

CONTENTS

FOREWORD	xiii
PREFACE	xv
CONTRIBUTORS	xvii
I PRINCIPLES	1
1 Introduction to Electron Paramagnetic Resonance	3
<i>Carlo Corvaja</i>	
1.1 Chapter Summary	3
1.2 EPR Spectrum: What Is It?	4
1.3 The Electron Spin	5
1.4 Electron Spin in a Magnetic Field (Zeeman Effect)	6
1.5 Effect of Electromagnetic Fields	8
1.6 Macroscopic Collection of Electron Spins	8
1.7 Observation of Magnetic Resonance	10
1.8 Electron Spin in Atoms and Molecules	11
1.9 Macroscopic Magnetization	14
1.10 Spin Relaxation and Bloch Equations	16
1.11 Nuclear Spins	18
1.12 Anisotropy of the Hyperfine Interaction	22
1.13 ENDOR	25
1.14 Two Interacting Electron Spins	28
1.15 Quantum Machinery	31
1.16 Electron Spin in a Static Magnetic Field	32
1.17 Electron Spin Coupled to a Nuclear Spin	32
1.18 Electron Spin in a Zeeman Magnetic Field in the Presence of a Microwave Field	34
2 Basic Experimental Methods in Continuous Wave Electron Paramagnetic Resonance	37
<i>Peter Höfer</i>	
2.1 Instrumental Components of a Continuous Wave Electron Paramagnetic Resonance (CW-EPR) Spectrometer	37
2.2 Experimental Techniques	52

Acknowledgment	80
References	80
Bibliography	82

3 What Can Be Studied with Electron Paramagnetic Resonance? 83

Marina Brustolon

3.1 Introduction	83
3.2 Organic Radicals	84
3.3 Organic Molecules with More than One Unpaired Electron	92
3.4 Inorganic Radicals, Small Paramagnetic Molecules, and Isolated Atoms	96
3.5 Transition Metal Ions	98
3.6 Natural Systems and Processes	100
3.7 Tailoring and Assembling PS for Magnetic Materials	102
3.8 Industrial Applications of EPR	104
References	105
Bibliography	107

4 Electron Paramagnetic Resonance Spectroscopy in the Liquid Phase 109

Georg Gescheidt

4.1 General Considerations	109
4.2 Generation of Radicals and Radical Ions	110
4.3 Basic Interactions and Principles	116
4.4 Patterns and Line Shapes of Fluid-Solution EPR Spectra	120
4.5 Transition-Metal Ions	132
4.6 Biradicals	133
4.7 Simulation Software	134
4.8 How Fluid-Solution Spectra are Analyzed	135
4.9 Calculation of EPR Parameters	138
4.10 Molecular Properties Mirrored by EPR Spectra in Fluid Solution	139
4.11 Chemically Induced Dynamic Electron Polarization (CIDEP) and CID Nuclear Polarization (CIDNP): Methods to Study Short-Lived Radicals	151
Acknowledgments	154
References	154
Further Reading	157

5 Pulsed Electron Paramagnetic Resonance 159

Michael K. Bowman

5.1 Introduction	159
5.2 Vector Model for Pulsed EPR	162
5.3 Pulse Sequences	172

5.4	Data Analysis	185
5.5	Spectrometer	187
	References	193
6	Electron Paramagnetic Resonance Spectra in the Solid State	195
	<i>Marina Bennati and Damien M. Murphy</i>	
6.1	Introduction	195
6.2	Anisotropy of the Zeeman Interaction: The \mathbf{g} Tensor	198
6.3	The Hyperfine Interaction in the Solid State	209
6.4	TMIs	229
6.5	EPR Spectra for $S > 1/2$: ZFS	233
	References	237
	Appendix A.6.1 Simple Matrix Manipulations	239
	Appendix A.6.2 Pauli Matrices	241
	Appendix A.6.3 Transformation of Tensor Coordinates Via Matrices	241
	Appendix A.6.4 Euler Angles	243
	Appendix A.6.5 Matrix Elements of Spin–Orbit Coupling	246
	Appendix A.6.6 Origin of the g and A Values for simple TMIs	246
	Appendix References	249
7	The Virtual Electron Paramagnetic Resonance Laboratory: A User Guide to <i>ab initio</i> Modeling	251
	<i>Vincenzo Barone and Antonino Polimeno</i>	
7.1	Introduction	251
7.2	Modeling Tools	255
7.3	Tutorial and Case Studies	262
7.4	Conclusions	281
	References	283
II	APPLICATIONS	285
8	Spin Trapping	287
	<i>Angelo Alberti and Dante Macciantelli</i>	
8.1	What Is Spin Trapping and Why Use It?	287
8.2	Spin Traps	288
8.3	Experimental Methods	317
8.4	Applications	317
8.5	Spin Trapping in the Gas Phase or in the Solid State	320
8.6	Availability of Spin Traps	321
8.7	FAQs	321
	Further Readings	322

