accurately by Sternheimer.[6] From his paper one finds for our case -0.187 Mev for this correction, yielding 0.968 Mev for the most probable energy loss, Δ_p. Finally, a small correction for multiple scattering should be applied. This can be done by replacing the target thickness by an effective thickness[7] which in this case increases Δ_p by 0.9 percent or 0.009 Mev. Thus, the final theoretical value in Cu is

$$\Delta_p = 0.977 \text{ Mev.}$$

The theoretical straggling distribution, $f(\Delta)$, is shown in Fig. 1 together with the uncorrected Landau curve $f_L(\Delta)$ (both normalized to unity). For the purpose of comparing the shapes of these two distributions, $f_L(\Delta)$ is also plotted in a reduced vertical scale and a shifted energy scale so that its maximum coincides with the maximum of $f(\Delta)$. The experimental points with errors of ± 0.015 Mev in energy and ± 5 percent in counting rate are also shown.[8] Both the shape and the most probable energy loss are seen to be in very satisfactory agreement.

If we use for Au the polarization correction of Sternheimer[6] (-0.134 Mev) instead of the approximate Fermi value (-0.055 Mev), we find $\Delta_p = 0.966$ Mev compared with an experimental value of 0.902 Mev. The reduction of the discrepancy from 0.143 Mev to 0.064 Mev is appreciable but not sufficient. However, the good agreement for all the other elements including Cu suggests that further experiments and a careful check of the calculations will yield agreement also for Au.

We are grateful to Dr. Yang for letting us see the unpublished calculations on Au by him and Dr. Kennedy and for two profitable discussions.

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[6] R. M. Sternheimer, Phys. Rev. 88, 851 (1952), and 91, 256 (1953).

[7] C. N. Yang, Phys. Rev. 84, 599 (1951).

[8] We are grateful to Dr. Hanson for communicating these results to us.

PHYSICAL REVIEW VOLUME 93, NUMBER 3 FEBRUARY 1, 1954

One-to-Two Millimeter Wave Spectroscopy. IV. Experimental Methods and Results for OCS, CH_3F, and H_2O†

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(Received September 17, 1953)

Design details are given of the harmonic generator and detector which made possible precision spectroscopy in the one-to-two mm wave region. The signal-to-noise ratio obtained on OCS rotational lines is 7 to 1 at 1.0-mm wavelength; 30 to 1 at 1.1 mm; and better than 100 to 1 at 1.4 mm and above. A useful tuning and measuring technique is made possible by the ability of the new system to detect several klystron harmonics at once and, hence, spectral lines in several different regions at the same time. The applications of the methods in the measurement of centrifugal distortion of molecules is illustrated with OCS, for which $D_J = 1.310 \pm 0.010$ kc/sec is obtained, and with CH_3F, for which $D_J = 57.8 \pm 1.0$ kc/sec and $D_{JK} = 445 \pm 4$ kc/sec are obtained. A new water-vapor line, the $2_{2,0} \rightarrow 3_{1,3}$ rotational line, has been measured at 183 311.30±0.30 Mc/sec.

INTRODUCTION

THE present paper is the fourth in a series reporting measurements of spectral lines in the one-to-two mm wave region. The experimental methods which made possible high-resolution spectroscopy in this essentially uncharted region of the electromagnetic spectrum will be described here in some detail. These methods were described earlier by one of us (W.G.) at the North Carolina Meeting of the American Physical Society (March, 1953) and briefly in the first paper of this series.[1]

EXPERIMENTAL METHODS

Harmonic Generator and Detector

The instrument and techniques developed earlier in this laboratory[2] extended high-resolution spectroscopy down to approximately 2 mm. Like the earlier methods, the present ones employ crystal harmonic generators driven by klystrons as the source of energy and crystal rectifiers for detection. The improvement in performance results principally from the changes in details of design of these components. The limit of applicability of the earlier harmonic generators and detectors which employed commercial, coaxially mounted crystals was found to be near 2-mm wavelength. Some improvement in the multiplier design

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† This research was supported by the United States Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command. It is part of a thesis submitted by W. C. King in partial fulfillment of the requirements for the Ph.D. degree at Duke University.

