MILLIMETER AND SUBMILLIMETER WAVES IN PHYSICS

Walter Gordy
Department of Physics, Duke University
Durham, North Carolina

Reprinted from the PROCEEDINGS OF THE SYMPOSIUM ON MILLIMETER WAVES

POLYTECHNIC INSTITUTE OF BROOKLYN March 31, April 1, 2, 1959

MILLIMETER AND SUBMILLIMETER WAVES IN PHYSICS*

Walter Gordy
Department of Physics, Duke University
Durham, North Carolina

The millimeter and submillimeter range of the electromagnetic spectrum is a rich, but largely undeveloped, region. In this range many atoms, molecules, and crystals have sharp, strong, spectral lines that can now be measured with the remarkably high-resolution and high-precision methods that characterize microwave spectroscopy. The principal class of spectra studied extensively in the region is that arising from the rotation of molecules in the gaseous state. A potentially large class yet unexplored is vibrational spectra in solids. A third large class of spectra observable in the range can be broadly classified as electronic resonance, which encompasses cyclotron resonance, paramagnetic resonance, ferromagnetic and antiferromagnetic resonance, and plasma oscillations. An unusual class of millimeter-wave spectra is thought to arise from quantum transitions in superconducting solids at low temperature. Millimeter-wave measurements are proving useful in the evaluation of important physical constants and in the critical testing of basic physical theory.

I. 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 radiation 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 he had to discover microwaves; for it is difficult 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 extend his beach-head in both directions. Those who went to the longer wavelengths 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 thousands 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. I would like to point out

*This research was supported by the U.S. Air Force through the A.F. Office of Scientific Research, Air Research and Development Command.

Presented at the Symposium on Millimeter Waves, Polytechnic Institute of Brooklyn, March 31, April 1 and 2, 1959 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.

While reading the account of Hertz's discovery in the Encyclopedia Brittanica, 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 favor of physical science."

Despite Hertz's abandonment of engineering, centimeter waves were first used extensively for a practical device: radar. We can point to only one very significant pre-radar application of centimeter waves in physics: the measurement of the ammonia inversion frequency by Cleeton and Williams 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, using methods similar to his, generated and detected waves which he estimated to be only 6mm in length. The following year Lampa² reported the similar detection of wavelengths of 4 mm. Mobius³ in 1918 was unable to get waves shorter than 7 mm and expressed doubt that Lebedew or Lampa had done so. In 1923 Nichols and Tear⁴ 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 those of the present day 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 wavelength 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 Baeyer⁵ had reached wavelengths as long as 0.314mm as early as 1911. Thus the work of Nichols and Tear overlapped these earlier optical measurements and closed the gap between the radio and optical regions. A more extensive overlapping was performed the following year, 1924, by a Russian scientist, Glagolewa-Arkadiewa, ⁶ who produced and detected waves from 0.082 mm to 50 mm. 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? 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 and Cooley and Rohrbaugh 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 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 an engineering sense we can say that the microwave region was not effectively "thrown open" until cavity resonators and waveguide techniques were developed.

II. 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 millimeter or submillimeter regions. Therefore, from the initiation of the microwave 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 microwave 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 spectrometer, 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 broadbanded 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 type) as the nonlinear 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 centimeters in length, which connected the millimeter waveguide to the input waveguide. The center conductor was made to project into the centimeter guide in order to pick up the fundamental energy to be transmitted to the crystal. There were

various tuners to maximize the input and output energy, and 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 removed. To our satisfaction, this stripped-down version was not only more broad-banded but also 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 useable 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 region, 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, since they are adequately described in the original publications 13 and 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 $60 \, \mathrm{kmc/sec}$ in frequency for 29 molecules, was given at the New York Academy Conference on Microwave Spectroscopy, November 1952. 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. His predecessors, 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, Mr. 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. Detecting crystals had been effectively

