

MOLECULAR SPECTRA *and* MOLECULAR STRUCTURE

I. SPECTRA OF DIATOMIC MOLECULES

By

GERHARD HERZBERG, F.R.S.
National Research Council of Canada

With the co-operation, in the first edition, of
J. W. T. SPINKS, F.R.S.C.

SECOND EDITION

II. Physikalisches Institut
der Technischen Hochschule
Darmstadt

E/187



VAN NOSTRAND REINHOLD COMPANY

NEW YORK

CINCINNATI

TORONTO

LONDON

MELBOURNE

CONTENTS

	PAGE
INTRODUCTION.....	1
General remarks, 1—Physical constants, 2—Units and conversion factors, 3	
CHAPTER I: RÉSUMÉ OF THE ELEMENTS OF ATOMIC STRUCTURE.....	5
1. BOHR THEORY.....	5
Stationary energy states, 5—Radiation, 6—Terms, 8—Continuous spectra, 8	
2. WAVE MECHANICS (QUANTUM MECHANICS).....	9
Fundamental equations, 9—Physical interpretation of the Ψ function, 12—Orthogonality and normalization of eigenfunctions, 13—Perturbation theory, 13—Heisenberg's uncertainty principle, 15—Momentum and angular momentum, 15—Space quantization, 17—Electron spin, 18—Emission and absorption of radiation, 18	
3. ATOMS WITH SEVERAL ELECTRONS; VECTOR MODEL.....	22
Quantum numbers of the individual electrons, 22—The Pauli principle, 22—Quantum theoretical addition of angular momentum vectors, 24—Quantum numbers and angular momenta of the whole atom; term symbols, 26—Influence of a magnetic or electric field, 28—Selection rules, 28—Nuclear spin, 29	
CHAPTER II: OBSERVED MOLECULAR SPECTRA AND THEIR REPRESENTATION BY EMPIRICAL FORMULAE.....	30
1. SPECTRA IN THE VISIBLE AND ULTRAVIOLET REGIONS.....	30
Coarse structure, 30—Fine structure, 42—Intensity distribution, 50	
2. SPECTRA IN THE INFRARED REGION.....	53
Near infrared spectra, 53—Far infrared spectra, 57	
3. RADIOFREQUENCY (MICROWAVE) SPECTRA.....	59
Microwave absorption, 59—Magnetic resonance spectra, 60	
4. RAMAN SPECTRA.....	61
Nature of the Raman effect, 61—Large Raman displacements, 61—Small Raman displacements, 63	
CHAPTER III: ROTATION AND VIBRATION OF DIATOMIC MOLECULES; INTERPRETATION OF INFRARED AND RAMAN SPECTRA.....	66
1. INTERPRETATION OF THE PRINCIPAL FEATURES OF INFRARED AND RAMAN SPECTRA BY MEANS OF THE MODELS OF THE RIGID ROTATOR AND OF THE HARMONIC OSCILLATOR.....	66

	PAGE
(a) The Rigid Rotator.....	66
The molecule as a rigid rotator, 66—Energy levels, 67—Eigenfunctions, 69—Spectrum, 70	
(b) The Harmonic Oscillator.....	73
The molecule as a harmonic oscillator, 73—Energy levels, 75—Eigenfunctions, 76—Spectrum, 79	
(c) Comparison with the Observed Infrared Spectrum.....	81
(d) The Raman Spectrum of the Rigid Rotator and of the Harmonic Oscillator.....	82
Classical theory of light scattering and of the Raman effect, 82—Quantum theory of the Raman effect, 85—Vibrational Raman spectrum, 86—Rotational Raman spectrum, 88—General remarks, 90	
2. INTERPRETATION OF THE FINER DETAILS OF INFRARED AND RAMAN SPECTRA.....	90
(a) The Anharmonic Oscillator.....	90
The molecule as an anharmonic oscillator, 90—Classical motion, 91—Energy levels, 92—Eigenfunctions, 93—Infrared spectrum, 94—Raman spectrum, 97—Vibrational frequency and force constant, 97—Continuous term spectrum and dissociation, 98—Mathematical representation of the potential curves, 101	
(b) The Nonrigid Rotator.....	103
Energy levels, 103—Spectrum, 105	
(c) The Vibrating Rotator.....	106
Energy levels, 106—Eigenfunctions, 109—Infrared spectrum, 110—Raman spectrum, 114	
(d) The Symmetric Top.....	115
The diatomic molecule as a symmetric top, 115—Angular momenta, 116—Energy levels, 117—Eigenfunctions, 118—Infrared spectrum, 119—Raman spectrum, 121	
(e) Thermal Distribution of Quantum States; Intensities in Rotation-Vibration Spectra.....	121
Vibration, 122—Rotation, 124	
(f) Symmetry Properties of the Rotational Levels.....	128
Positive and negative rotational levels, 128—Symmetric and anti-symmetric rotational levels for homonuclear molecules, 130—Influence of nuclear spin, 133—Influence of nuclear statistics, 135—Ortho and para modifications, 139—Isotopic molecules, 141	
(g) Isotope Effect.....	141
Vibration, 141—Rotation, 143	
CHAPTER IV: ELEMENTARY DISCUSSION OF ELECTRONIC STATES AND ELECTRONIC TRANSITIONS.....	146
1. ELECTRONIC ENERGY AND TOTAL ENERGY.....	146
Electronic energy and potential curves; stable and unstable molec-	

