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2-mm WAVE BAND  
EPR SPECTROSCOPY of  
CONDENSED SYSTEMS

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Victor I. Krinichnyi

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## PREFACE

Recent years have been characterized by widespread development of electron paramagnetic spectroscopy (EPR spectroscopy) in the millimeter and submillimeter ranges, which seems to be more promising in the studies of condensed systems. However, this development faces some difficulties associated mainly with a weak and complicated element base (SHF elements, including a cavity, cryogenic equipment, etc.), sample preparation procedure, and appropriate investigation methods.

From its appearance in the 1960s, the idea of broadening the EPR spectroscopy frequency range seemed to be mainly an intellectual game without concrete theoretical and practical future application. It was stipulated mainly by fragmentary investigations of specific objects in the millimeter EPR range, which could not enable full and clear arguments, thus proving the necessity of the development of EPR spectroscopy directed towards the increase of registration frequency. However, the elaboration and creation of the first multifunctional universal 2-mm wave band EPR spectrometer at the Russian Institute of Chemical Physics allowed the successful investigation of various condensed systems (solutions, polymers, etc.), in which complex molecular and relaxation processes occur, including slow anisotropic motions, cross-relaxation, etc. This development resulted in a wave of enthusiasm among chemists, physicists and biologists, and an explosive development of applications of various methods. However, today the importance of 2-mm EPR spectroscopy is not its successful application but the potential to obtain new qualitative information on well-known compounds and to understand various phenomena, from specific interactions and correlated relaxation in condensed media to charge transfer in biological systems and polymer semiconductors. This new appreciation of the essence of quantum mechanical phenomena lies beyond the framework of electron paramagnetic resonance as a special discipline and no doubt will promote a breakthrough in such other fields as biology, physics, and chemistry.

The present book appears as a monograph on the application of high-frequency 2-mm EPR spectroscopy to the study of physical-chemical properties of various condensed systems and their interpretation from the standpoint of modern conceptions of molecular physics. The methods of measurements at 2-mm wave band EPR considered here found their application in the investigation of both simple (solutions, ion crystals) and complex (biopolymers, enzymes, conducting polymers, ion-radical salts, etc.) condensed systems, and their potential is not yet exhausted. 2-mm wave band EPR spectroscopy enables the profound investigation of the structure, dynamics, other specific characteristics of radical centers and their local environment, and elementary charge transfer processes in these systems.

The monograph contains mainly the original results, obtained by the author in the last decade, of the investigation of various model, biological, and other high-molecular weight compounds by 2-mm wave band EPR spectroscopy. Therefore, special attention is paid to the description of various practical applications of the method in the study of liquids and solids.

The first chapter follows the Introduction, which appears as a brief survey of the main stages of millimeter EPR spectroscopy development. Chapter 1 presents a concise summary of the theoretical fundamentals of EPR spectroscopy and a body of mathematics necessary for the interpretation of

experimental results. It considers the most important magnetic resonance parameters of paramagnetic centers, the processes of spin relaxation, and the factors affecting it. Among them various experimental approaches of EPR spectroscopy are considered such as steady-state signal saturation, the saturation transfer method, and the method of spin label and probe, which is necessary for the investigation of various properties of condensed systems.

The success of 2-mm EPR spectroscopy is attributed mainly to a high spectral resolution over the  $g$ -factor. Chapter 2 describes the reason for the choice of the 2-mm wave band for registering EPR spectra of organic radicals, and the advantages of 2-mm wave band EPR spectroscopy are manifested by using organic peroxide and nitroxide radicals in model systems. This chapter contains the description of the development of steady-state saturation of spin-packets, microspin label and probe, macrospin probe, and saturation transfer methods applied to 2-mm wave band registration, which enables a more accurate and complete analysis of dynamic and relaxation properties of radical microenvironments in condensed systems.

Chapter 3 starts with the analysis of the restrictions of the common EPR method in the study of biological systems and exhibits the data, confirming the advantages of 2-mm EPR spectroscopy in investigating the structure, dynamics, and polarity of radical microenvironments in real biological objects.

And finally, Chapter 4 contains the discussion of the principal results obtained by using 2-mm wave band EPR for studying structural and electrodynamic peculiarities of the known conducting compounds, such as conjugated polymers, ion-radical salts, and high-temperature superconductors.

