REVIEWS OF MODERN PHYSICS VOLUME 20, NUMBER 4 OCTOBER, 1948

Microwave Spectroscopy*

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I. INTRODUCTION

SO often in the past has an instrument or a body of knowledge developed by the pure scientist found use in practical affairs that it is gratifying to find an outstanding example of reciprocity. The microwave techniques and instruments developed almost exclusively for the very practical device, radar, are now of great help to those seeking to extend further the bounds of basic knowledge of nature. The already large and rapidly growing new field in pure physics, "microwave spectroscopy," owes its existence almost wholly to the wartime developments in microwave radar. So far as I know, only one paper on microwave spectroscopy exists in prewar literature. This reports the pioneering experiment by Cleeton and Williams,[1] who used semi-optical methods to detect absorption of ammonia in the wave-length region of 1.25 cm. Yet in the brief period since the ending of World War II no less than 100 research papers dealing with microwave spectra have appeared, and it is now timely that a review article be written on the subject.

It is appropriate that this review begin with a comparison, or contrast, of optical with microwave spectroscopy. Though the two methods yield the same type of information because both of them are used to measure the quantitized energy changes in atoms and molecules, yet the techniques and instruments used in the two are completely different. Furthermore, the regions of the electromagnetic spectrum which can be effectively covered by the two methods do not overlap.

Though electronic devices have long been used in optical spectroscopy as auxiliary aids such as automatic recorders, microphotometers, etc., the

* This work was supported by Contract No. W-28-099-ac-125 with the Army Air Forces, Air Materiel Command.

[1] C. E. Cleeton and N. H. Williams, Phys. Rev. **45**, 234 (1934).

basic components of a spectroscope remained optical in nature until the advent of the "microwave spectroscope." In microwave spectroscopy the instrument of dispersion, prism or grating, which is the heart of the optical spectroscope, has been removed. This elimination of the dispersive instrument is made possible by the use of a fundamentally different source of radiation, which is an electronically controlled oscillator. This oscillator generates essentially monochromatic, single-phase radiation which makes possible the use of an electrically tuned receiver or detector. Because of its controlled source and tuned detector, the microwave spectroscope is an instrument of exceptional sensitivity and resolving power. Its resolving power is of the order of 100,000 times that of the best infra-red grating spectrometer. The wave-length or frequency measurements are also made electronically and are now being made to seven figures. The indicator is usually an electronic instrument, the cathode-ray oscilloscope. The synchronization of the cathode-ray sweep with the frequency modulation of the source allows a visual display of the spectral lines under study.

Since the regions of microwave and optical spectroscopy do not overlap, the two methods do not compete but rather complement each other. Microwave spectroscopy can be used to study heavy molecules which cannot be studied very effectively with optical techniques. It can be used with much more success than can optical methods for investigating the effects of the nucleus upon the molecular spectra. Indeed, because of exceptional resolving power microwave spectroscopy promises to be one of the most powerful methods yet developed for the study of nuclear spins and nuclear quadrupole moments.

The experiment of Cleeton and Williams in 1934 is of interest not only because it represents the first spectral measurements in the microwave region, but also because this first spectral work between the optical and radio regions of the electromagnetic spectrum was done by a hybrid spectroscope which employed in a fundamental way methods both optical and electronic. The source was essentially electronic, being a split-anode magnetron which Cleeton and Williams constructed by scaling down models of 9-cm tubes supplied them by Westinghouse. They were able to obtain radiation at a wave-length as low as 1 cm, at that time the lowest wave-length obtained with a vacuum tube. These tubes were tunable over a range of about 30 percent. They used four tubes to map the ammonia inversion spectrum at atmospheric pressures in the region of 1.06 to 3.8-cm wave-length. The collimating system consisted of parabolic mirrors, and though the light was essentially monochromatic, an echelette grating was used for wave-length measurement. No electronic amplification was employed. The signals, after being detected by an iron pyrite-phospho-bronze crystal, were passed directly to a sensitive galvanometer. The absorption cell which they employed is probably unique in spectral measurements: it was essentially a rubber cloth bag.

Despite this hopeful beginning, it was not until after the wartime development of microwave instruments and techniques that further significant advances in microwave spectroscopy were made.

Though its boundaries are not definite, the microwave region has apparently come to mean that part of the electromagnetic spectrum between the long wave-lengths of infra-red where optical methods must be used and the region where more conventional electronic tubes and r-f components begin to be effective. It is the region where cavity oscillators, cavity wave meters, and wave-guide components become effective and convenient in size. With these typically microwave components it is now possible to make spectral measurements in the region from about 3-mm wave-length to about 20-cm wave-length. Because absorption lines of molecules are generally more abundant and stronger in the shorter wave-length regions, the millimeter region is probably of most interest for microwave spectroscopy. In the Massachusetts Institute of Technology Radiation Laboratory, Beringer,[2] who used second-harmonic power from centimeter-wave oscillators to measure the absorption of oxygen from 4.8 to 6.1 millimeters, was the first to make spectral measurements in the millimeter-

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

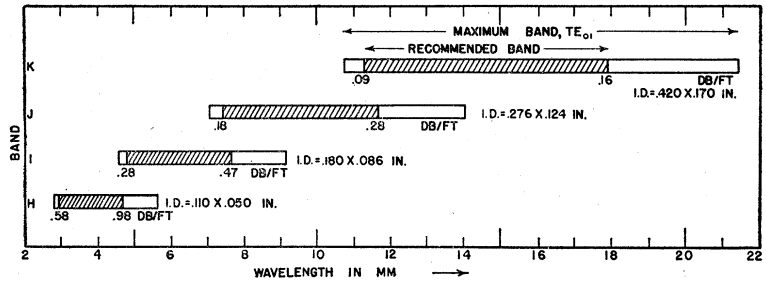


FIG. 1. Sizes and losses for millimeter wave guide (coin silver). The designation *H*, *I*, *J* is that adopted at Duke for the sub-*K*-bands as indicated.

wave region. We at Duke[3] have extended the range of measurement from 6 mm to the centimeter region and down to wave-lengths of 3 millimeters.

II. INSTRUMENTS AND EXPERIMENTAL METHODS

Notwithstanding the newness of the field, there is a considerable body of knowledge and a variety of instruments and techniques which can be employed to advantage in microwave spectroscopy. In an article of this scope it is impossible to give more than a fraction of this information. Fortunately, the Massachusetts Institute of Technology Radiation Laboratory Series,[4] which is now coming off the press, other recent books,[5] and articles[5] provide remarkably complete and up-to-date source of information about microwave theory, components, and techniques, and make inclusion of much detail unnecessary. It will be the purpose of this discussion to describe the adaptations and alterations in microwave radar instruments for microwave spectroscopy, and to indicate the type of knowledge which is needed and where it may be found.

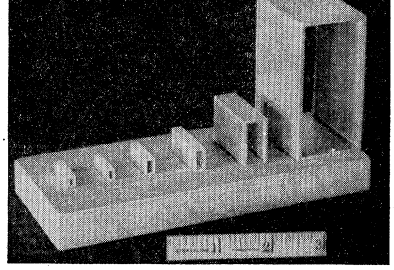


FIG. 2. Segments of wave guide. Left to right: *H*, *I*, *J*, *K*, *X*, *S* bands. An inch scale is shown.

A. Wave Guide and Associated Components

Wave guide.—Usually rectangular wave guide is used in microwave spectroscopy. Several sizes are required to cover the region defined above. The longer wave-length limit for a given size of rectangular guide is determined by the cut-off wave-length given in terms of the guide dimensions a and b, by the formula:

$$\lambda_c = 2/((m/a)^2+(n/b)^2)^{\frac{1}{2}}, \qquad (1)$$

which holds for both TE (transverse electric) and TM (transverse magnetic) modes. Here m and n are integers designating the particular mode. Thus, for the lowest mode TE_{01}, $\lambda_c = 2b$, or twice the longer dimension of the guide. The same formula is used in choosing a and b to cut out higher modes so that this formula defines the band width of the wave guide for propagation of the dominant mode. In Fig. 1** are given the different sizes of wave guide*** appropriate to the different regions indicated with the losses given for the recommended upper and lower wave-length ranges. Following the convention for the centimeter waves, it is convenient to designate the millimeter bands covered by different sized wave guide with letters: *H*, *I*, *J*, etc. Segments of wave guides are shown in Fig. 2.

[3] W. Gordy, W. V. Smith, and A. G. Smith, Phys. Rev. **72**, 259 (1947); J. W. Simmons and W. Gordy, Phys. Rev. **73**, 713 (1948); A. G. Smith, W. Gordy, J. W. Simmons, and W. V. Smith, to be published.

[4] Massachusetts Institute of Technology, L. N. Ridenour, editor-in-chief, *Radiation Laboratory Series* (McGraw-Hill Book Company, Inc., New York, 1947), Vol. 1–28.

[5] E. U. Condon, "Principles of microwave radio," Rev. Mod. Phys. **14**, 341 (1942); J. C. Slater, "Microwave electronics," Rev. Mod. Phys. **18**, 441 (1946). Radio Research Laboratory Staff, Harvard University, H. J. Reich, editor, *Very High-Frequency Techniques* (McGraw-Hill Book Company, Inc., New York, 1947), Vol. I–II.

** I am indebted to A. G. Smith for making this figure.

*** Coin silver wave guide in these sizes is obtainable from Horton-Angell Company, Attleboro, Massachusetts.

The attenuation for the dominant TE_{01} mode of a rectangular silver guide in terms of its smaller and larger dimensions a and b and the wave-length λ, all in cm, is:

$$\alpha_c = 0.142 b^{-\frac{3}{2}}[(b/2a)(2b/\lambda)^3+1] \times[(2b/\lambda)^3-(2b/\lambda)]^{-\frac{1}{2}} \text{ db per meter.} \quad (2)$$

For gold plated guide these values should be multiplied by 1.23, for copper by 1.03, and for brass by 2.08.

Cells.—Like most microwave components, absorption cells can be, and are, made in a variety of ways. They are most frequently made from sections of rectangular wave guide, with thin mica windows to seal the cells. Since there are no couplers, T-sections, slots, etc., in the absorption cell, it is possible to use oversized guide without exciting unwanted modes. This is particularly desirable for the millimeter-wave region where the very small-sized guide required to suppress higher modes attenuates heavily the dominant mode. Figure 3 gives the losses for 5-mm waves in wave guide of different sizes as measured in this laboratory by A. G. Smith. Here at Duke we have used S-band guide ($3'' \times 1\frac{1}{2}''$) very effectively for absorption cells in the region from 3- to 5-mm wave-length.[3] Losses were very low even for the shortest wave-length, and no more than the usual troubles were encountered with reflections. In other regions oversized cells are desirable to avoid saturating the molecules with radiation. With a gradually tapered section it is possible to connect the oversized guide to the smaller guide without objectionable reflections. The absorption of gas in a wave-guide cell is greater than that in a free-space cell of equal length by a factor, λ_g/λ, where λ is the free-space wave-length and λ_g is the wave-length in the guide, which is given by

$$\lambda_g = \lambda \Big/ \left[1-\left(\frac{\lambda}{\lambda_c}\right)^2\right]^{\frac{1}{2}}. \quad (3)$$

Here λ_c is the cut-off wave-length defined by (1).

Resonant cavities also are frequently used. It can be shown that the effective absorbing path in a resonant cavity is of the order of $(\lambda^2/\pi\lambda_g)Q_L$, which for a high Q cavity is equivalent to a very long cell. Q_L here represents the Q of the loaded cavity. The resonant cavity is especially suited to studies of the Zeeman effect because the magnetic field may be applied easily. Since cavities of small volume can be used, it is also desirable when rare gases are being investigated.

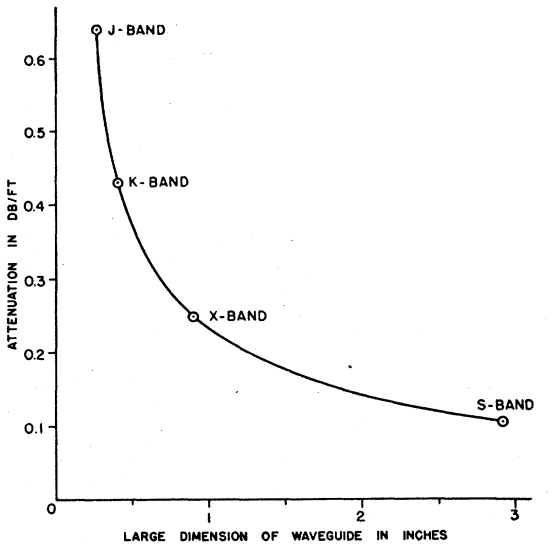


FIG. 3. Experimental losses of 5-mm. waves in rectangular guide of different sizes. The J- and K-band guide is of coin silver. The X- and S-band is of brass.

Free-space cells can also be used. For millimeter waves, broad-banded horns of convenient size can be made to focus and to receive the radiation.

For modulating the lines with an electrical field a semi-free-space cell might be used to advantage. A horn, designed to focus the radiation in one dimension only, would feed the energy across a small gap, or choke coupling, into a plane wave-guide cell open at the sides. The cell would then feed into a second horn, connected to the receiver. To put a long cell of this type into a short tank for convenient evacuation, a labyrinth construction may be used, or, as W. V. Smith has suggested, the cell may be folded into a compact spiral. Since the opposite plates of the plane wave guide are not in electrical contact, the electric field can be applied across these plates. It is believed that lower losses as well as a more uniform field can be obtained with this system than with the usual method of putting a metal strip supported by a dielectric material down the center of a rectangular wave guide. The method allows a spreading of energy in a cell to decrease molecular

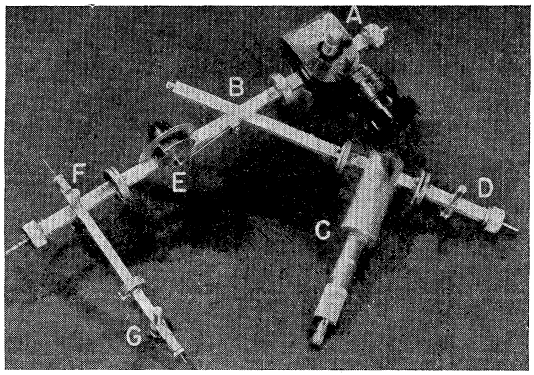


FIG. 4. Some Duke millimeter-wave components: (a) J-band oscillator; (b) J-band directional coupler; (c) J-band wave meter; (d) J-band crystal detector; (e) J-band attenuator; (f) crystal converter for J to H band; (g) H-band crystal detector.

saturation, while maintaining the electrodes close together so that a high voltage source is not required for modulation. It is also a broad-banded device.

Other wave-guide components.—Other wave-guide components needed, such as choke and flange couplers, crystal mounts, directional couplers, T-sections, and attenuators, are usually more narrow-banded than the wave guide itself. Hence, a considerable number of components of the same type but of different size are necessary to cover the workable microwave region. Descriptions and details of the design of such components are available elsewhere[4,5] for certain regions above 1-cm wave-length. These can usually be scaled down for the millimeter-wave region. However, as the wave-length is decreased, increasing precision is required to make these components. For this reason it is often necessary to alter the designs. It is usually much easier to make a good contact joint in the millimeter-wave region than to make a satisfactory choke joint. Increasing use should be made of the TE_{01} mode in circular wave guide and in cylindrical cavities. This mode has the unique property that attenuation actually decreases as the frequency increases. Details on some essential millimeter-wave components will be given in later sections. See Figs. 4 through 7.

B. Sources

Klystrons and associated power supplies.—The most common source of radiation is the reflex klystron oscillator. Though this tube is of rather recent development,[6] it is now a familiar instrument to most physicists. There are a number of variations of the tube which are due to differences in details of construction—for example, Oxford, Shepherd-Pearce, Neher, or McNally tubes. These differ in such details as the arrangement of the cavity, internal or external, and the manner in which the cavity is tuned. However, they all operate on the same principle of velocity modulation of an electron beam and a drift space in which the velocity modulated electrons form bunches and are reversed by a reflector and sent back through the same cavity in such a phase as to give up energy to the oscillating field of the cavity. The reflex klystron which has only one cavity is considerably easier to tune than the earlier models which employed a separate cavity for bunching of electrons and for generation of power. The two-cavity klystron has been used advantageously as a frequency multiplier in measuring frequencies of absorption lines. In this operation, however, it is not necessary to retune the klystron once it is set to the desired frequency.

There are certain features of the klystron which make it a very satisfactory source of radiation for spectroscopy. Though it generates relatively low power, only a few milliwatts as compared to a few megawatts peak power which can be generated by some magnetrons, this is not a particular disadvantage because of the saturation effect in molecules and because of the

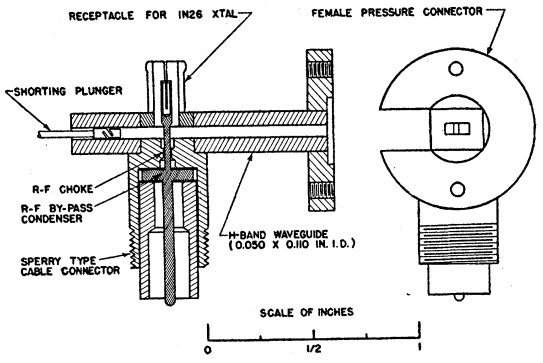


FIG. 5. Details of H-band crystal mount. (From Smith, Gordy, Simmons, and Smith (reference 25).)

[6] R. H. Varian and S. F. Varian, J. App. Phys. **10**, 321 (1939); W. G. Hahn and G. F. Metcalf, Proc. I.R.E. **27**, 106 (1939).

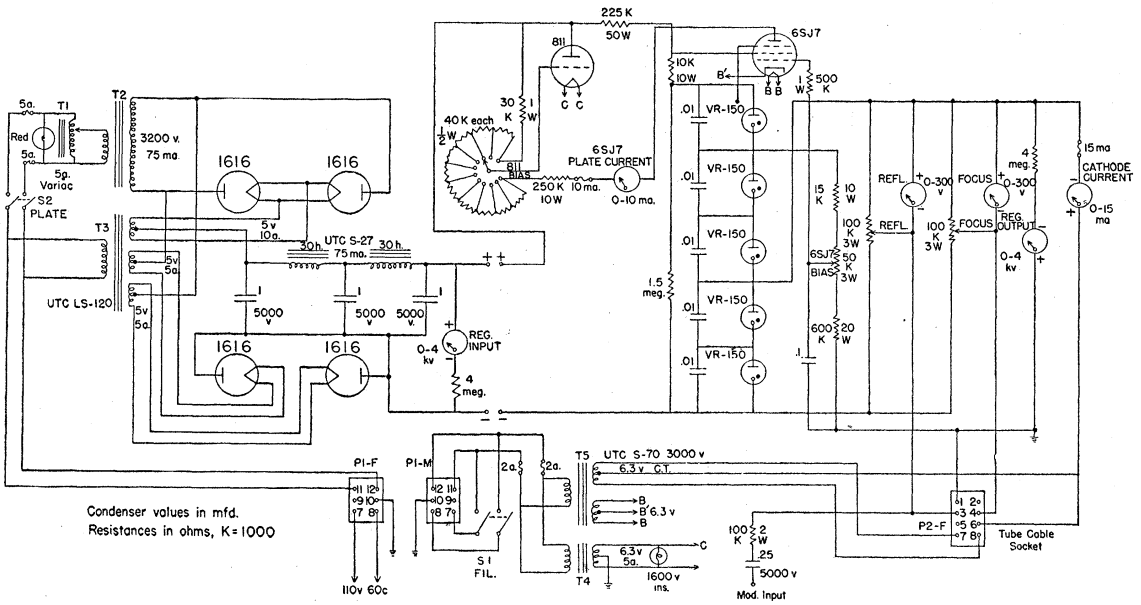


FIG. 6. Power supply for Raytheon millimeter-wave oscillators, *QK*140, 141, 142.

fact that the extremely sensitive crystals most widely used as detectors cannot detect high powers. In addition to its simplicity and ease of operation, the klystron can be stabilized by the Pound method[7] with an external cavity so as to provide an unusually high resolution. The frequency of this stabilized monochromatic source can be easily changed by varying the controlling cavity. Probably the most valuable feature for spectroscopy is the ease with which the tube can be frequency modulated electrically at any desired rate over any range, from a few kilocycles to thirty or forty megacycles, by simply imposing a varying voltage upon the reflector. When the sweep method is used, the oscillator need not be stabilized to obtain high resolution or, indeed, to obtain accurate measurements of the frequencies of absorption lines, since it is possible to superimpose a visual marker upon the absorption line displayed on the oscilloscope. This marker may be obtained by beating the frequency-modulated source against a monochromatic frequency used as a standard, or more conveniently but less accurately by superimposing the pip of a cavity wave meter upon the line.

Klystron oscillators can now be obtained to cover the microwave region from about 5.7-mm to 1.6-cm, and from about 2.7-cm to above 15-cm wave-length. The former region is the one of most interest for molecular absorption spectroscopy. Raytheon Manufacturing Company, Waltham, Massachusetts, makes a series of klystron tubes to cover the entire 0.57–1.6-cm range. In Table I are listed the pertinent characteristics of these tubes. Characteristics of other klystron oscillators for the region above 1 cm are given elsewhere.[8]

In Fig. 6 is given a circuit diagram of a power supply designed for the Raytheon tubes by

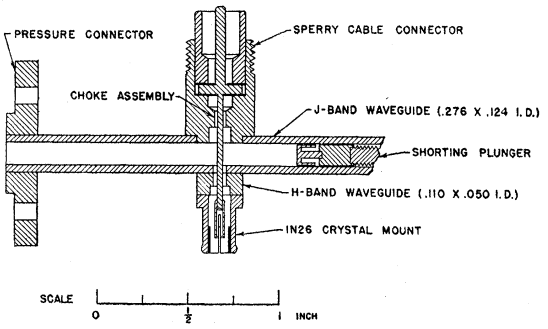


FIG. 7. Details of *J* to *H* harmonic converter. (From Smith, Gordy, Simmons, and Smith (reference 25).)

[7] R. V. Pound, Rev. Sci. Inst. **17**, 490 (1946).

[8] D. R. Hamilton, J. K. Knipp, and J. B. H. Kuper, *Klystrons and Microwave Triodes* (McGraw-Hill Book Company, Inc., New York, 1948); J. R. Pierce, Proc. I.R.E. **33**, 112 (1945); E. L. Ginzton and A. E. Harrison, Proc. I.R.E. **34**, 97 (1946).

TABLE I. Characteristics of Raytheon klystron tubes.

Type no.	Typical resonator potential in volts	Typical power output in milli-watts	Wave-length range covered in centimeters	Dimensions of wave-guide output in inches
RK-2K33	1800	40	1.1 -1.6	0.460″×0.210″ I.D. 0.500″×0.250″ O.D.
QK-140B	2200–2500	18	0.96–1.14	0.280″×0.140″ I.D. 0.320″×0.180″ O.D.
QK-140A	2200–2500	18	0.85–1.0	0.280″×0.140″ I.D. 0.320″×0.180″ O.D.
QK-141	2200–2500	10	0.80–0.90	0.280″×0.140″ I.D. 0.320″×0.180″ O.D.
QK-142	2500–3600	5	0.74–0.86	0.280″×0.140″ I.D. 0.320″×0.180″ O.D.
QK-226	2500–3600	≈5	0.68–0.80	0.224″×0.112″ I.D. 0.246″×0.152″ O.D.
QK-227	2500–3600	≈5	0.57–0.70	0.224″×0.112″ I.D. 0.246″×0.152″ O.D.

William Bennett at Duke. This is an electronically regulated power supply designed especially for the millimeter-wave tubes. It can easily be stepped down for use with those for the 1- to 2-cm range. A modulating voltage is not provided in this power supply, but one can easily be superimposed upon the reflector voltage from an external source. The modulating voltage varies considerably according to the type of measurements being made. In *cw* measurements the tube is usually modulated with a square-wave voltage. With the frequency-sweep method a saw-tooth wave is used. Frequently, double modulation is employed in which a radiofrequency sine wave is superimposed upon the slow saw-tooth voltage used to sweep the tube over its mode. With some amplification the saw-tooth wave from the indicator oscilloscope may be used to sweep the tube. When this is done, obviously no synchronization is required. Radiofrequency oscillators, available commercially, can be used to modulate the tube sinusoidally at high frequencies. A conventional multivibrator provides a good square-wave modulation.

Crystal harmonic generators.—For the region below about 5.7-mm wave-length no klystron oscillators are at present available. Crystal multipliers operating on the second-harmonic energy from the Raytheon tubes listed in Table I have been used successfully at Duke[3] as power sources to cover the region from 3 mm to 7 mm. Figure 7 gives a detailed sketch of the converter which has been used from 3 mm to 5 mm. The earlier work of Beringer[2] on oxygen in the 5-mm region was made with a crystal-harmonic generator driven by a 1-cm klystron oscillator.

Unfortunately, no precise measurements are available on the efficiency of harmonic generators for millimeter waves. This is, of course, because instruments for absolute power measurement in the millimeter region are not yet developed. Harmonic power in the 3.2-cm region from tubes operating at 6.4 cm has been obtained, which is 11 to 14 db down on the input 6.4-cm power.[9] One would expect second-harmonic power generated from K-band oscillators to be down 20 to 25 db from the fundamental. Since an output of 20 milliwatts is easily obtainable from K-band klystrons, harmonic power of the order of 150 microwatts is thus available for the 5- to 7-mm region. This amount of power is satisfactory for operation of a spectrometer with a video receiver and is on the borderline of the local oscillator power required to operate a superheterodyne receiver without excessive conversion loss. In the region of 5.7 mm to 10 mm, klystrons are available with output powers of 5 milliwatts. If we make the optimistic assumption that second-harmonic power which is only 25 db down on the fundamental can be obtained from these, then about 15 microwatts are available for spectroscopy in the region from 3 mm to 5 mm. This is adequate for operation of a video type receiver or an evacuated thermocouple, but with a superheterodyne receiver the conversion loss would be excessive. With 1N26 crystals for both multiplier and detector an over-all spectrometer sensitivity of about 3×10^{-4} cm^{-1} has been obtained at 3.4-mm wave-length.[3]

Considerable data[10] have been obtained which show that the welded germanium crystals developed by H. Q. North[11] are very superior to silicon crystals for both second and third harmonic generation. Unfortunately, the General Electric Company, which produced these crystals, ceased production at the end of the war, and I am unaware of any present commercial source for them.

[9] D. L. Falkoff, Rad. Lab. Report quoted by H. C. Torrey and A. C. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), p. 173.

[10] D. Montgomery, Rad. Lab. Report, quoted by Torrey and Whitmer, see reference 9, p. 173.

[11] H. Q. North, J. App. Phys. **17**, 912 (1946).

