A new and rapidly expanding field of research, microwave spectroscopy was practically nonexistent before World War II. Some of the consequences of the research that microwave radar developments made possible are discussed below.

MICROWAVE SPECTROSCOPY

By *Walter Gordy*

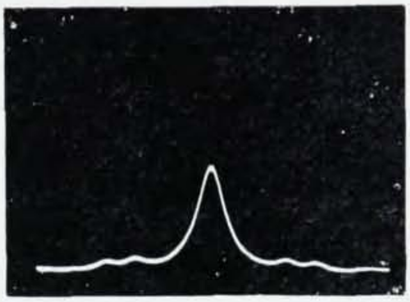

Fig. 1. Hyperfine structure found by W. E. Good in one of the ammonia inversion lines.

THE SPECTROSCOPIST in the past has been a fortunate fellow. When he could no longer find something new to measure with his old spectrometer (or if he became bored with repeated use of the same old frequencies) he could always move on to a new place in the spectrum, provided of course that he could generate and detect radiation there. Until very recently there was a vast unexplored island in the electromagnetic spectrum, the region between the infrared waves and the conventional radio waves, now known as the microwave region.

It is not strictly correct to speak of the microwave region as new. The last gap in the electromagnetic spectrum was closed in 1923 by Nichols and Tear. The development of the region did not follow, however. The early methods of generating and detecting microwave radiation did not prove practical either for spectrographic measurements or for engineering purposes. Although one important spectral measurement in this region occurred before World War II, that of the ammonia inversion frequency by Cleeton and Williams in 1934, it was not until after the advanced developments of components for microwave radar during World War II that the region was opened up in a practical way. It is now being explored at a rapid rate by hundreds of scientists (usually at government expense*). The rapid growth of microwave spectroscopy is illustrated by a recent bibliography which lists only one paper before 1946, 27 in 1946, 60 in 1947, 79 in 1948, 88 in 1949, 129 in 1950, and 157 in 1951.

Although the boundaries of the microwave region are not well defined, its wavelengths are usually regarded as lying approximately between one millimeter and 30 centimeters (between 300 kilomegacycles and one kilomegacycle). Hence, microwaves are millimeter or centimeter waves. Usually a given region of the spectrum is distinguished by the methods employed in generating, detecting, and measuring the waves. Microwaves are generated by cavity oscillators, transmitted by hollow waveguide, and detected by crystal rectifiers. The familiar resistors, coils, and capacitors of conventional radio circuits are not evident in microwave circuits. The *L*, *C*, and *R*, if one wishes to think in terms of them, are distributed rather than lumped parameters. Neither are the globars, prisms, gratings, and mirrors of the infrared spectroscope present.

In its simplest form a microwave spectroscope consists of a radiation source (usually a reflex klystron), a frequency meter, an absorption cell (usually a hollow waveguide stopped at either end by mica windows), a radiation detector (usually a silicon crystal), an amplifier of the detected energy, and an indicator (usually a cathode-ray scope or a pen-and-ink recorder). This is not the place for discussion of the complex ramifications of the spectroscope, but it may be appropriate to say that the spectral lines are usually measured to seven-place accuracy from a comparison of them with frequencies obtained by multiplying electronically certain standard low-frequency signals, 5 or 10 Mc, broadcast by station WWV, of the National Bureau of Stand-

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* The tax payers who read this should not become alarmed. Many times the total amount spent on microwave spectroscopy was wasted during World War II in developing a radar band on top of an uncharted absorption line of water vapor.

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ards. A distinguishing feature of the region is the exceptionally high resolution obtainable, more than ten thousand times that of infrared spectroscopy.

The interest of the spectroscopist is focused primarily upon the quantities he measures rather than upon the electromagnetic radiation he uses. Only rarely does he discover any new property of the radiation itself. We shall therefore describe the microwave region in terms of the energy transformations which occur at microwave frequencies in various systems. According to the famous Bohr relation, the transformed energy ΔE is related to the absorbed or radiated frequency ν by $\Delta E = h\nu$ where h is Planck's constant.

