

Microwave Spectroscopy in the Region from Two to Three Millimeters*

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(Received January 10, 1950)

A completely electronic sweep spectroscope of high resolution has been developed for the wave-length region from 2 to 3 millimeters (150,000 mc/sec. to 100,000 mc/sec.). The radiation source is a silicon crystal harmonic generator driven by Ratheon klystrons. Silicon crystals are used also as detectors. Radiation of wave-length 1.96 mm (154,000 mc/sec.) has been generated and detected with strength more than ten times the noise level. Some lines in the hyperfine structure of the $J=19 \rightarrow 20$ rotational transition of ICN at 2.32 mm have been observed. The $J=1 \rightarrow 2$ transition of CH_3F has been observed at 2.93, and the separation of the $K=1$ and $K=0$ lines has been determined as 1.8 mc. Precision measurements on the first rotational line ($J=0 \rightarrow 1$) of $\text{C}^{12}\text{O}^{16}$ and $\text{C}^{13}\text{O}^{16}$ in the 2.6-mm region have been made with an electronic frequency standard monitored by the 10 mc/sec. signal of station WWV. The following molecular constants were determined: for $\text{C}^{12}\text{O}^{16}$, $B_0=1.92262_3 \text{ cm}^{-1}$, $B_e=1.93136_7 \text{ cm}^{-1}$, $I_0=14.5553_1 \times 10^{-40} \text{ g cm}^2$, $I_e=14.4894_3 \times 10^{-40} \text{ g cm}^2$, $r_0=1.13078_9 \text{ \AA}$, $r_e=1.12822_7 \text{ \AA}$; for $\text{C}^{13}\text{O}^{16}$, $B_0=1.83806_9 \text{ cm}^{-1}$, $I_0=15.2248_9 \times 10^{-40} \text{ g cm}^2$, $r_0=1.13072_6 \text{ \AA}$. The last three digits quoted for r and I have relative significance only, because of possible error in Planck's constant.

1. INTRODUCTION

IT is well known that for many years the gap in the electromagnetic spectrum between the optical and radio regions has been closed.¹ That is, energy has been detected throughout this region. However, the earlier methods of generating and detecting the radiation have not proved effective for spectroscopic measurements. Consequently, much of this spectral region is still relatively unexplored.

For the past three years a program has been underway in this laboratory for extending to higher frequencies the region in which spectroscopic measurements can be made with essentially electronic or radiofrequency instruments and techniques. A survey of the progress up to August 1948 has been given by one of us.² Measurements in the region from 3- to 5-mm wave-length have been reported by Smith, Gordy, Simmons, and Smith.³ Their observations were made with a sweep spectrograph capable of high resolution, but measurements of the line frequencies were made with a cavity wave meter accurate to only a few megacycles. Since that time, Simmons, Anderson, and Gordy⁴ have made spectrum line measurements in the latter region to an accuracy of 3 parts in 10^6 . They used an electronic frequency standard monitored by Station WWV.

The present work extends the range of precision electronic frequency measurements above 100,000 mc. The $\text{C}^{12}\text{O}^{16}$ absorption line frequency was measured as $115,270.56 \pm 0.25 \text{ mc}$ —a frequency over 11,000 times the WWV frequency used as a monitoring standard.

* The research reported in this document has been made possible through support and sponsorship extended by the Geophysical Research Directorate of the Air Force Cambridge Research Laboratories under Contract No. W(19-122)ac-35. It is published for technical information only and does not represent recommendations or conclusions of the sponsoring agency.

¹ E. F. Nichols and J. D. Tear, Annual Report of the Smithsonian Institution, pp. 175-185 (1923).

² W. Gordy, Rev. Mod. Phys. **20**, 668 (1948).

³ Smith, Gordy, Simmons, and Smith, Phys. Rev. **75**, 260 (1949).

⁴ Simmons, Anderson, and Gordy, Phys. Rev. **77**, 77 (1950).