ular states, 146—Resolution of the total eigenfunction, 147—Resolution of the total energy, 149

2. VIBRATIONAL STRUCTURE OF ELECTRONIC TRANSITIONS.....	151
General formulae, 151—Examples; graphical representation, 153—Absorption, 155—Excitation of single progressions in emission, 158—Sequences (diagonal groups), 159—Vibrational analysis, 161—Isotope effect, 162—Applications of the isotope effect, 165	
3. ROTATIONAL STRUCTURE OF ELECTRONIC BANDS.....	168
General relations, 168—The branches of a band, 169—Band-head formation; shading (degrading) of bands, 171—Combination relations and evaluation of the rotational constants for bands without Q branches, 175—Combination differences and evaluation of rotational constants for bands with Q branches, 183—Determination of the band origins (zero lines), 185—Determination of the numbering in the branches of incompletely resolved bands, 189—The picking out of branches, 191—Isotope effect, 192	
4. INTENSITIES IN ELECTRONIC BANDS.....	193
(a) Intensity Distribution in the Vibrational Structure.....	193
Observed intensity distribution in absorption, 193—The Franck-Condon principle: absorption, 194—The Franck-Condon principle: emission (Condon parabola), 196—Wave-mechanical formulation of the Franck-Condon principle, 199—Vibrational sum rule and vibrational temperature, 203	
(b) Intensity Distribution in the Rotational Structure.....	204
$^1\Sigma$ — $^1\Sigma$ transitions, 204—Other transitions, 207—Intensity alternation, 209—Wood's resonance series, 210	

CHAPTER V: FINER DETAILS ABOUT ELECTRONIC STATES AND ELECTRONIC TRANSITIONS..... 212

1. CLASSIFICATION OF ELECTRONIC STATES; MULTIPLY STRUCTURE.....	212
Orbital angular momentum, 212—Spin, 214—Total angular momentum of the electrons; multiplets, 214—Symmetry properties of the electronic eigenfunctions, 217	
2. COUPLING OF ROTATION AND ELECTRONIC MOTION.....	218
(a) Hund's Coupling Cases.....	219
Hund's case (a), 219—Hund's case (b), 221—Hund's case (c), 224—Hund's case (d), 225—Hund's case (e), 226	
(b) Uncoupling Phenomena.....	226
Λ -type doubling, 226—Transition from case (b) to case (d) (L uncoupling), 229—Transition from case (a) to case (b) (spin uncoupling, 231—Transition from case (b) to case (c), 237	
(c) Symmetry Properties of the Rotational Levels.....	237
Σ states, 237— Π , Δ , . . . states, 239	

