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Microwave Spectroscopy in the Region of Three to Five Millimeters*

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Exploratory investigations in the region of the electromagnetic spectrum between 3.3- and 5-mm wave-length have shown that useful work can be done here with available sources and detectors. Higher rotational transitions of BrCN and ICN have been observed with satisfactory signal-to-noise ratios at pressures low enough to resolve the nuclear quadrupole splittings. These measurements indicate that the minimum detectable absorption is 10^{-5} neper per cm with the present spectroscope. The B_0 value of HCN has been determined as 1.4789 cm^{-1}, in agreement with infra-red results. The quadrupole coupling factor for the nitrogen nucleus in this molecule has been found to be 4.7 mc.

I. INTRODUCTION

THE application of microwave harmonic generators to the study of gas absorptions was first described by R. Beringer, who used the technique in the study of oxygen-nitrogen mixtures at relatively high pressures in the wave-length region from 4.8 mm to 6.1 mm.[1] A silicon-tungsten crystal driven by a one-centimeter signal generator was used as an energy source, the harmonics arising in the crystal being isolated from energy of the fundamental wave-length by means of a wave-guide filter. Although harmonics higher than the second are also present in a signal thus derived, they are considerably less intense, and need occasion no confusion in working with the second harmonic. In this laboratory we have employed the second harmonic of the shorter wave-length klystron sources now available to make spectroscopic studies at wave-lengths as short as 3.3 mm.

FIG. 1. Microwave components. *A* is the reflex klystron, *B* a directional coupler, *C* the *J*-band cavity wavemeter, *D* a *J*-band crystal mount, and *E* a variable attenuator. *F* is the frequency multiplier and *G* an *H*-band crystal mount. Normally, the cell is inserted between the multiplier and the *H*-band crystal mount.

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[1] R. Beringer, Phys. Rev. **70**, 53 (1946).

The most obvious advantages resulting from extending the high frequency coverage of microwave spectroscopy are the possibilities of studying a greater variety of molecules and of observing higher rotational transitions where centrifugal distortions may be studied. For example, the first rotational transition of carbon monoxide and the fifteenth rotational line of ICN both occur near three millimeters. Ultimately, the over-all ability to detect absorption lines should be greater in the millimeter than in the centimeter region. Even now, the considerable losses in source and detector sensitivities are largely balanced by the marked increase in gas absorption with frequency (varying as ν^3 in the case of a linear molecule). An analysis of the results for BrCN indicates that an absorption of 10^{-5} neper per cm is detectable with the present spectroscope.

II. INSTRUMENTATION

Figure 1 is a photograph of the essential microwave components, with the cell omitted. The multiplier unit is driven by Raytheon reflex klystrons operating in the region of six to ten millimeters. The magnitude of the fundamental energy is of the order of ten milliwatts. The wave guide components used in this band are made from scaled and simplified designs of standard centimeter-wave-length equipment. They have been employed extensively in this laboratory for spectroscopic work in the region below *K*-

band.[2-4] Figure 2A shows the design of the multiplier. This simple crossed wave-guide construction has proven as efficient in practice as a more complex model embodying chokes to prevent feedback of second harmonic energy into the larger wave guide. The small guide cuts off at 5.6 mm, so that it is useful as a filter for all fundamental wave-lengths longer than this. For fundamental wave-lengths between seven and ten millimeters the larger guide is made of the size indicated in the drawing; for shorter wave-lengths it is reduced to 0.180×0.086 inch. By connecting an indicator to the Sperry cable fitting, all of the components associated with the fundamental wave-length may be put in tune, including the multiplier crystal. For detection of the second harmonic energy, scaled-down versions of conventional crystal mounts are employed (Fig. 2B). Sylvania 1N26 crystals are used both for multiplication and for detection. Germanium crystals probably would be greatly superior as multipliers, but these are at present unavailable. It has been necessary to select crystals with great care, and their frequency sensitivity is such that the selection must be repeated every two or three thousand megacycles. There appears to be little correlation between the performance of a crystal as a multiplier and as a detector. Approximate measurements made at five millimeters indicate that the detected second

