

CONTENTS

LIST OF ABBREVIATIONS

ix

1. BASIC PRINCIPLES

- 1.1. The Nature of Light and the Uncertainty Principle, 1
- 1.2. Absorption of Light: The Lambert–Beer Law, 2
- 1.3. Photochemical Laws, 7
- 1.4. Photostationary State and the Rate Law, 9
- 1.5. Continuous Photolysis, Quantum Yields, and Measurement of Light Intensity, 13
- 1.6. Photochemical Reactions in Condensed Media, 21

2. DETECTION OF INTERMEDIATES

31

- 2.1. Scavenging of Reaction Intermediates, 31
- 2.2. Conventional Flash Photolysis and Single Photon Counting, 38
- 2.3. The Rotating Sector Technique, 45
- 2.4. Flow Techniques, 46
- 2.5. Picosecond Transient Kinetics, 49

3. ELEMENTS OF INORGANIC SPECTROSCOPY

52

- 3.1. Born–Oppenheimer Approximation, 52
- 3.2. Potential Surfaces—The Nuclear Motions, 55
- 3.3. Distortion of Potential Surfaces: The Jahn–Teller Effect, 62
- 3.4. Vibronic Coupling, 64
- 3.5. Spin–Orbit Coupling and Magnetic Field Perturbations, 66

vii

3.6.	Time-Dependent Perturbations: Absorption and Emission of Radiation,	74
3.7.	Intensity of Electronic Transitions (Absorption Bands),	79
4.	KINETICS OF PHOTOLUMINESCENCE	87
4.1.	Thermal Effects on Photoluminescence,	87
4.2.	Dependence of Photoluminescence Yields on the Wavelength of Excitation,	94
4.3.	Time-Resolved Detection of the Excited State (Prompt and P- or E-Delayed Fluorescence),	95
4.4.	Radiative Transitions,	100
4.5.	Radiationless Processes in Polyatomic Molecules,	101
4.6.	Energy Transfer,	111
5.	PHOTOREDOX REACTIONS	
5.1.	Mulliken's Concept of Charge Transfer Complexes,	122
5.2.	Jørgensen's Scale of Optical Electronegativities,	127
5.3.	Charge Transfer Transitions in Ion Pairs,	133
5.4.	Reactivity of CTTM and CTTL Excited States,	134
5.5.	Models for Charge Transfer to Solvent (CTTS) Transitions,	141
5.6.	Specific Medium Effects on CTTM Photochemistry,	148
6.	LIGAND FIELD PHOTOCHEMISTRY	
6.1.	General Features of Ligand Field Photochemistry,	152
6.2.	Photoreactive Excited States of Cr(III) Complexes,	156
6.3.	Photosubstitution Reactions of d^6 Metal Ions,	168
6.4.	Exceptional Photoreactivity of Ligand Field Excited States,	171
7.	ELEMENTS OF ORGANOMETALLIC PHOTOCHEMISTRY	
7.1.	Excited States in Organometallic Compounds,	173
7.2.	Metal Carbonyls,	174
7.3.	Compounds with σ (Alkyl) or π (Olefinic) Carbon–Metal Bonds,	177
7.4.	Hydride Complexes,	183
APPENDIX	PHYSICAL CONSTANTS AND CONVERSION FACTORS FOR PHOTOCHEMICAL WORK	186
APPENDIX II.	CHARACTER TABLES FOR SYMMETRY GROUPS	188
APPENDIX III.	VIBRATIONAL MOTIONS	

APPENDIX IV. DESCRIPTION OF THE CHEMICAL BONDING IN COORDINATION COMPLEXES	214
APPENDIX V. CHARGE TRANSFER TRANSITIONS	223
APPENDIX VI. BORN CYCLES RELATED TO CHARGE TRANSFER PROCESSES	225
REFERENCES	229
INDEX	243