4 October 1968, Volume 162, Number 3849 **SCIENCE**

Microwave Spectroscopy in Chemistry

The use of short radio waves has yielded accurate detailed information on many molecular properties.

E. Bright Wilson, Jr.

Gas-phase microwave spectroscopy is now somewhat more than 20 years old, and it is time to take a backward look with the object of assessing the impact it has had on chemistry. This article is an attempt to describe, for chemists and others, some of the applications which have proved useful. For readers who are not familiar with this field, suffice it to say that this is a branch of spectroscopy which employs electromagnetic radiation with wavelengths ranging from millimeters to a few centimeters—that is, frequencies of from perhaps 5000 to several hundred thousand megahertz (*1–3*). The absorption of such radiation by moderate-sized polar molecules at pressures of a few hundredths of a torr can be observed and accurately measured by equipment, largely electronic in nature, which I make no attempt to describe here. The outstanding features of the technique, from an experimental viewpoint, are the ease with which frequencies can be measured to an accuracy of better than one part in a million and the effectiveness with which adjacent absorption frequencies can be resolved, even though they may be separated by a mere fraction of a megahertz—that is to say, by less than 1/30,000 of a wave number. Furthermore, a very small amount of material, of the order of micrograms, is required.

By way of introduction it should also be stated that, in nearly all cases, the absorption of the electromagnetic radiation produces a change of rotational energy in the free gas molecule. This rotation is, of course, quantized and is governed by well-known quantum mechanical formulas. To a first and very good approximation, a rigid rotating body with three principal mechanical moments of inertia serves as an adequate molecular model for many of the observations.

A number of types of information about individual molecules can be obtained by means of this technique, including very accurate molecular structures, dipole moments, nuclear quadrupole coupling constants, nuclear masses, molecular magnetic moments, low-lying vibration frequencies, conformations and energy differences of rotational isomers, and various types of magnetic interaction energies; the end is nowhere in sight. Only a sample (and probably a biased one) of the many applications can be discussed here, and many very interesting topics must be omitted. In addition an article of this length cannot do justice to the work of all of the 50 or so laboratories around the world where active work in this field is being carried out (*4*).

Structure

The most obvious contribution of this branch of spectroscopy to chemistry is a massive collection of quite accurate and reliable data on molecular structures. Nearly 1000 molecules have been studied in greater or less detail, the studies yielding in each case partial or complete information about the interatomic distances and angles. In the more favorable cases the values for interatomic distances have at least consistency and some kind of meaning down to a few thousandths of an angstrom, and in most cases they probably have an absolute accuracy of approximately a hundredth of an angstrom. The values for angles are roughly accurate to within about 1 degree and often less. For determining the structure of gas-phase species, microwave spectroscopy has only one serious rival—the electron diffraction method. This latter method has one great advantage: it can be used for studying completely nonpolar molecules, while so far this has not been possible with the microwave technique. Furthermore, the best electron diffraction studies on simple molecules give results of probably about the same accuracy as those obtained with the microwave technique. Both methods are limited by the difficulty of taking into account the vibrational motions of the atoms. However, although errors have been made with the microwave technique—it is possible to make mistakes in any field—the microwave method does have a great advantage over the electron diffraction technique for studying polar molecules in that it is less subject to errors due to impurities or decomposition of the sample, or to incorrect interpretation. The analysis of complicated microwave spectra, which means the assignment of quantum numbers for a certain number of transitions so that the quantum mechanical formulas can be applied and the moments of inertia and other parameters can be extracted from the resulting formulas, may be very simple in some cases and quite difficult in oth-

---

The author is on the staff of the Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts.

ers. However, once the analysis is accomplished, it is very easy to apply a large number of checks, so the microwave spectroscopist seldom has much excuse if he publishes incorrect assignments. Since structure is very important in chemistry, the quantitative structural results that have been obtained from electron diffraction and microwave spectroscopy are a very basic part of chemical knowledge and are constantly drawn upon (*5*).

Characterization

Perhaps the most obvious use of microwave spectroscopy historically, but not the most important, is its use as a tool for characterizing chemical species. So far such characterization has been made only for molecules of moderate size—molecules with up to perhaps 10 or 12 carbon atoms.

This is a severe limitation, because the organic chemist, at least, is nowadays usually interested in much bigger molecules, of a size at present beyond the reach of our spectrometers. However, for the smaller molecules, no other known type of spectrum is nearly as unique and characteristic as a microwave spectrum. Figure 1 shows a very small portion of the microwave spectrum of propionyl fluoride as an example. When one remembers that each peak on this chart can be measured to an accuracy of one part in a million and that, in addition, there are tricks, such as double-resonance, which multiply the specificity by factors of thousands, one sees that this is a means of characterization which has absolutely no rival. Once a molecule has been caught and finger-printed by this method, it is forever recognizable (*6*).

This, of course, leads to the notion that microwave spectroscopy should be a marvelously useful technique for analytical chemistry, both qualitative and quantitative. In principle it should be, but in practice this aspect of its capabilities is only now being developed, partly because of the power of gas chromatography, mass spectroscopy, infrared spectroscopy, and nuclear-magnetic-resonance spectroscopy. Nevertheless, it seems certain that problems do exist for which new tools are needed, and for some of them microwave spectroscopy may very well turn out to be the method of choice.

Dipole Moments

Microwave spectroscopy has proved to be an excellent method of obtaining molecular dipole moments—that is, the total electronic charge times the distance between the centers of negative and positive charge in a molecule. These values are obtained from the measured intervals in the Stark effect patterns—the sets of components which arise from a single rotational absorption line when a uniform electric field is applied to the gas. Figure 2 shows such a Stark pattern (admittedly an unusually symmetrical and beautiful one) for a transition of methyl alcohol.

