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Inhaltsverzeichnis.

Microwave Spectroscopy.

By

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With 25 Figures.

A. Introduction.

1. The microwave region. Microwaves are HERTZian waves ranging in length from about thirty centimeters to a fraction of a millimeter, or in frequency from about one billion[1] to five hundred billion cycles per second. The microwave region is thus the billion cycle range of the electromagnetic spectrum. Its low-frequency border is the upper megacycle range where ordinary radio tubes and circuits become ineffective and where the hollow cavity and wave-guide components of the microwave region must be adopted. Its high-frequency border, the upper submillimeter wavelengths, is the region where tunable sources and detectors which characterize radio waves become ineffective and where optical and semi-optical infrared methods must be adopted. Fig. 1 is a chart which locates the microwave region within the spectrum and suggests the principal types of spectral transitions which occur within its bounds.

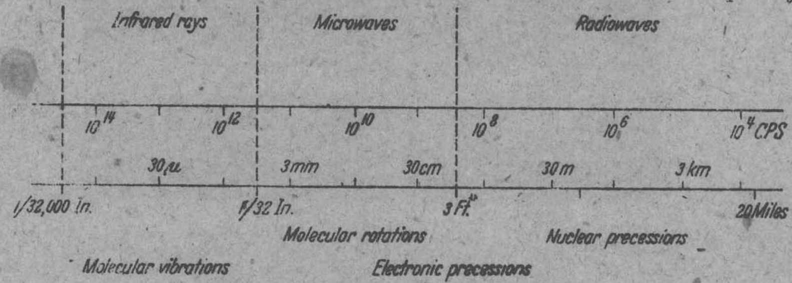

Fig. 1. A chart locating the microwave region within the spectrum.

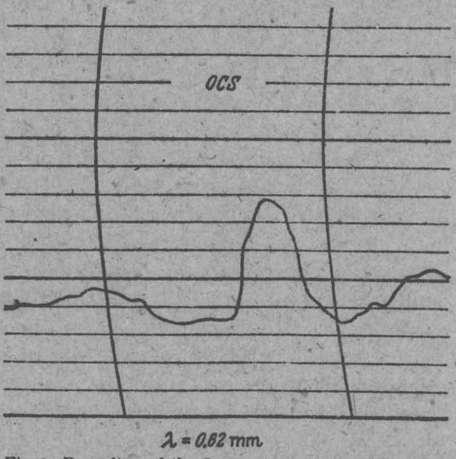

Fig. 2. Recording of the $J = 39 \rightarrow 40$ rotational frequency of carbonyl sulfide ($O^{16}C^{12}S^{32}$) at 486184.2 Mc/sec (wavelength = 0.617 mm), obtained with the 20th harmonic power of a 2 K 33 klystron. The line half-width is about 1 Mc/sec. (From M. COWAN and W. GORDY.)

Even though microwaves were the first radio waves to be discovered by HERTZ, they were the last radio waves to become useful to man. Although the klystron, the magnetron, the wave-guide propagation were discovered before 1940, refined and versatile microwave

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[1] One billion means 10^9. The abbreviation cps means "cycles per second".

instruments and techniques were not developed until the need for them arose in wartime radar, 1940 to 1945. The large and important field of microwave spectroscopy has been developed almost wholly since 1945. The single pre-war spectral measurement which is generally classified as microwave is the low-resolution measurement of the inversion frequency of ammonia in the centimeter-wave region by CLEETON and WILLIAMS[1] in 1934. Not until 1954 were spectral measurements with microwave electronic (radio) methods[2] made to overlap those with infrared grating spectrometers[3]. As early as 1923, however, NICHOLLS and TEAR[4] in a sense closed this last gap in the electromagnetic spectrum by detecting energy from a spark gap generator similar to that employed by HERTZ. Measurements are now made with microwave electronic methods down to 0.587 mm wavelength or 510 billion cps by our Duke University group[5]. Fig. 2 shows a spectral transition at 0.617 mm/sec detected with microwave methods. Spectral lines above 0.65 mm wavelength can now be displayed on the cathode ray scope (see Fig. 3). The sub-millimeter wave measurements[2, 5] are made with the same high precision and resolution as those which characterize the centimeter region.

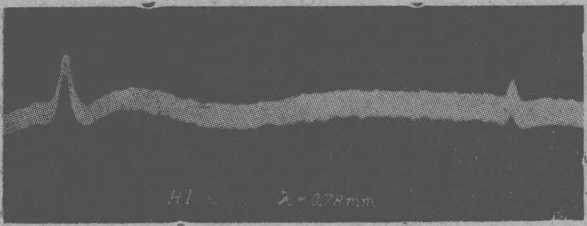

Fig. 3. Cathode ray display of two of the three hyperfine components of the $J=0\rightarrow 1$ transition of HI at 0.778 mm wavelength. The line to the left is the $F=\frac{5}{2}\rightarrow\frac{7}{2}$ component at 385 385.11 Mc/sec, and the one to the right is the $F=\frac{5}{2}\rightarrow\frac{3}{2}$ component at 385 548.80 Mc/sec. [From M. COWAN and W. GORDY: Phys. Rev. 104, 551 (1956).]

B. Microwave spectrometers.

2. Spectrometers for investigation of gases. Microwave spectrometers for the study of gases are usually designed for observation and measurement of sharp absorption lines—lines which are of the order of kilocycles or megacycles in width.

Various types of spectrometers for studying gases are in use [*1*], [*2*], [*4*], [*5*], [*6*], [*16*]. The particular design depends upon several factors such as the availability of components, the part of the microwave region for which the instrument is designed to operate, and the nature of the information which one wishes to gain from the measurements. Nevertheless, the various types have certain basic elements in common. They are: (1) a tunable microwave source; (2) a microwave detector; (3) a frequency meter; (4) an absorption cell; (5) a frequency modulator either for the source or for the absorption line; (6) an amplifier of the detected signal; and (7) a signal indicator. A diagram of a typical microwave spectrometer for gases is given in Fig. 4.

