

E. S. Medvedev V. I. Osherov

Radiationless Transitions in Polyatomic Molecules

With 31 Figures

Springer-Verlag

Berlin Heidelberg New York

London Paris Tokyo

Hong Kong Barcelona

Budapest

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{L} -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 |