MICROWAVE SPECTROSCOPY ABOVE 60 KMc.

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The present report is a survey of the methods used at Duke for millimeter wave spectroscopy at frequencies above 60 KMc. The results obtained are described only as they are needed to illustrate these methods. Several of the Duke group have made measurements in the region about 60 KMc. Those who have contributed most to the development of the millimeter wave components and spectrographic techniques for this region are former Duke students, A. G. Smith, O. R. Gilliam, R. S. Anderson and C. M. Johnson.

The region of 60 KMc. is chosen as the lower frequency boundary for the present discussion because it represents the upper frequency limit for the coverage obtainable with present day klystrons. Higher frequencies are obtainable with experimental magnetrons, but magnetrons are not satisfactory sources for high resolution spectroscopy. To date, all precise measurements of spectral frequencies above 60 KMc. have been made with crystal harmonic generators driven by klystrons. Therefore, I shall limit my discussion to spectrographs which employ this type of source. With these sources, sharp spectral lines have been measured at frequencies as high as 125 KMc. to an accuracy of 0.2 Mc. With special precautions, this accuracy can be improved by a factor of 2 or more.

Despite the limited power available from crystal harmonic generators (only a few microwatts), spectroscopy in the range 60 to 150 KMc. (5 to 2 mm wave lengths) is very promising for the following reasons: (1) Because the harmonics are precise multiples of the klystron driver frequency, the frequency measurements need not be made directly at the frequency of the spectral line but can be made at the lower frequency of the driver. The driver thus provides a convenient relay in the standard marker system. (2) With powers of only a few microwatts, excessive low-frequency noise is not generated in the crystal detector. Even at audio frequencies, the noise is essentially the Johnson type. (3) The output impedance of the crystal detector is virtually independent of variations of the input power at the low powers levels which are available. This simplifies the problem of matching the detector to the amplifier. (4) The saturation effect is not encountered even at the low pressures required for high resolution. (5) Because harmonics from the second through the fifth or higher can be used, a wide spectral range can be covered with a single klystron (This advantage is largely a monetary one). (6) Rotational lines of molecules increase in intensity with increase in frequency (they increase as the cube of the frequency for some molecules) throughout the microwave region. In general, the spectral lines are much stronger in the millimeter-wave than in the centimeter-wave region.

The most serious limitation to the sensitivities of spectrometers for the region above 60 KMc. is the inefficiency of the detectors. Although 1N26 silicon

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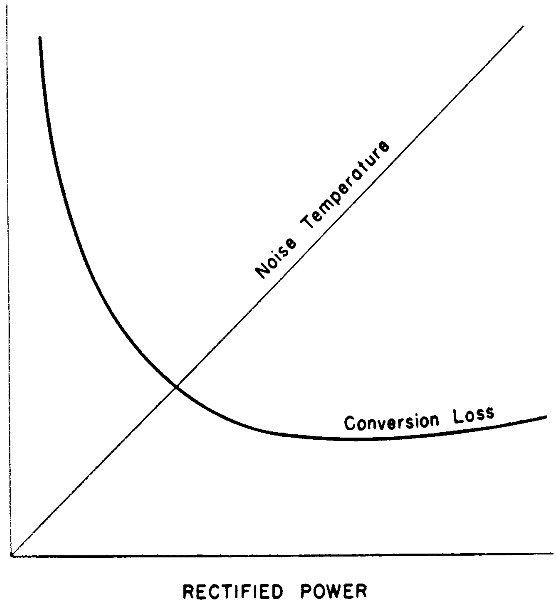
crystal detectors designed for 25 KMc. waves perform much better at 125 KMc than anticipated, their performance is understandably many times worse at 125 KMc. than at 25 KMc. The lowered efficiency appears to be more a consequence of the drop in power level than a result of the increased frequency. It is well known that below a certain power level, which is of the order of 100 microwatts, the conversion efficiency of a crystal drops rapidly with further decrease in detected power (local oscillator power in superheterodyne receivers). This is illustrated in FIGURE 1, which shows the forms of the variation of the conversion loss and noise temperature with the rectified r-f power. It is seen that while the noise temperature goes down, the conversion loss goes up rapidly with decrease of power below a certain limit.

In the region of 125 KMc., sensitivities of the order 5×10^{-5} cm^{-1} have been obtained with the simple video type spectrometer, and of 5×10^{-7} cm^{-1} with a narrow band amplifier having a phase lock-in detector.* These sensitivities, while impressive, are a hundred times lower than those obtainable with similar detectors and receivers in the K-band region. The decreased sensitivities approximately nullify the advantage of the increase in the strength of the absorption lines at the higher frequencies. With improved klystron drivers, further improvements can be made, but, of course, it is not to be expected that the same sensitivities will be obtained as for centimeter waves. The principal advantage arises from the wider frequency coverage afforded by the harmonic generators.



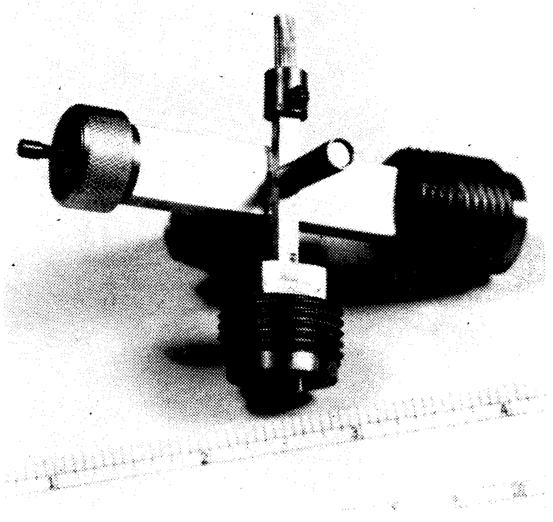


FIGURE 1 (left). Illustration of characteristic variation of noise temperature and conversion loss with rectified r-f power.

FIGURE 2 (right). Photograph of cross wave guide multiplier.

Wave Guide Components

Most of our studies have been made with silicon crystals mounted on crossed wave guide mounts, like that shown in FIGURE 2. This particular multiplier

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* A sensitivity of better than 10^{-7} cm.$^{-1}$ has now been obtained in this region.

is a quintupler, for converting energy from K-band klystrons to waves of approximately 2.5 mm. in length. Cross section details of it are given in FIGURE 3. The multiplier is tuned by adjustment of the two plungers and by movement of the co-axial crystal cartridge on its mount. We have also made multipliers of this type for doubling, tripling, and quadrupling, as well as quintupling energy, from K-band tubes as well as from klystrons of higher frequency.

