

Contents

1. Introduction	1
2. Qualitative Theory of Radiationless Transitions	5
2.1 Balance Equation	5
2.2 Experimental Observations and Empirical Rules	8
2.3 Molecular Energy Level Model	12
2.4 Physical Nature of Radiationless Transitions	15
2.4.1 The Nature of the Initial State	15
2.4.2 Freed–Jortner Irreversibility Criterion	25
2.5 General Description of Luminescence Kinetics:	
Intermediate Case and Statistical Limit	27
2.5.1 Strong Coupling	30
2.5.2 Experimental Criterion for the Statistical Limit	36
2.5.3 Upper Limit for Radiationless Transition Rates	36
2.5.4 Weak Coupling	38
2.6 Strong-Coupling Limit	39
2.6.1 The Bixon–Jortner Model	39
2.6.2 Inclusion of Level Broadening	46
2.6.3 Mono- and Biexponential Decays	48
2.7 Weak-Coupling Limit	53
2.7.1 The Role of Vibrational Relaxation in the Final Electronic State	53
2.7.2 The Robinson–Frosch Theory	55
2.7.3 The Trifonov–Shekhtman Model	60
2.7.4 Periodic Quantum Beats and Biexponential Decay	63
2.8 Time-Dependent Perturbation Theory	68
2.9 Comparison of Various Expressions for the Transition Rate	72
2.10 Characterization of the Final States of an Isolated Molecule	74
2.11 Small, Large and Intermediate Molecules	80
3. Luminescence Intensity as a Function of Time and the Radiationless Transition Rate	89
3.1 Formulation of the Problem	89
3.2 Laplace Transformation, Green's Functions and Resonant States	92
3.3 Computation of the Green's Functions	95
3.4 Evolution of the Initial State and the Luminescence Intensity	98

3.5	Resonant States	101
3.5.1	Small Molecules	102
3.5.2	Intermediate Case	107
3.5.3	Statistical Limit	110
3.6	Method of Projection Operators	112
4.	Matrix Elements of Intramolecular Interactions	118
4.1	Adiabatic Approximation	118
4.2	Accuracy of the Adiabatic Approximation	128
4.3	Crude Adiabatic Approximation	135
4.4	Coupling Operators	138
4.4.1	Nonadiabatic Coupling	138
4.4.2	Spin–Orbit Coupling	139
4.4.3	Rotational Matrix Elements	144
4.4.4	Coriolis Coupling	150
4.5	Condon Approximation	152
4.6	Model of Noninteracting Oscillators	159
4.7	Mechanisms and Selection Rules for Radiationless Transitions	164
4.8	Overlap Integrals for Harmonic and Morse Oscillators	170
5.	Quasiclassical Methods	175
5.1	Introductory Remarks	176
5.2	Overlap Integral for a Harmonic Oscillator	178
5.2.1	Basic Derivation	178
5.2.2	Conditions for Applicability of the Quasiclassical Approximation	189
5.2.3	Comparison of Frequency and Displacement Effects	190
5.3	Overlap Integral for an Anharmonic Oscillator	192
5.3.1	Morse Oscillator with $\Delta\alpha = 0$	192
5.3.2	Morse Oscillator with $\Delta\alpha \neq 0$ and Arbitrary Potentials	201
5.3.3	Selection Rule for the Morse Oscillator	204
5.4	Franck–Condon Principle for Radiationless Transitions	207
5.4.1	General Formulation	207
5.4.2	Real and Complex Term Intersections	208
5.4.3	Classical Franck–Condon Factor	209
5.4.4	Franck–Condon Principle and the Selection Rules	211
5.5	Transitions Between Parallel Terms	212
5.5.1	Model of Parallel Terms	213
5.5.2	Tunneling Nonradiative and Radiative Transitions	215
5.6	Overtone Vibrational Transitions	219
5.6.1	Derivation of the Quasiclassical Formula	220
5.6.2	Comparison with Exact Calculations	225
5.6.3	Normal Intensity Distributions	228
5.6.4	Dynamical Tunneling Depth	233
5.6.5	Intensity Anomalies in Absorption Spectra	234

5.7	Collision Model	237
5.7.1	Transition Matrix in the Linear Model	239
5.7.2	Perturbation Theory for Nonadiabatic Transitions	254
5.7.3	Method of the Classical $\mathcal{S}$ -Matrix	259
5.8	Two-State Vibronic Levels	261
6.	The Statistical Limit	266
6.1	Accepting Modes, Effective States and the Transition Rate ..	266
6.2	Generating-Function Method	274
6.3	Saddle-Point Method	278
6.3.1	First Saddle-Point Approximation (FSPA)	278
6.3.2	Validity Conditions for the FSPA	281
6.3.3	Saddle-Point Method Versus Effective-States Method ..	290
6.4	Single Vibronic Level (SVL) Transition-Rate Dependence upon Initial Vibrational Energy	290
6.5	Transition Rate from Statistically Equilibrated Initial States ..	296
6.6	Summation of the Franck–Condon Factors	303
6.7	Inductive-Resonant-Transfer Mechanism	305
7.	The Intermediate Case	310
7.1	Physical Effects	310
7.1.1	Absorption Spectra and Luminescence Kinetics	311
7.1.2	Pressure Dependence of the Transition Rate	312
7.1.3	Energy-Gap Dependence	313
7.1.4	Vibrational and Rotational Energy Dependence	315
7.1.5	Deuteration Effect	317
7.1.6	Comparative Description of the Intermediate Case and the Statistical Limit	317
7.2	Correlation-Function Method	318
7.3	Kinetic Model	329
8.	Conclusion	332
Appendix. Commutation Rules for Angular Momentum in the Laboratory and Molecular Frame		334
References		339
Subject Index		367