In order to appeal to a wide range of readers, the book provides the examples of experimental investigation of various classes of compounds, offering a more complete study of the systems.

Although this monograph is devoted almost entirely to EPR spectroscopy, it should be emphasized that it might be considered only as one of numerous useful and fruitful methods on the general background of physics and chemistry of condensed media. All the results obtained with this method attain their whole significance only by being combined with the data obtained by other methods. The results, presented in Sections 2.IV, 3.II, and 4.I may be considered as examples.

The author hopes that this book will be valuable to radio spectroscopists and investigators in neighboring branches of science such as molecular biology, radiation and photochemistry, organic and analytical chemistry, liquid and solid state physics, and for students specializing in chemistry, physics, and biology.

The author is very grateful to his teachers Professor Ya. S. Lebedev and Professor G. I. Likhtenstein, who promoted the development of his interests in classic and millimeter EPR spectroscopy.

The author expresses his gratitude to his colleagues, who contributed by carrying out the experiments and taking part in the discussion. The author is especially grateful to O. Ya. Grinberg, A. A. Dubinski, A. V. Kulikov, L. M. Goldenberg, I. B. Nazarova, S. D. Cheremisov, H.-K. Roth, K. Lüders, F. Lux, A. E. Pelekh, S. A. Brazovskii, L. I. Tkachenko, and O. N. Efimov.

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## THE AUTHOR

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Dr. Krinichnyi received his higher education at Kazan State University. His Ph.D. thesis research concerned 2-mm wave band EPR spectroscopy as a method of investigation of paramagnetic centers in biological and conducting organic polymers. After obtaining his Ph. D. in 1986 he joined the Institute of Chemical Physics in Chernogolovka as a scientific researcher, and since 1991 he has been employed as a senior scientific researcher in the same institute. He received his Dr. Sci. degree in physics and mathematics in 1992 after completing research on high resolution 2-mm wave band EPR spectroscopy in the study of biological and conducting polymers.

From 1989 to 1991 he headed a group of young scientists dealing with the synthesis and study of organic conducting and inorganic superconducting compounds as basic materials for molecular electronics, a project sponsored by the Russian Academy of Sciences.

Since 1975 Dr. Krinichnyi has published over 60 scientific papers relating mainly to the development of high resolution EPR spectroscopy for the investigation of various model, biological, and organic high-molecular weight compounds. He has collaborated with colleagues in Russia, Germany, France, Israel, and Japan.

Dr. Krinichnyi is also the author of three reviews concerned with the investigation of biological systems by high resolution 2-mm wave band EPR, published in the *Journal of Applied Spectroscopy* (in Russian), the *Journal of Biochemical and Biophysical Methods*, and *Applied Magnetic Resonance*.

At present his research in the physics of condensed matter is mainly concerned with the practical application of 2-mm wave band EPR spectroscopy in the study of biological systems with emphasis on the study of conducting polymers and high-temperature superconductors. Concerning these materials Dr. Krinichnyi's focus is on the analysis of dynamic properties of nonlinear excitations in conducting polymers and other compounds. The results of his investigations were reported at the Technology Universities of Leipzig and Berlin.



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## LIST OF SYMBOLS AND ABBREVIATIONS

