

## RADIO SPECTROSCOPY AND CONTEMPORARY THEORETICAL CHEMISTRY\*

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THE history of science shows that the development of new methods of research into various properties of matter, usually developed for some specific problem, eventually lead to a host of new discoveries and scientific advances in a number of related fields. For example, optical spectroscopy, which was developed primarily for studying the spectral composition of solar radiation, was for many years one of the basic physical methods for studying the structure of atoms, molecules and the kinetics of chemical reactions. Mass spectroscopy, which was developed as a method of isotope analysis, has become a powerful and precise method for the measurement of chemical binding energies and the study of free radicals and has been used widely in the analysis of gaseous mixtures under a wide variety of conditions, for example, even in the analysis of the natural gases in the petroleum industry. The development of electron microscopes with resolving powers as great as 10 Å in a very short time has resulted in the acquisition of fundamental new information on the structure and mechanisms of important biological structures such as muscle and nerve tissues.

The present survey has been undertaken to describe methods of solving some of the basic problems of contemporary theoretical chemistry by means of new physical techniques which are based on the absorption of high and ultrahigh frequency radiation by matter—the field of radio spectroscopy.

The development of radio spectroscopy is in many ways a result of achievements in modern electronic technology, particularly the microwave techniques used in radar. At the beginning radio spectroscopy was used exclusively by physicists for solving specialized problems, i.e., measurement of nuclear spins, magnetic moments, and quadrupole moments and the determination of the

\*This paper is an expanded version of a report delivered by the author to the 12th All-Union Conference on Spectroscopy, 1958. The author does not propose to describe the history of radio spectroscopy or its complete modern theory, or to consider the numerous papers devoted to physics of this field. Inasmuch as the electronic paramagnetic resonance method has been applied widely in the Soviet Union for chemical purposes this technique has been given greatest emphasis.

structure of complicated atoms and crystals, dipole moments, and the geometric parameters of certain simple molecules. In recent years, however, radio spectroscopy has been used in structural investigations and the study of chemical transformations and interactions; hence these techniques have become important in chemistry and biology.

At the present time, radio spectroscopy is being applied in the following fields of research in the Soviet Union and abroad:

- a) mechanisms involving radicals and chemical chain reactions, including polymerization;
- b) reactions which take place in liquids in times of the order of a microsecond (the interaction of ions, charge-exchange reactions in ions, fast isotope-exchange reactions);
- c) processes which take place in living tissues, in particular the mechanism of enzymatic catalysis, i.e. the action mechanism of the complex proteins which make possible the numerous chemical transformations in plant and animal cells at high reaction rates with extraordinary guidance and high efficiency;
- d) structural changes in various materials and polymers under the effect of heat, ionizing radiation, and mechanical disruption of the chemical structure (mechano-chemistry). It has been found that in interactions of this type it is possible to form and maintain broken chemical bonds (free radicals), which are capable of entering into highly-varied chemical reactions.

This field of research is very closely related to studies of the effect of ionizing radiation on biological structures, which are pertinent to such important problems as an understanding of the nature of radiation sickness and the effect of radiation on heredity.

It is to be hoped that existing radio spectroscopy techniques and those which will be developed in the near future will lead to the solution of still more interesting problems:

- a) problems of long-range effects in chemical reactions, in heterogeneous catalysis and in biochemical processes (the migration of charges and energy almost without loss to large distances within an ordered structure);
- b) the mechanism involved in such important

processes as photosynthesis of organic compounds from carbon dioxide and water, muscle contraction, and nerve conduction;

c) low temperature chemistry, associated with the possibility of forming active chemical agents which are capable of chemical reactions at very low temperatures.

Formally radio spectroscopy may be considered as the extension of conventional spectroscopy to the longer wavelength region of the spectrum. Microwave gas spectroscopy (the region of the spectrum between approximately 1.5 mm and 30 cm) is concerned, to a considerable extent, with the same rotational transitions which, for light molecules, fall in the far infrared. However, in using radio spectroscopy one achieves a marked increase in resolution and sensitivity. Although not different in principle, in practice radio spectroscopy techniques allow a considerable expansion in the application of spectroscopy in structural studies and for analytic purposes. In addition to the pure rotational transitions, this region contains transitions between magnetic fine structure levels of rotational states in paramagnetic molecules (for example  $O_2$ , NO,  $ClO_2$ ) and simple radicals (for example, CH, OH, NH, SH, etc.).

In dealing with the transitions in the longer wavelength region of the spectrum (up to wavelengths of the order of hundreds of meters) we deal with transitions connected with the different orientations of nuclei with electric quadrupole moments in the highly inhomogeneous electric fields produced by the valence electrons. In essence, these inhomogeneous fields lift the spatial spin degeneracy of nuclei with quadrupole moments. This region of radio spectroscopy, which has been developed in recent years, is called nuclear quadrupole resonance.

However, radio spectroscopy need not be limited to the study of transitions under the effect of high frequency fields. It is probable that the most interesting fields of present-day radio spectroscopy concern investigations of transitions between levels produced by Zeeman splitting of paramagnetic structures in appropriate fixed magnetic fields, perpendicular to the magnetic component of the radio-frequency field. Depending on the paramagnetic structure this region of radio spectroscopy can be divided into two categories: nuclear paramagnetic resonance and electronic paramagnetic resonance. Since the greatest amount of radio spectroscopic research as applied to chemistry has been concerned with these methods, we shall start our survey with a detailed description of principles and applications of these methods.

## ELECTRONIC PARAMAGNETIC RESONANCE (EPR)\*

The condition which must be satisfied to observe a magnetic resonance in absorption by a paramagnetic structure can be written in the form

$$h\nu = g\beta H, \quad (1)$$

where  $\nu$  is the frequency of the radio-frequency field,  $H$  is the intensity of the fixed magnetic field,  $\beta$  is the Bohr magneton and  $g$  is the so-called spectroscopic splitting factor which, in the case of free atoms, is the same as the Landé factor. The  $g$ -factor for the free electron (magnetic moment due to the spin alone) is 2.0023. In most cases studied up to now, there has been either no orbital moment or it has been quenched; the spin-orbit interaction is small and the  $g$ -factor is approximately 2. For this value of the  $g$ -factor and for magnitudes of  $H$  of the order of several thousand oersteds, easily achieved under laboratory conditions, electronic paramagnetic resonances can be observed in the centimeter and millimeter regions of the spectrum. It is more convenient for these measurements to work at a constant frequency and to obtain the resonance curve by varying  $H$ . A system which has found wide application at the present time operates in the three-centimeter region, in which case the resonance for  $g = 2$  is observed at  $H \cong 3000$  oersteds. The high sensitivity and the absence of any diamagnetic effects make it possible to carry out quantitative measurements of the parameters up to very small values ( $10^{12} - 5 \times 10^{12}$ ) at line widths of the order of oersteds at room temperature with recording times of the order of several minutes.

