Contents

Prefa Intro	ace	ix xiii	
Chapter 1 General Problems of Methodology of Spectrum Analysis of Complex Molecules. Chapter 2 General Principles of Calculating the Electronic and Vibration			
2.1	Separating Electronic and Nuclear Motions and the Adiabatic		
	Approximation	13	
2.2	The Franck–Condon Principle	24	
2.3	Types of Electronic Spectra and Some Important Patterns.	32	
2.4	Symmetry of Wave Functions and Selection Rules by Symmetry	37	
2.5	Solving the Non-adiabatic Vibronic Problem	38	
2.6	The Hertzberg–Teller Approximation	42	
2.7	Algorithm for Solving the Vibronic Problem	44	
Char	oter 3 Non-interacting Electron Approximation	52	
3.1	The Variational Method for Solving Schroedinger's Equation	52	
3.2	The Approximation of Non-interacting Electrons	58	
Char	oter 4 General Solution of the Polyelectronic Problem	71	
4.1	The Method of Configuration Interaction	71	
4.2	Spin-degeneracy Multiplets.	77	
4.3	The Matrix Method of Constructing Spin Multiplets.	81	
4.4	The Self-consistent Field Method	92	
4.5	Approximate Expressions for the Matrix Elements of the Hartree-		
	Fock Operator	101	
4.6	Expressions for the Matrix Elements of Dipole Transitions	105	
4.7	Use of Overcomplete Basis Sets	108	
Chaj	pter 5 The Symmetries of Molecular Orbitals and Normal Co-		
ordir	nates	111	
5.1	The Symmetry Elements of Polyatomic Molecules	111	
5.2	Symmetricized Linearly Combined Atomic Orbitals:		
	Hybridization	115	

5.3	The Construction of Molecular Orbitals of Symmetry and Symmetry Co-ordinatestry Co-ordinates12'
Chap	ter 6 Separation of Motions of Nuclei of Polyatomic Molecules:
Equa	tion for Vibrations
6.1	Separation of Types of Nuclear Motions in Polyatomics 15
6.2	Derivation of an Expression for the Kinetic Energy Operator in the Theory of Vibration of Polyatomic Molecules
Chap	ter 7 Solving the Vibrational Problem in the Harmonic
Appr	
7.1	Description of a Malacula's Configuration at Different Vibrational
1.2	Levels 18
73	Calculating the Mean Square Amplitudes of the Vibrational Co-
1.5	ordinates 19
71	Calculating Partial Derivatives of Vibration Frequencies with
7.4	Respect to a Molecule's Parameters 19
75	Relationships Between the Squares of Vibrational Frequencies in
1.0	Isotopic Molecules
7.6	The Use of Dependent Co-ordinates
Chap	ter 8 Computation of Matrices of Transition to Curvilinear Co-
ordin	ates and of Kinematic Coefficients
8.1	Natural Vibrational Co-ordinates and Classification of Vibrations 21
8.2	Classification of Molecular Vibrations
8.3	Derivation of Formulae for Elements of Matrix \overline{B}
8.4	Derivation of Expressions for Non-planar Co-ordinates 23
8.5	Co-ordinates Suitable for Specifying the Vibrations of Ligands in
	the Proximity of Heavy Complexing Atoms
8.6	Properties Element of the Matrix of Kinematic Coefficients 23
8.7	Standard Formulae for Kinematic Coefficients
8.8	Expression for the Displacements of Atoms from the Equilibrium
0.0	Positions through the Natural Co-ordinates
8.9	Expression for Derivatives of Bond Vectors with Respect to the
	vibrational Co-ordinates 24
Char	tor Q. The Detential Function of a Delvatomic Molecule and its
Pron	erties 24
9 1	An Analytical Form of the Potential Function 24
92	General Properties of the Force Constants of a Polyatomic
1.4	Molecule
9.3	The Ouantum Theory of Force Constants 25
9.4	Calculating the Force Constants
-	