With one exception all microwave spectra so far observed are absorption spectra. The one exception is the recent observation by Ewen and Purcell of an emission line in atomic hydrogen from an extended astronomical source. Because the probability of spontaneous emission decreases as the cube of the emitted frequency, emission lines are incomparably weaker at microwave than at optical frequencies. Indeed, it does not seem probable that a microwave emission line will soon be observed from a laboratory source. Absorption lines are also much weaker at microwave than at optical frequencies, but not incomparably so. Actually, the Einstein coefficient of absorption is independent of frequency. This is not the whole story, however. The coefficient of induced emission (not to be confused with the coefficient of spontaneous emission) is equal to the coefficient of absorption. Since the induced emission is coherent with the inducing radiation, it adds to the source radiation an amount of energy which at microwave frequencies is almost equal to the total absorbed energy. The net loss (observable absorption) is the total absorption less the induced emission. The net absorption then depends upon the excess population of the lower over the upper state involved in the transition or upon the Boltzmann factor $(1-e^{-h\nu/kT})$. This quantity, which is approximately unity at optical frequencies, is of the order of one percent at microwave frequencies. Only the high sensitivities of microwave spectroscopes (caused primarily by the strong and nearly monochromatic microwave sources now available) make it possible for microwave absorption spectra to be observed with relative ease.

The ammonia inversion spectrum is not a typical microwave spectrum but is a uniquely important one. Most of the new effects in microwave spectra were noticed first in the ammonia spectrum. It was the first spectral frequency to serve as a controlling pendulum in the now famous atomic clock.

The ammonia molecule NH_3 is in the form of a pyramid with the N at the apex and the three H's at the base corners. Its microwave absorption arises from a periodic turning inside out of the pyramid. This effect, which cannot be accounted for by classical mechanics, is one of the many predictions of quantum mechanics which has been confirmed by experience. We shall mention later one which microwave spectroscopy failed to confirm.

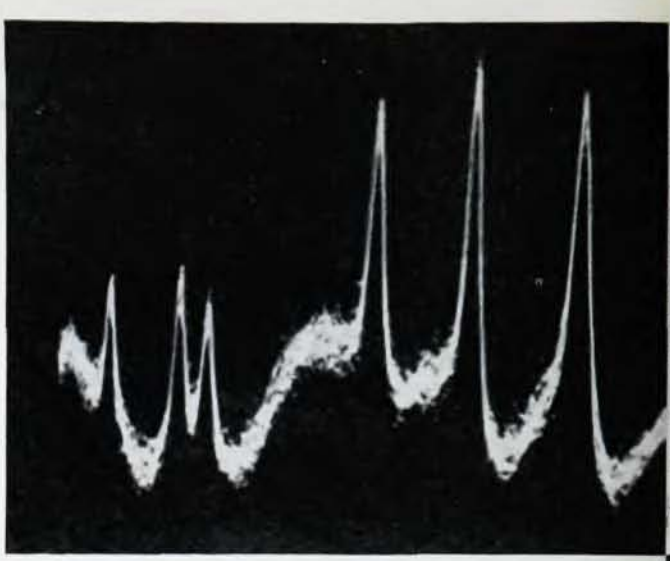

Fig. 2. Hyperfine structure of a rotational line of ICN at 5.81 mm wavelength.

The ammonia inversion absorption observed first by Cleeton and Williams in 1936 was rediscovered in a most interesting fashion during World War II. A group of scientists at the MIT Radiation Laboratory were testing the new K-band radar by observing signals from buildings in Back Bay across the Charles. Mysteriously, the signals blacked out temporarily each day at almost the same time. This puzzling phenomenon was solved when an alert technician correlated the blackout with the daily passing of a garbage boat up the river. From the boat came the unmistakable smell of ammonia.*

After World War II the ammonia spectrum was quickly and exhaustively examined by many researchers. This was a natural development. Ammonia is not only a very strong absorber, but its absorption falls conveniently in a radar band where discarded components were plentiful. Most physicists believe in tackling the easiest problem first—if not always in the easiest manner.