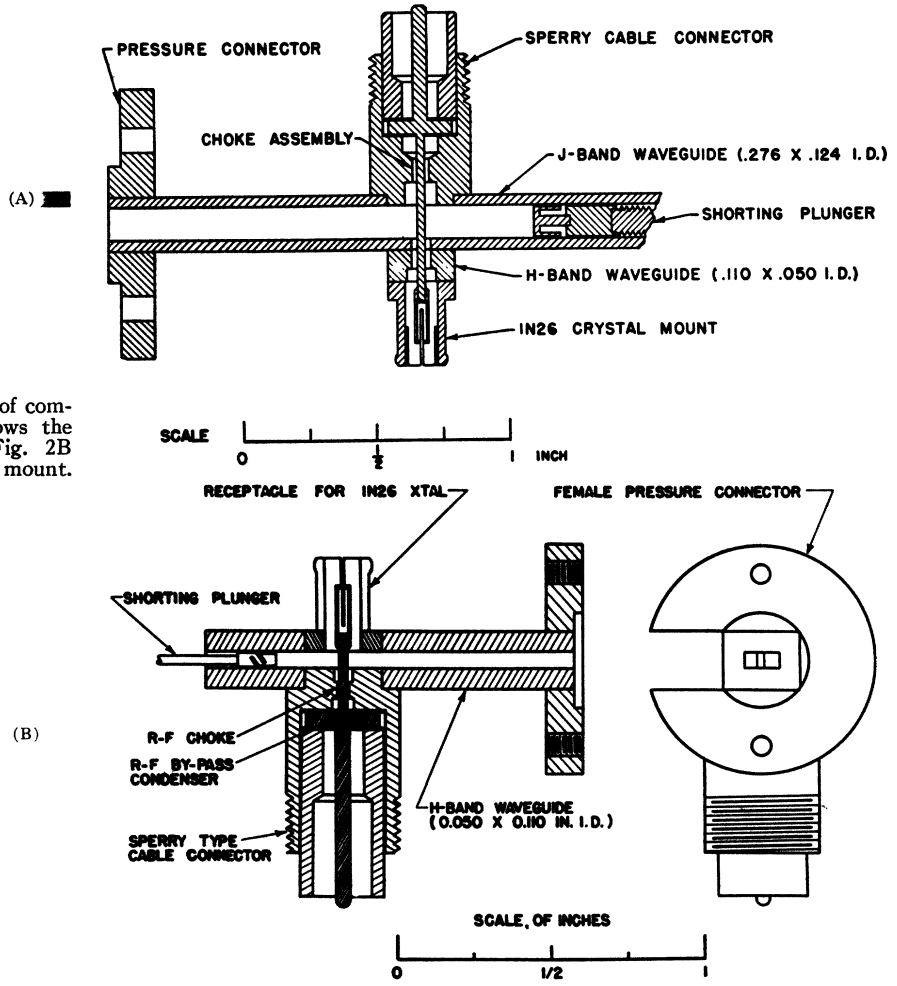


FIG. 2. Cross sections of components. Figure 2A shows the frequency multiplier; Fig. 2B shows the *H*-band crystal mount.

[2] W. Gordy, A. G. Smith, and J.W. Simmons, Phys. Rev. **71**, 917 (1947).
[3] O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. **73**, 635 (1948).
[4] A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. **74**, 370 (1948).

TABLE I. Observed attenuation of 5-millimeter radiation by various wave guides.

Wave-guide dimensions	Band designation	Wave-guide material	Attenuation, db/ft.
2.92 ×1.42 in.	*S*	Brass	0.10
0.95 ×0.45	*X*	Brass	0.25
0.420×0.170	*K*	Silver	0.43
0.276×0.124	*J*	Silver	0.64
0.110×0.050	*H*	Silver	1.25*

* Calculated.

harmonic signal is of the order of thirty decibels below the level of the detected fundamental signal.

For spectroscopy, a 15-foot cell is inserted between the multiplier unit and the detector. The cell is 2.92×1.42 inches in cross section, tapering eighteen inches at either end to the dimensions of the *H*-band components, which are joined to it by means of choke-to-flange connections. Thin mica windows are sealed on at these points to permit evacuation of the cell. The reason for the choice of a cell of such large cross section is made clear by Table I, which shows the results of empirical studies made at five millimeters. At these wave-lengths the losses occurring in wave guide of "normal" proportions would be prohibitive in view of the small amount of energy that is available. No difficulty has been experienced with modes or resonances in the oversize wave guide.

The method of presentation is that originally described by Gordy and Kessler.[5] The klystron is frequency-modulated by means of a saw-tooth voltage of about 15 cycles per second applied to the reflector electrode. The resulting mode envelope (Fig. 3D) is rejected by a preamplifier with a narrow pass-band extending from 150 c.p.s. to 500 c.p.s., whereas absorption lines are sufficiently sharp at the gas pressures ordinarily used to be passed and presented on an oscilloscope. The filtering action of the amplifier also eliminates the baseline "roll" caused by r-f reflections in the wave-guide system. Frequency measurements are made at the fundamental frequency, using a cavity wavemeter whose pip is added to the signal from the cell in a push-pull transformer preceeding the amplifier.