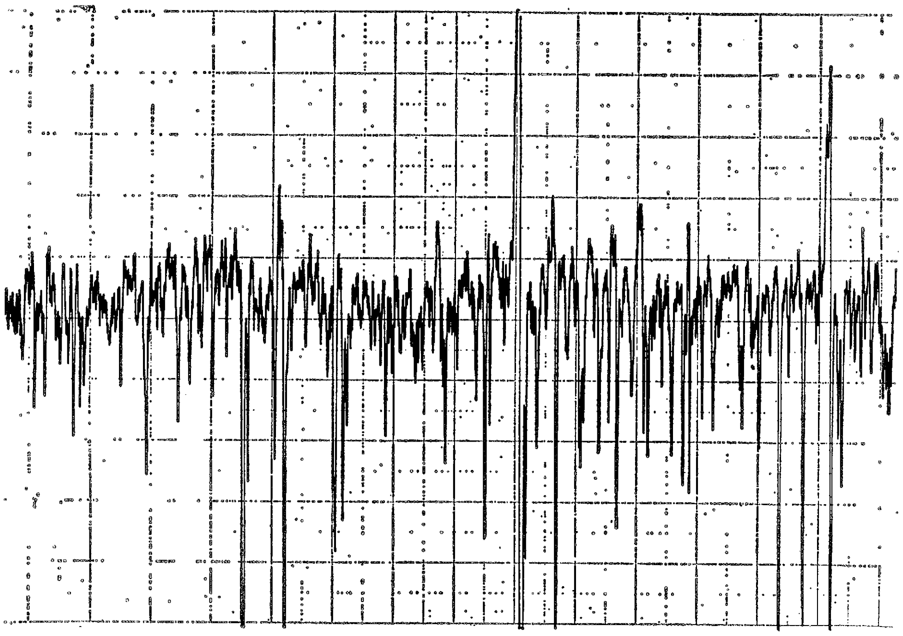


Fig. 1. A portion of the microwave spectrum of propionyl fluoride, showing more than 100 rotational transitions above the noise level, in the range 38 to 39 gigahertz. The same instrument can record transitions in the range 26 to 40 gigahertz.

Quantum mechanics is, as usual, required in order to proceed from the experimental measurements to the derived molecular property. The required quantum mechanical formulas are available and give the frequencies which should be observed for a rigid rotor carrying a given fixed dipole moment and rotating in a known electric field (*1*, *2*). The components of the dipole moment along the three principal axes of inertia of the molecule are treated as parameters and adjusted until the calculated frequency intervals agree with the observed ones. Again, a number of independent data can be obtained, so that parameters can be checked as well as determined.

The usual accuracy of these dipole-moment values is about 1 to 2 percent, but, through the use of specially designed equipment, a relative accuracy perhaps ten times greater has been achieved (*7*). With such accuracy, one can easily distinguish the moment values of molecules in various vibrational states and of different isotopically substituted species.

The microwave method has very great advantages: it requires no corrections for solvent and for gas nonideality; it should not be affected by impurities; and it is capable of greater accuracy than any other method except for the related molecular beam techniques. Furthermore—and this is a very interesting point—it yields the components along the principal axes separately.

Since the squares of the components are obtained experimentally, uncertainties in sign may exist. By isotopic substitution, the principal axes may often be rotated enough to produce observable changes in the relative sizes of the components, from which the relative signs (but not the overall sign of μ, the dipole moment) can be determined experimentally.

Dipole moments have historically been important in chemistry partly because the existence of a nonvanishing moment shows that certain symmetry elements (for example, a center of symmetry) are absent. It is difficult to prove, by any method, that a dipole moment is strictly zero. The microwave method can sometimes, but not always, detect quite small values (for example,

$\mu \sim 0.01$ D in H—C≡C—D), but of course the absence of any observable spectrum may be due to other causes besides the vanishing of the dipole moment.

The principal interest today is in the comparison between experimental values and values calculated by various approximate theories of the electron distribution in molecules.

Nuclear Quadrupole Fine Structure

When a molecule contains a nucleus with a nuclear spin of unity or greater —for example, ^{14}N, ^{35}Cl, ^{79}Br—the different possible orientations of the nuclear spin relative to the molecular axis can give rise to an experimentally observable splitting of a single rotational transition into several components (*1, 2*). These nuclei are not strictly spherical, so the electrostatic interaction of the nuclear charge with the charges of the electrons and other nuclei depends upon the orientation of the nucleus.

The pattern to be expected can be predicted by quantum mechanical treatments in terms of the magnitude of the nuclear electrical quadrupole moment and the components of the gradient of the electrical field at the nucleus arising from the electrons and other nuclei. Since the nuclear quadrupole moment is constant for a given nucleus (it is known for some), analysis of the experimental patterns gives information about the field gradient, at least on a relative basis, and hence about the electron distribution.

A spherically symmetric electron distribution, such as is postulated as a first approximation for an ionically bound atom, should give a vanishing field gradient. It is indeed found that chlorine in NaCl, a quite ionic compound, has an almost negligible field gradient in comparison with covalently bound chlorine, as in CH_3Cl. Similarly *s* electrons and also filled shells should not contribute to the field gradient. A rather considerably simplified theory attributes all of the effect to the *p* electrons in the covalent bond to the chlorine. Generally, the field gradient is found to be oriented along the direction of the chemical bond (even in some cases where this was not expected because "bent" bonds were predicted). The field gradient is approximately symmetrical about the bond direction for pure single bonds, but not for bonds that, according to conventional chemical ideas, have some double-bond character.

Table 1. Some barriers to internal rotation.

Molecule	Barrier (kcal/mole)
CH_3OH	1.07
CH_3CHO	1.17
CH_3CFO	1.04
$CH_3CH_2CH_3$	3.56
$CH_3CH{=}CH_2$	1.98
CH_3CH_2Cl	3.69
CH_3NO_2 (6-fold)	0.006

Although the available quantum mechanical approximations are usually inadequate to account for observed field gradients in a truly quantitative way, the inverse process of inferring some features of the bonding and electron distribution from observed spectra has been frequently used.

Barriers to Internal Rotation

The study of potential barriers hindering internal rotation is an area in which microwave spectroscopy has made a major and almost unique contribution.

In the last century chemists decided that a single bond, such as carbon-to-carbon in ethane (CH_3–CH_3), acted like a well-greased axle about which the two groups rotate freely. Some years ago it was proved that there is usually a small potential energy interfering with this rotation, the "barrier" to internal rotation being the maximum value of the potential.