In the centimeter and lower frequency millimeter wave region the reflex klystron is usually employed as a microwave source. This convenient, versatile

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[1] C. E. CLEETON and N. H. WILLIAMS: Phys. Rev. **45**, 234 (1934).

[2] C. A. BURRUS and W. GORDY: Phys. Rev. **93**, 897 (1954); **101**, 599 (1956).

[3] L. GENZEL and W. ECKHARDT: Z. Physik **139**, 592 (1954).

[4] E. F. NICHOLLS and J. D. TEAR: Phys. Rev. **21**, 378, 587 (1923). — Proc. Nat. Acad. Sci. U.S.A. **9**, 221 (1923).

[5] M. COWAN and W. GORDY: Phys. Rev. **104**, 551 (1956).

instrument is a highly stable, nearly monochromatic source of ample energy which can be mechanically tuned over a frequency range of about 20%, or electrically swept at almost any desired rate over a range of approximately 50 megacycles. In the region above 60 kMc/sec (wavelengths below 5 mm) no klystrons are yet available. Silicon crystal harmonic generators driven by klystrons are generally employed. That shown in Fig. 5 employs a small crystal mounted

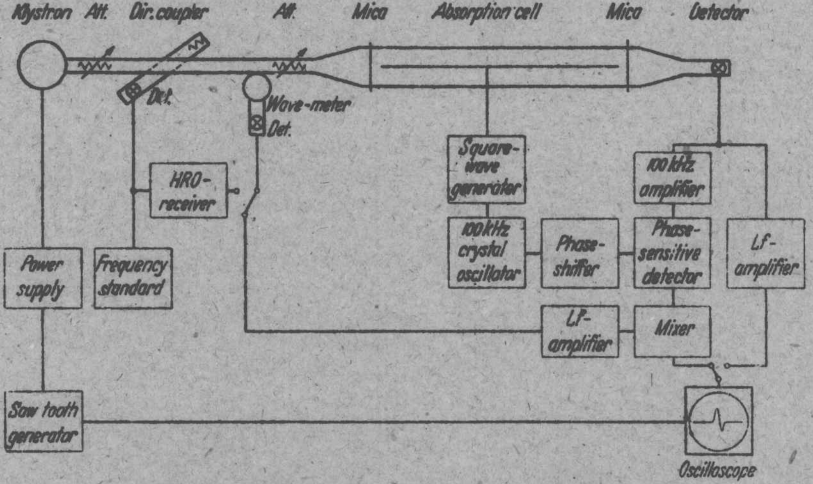

Fig. 4. Diagram of a STARK modulation spectrometer for gases. [From G. ERLANDSSON: Ark. Fysik 9, 399 (1955).]

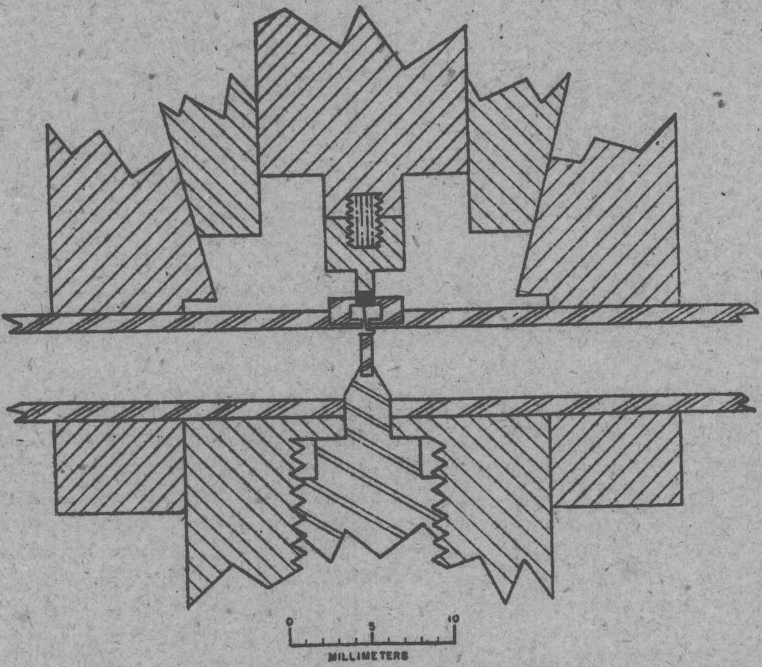

Fig. 5. Cross-section diagram of crystal multiplier employed for the lower millimeter and the sub-millimeter wave regions See also Fig. 6. [From KING and GORDY: Phys. Rev. 93, 407 (1954).]

directly in the waveguide with a differential screw mechanism for adjustment of the pressure of the tungsten "whisker". This design led to the first spectral measurements in the shorter millimeter[1] and sub-millimeter wave region[2].

Silicon crystals are almost universally used as detectors in spectrometers for gases, whereas in spectrometers for study of paramagnetic resonance in solids bolometers are most often used. The difference arises because much larger amounts of power can be employed for paramagnetic resonance than can be used for gases without limitation of absorption through radiation saturation of the sample under investigation. Powers of the order of milliwatts generate excessive lowfrequency noise in crystals but not in thermal detectors. For the centimeter region commercially available, coaxially mounted silicon crystals such as the 1N26 are used. For the 3 to 10 mm wave region the similar but smaller 1N53 crystal can be used. For the 1 to 3 mm region and for the sub-millimeter region small silicon crystals mounted directly in the millimeter waveguide with a differential screw mechanism, for adjustment of the pressure of the "whisker" have proved more satisfactory[1]. Fig. 6 shows a cross section of such a mount used at Duke University for measurements in the 0.6 to 4 mm wave region. This design makes possible easy removal of the crystal for repolishing of its surface and easy removal of the tungsten "whisker" for repointing, which is accomplished by electrolytic etching.