III. MOLECULAR ABSORPTIONS

Table II lists the rotational transitions of ICN, BrCN, and HCN which have been observed in the three-to-five-millimeter region. Each transition was found to be split into several lines (Fig. 3) by nuclear quadrupole interactions. Wavemeter measurements are not sufficiently

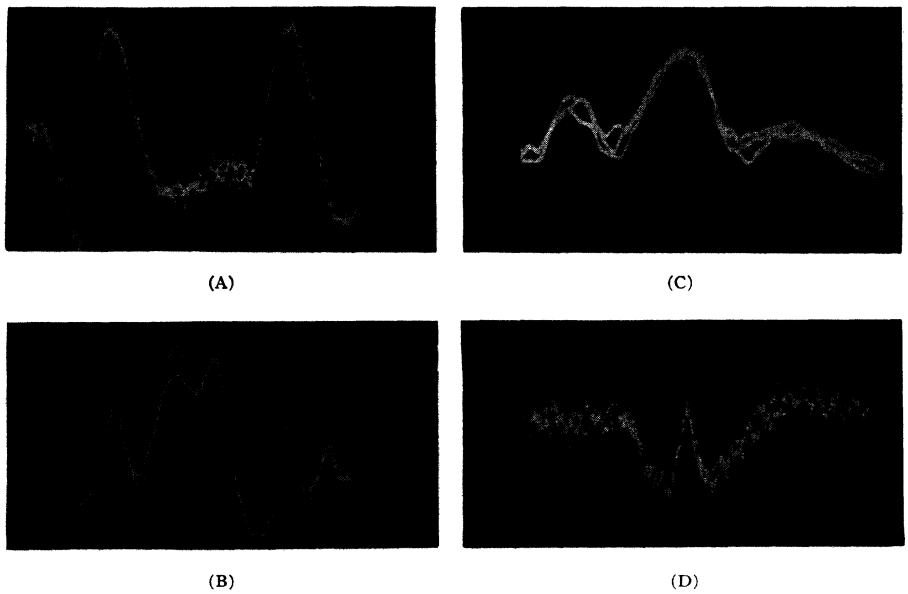


FIG. 3. Oscilloscope photographs of molecular rotational transitions in the three to five millimeter region: 3A, $Br^{81}C^{12}N^{14}$ at 73,742 mc; 3B, $IC^{12}N^{14}$ at 83,864 mc; 3C, $H^{1}C^{12}N^{14}$ at 88,671 mc, all at gas pressures of 5×10^{-3} mm of Hg. Figure 3D shows HCN at a pressure of 1 mm, the entire klystron mode envelope being presented here.

accurate to permit evaluation of the centrifugal distortions of the molecules, but measurements will be made later in this laboratory with a frequency standard to investigate this effect. The $J=4\rightarrow5$ transition of ICN and the $J=3\rightarrow4$ transition of BrCN have been measured to an accuracy of 0.1 mc in this way.[5]

Figure 3C shows the spectrum of the $J=0\rightarrow1$ transition of $H^1C^{12}N^{14}$ observed at 88,671 mc (3.38 mm), with a gas pressure of 5×10^{-3} mm of mercury. The B_0 value determined from this frequency is 1.4789 ± 0.0002 cm^{-1}, which is in good agreement with the value of 1.4784 cm^{-1} derived by Herzberg[6] from infra-red data.[7,8] The splitting of the lines resulting from quadrupole interaction of the nitrogen nucleus was measured by producing frequency markers through modulation with a calibrated signal generator in the manner described by Dailey *et al.*[9] The separations measured in this way were 1.4 mc and 2.1 mc, corresponding to a quadrupole coupling factor $eQ(\partial^2V/\partial z^2)$ of 4.7 mc. This value is appreciably larger than the factors previously determined for the cyanogen halides,[4] and is essentially the same as that found by Ring, Edwards, Kessler, and Gordy for CH_3CN.[10]

In Fig. 3D is shown the unresolved transition at a pressure of one millimeter. Here no filtering has been used in the detecting circuit, so that the entire klystron mode envelope is presented. (The poor signal-to-noise ratio results from the use of an amplifier of 200-kc band width to provide high fidelity.) The peak absorption α in cm^{-1} of a linear molecule in the microwave region ($h\nu\ll kT$ and J small) may be expressed as[11]

$$\alpha=\frac{4\pi^2Nf_vh\mu^2\nu^3}{3c(kT)^2\Delta\nu},$$

TABLE II. Observed rotational transitions of ICN, BrCN, and HCN.

