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SUMMARY

Summaries or abstracts of results obtained are given in the enclosed technical reports. Summaries of work on other projects will be given in later reports when the results are more definite or final.

MILLIMETER AND SUBMILLIMETER WAVES IN PHYSICS.*

Walter Gordy

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1. Detection of Millimeter and Submillimeter Radiation. The Spark-
Gap Era.

Neither microwaves nor millimeter waves are new. Microwaves
are the radio waves which were discovered by Hertz in 1888. His first
recorded wavelengths were in the centimeter range. He made this radia-
tion with a spark-gap generator and measured the wavelengths by detecting
nodes in standing waves set up by reflectors from the walls of the room in
which he worked. With such an arrangement as this he had to discover
microwaves, for it is difficult even to imagine a room large enough for him
to detect standing waves of kilocycle or megacycle frequencies ordinarily
used in radio communications.

Hertz was like an explorer who travels by air and lands in the middle
of an unknown world. The radio explorers who came after him tried to ex-
tend his beach head in both directions. Those who went to the longer wave-
lengths were the first to strike gold. In the gold rush that followed the

lonely explorers who went in the other direction were all but forgotten. Not only were radio and television developed on wavelengths thousand to millions of times longer than those discovered by Hertz, but also the first significant applications of radio waves in physics, the molecular beam resonance experiments, were at these non-Hertzian frequencies. For the glory of those of you who call yourselves engineers I would like humbly to point out that with few exceptions the practical applications of radio waves have preceded the fundamental applications of these waves in physics. The paramount exception is Hertz's original experiment which confirmed Maxwell's theory predicting the possibility of radio waves.

In reading the account of Hertz's discovery in the Encyclopaedia Britainica I came upon this statement which I cannot refrain from quoting to this illustrious congregation of engineers:

"On leaving school Hertz determined to adopt the profession of engineering, and in the pursuance of this decision went to study in Munich in 1877. But soon coming to the conclusion that engineering was not his vocation he abandoned it in favour of physical science."

Despite Hertz abandonment of engineering, centimeter waves were first used extensively for a practical device, radar. Ve can point to only one very significant preradar application of centimeter waves in physics, the measurement of the ammonia inversion frequency by Cleeton and Villiams in 1934.

To avoid the possibility of misleading you, let me hasten to add that the fundamental scientific applications and the practical engineering

applications of any new facility or knowledge - like theory and experiment - feed on each other and are therefore usually found together. At different times and in different areas it may be said that one or the other is progressing more rapidly, but in these times they are seldom far apart. However, the very existence of a new facility or new knowledge presupposes that some kind of species, be he engineer or physicist, has already thought or worked and most probably has spent a great deal of government money!

In the millimeter and submillimeter wave region the applications in physics seem, at last, to have come first, but despite an early start they have come first at a slow pace. In 1895, only three years after Hertz's discovery, Lebedew, [1] using methods similar to his, generated and detected waves which he estimated to be only 6 mm in length. The following year Lampa[2] reported the similar detection of wavelengths of 4 mm. Mobius[3] in 1913 was unable to get waves shorter than 7 mm and expressed doubt that Lebedew or Lampa had done so. In 1923 Nichols and Tear[4] stated: "If probable values be assigned to the λ / ℓ ratio of Lebedew and Lampa oscillators, it seems very probable that both investigators underestimated the wavelengths with which they were dealing." They state further: "A ten year old rumor concerning 2 mm fundamental waves obtained by von Baeyer apparently still lacks confirmation." Evidently physicists in those days were like present day ones in at least two ways: (1) they often overstated their claims, and (2) they sometimes published their results through the medium of rumor.

Nichols and Tear were not exactly conservative in evaluating their own contributions. In concluding their paper they state[4b]: "The present methods and results throw open for intensive study practically the last unexplored region in the whole extent of the electric wave spectrum which spans the enormous interval from the long radio waves to the shortest gamma rays of radium, a wave-length ratio of 20 million billion to one." They used a Hertzian spark-gap generator, a reflecting echelon grating to separate and measure the wavelengths, and a radiometer for detection. They state that by patient development and use of these instruments shorter and shorter electric waves were isolated and measured, from Lampa's and Mobius' limit of 7 mm down to 0.22 mm in length. Approaching from the optical side with a heat source, a dispersive instrument, and a bolometer detector, Rubens and von Baeyer[5] as early as 1911 had reached wavelengths as long as 0.314. Thus the work of Nichols and Tear overlapped this earlier optical measurements and closed the gap between the radio and optical regions. A more extensive overlapping was performed the following year, in 1924, by a Russian scientist, Glagolewa-Arkadiewa,[6] who produced and detected waves from 0.082 mm to 50 mm. As a source she employed metal filings immersed in mineral oil and energized by a spark gap.

Despite the enthusiastic claims of Nichols and Tear, these pioneering efforts did not "throw open for intensive study" the millimeter and submillimeter wave region, as you who have tried to make measurements in this region are well aware. In fact, no discrete spectral transitions were measured in this vast region during the entire spark-gap age. In the

millimeter wave region a few qualitative physical measurements were made on non-resonant, Debye-type absorption of liquids, as is illustrated by the work of Tear[7] on liquid water, alcohol, and glycerin. In the overlapping infrared region, low-resolution measurements of a few rotational transitions of simple gaseous molecules were made with infrared optical techniques, as is illustrated by the work of Czerny[8] and of Cooley and Rohrbaugh[9] on HI.

The millimeter and submillimeter wave regions remained undeveloped after these early starts primarily, I think, because the methods employed were essentially optical rather than radio. The spark-gap generator is not a stable, monochromatic source of radiation. Its output more nearly resembles that of an infrared heat source than it does that of a coherent radio oscillator. The first resonant spectral frequency measured in the microwave region, the ammonia inversion,[10] was observed not with a spark-gap generator but with split anode magnetrons. Thus microwave spectroscopy, like microwave radar, had to await the development of coherent radio methods. In a scientific as well as in an engineering sense we can say that the microwave region was not effectively 'thrown open" until cavity resonators and waveguide techniques were developed.

2. Development of Millimeter and Submillimeter Wave Spectroscopy.

At the close of World War II a unique opportunity faced spectroscopists: the vast centimeter wave region where only one discrete spectral transition had been measured[10] in all the pre-war years was accessible

to the most precise of spectral methods. Naturally. I was one of those who could not resist such an opportunity. Nevertheless, to me the proverbial pastures beyond the centimeter region seemed still greener. I knew that the spectral transitions of matter become stronger and more abundant as the frequency increases toward the optical region. Thus it seemed to me that the heart of microwave spectroscopy would eventually be in the milli-meter or submillimeter regions. Therefore from the beginning of the micro-wave laboratory at Duke University in 1946 I concentrated a large portion of our efforts on the extension of the high-resolution microwave spectral methods to higher and higher frequencies. A start in this direction had already been made during the war years by Beringer,[11] who with a crystal harmonic generator obtained sufficient second-harmonic energy from a centimeter wave klystron to measure the 5-mm wave absorption of oxygen, but not to resolve its fine structure. We were fortunate enough to obtain from Raytheon a few of the first klystrons developed for the region of 6 mm to 1 cm. With this encouragement we quickly developed other components needed for microwave spectroscopy in the 6-to 10-mm range, and in 1947 we made several high-resolution spectral measurements in this region.[12]

At that time no primary oscillators were available to us for the region beyond 5 mm. Although a few magnetrons had been made to operate at frequencies above 60 kMc/sec, they were not generally available, nor were they suitable for high resolution spectroscopy. Furthermore, it seemed that extension to much higher frequencies of conventional micro-wave oscillators would be difficult, as indeed it has proved to be. (See

other papers of this Symposium.) For this reason we looked carefully

at the crystal harmonic generator with which Beringer had measured the

5-mm oxygen absorption. It was a highly tuned, frequency-sensitive

device. Beringer had not attempted to develop a frequency-sweep spectrom-

eter but chose instead to measure the oxygen attenuation point by point so

that the multiplier could be tuned for maximum output at a fixed frequency.

Our first problem was to make the harmonic multiplier sufficiently broad

banded for sweep spectroscopy. Our second problem was to increase its

power output; our third, to increase its range of operation to higher

harmonics.

Beringer employed a crystal premounted in a coaxial mount (1N26)

as the non-linear multiplier unit. This coaxial crystal was connected by a

short coaxial section mounted on the 5-mm wave output guide. The center

conductor of this coaxial line extended across the millimeter waveguide

and formed the center conductor of another coaxial section, a few centi-

meters in length, which connected the millimeter waveguide to the input

waveguide. The center conductor was made to project into the centimeter

guide so as to pick up the fundamental energy to be transmitted to the

crystal. There were various tuners to maximize the input and output

energy, also chokes to prevent leakage of the millimeter wave energy from

the millimeter guide back through the coaxial line into the centimeter guide.

My first graduate students to work on millimeter wave spectroscopy

above 60 kMc/sec were Alex. G. Smith and J. W. Simmons. As a first

attempt to make a crystal harmonic generator we decided to retain the basic

features of the Beringer multiplier with its premounted coaxial crystal

and to try to make it more broad banded by removing some of the chokes

and tuners and by shortening all line dimensions as much as possible.

The coaxial line between the two waveguides was reduced in length to the

thickness of a milled-down waveguide wall, and its choke units were re-

moved. To our satisfaction, this stripped-down version not only was more

broad banded but gave more second-harmonic output, was much easier to

operate than the duplicate of the Beringer multiplier we had made earlier,

and, best of all, gave usable third and fourth harmonic energy. The first

spectral measurements in the 3- to 5-mm range[13] were made with it in

1948.   After some later improvements and with carefully selected 1N26

crystals the first measurements of spectral lines in the 2- to 3-mm

range[14] were made during 1949. The improved operation in the 5-mm

region allowed us to resolve and measure the individual fine-structure

components of the oxygen absorption,[15] where Beringer had earlier

measured the unresolved absorption. The extension of the harmonic range

allowed us to reach and measure the oxygen resonance in the 2.5-mm

range,[16] which had been theoretically predicted but had not been observed

before. For detection in these earlier experiments we also employed 1N26

crystals for which suitable mounts were designed for different waveguide

sizes. I shall not give further details of these units, which are adequately

described in the original publications[13] and which have now been replaced

by more effective ones.

During the years 1949, 1950, and 1951 our Duke group made numerous high-precision measurements of spectral lines of gaseous molecules in the region from 2 to 5 mm. A review of the methods and results together with a listing of measured spectral lines above 60 kMc/sec in frequency for 29 molecules was given at the New York Academy Conference on Microwave Spectroscopy, November 1952, the proceedings of which were published.[17]

Late in 1952, after much effort to extend the range of our harmonic chain below 2 mm, we realized that we must make some basic changes to reach higher frequencies. At this stage I had a new graduate student, W. C. King. The earlier ones, O. R. Gilliam and C. M. Johnson, who had worked effectively in the 2- to 3-mm region had just been graduated and had gone, C. M. Johnson to initiate a very successful program in millimeter wave spectroscopy in the Johns Hopkins Radiation Laboratory. King and I decided to take the multiplier and detector crystals out of their prefabricated mount and put them directly in one edge of the waveguide. During World War II detecting crystals had been effectively mounted within K-band waveguide in the M.I.T. Radiation Laboratory. We reduced the size of the commercial crystals considerably so that we could mount them in the small 2-mm waveguide without cutting a large hole in the guide or creating an abnormally large obstruction. We decided to make the position of the crystal adjustable so that contact and pressure of the whisker could be used as a tuning aid to optimize the over-all performance. A differential screw mechanism was provided for sensitive adjustment of the pressure.

We also constructed the device so that the whisker could be removed easily and resharpened at intervals. We did the resharpening electrochemically and each time examined the sharpened point under a microscope. Cross sections of the multiplier and detector are shown in Fig. 1. A photograph of the fabricated units attached to an absorption cell are shown in Fig. 2.

The results of these modifications were gratifying beyond our expectations. We were immediately able to detect and measure spectral lines down to 1 mm (300,000 Mc/sec). Furthermore, the devices were so broadbanded that several harmonics could be displayed in one sweep of the klystrons. In April 1953 the first results were published,[18] and during the same month, when the spring meeting of the American Physical Society was held at Duke, these units were displayed, and the techniques were described and demonstrated to other microwave spectroscopists. During the following months in addition to other measurements at Duke[19] one spectral measurements in the 1- to 2- mm region was made in the Columbia Radiation Laboratory,[20] and one in the Johns Hopkins Radiation Laboratory.[21] Near the end of the year the same multiplier and detector, with some improvements in techniques, were used in our laboratory to extend microwave spectral measurements into the submillimeter wave region to 0.77 mm and thus to open to the spectroscopist the last closed gap in the spectrum.[22] This accomplishment was achieved with my former student, C. A. Burrus, Jr., who has initiated a very successful program in millimeter wave spectroscopy at the Bell Telephone Laboratories and who has recently made both Stark[23] and Zeeman[24] measurements down to

Figs. 1 and 2. Omitted.

wavelengths of about one millimeter.