* Present address: Radiation Laboratory, The Johns Hopkins University, Baltimore, Maryland.

[1] W. C. King and W. Gordy, Phys. Rev. 90, 319 (1953).

[2] Smith, Gordy, Simmons, and Smith, Phys. Rev. 75, 260 (1949); Gilliam, Johnson, and Gordy, Phys. Rev. 78, 140 (1950).

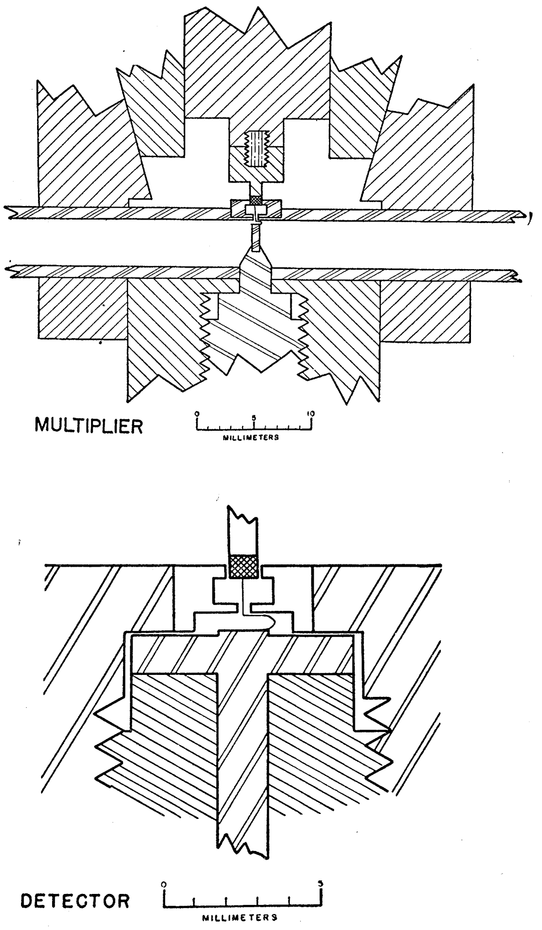

FIG. 1. Cross-section details of multiplier and detector (see also Fig. 2).

was made by Johnson,[3] who cut windows in the coaxial crystal cartridge of the harmonic generator so that the harmonic energy could be radiated directly down the mm waveguide. He also improved the mm wave detector by removing the crystal from its coaxial cartridge and mounting it in one face of the waveguide. With these improvements he was able to detect energy from klystron harmonics at wavelengths as short as 1.8 mm but measured no spectral lines below 2-mm wavelength. Simmons[4] reported making an improvement in the crystal multiplier by similarly mounting the crystal directly in the smaller waveguide. The Columbia group[5] were able by similar methods to measure spectral frequencies as high as 88 kMc/sec (3.4-mm wavelength).

While some improvement in performance in the previously worked two-to-three mm region was apparently obtained by use of waveguide mounts of silicon crystals, efforts to extend their range to shorter wavelengths were unsuccessful. It occurred to us that one cause of this failure might be the large size of the crystal and pick-up probe which were being employed. Consequently, we removed a 1N26 silicon crystal from its mount, fractured it into a number of pieces, and selected and repolished a piece which was small as compared with the wavelength which we hoped to detect. We constructed a small pick-up probe by simply extending a 2-mil tungsten cat-whisker directly across the smaller guide. It was then possible to mount these small elements into the mm waveguide through holes which were small as compared with the size of the guide. Thus, no drastic cutting of the guide was necessary. With the first multiplier and detector units made in this way, spectral lines were immediately detected near one mm wavelength.

We now cut and shape the crystal chips with a small diamond wheel and if necessary polish the face of the chip to flatness with optical rouge. The back side of the silicon slab is sputtered or plated with nickel to make it easier to solder it to the conducting post.[6]

Cross-section details of the detector and multiplier are given in Figs. 1 and 2. Photographs of the components are shown in Fig. 3. The loop or bend necessary to give flexibility to the cat-whisker is placed just outside the smaller guide so that it also gives some choking action to decrease the loss of harmonic energy. However, in line with previous experience gained in this laboratory, we have avoided the use of ordinary chokes in order to make the system broad banded.