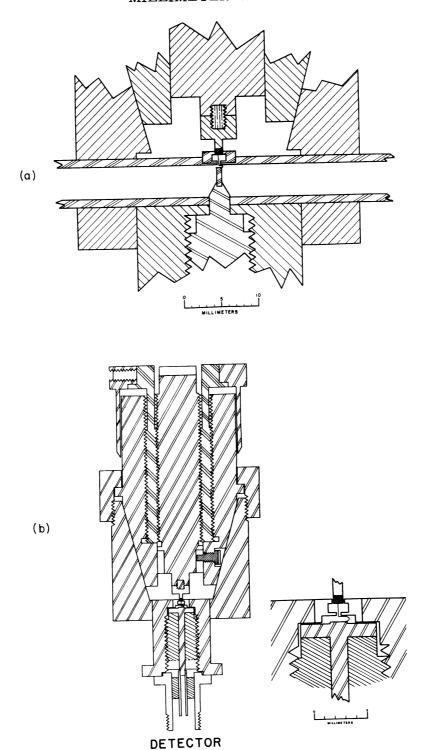


Fig. 1 (a) Cross section of millimeter and submillimeter harmonic generator, by King and Gordy. ^{19c} The differential screw mechanism not shown is the same as that for the detector unit. (b) Cross section of millimeter and submillimeter detector, by King and Gordy. ^{19c}

mounted within K-band waveguide in the M.I.T. Radiation Laboratory during World War II. 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 easily removed 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.

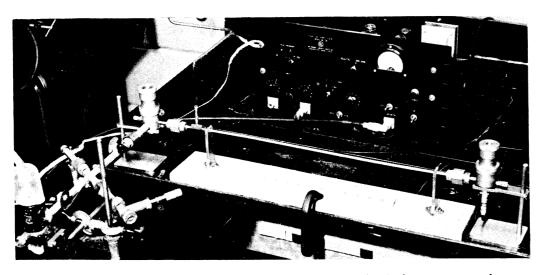


Fig. 2. The harmonic generator and detector units of Fig. 1 shown connected to the driver klystron and absorption cell as used in a microwave spectrometer.

The results of these modifications were gratifying beyond our expectations. We were immediately able to detect and measurg spectral lines down to 1 mm (300,000 mc/sec). Furthermore, the devices were so broad-banded 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. In addition to other measurements at Duke, 19 during the following months, one spectral measurement in the 1 to 2 mm region was made in the Columbia Radiation Laboratory, 20 and one in the Johns Hopkins Radiation Laboratory. Near the end of the year the same multiplier and detector, with some

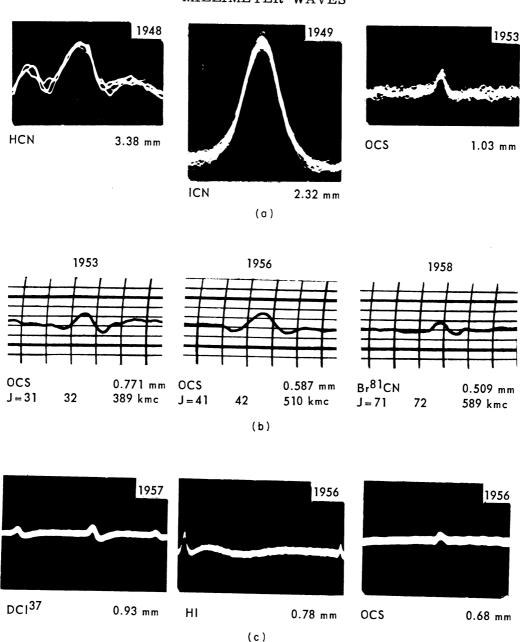


Fig. 3 (a) Chronological order of observation of spectral lines of increasing frequency in the 1- to 5 mm wave region. Left photograph from Ref. 18, middle from Ref. 14, right from Ref. 22. (b) Chronological order of observation of submillimeter lines of increasing frequency in the 0.50 to 1.0 mm region. Left curve from Ref. 22, middle from Ref. 25, right curve is unpublished results by Cowan and Gordy. (c) Cathode ray display of spectral lines demonstrating resolution and sensitivity now obtainable in the submillimeter 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)].

improvements in techniques, were used in our laboratory to extend microwave spectral measurements into the submillimeter wave region to 0.77 mm and thus open to the spectroscopist the last closed gap in the spectrum. This was accomplished with the aid of 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 and Zeeman 24 measurements down to wavelengths of about one millimeter.