3. TYPES OF ELECTRONIC TRANSITIONS	240
(a) Selection Rules	240
General selection rules, 240—Selection rules holding for case (a) as well as case (b), 241—Selection rules holding only in case (a), 242—Selection rules holding only in case (b), 244—Selection rules holding only in case (c), 244—Selection rules holding only in case (d), 244—More general cases, 245	
(b) Allowed Electronic Transitions	245
Notation, 245— $^1\Sigma$ — $^1\Sigma$ transitions, 245— $^2\Sigma$ — $^2\Sigma$ transitions, 247— $^3\Sigma$ — $^3\Sigma$ transitions, 250— $^1\Pi$ — $^1\Sigma$ transitions, 251— $^1\Sigma$ — $^1\Pi$ transitions, 256— $^2\Pi$ — $^2\Sigma$ transitions, 257— $^2\Sigma$ — $^2\Pi$ transitions, 264— $^3\Pi$ — $^3\Sigma$ transitions, 264— $^3\Sigma$ — $^3\Pi$ transitions, 265— Π — Σ transitions of higher multiplicities, 266— $^1\Pi$ — $^1\Pi$ transitions, 266— $^2\Pi$ — $^2\Pi$ transitions, 268— $^3\Pi$ — $^3\Pi$ transitions, 271— Π — Π transitions of higher multiplicity, 272— Π — Δ transitions, 273— Δ — Δ transitions, 273—Band structures in Hund's cases (c) and (d), 273—General remarks on the technique of the analysis of multiplet bands, 274	
(c) Forbidden Electronic Transitions	275
Violation of approximate selection rules, 275—Quadrupole and magnetic dipole radiation, 277—Enforced dipole radiation, 280	
4. PERTURBATIONS	280
Observed phenomena, 280—General considerations, 282—Selection rules for perturbations, 284—Rotational perturbations, 286—Vibrational perturbations, 292—Intersection of potential curves and the non-crossing rule, 295	
5. ZEEMAN EFFECT AND STARK EFFECT	298
General remarks on the splitting of molecular energy levels in a magnetic field, 298—The Zeeman splitting of $^1\Sigma$ states, 299—Zeeman effect in Hund's case (a), 300—Zeeman effect in Hund's case (b), 303—Other cases, 304—Polarization of resonance fluorescence, 305—Magnetic rotation spectra, 306—Stark effect, 307	
6. HYPERFINE STRUCTURE	308
Hyperfine structure without field, 308—Zeeman effect of hyperfine structure, 311	
CHAPTER VI: BUILDING-UP PRINCIPLES, ELECTRON CONFIGURATIONS, AND VALENCE	315
1. DETERMINATION OF THE TERM MANIFOLD FROM THE STATES OF THE SEPARATED ATOMS	315
Unlike atoms, 316—Like atoms, 320	
2. DETERMINATION OF THE TERM MANIFOLD FROM THE STATES OF THE UNITED ATOM	322
Unlike atoms, 322—Like atoms, 322	

	PAGE
3. DETERMINATION OF THE TERM MANIFOLD FROM THE ELECTRON CONFIGURATION.....	322
(a) Quantum Numbers of the Individual Electrons.....	322
Single electron in an axially symmetric electric field, 323—Several electrons, 331	
(b) The Pauli Principle in the Molecule.....	331
(c) Derivation of the Term Type (Species) from the Electron Configuration in Russell-Saunders Coupling.....	333
Terms of non-equivalent electrons, 333—Terms of equivalent electrons, 335—Electron configurations with equivalent and non-equivalent electrons, 336—Like atoms, 337	
(d) Derivation of the Term Type (Species) for Other Types of Coupling.....	337
(ω, ω) coupling, 337—(Ω_c, ω) coupling, 338—Other types of coupling, 338	
(e) Term Manifold of the Molecule, Examples.....	338
General considerations, 338— H_2 and the hydrides, 339—Molecules with nuclei of equal charge, 344—Other molecules, 346	
4. STABILITY OF MOLECULAR ELECTRONIC STATES; VALENCE.....	348
(a) Homopolar Binding (Atomic Binding).....	349
Treatment of the H_2 molecule according to Heitler and London, 350—Generalization of the Heitler-London theory for more complicated cases, 354—Theory of bonding and antibonding electrons for equal nuclear charges, 359—Unlike nuclear charges, 367	
(b) Heteropolar Binding (Ionic Binding).....	371
Ionic molecules, 373—Transition cases, 374—Ionicity and polarity, 375	
(c) Van der Waals Binding.....	377
5. INTENSITIES OF ELECTRONIC TRANSITIONS.....	381
General formulae, 382—Rydberg transitions, 383—Charge-transfer spectra, 384—Other sub-Rydberg transitions, 385	
CHAPTER VII: CONTINUOUS AND DIFFUSE MOLECULAR SPECTRA: DISSOCIATION AND PREDISSOCIATION.....	387
1. CONTINUOUS SPECTRA AND BAND CONVERGENCE LIMITS: DISSOCIATION OF DIATOMIC MOLECULES.....	387
(a) Absorption.....	387
Ionization continua, 387—Dissociation continua, 388—Upper state continuous, 388—Lower state or both lower and upper state continuous, 394	
(b) Emission.....	400
Upper state continuous (molecule formation in a two-body collision), 400—Lower state continuous, 402—Both upper and lower state continuous, 405	