In both the multiplier and detector a differential screw mechanism is used so that a critical adjustment of the pressure of the whisker upon the face of the crystal can be made (see Figs. 1–3). The effective pitch of the differential screw is 364 turns per in. The cone into which the screw mechanism fits must be accurately machined and lapped so that the crystal will pass through the small hole without striking the wall of the guide. To avoid breaking the crystal, one will find it a good practice to adjust the screw so that the crystal will be outside the wall of the guide before he inserts the assembly into the cone. He then advances the crystal through the hole until it makes contact with the whisker. For the multiplier, the instant of contact can be judged by the sudden change in the output power of the klystron caused by the change in impedance resulting from the contact. Usually the first contact is the best, although an improvement can sometimes be made by a slight increase in the pressure or by a shift to a new spot on the crystal. In both the multiplier and detector, provision is made for rotation of the crystal mount so

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[3] Johnson, Slager, and King, Rev. Sci. Instr. (to be published). Also given by C. M. Johnson at the third conference on Ultra-High Frequencies, held in Washington, D. C., February 1953 (unpublished).

[4] Reported orally by J. W. Simmons at the conference on Microwave Spectroscopy held by the New York Academy of Sciences (November 9–10, 1951).

[5] Nethercot, Klein, and Townes, Phys. Rev. **86**, 798 (1952).

[6] We are indebted to R. B. Belser, of the Georgia Institute of Technology, for suggesting this soldering aid.

that different points of contact can be made. Before the crystal is rotated, it should be screwed back so that it will not strike the whisker while the rotation is being made.

For the detector, one can usually judge when contact is made by the change in the noise output of the amplifier. However, evidence of detected energy is a much more reliable indication of contact. Hence it is desirable whenever possible to know that a detectable amount of harmonic energy is being generated by the multiplier. If the contact of the multiplier crystal is adjusted as directed, one can usually obtain detectable harmonic power with only a few trial settings of the waveguide tuning plungers. Nevertheless, it is good practice when one is making readjustments or changes in the detector to make sure that the harmonic generator is left in good adjustment. Likewise, it is advisable when one is readjusting the multiplier to leave the detector undisturbed.