In 1956 we received from Bell Labs some improved silicon multiplier crystals, developed and kindly given us by R.S. Ohl. Fortunately, these crystals fitted into the multiplier units we had already made. With these 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 easily able to extend the boundary of millimeter wave spectroscopy²⁵ from 0.77 to 0.58 mm in 1956, and, with some difficulty, down to 0.50 mm in 1958. A brief historical picture of our progress in extending the range of microwave spectroscopy by a factor of 10, from a half-centimeter to a half-millimeter, is given in Fig. 3.

We were also kindly supplied with some new silicon detector crystals by Microwave Associates. These crystals somewhat improved the submillimeter wave spectroscopy, 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 will, I understand, be given in a forthcoming paper from Bell Labs. 26 Although other laboratories were supplied with 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.

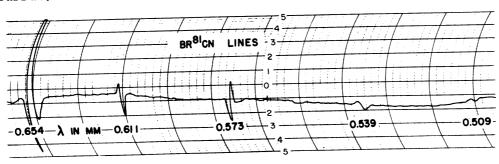


Fig. 4 Recording of Br⁸¹ CN rotational lines in the wavelength region of 0.65 mm (459 mc/sec) to 0.509 mm (589 mc/sec) obtained with 14th to 18th harmonics from E.M.I. klystron operating at 32,700 mc/sec with output power of 100 milliwatts. From left to right the rotational transitions are $J = 55 \longrightarrow 56$, $59 \longrightarrow 60$, $63 \longrightarrow 64$, $67 \longrightarrow 68$, and $71 \longrightarrow 72$. The line widths are of the order of 3 mc. Unpublished curve by Cowan and Gordy, obtained in 1958.

Molecule	Transition	Frequency Mc/sec	Reference
N ₂ O	J = 11 - 12	301,442.38 ± 0.60	27
CL37C12N14	J = 25 - 26	303,943.87 ± 0.65	27
ND ₃	J = 0 - 1, F = 1 - 1 F = 1 - 2 F = 1 - 0	309,908.24 309,909.54 309,911.41	а
Cl 35C 12N 14	J = 25 - 26	310,365.90 ± 0.65	27
O ¹⁶ C ¹² Se ⁸⁰	J = 38 - 39	313,217.57 ± 0.65	27
Br ⁸¹ C 12 _N 14	J = 38 - 39	319,345.52 ± 0.65	27
Br ⁷⁹ C 12N 14	J = 38 - 39	321,167.10 ± 0.65	27
DC l ³⁷	J = 0 - 1, F = 3/2-3/2 F = 3/2-5/2 F = 3/2-1/2	322,339.09 ± 0.13 322,352.33 ± 0.13 322,362.94 ± 0.13	Ь
DCl 35	J = 0 - 1, F = 3/2-3/2 F = 3/2-5/2 F = 3/2-1/2	323,282.28 ± 0.13 323,299.17 ± 0.13 323,312.52 ± 0.13	Ь
C ¹² O ¹⁶	J = 2 - 3	345,795.900 ± 0.090	36
ні ¹²⁷	J = 0 - 1, F = 5/2-5/2 F = 5/2-7/2 F = 5/2-3/2	385,000.11 ± 0.70 385,385.52 ± 0.70 385,548.80 ± 0.70	25
Br ⁸¹ C ¹² N ¹⁴	J = 47 - 48 J = 51 - 52 J = 55 - 56	492,907.0 425,575.9 458,226.2	С
O 16 C 12 S 32	J = 39 - 40 J = 41 - 42	486,184.7 510,457.3	с

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

Figure 4 illustrates the signal-to-noise ratio now obtainable on absorption lines in the submillimeter-wave region. At 0.57 mm $\,$

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

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

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 do not appear to be widely spaced relative to their widths, whereas actually each spectral line seen in the figure 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 useable 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, in a sweep like this one can 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 directly and accurately obtain 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. One often 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 submillimeter 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 that 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 that have been proposed or developed for giving milliwatts 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 $\rm\,H_2S^{33}\,$ showing resolution of the closely spaced $\rm\,S^{33}\,$