The very presence of an EPR spectrum gives the chemist important information. In the study of chemical processes by this technique certain conclusions can be drawn as to the radical or ion-radical mechanism involved; in investigating the structure of complexes or solids which contain heavy atoms with unpaired electrons in inner shells the absence of an EPR signal gives information on the electronic structure. The application of the EPR technique allows us to discover unpaired electrons in complicated organic compounds with conjugated bonds in which the thermal excitation in the triplet state occurs even at low temperatures (for example, dianthrone<sup>3</sup> and violanthrone<sup>4</sup>) under the effect of ionizing radiation on solid matter<sup>5,6</sup> and the free radicals which are produced in animal tissue during the course of enzymatic processes.<sup>7</sup>

\*Electronic paramagnetic resonance was reported by E. K. Zavoiskiĭ<sup>1</sup> in 1944. The first theoretical analysis of EPR was given by Ya. I. Frenkel'.<sup>2</sup>

An important feature of the EPR line is its position, i.e., the value of the  $g$ -factor. Any deviation of the  $g$ -factor from its value for the free electron by an amount which is larger than several units in the third place indicates the existence of heavy atoms and the localization of an unpaired electron near these atoms. Thus, for example, in the localization of the unpaired electron in the S atom the  $g$ -factor is found to be 2.024.<sup>8</sup> We note that in ordinary organic radicals, which contain only C, O, N and H, the deviation of the  $g$ -factor from the value 2.0023 never exceeds several units in the third place. In cases in which the departure of the  $g$ -factor from the ordinary value is large this fact is generally a unique indication of the type of chemical bonding. For example, the  $g$ -factor for the ferric ion in compounds such as  $\text{FeCl}_3$  is not very different from 2. On the other hand, the  $g$ -factor in methaemoglobin (the oxidized form of hemoglobin, which contains trivalent iron as the central atom) the  $g$ -factor is found<sup>9</sup> to be close to 6. This allows us to draw a very important conclusion as to the inadequacy of earlier ideas concerning the purely ionic nature of the bonding of the iron in this complex.

Another method of studying the properties of paramagnetic materials lies in an analysis of the shape of the EPR line. At centimeter wavelengths, the line shape is determined by the dependence of the absorption intensity on frequency or on magnetic field strength [ $I = f(\nu)$  or  $f(H)$ ] and by the single parameter which appears in this functional relationship. The parameter which is usually chosen is the width of the line at half-height ("half-width") or the spacing between points of maximum slope. In the absence of exchange interactions the line shape is Gaussian.

$$I = I_0 \exp\left(-\frac{\Delta\omega^2}{2\Delta\omega_{0f}^2}\right), \quad (2)$$

where  $\Delta\omega$  is the distance from the center of the line and  $\Delta\omega_{0f}$  is half of the half-width. In the presence of an exchange interaction or frequency translational effects at frequencies  $\omega_e$ , greater than the half-width of the line, the main part of the line is described by the Lorentz expression

$$I = \frac{I_0}{1 + \frac{\Delta\omega^2}{\Delta\omega_{0L}^2}}, \quad (3)$$

where  $\Delta\omega_{0L}$  has the same significance as  $\Delta\omega_{0f}$  in Eq. (2). As Van Vleck has shown<sup>10</sup>

$$\Delta\omega_{0L} \cong \frac{\Delta\omega_{0f}^2}{\omega_e}. \quad (4)$$

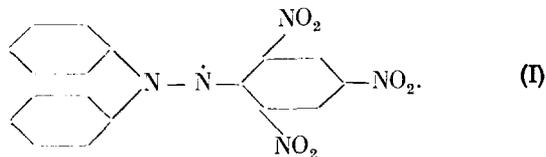
Whence it follows that the presence of an exchange interaction leads to a narrowing of the central part

of the line. It should be kept in mind, however, that at the edge of the line, where  $|\Delta\omega| > \omega_e$ , the line maintains its Gaussian shape. The presence of exchange narrowing of the line indicates to the chemist the presence of fast (frequency  $\omega_e$ ) interchange of the unpaired electron in the system. This effect appears in the so-called transfer of the reaction center along a chain of conjugated double bonds. Thus, for example, the relatively small width of the EPR signal of Lorentz shape from different coals, in spite of the extremely high concentration of unpaired electrons, uniquely indicates the presence of a large number of highly conjugated systems. As is well-known, this conclusion is in complete agreement with the chemical and x-ray studies of coals.<sup>11</sup> Another example is the EPR line due to unpaired electrons in proteins which have been irradiated by  $\gamma$ -rays where, by virtue of the delocalization of electrons in the regular grid of inter-chain hydrogen bonds the EPR lines are narrowed by a factor of 10 as compared with the EPR lines of unpaired electrons in  $\gamma$ -irradiated individual amino acids.<sup>12</sup>

Very interesting information as to the structure of radicals and the nature of the environment of these radicals can be obtained from an analysis of asymmetric EPR lines in cases in which the asymmetry is due to  $g$ -factor anisotropy. This method was used to obtain precise information on the structure of the lattices in a number of crystals.<sup>13</sup> Similar methods have been used to establish the C—O—O angle in the peroxide radical in irradiated teflon.<sup>14,32</sup>

There is another characteristic which is of special importance for the identification of the structure of complex radicals and paramagnetic complexes. This is the study of nuclear hyperfine structure in electronic paramagnetic resonances. This hyperfine structure is due to the interaction of the magnetic moment of the unpaired electron with the magnetic moments of nuclei in the material. As Gordy has shown,<sup>15</sup> nuclear hyperfine splitting in solids and solutions can be observed only by virtue of an admixture of the  $s$ -state in the wave function of the unpaired electron. The number of components in the hyperfine structure, the magnitude of the splitting, the distribution of intensities over the components, and the widths of the individual components allow us to obtain information on the details of the chemical structure as well as the density distribution of the unpaired electron between different atoms, the electronic structure of the atom with the magnetic nucleus, and the interaction of the paramagnetic structure with the surrounding medium.

