Translated from *Uspekhi Khimii*, 52 1490-1513 (1983) U.D.C. 543.422

# Electron Paramagnetic Resonance of Free Radicals in the Two-millimetre Wavelength Range

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Experimental data obtained in recent years on the electron paramagnetic resonance (EPR) of free radicals in the two-millimetre wavelength range are surveyed. It is shown that measurement of the spectra in this range makes it possible to increase greatly the amount of information derivable by the EPR method and its absolute sensitivity. The results of measurements of the magnetic resonance parameters of nitroxy-radicals, nitroxy-biradicals, and peroxy-radicals as well as data on the molecular mobilities of the above radicals in various matrices are presented.
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## I. INTRODUCTION

The vigorous development of experimental methods whereby the amount of information derivable by the EPR method is increased and which open up completely new fields in which the method can be applied has taken place at the present time. The new fields include magnetic resonance laser spectroscopy in the submillimetre and near infrared ranges, used to investigate free radicals in the gas phase[1-3], the spin echo electron spectroscopy[4,5], used mainly to investigate the paramagnetic centres in solids, various combined methods employing the spin polarisation effects in which the EPR signal is recorded optically or from the change in the yield of the chemical reaction[6-10], saturation transfer spectroscopy[11], EPR in inhomogeneous fields (EPR tomography)[12], and a number of other new methods.

However, the majority of the methods indicated are applicable only to the solution of specific problems and to the investigation of specific objects. We shall consider the development of a new universal EPR technique associated with a sharp increase of the frequency of the measurements. For species with spin paramagnetism, an increase of the frequency of the measurements is associated simultaneously with the necessity to increase the magnetic field strength. Therefore, in contrast to experiments in the gas phase where the rotational or vibrational Zeeman transitions are used, in the case of spin-only resonance progress has been made virtually only in the two-millimetre wavelength range. However, in this range studies on the EPR of free radicals, biradicals, and certain paramagnetic complexes carried out in recent years at the Institute of Chemical Physics of the USSR Academy of Sciences have already yielded what we believe to be extremely interesting and very promising results. The state of this field is considered in the present review.

## II. EPR IN THE MILLIMETRE RANGE: GENERAL PRINCIPLES AND POSSIBILITIES OF MEASUREMENT

The switch to stronger magnetic fields and the corresponding increase of the frequency of the measurements should in principle improve the fundamental characteristics of the magnetic resonance spectrometers: sensitivity and resolving power. Thus the sensitivity of EPR spectrometers is proportional to $\omega^{\alpha}$, where $\alpha$ assumes values ranging from 1/2 to 9/2 depending on the conditions of the measurement. It follows from the condition for magnetic resonance $\omega = \gamma H$ that, for centres of different types differing in the gyromagnetic ratio $\gamma$, the resonance fields at a fixed frequency of the measurement $\omega$ differ more the higher this frequency.

It can be shown on the basis of the most general physical considerations that the optimum, from the standpoint of the amount of information which can be derived, frequency of the observation of the magnetic resonance corresponds to $kT/h$ in order of magnitude and occurs in the range $10^{12}$–$10^{13}$ Hz at the usual temperatures, i.e. constitutes the "physically optimal" submillimetre wavelength range.

Practice gained in NMR research has shown that a switch to the measurement of magnetic resonance in strong fields with a corresponding increase of the resonance frequency makes it possible to realise the possibilities underlying this procedure for the improvement of the sensitivity and spectral resolution. Whereas 20 years ago the 10–40 MHz wavelength range was usually employed, at the present time NMR is recorded in the wavelength range 300–400 MHz. On the other hand, in EPR the three-centimetre or X-range has been dominant during three decades. The explanation is that the experimental basis of the EPR spectroscopy, which was for a number of reasons developed from the very beginning in the 3-cm range, proved to be extremely successful and satisfied for many years the requirements of experimenters as regards sensitivity and resolution and also made it possible to combine readily EPR with various sources of the generation of paramagnetic species and with other research techniques. Another cause is probably that, in contrast to NMR, the usefulness of using high transitions in EPR is not quite so evident. Indeed, the basis of the increase of the spectral resolution with increasing magnetic field strength in NMR is the great variety and specificity of the chemical shifts for nuclei of different functional groups. The analogue of the chemical shift in EPR, which determines the displacement of the resonance lines with increasing field strength, is the $g$-factor.

For free radicals, which are the main objects of EPR studies in chemical physics, biology, and medicine, the values of $g$ are near those of the $g$-factor of the free electron ($g_e = 2.0023$) and in most cases are not characteristic as the chemical shift in NMR. Bearing

in mind that experimenters have a large source of information in the field of EPR, namely the hyperfine and fine structures, one can imagine that interest in EPR studies in strong fields was insufficient to overcome the technical difficulties arising in this connection, which significantly held back the development of millimetre EPR spectroscopy. In particular, in the millimetre range not all the elements of the microwave technique are equivalent to those employed at the 3-cm range. Furthermore, here it is not always possible to use the best constructional solutions found for 3-cm EPR spectrometers. It was therefore expected that the sensitivity of a spectrometer of the millimetre range would not exceed or would even be inferior to the sensitivity of spectrometers for the 3-cm range.

Thus, general considerations alone are insufficient to provide an answer to the question of the likely usefulness of the development of high-frequency EPR; a special and broadly based series of experiments is necessary.

Fairly numerous studies in wavelength ranges below 3 cm are now available : in the *K*-range (12 mm) and the *Q*-range (8mm). An improvement of the absolute sensitivity of $2 \times 10^{10}$ spins $G^{-1}$ in the 3-cm range to $5 \times 10^{9}$ spins $G^{-1}$ in the *Q*-range was indeed achieved. However, in view of the increase of the working volume of the specimen, due to the decrease of the size of the measuring cell, the concentration sensitivity of such spectrometers was not improved.

We shall now turn to the problem of spectral resolution. At the present time one of the significant difficulties in the interpretation of the spectra consists in the identity of the g-factors for different radicals, which leads to the superposition of their spectra. This hinders greatly the interpretation of the spectra and the derivation of information from them; in particular, it precludes the use of the values of $g$ as a source of information about the structure of the radicals. An analogous situation arises also in the absence of superimposed signals in the analysis of weakly anisotropic spectra in frozen solutions and powders[13].

The values of $g$ for typical organic radicals differ from one another by $(1-10) \times 10^{-4}$. In the study of the signals in the three-centimetre range usually employed this leads to a line shift with respect to the field of 1–10 G and the overall extent of the spectra (taking into account the hyperfine structure) is 10–100 G. Comparison of the above values shows that, for an effective resolution of the spectral components of different free radicals, it is necessary to increase the working frequency by more than an order of magnitude compared with the centimetre EPR range, i.e. it is necessary to switch to the millimetre range for the measurement of EPR. According to estimates, a switch to the 12- and 8-mm ranges is in most cases insufficient for the effective resolution of the spectral lines.

In measurements at a wavelength $\lambda < 3$ mm the resolution should be sufficient in most cases, provided that the width of the individual line at least does not increase in this frequency range. Theoretical models predict a wide variety of line width–frequency relations, involving both a sharp increase and a sharp decrease, so that only systematic measurements can solve the problem of the likely usefulness of the millimetre range in high-resolution EPR.

The creation of spectrometers for the 1–3 mm range, suitable for the solution of physicochemical problems, requires the elucidation of a set of questions: (1) the question of sources, transmitting elements, and detectors for the millimetre and submillimetre radiations; (2) the question of the magnetic system of the spectrometer ensuring sufficiently intense fields, which must be varied and scanned over a wide range with retention of the high stability and homogeneity of the field; (3) the question of temperature control and the replacement in the course of the experiment of specimens of different types, including liquid and vitreous specimens.

Sources of the most traditional type in EPR spectroscopy consist of klystron oscillators. A series of their instruments and devices using wavelength ranges down to 2 mm have now been made based on the klystron. Thus the second harmonic of the klystron oscillator for the 4-mm range is used in the specrometer described in a monograph[14]. A specially developed klystron for the 2-millimetre range has been employed[15]. Backward-ware oscillators (carcinotrons[16]) have found extensive applications in spectrometers for the millimetre range; with their aid, it is possible to proceed to still shorter wavelengths[17].

With the aid of laser sources, it is possible to move into the infrared range and beyond. However, one must not forget that in the spectroscopy of free radicals an increase of the frequency of the spectrometer requires a proportional increase in the polarising magnetic field. Thus a field of ~1 MG is required for $\lambda = 0.1$ mm. Field strengths of 1 MG in an EPR spectrometer have been achieved[18] under pulsed conditions within a multisection solenoid of special design and pulsing lasers with the working wavelengths $\lambda = 337$ μm (based on HCN vapour) and $\lambda = 119$ μm (based on $H_2O$ vapour) have been used as sources of radiation. Unfortunately, a spectrometer constructed on this principle cannot apparently be used for extensive studies of free radicals in view of its low concentration sensitivity due both to the obligatory broad recording band (for an amplitude of 1 MG of a pulsing field with a duration of 200 μs, the time taken to traverse a signal with a width of 10 G is 2 ns) and to the large on-off time ratio of the pulses. Furthermore, it is impossible to avoid the occurrence of large distortions in the shape of the spectrum which are difficult to analyse. Nevertheless, in cases where these factors do not play a significant role, such a spectrometer does indeed make it possible to obtain interesting information, which is not accessible by other methods[19].