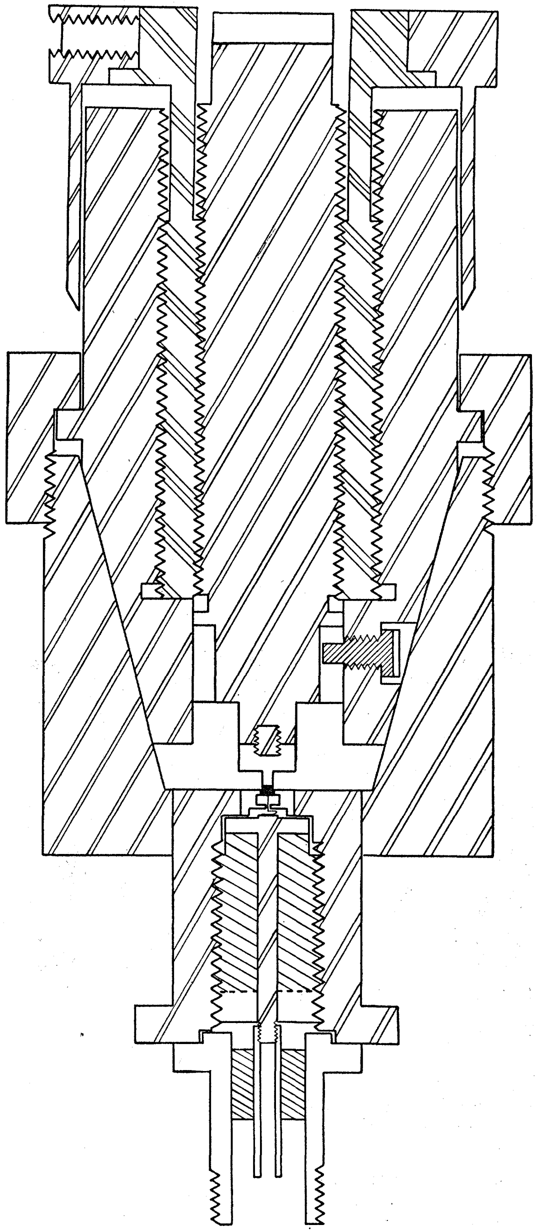

FIG. 2. Cross-section details of detector showing differential screw mechanism and the output connector. An identical differential screw arrangement is used for the multiplier unit.

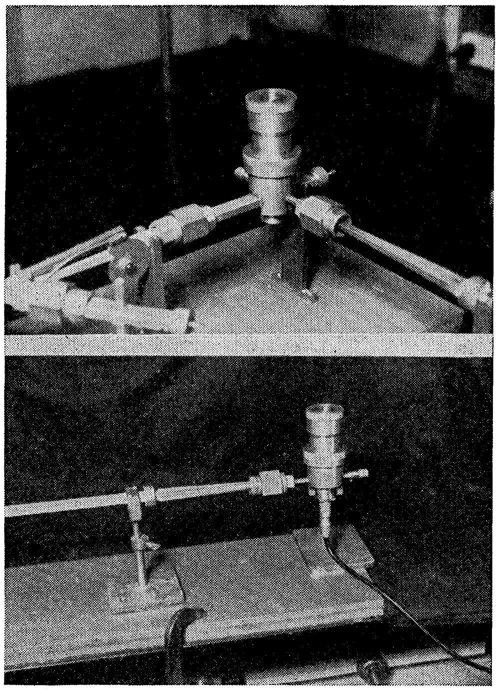

FIG. 3. Photograph of multiplier unit (upper figure) showing connector to klystron (left) and to absorption cell (right). Lower figure shows detector unit with electroformed transition section to K-band absorption cell.

The tungsten cat-whisker is pointed by electrolytic etching.[7] The end to be pointed is allowed barely to make contact with the surface film of a 10 normal solution of KOH. (The concentration is not critical, and other electrolytic agents can be used). An ac current is then passed through the whisker and solution until action at the end of the whisker ceases, usually in about one second. The amount of the current is not particularly critical. We use a 6-v 60-cy ac source. After the pointing, the solution is washed off, and the point is examined under a microscope. Often it is necessary to repeat the process in order to obtain a satisfactory point. A resharpening of the whisker is necessary after a few readjustments of the point of contact. Sometimes the point of the whisker is blunted by excess pressure, and sometimes it is burned off in the multiplier unit by excess power. If for unknown reasons the performance of the units drops, it is advisable for one to examine the whisker points under the microscope.

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

Some evidence has been obtained which indicates that high humidity adversely effects the operation of the multiplier and detector in the shorter mm range. This is believed to result from a water film which collects on the crystal surface. We consequently use a heating coil to keep the multiplier and detector units slightly warmer than the room temperature.

Electronic Components

The electronic amplifiers and display systems are the same as those used for the lower-frequency mm wave region.[2] The most convenient and rapid of these is the simple video system which employs a modified type *P* amplifier having a band width of about 6000 cps with a low frequency cutoff of about 100 cps. The sweep rate is adjusted so that the mode contour and broad signals from reflections are filtered, whereas the sharp absorption line signal is largely passed. With this broad-banded amplifier, and absorption line has been seen and measured on the cathode-ray oscilloscope at 1.03-mm wavelength.