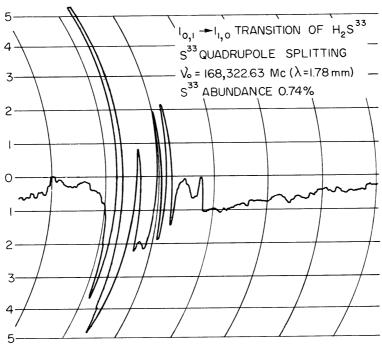


Fig. 5 Illustration of the sensitivity and resolution obtainable in the shorter millimeter wave region. The structure is due to S³⁵ nuclear quadrupole coupling. Total spread of the four stronger components is 10.1 mc, and the separation of the two equally intense, well resolved components to the right is 2.13 mc. From Burrus and Gordy, 1953. 19

nuclear quadrupole hyperfine structure with the S^{33} in its normal abundance of only 0.7%. This curve was obtained in 1953. ¹⁹ 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 Burrus and Graybeal ²³

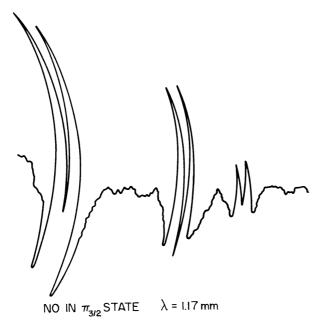


Fig. 6 Recording at 1.17 mm wavelength of the $J=3/2 \longrightarrow 5/2$ rotational transition of N14O in the upper $\pi_3/2$ electronic state. The gross splitting is due to N14 nuclear magnetic coupling; the small doublet splitting is due to interaction of electronic and rotational motions (Λ doubling). The components of the well resolved central doublet are spaced 2.49 mc apart. From Favero, Mirri and Gordy.²⁹

at Bell Laboratories have recently measured the Stark splitting of these components as well as those for the second rotational transition in the 1.2 mm region. Figure 7 illustrates the beautiful results that

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.

quency coverage of the spectrometer caused by its expanded sweep at a given harmonic: The HI lines displayed in Fig. 3 are 163 mc/sec apart and are displayed on the scope by a sweep through a single mode of the klystron, whereas the

STAR EFFECT OF NO, I.2 mm

6000 V/cm

ZERO FIELD

Fig. 7 Stark effect at 1.2 mm of the $3/2 \longrightarrow 5/2$ transition of $N^{14}O$ in the ground $\pi_{1/2}$ electronic state. From Burrus and Graybeal.²³

entire mode of the klystron covers only about 60 mc/sec. Likewise the mechanical 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 can be obtained.

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 accuracy of measurement is incurred over that obtainable with the fundamental power.

(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 submillimeter 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 $3\,\mathrm{mm}$ wavelength and mentioned some fixed-frequency gaseous attenuation measurements in progress on $\,\mathrm{DI}\,$ and $\,\mathrm{ND}_3.\,$ Apparently, however, the only spectral resonance observed with these techniques was the broad, unresolved inversion spectrum of $\ensuremath{\mathrm{ND}}_3$ 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 remeasurement 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, 34 and CO, 35 with a klystron-driven, crystal harmonic generator. So far as I know, they have made no further measurements with magnetron harmonics.

III. TYPES OF MEASUREMENT THAT CAN BE MADE WITH MILLIMETER AND SUBMILLIMETER 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 that 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.

Many subheads can be written under each of these eleven headings. 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 predominantly in the millimeter and submillimeterwave region. Some of the information that has already been obtained from millimeter and submillimeter-wave rotational spectra is listed in Tables 2, 3, 4, and 5.

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 c = 299,793.7 \pm 0.6 km/sec. Perhaps the largest potential application of millimeter and submillimeter—wave rotational spectra is for chemical analysis, for in this region the characteristic spectral transitions are sharp, strong, and abundant.