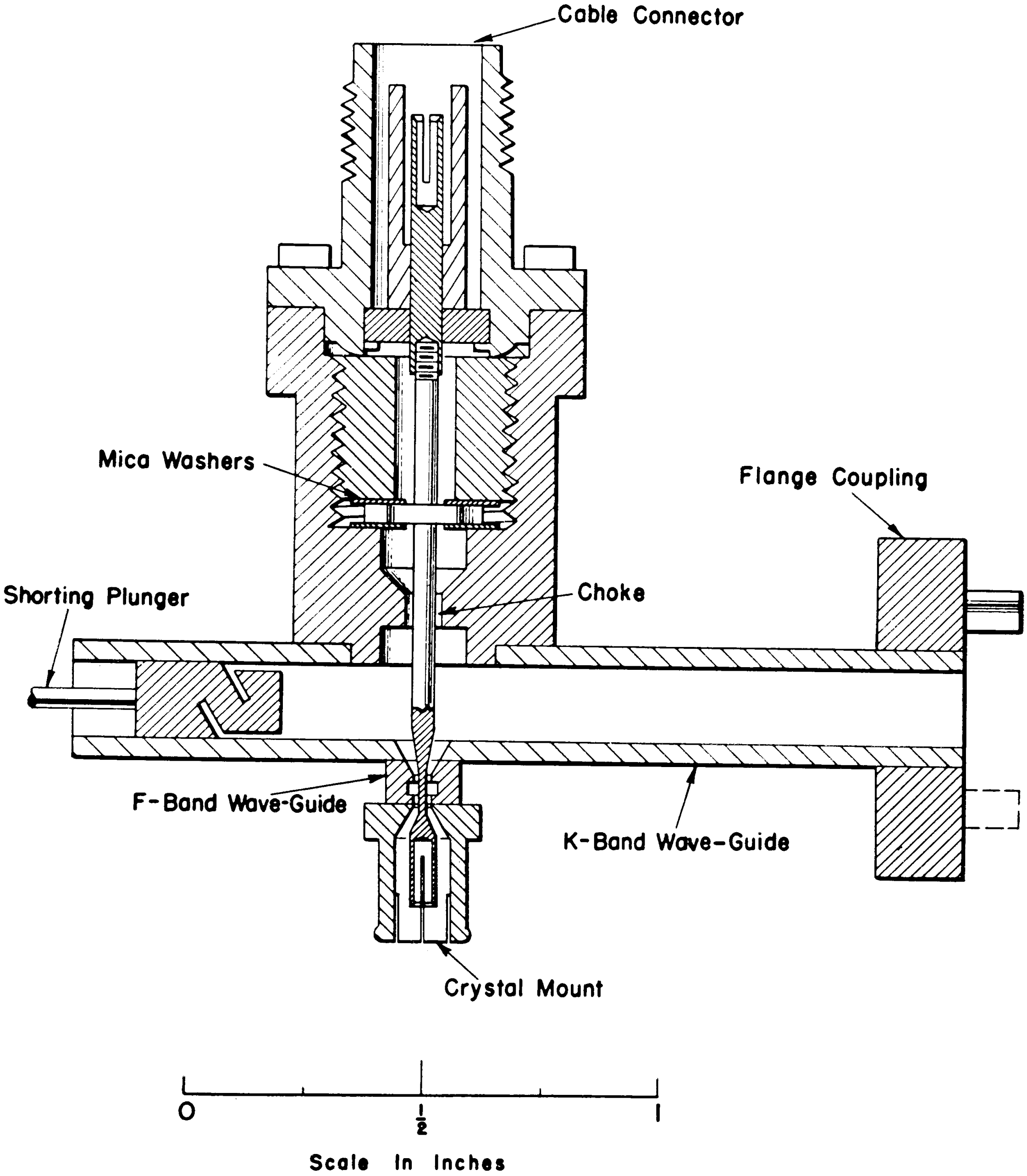

FIGURE 3. Cross section of crystal harmonic multiplier for obtaining fifth harmonic energy from K-band klystron. (From C. M. Johnson's Ph.D. thesis, Duke University. 1951.).

Extensive comparisons made in our laboratory, primarily by C. M. Johnson, have shown that approximately the same output in the region of 125 KMc. can be obtained by quintupling the K-band energy as can be obtained from lower harmonics of the higher frequency millimeter-wave tubes available to us. Although the filtering requirements are more strenuous for the higher harmonics, the frequency measurements are more easily made with K-band than with the higher frequency drivers. To obtain energy above 60 KMc., we are inclined at present to favor the use of higher harmonics from tubes operating below 30 KMc. over the use of lower harmonics from the millimeter wave tubes. All of our tests have been made with Raytheon klystrons, many of which were not the most recent types. If the power output of the millimeter-wave tubes can be stepped up by a factor of 3 or 4, it is probable that more

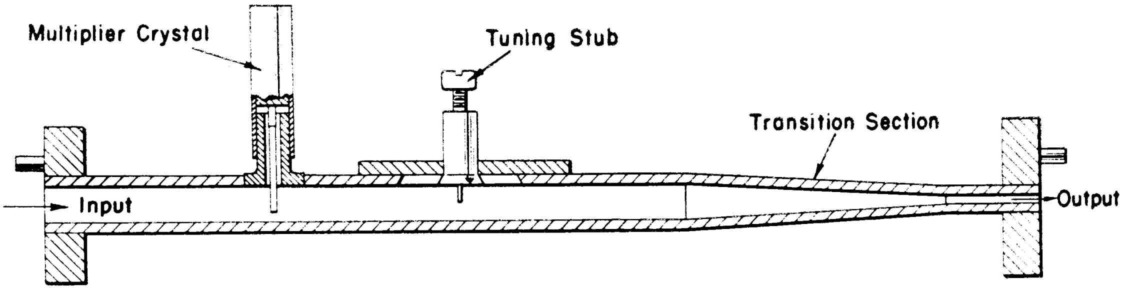

FIGURE 4. Simple straight-through multiplier. (From C. M. Johnson's Ph.D. thesis, Duke University. 1951.

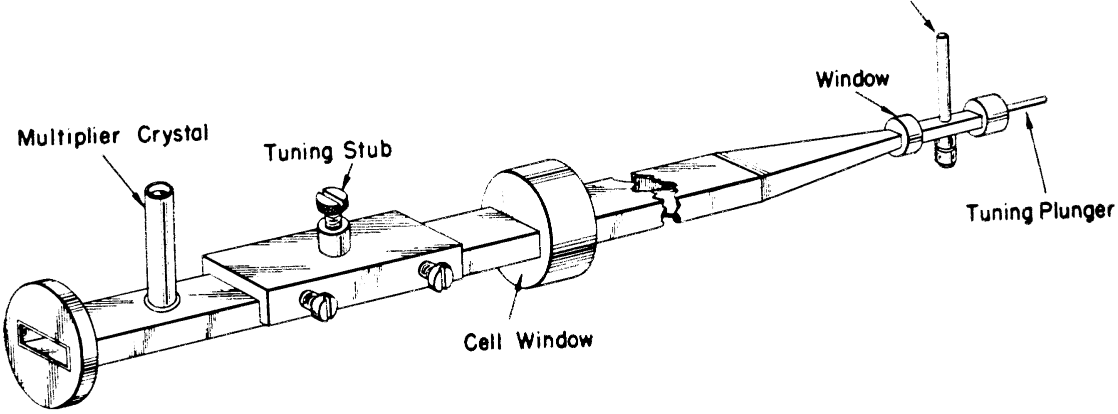

FIGURE 5. Illustration of simple high frequency spectrograph with the straight-through type multiplier.

satisfactory results can be obtained by using lower harmonics from the higher frequency tubes. The output from a crystal multiplier drops very rapidly when the driver power falls below a certain minimum, which varies with different crystals but which appears to be around 25 milliwatts for most crystals.

