Extension of Submillimeter Wave Spectroscopy below a Half-Millimeter Wavelength*

Gordon Jones† and Walter Gordy

Department of Physics, Duke University, Durham, North Carolina

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The methods of high-resolution microwave spectroscopy have been extended to $\lambda = 0.43$ mm. The $J = 5 \rightarrow 6$ rotational line of $C^{12}O^{16}$ has been measured to be $691\ 472.60 \pm 0.60$ Mc/sec. With other measured lower frequency transitions, this value leads to a centrifugal stretching constant $D_0 = 0.18390 \pm 0.00014$ Mc/sec and to $B_0 = 57\ 635.970 \pm 0.003$ Mc/sec for $C^{12}O^{16}$. Measurements of the three hyperfine components of the $J = 0 \rightarrow 1$ transition of HC^{135} at $\lambda = 0.48$ mm yield for this molecule $\nu_0 = 625\ 919.24 \pm 0.52$ Mc/sec and $B_0 = 312\ 991.30 \pm 0.26$ Mc/sec. With the infrared value of B_0 in wavelength units measured with great accuracy by Rank and his associates, our B_0 value yields the spectral value

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

for the velocity of light. This value is in agreement with, and is of comparable accuracy to, the best values obtained by other more direct methods for the measurement of c.

THE submillimeter wave region from 0.1- to 1.0-mm wavelength is potentially one of the most useful segments of the entire electromagnetic spectrum, yet this region has held out longest against modern scientific and technological onslaughts. The maser has not yet been made operable in this region.

In 1953, Burrus and Gordy[1] employing the crystal harmonic generator and detector which had been used for microwave spectroscopy in the 1- to 2-mm wave region,[2] penetrated the submillimeter wave region for the first time with the accurate, high-resolution methods of microwave electronics. They were able to reach and measure spectral lines at wavelengths as short as 0.77 mm. In 1956, Cowan and Gordy[3] extended microwave electronic measurements to approximately a half-millimeter wavelength. Until these advances, only a few unprecise measurements with over-extended optical methods had been made in the region of 0.5 to 1.0 mm. Since that time, it has become common practice in this laboratory to detect and measure spectra throughout this first octave of the submillimeter region with high precision and resolution.[4]

The earlier measurements in the region above one-half millimeter were made with harmonic generators driven by centimeter-wave klystrons. Attempts to extend the coverage below a half-millimeter with centimeter-wave fundamental energy failed. Recently, however, klystrons in the 5-mm range with output power of the order of 100 mW have become available. With a 55 V 10 klystron made by OKI Electric Industry Company, Ltd. (Tokyo, Japan) we have been able to extend high-precision microwave spectroscopy to wavelengths of 0.43 mm. The $J = 5 \rightarrow 6$ rotational transition of $C^{12}O^{16}$ was measured at this frequency, 691 472.6 Mc/sec, with a multiple of the 5-Mc/sec standard broadcast by Station WWV.

The pip to the right on the recorder trace of Fig. 1 shows the highest recorded microwave spectral line to be approximately three times the noise level. It is recorded with the 12th harmonic of the klystron frequency and has a linewidth of approximately 5 Mc/sec. The stronger pip to the left is the $J = 4 \rightarrow 5$ transition observed with the 10th harmonic and occurring at 0.52 mm. Actually, the 0.52-mm line was observed and measured on the cathode-ray scope. To date, lines below a half-millimeter have been detected only with the more sensitive recording techniques.

The components of the submillimeter spectroscopic system used in the present extension are similar to those used earlier.[2] A silicon crystal developed by R. S. Ohl,[5] of the Bell Telephone Laboratories, was used in the multiplier, and a silicon crystal from Microwave Associates was used as the detector. A dc bias was
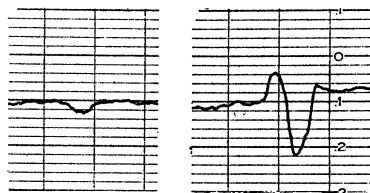
[1] C. A. Burrus and W. Gordy, Phys. Rev. **93**, 807 (1954).

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

[3] M. Cowan and W. Gordy, Phys. Rev. **104**, 551 (1956).

[4] C. A. Burrus and W. Gordy, Phys. Rev. **101**, 599 (1956), G. Erlandsson and W. Gordy, *ibid*. **106**, 513 (1957), M. Cowan and W. Gordy, *ibid*. **111**, 209 (1958); See also the review by W. Gordy, in *Proceedings of the Symposium on Millimeter Waves* (Polytechnic Press of the Polytechnic Institute of Brooklyn, Brooklyn, New York, 1960).

Fig. 1. Recorder tracing of the $J = 4 \rightarrow 5$ rotational transition of $C^{12}O^{16}$ at 0.52-mm wavelength (576 267.7 Mc/sec), at left; and of the $J = 5 \rightarrow 6$ transition at 0.43-mm wavelength (691 472.6 Mc/sec), at right. The lines are approximately 5 Mc/sec in width.