Magnetrons.—Mention has been made of the use of split-anode magnetrons in the early work of Cleeton and Williams. During the war magnetrons were used in measurements of the absorption of water vapor in the K-band region.[12] Theoretically, the sensitivity of a spectrometer increases with power, and the much higher powers obtainable with magnetrons suggest that they may be superior to klystrons as sources. There are certain factors which prevent this advantage from being realized. Perhaps the most serious of these is the saturation effect,[13] which limits the power which can be absorbed by a gas at low pressure. One can, of course, spread the power over a large volume of gas by the use of oversized wave guide, large resonant cavities, or free-space methods. The experimental difficulties are thereby increased. In addition, the most sensitive microwave detectors are incapable of handling powers available from magnetrons. One can use r-f balancing to reduce the power falling on the detector, but again the experimental difficulties are increased. Though some types of magnetrons are tunable, they are, in general, not as conveniently tuned as are klystrons. For these reasons magnetrons have not yet found wide use in microwave spectroscopy. They may come into wider use in the future as more practical means are developed for overcoming the difficulties mentioned. In the shorter millimeter region, where power generation is difficult, magnetrons may prove to be the most advantageous sources. Volume VI in the Radiation Laboratory Series[4] and other reports[14] give up-to-date and detailed information on all the different types of magnetrons.

C. Detecting Systems

Superheterodyne receivers.—In defining the noise figure of a receiver the usual reference level is the available Johnson noise power, $kT\Delta f$. If we assume that the minimum detectable signal power, $P_{\min}$, is that which at receiver output just equals the noise power, then

$$P_{\min}=F_r kT\Delta f, \tag{4}$$

where F_r is the noise figure of the receiver, which incorporates the conversion loss and noise of the detector as well as the noise arising from the amplifier, k is Boltzmann's constant, T is the absolute temperature, and Δf is the effective noise band width of the receiver. The function of a receiver used in microwave spectroscopy is somewhat different from that of a radar receiver since the receiver in microwave spectroscopy is not required to detect small amounts of signal power but rather to detect small variations, or decrements, in a relatively large signal power. One can, however, use r-f balancing to cancel the power around the absorption line and thus cause the spectrum line to appear as a small amount of unbalanced power $(\Delta P)'$. It is easy to show that

$$(\Delta P)'\approx(\Delta P)^2/4P_i\exp[-\alpha_c l], \tag{5}$$

where ΔP is the power absorbed by the gas, P_i the input power to the cell, l the equivalent cell length, and α_c the attenuation coefficient of the cell. When the input impedance of the receiver is coupled to a source, as is the case in microwave spectroscopy, there is an additional $F_s kT\Delta f$ of available noise power (where F_s is the noise figure of the power source) so that

$$(\Delta P)'_{\min}=F_r kT\Delta f+F_s kT\Delta f=FkT\Delta f, \tag{6}$$

where F is now the over-all noise figure of the spectrometer. Combining (5) with (6) one obtains:

$$(\Delta P)_{\min}=(4FkT\Delta f P_i\exp[-\alpha_c l])^{\frac{1}{2}}, \tag{7}$$

where $(\Delta P)'_{\min}$ is the minimum detectable unbalanced power and $(\Delta P)_{\min}$ is the minimum detectable absorption of power by the gas.

To obtain the optimum cell length and the minimum detectable absorption coefficient of a gas with this type of receiver, one must maximize the detected power, $(\Delta P)'$, rather than, as was done by Hershberger,[15] the absorbed power (ΔP). We have

$$\begin{aligned}(\Delta P)'&=(P_i\exp[-\alpha_c l]/4)(1-\exp[-\alpha_g l])^2\\&\approx(P_i\exp[-\alpha_c l]/4)(\alpha_g l)^2.\end{aligned} \tag{8}$$

By setting $\partial(\Delta P)'/\partial l$ equal to zero and solving, it is seen that

$$l_{\text{opt}}=2/\alpha_c, \tag{9}$$

[12] G. E. Becker and S. H. Autler, Phys. Rev. **70**, 300 (1946).
[13] C. H. Townes, Phys. Rev. **70**, 665 (1946).
[14] J. B. Fisk, H. D. Hagstrom, and P. L. Hartman, Bell Sys. Tech. J. **25**, 167 (1946).
[15] W. D. Hershberger, J. App. Phys. **19**, 411 (1948).

which yields with (8):

$$(\Delta P)'_{\max}=P_i(\alpha_g/e\alpha_c)^2. \tag{10}$$

Substituting this value in (6) one obtains

$$(\alpha_g)_{\min}=e\alpha_c(FkT\Delta f/P_i)^{\frac{1}{2}} \tag{11}$$

for the minimum detectable absorption coefficient, α_g, of a gas.

Though r-f balancing is assumed in the above analysis, essentially the same results are obtained for a receiver employing linear detection without r-f balancing. Detection in the usual superheterodyne receiver is linear. Also, the detection in a crystal video receiver for large-signal reception is approximately linear. For these we have

$$V_o=GV_s, \tag{12}$$

where V_o is the output voltage, V_s is the r.m.s. signal voltage, and G is a constant which incorporates the gain of the amplifier and the conversion gain (or loss) of the detector. For a small change in V_s,

$$(\Delta V_o)=G(\Delta V_s). \tag{13}$$

The output noise voltage N_0 of the receiver is

$$N_o=G(4FkTR\Delta f)^{\frac{1}{2}}, \tag{14}$$

where F again is the over-all noise figure and R is the input impedance. To meet the usual criterion for detectability, we equate ΔV_o to N_o. By combining (13) and (14) we obtain

$$(\Delta V_s)_{\min}=(4FkTR\Delta f)^{\frac{1}{2}}. \tag{15}$$

It is easily shown that

$$(\Delta V_s)=R(\Delta P)/2V_s=(R/4P)^{\frac{1}{2}}(\Delta P), \tag{16}$$

which with (15) yields

$$(\Delta P)_{\min}=(16FkT\Delta fP)^{\frac{1}{2}}$$
$$=(16FkT\Delta fP_i\exp[-\alpha_c l])^{\frac{1}{2}}. \tag{17}$$

This expression, except for a factor of 2, is identical with (7), obtained with r-f balancing. The optimum cell length is again $2\alpha_c^{-1}$, and

$$\alpha_{g\ \min}=2\alpha_c e(FkT\Delta f/P_i)^{\frac{1}{2}}. \tag{18}$$

The result indicates that there is no significant gain in r-f balancing as long as it is assumed that the over-all noise figure is independent of the power received. This assumption is not justified except for relatively low signal power, and r-f balancing could be an advantage when high power sources are available if cells are employed which have sufficiently large volume to prevent molecular saturation.

Though Hershberger[15] was the first to define the minimum detectable absorption coefficient, his results appear to be incorrect by orders of magnitude because he equated the absorbed power $(\Delta P)_{\min}$ to $FkT\Delta f$. Townes and Geschwind[16] have pointed out this error and through a somewhat different approach have obtained results in essential agreement with those given above. The latter researchers take the reference level of the noise voltage as $(2kT\Delta f)^{\frac{1}{2}}$ rather than $(4kT\Delta f)^{\frac{1}{2}}$. They assume the gas to be introduced and withdrawn from the cell at a constant frequency, and they employ the principle that an amplitude-modulated wave is equivalent to the unmodulated carrier with side-band frequencies containing the signal power.

Estimates of the performance to be expected of a spectrograph with a heterodyne receiver can be obtained by assuming the easily realizable parameter values: $\alpha_c=5\times10^{-4}$ neper per cm, $P_i=10^{-5}$ watt, $f=300$ c.p.s., $F=40$, or 16 db. For these

$$l_{\text{opt}}=40 \text{ meters},$$

and

$$\alpha_g \text{ min.}=6\times10^{-9} \text{ neper/cm}=1.2\times10^{-8} \text{ cm}^{-1}.$$

Considerably more than 10^{-5} watt is available in the K-band region. Here it is assumed that K-band guide is used and that the gas is being observed at such a low pressure that powers higher than 10^{-5} watt would be ineffective because of molecular saturation. Also, a band width which allows a convenient sweep speed is chosen. To obtain an estimate of the probable limits of detection, it is instructive to assume the idealized parameter values: $P_i=5\times10^{-3}$ watt, $\Delta f=30$ c.p.s., $F=2$, $\alpha_c=10^{-4}$ neper/cm. Then,

$$l_{\text{opt}}=100 \text{ meters},$$

and

$$\alpha_{g\ \min}=3.8\times10^{-12} \text{ neper/cm}=7.6\times10^{-12} \text{ cm}^{-1}.$$

With the assumed power, r-f balancing would

[16] C. H. Townes and G. Geschwind, J. App. Phys. 19, 795 (1948).

have to be employed to prevent excessive crystal noise, and a cell of large volume would be needed to prevent molecular saturation. In these estimates such loss factors as are caused by the output-cell window, impedence mismatch, etc., are neglected. Spurious signals caused by r-f mismatch can be eliminated by methods which will be described later, but not without significant loss.

The superheterodyne receiver is somewhat more complex than other receivers which can be used effectively. If one uses separate klystrons for the source and local oscillator power, some form of automatic frequency control is needed to keep the oscillators tuned, especially if the sweep method is employed. The automatic frequency control circuits[17] used in microwave radar are feasible for slow rates of sweep.

Leo C. Levitt has suggested to me the possibility of using the same oscillator to provide the source and the local oscillator power so that no automatic frequency control would be needed. This can be achieved by allowing a part of the source power to be reflected by a crystal which is modulated by an i-f oscillator. Thus side bands are produced which have frequencies

$$\nu_s+\nu_{if} \text{ and } \nu_s-\nu_{if},$$

where ν_s is the frequency of the source and ν_{if} that of the oscillator. One of these side-band frequencies can then be used as a source of power for the absorption cell when a part of the direct power from the oscillator of frequency ν_s which is not passed through the cell is used for local oscillator power. Crystals have been used for this type of modulation by Pound[18] in the stabilization of oscillators. Using 1 N 23 B crystals at X band, Pound[19] obtained a conversion loss, $L\approx 6$ db, for this type of frequency conversion. Thus it appears that adequate local oscillator power may be obtained in this manner for K-band and perhaps also for J-band spectroscopy.

As will be shown later, the enormous advantage in sensitivity of the superheterodyne receiver in radar over the simple video receiver operating with a square-law detector is not maintained in microwave spectroscopy, where small changes of power rather than small pulses of power must be detected. For this reason and because of its complexity which makes it slow as a search system, the superheterodyne receiver has not yet found wide use in microwave spectroscopy.

Crystal video receivers.—A simple, rapid, and rather sensitive microwave spectrograph can be made by employing the frequency sweep method with a crystal video receiver. In this receiver the crystal detector is mounted in a wave-guide holder and is matched to the microwave line. The crystal is then connected directly to a video amplifier. Very narrow-band audio amplifiers are actually used, but these are here referred to as video receivers.

The noise generated in a crystal with no d.c. bias nor r-f excitation greater than $\approx 5\times 10^{-6}$ watt is almost completely the Johnson noise. The output noise voltage, N_0, from a crystal video receiver operating in the square-law region can therefore be expressed as[20]

$$N_0\approx G[4kT(R+R_A)\Delta f]^{\frac{1}{2}}, \tag{19}$$

where R is the video resistance of the crystal and R_A is a resistance which, if in series with the crystal, would generate a noise equivalent to that generated in the amplifier. Usually, $R_A \approx 1000$ ohms.[20] In the square-law region the voltage detected by the crystal, V_d, is

$$V_d=SV_s^2, \tag{20}$$

where S represents sensitivity of the detector and V_s is the r.m.s. input voltage. The output voltage of the receiver is

$$V_o=GSV_s^2, \tag{21}$$

and for a small change in P

$$\begin{aligned}\Delta V_o &\approx GS(2V_s\Delta V_s)\\ &\approx GS(R\Delta P),\end{aligned} \tag{22}$$

since G, the voltage gain, and S are constants. To meet the usual criterion for detectability we equate

$$\Delta V_o=GS(R\Delta P)=G[4kT(R+R_A)\Delta f]^{\frac{1}{2}},$$

[17] R. V. Pound, *Microwave Mixers* (McGraw-Hill Book Company, Inc., New York, 1947), see Eric Durand, Ch. 7, p. 240.

[18] R. V. Pound, Rad. Lab. Report, quoted by Torrey and Whitmer, see reference 9, p. 174.

[19] R. V. Pound, quoted by Torrey and Whitmer, see reference 9, p. 178.

[20] H. C. Torrey and C. A. Whitmer, see reference 9, p. 346.

and obtain

$$\Delta P=[(4kT(R+R_A)/RS)\Delta f]^{\frac{1}{2}} =[4kT\Delta f/M]^{\frac{1}{2}}, \quad (23)$$

where

$$M=RS/(R+R_A)^{\frac{1}{2}} \quad (24)$$

is the figure of merit.[20] By definition,

$$\Delta P=P_i\exp[-\alpha_c l]-P_i\exp[-(\alpha_c+\alpha_g)l] \approx P_i\exp[-\alpha_c l](\alpha_g l). \quad (25)$$

Substituting this value of ΔP in (23) we obtain

$$\alpha_{g\,\min}=(4kT\Delta f)^{\frac{1}{2}}/MlP_i\exp[-\alpha_c l]. \quad (26)$$

If it is assumed that M is independent of the received power, $P_i\exp[-\alpha_c l]$, then it is appropriate to determine l_{opt} from (26) by setting $\partial(\alpha_g)/\partial l=0$. In this way we obtain

$$l_{\text{opt}}=\alpha_c^{-1}, \quad (27)$$

and

$$\alpha_{g\,\min}=2e\alpha_c(kT\Delta f)^{\frac{1}{2}}/P_iM. \quad (28)$$

No measured values of M are available for the K-band or the millimeter region. Figures of merit as high as 55 are easily attainable in the 3-cm region. In order to estimate the performance to be expected in the 1-cm region, we assume the reasonable values $M=20$; $P_i=5\times10^{-6}$ watt; $\alpha_c=5\times10^{-4}$ neper/cm; $\Delta f=300$ c.p.s.; then,

$$l_{\text{opt}}=20 \text{ meters}$$

and

$$(\alpha_g)\ \min=3\times10^{-8}\text{ neper/cm}=6\times10^{-8}\text{ cm}^{-1}.$$

If more power is available than can be efficiently detected, as is usually the case, it could be advantageous to use a longer cell than the l_{opt} as defined above. Suppose that the detected power must be $\approx10^{-6}$ watt, that much greater power than this is available, and that molecular saturation can be avoided. To minimize α_g then,

$$l_{\text{opt}}\approx(6\log_e 10+\log_e P_i)\alpha_c^{-1}.$$

For example, when $P_i=10^{-4}$ watt, the optimum length is then $4.6\alpha_c^{-1}$. If these values are substituted in (28) with $\alpha_c=5\times10^{-4}$ neper/cm, $\Delta f=300$ c.p.s., $M=20$, then,

$$l=92 \text{ meters}$$

and

$$(\alpha_g)_{\min}=1.3\times10^{-8}\text{ neper/cm}.$$

Thus it appears that the simple video receiver compares favorably in sensitivity with the more complex superheterodyne receiver for the detection of absorption spectra. This result is probably not generally realized because of the much greater sensitivity of the superheterodyne receiver for the detection of radar pulses, $\approx10^5$ times greater for the usual pulse width of 1 μsec.

The appearance of $\alpha_{g\,\min}$ as an inverse function of power suggests that one may increase sensitivity indefinitely by increasing the source power. This is not true because M, the figure of merit, remains constant for only a small range of powers in the microwatt region. A considerable amount of experimental data has been obtained by Miller, Greenblatt, and others[21] at the University of Pennsylvania, to show that the noise "temperature" of silicon crystal rectifiers at low frequency is very high when either d.c. or r-f excitation beyond a few microwatts is applied and that it varies inversely with frequency. Over the entire range covered by these measurements, 50 c.p.s. to several kc/sec., the inverse relation was found to hold. This inverse relation makes it impossible to suppress the excess noise by the usual method of employing slow rates of sweep so that narrow-band receivers can be used. For example, suppose that an oscillator is swept over an absorption line at such a rate that the time of sweeping through the line width, d_t, is 1/1000 c.p.s. The optimum band width, that which gives the best ratio of signal to noise, is $\approx1/d_t$ $=1000$ c.p.s. If one covers the line at 1/10 this rate, a band width of only 100 c.p.s. can be used. This indicates an increase in sensitivity of 10 db. However, in order to cover the same section of the microwave spectrum with the slower sweep, the recurrence rate must be reduced by a factor of 10. The Fourier component frequencies which comprise the signal are reduced by the same factor. The low frequency cut-off of the receiver must accordingly be lowered by a factor of 10. Because of the increase of the noise "temperature" of the crystal with decrease of frequency, the noise factor is increased by 10. The db gained by decreasing the band width of the receiver is thereby nullified. The advantages of the superheterodyne receiver or one of its equiva-

[21] P. H. Miller and M. H. Greenblatt, N.D.R.C. report, quoted by Torrey and Whitmer, see reference 9, p. 192.

lents, discussed in the next section, become evident when powers much beyond the microwatt range can be used without molecular saturation. However, when welded-contact germanium crystals become available it may be possible to obtain high sensitivity with a video receiver operating at powers well above the microwatt range. High figures of merit have been obtained with these crystals when appreciable d.c. bias was applied.[22]

Of great interest is the low power level performance of crystals in the millimeter region, particularly in the shorter wave-length region, 3–5 mm, where not enough local oscillator power is available to operate a superheterodyne receiver without great conversion loss. No quantitative data seem to be available for wave-lengths lower than 3 cm. Qualitative theoretical considerations lead to an approximate relation of the form[23]

$$\beta = a/(1+bf^2),$$

where β is the current sensitivity of the crystal which is equivalent to the proportionality constant S in (20), and where a and b are other constants which depend upon the characteristics of the crystal. To evaluate the constants a and b, I have used two experimental points determined for a 3-cm crystal by Beringer[24] at frequencies of 9300 mc/sec. and 3300 mc/sec., and have thereby obtained

$$b = 2/(1+1.7\times 10^{-20}f^2).$$

This relation indicates that the figure of merit of a video receiver in which this crystal is used would be down at 1 cm to 15 percent of its 3-cm value and at 3 mm to 1.4 percent of the 3-cm value. Better performance in the millimeter region than that indicated might be obtained by selecting from K-band crystals those most suitable for millimeter waves. Results obtained in this laboratory[25] on IN26 crystals operated near 3 mm are in rough agreement, though no quantitative comparisons are yet possible.

A double-crystal balanced video receiver is sometimes used.[13,26] One of the crystals detects energy which has passed through the absorption cell while the other detects a fraction of the source power which is not passed through the cell. The signals from the two crystals are then mixed in phase opposition and their relative strengths adjusted by attenuators until the receiver is balanced when no absorption occurs. With the frequency sweep method this type of balancing is not very satisfactory because of the difficulty of obtaining a sufficiently good impedance match over a large fraction of the oscillator mode.

A single crystal video receiver[27] which employs an amplifier with a rather sharp low frequency cut-off filter to eliminate contour of the mode and spurious signals caused by r-f mismatch has been used successfully with the frequency sweep method. With this system the gas pressure is adjusted to make the absorption line narrow as compared to the mode contour or any spurious signals caused by r-f mismatch. The rate of sweep is then adjusted so that the significant Fourier components of the mode contour and of the spurious signals fall below the cut-off frequency while a major portion of the absorption line components fall in the band width covered by the amplifier. Some distortion of the signal is obviously unavoidable with this system. Though this is not objectionable in a search system, it makes the method unusable for the study of line shapes. One feature of the system which has proved useful in distinguishing absorption lines from spurious electronic disturbances is that an absorption-line signal can be instantly erased by increasing the pressure in the cell by a factor of 8 to 10 so as to broaden the line sufficiently to cause its major Fourier components to fall below the filter cut-off frequency.

Modulation methods.—To avoid the excessive low frequency noise when silicon crystals are used to detect powers above the microwatt range and to avoid low-frequency noise from other sources such as the flicker effect in tubes,[28]

[22] H. C. Torrey and C. A. Whitmer, see reference 9, p. 348.
[23] H. C. Torrey and C. A. Whitmer, see reference 9, p. 339.
[24] R. Beringer, Rad. Lab. Report, quoted by Torrey and Whitmer, see reference 9, p. 338.
[25] A. G. Smith, W. Gordy, J. W. Simmons, and W. V. Smith, to be published.
[26] W. E. Good, Phys. Rev. **69**, 539 (1946); **70**, 213 (1946).
[27] W. Gordy and M. Kessler, Phys. Rev. **71**, 640 (1947).
[28] J. B. Johnson, Phys. Rev. **26**, 71 (1925); W. Schottky, Phys. Rev. **28**, 74 (1926).

it is desirable to amplify the signal at frequencies of 100 kc or higher. Two methods have been evolved which make this possible without the complexity of the superheterodyne receiver. These methods are similar in principle in that they both use the absorption line itself to produce a high frequency amplitude modulation of the microwave radiation and a narrow-band communication receiver to amplify the signal at the modulation frequency. The principle involved is not unlike the familiar "beam-chopper" which makes possible the use of an a.c. rather than a d.c. amplifier in infra-red spectroscopy. However, it is not possible to use a mechanical chopper at the frequencies desired here, and hence the modulation must be achieved electrically. The two methods of achieving this electrical modulation I shall designate as molecular modulation and source modulation.

Molecular modulation.—Shortly after the first demonstration of the Stark effect in rotational spectra by Dakin, Good, Coles,[29] the electrical modulation of the absorption lines at low radio-frequencies was introduced by Hughes and Wilson[30] as an aid to detection. It is easy to see that amplitude modulation can be produced by this method if we imagine the source oscillator tuned to a fixed frequency at some point on a sharp absorption line. As the position of the absorption line is moved, the amount of absorption will be changed and the intensity of the radiation reaching the detector will be modulated. In practice the source oscillator is electrically swept over the absorption line at a rate which is slow compared to the molecular modulation frequency, so that the absorption lines can be displayed on a cathode-ray oscilloscope in the usual manner. In addition to increasing sensitivity by avoiding low frequency noise, this ingenious method also completely eliminates the troublesome problem of spurious signals arising from mismatch in the microwave line. Since only the absorption line produces amplitude modulation of the microwaves at the frequency to which the highly selective receiver is tuned, spurious signals of all types are minimized. Though a more complex spectrum is observed, because of the Stark splitting of the lines, the additional information which is obtained is of value. If a square-wave voltage[31] is used to modulate the molecules, the Stark pattern can be resolved and used as an aid to identification of the lines. It can also be used to determine the dipole moment of the molecule under study.

As with other methods, certain difficulties are encountered. Some of the gain in sensitivity is lost because of the splitting of the line into a number of components. Also, with the usual methods of achieving the modulation, conducting strips are placed down the center of a wave guide cell. The impedance mismatch thereby introduced and the dielectric losses in the posts or wedges used to support the conducting strips again tend to offset the gain in sensitivity. A cell which avoids some of these difficulties is described in the section on wave guide and associated components. Good shielding is needed to prevent direct pick-up between the high voltage modulation source and the high gain receiver which is tuned to the same frequency. Because of the large electrical capacity introduced, it is difficult to obtain the necessarily high voltage modulation with a cell of optimum length. This is particularly true for square-wave modulation. Much of the advantage in sensitivity of this method over the simpler video receiver comes from the detection of higher powers without excessive noise. If this advantage is to be realized, a cell sufficiently large to avoid molecular saturation must be employed.

With the Stark modulation Hughes and Wilson[30] report that the 1,1 line in the $N^{15}H_3$ inversion spectrum has been detected with N^{15} in its naturally occurring concentration of 0.37 percent.

The Massachusetts Institute of Technology group[32] applies a square-wave Stark modulation at an audiofrequency and uses with this a superheterodyne receiver. After preamplification at a high i-f frequency, 30 mc, the audiofrequency is detected and amplified by a narrow-band audio amplifier. Thus, only signals from an absorption line appear on the indicator. At this low frequency the impedance across the cell electrodes is high, and an electric field of several thousand

[29] T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (1946).
[30] R. H. Hughes and E. B. Wilson, Phys. Rev. **71**, 562 (1947).
[31] B. P. Dailey, Phys. Rev. **72**, 84 (1947).
[32] M. W. P. Strandberg, private communication.

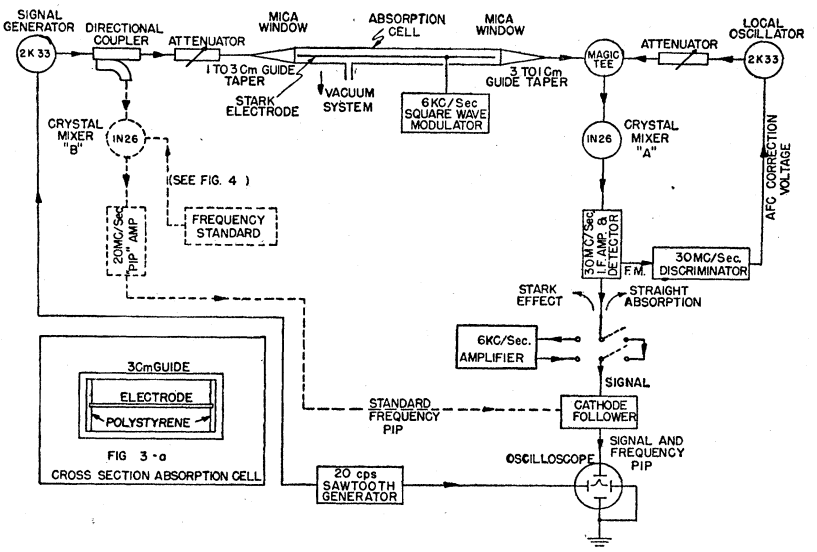


FIG. 8. Block diagram of M.I.T. Stark effect microwave spectrograph. (From Strandberg, Wentink, and Kyhl (reference 32).)

volts/cm can be applied to the molecules. The Stark pattern can be resolved and studied. Though it lacks the advantage of simplicity, the system has been used very effectively. Figure 8 shows a block diagram of this spectrometer.

A theoretical analysis of the effects of different forms and frequencies of modulation on line shape has been given by Karplus.[33] For a treatment of sinusoidal modulation, see also Townes and Merritt,[34] Blochinzew,[35] and Hershberger.[15]

A magnetic field can also be used to frequency modulate spectral lines. Indeed, the Zeeman effect has already been used to aid detection. (See the section on specialized methods.)