9 Radiation Produced Radicals 325

Einar Sagstuen and Eli Olaug Hole

- 9.1 Introduction 325
- 9.2 Interaction of Radiation with Matter 326
- 9.3 Qualitative Detection of DNA Radicals 327
- 9.4 Tools and Procedures for Radical Structure Determinations 341
- 9.5 Quantitative Detection of Radicals 361
- 9.6 Highlighted Reading 374
- Acknowledgments 375
- References 375

10 Electron Paramagnetic Resonance in Biochemistry and Biophysics

383

Part I: Spin Labels, Paramagnetic Ions, and Oximetry 383

Michael K. Bowman

- 10.1 Introduction 383
- 10.2 Experimental Considerations 386
- 10.3 Dynamics 390
- 10.4 Saturation Transfer 393
- 10.5 Two-Dimensional Pulsed EPR 393
- 10.6 Protein Topology and SDSL 394
- 10.7 Surface Potentials/Accessibility and SDSL 394
- 10.8 Oximetry 395
- 10.9 Nanoscale Distance Measurement 396
- References 402

Part II: Photosynthesis 403

Donatella Carbonera

- 10.10 Introduction 403
- 10.11 Oxygenic Photosynthesis 405
- Appendix A.10.1: Pulse EPR Experiments on Radical Pairs 419
- Appendix A.10.2: Recombination Triplet States of the Primary Donors 421
- References 423
- Further Reading 425

11 Electron Paramagnetic Resonance Detection of Radicals in Biology and Medicine

427

Michael J. Davies

- 11.1 Free Radicals in Disease Processes 427
- 11.2 Nature of Free Radicals Involved in Disease Processes and Potential Catalysts for Radical Formation 428

11.3	Direct EPR Detection of Reactive Radicals <i>In Vivo</i> and <i>Ex Vivo</i>	428
11.4	Spin Trapping of Reactive Radicals <i>In Vivo</i> and <i>Ex Vivo</i>	430
11.5	Spin Scavenging of Reactive Radicals <i>In Vivo</i> and <i>Ex Vivo</i>	439
11.6	Spin Trapping of Nitric Oxide	440
11.7	Verification of the Occurrence of Radical-Mediated Processes	443
11.8	Conclusions	445
	Acknowledgments	445
	References	446
12	Electron Paramagnetic Resonance Applications to Catalytic and Porous Materials	451
	<i>Daniella Goldfarb</i>	
12.1	Introduction	451
12.2	Paramagnetic TMI's	453
12.3	Spin Probes	475
12.4	Reaction Intermediates and Trapped Radicals	482
12.5	Sample Preparation Considerations	483
12.6	Summary and Outlook	484
	References	484
13	Electron Paramagnetic Resonance of Charge Carriers in Solids	489
	<i>Mario Chiesa and Elio Giamello</i>	
13.1	Introduction	489
13.2	Point Defects, Charge Carriers, and EPR	490
13.3	Localized Electrons: Color Centers in Ionic Solids	492
13.4	Aggregate Color Centers	499
13.5	Localized Holes in Ionic Solids	500
13.6	Charge Carriers in Semiconductors	505
13.7	CESR in Metals	510
	References	517
	Appendix	519
	SUBJECT INDEX	527
	CHEMICAL INDEX	537