The most promising magnetic systems are based on a superconducting solenoid. Superconducting 50–100 kG systems, in which the magnetic fields are generated in fairly large volumes, are nowadays commercially available and are fairly widely used in NMR. It is noteworthy that, since fairly large changes in the magnetic field strength are necessary in the course of the experiment during EPR measurements, the magnet of the EPR spectrometer must operate under the given power supply conditions and the cryomagnetic systems of NMR spectrometers operating under frozen field conditions are unsuitable for direct use in an EPR spectrometer. Appropriate modification of the magnetic system and its power supply do not apparently present fundamental difficulties.

The availability of the principal elements of EPR microwave spectrometers—magnetic systems, oscillators, and detectors (high-temperature crystalline and low-temperature *n*-InSB detectors)—made it possible to create a whole series of specialised EPR devices for the millimetre range[16,20–24]. It is noteworthy that the apparatus employed in the above studies had a limited scope with respect to two parameters which are of central importance in physicochemical research, namely sensitivity and the possibility of extensive variation of the temperature of the measurement.

The greatest possibilities for an increase of sensitivity involve the optimisation of the measuring cell of the spectrometer. In measurements using the simplest "through" circuits without a resonator, the sensitivity is minimal and amounts to $10^{13}$–$10^{14}$ spins $G^{-1}$.[24] The situation improves when extra large resonators[15] or Fabry–Perrault resonator interferometers[25] are used. However, these resonators

cannot be regarded as the best: in order to avoid unduly large losses of energy, it is necessary to employ specimens of special shape (which to not distort the distribution of the microwave field) and small size, i.e. to ensure low filling coefficients. We believe that the best solution involves the employment of low-mode volume resonators analogous to those employed in the X-range. Thus an absolute sensitivity of $4\times10^7$ spins $G^{-1}$ and a concentration sensitivity of $2\times10^{11}$ spins $cm^{-3}$ $G^{-1}$ have been obtained for a resonator of type $H_{011}$ in the 2-mm range[26].

In spectrometers with a superconducting solenoid the specimen is placed within the solenoid and hence within a helium cryostat. The conditions in the EPR measurements are then necessarily limited to temperatures in the vicinity of 4 K; access to this specimen for its replacement and various manipulations is also hindered. In order to ensure the possibility of regulating the temperature of the specimen within a wide range, it is essential that the cryostat be provided with a thermally insulated working chamber for the measuring cell (as, for example, in the study of Galkin et al.[15]).

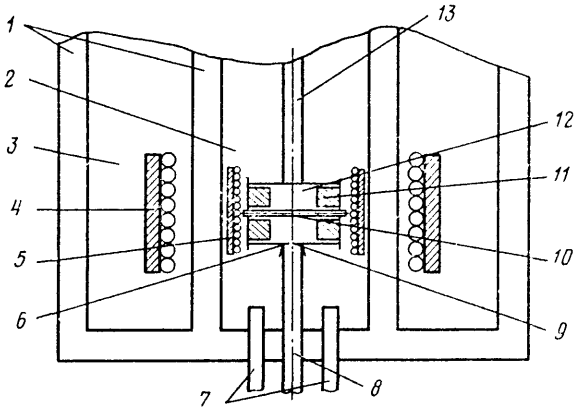



**Figure 1.** Schematic illustration of the positioning of the resonator in the working chamber of the cryostat of the EPR spectrometer for the two-millimetre range: *1*) thermally insulated vacuum jackets; *2*) working chamber; *3*) liquid helium; *4*) superconducting solenoid; *5*) magnetic modulation coils; *6*) disconnectable junction between the resonator and the UHF supply waveguide; *7*) inlet and outlet for the heat exchanger in the thermal stabilisation system; *8*) UHF supply waveguide; *9*) aperture for the adjustable linkage; *10*) bulb for the specimen 0.7 mm in diameter; *11*) adjustable piston for the adjustment of the volume of the resonator; *12*) cylindrical $H_{011}$ resonator; *13*) fixing rod for the resonator and the regulating mechanims[26].

The above discussion shows that an EPR spectrometer for the 2-mm range with a polarising field up to 70 kG, with provision for the regulation of the temperature of the measurement within a wide range and with a sensitivity sufficient for the investigation of the majority of objects traditional in EPR spectroscopy, is at present entirely realistic. The concentration sensitivity attained in the 2-mm range is comparable to the sensitivity of standard spectrometers for the 3-cm range and the absolute sensitivity is greatly superior to the latter. This created conditions for the formulation of experiments designed to elucidate the prospects for the employment of EPR in the millimetre range in the study of free radicals.

A cryostat with a temperature controlled working chamber, in which was placed a type $H_{011}$ resonator with a special tuning system and the junctions between the resonator and the waveguide, ensuring a rapid replacement of the specimens in the course of measurements, was incorporated in the EPR spectrometer for the two-millimetre range[15] which is used nowadays in the Institute of Chemical Physics of the USSR Academy of Sciences (Fig.1). So far as we are aware, this is at present the only experimental apparatus permitting the measurement of electron spin resonance spectra in the two-millimetre wavelength range for liquid, vitrified, and powdered specimens over a wide temperature range (100–350 K) and with a fairly high concentration sensitivity ($2\times10^{11}$ spins $G^{-1}$ $cm^{-2}$). As already mentioned, the absolute sensitivity is $4\times10^7$ spins $G^{-1}$ at room temperature and is maximum for EPR (a higher sensitivity can be achieved only in "on-equilibrium" experiments with optical or "chemical" recording of the signal[7,8] but such experiments are possible only for special objects). Liquid, frozen, and friable specimens were placed in a capillary ~0.7 mm in diameter (0.2 mm) for aqueous solutions), which was located on the resonator axis: solid single crystal specimens can be attached on the bottom of the resonator or on a special rod. The majority of the results described above were obtained on this apparatus. The system illustrated in Fig.1 is unsuitable for the study of specimens in the form of suspensions, native tissues, etc., which are difficult to insert into a thin capillary. Resonators of the Fabry–Perrault type can probably be usefully employed for specimens of this kind.

## III. DETERMINATION OF THE MAGNETIC RESONANCE PARAMETERS AND THE STRUCTURE OF FREE RADICALS AND BIRADICALS

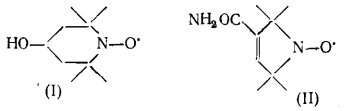
The $g$- factor of the paramagnetic centre (or the set of $g$-tensors) is one of the fundamental magnetic-resonance parameters[27]. The first systematic study undertaken in order to employ the $g$-factors to obtain physicochemical information about free radicals is apparently that of Stone[28]. He developed a general theory relating to $g$-factor to the molecular and electronic structure of the radical, devised a semi-empirical method for the calculation of $g$-factors, and compared the calculated and experimental data. Subsequently a whole series of similar studies were carried out in which the influence of solvents on the $g$-factor was considered apart from structural aspects and various modifications of Stone's theory were developed. Aromatic radicals[29], semiquinones[30], phenoxy-radicals[31], nitrofuran radical-anions[32], nitroxy-radicals[33], peroxy-radicals[34], and other radicals were investigated in succession. The possibility of the experimental observation and fairly accurate measurement of the changes in the $g$-factors within a "homologous" series of compounds or solvents was of decisive importance in these investigations.

Several studies devoted the the analysis of the accuracy of the experimental determination of the $g$-factor have been described[35,36]. The procedure involving the relative measurement of the $g$-factor on the basis of the shift of the given line relative to the reference signal is most widely used and is most convenient. In measurements of this type there is no need for the simultaneous accurate determination of the absolute frequency and field strength and it is sufficient to measure the resonance field of the reference line and the distance from the latter to the measured line with a much lower accuracy. The precision of such measurements is,

however, lower the greater the width of the individual components of the spectrum. Thus only solutions of radicals having EPR spectra with fairly narrow lines, whose width does not exceed 0.1–0.3 G, are susceptible to studies in the 3-cm range. The switch to the millimetre EPR range makes it possible, in principle, to increase greatly the accuracy of the measurements of the components of the $g$-tensor and thus to extend greatly the class of objects susceptible to investigation.

However, one should bear in mind that an improvement of resolution would be observed when addtional line broadening does not occur following an increase of the resonance frequency. As already mentioned, only experiment can lead to the discovery of systems in which a real improvement of the resolution of the spectra in measurements in the millimetre EPR range is possible.

Measurements in the millimetre range of the EPR spectra of free radicals with $g = 2$ in solution at room temperature were achieved for the first time in 1976.[37] Fig. 2 presents the spectra of a solution ($10^{-3}$M) of a mixture of stable radicals (I) and (II) in dioxan[37]:




Spectrum $a$, obtained on a standard spectrometer for the three-centrimetre range, demonstrates a virtually complete superspositon of the components of the individual spectra. Fig. 2$b$ illustrates the complete resolution of the components of the individual spectra in measurements on a spectrometer for the two-millimetre range. The difference between the $g$-factors for radicals (I) and (II) is $\Delta g = 2.40 \times 10^{-4}$. The accuracy of the relative measurements is to within a factor reaching $10^{-5}$, which makes it possible to employ the $g$-factor as an effective characteristic of individual paramagnetic compounds. Fig. 2$b$ also shows that the width of the individual lines of the spectrum hardly changes on passing from the three-centimetre to the millimetre range.

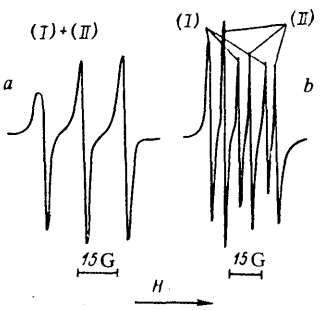



**Figure 2.** EPR spectra of solutions of a mixture of radicals (I) and (II) (1:1), $10^{-3}$M) in dioxane. Measurements at 300 K on spectrometers for the 3-cm ($a$) and 2-mm ($b$) ranges[37].