Bleaney and Penrose found that the inversion band could be resolved into a number of separate lines. This fine structure was not unexpected. While turning inside out, the molecule is also rotating. Because of the interaction of the rotation and the inversion, the molecule has slightly different inversion frequencies when in different rotational states. Effects of this interaction on the rotational spectrum had already been detected by infrared spectroscopists. Indeed, it was this infrared evidence for inversion that led to the experiment of Cleeton and Williams.

W. E. Good, with higher resolution than that used by Bleaney and Penrose, found that the individual fine structure lines of the NH_3 spectrum have satellites. These satellites are readily evident in Fig. 1, which is a reproduction of one of the lines as originally seen by Good on the cathode ray screen. This beautifully symmetric hyperfine structure arises from the nonspherical shape of the N^{14} nucleus. The $N^{15}H_3$ spectrum has no

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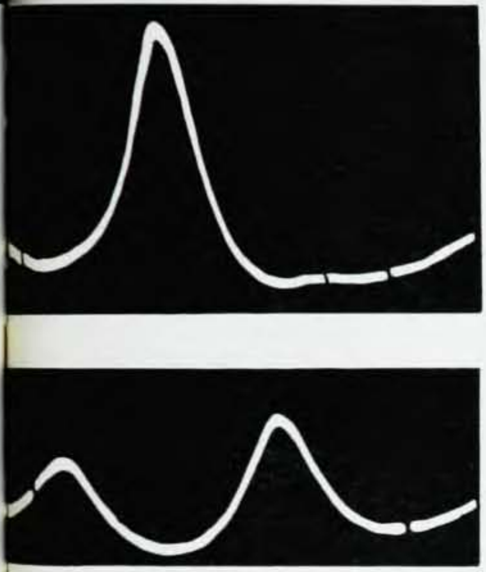
* To his regret the author was not a participant in this experiment and cannot testify to its authenticity.

such satellites. In addition to the rotation and inversion motions already mentioned, the various nuclei are spinning rapidly about their own internal axes. A nonspherical distribution of electric charge causes the nucleus to have an electric quadrupole moment which couples its spin axis to the molecular frame. This coupling causes a precession of the N^{14} spin axis as well as the molecular rotational axis about a direction fixed in space, along which the vector representing the total angular momentum points. Nuclear precession is analagous to the precession of the earth's axis, which results from the torque exerted by the gravitational interaction of the sun on the not-exactly-round earth. The N^{14} precession gives rise to the hyperfine structure of Fig. 1.



ig. 3. Stark splitting of a rotational ne of OCS by Dakin, Good, and Coles.

One of the largest classes of spectra observed in the microwave region is the pure rotational spectra of molecules. Most, but not all, observable rotational lines fall in this region. It is a well-known but still strange fact that rotational motion is quantized. An isolated molecule of a gas cannot rotate with just any energy or momentum but is restricted to certain discrete values of these quantities. Microwave absorption results from a sudden jump of the molecule from one quantized rotational frequency to another. And as much as we would like to think it so, neither of these molecular rotational frequencies corresponds to the radiation frequency which is absorbed. To find the latter, we must subtract the energy of the lower rotational state from that of the upper and divide the remainder by Planck's constant h. That's all the meaning any spectral frequency has at this stage in the development of physics. But the principal moments of inertia of the molecule are related by quantum mechanical formulas to the absorbed radiation frequency. By measurement of the spectral frequency we can then obtain the moments of inertia and from them can calculate the distances between the atoms of the molecule. Microwave spectroscopists have already found the precise structures of dozens of molecules in this manner. A recently measured one is the simple ozone molecule O_3, which has escaped or deceived both optical spectroscopists and electron diffraction experts who sought to find its correct triangular shape. When there are more unknown molecular dimensions than there are principal moments of inertia to be measured, one must resort to isotopic substitution for some of the atoms to obtain the complete structure from microwave spectroscopy.

