

Preface

Electron paramagnetic resonance (EPR) spectroscopy [1-3] is the most selective, best resolved, and a highly sensitive spectroscopy for the characterization of species that contain unpaired electrons. After the first experiments by Zavoisky in 1944 [4] mainly continuous-wave (CW) techniques in the X-band frequency range (9-10 GHz) were developed and applied to organic free radicals, transition metal complexes, and rare earth ions. Many of these applications were related to reaction mechanisms and catalysis, as species with unpaired electrons are inherently unstable and thus reactive. This period culminated in the 1970s, when CW EPR had become a routine technique in these fields. The best resolution for the hyperfine couplings between the unpaired electron and nuclei in the vicinity was obtained with CW electron nuclear double resonance (ENDOR) techniques [5].

Starting in the 1960s, stable free radicals of the nitroxide type were developed as spin probes that could be admixed to amorphous or weakly ordered materials and as spin labels that could be covalently attached to macromolecules at sites of interest [6,7]. In parallel, theory was developed for analyzing linewidths and lineshapes in CW EPR spectra in terms of molecular dynamics [8-10]. At about the same time a few select groups in the Soviet Union and the USA worked on pulse experiments, using spin echo phenomena to measure electron spin relaxation [11], to detect hyperfine couplings by electron spin echo envelope modulation (ESEEM) techniques [12], to acquire ENDOR spectra in a broader temperature range than with CW methods [13], and to measure distances between electron spins [14]. These developments were pursued by physicists, were heavily focused on methodology, and were hardly recognized by mainstream chemists even by the end of the 1980s when the groundwork was all done. As a result, EPR spectroscopy acquired the reputation of an old-fashioned, somewhat obscure technique applicable to only a small range of compounds. Many chemistry departments considered it as dispensable.

Several developments in the 1990s prepared the stage for the renaissance of EPR spectroscopy that we now experience. Concepts of pulse NMR were introduced into pulse EPR [15,16], which lead to a zoo of new experiments for the separation of different interactions of the electron spin with its environment [3]. After an

induction period a new generation of EPR spectroscopists started using these techniques in the established application fields of transition metal catalysis and metalloenzymes. Within the same decade the application field in structural biology was extended tremendously by the introduction of site-directed spin labeling [17], which made diamagnetic proteins accessible to EPR spectroscopy, among them many that were difficult to study by x-ray crystallography or NMR spectroscopy. The third major development of the 1990s was the systematic combination of EPR measurements at multiple frequencies (multi-frequency EPR) to study more complex problems, and, in particular, the extension to higher fields and frequencies, made possible by new microwave technology and by the superconducting magnet technology developed for NMR spectroscopy [18,19].

This volume of *Topics in Current Chemistry* is devoted to the consequences that these three parallel developments have had on the application field of EPR spectroscopy. It is no exaggeration to state that the major part of the systems studied nowadays by EPR spectroscopy was inaccessible two decades ago and that for the remaining systems information can be obtained, which was inaccessible at that time. The scope of EPR spectroscopy arising from this combination has been hardly realized even by the most advanced practitioners.

This volume starts with three chapters that illustrate the wealth of information which can now be obtained in some of the traditional application fields of EPR spectroscopy. Chapter 1 by S. Van Doorslaer and D. Murphy is an in-depth review on work in catalysis focusing on the mechanistic information that can be obtained from EPR spectra. Work on radical enzymes is exemplified in Chapter 2 by S. Weber and E. Schleicher on the example of flavoproteins which play a role in both chemically and light-activated electron transfer processes. Chapter 3 on synthetic polymers by D. Hinderberger argues that careful analysis of mundane nitroxide spin label or spin probe CW EPR spectra can reveal a lot of information which is hard to obtain by any other characterization technique.

The following three chapters explore the opportunities provided by site-directed spin labeling of diamagnetic biomacromolecules. Intrinsically disordered proteins are one class of such biomacromolecules that is hard to characterize by established techniques. Chapter 4 by M. Drescher discusses how EPR spectroscopy can contribute to better understanding of these proteins. The main application of site-directed spin labeling techniques is on membrane proteins, which are more difficult to study by crystallography and high-resolution NMR spectroscopy than soluble proteins. EPR on membrane proteins is treated in Chapter 5 by E. Bordignon, with an emphasis on the nuts and bolts of the approach. During the past few years application of spin label EPR to nucleic acids has emerged, and Chapter 6 by I. Krstić, B. Endeward, D. Margraf, A. Marko, and T. Prisner provides a comprehensive overview of both spin labeling and EPR techniques applied in this field and on the information that can be obtained.

Finally, an emerging application field is discussed. The application to molecular magnets is a result of parallel development of new approaches in inorganic chemistry and new high-field and high-frequency EPR technologies. In Chapter 7 J. van Slageren discusses the newly emerging technologies of frequency-domain

magnetic resonance and Terahertz spectroscopy and the importance of relaxation studies in the field of molecular nanomagnetism.