In certain systems, usually in solids, such a transition leads to an additional broadening of the lines, but an improvement of the resolution is nevertheless still attained. An example of this type is provided by the peroxy-radicals $RO_2^{\cdot}$ investigated by Grinberg et al.[38], The simplest radicals of this series, namely $HO_2^{\cdot}$, were obtained in the photolysis of a 30% frozen $H_2O_2/H_2O$ solution at 77 K. In contrast to the 3-cm range, in the 2-mm range the resonance lines corresponding to the radicals in which the principal axes of the $g$-tensor are directed along the external magnetic field canonical components) are fully resolved (Fig. 3$a$), which made it possible to determine the main values of the $g$-tensor ($g_1 = 2.00382$, $g_2 = 2.00821$, and $g_3 = 2.03362$). After heating the specimen to 140 K, some of the $HO_2^{\cdot}$ radicals recombined, which led to a narrowing and shift of the lines: $\delta g_1 = -1.05 \times 10^{-3}$ and $\delta g_2 = 1.33 \times 10^{-3}$. These changes in the EPR spectrum indicate, on the one hand, the structural inhomogeneity of the specimen as a possible cause of the additional line broadening in the two-millimetre spectra; on the other hand, they indicate a correlation between the stability of the radicals and their environment. Differences between the magnetic parameters of the middle ($R_mO_2$) and terminal ($R_tO_2$) peroxy-radicals in polytetrafluoroethylene have also been observed[38] (Fig. 3$b$). The principal values of the $g$-tensor were obtained: $g_1^m = 2.00232$; $g_2^m = 2.00743$; $g_3^m = 2.03813$; $g_1^t = 2.00278$; $g_2^t = 2.00770$; $g_3^t = 2.03963$.

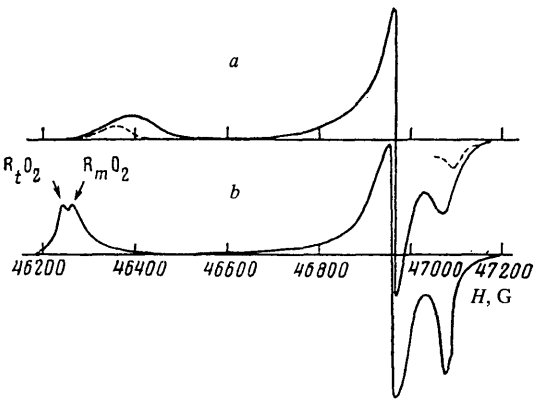



**Figure 3.** EPR spectra of peroxy-radicals in the 2-mm range: $a$) in $H_2O_2/H_2O$ at 77 K; dashed line—after annealing at temperatures up to 140 K; $b$) in polytetrafluoroethylene[38].

Fig. 4$a$ presents yet another example which demonstrates the complete separation of the spectra of the peroxy-, alkyl, and allyl radicals in polytetrafluoroethylene as a result of the effective resolution by the spectrometer in the two-millimetre range. The spectrum for the same specimen recorded in the 3-cm range, illustrated in Fig. 4$b$, is an unresolved blend of overlapping spectra unsuitable for analysis. The examples presented show clearly that the switch to the millimetre EPR range for free radicals in condensed media does indeed entail an improvement of the resolution with respect to the g-factor, which permits the separate recording of the group of lines of different radicals. On the other hand, the advantages of high-resolution spectroscopy can be used for the analysis of complex spectra of radicals of the same type when canonical groups of lines are resolved with increase of the resonance field strength. Figs. 5 and 6 present as examples the spectral solutions of the familiar compound $VOSO_4$ in $H_2O$ and of the stable diphenylpicrylhydrazyl radical (DPPH) in toluene. Fig. 5 shows how appreciable is the simplification of the overall form of the spectrum of the vanadyl group in

the two-millimtre range compared with the spectrum in the three-centimetre range as a result of the separation of the components with perpendicular and parallel orientations to give isolated groups. On the other hand, the DPPH spectrum (Fig.6) shows the appearance of additional components but their positions make it possible to extract new information, inaccessible in measurements in the 3-cm range, about the components of the $A$ and $g$ tensors of the radical in a frozen toluene solution: $A = 20.9$ G and $g_{\parallel} = 2.00254$. It is noteworthy that a qualitative demonstration of the possibility of the resolution of the anisotropic doublet in the spectrum of DPPH powder was achieved as early as 1964.[16]

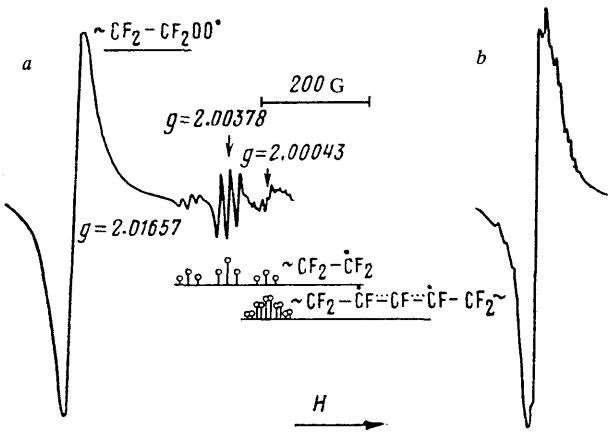



**Figure 4.** *a*) Separation of the EPR signals of the allyl, alkyl, and peroxy-radicals in polytetrafluoroethylene in the 2-mm range; *b*) spectrum of the same specimen in the 3-mm range[38].

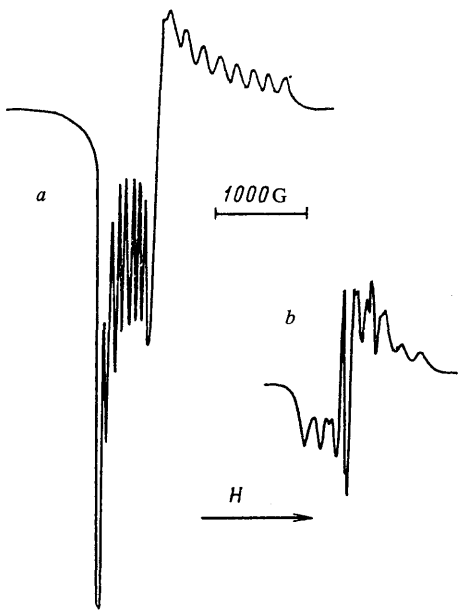



**Figure 5.** EPR spectra of $VO^{2+}$ ions in sulphate glass in the 2-mm (*a*) and 3-cm (*b*) ranges[26].

The possibility of determining the principal values of the $g$- and $A$-tensors, which appears in the two-millimetre range, is particularly valuable in the case of nitroxy-radicals, which are widely used in chemical, biological, and medical research as spin probes and labels[39]. In order to obtain such information in the 3-cm range, the EPR spectra of single crystals, containing radicals as regular inclusions, were investigated. The preparation of such single crystals is difficult. Furthermore, the application of the method of spin labels and probes requires the introduction of radicals into different and as a rule non-single crystal matrices. Since the medium can influence the magnetic parameters[40], the employment of data obtained for single crystals is not always correct and inaccurate calculations of these data must be regarded solely as the zeroth approximation for undetermined variable parameters[39]. The magnetic resonance parameters measured directly in real polyoriented objects are therefore particularly valuable.

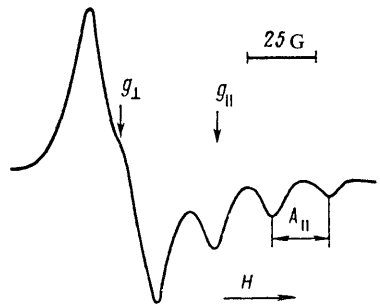



**Figure 6.** EPR spectrum of a frozen solution of DPPH in toluene in the 2-mm range[26].

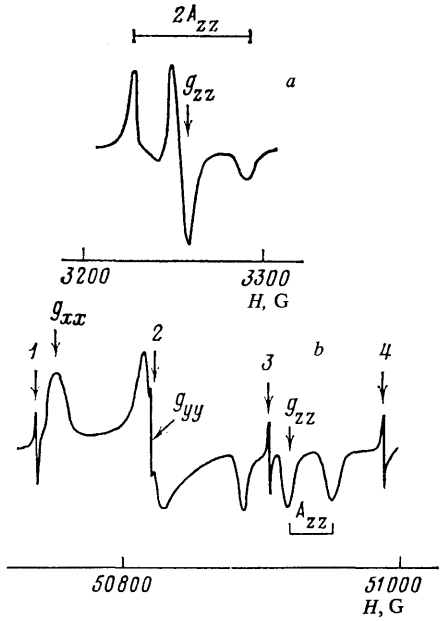



**Figure 7.** EPR spectra of a radical (III) solution in polystyrene at 77 K in the 3-cm (*a*) and 2-mm (*b*) ranges. The arrows indicate the components of the 1–4 spectrum of the $Mn^{2+}$ lateral standard in MgO.

Fig.7 presents the spectra of a solid solution ($10^{-3}$M) of the stable radical (III) in polystyrene at 77 K.[37] Components corresponding to the three principal values of the anisotropic $g$-factor are distinctly seen in the spectrum obtained in the 2-mm range. One of the values of the anisotropic $A$-tensor can also be readily measured. Determination of the remaining principle values of the $A$-tensors ($A_{xx}$ and $A_{yy}$) from the spectra of nitroxy-radicals of the type illustrated in Fig.7 is evidently difficult ($z$ represents the direction at right angles to the plane of the radical fragment and $x$ the direction along the N–O bond).