The millimeter wave components employed in the present work are similar to those referred to above for the 3- to 5-mm wave region. A silicon crystal multiplier driven by Raytheon klystrons is again used as a source. The klystron source frequency is here tripled rather than doubled, as was done in the previous work. Though it has not yet been used to measure spectral lines, a frequency quadrupler similarly designed and energized by a QK142 Raytheon klystron has been found to give usable power at wave-lengths slightly below 2 mm.

Obviously, because of their much greater output, magnetrons would be more powerful sources for millimeter wave harmonic energy. But, because of the greater difficulty in tuning them and because of their more impure (less monochromatic) spectrum as compared to that of the klystron, we have not used them. Recently, however, energy of magnetron harmonics has been detected in the region from 1.5- to 2-mm wave-length by Loubser and Townes.⁵ They used an infra-red type detector (Golay cell). With this combination they were able to detect absorption of DI and NH_3 at high pressures, but to our knowledge no resonant absorption peaks have been measured with accuracy by this method.

2. MILLIMETER WAVE BANDS AND COMPONENTS

Several different sizes of wave guide are required for the millimeter wave region. The diagram given in an earlier report,⁶ which shows the wave guide sizes and the band designations as employed in this laboratory, has been extended (see Fig. 1) to include the G band (2 to 3 mm) covered in the present report and the projected F band (1.3 to 2 mm), for which wave guide components are now being developed. The dimensions of the H band guide have been changed slightly from those previously used so that more effective overlapping

⁵ J. H. N. Loubser and C. H. Townes, Phys. Rev. **76**, 178 (1949).

⁶ W. Gordy, reference 2, p. 670.

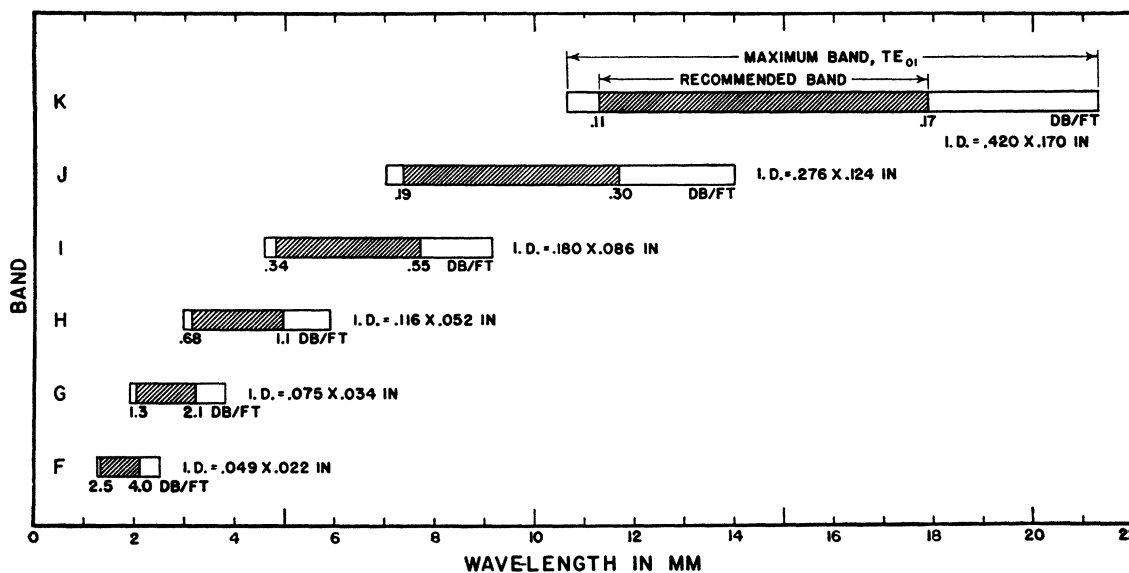


FIG. 1. Dimensions and losses for coin silver wave guide covering the region from 1.3 mm to 18 mm. The designation *F*, *G*, *H*, *I*, *J* is that adopted at this laboratory for the sub-*K* bands as indicated.