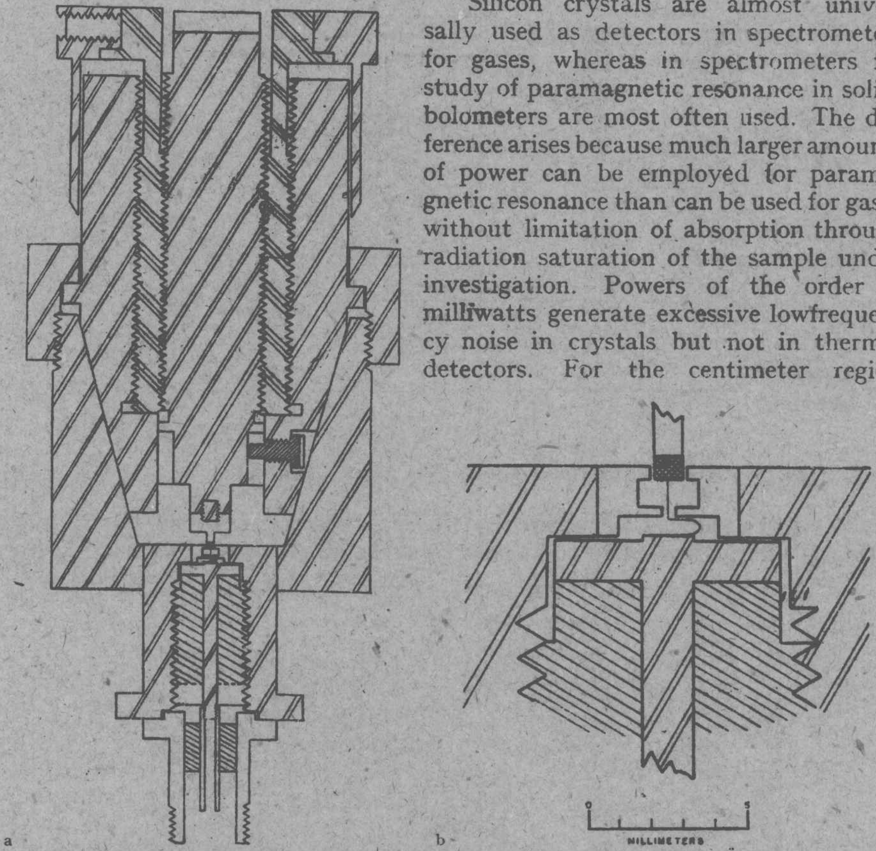

Fig. 6a and b. Cross-section diagram of crystal detector employed for the lower millimeter and the sub-millimeter wave regions. The diagram at the left shows details of the differential screw mechanism used for the critical adjustment of the pressure of the crystal against the tungsten "whisker" in both the multiplier (Fig. 5) and the detector. An enlargement of the waveguide section which contains the crystal and "whisker" is given on the right. [From KING and GORDY: Phys. Rev. 93, 407 (1954).]

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[1] W. C. KING and W. GORDY: Phys. Rev. **90**, 319 (1953). — C. A. BURRUS and W. GORDY: Phys. Rev. **92**, 274 (1953).

[2] C. A. BURRUS and W. GORDY: Phys. Rev. **93**, 897 (1954); **101**, 599 (1956). — M. COWAN and W. GORDY: Phys. Rev. **104**, 551 (1956).

Two devices for frequency measurement are used in combination in most microwave spectrometers for gases. One of these is a simple, tunable, resonant cavity, accurate only to about 5 to 25 megacycles. This is used in the search for spectral lines and for identification of the more accurate markers used in the final measurement of the spectral lines. The second frequency meter is a more elaborate device which provides sharp, standard frequency markers, accurate to a few parts in 10^8. Such markers are customarily produced by multiplication of standard low frequencies to the desired microwave region. The low frequency signals, usually in the megacycle range, are generated by a crystal-controlled oscillator. The crystal which controls the frequency of the oscillator is kept at a constant temperature. In the United States, the master oscillator is continuously monitored with the standard frequencies broadcast by the National Bureau of Standards. The multiplier[1] in its lower frequency stages consists of conventional radio tube circuits; in its intermediate stages, of a double cavity klystron multiplier; and in its final stages, of a crystal multiplier circuit. In many systems the klystron multiplier is omitted[2]. Such frequency standards usually provide markers separated by 30 to 90 megacycles. Markers spaced closer than 30 Mc are difficult to identify with the cavity wave meter. Either a calibrated radio receiver or a beat-frequency oscillator is employed for interpolation between the markers.

When the Stark effect is not employed, the gas to be studied is most often placed in a simple metallic waveguide cell sealed at either end with thin mica windows. Stark cells are most often constructed with a metallic conducting strip placed in the center of the waveguide cell perpendicular to the electric vector of the microwave radiation. The strip is supported at either side by a dielectric material such as Teflon.

In searching for absorption lines one tunes the source oscillator so as to sweep its frequency over that of the spectral line. The absorption line is detected as a decrement in the received power when the oscillator passes over its characteristic frequency. In the simple video system the source is swept over the line several times a second, and the sweep rate is synchronized with a cathode-ray trace which displays the response of the amplifier. Fig. 3 shows absorption lines displayed in this way. The amplifier is designed to amplify the Fourier components of the spectral line for the chosen rate of sweep. This system, although convenient, is not particularly sensitive for two reasons. First, the video amplifier for the Fourier components of such a signal must be in the audio region, where the crystal noise generated by microwave power of the order of milliwatts is high. Second, for passing the signal components with such rapid sweep, an amplifier with a wide noise bandwidth, of the order of kilocycles, must be used. The required amplifier bandwidth decreases with decreasing rate of sweep over the spectral line. When high sensitivity is required, one must sweep so slowly that a cathode ray tracing of the line cannot be made, and an automatic, pen-and-ink recorder is used to trace out the signal.

To avoid amplification of low-frequency noise of the detector crystal and of the tubes it is necessary to amplify the signal at high audio or radio frequencies. Some form of intensity modulation of the signal power at the amplifier frequency is necessary. The intensity modulation can be achieved through Stark effect modulation of the spectral line itself[3], or through frequency modulation of the

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[1] R. R. Unterberger and W. V. Smith: Rev. Sci. Instrum. **19**, 580 (1948).