C. M. Johnson has tried the straight-through mount for the crystal multiplier shown in FIGURE 4. Although the results were very encouraging, he was not able to obtain quite as much output from this arrangement as from the crossed wave guide design of FIGURE 2. This is probably because of the difficulty of obtaining as good an impedance match with the straight-through as with the crossed type. The straight-through design is nevertheless attractive because of the extremely simple, high frequency spectrograph which it allows. See FIGURE 5. Only one transition section is required. The wave guide mount for the output detector serves as the filter. To use a different harmonic, it is necessary only to change this crystal mount. A high frequency spectrometer of wide coverage can be made in this way, quickly, and at low cost.

The wave guide mount for the crystal detectors which we use are of the same design as those used for centimeter waves, except that we have dispensed with the usual chokes in the sliding plunger. No tuning screws are used. Tuning is accomplished by movement of the crystal cartridge and by sliding the shorting plunger. A cross-section of one of these crystal mounts is shown in FIGURE 6. When the fourth, fifth, or a higher harmonic energy is to be employed, the dimensions of the wave guide must be carefully chosen if it is to serve as a filter as well as a crystal mount. FIGURE 7 shows the sizes required for various filters.

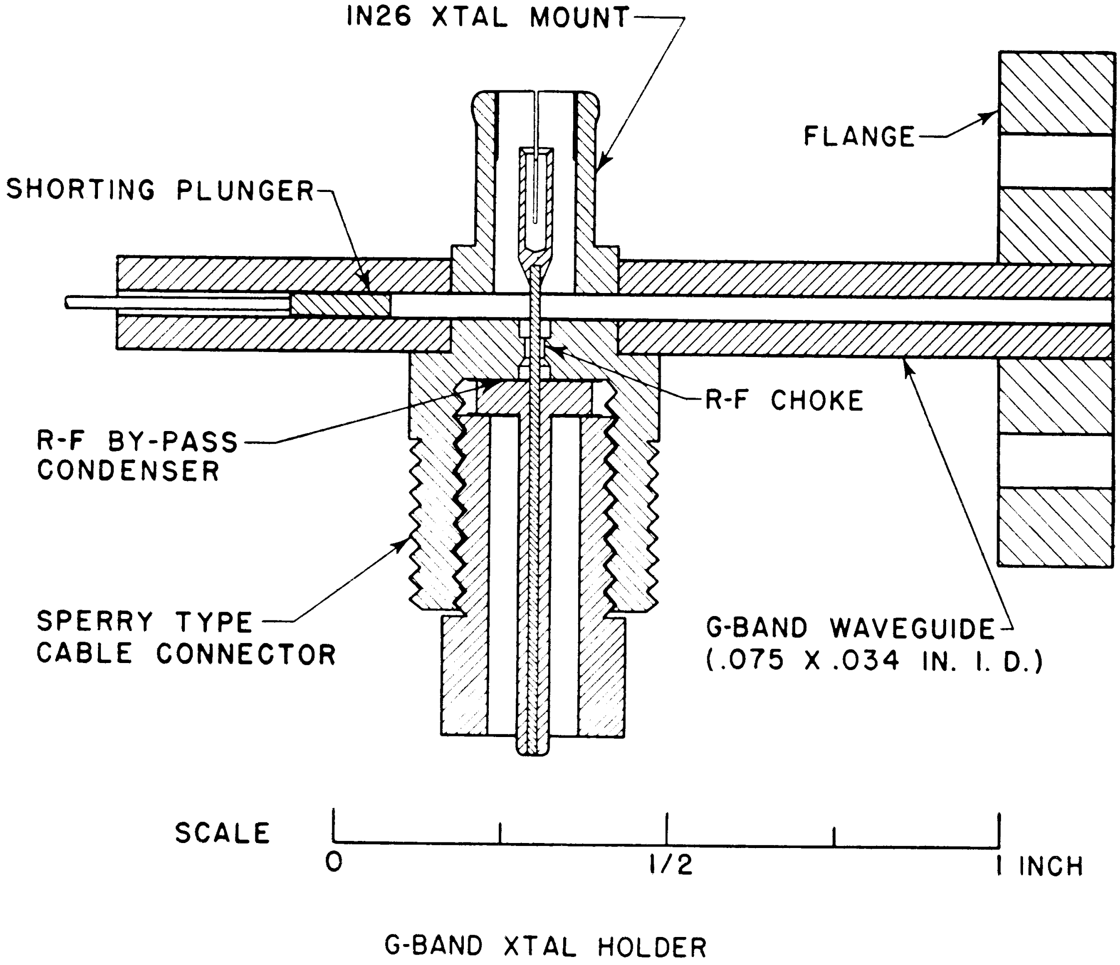

FIGURE 6. G-band crystal holder. (From C. M. Johnson's Ph.D. thesis, Duke University. 1951.)

The multiplier crystals as well as the detectors must be carefully selected. Only one in 10 or 20 crystals designed for K band is likely to be satisfactory, either as a detector or as a multiplier for the region above 60 KMc. Sylvania now produces a silicon crystal, the IN53, designed for a somewhat higher frequency than K-band region, which is superior to the IN26 for millimeter-wave spectroscopy. Crystals which are unsatisfactory detectors may be very good multipliers and *vice versa*. Also, crystals which are unsatisfactory in one region may perform well a few thousand Mc. away. Some crystals which are good today are bad tomorrow and *vice versa.* A spectroscopist who works above 60 KMc. should obtain a large number of crystals and never throw any away. In other words, he should become a crystal collector.

