

Contents

1	Excited-State Properties	1
1.1	Introduction	1
1.2	The Nature of Light	2
1.3	Potential Energy Surfaces	4
1.4	Electronic States and Electronic Configurations	7
1.4.1	Organic Molecules	7
1.4.2	Metal Complexes	9
1.5	Light Absorption	12
1.6	Intramolecular Excited State Decay	15
1.6.1	Vibrational Relaxation	15
1.6.2	Radiative Deactivation	15
1.6.3	Radiationless Deactivation	16
1.6.4	Chemical Reaction	18
1.6.5	Kinetic Aspects	19
	References	20
2	Photoinduced Energy and Electron Transfer Processes	21
2.1	Bimolecular Processes	21
2.1.1	General Considerations	21
2.1.2	Thermodynamic Aspects	22
2.1.3	Kinetic Aspects of Bimolecular Processes	23
2.2	Supramolecular Photochemistry	25
2.2.1	Definition of a Supramolecular System	25
2.2.2	Photoinduced Energy and Electron Transfer in Supramolecular Systems	26
2.2.3	Excimers and Exciplexes	27
2.3	Electron Transfer Processes	28
2.3.1	Marcus Theory	28
2.3.2	Quantum Mechanical Theory	31
2.4	Optical Electron Transfer	33

2.5	Energy Transfer Processes	34
2.5.1	Coulombic Mechanism.	35
2.5.2	Exchange Mechanism.	36
2.6	The Role of the Bridge in Supramolecular Systems.	37
	References	38
3	Spectrophotometry, Measurements in Solution	39
3.1	Introduction	39
3.2	The Absorption Spectrum.	40
3.3	The General Absorption Characteristics of Molecules	43
3.4	Qualitative Analysis.	45
3.5	Quantitative Treatment of the Absorption Intensity	47
3.6	Quantitative Analysis.	50
3.6.1	The Method of the Standard Additions.	51
3.6.2	Analysis of Mixtures of Absorbing Species	51
3.6.3	Spectrophotometric Titrations	52
3.7	Instrumentation	52
3.7.1	The Light Source.	53
3.7.2	The Monochromator	53
3.7.3	The Sample Holder	55
3.7.4	The Detector.	56
3.7.5	The Spectrophotometers	57
3.8	The Sample Measurement.	59
3.8.1	The Cells	59
3.8.2	The Solvent	60
3.8.3	The Diffusion	61
3.8.4	The Instrumental Precision	61
3.9	Experimental Examples	62
	References	66
4	Photochemical Techniques	67
4.1	Photochemical Apparata.	67
4.1.1	Light Sources	68
4.1.2	Selection of the Exciting Radiation	71
4.1.3	Reaction Cells.	72
4.1.4	Optical Material	73
4.1.5	Control of Temperature and Stirring	73
4.2	Photoreaction Quantum Yield	74
4.3	Chemical Actinometers	77
4.3.1	Potassium Ferrioxalate	78
4.3.2	Potassium Reineckate.	81
4.3.3	Azobenzene	83
4.3.4	Aberchrome 540	85
4.4	A Photochromic Diarylethene Compound.	88

4.4.1	Irradiation Experiments	89
4.4.2	Photochemical Behaviour	90
4.4.3	Compound 1 as Actinometer.	92
	References	95
5	Spectrofluorimetry	97
5.1	Introduction	98
5.2	The Instrumentation for Measuring Luminescence.	99
5.2.1	Light Source S	100
5.2.2	Excitation and Emission Monochromators M1 and M2	102
5.2.3	Sample-Holder C.	102
5.2.4	Detector R	103
5.3	Emission and Excitation Spectra and Their Correction.	104
5.3.1	Emission Spectra	104
5.3.2	Excitation Spectra	107
5.3.3	Presence of Spurious Bands in Spectra.	109
5.4	Quantitative Measurements at Fixed Wavelength.	111
5.4.1	Correction for the Sample Absorption at the Excitation Wavelength	111
5.4.2	Correction for the Sample Absorption at the Emission Wavelength	115
5.4.3	Determination of the Stability Constant of a [2]Pseudorotaxane.	118
5.5	Determination of Luminescence Quantum Yields	122
5.5.1	Reference Standards for the Determination of Fluorescence Quantum Yields.	123
5.5.2	Reference Standards for the Determination of Phosphorescence Quantum Yields	125
5.6	Luminescence Measurements on Solid Samples	126
5.6.1	Introduction	126
5.6.2	Front-Face and Right-Angle Geometries.	126
5.6.3	Sample Inhomogeneity.	127
5.6.4	Concentration Effects.	128
	References	128
6	Absorption and Emission Spectroscopy with Polarized Light.	131
6.1	Linear and Circular Dichroism Spectroscopy	131
6.1.1	Introduction	131
6.1.2	Polarized Light	132
6.1.3	Birefringence and Circular Dichroism	134
6.1.4	Linear Dichroism.	139
6.1.5	Observables in Circular Dichroism Spectroscopy.	140