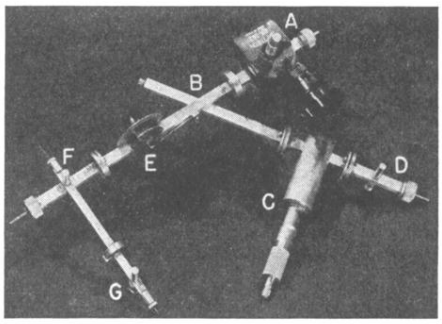
Molecule	Transition	Frequency in mc	Wave-length in mm
$Br^{81}C^{12}N^{14}$	$J=8\rightarrow9$ (Fig. 3A)	73,742	4.07
$Br^{79}C^{12}N^{14}$	$J=8\rightarrow9$	74,165	4.04
$IC^{12}N^{14}$	$J=11\rightarrow12$	77,413	3.88
$Br^{81}C^{12}N^{14}$	$J=9\rightarrow10$	81,936	3.66
$Br^{79}C^{12}N^{14}$	$J=9\rightarrow10$	82,405	3.64
$IC^{12}N^{14}$	$J=12\rightarrow13$ (Fig. 3B)	83,864	3.58
$H^1C^{12}N^{14}$	$J=0\rightarrow1$ (Fig. 3C)	88,671	3.38

where $N=$No. of molecules per cc in absorbing path, $f_v=$fraction of molecules in lowest vibrational state, $\mu=$permanent dipole moment in e.s.u., $2\Delta\nu=$line width at half-power points, and h, c, ν, k, T are standard nomenclature. For HCN, $\mu=2.65\times10^{-18}$ e.s.u.[12] Our observed line width is $2\Delta\nu=50\pm15$ megacycles at a pressure of one millimeter and temperature of 300°K. The sample contained 86 percent C^{12}, while $f_v=97$ percent. The calculated intensity is $\alpha=9\times10^{-3}$ cm^{-1} (or 4.5×10^{-3} neper per cm), almost ten times as strong as the 3,3 ammonia line at 23,870 megacycles, heretofore the strongest observed microwave absorption.

For the 15-foot cell used, the calculated absorption at the resonant frequency is 98 percent. The observed absorption was between 90 and 100 percent. This intense absorption accounts for the large probable error in the line width, since the line shape is quite distorted.

The results thus far obtained in this undeveloped region of the electromagnetic spectrum show that useful work can be done with available equipment. Considerable improvement can be achieved in sensitivity and in precision measurements. Development of the region along each of these lines is proceeding in this laboratory. As an extension of the techniques described above, quite useful quantities of third harmonic energy have been obtained from a multiplier driven by standard 2K33 K-band klystrons. The third harmonic of these oscillators (fundamental power of the order of 30 milliwatts) is comparable in intensity to the second harmonic of the less energetic millimeter tubes. Experiments with the fourth harmonic are now being undertaken.

[5] W. Gordy and M. Kessler, Phys. Rev. **71**, 540 (1947).
[6] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 391.
[7] P. F. Bartunek and E. F. Barker, Phys. Rev. **48**, 516 (1935).
[8] G. Herzberg and J. W. T. Spinks, Zeits. Physik **91**, 386 (1934).
[9] Dailey, Kyhl, Strandberg, Van Vleck, and Wilson, Phys. Rev. **70**, 984 (1946).
[10] H. Ring, H. Edwards, M. Kessler, and W. Gordy, Phys. Rev. **72**, 1262 (1947).
[11] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945), inserting value of $|\mu_{ij}|^2$ appropriate for a linear rotator.
[12] S. Werner, Zeits. f. physik. Chem. (B), 371 and 391 (1929).



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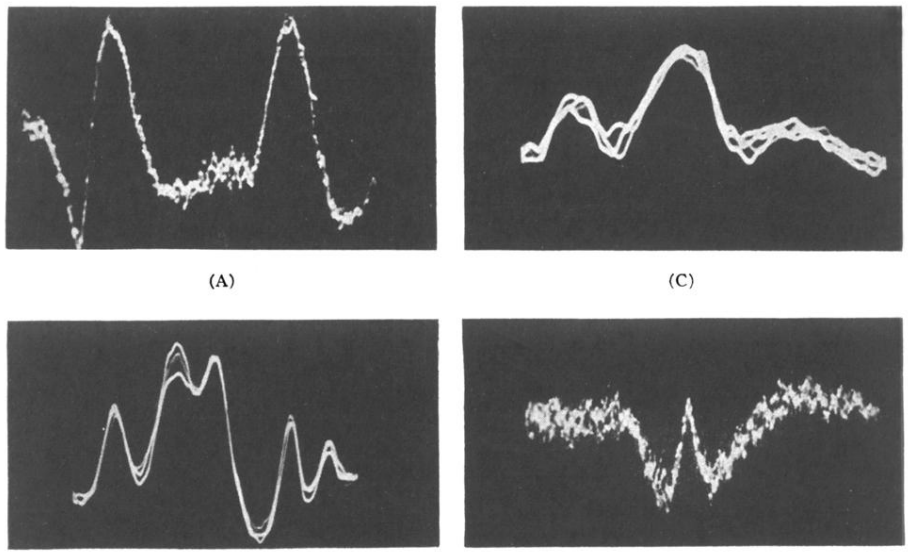

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