- A** tensor of hyperfine interaction  
**A** anisotropic hyperfine interaction constant  
**A** orientation degree of chains (Eqs. 161-164)  
**a** isotropic hyperfine interaction constant  
 $\langle a \rangle = \frac{1}{3} \sum A_{ii}$  averaged hyperfine interaction constant  
 $a_N^0$  unperturbable hyperfine interaction constant (Eqs. 102, 104, 107, 108)  
**A/B** asymmetry factor of EPR spectrum  
**B<sub>0</sub>** external magnetic field vector  
**B<sub>0</sub>** external magnetic field modulus ( $1T = 10^4$  Oe, G)  
**B<sub>1</sub>** amplitude of magnetic component of polarizing field  
**B<sub>c1</sub>** lower critical magnetic field in superconductor  
**B<sub>m</sub>** amplitude of modulation of external magnetic field  
**B<sub>loc</sub>** local magnetic field strength  
**c** light velocity ( $c = 2.9979 \cdot 10^8$  m s<sup>-1</sup>)  
**D** diffusion coefficient (m<sup>2</sup>s<sup>-1</sup>)  
**d** dimensionality of a disordered system (Eqs. 58, 150, 152)  
**E** energy (1 eV =  $1.6021 \cdot 10^{-19}$  J =  $8.0660 \cdot 10^3$  cm<sup>-1</sup>)  
**E<sub>α(β)</sub>** eigenvalues of spin Hamiltonian  
**E<sub>a</sub>** activation energy (eV)  
**E** electrostatic field strength  
**e** elementary charge ( $e = 1.6022 \cdot 10^{-19}$  K)  
**f(r)** spherically symmetric function  
**g** splitting tensor  
**g** Lande splitting factor ( $g_e = 2.00232$  for free electron)  
 $\langle g \rangle = \frac{1}{3} \sum g_{ii}$  averaged *g*-factor  
**g<sub>iso</sub>** isotropic *g*-factor  
**g(ω)** factor of line shape  
**H** enthalpy  
**ℋ** Hamiltonian of magnetic interaction  
**h = 2πℏ** Planck quantum constant ( $h = 6.6262 \cdot 10^{-34}$  Js)  
**I** transfer integral  
**I** nuclear spin  
**I** ionization potential  
**I<sub>c</sub>** Coulombic integral (Eq. 120)  
**I<sub>c</sub>** critical current for type-II superconductor  
**I<sub>i</sub>** intensity of *i*th spectral component (Eq. 109)  
**J** total electron angular momentum  
**J(ω)** spectral density function  
**k** Boltzmann constant ( $k = 1.3807 \cdot 10^{-23}$  JK<sup>-1</sup>)



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- $k$  reaction rate constant (Eqs. 140–142)
- $k_f$  coefficient of cavity filling (Eq. 116)
- $L$  total orbital moment of electron
- $M_0$  equilibrium magnetization of spin ensemble
- $M$  total magnetization of spin ensemble
- $M$  molecular mass (Eqs. 108, 124)
- $m_e$  mass of electron ( $m_e = 9.1095 \cdot 10^{-31}$  kg)
- $m$  orientation magnetic number (Eqs. 3, 5, 6, 30, 34, 91, 92)
- $N_{\alpha, \beta}$  population of electron energy levels (Eqs. 12, 13)
- $N$  number of spins in volume unit ( $m^{-3}$ )
- $N$  halfwidth of nonlinear excitations in cell units (Eq. 165)
- $n(\epsilon_F)$  density of states at the Fermi level  $\epsilon_F$
- $n$  concentration of paramagnetic centers per monomer unit
- $P$  probability (Eqs. 52–54, 135)
- $P(r_0, r, t)$  spin motion propagator (Eqs. 55–57, 61, 62)
- $P$  power of microwave oscillator (Eq. 116)
- $Q$  quality of MWF cavity (Eq. 116)
- $Q$  McConnell proportionality constant (Eq. 38) ( $Q = 2 \div 3$  mT)
- $R$  relative humidity degree
- $r$  radius vector between two dipoles
- $r_{NO}$  distance between N and O atoms in nitroxide radical
- $r'$  hydrodynamic radius of nitroxide probe
- $S$  spin quantum number
- $S$  total electron spin of molecule
- $s$  saturation factor
- $T_1$  electron longitudinal (spin-lattice) relaxation time
- $T_2$  electron transverse (spin-spin) relaxation time
- $t$  time
- $T$  absolute temperature (K)
- $U_n(\omega)$  dispersion signal component detected in phase with respect to applied Zeeman modulation at the  $n$ th harmonic of modulation
- $U'_n(\omega)$  dispersion signal component in  $\pi/2$ -out-of-phase (in phase quadrature) with respect to applied modulation detected at the  $n$ th harmonic of modulation
- $u_i$  amplitude of dispersion signal  $i$ th component (Eqs. 100, 136–139)
- $V$  sample volume
- $V_n(\omega)$  absorption signal component detected in phase with respect to applied Zeeman modulation at the  $n$ th harmonic of modulation
- $V'_n(\omega)$  absorption signal component  $\pi/2$ -out-of-phase (in phase quadrature) with respect to applied modulation detected at the  $n$ th harmonic of modulation
- $V$  potential with matrix elements  $V_i$  (Eqs. 102, 103)
- $v$  velocity (Eq. 166)