A more sensitive system employs low-frequency repeller modulation[8] (of the order of 4000 cps) with a phase lock-in detector and a narrow-band amplifier and automatic recording of the line. The system used for the present work is essentially that given in a paper by Gilliam, Johnson, and Gordy[2] on techniques for the two-to-three mm region. We have found, however, that we obtain better discrimination against reflections by tuning the amplifier to twice the frequency of the repeller modulation (compare, for example, Figs. 6 and 7). To give this system best sensitivity, one must optimize the amplitude of repeller modulation for the line width expected (this is best accomplished by recording a known line), and one must, of course, make proper phase adjustment of the reference voltage which controls the lock-in detector. Another obvious but important adjustment is the tuning rate of the tube. The latter must be properly regulated for the time constants of the recorder and the bandwidth of the amplifier. For the optimum sensitivity and resolution, the klystron frequency must be stabilized by an external cavity.

Experience has shown that for the mm wave region, where harmonic generators of low power must be used as sources, better results are obtained with the repeller modulation at audio rather than at radio frequencies. Furthermore, at this time, repeller modulation is superior to Stark modulation because no Stark cells of sufficiently low loss for the shorter mm region have yet been developed. Parallel plate-type cells are under development.

A New Tuning Technique

A useful aid to tuning and measuring was evolved during the course of this work. Since the harmonics generated by the crystal are integral multiples of the klystron frequency whereas the rotational lines of linear or symmetric-top molecules are almost, but because of centrifugal stretching not exactly, integral multiples of $2B_0$, it is possible with the spectrometer described here to observe more than one molecular rotational line at a time (see Figs. 4 and 5). This multiple display of rotational lines has useful applications. Already it has been used as an aid to tuning, for accurate evaluation of centrifugal stretching, and for measurement of line breadths[9] as a function of rotational quantum number. Perhaps the most important of these uses is the aid to tuning. This trick circumvents the need for stringent waveguide filtering in the shorter mm wave region and is one factor which has led to the rapid exploitation[10] of the one-to-two

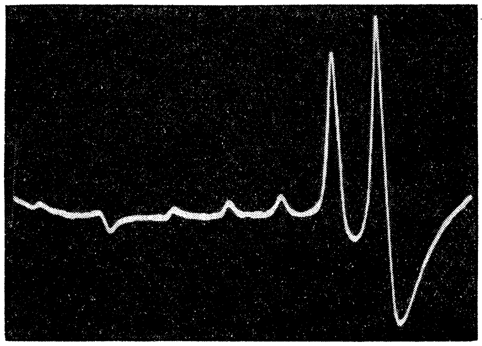

FIG. 4. The 8th, 10th, 12th, 14th, 16th, 18th, and 20th (from right to left) rotational lines of OCS obtained with the 4th to 10th klystron harmonic. Frequencies range from 97 kMc/sec to 243 kMc/sec (3.08 mm to 1.23 mm wavelength).

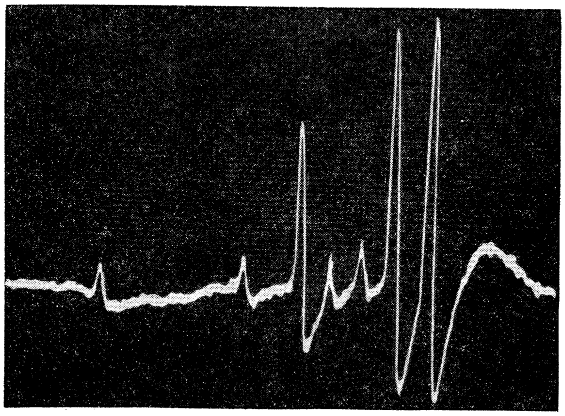

FIG. 5. Cathode-ray presentations of the $J=2\rightarrow3$ transition (the three tall lines) of CH_3F at 1.96-mm wavelength and of the $J=3\rightarrow4$ transition (the four weaker lines) of CH_3F at 1.47-mm wavelength.

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[8] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), Chap. I.

[9] R. S. Anderson (to be published).

[10] In addition to the measurements made in our own laboratory, spectral measurements are now being made in the region at Columbia University [J. A. Klein and A. H. Nethercot, Phys. Rev. **91**, 1018 (1953)] and at John Hopkins University [Gallagher, Bedard, and Johnson (private communication)].