In 1956 we received from the Bell Telephone Laboratories some improved silicon multiplier crystals, developed and kindly given us by R. S. Ohl. Fortunately these crystals fitted into our multiplier units already made. With the improved multiplier crystals and a new 9-mm wavelength klystron produced by E. M. I. Electronics, Ltd. and with another good graduate student, Monroe Cowan, we were able with ease to extend the boundary of millimeter wave spectroscopy[25] from 0.77 to 0.58 mm in 1956, and, with some difficulty, down to 0.50 mm in 1953. A brief historical picture of our progress in extending the range of microwave spectro: copy by a factor of 10, from a half-centimeter to a half-millimeter, is given in Fig. 3.

We were also kindly supplied some new silicon detector crystals by Microwave Associates. These crystals improved the submillimeter wave spectroscopy somewhat but not so much as did the multiplier crystals from Ohl. The method of preparation of the Ohl crystals and information on their operation and performance are, I understand, to be given in a forthcoming paper from the Bell Laboratories.[26] Although other laboratories were supplied the Ohl crystals, some before and some after our laboratory received them, so far as I know, ours is the only laboratory to report submillimeter wave measurements with them. However, a recent paper[26] refers to some submillimeter wave measurements down to 0.9 mm in progress by C. A. Burrus.

Fig. 3a.   Chronological order of observation of spectral lines of
           increasing frequency in the 1- to 5-mm wave region.
           Upper photograph from Ref. 18, middle from Ref. 14,
           lower from Ref. 22.

Fig. 3b.   Chronological order of observation of submillimeter lines
           of increasing frequency in the 0.50 to 1.0 mm region.
           Upper curve from Ref. 22, middle from Ref. 25, bottom
           curve is unpublished results by Cowan and Gordy.

Fig. 3c.   Cathode ray display of spectral lines demonstrating
           resolution and sensitivity now obtainable in the submilli-
           meter wave region. The two components to the right
           of the DCl triplet are spaced 10.61 Mc apart. The two
           components shown for HI are spaced 163.28 Mc apart.
           The width of the OCS line is of the order of a megacycle.
           From M. Cowan and W. Gordy (Ref. 25 and Bull. Phys.
   Soc. 2, 212 (1957)).

HCN
3.38 mm

1948

ICN
2.32 mm

1949

OCS
1.03 mm

1953
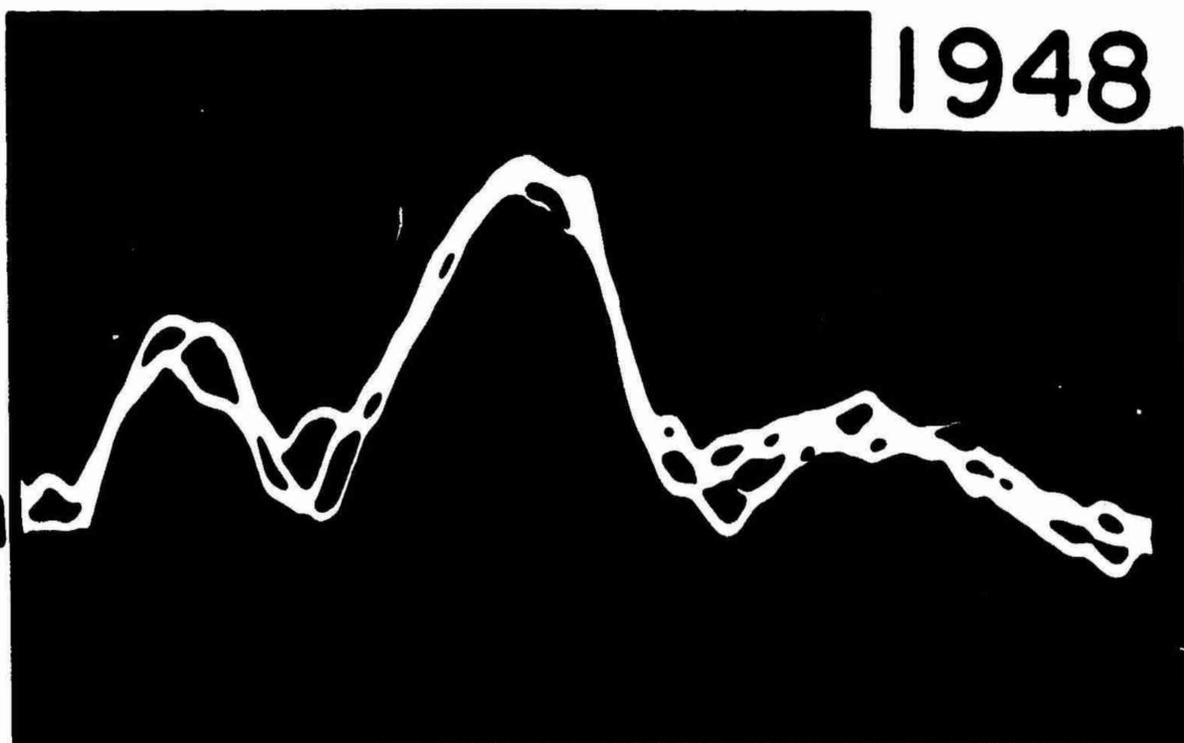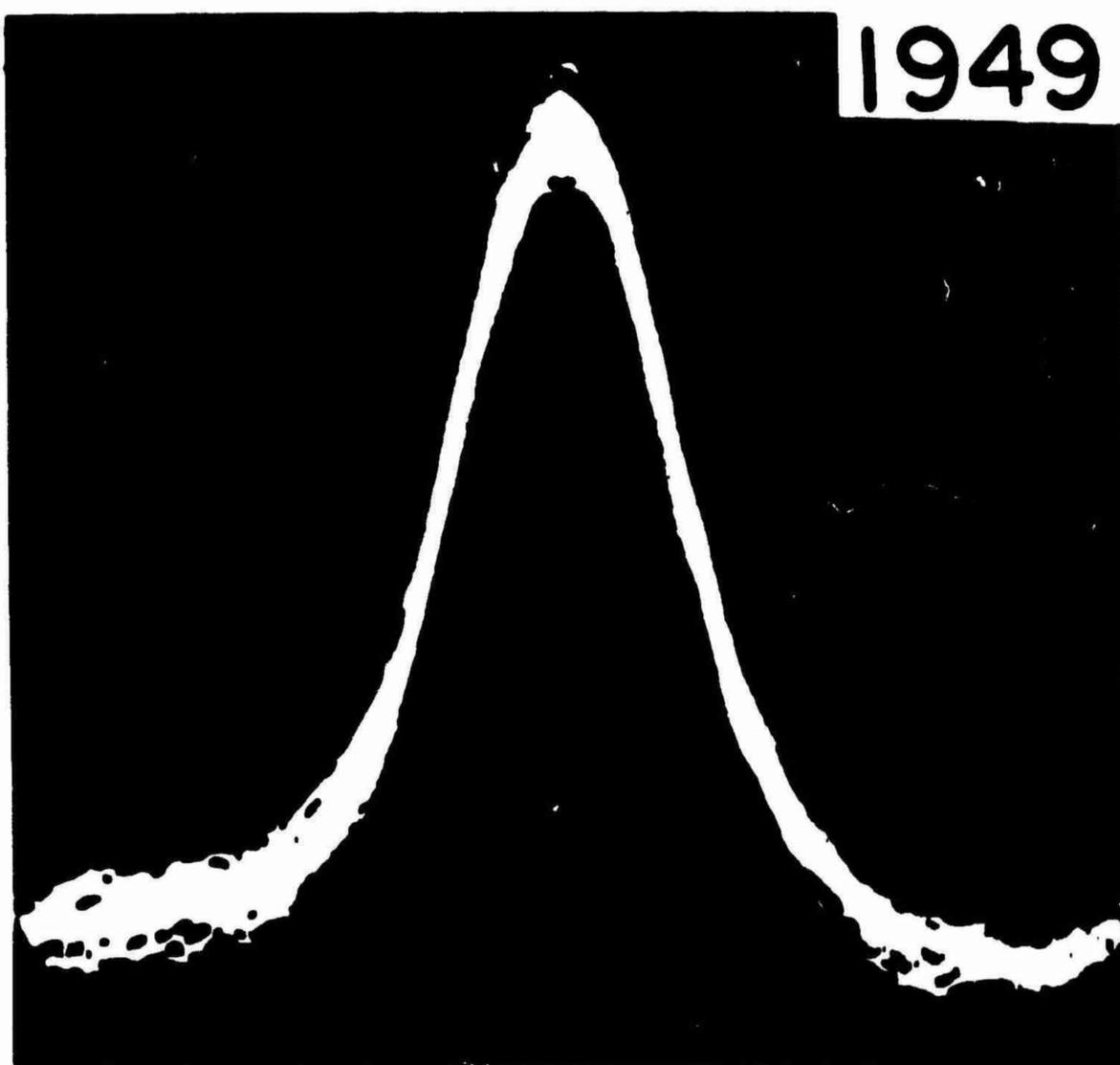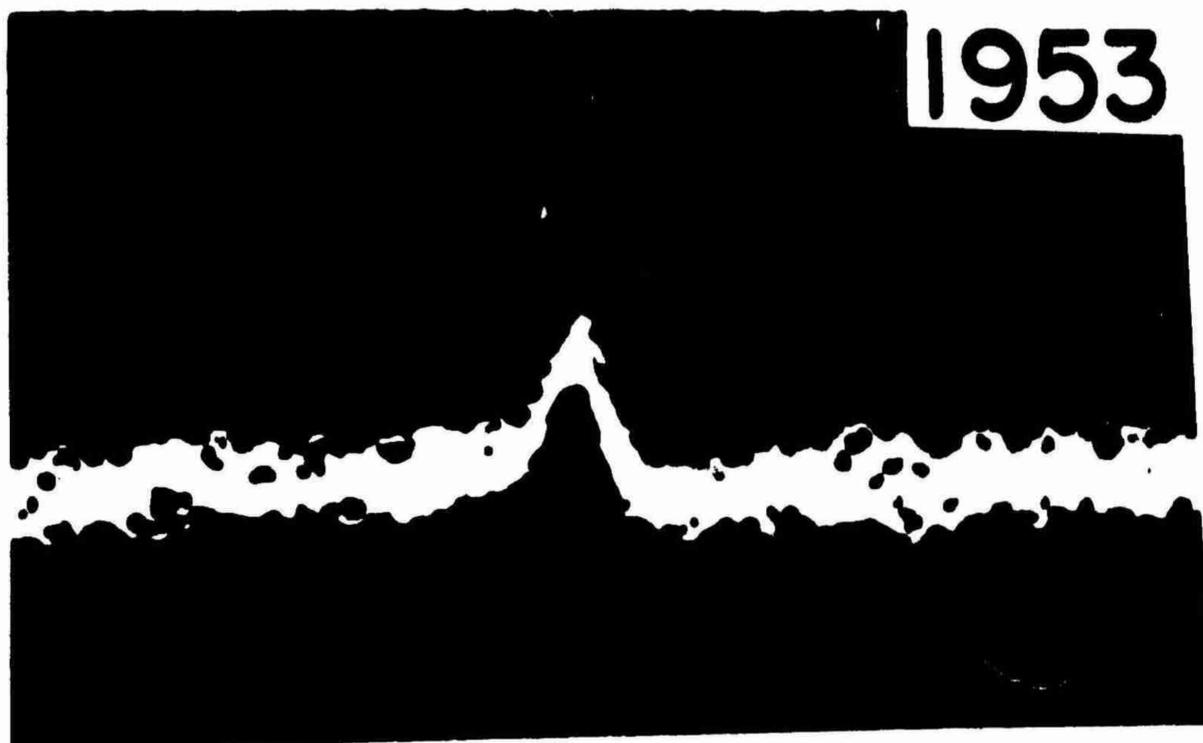
OCS