- $W_{\alpha\beta}$  power absorbed by spin ensemble at  $\alpha \rightarrow \beta$  transition (Eq. 13)  
 $x, y, z$  axes of molecular coordinate system  
 $\alpha$  decay length of localized state  
 $\alpha, \beta$  spin levels  
 $\langle \alpha | \mu | \beta \rangle$  matrix element of magnetic moment component  
 $\beta$  resonance integral of C = C coupling (Eqs. 102, 104, 107, 108)  
 $\gamma_e$  gyromagnetic ratio for electron ( $\gamma_e = 1.7608 \cdot 10^{11} \text{ T}^{-1}\text{s}^{-1}$ )  
 $\gamma_p$  gyromagnetic ratio for proton ( $\gamma_p = 2.6751 \cdot 10^8 \text{ T}^{-1}\text{s}^{-1}$ )  
 $\Delta B_{pp}$  linewidth from peak to peak  
 $\Delta E_{\alpha\beta}$  difference in electron energy  $\alpha$  and  $\beta$  levels  
 $\Delta G$  profile of reaction (Eq. 143)  
 $\Delta\omega$  anisotropy of magnetic interaction  
 $\Delta\omega_{ij}$  distance between a spin packets in frequency units  
 $\langle \Delta\omega^2 \rangle$  second momentum of absorption signal  
 $\delta$  skin layer thickness  
 $\delta\Delta B_{pp}$  spectral line broadening  
 $\delta B$  shift of spectral line  
 $\epsilon$  dielectric constant  
 $\epsilon_F$  Fermi energy level  
 $\xi$  decay length for charge carries (Eq. 146, 147)  
 $\xi$  superconducting coherence length  
 $\eta$  coefficient of dynamic viscosity  
 $\eta_r$  anisotropy parameter of radical rotation (Eq. 125)  
 $\kappa$  parameter of rotation diffusion of a radical (Eq. 110)  
 $\Lambda$  soliton width (Eq. 166)  
 $\lambda$  spin-orbit coupling constant (eV)  
 $\mu_e$  electron magnetic moment  
 $\mu_I$  nuclear magnetic moment  
 $\mu_B$  Bohr magneton ( $\mu_B = 9.2741 \cdot 10^{-24} \text{ J T}^{-1}$ )  
 $\mu_0$  permeability for vacuum ( $\mu_0 = 4\pi \cdot 10^{-7} \text{ VsA}^{-1}\text{m}^{-1}$ )  
 $\mu$  dipole moment (Eqs. 105–108)  
 $\mu$  mobility  
 $\nu_e$  resonance frequency for free electron  
 $\nu_{ex}$  frequency of spin-packets exchange  
 $\rho(r)$  density of unpaired electron at  $r$  distance from nucleus  
 $\rho$  apparent density of radical microenvironment  
 $\sigma_{AC}$  alternating current electric conductivity ( $\text{Sm}^{-1}$ )  
 $\sigma_{DC}$  direct current electric conductivity ( $\text{Sm}^{-1}$ )  
 $\sigma_{nD}$  nD specific conductivity  
 $\sigma$  cross section of irradiation process (Eqs. 140, 141)  
 $\tau$  effective relaxation time

**x**

- $\tau_c$  correlation time of radical rotation  
 $\tau_m$  mechanical relaxation time (Eqs. 132, 133)  
 $\chi$  magnetic susceptibility with real ( $\chi'$ ) and imaginary ( $\chi''$ ) components  
 $\chi_0$  static magnetic susceptibility of spin ensemble  
 $\Psi(r)$  wave function for electron localization ( $\Psi^2(r) = \rho(r)$ )  
 $\omega_e$  resonance angular frequency of electron transition between  $\alpha$  and  $\beta$  levels  
 $\omega_L$  Larmor angular frequency of electron precession  
 $\omega_m$  angular frequency of Zeeman magnetic modulation  
AC alternating current  
DC direct current  
EPR electron paramagnetic resonance  
HFI hyperfine interaction  
HFS hyperfine structure  
HTSC high-temperature superconductor  
MRP magnetic resonance parameter  
MWF microwave frequency  
NMR nuclear magnetic resonance  
NR nitroxide radical  
PR peroxide radical  
*ppm* percents per million cell units  
SOI spin-orbital interaction

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## INTRODUCTION

EPR spectroscopy is one of the most widely used and productive physical methods in structural and dynamic studies of various condensed systems that contain free radicals, ion-radicals, molecules in triplet states, transition metal complexes, and other paramagnetic centers (PCs).