6.1.6	Instrumentation and Experimental Procedures	141
6.1.7	Applications	143
6.2	Circularly Polarized Luminescence Spectroscopy	146
6.2.1	Introduction	146
6.2.2	Observables in CPL spectroscopy	147
6.2.3	Instrumentation and Experimental Procedures	149
6.2.4	Applications	150
6.3	Steady State and Time Resolved Fluorescence Anisotropy	151
6.3.1	Introduction	151
6.3.2	Definition of Fluorescence Anisotropy	152
6.3.3	Fluorescence Polarization	153
6.3.4	Fluorescence Anisotropy and Electronic Transition	153
6.3.5	Depolarization due to Rotation	156
6.3.6	Depolarization due to Energy Transfer	157
6.3.7	Emission Anisotropy Spectra	157
6.3.8	The G Factor	158
6.3.9	Calculation of the Emission Anisotropy Spectra	159
6.3.10	Effect of Concentration and Scattering on the Anisotropy	160
6.3.11	Instrumental Configurations	160
6.3.12	Fluorescence Anisotropy of a Mixture of Fluorophores	160
6.3.13	Excitation Anisotropy Spectra	161
6.3.14	Time Resolved Fluorescence Anisotropy	161
6.3.15	Fluorescence Anisotropy Decay	161
6.3.16	Fundamental Fluorescence Anisotropy in Time-Resolved Measurements	162
6.3.17	Acquisition of the Decay	163
6.3.18	Interpretation of the Results	163
	References	164
7	Time-Resolved Luminescence Techniques	167
7.1	General Concepts	167
7.2	Experimental Methods for Lifetime Measurements	170
7.2.1	Single Flash	170
7.2.2	Gated Sampling	172
7.2.3	Single Photon	173
7.2.4	Phase Shift	176
7.3	Analysis of Decay Data	178
7.4	Example of Lifetime Measurements on a Supramolecular System	180
7.5	Luminescence Lifetime Standards	183
	References	183

8	Transient Absorption Spectroscopy	185
8.1	Introduction	185
8.2	Transient Absorption with Nanosecond Resolution	186
8.2.1	Measure of Absorbance Change	187
8.2.2	The Sample Compartment	189
8.2.3	The Optical System	190
8.2.4	The Electronic Detection System	191
8.3	Transient Absorption Spectroscopy in Supramolecular Systems	193
8.3.1	Fullerene Derivatives	193
8.3.2	Ligand-Protein Complexes	195
8.4	Sub-Nanosecond Transient Absorption	197
8.4.1	Shortening the Laser Pulse	198
8.4.2	Ti: Sapphire Laser	199
8.4.3	Chirped Pulse Amplification	199
8.4.4	Regenerative Amplification	200
8.5	Ultrafast Transient Absorption Spectroscopy	200
8.5.1	Femtochemistry	200
8.5.2	Pump and Probe Experiments	201
8.6	Photoinduced Electron Transfer in a Multichromophoric System	202
8.7	Femtosecond Systems, Experimental Suggestions	205
	References	206
9	Spectroelectrochemistry	209
9.1	Introduction	209
9.2	General Considerations	217
9.3	Absorption Measurements	219
9.4	Emission Measurements	223
	References	225
	Index	227