Primarily, microwave spectroscopy can be used to study a special class of internal rotations—namely, internal rotation of methyl groups in simple molecules. Here it is found that suitable pure rotational transitions are split into doublets, usually with spacings of a megahertz or so. Several different forms (*2*) of the quantum mechanical theory of this phenomenon have been developed, so measurements of the splittings of a few transitions can give the value of the potential barrier to an accuracy of 5 percent or perhaps even better. The restriction has been that the rotating group must be symmetric; with a few exceptions, it has been a methyl group, although in several transitions studied it has been a silyl group and, in one instance, a CF_3 group. The effect is caused by the tunneling of the atoms through the potential barrier; this quantum mechanical effect depends strongly on the mass and therefore is most likely to be observed with hydrogen atoms, as in CH_3 groups.

Table 1 shows a list of some barriers, selected from nearly a hundred, determined by the frequency-splitting microwave method. The important feature of these barrier values is their presumed reliability. There may be errors of a few percent, but it seems quite unlikely that there are any large errors. A certain degree of checking has been done, since there is now a quite effective technique involving use of the far-infrared spectrum and, in addition, rough checks can be made by a microwave intensity method. Of course, as vibrational anal-

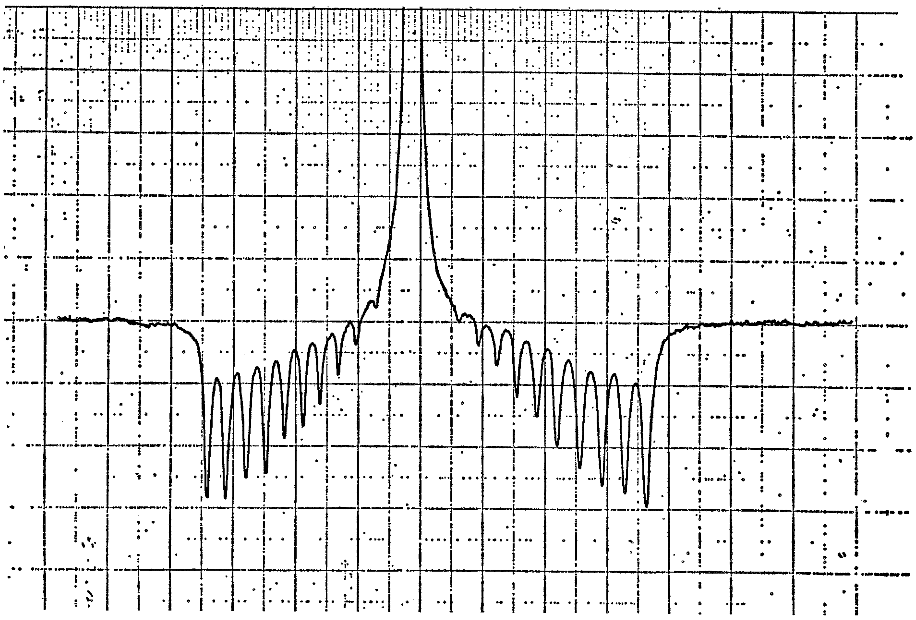


Fig. 2. The Stark effect on a rotational transition of methyl alcohol.

yses are made more certain, the thermodynamic methods also become more reliable.

The availability of these new barrier data has led to a considerable effort on the part of theoretical chemists. At first it seemed difficult to explain the origin of barrier forces, but as computers grew more powerful and it became practical to make calculations with fewer unsatisfactory approximations, treatments based on molecular orbital theory began to give results that were in rough accord with observations for the simplest case, ethane (*8*). It now is fairly clear that barriers arise from a balance between the various coulombic electrostatic attractions and repulsions of the electrons and nuclei, the electrons being distributed in more or less the way one would expect from quite simple quantum mechanical treatments.

Barrier heights are quite small energies, even by comparison with the errors in the best present calculations of total molecular energies. Nevertheless, they are important among the factors determining the stabilities of particular species and are of quite far-reaching importance for an understanding of conformations of small molecules and polymers and proteins—that is, for understanding the way in which chains fold up. It is therefore desirable to have much more understanding of barrier heights than we now possess. The theory has not yet reached a point where it can reliably predict differences from one molecule to the next, and it is incapable, as most applications of quantum chemistry are, of giving estimates of the error limits of predicted values. It is still important, therefore, to collect experimental barrier values and to seek empirical regularities.

Conformations

When a molecule contains a single bond connecting two unsymmetrical groups [for example (*9*), $CH_2F–CH=CH_2$ (Fig. 3)], complete specification of its structure requires that the equilibrium angle of rotation of one group (for example, CH_2F above) with respect to the other ($–CH=CH_2$) about the single bond be given. This angle defines the molecule's conformation. It may or may not happen that the energy of the molecule shows more than one minimum as this angle is changed; in other words, the molecule may exist in two or more forms, here called rotational isomers. Where these occur, it is ordinarily true that the molecule, as a result of collisions, can be rapidly transformed from one conformation to another, even at room temperature. Consequently the different rotational isomeric forms cannot be separated from one another, bottled up, and studied. This behavior is in contrast with the situation existing for *cis-trans* isomers, such as the pair in Fig. 4, where quite high temperatures are usually required to cause interconversion (here rotation by 180 degrees around the C=C double bond). *Cis-trans* isomers can usually be separated and purified.

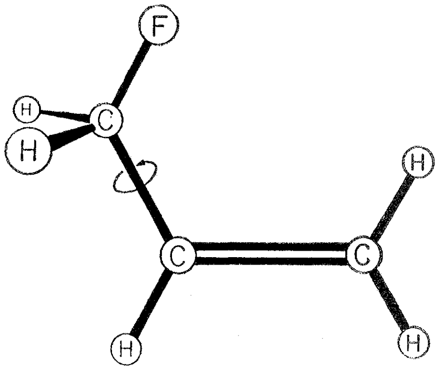


Fig. 3. One conformation of 3-fluoropropene. Other conformations are achieved through approximately 120-degree rotation of the CH_2F group.