EPR spectroscopy became a powerful investigation tool after Zavoiskii carried out the first electron relaxation studies in salts.<sup>1</sup> From that moment this method began to play an important role and is used successfully in physical, chemical, and biological investigations. Many fundamental and general works concerning this field of knowledge<sup>2-20</sup> are evidence of this process.

This method can be applied the most effectively to the study of elementary chemical reactions. Voevodskii, who was the first in these investigations, found<sup>21</sup> that transformation mechanisms in oxidation and cracking, radiolysis and photolysis, homogeneous and heterogeneous catalysis, and chemical processes were stipulated mainly by the properties of PC and especially free radicals, involved in these processes.

EPR has been widely used in recent decades for solving such important problems of chemical and biological physics as the elucidation of the role of electron transport in biological processes, the effect of molecular dynamics in viscous and heterogeneous media on the rate and mechanism of transformations which occur there,<sup>6, 16, 18</sup> etc.

EPR gave rise to the development of the method of spin labels and probes, suggested by Hamilton and McConnell,<sup>22</sup> which provided significant progress in the study of biological substrates, polymers, and other condensed systems.<sup>23-30</sup> The success was achieved due to the unique properties of nitroxide radicals, which were commonly used as spin labels and probes, and the development of biochemistry. However, the utilization of the EPR method as a sensitive and informative instrument<sup>26, 27</sup> played a dominant role in these investigations.

In solving these problems the restrictions of the EPR method emerged clearly, being associated in particular with the fact that the signals of organic free radicals were registered in a narrow magnetic field range, which resulted in the overlapping of the lines of complex spectra or spectra of different radicals with close  $g$ -factor values. Thus, new experimental techniques that improve the efficiency of the method and open absolutely new fields of application have been recently developed. They are laser spectroscopy of magnetic resonance at submillimeter<sup>31</sup> and near-infrared<sup>32</sup> wave bands, which are generally used to study radical reactions in gas phase; electron spin echo spectroscopy,<sup>33, 34</sup> which is used mainly to study PC in solids; different methods based on the effect of spin polarization, in which the EPR signal is registered optically<sup>35</sup> or, depending on the change of chemical yield,<sup>36-38</sup> methods of double electron-nuclear resonance;<sup>39, 40</sup> EPR spectroscopy with microwave frequency (MWF) saturation transfer;<sup>41</sup> EPR in inhomogeneous fields;<sup>42</sup> and some others.

However, most of these methods may be applied only to solve specific problems and investigate special objects. The transition to higher magnetic fields and registration frequencies is known to be the most common method to elevate the precision and informativeness of the method.

This practice was already used successfully to enhance the sensitivity and resolution of nuclear magnetic resonance (NMR),<sup>43</sup> which is complementary to EPR. However, a similar approach was almost not applied to widen EPR

spectroscopy possibilities. This may be explained by the fact that the element base of 3-cm and 8-mm wave bands was found to be suitable initially, since it satisfied the standards of resolution and sensitivity,<sup>4,49</sup> and, thus, was widely used. Besides, some difficulties exist with the selection of MWF radiation source of sufficient power in the millimeter wave band as well as with the generation of strong magnetic fields with the intensity of several Tesla.

In the 1970s an EPR spectrometer of 2-mm wave band containing superconducting solenoid<sup>44</sup> was designed at the Institute of Chemical Physics, Russia, for physical-chemical investigations. It was the first in a series of analogous devices, which are still unique. These spectrometers are especially characterized by a high spectral resolution and an absolute sensitivity of  $5 \cdot 10^{11}$  spin/T.

This book reports on the possibilities of 2-mm wave band EPR spectroscopy of high spectral resolution over  $g$ -factor and reviews the principal results obtained in the investigation of various condensed systems at this wave band.

The first chapter includes a brief description of some EPR fundamentals, which are to be used to interpret experimental results.

The second chapter contains a consideration of the methodic foundation of 2-mm wave band EPR spectroscopy, and some results of the study of model systems are presented, which reveal the possibilities of high resolution over  $g$ -factor in the study of different condensed systems.

The results presented in the third chapter confirm the principal advantages of the method in investigating the structure, conformation, and molecular dynamics of biological objects with spin labels and probes.

The fourth chapter considers 2-mm EPR spectroscopy possibilities in the study of a large group of organic polymer semiconductors and other conducting compounds.