[5] R. S. Ohl, Bell System Tech. J. **31**, 104 (1952); see also R. S. Ohl, P. P. Budenstein, and C. A. Burrus, Rev. Sci. Instr. **30**, 765 (1959).
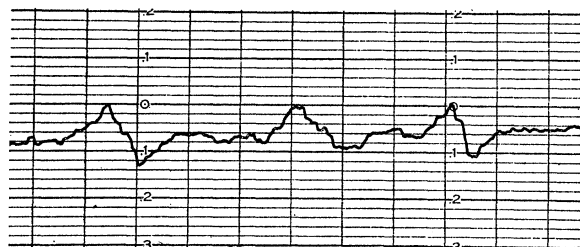
FIG. 2. Recorder tracing of the three hyperfine components of the $J=0 \rightarrow 1$ rotational transition of HCl^{35} at 0.48-mm wavelength. The two outside components are separated by approximately 35 Mc/sec. Observed frequencies are listed in Table I.

applied to the multiplier crystal but not to the detector crystal.

Figure 2 shows the three hyperfine components of HCl^{35} observed on the recorder at 0.48-mm wavelength. Table I gives the measured frequencies and derived constants. The rotational constants of HCl^{35} have been obtained with great accuracy from wavelength measurements in the near infrared by D. H. Rank[6] and his associates. By taking the ratio of the B_0 value of HCl^{35} in frequency units obtained in the present work to the infrared value[6] 10.440254 ± 0.000010 cm^{-1} obtained in wavelength units, one can get a new spectral measurement of the velocity of light. The value thus obtained is:

$$c = 299\ 792.8 \pm 0.4\ \text{km/sec.}$$

Because of its larger B value which leads to more widely

TABLE I. Observed and calculated frequencies of the $J = 0 \rightarrow 1$ transition of HCl^{35}.

Transition $F \rightarrow F'$	Nuclear hyperfine displacement (Mc/sec)	Frequencies (Mc/sec) Calculated	Observed
$3/2 \rightarrow 3/2$	-13.60	625 905.65	625 905.65±0.52
$3/2 \rightarrow 5/2$	3.40	625 922.65	625 922.74±0.52
$3/2 \rightarrow 1/2$	17.00	625 936.25	625 936.06±0.52

$\nu_0 = 625\ 919.24 \pm 0.52$ Mc/sec
$B_0 = 312\ 991.30 \pm 0.26$ Mc/sec[a]

[a] In the calculation of B_0 correction for the small effect of centrifugal distortion on the $J = 0 \rightarrow 1$ transition are made with the D_J from optical spectroscopy (Ref. 6).

[6] D. H. Rank, D. P. Eastman, R. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. 52, 1 (1962).

TABLE II. Observed millimeter and submillimeter wave frequencies of $C^{12}O^{16}$.

Transition	Observed frequency (Mc/sec)	Wavelength (mm)
	Previous work	
$J=0 \rightarrow 1$	115 271.195±0.015	2.60[a]
	115 271.204±0.005	2.60[b]
$J=1 \rightarrow 2$	230 537.974±0.030	1.30[a]
$J=2 \rightarrow 3$	345 795.900±0.090	0.87[a]
	Present work	
$J=3 \rightarrow 4$	461 040.68 ±0.06	0.65
$J=4 \rightarrow 5$	576 267.75 ±0.10	0.52
$J=5 \rightarrow 6$	691 472.60 ±0.60	0.43
	Derived constants	

$B_0 = 57\ 635.970 \pm 0.003$ Mc/sec
$D_0 = 0.18390 \pm 0.00014$ Mc/sec

[a] See Ref. 8.
[b] See Ref. 9.

spaced lines in the infrared spectrum, HCl is a more suitable molecule for measurement of the velocity of light than are the CO and HCN molecules which have been used for this purpose before. Although the precise wavelength measurements were made more than two years ago, it was not possible at that time to reach the rotational lines at lowest frequency with microwave methods. The above value, which we believe represents the best spectral value for c, is comparable in accuracy to the best measurements of other types.[7]

Table II lists the newly measured submillimeter wave lines of $C^{12}O^{16}$ with those measured earlier.[8,9] These accurately measured lines provide a convenient set of secondary frequency markers throughout the present range of submillimeter wave spectroscopy.

The authors wish to thank Monroe Cowan, now at the Bell Telephone Laboratories, who helped in the initial phases of these experiments.

[7] J. W. M. Dumond and E. R. Cohn, in Handbook of Physics, edited by E. U. Condon and H. Odishaw (McGraw-Hill Book Company, Inc., New York, 1958), Chap. 10, pp. 7–173.

[8] M. Cowan and W. Gordy, Bull. Am. Phys. Soc. 2, 212 (1957).

[9] B. Rosenbloom, A. H. Nethercot, Jr., and C. H. Townes, Phys. Rev. 109, 400 (1958).