

# *Electron Spin Resonance in Chemistry*

PETER B. AYSCOUGH

MA, PhD(Cantab)

*Senior Lecturer, Department of Physical Chemistry,  
The University of Leeds*

METHUEN & CO LTD

11 NEW FETTER LANE · LONDON EC4

# Contents

PREFACE	page xv
1 INTRODUCTION	
1.1 Paramagnetism	1
1.2 Magnetic properties of the electron	2
1.2.1 <i>Orbital and spin magnetic moments</i>	
1.2.2 <i>Interaction with a magnetic field</i>	
1.2.3 <i>The Zeeman effect</i>	
1.2.4 <i>The Paschen-Back effect</i>	
1.3 Paramagnetic susceptibility	10
1.4 Electron spin resonance	12
1.4.1 <i>The resonance condition</i>	
1.4.2 <i>Energy absorption</i>	
1.4.3 <i>Relaxation processes</i>	
1.4.4 <i>Line shapes</i>	
1.4.5 <i>Fine structure</i>	
1.4.6 <i>Nuclear hyperfine structure</i>	
1.4.7 <i>Atoms and radicals in the gas phase</i>	
<i>References</i>	28
2 BASIC THEORY: <i>g</i> -FACTORS	
2.1 The <i>g</i> -factor	29
2.2 The general Hamiltonian	30
2.3 The crystal field and orbital symmetry	33
2.3.1 <i>Symmetry of p- and d-orbitals: effect of crystal field</i>	
2.3.2 <i>Jahn-Teller distortion and Kramer's theorem</i>	
2.3.3 <i>Magnitude of the crystal field</i>	
2.4 Calculation of <i>g</i> -factors	39
2.4.1 <i>Ti<sup>3+</sup> in an octahedral field</i>	
2.4.2 <i>Weak crystal field: the Ce<sup>3+</sup> ion</i>	
2.4.3 <i>Strong crystal field: Cu<sup>2+</sup> phthalocyanines</i>	
2.4.4 <i>Free radicals</i>	
2.5 The spin Hamiltonian	48
2.5.1 <i>Effect of field orientation</i>	
2.6 Fine structure: zero-field splittings	51
2.6.1 <i>The spin Hamiltonian for V<sup>3+</sup> and FeO<sub>4</sub><sup>2-</sup></i>	
2.6.2 <i>S-state ions: Mn<sup>2+</sup></i>	
<i>References</i>	56

<b>3</b>	<b>NUCLEAR HYPERFINE STRUCTURE</b>	
3.1	Introduction	58
3.1.1	<i>General treatment</i>	
3.1.2	<i>Special cases</i>	
3.2	Isotropic hyperfine interaction	61
3.2.1	<i>The spin Hamiltonian: energy levels</i>	
3.2.2	<i>The high-field approximation</i>	
3.3	Interpretation of isotropic hyperfine coupling constants	69
3.3.1	<i>Unpaired spin density</i>	
3.3.2	<i>Configurational interaction: admixture of excited states</i>	
3.3.3	<i><math>\alpha</math>-protons in organic radicals: spin polarization</i>	
3.3.4	<i><math>\beta</math>- and <math>\gamma</math>-protons in organic radicals</i>	
3.3.5	<i>Interaction with other nuclei</i>	
3.4	Anisotropic hyperfine interaction	79
3.4.1	<i>The spin Hamiltonian: energy levels</i>	
3.5	Interpretation of anisotropic hyperfine coupling constants	82
3.5.1	<i>The term <math>\langle(1 - 3 \cos^2 \phi)/r^3 \rangle_{av}</math></i>	
3.5.2	<i>s- and p-character</i>	
3.5.3	<i><math>\alpha</math>-protons in organic radicals</i>	
3.5.4	<i><math>\beta</math>-protons in organic radicals</i>	
3.6	Second-order effects	89
3.6.1	<i>Second-order effects on radicals in solution</i>	
3.6.2	<i>Second-order effects in orientated radicals</i>	
3.6.3	<i>Nuclear quadrupole interactions</i>	
	<i>References</i>	104
<b>4</b>	<b>RELAXATION PROCESSES AND LINE WIDTHS</b>	
4.1	General theories	105
4.2	The Bloch susceptibilities	106
4.3	Interactions with other spins	108
4.3.1	<i>Exchange interactions</i>	
4.4	Spin-lattice relaxation	113
4.4.1	<i>Mechanisms of spin-lattice relaxation</i>	
4.5	Motional modulation	119
4.5.1	<i>Line widths in liquids</i>	
4.5.2	<i>Correlation times</i>	
4.5.3	<i>Micro-crystalline model for ions in solution</i>	
4.5.4	<i>Free radicals in solution</i>	
4.6	Saturation	126
4.6.1	<i>Two-level systems</i>	
4.6.2	<i>Multi-level systems</i>	
4.6.3	<i>Double-resonance phenomena</i>	
	<i>References</i>	134