Source modulation.—Gordy and Kessler,[36] and independently Hershberger,[15] have shown that high frequency source modulation can be employed to achieve high sensitivity without a superheterodyne receiver.† Upon the slowly varying saw-tooth voltage used to sweep the klystron over its mode, there is superimposed a voltage wave of a much higher frequency (it may be as high as several mc) which causes the oscillator to make rapid excursions into and out of regions of greater absorption as the spectrum line is gradually passed over by the slow sweep. The spectrum line then acts as a discriminator to convert the frequency modulation into an intensity modulation of the same frequency.†† After detection by a crystal the signal is then amplified by a narrow-band radiofrequency amplifier which is tuned to the modulation frequency. It is then passed through an audio amplifier with a rather sharp low frequency cut-off filter which discriminates against low frequencies generated as a result of reflections in the microwave line.***

The early results obtained by Gordy and Kessler, which are reproduced in Fig. 9, demonstrate that good resolution as well as good sensitivity can be obtained with this system. The $N^{15}H_3$ line shown here about 10 db above the noise level indicates a sensitivity of approximately 10^{-7} neper/cm. These results were obtained with a receiver having a receiver band width of approximately 3000 c.p.s. and with a *K*-band cell which, because of molecular saturation, severely limited the effective power level. The distortion apparent in these photographs is caused by the low frequency cut-off filter men-

[33] R. Karplus, Phys. Rev. **73**, 1027 (1948).
[34] C. H. Townes and F. R. Merritt, Phys. Rev. **72**, 1266 (1947).
[35] D. Blochinzew, Phys. Zeit. U.S.S.R. **4**, 501 (1933).
[36] W. Gordy and M. Kessler, Phys. Rev. **72**, 644 (1947).

† Apparently, Wilson and his colleagues earlier tried a square-wave source modulation at 50 kc without achieving marked advantage over the low frequency system [unpublished report quoted by R. J. Watts and D. Williams, Phys. Rev. **72**, 1122 (1947)]. Watts and Williams state that they have used this method successfully.

†† It appears that the sharp slope of an absorption line might provide a practical discriminator for an f-m communication receiver operating in the microwave region.

*** As an alternative, one could use a low frequency Stark modulation in combination with the high frequency source modulation.

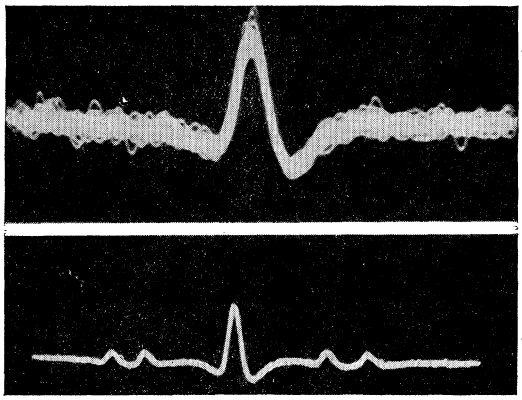


FIG. 9. Upper curve: 3,3 line of $N^{15}H_3$ at natural concentration (0.3 percent) in normal ammonia. (3.6-meter cell, 2×10^{-3} mm of Hg pressure, 100 kc source modulation). Lower curve: 3,3 line of $N^{14}H_3$ showing satellite structure with 100-kc source modulation. (From Gordy and Kessler (reference 36).)

tioned above. At least 3 db of signal strength is also lost to achieve this low frequency filtering.

Specialized methods.—The sensitive detecting system used by Roberts, Beers, and Hill[37] for observing directly the hyperfine structure in the 3-cm wave region of Cs vapor can be used for many other studies. With this method a Pound stabilizer is employed to couple a microwave oscillator to the frequency of an external, tunable cavity which contains the gas or vapor at low pressures, $\sim10^{-2}$ mm of Hg. The anomalous dispersion of the vapor in the region of an absorption line alters slightly the resonant frequency of the cavity. By frequency modulating the absorption line with an alternating magnetic field, the coupled klystron is frequency modulated at the alternation rate. An f-m receiver is then used to detect the absorption line.

A somewhat more specialized but extremely sensitive method is the atomic beam technique used by Lamb and Retherford[38] in the celebrated hydrogen experiment at microwave frequencies. In the future, certain other features of the atomic and molecular beam[39] methods will no doubt be adapted to microwave frequencies. Likewise the sensitive radiofrequency methods[40] recently devised for the detection of nuclear resonance in solids and liquids may later be applied to problems in the microwave region.

A very effective method for studying the Zeeman effect in gases is described in a forthcoming publication by C. K. Jen.††† A high Q cavity is used as the cell. The pressure of the gas is such that the absorption line is sharp as compared to the response curve of the cavity. The high frequency source modulation described above is used to increase the sensitivity. The minimum detectable signal as given by Jen is

$$(\alpha)_{\min}=(4kTN\Delta f/P_0)^{\frac{1}{2}}(2\pi/Q\lambda), \qquad (29)$$

where P_0 is the incident power, N the receiver noise figure, Δf the noise band width of the receiver, λ the free-space wave-length, and Q the usual quality factor of the cavity. Figure 10 gives a block diagram of this apparatus, with illustrations of spectral lines as they appear on the cathode-ray oscilloscope.

Thermal detectors.—Thermocouples and bolometers have not yet found wide use as detectors in microwave spectroscopy. Nevertheless, because they have capacity to detect relatively high powers as compared to crystals and because they have possibly greater sensitivity than have crystals for the shorter millimeter waves, they merit consideration. The outstanding disadvantage, particularly for thermocouples, is their slow response time. Unlike crystals, low level (microwatt range) thermal detectors of microwave radiation were not highly developed during the war, although rather refined thermister bridges were developed for power measurement in the milliwatt range for the K, X, and S bands. Research and developmental work on thermal detectors for microwave spectroscopy should yield high returns, particularly in the shorter millimeter-wave region where the effectiveness of crystals decreases rapidly with increase in frequency.

Though receivers having thermal detectors are much inferior to crystal heterodyne receivers for

[37] A. Roberts, Y. Beers, and A. G. Hill, Phys. Rev. **70**, 112A (1946).
[38] W. E. Lamb, Jr. and R. C. Retherford, Phys. Rev. **72**, 241 (1947).
[39] I. Esterman, Rev. Mod. Phys. **18**, 300 (1946); J. B. M. Kellogg and S. Millman, Rev. Mod. Phys. **18**, 323 (1946); H. K. Hughes, Phys. Rev. **72**, 614 (1947).
[40] E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev. **69**, 137 (1946); F. Bloch, W. W. Hansen, and M. Packard, Phys. Rev. **70**, 474 (1946); A. Roberts, Rev. Sci. Inst. **18**, 845 (1947).
††† C. K. Jen, Tech. Report, No. 51, Cruft Laboratory, Harvard University, July 10, 1948.

the detection of small amounts of centimeter-wave power such as is required in radar, theoretical considerations indicate that for the detection of small changes in relatively large powers, as is required for observation of absorption spectra, they are comparable to crystals in sensitivity. If, as was done with crystals, we assume that they can be matched to the microwave line and that the Johnson noise is the limiting factor, a simple analysis is possible. The thermoelectric voltage V set up in a thermocouple as a result of incident power P is:

$$V=SP, \tag{30}$$

where S is the sensitivity of the thermocouple. For a small change of P,

$$\Delta V=S\Delta P. \tag{31}$$

Here it is assumed that ample response time is allowed so that S remains constant. We equate ΔV to the Johnson noise voltage and from (31) obtain:

$$\Delta P_{\min}=\frac{[4kT(R_t+R_A)\Delta f]^{\frac{1}{2}}}{S}, \tag{32}$$

where R_t is the thermocouple resistance and R_A is a resistance which would generate a thermal noise equivalent to that generated in the galvanometer or amplifier to which the thermocouple is connected. Combining (32) with (25) we obtain:

$$\alpha_{g\,\min}=\frac{[4kT(R_t+R_A)\Delta f]^{\frac{1}{2}}}{SlP_i\exp[-\alpha_c l]}, \tag{33}$$

which for the optimum cell length, $l_{\text{opt}}=\alpha_c^{-1}$, becomes:

$$\alpha_{g\,\min}=\frac{2\epsilon\alpha_c[kT(R_t+R_A)\Delta f]^{\frac{1}{2}}}{SP_i}. \tag{34}$$

If we set

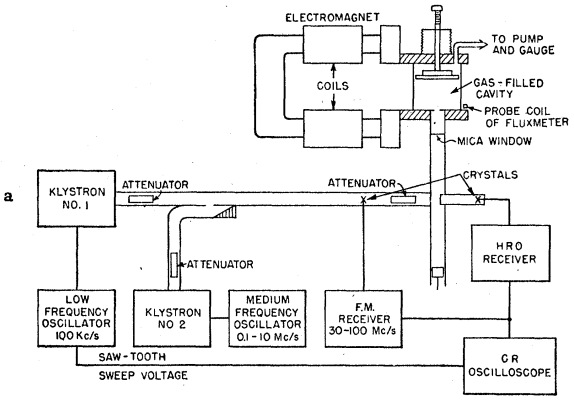
$$M=S/(R_t+R_A)^{\frac{1}{2}},$$

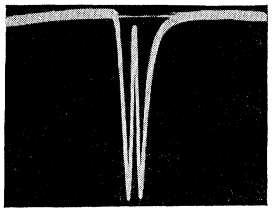
this expression is identical to (28), where M now represents the figure of merit of a thermocouple receiver. The resistances and sensitivities for a number of microwave thermocouples are listed in Volume XI of the Radiation Laboratory Series.[41] For one evacuated type which has a power limit of 5 milliwatts, $S=20$ mv/mw and $R=38$ ohms. If this is used with an amplifying system of equivalent resistance, a very small α_g can be detected, provided the absorption of the gas can be distinguished from deviations in power caused by r-f reflections. The value of M indicated is 2, and if we assume for K band the reasonable values, $\Delta f=30$ c.p.s., $P_i=5\times10^{-3}$ watt, $\alpha_c=10^{-4}$ neper/cm, then

$$\alpha_{g\,\min}=2\times10^{-11}\text{ neper/cm}.$$

This compares favorably with the value 3.8×10^{-12} neper/cm obtained for a superheterodyne receiver with idealized noise figure and with other parameters the same as those assumed here.

Considerable work has been done on thermocouples and bolometers for the detection of submicrowatt powers in the infra-red region. Data on the performance of these can be used to estimate the minimum detectable α_g which





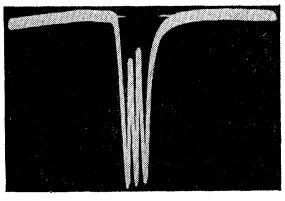


FIG. 10. a: Harvard microwave spectrograph for studies of Zeeman effect; b: oscilloscopic pattern of spectral line of a gas in resonant cavity cell; c: Zeeman splitting of a spectral line of a gas in a resonant cavity cell. (From C. K. Jen (reference †††).)

[41] C. S. Montgomery, *Techniques of Microwave Measurements* (McGraw-Hill Book Company, Inc., New York, 1947), p. 187.

may be expected in the microwave region, provided these can be made to absorb effectively the incident power. With square-law detectors it is permissible to assume that the minimum ΔP which can be detected is comparable to the minimum detectable power over the power range for which the sensitivity remains constant. Thus,

$$\Delta P_{\min} \approx P_i \exp[-\alpha_c l](\alpha_{g\,\min}) = P_{\min} \quad (35)$$

or

$$\alpha_{g\,\min} = P_{\min}/P_i \exp[-\alpha_c l] = \epsilon\alpha_c P_{\min}/P_i,$$

when

$$l = l_{\text{opt}} = \alpha_c^{-1}. \quad (36)$$

Here $P_{\min}$ is the minimum detectable power with the particular thermocouple or bolometer. For the usual thermocouples and bolometers operated in the infra-red region, the minimum detectable power is about 10^{-8} watt.[42,43] With $P_i = 5\times10^{-5}$ watt and $\alpha_c = 5\times10^{-4}$ neper/cm this gives

$$\alpha_{g\,\min} = 2.7\times10^{-7} \text{ neper/cm}.$$

Powers of the order of 10^{-10} watt have been detected with both bolometers and thermocouples.[43] Thus it appears that the estimate here is conservative. With the exception of the Andrews superconductivity bolometer, d.c. thermocouples seem to be slightly more sensitive than bolometers. However, for microwave spectroscopy this advantage in sensitivity is probably more than offset by the much more rapid response-time obtainable with bolometers. With bolometers one can use a.c. modulations of frequency greater than a thousand if desirable. Thus the Stark modulation method can be used to prevent the indicator from responding to variations in power not caused by the gas absorption. Recently, thermocouples[44] which are sufficiently rapid for use with transformers and a.c. amplifiers have been constructed.[40] Special low frequency amplifiers have been designed[45] for use with them.

It appears that a microwave spectrometer of good stability and sensitivity could be made with a bolometer detector used with a narrow-band lock-in-amplifier[46] and with Stark modulation of the molecules to provide the alternation of beam intensity. It would be advantageous to stabilize the source oscillator by coupling it to a tunable cavity[7] and to use an automatic recorder. As an alternative, one could use the frequency-sweep method with a persistent-screen, slow-sweep cathode-ray oscilloscope. Daly and Sutherland[47] have developed a system for cathode-ray display of infra-red absorption spectra which employs a bolometer with a response-time of 0.01 sec.

Thermocouples have been used effectively by Autler and Becker[12] to measure the absorption of water vapor in the 1.32-cm region. The measurements were made with the water vapor at various partial pressures in air at one atmosphere. Magnetrons were used as sources. The water vapor was contained in an approximately cubical cavity having a volume of 15.8 cubic meters. The thermocouple system used for detection contained 360 junctions. These were distributed throughout the cavity with alternate junctions coated with lossy material. Their measurement consisted of the determination of the change in Q of the cavity caused by the absorption of the water vapor and of the evaluation of the absorption coefficient for this change. To provide uniform radiation density throughout the cavity a "mode mixer" in the form of an electric fan was used to "stir" the large number of modes in the cavity. It was assumed that the steady-state response of the thermocouple is proportional to the Q of the cavity. The theory of this spectroscope is discussed by Lamb.[48]

D. Evaluation of Spectrometer Sensitivity

Methods used to measure the noise figures of radar receivers can be applied in checking the performance of a microwave spectrometer. Thermister bridges[49] are available for power measurement in the K-band region, also calibrated attenuators[50] for reducing the measured power by known amounts considerably below

[42] E. E. Bell, R. F. Buhl, A. H. Nielsen, and H. H. Nielsen, J. Opt. Soc. Am. **36**, 355A (1946).
[43] V. Z. Williams, Rev. Sci. Inst. **19**, 135 (1948).
[44] D. R. Horning and B. J. O'Keefe, Rev. Sci. Inst. **18**, 474 (1947).
[45] L. C. Roess, Rev. Sci. Inst. **16**, 173 (1945).
[46] R. H. Dicke, Rev. Sci. Inst. **17**, 268 (1946); R. H. Dicke, E. R. Beringer, R. L. Kyhl, and A. B. Vane, Phys. Rev. **70**, 340 (1946).
[47] E. F. Daly and G. B. B. M. Sutherland, Proc. Phys. Soc. **59**, 77 (1947).
[48] W. E. Lamb, Phys. Rev. **70**, 308 (1946).
[49] R. N. Griescheimer, see reference 41, Chapter 3.
[50] R. N. Griescheimer and E. Weber, see reference 41, Chapters 11–13.

that which can be measured directly. With these one can measure the input power which is required to equal $F_r kT\Delta f$ at the output or $(4kT\Delta f)^{\frac{1}{2}}/M$ for video receivers, and can thus obtain F_r or M. Similar methods can be applied to receivers with thermal detectors. P_i is easily measured with a thermister bridge. With these values one can compute the $\alpha_{g\ \min}$ expected with a given spectrometer. R-f and i-f noise sources are also available[51] for convenient determination of noise factors.[51]

When the i-f amplifier-noise factor F_{if}, the crystal noise "temperature" t_c, and conversion loss L of the crystal are measured separately, they can be used to compute the receiver noise figure for a heterodyne receiver, with the equation

$$F_r = 10 \log L + 10 \log(t_c + F_{if} - 1). \qquad (37)$$

For an i-f frequency of 30 mc the conversion loss, $10 \log L$, of a typical 1N26 crystal for K-band operation is ≈ 7 db, and t_c is ≈ 2. A good i-f noise factor is 2 or 3 db. With these values, $F_r \approx 12$ db. If a balanced mixer is not used to cancel the local-oscillator noise, a figure greater by 3 to 8 db may be obtained.[52] Also the source noise must be added. In a system without r-f balancing, this could increase the over-all noise by several db. The increase in the noise figure which is caused by local oscillator or source noise is quite different for different klystron modes even when the power is maintained at a constant level. For a given mode the contribution of klystron noise is least for the center of the mode and is less for the low frequency side of the mode than for the high frequency side.[52] Since the conversion loss is not affected by the local oscillator or source noise, this additional noise can be included in the over-all receiver noise by increasing t_c in (36) by an appropriate amount.

The most direct method of determining the over-all sensitivity or figure of merit of any type of microwave spectroscope is the measurement of the signal-to-noise ratio obtainable for weak spectral lines of known absorption coefficient. The coefficient for the 3,3 line of the $N^{14}H_3$ inversion spectrum has been measured by several observers[13, 26, 53] as near 7×10^{-4} cm^{-1}. The strength of the $N^{15}H_3$ lines for naturally occurring concentrations, 0.37 percent of N^{15}, provides weak signals in the K-band region, the strength of which can be calculated from measurement on the lines of $N^{14}H_3$. The $N^{14}H_3$ lines in the region between 7 mm and 1 cm are suitable for purposes of calibration since they are, in general, less than one percent of the 3,3 line.[54] The absorption coefficients of all measured ammonia lines have been calculated and the resulting values listed with their frequencies in Table II. Other molecules can be similarly used when their line-breadth parameters are measured, as it is then possible to obtain their absorption theoretically. For example, the stronger ICN lines with C^{13} in its normal concentration of one percent are barely above the noise level of present spectrometers, and the $IC^{12}N^{15}$ lines are about $\frac{1}{3}$ as strong as these. Thus the small but known concentrations of naturally occurring isotopes such as S^{34}, N^{14}, and C^{13} provide useful calibrated "attenuators" many db down from the attenuation of the corresponding, most abundant isotope.

E. Intensity Measurements

Absolute intensities.—Measurements of the absorption coefficients of oxygen,[2] water,[47] and ammonia,[13, 53] in regions of resonant absorption have been made. Also, the attenuation of certain other gases in non-resonant regions has been measured.[55] All these measurements have been made at fixed frequencies (non-sweep method) with the gas at relatively high pressure. Under these conditions the problem is not unlike that of measuring the usual losses in a microwave transmission line or in a resonant cavity, except that one must consider the cell windows and the dielectric effects of the gas. Hence, the wealth of information accumulated during the war for the measurement of attenuation is pertinent.[49]

Measurement in wave guide cell.—One of the simpler methods is to measure the attenuation of a gas in a wave-guide cell. A detector whose response is proportional to power is placed at

[51] R. Beringer, C. G. Montgomery, R. A. Howard, and S. Katz, see reference 41, Chapter 4.

[52] R. V. Pound, *Microwave Mixers* (McGraw-Hill Book Company, Inc., New York, 1947), p. 240.

[53] B. Bleaney and R. P. Penrose, Nature **157**, 339 (1946); Proc. Roy. Soc. **A89**, 358 (1947).

[54] J. W. Simmons and W. Gordy, Phys. Rev. **73**, 713 (1948).

[55] W. D. Hershberger, J. App. Phys. **17**, 495 (1946).

the output of the cell, and a linear amplifier is used. An indicator reading is taken before and after the gas is admitted into the cell. The absorption coefficient is:

$$\alpha=[10\lambda/L\lambda_g]\log_{10}[(d-\Delta d)/d] \quad \text{db per unit length,}$$

where d is the deflection or reading of the indicator before the gas is admitted, and Δd represents the change caused by the gas. Usually, a balanced detector is employed. The change in wave-length in the cell which is due to the dielectric changes upon admission of the gas can cause errors when there are reflections in the line. These and other extraneous effects are discussed in detail by Beringer.[2] See also Bleaney and Penrose.[56]

The requirement of a square-law detector and a linear amplifier can be avoided by the use of a calibrated microwave attenuator to restore the indicator reading after the gas is admitted to its value before the gas was admitted. The gas absorption is then equal to the difference in attenuator settings. This method has been used by Good.[51] To determine α_g Townes[13] has measured the change in the standing-wave ratio resulting from the gas absorption in a shorted wave-guide cell. To avoid possible detector and amplifier errors he used a calibrated attenuator to adjust the indicator reading to the same value at the maximum and minimum. Townes estimates the accuracy obtainable with this method as about 2×10^{-5} neper/cm.

Tuned cavity method.—Bleaney and Penrose[53] have used a tuned, resonant cavity to measure the absolute absorption of NH_3. The absorption coefficient at the given wave-length is

$$\alpha_g=(2\pi/\lambda)((1/Q_1)-(1/Q_0)), \qquad (38)$$

where Q_0 and Q_1 represent the effective cavity Q values before and after the gas is admitted.‡ Q_0 and Q_1 are measured by detuning the cavity. Bleaney and Penrose estimate that α values of $\sim5\times10^{-4}$ cm^{-1} can be measured in this way without oscillator frequency stabilization. A similar but more sensitive method used by the same authors is to measure the power registered by a loosely coupled crystal detector at the peak of the cavity-response curve with and without the gas. Under these conditions

$$Q_1/Q_0=(d_1/d_0)^{\frac{1}{2}}, \qquad (39)$$

where d_1 and d_0 are the indicator responses with and without gas in the cavity. Substituting (39) in (38) we obtain

$$\alpha=(2\pi/\lambda Q_1)[1-(d/d_0)^{\frac{1}{2}}]$$
$$=(2\pi/\lambda Q_0)[(d_0/d_1)^{\frac{1}{2}}-1]^{\frac{1}{2}}. \qquad (40)$$

The sensitivity depends primarily upon the power stability of the oscillator. Bleaney and Penrose were able to detect absorption as low as 2×10^{-6} cm^{-1} with the latter method. Recently Weidner[57] has achieved a sensitivity of 6×10^{-8} cm^{-1} with this method in the $4\frac{1}{2}$-cm wave region.

The use of the Pound frequency stabilizer[7] should improve this type of cavity measurement. Also, the frequency sweep method may be employed effectively. Then the cavity response curve may be displayed on a cathode-ray oscilloscope. When the pressure of the gas is such that the absorption line is very broad as compared to the cavity response curve, the visual changes in the curve as the gas is admitted may be used to calculate the absorption coefficient from the above equations.

Other methods.—Reference has been made to the use of a large, non-resonant cavity by Becker and Autler.[12] This method, though rather slow, is sensitive. Other methods designed specifically for measuring the absorption of gases in the atmosphere[58] will not be discussed here. However, the phase-lock-in amplifier principle of the ingenious microwave radiometer of Dicke[58] can be adapted to many types of laboratory instru-

[56] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. **59**, 418 (1947).

‡ A simple proof of this equation is possible. By definition

$$Q=2\pi\nu W/(-dW/dt),$$

where W is the energy stored and $-dW/dt$ is the rate of energy loss. By definition of α_g,

$$\alpha_g=-1/W\cdot dW/dx=1/W\cdot dW/dt\cdot dt/dx$$
$$=1/W\cdot dW/dt\cdot 1/c.$$

Combining these, we have

$$Q_g=2\pi\nu/\alpha_g c=2\pi/\alpha_g\lambda.$$

Now,

$$(1/Q_1)=(1/Q_0)+(1/Q_g)=(1/Q_0)+(\alpha_g\lambda/2\pi),$$

which, on rearrangement, is identical with (37).

[57] R. T. Weidner, Phys. Rev. **72**, 1268 (1947).

[58] G. C. Southworth, J. Franklin Inst. **239**, 285 (1945); R. H. Dicke, E. R. Beringer, R. L. Kyhl, and A. B. Vane, Phys. Rev. **70**, 340 (1946); R. W. Bender, Rad. Lab. Report No. 41 (10/21/44).

ments designed to measure absorption spectra. In fact, this principle has already been used by Beringer[2] in the measurement of the oxygen absorption mentioned above.

Relative intensities.—The methods described above for obtaining absolute values of absorption coefficients are not applicable to measurement at low pressures, $\sim 10^{-3}$ mm of Hg or lower. At these pressures the widths of the absorption lines are a fraction of a megacycle, and extreme oscillator frequency stability would be required for even approximate measurements. Studies at low pressures are usually made with a frequency-modulated source and with a cathode-ray oscilloscope display of the lines. With certain of the methods described under the section on detecting systems it is possible to detect sharp and extremely weak absorption lines, but the methods employed do not yield directly absolute values of α_g. However, it is possible to obtain relative intensities of a group of lines located in the same spectral region by comparing the heights of the different lines with the same conditions of power, receiver gain, and sensitivity. If the lines differ greatly in strength, the receiver gain can be varied with a calibrated attenuator. The difficulty arises in monitoring the power and the receiver sensitivity. The usual monitors are themselves frequency sensitive. But conditions do not usually vary much over ranges of a few megacycles, and fairly accurate comparison can be made of closely spaced lines. Usually the accuracy obtainable is sufficient to allow identification of the different components of the hyperfine pattern by comparison with the theoretical intensities. Best results are obtained with a high fidelity receiver. High frequency Stark modulation or source modulation greatly increases the uncertainty of relative intensities.

F. Frequency Measurements

For many purposes in microwave spectroscopy the simple and rapid cavity wave meter is adequate. Nevertheless, when one makes use of different isotopes of the same element in the determination of the structures of polyatomic molecules, the accuracy of the evaluation of the molecular dimensions depends, among other things, upon the percent accuracy of the differences of the frequencies obtained for the different isotopes. These differences are frequently of the order of 100 mc/sec. Thus, if an ordinary cavity wave meter is used for the measurement, the structural determinations would be so inaccurate as to be almost useless, whereas with the frequency standards discussed in the following sections such differences can easily be measured to an accuracy of a tenth of a percent. There is a similar need for accurate measurement in determining nuclear quadrupole coupling factors, which also depend upon relatively small differences in frequency. When a frequency standard is not available, the simpler methods described for measuring differences in frequency often can be applied effectively.

Resonant cavity wave meters.—For regions above 1-cm wave-length a variety of cavity wave meters have been designed which have accuracies ranging from about ± 3 to ± 10 mc. Details of construction and other information on these are available elsewhere.[59,60] The coaxial type is self-calibrating and can be made to tune over a very wide frequency range. The cylindrical cavity operating in TE_{01n} is easier to construct, especially for the millimeter region; and because of its higher Q it is capable of greater accuracy than either the coaxial type or the cylindrical cavity TE_{11n} type.

The frequencies of the different modes of a cylindrical cavity are given by the formula

$$f=(c/2)[(2x_{lm}/\pi D)^2+(n/L)^2]^{\frac{1}{2}}, \qquad (41)$$

where c is the velocity of light in free space, D and L are the cylinder diameter and length, respectively. For TM modes x_m represents the mth root of the Bessel function $J_l(x)=0$, and for TE modes the mth root of $J_l'(x)=0$. Tables of roots of Bessel functions, also charts of modes, which are helpful in designing cavity wave meters, are available in several places.[59,60] Because in the TE_{01n} mode no axial currents exist, it is not necessary to provide plunger chokes nor to make a tight-fitting plunger in order to obtain a high Q. This makes construction easy and also makes it possible to suppress unwanted modes simply by making a loose-fitting piston. Usually polyiron is placed behind the piston to aid in suppression of these modes. For the TE_{01n} case,

[59] R. Beringer, see reference 41, Chapter 5, p. 285.
[60] I. G. Wilson, C. W. Schramm, and J. P. Kinger Bell Sys. Tech. J. **25**, 408 (1946).