We consider the hyperfine structure and its chemical interpretation, using the example of the free stable radical in diphenylpicrylhydrazyl, to which chemists ordinarily ascribe a structure



The EPR spectrum of this material is well known since it is used as a standard for calibration in EPR spectra. One milligram of DPPH contains approximately  $1.5 \times 10^{18}$  unpaired electrons. In the solid state DPPH gives a narrow single EPR line without hyperfine structure (Fig. 1a). The absence of hyper-

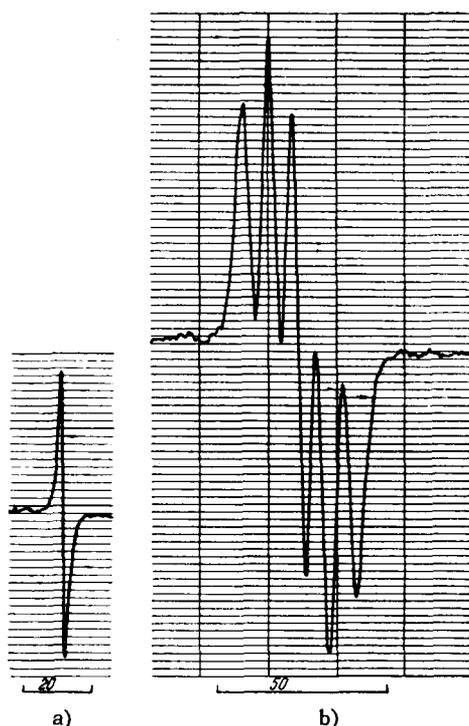
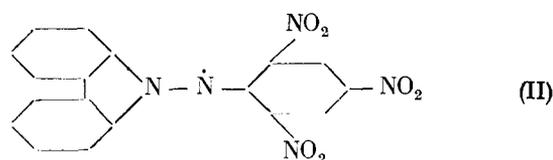


FIG. 1. a) EPR spectrum of polycrystalline diphenylpicrylhydrazyl; b) EPR spectrum of diphenylpicrylhydrazyl in benzene solution. The first derivatives of the absorption curves are shown.

fine structure, in spite of the presence of H and N nuclei, which have magnetic moments, is due to the strong intermolecular exchange interaction, which leads to an averaging of the local magnetic fields of the nuclei. In a solution the exchange interaction is reduced because of the increased distance between radicals. Because of the rather small width of the components, it then becomes possible to observe the hyperfine splitting (Fig. 1b). As is apparent from the figure, in this case the EPR spectrum consists of five components with unequal

spacings and with intensity ratios 1:2:3:2:1. If, in accordance with the structural formula, the splitting were due to only one nitrogen atom (nuclear spin  $I_N = 1$ ), the spectrum would consist of three lines of equal intensity. The effect of the second nitrogen atom should mean, in the general case, arbitrary splitting ( $\Delta H_1$  and  $\Delta H_2$ ) at each end atom, the splitting of each line into three components, and the appearance of nine hyperfine structure components with different intensities (Fig. 2a). It is apparent that only when  $\Delta H_1 = \Delta H_2$  is it possible to obtain a hyperfine structure pattern which matches the observed spectrum (Fig. 1b and Fig. 2b). The spectral pattern is sensitive to small changes in the molecular structure. Thus, for example, the spectrum of the radical



consists of seven hyperfine structure components with intensity ratios 1:1:2:1:2:1:1, corresponding to the condition  $\Delta H_1 = 2\Delta H_2$ . Usually these observations are explained by saying that the density distribution of the unpaired electron between the two nitrogen atoms is uniform in the case of the radical given in (I) while in the radical described by (II) the density at one of the nitrogen atoms is twice as large

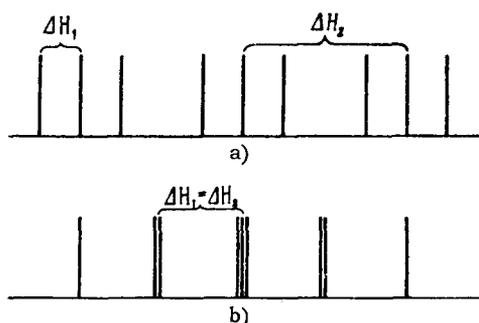


FIG. 2

as at the other. However, this interpretation is valid only for identical hybridization of the wave function of the unpaired electron (same admixture of s-state) in both nitrogen atoms. Because these are not chemically equivalent, this situation is not very probable. It would seem more reasonable to interpret these data as an indication that there is a definite ratio between the s-hybridizations of the wave function of the unpaired electron in both nitrogen atoms. The absence of a hyperfine splitting due to the nitrogen atoms of the  $\text{NO}_2$ -group and the hydrogen atoms in the benzene rings indicates that the unpaired electron is localized at

the two central nitrogen atoms.

Another example of the use of hyperfine structure in the EPR spectrum for explaining the details of the distribution of the electron cloud is the spectrum of the  $(\text{IrCl}_6)^{-}$ -ion, which contains one unpaired electron.<sup>13</sup> In addition to the splitting due to the nuclear components of the two Ir isotopes, the spectrum exhibits completely separate lines as a consequence of the splitting at the six chlorine nuclei ( $I_{\text{Cl}} = 3/2$ ). This example was the first experimental proof of the existence of the donor-acceptor bond, in which an unshared pair of electrons (in the present case a pair of electrons of the  $\text{Cl}^-$  ion) provides a two-electron bond with the other atom.

A very graphic example of the effect of the admixture of the s-state on the hyperfine splitting is the EPR spectrum of ion-radicals such as the semiquinones. We consider this problem using the example of the simplest radical of this kind: n-benzosemiquinone



(III)

The EPR spectrum consists of five components with the intensity ratio 1:4:6:4:1,<sup>16</sup> which indicates that all four equivalent protons of the radical (III) participate in the splitting. According to classical quantum chemistry ideas the unpaired electron is the  $p_z$ -electron, which has zero density in the plane of the aromatic ring. The hyperfine splitting on protons located in this plane indicates that the wave function of the unpaired electron is not a pure  $p_z$ -function. According to a suggestion made by McConnell<sup>17</sup> the hyperfine splitting can be explained by the fact that the s-hybridization of the unpaired electron on the C atom leads to the appearance of a certain density of unpaired electrons with the opposite spin orientation at neighboring protons. The calculations by McConnell indicate that to explain the observed splitting it is sufficient to assume that the admixture of s-state is approximately 20%.

Up to this point we have considered investigations in which the analysis of the hyperfine structure of the EPR spectrum makes it possible to refine or improve existing ideas as to the nature of chemical bonds. As another example we have chosen a series of compounds which have opened up completely new possibilities in modern chemistry. There are as yet no firmly established concepts of the nature of

the chemical bond in these compounds. We have in mind the recently discovered and intensively investigated (both in the U.S.S.R. and abroad) metallocenes—metal-aromatic compounds of the general form



The basic structural characteristic of compounds of this type is the fact that the metal atom (or ion) is "pressed" between two cyclopentadienyl or benzene rings located in parallel planes. For this reason they are frequently called "sandwich" compounds. It is clear that the chemical bond in these compounds must have some new peculiar characteristics since they cannot be described within the framework of the two-electron bonds used in chemistry. A theoretical quantum-mechanical analysis of this problem on the basis of the known information on electron orbits in metal atoms and aromatic ligands has been given by a number of authors.<sup>18</sup> M. E. Dyatkina and E. M. Shustarovich<sup>19</sup> have shown that it is possible to explain the relative stability of compounds of this type. There is great interest, however, in direct investigations of the electronic distribution in this molecule. The distribution of spins of the unpaired electrons in this system can be investigated by the EPR method, as has been shown above. These data may provide valuable evidence on the possibility of delocalization of free electrons over the entire molecule.