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

[3] R. H. Hughes and E. B. Wilson: Phys. Rev. **71**, 562 (1947).

source power[1]. In the first method the STARK components are moved into and out of the frequency of the microwave source. The microwave power is thus modulated in intensity at the rate of the STARK modulation. An amplifier tuned to the modulation frequency will amplify the fundamental component of the signal power. In the second method, a rapid frequency modulation is superimposed upon the slower sweep of the source oscillator. The microwave frequency is then moved rapidly into and out of the regions of greater absorption as it sweeps slowly over the line. An intensity modulation of the detected power is thus produced which allows amplification of the signal at the modulation frequency. In both systems the modulation amplifier is followed by a second detector, usually a phase-sensitive detector, which detects the absorption line signal superimposed upon the "carrier wave" or the modulation frequency. Of the two, the STARK modulation method is preferable for the centimeter and upper millimeter wave range, where ample microwave power is available. Source modulation is used in the shorter millimeter and sub-millimeter region, where the power is severly limited. The recording of Fig. 2 was obtained with source modulation.

Sine wave and square wave STARK modulation are both commonly used. A sine wave modulator is simple to construct, and the sensitivity achieved with it is comparable to that achieved in square wave modulation. With square wave modulation the STARK-components can be resolved and measured. Suitable square wave modulators are described by HEDRICK[2] and by SHARBAUGH[3].

3. Spectrometers for study of paramagnetic resonance. Fig. 7 is a diagram of a typical spectrometer for the study of magnetic resonance of electrons in solids.

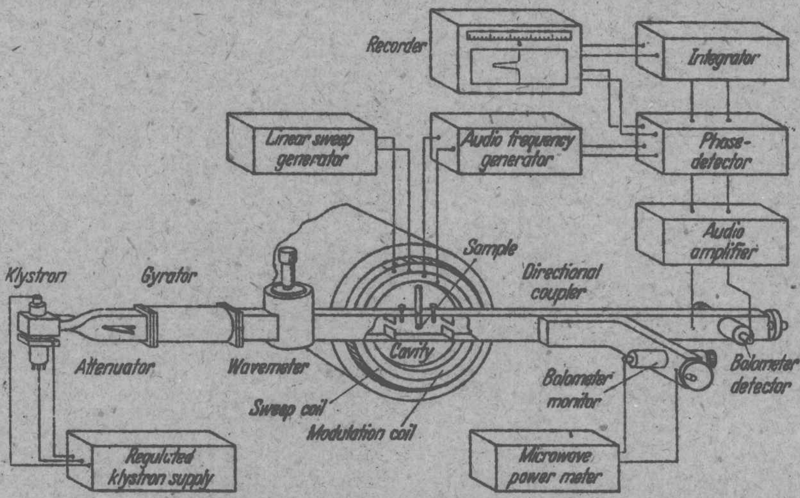

Fig. 7. Diagram of a typical microwave spectrometer for measurement of electron-magnetic resonance in solids and liquids. (From J. E. WERTZ [22].)

It can also be used for observation of magnetic resonance of liquids and gases. Some of its components are common to spectrometers designed for observation of rotational spectra of gases. A basic difference in design results from the fact that the frequency of a magnetic resonance is determined by an imposed magnetic

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[1] W. GORDY and M. KESSLER: Phys. Rev. **72**, 644 (1947). — W. D. HERSHBERGER: J. Appl. Phys. **19**, 411 (1948).

[2] L. C. HEDRICK: Rev. Sci. Instrum. **20**, 781 (1949); **22**, 537 (1951).

[3] A. H. SHARBAUGH: Rev. Sci. Instrum. **21**, 120 (1950).

field and can be tuned to any desired microwave frequency by variation of this field. This circumstance makes unneccessary the sweeping of the microwave oscillator and thus makes possible the use of fixed-frequency resonant cavities for absorption cells and fixed, sharply tuned source oscillators and receivers. Also, the possibility of using many milliwatts of power without saturating the paramagnetic resonance of most samples makes simple, convenient bolometer detection as sensitive as superheterodyne detection employing a crystal mixer. Such amounts of microwave power do not generate extra low-frequency noise (above the JOHNSON noise) in the bolometer as they do in the crystal mixer or detector. The greater power required for saturation in paramagnetic resonance over that in rotational spectra is caused primarily by the much smaller coupling dipole effective in the paramagnetic resonance transitions. The magnetic dipole responsible for the absorption of radiation in paramagnetic resonance is of the order of a BOHR magneton, whereas the electric dipole moment responsible for the absorption in rotational spectra is of the order of a DEBYE unit. The latter is 100 times as strong as the former, and its coupling to the radiation field is $(100)^2$, or 10000, times more effective.

As in the detection of rotational spectra, some form of modulation of the received microwave power is needed for detection of the resonance. In magnetic resonance this modulation is most easily achieved with an alternating component superimposed upon the magnetic field which determines the resonance frequency. This modulates the magnetic resonance frequency and thereby the intensity of absorption of microwave power at the fixed microwave frequency. Usually the range of the frequency modulation is small as compared with the line width. With this small modulation and the customary phase-sensitive detector, the detected shape of the magnetic resonance appears as the first derivative of the actual absorption contour when the receiver is tuned to the fundamental of the modulating frequency, and as the second derivative when the receiver is tuned to the second harmonic of the modulating frequency. It is not easy to achieve the necessary modulation amplitude with iron-core magnets at high frequencies, nor will the usual bolometer respond to modulating frequencies much in excess of a kilocycle. Hence the modulating frequency is usually in the low audio range.

The phase-lock-in detector and automatic recorder are used for high sensitivity, as they are in spectrometers for gases, but cathode ray scopes can be used to display the stronger magnetic resonances. The resonance is swept out by variation of the magnetic field. The magnetic resonance is thus a plot of intensity of absorption versus magnetic field strength, rather than a plot of intensity of absorption versus frequency as in ordinary spectroscopy.