(41) becomes

$$f=(c/2)[(7.6634/\pi D)^2+(n/L)^2]^{\frac{1}{2}}. \quad (42)$$

This equation can be used to obtain a calibration which in most instances is sufficiently accurate for identification of absorption lines already measured by more accurate methods. These spectral lines can then be used to obtain a more accurate calibration of the meter, or it can be calibrated with the frequency standard described in the next section. Because the extraneous modes are not entirely suppressed, meters of this type must be used with a certain amount of caution. Figure 11 shows a cross section of a cylindrical cavity TE_{01n} wave meter, with the cylinder dimensions for different millimeter wave-length ranges.

For a silver cylindrical cavity operating in a TE_{01n} mode the Q, which determines the sharpness of tuning, can be determined approximately from the equation

$$Q=2.73\times10^6[1+0.168(D/L)^2n^2]^{\frac{3}{2}}/ f^{\frac{1}{2}}[1+0.168(D/L)^3n^2], \quad (43)$$

where f is in megacycles. This value will be lowered somewhat by the coupling window. The accuracy of the meter is dependent on the half-width of its response curve, which is

$$\Delta f=\frac{f}{Q_{\text{eff}}}, \quad (44)$$

where Q_{eff} is the loaded or effective Q. Thus for a given accuracy the required Q increases with frequency. The TM_{11n} mode, which is degenerate with the TE_{01n} one, can lower the Q of the latter if there is cross coupling. (For ways of preventing this, see reference 59.) The meters which we have constructed at Duke for the 5 to 10 millimeter region have experimentally determined Q's of about 30,000.

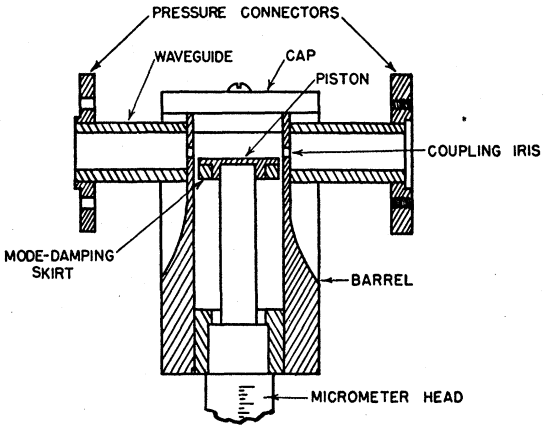


FIG. 11. Cross section of TE_{01n} cavity wave meter. Diameter of cylinder: 0.563″ for upper J band (~8.1- to 11-mm wave-length); 0.469″ for I–J region (~7- to ~8.5-mm wave-length); 0.375″ for upper I band (~5.5- to ~7.1-mm wave-length).

Cylindrical cavity wave meters which employ the TE_{11n} mode have been constructed for the 1.2-cm region.[59] These are self-calibrating and have the additional advantage that extraneous modes can be eliminated by limiting the diameter of the cavity. Because of the chokes required in the plunger, these are more difficult to construct for millimeter waves. The Q obtainable is also somewhat lower than that for the TE_{01n} mode.

Wave meters can be conveniently coupled to the microwave line with directional couplers or with T-sections. Usually several db of attenuation must exist between the meter and the oscillator to prevent pulling of the oscillator. With the frequency sweep method the wave meter "pip" is superimposed upon an absorption line appearing on the oscilloscope.

Standard frequency multipliers.—Through the cooperative effort of the National Bureau of Standards and the Massachusetts Institute of Technology Radiation Laboratory during the war, accurate frequency standards for the centimeter wave region were obtained by multiplying the standard low frequencies which are maintained by the Bureau to an accuracy better than one part in 10^7. Though these standards were constructed for the calibration of secondary standards such as cavity wave meters, the one at Massachusetts Institute of Technology is being used for the direct measurement of spectral lines.[61] Descriptions of these multipliers are available.[62] Less elaborate standards based upon the same principle have been constructed at Westinghouse Research Laboratory[63] and at Duke[64] for use in microwave spectroscopy.

[61] M. W. P. Strandberg, R. L. Kyhl, T. Wentink, and R. E. Hillger, Phys. Rev. **71**, 326 (1947).

[62] L. B. Young, see reference 41, Chapter 6; W. D. George, H. Lyons, J. J. Freeman, and J. M. Shaull, "The microwave frequency standard at the central radio propagation laboratory," Nat. Bur. of Stand. Report No. CRPL–8–1, 9–4.

[63] W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947).

[64] R. Unterberger and W. V. Smith, Rev. Sci. Inst. **19**, 580 (1948).

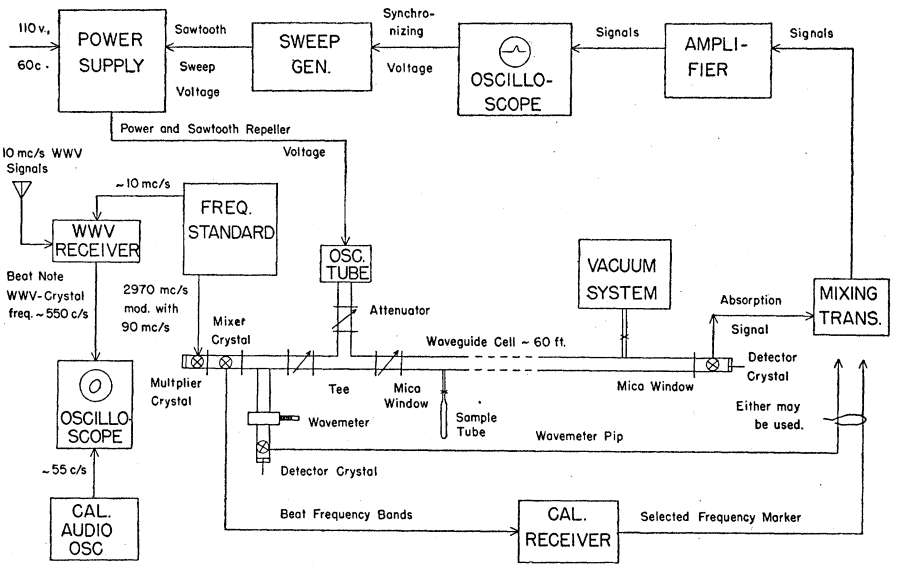


FIG. 12. Diagram of Duke millimeter wave spectrometer.

The Duke system was constructed for obtaining standards in the millimeter region as well as for direct measurement of absorption lines. The initial frequency comes from a 10-mc, temperature-controlled oscillator monitored with Station WWV. Continuous monitoring is achieved by a Lissajous figure, as indicated in Fig. 12. The 10-mc frequency is multiplied to 270 mc with conventional electronic tubes. A Sperry 2K47 klystron multiplier is used to convert the 270 mc to 2970 mc. This output frequency is multiplied by a crystal to the desired region. Strong markers are thus obtained which are separated by 2970 mc. The crystal is also modulated by the 270-mc power and by some of the 90-mc power which is made to by-pass the klystron. The side-band frequencies produced by this modulation provide markers which cover the microwave region at 90-mc intervals.‡‡ A calibrated communications receiver, also monitored by radio station WWV is used to interpolate between the 90-mc markers in the following manner. The marker power is mixed with the source energy in a conventional microwave crystal mixer. The receiver is tuned to the beat note between the source oscillator irradiating the cell and the standard markers nearest the absorption line. With the frequency-sweep method it is easy by mixing the two signals to superimpose the "pip" from the receiver upon the absorption line appearing on the scope. See Fig. 12. The frequency range of the tunable receiver covers 90 mc so that the readings from markers on each side of the spectral line are possible. Since the two receiver readings thus made must add to 90, this allows a constant check on accuracy. Cavity wave meters are used to identify the markers. With this system the NH_3 lines in the millimeter region have been measured[54] to the 16,16 line at 39941.5 mc. Strong markers were obtained at this point. It appears that workable energy can be obtained at least to the 20th harmonic‡‡‡ of the 2920 klystron frequency, so that direct measurements at 5 mm seem feasible. When the second-harmonic power is used to irradiate the cell the first-harmonic output of the source oscillator is measured and the frequency doubled. In this way accurate measurements can be made in the region below 5-mm wave-length. With this standard, spectral lines can be measured to an accuracy of about 50 kc at 25,000 mc and about 70 kc at 40,000 mc. Good and Coles,[63] of Westinghouse, quote an accuracy of 20 kc on the NH_3 lines measured in the 25,000-mc region. The Duke standard has been described in more detail

‡‡ This method for increasing the population of the markers was suggested to us by W. E. Good.

‡‡‡ The Massachusetts Institute of Technology standard employs crystal harmonics down to the 35th to obtain markers at 32,256 mc.

by Unterberger and Smith.[64] Description[65] of other frequency standards are also accessible.

Measurement of differences in frequency.—Dailey and others[66] have suggested the method of producing images of the absorption line by frequency-modulating the source oscillator with a calibrated, tunable, low frequency oscillator. This has been used for accurate measurement of small separations of closely spaced absorption lines such as those of the hyperfine components of the ammonia inversion spectrum. Carter and Smith[67] have suggested the use of a secondary cw oscillator which is tuned in the range covered by the sweep of the source oscillator. The interference of the two oscillators was found to produce sharp signals. By modulation of the secondary oscillator side-band frequencies are produced which provide a ladder of markers of adjustable and known separation. These methods require less equipment than the frequency-multiplier standards and can be used for measuring accurately small differences in frequency. For measuring wider differences in frequency a convenient method,[68] is to employ a calibrated receiver to measure the beat note between two oscillators, one of which is maintained as a reference oscillator at a constant frequency. This method can be used to measure absolute frequencies, provided the reference oscillator is set upon a known absorption line. However, for high accuracy the reference oscillator must be stabilized on the known absorption line.

III. ABSORPTION SPECTRA OF GASES AND VAPORS

A. Atomic Spectra

The range, 0.05 cm^{-1} to 3.5 cm^{-1}, which in waves per centimeter designates approximately the workable microwave region, covers the energy difference between many fine structure terms as well as hyperfine structure terms of a large number of atoms. For example, through interaction of the nuclear magnetic moment with the magnetic field of the valence electron, the ground states of Na^{23}, Rb^{87}, and Cs^{113} are split into doublets with separations of 0.059, 0.228, and 0.307 cm^{-1}, respectively.[69] The separations of the doublet fine structure levels, $2\,^2P_{1/2}-2\,^2P_{3/2}$, for *H* and *Li* are 0.365 and 0.338 cm^{-1}, respectively. The advantage of the greater accuracy of the microwave over the optical method in measuring these intervals need not be emphasized. The experimental difficulties of observing atomic spectra in the microwave region are great, however. That ingenuity can overcome these difficulties in some instances is illustrated by the observation of the hyperfine structure of cesium by Roberts, Beers, and Hill[37] and by the classic hydrogen experiment of Lamb and Retherford.[38] The former observers were able to measure 14 of the components of the Cs transition. Their method has been described in a previous section.

The results obtained by Lamb and Retherford are of considerable consequence because they represent the first definite experimental disagreement with modern quantum theory. According to the Dirac theory, the levels of the same n and j should be degenerate, i.e., $2\,^2S_{1/2}$ with $2\,^2P_{1/2}$, etc. Contrary to theory, Lamb and Retherford showed that the $2\,^2S_{1/2}$ state is actually higher than the $2\,^2P_{1/2}$ state by about 1000 mc/sec.

Though their measurements were made in the microwave region, Lamb and Retherford did not measure directly the transition, $2\,^2P_{1/2}$ to $2\,^2P_{3/2}$, which represents a wave-length of 2.74 cm. They used the atomic beam technique with a detector which was sensitive only to atoms in excited states. Atoms in the metastable $2\,^2S_{1/2}$ state were used to energize the detector. When these were passed through weak microwave radiation of the correct frequency, some were lifted to the $2\,^2P_{3/2}$ state from which they could rapidly decay to the $1\,^2S_{1/2}$ ground state. Thus a drop in indicator current resulted, because fewer excited atoms arrive dat the detector. Measurements were made on weak-field Zeeman components of the $2\,^2S_{1/2}\rightarrow 2^2P_{3/2}$ transition, and by projec-

[65] E. Ginzton, A. Harrison, and R. Hatch, "A frequency standard in the microwave region," Report No. 105-5220, Research Laboratory, Sperry Gyroscope Company, Inc. (1943); R. G. Talpey and H. Goldberg, Proc. I.R.E. **35**, 965 (1947); L. E. Hunt, Proc. I.R.E. **35**, 979 (1947).

[66] B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. **70**, 984 (1946).

[67] R. L. Carter and W. V. Smith, Phys. Rev. **72**, 1265 (1947).

[68] This method, which has been used at several places was originated, I think, by the Westinghouse group.

[69] I. B. M. Kellogg and S. Millman, Rev. Mod. Phys. **18**, 323 (1946).

tion the energy difference for zero field was determined. By refinement of their method these observers hope to resolve the hyperfine structure of the $2\,^2S_{1/2}$ state.

Bethe[70] has shown that the anomalies in the hydrogen fine structure may result from interaction of the electron with the radiation field. This possibility was suggested by Schwinger, Weisskopf, and Oppenheimer.[70] From this effect, Bethe predicted a shift of 1050 mc/sec. for the $2S$ level and a negligible shift in the $2P$ level. This is in good agreement with the Lamb-Retherford results. According to the Bethe theory, this electromagnetic shift of levels increases with Z and decreases rapidly with n. Thus the shift of the $2\,^2S_{1/2}$ level for He^+ should be much greater—Bethe predicts 13 times greater—than for H; and the shifts of the $3S$ levels should be shifted less than the $2S$ levels of the same atom. Hence, a critical test of the Bethe theory can be made.‡‡‡‡ It is my understanding that studies of He^+ are planned by Lamb and Retherford.

B. Molecular Spectra

1. *Inversion Spectra*

(a) *Ammonia.*—Not only was the ammonia inversion spectrum the first to be investigated in the microwave region; it is the most thoroughly studied microwave spectrum. As is well known, ammonia absorbs microwave radiation because of its capacity to turn inside out. The two equilibrium positions of the nitrogen on either side of the plane defined by the three hydrogens are separated by a potential barrier of about 0.38 cm^{-1}. By quantum-mechanical resonance the nitrogen "tunnels through" the barrier. This phenomenon has been explained theoretically[71] and has been investigated in the infra-red region through its effect on the pure rotation spectrum.[72] The ammonia inversion spectrum consists of a number of different lines arising from molecules in different rotational states. This fine structure was apparently first detected by H. S. Howe.[73] It has been explained theoretically by Sheng, Barker, and Dennison,[74] and beautifully resolved by Bleaney and Penrose,[75] by Good,[76] and later by a large number of researchers.

The formula for the fine structure as derived by Sheng, Barker, and Dennison[74] does not contain enough terms to fit the microwave data. A fourth-power formula,

$$\nu=\nu_0+AJ(J+1)+BK^2+CJ^2(J+1)^2 +DJ(J+1)K^2+EK^4, \quad (45)$$

which is the form used by Slawsky and Dennison[77] to account for the pure rotation spectra of non-rigid, symmetric-top molecules, has been employed by Bleaney and Penrose,[75] by Good,[76] and more recently by Simmons and Gordy[54] to calculate the fine structure of the NH_3 inversion spectrum. The work of the last-mentioned observers included measurements into the millimeter wave regions, to the $J=16$, $K=16$ line, and resulted in the particular form

$$\nu(\text{mc/sec.})=23{,}787-151.3J(J+1) +211.0K^2+0.5503J^2 -1.531J(J+1)K^2+1.055_5K^4 \quad (46)$$

for the fine structure lines. The formula fits the results only approximately, to ~25 mc. Thus, still higher order terms are required for a satisfactory agreement. The observed positions of the fine structure lines are given in Table II. Strandberg, Kyhl, Wentink, and Hillger[61] detected an anomaly in the positions of the $K=3$ lines, which has been accounted for by Nielsen and Dennison[78] on the basis of a K-type splitting of these levels.

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[70] H. A. Bethe, Phys. Rev. **72**, 339 (1947).

‡‡‡‡ After this section was written, a note by G. R. Fowles appeared (Phys. Rev. **74**, 219 (1948)) reporting that the predicted S-level shift in ionized helium has been detected with optical spectra.

[71] P. M. Morse and E. C. G. Stueckelberg, Helv. Phys. Acta. **4**, 335 (1931); D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932); M. F. Manning, J. Chem. Phys. **3**, 136 (1935).

[72] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

[73] Unpublished work, quoted by William E. Good, Phys. Rev. **70**, 213 (1946).

[74] H. Y. Sheng, E. F. Barker, and D. M. Dennison, Phys. Rev. **60**, 786 (1941).

[75] B. Bleaney and R. P. Penrose, Nature **157**, 339 (1946); Proc. Roy. Soc. **A189**, 358 (1947).

[76] W. E. Good, Phys. Rev. **69**, 639 (1946); **70**, 213 (1946).

[77] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939).

[78] H. H. Nielsen and D. M. Dennison, Phys. Rev. **72**, 1101 (1947).

TABLE II. Microwave frequencies and absorption coefficients of ammonia.

J	K	Frequency, mc/sec. C. and G.*	S., K., W., and H.**	S. and G.***	Absorption coefficient $cm^{-1}\times10^{6}$†
		$N^{14}H_3$			
1	1	23,694.49	23,694.48		140.
2	2	23,722.63	23,722.59		320.
2	1	23,098.79	23,098.78		62.
3	3	23,870.13	23,870.09		720.
3	2	22,834.17	22,834.02		130.
3	1	22,234.53	22,234.49		30.
4	4	24,139.41	24,139.38		390.
4	3	22,688.29	22,683.73		340.
4	2	21,703.36	21,703.32		77.
4	1	21,134.29	21,134.46		14.
5	5	24,532.98	24,532.90		370.
5	4	22,653.00	22,653.00		170.
5	3	21,285.27	21,285.32		150.
5	2	20,371.46	20,371.51		28.
6	6	25,056.02	25,056.06		320.
6	5	22,732.43	22,732.47		150.
6	4	20,994.61	22,994.63		54.
6	3	19,757.57	19,757.55		63.
7	7	25,715.17	25,715.11		260.
7	6	22,924.94	22,924.88		240.
7	5	20,804.83	20,804.76		56.
7	4		19,218.52		26.
8	8			26,518.91	190.
8	7	23,232.24	23,232.16		10.
8	6	20,719.21	20,719.19		80.
9	9			27,478.00	230.
9	8	23,657.48	23,657.44		58.
9	7	20,735.44	20,735.47		26.
10	10			28,604.73	88.
10	9	24,205.29	24,205.20		72.
10	8	20,852.51	20,852.50		16.
11	11			29,914.66	55.
11	10	24,881.90			19.
11	9	21,070.70	21,070.76		17.
12	12			31,424.97	50.
12	11	25,695.23			11.
12	10		21,391.55		4.6
13	13			33,156.95	16.
13	12			26,655.00	12.
14	14			35,134.44	8.8
14	13			27,772.52	2.8
15	15			37,385.18	8.3
15	14			29,061.14	1.3
16	16			39,941.54	2.0

TABLE II.—*Continued.*

J	K	Frequency, mc/sec. C. and G.*	S., K., W., and H.**	S. and G.***	Absorption coefficient $cm^{-1}\times10^{6}$†
		$N^{15}H_3$			
1	1	22,624.96			6.0
2	2	22,649.85			12.8
2	1	22,044.28			2.3
3	3	22,789.41			27.1
3	2	21,783.98			5.0
3	1	21,202.30			1.1
4	4	23,046.10			14.7
4	3	21,637.91			12.8
4	2	20,682.87			2.9
5	5	23,421.99			13.5
5	4	21,597.86			6.4
5	3	20,272.04			5.7
6	6	23,922.32			11.7
6	5	21,667.93			5.6
7	7	24,553.42			9.0
7	6	21,846.41			8.9
8	8	25,323.51			6.8
8	7	22,134.89			0.38
9	8	22,536.26			2.2
10	9	23,054.97			2.7

* W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947).
** M. W. P. Strandberg, R. Kyhl, T. Wentink, Jr., and R. E. Hillger, Phys. Rev. **71**, 326 (1947).
*** J. W. Simmons and W. Gordy, Phys. Rev. **73**, 713 (1948).
† For the naturally occurring concentrations of the isotope.

The Van Vleck-Weisskopf formula,[79] when specialized to the ammonia inversion spectrum, becomes for particular lines at the resonant frequency and for $T=300°C$, very nearly,

$$\alpha=18\nu^2[K^2(2J+1)/J(J+1)]g \times\exp[-0.0475J(J+1)+0.0174K^2], \quad (47)$$

where

$$g=1 \quad \text{for} \quad K=1, 2, 4, 5, \cdots$$
$$g=2 \quad \text{for} \quad K=3, 6, 9, \cdots,$$

and where ν is in mc. This specialization neglects the nuclear quadrupole hyperfine splitting of the lines. It assumes a line-breadth parameter, $\Delta\nu$, of 13 mc for 1 mm of Hg pressure. Bleaney and Penrose[75] have obtained empirical evidence that this parameter varies as $(K^2/J(J+1))^{\frac{1}{2}}$. This variation is, however, neglected here. In the above transformation,

$$(\mu_{ij})^2=(1.44\times10^{-18})^2(K^2/J(J+1).$$

Equation (47) was used to calculate the absorption coefficients of NH_3 in Table II.

The $N^{14}H_3$ hyperfine structure, the line shapes, and other properties of the NH_3 spectrum will be discussed in later sections.

(b) *Other molecules.*—Though the inversion-type spectrum has so far been investigated only in NH_3, it appears that this type of spectrum in the microwave region may now be observed in certain other molecules. In the infra-red region, Sutherland, Lee, and Wu[80] have observed a splitting of 2.4 cm^{-1} for the excited vibrational state ν_2 of PH_3. This will give rise to a microwave inversion spectrum near 4.2-mm wave-length. Only about one percent of the molecules exist in the ν_2 state at room temperature. Nevertheless,

[79] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945); see also H. Frohlich, Nature **157**, 478 (1946).

[80] G. B. B. M. Sutherland, E. Lee, and C. K. Wu, Trans. Faraday Soc. **35**, 1373 (1937).

by moderate heating it should be easy to observe this spectrum. Similarly, it should be possible to observe the inversion spectrum for the ν_2 state of ND_3, which from infra-red work[81] is predicted at about 4.1-mm wave-length. The population of the ν_2 state of ND_3 is about three percent. Inversion-type spectra in other molecules[81] such as H_2O_2 may well occur in the microwave region.

2. *Electronic Spectra*

Oxygen.—Unlike most microwave absorption spectra, the oxygen spectrum[82] arises through a magnetic rather than through an electric coupling to the radiation field. Because of its symmetry O_2 has no permanent electric dipole moment but does have, because of its $^3\Sigma$ ground state, a permanent magnetic dipole moment of 2-Bohr magnetons. The resonance absorption, which occurs in the 5-mm wave-length region[2, 82] does not represent a transition between different rotational levels but rather a transition between the fine-structure terms of given rotational levels. This fine structure arises from an interaction between the end-over-end rotational momentum of the molecules, defined by the quantum number K, and the total electronic spin momentum, defined by the quantum number S. Since in a Σ state, there is no electronic orbital momentum, the total momentum number J is represented by

$$J=K+S,\ K+S-1\cdots K-S.$$

The selection rules are $\Delta J=\pm 1$ and $\Delta K=0$. For O_2, $S=1$, and there are three values of J for each K. Hence, each rotational level K is split into a triplet. The triplet intervals depend on the nature and magnitude of the coupling of S to the molecular axis.[83] A formula for the fine-structure intervals derived by Kramers[84] and refined and extended by Schlapp[83] yields the microwave frequencies

$$\nu(\text{cm}^{-1})=-(2K+3)B+\lambda+[(2K+3)^2B^2+\lambda^2-2\lambda B]^{\frac{1}{2}}-\mu(K+1) \quad \text{for } J=K+1\rightarrow K, \quad (48)$$

and

$$\nu(\text{cm}^{-1})=+(2K-1)B+\lambda-[(2K-1)^2B^2+\lambda^2-2\lambda B]^{\frac{1}{2}}+\mu K \quad \text{for } J=K-1\rightarrow K.$$

Here $K=1, 3, 5, 7\cdots$ and $B=h/(8\pi^2cI_B)$, where I_B represents the moment of inertia for the molecule. λ and μ are coupling coefficients which must be evaluated empirically. From optical data they have been determined as $B=1.43777$ cm^{-1}, $\lambda=1.985$ cm^{-1}, and $\mu=0.00837$ cm^{-1}.[82, 83] The above formulas predict two series of closely spaced lines, all but one of which occur in the 5-mm region. The $K=1$ line for $J=K-1\rightarrow K$ falls near 2.5-mm wave-length. Beringer[2] has measured the absorption of oxygen¶ in the region 4.8 to 5.9 mm at pressures so high that the structure was not resolved. Measurements on the lines at lower pressures should now be possible. They would be useful in obtaining more accurate values of the fine-structure intervals and the parameters λ and μ.

Van Vleck[82] has calculated the microwave absorption of oxygen in both resonant and non-resonant regions and has compared the results with the measurements of Beringer[2] and others. The agreement of theory and experiment was considered to be satisfactory. He chose $\delta\nu=0.02$ cm^{-1} as the most probable value of the line-breadth parameter for atmospheric pressure. Beringer's measurement of the peak absorption of pure oxygen in the 5-mm region, at atmospheric pressure, is about 67 db per km, or 7.7×10^{-5} neper/cm.

Though oxygen is the only known example of this type of spectrum occurring in the microwave region, it is possible that similar absorption in other molecules having unpaired electrons—for example, S_2, SO, or Se_2—may fall in the workable microwave region.

3. *Pure Rotational Spectra*

(a) *Diatomic and linear polyatomic molecules.*—The rotational frequencies of diatomic molecules are given with sufficient accuracy for our purposes by the formula[85]

$$\nu(\text{cm}^{-1})=2B(J+1)-4D(J+1)^3, \quad (49)$$

[81] G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 224.
[82] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947).
[83] R. Schlapp, Phys. Rev. **51**, 342 (1937).
[84] H. A. Kramers, Zeits. f. Physik **53**, 422 (1929).

¶ See H. R. L. Lamont, Phys. Rev. **74**, 353 (1948).
[85] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939), p. 111.

where

$$J=0,\ 1,\ 2\cdots;\quad B=h/(8\pi^2cI);\quad D=(4B^3)/\omega^2.$$

I is the moment of inertia and ω is the fundamental vibrational frequency.