vi

9.5	Effective Algorithm of a Quantum-mechanical Search of Para- meter Values of the Potential Function of Polyatomic Molecules in an Arbitrary System of Internal Co-ordinates	272		
Chapter 10 Solution of the Problem for Anharmonic Vibrations and				
Vibrat	tions with Large Amplitudes	279		
10.1	General Comments	279		
10.2	The Variational Method for Solving Anharmonic Problems	283		
10.3	Examples of the Solutions of Anharmonic Vibrational Problems	288		
10.4	Use of Variational Method for Calculation of Highly Excited Vibration Levels of Polyatomic Molecule Energy	303		
10.5	An Anharmonic Analysis of the Vibrations of A—H and AH bonds in Ion-molecular and Intermolecular H Complexes of			
	Hydroxyl-containing Compounds	308		
10.6	Investigation of the Excited Vibrational State of Small Polyatomic	313		
10.7	Variational Solving of the Problem of Arbitrary Internal Motions			
10.7	in Polyatomic Molecules: Internal Rotation	320		
Chapt	ter 11 The Theory of Intensity in the Infra-red Spectra of	225		
Polya		335		
11.1	Expressions of the Dipole Transitions for Matrix Elements	335		
11.2	The Valence-optical Scheme	340		
11.3	General Formula for $(\partial \vec{\mu} / \partial Q_i)_0$	356		
11.4	The Symmetry of Molecules and the Selection Rules with Respect	262		
	to Symmetry.	303		
11.5	Additional Relationships Between the Co-ordinates	30/		
11.6	Examples of Compiling General Formulae for $(\partial \mu / \partial Q_i)_0$	308		
11.7	Relationships between the Intensities of Isotopically Substituted Molecules.	376		
11.8	The Intensity Theory of Overtone and Combination Bands	378		
11.9	The Valence-optical Theory of Band Intensities in Infra-red			
	Spectra of Molecules with Internal Rotations	392		
11.10	The Valence-optical Theory of Intensities in the Infra-red Spectra			
	of Molecular Ions	398		
Chap	ter 12 Characteristic Vibrations of Polyatomic Molecules	401		
12.1	General Principles.	401		
12.2	I ne I neory of Characteristic Intensities and Polarizations in Infra-	410		
10.0		410		
12.3	The Intensities of Infra-red Absorption Bands of a Polyatomic	417		
10.4	Molecule that Contains Several Identical Groups	41/		
12.4	Characteristic Intensities and Polarizations for Primary Overtones and Combination Bands.	420		

vii

viii

12.5	The Dependence of the Overtone and Combination Band Intens-	100
	ities on the Number of Identical Groups in a Molecule	423
12.6	Characteristic Electronic Transitions	425
Chap	ter 13 Solutions of Inverse Spectral Problems	429
13.1	General Aspects	429
13.2	Symbolic Logic Methods for Spectrochemical Investigations	435
13.3	Mathematical Formulation of the Inverse Spectral Problem for	
	Continuous (Functional) Models.	465
13.4	The Inverse Electro-optical Problem	477
Chap	ter 14 Methods of Calculation of Vibronic Spectra of Polyatomic	
Mole	cules	495
14.1	The Calculation of Matrix Elements	495
14.2	Spectral Distribution Curves of Absorption Coefficients.	519
14.3	Calculation of the Electronic Spectra of Polyatomic Molecules	
	Taking into Account Vibrational Anharmonicity and Internal	
	Rotation	537
14.4	Determination of Potential Surface Parameters of Excited States	
	for Small Changes in the Latter Compared with the Ground States	540
14.5	The Valence-optical Theory of Intensities in the Vibronic Spectra	
	of Polyatomic Molecules	544
14.6	Transitions between very different States of Polyatomic Molecules	554
Chap	ter 15 Theory of Intensities in the Raman Spectra of Polyatomic	
Mole	cules	563
15.1	General Problems and the Construction of the Parametric Theory	563
15.2	General Formulae for the Intensity and Depolarization of a Raman	
	Line	570
15.3	The Valence-optical Scheme and the Formulae for Components of	
	a Polarizability Tensor's Derivative with Respect to a Normal	
	Co-ordinate	574
15.4	Propeties of the Intensities and Degree of Polarization of the Lines	592
155	in Raman Spectra of Symmetrical Molecules	202
15.5	An Example of Calculating the Components of the Derivative	586
151	Tensor of Polarizability: The H_2O molecule	200
15.0	Solution of the Inverse Spectral Floblen in the Theory of	500
	Intensities in Raman Spectra	590
App	endix by B. K. Novosadov	
Metl	hods for Computing Matrix Elements in the Theory of Electronic	
Spec	tra of Polyatomic Molecules	596
Inde	x	627