of the *I* band is obtained. The *I* and *J* band sizes here shown do not correspond exactly to the output sizes of the present Raytheon tubes. Hence, slightly tapered connectors are used. It will be noted that wave guide of six different sizes is required for making the usual wave guide components—attenuators, multipliers, crystal mounts, etc.—for the region from 1.3 mm to 18 mm. For absorption cells oversized wave guide can be used. When the third, fourth, or higher harmonics are used, additional wave guide sizes are needed for filtering the lower harmonics.

Figure 2 represents a photograph of the essential wave guide components with the exception of the absorption cell and the mixer for the frequency standard. The crystal multiplier and detector previously described³ are reduced in size to conform to the shorter wave-lengths. For the present work the absorption cell was made of *K* band rather than of *S* band guide, as previously used. The *K* band guide was found to be more satisfactory, probably because of smaller losses in the transition sections. The cell length was 7 feet. A mica window (0.001-in. thickness) and a lead gasket (0.003 in.) pressed tightly between coupling flanges were used to seal each end of the absorption cell. This type of vacuum seal permitted the cell to be cooled to liquid air temperature. To energize the frequency tripler, Raytheon klystrons QK142 and QK226 were used. Approximately 10 milliwatts is available from the QK142 and 5 milliwatts from the QK226. No attempts were made to measure the power output from the tripler, but it was probably of the order of a microwatt. Selected Sylvania 1N26 crystals were employed both for the multiplier and detector, and for the mixer and detector of the frequency standard.

3. DETECTING METHODS

Video

As has been previously shown,² the simple "video" receiver compares favorably with the more awkward superheterodyne one for the detection of absorption lines whenever the available power is so small (the order of a microwatt) that the low frequency noise generated in the crystal by the microwave power is

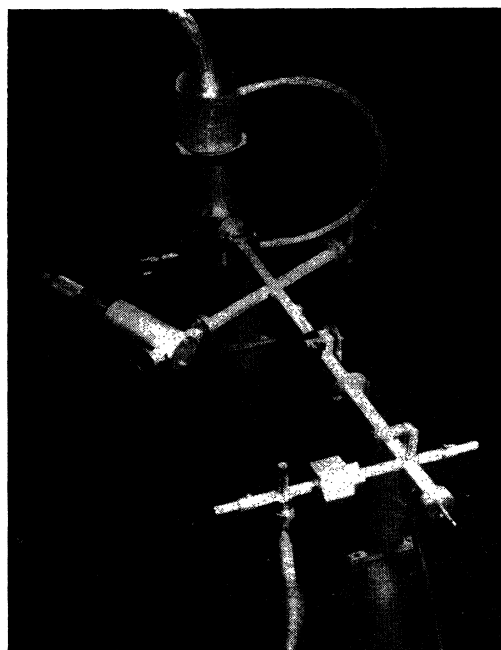


FIG. 2. Microwave components (less absorption cell and mixer for frequency standard) showing a frequency tripler and detector in the *G* band region, and associated *J* band components.

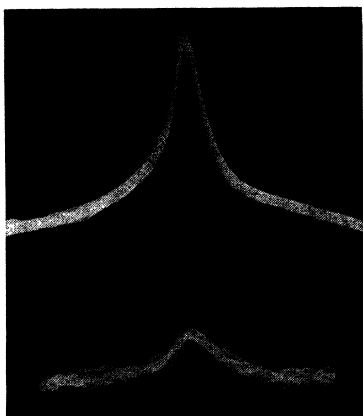


FIG. 3. Oscillograms of the lowest rotational transition of $C^{12}O^{16}$ at 115,270 mc. The upper curve was taken at the temperature of liquid air, the lower at the temperature of dry ice.