V. M. Chibrikin, Yu. D. Tsvetkov and G. A. Razuvaev have carried out work<sup>20</sup> with the purpose of making a detailed investigation of the EPR spectrum of paramagnetic cationic complexes of the type



in which  $\text{X} = \text{H}, \text{C}_6\text{H}_6, \text{cyclo-C}_6\text{H}_{11}, \text{COOH}, \text{etc.}$  The most important result of this work is the establishment of the very clearly defined hyperfine structure of the spectrum with a number of components corresponding to the number of hydrogens on the two aromatic rings (Fig. 3). The binomial nature of the intensity distribution indicates the equivalence of all hydrogens. The magnitude of the splitting, approximately 3.5 oersteds, is the same for any X, indicating that these substitutions have little effect on the distribution of electrons in the Ph-Cr bonds. If one assumes that the hybridization of the atomic orbitals of the carbon atoms in the system (IV) is the same as in the semiquinone ions (III), this large splitting indicates that in each CH group in (IV) there are not 0.1 unpaired electron (this is the figure reached

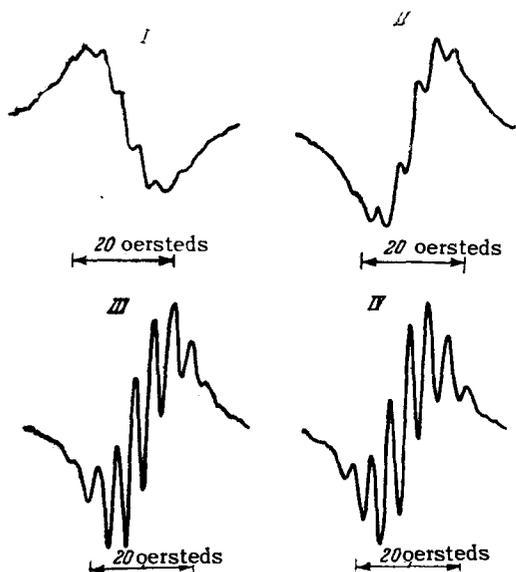


FIG. 3. EPR spectrum of compounds:  $(C_6H_6)_2CrI$  (I);  $(C_6H_5 - C_6H_{11})_2CrI$  (II);  $(C_6H_5 - C_6H_5)(C_6H_6)CrI$  (III);  $(C_6H_5 - C_6H_5)_2CrI$  (IV).

by McConnell in his estimates for the semiquinone ion) but approximately 0.16. It follows from this that the total spin density on all twelve carbon atoms in both aromatic rings is 1.92. Since, as follows from direct measurements of the magnetic permeability and from measurements of the total concentration of spins by the EPR method, each ion (IV) has only one unpaired electron, this result indicates, (according to McConnell) that at each chromium atom there are 0.92 free electrons, but with opposite spin orientations. Qualitatively this result is supported by the results obtained by the same authors in taking spectra at highest amplification. As is apparent from Fig. 4, on both sides of the main absorption line there are satellite lines with the same hyperfine structure and with an intensity approximately 50 times smaller than that of the main line. These lines are the two outside components of the quadruplet due to the  $Cr^{53}$  isotope, which has a nuclear spin of  $3/2$ . The natural abundance of  $Cr^{53}$  is 9.4%; hence the intensity of each of the four components of the quadruplet should be approximately 2.35% of the main line. According to the data of A. A. Manenkov and A. M. Prokhorov<sup>21</sup> the hyperfine splitting in  $Cr^{53}$  in inorganic salts is 18.4 oersteds. In the case of the compound (IV) at the  $Cr^{53}$  we have 0.92 free electrons and the splitting is 19 oersteds. The discrepancy which is obtained, approximately 11%, is not a serious objection against the proposed distribution pattern of the unpaired electron in the molecule since in this estimate it is assumed that the conditions of hybridization for the chromium are the same in the salts and in (IV), which is obviously not precisely true.

On the basis of an investigation of hyperfine structure in EPR in chromocenes V. M. Chibrikin, A. I. Burshtein and S. P. Solodovnikov<sup>22</sup> have been able to reach a number of interesting conclusions concerning the interaction of these compounds with the surrounding medium. These authors have found that the width of the individual component is very sensitive not only to the substitution but also to the solvent and temperature. In the present case, because of the constancy of the splitting, the resolution of the hyperfine structure is determined only by the width of the individual component. In most of the samples which have been investigated there is a sharp reduction in the width of the component as the temperature is reduced. This effect can only be partially due to a change of viscosity in certain solvents. According to existing ideas an increase in viscosity should lead to a broadening of the component because of the reduction in the averaging of the local fields. In a number of cases a change in the width of the components in (IV) occurs in opposite directions than would be expected on the basis of the change in viscosity. Thus, for example, the resolution of the spectrum of  $(C_6H_6)_2CrI$  in acetic acid improves as the temperature is reduced from +25 to  $-30^\circ C$  whereas acetic acid solidifies at  $+14^\circ C$ .

Without dwelling in detail on the numerous effects of this type and the theoretical interpretation of these effects, which in our opinion is of great interest for physicists, we may point out that for the chemist the marked systematic change in the resolution of the spectrum with a change in the solvent and with a change in temperature furnishes evidence as to the formation of complexes of these ions with the medium. This interpretation is supported by a large amount of data obtained by the indicated authors on the effect of different additives on the resolution of the spectrum of the (IV) compound with  $X = COOH$ . It has been shown that the width of the individual components is reduced sharply when one adds to the pyridine solution (IV) such materials as

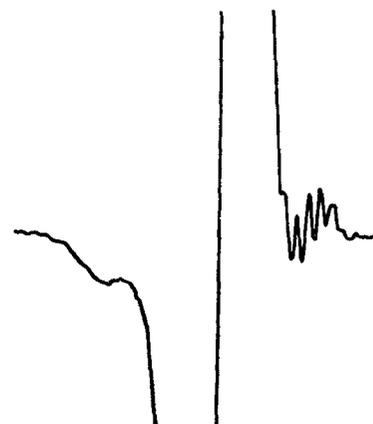


FIG. 4. Hyperfine structure due to  $Cr^{53}$  in the EPR spectrum of  $(C_6H_5 \cdot C_6H_{11})_2CrI$  in alcohol.

water, methyl and ethyl alcohols, phenol, acetic acid, and so on; that is to say, the material is energetically bonded with the  $\text{COO}^-$  by hydrogen bonds. The described effect would seem to open the possibility of new methods of studying unstable complexes with the participation of molecules of the solvent and this is of great interest for the chemistry of the liquid phase. In the example being considered the improvement in resolution seems to take place because the formation of the complexes has no apparent effect on the distribution of the electrons which form the Cr-PhX bond and only changes the relaxation conditions. In cases, however, in which the central atom carrying an unpaired electron takes part in the formation of the complex, the hyperfine structure of the spectrum undergoes a much more significant change.