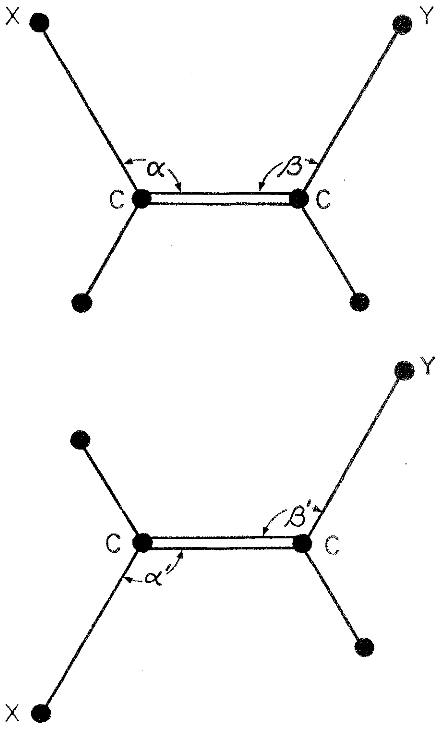


Fig. 4. A *cis-trans* isomer pair.

A good deal of information about rotational isomers has been obtained by infrared, Raman, and nuclear-magnetic-resonance spectroscopy, as well as by other methods, but the techniques of microwave spectroscopy provide very detailed and quantitative information. Collisions almost always cause polar molecules to undergo a transition from one rotational state to another, so the absorption of a microwave photon of a particular frequency by a molecule can only be accomplished in the short time between collisions. The conversion of one rotational isomer to another requires collisions, so it is a slower process than microwave absorption. Therefore, the microwave spectrum of a mixture of rotational isomers is just the superposition of the spectra of the separate forms, despite their rapid interconversion. Since the resolution is so great, there is relatively little trouble with overlapping lines (at least for the stronger lines), and the spectrum of each form can be separately analyzed. Thus the structures, including especially the dihedral angles, can be obtained, as well as much other information. Figure 5 shows some rotational isomeric conformations determined in this manner (*10, 11*).

In addition to the conformations, it is possible, in appropriate cases, to get approximate information about the potential energy function associated with changing the dihedral angle. Figure 6 shows such a result for ethyl formate (*10*). This function is certainly related to the problem, discussed above, of barriers to internal rotation, and to the very general and basic problem of nonbonded forces—that is, the forces within a molecule between atoms not directly bonded to one another. Altogether too little is known about such forces, despite the chemist's long acquaintance with the fact that atoms cannot be too closely crowded together (steric hindrance).

Conformational preferences are fundamentally important for an understanding of protein structure and hence of enzyme action, as well as being important in the theory of polymers. Today, many physical organic chemists are engaged in trying to fit various empirical formulas for nonbonded forces, barrier energies, and so on, to the known facts about conformations (*12*). More quantitative experimental data for testing these procedures are greatly needed.

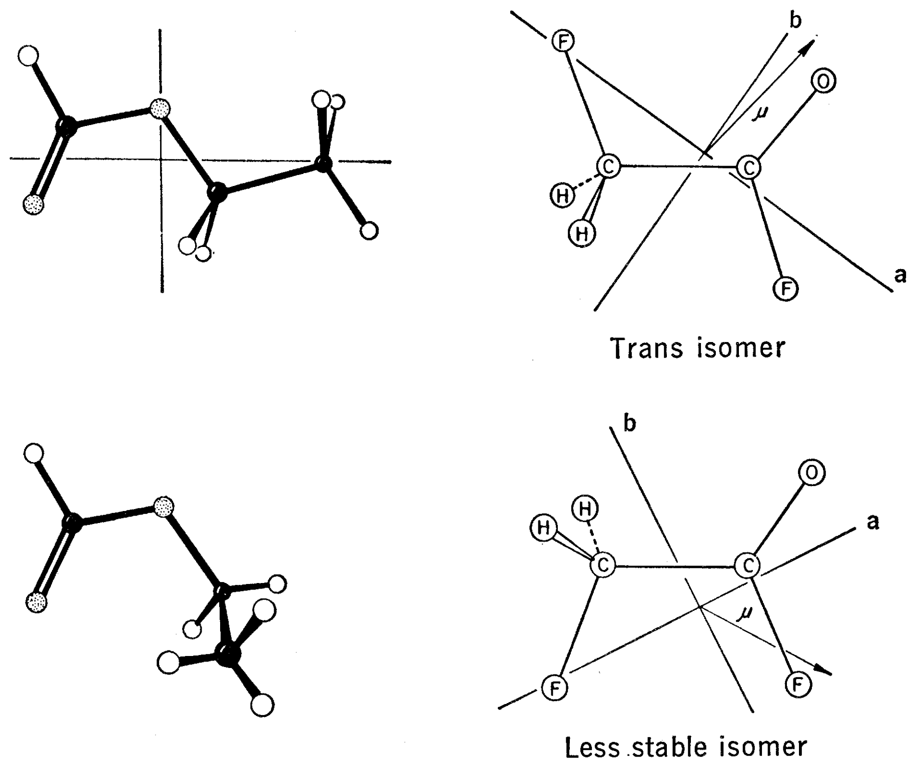
Centrifugal Distortion and Chemical Bonds

Although the pure rotational transitions of lower energy of most molecules so far studied can be understood quite accurately in terms of the rigid rotor model (sometimes elaborated by including internal rotation), the deviations can become quite measurable for the higher energy levels, where the molecule is rotating very rapidly. At this point we need to use a more accurate model, one which allows for the fact that the nuclei are not held apart at exactly fixed distances but can be displaced somewhat by the centrifugal force of the rapid rotation. If we use a model of point masses (the nuclei) held together by spring-like forces (provided by the chemical bonds based on the electrons which hold the nuclei together), it becomes possible to use the deviations from the rigid rotor fit to learn about the valence forces in a quantitative way (*1, 2*). This procedure is particularly effective for the weak forces which determine the equilibrium valence angles, such as the F–O–F angle in the bent molecule F_2O. The stiffness of valence bonds and valence angles determines the vibrational frequencies of molecules, which give rise to their usual infrared spectra. So here two different branches of spectroscopy are linked, and their conclusions are found to agree quite well. Further, the use of data from both sources yields even sharper information about the internuclear forces in simple molecules (*13*).