negligible. For most of the work we have used a single crystal detector followed by an amplifier with a band width of approximately 500 c.p.s. The lower frequency "cut-off" occurs at about 60 c.p.s. and is fairly sharp so that by proper adjustment of the rate of oscillator sweep the mode contour and variations caused by r-f reflections can be "filtered." Figure 3 shows the $J=0 \rightarrow 1$ rotational line of $C^{12}O^{16}$ at 2.60-mm wavelength, and Fig. 4 shows a section of the $J=19 \rightarrow 20$ rotational transition of ICN at 2.32-mm wavelength, both detected by this method.

Phase-Sensitive Amplifier with Source Modulation

A second method, which was found to be more sensitive and only slightly more complicated than the method just described, employs a narrow-band phase-sensitive detector with the reference signal applied to the reflector of the oscillator so as to frequency modulate the oscillator at the reference frequency. Figure 5 shows a block diagram of this system. The principle of operation is similar to the modulation method already described by Gordy and Kessler⁸ except that the phase-sensitive amplifier is used instead of the ordinary A.M. receiver. For the present work a 4000 c.p.s. receiver was used. Figure 6 shows the same ICN lines as those in Fig. 4, detected by this method and displayed on an Esterline-Angus automatic recorder. Stark modulation instead of source modulation would offer some advantages if a Stark cell of sufficiently low loss can be made for these high frequencies. The present method, however, has the advantage that the power can be detected when no absorption line is being observed. This is very desirable in this region where frequently the power drops below that necessary for satisfactory operation.

⁷ W. Gordy and M. Kessler, *Phys. Rev.* **71**, 640 (1947).

⁸ W. Gordy and M. Kessler, *Phys. Rev.* **72**, 644 (1947).

Superheterodyne

One of the difficulties in employing energy of harmonics higher than the third is the stringent requirement on the wave guide filters. Dr. Robert Carter has suggested to us a heterodyne detecting method which discriminates between the different harmonics. Two harmonic generators driven by separate klystrons are required for operation of the system. The outputs from the two sources are mixed, and the difference frequency is amplified by an I.F. amplifier. One of the oscillators has a fixed frequency (or its frequency is varied very slowly), and the other has a frequency sweep synchronized with the C.R.O. sweep used to display the output signal. This is equivalent to viewing the output of the fixed frequency source with a spectrum analyzer. However, the signal resulting from the beating of any two harmonics appears at a place on the scope-trace different from that of any other two. This useful result follows simply from the fact that the difference frequency of the different harmonic pairs is not the same. Thus, to obtain the same beat frequency with different harmonic combinations, the difference frequency of the fundamental sources must be changed. We have found this method useful for selecting crystals, for tuning multipliers, and for estimating the relative energies in the different harmonics. It could be used for observing absorption lines, but it would be slower than the other methods described. By mixing fourth harmonic power we have obtained signals more than ten times the noise level at a frequency of 154,000 mc (1.96-mm wavelength).



FIG. 4. Upper curve shows the unresolved $J=19 \rightarrow 20$, $\Delta F = +1$ transitions of ICN at $\lambda = 2.32$ mm. Lower curve shows the same transition partially resolved.