For example,  $\text{Mn}^{++}$  ions in a solution at sufficiently low concentration exhibit a clear hyperfine structure consisting of six components, due to the interaction of the unpaired electrons with the  $\text{Mn}^{55}$  nucleus ( $I_{\text{Mn}} = 5/2$ ). In this case the hyperfine structure results from the admixture in the ground electron state  $\text{Mn}^{++} 3s^2 3p^6 3d^5$  of the excited state  $3s^1 3p^6 3d^5 4s^1$  with unpaired s-electrons. The resolution of the hyperfine structure depends very strongly on the formation of the complex. Very small amounts of such complex formers as ethylene diamine tetraacetic acid, glucose-6-phosphate or adenosine triphosphate cause the hyperfine structure to vanish.<sup>23</sup> Apparently the formation of additional coordination bonds by the paramagnetic atom leads to a change in its electron structure, in the present case to a reduction of the weight of the s-state; this results in the disappearance of the hyperfine structure. These effects are the best indications of the formation of complexes. Thus, a determination has been made of the dissociation constant for the  $\text{Mn}^{++}$  complex in a number of biologically active materials.

This work opens up new approaches to the study of the role of the infinitesimal amounts of ions of the heavy metals and their complexes in biological processes.

The fact that a hyperfine structure does exist in these complexes indicates that, although they may be very unstable, the lifetime of these complexes is greater than the reciprocal of the splitting expressed in seconds. A splitting of 10 oersteds with  $g \cong 2$  corresponds to  $\Delta\nu \cong 3 \times 10^7 \text{ sec}^{-1}$ . This means that a complex which exhibits a splitting of this order of magnitude has a lifetime greater than  $3 \times 10^{-8} \text{ sec}$ . If the lifetime of the complex becomes smaller than this the hyperfine structure pattern is changed and may vanish completely. It is completely reasonable, therefore, that the EPR spectrum can be used for

kinetic studies of very fast processes in which paramagnetic structures take part.

Among the processes investigated by this method are, for example, the reaction in which electrons are transferred between negative naphthalene ions and naphthalene molecules in solution.<sup>24</sup> At suitable naphthalene concentrations the exchange of the unpaired electron takes place so rapidly that the frequency at which the unpaired electron is exchanged between the molecules becomes greater than the  $\Delta\nu$  of the hyperfine splitting.

The hyperfine splitting noted above in the EPR spectrum of  $\text{Mn}^{++}$  ions vanishes as the concentration is increased, although the total width of the line is not changed under these conditions.<sup>25</sup> This is a result of the acceleration of the exchange of electrons between two neighboring ions. The hyperfine structure becomes smeared out at concentrations of approximately 2N. Under these conditions the width of the components becomes comparable with the spacing between them, 90 oersteds. It follows from these data that an exchange with a frequency greater than  $3 \times 10^8 \text{ sec}^{-1}$  can take place at distances between the centers of the neighboring solvated ions of approximately 10 Å. At zero activation energy and absolute ordering of the lattice the exchange frequency should be of the order of magnitude of the vibration frequency, i.e.  $10^{13}$  to  $5 \times 10^{13} \text{ sec}^{-1}$ . Even in the complete absence of solvation and completely chaotic motion the exchange frequency should not be less than  $zm \cong 10^{11} \text{ sec}^{-1}$ , where  $z$  is the number of double collisions ( $\cong 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ ) and  $m$  is the ion concentration. Thus, the electron exchange process in the case being considered here should have a spatial factor  $f$  and an activation energy  $E$  such that the quantity  $fe^{-E/kT}$  at room temperature is  $10^{-3}$  to  $10^{-5}$ . A measurement of the dependence of the effect on concentration at various temperatures can then furnish information as to the activation energy for the process.

In principle, this same method can be used to study electron transfer between nonequivalent ions.

We may note that in the work cited above<sup>12</sup> on the EPR spectrum of  $\gamma$ -irradiated proteins observations have also been made of the disappearance of the hyperfine structure characteristic of  $\gamma$ -irradiated individual amino acids, as a consequence of the rather rapid migration of the unpaired electrons.

The last example shows that the EPR method can be used not only for studying paramagnetic materials but for studying those interactions in non-paramagnetic materials which result in the formation of more or less stable paramagnetic

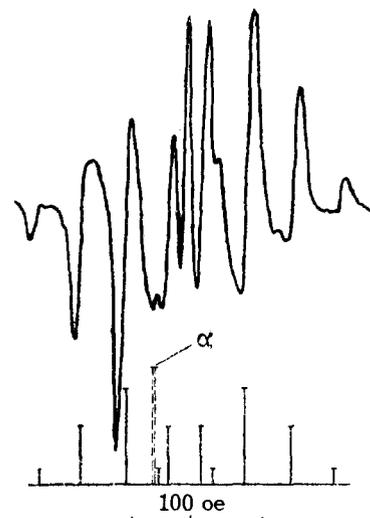
structures. These interactions include a number of radiation-chemical and mechanical interactions. By means of the EPR method it may be possible to carry out detailed investigations of these interactions and to understand the structure and properties of the primary products which are formed. The prospect of studying the mechanism and the subsequent action of penetrating radiation on various kinds of substances and materials, including biological substances, is one of great promise. This problem is especially interesting in connection with the possibility of studying changes which take place in solid materials which are not amenable to analysis by simple chemical methods. Another interesting possibility is that of forming active free radicals at low temperatures (in which case they become stable) and studying their transformations under these conditions (low temperature chemistry). The literature contains an enormous amount of material on this subject. We shall limit ourselves here to several examples.