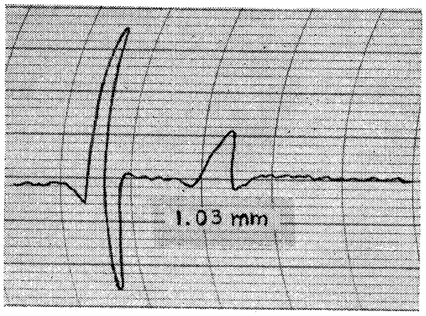

FIG. 6. Recorder tracing of the $J=21\rightarrow22$ (stronger) and $J=23\rightarrow24$ (weaker) lines of OCS occurring at 1.12 and 1.03-mm wavelength respectively. These results were obtained with the 11th and 12th harmonic energy from a K-band Raytheon klystron and with a small G-band cell of 20-cm length. The receiver is tuned to twice the klystron modulation frequency. The tracing represents approximately the second derivative of the absorption line contour.

mm region since the first description of our experiments. But the primary factors responsible for this development are the exceptionally broadbanded and effective multiplier and detector units described above.

To tune the microwave components with this method, one must choose a convenient "tuner" molecule such as OCS or OCSe, which has a rotational line in the region to be searched as well as a number of lines at lower frequencies. A klystron is then selected which gives harmonics coinciding with a group of rotational lines of the "tuner" molecule, including the one in the region of search. This allows a stepwise peaking of rotational lines of higher and higher frequency until the spectrometer is tuned in the desired region. The "tuner" molecules are then replaced by the ones to be investigated. A new line found in this way does not necessarily lie in the expected region but may correspond to an absorption of any harmonic passed by the waveguide filter. To verify the harmonic identification one can tune the klystron (or use a different one) so that the same line is observed by a different order of harmonic. This "crossfire" method was used in making certain the frequency of the H_2O line reported here. We found the line by first peaking the system on the sixteenth rotational line of OCS with the energy of the eighth harmonic of a K-band tube; we found the line again with a sixth harmonic from a J-band QK-291 klystron by first peaking the system on the tenth and fifteenth OCS lines.

Sensitivity

The signal-to-noise ratio obtained thus far on OCS rotational lines with the use of the recorder techniques is 7 to 1 at 1.0-mm wavelength, 30 to 1 at 1.1 mm, and better than 100 to 1 at 1.4 mm and above. In obtaining these signal-to-noise ratios we used a cell of 20-cm length and only $\frac{1}{3}$-cc volume. Most molecules absorb so strongly in this region that a longer cell is less effective. In the region of 2 mm and above, where it is now possible to obtain signal to noise ratios on power better than a thousand to one, a cell of K-band guide 6 m long has been used with excellent results on weak lines.

TABLE I. Observed transitions of $O^{16}C^{12}S^{32}$. $B_0=6081.494\pm0.10$ Mc/sec; $D_J=1.310\pm0.010$ kc/sec.

Oscillator harmonic	Transition	Frequency in Mc/sec Calculated	 Observed	Wavelength in mm
6	11→12	145 946.80	145 946.79±0.30	2.06
7	13→14	170 267.45	170 267.49±0.35	1.76
8	15→16	194 586.35	194 586.44±0.40	1.54
9	17→18	218 903.22	218 903.27±0.45	1.37
10	19→20	243 217.84	243 218.09±0.50	1.23
11	21→22	267 529.94	267 529.56±0.55	1.12
12	23→24	291 839.27	291 839.22±0.60	1.03

MEASUREMENT OF CENTRIFUGAL STRETCHING IN MOLECULES

Rotational lines up to the $J=23\rightarrow24$ transition at 291.8 kMc/sec (1.027 mm) have been measured for $O^{16}C^{12}S^{32}$. The twenty-fourth line, which represents the highest spectral frequency measured to date with microwave spectroscopy, could barely be seen on the scope with the wide-band audio-amplifier but with a cell length of 20 cm gave a signal about 7 times the noise level on the recorder (see Fig. 6). The rotational lines were found to fit, within the limits of error, the theoretical formula