It is perhaps worth noting that this somewhat esoteric effect—a molecule's distortion because of centrifugal force when it rotates rapidly—affects our electricity bills. Centrifugal distortion contributes about 1 percent to the specific heat of steam at high temperatures, hence the effect had to be included in the calculations for the engineers' steam tables (*14*).

Magnetic Effects

When a magnetic field is applied to a molecule, the energy levels are altered by a small amount and may be split into components; this is the so-called Zeeman effect. If the molecule has unpaired electrons (examples are oxygen, NO_2, and ClO_2), the effect, though still small, is thousands of times larger than in the more common case where all electrons are paired. These latter molecules can still act as very weak magnets because they generate a magnetic field on rotation, or because they contain nuclei with magnetic moments. These nuclear magnetic moments can interact with each other and with the rotational magnetic moment. There is also the diamagnetic effect, a magnetic moment induced in the molecule by the influence of the external magnetic field on the motion of the electrons. These several effects are all very small, and special high-resolution experimental equipment is needed for seeing and measuring them, but they have been observed for a number of molecules (*15*). Together with information on the bulk diamagnetic



Trans isomer

Less stable isomer

Fig. 5. Rotational isomers for ethyl formate (CH_3CH_2OCHO) and fluoromethyl acetyl fluoride (CH_2FCOF).

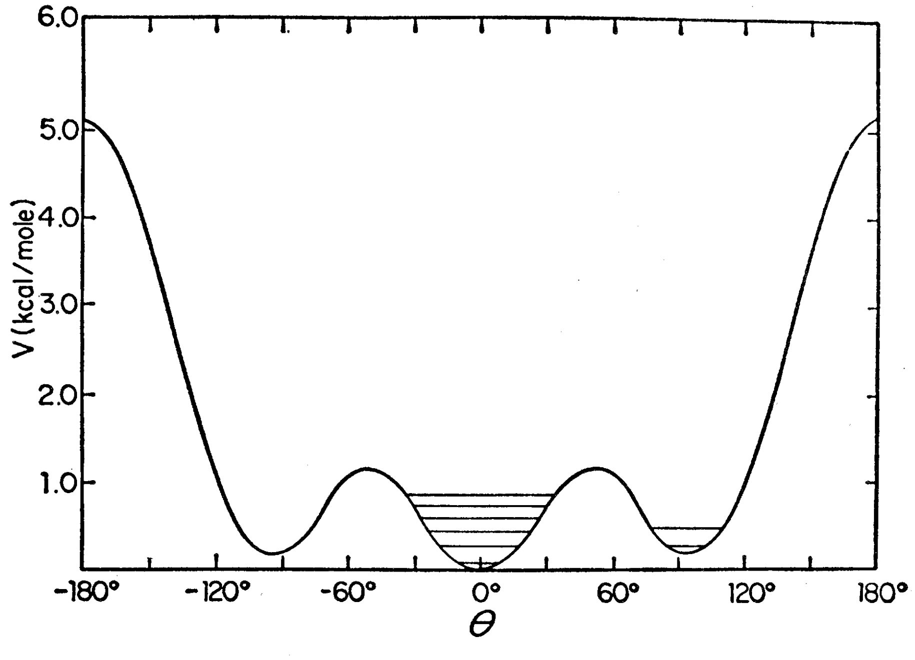


Fig. 6. Potential energy function for ethyl formate.

susceptibility and data of the kind provided by nuclear magnetic resonance, they yield some very detailed information about the way in which the electrons are distributed in the molecule.

The chief value of these various quantities (such as the average squared distance of the electrons from the center of mass) indicative of electron distribution is that they are experimentally obtained values which can be used to test various approximate quantum mechanical calculations of the distribution. A particularly searching comparison has recently been made (*16*) for formaldehyde (H_2CO), a molecule small enough so that various quantum mechanical approximations of at least moderate respectability can be made numerically. A considerable number of properties were measured by microwave spectroscopy.

The calculated values agree moderately well with experimental values for some of these properties, not so well for others; the net result was not a great success for the particular version of molecular orbital theory used. However, there is a measure of agreement, so there seems little doubt that the theoretical procedure is basically sound, even though not very accurate.

Inorganic Species

Inorganic chemistry provides a rich collection of small molecules with very varied properties, reactivities, and stabilities. There still exist situations in which unauthenticated claims have been made—and disputed—concerning the very existence, not to mention the structure, of simple species. Where the vapor pressure is adequate and a dipole moment is expected, microwave spectroscopy can be the method of choice for clarifying these puzzles.

An early example is provided by a species variously claimed to be SO, S_2O_2, and other formulas. A microwave study (*17*), in combination with standard physical chemical techniques, conclusively showed that the compound in question is S_2O, with the geometry shown in Fig. 7 and a dipole moment of 1.47 Debye.

In another confused situation there were claims that a particular compound had the formula SNF and that another species NSF also existed. With support from the Office of Naval Research it was proved (*18*) that the compound said to be SNF has the structure shown in Fig. 8—that is, it is NSF.

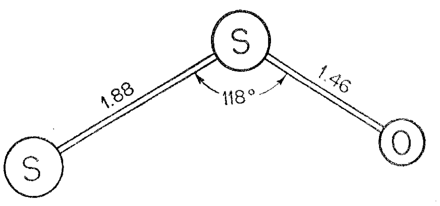


Fig. 7. Structure of S_2O.

The sulfur fluorides are an interesting series. So far, SF, SF_4, and S_2F_2 have been studied by the microwave method; SF_6 is a well-known compound with no dipole moment. The situation with respect to S_2F_2 a few years ago was quite unsatisfactory. Although the literature contained claims, dating back several decades, that such a compound had been synthesized, the evidence presented was regarded as unconvincing by most writers of books on inorganic chemistry, who generally doubted that such a compound existed. Microwave studies (*19*) and independent and simultaneous infrared investigations (*20*) showed that not only is there a compound with the formula S_2F_2, there are actually two of them; the structures are shown in Figs. 9 and 10. The difficulty with the earlier work was that the method of preparation yields a complex mixture and the earlier tools were inadequate for characterizing such a system. The microwave spectrum of the product immediately showed that the mixture contained SO_2, SOF_2, SF_4, and two different unidentified species. (Nonpolar SiF_4, which has no microwave spectrum, was also present.) That the unidentified lines were from different species was clear because one set faded out faster than the other.