The first problem which arises in a consideration of the effect of penetrating radiation on solids is an understanding of the formation of those radicals which are already known to the chemist from gas and liquid reactions. In the irradiation by  $\gamma$ -rays ( $\text{Co}^{60}$ ) of frozen methane at 20.4°K a radical is formed, the EPR spectrum of which consists of four hyperfine components with an intensity ratio 1:3:3:1,<sup>26</sup> indicating the formation of the methyl group  $\dot{\text{C}}\text{H}_3$ . The EPR spectrum shown in Fig. 5 was obtained by irradiating teflon (polyfluoroethylene —  $(\text{CF}_2 - \text{CF}_2)_n$  —) at 77° K and then warming it in the absence of air.<sup>32</sup> An analysis of this spectrum shows that it consists of eleven lines, ten of which represent components of two partially overlapping quintuplets, in which the intensity ratio of the three outermost components of each quintuplet is 1:4:6. An analysis of the structural formula of teflon allows us to assign the observed spectrum to the radical



Since  $I_F = 1/2$ , the interaction of the unpaired electron with the nucleus of the central fluorine atom should lead to a splitting of the line into two components of equal intensity. A weaker interaction with four equivalent nuclei in the fluorine of the neighboring  $\text{CF}_2$  groups should lead to additional splitting of each component of the doublet into five components with a binomial intensity distribution. Supplementary experiments indicate that the eleventh line ( $\alpha$ ) is due to the peroxide radical  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OO}$  which has been discussed above. In air the entire spectrum of the radical (V) becomes one asymme-

FIG. 5. EPR spectrum of  $\gamma$ -irradiated teflon.

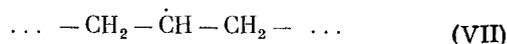


tric line which coincides in position with the  $\alpha$  line. The appearance of the latter in an inert atmosphere is apparently due to the small amount of oxygen dissolved in the original teflon.

Conclusions concerning the structure of the radicals formed in the irradiation of solids can be drawn without such careful analysis. For example, the odd or even nature of the spectrum, i.e. the presence of respectively one or two central components of maximum intensity in the EPR spectrum of the irradiated hydrocarbons indicates uniquely whether the number of equivalent hydrogens nearest to the free valence is odd or even. Thus, in the irradiation of normal individual paraffin hydrocarbons frozen at 77°K, it has been found<sup>27,28</sup> that when there is a small number of carbon atoms in the chain ( $\text{C}_6$ ,  $\text{C}_7$ ,  $\text{C}_8$ ) the spectrum is odd whereas in the irradiation of higher molecular compounds with a higher relative content of  $\text{CH}_2$ -groups ( $\text{C}_{16}$ , polyethylene —  $(\text{CH}_2 - \text{CH}_2)_n$  —) the spectrum is even. Apparently the nature of the spectrum is due to the fact that in the first group we find radicals of the following type



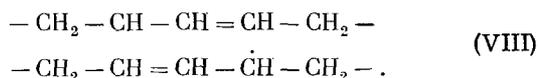
which arise in the removal of the hydrogen atom from the end  $\text{CH}_3$ -group whereas in the second case we are dealing with the disruption of the  $\text{CH}$ -bond in the chain with the formation of the radical



At low temperatures it is even possible to stabilize hydrogen atoms as well as the heavy organic radicals. Thus, in reference 29 it has been shown that in  $\gamma$ -irradiation of methane at 4.2°K, in addition to the quadruplet for methyl described above, the spectrum exhibits a doublet with a splitting of approximately 500 gauss, corresponding to the free hydrogen atom. Still earlier a doublet

with this same splitting had been observed at a temperature of 77°K in  $\gamma$ -irradiated solid acids ( $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ).<sup>30</sup> At 77°K the hydrogen atoms which are produced in the irradiation of quartz, glass, and silica which contain surface OH and adsorbed water<sup>31</sup> become stabilized at the surface. In all these cases the EPR signal from the hydrogen atoms vanishes upon warming. It is interesting to note that the splitting is the same in all cases and is essentially the same as the hyperfine splitting in the magnetic spectrum of the hydrogen atom in an atomic beam. This indicates that the bonds which stabilize the hydrogen atoms under these conditions do not affect the density of the unpaired electron at the nucleus. This situation requires still further investigation.

The study of the spectra of  $\gamma$ -irradiated organic compounds, including polymers, makes it possible to establish the structure of the radicals which are formed and, in a number of cases, allows us to follow the behavior of these radicals in time. For example, as has been mentioned above, in the  $\gamma$ -irradiation of polyethylene at 77°K an even EPR spectrum was observed at this same temperature.<sup>32</sup> Upon warming the spectrum changes in the following way: the parity changes and the splitting between components is reduced by approximately a factor of 2. It has also been found that similar changes can be observed at room temperature in measurements of the EPR spectrum when polyethylene is bombarded by fast electrons.<sup>33</sup> As a possible explanation of this change the authors have proposed the migration of the free valence along the irradiated polymer with subsequent localization of the double bond. In this case the alkyl radical (VII) is converted into a radical of the allyl type, in which the distribution of the unpaired electron may be given by the superposition of two spin-valence systems



The density of the unpaired electron is distributed equally between the two carbon atoms and this explains the reduction in the hyperfine splitting while the fact that the spectrum is odd shows the strongest interaction takes place with only two protons.

#### NUCLEAR MAGNETIC RESONANCE (NMR)

In principle nuclear magnetic resonance is no different from electron resonance. However, because of the fact that nuclear magnetic moments are considerably smaller than the magnetic moment

of the electron (approximately three orders of magnitude), at reasonable field values ( $H_0$  approximately 10,000 oersteds) the absorption is observed at much longer wavelengths (frequencies ranging from 1 to 30 Mcs). For the chemist the most important elements which exhibit nuclear magnetic resonance spectra are H, N and P. Nuclear magnetic resonance spectroscopy can be divided into two categories: a) spectroscopy with high resolving power, and b) spectroscopy with low resolving power. In the first case the uniformity of the magnetic field must be at least  $10^{-7}$ . In the second case it is possible to carry out operations with field uniformities which are the same as those used in measuring electronic paramagnetic resonance (approximately  $10^{-4}$ ).

a) Low-resolution nuclear magnetic resonance spectroscopy is used chiefly for studying line widths in nuclear magnetic resonance of solid compounds and certain liquids, and changes in these spectra which occur as a result of phase transformation. This method is based on the fact that rather fast (as compared with the line width) motion of the molecules in the lattice leads to the averaging of the magnetic fields as seen by the nuclei being studied. The line width of a nuclear paramagnetic resonance can be taken as an indication of the rigidity of the structure. On the other hand, unfreezing of degrees of freedom of the molecules being investigated in the lattice upon increase of temperature leads to discontinuous narrowing of the proton resonance lines.

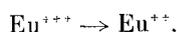
For example,<sup>34</sup> upon elevating the temperature of frozen polycrystalline benzene ( $\text{C}_6\text{H}_6$ ) a sharp reduction in the line width in the temperature range between 90 and 120°K is observed, i.e. long before the melting point (5°C). This is explained by the fact that at this temperature the rotation of the benzene molecules about the axis of six-fold symmetry is unfrozen. It should be noted that no change in the line width is observed at the melting point. This means that in solid benzene the averaging of the motion takes place rather rapidly, (cf. above).

