± 1.4	447.9 ± 1.4	-1831.0 ± 3.0^c
C_I (hal.) in Mc/sec	0	0.29 ± 0.20	0.31 ± 0.20	0.26 ± 0.2^c
D_0 in Mc/sec	15.84^a	11.58^b	11.59^b	6.09^d
B_0 in Mc/sec	$312\,991.30 \pm 0.26$	$250\,360.78 \pm 0.13$	$250\,282.88 \pm 0.13$	$192\,658.8 \pm 0.5^c$
B_e in Mc/sec	$317\,587$	$253\,790$	$253\,710$	$195\,200$
r_0 in Å	1.2838_7	1.4243_9	1.4240_2	1.6197_2
r_e in Å	1.2745_5	1.4146_0	1.4146_0	1.6091_4

a From Rank *et al.* (Ref. 14).
b From Thompson, Williams, and Callomon (Ref. 13).
c From Cowan and Gordy (Ref. 4).
d From infrared data by Boyd (Ref. 10).

Williams, and Callomon.[13] Table III shows the various corrections applied to the B_0 value for calculation of the B_e value from which the equilibrium value of the internuclear distance r_e was obtained.

HYDROGEN CHLORIDE AND HYDROGEN IODIDE

The submillimeter wave frequencies of the $J=0 \to 1$ transition of HCl^{35} have been reported in an earlier note.[1] However, no analysis of the data was given except for the evaluation of B_0, from which a new spectral velocity of light was obtained by a combination of this B_0 (in frequency units) with the B_0 from infrared spectroscopy (in wave-length units) which was accurately measured by D. H. Rank and his associates.[14] The resulting value,

$$c = 299\,792.8 \pm 0.4 \text{ kMc/sec},$$

TABLE III. Corrections applied to B_0 for derivation of B_e for hydrogen bromide and for hydrogen chloride.

	HBr^{79}	HBr^{81}	HCl^{35}
B_0(Mc/sec)	250 360.78	250 282.88	312 991.30
Correction for vibration-rotation interaction:			
$\frac{1}{2}\alpha_e - \frac{1}{4}\gamma_e$(Mc/sec)	3467	3467	4591.24
Correction for rotation-electron interaction:			
ΔB(Mc/sec)	-48	-50	~ 0
Dunham correction:			
δ(Mc/sec)	-10.40	-10.37	-5.01
B_e(Mc/sec) $= B_0 + \frac{1}{2}\alpha_e - \frac{1}{4}\gamma_e + \Delta B + \delta =$	253 790	253 710	317 587.6

[13] H. W. Thompson, R. L. Williams, and H. J. Callomon, Spectrochim. Acta 5, 313 (1952).
[14] D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. 52, 1 (1962).

compares favorably with the best values of the velocity of light measured by more direct methods. The $J=0 \to 1$ lines of HCl fall at a wavelength of less than a half-millimeter ($\lambda=0.48$ mm). They could not be observed on the CRO scope, but were recorded with a signal-to-noise ratio of about eight to one. (See Fig. 2 of the previous paper.[1])

In Table I are given experimental and derived constants for HCl^{35}. These were obtained from a combination of our submillimeter-wave measurements with the precise infrared measurements of g_e, γ_e, etc., by Rank and his associates.[14] Because the magnetic interaction of HCl^{35} was too small to be measured reliably, no correction of B_e for electronic distortions was made.

The submillimeter-wave frequencies of the $J=0 \to 1$ transition of HI^{127} have been published by Cowan and Gordy,[4] but in their analysis of the data no correction was made on B_e for the electronic distortion indicated by the observed magnetic nuclear coupling, and no Dunham correction was applied. These corrections were made and applied later in the Ph.D. thesis of M. Cowan. The revised values for B_e and r_e are given in Table II, along with other spectral constants, so that comparison with HBr and HCl may be made easily. Similar results for the corresponding deuterides are summarized in an earlier paper.[15] The only hydrogen halide which has not been reached with submillimeter-wave spectroscopy is the fluoride.

ACKNOWLEDGMENT
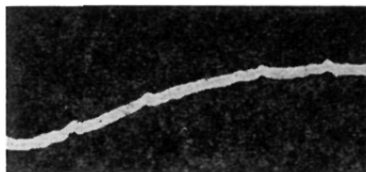
[15] M. Cowan and W. Gordy, Phys. Rev. 111, 209 (1958).

FIG. 1. Photograph of the oscilloscope display of part of the $J=0 \rightarrow 1$ transition of HBr. Only four of the six hyperfine components of HBr^{79} and HBr^{81} at 0.599 mm are shown. From left to right the components are $F=\frac{3}{2} \rightarrow \frac{5}{2}$ of HBr^{81}, $F=\frac{3}{2} \rightarrow \frac{1}{2}$ of HBr^{79}, $F=\frac{3}{2} \rightarrow \frac{3}{2}$ of HBr^{81} and $F=\frac{3}{2} \rightarrow \frac{5}{2}$ of HBr^{79}. The two outside components shown are separated by approximately 150 Mc/sec.