C. Microwave molecular spectra.

4. Inversion spectra. The first and most thoroughly studied microwave spectrum is the inversion spectrum of ammonia[1-3]. Furthermore, ammonia including its various isotopic forms seems to be unique in exhibiting a microwave inversion spectrum, despite the fact that inversion is theoretically conceivable, given unlimited time, in any non-planar molecule. Inversion may be described as the reflection of all the nuclei of a non-planar molecule at its center of mass. In this way a new equilibrium configuration of the molecule is obtained which

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[1] C. E. CLEETON and N. H. WILLIAMS: Phys. Rev. **45**, 234 (1934).

[2] B. BLEANEY and R. P. PENROSE: Nature, Lond. **157**, 339 (1946).

[3] W. E. GOOD: Phys. Rev. **70**, 213 (1946).

in non-planar molecules cannot be obtained from the original one through any succession of simple rotations. To obtain the new equilibrium configuration, the molecule must pass through a potential barrier, a feat which is described quantum mechanically as "barrier tunneling". In practically all non-planar molecules the barrier is so great that inversion is not achieved because the inversion time, if not infinite, is too long to observe. For NH_3, however, the inversion frequency in the ground vibrational state falls in the microwave region at about 24 kMc (kilomegacyles per second), and in ND_3 it falls near 16 kMc. For molecules of this symmetry the inversion consists simply of a turning inside out of the molecule. It may be regarded as a form of molecular vibration.

In inversion, a pyramidal molecule like ammonia can be treated simply as a one-dimensional oscillator of reduced mass μ, oscillating in a double minima potential field like that in Fig. 8. There are equivalent vibrational energy levels on either side of the hill, and the oscillator has equal probability of existing in either. If the barrier is not infinite, the oscillator will "resonate" between these two states with a "resonant" frequency inversely related to the height of the barrier.

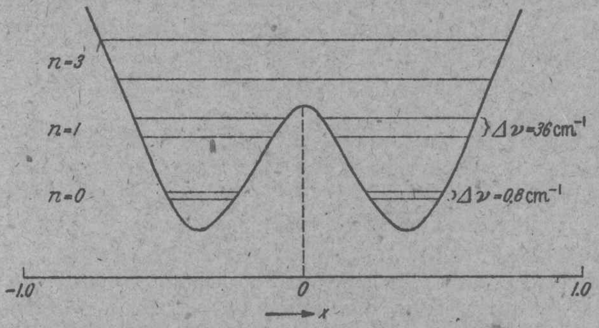

Fig. 8. Double minima of the potential curve for ammonia which give rise to the inversion splitting of the vibrational levels. The NH_3 absorption in the 1.25 cm wave region results from transition between the two components of the ground vibrational state ($n = 0$). The diagram is not drawn to scale.

The wave functions of the equivalent vibrational states on either side of the hill overlap to some extent. The resulting interaction leads to a splitting of the vibrational levels into doublets of separation ΔE_{inv}, as shown in Fig. 8. The splitting varies inversely as the height of the barrier and hence increases with the vibrational quantum number for the symmetrical bending mode in which the N vibrates along the symmetry axis perpendicular to the plane of the three hydrogens. The two inversion sub-levels of the vibrational state have opposite symmetry. The dipole matrix elements connecting the states do not vanish, and therefore transition between them giving rise to an absorption frequency $\nu_{\mathrm{inv}} = \Delta E_{\mathrm{inv}}/h$ is possible.

The inversion splitting ΔE_{inv} is related[1] to ΔE_v, the over-all separation of the vibrational levels considered, and to A, the area under the potential barrier, by:

$$\Delta E_{\mathrm{inv}} = \Delta E_v / \pi A^2 \tag{4.1}$$

or

$$\nu_{\mathrm{inv}} = \nu_v / \pi A^2 \tag{4.2}$$

where

$$A = \exp\left[\left(\frac{2\pi}{h}\right) \int\limits_0^{x_1} [2\mu (V - E_v)]^{\frac{1}{2}}\, dx\right] \tag{4.3}$$

and μ = reduced mass;
x = inversion coordinate;
V = potential energy;
$x = 0$ at potential maximum and $x = x_1$ at $V = E_v$.

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[1] D. M. DENNISON and G. E. UHLENBECK: Phys. Rev. 41, 313 (1932).

The inversion frequency is lowest therefore for the ground vibrational state and increases with the vibrational quantum number. Since A increases exponentially as μ, the inversion frequency decreases rapidly with increasing μ. For these reasons the inversion frequency for the next lightest molecule similar to ammonia, PH_3, the expected inversion frequency for the ground vibrational state is only a fraction of a megacycle. Something like a year would be required for AsH_3 to execute one inversion; some centuries would be required for SbH_3 to do so.

As a result of interaction of vibration and rotation, the inversion splitting varies slightly for the different rotational states of the molecule. This leads to the fine structure of the inversion transition. Some sixty-six components of this fine structure have been measured for $N^{14}H_3$. The frequency of these in Mc/sec fit approximately the relation[1]:

$$\left.\begin{aligned}\nu = 23787 - 151.3\,J(J+1) + 211.0\,K^2 + 0.5503\,J^2(J+1)^2 - \\ - 1.531\,J(J+1)\,K^2 + 1.055\,K^4,\end{aligned}\right\} \tag{4.4}$$

where J and K are the usual rotational quantum numbers for the symmetric-top molecule.

The inversion frequency of NH_3 was originally observed by CLEETON and WILLIAMS[2] in 1934. Its fine structure was observed by BLEANEY and PENROSE[3] and independently by GOOD[4] in 1946. The inversion spectrum of ND_3 has been observed by LYONS, RUEGER, NUCKOLLS and KESSLER[5], and of mixed form ND_2H and NH_2D by WEISS and STRANDBERG[6].