$J = 31 \rightarrow 32$
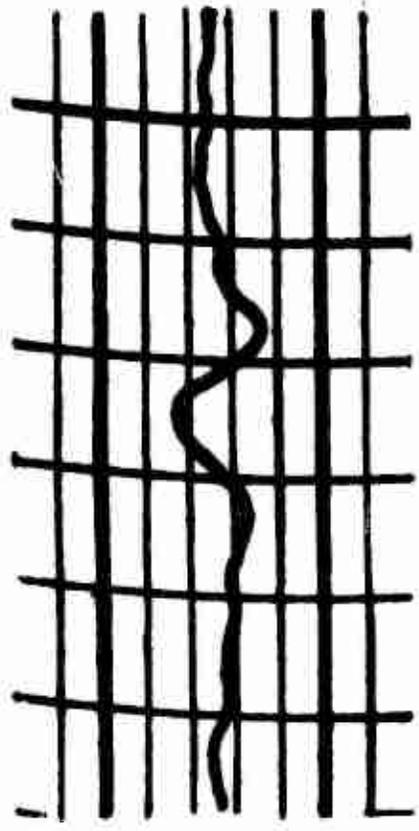
0.771 mm

389 kMc

1956

OCS

$J = 41 \rightarrow 42$
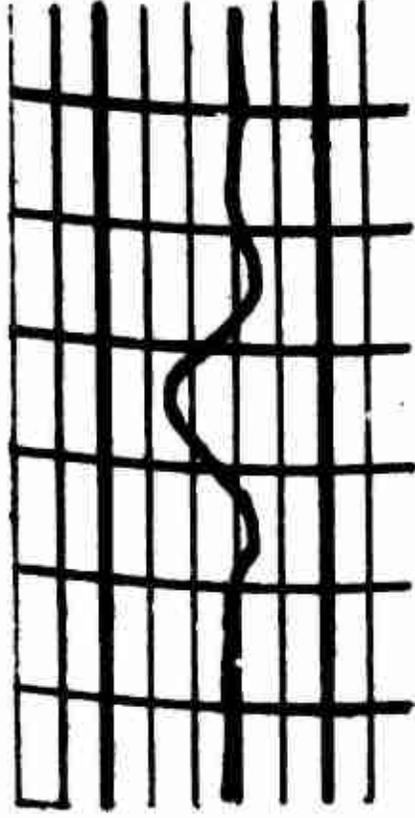
0.587 mm

510 kMc

1958

$Br^{81}CN$

$J = 71 \rightarrow 72$

0.509 mm

589 kMc

D Cl^{37}
0.93mm
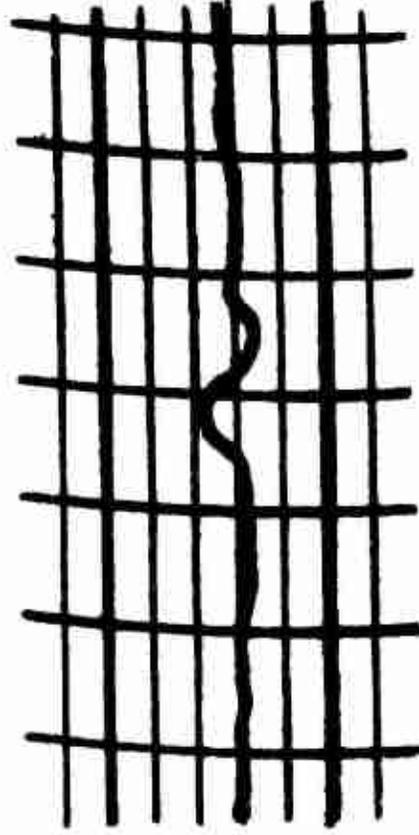
1957
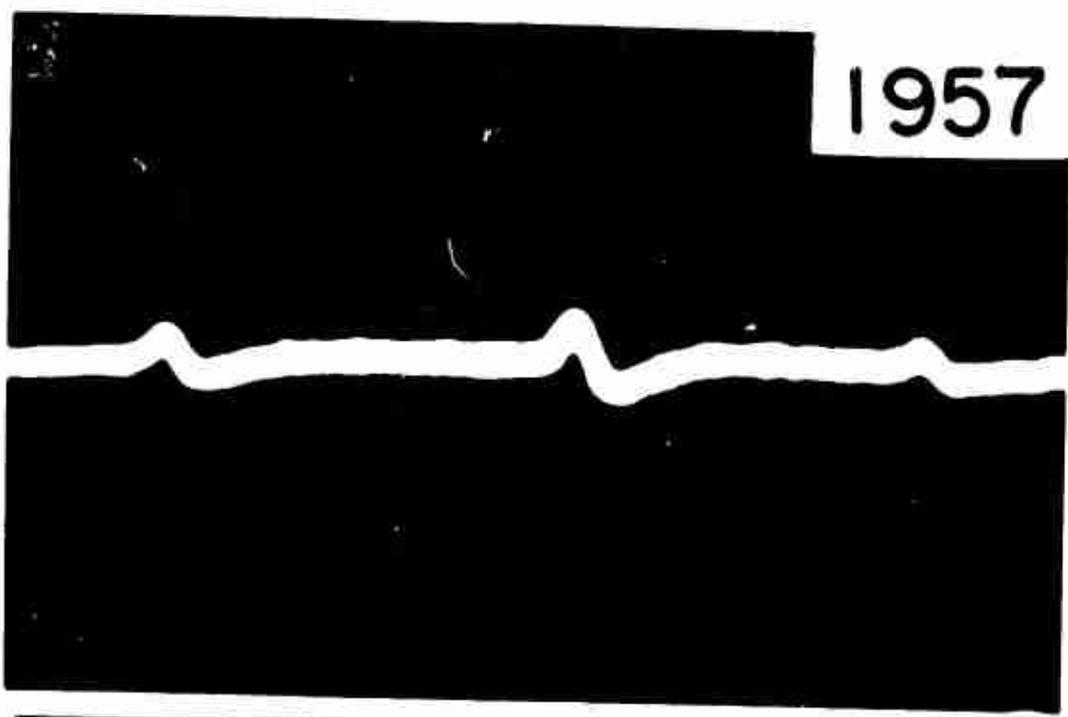
H I
0.78mm

1956

OCS
0.68 mm
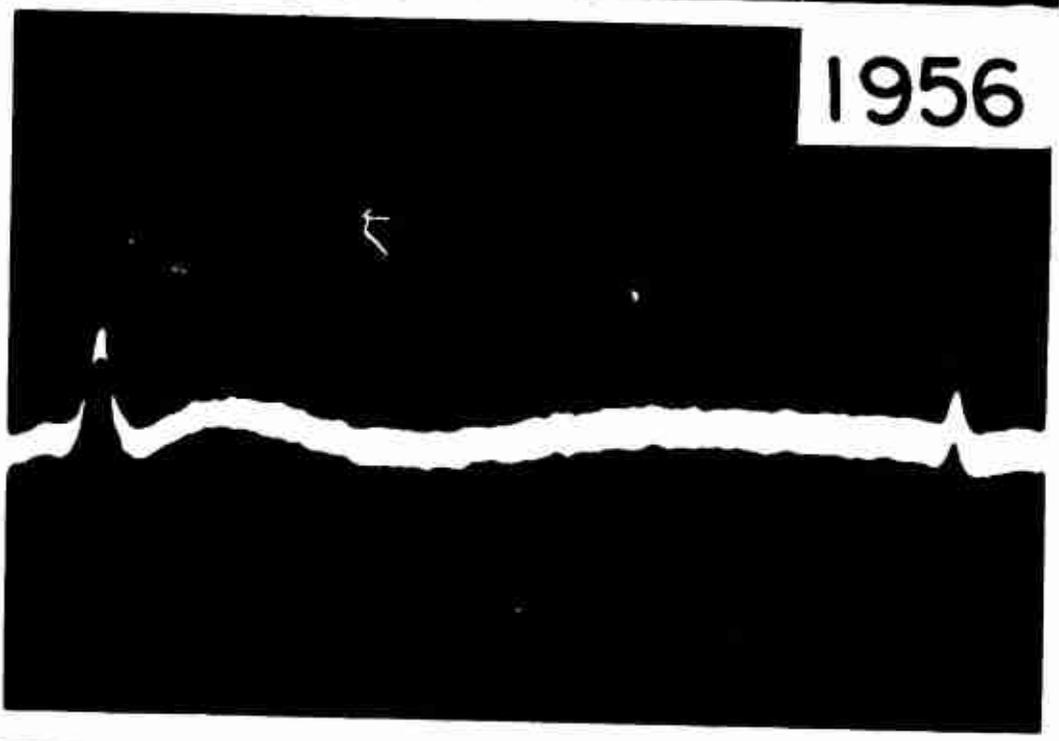
1956
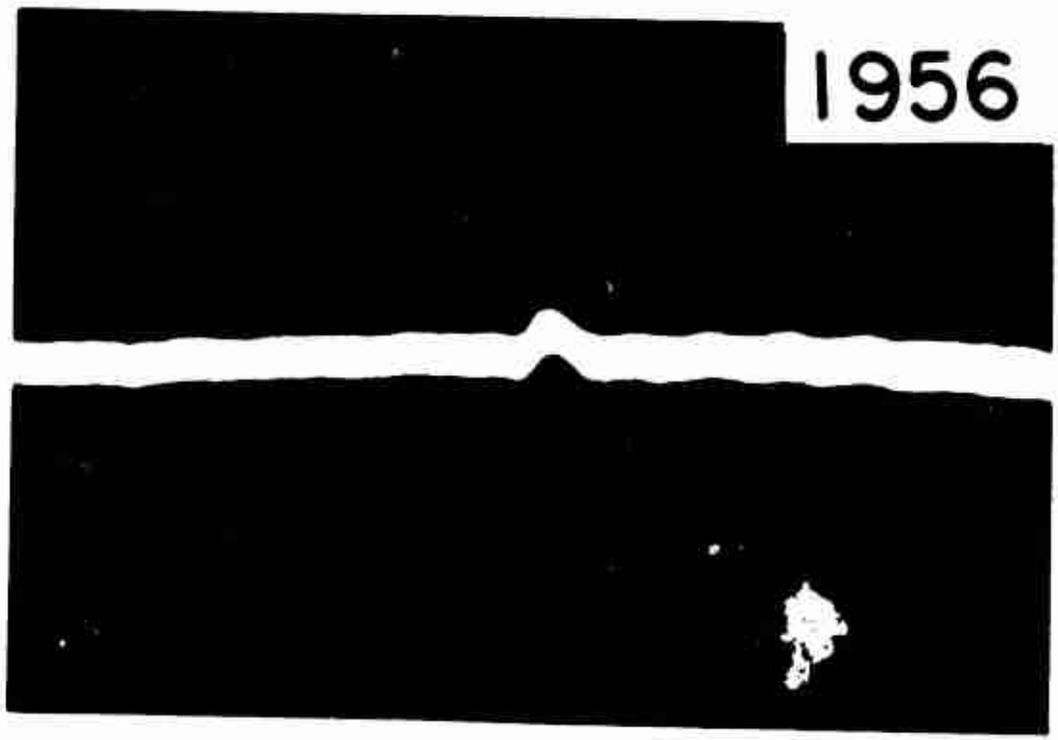
Figure 4 illustrates the signal-to-noise ratio now obtainable on absorption lines in the submillimeter wave region. At 0.57 mm wavelength the signal-to-noise ratio is about 25 to 1, and at 0.65 mm wavelength it is better than 100 to 1. Table I lists some spectral frequencies measured in the submillimeter range with the accuracy to which each was obtained.

Figure 4 illustrates the possibility of displaying with these devices several harmonics in a single klystron sweep. This recording is a bit deceptive in that the different rotational lines appear to be not widely spaced relative to their widths, whereas actually each spectral line seen in the figures appears at a different klystron harmonic and is of the order of 32,000 Mc/sec from its nearest neighbor though its width is of the order of only 1 Mc/sec. This display is possible because usable energy is present from many klystron harmonics above the waveguide cut-off frequency (about 2 mm wavelength here). Although to prevent reduction of the figure we did not show the lower frequencies, one can in a sweep like this display a series of similar spectral lines ranging the whole gamut from a half millimeter to a half centimeter. The ability to display these lines results from the fact that the rotational frequencies of linear molecules fall in an approximate but not an exact harmonic series, whereas the klystron harmonics are exact multiples within the discrimination of these experiments. Thus to display two of these rotational frequencies with different harmonics one must sweep the klystron frequency over a small frequency range determined entirely by the centrifugal distortion of the molecule by rotation. By measurement of the frequency spacing of the lines one can

Fig. 4.   Recording of $Br^{81}CN$ rotational lines in the wavelength region of 0.65 mm (458 Mc/sec) to 0.509 mm (589 Mc/sec) obtained with 14th to 18th harmonics from E. M. I. klystron operating at 32,700 Mc/sec with output power of 100 milliwatts. From left to right the rotational transitions are J = 55 → 56, 59 → 60, 63 → 64, 67 → 68, and 71 → 72. The line widths are of the order of 3 Mc. Unpublished curve by Cowan and Gordy, obtained in 1958.