In solid cyclohexane ( $t_{\text{melt}}^0 = 6.5^\circ\text{C}$ ) changes in the line width are observed at higher temperatures than in benzene; the temperatures are 150, 186, and 220°K.<sup>35</sup> On the basis of these data it may be maintained that below 150°K the crystal structure is rigid. At this temperature the motion of the molecules about the axis of three-fold symmetry is unfrozen. At 186°K there is a discontinuous change in the crystal structure (with high latent heat), which is accompanied by an increase in volume. At 220°K, in the author's opinion, the molecules can diffuse in

the solid lattice.

Similar discontinuous changes in line width with elevation of temperature are observed in solid polymers: polyethylene,<sup>36</sup> polymethylmethacrylate and rubber.<sup>37</sup> Thus, it may be possible to obtain entirely new kinds of data on the internal molecular motions in solid polymers, in particular the motion of the individual elements of the polymer chains, the rigidity of the molecules, and temperature changes in polymers. This would be of great value in connection with studies of the properties of stereospecific polymers with different degrees of crystallinity.

Nuclear paramagnetic resonance at low resolving power can be used for solving certain other chemical problems. As is well known, in liquids the lifetime of a nucleus in a given magnetic state is determined by the spin-lattice relaxation. With a sufficiently large spin-lattice relaxation time  $T_1$ , as is found in the case of protons in pure water, saturation sets in and the resonance line is not observed. The introduction of paramagnetic materials reduces this effect. Thus, if during the course of the reaction there is a change in the number of unpaired electrons or, if a sufficiently high stationary concentration of free radicals is established, the intensity of the proton resonance line is enhanced markedly. By this means a measurement has been made of the reaction rate for the reduction of trivalent europium:



in which the magnetic moment of the  $\text{Eu}^{++}$  ion is 15 times greater than the magnetic moment of the  $\text{Eu}^{+++}$  ion.<sup>38</sup> This same method has been used to give direct evidence of the participation of free radicals in the mechanism for thermal dissociation of hydrogen peroxide.<sup>39</sup>

b) High resolution nuclear magnetic resonance spectroscopy is applied chiefly for measuring small differences in the position in a spectrum of a magnetic resonance line for one kind of nucleus. These differences may be due to different degrees of shielding of the nucleus by electrons of the chemical bond, meaning ultimately the density and polarizability of the valence electron shell (chemical shift) or the existence of fast processes of transfer of the magnetic nuclei from one molecule to another.

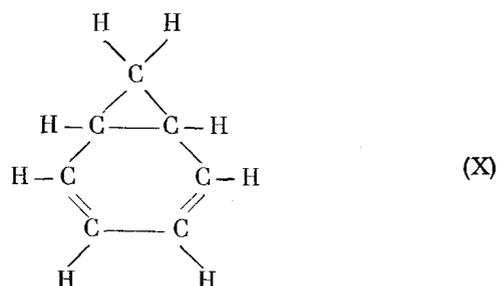
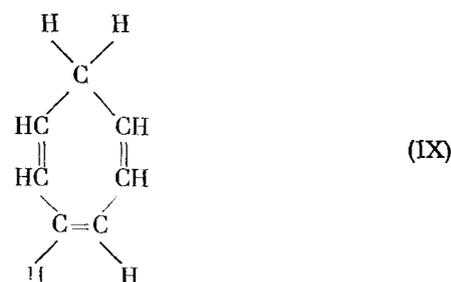
A measure of the chemical shift is the quantity

$$\delta = \frac{H_r - H_x}{H_r},$$

where  $H_r$  is the field at which the resonance absorption for a given nucleus is observed in a compound chosen as a standard (for proton resonance

in organic compounds the standard is usually cyclohexane) and  $H_x$  is the field at which the resonance is observed in the compound being studied.

Chemical shifts are dimensionless quantities and, in the case of proton resonance, are generally expressed in units of  $10^{-5}$ . The presence in the system of chemically non-equivalent magnetic nuclei of the same kind (for example protons) leads to the appearance of several resonance signals with characteristic shifts; the integrated intensity of each of these is proportional to the concentration of equivalent atoms. This situation makes it possible to carry out a structural analysis of various kinds of compounds. For example, two structural formulas were proposed for the compound  $\text{C}_7\text{H}_8$ :<sup>40</sup>

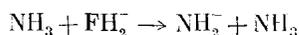


The proton resonance spectrum consisted of two signals with an intensity ratio of 3:1, which completely verified the formula (IX), since the hydrogens on the double-bonded carbon atoms must be characterized by high magnetic shielding and, consequently, should give a signal at a higher value of the magnetic field. In the case of the structure given in (X) the spectrum should consist of two lines, but with an intensity ratio of 1:1.

At the present time the literature contains detailed tables of chemical shifts in various compounds and in this respect the high resolution nuclear magnetic resonance method may be taken as a standard analytical tool. We may recall, that high precision magnets are required for work with protons and nitrogen atoms etc. A record achievement in this field is represented by the work carried out by Shuler, who in aniline ( $\text{C}_6\text{H}_5-\text{NH}_2$ ), was not only able to distinguish the lines for the proton

resonance in the  $\text{NH}_2$ -group and in the ring but was also able to distinguish the proton lines located in the ortho, para and meta positions of the benzene ring.<sup>15</sup>

If the system exhibits any process in which magnetic nuclei (for example protons) are transferred from one compound to another, and the position and line shape of the proton resonance is different in these compounds, the nuclear magnetic resonance method allows us to measure the position of equilibrium and the reaction rate for these processes in cases in which this rate is comparable with the chemical shift expressed as a frequency. Among processes of this kind, which can scarcely be studied by other methods, are the dissociation of acids and bases and fast proton-exchange reactions. For example, Ogg<sup>41</sup> has investigated the kinetics of proton exchange in liquid ammonia between  $\text{NH}_3$ ,  $\text{NH}_2^-$  and  $\text{NH}_4^+$ . For the reaction



he has obtained a reaction rate constant  $4.6 \times 10^{+11} \text{ mol}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ , i.e. a quantity which is two orders of magnitude smaller than the number of collisions computed without taking account of solvation. Gutowsky and his colleagues<sup>42</sup> have investigated in detail the dissociation of strong acids and bases and proton exchange between water and these compounds. The frequency of proton exchange in this case is approximately  $10^6 \text{ sec}^{-1}$ , which corresponds (for two-fold dilution of the acid by water) to a bimolecular rate constant  $4 \times 10^7 \text{ mol}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ .