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

TABLE 2. Sp		s for some hydrogen vave spectroscopy a		from millimeter-
Molecule	B _o in mc∕sec	eQq coupling for CL, Br, or l in mc/sec	Bond length r _o in A	Reference
DC/25	161656.10	-67.3	1.28125	a
DCℓ ³⁷	161183.02	-53.0	1.28124	a
тс / ³⁵	111075.76	-67.0	1.28003	Ь
TCℓ ³⁷	110601.53	-53.0	1.28002	Ь
DBr ⁷⁹	127358.06	530.5	1.42144	a
DBr ⁸¹	127280.14	443.5	1.42144	a
TBr ⁷⁹	86252.24	530	1.42012	Ь
TBr ⁸¹	86174.33	443	1.42011	ь
DI 127	97537.10	-1823.3	1.61660	a
HI 127	192658.8	-1831	1.61972	c

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

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

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

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

TABLE 3. Spectral constants of hydrides and deuterides of nitrogen, phosphorus,	
arsenic, and antimony obtained from millimeter-wave spectroscopy at Duke	

Molecule	B _o	eQq coupling for N, As, or Sb	Bond angle	Bond length	Reference
N ¹⁴ D ₃	154162.7	-4.10	10 7°	1.0144	α
PH ₃	133478.3		93°27'	1.4206	ь
PD ₃	69470.41		93°10′	1.4166	Ь
As ⁷⁵ H ₃	112468.46	-160.1	91°50'	1.5192	С
As ⁷⁵ D ₃	57477.15	-165.9	91°30'	1.5145	С
Sb 121H3	88031.92	458.7	91°18′	1.7073	d
Sb121D3	44693.29	465.4	90°56'	1.7021	d
Sb 123H3	88015.54	586.0	91°18′	1.7073	d
sb ¹²³ D ₃	44677.13	592.8	90°56'	1.7021	d

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

has recently been made 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 thing, 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 occuring in

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

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

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

TABLE 4.	Some dipole moments	s from millimeter-wave s	pectroscopy
Molecule	Moment (Debye units)	Wavelength of Measurement (mm)	Reference
НСИ	2.986 ± 0.002	3.38	a
C0	0.112 ± 0.005	2.6	23
03	0.53 ± 0.02	2.5	Ь
H ₂ Se	0.24 ± 0.02	2.1	с
DI	0.316 ± 0.010	1.5	23
NO $(2\pi_{1/2})$	0.158 ± 0.006	1.2	23
PH ₃	0.578 ± 0.010	1.1	23

- a. Bhattacharya and Gordy, unpublished results.
- b. Trambarulo, Ghosh, Burrus and Gordy, J. Chem. Phys., Vol. 21, p. 85 (1953).
- c. Jache, Moser and Gordy, J. Chem. Phys., Vol. 25, p. 209 (1956).

Halogen Halide	C _l in mc/sec	C _l /g _l	C _I /g _I B _o	References
DC ℓ^{35}	< 0.05	~ 0	~ 0	α
DCL37	< 0.05	~ 0	~ 0	a
DBr ⁷⁹	0.15 ± 0.04	0.11	0.9	а
DBr ⁸¹	0.16 ± 0.04	0.11	0.9	а
DI ¹²⁷	0.16 ± 0.02	0.14	1.4	а
HI 127	0.26 + 0.05	0.23	1.2	25

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 super-heterodyne 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.

I hear by rumor that plasma investigations with millimeter waves (7) are in progress in many places. Certain other papers given at this symposium deal with this subject.

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 (kilogauss) =
$$\frac{\nu \,(\text{mc/sec})}{1400 \,\text{g}_{\text{eff}}}$$
,

where $g_{\rm eff}$ 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 required for observation of the resonance at 1 mm wavelength (300,000 mc/sec). However, in many crystals there is zero field splitting of the magnetic states or residual spin orbit coupling which makes $g_{\rm eff}$ 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 $\rm MnF_2$ 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 a 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 at 72 kmc/sec. The principal advantage of observing cyclotron resonance at high frequencies is that the resonance period can be made short 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 sufficient increase of the relaxation time to make cyclotron resonance observable. Low pressures must be used for electrons in gases. 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 superconducting state in superconducting solids. The late 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 Schrieffer⁴⁴ have recently evolved a more specific theory of superconductivity based on the postulate of the quantum gap. This quantum gap, which is of the order of kT, where T, is the critical temperature for reaching the superconducting state, falls in the millimeter or submillimeter 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 have been made by Glover and Tinkham⁴⁶ on thin films of tin on the other side of the gap with far-infrared techniques. 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 and for lead as 4.1 kT 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. 48 The superconducting gap in this substance falls at a lower frequency (~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, $E_g(0) = 3.25 \text{ kT}_c$, compares favorably with the value theoretically predicted, 3.52 ${
m kT}_{
m C}$, 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.