BR^{81}CN LINES

λ IN MM — 0.654 — 0.611 — 0.573 — 0.539 — 0.509
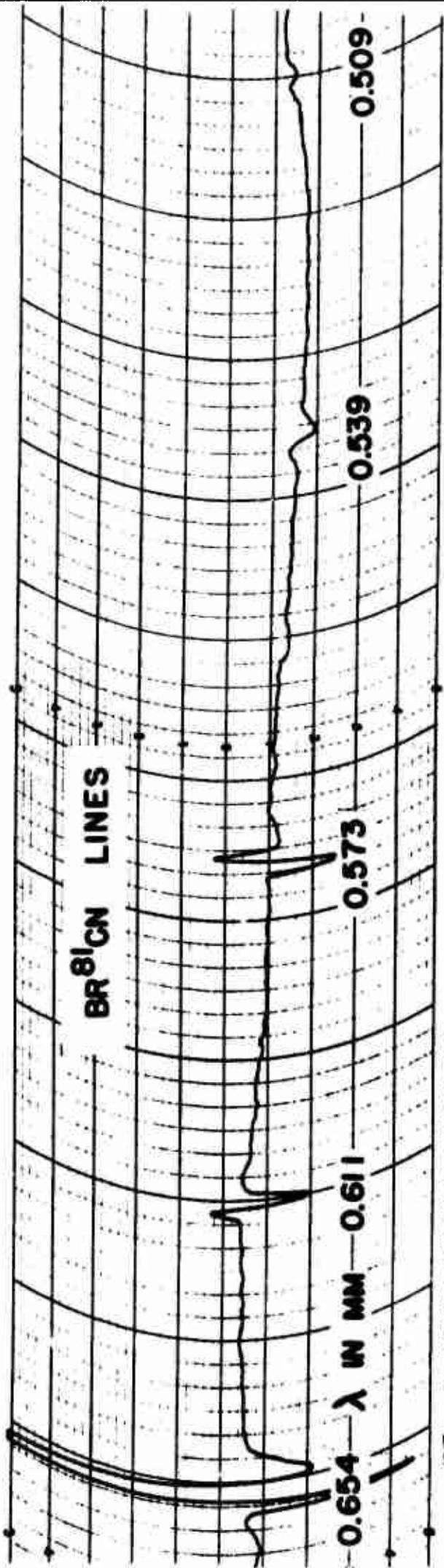
TABLE I. Some Representative Submillimeter Wave Spectral Lines
Measured at Duke

Molecule	Transition	Frequency Mc/sec	Reference
N_2O	$J = 11 \rightarrow 12$	$301,442,30 \pm 0.60$	27
$Cl^{37}C^{12}N^{14}$	$J = 25 \rightarrow 26$	$303,943.7 \pm 0.65$	27
ND_3	$J = 0 \rightarrow 1, \ F = 1 \rightarrow 1$	$309,908.24$	
	$F = 1 \rightarrow 2$	$309,909.54$	a
	$F = 1 \rightarrow 0$	$309,911.41$	
$Cl^{35}C^{12}N^{14}$	$J = 25 \rightarrow 26$	$310,965.90 \pm 0.65$	27
$O^{16}C^{12}Se^{80}$	$J = 3 \rightarrow 29$	$313,217.57 \pm 0.6$	27
$Br^{81}C^{12}N^{14}$	$J = 3 \rightarrow 39$	$319,345.52 \pm 0.65$	27
$Br^{79}C^{12}N^{14}$	$J = 33 \rightarrow 39$	$321,167.10 \pm 0.65$	27
DCl^{37}	$J = 0 \rightarrow 1, \ F = 3/2 \rightarrow 3/2$	$322,339.09 \pm 0.13$	
	$F = 3/2 \rightarrow 5/2$	$322,352.33 \pm 0.13$	b
	$F = 3/2 \rightarrow 1/2$	$322,362.94 \pm 0.13$	
DCl^{35}	$J = 0 \rightarrow 1, \ F = 3/2 \rightarrow 3/2$	$323,232.28 \pm 0.13$	
	$F = 3/2 \rightarrow 5/2$	$323,299.17 \pm 0.13$	b
	$F = 3/2 \rightarrow 1/2$	$323,312.52 \pm 0.13$	

Table I (continued)

Molecule	Transition	Frequency Mc/sec	Reference
$C^{12}O^{16}$	$J = 2 \rightarrow 3$	$345,795.900 \pm 0.090$	36
HI^{127}	$J = 0 \rightarrow 1$, $F = 5/2 \rightarrow 5/2$	$385,000.11 \pm 0.70$	
	$F = 5/2 \rightarrow 7/2$	$385,315.52 \pm 0.70$	25
	$F = 5/2 \rightarrow 3/2$	$385,543.0 \pm 0.70$	
$Br^{81}C^{12}N^{14}$	$J = 47 \rightarrow 48$	$392,807.0$	
	$J = 51 \rightarrow 52$	$425,575.9$	c
	$J = 55 \rightarrow 56$	$458,226.2$	
$O^{16}C^{12}S^{32}$	$J = 39 \rightarrow 40$	$486,135$	
	$J = 41 \rightarrow 42$	$510,457$	c

a.   G. Erlandsson and W. Gordy, Phys. Rev. 106, 513 (1957).

b.   M. Cowan and W. Gordy, Phys. Rev. 111, 209 (1958).

c.   M. Cowan and W. Gordy, unpublished results.

obtain directly and accurately the centrifugal distortion constants of the molecule.[27,28]

I am sometimes asked how one knows at which harmonic an unknown line is detected when several harmonics are present in the detected energy. Often one already knows enough about the molecule to predict at which harmonic the line must occur. When this is not true, one can readily identify the harmonic by a "cross-fire" method which consists of finding the line again with another harmonic. From the two klystron frequencies which give the same rotational frequency with two different harmonics one can deduce what the frequency of the spectral line must be.

The klystron harmonic method described here is no stop-gap measure in microwave spectroscopy. The method actually has many advantages over those which employ the fundamental power from microwave oscillators. For high-resolution spectroscopy where sharp spectral lines are of necessity observed, one cannot effectively employ high power because of saturation broadening of the spectral lines. Only the order of microwatts is required for sensitive, high-resolution spectroscopy in the millimeter and sub-millimeter range provided that the power is concentrated in a narrow band of only a few kilocycles, as is the case with the klystron harmonic power described. It is not the total power but the power within a given bandwidth which is significant for spectroscopy and for most other precise physical measurements. To yield the same amount of submillimeter wave power as that available from our harmonic generator and within the same bandwidth, a heat source would have to operate at millions of degrees. Furthermore,

some generators which have been proposed or developed for giving milli-
watts or even watts of millimeter-wave power will actually give less power
within a narrow kilocycle band range than is available from these klystron
harmonics.

To illustrate both the high sensitivity and high resolution obtainable
with klystron harmonics, I have shown in Fig. 5 a rotational transition of
H_2S^{33} showing resolution of the closely spaced S^{33} nuclear quadrupole
hyperfine structure with the S^{33} in its normal abundance of only 0.7%.
This curve was obtained[19] in 1955. Recently the $J = 3/2 \rightarrow 5/2$ rotational
transition of NO in the excited $\pi_{3/2}$ electronic state has been observed[29]
in the 1.2 mm region and its N^{14} hyperfine structure resolved as is shown
in Fig. 6. This, I think, is the only observation of the spectrum of a
molecule in an excited electronic state in the microwave region, and yet
the NO molecule has an exceptionally small dipole moment of only 0.158
Debye. In our laboratory the Zeeman splitting of the hyperfine components
in the $J = 1/2 \rightarrow 3/2$ transition of the $\pi_{1/2}$ electronic ground state of
NO at 1.9 mm has been measured,[30] and in the Bell Laboratories Burrus
and Graybeal[23] have recently measured the Stark splitting of these compo-
nents as well as those for the second rotational transition in the 1.2 mm
region. Figure 7 illustrates the beautiful results which Burrus and
Graybeal obtained at 1.2 mm. One can do no better in the centimeter wave
region.

There are several advantages in doing microwave spectroscopy with
klystron harmonic power. (1) The increased frequency coverage of the

Fig. 5. Illustration of the sensitivity and resolution obtainable in the shorter millimeter wave region. The structure is due to S^{35} nuclear quadrupole coupling. Total spread of the four stronger components is 10.1 Mc, and the separation of the two equally intense, well resolved components to the right is 2.13 Mc. From Burrus and Gordy, 1953 (Ref. 19).

$1_{0,1} \rightarrow 1_{1,0}$ transition of H_2S^{33}

S^{33} quadrupole splitting

ν_0 = 168, 322. 63 Mc $(\lambda$ = 1. 78 mm$)$

S^{33} abundance 0. 74 %
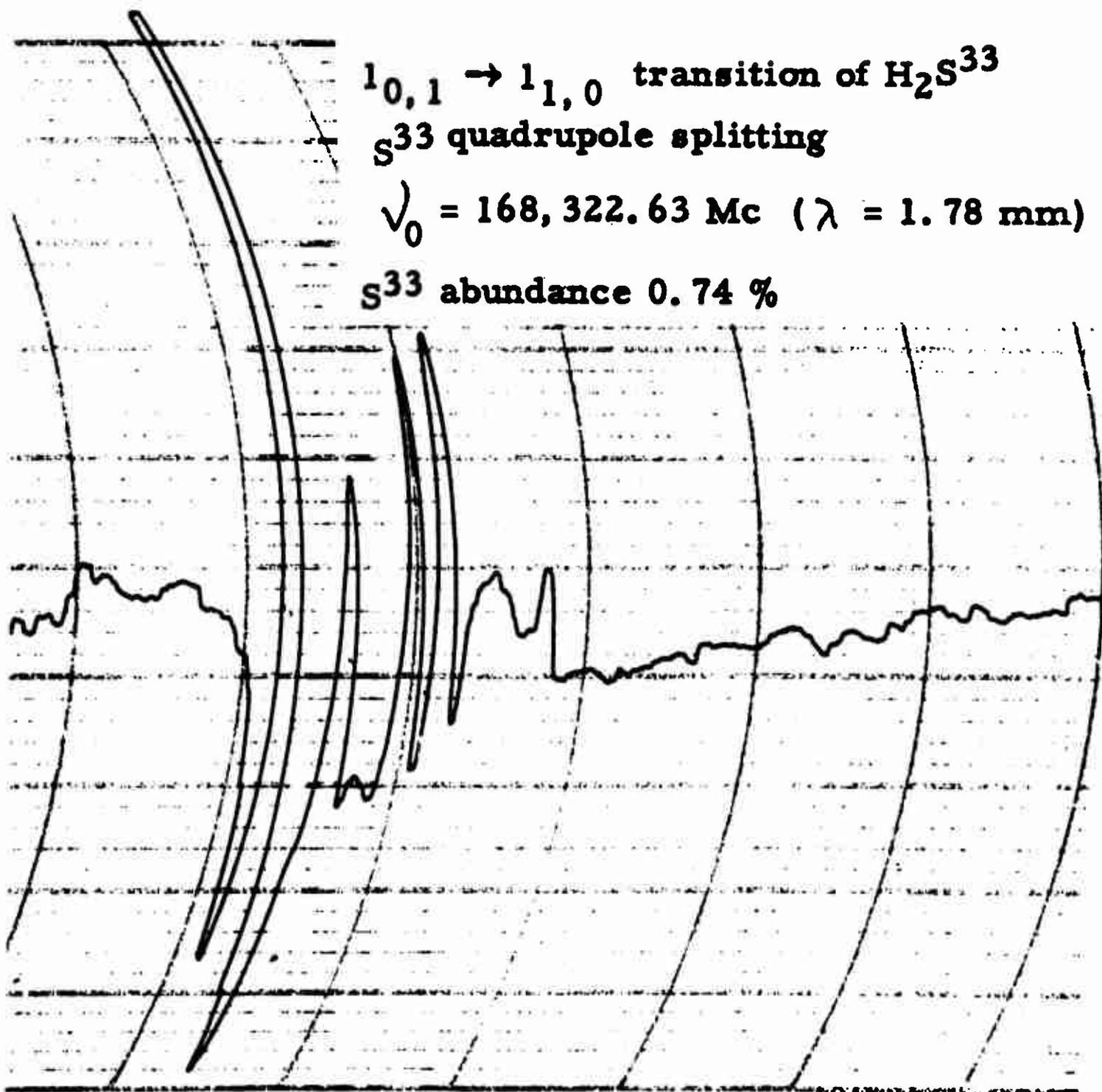
Fig. 6.   Recording at 1.17 mm wavelength of the $J = 3/2 \rightarrow 5/2$
rotational transition of $N^{14}O$ in the upper $\pi_{3/2}$ electronic
state. The gross splitting is due to N^{14} nuclear magnetic
coupling; the small doublet splitting is due to interaction
of electronic and rotational motions (Λ doubling). The
components of the well resolved central doublet are
spaced 2.49 Mc apart. From Favero, Mirri, and Gordy
(Ref. 29).

NO IN $\pi_{3/2}$ STATE $\lambda = 1.17$ MM

Fig. 7.   Stark effect at 1.2 mm of the $3/2 \to 5/2$ transition of $N^{14}O$ in the ground $\pi_{1/2}$ electronic state. From Burrus and Graybeal (Ref. 20).