5	EXPERIMENTAL ASPECTS	
5.1	Basic features of ESR spectrometers	136
5.2	Microwave components	138
5.2.1	<i>The klystron</i>	
5.2.2	<i>The waveguide</i>	
5.2.3	<i>Attenuators</i>	
5.2.4	<i>Matching units</i>	
5.2.5	<i>The sample cavity</i>	
5.2.6	<i>Detectors</i>	
5.2.7	<i>The hybrid ring, circulator and magic tee</i>	
5.3	Magnets	146
5.3.1	<i>Field range</i>	
5.3.2	<i>Homogeneity and stability</i>	
5.4	High-sensitivity spectrometers	147
5.4.1	<i>Design and operation</i>	
5.4.2	<i>Phase-sensitive detection</i>	
5.4.3	<i>Automatic frequency control</i>	
5.4.4	<i>Sensitivity</i>	
5.5	Measurement and interpretation of spectra	154
5.5.1	<i>Frequency</i>	
5.5.2	<i>Magnetic field</i>	
5.5.3	<i>Microwave power</i>	
5.5.4	<i>g-factors</i>	
5.5.5	<i>g-tensors in single crystals</i>	
5.5.6	<i>Nuclear hyperfine spectra in solution</i>	
5.5.7	<i>Nuclear hyperfine spectra in single crystals</i>	
5.5.8	<i>Concentrations</i>	
	<i>References</i>	168
6	TRANSITION-METAL IONS	
6.1	Introduction	169
6.2	Host crystals	171
6.3	Ions of the first transition series: the iron group	174
6.3.1	<i>General considerations</i>	
6.3.2	<i>Results for individual ions</i>	
6.4	Ions of the second and third transition series: the palladium and platinum groups	193
6.5	Ions of the rare earths (lanthanides)	195
6.6	Ions of the actinides	202
6.7	Effects of ultra-violet and ionizing radiation	204
	<i>References</i>	206

7	RADICALS IN SINGLE CRYSTALS	
7.1	Introduction and experimental methods	209
7.2	Inorganic radicals	212
7.2.1	<i>Irradiated alkali-metal halides and azides</i>	
7.2.2	<i>Hydroxyl radicals</i>	
7.2.3	<i>Nitrogen oxy-radicals</i>	
7.2.4	<i>Phosphorus oxy-radicals</i>	
7.2.5	<i>Sulphur oxy-radicals</i>	
7.2.6	<i>Carbon oxy-radicals</i>	
7.2.7	<i>Chlorine oxy-radicals</i>	
7.2.8	<i>Other inorganic radicals</i>	
7.3	Organic radicals	227
7.3.1	<i>Carboxylic acids</i>	
7.3.2	<i>Halogen interactions</i>	
7.3.3	<i>Carbohydrates</i>	
7.3.4	<i>Other organic radicals</i>	
	<i>References</i>	236
8	RADICALS AND IONS IN SOLUTION	
8.1	Introduction and experimental methods	239
8.2	Anions of benzene and its derivatives	244
8.2.1	<i>Symmetric and anti-symmetric orbitals</i>	
8.2.2	<i>Orbital degeneracy in benzene anions: the Jahn-Teller effect</i>	
8.2.3	<i>Cyanobenzene anions</i>	
8.2.4	<i>The anion of cyclo-octatetrene</i>	
8.3	Ions of polynuclear aromatic hydrocarbons	250
8.3.1	<i>Alternant and non-alternant systems</i>	
8.3.2	<i>Even-alternant systems</i>	
8.3.3	<i>Odd-alternant systems: negative spin densities</i>	
8.3.4	<i>Non-alternant systems</i>	
8.4	Ions of heterocyclic aromatic compounds	257
8.4.1	<i>Nitrogen heterocyclic ions</i>	
8.4.2	<i>Oxazines and thiazines</i>	
8.4.3	<i>Other heterocyclic ions containing oxygen and sulphur</i>	
8.5	Semiquinones and related ions	262
8.5.1	<i>p-benzosemiquinones</i>	
8.5.2	<i>o-benzosemiquinones</i>	
8.5.3	<i>m-benzosemiquinones</i>	
8.5.4	<i>Alicyclic and aliphatic semiquinones</i>	
8.5.5	<i>Amino-benzene derivatives</i>	
8.6	Anions of nitro-compounds	268
8.6.1	<i>Derivatives of nitrobenzene</i>	
8.6.2	<i>Dinitro- and polynitro-benzene anions</i>	