REFERENCES

- 1. Lebedew, Wied. Ann. Physik, Vol. 56, p. 1 (1895).
- Lampa, Wien. Ber., Vol. 105, pp. 587 and 1049 (1896).
 105, pp. 587 and 1049 (1896).
- 3. W. Mobius, "Über die Dispersion von Wasser und Athylalkohol zwischen 7 und 35 mm Wellenlänge und Vorversuche zur Verwendung noch kürzerer elektrischer Wellen", Ann. Der Phys., Vol. 62, pp. 293-322 (December 1920).
- (a) E. F. Nichols and J. D. Tear, "Short Electric Waves", Phys. Rev., Vol. 21, pp. 587-610 (June 1923).
 - (b) E. F. Nichols and J. D. Tear, "Joining the Infra-red and Electric Wave Spectra" Proc. Nat. Acad. Sci. U.S.A., Vol. 9, pp. 211-214 (June 1923).
- H. Rubens and O. von Baeyer, "On Extremely Long Waves emitted by the Quartz Mercury Lamp", Phil. Mag. (London), Vol. 21, pp. 689-695 (May 1911).
- 6. A. Glagolewa-Arkadiewa, "Short Electromagnetic Waves of Wavelength up to 82 Microns', Nature (London), Vol. 113, p. 640 (1924).
- 7. J. D. Tear, "The Optical Constants of Certain Liquids for Short Electric Waves", *Phys. Rev.*, Vol. 21, pp. 611-622 (June 1923).
- 8. M. Czerny, "Die Rotationsspektren der Halogenwasserstoffe", Z. Physik, Vol. 44, pp. 235-255 (August 8, 1927).
- 9. J. P. Cooley and J. H. Rohrbaugh, "The Production of Extremely Short Electromagnetic Waves", Phys. Rev., Vol. 67, p. 296 (1945).
- C. E. Cleeton and N. H. Williams, "Electromagnetic Waves of 1.1 cm Wave-Length and the Absorption Spectrum of Ammonia", Phys. Rev., Vol. 45, pp. 234-237 (February 15, 1934).
- 11. R. Beringer, "The Absorption of One-Half Centimeter Electromagnetic Waves in Oxygen", Phys. Rev., Vol. 70, pp. 53-57 (July 1946).
- (a) W. Gordy, A. G. Smith and J. W. Simmons, "Microwave Spectra: Methyl Iodide", Phys. Rev., Vol. 71, p. 917 (June 15, 1947).
 - (b) W. Gordy, W. V. Smith, A. G. Smith and H. Ring, "Millimeter-Wave Spectra: Hyperfine Structure of BrCN and ICN", Phys. Rev., Vol. 72, pp. 259-260 (August 1, 1947).
 - (c) W. Gordy, J. W. Simmons and A. G. Smith, "Nuclear and Molecular Constants from Microwave Spectra: Methyl Chloride and Methyl Bromide", *Phys. Rev.*, Vol. 72, pp. 344-345 (August 15, 1947).
 - (d) H. Ring, H. Edwards, M. Kessler and W. Gordy, "Microwave Spectra: Methyl Cyanide and Methyl Isocyanide", *Phys. Rev.*, Vol. 72, pp. 1262-1263 (December 15, 1947).
- 13. (a) W. Gordy, "Microwave Spectroscopy", Revs. Modern Phys., Vol. 20, pp. 668-717 (October 1948).
 - (b) A. G. Smith, W. Gordy, J. W. Simmons and W. V. Smith, "Microwave Spectroscopy in the Region of Three to Five Millimeters" *Phys. Rev.*, Vol. 75, pp. 260-263 (January 15, 1949).
- 14. O. R. Gilliam, C. M. Johnson and W. Gordy, "Microwave Spectroscopy in the Region from Two to Three Millimeters", *Phys. Rev.*, Vol. 78, pp. 140-144 (April 15, 1950).