Due to space limitations only a selected range of systems can be covered. Recent good reviews exist about EPR spectroscopic studies on photosynthesis [20-22] and metalloproteins [23-26]. Strongly physics-related application fields, such as quantum computing [27], electrically detected [28] and optically [29] detected EPR spectroscopy of dopants and defects in solids are left out. Furthermore, this volume does not cover technical issues that are mainly of interest to method developers rather than chemists. Pulse EPR spectroscopy [3], high-field EPR spectroscopy [19], and quantum chemical computation of EPR parameters [30] were all subject of monographs. Note also that EPR distance measurements between spin labels in biological systems are covered by two forthcoming volumes of the series *Structure and Bonding* that are edited by C. Timmel and J. Harmer.

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References

1. J. A. Weil, J. R. Bolton, J. E. Wertz, *Electron Paramagnetic Resonance*, Wiley, New York (1994)
2. N. M. Atherton, *Principles of Electron Spin Resonance*, Ellis Horwood, New York (1993)
3. A. Schweiger, G. Jeschke, *Principles of Pulse Electron Paramagnetic Resonance*, Oxford University Press, Oxford, 2001.
4. E. Zavoisky, *J. Phys. USSR* **1945**, 9, 211-216.
5. H. Kurreck, B. Kirste, W. Lubitz, *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*, VCH Publishers, New York (1988)
6. A. K. Hoffmann, A. T. Henderson, *J. Am. Chem. Soc.* **1961**, 83, 4671-4672.
7. O. H. Griffith, A. S. Waggoner, *Chem. Rev.* **1969**, 2, 17-24.
8. D. Kivelson, *J. Chem. Phys.* **1960**, 33, 1094-1106.
9. J. H. Freed, G. K. Fraenkel, *J. Chem. Phys.* **1963**, 39, 326-348.
10. J. H. Freed, G. V. Bruno, C. F. Polnaszek, *J. Phys. Chem.* **1973**, 75, 3385-3399.
11. A. M. Raitsimring, K. M. Salikhov, B. A. Umanskii, Y. D. Tsvetkov, *Fiz. Tverd. Tela* **1974**, 16, 756-766.
12. W. B. Mims, *Phys. Rev. B* **1972**, 5, 2409-2419.
13. W. B. Mims, *Proc. Roy. Soc. London A*, **1965**, 283, 452-457.
14. A. D. Milov, K. M. Salikhov, M. D. Shirov, *Fiz. Tverd. Tela* **1981**, 23, 975-982.
15. P. Höfer, A. Grupp, H. Nebenführ, M. Mehring, *Chem. Phys. Lett.* **1986**, 132, 279-282.
16. J. M. Fauth, A. Schweiger, L. Braunschweiler, J. Forrer, R. R. Ernst, *J. Magn. Reson.* **1986**, 66, 74-85.
17. W. L. Hubbell, D. S. Cafiso, C. Altenbach, *Nat. Struct. Biol.* **2000**, 7, 735-739.
18. A. K. Hassan, L. A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer, L. C. Brunel, *J. Magn. Reson.* **2000**, 142, 300-312.
19. K. Möbius, A. Savitsky, *High-Field EPR Spectroscopy on Proteins and their Model Systems: Characterization of Transient Paramagnetic States*, RSC Publishing, Cambridge, 2008.
20. A. Savitsky, K. Möbius, *Photosynth. Res.* **2009**, 102, 311-333.
21. A. van der Est, *Photosynth. Res.* **2009**, 102, 335-347.

22. G. Kothe, M. C. Thurnauer, *Photosynth. Res.* **2009**, *102*, 349-365.
23. M. E. Pandelia, H. Ogata, W. Lubitz, *ChemPhysChem* **2010**, *11*, 1127-1140.
24. B. M. Hoffman, D. R. Dean, L. C. Seefeldt, *Acc. Chem. Res.* **2009**, *42*, 609-619.
25. R. Davydov, B. M. Hoffman, *Arch. Biochem. Biophys.* **2011**, *507*, 36-43.
26. J. Harmer, G. Mitrikas, A. Schweiger *Biol. Magn. Reson.* **2009**, *28(1)*, 13-61.
27. M. Mehring, J. Mende, W. Scherer, *Phys. Rev. Lett.* **2003**, *90*, 153001.
28. A. R. Stegner, C. Boehme, H. Huebl, M. Stutzmann, K. Lips, M. S. Brandt, *Nature Physics* **2006**, *2*, 835-838.
29. L. Childress, M. V. G. Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hemmer, M. D. Lukin, *Science* **2006**, *314*, 281-285.
30. M. Kaupp, M. Bühl, V. G. Malkin, *Calculation of NMR and EPR Parameters. Theory and Applications*, Wiley-VCH, Weinheim, 2004.

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