The second terms in (49) can usually be neglected for J less than about 3. For ICl, for example, when $J=4$, the second term amounts to only 80 kc, but for $J=10$ it is 1.6 mc. Fairly accurate values of D can be obtained from microwave measurements on the rotational spectra alone when rotational lines higher than about $J=10$ can be measured. Thus certain vibration frequencies can be determined from rotational spectra.

For diatomic molecules, measurement of the position of only one rotational line of low J value allows an accurate determination of the internuclear distance for the ground vibrational state. If measurements can also be made on molecules in an excited vibrational state, equilibrium values of the parameters can be made. To first-order approximation,[86]

$$B_n=B_e-\alpha(n+\tfrac{1}{2}),$$

where n is the vibrational quantum number and α is a small constant. If, as is usually the case, the ground state and first excited state are employed,

$$B_e=1/2(3B_0-B_1),\quad \alpha_e=B_0-B_1.$$

Iodine monochloride is the only diatomic molecule whose pure rotational spectrum has been investigated in the microwave region. Detection of this spectrum was first reported by Weidner,[57] who observed the $J=0\rightarrow1$ transition in the 4.5-cm region. Later, it was studied more in detail by Townes, Merritt, and Wright[87] in the 1.2-cm region. The molecular and nuclear constants determined are listed in Tables IV–XI.

One can also determine mass ratios of different isotopes from microwave rotational spectra of diatomic molecules. The frequency difference in the corresponding isotopic frequencies (corrected for nuclear quadrupole and nuclear magnetic perturbations) for the ground vibrational state is[88]

$$\Delta\nu_r=\nu_r-\nu_r{}^i=2B_e(J+1)(1-\rho^2)-\alpha_e(1-\rho^3)(J+1)-4D(1-\rho^4)(J+1)^3,\quad(50)$$

where the B_e, α_e, and D refer to the isotope corresponding to ν_r, and $\rho=(\mu/\mu_i)^{\frac{1}{2}}$. Thus, ρ can be evaluated from (50) and the mass ratios determined from the reduced mass ratio μ/μ_i. Again, if one employs lines of a low J, the last term of (50) can be neglected. With the microwave method applied to ICl, Townes, Merritt, and Wright[87] have evaluated the mass ratio Cl^{35}/Cl^{37} as 0.9459801 ± 0.0000050. This agrees with the value given by Aston,[89] 0.9459806 ± 0.0000300, but not with the more recent value listed by Mattauch,[90] 0.9459441 ± 0.0000065. No doubt a number of other isotopic ratios will be thus evaluated in the future.

The rotational frequencies of linear polyatomic molecules are also given by Eq. (49). The parameter D cannot always be evaluated from vibration frequencies, but when it is not negligible it can be evaluated from measurements on the microwave rotational spectra. Equilibrium values of B are, to a first approximation,[91]

$$B_v=B_e-\sum_i \alpha_i(n_i+d_i/2),$$

where the summation extends over all vibrations, with degenerate ones included only once. n_i is the vibration quantum number, d_i is the degeneracy of the vibration, and α_i are small constants characteristic of the different modes. Thus, to obtain B_e one must make measurements on molecules in $(m+1)$ different vibration states, where m is the number of modes of vibration which the molecule has. As a result of the interaction between vibration and rotation, a doubling of the rotational lines, termed l-type doubling, occurs for the degenerate bending modes. The separation of the doublet increases with J and is given by[92]

$$\Delta\nu=2q(J+1),$$

where q is a small constant which has been

[86] G. Herzberg, reference 85, p. 114.
[87] C. H. Townes, F. R. Merritt, and B. D. Wright, Phys. Rev. **73**, 1334 (1948).
[88] G. Herzberg, reference 85, p. 154.
[89] F. W. Aston, Proc. Roy. Soc. **163**, 391 (1937).
[90] J. Mattauch, *Nuclear Physics Tables* (Interscience Publishers, Inc., New York, 1946).
[91] G. Herzberg, reference 81, p. 370.
[92] A. Herzberg, reference 81, p. 378.

evaluated theoretically by Nielsen and Shaffer.[93] This constant has been determined for certain molecules by direct microwave measurement.[94, 95] The agreement with the theoretical values was found to be only approximate.

Since in a linear polyatomic molecule there are, in general, $(n-1)$ independent molecular-structure parameters, one cannot determine the structure from a single moment of inertia, as is done for diatomic molecules. To a very close approximation, however, the internuclear distances remain the same when different isotopes of a given atom are substituted. By making measurements on molecules with $(n-1)$ different isotopic combinations, one can determine the molecular structure completely. Because of the different zero-point vibration energies for the different isotopes, the average internuclear distance in the ground vibrational state is not quite the same in the molecules containing different isotopes. In most instances, however, this difference does not cause errors greater than a few parts in a thousand in the structural determinations.

If one neglects the hyperfine structure or other splitting, the absorption coefficient of a particular microwave rotational line at the resonant frequency is found to be very nearly

$$\alpha(\mathrm{cm}^{-1})=[8\pi^2 NF_v\nu^2|\mu_J|^2/3ckT\Delta\nu]\times[g_I g_J \exp[-E_r/kT]/Q_r]. \quad (51)$$

This applies to linear, symmetric, or asymmetric molecules. Here,

N = number of molecules per cc in absorbing path;

ν = frequency of the rotational line in vib./sec.;

$|\mu_J|^2$ = the squared matrix element for the transition moment averaged over all orientations of J;

c, k, and T = the velocity of light, Boltzmann's constant, and the absolute temperature, respectively;

$\Delta\nu=1/2\pi\tau$ = line breadth parameter or half of width of line between half-intensity points. Here τ is the mean time between collisions which interfere with the molecular oscillations.

$F_v=g_i\exp[-\omega_i hc/kT]/Q_v$ = the fraction of the molecules in the particular vibration state observed. Here, g_i is the weight of the state; $\omega_i hc$ is the energy above the ground vibrational state; and Q_v is the vibration partition function.

$g_I g_J \exp[-E_r/kT]/Q_r$ = the fraction of the molecules in the lower rotational state of the transition. $g_I g_J$ is the weight of the state, and Q_r is the rotational partition function.

For non-symmetric diatomic and linear polyatomic molecules, which are the ones of interest here,

$$g_n=1,\quad g_J=2J+1,\quad |\mu_J|^2=\mu^2[(J+1)/(2J+1)],$$
$$Q_r=kT/hcB,\quad E_r=hcBJ(J+1),$$

and the above relation reduces to

$$\alpha=[4\pi^2 NF_v hc\nu^3\mu^2/3(kT)^2\Delta\nu]\times\exp[-hcBJ(J+1)/kT], \quad (52)$$

where α, B, ν, and $\Delta\nu$ are in cm^{-1}, and μ, the dipole moment, is in e.s.u. Here J refers to the lower state. Kinetic theory dictates that the average time between collisions, τ, is proportional to $(T)^{\frac{1}{2}}$ and inversely proportional to the pressure. With conditions such that molecular collision is the predominant cause of broadening and for pressures not much greater than 10 cm of Hg, it has been fairly well established experimentally that the line-breadth constant is proportional to pressure. For these conditions we can write

$$\Delta\nu=(\Delta\nu)_1 P_{\mathrm{mm}}(300/T)^{\frac{1}{2}}, \quad (53)$$

where $(\Delta\nu)_1$ is the line-breadth constant for a pressure of 1 mm of Hg and a temperature of 300°K. This idealization assumes that all collisions are equally effective in interrupting the molecular oscillations regardless of the molecular velocity. The number of molecules per cc in the absorbing path is given by

$$N=9.68\times10^{18}(P_{\mathrm{mm}}/T).$$

With these expressions the above equation reduces to the form convenient for calculations:

$$\alpha=[76.7\times10^{-3}F_v\mu^2\nu^3/T^{5/2}(\Delta\nu)_1]\times\exp[-0.72J\nu/T], \quad (54)$$

[93] H. H. Nielsen and W. Shaffer, J. Chem. Phys. **11**, 140 (1943).

[94] C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. **72**, 513 (1947); A. Roberts, *ibid.* **73**, 1405 (1948).

[95] C. H. Townes, A. N. Holden, and F. R. Merritt, private communication.

where μ is expressed in Debye units, and ν_1, $(\Delta\nu)_1$, and α are again in cm^{-1}. Some line-breadth parameters are given in Table IV. This equation illustrates the advantages of studying molecules at low temperatures and high frequencies to obtain strong absorption.

A number of linear molecules have now been investigated in the microwave region. The results obtained are summarized in Tables VI and VII.

Symmetric-top molecules.—The rotational energy of a non-rigid symmetric-top molecule has been derived by Slawsky and Dennison,[77] and in the notation of Herzberg it is[96]

$$E_r/hc=BJ(J+1)+(A-B)K^2-D_JJ^2(J+1)^2 -D_{JK}J(J+1)K^2-D_KK^4; \quad (55)$$

$A=h/(8\pi^2cI_A)$, where I_A is the moment of inertia about the symmetry axis; $B=h/(8\pi^2cI_B)$, where I_B is the moment of inertia about an axis perpendicular to the symmetry axis; D_J, D_{JK}, and D_K, the distortion coefficients, are extremely small constants in comparison to A or B.

Applying the usual Bohr relation with the selection rules,

$$\Delta J=+1, \quad \Delta K=0,$$

one finds the rotational frequencies are:

$$\nu_r(cm^{-1})=2B(J+1)-4D_J(J+1)^3 -2D_{JK}(J+1)K^2, \quad (56)$$
$$J=0, 1, 2, \cdots.$$

For low rotational states the latter terms can be neglected, and

$$\nu_r=2B(J+1)=1677929(J+1)/I_B,$$

where ν_r and B are in mc/sec. and I_B is in $gmcm^2\times10^{-40}$ and where the value $h=6.6242\times10^{-27}$ erg/sec. has been used.

The above expression does not include the nuclear perturbations frequently encountered, but these can be accounted for by adding to the above energy the appropriate expressions, to be given in the section on hyperfine structure. Also it does not hold exactly for molecules in certain excited vibrational states. Formulas for excited vibrational states have been derived. For a discussion, see Herzberg.[97]

[96] G. Herzberg, reference 81, p. 400.
[97] G. Herzberg, reference 81, p. 403.

The absorption coefficient of a given rotational line at the resonant frequency can be calculated by means of formula (51), with the following parameter values, which differ from those of linear molecules,[98, 99]

$$|\mu_J|^2=\mu^2[((J+1)^2-K^2)/(J+1)(2J+1)],$$
$$E_r=hcBJ(J+1)+(A-B)K^2,$$
$$g_J=2(2J+1), \quad \text{for} \quad K\neq0,$$
$$=2J+1 \quad \text{for} \quad K=0.$$

For cases of three identical corner atoms (PF_3 or CH_3Cl type),

$$g_I=\tfrac{1}{3}(2I+1)(4I^2+4I+3), \quad \text{for } K \text{ divisible by 3,}$$
$$=\tfrac{1}{3}(2I+1)(4I^2+4I), \quad \text{for } K \text{ not divisible by 3,}$$
$$Q_r=[(2I+1)^3/3][(\pi/B^2A)(KT/hc)^3]^{\frac{1}{2}},$$
$I=$ nuclear spin of the identical corner atoms.

The microwave rotation spectra of a number of symmetric-top molecules have been investigated. The pertinent results obtained are summarized in the tables on molecular and nuclear constants. As with linear polyatomic molecules, one must always employ molecules with different isotopes to make complete determination of molecular structure, since only I_B values are obtained from the measurements.

The structure of the methyl halides has long been a subject of speculation. Fairly reliable estimates (to about three percent) of the C—Hal distance were made by means of electron diffraction, but with this method no determination of the bond angles or the C—H distances could be made because of the low electron-scattering power of hydrogen. From infra-red rotation-vibration spectra it has not been possible to obtain accurate values of either I_A or I_B alone. But, with the Johnson and Dennison relation,[100]

$$\sum\Delta\nu_i=[6/I_A-7/I_B][h/(8\pi^2c)],$$

one of the moments can be determined in terms of the other, from measurements of the separations of zero branch lines in the three fundamental perpendicular-type vibration bands. Now that I_B has been accurately determined from microwave rotation spectra, I_A can be evaluated

[98] G. Herzberg, reference 81, pp. 28, 32, 506.
[99] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[100] M. Johnson and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

with the help of the above formula. With this help and by microwave measurements on molecules containing different isotopes, complete determinations of the structures of all four methyl halides have been made in this laboratory.[101,102] As might be expected, C−H distances are not the same in these molecules but vary in a uniform manner from F to I. The C−H distances are in inverse sequence to the C−H bond-stretching force constant. With the exception of C−F, the C−Hal bonds are longer than had been anticipated. They are significantly longer than the added single-bond covalent radii if the C radius 0.77A proposed by Pauling[103] is used. The agreement is improved by use of the revised C radius 0.79A suggested by the author[104] from a consideration of the work on hydrocarbons by Mulliken, Rieke, and Brown.[105] The exceptionally short C−F distance in methyl fluoride, 1.385A indicates a considerable amount of double-bond character from contributions of structures of the types $H-\underset{H}{\overset{H^-}{C}}=F^+$. The Schomaker-Stevenson[106] correction for ionic character, $-.09|x_1-x_2|$, may explain some of the decrease from the radii sum for C−F, but for the other halides this correction makes agreement with the measured values even worse. Since the complete determination of the structures depends partly on infra-red data, some improvement in the accuracy of C−H distances and bond angles can be made through microwave measurements on molecules containing additional isotopic combinations. In this way complete determinations of structure can be made with microwave data alone. Such measurements are already planned by J. W. Simmons.

Methyl cyanide,[107] methyl isocyanide,[107] methyl acetylene,[108] and borine carbonyl[109] have been shown to have symmetric structures. Other methods have indicated a symmetric structure, but a slight asymmetry could not have been detected by previously used methods. In the preliminary report from this laboratory[110] it was stated that the extra lines for the $J=1\rightarrow2$ transition of CH_3NC might possibly indicate a slightly asymmetric structure. These extra lines have now been proved to arise from molecules in excited vibrational states. Some of their molecular parameters have been evaluated and are listed in Tables VI and VII. Further work is in progress on these compounds with molecules having different carbon isotopes. It is hoped that complete determinations of structure can soon be made for each of them.

Results obtained on these and other symmetric-top molecules are listed in Tables VI and VII. Nuclear effects will be discussed in a later section.

Asymmetric-top molecules.—The rotational energy for asymmetric-top molecules has been expressed by Wang in the form[111]

$$E_\tau/hc=\tfrac{1}{2}(B+C)J(J+1)+[A-\tfrac{1}{2}(B+C)]W_\tau, \quad (57)$$

where

$$A=h/(8\pi^2cI_A),\quad B=h/(8\pi^2cI_B),\quad C=h/(8\pi^2cI_C),$$

and where I_A, I_B, and I_C are the three principal moments of inertia, which are all unequal. W_τ here is analogous to K^2 for symmetric tops. However, unlike K^2, it is not limited to integral values but is, in general, a complicated algebraic function of the moments of inertia. For each J there are $(2J+1)$ values of W_τ, identified by the quantum number τ, which takes integral values ranging from $-J$ to $+J$. Algebraic expressions for W_τ in terms of the parameter, $b=(C-B)/[2A-(B+C)]$, have been derived for J values up to 10 by Nielsen,[112] and for $(J=11)$ by Randall, Dennison, Ginsberg, and Weber.[113] These equations are reproduced for J values up to 6 by Herzberg.[114] The powers of these equa-

[101] W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).
[102] O. R. Gilliam, H. D. Edwards, and W. Gordy, to be published.
[103] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.
[104] W. Gordy, J. Chem. Phys. **15**, 81 (1947).
[105] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).
[106] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).
[107] M. Kessler, H. Ring, and W. Gordy, to be published.
[108] H. Ring and W. Gordy, to be published.
[109] W. Gordy, H. Ring, and A. B. Burg, to be published.
[110] H. Ring, H. D. Edwards, M. Kessler, and W. Gordy, Phys. Rev. **72**, 1262 (1947).
[111] S. C. Wang, Phys. Rev. **34**, 243 (1929).
[112] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).
[113] H. N. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, Phys. Rev. **52**, 160 (1937).
[114] G. Herzberg, reference 81, pp. 46–47.

tions increase with J. Hence, an exact solution is possible only for very low J values.

Tables have been made by King, Hainer, and Cross[115] which are designed to eliminate much of the tedious calculation involved in the analysis of asymmetric-top molecules. These were constructed primarily for infra-red spectra and need to be greatly expanded for the accuracy required in microwave work. Nevertheless, they are very useful in their present form. These authors express the rotational energy in the form

$$E_r/hc=\tfrac{1}{2}(A+C)J(J+1)+\tfrac{1}{2}(A-C)E_\tau{}^J, \quad (58)$$

where A and C have their usual significance, and the third moment of inertia is expressed as an implied function of $E_\tau{}^J$. $E_\tau{}^J$ is developed as a function of κ, where

$$\kappa=[2B-(A+C)]/[A-C].$$

In Table I of the paper mentioned[115] are given $E_\tau{}^J$ values for 11 values of the parameter κ ranging from -1 (symmetric top) to 0 (most asymmetric) for J as high as 12. Interpolations¶¶ between the $E_\tau{}^J$ values given are usually not sufficiently accurate for microwave spectra. Table II in their paper gives an expansion of $E_\tau{}^J$ in power series in κ:

$$E^J=\sum A_{\tau n}\kappa^n.$$

The expansion is carried only to second order and hence is useful only for very small values of κ, i.e., for the most asymmetric types. Table III of the same paper expresses $E_\tau{}^J$ as a power series in δ:

$$E_\tau{}^J=\sum B_{\tau n}\delta^n,$$

where

$$\delta=(\kappa+1)/2=(B-C)/(A-C).$$

The expansion is carried to third order. It is useful only for very slightly asymmetric rotators, i.e., for δ very small, and for relatively small J values as the series converges slowly for J high.

Recently Golden[116] has developed a method which in certain cases allows accurate determination of asymmetric rotator levels of high J. It is shown that solutions of Mathieu's equation (which are already tabulated) can be transformed to provide energy level values to good approximation for levels of large J which correspond to small K in the limiting symmetric-top case. Perturbation methods are then applied to obtain accurate values of the levels. The correspondence principle has also been applied[117] to obtain a satisfactory solution for the slightly asymmetric rotator of high J, corresponding to high K of the limiting symmetric-top case. In addition to other difficulties, the centrifugal distortion for states of high J greatly increase the difficulties of interpretation of the spectrum of an asymmetric rotator. These are treated in a second paper by Golden.[118]

In addition to the laborious task of obtaining the numerical solutions, the problem of correct assignment of the levels is great. The Stark effect has proved extremely valuable for this purpose.[119]

Selection rules for slightly asymmetric rotators can be obtained immediately by identification of the levels with the corresponding K of the limiting symmetric rotator. For a discussion of different cases, see Herzberg,[120] also Cross, Hainer, and King.[121]

Cross, Hainer, and King have also constructed tables[121] which allow easy calculation of line intensities of asymmetric rotators. Equation (51) above can be used with these tables to calculate absorption coefficients if we set

$$\mu_J=\mu^2|\Phi|^2,$$

where μ is the permanent dipole moment of the molecule and where, in their notation,

$$|\Phi|^2=\sum_{X,Y,Z}\sum_{M''}\sum_{M'}|(\Phi_{F_g}A)J'',\tau'',M'';J',\tau',M'|^2.$$

Numerical values of this function are given by these researchers for J up to 12 and for five

[115] W. G. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943).

¶¶ A method of making rapid interpolation with the punched-card I.B.M. system has been described. (G. W. King, P. C. Cross, and G. B. Thomas, J. Chem. Phys. **14**, 35 (1946).)

[116] S. Golden, J. Chem. Phys. **16**, 78 (1948).

[117] E. E. Witmer, Proc. Nat. Acad. Sci. **13**, 60 (1927); Monthly Progress Reports of the University of Pennsylvania, Thermodynamics Research Laboratory, Contract NObs-2477, Navy Department Bureau of Ships; Bull. Am. Phys. Soc. **23**, No. 3, 55 (1948).

[118] S. Golden, J. Chem. Phys. **16**, 250 (1948).

[119] (a) B. P. Dailey, S. Golden, and E. B. Wilson, Jr., Phys. Rev. **72**, 871 (1947); (b) S. Golden and E. Bright Wilson, J. Chem. Phys. **16**, 669 (1948).

[120] G. Herzberg, reference 81, Chapter I.

[121] P. C. Cross, R. M. Hainer, and W. G. King, J. Chem. Phys. **12**, 210 (1944).

different values of κ (degrees of asymmetry). These authors[122] have calculated the microwave absorption coefficients expected for H_2O, HDO, D_2O, and similar molecules.

So far only two complete structural determinations of asymmetric molecules from microwave spectra have been reported (see Table VII). Nevertheless, because of the great abundance of relatively simple asymmetric molecules, considerable work will no doubt be done in the future. Studies on several other molecules of this type are already in progress, and preliminary results on some of these are given in Tables VI and VII. The large amount of work required in the analysis of the asymmetric rotator is partly offset by the greater amount of information which is obtained. Since all the moments of inertia can be evaluated from the pure rotation spectra alone, one can, for example, determine the structure of a triatomic molecule without the use of different isotopic combinations.

Internal rotation.—Molecules in which one part can rotate with respect to another part are of interest. Those for which one of the rotating parts has a dipole moment with a component perpendicular to the axis of rotation and a sufficiently large moment of inertia, per se, would be expected to have microwave internal rotational spectra. No free internal rotational spectra have yet been reported in the microwave region, though spectra apparently caused by a hindered internal rotation of the OH group in CH_3OH and of the NH_2 group in CH_3NH_2 have been reported.[123]

The theory for internal rotation has been worked out by Nielsen[124] for the symmetric-top case. (See also Koehler and Dennison.[125]) This theory is also applicable to the slightly asymmetric rotator. It predicts two series of lines, given in Herzberg's notation as[126]

$$\nu = A_1 - B \pm 2BK \pm 2A_1K_1, \qquad (59)$$

with

$$B = h/(8\pi^2 I_B c),$$

and

$$A_1 = h/(8\pi^2 I_{A_1} c),$$

where I_A is the moment of inertia about the symmetry axis of the internally rotating part which has the dipole moment and where K_1 is the absolute value of the quantum number for this rotation. No internal rotational spectra would be expected for symmetrical molecules such as H_3C-CF_3, but internal rotation might, nevertheless, be detected indirectly through its centrifugal effects on the ordinary rotational spectra.

A series of lines for CH_3OH and CH_3NH_2 have been detected by Hershberger and Turkevitch[123] in the 1.2-cm region. This series of CH_3OH lines has been studied by Dailey[31] and by Coles[127] with the Stark modulation method. The lines have been interpreted by Burkhead and Dennison¶¶¶ as arising from hindered internal rotation of the OH group corresponding to the transition $J=2\rightarrow2$ and $K=2\rightarrow1$. Lines corresponding to free internal rotation of the OH would fall in the infra-red region.[128] However, the energy restricting rotation,[125] which can be negative, is sufficient to make lines fall in the 1-cm region, provided the barrier height is of the right amount. The barrier height tentatively chosen by Burkhead and Dennison is 320 cm^{-1}, somewhat lower than that previously estimated from infra-red spectra.[128] They treat the molecule as an asymmetric rotator with hindered internal rotation. By a proper choice of the three parameters in their formula they were able to calculate the positions of the ten lines observed near 1.2 cm, with an average deviation of only 0.18 mc. Certain features of the methyl alcohol spectrum are yet to be cleared up. One of these is the correct interpretation of a group of lines in the 6-mm region, observed by Edwards, Gilliam, and Gordy,[129] which apparently correspond to the $J=0\rightarrow1$, $K=0\rightarrow0$ transition.

[122] G. W. King, R. M. Hainer, and P. C. Cross, Phys. Rev. **71**, 433 (1947).
[123] W. D. Hershberger and J. Turkevitch, Phys. Rev. **71**, 554 (1947).
[124] H. H. Nielsen, Phys. Rev. **40**, 445 (1932).
[125] J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1006 (1940).
[126] G. Herzberg, reference 81, p. 498.
[127] Quoted by D. M. Dennison, Symposium on Molecular Spectroscopy, Ohio State University, June, 1948.
¶¶¶ A report on this work was given by D. M. Dennison at the Ohio State Symposium on Molecular Spectroscopy, June, 1948. The theory has not yet been published. I am indebted to him for communicating their results to me.
[128] A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1938).
[129] H. D. Edwards, O. R. Gilliam, and W. Gordy, to be published.

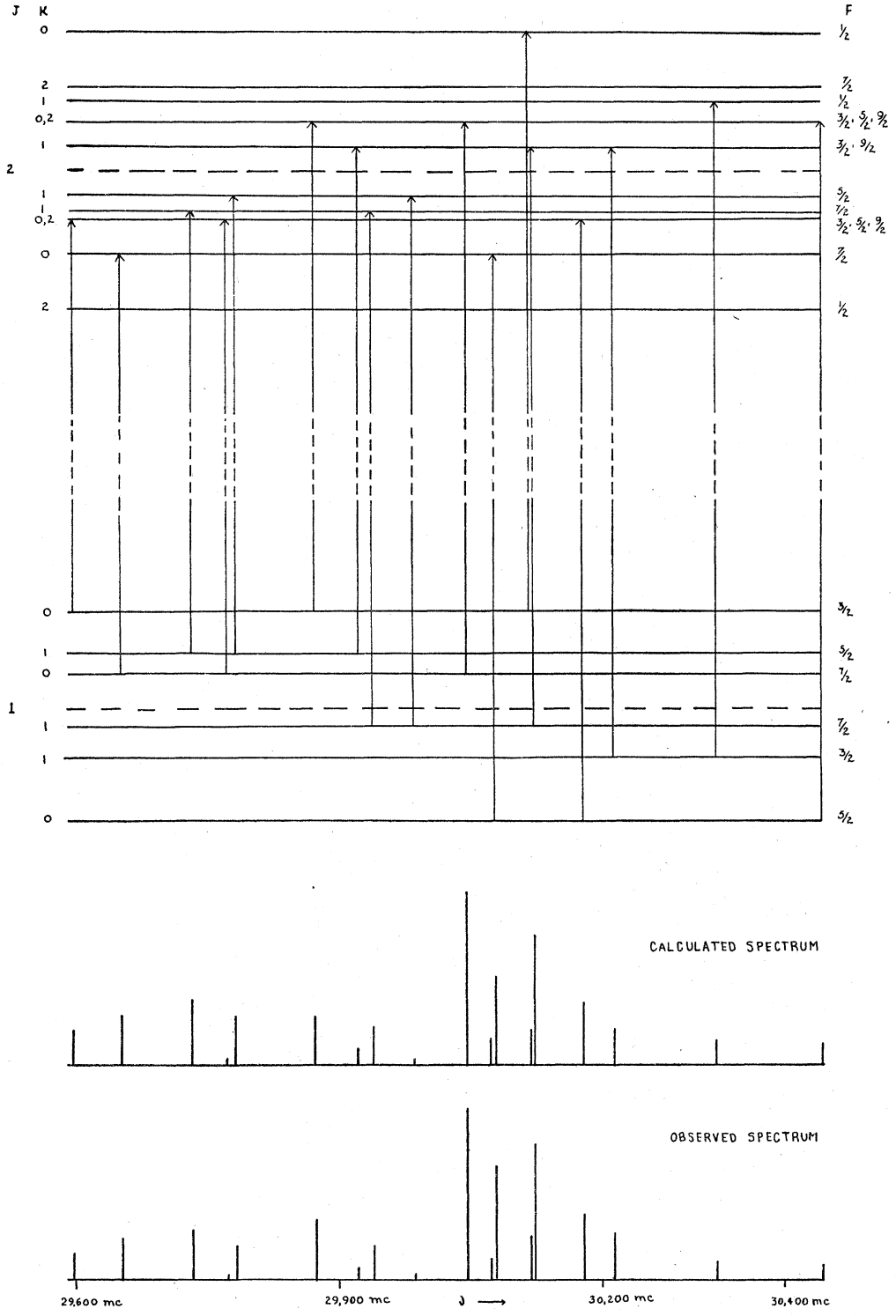


FIG. 13. Illustration of hyperfine structure in a symmetric rotator. $J=2\rightarrow 3$ transition of $C^{12}H_3I^{127}$. (Data from Gordy, Simmons, and Smith (reference 101).)