Stark Effect of NO, 1.2 mm

6000 v/cm
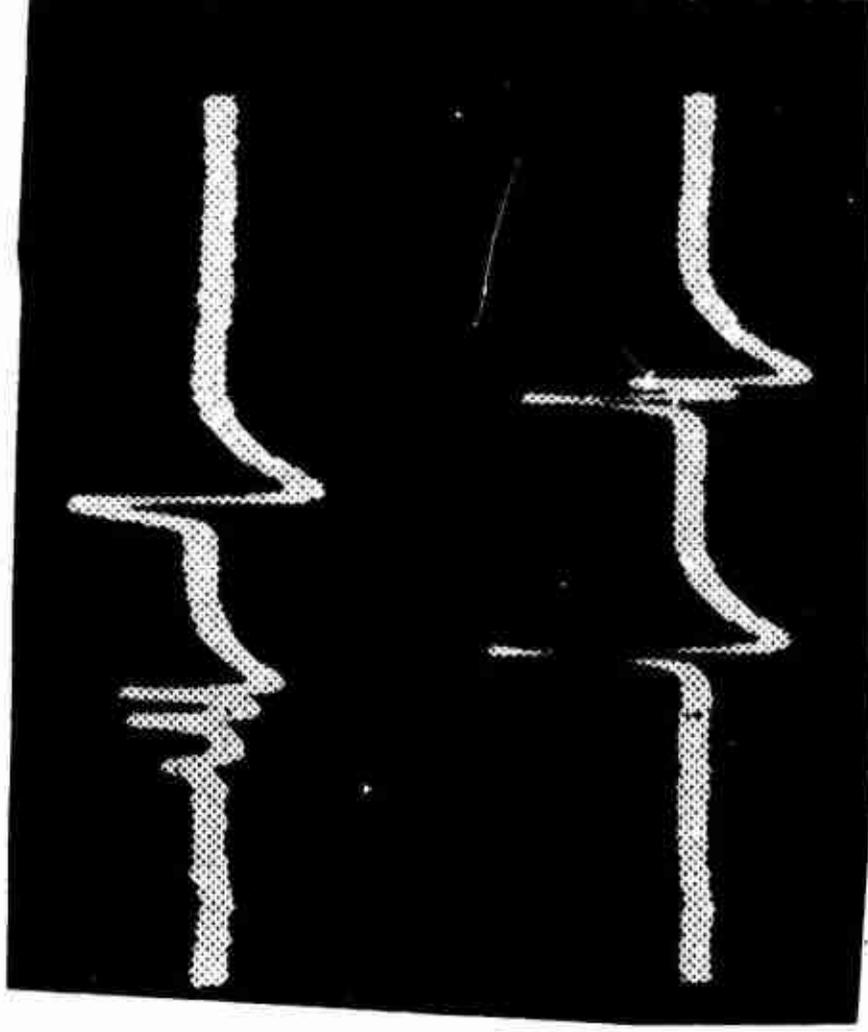
Zero field

spectrometer caused by its expanded sweep at a given harmonic. The
HI lines displayed in Fig. 3 are 13. Mc/sec apart and are displayed on the
scope by a sweep through a single mode of the klystron, whereas the entire
mode of the klystron covers only about 60 Mc/sec. Likewise the mechani-
cal tuning range of the spectrometer is increased. This extra range comes
from the fact that the harmonic multiplier also multiplies the frequency
span of the klystron. (2) Increased frequency coverage of the spectrometer
because of its capacity to employ several different harmonics. This is
illustrated in Fig. 4. This magnification in range is great since useful
power up to the twentieth harmonic is usable. Features (1) and (2) together
reduce the amount of equipment required for coverage of the range from
half a millimeter to half a centimeter by orders of magnitude over that
required for a search of the region with fundamental power. They likewise
reduce by orders of magnitude the time required to search through this
vast region for spectral lines. Despite this great advantage in extent and
rapidity of frequency coverage, no significant loss in resolution or accurac:
of measurement is incurred over that obtainable with the fundamental powe1
(3) Ability to measure the detected spectral frequency by comparison with
standard broadcast frequencies such as those of WWV. If one could
develop a sharp, coherent, tunable, primary source in the submillimeter
region, one would still need the harmonic chain which has been established
to provide a movable ladder of standard frequency markers in the submilli-
meter region.

While we at Duke were developing the methods for millimeter wave spectroscopy based on the klystron-driven, crystal harmonic generator and crystal detector, the Columbia group was experimenting with filtered harmonic energy directly from high-powered magnetrons without the aid of the crystal harmonic generator. They announced detection[31] of harmonic energy from magnetrons with an infrared Golay detector as early as 1949 in the region of 1.5 to 3-mm wavelength and mentioned some fixed-frequency gaseous attenuation measurements in progress on DI and ND_3. Apparently, however, the only spectral resonance observed with these techniques was the broad, unresolved inversion spectrum of ND_3 at high pressure in the 2- to 3-mm wave region.[32] They published their first results with the crystal-multiplier, klystron-harmonic method in 1952, a re-measurement of some lines in the 3- to 4-mm region[32a] previously measured at Duke. Since that time they have made high-resolution measurements in the region of 1.5- to 3-mm wavelength on DI,[20] TBr,[32] and CO,[35] with a klystron-driven, crystal harmonic generator. So far as I know, they have made no further measurements with magnetron harmonics.

3. Types of Measurement Which Can Be Made With Millimeter and Sub-Millimeter Waves.

I do not pretend to forsee all, or even most, of the possible future applications of this vast and relatively unexplored portion of the spectrum. Nevertheless, I list below eleven types of measurement which have been made or can be made:

(1) Rotational spectra of molecules

(2) Fine and hyperfine intervals of atomic spectra

(3) Vibration spectra of solids or molecular crystals

(4) Dielectric absorption of liquids and solids

(5) Millimeter wave astronomy

(6) Atmospheric investigations

(7) Plasma investigations

(8) Electron paramagnetic resonance

(9) Antiferromagnetic resonance in solids

(10) Cyclotron resonance of electrons in solids and gases

(11) Study of the superconducting state.

Under each of these eleven headings many subheads can be written. Here I can give only an indication of the magnitude of the studies which are possible. Perhaps (1), rotational spectra of molecules is the largest of these fields of investigation. At least it is the one in which the most work has been done to date. Rotational transitions of molecules fall predominently in the millimeter and submillimeter wave region. Some of the information which has already been obtained from millimeter and submillimeter wave rotational spectra is listed in Tables II, III, IV, and V.

In addition to information of the type illustrated in the tables, rotational lines have provided a means of evaluation of mass ratios of several atomic isotopes and of measurement of a number of nuclear spins, magnetic dipole and electric quadrupole moments. Measurements of millimeter and submillimeter wave rotational lines[36] of CO have been combined with near-infrared measurements by Rank[37] to obtain a highly accurate spectral measurement of the velocity of light. The value obtained is

TABLE II. Spectral Constants for Some Hydrogen Halides Obtained from
Millimeter Wave Spectroscopy at Duke

Molecule	B_0 in Mc/sec	eQq coupling Cl, Br, or I in Mc/sec	Bond length r_0 in A	Reference
DCl^{35}	161,656.10	-67.3	1.23125	a
DCl^{37}	161,133.02	-53.0	1.23124	a
TCl^{35}	111,075.76	-67.0	1.23003	b
TCl^{37}	110,601.51	-53.0	1,23002	b
DBr^{79}	127,358.06	530.5	1.42144	a
DBr^{81}	127,260.14	443.5	1.42144	a
TBr^{79}	76,252.24	530	1.42012	b
TBr^{81}	86,174.33	443	1.42011	b
DI^{127}	97,537.10	-1023.3	1.61630	a
HI^{127}	192,655.0	-1331	1.61972	c

a. M. Cowan and W. Gordy, Phys. Rev. **111**, 209 (1958).

b. C. A. Burrus and W. Gordy, B. Benjamin and R. Livingston, Phys. Rev.
   97, 1661 (1955).

c. M. Cowan and W. Gordy, Phys. Rev. **104**, 551 (1956).

TABLE III. Spectra Constants of Hydrides and Deuterides of Nitrogen, Phosphorus, Arsenic, and Antimony Obtained from Millimeter Wave Spectroscopy at Duke.

Molecules	B_0 in Mc/sec	eQq coupling for N, As, or Sb	Bond angle	Bond length	Reference
$N^{14}D_3$	154,162.7	-4.10	107°	1.0144	a
PH_3	133,478.3		$93^{\circ}27'$	1.4206	b
PD_3	69,470.41		$93^{\circ}10'$	1.4166	b
$As^{75}H_3$	112,462.46	-160.1	$91^{\circ}50'$	1.5192	c
$As^{75}D_3$	57,477.15	-165.9	$91^{\circ}30'$	1.5145	c
$Sb^{121}H_3$	88,031.92	452.7	$91^{\circ}13'$	1.7073	d
$Sb^{121}D_3$	44,693.29	465.4	$90^{\circ}56'$	1.7021	d
$Sb^{123}H_3$	88,015.54	586.0	$91^{\circ}18'$	1.7073	d
$Sb^{123}D_3$	44,677.13	592.8	$90^{\circ}56'$	1.7021	d

a. G. Erlandsson and W. Gordy, Phys. Rev. 106, 513 (1957).

b. C. A. Burrus, A. W. Jache, and W. Gordy, Phys. Rev. 95, 706 (1954).

c. G. S. Blevins, A. W. Jache, and W. Gordy, Phys. Rev. 97, 684 (1955).

d. A. W. Jache, G. S. Blevins, and W. Gordy, Phys. Rev. 97, 680 (1955).

TABLE IV. Dipole Moments from Millimeter Wave Spectroscopy.

Molecule	Moment (Debye units)	Wavelength of measurement (mm)	Reference
HCN	2.936 ± 0.002	3.33	a
CO	0.112 ± 0.005	2.6	23
O_3	0.53 ± 0.02	2.5	b
H_2Se	0.24 ± 0.02	2.1	c
DI	0.316 ± 0.010	1.5	23
NO ($^2\pi_{1/2}$)	0.158 ± 0.006	1.2	23
PH_3	0.573 ± 0.010	1.1	23

a.   Bhattacharya and Gordy, unpublished results.

b.   Trambarulo, Ghosh, Burrus, and Gordy, J. Chem. Phys. 21, 85 (1953).

c.   Jache, Moser, and Gordy, J. Chem. Phys. 25, 209 (1956).

TABLE V. Nuclear Magnetic Coupling C_I of Halogens in Halogen Halides.

Halogen Halide	C_I in Mc/sec	C_I/g_I	$C_I/g_I B_0$	Reference
DCl^{35}	$< |0.05|$	~ 0	~ 0	a
DCl^{37}	$< |0.05|$	~ 0	~ 0	a
DBr^{79}	0.15 ± 0.04	0.11	0.9	a
DBr^{81}	0.16 ± 0.04	0.11	0.9	a
DI^{127}	0.16 ± 0.02	0.14	1.4	a
HI^{127}	0.26 ± 0.05	0.23	1.2	25

a. M. Cowan and W. Gordy, Phys. Rev. **111**, 209 (1958).

c = 299, 793. 7 $\pm$ 0. 6 kMc/sec.   Perhaps the largest potential application of millimeter and submillimeter wave rotational spectra is for chemical analysis, since the characteristic spectral transitions are sharp, strong, and abundant in this region.

Many fine and hyperfine intervals of atoms have spacings equivalent to millimeter and submillimeter wave quanta. So far as I know, atomic spectra have not yet been measured in the region. Probably many measurements on atoms will eventually be made with optical pumping techniques employing millimeter waves.

Millimeter and particularly submillimeter wave vibration spectra in solids (3), especially in crystals containing large organic molecules, is a potentially great but yet untouched field. Debye type dielectric absorption measurements of liquids and solids (4) can of course be made at any point in the radio region. There is, however, a great advantage in having a wide frequency range for such measurements so that the measurements can be made with vibrational periods approximately equivalent to the relaxation times of the molecules. An extension of dielectric absorption measurements to the 3-mm region has been made recently by C. P. Smyth and his group[38] at Princeton. Jurgen Schneider, in our laboratory, has also made unpublished measurements in the same region.

Millimeter and perhaps submillimeter wave astronomy (5) is a potentially important field because, for one reason, a sharp probing of the sky, sun, moon, or planets can be made with an antenna which is small enough to be paid for and maneuvered. Like many other things that can be

done in the region, millimeter wave astronomy combines advantages of both optical and radio astronomy. Some free radicals, or molecular species, and excited atoms in the solar atmosphere, and perhaps some in outer space, have spectral transitions occurring in the region. Astronomical investigations in the millimeter range are already being made at the Naval Research Laboratory and at the University of Alabama. A few years ago a group in our laboratory detected solar radiation in the 3-mm region using our harmonic multiplier as a local oscillator in a superheterodyne receiver with an inefficient, improvised antenna.

Millimeter waves should be very useful for atmospheric studies (6). Many molecules in the atmosphere have rotational transitions in the region. Millimeter wave lines of atmospheric molecules - O_2, O_3, CO, H_2O, NO, and N_2O - have already been measured by our group in the laboratory but not in the atmosphere.

Plasma investigations with millimeter waves (7) I hear by rumor are in progress in many places. Certain other papers given at this Symposium deal with this subject, which I shall not discuss.

Our laboratory has made electron spin resonance measurements (8) on single crystals of organic free radicals[39] up to frequencies of 79,000 Mc/sec. There are certain advantages in making measurements at still higher frequencies, but the magnetic field is the limitation for us. The magnetic field required for observation of spin resonance at a frequency ν is

$$H \text{ (kilogauss)} = \frac{\nu \text{ Mc/sec}}{1400 \, g_{eff.}} \quad ,$$

!

where $g_{eff.}$ is the g factor, which for the free electron spin is 2.0023.
Thus for an approximately free electron spin (as is found in most organic
free radicals or electron gases), a magnetic field of 107 kilogauss is re-
quired for observation of the resonance at 1 mm wavelength (300,000 Mc/
sec). However, in many crystals there is zero field splitting of the mag-
netic states or residual spin orbit coupling which makes $g_{eff.}$ greater than
2.00 and thus reduces the field required for resonance.