- J. H. Burkhalter, R. S. Anderson, W. V. Smith and W. Gordy, "The Fine Structure of the Microwave Absorption Spectrum of Oxygen", Phys. Rev., Vol. 79, pp. 651-655. (August 15, 1950).
- R. S. Anderson, C. M. Johnson and W. Gordy, "Resonant Absorption of Oxygen at
 2.5 Millimeter Wavelength", Phys. Rev., Vol. 83, pp. 1061-1062 (September 1,1951).
- 17. W. Gordy, "Spectroscopy above 60 kmc", Ann. N. Y. Acad. Sci., Vol. 55, pp. 774-788 (November 21, 1952).
- 18. W. C. King and W. Gordy, "One-to-Two Millimeter Wave Spectroscopy, Part I", Phys. Rev., Vol. 90, pp. 319-320 (April 15, 1953).
- 19. (a) C. A. Burrus and W. Gordy, "One-to-Two Millimeter Wave Spectroscopy, Fart II", Phys. Rev., Vol. 92, pp. 274-277 (October 15, 1953).
 - (b) C. A. Burrus and W. Gordy, "One-to-Two Millimeter Wave Spectroscopy, Part III: NO and DI", Phys. Rev., Vol. 92, pp. 1437-1439 (December 15, 1953).
 - (c) W. C. King and W. Gordy, "One-to-Two Millimeter Wave Spectroscopy, Fart IV: Experimental Methods and Results for OCS, CH₃F, and H₂O", Phys. Rev., Vol. 93, pp. 407-412 (February 1, 1954).
 - (d) W. Gordy and C. A. Burrus, "Spectrum of DBr in the One-Millimeter Wave Region", Phys. Rev., Vol. 93, pp. 419-420 (February 1, 1954).
- 20. J. A. Klein and A. H. Nethercot, "Microwave Spectrum of DI at 1.5-mm Wavelength", Phys. Rev., Vol. 91, p. 1018 (August 15, 1953).
- F. D. Bedard, J. J. Gallagher and C. M. Johnson, "Microwave Measurement of Do for CO", Phys. Rev., Vol. 92, p. 1440 (December 15, 1953).
- 22. C. A. Burrus and W. Gordy, "Submillimeter Wave Spectroscopy", Phys. Rev., Vol.93, pp. 897-898 (February 15, 1954).
- 23. (a) C. A. Burrus, "Stark Effect from 1.1 to 2.6 Millimeter Wavelength: PH3, PD3, DI, and CO", J. Chem. Phys., Vol. 28, pp. 427-429 (March 1958).
 - (b) C. A. Burrus and J. D. Graybeal, "Stark Effect at 2.0 and 1.2 Millimeters Wavelength: Nitric Oxide", Phys. Rev., Vol. 109, pp. 1553-1556 (March 1, 1958).
- 24. C. A. Burrus, "Zeeman Effect in the 1- to 3-Millimeter Wave Region: Molecular g Factors of Several Light Molecules" J. Chem. Phys., Vol. 30, pp. 976-983 (April 1959).
- 25. M. Cowan and W. Gordy, "Further Extension of Microwave Spectoscopy in the Submillimeter Wave Region", Phys. Rev., Vol. 104, pp. 551-552 (October 15, 1956).
- 26. R. S. Ohl, P. P. Budenstein and C. A. Burrus, "Improved Diode for the Harmonic Generation of Millimeter- and Submillimeter-Waves", Rev. Sci. Instr., (Sept. 1959).
- 27. C. A. Burrus and W. Gordy, "Millimeter and Submillimeter Wave Spectroscopy", *Phys. Rev.*, Vol. 101, pp. 599-602 (January 15, 1956).
- 28. C. A. Burrus and W. Gordy, "Spectra of Some Symmetric-Top Molecules in the One-to-Four Millimeter Wave Region", J. Chem. Phys., Vol. 26, pp. 391-394 (February 1957).
- 29. P. G. Favero, A. M. Mirri, and W. Gordy, "Millimeter-Wave Rotational Spectrum of NO in the $2\pi 3/2$ State", Phys. Rev., Vol.114, pp.1534-1537 (June 15, 1959).
- 30. M. Mizushima, J. T. Cox and W. Gordy, 'Zeeman Effect in the Rotational Spectrum of NO" Phys. Rev., Vol. 98, pp. 1034-1038 (May 15, 1955).
- 31. J. H. N. Loubser and C. H. Townes, "Spectroscopy between 1.5 and 2 mm Wavelength using Magnetron Harmonics" *Phys. Rev.*, Vol. 76, p. 178 (A) (1949). [See also, J. H. N. Loubser and J. A. Klein, "Absorption of Millimeter Waves in ND3", *Phys. Rev.*, Vol. 78, p. 348 (A) (May 1, 1950)].
- 32. A. H. Nethercot, J. A. Klein, J. H. N. Loubser and C. H. Townes, "Spectroscopy near the Boundary between the Microwave and Infrared Regions", Nuovo Cimento, Suppl. Vol. 8, pp. 358-363 (June 1952).
- 32a. A.H. Nethercot, J.A. Klein and C.H. Townes, "Microwave Spectrum and Molecular Constants of Hydrogen Cyanide", Phys. Rev., Vol. 86, pp. 789-799 (June 1, 1952).