4. *Hyperfine Structure*

Nuclear quadrupole interactions.—The work of Good[76] disclosed a definite hyperfine structure in the inversion spectrum of ammonia. The observed satellite structure was later interpreted by Coles and Good,[130], and by Dailey, Kyhl, Strandberg, Van Vleck, and Wilson[66] as caused by interaction of the nuclear quadrupole moment of N^{14} with the molecular field. Since this initial discovery, hyperfine structure caused by nuclear quadrupole interaction has been found in the microwave spectrum of a large number of molecules. Indeed, it appears that such hyperfine structure may confidently be expected for any molecule having an atom with a nuclear spin greater than $\frac{1}{2}$. Nuclear quadrupole interaction had, of course, been detected previously in atomic spectra, and with the molecular beam radiofrequency method for certain diatomic molecules. The theory of these interactions developed by Casimir[131] was adapted to symmetric-top molecules by Coles and Good[130] and by Van Vleck.[66,132] The resulting formula for the interaction energy is

$$E_Q = eQ\frac{\partial^2 V}{\partial z^2}\left(\frac{3K^2}{J(J+1)}-1\right) \times \frac{3/4C(C+1)-I(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)} \quad (60)$$

$$C = F(F+1)-I(I+1)-J(J+1),$$

$$F = J+I,\ J+I-1\cdots|J-I|,$$

where I is the spin of the interacting nucleus, e is the electronic charge, Q is the nuclear quadrupole moment, and $(\partial^2 V)/(\partial z^2)$ is the divergence along the molecular axis of the molecular field at the interacting nucleus. The pertinent selection rules are

$$\Delta J = +1, \quad \Delta K = 0, \quad \Delta F = 0, \pm 1.$$

This formula also applies to linear molecules if we set $K=0$. It applies to molecules with only one interacting nucleus.

[130] D. K. Coles and W. E. Good, Phys. Rev. **70**, 979 (1946).

[131] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, E. F. Bohn, Haarlem, 1936); Physica **2**, 719 (1935).

[132] J. H. Van Vleck, Phys. Rev. **71**, 468A (1947).

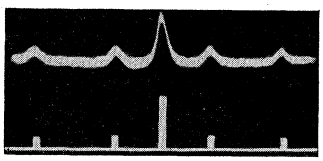


FIG. 14. Hyperfine structure of the 1,1 line of $N^{14}H_3$. $J=1$, $K=1$. (From Simmons and Gordy (reference 54).)

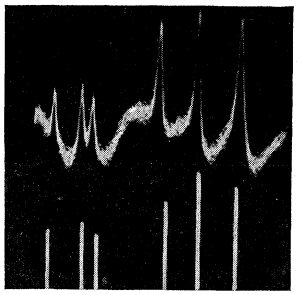


FIG. 15. Theoretical and observed $F_1 \rightarrow F_1+1$ hyperfine lines of the $J=7\rightarrow 8$ rotational transition of $I^{127}C^{12}N^{14}$ at 5.81-mm wave-length. (From Gilliam, Edwards, and Gordy.)

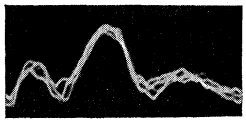


FIG. 16. Hyperfine structure of the $J=0\rightarrow 1$ rotational transition of $HC^{12}N^{14}$ at 3.38 mm wave-length. (From Smith, Gordy, Simmons, and Smith (reference 25).)

The above formula is slightly different from the formula as originally stated. Different forms of it exist in the literature because of the existence of different definitions of the unit quadrupole coupling.[133] The above form now seems to be generally used, and the quadrupole coupling factors determined earlier have all been converted to conform to it.

As an illustration of the theory I have sketched in detail the energy-level diagram and theoretical spectrum for the $J=1\rightarrow 2$ transition of CH_3I^{127} (see Fig. 13). The observed spectrum is given for comparison. Some of the levels here are accidentally degenerate. The second-order effects mentioned below were included to bring the observed and calculated spectrum into agreement. However, these effects, though large in comparison to the experimental error, are too small to be readily apparent in a graph of this

[133] B. T. Feld, Phys. Rev. **72**, 1116 (1947).

TABLE III.* Second-order effects in the hyperfine structure of the $J=1$ to $J=2$, $K=0$ to $K=0$ line of CH_3I in the ground vibrational state. Frequencies are given in mc/sec. relative to the strongest line, $F=7/2$ to $F=9/2$, $K=0\rightarrow 0$. $eQ(\partial^2V/\partial z^2)=-1934$ mc/sec.

F transition	Experimental	First-order theory	Experiment minus first-order theory	Second-order theory
3/2→1/2	+ 74.33	+ 74.59	−0.26	−0.27
3/2→3/2	−174.47	−174.06	−0.41	−0.37
3/2→5/2	−448.04	−450.35	+2.31	+2.19
5/2→3/2	+406.47	+406.14	+0.33	+0.40
5/2→5/2	+132.72	+129.85	+2.87	+2.95
5/2→7/2	+ 32.73	+ 33.15	−0.42	−0.39
7/2→5/2	−273.04	−276.29	+3.25	+3.35
7/2→7/2	−373.04	−372.99	−0.05	0
7/2→9/2	0	—	—	—

* From W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).

kind. For further illustration, the 1,1 line of $N^{14}H_3$ and selected sections of the spectra of ICN and HCN are shown in Figs. 14–16.

Second-order effects.—In the Bell Telephone Laboratories[87,134] and in this laboratory[135] it was found that the first-order nuclear quadrupole interaction is an inadequate explanation of the observed hyperfine structure of some molecules. In the case of ICN and of CH_3I, deviations of the order of megacycles were detected. The theory extended to second order by Bardeen and Townes,[134] however, was found to account for the observation. In Table III the observed and calculated second-order effects for one transition of CH_3I are repeated from a paper by Gordy, Simmons, and Smith.[101] It appears that second-order effects may be encountered frequently, since in a number of molecules the nuclear interactions are sufficiently large to cause such effects. The energy of second-order interaction, as derived by Bardeen and Townes, is of the form[134]

$$E_Q=\sum_{J'}[(IJFM_F|H_Q|IJ'FM_F)/(E_r-E_r')], \quad (61)$$

where J' can differ from J by 1 or 2. Physically, this represents an interaction between levels of different J but of the same total momentum F and with the same M_F. The formulas for numerical evaluation of the squared matrix element in the numerator are

$$(IJFM_F|H_Q|IJ+1FM_F)^2$$
$$=\left[3eQ\frac{\partial^2V}{\partial z^2}\cdot\frac{K}{8I(2I-1)J(J+2)}\right]^2\left[1-\frac{K^2}{(J+1)^2}\right]$$
$$\times\frac{[F(F+1)-I(I+1)-J(J+2)]^2}{(2J+1)(2J+3)}$$
$$\times(I+J+F+2)(J+F-I+1)$$
$$\times(I+F-J)(J+I-F+1), \quad (62)$$

$$(IJFM_F|H_Q|IJ+2FM_F)^2$$
$$=\left[3eQ\frac{\partial^2V}{\partial z^2}\cdot\frac{1}{16I(2I-1)(2J+3)}\right]^2\left[1-\frac{K^2}{(J+1)^2}\right]$$
$$\times\left[1-\frac{K^2}{(J+2)^2}\right]\frac{1}{(2J+1)(2J+5)}$$
$$\times(F+I+J+5)(F+I+J+2)$$
$$\times(J+I-F+2)(J+I-F+1)$$
$$\times(J+F-I+2)(J+F-I+1)$$
$$\times(I+F-J)(I+F-J-1). \quad (63)$$

Levels below as well as above a given level interact with it. However, since the matrix element is symmetric in J and J', the above formulas are all that are necessary for calculations. The matrix element vanishes when J' differs from J by more than 2.

Quadrupole coupling involving two nuclei.—The case of two nuclei in the same molecule having quadrupole interactions has also been treated by Bardeen and Townes.[136] If the interaction energy of one of these, E_1, is large compared to that of the other, E_2, the latter can be treated as a perturbation of the first and the energy expressed as

$$E_Q=E_1(F_1)+\sum_{F_2}c(F_1F_2)^2\cdot E_2(F_2), \quad (64)$$

where

$$F_1=J+I,\ J+I-1,\ \cdots|J-I_1|$$
$$F_2=J+I_2,\ J+I_2-1,\ \cdots|J-I_2|.$$

$E_1(F_1)$ and $E_2(F_2)$ are obtained by substituting F_1 and F_2 in formula (60). The transformation

[134] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627, 1204 (1948).

[135] O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. **73**, 635 (1948).

[136] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

coefficient $c(F_1F_2)$ is given by Bardeen and Townes for the cases

(1) $I_1=1$, I_2 and J arbitrary,
(2) $I_1=\frac{3}{2}$, I_2 and J arbitrary.

The total momentum is

$$F=J+I_1+I_2,\ J+I_1+I_2-1\cdots J-I_1-I_2$$
$$=F_1+I_2,\ F_1+I_2-1\cdots F_1-I_2.$$

Thus for $J\geqq I_1+I_2$, each J level is split into $(2I_1+1)(2I_2+1)$ hyperfine levels. Since here $E(F_1)$ is considered large as compared to $E_2(F_2)$, each F_1 level may be regarded as split into $(2I_2+1)$ sublevels. The summation in the above formula extends over the F_2 values for a given F and F_1.

The first-order theory was found to hold fairly accurately for $(\alpha)<0.1$ or $(1/\alpha)<0.1$, where α is the ratio of the quadrupole coupling for the two nuclei. For ClCN, $\alpha=0.05$, the deviations from first order were barely noticeable. Smith, Ring, Smith, and Gordy[137] have applied the theory to ICN and N_2O, where the ratio of the coupling of the central to the end atom is 0.0015 and 0.261, respectively. Quadrupole effects of two atoms in the same molecule are illustrated by Fig. 17.

Quadrupole coupling in asymmetric rotators.—A theoretical treatment of nuclear quadrupole interaction in asymmetric-top molecules has been made by Bragg[138] and by Knight and Feld.[139] The matrix elements of the coupling operator

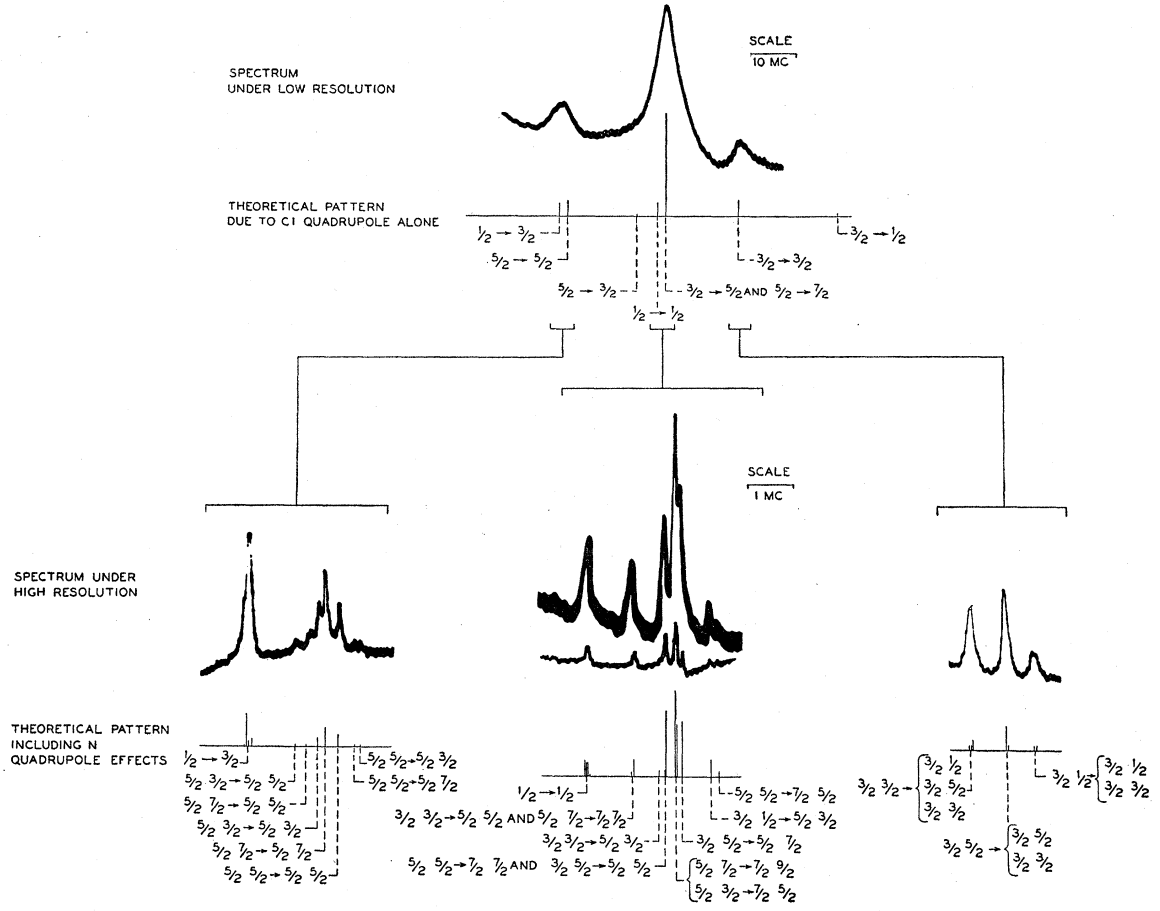


FIG. 17. Illustration of quadrupole splitting by two nuclei: the hyperfine structure of the $J=1\rightarrow2$ transition of $Cl^{35}C^{12}N^{14}$. Upper curve shows splitting caused by Cl^{35} with N^{14} splitting unresolved. Lower curves show N^{14} effects resolved. (From Townes, Holden, and Merritt (reference 95).)

[137] A. G. Smith, H. Ring, W. V. Smith, and W. Gordy Phys. Rev. **73**, 633 (1948).
[138] J. K. Bragg, Phys. Rev. **73**, 1250A (1948).
[139] G. Knight and B. T. Feld, Phys. Rev. **74**, 354A (1948).

$F(I, J)$ are the same as those for linear and diatomic molecules, but the factor $\langle 3\cos^2\theta-1\rangle_{Av}$ is different and involves two molecular coupling parameters $(\partial^2V)/(\partial z^2)$ and $(\partial^2V)/(\partial x^2)-(\partial^2V)/(\partial y^2)$, where x, y, and z are coordinates of the principal molecular axis and V is the potential at the interacting nucleus. Details of the calculations have not yet been published.

Intensities.—Relative intensities of the different hyperfine components of a given rotational transition may be determined from the weights $(2F+1)$ of the upper and lower hyperfine levels with the methods commonly applied in atomic spectra. The relevant formulas for the calculation are[140]

$$\left.\begin{aligned} I_+ &= (1/F)\cdot Q(F)\cdot Q(F-1) && \Delta F=+1 \\ I_0 &= (2F+1)/F(F+1) && \\ &\quad \cdot P(F)\cdot Q(F) && \Delta F=0 \\ I_- &= (1/F)\cdot P(F)\cdot P(F-1) && \Delta F=-1 \end{aligned}\right\} \begin{array}{l}\Delta J=+1\\ \text{Pure}\\ \text{rotation}\\ \text{spectra}\end{array} \tag{65}$$

$$\left.\begin{aligned} I_0 &= (2F+1)/F(F+1)\cdot R^2(F) && \Delta F=0 \\ I_\pm &= 1/F\cdot P(F)\cdot Q(F-1) && \Delta F=\pm 1 \end{aligned}\right\} \begin{array}{l}\Delta J=0\\ \text{Inversion}\\ \text{type}\\ \text{spectra}\end{array} \tag{66}$$

where

$$P(F)=(F+J)(F+J+1)-I(I+1),$$
$$Q(F)=I(I+1)-(F-J)(F-J+1),$$
$$R(F)=F(F+1)+J(J+1)-I(I+1).$$

J and F in these formulas are for the upper state. For J values up to 6 and I values to 7/2, numerical values of the relative intensities are tabulated in various places.[141,142] For symmetric-top molecules, the relative intensities for the different K values in a given J transition must first be determined by the theory of Dennison (outlined in the section on symmetric rotators above), since K does not appear here. These formulas are very useful in identifying the different lines of a hyperfine pattern. However, the present methods of measuring relative intensities in the microwave region are not sufficiently accurate to provide a test of the theory.

Magnetic interaction.—The work of Simmons and Gordy[54] on the inversion spectrum of ammonia revealed that the nuclear quadrupole interaction alone is an inadequate explanation of the hyperfine structure. In this instance, the rotational levels are too widely spaced in comparison to the nuclear quadrupole splitting for second-order interactions of the type discussed above to be significant. Interaction of the nuclear magnetic moment of nitrogen with the magnetic field arising from molecular rotation was suggested as a possible cause of this additional perturbation. By quantitative calculations Jauch[143] and Henderson[144] have shown that this is very probably the correct explanation. The energy contributed by this interaction as stated by Henderson is

$$\Delta E=[(aK^2)/(J(J+1))+b]\times[F(F+1)-J(J+1)-I(I+1)], \tag{67}$$

where $a=0.0011$ and $b=0.0057$. The quadrupole coupling, $eQ(\partial^2V/\partial z^2)$, used to obtain the best fit is 4.10.

Henderson and Van Vleck[145] have worked out the theory of the coupling of electron spins in rotating polyatomic molecules. When molecules with unpaired electrons such as NO_2, NO_3, and ClO_2 are investigated in the microwave region, this theory will be particularly helpful. Henderson points out that it can also be applied when nuclear rather than electronic spins interact with the electronic orbital moments.

5. *Line Shapes*

(a) *Natural width.*—The natural line width, that caused by spontaneous emission alone, is so small for microwave frequencies that it is entirely insignificant in comparison to other factors determining line breadths. For K-band wavelengths it is of the order of 10^{-8} cycle/sec.

(b) *Pressure broadening.*—The most significant factor influencing line shapes, when the pressure is not extremely low, is molecular collision. The most general expression for the shape of lines broadened by collision is that recently

[140] A. C. Candler, *Atomic Spectra and the Vector Model* (University Press, Cambridge, 1937), Ch. XI, p. 187.
[141] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), p. 439; E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).
[142] A. C. Candler, reference 138, p. 95.
[143] J. M. Jauch, Bull. Am. Phys. Soc. **23**, No. 4, 14 (1948).
[144] R. S. Henderson, Phys. Rev. **74**, 107, 626, (1948).
[145] R. S. Henderson and J. H. Van Vleck, Phys. Rev. **74**, 106 (1948).

TABLE IV. Line-breadth parameters.*

Molecule	$\Delta\nu$ in mc	Pressure	Temperature	$\Delta\nu$ for 1 mm Hg**
O_2	600–1000[a]	1 atmos.	27°C	0.8–1.3
ICl	6.65[b]	1.2 mm Hg	−15°C	5.5
	2400[c]	1 atmos.	room	3.2
HCN	25[d]	1 mm Hg	27°C	25
ClCN	25±4[e]	1 mm Hg	room	25
BrCN	21±3[e]	1 mm Hg	room	21
ICN	2.0±3[e]	0.1 mm Hg	0°C	20
H_2O	0.72[f]	0.103 mm Hg	room	7
NH_3	6–10[g] (depending on J, K values)	0.5 mm Hg	room	12–20
	29.2[h]	1 mm Hg	room	29.2

* Line breadths here are half-line widths measured at half-intensity points.
** Conversion to pressure of 1 mm Hg assumes linear variations of $\Delta\nu$ with pressure.
[a] R. Beringer, Phys. Rev. **70**, 53 (1946).
[b] C. H. Townes, F. R. Merritt, and B. D. Wright, Phys. Rev. **73**, 1334 (1948).
[c] R. T. Weidner, Phys. Rev. **72**, 1268 (1947).
[d] A. G. Smith, W. Gordy, J. W. Simmons, and W. V. Smith, to be published.
[e] C. H. Townes, A. N. Holden, and F. R. Merritt, private communication.
[f] C. H. Townes and F. R. Merritt, Phys. Rev. **70**, 558 (1946).
[g] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. **59**, 418 (1947).
[h] C. H. Townes, Phys. Rev. **70**, 665 (1946).

derived by Van Vleck and Weisskopf.[79] Their expression for molecular absorption coefficient in the microwave region (where $h\nu \ll kT$) has the form

$$\alpha = \left(\frac{4\pi^3 \nu N}{3ckT}\right) \times \frac{\sum_i \sum_j |\mu_{ij}|^2 \nu_0 f(\nu_0, \nu) \exp[-W_j/kT]}{\sum_j \exp[-W_j/kT]} \quad (68)$$

The line-shape factor in this equation is

$$f(\nu_0, \nu) = \frac{\nu}{\pi\nu_0}\left[\frac{\Delta\nu}{(\nu_0-\nu)^2+\Delta\nu^2} + \frac{\Delta\nu}{(\nu_0+\nu)^2+\Delta\nu^2}\right]. \quad (69)$$

It reduces approximately to the familiar Lorentz expression,

$$f(\nu_0, \nu) = \frac{1}{\pi}\left[\frac{\Delta\nu}{(\nu_0-\nu)^2+\Delta\nu^2}\right], \quad (70)$$

for frequencies near the resonance frequency ν_0. At resonance $f(\nu_0, \nu)$ becomes $1/\pi\Delta\nu$, and the absorption equation reduces to the form used to calculate peak absorption coefficients. Van Vleck[82] has pointed out that for very broad lines the equation becomes similar in form to the Debye expression for non-resonant absorption. The theory has received confirmation for pressures of the order of an atmosphere by Beringer's work on oxygen.[2] However, the results of

TABLE V. Some results of Bleaney and Penrose* on collision broadening of NH_3 lines by non-polar gases.

Gas mixed with NH_3	Polarizability (in 10^{-24} cm^3)	Collision diameters in A: Measured	Collision diameters in A: Calculated from kinetic gas theory
Helium	0.21	2.35	3.20
Hydrogen	0.78	3.50	3.58
Nitrogen	1.72	6.4	4.09
Oxygen	1.51	4.85	4.02
Argon	1.74	4.6	4.04
Carbon disulfide	8.6	7.5	—
Ammonia	—	13.8	4.4

* Proc. Phys. Soc. **60**, 540 (1948).

Bleaney and Penrose[56] on NH_3, while confirming the theory for pressures of 10 cm of Hg, show a definite departure from this theory for pressures of 60 cm of Hg. Measurements have been made by Weingarten[146] on NH_3 at pressures varying from 10 cm to 538 cm of Hg in the wave-length range from 0.86 cm to 3.2 cm. In agreement with Bleaney and Penrose, he found that the resonant frequency shifts to lower frequencies at the higher pressures and that the line width is not then directly proportional to pressure. Specifically, he found the line width to remain essentially constant between pressures of 76 and 228 cm of Hg. Preliminary results by Weidner[57,147] on ICl, at pressures of 2 to 20 mm of Hg, shows the absorption in the wings of the lines to be in excess of that predicted by Van Vleck and Weisskopf[79] by a factor of about 5.

In Table IV are listed the line-breadth parameters for a number of molecules. These can be used with Eq. (51) to calculate the peak intensities of the lines over the range of pressures for which the line width varies linearly with pressure. To my knowledge, no significant exceptions to the linear law have been reported in the medium pressure range, i.e., $\sim 10^{-1}$ to $\sim 10^{2}$ mm of Hg. The line-breadth constant can also be used with kinetic theory to calculate the "optical cross section" or collision diameter. The optical diameter is proportional to $M^{\frac{1}{2}}(\Delta\nu)^{\frac{1}{2}}$, where M is the mass of the colliding particles (or $(Mm)/(m+M)$ for unlike molecules). The wide differences in collision diameter for the molecules listed is of interest. That for ICN is more than

[146] I. R. Weingarten, Ph.D. thesis, Columbia University, 1948.
[147] R. T. Weidner, Phys. Rev. **73**, 254 (1948).

7 times that for O_2. This difference is, of course, due largely to the large dipole moment of ICN.

Bleaney and Penrose|| have made a systematic study of the effects of various non-polar foreign gases on the line widths in the inversion spectrum of NH_3. Table V summarizes some of their results. Note the rough correlation of collision diameter with polarizability.

(c) *Collision with cell walls.*—Collision with cell walls becomes a significant broadening factor at pressures such that the mean free path in the gas becomes comparable with the cell dimensions. For a long rectangular wave-guide cell with cross-section dimensions a and b, it is easy to show that

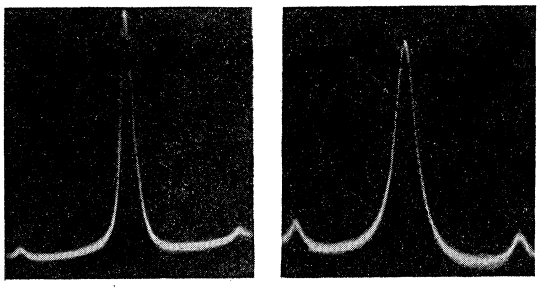
$$2\Delta\nu=\frac{2}{3\pi}\left(\frac{a+b}{ab}\right)\left(\frac{2RT}{M}\right)^{\frac{1}{2}}$$

$$=1.54\times10^{3}\left(\frac{a+b}{ab}\right)\left(\frac{T}{M}\right)^{\frac{1}{2}}\text{c.p.s.,}\quad(71)$$

or, for a cavity of volume V and surface S, that

$$2\Delta\nu=\frac{S}{3\pi V}\left(\frac{2RT}{\pi M}\right)^{\frac{1}{2}}=7.7\times10^{2}\frac{S}{V}\left(\frac{T}{M}\right)^{\frac{1}{2}}\text{c.p.s.,}\quad(72)$$

where $2\Delta\nu$ is the width of the line between half-intensity points caused by collision with walls alone, M is the molecular weight, and T is the absolute temperature. For NH_3 in K-band guide at room temperature this broadening factor is 113 kc.