Detecting Systems

The great advantage of the Stark-modulation method over other detecting systems in the centimeter wave region is not evident in the region above 60 KMc. To understand this difference, one needs to examine the causes for the greater sensitivity of the Stark method in the centimeter wave region. In the first place, Stark-modulation allows the amplification of the signal at fairly high frequencies, so that the excessive low-frequency noise generated in the detector crystal by the microwave power can be partly avoided. This allows the use of sufficient power (without excessive noise) to operate the detector crystal at a point where the conversion efficiency is good. At the same time since no filtering is required to cope with reflections the pressure of the gas in the cell can be increased sufficiently to avoid the saturation effect. In other words, the Stark-modulation allows one to make effective use of the milliwatt powers available in the region below 60 KMc. In the region above 60 KMc., there is insufficient power to produce the excessive low frequency noise or to saturate the molecules even at relatively low pressures, and the advantages of

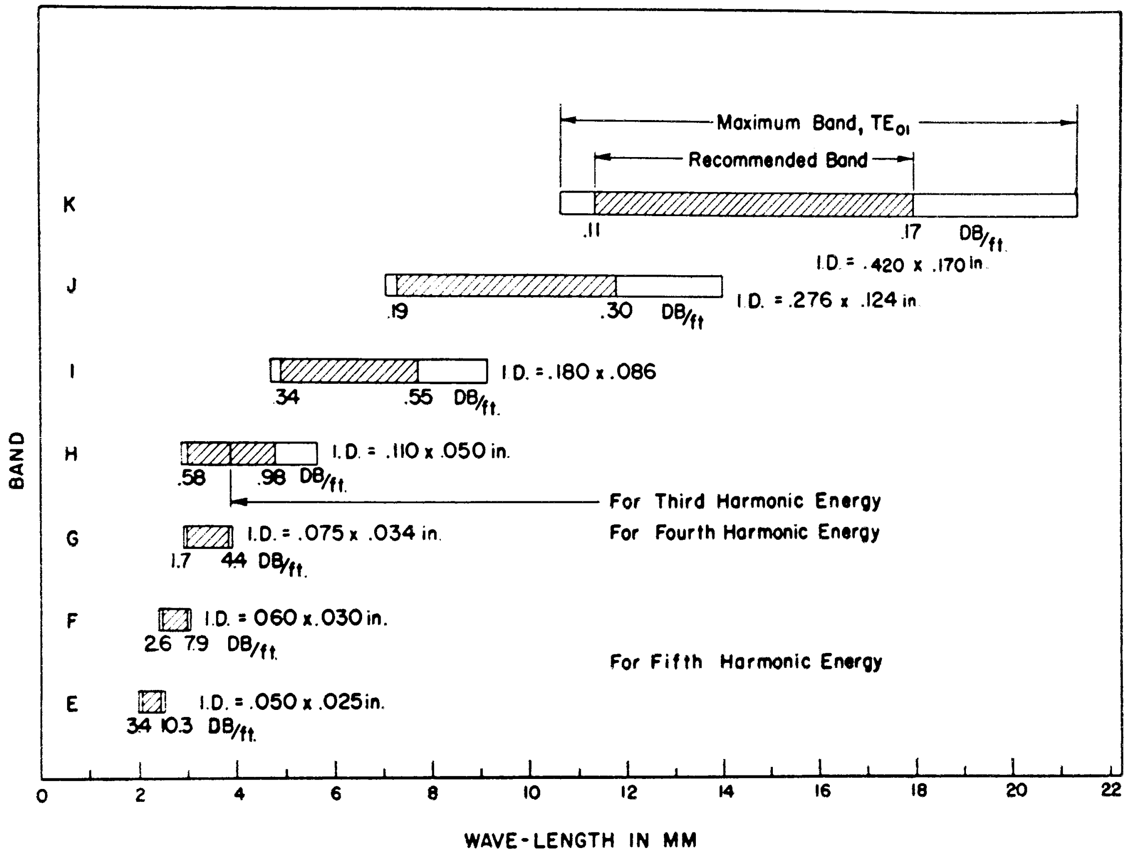

FIGURE 7. Dimensions of wave guide filters. (From C. M. Johnson's Ph.D. thesis, Duke University, 1951.).

Stark-modulation mentioned above are not evident. In fact, the greater losses introduced by the Stark electrode lowers the power falling on the detector crystal still further and hence decreases the conversion efficiency.

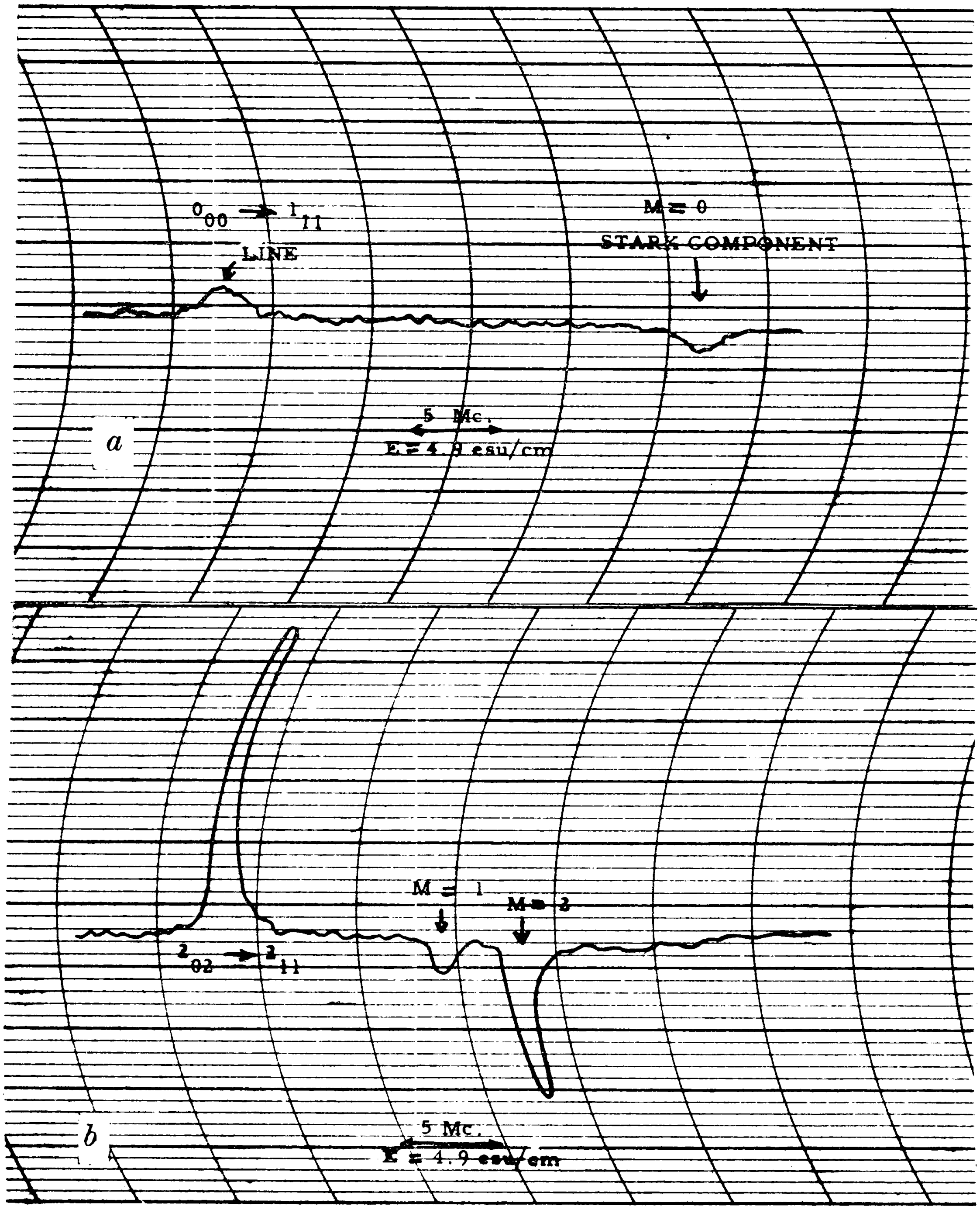

FIGURE 8. (a) Recording of SO_2 $0_{00} \rightarrow 1_{11}$ transition at 69,576 Mc. (b) Recording of SO_2 $2_{02} \rightarrow 2_{11}$ transition at 53,529 Mc. (From G. F. Crable's Ph.D. thesis, Duke University. 1951.).