5. Pure rotational spectra. The principal class of microwave molecular spectra arises from transitions between quantized rotational energies of molecules in singlet electronic ground states. Although pure rotational spectra of a few light molecules have been resolved with optical techniques in the far infrared region and although the rotational spectra of many heavy molecules originate in the longer wave radio region, the greater part of all measurements of pure rotational spectra has been made at microwave frequencies. The microwave region appears to be the optimum one for the study of rotational spectra. The theory of rotational spectra, which was developed by infrared spectroscopists long before the microwave region was opened up, is generally adequate, even though the great resolution of microwave spectroscopy makes it necessary to extend it to include fine or hyperfine structure normally unresolvable in the infrared region. This structure may arise from externally imposed electric or magnetic fields or from such weak internal interactions of the molecule as those of molecular electrons with magnetic dipole or electric quadrupole moments of the nuclei. The perturbations giving rise to fine and hyperfine structure are treated in Sects. 10 and 11.

For discussion of their rotational spectra molecules are classified as linear, symmetric-top, and asymmetric rotors. In a linear rotor, two of the principal moments of inertia are zero; in a symmetric-top, two principal moments of inertia are equal, but none is zero; and in an asymmetric rotor, none of the principal moments of inertia is equal to another, and none is zero. Because the spherical-top rotor, in which all three principal moments of inertia are equal, has no observable rotational spectrum, it will not be treated here.

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[1] J. W. SIMMONS and W. GORDY: Phys. Rev. **73**, 713 (1948).

[2] C. E. CLEETON and N. H. WILLIAMS: Phys. Rev. **45**, 234 (1934).

[3] B. BLEANEY and R. P. PENROSE: Nature, Lond. **157**, 339 (1946).

[4] W. E. GOOD: Phys. Rev. **70**, 213 (1946).

[5] H. LYONS, L. T. RUEGER, R. G. NUCKOLLS, and M. KESSLER: Phys. Rev. **81**, 630 (1951).

[6] M. T. WEISS and M. W. P. STRANDBERG: Phys. Rev. **83**, 567 (1951).

α) Diatomic and linear polyatomic molecules. Diatomic or linear polyatomic molecules having no unbalanced electronic angular momenta can be treated in the first approximation as rigid rotors. The wave equation for such a rotor is:

$$\frac{1}{\sin\vartheta}\cdot\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial\psi}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\cdot\frac{\partial^2\psi}{\partial\varphi^2}+\frac{8\pi^2 I E}{h^2}=0 \tag{5.1}$$

where ϑ is the polar angle with reference to the space-fixed Z axis, φ is the azimuthal angle, h is PLANCK'S constant, I is the moment of inertia, and E is the rotational energy. Solutions of this equation which have physical significance are possible only for discrete values, E_J, of the rotational energy,

$$E_J=\frac{h^2}{8\pi^2 I}\,J(J+1)\,, \tag{5.2}$$

where J, the rotational quantum number, can have only the values: $J=0, 1, 2, \ldots$. Complete solution of Eq. (5.1) yields the rotational wave functions:

$$\psi_J=N_{JM}\,e^{iM\varphi}P_J^{|M|}(\cos\vartheta)\,, \tag{5.3}$$

where N_{JM} is a normalizing factor determined by $\int\psi_J\,\psi_J^*\,d\tau=1$ to be

$$N_{JM}=\frac{1}{\sqrt{2\pi}}\left[\frac{(2J+1)}{2}\cdot\frac{(J-|M|)!}{(J+|M|)!}\right]^{\frac{1}{2}}. \tag{5.4}$$

$P_J^{|M|}(\cos\vartheta)$ is the associated LEGENDRE function. M, the "magnetic" quantum number, can take the integral values:

$$M=J,\ J-1,\ J-2,\ \ldots\ -J\,. \tag{5.5}$$

With the BOHR postulate,

$$h\nu=E_1-E_2\,, \tag{5.6}$$

and the selection rule for absorption of radiation through rotational transition, $J\rightarrow J+1$, the rotational frequencies of a "rigid" linear molecule are found from Eq. (5.2) to be

$$\nu_r=2B(J+1)\,, \tag{5.7}$$

where $B=h/(8\pi^2 I)$ is the spectral constant in frequency units and J is the quantum number of the lower of the two energy levels between which the transition occurs. From Eq. (5.7) it is obvious that the rotational spectrum of a rigid linear molecule is a series of equally spaced lines of separation $2B$ and with the lowest frequency having the value $2B$.

If B is sufficiently large (I, sufficiently small), the rotational spectrum of a linear molecule may originate in the infrared region and therefore not have a microwave rotational spectrum. Actually, however, all but the lighter diatomic hydrides such as HF or HCl have their rotational spectra originating at frequencies which can now be reached with microwave or radiofrequency methods. Rotational lines of simple molecules such as DBr, TCl and HI have already been measured with microwave methods (see Table 1), and the first rotational lines of DCl and HBr fall in the workable microwave region.

If an observable transition between the rotational levels J and J' is to occur, all the matrix elements of the electric dipole moment μ along space-fixed axes,

$$\mu_J^{J'}=\int\psi_J\,(\mu_f)\,\psi_{J'}\,d\tau\,, \tag{5.8}$$

must not vanish. This will occur only when $\mu\neq 0$ or when the molecule has a permanent dipole moment. From the wave function of Eq. (5.3) substituted in Eq. (5.8) it is found that even if $\mu \neq 0$, all the matrix elements vanish unless $J = J' \pm 1$. This latter condition is the basis for the selection rule already stated.

Although the simple formula (5.7) represents a good first approximation to the rotational spectra of diatomic and linear polyatomic molecules, it is inadequate for refined measurements. In addition to the nuclear and external field perturbations treated in later sections, effects of centrifugal distortion and vibrational motions are easily detected in microwave measurements. Theoretically, such effects can be included in the original HAMILTONian used in obtaining the wave equation for the rotational motion. It is simpler, however, to treat them as perturbations upon the rigid rotor states already found.