(a) (b)

FIG. 18. Illustration of saturation broadening. The 3,3 line of NH_3, with $2\Delta\nu_0\approx200$ kc, and the gain adjusted for approximately constant height. (a) Input power, 1.5×10^{-6} watt; (b) input power, 150×10^{-6} watt. (From Carter and Smith (reference 150).)

|| B. Bleaney and R. P. Penrose, Proc. Phys. Soc. **60**, 540 (1948).

(d) *Doppler broadening.*—The line width caused by Doppler effect alone is

$$2\Delta\nu=72\times10^{-8}(T/M)^{\frac{1}{2}}\text{ c.p.s.,}\quad(73)$$

where T is the absolute temperature and M is the molecular weight. For $N^{14}H_3$ and ICN, with $\nu=24{,}000$ mc and $T=300$, this amounts to 70 kc and 30 kc, respectively.

(e) *Saturation effects.*—Effects of saturating the molecules with resonant radiation were first noticed in the microwave region by Townes[13] and by Bleaney and Penrose.[148] The principal results of saturation are a decrease in the absorption coefficient and a broadening of the absorption line. These effects, which result from a disturbance of the thermal equilibrium, have been confirmed a number of times[149–151] and have been theoretically explained by Karplus and Schwinger[152] and less precisely by others. Saturation broadening is illustrated by Fig. 18, which was obtained by Carter and Smith.[150]

Saturation effects become evident when the incident power is sufficient to lift molecules from the lower to the higher state considered at a rate comparable with their return to the former state. Since collision with other molecules is the principal mode of relaxation of the molecules, the effects become significant only at relatively low pressures. The limit to the power which can be absorbed is obviously determined by the thermal relaxation power,

$$P_{\max}=1/2((N_1-N_2)/\tau)h\nu,\quad(74)$$

where N_1 and N_2 are the populations of the two states considered, τ is the average relaxation time, and $h\nu$ is the energy difference between the states. For pure rotation spectra this is

$$P_{\max}=\frac{1}{2}\frac{N_J(1-\exp[-h\nu/kT])h\nu}{\tau}$$

$$\approx\frac{1}{2}\frac{N_J(h\nu)^2}{kT\tau},\quad(75)$$

[148] B. Bleaney and R. P. Penrose, Phys. Rev. **70**, 775 (1946); Proc. Phys. Soc. **60**, 83 (1948).

[149] T. A. Pond and W. F. Cannon, Phys. Rev. **72**, 1121 (1947).

[150] R. L. Carter and W. V. Smith, Phys. Rev. **73**, 1053 (1948).

[151] J. Pietenpol, J. D. Rogers, and D. Williams, Bull. Am. Phys. Soc. **23**, No. 3, 54 (1948).

[152] R. Karplus, Phys. Rev. **73**, 1120 (1948); **74**, 223 (1948); R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

where N_J is the population of the lower state. The absorption coefficient in terms of that for no saturation α_0, as expressed by Carter and Smith,[150] is

$$\alpha=\frac{\alpha_0}{[(\nu-\nu_0)/\Delta\nu_0]^2+1+[AP/(\Delta\nu_0)^2]}. \quad (76)$$

The line width, $2\Delta\nu$, with saturation in terms of that without saturation, $\Delta\nu_0$, is

$$2\Delta\nu=2\Delta\nu_0[1+(AP/(\Delta\nu_0)^2)]^{\frac{1}{2}}, \quad (77)$$

where

$$A=8\pi(\mu_{ij})^2/3ch^2$$

and where $(\mu_{ij})^2$ is the square of the matrix element of the transition moment averaged over the Zeeman components. Karplus and Schwinger[152] have shown that one must average the absorptions produced by the (independent) Zeeman components rather than the squares of the matrix elements.

(f) *Effects of external field.*—The shape of an absorption line can, of course, be modified by external magnetic or electric fields. The effects of certain types of modulation on line shapes have been derived theoretically by Karplus.[33] See also Blochinzew[35] and Townes and Merritt.[34]

6. *Stark Effect*

In the early stages of microwave spectroscopy, Dakin, Good, and Coles[29] observed the effects of an electric field on an absorption line. Figure 19 reproduces their original photographs which show in a convincing way the power of the microwave method for investigation of the Stark effect in pure rotational spectra. Mention has been made of the application of this effect as an aid to detection. It is also an aid to identification of lines, and provides an accurate means of measuring dipole moments of gases in excited as well as ground states.

The theory of the Stark effect in rotational spectra[153] has been developed for many years though effective application of it became possible only with the coming of microwave spectroscopy. For linear molecules in Σ states the first-order effect does not appear. The second-order rotational energy perturbation for the ground vibrational state is given by

$$W_{JM}^{(2)}=[4\pi^2\mu E^2I/h^2]\times[(J(J+1)-3M^2)/J(J+1)(2J-1)(2J+3)],$$

where E = strength of applied electric field, μ = molecular dipole moment, and $|M|=J,\ J-1,\ \cdots 0$. The usual $\Delta J=+1$ selection rule applies for an electric dipole transition; $\Delta M=0$ when the applied field is parallel to the electric vector of the microwaves; $\Delta M=\pm 1$ when it is perpendicular to this vector. The case for $\Delta M=0$ (π-type transition) is the usual one observed because it is more convenient to apply a parallel than a perpendicular field in wave guide. The Stark effect in several linear molecules has now been investigated. The dipole moments determined by this method are listed in Table VIII.

For the symmetric-top molecule, first- and second-order Stark perturbation energies are

$$W_{JM}^{(1)}=-\mu EMk/J(J+1),$$

$$W_{JM}^{(2)}=\frac{4\pi^2I\mu^2E^2}{h^2}\left\{\frac{(J^2-M^2)(J^2-K^2)}{J^3(2J-1)(2J+1)}-\frac{[(J+1)^2-M^2][(J+1)^2-K^2]}{(J+1)^3(2J+1)(2J+3)}\right\},$$

where the selection rules for linear molecules apply, with the additional requirement that $\Delta K=0$. So far as I know, the Stark effect in

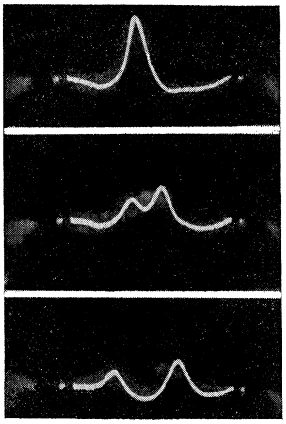
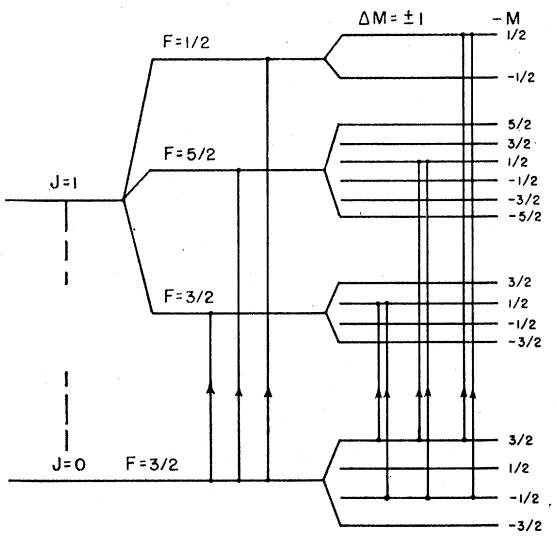


FIG. 19. Illustration of Stark splitting of a rotational line. The $J=1\rightarrow 2$ transition of OCS. Upper curve for zero field; middle for 750 volts/cm; lower for 1070 volts/cm. (From Dakin, Good, and Coles (reference 29).)

[153] R. de Kronig, Proc. Nat. Acad. Sci. **12**, 608 (1926); P. Debye and C. Manneback, Nature **119**, 83 (1927); P. Debye, *Polar Molecules* (Dover Publications, New York, 1929), Ch. IX; J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), Ch. VI.

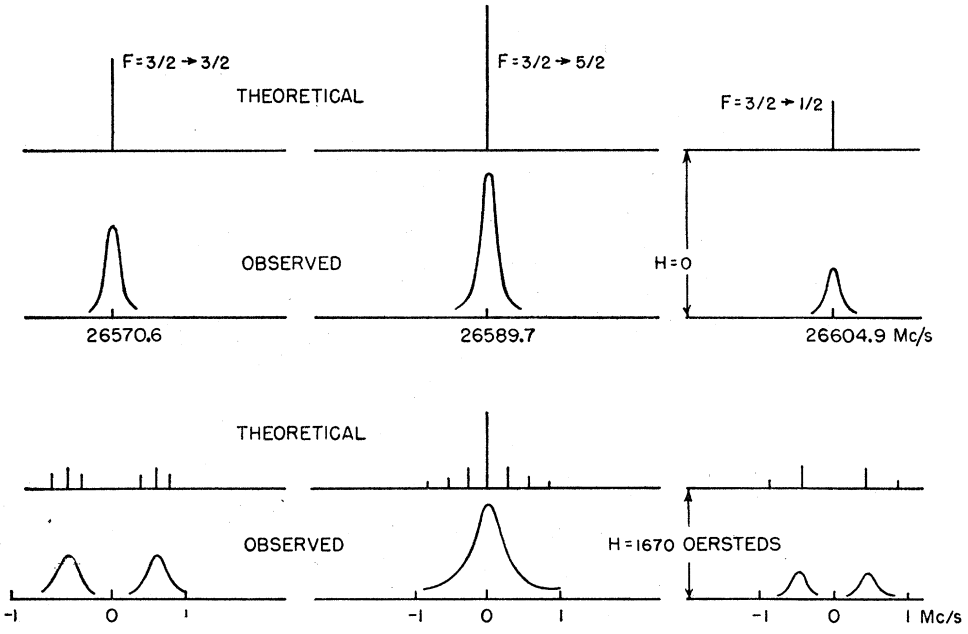


$I(Cl^{35}) = 3/2$ $g(Cl^{35}) = 0.547$

$I(Cl^{37}) = 3/2$ $g(Cl^{37}) = 0.454$

$g_{mol} \ll g(Cl)$

ENERGY LEVEL DIAGRAM AND ZEEMAN SPLITTING FOR CH_3Cl.



THE $J=0 \rightarrow 1$ LINES OF CH_3Cl^{35} WITH AND WITHOUT MAGNETIC FIELD

$I(Cl^{35}) = 3/2$ $g(Cl^{35}) = 0.547$ $g_{mol} \ll g_N(Cl^{35})$

FIG. 20. Illustration of Zeeman splitting. The $J=0 \rightarrow 1$ transition of CH_3Cl^{35}. (From C. K. Jen (reference †††).)

symmetric top molecules has not yet been studied in the microwave region.

For a theoretical discussion of the Stark effect on the inversion spectra of ammonia, see that by Jauch.[154] Stark effect in asymmetric rotators has been treated by Golden and Wilson.[119(b)]

7. *Zeeman Effect*

The splitting of microwave absorption lines by a magnetic field was first accomplished by Coles and Good[130] on lines of the ammonia inversion spectrum. The work was taken up by C. K. Jen,[‖ ‖] of Harvard, who, through development of experimental techniques and through interpretation of his results on several molecules, has demonstrated the value of the Zeeman effect in microwave spectroscopy.

The interaction energy with an external magnetic field of a molecule having a molecular g factor and a single nucleus coupled to the molecular axis, as stated by Jen, is

$$\Delta W = -M\mu_0 H(\alpha_J g_{\mathrm{mol}} + \alpha_I g_N), \qquad (78)$$

where

$\alpha_J = F(F+1)+J(J+1)-I(I+1)$,
$\alpha_I = [F(F+1)+I(I+1)-J(J+1)]/2F(F+1)$,
$M = F, F-1, F-2 \cdots -F$,
μ_0 = nuclear magneton,
g_{mol} = g factor for the molecule along J,
g_N = g factor of the nucleus considered,
H = external magnetic field.

Neglecting interactions of higher order, one finds that this energy is simply added to the energy of the vibrational, rotational, and nuclear quadrupole interactions. By applying the appropriate selection rules the positions of the absorption lines are determined. This theory is applicable to a large fraction of the molecules which will be of interest.

As pointed out by Jen, the above case is completely analogous to the nuclear Zeeman effect in atomic spectra except that here no fixed ratio exists between g_{mol} and g_N. In fact, this formula is parallel with that first derived by Back and Goudsmit[155] for Zeeman effects in the hyperfine structure of atoms. For a simple derivation, see White's *Introduction to Atomic Spectra*.[156] The selection rules:

$\Delta M = \pm 1$ for H parallel to the E vector of the radiation field,
$\Delta M = 0$ for H perpendicular to the E vector of the radiation field,

and the intensity rules apply as they do for atomic spectra.

There are interesting differences, however, in the applications of the Zeeman effect in microwave molecular spectra and in optical atomic spectra. In the latter case $g_I \ll g_J$, whereas in molecular spectra frequently $g_N \gg g_{\mathrm{mol}}$. Generally the field required to produce a resolvable splitting in optical spectra is so strong that the IJ coupling is broken down and it is the Back-Goudsmit effect (analogous to the Paschen-Back effect in fine structure) which is actually observed. In the microwave region effects of extremely weak fields can be observed. It is possible with microwaves to detect very small magnetic moments of molecules in $^1\Sigma$ ground states. An interesting case is that of a molecule for which $g_N = 0$. For it

$$\Delta W = \mu_0 g_{\mathrm{mol}} H M, \qquad (79)$$

which for the parallel field, $\Delta M = \pm 1$, gives a doublet splitting:

$$\Delta \nu = \pm \mu_0 g_{\mathrm{mol}} H/h. \qquad (80)$$

With a field of 1670 gauss Jen detected a broadening of the rotational lines in SO_2 but could not resolve the predicted splitting. A field of 10 times this strength would no doubt allow investigation of a large number of molecules of this type.

Molecules for which $g_N \neq 0$ and of $g_{\mathrm{mol}} \neq 0$ but in which the coupling between I and J is negligible can also be treated with the simple equation (79). Here, of course, I precesses around H, but this produces no significant change in the rotational frequency because of the small coupling with J. This type of molecule is illustrated by $N^{15}H_3$, which was investigated by Jen. A doublet-splitting conforming to that expected for g_{mol} alone was observed.

An important case is that for which $g_{\mathrm{mol}} \approx 0$ and for which one nucleus is coupled to the

[154] J. M. Jauch, Phys. Rev. **72**, 715 (1947).
[‖ ‖] C. K. Jen, Tech. Report No. 51, Cruft Laboratory, Harvard University, July 10, 1948.
[155] E. Back and S. A. Goudsmith, Zeits. f. Physik **47**, 174 (1928). S. Goudsmit and R. F. Bacher, Zeits. f. Physik **66**, 13 (1930).
[156] H. E. White, reference 141, p. 373.

TABLE VI. Pure rotational spectra.

Molecule	J transition	Observed frequency mc/sec.	B_0 mc/sec.	Reference
Linear molecules				
$I^{127}Cl^{35}$	0→1	Hyperfine structure unresolved.		a
	3→4	21 lines between 27194.75 and 27357.73 H*	(B_e=3422.300)	b
$I^{127}Cl^{37}$	0→1	Hyperfine structure unresolved.		a
$HC^{12}N^{14}$	0→1	Triplet at 88671 H	44336	c
$Cl^{35}C^{12}N^{14}$	1→2	17 lines between 23862.57 and 23984.60 H	5970.820	d
	2→3	4 lines between 35805.05 and 35835.75 H	5970.823	e
$Cl^{37}C^{12}N^{14}$	1→2	5 lines between 23372.72 and 23402.47 H	5847.260	d
	2→3	4 lines between 35067.97 and 35091.87 H	5847.243	e
$Cl^{35}C^{13}N^{14}$	2→3	4 lines between 35615.88 and 35649.58 H	5939.795	e
$Cl^{37}C^{13}N^{14}$	2→3	34889.05 (F=7/2→9/2) H	5814.710	e
$Br^{79}C^{12}N^{14}$	2→3	10 lines between 24583.00 and 24884.57 H	4120.190	d
	3→4	5 lines between 32804.56 and 32956.78 H	4120.224	e
$Br^{81}C^{12}N^{14}$	2→3	11 lines between 24465.87 and 24717.19 H	4096.760	d
	3→4	7 lines between 32643.10 and 32913.52 H	4096.797	e
$Br^{79}C^{13}N^{14}$	3→4	4 lines between 32581.71 and 32601.53 H	4073.355	e
$Br^{81}C^{13}N^{14}$	3→4	4 lines between 32392.56 and 32409.12 H	4049.606	e
$I^{127}C^{12}N^{14}$	4→5	9 lines between 31848.77 and 32386.29 H	3225.555	e
$I^{127}C^{13}N^{14}$	4→5	6 lines between 31718.28 and 31793.46 H	3177.035	e
$O^{16}C^{12}S^{32}$	1→2	24325.92	6081.480	f,g
	1→2	24355.49 (v_2=1, l=1)		g
	1→2	24355.50 (v_2=1, l=1)		d
	1→2	24380.70 (v_2=1, l=2)		g
	1→2	24381.07 (v_2=1, l=2)		d
	2→3	36488.82	6081.470	g
	3→4	48651.64	6081.455	g
	4→5	60814.08	6081.408	g
$O^{16}C^{12}S^{33}$	1→2	4 lines between 24013.04 and 24032.75 H	6005.053	h
$O^{16}C^{12}S^{34}$	1→2	23731.33		f
	3→4	47462.40		g
$O^{16}C^{13}S^{32}$	1→2	24247.82	6061.955	g
	1→2	24247.69	6061.923	d
	1→2	24275.25 (V_2=1, l=1)		g
	1→2	24301.05 (V_2=1, l=2)		g
$O^{16}C^{13}S^{34}$	1→2	23646.92	5911.730	d
$O^{16}C^{14}S^{32}$	1→2	24173.	6043.25	i
	1→2	24197. (V_2=1, l=1)		i
	1→2	24224. (V_2=1, l=2)		i
$N^{14}N^{14}O^{16}$	0→1	25123.03 (F=1→1)		
		25123.28 (F=1→2) H		
		25123.64 (F=1→0)	12561.64	j
$N^{15}N^{14}O^{16}$	0→1	24274.53 (F=1→1)		
		24274.61 (F=1→2) H		
		24274.73 (F=1→0)	12137.31	j
OCSe	2→3	Several lines observed between 23500 and 24500		k

* H indicates that hyperfine structure is observed.

[a] R. T. Weidner, Phys. Rev. **72**, 1268 (1947); **73**, 254 (1948).
[b] C. H. Townes, F. R. Merritt, and B. D. Wright, Phys. Rev. **73**, 1334 (1948).
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[e] A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. **74**, 370 (1948).
[f] T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (1946).
[g] M. W. P. Strandberg, T. Wentink, Jr., and R. L. Kyhl, Tech. Report, No. 59, Research Lab. of Electronics, M.I.T., May 13, 1948.
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[k] M. W. P. Strandberg and T. Wentink, Jr., Bull. Am. Phys. Soc. **23**, No. 2, 17 (1948).

TABLE VI. (*Continued*).

Molecule	J transition	Observed frequency mc/sec.	B_0 mc/sec.	Reference
Symmetric-top molecules				
PF_3	1→2	31279.60	7819.900	l
	2→3	46918.90		l
AsF_3	1→2	12 lines near 23500 H	5883.0	m
HCF_3	1→2	41394.95	41394.96	n
$C^{12}H_3F$	0→1	51071.69	25535.85	n
$C^{13}H_3F$	0→1	49724.73	24862.37	n
$C^{12}H_3Cl^{35}$	0→1	26570.77 ($F=3/2\rightarrow1/2$) 26589.49 ($F=3/2\rightarrow5/2$) H 26604.57 ($F=3/2\rightarrow3/2$)	13292.89	o
$C^{12}H_3Cl^{37}$	0→1	26164.57 ($F=3/2\rightarrow1/2$) 26179.30 ($F=3/2\rightarrow5/2$) H 26191.13 ($F=3/2\rightarrow3/2$)	13088.19	o
$C^{12}H_3Br^{79}$	1→2	12 lines between 38128.40 and 38417.09 H	9568.100	o
$C^{12}H_3Br^{81}$	1→2	12 lines between 38006.47 and 38247.77 H	9531.743	o
$C^{12}H_3I^{127}$	1→2	17 lines between 29598.95 and 30179.71 H	7501.250	o
$C^{13}H_3I^{127}$	1→2	11 lines between 28069.99 and 28687.21 H	7119.040	o
$B^{10}H_3CO$	1→2	8 lines between 35917.61 and 25920.16 H	8979.90	p
$B^{11}H_3CO$	1→2	7 lines between 34627.24 and 34629.32 H	8657.21	p
$C^{13}H_3C^{12}C^{12}H$	2→3	15 lines between 51260 and 51464	8544.	q
$C^{12}H_3C^{12}N^{14}$	1→2	11 lines between 36942.15 and 36793.64 H	9198.845	r
$C^{12}H_3N^{14}C^{12}$	1→2	6 lines between 40210.27 and 40424.49	10052.79	r
$C^{12}H_3N^{14}C^{13}$	1→2	38782.20 38783.21	9695.802	r
CH_3CF_3	1→2	20741.	5185.	s
Asymmetric-top molecules				
H_2O	$5_{-1}\rightarrow6_{-5}$	22235.22		t
HDO	$5_{3,3,0}\rightarrow5_{3,2,1}$	22307.67		t
SO_2	$13_{2,12}\rightarrow12_{3,9}$	20420	$I_c^0=95.14\times10^{-40}$	u
	$6_{1,5}\rightarrow5_{2,4}$	23413	$I_b^0=81.16\times10^{-40}$	u
	$9_{1,9}\rightarrow8_{2,6}$	24037 or 24083	$I_a^0=13.78\times10^{-40}$	u
	$7_{2,6}\rightarrow8_{1,7}$	25392		u
	$3_{1,3}\rightarrow4_{0,4}$	29460		u
$HNC^{12}S^{32}$	1→2	23464	$\frac{1}{2}(B+C)=5866.0$	v
$DNC^{12}S^{32}$	1→2	21897	$\frac{1}{2}(B+C)=5474.3$	v
$HNC^{13}S^{32}$	1→2	23389	$\frac{1}{2}(B+C)=5847.3$	v
$CNC^{13}S^{32}$	1→2	21839	$\frac{1}{2}(B+C)=5459.8$	v
$HNC^{12}S^{34}$	1→2	22915	$\frac{1}{2}(B+C)=5728.8$	v
CH_3OH	0→1	7 lines between 47840 and 48010	$\frac{1}{2}(B+C)=24353.85$	w
CH_3OD	0→1	47346 47266 47052	$\frac{1}{2}(B+C)=23673$	w
CH_3NH_2	0→1	45324.24 45324.94	$\frac{1}{2}(B+C)=22662.12$	w

[l] O. R. Gilliam, H. D. Edwards, and W. Gordy, to be published.
[m] B. P. Dailey, K. Rusinow, R. G. Shulman, and C. H. Townes, Bull. Am. Phys. Soc. **23**, No. 3, 53 (1948).
[n] O. R. Gilliam, H. D. Edwards, and W. Gordy, to be published.
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[p] W. Gordy, H. Ring, and A. B. Burg, to be published.
[q] H. Ring and W. Gordy, to be published.
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[t] S. Golden, T. Wentink, Jr., R. Hillger, and M. W. P. Strandberg, Phys. Rev. **73**, 92 (1948).
[u] B. P. Dailey, S. Golden, and E. B. Wilson, Jr., Phys. Rev. **72**, 871 (1947).
[v] C. I. Beard and B. P. Dailey, J. Chem. Phys. **15**, 762 (1947).
[w] H. D. Edwards, O. R. Gilliam, and W. Gordy, to be published.

TABLE VII. Molecular structures determined by microwave spectroscopy.

Molecule	Ground state distance in A	Angle
Linear molecules		
HCN[a]	C—H =1.059 (assumed) C—N =1.157	
ClCN[b,c]	C—Cl =1.630 C—N =1.163	
BrCN[b,c]	C—Br =1.789 C—N =1.160	
ICN[b,c]	C—I =1.995 C—N =1.159	
OCS[c-e]	C—O =1.161 C—S =1.560	
N_2O[f]	N—N =1.126 N—O =1.191	
Symmetric-top molecules		
PF_3[g]	P—F =1.546±0.008	∠FPF =104°±3° (assumed)
AsF_3[h]	As—F =1.712±0.006	∠FAsF =100°±5° (assumed)
HCF_3[i]	C—F =1.322 C—H = 1.111 (assumed)	∠FCF =111° (assumed)
CH_3F[i]	C—F =1.384 C—H =1.111	∠HCH =110° 6′
CH_3Cl[j]	C—Cl =1.779 C—H =1.109	∠HCH =110° 0′
CH_3Br[j]	C—Br =1.936 C—H =1.104	∠HCH =110° 15′
CH_3I[j]	C—I =2.139 C—H =1.100	∠HCH =110° 58′
CH_3NC[k]	C—N =1.426 N—C =1.167 C—H =1.093 (assumed)	∠HCH =109° 28′ (assumed)
BH_3CO[l]	B—H =1.20 (assumed) C—O =1.13 (assumed) B—C =1.540	∠HBH =113° 52′ ∠OSO =119.5°
Asymmetric-top molecules		
SO_2[m]	S—O =1.433	
HNCS[n]	H—C =1.2 ±0.1 N—C =1.21±0.01 C—S =1.57±0.01	∠HNC =112°±10°

[a] A. G. Smith, W. Gordy, J. W. Simmons, and W. V. Smith, to be published.
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molecular axis through its nuclear quadrupole moment. In this instance the splitting of the hyperfine levels is given by (81), obtained with g_{mol} set equal to zero. Figure 20, which is reprinted from Jen's paper, illustrates in detail the microwave Zeeman effect for a molecule of this type. Though the nuclear g factor of both Cl^{35} and Cl^{37} are already known accurately, this example illustrates the way the method may be applied in other instances to determine unknown nuclear magnetic moments. Since a small cavity cell can be used, the method is applicable to radioactive nuclei. For example, the nuclear g factor of I^{131} could be determined through measurements on CH_3I^{131}.