Stark-modulation is still useful, of course, for the identification of transitions of asymmetric rotators and for the measurement of dipole moments. Although it can be achieved in other ways, the Stark method provides a convenient modulation for use with phase-lock-in detectors.

FIGURE 8 shows a recorder trace of two SO_2 lines, one at approximately 70 KMc. and the other near 53 KMc. Both were obtained with 4 Kc. square-wave Stark-modulation and a lock-in-amplifier followed by a pen and ink recorder. The cell was made of K-band guide six feet in length with the Stark electrode supported in the usual way by Teflon. The losses in this Stark cell become prohibitive above 90 KMc., although it appears that a shorter one of

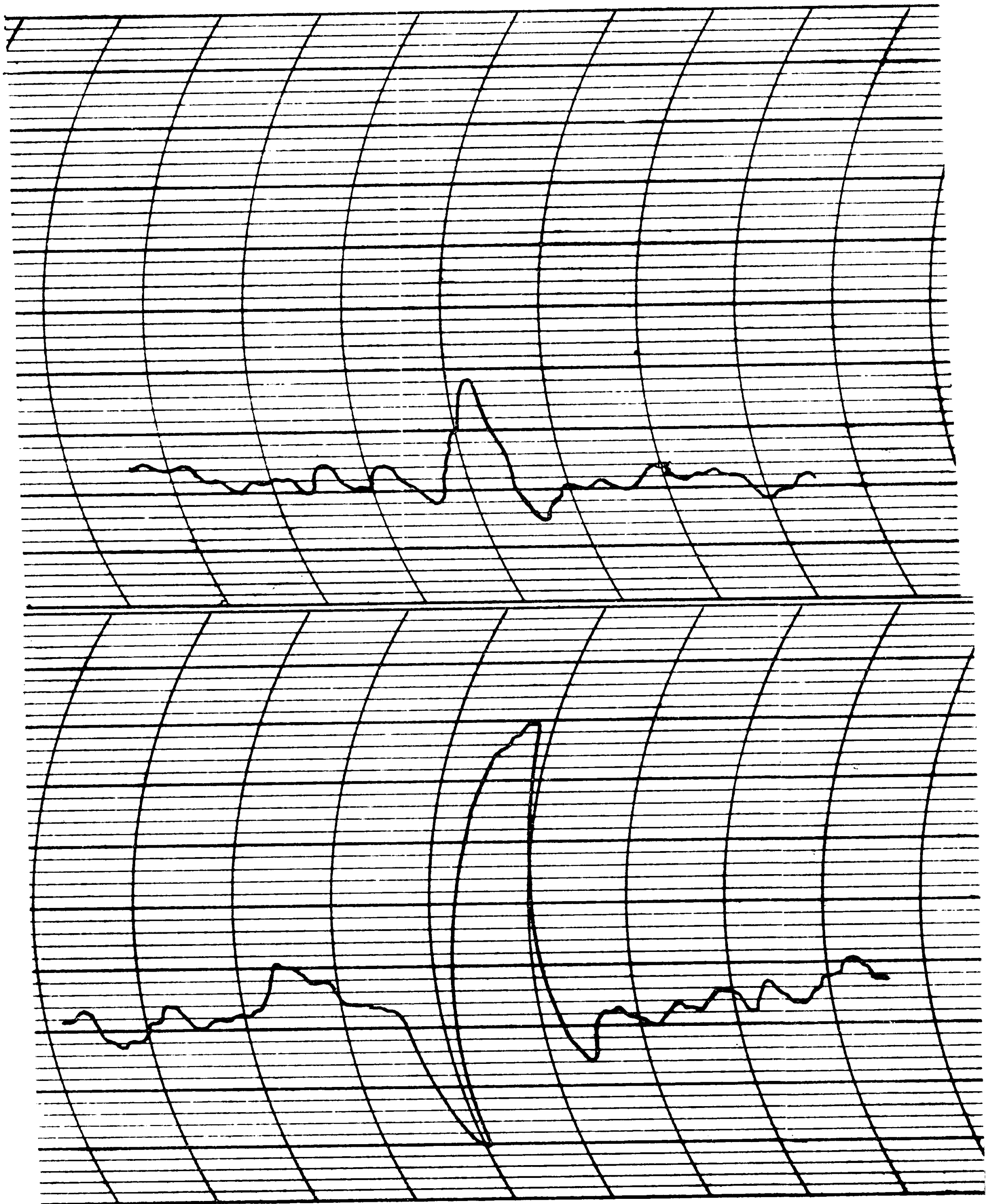

FIGURE 9. Recorder tracings of the $J = 0 \rightarrow 1$, $K = 1$ transition of oxygen occurring at 118,745.5 Mc. The upper recording shows the line at room temperature and the lower at dry ice temperature. (From Anderson, Johnson, and Gordy. Phys. Rev. **83:** 1061. 1951.).

the same type might be used at least to 100 KMc. We have passed energy at about 90 KMc. through the above-mentioned cell and through a paralled-plate cell of approximately the same length. The losses were found to be comparable and were estimated at 7 to 8 db. Because of the low energy available in this region, such losses are severe. At present, we are constructing an experimental wave guide Stark cell approximately two feet in length, with the inner conductor held by dielectric supports placed at intervals.