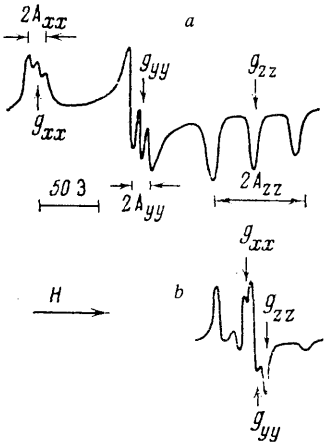
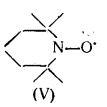




**Figure 8.** EPR spectra of a solution of deuterated radical (IV) in toluene at 140 K: *a*) 2-mm range; *b*) 3-cm range.

In order to improve the resolution of the UHF lines in the 2-mm EPR spectra, the familiar procedure of isotope substitution of H by D or of $^{14}$N or $^{15}$N has been used[41]. Fig.8*a* illustrates the spectrum of radical (IV) and the characteristic points from which the complete set of magnetic resonance parameters were determined directly. For comparison, Fig.8*b* presents the spectrum of the same radical in the three-centimetre range. It is noteworthy that for deuterium-substituted radicals there is a possibility, in principle, of determining the parameters also from the spectra in the 3-cm range[49]. However, this entails necessarily a complex analysis involving a theoretical calculation of the spectrum, which lowers the accuracy of the determination of the parameters and leads to a sharp increase of the time consumed. All the magnetic-resonance parameters of radical (V) with the $^{15}$N isotope can be determined directly from the spectrum in Fig.9, as for the spectrum in Fig.8*a*.




The magnetic parameters of nitroxy-radicals of different types (about 70 individual structures) have been determined[43] from the EPR spectra in the 2-mm range. The principal values of the $g$-tensor of the nitroxy-radicals determined in the above study are presented in Fig.10 in terms of plots of $g_{xx}$ against $g_{yy}$ and $g_{zz}$. The figure shows that $g_{xx}$ is most sensitive to the structure of the radical. It is noteworthy that the points corresponding to different radicals in the "space of $g$-factors" do not coincide in most cases, which permits the conclusion that the EPR resolution attained in the 2-mm range makes the $g$-tensor of nitroxy-radicals a characteristic parameter which extends the availabel range of analytical procedures. Analysis of Fig.10 shows that the values of $g$ for nitroxy-radicals with identical structures of the radical ring are grouped in a definite region corresponding mainly to radicals of the given series. The values of $g_{xx}$ for nitroxy-radicals of the piperidine series are in the range from 2.00975 to 2.01005, those for radicals of the 4-piperidine series are between 2.00955 and 2.00970, those for radicals of the 3-imidazoline series with the nitrone group are between 2.00917 and 2.00930, and those for radicals of the series without the nitrone group are in the range from 2.00905 to 2.00915, i.e. they decrease in the series of radical structures enumerated.

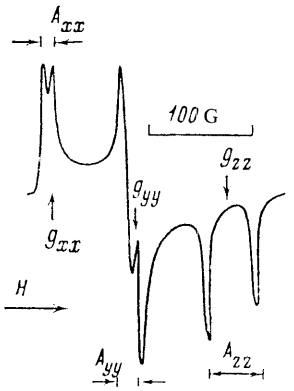



**Figure 9.** EPR spectrum of a solutlion of radical (V) with nitrogen substituted by $^{15}$N in toluene at 140 K in the 2-mm range.

This behaviour, established in relation to a large number of radicals, is useful both in the assignment of the radicals to a particular class (i.e. in identification on the basis of EPR spectra) and in estimating the magnetic parameters of the radical on the basis of the type of its structure. These data are particularly important for the theoretical analysis of the structure of the radicals and its influence on the spectroscopic parameters. Thus in the series enumerated, there is a successive intensification of the interactions of $\pi$ orbitals localised in the peripheral part of the radical with the $\pi^*$ orbital of the N–O bond (the interatomic distance diminishes and the overlap of the orbitals improves), which alters the energy of the singly populated $\pi^*$ orbital:

$$\delta E_{\pi^*} \simeq \Sigma \frac{V^2_{\pi^*\alpha}}{\Delta E_{\pi^*\alpha}} \qquad (1)$$

where $\alpha$ is the index of the peripheral orbital, $V^2_{\pi^*\alpha}$ the square of the matrix element approximately proportional to the overlap integral of the $\pi^*$ and $\alpha$ orbitals, and $\Delta E_{\pi^*\alpha}$ the

difference between the energies of these orbitals. Overlap with the bonding peripheral $\pi$ orbitals is more effective than with the antibonding orbitals, because in the latter there is partial compensation of the contributions by individual atomic orbitals. Terms with positive $\Delta E$ therefore predominate in the sum defined by Eqn.(1), which leads to an overall increase of the level of the singly populated $\pi^*$ orbital of the NO group. The approximation[44]

$$\Delta g_{xx} = \lambda \rho_O^{\pi} / \Delta E_{n\pi^*}$$

is used for $\Delta gxx$. Here $\lambda$ is the spin-orbital coupling constant for the oxygen atom, $\rho_O^{\pi}$ the spin density at the oxygen atom, and $\Delta E_{n\pi^*}$ the energy of the $n-\pi^*$ transition.

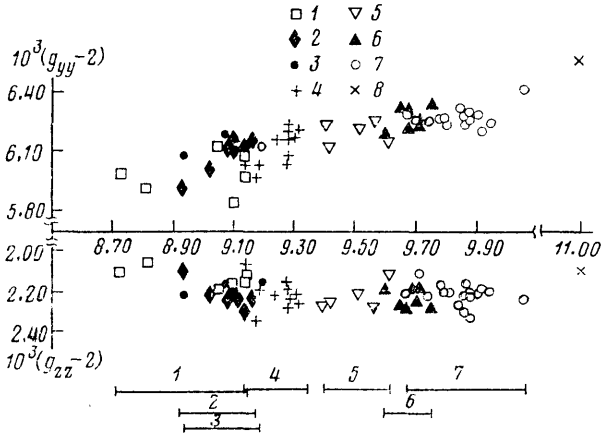



**Figure 10.** Principal values of the $g$-tensors for nitroxy-radicals having different structures; radicals derived from: *1*) imidazolidines; *2*) imidazolines; *3*) pyrrolidines; *4*) imidazolines with the N → O group; *5*) imidazolidines with phenyl substituents in the 4,4′-positions; *6*) 4-piperidines; *7*) piperidines; *8*) nitronylnitroxy-radical. The ranges incorporating the values of $g_{xx}$ for radicals with the same ring structure are indicated below.

The positive shift $\delta E_{\pi^*}$ leads to a decrease of $gxx$, which agrees with the relation discovered. Apart from the "direct" influence of peripheral orbitals described above, there are also other factors acting on $gxx$. It has been noted[43] that an increase of $gxx$ is accompanied by an increase of the N-O bond length, a decrease of the angle between the N-O bond and the -C-N-C- plane, and the decrease of the CNC angle in the radical fragment. The examples presented show that high-resolution EPR (millimetre range) makes it possible to increase the accuracy of the measurement of the $g$-tensor components and to observe experimentally the fine changes in these quantities under the influence of various factors. The measured principal values of the $A$- and $g$- tensors can apparently be used to identify the radicals, in the study of the interaction of the radicals with the molecules of the medium, and in comparing spectroscopic data with the results of quantum-chemical calculations for radicals of different structures.

In certain cases it is possible to obtain from spectra in the two-millimetre range information about the structure of the centres investigated. The spectrum (Fig.11) of the middle peroxy-radical in polytetrafluoroethylene (PTFE), characterised by an axially-symmetrical $g$-tensor owing to the movement of the radical fragment around the polymer axis, has been recorded[44] at 300 K.

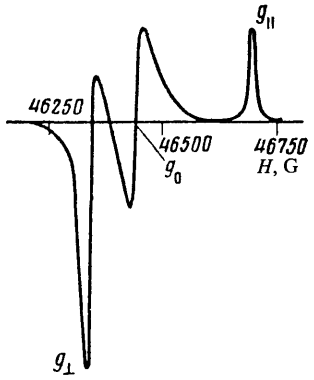



**Figure 11.** Spectrum of peroxy-radicals in polytetrafluoroethylene at 300 K; $g_{\parallel}$ and $g_{\perp}$ are components of the $g$-factor of the middle radical $R_mO_2$; $g_0$ is the component of the $g$-factor of the residual terminal $R_tO_2$ radical.

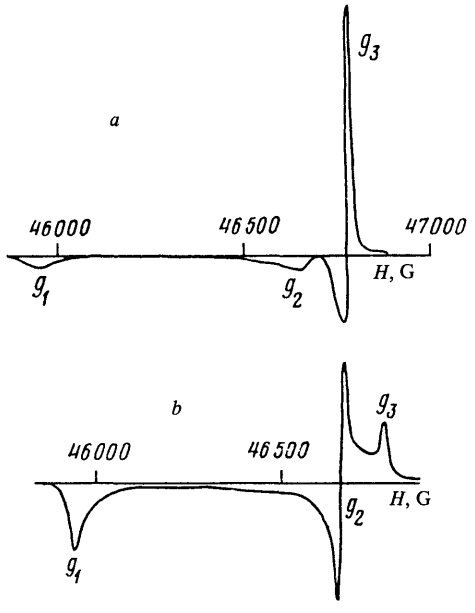



**Figure 12.** EPR spectrum at 100 K in the 2-mm range of the middle radical in polytetrafluoroethylene specimens oriented by stretching: *a*) extension axis parallel to the field; *b*) axis perpendicular to the field[44].