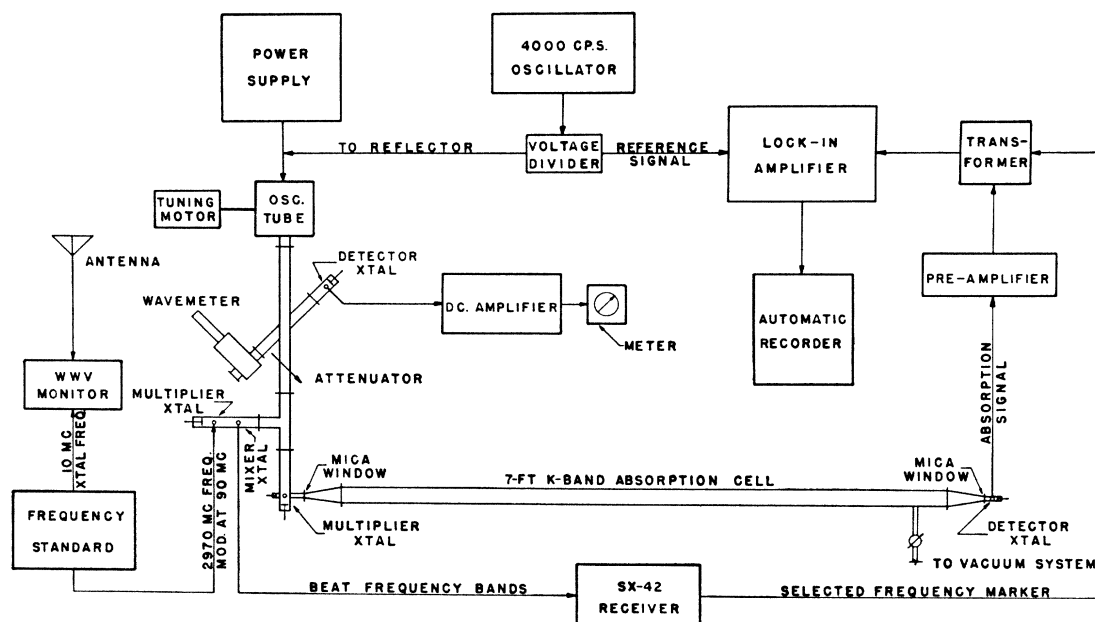


FIG. 5. Block diagram of the 2- to 3-millimeter wave spectrometer employing a phase-sensitive amplifier with source modulation and automatic recording.

4. MICROWAVE SPECTRUM AND MOLECULAR CONSTANTS OF CARBON MONOXIDE

The first rotational lines of $C^{12}O^{16}$ and $C^{13}O^{16}\dagger$ have been measured for the ground vibrational state. From these measurements precise values of the molecular constants were calculated (see Table I). Since microwave data could not be obtained on excited vibrational states, equilibrium values B_e , I_e , and r_e are not completely determined from the present work. Nevertheless, the present work improves the accuracy in these values by a factor of 10 or more because the error introduced by the anharmonicity corrections is an order of magnitude smaller than the total error in the previously determined B values. The frequency of the first rotational line is altered slightly by centrifugal stretching. Fortunately, this does not limit the accuracy of the final results since the small stretching constant can be estimated with sufficient accuracy from B and from the known vibrational frequency.

The rotational frequencies of a diatomic molecule are:

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

where

$$\begin{aligned} J &= 0, 1, 2, \dots \\ B_v &= B_e - \alpha_e(v+1/2), \\ B_e &= h/(8\pi^2cI_e), \end{aligned}$$

and

$$D_v = 4B_v^3/\omega^2.$$

For the first rotational line ($J=0 \rightarrow 1$) and the ground vibrational state ($v=0$),

$$\nu(\text{cm}^{-1}) = 2B_0 - 4D_0,$$

\dagger The C^{13} was concentrated to 14 percent.

where

$$B_e = B_0 + \frac{1}{2}\alpha_e, \quad D_0 = 4B_e^3/\omega_e^2.\ddagger$$

For $C^{12}O^{16}$ we use $\alpha_e = 0.017485 \pm 0.000015 \text{ cm}^{-1}$ and $D_0 = 6.45 \times 10^{-6} \text{ cm}^{-1}$, as determined by Herzberg and Rao.⁹ For $C^{13}O^{16}$ we calculate $D_0 = 5.89 \times 10^{-6} \text{ cm}^{-1}$, with the easily derived formula,

$$D_0' = (\mu/\mu')^2 D_0,$$

where the prime indicates the constants for $C^{13}O^{16}$. The value of α_e listed in Table I for $C^{13}O^{16}$ is obtained from our measurements by assuming r_e for $C^{13}O^{16}$ to be the same as that for $C^{12}O^{16}$. For Planck's constant we



FIG. 6. Automatic recording tracings of $J=19 \rightarrow 20$, $\Delta F = +1$ transitions of ICN at $\lambda = 2.32 \text{ mm}$ obtained by use of phase sensitive amplifier with source modulation. Left curve shows unresolved line. Right curve is partially resolved. The presentation represents the first derivative of the absorption curve.