#### NUCLEAR QUADRUPOLE RESONANCE

Many of the nuclei which are of interest to the chemist have spins greater than unity and thus an electric quadrupole moment. As has been indicated above, these nuclei can be found in various energy states, corresponding to the various orientations of the quadrupole moment in the inhomogeneous electric fields produced by the valence electrons. The energy levels of a nucleus with a quadrupole moment  $Q$  and a nuclear spin  $I$  in a field whose gradient is given by  $q = \frac{\partial E}{\partial Z} = \frac{\partial^2 V}{\partial Z^2}$  is

$$E = eqQ \left[ \frac{3M_y^2 - I(I+1)}{4I(2I-1)} \right],$$

where  $e$  is the charge in the electron and  $M_y$  is the projection of the nuclear spin in the  $z$  direction, which may take on values ranging from  $-I$  to  $+I$ . In accordance with the selection rule  $|\Delta M_y| = 1$  the frequencies of the transitions which are observed must be

$$\nu = \frac{eqQ}{h} \left[ \frac{3}{4I(2I-1)} \right] (2|M_y| - 1).$$

The quantity  $eqQ$ , which is called the quadrupole interaction constant, is usually expressed in frequency. Its magnitude is determined basically by the quadrupole moment of the nucleus and the nature of the chemical bond. In the case of covalent compounds, in which the difference in electronegativity of the atom which possesses the quadrupole moment and the neighboring atom is small, the quantity  $eqQ$  and, consequently,  $\nu$ , are determined basically by  $Q$  and are very much the same for all compounds of a given atom. It is known from the literature (cf. for example reference 1 in the bibliography of general references) that for covalent compounds of  $\text{Cl}^{35}$  the observed frequencies lie between 30 and 70 Mcs, for  $\text{Br}^{79}$  between 270 and 300 Mcs, for  $\text{I}^{127}$  between 1500 and 3000 Mcs and for  $\text{N}^{14}$ , between 1 and 3 Mcs. In the case of highly polar compounds, in which the field around the atom with the quadrupole moment is almost completely symmetrical,  $q$  is very small; and this means very small values for the transition frequencies.

It should be noted that the accuracy in the determination of the frequency of the nuclear quadrupole resonance in the ranges of tens and hundreds of megacycles reaches several kilocycles. Hence this method makes it possible to examine small differences in the chemical bonds.

For example, the introduction of the  $\text{NO}_2$ -group into the chlorobenzene molecule in the para position shifts the resonance frequency of the  $\text{Cl}^{35}$  by 700 kcs.<sup>43</sup> Thus, by a direct experiment it was possible to establish the known qualitative rule that electro-negative groups of the  $\text{NO}_2$  type displace the center of gravity of the  $\pi$ -electron cloud of an aromatic ring toward themselves. The solution of this problem and similar problems is extremely important for an understanding of the true mechanism of many reactions in organic chemistry. Results obtained by the nuclear quadrupole resonance technique can be used for making quantitative estimates of quantities which are of importance for contemporary theoretical chemistry such as the degree of ionic character of the bond and the hybridization of the valence electrons (cf. reference 1 in the bibliography of general references).

Thus, the nuclear quadrupole resonance method, which has not been developed as much as it should have been in the Soviet Union up to this time, will undoubtedly be one of the most powerful methods for studying the structure of molecules. An especially promising application of this method lies in the study of atoms such as nitrogen, which are of

great importance to the chemist.

#### MICROWAVE SPECTROSCOPY OF GASES

The widest application of microwave spectroscopy has been in connection with the study of rotational spectra. As is well known, a necessary condition for obtaining these spectra is the existence of a molecular dipole moment. This imposes some limitation on the method although, generally speaking, the number of molecules with dipole moments is rather large. The method is extremely sensitive. For example, in work in the submillimeter region of the spectrum it is possible to observe  $5 \times 10^{12}$  molecules of OCS, corresponding to  $10^{-9}$  grams of the material.

In the investigation of chemical reactions in the gaseous phase microwave spectroscopy allows us to observe infinitesimal amounts of free radicals in the reaction zone. As an example of the sensitivity of the method we may carry out measurements of the concentration of radicals of OH which are formed in a high-frequency discharge in water vapor. For a total pressure of 1 mm Hg it is possible to observe the OH radical at partial pressure of  $10^{-6}$  mm Hg, corresponding to approximately  $3 \times 10^{10}$  particles per  $\text{cm}^3$ .

A very important advantage of microwave spectroscopy as compared, say, with infrared spectroscopy of gases, is the high resolution. In the present case the resolution is limited only by the line width (in contrast with infrared spectroscopy). At low pressures the line width is independent of pressure and frequently is as small as 50 kcs. Hence in the microwave region (1.5 mm — 30 cm) it is possible to record simultaneously more than  $10^6$  lines (under optimum conditions). In order to cover the entire region it is necessary to have a number of klystrons. However, even with one klystron in the centimeter region (20,000 — 26,000 Mcs) it may be possible to cover 100,000 lines. We may note that in the entire infrared region (from 500 to 3500  $\text{cm}^{-1}$ ) it is not possible to resolve more than 3000 lines. Thus, in principle, microwave spectroscopy of gases can be a powerful analytical tool.

Unfortunately, for complicated molecules with high moments of inertia the lines lie in the region of longer wavelengths, where the absorption intensity is correspondingly smaller.

Up to now, rotational spectra have been used basically for structural investigations. It is possible to determine the moment of inertia directly from the position of the lines in the spectrum. It has been possible to compute the interatomic distances and the valence angles directly for simple mole-

cules. For more complex molecules the method of isotopic substitution is used. The most exact measurement is the one made for diatomic molecules. For example the CO distance is measured in Angstroms with an accuracy to the sixth place.<sup>45</sup> As an example of the determination of valence angles by the methods of microwave spectroscopy we may cite the determination of the HCH angle in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) (see reference 1 in the general bibliography). This angle was found to be  $112.0^\circ$ , i.e. considerably different from the tetrahedral angle of unsubstituted methane.

This method is extremely effective for the analysis of isotopic molecules. For example the distance between the rotational levels of  $\text{CsCl}^{35}$  and  $\text{CsCl}^{37}$  in the spectrum is approximately 100 Mcs whereas the position of the lines can be measured with an accuracy of 15 kcs.

From the short description of the results of the application in chemistry of the four basic methods of radio spectroscopy it is apparent that in spite of the relatively short time which has passed since the introduction of this technique it has already given much new information for the understanding of chemical processes and details of chemical structure. This results most of all from the fact that these techniques make it possible to actually examine the physical mechanisms involved in chemical processes. Hence it will be most fruitful to have cooperation between theoretical physicists, experimental physicists, and various kinds of chemists in this field of endeavor.

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