For radicals the axis of rotation of which is parallel to the external magnetic field, the presence or absence of rotation is in no way manifested in the EPR spectra. In the absence of rotation, the spectrum of these species are characterised by its $g$-factor

$$g = (g_1^2 l_1^2 + g_2^2 l_2^2 + g_3^2 l_3^2)^{1/2}, \qquad (2)$$

where $l_i$ are the directional cosines of the axis of rotation relative to the principal axes of the $g$-tensor. For rapid rotation, the spectrum of these species in semioriented specimens corresponds to the components with $g = g_{\parallel}$. The above equation together with the relation

$$l_1^2 + l_2^2 + l_3^2 = 1 \qquad (3)$$

defines the curve on the surface of a single sphere—the geometrical locus of the possible positions of the end of the vector of the directional axis of rotation. Additional data about the position of the axis of rotation have been obtained from the spectra of partially oriented polytetrafluoroethylene specimens. Fig.12 shows that, when the axis of extension of the specimen is oriented along the magnetic field, the intensity of the $g_2$ component falls sharply. Consequently the molecular axis corresponding to this component is located near the plane perpendicular to the axis of extension. Having assumed that the axis of rotation coincides with the longitudinal axis of the molecule, which is oriented along the axis of extension during the stretching process, one can find that $l_2 \cong 0$. This estimate and Eqns.(2) and (3) made it possible to establish, after substituting the values of $g_i$, that the polymer axis in the $XY$ plane makes an angle $\theta = 72°$ with the direction of the O–O bond. The location of the $CO_2$ fragment in the polytetrafluoroethylene molecule and the orientation of the principal axis of the $g$-tensor relative to the molecular axis are shown in Fig.13.

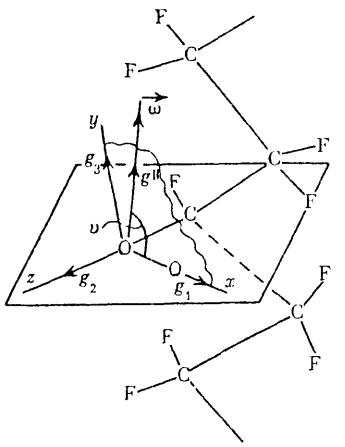



**Figure 13.** Disposition of the $CO_2$ fragment and of the principal axes of the $g$-tensor for the middle peroxy-radical relative to the polytetrafluoroethylene molecule[44].

The application of two-millimetre EPR holds out promise for extensive possibilities in the study of the structures of biradicals. Fig.14 illustrates the EPR spectra of a toluene solution of the *trans*-bis(2,2,5,5-tetramethyl-3-oxo-3-imidazolin-1-oxy-4-yl)ethylene biradical in the 3-cm and 2-mm ranges. Preliminary inspection showed already that the spectrum in the two-millimetre range is simpler and more convenient for analysis. The components in the spectrum in Fig.14 can be assigned by comparison with the spectrum of the monoradical (Fig.7). The spectrum of the biradical has a greater multiplicity of lines in the hyperfine structure (HFS) compared with the spectrum of the monoradical: the electrons of the biradical interact with the magnetic nuclei of both fragments. Furthermore, a doublet dipole–dipole line splitting appears. The spectrum illustrated in Fig.14*a* results precisely from the splitting of the canonical components in the spectrum of the monoradical (Fig.7) into dipole doublets when account is taken of the increase of the HFS multiplicity manifested in the $z$ components.

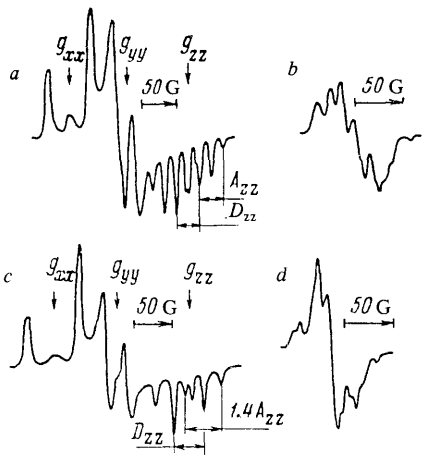



**Figure 14.** EPR spectra of nitroxy-biradicals (structure shown in Fig.15) in a $10^{-3}$ M solution in toluene at 140 K: *a*) and *b*) with $^{14}N$ atoms; *c*) and *d*) with $^{15}N$ atoms; *a*) and *c*) in the 2-mm range; *b*) and *d*) in the 3-cm range[45].

The positions of the components in the spectrum of the biradical are determined by the set of parameters characterising its structure and magnetic interactions, in particular the principal values of the fine structure $D$-tensor and the relative orientations of the axes of the $g$- and $D$-tensors. It has been established[45] that the axes of the $g$-tensors of both nitroxy-fragments of the biradical have the same directions and that the symmetry axis of the $D$-tensor is in the $xy$ plane of the $g$-tensor and makes an angle of 14° with the $x$ axis of the $g$-tensor.

The geometrical structure of the biradical was established on the basis of the data obtained: the molecule has a planar structure and the *cis*, *trans*, *cis*-conformation relative to the C(5)–C(6), C(6)–C(6′), and C(6′)–C(5′) axes (Fig.15). Quantitative estimates of the delocalisation of the spin density from the NO radical fragment to the π-system of the C(3)–C(4)...C(4′)–C(3′) biradical have shown that the spin densities in the atomic orbitals of these nuclei are ~1%.

The examples considered demonstrate that, in the measurement of the spectra of free radicals in the 2-mm range in condensed media, an additional broadening of the individual lines is not as a rule observed. An increase of the resonance frequency entails a real increase of the resolution of the EPR spectra of free radicals which makes it possible to record separately the spectra of different radicals in the mixture, increases the accuracy of the measurement of the $g$-factors, and simplifies or simply makes possible the analysis of the spectra of the paramagnetic centres. From our point of view, the results presented justify the treatment of the spectroscopy in the millimetre range as high-resolution EPR spectroscopy with respect to the $g$-factor, which can yield valuable

physicochemical information about the structure of the paramagnetic species and their interaction with the medium.

## IV. THE STUDY OF MOLECULAR MOVEMENTS

Studies of the molecular mobility in condensed media occupy a notable place in modern researches by EPR. Such investigations are based on the sensitivity of the form of the EPR spectra to the relaxation processes caused by the movements of the paramagnetic centres and their environment. The method of spin labels and probes, developed largely for the investigation of molecular mobility in biological objects[39] and polymeric matrices[46], has become particularly widespread. However, one already has to reckon with the limitations to this method associated, in particular, with the inadequate resolution in the spectra of typical labels (stable nitroxy-radicals are usually employed as labels and probes[39]). In this situation it is natural to use procedures which improve the spectral resolution, the most effective of which involves the measurement of the EPR spectra in strong fields.

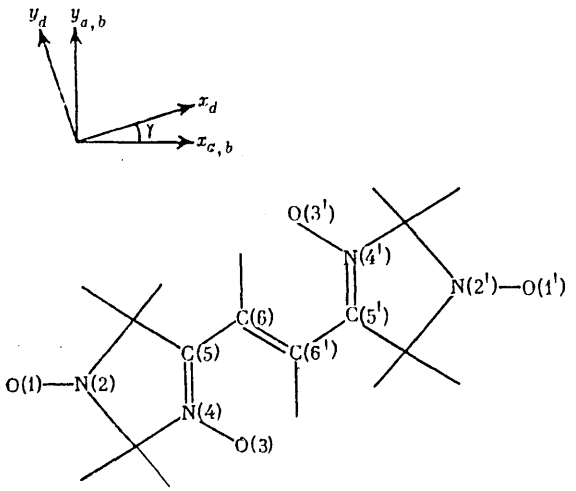


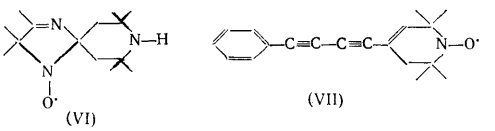

**Figure 15.** The structure of the *trans*-bis(2,2,5,5-tetramethyl-3-oxo-3-imidazolin-1-oxy-4-yl)ethylene biradical. Above —the relative dispositions of the axes of the $D(x_d, y_d)$ and $g(x_{a,b}, y_{a,b})$-tensors[45].

As early as 1976, interesting possibilities for the employment of EPR spectra in the two-millimetre range in the study of molecular mobility were noted[37]: in the fully resolved $z$ components of the spectra of probe nitroxy-radicals, it is easy to observe the broadening (Fig.16) in which the frequencies of molecular movements in the range $10^7$–$10^8$ $s^{-1}$ can be determined directly (in the centimetre range a complex calculation of the line form is usually needed for this purpose. We shall consider the studies whose results demonstrate new, compared with the centimetre range, qualitative and quantitative possibilities for the employment of the millimetre EPR range. Studies of the anisotropy of the rotational lines are particularly instructive in this respect.

The procedure for the analysis of the anisotropy of the rotation developed for the EPR spectra in the three-centimetre range are more suitable for the region of rapid movements[47]. The knowledge of much more accurate values of all the magnetic parameters of the probe radical proved important under these conditions. In the previous Section it was shown that a realistic possibility for the determination of such data arises only in EPR measurements in the millimetre range. Thus progress in the determination of the magnetic parameters of nitroxy-radicals with the aid of millimetre EPR can serve as a basis for extensive studies of the anisotropy of rapid rotations in the centimetre range.