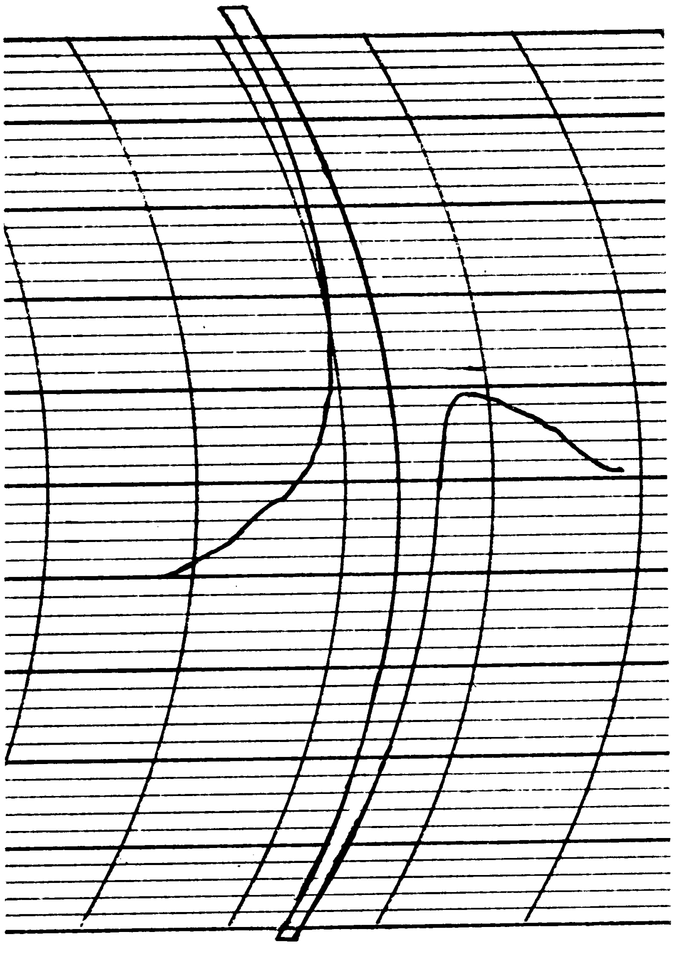

FIGURE 10. ICN line at 129 KMc. Repeller modulation at 4 Kc. (From Gilliam, Johnson, and Gordy, Phys. Rev. **78:** 140. 1950.).

For measuring the fine structure of the oxygen spectrum in the region 50 to 65 KMc., a Zeeman-modulation spectrograph with a phase-lock-in detector was used. Recently, with this method, the oxygen line at 118 KMc. was detected. At room temperature, this line is of the order of 5×10^{-6} cm^{-1} in strength. FIGURE 9 shows a recorder tracing of it at room temperature and at the temperature of dry ice. This result demonstrates that good sensitivity can be obtained at 2.5 mm. wave length.*

FIGURE 10 illustrates the use of a lock-in-amplifier with source modulation at 4 Kc. For the small modulations employed, the trace represents the first derivative of the line contour. This type modulation, like Zeeman-modula-

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* A tracing has now been obtained with a signal-to-noise ratio better than ten times that indicated in FIGURE 9.

tion, requires no lossy electrode inside the cell and is very promising for the region above 90 KMc. Some trouble is encountered with reflections unless the lines are sharp, compared with the reflections, and the modulation amplitude is accordingly small.

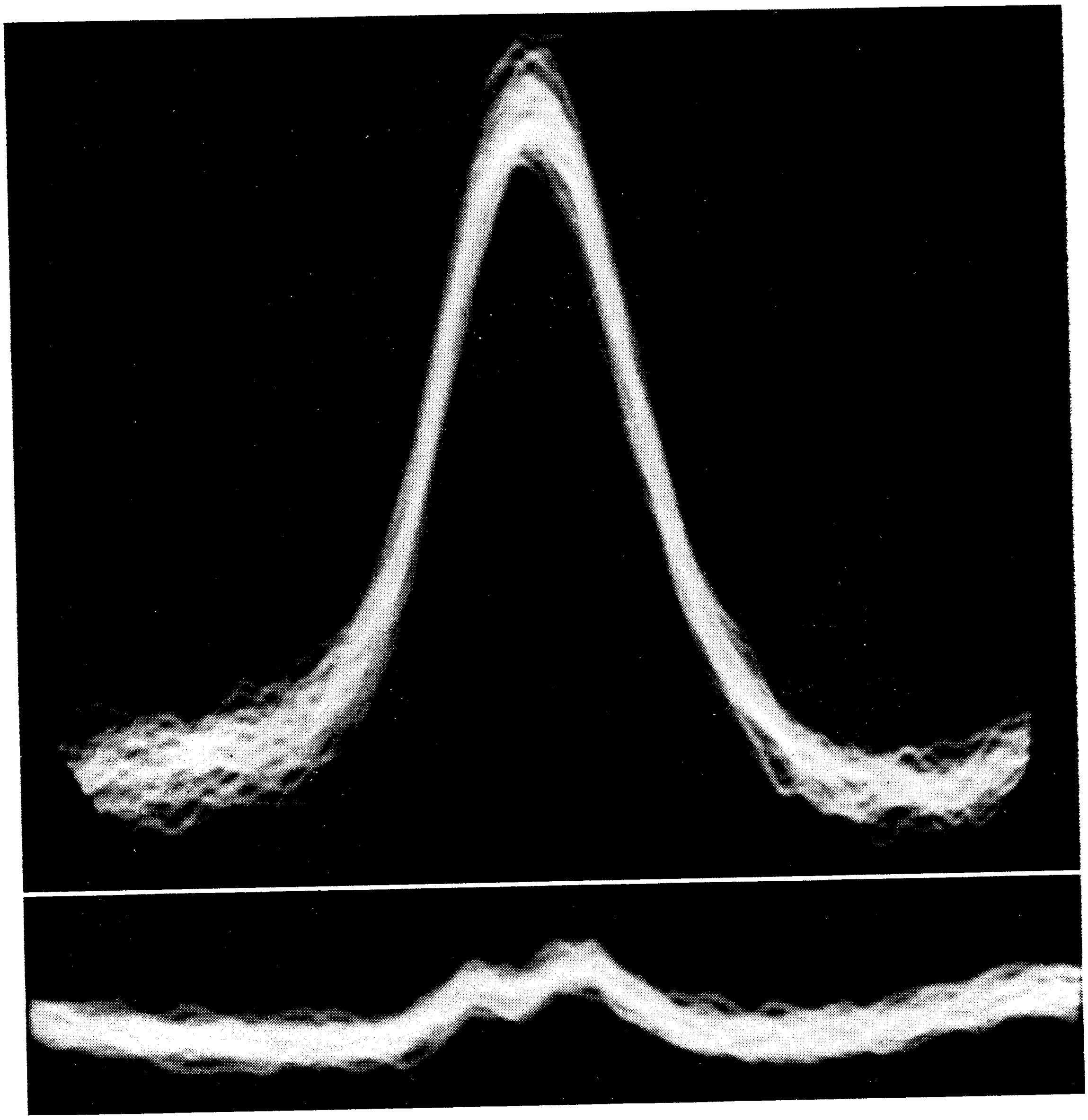

FIGURE 11. Lines obtained with simple video type detection. Upper curve shows the unresolved $J = 19 \rightarrow 20$, $\Delta F = +1$ transitions of ICN at $\lambda = 2.32$ mm. Lower curve shows the same transition partially resolved. (From Gilliam, Johnson, and Gordy. Phys. Rev. **78:** 140. 1950.).