The nuclear quadrupole hyperfine structure seen in the ammonia spectrum is also prevalent in microwave rotational spectra. Whenever there is a nucleus in the molecule with a spin greater than 1/2, it is likely to have a nuclear quadrupole moment of sufficient magnitude to split the rotational lines to an observable extent. Nuclei with spins of zero or 1/2 have no quadrupole moments. Fig. 2* shows how a rotational line of the linear molecule ICN is split by the nuclear interaction of the I^{127}. But for the nuclear interaction with the molecular rotation there would be only a single line here. From such microwave hyperfine structure several unknown nuclear spins and quadrupole moments have been ascertained. An example is boron ten. Its spin, long thought to be one, was shown by microwave spectroscopy to be three. The same rotational hyperfine structure, that of borine carbonyl, revealed further that the B^{10} nucleus is elongated, or football-shaped. Nuclei with positive quadrupole moments are prolate (elongated), and those with negative quadrupole moments are oblate, or flattened like a door knob. From rotational hyperfine structure the moments of a few radioactive nuclei have been obtained. Because exceptionally small quantities of the material are required, this method is one of the most promising for investigation of moments of radioactive nuclei.

Although the theory of the Stark effect in rotational spectra was developed in the early days of quantum mechanics, this theory lay idle for many years because the resolution in optical spectroscopy was inadequate for its application. The Stark effect in rotational spectra was demonstrated first, and in a spectacular manner, by Dakin, Good, and Coles, who in the early days of microwave spectroscopy applied an electric field to the molecules and saw a single rotational line of OCS suddenly divide and become two. Photographs of this event are shown in Fig. 3, but I assure you that it is more exciting to see these things on the screen directly as they happen. The Stark effect has now become a powerful adjunct to microwave spectroscopy. It is used to obtain precise values of electric dipole moments of molecules, to identify rotational lines, and to aid in detection. In the last mentioned function, introduced by Hughes and Wilson, the spectral line is shaken at a certain frequency with an alternating electric field, and the receiver is tuned to the alternating frequency. Fig. 4 is an automatic recording of a methyl alcohol line

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* I am indebted to O. R. Gilliam, John Cox, and R. M. Hill for obtaining illustrations and to B. Bleaney for sending the photograph of Fig. 5.

and its Stark pattern obtained by square wave voltage modulation. This represents the first-order Stark effect in which the components are symmetrically placed. With this type of modulation the undisturbed line appears along with its Stark components. For ready identification the components are made to point downward while the undisturbed line points upward. These tricks illustrate some of the advantages of doing spectroscopy the electronic way.

The Zeeman effect, magnetic field splitting, of microwave spectral lines is also frequently observed and has been used to measure a few unknown magnetic moments. Both the Stark and Zeeman effects result from the amazing fact that the space orientation of a molecule is quantized. A molecule cannot be oriented at just any angle with an applied electric or magnetic field but is doomed to precess about the field at one of a few fixed orientations which are predetermined by the strength of the field and of the molecular dipole moment. Because of the classical interaction of the dipole with the field, the molecule has potential energy in the field. This energy varies with the orientation. When the molecule shifts from one of its allowed orientations to another, its potential energy must change. The allowed orientation energies perturb the rotational levels and cause the Stark or Zeeman splitting of the rotational lines.

Another large class of microwave spectra is that of electronic paramagnetic resonance. These resonances were discovered in 1946 by a Russian scientist, Zavoisky. Many solids and a few gases are paramagnetic, that is, they contain atoms or ions which have uncancelled electronic-spin or orbital-magnetic moments. Others can be made so by bombardment with x-rays, neutrons, and the like. Paramagnetic substances will absorb microwave radiation if a magnetic field of proper magnitude is imposed. The field interacts with the magnetic moment of the paramagnetic atom or ion and causes its angular momentum vector to precess about the direction of the field. Just as in molecular rotation, the precessional or orientation angle is quantized. The process is similar to that of the Stark or Zeeman effect just described. The flipping of the magnetic moment from one allowed orientation to another gives rise to a change in potential energy which is supplied directly by the radiation field. To find the absorbed frequency one divides the energy difference of the two orientations by h.