For a particular vibrational state the rotational levels and frequencies of the non-rigid diatomic or linear polyatomic molecule with no unbalanced electronic momentum are given with sufficient accuracy for microwave measurement by the equations:

$$E_J = c\left[B_v J(J+1) - D_v J^2 (J+1)^2\right] \tag{5.9}$$

and

$$\nu_r = 2B_v(J+1) - 4D_v(J+1)^3, \tag{5.10}$$

where B_v is the "effective" spectral constant, $h/(8\pi^2 I_v)$, for the particular vibrational state for which the rotational spectrum is observed, and where D_v is the centrifugal stretching constant for that state.

In terms of the constants B_e and D_e for the hypothetical vibrationless state, B_v and D_v for diatomic molecules are:

$$B_v = B_e - \alpha\left(v + \tfrac{1}{2}\right), \tag{5.11}$$

$$D_v = D_e + \beta\left(v + \tfrac{1}{2}\right), \tag{5.12}$$

where α and β are interaction constants which are very small in comparison with B and D respectively, and where v is the vibrational quantum number. For linear polyatomic molecules there is more than one vibrational mode, and the above equations must be written in the more general form:

$$B_v = B_e - \sum_i \alpha_i\left(v_i + \frac{d_i}{2}\right), \tag{5.13}$$

$$D_v = D_e + \sum_i \beta_i\left(v_i + \frac{d_i}{2}\right), \tag{5.14}$$

where the summation is taken over all the fundamental modes of vibration. The subscript i refers to the i-th mode, and d_i represents the degeneracy of that mode.

There is an additional complication for degenerate bending modes. A splitting of the rotational lines into doublets, known as l-type doublets, arises from the interaction between rotation and vibration. This splitting increases with J according to the equation,

$$\Delta\nu = 2q_l(J+1), \tag{5.15}$$

where q_l, the interaction constant, is of the order of $2B^2/\omega$, in which ω is the frequency of the bending vibration. In applying Eq. (5.10) one can simply employ the mean of the doublet frequencies.

When it is possible to make measurements of rotational transitions in all the fundamental vibrational modes, one can find the interaction and stretching constants and the equilibrium value B_e from microwave measurements alone. Since D is itself a small, second-order constant in comparison with B, it is usually possible to neglect its variations with the vibrational state.

When the B values are measured for a diatomic molecule, the corresponding moments of inertia and internuclear distances can be immediately calculated. In terms of the moments of inertia and two atomic masses, m_1 and m_2, the internuclear distance r is:

$$r = \left[I\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\right]^{\frac{1}{2}}. \tag{5.16}$$

The effective internuclear distance varies slightly for different vibrational states. Because of the zero point vibrational energy, the effective value r_0 for the ground state differs slightly from the value r_e for the hypothetical, vibrationless state.

Table 1. *Spectral constants for some hydrogen halides obtained from millimeter wave spectroscopy.*

Molecule	B_0 in Mc/sec	eQq coupling for Cl, Br, or I in Mc/sec	Bond length r_0 in Å	References
DCl^{35}	161656.09	-67.3	1.28125	g
DCl^{37}	161182.93	-53.1	1.28124	g
TCl^{35}	111075.76	-67.0	1.28003	a
TCl^{37}	110601.51	-53.0	1.28002	a
DBr^{79}	127358.2	533	1.42136	b
DBr^{81}	127280.0	445	1.42136	b
TBr^{79}	86252.24	530	1.42012	a, c
TBr^{81}	86174.33	443	1.42011	a, c
DI^{127}	97537.2	-1823	1.6165	d, e
HI^{127}	192658.6	-1831	1.60904	f

a) C. A. BURRUS and W. GORDY, B. BENJAMIN and R. LIVINGSTON: Phys. Rev. **97**, 1661 (1955).
b) W. GORDY and C. A. BURRUS: Phys. Rev. **93**, 419 (1954).
c) A. E. NETHERCOT and B. ROSENBLUM: Phys. Rev. **97**, 84 (1955).
d) J. A. KLEIN and A. H. NETHERCOT: Phys. Rev. **91**, 1018 (1953).
e) C. A. BURRUS and W. GORDY: Phys. Rev. **92**, 1437 (1953).
f) M. COWAN and W. GORDY: Phys. Rev. **104**, 551 (1956).
g) From M. COWAN and W. GORDY.

Table 1 lists spectral constants and internuclear distances evaluated for hydrogen halides from microwave spectroscopy. In the evaluation of these constants the observed rotational transitions were corrected for any nuclear coupling effects, as described in Sect. 10 and Sect. 11.

A linear molecule of n atoms has in general $(n-1)$ independent internuclear dimensions. To evaluate the complete structure of a linear molecule having more than two atoms from its rotational constants alone, one must make measurements on different isotopic species of the molecule and assume that the internuclear distances are not altered by the isotopic substitution. Because of differences in zero point vibrational energies of the different isotopic species, the latter assumption is not exactly true. Nevertheless, internuclear distances evaluated with different isotopic combinations, when more observables than unknown parameters are available, usually agree within 0.1%. To evaluate the complete structure of a linear molecule with n unknown structural parameters, one must make measurements on at least n different isotopic combinations of the molecule, with only one isotopic substitution per atom. Only one substitution per atom leads to additional independent structural equations. However, additional substitutions are useful as a check on the evaluations and in the estimation of the error caused by the zero point vibrations. Simplified methods for such calculations with discussion of the inherent errors are available[1] [*2*], [*4*], [*6*]. Results on some

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[1] J. KRAITCHMAN: Amer. J. Phys. **21**, 17 (1953).

representative linear molecules are given in Table 2. Comprehensive tabulations of spectral constants for linear molecules are given elsewhere [*3*], [*4*], [*6*].

Table 2. *Structures of some linear molecules measured with microwave spectroscopy.*

XYZ	d_{XY} in Å	d_{YZ} in Å	XYZ	d_{XY} in Å	d_{YZ} in Å
HCN	1.064	1.156	NNO	1.126	1.191
ClCN	1.629	1.163	OCS	1.1637	1.5584
BrCN	1.790	1.159	OCSe	1.1588	1.7090
ICN	1.995	1.159	TeCS	1.904	1.557

Remarks: Values taken from [*4*].