In the various modulation techniques, the optimum modulation frequency is much lower for the region above 60 KMc. than it is in the centimeter wave region. This is because there is no need to amplify at the high frequencies to avoid crystal noise. Less pick-up disturbance and less distortion of the spectral lines are experienced at low than at high frequency modulation. Also, a more effective lock-in-amplifier can be made at audio than at radio frequencies. If the frequency is too low, however, the flicker effect in tubes and other low

TABLE 1

SOME ABSORPTION LINE FREQUENCIES MEASURED ABOVE 70 KMC.

Measured frequency	*Transition*	*Molecule*	*Reference*
	J = 10 → 11		
70,949.66 ± 0.18	F = 17/2 → 19/2	ICN	1
70,959.14 ± 0.18	F = 21/2 → 23/2		
70,963.90 ± 0.18	F = 23/2 → 25/2		
70,961.30 ± 0.18	F = 25/2 → 27/2		
	J = 0 → 1		
72,413.25 ± 0.20	F = 1 → 1	$DC^{12}N^{14}$	2
72,414.62 ± 0.20	F = 1 → 2		
72,416.68 ± 0.20	F = 1 → 0		
	J = 8 → 9		
73,738.42 ± 0.18	F = 13/2 → 15/2 F = 15/2 → 17/2	$Br^{81}CN$	1
73,741.20 ± 0.18	F = 17/2 → 19/2 F = 19/2 → 21/2		
	J = 8 → 9		
74,159.48 ± 0.18	F = 13/2 → 15/2 F = 15/2 → 17/2	$Br^{79}CN$	1
74,162.76 ± 0.18	F = 17/2 → 19/2 F = 19/2 → 21/2		
	J = 4 → 5, K = 0		
74,986.14 ± 0.16	F = 3/2 → 5/2	CH_3I^{127}	1
74,967.66 ± 0.16	F = 5/2 → 7/2		
74,977.62 ± 0.16	F = 7/2 → 9/2		
75,004.28 ± 0.16	F = 9/2 → 11/2		
75,027.58 ± 0.16	F = 11/2 → 13/2		
75,019.28 ± 0.16	F = 13/2 → 15/2		
	J = 3 → 4, K = 0		
76,554.82 ± 0.18	F = 3/2 → 5/2 F = 5/2 → 7/2	CH_3Br^{79}	1
76,538.02 ± 0.18	F = 7/2 → 9/2 F = 9/2 → 11/2		
	J = 2 → 3, K = 0		
78,512.80 ± 0.16	F = 7/2 → 7/2	CH_3Cl^{37}	1
78,523.32 ± 0.16	F = 1/2 → 3/2 F = 3/2 → 5/2		
78,527.10 ± 0.16	F = 5/2 → 7/2 F = 7/2 → 9/2		
	J = 2 → 3, K = 0		
79,769.94 ± 0.16	F = 3/2 → 3/2	CH_3Cl^{35}	1
79,764.56 ± 0.16	F = 5/2 → 5/2		
79,736.96 ± 0.16	F = 7/2 → 7/2		
79,751.02 ± 0.16	F = 1/2 → 3/2 F = 3/2 → 5/2		
79,755.68 ± 0.16	F = 5/2 → 7/2 F = 7/2 → 9/2		
	J = 0 → 1		
86,338.12 ± 0.30	F = 1 → 1	$HC^{13}N^{14}$	2
86,339.49 ± 0.30	F = 1 → 2		
86,341.54 ± 0.30	F = 1 → 0		

TABLE 1
(CONTINUED)

Measured frequency	*Transition*	*Molecule*	*Reference*
88,630.11 ± 0.30	J = 0 → 1 F = 1 → 1	$HC^{12}N^{14}$	2
88,631.49 ± 0.30	F = 1 → 2		
88,633.56 ± 0.30	F = 1 → 0		
91,879.26 ± 0.40	J = 9 → 10, K = 9	$PO^{16}F_3$	3
91,879.58 ± 0.20	K = 8		
91,879.96 ± 0.25	K = 7		
91,880.34 ± 0.30	K = 6		
91,880.50 ± 0.40	K = 5		
91,880.95 ± 0.20	K = 3		
91,881.24 ± 0.20	K = 0		
95,319.12 ± 0.27	J = 4 → 5, K = 0 F = 5/2 → 7/2 F = 7/2 → 9/2	CH_3Br^{81}	1
95,310.78 ± 0.27	F = 9/2 → 11/2 F = 11/2 → 13/2		
95,683.62 ± 0.27	J = 4 → 5, K = 0 F = 5/2 → 7/2 F = 7/2 → 9/2	CH_3Br^{79}	1
95,673.51 ± 0.27	F = 9/2 → 11/2 F = 11/2 → 13/2		
97,301.31 ± 0.20	J = 7 → 8	$O^{16}C^{12}S^{34}$	3
100,491.76 ± 0.25	J = 3 → 4	$N_2^{14}O^{16}$	3
101,066.06 ± 0.20	J = 10 → 11, K = 9	$PO^{16}F_3$	3
101,066.52 ± 0.20	K = 8		
101,066.91 ± 0.20	K = 7		
101,067.33 ± 0.20	K = 6		
101,067.62 ± 0.40	K = 5		
101,068.04 ± 0.20	K = 3		
101,068.35 ± 0.20	K = 0		
102,140.85 ± 0.20	J = 1 → 2, K = 1	$C^{12}H_3F$	3
102,142.62 ± 0.20	K = 0		
106,803.62 ± 0.20	J = 4 → 5, K = 3	$N^{14}F_3$	3
106,804.54 ± 0.50	K = 2		
106,805.93 ± 0.20	K = 0		
110,201.1 ± 0.4	J = 0 → 1	$C^{13}O^{16}$	4
115,270.56 ± 0.25	J = 0 → 1	$C^{12}O^{16}$	4
118,745.5 ± 0.3	J = 0 → 1, K = 1	O_2	5
119,441.32 ± 0.45	J = 12 → 13	$PO^{16}F_3$	3
119,555.62 ± 0.20	J = 6 → 7, K = 6	$C^{12}H_3C^{12}C^{12}H$	3
119,580.50 ± 0.20	K = 5		
119,601.06 ± 0.20	K = 4		
119,617.00 ± 0.20	K = 3		
119,628.50 ± 0.50	K = 2		
119,635.95 ± 0.20	K = 1		
119,637.90 ± 0.30	K = 0		

TABLE 1

(CONTINUED)