In the region of slow movements the manifestation of the anisotropy of the rotation leads to non-specific changes in the spectra in the 3-cm range[48] whose employment for the determination of the anistropy is difficult. On the other hand, in the millimetre EPR there is an entirely realistic possibility for the investigation of the anisotropy of the rotation precisely in the region of slow movements and important conclusions about the nature of the rotation (the presence of anisotropy, the direction of the preferential rotation axis) can be obtained directly from experimental data without resorting to a complex analysis of the spectra.

Radicals with different shapes, namely elongated[(VI) and (VII)] and nearly spherical [(V)], have been selected[49] for the study of the anistropy of the rotation of nitroxy-radicals in viscous matrices (liquid paraffin, vitrified toluene, etc.):



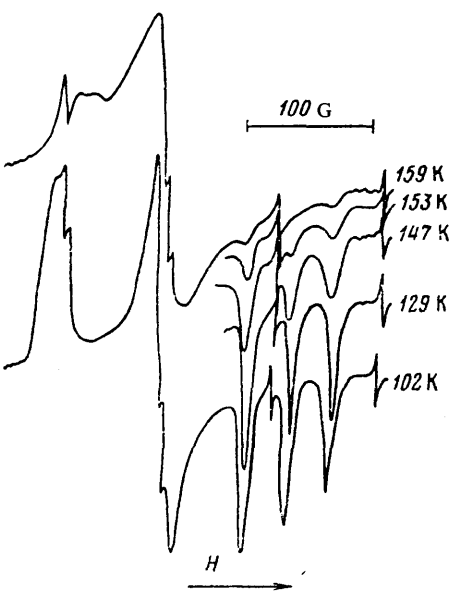




**Figure 16.** EPR spectra of radical (V) in a solution of polystyrene in toluene (15%) at different temperatures in the 2-mm range.

Furthermore, the long axes of radicals (VI) and (VII) are oriented in different ways relative to the principal axes of the $g$-tensor of the radical fragment. The direction of the long axis of radical (VII) is close to that of the $x$ axis of the $g$-tensor, while radical (VI) direction of this axis is close to

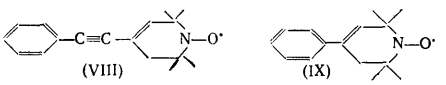
that of the $y$ axis. Fig.17 shows how the EPR spectra of the chosen radicals vary when the rotational mobility of the probes is "unfrozen" with the increase of temperature. The spectra were recorded in the two-millimeter range at 100–350 K. Fig.17 shows that the relaxation changes, manifested primarily in the broadening and displacement of the components of the spectrum, begin at lower temperatures for radical (VI) and are characterised by a greater depth for the $x$ and $z$ components than for the $y$ component.

The effect described has a simple qualitative explanation. For species with anisotropic magnetic parameters, different resonance frequencies correspond to different orientations in an extermal magnetic field. Rotation of the species leads to exchange between states with different resonance frequencies, which induces relaxation changes in the spectrum. However, each rotation is not involved in such exchange with identical efficiency. In particular, the rotation of the molecule about the axis directed along the magnetic field does not alter the angle between the field and the axes of the $g$- and $A$-tensors, i.e. does not affect the resonance frequency. For the "ellipsoidal" radicals distributed isotropically in the specimen, the axis of rotation in some of the centres is oriented along the field and no relaxation changes are manifested in the EPR signals corresponding to these centres. In the case of radicals (VI) the species oriented with the $y$ axis of the $g$-tensor along the field satisfy this condition. These species in fact give rise to the $y$ component of the EPR spectra, which does not therefore exhibit relaxation changes whatever the changes in the other parts of the spectrum—the $x$ and $z$ components. Only on further increase of temperature, when movements giving rise to a reorientation of the direction of the long axis of the radical are fairly effective, does the $y$ component begin to participate in the frequency exchange.

The anisotropy of rotation is manifested to an even greater extent in the spectra of radical (VII) which has a somewhat more extended shape. Here rotation takes place preferentially about the $x$ axis of the $g$-tensor and it can be seen from Fig.17 that the $x$ component of the spectrum is incorporated in the relaxation process significantly later than the $y$ and $z$ components. The longitudinal ($\nu_\parallel$) and tranverse ($\nu_\perp$) frequencies of the rotational correlation then differ so much that complete averaging of the spectral $y$ and $z$ components as far as the "exchange-narrowed" triplet is attained and the spectrum assumes the form characteristic of the axial symmetry of the $A$- and $g$-tensors. As in the case of radical (VI), further heating leads to the broadening of the parallel $x$ component and the perpendicular components and to their displacement towards the centre of gravity of the spectrum.

In the spectra of radical (V) relaxation changes are observed simultaneously and to an equal extent for all three canonical components. In this case there is apparently no separate axis of preferred rotations, in agreement with the approximately spherical shape of the radical.

The influence of the matrix on the degree of anisotropy of the rotation of the probe was investigated in greater detail in a study[50] where the spectra were analysed within the framework of the model involving changes in the orientation of the molecule in jumps by uncorrelated angles[51]. It was shown[50] that in the region of "slow" movements the effect reduces to a broadening of the canonical components of the spectrum equivalent to the convolution of the initial line form with a Lorentzian line whose width is different for different components in anisotropic rotation. Thus, in rotation about the $x$ axis of the $g$-tensor of the radical fragment along which radicals (VII), (VIII), and (IX) are extended, i.e.



(VIII) (IX)

the $y$ and $z$ components are convoluted with a Lorentzian line having a width

$$\delta_L = 1/\gamma\tau_\parallel + 1/\gamma\tau_\perp$$

and the $x$ component is convoluted with a line having a width

$$\delta_L = 2/\gamma\tau_\perp,$$

where $\tau_\parallel$ and $\tau_\perp$ are the correlation times of the axially symmetrical movement about the long and short axes of the probe respectively and $\gamma$ is the gyromagnetic ratio.

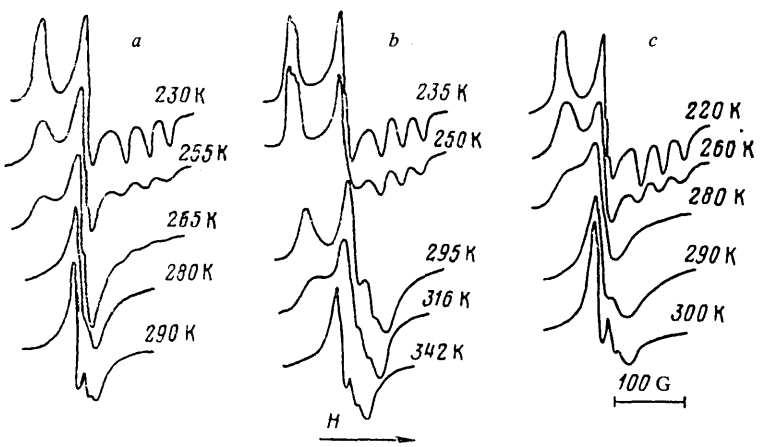



**Figure 17.** EPR spectra of solutions of the nitroxy-radicals (VI) (*a*), (VII) (*b*), and (V) (*c*) in liquid paraffin at different temperatures in the 2-mm range[49].

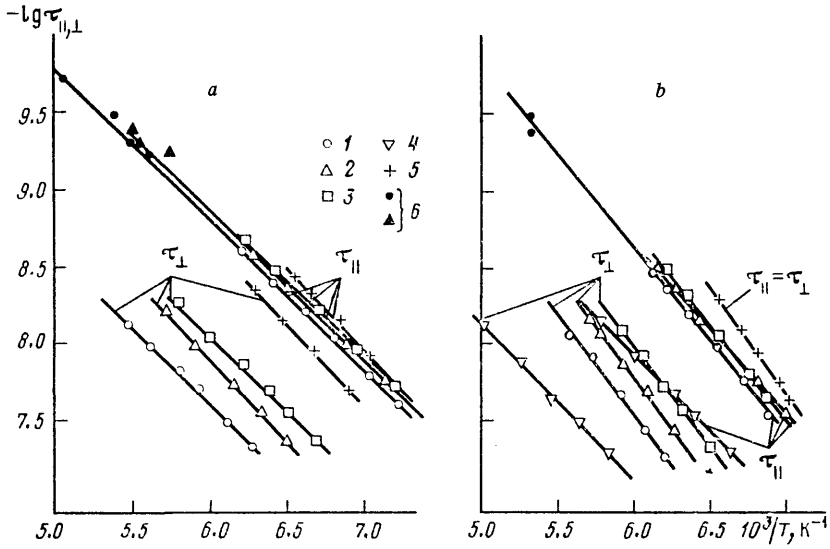



**Figure 18.** Arrhenius relations for the rotational correlation times of the radicals: *a*) in methanol; *b*) in toluene; *1*) radical (VII); *2*) radical (VIII); *3*) radical (IX); *4*) radical (X); *5*) radical (I); *6*) measurements based on the exchange-narrowed triplet[50].