There is zero field splitting of the electronic ground states in many
ferromagnetic materials which are of the order of a millimeter wave
quantum arising from exchange interaction of the electrons in neighboring
magnetic units. Transitions between these levels give rise to a class of
spectra called anti-ferromagnetic resonance.[40] This type of resonance
has been observed in single crystals of MnF_2 in the 1.2- to 3-mm region
by Johnson and Nethercot.[41] There are other crystals in which this
phenomenon can be profitably investigated in the millimeter region.

Cyclotron resonance of electrons in both solid and gaseous states
(10) can be studied most advantageously in the millimeter or submillimeter
range provided that a sufficiently high magnetic field can be obtained. The
magnetic field requirements for free electrons are similar to those of
spin resonance, and, if one is lucky enough to obtain sufficient funds for
purchase of a magnet with field strength of 100 to 200 kilogauss, he can
do important submillimeter measurements in both areas with the presently
available crystal multipliers and detectors. The effective masses of
electrons in crystals are often lower than those for free electrons, and

hence the resonances can be observed with correspondingly lower fields.

Cyclotron resonance in graphite has recently been observed[42] at 72 kMc/
sec. The principal advantage of observing cyclotron resonance at high
frequencies is that the resonance period can be made short as compared
with the collision time or the lifetime in the state. For observation of
resonance in solids within the centimeter range very pure crystals and low
temperatures are required for increase of the relaxation time sufficiently
to make cyclotron resonance observable. For electrons in gases low
pressures must be used. In the submillimeter range the phenomena should
be observable at room temperatures in some solids and at atmospheric
pressures in some gases.

Although it is not a large field of investigation such as rotational
spectra, one of the most significant types of millimeter wave studies is
the measurement of the quantum gap between the normal and the super-
conducting state in superconducting solids. The later Fritz London, of
Duke, believed,[43] but did not live to prove, that the electrons somehow
form a cooperative "macroscopic quantum state of long-range order"
to achieve the strange properties of superconduction. Bardeen, Cooper,
and Schrieffer[44] have recently evolved a more specific theory of super-
conductivity based on the postulate of the quantum gap. This quantum gap,
which is of the order of kT_c where T_c is the critical temperature for
reaching the superconducting state, falls in the millimeter or submilli-
meter region for most known superconductors. The first, but very skimpy,
evidence for the existence of a gap was obtained at Duke on tin.[45] Our

work on tin is still incomplete but is being actively pursued. Measurement of the gap in this substance with microwave methods is difficult because it falls approximately at 1 mm wavelength, and requires accurate attenuation measurements at low temperatures in this high frequency region. During the course of our work measurements on thin films of tin have been made on the other side of the gap with far-infrared techniques by Glover and Tinkham.[46] These observations gave good evidence for the existence of the gap. Recently evaluations of the gap with infrared methods for tin as $3.4 \, kT_c$ and for lead as $4.1 \, kT_c$ at $T = 0$ were made by Richards and Tinkham.[47] Measurements of the gap with microwave methods have been made on superconducting aluminum in the 3-mm region by Biondi and Garfunkel.[43] The superconducting gap in this substance falls at a lower frequency ($\sim 100 \, kMc/sec$) than it does in tin. Biondi and Garfunkel obtained a good measure of the gap by a projection of the onsets of absorption at different frequencies as the temperature was varied. Their value for the quantum gap in aluminum at absolute zero, $E_g(0) = 3.25 \, kT_c$, compares favorably with the value theoretically predicted, $3.52 \, kT_c$, by Bardeen, Cooper, and Schrieffer.[44]

I have not mentioned all the applications of millimeter waves in physics, but I think I have covered enough to convince you that the gate to the radio side of the millimeter wave region has at last been swung open.

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DIELECTRIC RELAXATION OF DILUTE SOLUTIONS

IN THE MILLIMETER WAVE REGION.*

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SUMMARY

The dielectric losses of benzophenone, diphenylether, diphenylamine, chlorobenzene and aniline, measured at 12.33, 6.19, 3.08 and 2.47 mm wavelength in dilute benzene solutions, have been found to fit Debye type relaxation curves within the limits of experimental error. The distinctly lower relaxation time of diphenylether and of diphenylamine, compared to the one for benzophenone, can be explained by a high internal mobility of the phenyl rings in these two molecules. Similarly, the mobility of the amino group in aniline results in a decrease of the relaxation time, compared to the rigid chlorobenzene molecule.

INTRODUCTION

The occurrence of internal mobilities in a dipolar molecule may result in a dielectric relaxation time which is considerably shorter than ϕ the one for a rigid molecule of comparable molecular dimensions. A striking example of this effect is the unusually short relaxation time of diphenylether and of diphenylamine, first reported by Fischer.[1,2] To obtain the relaxation curves of these molecules, it was necessary to extend dielectric loss measurements into the shorter millimeter wave region.

APPARATUS

Since absolute absorption measurements become increasingly difficult in the shorter mm-region, mainly due to the small size of the waveguide components, we have performed only relative measurements of the dielectric loss ε'' and calibrated the data by means of standard substances. Benzophenone and chlorobenzene are suitable for this procedure.

A. Reflection Method.

At wavelengths of 12 mm and 6 mm, dielectric losses were measured by means of a reflection method. A schematic diagram of the apparatus is given in Fig. 1. Microwave power was generated by a 2K33 K-band klystron and fed into a frequency multiplier M. After passing a crystal detector D and a tapered transition section T, the wave entered the absorption cell C, a vertical section of K-band waveguide shorted at the

Fig. 1. Schematic diagram of the reflection arrangement.

2K33

M

D

P

T

V

C
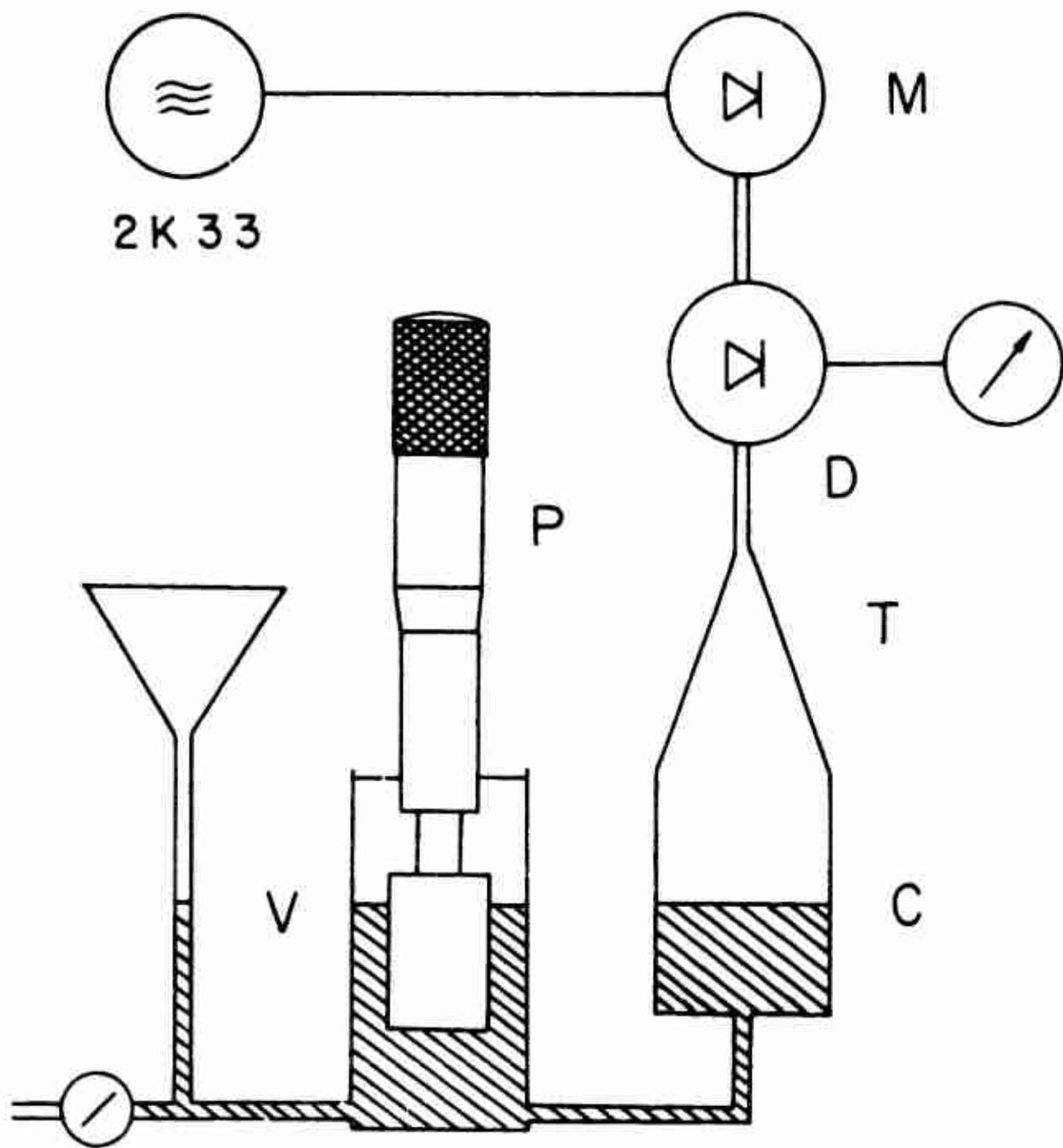
bottom by a metal plate. The height of the liquid in the cell could be changed with an accuracy of at least 1/1000 mm by immersing a micrometer plunger P into a second vessel V, connected to the cell. The micrometer vessel and the cell were surrounded by a thermostat jacket, with kept the temperature constant within $1/10^{\circ}$C. The detector signal, modulated by applying a 200 cps audio voltage to the klystron reflector, was fed into a sensitive amplifier (gain 100,000) and measured with a vacuum tube voltmeter.

As the height of the liquid in the cell is changed, the detector voltage passes through maxima and sharp minima, similar to a standing wave pattern. When a dipolar substance is added to the nonpolar solvent, both the real and the imaginary part of the dielectric constant of the liquid are increased, and this results in a shift and in a broadening of the nodes in the standing wave pattern. For sufficiently low losses, the position of the node is only dependent on the real part, and its width only on the imaginary part of the dielectric constant. Thus, the complex dielectric constant can be determined by measuring the width and position of a node, as a function of the height of the liquid. Compared with the usual method, in which the height of the dielectric material is kept constant and the detector is moved along the waveguide to measure the shape of the standing wave, the above method has the advantage of great simplicity, since no complicated driving device for the detector probe is required.[3] To obtain a quantity proportional to the loss of the dipole substance, the node width obtained for

the pure solvent was subtracted from that for the solution, and this differ-
ence was found to vary linearly with the concentration. In this work, only
the imaginary part ε'' of the dielectric constant has been measured.

Microwave power for measurements at 6 mm wavelength was produced
by a crossed multiplier, containing a slotted 1N26 crystal. A crystal of
this type was also used for detection. At 12 mm wavelength the fundamental
power of the klystron was used.

B. Transmission Method.

At higher frequencies, where the microwave power available is
comparatively small and unstable, the reflection method becomes inaccurate.
Therefore, a transmission method was used to measure the dielectric loss
at 3 mm and 2.5 mm wavelength. The absorption cell was a piece of K-band
waveguide, closed at its ends by two Teflon windows, and was located be-
tween a multiplier and a detector, of the type described by King and Gordy.[4]
Two cells of length 181 mm and 55 mm were used for measurements at 3 mm
and 2.5 mm wavelength, respectively. The attenuation, in db, of the micro-
wave was found to vary linearly with the concentration of the solutions.

The measurements at 3 mm wavelength were carried out with a
detector which responded to the fourth and all higher harmonics of the
klystron. To eliminate these higher harmonics, whose intensity was not
negligibly small, a 120 cm long absorption cell filled with OCS gas was
introduced between the multiplier and the liquid cell. The $0 \to 1$ rotational
transition of this linear molecule has a frequency of 12.163 kMc/sec. Due

to centrifugal distortion effects, the higher rotational transitions do not occur at exactly integral multiples of the fundamental frequency.[5] Therefore, when the detector output was displayed on an oscilloscope, a whole spectrum of absorption lines appeared, each one representing the intensity of a particular harmonic, generated by the multiplier. For instance, the fourth harmonic of the 2K33 klystron at 97 kMc/sec was represented by the 7 →8 transition of the OCS molecule. By proper adjustment of the detector and multiplier tuning plungers, it was possible to cancel out almost completely all harmonics above the fourth. In a similar way, the measurements at 2.5 mm wavelength were carried out with a fifth harmonic detector.

For rough absorption measurements, it is also possible to take the intensity decrease of the rotational lines as a direct measure of the attenuation of the harmonics in an absorbing medium, located between the gas cell and the detector. By this method, absorption measurements at many frequencies can be carried out simultaneously.