$$\nu=2B_0(J+1)-4D_J(J+1)^3,$$

with $B_0=6081.494\pm0.010$ mc/sec and $D_J=1.310\pm0.010$ kc/sec. Because of the cubic variation of the centrifugal stretching term, it is evident that D_J can now be measured much more accurately with microwave spectroscopy than it could when only the region above 2 mm could be reached. For the $J=7\rightarrow8$ transition at 3.09 mm, the centrifugal stretching term amounts to only 2.68 Mc/sec, whereas for the 23→24 transition at 1.03 mm it amounts to 72.44 Mc/sec. Furthermore, with the new technique of displaying several rotational lines, one can observe the stretching term directly by the separation of the lines on the scope or recorder without a measurement of the absolute frequencies or a knowledge of B_0. For this reason also, the centrifugal stretching constant D_J can now be more accurately obtained than was possible before. In Table I is a comparison of the measured frequencies of OCS with those calculated with the above formula.

In a symmetric-top molecule, there are two stretching constants, D_J and D_{JK}, which are observable from microwave measurements. These have already been measured at lower frequencies for the methyl halides but are being remeasured with the new techniques. This remeasurement has been completed for methyl fluoride. The results are given in Table II. The value of D_J, 57.8±1.0 kc/sec, agrees only roughly with the previous value, 32.5 kc/sec, obtained from the first

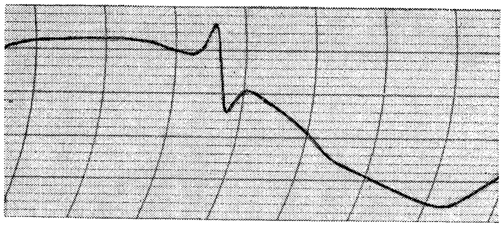

FIG. 7. Recorder tracing of the $2_{2,0}\rightarrow 3_{1,3}$ line of water vapor at 1.64-mm wavelength. The receiver is tuned to the fundamental frequency of the klystron modulation voltage (4 kc/sec). The tracing represents approximately the first derivative of the absorption line contour.

and second rotational lines only. Figure 5 is a photograph of the third and fourth transitions as displayed upon the scope.

WATER VAPOR LINE

A resonant absorption line has been found in water vapor at 183 311.30±0.30 Mc/sec. Its Stark effect has not yet been observed, but it can be identified with certainty from its position as the $2_{2,0}\rightarrow 3_{1,3}$ rotational line. Figure 7 shows a recorder tracing of the line.

Only two water vapor lines are expected[11] to fall in the entire microwave region between one mm and one m. A knowledge of the positions of these lines has practical significance for microwave propagation. Both have now been located experimentally. The $5_{2,3}\rightarrow 6_{1,6}$ transition occurring at 1.35 cm was first measured[12] during World War II after a radar band had unfortunately been developed in the same region.

The absorption coefficient and line-breadth parameter of the 1.62-mm line will be measured later in this laboratory. The observed frequency occurs only 1200 Mc/sec from that predicted by King, Hainer, and Cross.[11] Consequently, their predicted absorption coefficient of 6.838×10^{-3} cm^{-1} for the line should be approximately correct. Had the line occurred at a radically different frequency from that predicted, the predicted absorption coefficient, which varies rapidly with frequency, would also have been greatly in error.

If centrifugal distortion effects are ignored and the reasonable value of 0.96A as obtained from infrared spectroscopy is assumed for the OH distance, the $2_{2,0}\rightarrow 3_{1,3}$ frequency yields the rather large value of 105° 56′ for the bond angle. The value obtained from infrared spectroscopy[13] is 105° 3′. The larger value obtained here is almost certainly caused by the centrifugal distortion which would be expected to open up the HOH angle. In consideration of the large OH bond stretching force constant 8×10^{-5} d/cm, no significant lengthening of the bond is expected. Insufficient data are obtainable from microwave spectroscopy on H_2O alone for evaluation of its centrifugal distortion constant. Progress is being made, however, in the evaluation[14] of these constants for D_2O and HDO, which have more abundant microwave spectra.

