

Spectra of Atoms and Molecules

Peter F. Bernath

New York Oxford
OXFORD UNIVERSITY PRESS
1995

Contents

1 Introduction	3
Waves, Particles, and Units	3
The Electromagnetic Spectrum	6
Interaction of Radiation with Matter	7
Blackbody Radiation	
Einstein <i>A</i> and <i>B</i> Coefficients	
Absorption and Emission of Radiation	
Beer's Law	
Line-Shape Functions: Homogeneous and Inhomogeneous Line Shapes	
Natural Lifetime Broadening	
Pressure Broadening	
Doppler Broadening	
Transit-Time Broadening	
Power Broadening	
2 Molecular Symmetry	41
Symmetry Operations	41
Operator Algebra	
Symmetry Operator Algebra	
Groups	48
Point Groups	
Classes	
Subgroups	
Notation for Point Groups	53
3 Matrix Representation of Groups	58
Vectors and Matrices	58
Matrix Eigenvalue Problem	
Similarity Transformations	
Symmetry Operations and Position Vectors	65
Reflection	
Rotation	
Inversion	

Rotation-Reflection		
Identity		
Symmetry Operators and Basis Vectors	69	
Symmetry Operators and Basis Functions	72	
Function Spaces		
Gram-Schmidt Procedure		
Transformation Operators		
Equivalent, Reducible, and Irreducible Matrix Representations		77
Equivalent Representations		
Unitary Representations		
Reducible and Irreducible Representations		
Great Orthogonality Theorem	79	
Characters		
Character Tables	84	
Mulliken Notation		
4 Quantum Mechanics and Group Theory	92	
Matrix Representation of the Schrödinger Equation		92
Born-Oppenheimer Approximation	98	
Symmetry of the Hamiltonian	101	
Projection Operators	103	
Direct Product Representations	106	
Integrals and Selection Rules	107	
5 Atomic Spectroscopy	112	
Introduction	112	
Angular Momentum	114	
The Hydrogen Atom and One-Electron Spectra		119
Vector Model		
Spin-Orbit Coupling		
Many-Electron Atoms	128	
Selection Rules	139	
Atomic Spectra	142	
Hyperfine Structure		
Hydrogen Atom		
Zeeman Effect	147	
Paschen-Back Effect		
Stark Effect		
6 Rotational Spectroscopy	159	
Rotation of Rigid Bodies	159	
Pure Rotational Spectroscopy of Diatomic and Linear Molecules		168
Selection Rules		
Centrifugal Distortion		
Vibrational Angular Momentum		

Symmetric Tops	181
Molecule and Space-Fixed Angular Momenta	
Rotational Spectra	
Centrifugal Distortion	
Asymmetric Tops	187
Selection Rules	
Structure Determination	194
7 Vibrational Spectroscopy	201
Diatomic Molecules	201
Wavefunctions for the Harmonic and Anharmonic Oscillators	
Vibrational Selection Rules for Diatomic Molecules	
Determination of Dissociation Energies from Spectroscopic Data	
Vibration–Rotation Transitions of Diatomic Molecules	
Combination Differences	
Vibrational Motion of Polyatomic Molecules	220
Classical Mechanical Description	
Quantum Mechanical Description	
Internal Coordinates	
Symmetry Coordinates	
The Symmetry of the Normal Modes of Vibration	
Selection Rules for Vibrational Transitions	
Vibration–Rotation Transitions of Linear Molecules	
Nuclear Spin Statistics	
Excited Vibrational States of Linear Molecules	
Vibrational Spectra of Symmetric Tops	256
Coriolis Interactions in Molecules	
Infrared Transitions of Spherical Tops	264
Vibrational Spectra of Asymmetric Tops	267
Fermi and Coriolis Perturbations	270
Inversion Doubling and Fluxional Behavior	273
8 The Raman Effect	283
Background	283
Classical Model	
Quantum Model	
Polarization	
Rotational Raman Effect	290
Diatomic Molecules	
Vibration–Rotation Raman Spectroscopy	292
Diatomic Molecules	
9 Electronic Spectroscopy of Diatomic Molecules	297
Orbitals and States	297

Vibrational Structure	303	
Rotational Structure of Electronic Transitions of Diatomic Molecules		308
Singlet–Singlet Transitions		
Nonsinglet Transitions		
The Symmetry of Diatomic Energy Levels: Parity	324	
Total (+/–) Parity		
Rotationless (<i>e/f</i>) Parity		
Gerade/Ungerade (<i>g/u</i>) Parity		
Symmetric/Antisymmetric (<i>s/a</i>) Parity		
Dissociation and Predissociation	333	
10 Electronic Spectroscopy of Polyatomic Molecules		338
Orbitals and States	338	
Walsh's Rules: Qualitative Molecular Orbital Theory		
Hückel Molecular Orbital Theory		
Vibrational Structure of Electronic Transitions	352	
Vibronic Coupling: The Herzberg–Teller Effect	355	
Jahn–Teller Effect	358	
Renner–Teller Effect	359	
Nonradiative Transitions: Jablonski Diagram	361	
Photoelectron Spectroscopy	363	
Rotational Structure: H ₂ CO and HCN	364	
Appendix A Units, Conversions, and Physical Constants		375
Appendix B Character Tables	377	
Appendix C Direct Product Tables	386	
Appendix D Introductory Textbooks Covering All of Spectroscopy		389
Figure Acknowledgments	391	
Index	395	