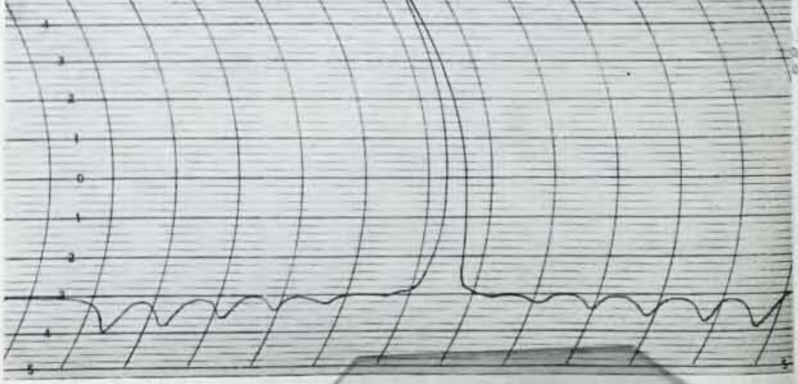
Though pure paramagnetic resonance is simple, it is hardly ever pure. Seldom is the spinning or revolving electron free to precess about an externally imposed field without hindrance from numerous neighbors. But it is the impure rather than the pure resonance which delights the physicist most and which gives him much information as well as trouble. The precessing electron is conveniently situated to give away secrets about the interior of solids. It sometimes even gives away nuclear secrets.

One prevalent effect detected in paramagnetic resonance is the quenching of the orbital momentum of the electrons by the internal electric fields so that only the electron spin vector is free to precess about the external magnetic field. Components of the orbital magnetic moments are thus "frozen" in certain directions according to the symmetry of the internal electric field. These components reveal the directions of the internal fields through their interaction with the spin magnetic moment. The "g factor" obtained from the resonance is frequently close to, but never exactly that of, the free electron spin. Its value usually varies with the orientation of the paramagnetic crystal in the external field.

A significant development in paramagnetic resonance was the resolution of nuclear hyperfine structure by Penrose. The most pronounced hyperfine splitting is caused by the interaction of the nuclear magnetic moment with the electronic magnetic moment. However, effects of nuclear quadrupole moments have been detected in this type of spectra. When the internal fields have axial symmetry, as often happens, the hyperfine structure is frequently simple and beautiful. Fig. 5 shows such hyperfine structure which was cobalt found by Bleaney and Ingram in the ammonium sulfate resonance. The nuclear spin I can be obtained by merely counting the lines. There are $(2I + 1)$ components in the group. It is readily seen that the spin of the nucleus causing the hyperfine structure of Fig. 5 is $7/2$. The nuclear magnetic moment can be obtained from the spacing of the components. From microwave spectra of this type Bleaney and his coworkers have recently obtained the nuclear moments of several of the rare earth elements.

Evidence for the swallowing of a single quantum by two neighboring copper ions in copper acetate was obtained by F. Lancaster and the author. A strong resonance was found at twice the frequency it should occur for the field applied. Since there is only one unpaired electron in each copper ion, the line could not arise from a "double jump" of a single ion. By making studies at low temperature Bleaney showed that this pairing up of two neighboring ions is unquestionably going

Fig. 4. Stark effect of a microwave line of methyl alcohol.



on. The hyperfine structure of the line, instead of having four components as it should have for the nuclear spin of 3/2, was found to have seven components, as it would have if the hyperfine structure represented the combined splitting by two nuclei with total spin 3.

Paramagnetic resonance of unpaired electrons in organic free radicals and of electrons trapped in *F* centers in crystals has been observed. Also, resonance has been found in certain plastics irradiated with x-rays.

The microwave absorption of oxygen is of special interest because of its effects on the propagation of radiation through the atmosphere. Fortunately, oxygen has no resonance frequencies in the centimeter wave region. It does, however, have a large number of peaks, unresolved at atmospheric pressure, between 4 and 6 mm wave lengths and a single resonant frequency at 2.5 mm wave lengths which are of sufficient intensity to affect seriously atmospheric propagation in these regions. The oxygen molecule has no electric dipole moment but does have a magnetic moment of two Bohr magnetons arising from the uncancelled spin of its two unpaired electrons. The microwave absorption energy results from a reorientation of this electronic spin moment in the weak rotational magnetic field of the molecule. Transitions are induced through a coupling of the spin magnetic moment to the magnetic component of the microwave radiation.