\ddagger Here we neglect the second-order term $\frac{1}{2}\beta_e$.

⁹ G. Herzberg and K. N. Rao, *J. Chem. Phys.* **17**, 1099 (1949).

TABLE I. Molecular constants of carbon monoxide.

	C ¹² O ¹⁶	C ¹³ O ¹⁶
ν_0 mc/sec. ($J=0 \rightarrow 1$)	115,270.56 \pm 0.25	110,201.1 \pm 0.4
B_0 cm ⁻¹	1.92262 ₅	1.83806 ₉
B_e cm ⁻¹	1.93136 ₇	1.84621 ₅
D_0 cm ⁻¹	(6.4 ₅ \times 10 ⁻⁶)	5.8 ₉ \times 10 ⁻⁶
α_e cm ⁻¹	(0.01748 ₆)	0.01629 ₂
* I_0 g cm ² \times 10 ⁻⁴⁰	14.5553 ₁	15.2248 ₉
* I_e g cm ² \times 10 ⁻⁴⁰	14.4894 ₃	15.1577 ₁
* r_0 10 ⁻⁸ cm	1.13078 ₉	1.13072 ₅
* r_e 10 ⁻⁸ cm	1.12822 ₇	(1.12822 ₇)

* The last three digits quoted for r and I have relative significance only, because of possible error in the value of Planck's constant.

use the latest value given by DuMond and Cohen,¹⁰ $h=6.62373\pm 0.0011\times 10^{-27}$ erg sec. With the value¹¹ $c=2.99776\pm 0.00004\times 10^{10}$ cm/sec. this gives

$$I = 27.98440 \times 10^{-40} / B \text{ g cm}^2$$

and

$$r = 5.290028 \times 10^{-20} / (\mu B)^{\frac{1}{2}} \text{ cm.}$$

Other constants used are:

$$\left. \begin{aligned} 1 \text{ A.M.U.} &= 1.65972 \times 10^{-24} \text{ g}^{12} \\ M_{C12} &= 12.00386 \text{ A.M.U.} \\ M_{C13} &= 13.00761 \text{ A.M.U.} \end{aligned} \right\}^{11}$$

With the above constants and equations we have calculated the molecular parameters listed in Table I. The values thus obtained are in remarkably good agreement with those recently obtained by Herzberg and Rao, who made observations with a 21-foot grating in the region of 1.2 microns on the third overtone of

¹⁰ J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. 21, 651 (1949).

¹¹ R. T. Birge, Rev. Mod. Phys. 13, 233 (1941).

¹² This was obtained from the value of Avogadro's number given by DuMond and Cohen, reference 10.

the CO vibrational band. Our B_0 values are apparently more precise than those of Herzberg and Rao by a factor of more than 10. They quote their error limits in B_0 for C¹²O¹⁶ as 1.5×10^{-4} cm⁻¹. We believe ours to be accurate to 7×10^{-6} cm⁻¹. The results obtained from the ultraviolet¹³ are also in good agreement but are considered less accurate than those of Herzberg and Rao. The values obtained in the longer infra-red region¹⁴ on the CO fundamental vibration-rotation band are in poor agreement with our results.

The rotational constants of C¹²O¹⁶ have now been measured in three widely different regions of the spectrum: the ultraviolet, the infra-red, and the microwave. This allows a checking of the calibration methods of one region against those of another. For example, one may now calibrate an infra-red or ultraviolet spectroscopy indirectly with station WWV by using the carbon monoxide lines as secondary frequency standards.