	PAGE
2. DIFFUSE MOLECULAR SPECTRA, PREDISSOCIATION, AND RELATED TOPICS.	405
(a) General Discussion of Spontaneous Radiationless Decomposition Processes.....	405
The Auger process, 405—Passage through potential barriers, 408	
(b) Radiationless Decomposition Processes in the Molecule.....	409
Diffuseness of the bands, 410—Photochemical decomposition, 411—Breaking-off of bands, 412—Different types of predissociation, 413—Preionization, 414—Inverse predissociation, 414—Accidental predissociation, 415	
(c) Selection Rules for Predissociation.....	416
Kronig's selection rules, 416—Forbidden predissociations, 419—Preionization, 419	
(d) The Franck-Condon Principle in Predissociation.....	420
Case I of predissociation, 420—Case III (predissociation by rotation); effective potential curves, 425—Influence of rotation in case I, 430	
(e) Pressure Effects in Predissociation.....	432
Induced predissociation, 432—Suppression of breaking-off by pressure, 433	
(f) Other Diffuse Molecular Spectra.....	435
3. DETERMINATION OF HEATS OF DISSOCIATION.....	437
(a) Determination of Dissociation Limits.....	438
(1) Band convergences, 438—(2) Extrapolation to convergence limits, 438—(3) Long-wave-length limit of an absorption continuum, 441—(4) Predissociation limits, 442—(5) Excitation of atomic fluorescence, 443—(6) Photodissociation, 443—(7) Chemiluminescence, 443	
(b) Determination of the Dissociation Products.....	444
(1) Energy differences of dissociation limits, 444—(2) Application of the Wigner-Witmer correlation rules, 445—(3) Application of the non-crossing rule, 445—(4) Observation of atomic fluorescence, 445—(5) Use of thermochemical data, 445	
(c) Examples.....	446
O ₂ , 446—N ₂ , 449	
CHAPTER VIII: EXAMPLES, RESULTS, AND APPLICATIONS.....	451
1. ENERGY LEVEL DIAGRAMS; MOLECULAR CONSTANTS.....	451
Empirical relations, 453—Ionization potentials, 459	
2. APPLICATIONS TO OTHER FIELDS OF PHYSICS.....	460
Nuclear physics, 460—Paramagnetism, 462—Collision processes, 463—Nature of the liquid and the solid state, 464—Determination of high temperatures, 465—Calculation of thermodynamic quantities, 466	

	PAGE
3. APPLICATIONS TO CHEMISTRY.....	472
Free radicals, 472—Elementary chemical reactions in gases and chemiluminescence, 473—Photochemical primary processes, 477—Chemical equilibria, 479—Atomic heats of formation and related topics, 480	
4. APPLICATIONS TO ASTROPHYSICS.....	482
Absorption spectrum of the earth's atmosphere, 482—Emission spectrum of the earth's atmosphere, 484—Planetary atmospheres, 486—Comets, 488—Stellar atmospheres, 491—Interstellar space, 496	
APPENDIX: VIBRATIONAL AND ROTATIONAL CONSTANTS FOR THE ELECTRONIC STATES OF ALL KNOWN DIATOMIC MOLECULES (TABLE 39)....	501
BIBLIOGRAPHY.....	582
AUTHOR INDEX.....	617
SUBJECT INDEX.....	627