RESULTS

Benzophenone, diphenylether, diphenylamine, chlorobenzene and aniline have been measured in dilute benzene solutions at 12.33 mm and 6.19 mm by the reflection method and at 3.08 mm and 2.47 mm by the transmission method. The temperature wa 25 ± 0.1 C. The molar fraction m of the solutions ranged from about 0.001 to 0.01. The dielectric losses of these substances, represented by quantities proportional to ε''/m,

are listed in Table I. The values for benzophenone have been taken equal to unity for all wavelengths, since this molecule has been used to calibrate the dielectric losses of the other substances on an absolute scale. The experimental error is about 1 to $2^o/o$ for the measurements at 12.33 and 6.19 mm, and 2 to $4^o/_o$ for those at 3.08 and 2.47 mm.

TABLE I. Dielectric loss relative to benzophenone.

Wavelength (mm)	12.33	6.19	3.08	2.47
Frequency (kMc/sec)	24.32	48.46	97.30	121.65
benzophenone[a]	1.000	1.000	1.000	1.000
diphenylether[b]	0.173	0.348	0.473	0.510
diphenylamine[c]	0.117	0.174	0.196	0.221
chlorobenzene[d]	0.426	0.483	0.545	0.575
aniline[e]	0.302	0.473	0.573	0.642

a.   melting point 48^oC.

b.   melting point 23^oC.

c.   melting point 53^oC.

d.   boiling point 132.5^oC.

e.   boiling point 132^oC.

DISCUSSION

The dielectric loss of a Debye type relaxation process, characterized by a single relaxation time τ, is represented by the formula

$$\mathcal{E}'' = m(a_0 - a_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2} \tag{1}$$

where m is the molar fraction of the solution and ω the circular frequency of the electric field. The quantity ma_0 is the static dielectric constant and ma_∞ that at very high frequencies, usually the far infrared, where only the electronic and the atomic polarizability contribute to the total polarization. Rigid molecules whose structure deviates not too much from a spherical shape, are usually found to be in fair agreement with Eq. (1). Therefore, it can be expected that this is also true for the two calibration substances measured in this work, benzophenone and chlorobenzene.

The conversion of the relative values of the dielectric loss, as given by Table I, to absolute units was done in the following way: Assuming benzophenone and chlorobenzene to be in agreement with Eq. (1), a value for the relaxation time τ was chosen for benzophenone, so that the dielectric loss of chlorobenzene, now calibrated by that of benzophenone, also gave a good fit to a Debye curve. In this way, the values 1.85×10^{-11} sec and 0.91×10^{-11} sec were obtained for the relaxation times of benzophenone and chlorobenzene, respectively. In general, this method is only applicable, if the relaxation times of the two calibration substances differ sufficiently, as in the above case.

The dielectric increment $a_0 - a_\infty$ is related to μ, the dipole moment in solution, by

$$a_0 - a_\infty = \frac{4\pi}{27\,kT} \frac{L}{M} \rho (\varepsilon + 2)^2 \mu^2 \ , \tag{2}$$

where k is Boltzmann's constant, T the absolute temperature, L Avogadros number and ρ, ε, M are respectively the density, dielectric constant and molecular weight of the solvent. For benzene solutions at $25^{o}C$, this equation becomes

$$a_o - a_\infty = 1.469 \mu^2 \qquad (3)$$

where μ is measured in Debyes. The dipole moment of benzophenone is 2.95 Debye,[6] this gives $a_o - a_o = 12.9$. The dielectric losses of diphenylether, diphenylamine and aniline, now calibrated by that of benzophenone, were found to be also in fair agreement with the assumption of a single relaxation time, see Table II.

TABLE II. Dielectric relaxation times τ, increments $a_o - a_o$ and dipole moments μ at $25^{o}C$.

	τ (10^{-11} sec)	$a_o - a_o$	μ^a (Debye)
benzophenone	1.35	12.9	2.95
diphenylether	0.41	1.53	1.04
diphenylamine	0.60	0.96	0.81
chlorobenzene	0.91	3.52	1.55
aniline	0.54	2.48	1.30
benzophenone[b]	1.37	12.1	2.91
chlorobenzene[b]	0.95	3.30	1.50
diphenylether[c]	0.37	2.06	1.20

a. calculated from Eq. (3).
b. values obtained by Bergmann, see reference 7.
c. values obtained by Maier, see reference 8.

The dispersion of the dielectric losses of these substances, in normalized units $\omega\tau/1 + \omega^2\tau^2$ is shown in Figs. 2 and 3 as a function of the logarithum of the frequency f. The values for μ and $\mathcal{C}$ are in fair agreement with those obtained by Bergmann[7] from ε' and ε'' measurements at 1, 3, and 14 cm wavelength and at 22°C. Measurements of the dielectric relaxation of diphenylether in dilute benzene solutions and at cm wavelengths have been recently reported by Mai.r.[8] His data also confirm the assumption of a single relaxation time, which is in rough agreement with the value given in Table II. However, his value for the dipole moment differs considerably from the one obtained in this work.

To explain the unusually short relaxation time of diphenylether, Maier[8] has proposed the following explanation: The whole dipole moment of this molecule can be reversed in direction by an internal motion around the molecular axis of greatest length. During this motion, the orientation of the two phenyl rings changes by considerably less than 180°, so that the orientation of the dipole moment will be associated with a relaxation time much shorter than that for a rigid molecule of comparable molecular dimensions. The same effect may be expected to occur in diphenylamine. In contrast, the longer relaxation time of benzophenone indicates a strong rigidity of the phenyl rings, probably due to conjugation between the rings and the CO double bond.

An internal mobility of the amino group in aniline is revealed by the distinctly shorter relaxation time, comparable to chlorobenzene, a
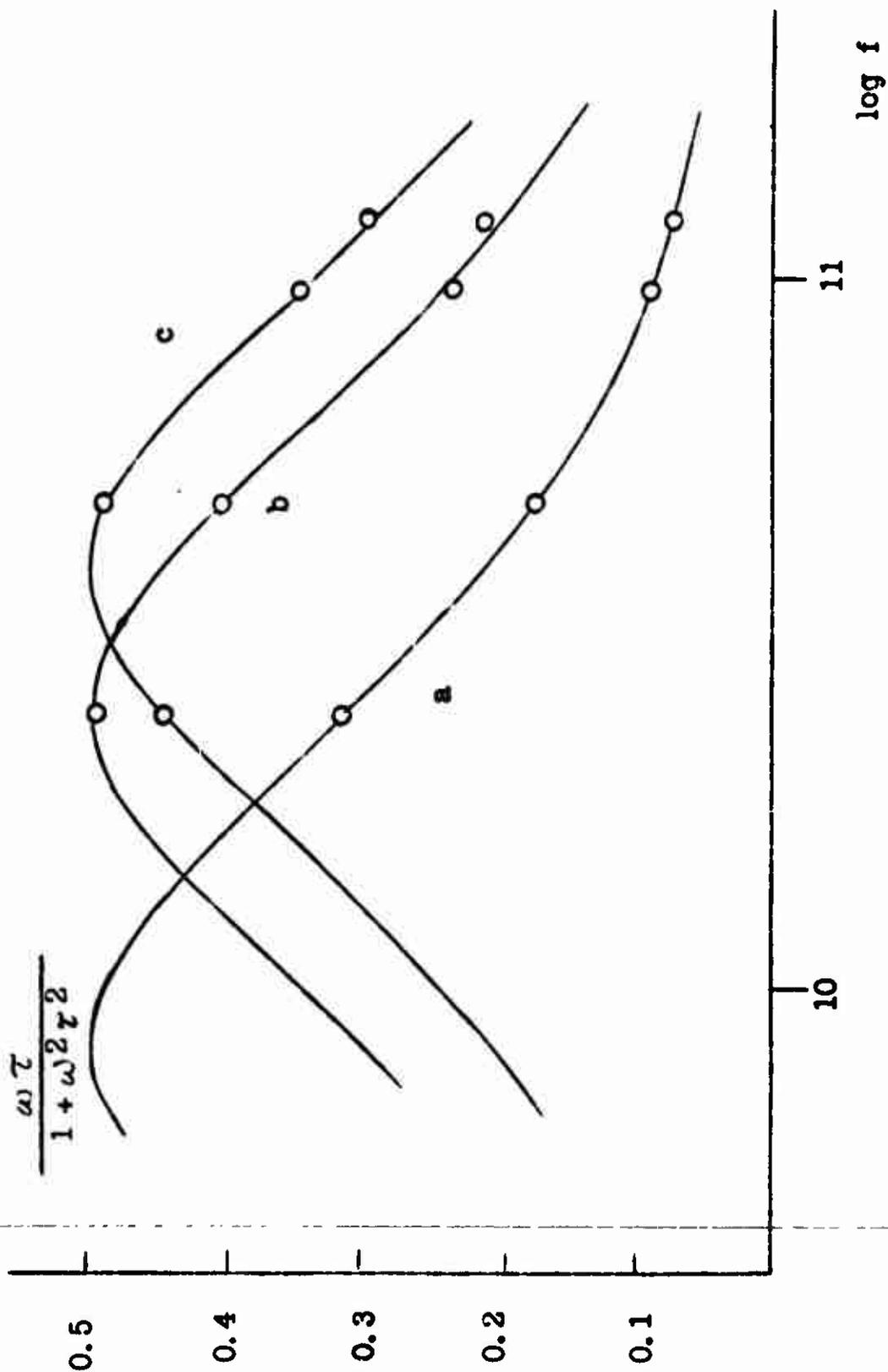
Fig. 2. Dielectric losses, in normalized units, of benzophenone
(a), diphenylamine (b), and diphenylether (c) measured
in dilute benzene solutions at 25°C. The solid lines are
Debye curves, calculated from the values given in Table II.
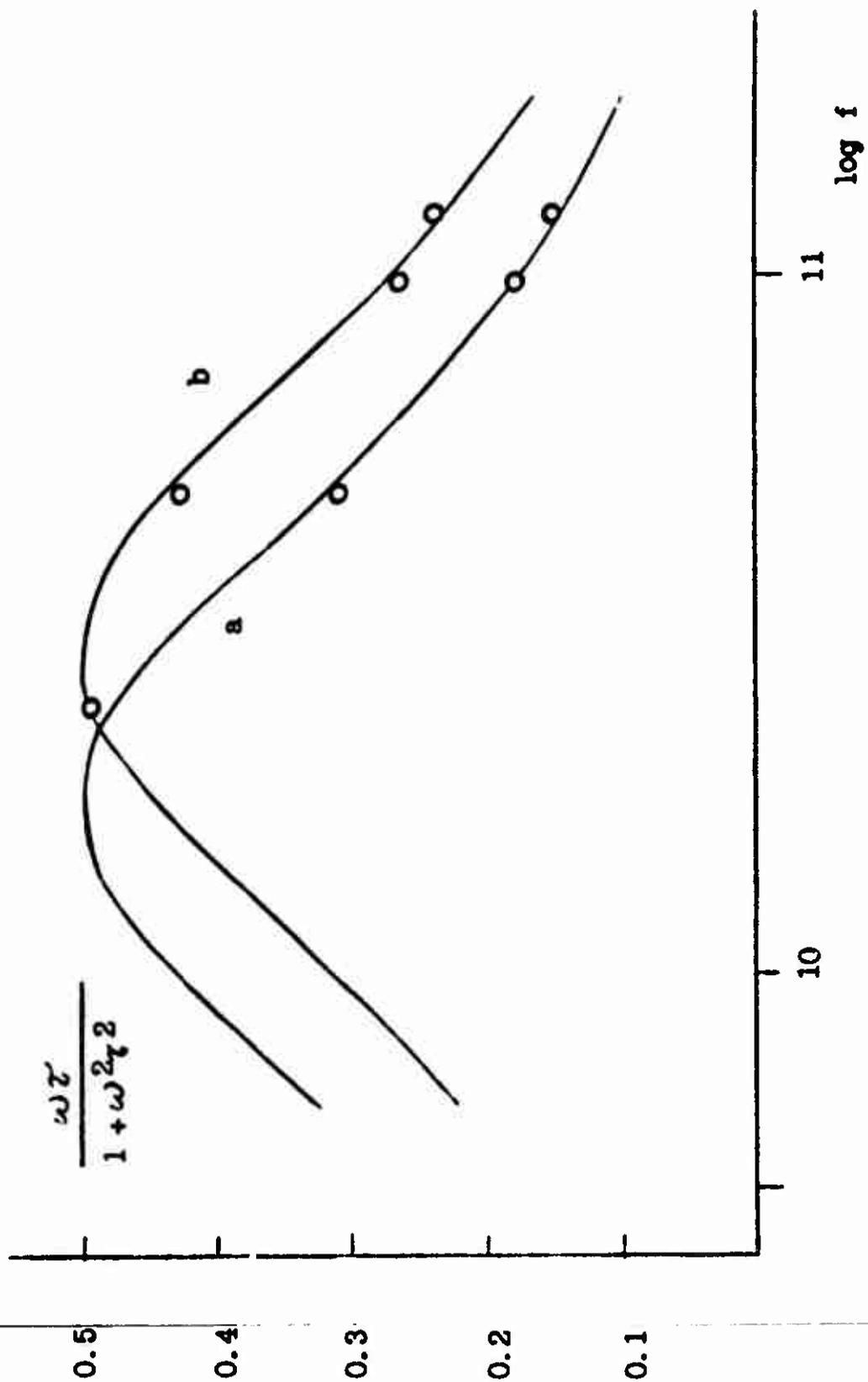
Fig. 3. Dielectric losses, in normalized units, of chlorobenzene (a) and aniline (b) measured in dilute benzene solutions at 25°C. The solid lines are Debye curves, calculated from the values given in Table II.

rigid molecule of similar dimensions. The same effect has been reported by Maier[8] for anisole, due to the mobility of the methoxy group. The dipole moment of aniline, 1.30 Debye, as determined in this work, is considerably lower than that reported in the literature,[6] 1.52 Debye. The latter was obtained from a static measurements of a_0 in benzene solution, with the assumption that the atomic polarizability does not exceed the electronic polarizability by much more than 10%. If, however, the atomic polarizability were unusually large, the dipole moment obtained by this method would be too high. A large atomic polarizability could possibly be explained by the existance of a low frequency vibration of the amino group. For α- and β-aminonapthalene, Bergmann[7] found atomic polarizabilities of 20%. However, since a_0 has not been measured in this work, further conclusions cannot be drawn.