Through spectral measurements in the microwave region Lamb and Retherford showed that the $2^2S_{1/2}$ and the $2^2P_{1/2}$ levels of the hydrogen atom are not degenerate, as predicted by long accepted Dirac quantum theory, but are actually separated by 1000 megacycles. This observation stimulated considerable theoretical activity. The effect, which has come to be known as the Lamb shift, has also been observed in ionized helium. It has been explained by Bethe and others as arising from the interaction of the electron with the radiation field.

The reader will be familiar with nuclear hyperfine structure in the optical spectra of atoms. One type of microwave spectra arises from direct transitions between the atomic hyperfine levels. These microwave transitions make possible highly accurate measurements of the small spacings of the hyperfine multiplets. Although hyperfine transitions of many atoms fall in the microwave region, because of experimental difficulties—which are in the process of being surmounted—such transitions have so far been observed for H, Na, and Cs only. That for H is the emission line already mentioned.

Although it took a war to get the microwave spectroscopist started, it has not required a war to keep him in business. He was happy but not contented with the narrow military radar bands which he inherited. There were no millimeter radar bands during World War II, yet microwave spectra are now measured with high precision in all regions between about two millimeters wave length and the centimeter region. The first measurements in the millimeter region were made by Beringer on the 5-mm oxygen absorption. He used crystal detectors and power from crystal multipliers driven by klystrons. At Duke these methods have been developed and extended in range so that spectral measurements are now made down to about 2-mm wavelength, and with an ease, resolution, and sensitivity comparable to that of the centimeter wave region. Fig. 6 shows a recorder tracing of the 2.5-mm wave oxygen line recently measured in this laboratory. Its strength as shown here represents a sensitivity of about 10^{-7} cm^{-1}.

A millimeter wave program is under development at Columbia University, which employs harmonic power from magnetrons. Much more power is available from magnetrons than from reflex klystrons, and harmonic power from them has been detected at wavelengths of 1.1 mm. Nevertheless, because they are not easily tuned and do not have very pure spectral outputs, magnetrons do not now appear promising for high resolution spectroscopy. It seems probable, however, that high resolution can be obtained by use of a grating in combination with a magnetron source. As the microwave spectroscopist approaches the infrared region it seems fitting that he should borrow some of the instruments of that region.

Microwave spectroscopy is still young, but it is no longer small. Already it is too late to describe all branches of the subject in a single article. Ferromagnetic resonance and the dielectric absorption of liquids and solids have been entirely omitted here, as have practical applications such as isotopic and chemical analysis and the regulation and control of electronic instruments. But I hope that enough has been said to suggest the scope and power of this new branch of physics.

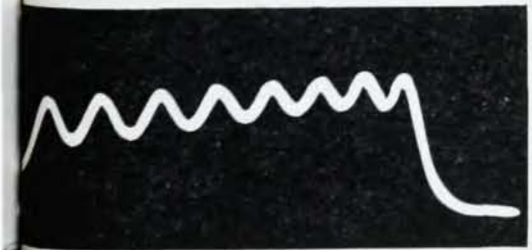


Fig. 5. Hyperfine structure in the paramagnetic resonance of cobalt ammonium sulfate by Bleaney and Ingram.

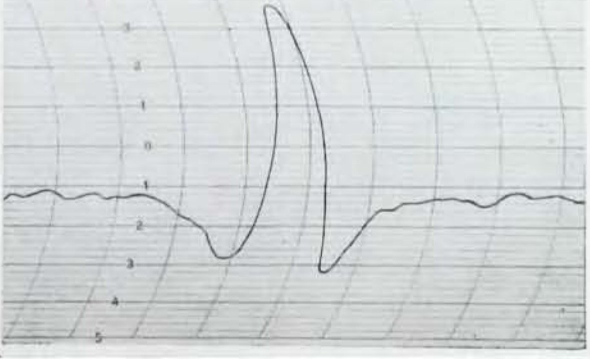


Fig. 6. Recorder tracing of the 2.5 mm line of oxygen at room temperature.