TABLE II. Observed transition of CH_3F. $B_0=25\,536.12\pm 0.05$ Mc/sec; $D_J=57.8\pm 1.0$ kc/sec; $D_{JK}=445\pm 4$ kc/sec.

Oscillator harmonic	Transition J	K	Frequency in Mc/sec Calculated	Observed	Wavelength in mm
4	1→2	0	102 142.59	102 142.56±0.20	2.94
		1	102 140.81	102 140.86±0.20	
6	2→3	0	153 210.30	153 210.44±0.30	1.96
		1	153 207.63	153 207.65±0.30	
		2	153 199.62	153 199.58±0.30	
8	3→4	0	204 273.70	204 273.69±0.40	1.47
		1	204 270.14	204 270.09±0.40	
		2	204 259.46	204 259.48±0.40	
		3	204 241.66	204 241.71±0.40	

Mr. W. B. Francis, of the Duke University Instrument Shop, constructed the multiplier and detector, and it is a credit to his careful machine work that even the first models performed well. Mr. Frank Trippe, electronics technician, of the microwave laboratory, made all electronic components for the spectrometer. Mr. C. A. Burrus helped to obtain the experimental results.

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[11] King, Hainer, and Cross, Phys. Rev. **71**, 433 (1947).

[12] G. E. Becker and S. H. Aulter, Phys. Rev. **70**, 300 (1946).

[13] G. Herzberg, *Infrared and Raman Spectra* (D. Van. Nostrand Company, Inc., New York, 1945), p. 489.

[14] D. W. Posener and M. W. P. Strandberg, J. Chem. Phys. **21**, 1401 (1953).

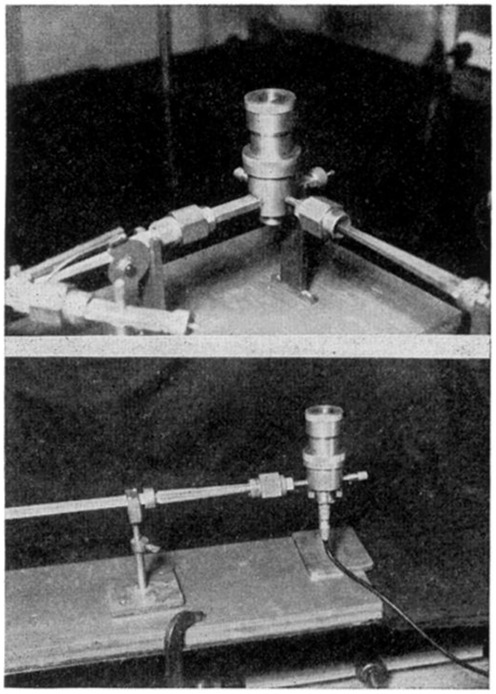
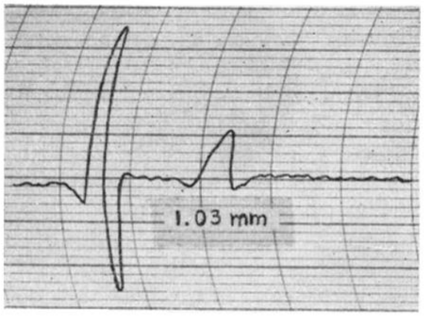


FIG. 3. Photograph of multiplier unit (upper figure) showing connector to klystron (left) and to absorption cell (right). Lower figure shows detector unit with electroformed transition section to K-band absorption cell.



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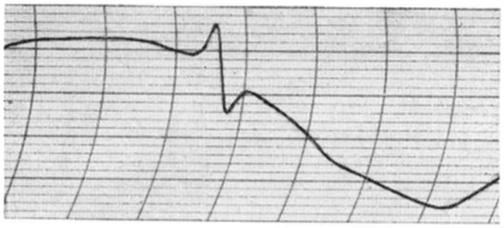

FIG. 7. Recorder tracing of the $2_{2,0} \rightarrow 3_{1,3}$ line of water vapor at 1.64-mm wavelength. The receiver is tuned to the fundamental frequency of the klystron modulation voltage (4 kc/sec). The tracing represents approximately the first derivative of the absorption line contour.