β) Symmetric-top molecules. Non-linear molecules which have axial symmetry about an internal axis such that two principal moments of inertia are equal are commonly designated as symmetric tops or symmetric rotors. When the two smaller principal moments of inertia are equal ($I_a = I_b < I_c$), they are oblate symmetric tops; when the two larger ones are equal ($I_a < I_b = I_c$), they are prolate symmetric tops. Solutions of the wave equation for a rigid prolate symmetric-top molecule[1] which have physical significance require that the rotational energies have only the values:

$$E_{J,K} = \frac{h^2}{8\pi^2}\left[\frac{J(J+1)}{I_b} + \left(\frac{1}{I_a} - \frac{1}{I_b}\right)K^2\right] \tag{5.17}$$

$$= h\left[B\,J(J+1) + (A-B)\,K^2\right], \tag{5.18}$$

where $A = h/(8\pi^2 I_a)$ and $B = h/(8\pi^2 I_b)$. Solutions for the oblate top requires an equation of the same kind, with the subscript a replaced by c. The quantum number J refers to the total angular momentum of the molecule, and as for a linear molecule it can take only integral values, including zero, whereas K is a quantum number which measures in units of $h/(2\pi)$ the component of the total momentum $J(J+1)\,h/(2\pi)$ which is directed along the symmetry axis, i.e. the a axis for the prolate top under discussion.

In all but the accidentally symmetric top the permanent dipole moment will lie along the symmetry axis. Under these conditions the selection rules for absorption of radiation through rotation are:

$$J \to J+1, \quad K \to K.$$

These rules, like those for linear molecules, are based upon the non-vanishing of the dipole moment matrix elements with reference to axes fixed in space. Application of these rules with the Bohr postulate to Eq. (5.18) gives for the rotational lines the values:

$$\nu = 2B(J+1), \tag{5.19}$$

exactly as obtained for the linear molecule. Since only B or I_b appears in this formula, it clearly applies equally well to both prolate and oblate tops. Furthermore, the spectrum of a rigid linear rotator should obviously be the same as that of a completely rigid symmetric top, since the former can be regarded as a special case of the latter for which $I_a = 0$ and $I_b = I_c$. Nevertheless, no molecule is completely rigid; differences in centrifugal stretching cause distinguishable differences in the rotational spectra of the actual linear and symmetric-top molecules.

The effects of centrifugal stretching on the rotational energies of the symmetric top have been calculated with perturbation theory by Slawsky and Dennison[2].

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[1] D. M. Dennison: Phys. Rev. **28**, 318 (1926); Rev. Mod. Phys. **3**, 280 (1931).

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

who obtained an equation for the energy of the non-rigid symmetric rotor:

$$E_{JK}=h[BJ(J+1)+(A-B)K^2-D_J J^2(J+1)^2-D_{JK}J(J+1)K^2-D_K K^4], \quad (5.20)$$

where the new quantities D_J, D_{JK}, and D_K are centrifugal stretching constants. Used with the selection rules, $J\rightarrow J+1$ and $K\rightarrow K$, this equation leads to the formula:

$$\nu=2B(J+1)-4D_J(J+1)^3-2D_{JK}(J+1)K^2 \quad (5.21)$$

for the rotational absorption frequencies. As before, J is the rotational quantum number for the lower of the two levels. Formula (5.21) differs from the corresponding one for the non-rigid linear molecule, Eq. (5.10), only in the additional stretching term, $-2D_{JK}(J+1)K^2$. Since this last term involves K^2, it leads to a splitting of a rotational transition of a symmetric-top molecule into $(J+1)$ components which are closely spaced but usually resolvable. Fig. 9 illustrates this splitting with the $J=8\rightarrow 9$ transition of fluoroform at 1.61 mm wavelength. A rotational transition of a symmetric-top molecule is both split into components and displaced by centrifugal stretching, whereas a rotational transition of a linear molecule is only displaced. In the centimeter region the splitting and the displacements are very small, usually of the order of kilocycles or megacycles, but in the region of one millimeter wavelength they may be of the order of tens to hundreds of megacycles. Tabulations of the constants are available [*3*], [*4*], [*6*].

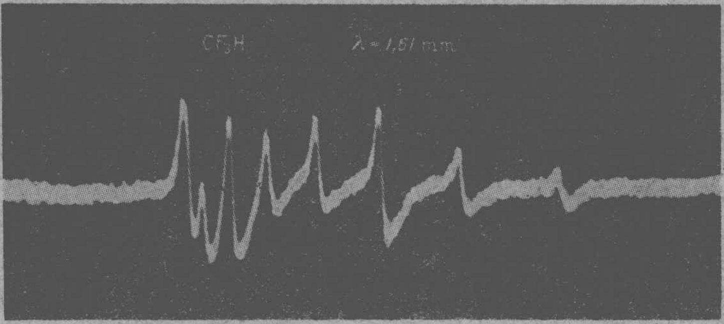

Fig. 9. Cathode-ray display of a rotational transition in a symmetric top molecule: the $J=8\rightarrow 9$ transition of CF_3H at 1.61 mm wavelength. The components corresponding to different values of K from 0 to 8 are separated by centrifugal distortions. There is no nuclear hyperfine structure. The total spread is 21 Mc/sec. [From BURRUS and GORDY: J. Chem. Phys. (in press).]

In the analysis of spectra the variations of the stretching constants D_J and D_{JK} with vibrational state are customarily neglected. It is seldom possible to obtain sufficient data even for evaluation of these effects upon B and for determination of B_e for the simpler symmetric tops. Formula (5.13) for the linear molecule applies for the symmetric top also. A complication due to interaction between rotation and vibration is encountered for degenerate bending modes of symmetric-top molecules. This condition, similar to l-type doubling in linear molecules, is treated by NIELSEN[1].

To obtain the molecular structure of a symmetric-top molecule one must apply the principle of isotopic substitution as described for linear polyatomic molecules. Since only one observable parameter involving the molecular dimensions can be obtained for each isotopic species, the number of isotopic species

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[1] H. H. NIELSEN: Phys. Rev. 77, 130 (1950).