Incidentally, the availability of modern tools, such as infrared, microwave, and nuclear-magnetic-resonance spectroscopy, for characterizing chemical species in mixtures is an enormous help in separating and purifying single substances. With the aid of these tools the chemist can monitor his operations and follow the path taken by a given species through the various distillations, crystallizations, chromatographic separations, and so on.

Some molecules containing one quite heavy atom have been successfully studied—for example, cyclopentadienyl complexes of thallium, manganese, and nickel (*21*). The identification of one of the recently discovered compounds of the rare gas xenon, the oxytetrafluoride $XeOF_4$, has likewise been verified, and its structure has been determined (*22*). Such compounds are of great interest because, until a few years ago, it was a firm principle of chemistry that the rare gases—helium, neon, argon, xenon, and krypton—formed no compounds, and that everyone understood why they could not.

The microwave technique has been applied to the study of very nonvolatile substances through observation at high temperatures (*23*). Examples of such substances are many alkali halides, AgCl, TlBr, and CsOH.

Unstable Species and Free Radicals

For many years microwave spectroscopists have believed that their techniques should be a highly effective tool for studying the structure and other molecular properties of short-lived chemical species. It is postulated that large numbers of such species occur as intermediates in chemical reactions, but direct evidence of their reality is limited, and in most cases very little information about their structure, dipole moments, and other properties has been obtained. These species are often pieces of broken molecules, and they may contain unpaired electrons.

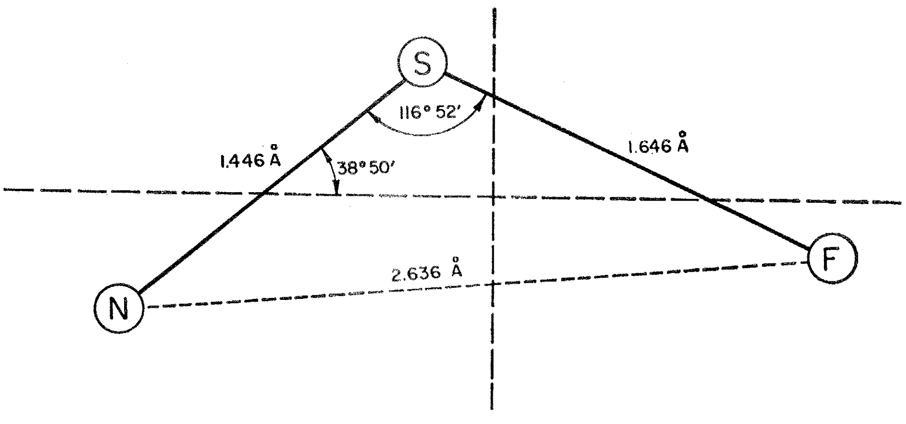


Fig. 8. Structure of NSF.

Unfortunately, most of these species, called free radicals, have turned out to be so reactive that their lifetimes are very short indeed—perhaps measurable in microseconds. Attack of this field by microwave spectroscopy has therefore proved very difficult, and progress has been slow.

The first success was detection of the spectrum of the OH radical, achieved by running an electric discharge through water vapor (*24*). This discovery has had most interesting astrophysical applications. The same spectrum, with very curious intensity anomalies, has been picked up from space; an explanation of these anomalies is only now being proposed.

Of course, stable species with unpaired electrons, such as O_2 (*25*) (the outstanding example of a nonpolar molecule showing a microwave spectrum), NO (*26*), NO_2 (*27*), and ClO_2 (*28*), have been studied. These show interesting, analyzable complications due to the magnetic moment of the unpaired electrons.

Other short-lived species which have been observed include CF_2 (*29*), SiF_2 (*30*), and SO (*31*).

Recently a number of transient vapor-phase paramagnetic species have been detected (*32*) by a special form of microwave spectroscopy—electron spin magnetic resonance (not discussed in this article except in this context). The transitions being observed by this method are transitions between different quantized orientations of the unpaired electron spin in a strong magnetic field, instead of transitions between rotational states. The species SF, SeF, SeO, NSe, and IO are among those found. It is fairly certain that more and more transient species will be detected, and this may well be one of the areas where microwave spectroscopy can be most useful to chemistry in the future. It is possible to smash up molecules by heat, light, electric discharges, shock waves, and other means, and microwave spectroscopy could prove to be capable of determining what the initial fragments look like before they recombine to form more stable species.

Energy Transfer and Intermolecular Forces

So far the discussion has dealt exclusively with the properties of individual molecules, but microwave spectroscopy has provided some information on intermolecular forces and collisional effects as well. The widths of microwave spectral lines have been associated with the forces between molecules and used to estimate molecular electrical quadrupole moments.

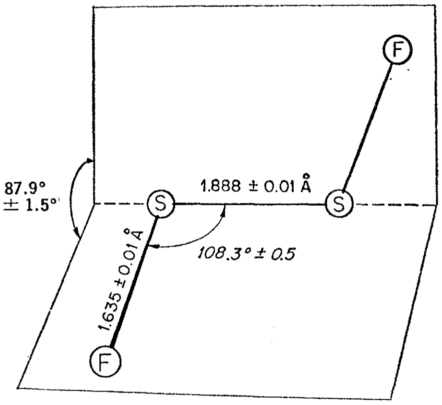


Fig. 9. Chain isomer of S_2F_2.

Recently it has been shown (*33*) that approximate collisional selection rules exist—that is, that when a molecule suffers a collision it is transferred preferentially into one or another of a small number of other rotational states, these being governed by a simple rule. Apparently, the main effect is due to the interaction of the dipole moments of two collision partners, and this interaction can occur at a distance several times greater than the normally defined "diameters" of the molecules concerned. Hence the molecules may transfer rotational energy and convert translational into rotational energy even when they do not truly collide in the simple hard-sphere sense. The technique for studying this involves the use of two microwave sources. A more powerful source saturates a rotational transition—that is, causes upward transitions to occur so rapidly that an excess of molecules appears in the upper level of the transitions. Collisions then transfer some of these excess molecules to other states, where they are detected because they change the intensity of a second microwave absorption line (see Fig. 11).