5. METHYL FLUORIDE

The $J=1 \rightarrow 2$ transition of methyl fluoride was observed at 2.93-mm wave-length. The separation of the $K=0$ and $K=1$ lines was found to be 1.8 mc. This gives the centrifugal stretching constant $D_{JK}=0.45$ mc. The molecular structure of methyl fluoride has already been determined from measurements on the $J=0 \rightarrow 1$ transition.¹⁵

We wish to thank W. V. Smith, R. L. Carter, and R. S. Anderson for their suggestions and assistance with the electronic problems, and R. Trambarulo for preparing the sample of carbon monoxide with concentrated C¹³.

¹³ Gerö, Herzberg, and Schmid, Phys. Rev. 52, 467 (1937).

¹⁴ Lagemann, Nielsen, and Dickey, Phys. Rev. 72, 284 (1947).

¹⁵ Gilliam, Edwards, and Gordy, Phys. Rev. 75, 1014 (1949).

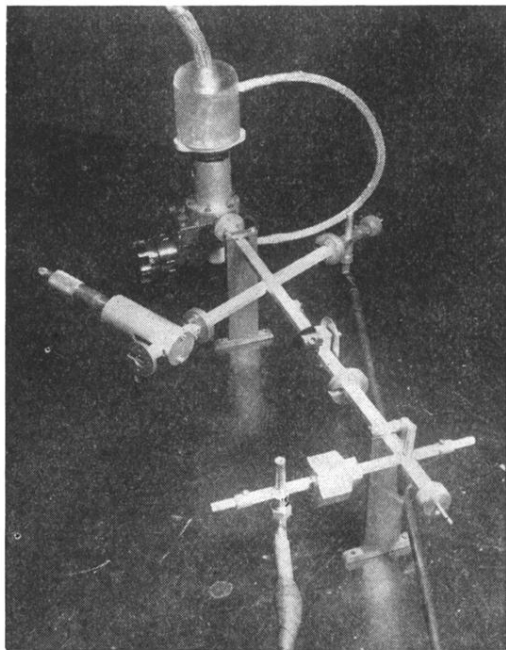


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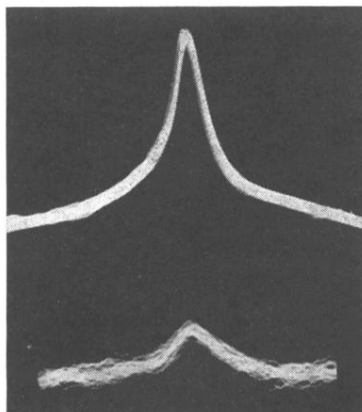


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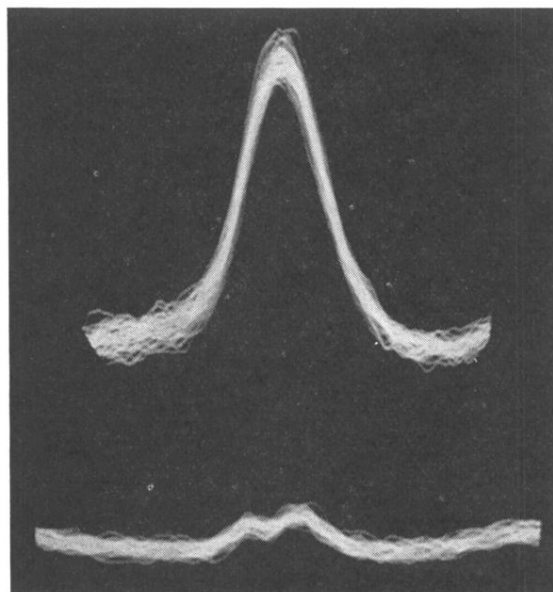


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