

Contents

	<i>page</i>
Preface	vii
List of Symbols	xiv
1. ATOMIC SPECTROSCOPY	1
Introduction to atomic spectroscopy	1
Simple line spectra	6
Five series of the hydrogen atom	
Combination terms	
The Bohr theory of the hydrogen atom	
Sommerfeld's refinements of the Bohr theory	
Energy level diagram of the hydrogen atom including fine structure	
Weaknesses of the Bohr-Sommerfeld theory	
Spectra of hydrogen-like ions	
Other simple line spectra	21
Multiplet fine structure	26
Elements with more than one outer valence electron	35
Forbidden transitions and selection rules	42
Space quantisation	45
Magnetic moment and space quantisation of angular momentum	
The Stern-Gerlach experiment	
The normal Zeeman effect	52
The anomalous Zeeman effect	53
The magnetic moment of the atom and g -factor	
Emitted frequencies in anomalous transitions	
The Landé g -formula	
The Paschen-Back effect	62
The Stark effect	65
Normal Stark effect	
Stark effect in a strong electric field	
Width of spectral lines	69
(i) Natural breadth of a spectral line	
(ii) The Doppler effect	
(iii) External effects	

	<i>page</i>
Hyperfine structure of spectral lines	71
Zeeman effect of hyperfine structure	
The Back-Goudsmit effect	76
The g -factors and the effects of various magnetic field strengths	
Rabi method for the determination of the nuclear spin quantum number	80
Effect of various magnetic strengths on Na 'D' lines	
Type of information derived from atomic spectra	82
Quantum numbers and the structure of the atom	
Determination of J and g_J -values from the Zeeman pattern	
Building up of the periodic table of elements	
Inadequacy in Dirac quantum-mechanical theory	
Ionisation potentials	
Qualitative emission spectroscopy	
Quantitative spectrochemical analysis	
Other applications	
Some recent advances in atomic spectroscopy	97
Atomic spectra studies of some heavier elements	
Spectrochemical analysis	
Examination of discharges in thermonuclear reactions	
<i>References</i>	105
 2. INTRODUCTION TO MOLECULAR SPECTRA	 106
Electronic, vibrational, and rotational energies	106
Energy changes within a molecule and selection rules	110
Microwave spectra	
Infra-red spectra	
Electronic spectra	
Potential energy curves	114
<i>References</i>	119
 3. MICROWAVE SPECTROSCOPY	 120
Experimental method	121
Information derived from work on gases	125
Linear molecules	
Spherical-top molecules	
Symmetric-top molecules	
Asymmetric-top molecules	
Accuracy of moment of inertia and internuclear distance	
Hyperfine structure and quadrupole moment	135
Quadrupole coupling constant	
Nuclear quadrupole moments	
Linear molecules and the Stark effect	141
Microwave determination of the electric dipole moment of gaseous molecules	

CONTENTS

xi

	<i>page</i>
Two special cases of microwave absorption	146
Inversion spectrum of ammonia	
The oxygen molecule	
Summary of general applications of microwave data on gaseous molecules	147
Fundamental information	
Qualitative and quantitative analysis	
Detection of free radicals	
Study of chemical reactions	
Applications of microwaves to atomic spectra	
Microwave studies of condensed systems	151
Study of potential energy barrier	
Microwave determination of electric dipole moment in solution	
<i>References</i>	153
 4. ELECTRON SPIN RESONANCE SPECTROSCOPY	 154
The resonance condition	154
Induction and magnetic field strength	160
The <i>g</i> -factor	161
Experimental technique and principles	162
Theory and applications of the electron spin resonance method	167
SECTION A. CRYSTALLINE SOLIDS	
Internal field effects	167
Symmetry effects of the internal crystalline field	168
Fine structure	169
Hyperfine structure	170
The major causes of line width in the ESR spectra of solids	172
The various interactions in crystalline solids and their relative magnitudes	173
Information derived from ESR studies on crystalline solids	175
Nuclear spin and hyperfine splitting	
Determination of the spectroscopic splitting factor	
Nuclear quadrupole moments	
The cupric acetate crystal	
Metallic derivatives of complex organic molecules	
Octahedral complexes	
SECTION B. FREE RADICALS IN SOLUTION	
Information derived from the study of solutions	180
Delocalisation of electrons	181
Delocalisation of electrons within the molecule	
Delocalisation of electrons amongst the radicals	
Determination of an electronegativity scale	188

SECTION C. OTHER ASPECTS OF ESR WORK		<i>page</i>
With a view to chemical analysis		189
With a view to the study of small free radicals		190
Biological studies		193
Biradicals and the triplet state		197
<i>References</i>		197
5. RADIO-FREQUENCY SPECTROSCOPY. NUCLEAR MAGNETIC RESONANCE		199
Introductory principles		199
Two different types of nuclear magnetic resonance study		204
Broad line nuclear magnetic resonance		
High-resolution nuclear magnetic resonance		
An NMR spectrometer and basic principles		205
The NMR spectrogram		209
Some applications of nuclear magnetic resonance results		211
Determination of nuclear magnetic moments		212
Magnetic interaction of adjacent dipoles in rigid solids		212
Scope and accuracy of internuclear distance determination		219
Quadrupole interaction		219
General principles		
Effect of the quadrupole on nuclear magnetic resonance spectrum of a solid		
Pure quadrupole resonance		
Molecular motion in solids and relaxation time		224
Interaction of a dipole with the crystal lattice		
Dipole-dipole interaction		
The magnitude of t_1 and t_2		
Restricted rotation studies		
Chemical shifts		230
Chemical exchange		234
Qualitative and quantitative analysis		235
Nuclear spin-spin interaction by means of the bonding electrons		237
<i>References</i>		242
APPENDIX		243
1. Quantum-mechanical considerations of the hydrogen atom and the emergence of the quantum numbers n , l and m_l		243
2. Energy levels of a linear rigid rotator		247
3. Angular momentum of a linear rigid rotator		248
4. Selection rules for the linear rigid rotator		249
5. Dependence of spectral intensity on the matrix element		251
<i>References</i>		251
AUTHOR INDEX		253
SUBJECT INDEX		256

CONTENTS

xiii

PLATES

(All figures are in the text except the following which are inserted as plates)

Figures 1.5, 1.6, 1.7	<i>facing page</i>	4
Figure 1.65		94
Figure 1.68		103
Figure 2.3		114
Figure 3.7		131
Figure 3.11		139