If the rotation of the probe was sufficiently anisotropic and a resolved triplet was formed as a result of the averaging of the *y* and *z* components of the spectrum, the correlation times $\tau_\parallel$ and $\tau_\perp$ were determined from the formulae

$$\delta_L^\parallel = 2/\gamma\tau_\perp$$

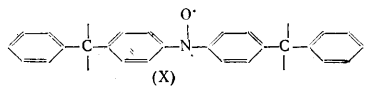
$$\delta_L^\perp = 2/\gamma\tau_\perp + \gamma(\Delta H_m)^2\tau_\parallel/8$$

for the parallel and perpendicular components respectively, where

$$\Delta H_m = g_0 H_0(1/g_{zz} - 1/g_{yy}) + m(A_{zz} - A_{yy});$$

$m = -1$, 0, +1 is the projection of the nuclear spin of nitrogen onto the magnetic field. Alcohols, (methyl, propyl, isodecyl, and isopentyl), toluene, liquid paraffin, and *p*-methoxybenzylidene-*p'*-butylaniline (MBBA) were chosen as the solvents.

Fig.18 presents the Arrhenius temperature variations of $\tau_\parallel$ and $\gamma_\perp$ for solutions of the radicals in toluene and methanol (in other solvents the relations were analogous). Over the entire range of measurements, the relations are linear. Fig.18 shows that a decrease of the length of the radical leads to a considerable (by a factor up to three) shortening of the time $\tau_\perp$. The time $\tau_\parallel$ for the same series of radicals diminishes by only 20%. For the radical




(X)

whose transverse dimension is greater than that of the radicals (VII)–(IX) and (V) and is close to the longitudinal dimension of radical (VIII), the variation of $\tau_\parallel$(X) is also close to that of $\tau_\perp$(VIII).

Thus the relations between the correlation times $\tau_\parallel$ and $\tau_\perp$ for different radicals in the same solvent are determined mainly by the dimensions of the radicals and $\tau_\parallel$ is influenced by the transverse dimension of the radical, while $\tau_\perp$ is influenced by its length.

The anisotropy parameters ($N = \tau_\perp/\tau_\parallel$) were measured for all the radicals at the temperature corresponding to the same $\tau_\parallel = 2\times10^{-9}$ s. The choice of this temperature was dictated by the fact that in its vicinity it is possible to determine simultaneously $\tau_\parallel$ and $\tau_\perp$ from the rotational broadening of the spectra. It was found that the anisotropy parameters *N* are either independent of temperature or decrease somewhat as the temperature is raised. However, the $N(T)$ relation could not be elucidated accurately, because the correlation times could be measured only over an inadequately wide temperature range. It was found that the anisotropy parameters depend greatly on the solvent and on the shape of the radicals. For example, in the series of alcohols *N* diminishes with increasing molecular weight of the alcohol: for radical (VIII), $N = 11.7$ in methanol and $N = 7$ in decyl alcohol. The lowest anisotropy parameters have been obtained for MBBA ($N = 5.7$) at temperatures below the region of its liquid-crystal state. A correlation with the parameters for different radicals in different solvents has been observed: firstly, the more extended molecule the greater the anistropy of its rotation in the given solvent and, secondly, if the anisotropy parameter of any one radical is greater in one solvent than in another, then an analogous relation is observed also for other radicals. The dependence of *N* on the properties of the radical and the solvent has been represented[50] by the empirical formula

$$N = KN_0, \qquad (4)$$

where $N_0$ is a parameter characterising the radical and depending solely on its geometrical dimensions; *K* is a parameter characterising the solvent for extended radicals; for spherical radicals, $N = 1$. Fig.19 illustrates the linear correlation between *N* and *K* in accordance with Eqn.(4). In order to account for the experimental data obtained, certain models of motion were examined[50] and it was shown that the model involving the "flickering of the free volume" yields the best agreement with experiment.

Another example of the study of the anisotropy of rotations in the millimetre range has been published by Grinberg et al.[44] They investigated the middle and terminal peroxy-radicals in polytetrafluoroethylene. In previous studies it had been found from three-centimetre[52] and eight-millimetre[53] data that the middle radical rotates as a rigid rotator in the vicinity of 300 K and that the axis of rotation is approximately perpendicular to the O–O bond. In the two-millimetre EPR range, not only all three principal values of the $g$-tensor but also the effective values of $g_\parallel$ and $g_\perp$ can be measured accurately by virtue of the full resolution of the components (Figs.3 and 11). The values of $g_\parallel$ and $g_\perp$ characterise the spectrum of the middle radical on partial averaging of the initial anisotropy to give cylindrical symmetry as a result of the rapid rotations about the axis of the rotator. The possibility of the accurate measurement of these parameters enabled the authors[44] to establish finally the disposition of the axis of rotation of the middle radical (the axis of the polymer chain) relative to the principal axes of the $g$-tensor. It was also found that, for the terminal peroxy-radicals the PTFE in the region of rapid movements (above 290 K), there is likewise no complete averaging of the spectra to give an isotropic singlet. It is noteworthy that these spectra (Fig.20) do not reduce either to the doublet characteristic of monoaxial rotation with the components $g_\parallel$ and $g_\perp$ (of the type shown in Fig.11), but consist of a set of such doublets with different parameters and statistical weighting factors. Thus it was possible to observe not only a definite "constraint" of the movement of the terminal groups at the polymer chain, leading to the anistropy of the rotation of the terminal $RO_2$ groups, but also the presence of a set of different structures of this fragment.

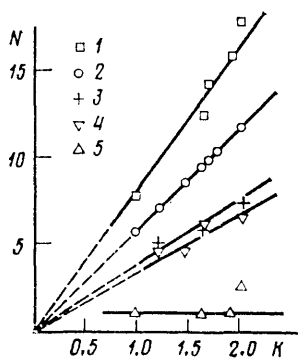



**Figure 19.** Dependence of the anisotropy parameter for different radicals on the solvent; radical: 1) (VII); 2) (VIII); 3) (X); 4) (IX); 5) (I).[50]

A certain distribution of properties is in general characteristic of condensed media. In particular, molecular mobility can be inhomogeneous, i.e. characterised by a distribution with respect to rotational correlation times. The influence of kinetic inhomogeneity on chemical processes is well known[54,55] and procedures for its description have been adequately developed. There exist data concerning the manifestation of multiple frequencies of molecular rotations and the relaxation changes in the EPR spectra, but analysis is extremely difficult. The point is that even in the simple case of motion with a single correlation time, the changes in the spectrum are extremely complex, so that, for example, the determination of $\tau_c$ does not reduce (except in the region of rapid rotations) to the measurement of simple spectral parameters and it is in fact necessary to carry out a full synthesis of the spectrum and to compare it with experiment.

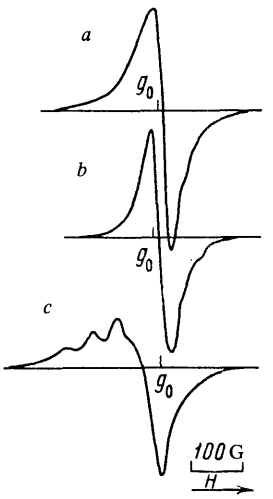



**Figure 20.** EPR spectra of terminal peroxy-radicals in the isotropic ($a$) and oriented by stretching ($b$,$c$) polytetrafluoroethylene specimens. The extension axis is parallel to the field at 300 K ($c$) or is perpendicular to the field ($b$); $g_0$—signal of the reference standard[44].

If one considers in addition the influence on the spectrum of the anisotropy of the rotation of the dynamic model of motion (diffusion, jump, or free rotation[56]), then the problem of the determination of the parameters of the distribution with respect to the correlation times of the molecular movement of the radicals from the EPR spectra in the three-centimetre range becomes virtually insoluble. Progress can be made in this field only in special cases of the so called "isolated", i.e. well resolved from the remainder of the spectrum, components. If the movement of the paramagnetic centre induces the frequency exchange of this component with the spectrum, the changes reduce simply to a broadening linear in terms of the exchange frequency and to its shift to an extent for which its overlap with other parts of the spectrum begins. An example of such components can be provided by the forbidden $\Delta M_S = 2$ transitions in radical dimers, on the basis of the spectra of which it proved possible[57,58] to establish the presence of distributions with respect to the correlation times and to determine the parameters of the distribution. Another example may be the canonical components in the spectra characterised by the anisotropy of the magnetic parameters. Since the effectiveness of the employment of these components in order to characterise the movement depends on the degree of their resolution, the best results can be obtained in the millimetre EPR range.

Such analysis of the relaxation changes of the $x$ component of the spectrum (Fig.3) of the middle peroxy-radical in polytetrafluoroethylene as a function of temperature has been carried out[44]. The decrease of the amplitude of the $x$ component is far in advance of its broadening, i.e. the integral

intensity diminishes, which is inconsistent with the hypothesis that relaxation processes influence spectra of this type. According to calculations[59], the changes in the canonical components of the anisotropic spectra reduce, as already mentioned, to their broadening and displacements and, so long as the component is observed as an isolated component, i.e. the overlap with the neighbouring components has not begun, its integral intensity remains unaltered. The decrease of the integral intensity of the $x$ component observed in the case under consideration can be induced by the scatter of the values of $\tau_C$ in the specimen, so that the component for some of the radicals characterised by short $\tau_C$ is greatly broadened and is not recorded.

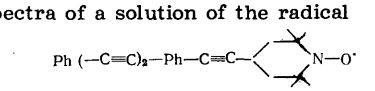
The analysis of the decrease of the intensity of the $x$ component with increase of temperature[44] established the distribution with respect to the activation energies for the movement of the radical and led to the determination of the parameters of this distribution. It must be specially emphasised that, whereas the data obtained previously for the inhomogeneity of the molecular mobility referred to movements involving different types of rotation, in the given instance one is dealing with rotations of a rigorously defined type—about the axis of the polymer chain.