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DETERMINATION OF THE COLLISION FREQUENCY OF FREE ELECTRONS IN FLAMES BY MICROWAVE ABSORPTION MEASUREMENTS. *

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In order to determine the concentration of free electrons in flame gases from microwave attenuation measurements it is necessary to know the collision frequency ν of the electrons. To the authors' knowledge only two not too well agreeing values of this parameter have been published by Belcher and Sugden[1] and by Kuhns,[2] respectively. In the course of the authors' research in flame spectroscopy a new determination of the electron collision frequency in flames of different temperatures suggested itself.

The acetylene-air flame of a Lundegårdh-type burner was placed between two waveguide horns (distance between horns 30 mm, burner slot perpendicular to waveguide axis, center of measuring zone 8 mm above burner top), and the flame was colored with atomized alkali salt solutions of known concentrations. The temperature of the flame gases, measured by a modified line reversal method, was 2480^{c}K. Thermal ionization of

the alkali atoms results in a concentration of free electrons of good time constancy. A microwave which traverses the flame plasma is attenuated by these free electrons. A more detailed description of the experimental setup and a brief resume of the theory on which these measurements are based is published elsewhere.[3]

The frequency dependence of the attenuation was measured in the range between 23,100 and 92,960 megacycles, using seven different frequencies. These measurements resulted in an electron frequency of 26×10^{10} sec^{-1}. Furthermore, the shape of the dispersion curve indicated that, within the experimental error, the electron collision frequency is independent of the electron velocity.[3]

Subsequent measurements at 24,665 megacycles and at 48,260 megacycles with flames of various temperatures and compositions showed that ν does not depend strongly on the flame conditions. In a propane-air flame of 2100°K, ν was found to be 27×10^{10} sec^{-1}. In acetylene flames of 2500°K and 2750°K a value of $\nu = 20 \times 10^{10}$ sec^{-1} resulted, in both cases. In these experiments a Meker-type burner was used whose flame is considerably more homogeneous in the direction of microwave propagation than that of a Lundegårdh burner in the direction perpendicular to the slot. The lower value of ν as obtained in the first determination can be qualitatively explained by the effect of the cooler boundary zones which is not negligible in this case.

Kuhns[2] measured a value of $\nu = 19 \times 10^{10}$ sec^{-1} for a propane-air flame of 2200°K. Belcher and Sugden[1] obtain $\nu = 8.8 \times 10^{10}$ sec^{-1} for a

coal gas air flame of the same temperature.

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MEASUREMENTS OF FREE ELECTRONS IN FLAMES.*

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* This article was written as an appendix to the paper on "Absorption and Dispersion of Microwaves in Flames" by Jürgen Schneider and F. W. Hofmann which appeared in the Air Force Technical Report No. 25.

APPENDIX

As in the case of Na, the microwave attenuation measurements in the vapors of heavy alkali elements, K, Rb and Cs, were carried out with 11 wavelengths ranging between 3 and 12 mm and widely varied concentrations of the aqueous metal salt solutions introduced into the flame. The concentrations ranged between 10^{-4} and 1 M. Accordingly, the attenuation values $\beta/d = 10 \log_{10} (P_o/P)/d$ ranged between 0.1 and 20 db/cm, and the rigorous equations (23) had to be applied to calculate the corresponding electron densities N and electron partial pressures p_e. The value of the electron-molecule collision frequency $\nu = 26 \times 10^{10}$ sec^{-1} gained from the investigation of Na vapor was used for the evaluation of N and p_e. The exact relationship between β/d and N can conviently be written as

$$ N = 2.169 \nu \ (1 + \omega^2/\nu^2) \beta/d \ \left[(1 + (1 + \omega^2/\nu^2) n''^2)^{1/2} - (\omega/\nu) n'' \right] $$

where $n'' = 3.452 \times 10^9 \ \beta/\omega d$

The results are consistent for all wavelengths applied.

The logarithms of the average values of the electron pressures p_e, in atm, for K and Cs are plotted in Figure 9, together with those for Na, vs. the logarithms of the molar concentrations C of the salt solutions of these metals. The correlation, i.e., the conversion factor between C and the total metal content $p(M_{tot})$ in the flame was obtained optically by measuring, on an absolute scale, the total line intensity of the resonance line of the Na vapor in the flame source. The

abscissa is labelled in both scales. It was assumed that, at the tempera-
ture of the flame (2430°K), all sodium compounds are completely dis-
sociated. Its degree of ionization is negligibly low at the relatively high
vapor densities at which the conversion factor was determined. Further-
more, it was assumed that this conversion factor is the same for all
metal solutions delivered into the flame by the same atomizer.

The solid curves in Figure 9 represent calculated values of the
electron pressure p_e as a function of the total metal content $p(M_{tot})$.
Equilibrium conditions with regard to the ionization of the vapors were
assumed, and the formation of hydroxides of K and Cs was taken into
account. Possible formation of OH^- -ions was disregarded. With
these assumptions the relationship between $p(M_{tot})$ and p_e is

$$p(M_{tot}) = p_e + p_e^2 (1 + \phi_M)/I_M$$

Here, I_M stands for the ionization equilibrium constant; its values for
Na, K, Cs were calculated with the Saha equation. The symbol ϕ_M
is introduced for the ratio $p(MOH)/p(M) = p(OH)/K_{MOH}$, following
H. Belcher and T. M. Sugden.* K_{MOH} stands for the chemical equili-
brium constant of the reaction ($MOH \rightleftharpoons M + OH$). The ratio ϕ_M remains
constant throughout the concentration range of added alkalis due to the

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* H. Belcher and T. M. Sugden, Proc. Roy. Soc. A202, 17 (1950).
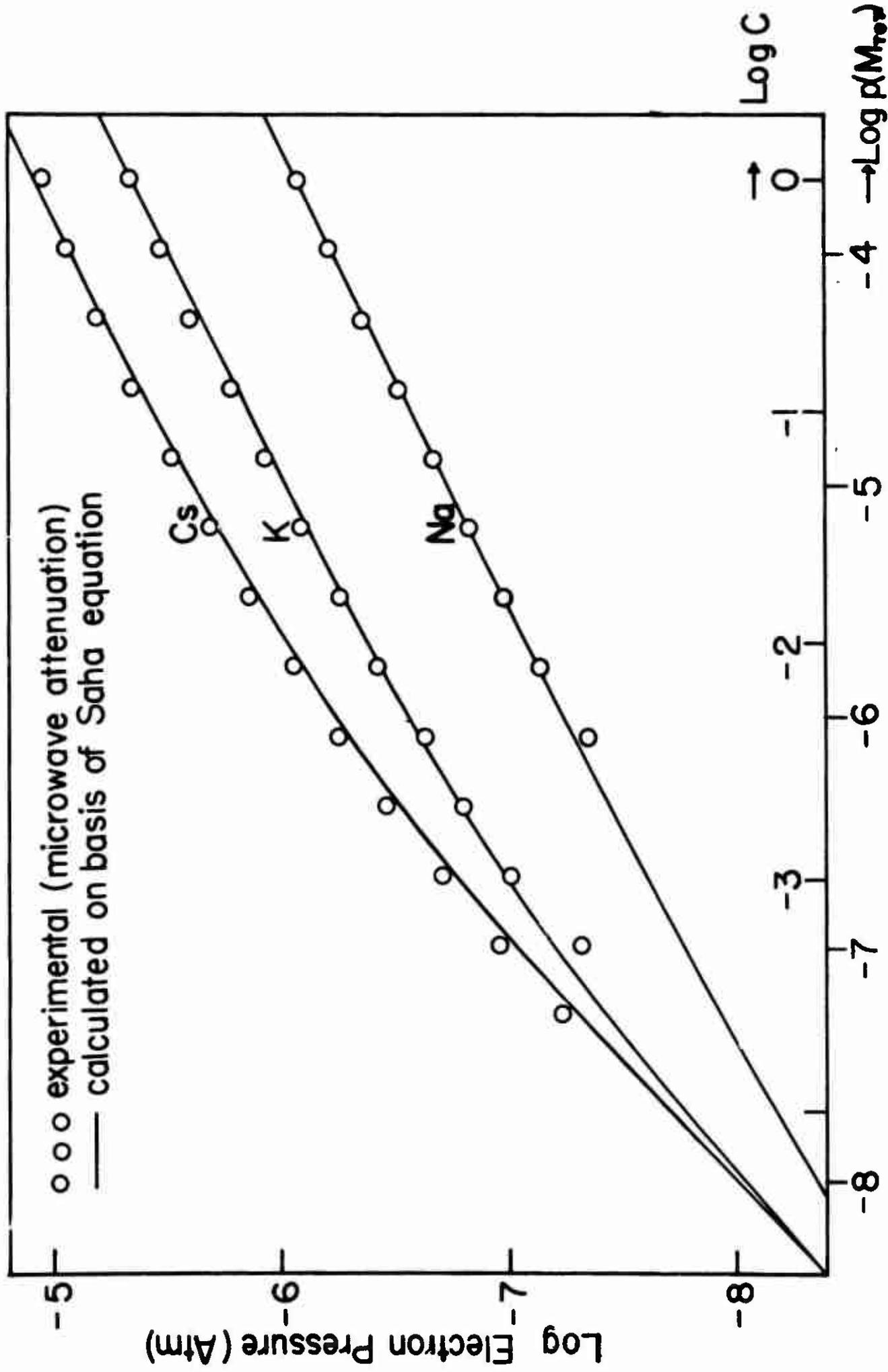
Figure 9. $p(M_{\text{TOT}})$ = total metal content in flame gases (in atm)

C = molar concentration of salt solution of metal

the relatively large OH-content of the flame. For large values of
$p(M_{tot})$ the general relation given above approaches asympototically
the form

$$p_e = \left[p(M_{tot}) I_M/(1 + \phi_M) \right]^{1/2}$$

Therefore, the ratio ϕ_M could be evaluated by comparing the asymptote
of the experimental high density curve (Log p_e vs Log C) for K and Cs
respectively with that for Na. An independent check on the ϕ_M-values
was obtained by comparing the photo-electrically measured absolute
total intensities of the resonance lines of the vapors at very low densities.

The fit of the calculated curves for the electron pressures to the
plotted measured values is rather satisfactory, considering the large
number of measured quantitites involved in the evaluation of p_e and
$p(M_{tot})$. A rather significant uncertainty arises from the somewhat vague
determination of the layer thickness of the vapors in the flame. The
flame thickness along the burner slot has to be known to find the conversion
factor between $P(M_{tot})$ and C. The flame thickness perpendicular to the
slot, i.e., in the direction of the microwave propagation is needed in
determining the electron density from the measured attenuation data. With
the relatively simple setup and method for the microwave attenuation
measurements the error limit of the plotted electron pressures - averaged
over the results with the 11 different wavelengths - was about $\pm 5\%$, for
medium and high vapor densities. At the lowest densities shown in

the graphs deviations of $\pm$ 10% occurred. In the case of Cs the deviations

of the experimental p_e values from the calculated curve amount to about 15%

and seem to be of a systematic nature, i.e. to the side of too high electron

pressures. Deviations from equilibrium conditions in the flame or the

neglect of side reactions in calculating the electron pressures may easily

account for differences of 15%. Possibly also the conversion factor which

correlates the molar concentrations of the solutions with the total amount

of metal in the flame may have slightly different values for different

elements.

In spite of the discussed deviations the results of these investigations

may be considered a good quantitative verification of the Saha equation. They

are of considerable significance for our studies of total line intensities

at low vapor densities where the heavy alkali atoms are largely ionized.

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