Measured frequency	*Transition*	*Molecule*	*Reference*
121,624.79 ± 0.25	J = 9 → 10	$O^{16}C^{12}S^{34}$	3
122,219.00 ± 0.30	J = 22 → 23, K = 15	$PS^{32}F_3$	3
122,225.50 ± 0.30	K = 12		
122,231.30 ± 0.30	K = 9		
122,235.80 ± 0.30	K = 5 or 6		
122,237.90 ± 0.30	K = 0		
122,690.02 ± 0.30	J = 2 → 3, K = 2	$C^{12}D_3F$	3
122,694.20 ± 0.30	K = 1		
122,695.50 ± 0.30	K = 0		
125,110.64 ± 0.30	J = 7 → 8, K = 6	PF_3	3
125,108.60 ± 0.20	K = 5		
125,106.85 ± 0.25	K = 4		
125,105.60 ± 0.20	K = 3		
125,103.89 ± 0.20	K = 0		
125,613.68 ± 0.30	J = 4 → 5	$N_2^{14}O^{16}$	3
128,626.60 ± 0.20	J = 13 → 14	$PO^{16}F_3$	3

1. SIMMONS, J. W. & W. E. ANDERSON. 1950. Phys. Rev. **80:** 338. *Errata.* Phys. Rev. **86:** 1055 (1952).
2. SIMMONS, J. W., W. E. ANDERSON & W. GORDY. 1950. Phys. Rev. **77:** 77.
3. JOHNSON, C. M., R. TRAMBARULO & W. GORDY. Phys. Rev. (In press).
4. GILLIAM, O. R., C. M. JOHNSON & W. GORDY. 1950. Phys. Rev. **78:** 140.
5. ANDERSON, R. S., C. M. JOHNSON & W. GORDY. 1950. Phys. Rev. **83:** 1061.

frequency disturbances become objectionable. We have found 4 Kc. to be a very satisfactory modulation frequency for spectrographs operating above 60 KMc., but the modulation frequency is not critical. Two kilocylces or 6 Kc. will, no doubt, be just as effective.

FIGURE 11 illustrates the simple video-type detection with a frequency sweep spectrometer employing C.R.O. display. The sensitivity of this method, although good for these high frequencies, does not compare with that obtainable with the lock-in-detector.

Frequency Measurements

In TABLE 1 are listed some spectral lines above 70 KMc. These were measured with frequency markers obtained by multiplying a 5 Mc. signal, monitored by comparison with station WWV, to the microwave region. The highest frequency here is 24,000 times the 5 Mc. standard.

In measuring the breadths of the O_2 lines, strong, closely-spaced markers were needed. To obtain these from the usual frequency standard would have required the use of appreciable local oscillator power from the klystron used to drive the source multiplier crystal. To avoid this drain on the driver power, an X-band oscillator was stabilized with the Pound method at a frequency which

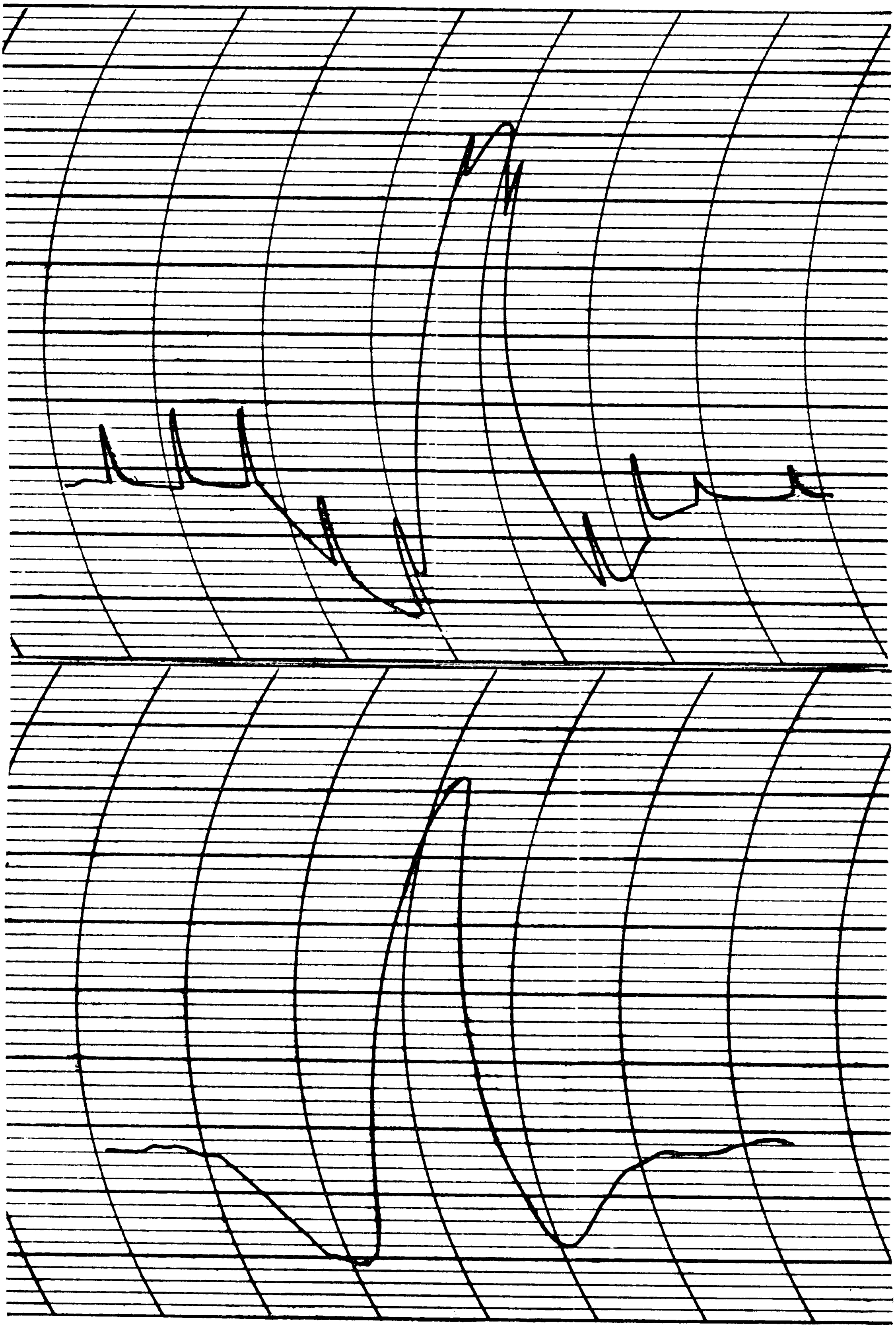

FIGURE 12. One of the 5 mm. oxygen lines with and without frequency markers. (From R. S. Anderson's Ph.D. thesis, Duke University. 1951.).

could be tripled with a crystal multiplier to give a strong marker in the mode covered by the driver klystron. The crystal was then modulated so that side bands of this frequency, spaced 5.70 Mc., were produced. FIGURE 12 illustrates the use of this marker system. Such a system can be used to measure absolute as well as relative frequencies if the 3 cm. klystron frequency is properly monitored by comparison with markers multiplied from WWV frequencies.