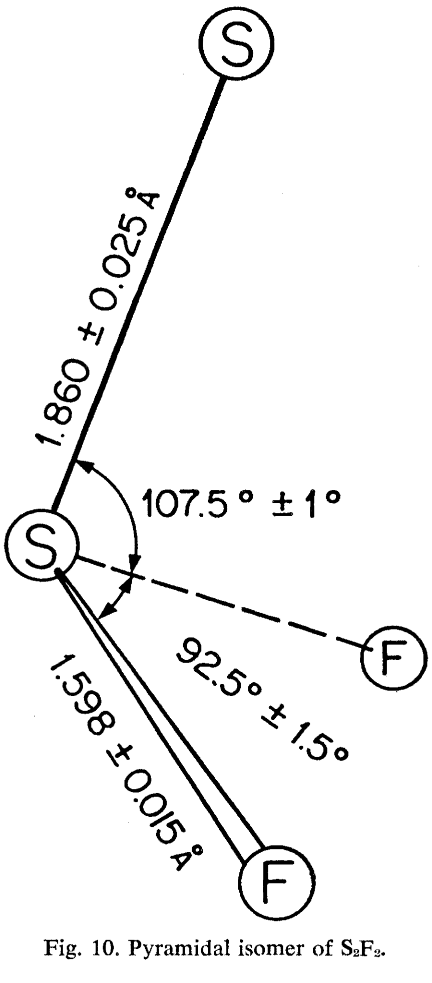


Fig. 10. Pyramidal isomer of S_2F_2.

Testing Theories

Any method giving quantitative molecular information can have an important role as a testing ground for current theories. Chemistry has so far acquired only a very limited basis of rigorous theory; its literature is flooded with theories which can make no claim to rigor but which nevertheless have provided much of the guidance for experimental advances over the years. It is important (but not easy) to sort these out and to try to define their respective areas of usefulness. Microwave spectroscopy has provided a vast number of data on bond distances, bond angles, nonbonded distances, conformations, dipole moments, quadrupole coupling constants, magnetic interactions, and so on, many of which can be matched against the predictions of various theories (*34*).

An interesting example is provided by the popular picture of hybridized bonding orbitals and the related concept of "bent bonds." In several very important but very approximate methods of describing chemical bonds (especially those involving carbon), the wave functions for the bond electrons are built up from the first two wave functions for one-electron atoms, the so-called *s* and *p* orbitals. In this concept, in order that four of these orbitals may be directed toward the corners of a tetrahedron, as in methane (CH_4), the orbitals are combined or hybridized. Angles other than tetrahedral angles can be obtained by varying the admixture, and there is a fixed relation between the angle and the amount of *s* character.

It further follows from the theory (at this very simple but often invoked level) that if one of the tetrahedral angles is opened up, the opposite orbitals must make an angle smaller than a tetrahedral angle. It is therefore interesting and disconcerting when microwave measurements (*35*) give values greater than a tetrahedral angle for the opposite angles in CH_2Cl_2—that is, the Cl–C–Cl and H–C–H angles.

Furthermore, no amount of hybridization can produce a 60-degree angle, such as occurs in the carbon ring of cyclopropane (C_3H_6). To explain this case the concept of bent bonds was developed (*36*). A bent bond is a bond in which the line from one atom to the next, following the line of highest electron density, is not the straight line between the two nuclei. In terms of the simple orbital theory, the angles between the orbitals in a bent bond can differ from the angles between the straight lines leading to adjacent atoms. Although this concept extricates the theory from the difficulty of the 60-degree angle, it of course also removes it from the realm of predictive theories.

Microwave measurements of methylene chloride (CH_2Cl_2) have provided further pertinent data. If the failure of the simple theory with respect to the opposite angles is to be explained in terms of bent bonds, one would expect the C–Cl bond electron distribution, as viewed from the chlorine nucleus, not to be exactly lined up with the Cl–C direction. But, as discussed above, the nuclear quadrupole fine structure can give information about the electric field gradient at the chlorine nucleus. Measurements show that this field gradient is here lined up with the carbon-chlorine bond direction (*37*); the expectation that the carbon-chlorine bond is bent is thus not fulfilled.

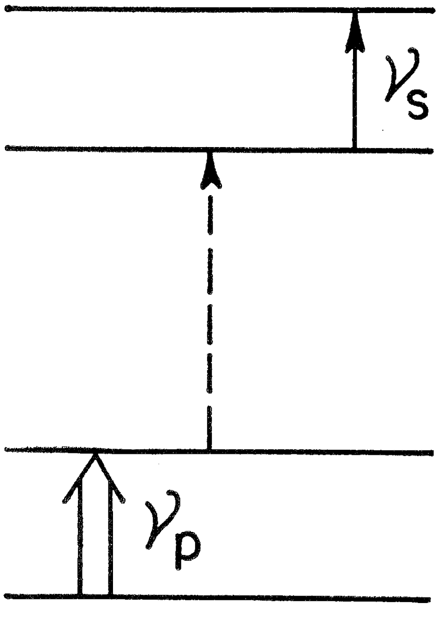


Fig. 11. Energy-level diagram for collisional transfer experiment.

So these microwave results shed some doubt on the universal usefulness of the concept of hybridization for the prediction of bond angles.

Since microwave spectroscopy is capable of providing refined information about electrons in molecules, it is serving more and more as the basis for severe tests of current theories.

Summary

It is clear that microwave spectroscopy has provided a considerable quantity of reliable data, often very detailed, on various molecular properties. These data are being built into the structure of chemistry. It is also important as the basis for testing existing theories and as a stimulus for new theoretical developments. Although the technique is limited at present to polar molecules (oxygen is an exception) which are not very large and which have some observable vapor pressure, large numbers of compounds and probably a good many new properties and effects remain to be studied. Furthermore, the possibilities of using microwave spectroscopy as an analytical tool have been very little explored.