The anisotropy of the rotational mobility is frequently accompanied by the orientational order of the molecules in the specimen. The character of the rotation of the probe molecule is determined by the structure of its immediate environment—the structure of the "cell" in which it is placed. The cell follows to some extent the shape of the probe and is elongated for an elongated species. The probe is oriented preferentially along the long axis of the chain. If the specimen as a whole is disordered, the cells are distributed isotropically. However, the specimen can be also non-isotropic—for example, it can consist of extended polymers, liquid crystals in external fields deposited on the support of the system, etc. In such cases the angular distribution of the probes is also non-isotropic, which is manifested in their EPR spectra.

The possiblity of the analysis of the angular distribution of the radicals on the basis of EPR spectra depends on the anisotropy of their magnetic-resonance parameters, i.e. on the extent to which the resonance fields for different orientations of the radical relative to the direction of the magnetic field of the spectrometer are different. The data presented in the preceding Sections show that only in the millimetre EPR range it is possible to achieve the optimum conditions for the investigation of the anisotropy of the distribution of the nitroxy-radicals widely used as probes and labels as well as peroxy-radicals for which the ~O–O· fragment can be regarded as a paramagnetic label on the "body" of the molecule.

We considered above, in relation to the study of Grinberg et al.[44], how the orientation of PTFE molecules by the stretching of the polymer is manifested in the EPR spectra of peroxy-radicals in the 2-mm range (Figs.12 and 20). It must be emphasised that an increase of the spectral resolution did in fact permit in the given instance a detailed description of the structure of the radical centre (Fig.12) and the differentiation of the individual structures of chemically equivalent radicals.

The study of the orientational order of nitroxy-radicals in the millimetre EPR range is very promising[60]. Fig.2 presents the spectra of a solution of the radical




in MBBA at different temperatures of the measurement. The compound MBBA is characterised by the presence of a nematic phase in the range 290–318 K. The spectrum (Fig.21*a*) of the isotropic liquid phase (above 318 K) has a structure characteristic of the axial symmetry of the $g$- and $A$-tensors and corresponds to probes rapidly rotating around the long $x$ axis of the radical ($g \cong g_{xx}$) and the directions of the $x$ axes are distributed isotropically (analogously to Fig.17*b*). On passing to the nematic phase (Fig.21*b*), the spectrum is localised in the vicinity of the resonance field corresponding to the orientation of the radical with the $x$ axis along the direction of the field. Thus the orientation of the domains of the nematic MBBA in the magnetic field leads to a pronounced (almost complete) orientation of the "cells" containing the probe. This structure of the matrix can be "frozen" by the rapid cooling of MBBA to below 250 K. Fig.21*c* presents the spectrum of the frozen specimen, which is close to the spectrum in Fig.21*b*.

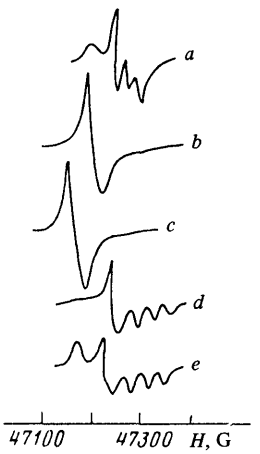



**Figure 21.** EPR spectra of a solution of nitroxy-radicals in MBBA in the 2-mm range. Temperature of the measurement (K): *a*) 320; *b*) 290; *c*)–*e*) 200; *c*) specimen of the nematic phase frozen at 200 K in the field of the spectrometer; *d*) specimen *c* frozen outside the field of the spectrometer; *e*) frozen specimen of the isotropic MBBA phase.

Ordering in the nematic MBBA phase can be induced also under the influence of the walls of the bulb. If the specimen (quartz capillary with an internal diameter of 0.5 mm) is kept at 300 K, is rapidly frozen outside the field, and the EPR is recorded without raising the temperature, then the corresponding spectrum (Fig.21*d*) does not contain the $x$ components, which corresponds to a distribution of the radicals with the $x$ axis preferentially perpendicular to the field [the axis of the bulb in the spectrometer (Fig.1) is perpendicular to the axis of the solenoid]. Freezing of an isotropic phase specimen leads to the spectrum illustrated in Fig.21*e*, which corresponds to a random distribution of the radicals. The loss of orientational order is also observed in frozen specimens subjected to preliminary orientation under the influence of the field of the spectrometer or the walls of the bulb. Under these conditions, in the initial spectrum of the type illustrated in Fig.21*c* the $y$ and $z$ components appear and increase in intensity, the intensity of the $x$ component falls, and in the limit the spectrum tends to the form shown in Fig.21*e*. Such randomisation apparently corresponds to a transition from the vitrified structure of the liquid crystal to the polycrystalline form and is extremely slow (tens of minutes at 250 K).

The example considered demonstrates the possibilities of the millimetre EPR range in the study of the angular distribution of radicals and the factors leading to the establishment and loss of orientational order in the substance.

Whereas in the case of slow molecular movements, the millimetre EPR makes it possible to obtain different qualitative characteristics of the movements of radicals, in the case of rapid movements such EPR permits a considerable expansion of the range of the measured correlation times. In the region of small values of $\tau_C$ the components of the spectrum occupy positions defined by the isotropic (averaged as a result of rotation) values of the magnetic parameters and the widths contain a contribution "incompletely averaged" by the movement. Thus in the simplest case of the frequency exchange between the components of a doublet with a 1:1 intensity ratio separated by a frequency interval $\Delta\omega$, the residual broadening is[61]

$$\delta H \simeq (\Delta\omega)^2\tau_c/\gamma \ .$$

The expresson for $\delta H$ relating to spectra with anisotropic parameters can be more complex (see Chapter III in Berlinger's book[39]), but here too the residual broadening is greater the greater the initial extent of the spectrum in the limit corresponding to slow molecular movements. The range of the averaged frequencies then increases with increase of the polarising field owing to the contribution determined by the anisotropy of the $g$-factor ($\Delta\omega \cong \gamma\Delta g H_0$), so that complete averaging in the spectra in the millimetre range requires higher frequencies of the movement than in the 3-cm range.

The limits within which $\tau_C$ is accessible to measurement which are attainable in the 3-cm and 2-mm ranges have been compared[62]. It was shown that, on the side of rapid movements, the boundary of the measured correlation times shifts from $6\times10^{-11}$ to $4\times10^{-12}$ s on passing from the three-centimetre range to the two-millimetre range. The above values change somewhat when the matrix is replaced or when the structure of the probe is altered as a result of a change in the limiting (not averaged by rotation) line width, but the overall effect of the transition to the 2-mm range (amounting to more than an order of magnitude) is preserved.

## V. CONCLUSION

The results presented above, obtained with the aid of EPR in the two-millimetre range, demonstrate, in the present authors' view, the possibility of obtaining qualitatively new information in fields such as the metrology of free radicals, the study of molecular mobility, the study of the electronic and geometrical structures of radicals and biradicals, the study of matrix effects, etc. It is important to note that the qualitative leap forward is due to the appearance of the possibility of measuring electron spin resonance in strong fields over a wide temperature range and in objects of different types, characteristic of both chemistry and biology. All the advances enumerated above are associated with the increase of the resolving power of the method. The relative increase of frequency on passing from the 8-mm range, adopted for a long time, to the 2-mm range does not exceed the increase of the frequency on passing from the 3-cm to the 8-mm range, but experiment confirmed the estimates presented at the beginning of this review, according to which conditions leading to a high resolution of the spectra of typical organic free radicals occur precisely in the wavelength range shorter than 3 mm. This makes it possible to regard the EPR spectroscopy in the two-millimetre range as a method for the investigation of free radicals which has a high resolving power with respect to the $g$-factors. Apart from the applications already tested, one may specify a series of further applications whose likely usefulness follows from the parmeters attained in the EPR in the millimetre range.

The high absolute sensitivity ($\sim5\times10^7$ spin $G^{-1}$) can be used for the investigation of micro-objects. With this sensitivity, it is easy to show by calculation that the signal due to $10^{-13}$ g of the stable DPPH radicals can be recorded. If a spin-labelled object with a concentration of the usual spin labels of $10^{-5}$ mole $cm^{-3}$ is used, then a specimen with a linear dimension of 2–3 μm can be used to measure the spectrum, i.e. in principle there is a possibility of investigating individual living cells, etc. For ferromagnetic particles with a narrow ferromagnetic resonance line, the lower limit of the size of the specimen may be only $10^{-15}$ $cm^3$.

The high absolute sensitivity combined with a high resolution with respect to the $g$-factor, which makes it possible to detect the perturbations induced by weak intra-electronic and interelectronic interactions, makes it possible, in principle, to use the EPR millimetre range for microchemical analysis using stable radicals as specific reagents. The high absolute sensitivity and also the high sensitivity to the angular orientation of the paramagnetic centre in the presence of the anisotropy of the $g$-factor make EPR in strong fields a promising procedure for tomography (zeugmatography) of small objects with a higher spatial resolution than in NMR or EPR in the centimetre range. Estimates have shown that in favourable situations (high concentrations, narrow lines) the spatial resolution can reach 0.1–1 μm.

The suppression of forbidden transitions and the weakening of the interaction between the individual resonances make EPR in intense fields a convenient method for the investigation of the relaxation effects, transmission effects, and the transfer of saturation.

Thus by no means all the possibilities inherent in the EPR spectroscopy of the two-millimetre range have been so far realised. All this gives rise to the hope that greater sophistication of the experimental technique associated with the transition to the range of millimetre wavelengths will be justified by the increase of the amount of information derivable from the measurements and the expansion of the applications of the EPR method.

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