- 33. J.A. Klein, J.H.N. Loubser, A. H. Nethercot, Jr., and C. H. Townes, "Magnetron Harmonics at Millimeter Wavelengths", Rev. Sci Inst., Vol. 23, pp. 78-82 (February 1952).
- 34. B. Rosenblum and A. H. Nethercot, "Microwave Spectra of Tritium Iodide and Tritium Bromide", Phys. Rev., Vol. 97, pp. 84-85 (January 1, 1955).
- B. Rosenblum, A. H. Nethercot, Jr., and C. H. Townes, "Isotopic Mass Ratios, Magnetic Moments and the Sign of the Electric Dipole Moment in Carbon Monoxide", Phys. Rev., Vol. 109, pp. 400-412 (January 15, 1958).
- 36. W. Gordy and M. J. Cowan, "Precision Measurements of Millimeter and Submillimeter Wavelengths", Bull. A. P. S., Vol. 2, No. 4, pp. 212-213 (April 1957).
- 37. D. H. Rank, "Velocity of Light Derived from Spectroscopic Measurements on Carbon Monoxide", Bull. A. P. S., Vol. 2, No. 4, p. 213 (April 1957).
- R. W. Rampalla, R. C. Miller and C. F. Smyth, "Measurements of Dielectric Constant and Loss at 3.1-mm Wavelength by an Interometric Method", J. Chem. Phys., Vol. 30, pp. 566-573 (February 1959).
- 39. A. van Roggen, L. van Roggen, "Paramagnetic Resonance of Free Radicals at Millimeter-Wave Frequencies", Phys. Rev., Vol. 105, pp. 50-55 (January 1,1957).
- 40. Charles Kittel, Introduction to Solid State Physics (New York: John Wiley, 1953)
 p. 193.
- 41. F. M. Johnson and A. H. Nethercot, Jr., "Antiferromagnetic Resonance in MnF₂", Phys. Rev., Vol. 114, pp. 705-716 (May 1, 1959).
- 42. P. Nozieres, "Cyclotron Resonance in Graphite", Phys. Rev., Vol. 109, pp. 1510-1521 (March 1, 1958).
- 43. F. London, Superfluids, Vol. I (New York: John Wiley, 1950) pp. 142-155.
- 44. J. Bardeen, L. N. Cooper and J. R. Schrieffer, "Theory of Superconductivity", *Phys. Rev.*, Vol. 108, pp. 1175-1204 (December 1, 1957).
- 45. G. S. Blevins, W. Gordy, W. M. Fairbank, "Superconductivity at Millimeter Wave Frequencies", Phys. Rev., Vol. 100, pp. 1215-1216 (November 15, 1955).
- R. E. Glover, III and M. Tinkham, "Conductivity of Superconducting Films for Photon Energies between 0.3 and 40 kT_c", Phys. Rev., Vol. 108, pp. 243-256 (October 15, 1957).
- F. L. Richards and M. Tinkham, "Far Infrared Energy Gap Measurements in Bulk Superconductors", Phys. Rev. Letters, Vol. 1, pp. 318-320 (November 1, 1958).
- M. A. Biondi and M. P. Garfunkel, "Measurement of the Temperature Variation of the Energy Gap in Superconducting Aluminum", Phys. Rev. Letters, Vol. 2, pp. 143-145 (February 15, 1959).