References and Notes

1. C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).
2. J. E. Wollrab, *Rotational Spectra and Molecular Structure* (Academic Press, New York, 1967).
3. W. Gordy, W. V. Smith, R. F. Trambarulo, *Microwave Spectroscopy* (Wiley, New York, 1953); M. W. P. Strandberg, *Microwave Spectroscopy* (Methuen, London, 1954); T. M. Sugden and C. N. Kenney, *Microwave Spectroscopy of Gases* (Van Nostrand, Princeton, N.J., 1965).
4. Since I make no attempt here to provide a review for specialists, the bibliography, except for the books, is incidental. For comprehensive bibliographies, see Townes and Schawlow (*1*), Wollrab (*2*), and P. G. Favero, *Microwave Gas Spectroscopy Bibliography 1954–1962* (Istituto di Chimica e Fisica dell' Università di Padova, Padova, Italy, 1963).
5. Recently a very convenient compilation of structures, dipole moments, barriers to internal rotation, and quadrupole coupling constants, as established by microwave spectroscopy, has appeared: B. Starck, *Molecular Constants from Microwave Spectroscopy* (Springer, Berlin, 1967).
6. For frequencies, see "Microwave Spectral Tables," *Nat. Bur. Std. Monograph No. 70* (1963), vol. 1; *ibid.*, vol. 3, in press; *ibid.*, vol. 4, in press, *ibid.*, vol. 5 (1968).
7. J. S. Muenter and V. W. Laurie, *J. Chem. Phys.* **45**, 855 (1966).
8. See, for example, R. M. Pitzer and W. N. Lipscomb, *ibid.* **39**, 1995 (1963).
9. E. Hirota, *ibid.* **42**, 2071 (1965).
10. J. M. Riveros and E. B. Wilson, *ibid.* **46**, 4605 (1967).
11. E. Saegebarth and E. B. Wilson, *ibid.* **40**, 3088 (1964).
12. See, for example, N. L. Allinger, M. A. Miller, F. A. Van Catledge, J. A. Hirsch, *J. Amer. Chem. Soc.* **89**, 4345 (1967).
13. L. Pierce, N. DiCianni, R. H. Jackson, *J. Chem. Phys.* **38**, 730 (1963); G. E. Herberich, R. H. Jackson, D. J. Millen, *J. Chem. Soc. A* **1966**, 336 (1966).
14. W. F. Giauque, *J. Amer. Chem. Soc.* **59**, 1157 (1937).
15. See W. H. Flygare, *Record Chem. Prog.* (*Kresge-Hooker Sci. Lib.*) **28**, 63 (1967).
16. W. H. Flygare, J. M. Pochan, G. I. Herley, T. Caves, M. Karplus, S. Aung, R. M. Pitzer, S. I. Chan, *J. Chem. Phys.* **45**, 2793 (1966).
17. D. J. Meschi and R. J. Myers, *J. Mol. Spectrosc.* **3**, 405 (1959).
18. W. H. Kirchhoff and E. B. Wilson, *J. Amer. Chem. Soc.* **85**, 1726 (1963).
19. R. L. Kuczkowski and E. B. Wilson, *ibid.*, p. 2028.
20. F. Seel and D. Gölitz, *Chimia* **17**, 207 (1963).
21. A. P. Cox, L. F. Thomas, J. Sheridan, *Nature* **181**, 1157 (1958); J. K. Tyler, A. P. Cox, J. Sheridan, *ibid.* **183**, 1182 (1959).
22. J. Martins and E. B. Wilson, *J. Chem. Phys.* **41**, 570 (1964).
23. L. C. Krisher, *ibid.* **44**, 974 (1966); D. R. Lide, Jr., *ibid.* **42**, 1013 (1965); J. Hoeft, *Naturforscher* **20A**, 313 (1965).
24. G. C. Dousmanis, T. M. Sanders, C. H. Townes, *Phys. Rev.* **100**, 1735 (1955).
25. See, for example, M. Mizushima and R. M. Hill, *ibid.* **93**, 745 (1954).
26. M. Mizushima, J. T. Cox, W. Gordy, *ibid.* **98**, 1034 (1955).
27. G. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl, A. C. Kunkle, J. W. Bransford, J. Rastrup-Anderson, J. Rosenthal, *J. Chem. Phys.* **40**, 3378 (1964).
28. R. F. Curl, J. L. Kinsey, J. G. Baker, J. C. Baird, G. R. Bird, R. F. Heidelberg, T. M. Sugden, D. R. Jenkins, C. N. Kenney, *Phys. Rev.* **121**, 1119 (1961).
29. F. X. Powell, *J. Chem. Phys.* **45**, 1067 (1966).
30. V. M. Rao, R. F. Curl, Jr., P. L. Timms, J. L. Margrave, *ibid.* **43**, 2557 (1965).
31. F. X. Powell and D. R. Lide, Jr., *ibid.* **41**, 1413 (1964); M. Winnewisser, T. V. L. N. Sastry, R. L. Cook, W. Gordy, *ibid.*, p. 1687.
32. A. Carrington and D. H. Levy, *ibid.* **44**, 1298 (1966).
33. T. Oka, *ibid.* **45**, 254 (1966); A. M. Ronn and E. B. Wilson, *ibid.* **46**, 3262 (1967).
34. See, for example, B. Bak, C. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen, *ibid.* **37**, 2037 (1962).
35. R. J. Myers and W. D. Gwinn, *ibid.* **20**, 1420 (1952).
36. C. A. Coulson and W. E. Moffitt, *Phil. Mag.* **40**, 1 (1949).
37. W. H. Flygare and W. D. Gwinn, *J. Chem. Phys.* **36**, 787 (1962); W. H. Flygare, A. Narath, W. D. Gwinn, *ibid.*, p. 200.
38. I thank B. Bak, R. F. Curl, W. H. Flygare, W. H. Kirchhoff, L. C. Krisher, D. J. Millen, and J. Sheridan for useful replies to my request for suggestions, and H. Harrington for Figs. 1 and 2.