Although ammonia, methyl chloride, and sulfur dioxide are the only molecules which have been investigated thus far, these few well chosen studies show that the Zeeman effect in microwave spectroscopy is likely to become a subject of much research.

C. Determination of Molecular and Nuclear Properties

Molecular structures.—In Tables VI and VII are summarized the B values and molecular dimensions determined to date. Several factors affect the accuracy of the determinations of the molecular structures. When molecules with different isotopic combinations are employed, differences in zero-point energy probably cause the largest error. This has been pointed out by

TABLE VIII. Dipole moments of gases from microwave data.

Molecule	Moment in Debye units	Method
ICl[a]	0.65	Intensity
ClCN[b]	2.54±0.25	Intensity
OCS[c]	0.732±0.007 for $O^{16}C^{12}S^{32}$ 0.722±0.007 for $O^{16}C^{13}S^{32}$	Stark
OCSe[d]	0.752±0.007 gr. vib. state 0.728±0.007 v_1 state	Stark
H_2O[e]	1.94±0.06	Stark
HDO[f]	1.78±0.06	Stark
NHI[g]	1.5	Stark

[a] C. H. Townes, F. R. Merritt, and B. D. Wright, Phys. Rev. **73**, 1334 (1948).
[b] C. H. Townes, A. N. Holden, and F. R. Merritt, private communication.
[c] M. W. P. Strandberg, T. Wentink, Jr., and R. L. Kyhl, Tech. Report No. 59, Research Lab. of Electronics, M.I.T.; see also, T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (1946).
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[g] D. K. Coles and W. E. Good, Phys. Rev. **70**, 979 (1946).

Strandberg, Wentink, and Kyhl[157] and has been emphasized by Townes, Holden, and Merritt.[95] Errors caused in this way differ greatly from molecule to molecule and are difficult to estimate since they depend upon the anharmonisities of the vibrational potential function as well as upon the differences in zero-point energy of the isotopes. The accuracy is indicated, however, by the degree of internal consistency of the interatomic distances determined from several different isotopic combinations. Deviations as great as one percent have been found, but usually the agreement is much better than this.

Dipole moments.—Dipole moments of gases can be accurately measured by the Stark modulation of the absorption lines, as indicated above. Moments determined in this way are listed in Table VIII. Since one can observe the Stark splitting of rotational lines of molecules in excited vibrational states, the change in the dipole moment caused by the vibration can be observed. Dipole moments can be determined also by measurement of line intensities, but the accuracy obtainable is not as good as that with the Stark method.

Nuclear couplings.—In Table IX are listed the coupling factors, $eQ(\partial^2 V)/(\partial z^2)$, which have been determined. Since eQ remains fixed, the different couplings of a given nucleus in different molecules reveal a difference in the electronic structures of the molecules. It is seen that significant differences exist. For example, the coupling of N^{14} varies from -0.27 mc to -4.7 mc. As more data are accumulated, a correlation of values of $(\partial^2 V)/(\partial z^2)$ with other molecular properties will no doubt throw considerable light on the nature of the chemical bond. Attempts have already been made to relate $(\partial^2 V)/(\partial z^2)$ to the amount of s-p hybridization.[158,159]

Nuclear quadrupole moments.—To evaluate nuclear quadrupole moments from microwave data, the factor $(\partial^2 V)/(\partial z^2)$ must be evaluated from other sources. No accurate calculations of this quantity have been made except for the simple hydrogen molecule.[160] For heavy atoms bonded by a simple covalent p bond, Townes[158] has suggested the application of the formula, $8e\Delta\nu/15Z_1R\alpha^2a_0^3$, used to determine nuclear

TABLE IX. Nuclear quadrupole couplings.

Molecule	Atom	$eQ(\partial^2V/\partial z^2)$ in mc	Reference
NH_3	N^{14}	$\lvert 4.08\rvert$ *	a
		$\lvert 4.10\rvert$ *	b
		$\lvert 4.26\rvert$ *	c
		$\lvert 4.08\rvert$	d
NNO	N^{14}	-0.27 central atom	e
		-0.84 end atom	e
		-1.03 end atom	f
HCN	N^{14}	-4.7	g
ClCN	N^{14}	-3.63	h
BrCN	N^{14}	-3.83	h
ICN	N^{14}	-3.80	f
CH_3CN	N^{14}	-4.67	i
CH_3NC	N^{14}	$<\lvert 0.5\rvert$	i
CH_3NH_2	N^{14}	$<\lvert\sim 1\rvert$	j
BH_3CO	B^{11}	-1.55	k
	B^{10}	-3.30	k
AsF_3	As^{75}	$-235.$	l
OCS	S^{33}	-28.5	m
ICl	Cl^{35}	-82.5	n
ClCN	Cl^{35}	-83.5	o
		-83.2	h
CH_3Cl	Cl^{35}	-75.13	p
ClCN	Cl^{37}	-65.0	o
		-65.7	h
CH_3Cl	Cl^{37}	-59.93	p
BrCN	Br^{79}	$+686.0$	o
		$+686.5$	h
CH_3Br	Br^{79}	$+577.0$	p
BrCN	Br^{81}	$+573.0$	o
		$+573.5$	h
CH_3Br	Br^{81}	$+482.0$	p
ICN	I^{127}	-2420	q, o, h
CH_3I	I^{127}	-1934	p
ICl	I^{127}	-2920	n

* For conversion of these values to this form, see B. T. Feld, Phys Rev. **72**, 1116 (1947).
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[c] R. J. Watts and D. Williams, Phys. Rev. **72**, 263 (1947).
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[e] D. K. Coles, E. S. Elyash, and J. G. Gorman, Phys. Rev. **72**, 973 (1947).
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[n] C. H. Townes, F. R. Merritt, and B. D. Wright, Phys. Rev. **73**, 1334 (1948).
[o] A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. **74**, 370 (1948).
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[160] A. Nordsieck, Phys. Rev. **58**, 310 (1940). See H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. **8**, 226 (1936).

TABLE X. Nuclear quadrupole moments in units of 10^{-26} cm^2.

Atom	Microwave value[a]		Other sources
N^{14}	$\sim+2$[b]		
S^{33}	~-5[c]		
Cl^{35}	-6.6[d]	-6.0[e]	$7.921\pm.05$[f]
Cl^{37}	-5.2[d]	-4.7[e]	$6.189\pm.05$[f]
Br^{79}	$+28$[d]	$+24$[e]	
Br^{81}	$+23$[d]	$+19$[e]	
I^{127}	-75[d]	-59[e]	-45.[g]

[a] With atomic orbital approximation of $(\partial^2V/\partial z^2)$, C. H. Townes, Phys. Rev. **71**, 909 (1957).
[b] C. H. Townes, Bull. Am. Phys. Soc. **23**, No. 3, 52 (1948).
[c] C. H. Townes and S. Geshwind, Phys. Rev. **74**, 626 (1948).
[d] Determined from quadrupole coupling in cyanogen halides, C. H. Townes, A. N. Holden, and F. R. Merritt, private communication, and A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. **74**, 370 (1948).
[e] Determined from quadrupole coupling in methyl halides, W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).
[f] L. Davis, B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. **73**, 525 (1948); L. Davis and C. W. Zabel, private communication.
[g] K. Murakawa, Zeits. f. Physik. **114**, 651 (1939).

quadrupole moments from atomic spectra. Here, $\Delta\nu$ is the fine structure separation of the atom in the corresponding p state. This idealization, when it can be applied, holds only approximately. Experience has shown that the extent and type of bonding heavily influence the coupling. When the nature of the bonding is known, one can estimate corrections for the amount of s-p hybridization, etc. Table X lists some quadrupole moments determined by the atomic orbital approximation from microwave data on different molecules.

Even when it is not possible to evaluate the quadrupole moment numerically, it is usually possible to determine its sign. This gives qualitative information about the nuclear structure. A positive quadrupole moment indicates that the nucleus is elongated along the spin axis, i.e., it is prolate. A negative one indicates that the nucleus is flattened along the spin axis, i.e., it is oblate.

Nuclear spins.—Microwave spectroscopy is the method par excellence for the determination of nuclear spins. For spins greater than 1/2 the hyperfine structure caused by nuclear quadrupole interaction provides indentification of the spin. The hyperfine pattern is so dependent upon the spin that there is no possibility of error when the structure is completely resolved. Spins less than unity can be determined by the usual method of intensity alternation in rotational lines when the atom can be observed in a molecule of sufficient symmetry. A less certain identification is the absence of a nuclear quadrupole effect. In Table XI I have listed the spins which have been either determined correctly for the first time or confirmed by the microwave method. In most instances there was no question about the previous value which was confirmed. However, it is of interest that the spins of Cl^{35} and Cl^{37}, evaluated from optical spectra as 5/2, were corrected to the value of 3/2 by the microwave method. In the near future no doubt a large number of determinations of spin will be made. Since measurements can be made on gases at pressures of the order of 10^{-4} mm of Hg in cavities of 10 cc or less, this method will prove extremely valuable for determination of the spins of radioactive or rare nuclei.

TABLE XI. Nuclear spins measured or confirmed by microwave spectroscopy.

Atom	I*	II**	Reference
B^{10}	1		a
B^{11}	3/2		a
N^{14}		1	b
S^{33}	3/2		c
As^{75}		3/2	d
F^{19}		1/2	e
Cl^{35}	3/2		f
Cl^{37}	3/2		f
Br^{79}		3/2	f
Br^{81}		3/2	f
I^{127}		5/2	g

* Measured correctly for first time.
** Previous value confirmed. A number of spin values of 0 and 1/2 have received supporting evidence from failure to detect a microwave hyperfine structure.
[a] W. Gordy, H. Ring, and A. B. Burg, to be published.
[b] D. K. Coles and W. E. Good, Phys. Rev. **70**, 979 (1946); B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. **70**, 984 (1946).
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IV. MICROWAVE STUDIES OF LIQUIDS AND SOLIDS

It is not the purpose of this review to treat comprehensively liquids and solids. This section is intended primarily to call attention to a few outstanding applications of microwaves in this field. The fairly recent symposium on dielectrics held by the Faraday Society[161] provides an integrated introduction to work on dielectric

[161] "A general discussion on dielectrics," Trans. Faraday Soc. **42**, Suppl. (1946).

properties of liquids, solids, and solutions. See also Roberts and von Hippel,[162] Crouch,[163] and Surber.[164]

In the microwave region many liquids and solutions have absorption peaks and associated regions of anomalous dispersion caused by orientation of the molecular dipoles in the radiation field. Such loss peaks occur at frequencies corresponding to $\nu=1/(2\pi\tau)$, where τ is the relaxation time of the molecular dipole. According to the Debye theory,[165] the loss factor, $\tan\delta$, is:

$$\tan\delta=[(\epsilon+2)^2/\epsilon]\times[8\pi^2\mu^2cN\nu\tau/27kT[1+(2\pi\nu\tau)^2]] \quad (81)$$

where δ = loss angle (complement of the phase angle), ϵ = the dielectric constant of the solution, μ, c = the dipole moment and the concentration of the solute, ν = frequency of the radiation, τ = relaxation time of the solute molecules, N, k, T = Avogadro's number, Boltzmann's constant, and the absolute temperature. A maximum occurs in $\tan\delta$ when $\tau=1/(2\pi\nu)$. Thus by a measurement of the frequency of maximum absorption, the relaxation time can be calculated. Also, by measurement of $\tan\delta$ for different frequencies or temperatures, ϵ, μ, and τ can be evaluated from the Debye equation. It is not known how accurately this equation holds. For solutions in benzene of nitrobenzene, bromobenzene, chloroform, acetone, and benzophenone, Jackson and Powles[166] obtained good agreement with this theory. The work of Whiffen and Thompson[167] has revealed decided anomalies for certain solutions. Cripwell and Sutherland[168] used the Debye equation to calculate from their microwave data the dipole moments of several liquids, including nitrobenzene, nitromethane, methyl acetate, acetone, and methyl cyanide. The agreement with values obtained by other methods was found reasonably satisfactory.

According to the Eyring theory,[169] the activation energy, ΔE, and the entropy of relaxation, ΔS, are related to τ by

$$1/\tau=((kT)/h)\exp(\Delta S/R)\exp(-\Delta E/RT). \quad (82)$$

The relaxation time is also related in a direct way to the internal viscosity.

When there are resonant frequencies present in the dielectric material, the tangent of the loss angle, according to Frolich,[79] is

$$\tan\delta=\frac{\Delta\epsilon}{2\epsilon_s}\left(\frac{2\pi\nu\tau}{1+(2\pi\nu+2\pi\nu_0)^2\tau^2}+\frac{2\pi\nu\tau}{1+(2\pi\nu-2\pi\nu_0)^2\tau^2}\right), \quad (83)$$

where ϵ_s is the static dielectric constant, $\Delta\epsilon$ the change in ϵ caused by the oscillating dipoles, and ν_0 the frequency of resonance. In addition to the possibilities of microwave resonant frequencies in solids, there exists the chance of resonant absorption in certain liquids or solutions arising from vibrations in molecular chains held together by weak intermolecular bonds such as hydrogen bonds. An interesting phenomenon is the transfer of a proton from molecule to molecule, or from group to group, along a molecular chain. This "tunneling through" of the proton from one potential well to another may in some instances give rise to microwave absorption.

Magnetic resonance absorption.—Because of the exceptionally high magnetic field required, the nuclear magnetic resonance method of Purcell, Torrey, and Pound[170] has not been employed in the microwave region. However, a development analogous to this one but involving the free electron spins in paramagnetic substances has been made by Zaboisky[171] and by Cummerow and Halliday.[172] In these experiments a paramagnetic salt is placed in a magnetic field, and absorption lines are observed in the microwave region, corresponding to the Larmor precession frequencies of the resultant electron spin of the

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[163] G. R. Crouch, J. Chem. Phys. **16**, 364 (1948).
[164] W. H. Surber, Jr., J. App. Phys. **19**, 514 (1948).
[165] P. Debye, *Polar Molecules* (Dover Publications, New York, 1929).
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[167] D. H. Whiffen and H. W. Thompson, reference 161, p. 114.
[168] F. J. Cripwell and G. B. B. M. Sutherland, reference 161, p. 149.
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[170] E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev. **69**, 37 (1946).
[171] E. Zavoisky, J. Phys. U.S.S.R. **9**, 211, 245, 447 (1945); **10**, 170, 197 (1946).
[172] R. L. Cummerow and D. Halliday, Phys. Rev. **70**, 433 (1946).

paramagnetic ion. The orbital momentum vector is effectively quenched by the internal electric field, leaving only the spin vector S to precess about the applied magnetic field. This causes a Stark splitting of the lines which depends on the relative orientations of the external magnetic field with the axis of the crystal. This crystalline Stark splitting has been observed by Bagguley and Griffiths and by others[173] and has been treated theoretically by Kittel and Luttinger.[174] The Stark splitting breaks down the degeneracy of the energy levels of the free ions and makes observable in the microwave region the magnetic dipole transitions even without an external field.

Bleaney and Penrose[175] have studied the crystalline Stark splitting of paramagnetic resonance absorption in ammonium chrome as a function of temperature. They found the Stark splitting to decrease linearly with decrease in temperature until a temperature of about 80°K was reached. At this point a sharp discontinuity occurred, representing a large increase in the splitting for lower temperatures. They suggested as the cause of the discontinuity a realignment of the crystalline field.

The absorption lines detected by Zavoisky[171] and by Cummerow and Halliday[172] were very much sharper than had been expected. The narrowness of the lines has been explained by Gorter and Van Vleck[176] on the basis of exchange interaction between electron spins.

Magnetic resonance effects have been observed for ferromagnetic materials by Griffiths[177] and confirmed by Yager and Bozorth.[178] Griffiths found that the observed frequencies in ferromagnetic materials were several times greater than those predicted for Larmor frequencies of electron spins. Kittel[179] has shown that this anomalous effect is due to the induced internal field. For the case of the plane surfaces he proposed substitution of the geometric mean $(BH)^{\frac{1}{2}}$ for H in the Larmor theorem. The predicted frequencies,

$$\omega_\nu = \sigma(BH)^{\frac{1}{2}}, \tag{84}$$

where σ is the magneto-mechanical ratio for the electron spin, were found to be in good agreement with the observations of Griffiths. Later, Kittel[180] showed that the correct form of the Larmor theorem depends upon the shape of the ferromagnetic material used. For a small sphere the usual form $\omega_\nu = \sigma H$ gives the correct frequency.

It is apparent that the magnetic resonance absorption of solids in the microwave region provides a new and powerful means of measuring closely spaced energy levels in paramagnetic substances and of studying the structures of certain crystals.

V. APPLIED MICROWAVE SPECTROSCOPY

A. Stabilization of Microwave Oscillators with Spectral Lines

Stabilization of a microwave oscillator by coupling it electrically to a spectrum line was accomplished first in this laboratory by Smith, García de Quevedo, Carter, and Bennett.[181] The possibility of a spectrum-line stabilizer had been suggested previously by Pound.[7] The use of spectrum lines for stabilization has been reported recently by Hershberger and Norton[182] of RCA. Details about the method of coupling an oscillator to an absorption line will not be given here. The Duke stabilizer employs the anomalous dispersion in the region of an absorption line and is similar in principle to the Pound cavity stabilizer. The degree of stabilization depends, among other things, upon the strength of the absorption line. In favorable cases it appears possible to stabilize the frequency of a klystron to much better than one part in a million. The inability to use crystals to stabilize oscillators in the microwave region, as is done at broadcast

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[181] W. V. Smith, J. L. García de Quevedo, R. L. Carter, and W. S. Bennett, J. App. Phys. **18**, 1112 (1947); J. L. García de Quevedo and W. V. Smith, J. App. Phys. **19**, 831 (1948).

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frequencies, makes it necessary to find some other form of stabilization. The use of sharp, unchangeable absorption lines of gases offers obvious advantages.

B. Spectral Lines as Frequency Standards

The absorption lines of gases at low pressures, once they are accurately measured, provide convenient frequency standards for the calibration of wave meters or the measurement of other lines by the beat frequency method already described. Tables II and VI give frequencies of some easily obtained and conveniently handled gases which cover the region from 5 mm to 1.5 cm wave-length. In this laboratory plans are underway for accurately measuring spectral frequencies in the 3- to 5-mm region which will provide similar standards in this region.

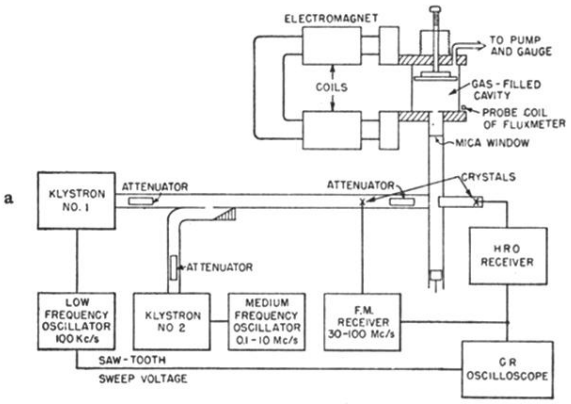
C. Qualitative and Quantitative Analysis of Gases

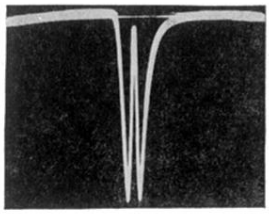
An application which has hardly begun but which in the future will be of incalculable value is the use of microwave spectroscopy in the qualitative and quantitative analysis of polar gases or vapors. The wide industrial use of infra-red spectroscopy for this purpose is an illustration of what may be expected. Infra-red spectroscopy has the advantage that certain non-polar molecules such as CO_2 can be observed. However, there is a very large group of molecules to which the microwave method can be applied. Wherever it can be used it promises to be much superior to infra-red methods. Its superiority comes from the much greater resolving power, which allows definite identification and accurate intensity measurement of the lines. When an absorption line is reduced to 50 kc in width, it is improbable that a line of some other gas would fall too close to be recognized as a separate line. When there is any question of identity, there are usually other lines in the same region which can be conveniently checked. The method provides the same certainty of identification of molecules as the line emission spectra provide for identification of the elements. In a number of instances we have used this method to identify impurities in a sample under investigation. Before the method can be used widely, however, the characteristic microwave spectra of a large number of compounds must be measured and catalogued. The different groups now engaged in microwave spectroscopy are making significant headway in this colossal task.

ACKNOWLEDGMENTS

I owe thanks to my wife, Vida Miller Gordy, who did the computations and assisted with the preparation of the manuscript. I should like to acknowledge many helpful discussions with my colleague, Dr. William V. Smith. Leo C. Levitt gave valuable help on the treatment of detecting systems. Much credit is due the several graduate students working in microwaves, particularly A. G. Smith and James W. Simmons, who prepared the figures on millimeter-wave equipment. I wish also to express thanks to the large number of researchers at other institutions who have sent me their unpublished results and who have allowed me freely to reproduce their figures.

I should like to express my gratitude to Dr. W. M. Nielsen, departmental chairman at Duke, and to Dr. M. D. O'Day, administrator of our contract with the Air Materiel Command, for their constant interest in our microwave program.





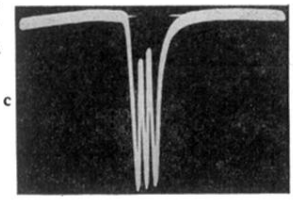


FIG. 10. a: Harvard microwave spectrograph for studies of Zeeman effect; b: oscilloscopic pattern of spectral line of a gas in resonant cavity cell; c: Zeeman splitting of a spectral line of a gas in a resonant cavity cell. (From C. K. Jen (reference †††).)

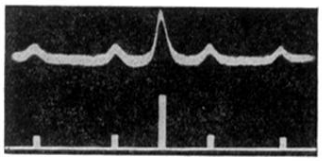


FIG. 14. Hyperfine structure of the 1,1 line of $N^{14}H_3$. $J=1$, $K=1$. (From Simmons and Gordy (reference 54).)

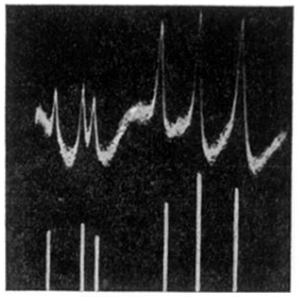


FIG. 15. Theoretical and observed $F_1 \rightarrow F_1+1$ hyperfine lines of the $J=7\rightarrow 8$ rotational transition of $I^{127}C^{12}N^{14}$ at 5.81-mm wave-length. (From Gilliam, Edwards, and Gordy.)

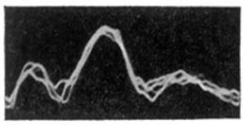
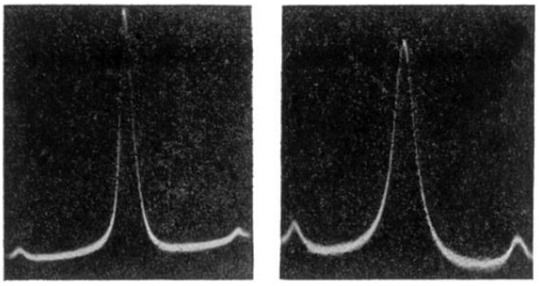


FIG. 16. Hyperfine structure of the $J=0\rightarrow1$ rotational transition of $HC^{12}N^{14}$ at 3.38 mm wave-length. (From Smith, Gordy, Simmons, and Smith (reference 25).)



(a) (b)

FIG. 18. Illustration of saturation broadening. The 3,3 line of NH_3, with $2\Delta\nu_0 \approx 200$ kc, and the gain adjusted for approximately constant height. (a) Input power, 1.5×10^{-6} watt; (b) input power, 150×10^{-6} watt. (From Carter and Smith (reference 150).)

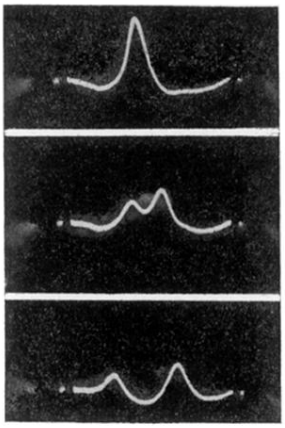


FIG. 19. Illustration of Stark splitting of a rotational line. The $J=1\rightarrow 2$ transition of OCS. Upper curve for zero field; middle for 750 volts/cm; lower for 1070 volts/cm. (From Dakin, Good, and Coles (reference 29).)

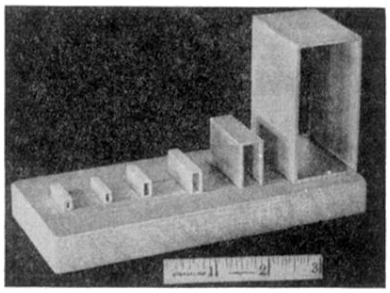


FIG. 2. Segments of wave guide. Left to right: *H*, *I*, *J*, *K*, *X*, *S* bands. An inch scale is shown.

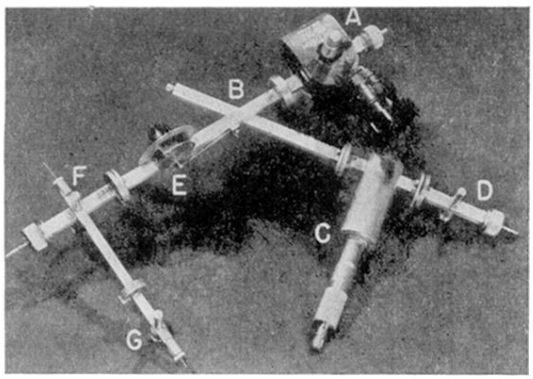


FIG. 4. Some Duke millimeter-wave components: (a) *J*-band oscillator; (b) *J*-band directional coupler; (c) *J*-band wave meter; (d) *J*-band crystal detector; (e) *J*-band attenuator; (f) crystal converter for *J* to *H* band; (g) *H*-band crystal detector.

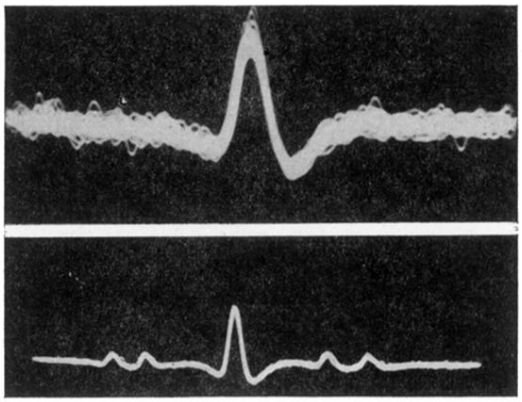


FIG. 9. Upper curve: 3,3 line of $N^{15}H_3$ at natural concentration (0.3 percent) in normal ammonia. (3.6-meter cell, 2×10^{-3} mm of Hg pressure, 100 kc source modulation). Lower curve: 3,3 line of $N^{14}H_3$ showing satellite structure with 100-kc source modulation. (From Gordy and Kessler (reference 36).)