8.7	Anions of carbonyl compounds	274
8.7.1	<i>Aromatic ketyls</i>	
8.7.2	<i>Other aromatic carbonyl compounds</i>	
8.7.3	<i>Aliphatic ketyls</i>	
8.8	DPPH and related radicals	279
8.9	Triphenylmethyl and related radicals	281
8.10	Nitroxide and related radicals	282
8.11	Anilino and phenoxy radicals	286
8.12	Alkyl radicals	288
8.12.1	<i>Interpretation of proton hyperfine splittings</i>	
8.12.2	<i>Mechanism of radiolysis of hydrocarbons</i>	
8.13	Other transient aliphatic radicals	294
8.14	Solvated electrons	300
8.15	Solvent effects	301
8.16	Exchange processes	303
8.16.1	<i>Electron exchange</i>	
8.16.2	<i>Rotational isomerization</i>	
	<i>References</i>	311
9	RADICALS IN POLYCRYSTALLINE AND AMORPHOUS MATRICES	
9.1	Introduction	318
9.2	Preparative methods	319
9.3	Line shapes in amorphous systems: computation of spectra	323
9.4	Atoms and radicals in inert-gas matrices	332
9.4.1	<i>Spectra of atoms produced by electric discharge</i>	
9.4.2	<i>Radicals produced by photolysis in argon and similar matrices</i>	
9.5	Irradiation of simple organic compounds	339
9.5.1	<i>Alkyl halides</i>	
9.5.2	<i>Hydrocarbons</i>	
9.5.3	<i>Alcohols, aldehydes, ketones</i>	
9.5.4	<i>Carboxylic acids (including amino-acids), amides, etc.</i>	
9.5.5	<i>Carbohydrates</i>	
9.5.6	<i>Oxygen-, sulphur- and selenium-containing radicals</i>	
9.6	Irradiation of aqueous systems	352
9.6.1	<i>Frozen H<sub>2</sub>O, D<sub>2</sub>O and neutral solutions containing H<sub>2</sub>O<sub>2</sub></i>	
9.6.2	<i>Alkaline aqueous glasses: trapped electrons</i>	
9.6.3	<i>Acid aqueous glasses</i>	
9.7	Radicals in polymers	361
9.7.1	<i>Radicals trapped during polymerization</i>	
9.7.2	<i>The effects of radiation on polymers</i>	
9.7.3	<i>Reactions of irradiated polymers with gases</i>	

9.8	Carbons	374
9.9	Radical reactions in solid matrices	377
	<i>References</i>	380
10	<b>F-CENTRES, CONDUCTION ELECTRONS AND SEMICONDUCTORS</b>	
10.1	<i>F-centres</i>	386
	10.1.1 <i>Colour centres in crystals</i>	
	10.1.2 <i>Structure of the F-centre</i>	
	10.1.3 <i>The wave-function for an F-centre</i>	
10.2	Conduction electrons	391
10.3	Semiconductors	394
	10.3.1 <i>Donor impurities in silicon and germanium</i>	
	10.3.2 <i>Acceptor impurities in silicon and germanium</i>	
	10.3.3 <i>Other impurity centres</i>	
	<i>References</i>	398
11	<b>BIRADICALS, TRIPLET STATE MOLECULES AND MOLECULAR COMPLEXES</b>	
11.1	Biradicals	401
11.2	Triplet state molecules	402
	11.2.1 <i>Triplet states in single crystals</i>	
	11.2.2 <i>Triplet states in glasses</i>	
	11.2.3 <i>Oxygen</i>	
11.3	Molecular complexes	413
	11.3.1 <i>Hydrocarbon-halogen complexes</i>	
	11.3.2 <i>Amine-quinone complexes</i>	
	11.3.3 <i>Hydrocarbon-quinone complexes</i>	
	11.3.4 <i>Amine-halogen complexes</i>	
	11.3.5 <i>Other complexes</i>	
	<i>References</i>	421
12	<b>PARAMAGNETIC SPECIES IN BIOLOGICAL SYSTEMS</b>	
12.1	Introduction	423
12.2	Structural investigations	424
12.3	Intermediates in metabolic processes	427
	12.3.1 <i>Photosynthesis</i>	
	12.3.2 <i>Oxidation-reduction systems</i>	
12.4	Radiation damage	431
	<i>References</i>	433

## CONTENTS

xiii

Appendix	1 The Landé $g$ -factor	435
	2 Probability of transitions for magnetic dipoles	437
	3 Calculated atomic parameters and nuclear hyperfine coupling constants	438
	4 Computation of spectra from isotropic hyperfine couplings	440
	5 Numerical double integration of the first derivative curve	442
Index		445