P	AGE
INTRODUCTION General remarks, 1—Symmetry elements and symmetry opera- tions, 1—Point groups, 5	1
CHAPTER I: ROTATION AND ROTATION SPECTRA	13
1. LINEAR MOLECULES Energy levels, 14—Symmetry properties, 15—Statistical weights and influence of nuclear spin and statistics, 16—Thermal distribu- tion of rotational levels, 18—Infrared rotation spectrum, 19— Rotational Raman spectrum, 20	13
2. SYMMETRIC TOP MOLECULES Classical motion (vector diagram), 22—Energy levels, 24—Sym- metry properties and statistical weights, 26—Thermal distribution of rotational levels, 29—Infrared spectrum, 29—Rotational Raman spectrum, 34	22
3. SPHERICAL TOP MOLECULES Classical motion, 38—Energy levels, 38—Statistical weights and symmetry properties, 38—Thermal distribution of rotational levels, 40—Infrared spectrum, 41—Rotational Raman spectrum, 41	37
4. ASYMMETRIC TOP MOLECULES Classical motion, 42—Energy levels, 44—Influence of non-rigidity, 49—Symmetry properties and statistical weights, 50—Infrared rotation spectrum, 55—Raman spectrum, 59	42
CHAPTER II: VIBRATIONS, VIBRATIONAL ENERGY LEVELS, AND VIBRATIONAL EIGENFUNCTIONS	61
 NATURE OF NORMAL VIBRATIONS: CLASSICAL THEORY	61
2. VIBRATIONAL ENERGY LEVELS AND EIGENFUNCTIONS General, 76—Energy levels, 77—Eigenfunctions, 78—Degenerate vibrations, 80	76
3. Symmetry of Normal Vibrations and Vibrational Eigenfunctions	82
(a) Effect of symmetry operations on non-degenerate normal vibrations	82
vii	

mal coordinates, 98-Triply degenerate vibrations, 99

- (c) Effect of symmetry operations on the vibrational eigenfunctions.. 101 Molecules with non-degenerate vibrations only, 101—Molecules with degenerate vibrations, 103—Generalization, 104
- (d) Symmetry types (species) of normal vibrations and eigenfunctions. 104 Point groups C_1 , C_2 , C_3 , and C_i , 105—Point groups C_{2v} , C_{2h} and $D_2 \equiv V$, 106—Point group $V_h \equiv D_{2h}$, 106—Degenerate symmetry types, 108—Point groups C_{3v} and D_3 , 109—Point group C_{5v} , 111— Point group $C_{\infty v}$, 111—Point groups C_{4v} , D_4 and $D_{2d} \equiv V_d$, 112 —Point groups C_{6v} and D_6 , 114—Point groups $D_{3d} (\equiv S_{6v})$ and $D_{4d} (\equiv S_{8v})$, 114—Point groups D_{3h} and D_{5h} , 116—Point groups D_{4h} and D_{6h} , 116—Point group $D_{\infty h}$, 118—Point groups C_p , 119— Point groups S_4 and S_6 , 120—Point groups C_{ph} , 120—Point groups T_d and O, 121—Point group O_h , 122—Point group T, 123
- (e) Symmetry types (species) of the higher vibrational levels...... 123 Non-degenerate vibrations, 124—Binary combinations of a nondegenerate and a degenerate vibration, 125—Multiple excitation of a single, degenerate vibration, 125—Binary combinations of two different degenerate vibrations, 129—More general cases, 130

4. Determination of Normal Modes of Vibration...... 131

- (a) Number of normal vibrations of a given symmetry type (species).. 131
 Sets of equivalent nuclei, 131—Non-degenerate vibrations, 131— Degenerate vibrations, 135
- (b) Methods for the general solution of the secular equation...... 140 Solution in Cartesian coordinates, 140—Solution in "internal" coordinates, 142—Solution by the use of symmetry coordinates, 145—Application to non-linear XY₂, 148—Application to symmetrical planar X₂Y₄, 150—Application to linear symmetrical XY₂, 153—Application to pyramidal XY₃, 154—Solution by the use of mechanical models, 157

page . 83

P	AGE
(e) Assumption of more general force fields	186
 (f) Intercomparison of force constants in different molecules, character- istic bond frequencies, stretching and bending vibrations, and related matters	192
5. Anharmonicity and Interaction of Vibrations: Limitations of the	901
 (a) Influence of anharmonicity for non-degenerate vibrations A simple potential surface, 201—Classical anharmonic motion, 204 —Energy levels, 205—Vibrational eigenfunctions, 209 	201
(b) Influence of anharmonicity for (non-accidentally) degenerate vibra- tions	210
(c) Accidental degeneracy, Fermi resonance Qualitative discussion, 215—Mathematical formulation, 215— Application to CO_2 and similar cases, 217—Application to H_2O , 218—Splitting of the l_i degeneracy, 219	215
(d) Several potential minima General remarks, 220—Inversion doubling in NH ₃ and similar molecules, 221—Optical isomers, 224—Torsional oscillations, 225	220
 Isotope Effect Introductory remarks, 227—Triatomic molecules, 228—The Teller-Redlich product rule, 231—Resolution of the symmetry types of a point group into those of a point group of lower sym- metry, 235—Application to the unsymmetrically substituted iso- topes of an XY₄ molecule, 236 	227
CHAPTER III: VIBRATIONAL INFRARED AND RAMAN SPECTRA.	239
1. CLASSICAL TREATMENT	239
(a) Infrared vibration spectra Active and inactive fundamentals, 239—Overtone and combina- tion vibrations, 241	239
(b) Vibrational Raman spectra	242

		P	AGE
2. 0	QUA	NTUM-THEORETICAL TREATMENT	249
((a)	Elementary treatment of fundamentals	249
((b)	Rigorous vibrational selection rules Infrared spectrum, 251—Raman spectrum, 254—The rule of mutual exclusion, 256—Inversion doubling, 256	251
((c)	More refined treatment of fundamentals General rule, 258—Examples, 258—Alternative treatment; inten- sities, 259	258
((d)	Overtone and combination bands	261
1	(e)	Polarization of Raman lines	269
3.	Ind	IVIDUAL MOLECULES	271
((a)	Triatomic Molecules Carbon dioxide, CO ₂ , 272—Carbon disulfide, CS ₂ , 276—Nitrous oxide, N ₂ O, 277—Hydrogen cyanide, HCN, 279—Water, H ₂ O, 280—Heavy water HDO and D ₂ O, 282—Hydrogen sulfide, H ₂ S, HDS, D ₂ S, 282—Nitrogen peroxide, NO ₂ , 284—Sulfur dioxide, SO ₂ , 285—Ozone, O ₃ , 285—Other triatomic molecules, 287	272
	(b)	Four-atomic molecules Acetylene, C_2H_2 , 288—Heavy acetylene, C_2HD and C_2D_2 , 289— Cyanogen, C_2N_2 , 293—Ammonia, NH ₃ and ND ₃ , 294—Trihalides of phosphorus, arsenic, antimony, and bismuth, 297—Boron tri- fluoride, BF ₃ , 298—Phosphorus, P ₄ , 299—Formaldehyde, H ₂ CO and D ₂ CO, 300—Hydrogen peroxide, H ₂ O ₂ , 301—Other four- atomic molecules, 303	288
	(c) ,	Five-atomic molecules	303
	(d)	Six-atomic molecules. Diacetylene, HC=C-C=CH, 323-Ethylene, C_2H_4 and C_2D_4 , 325-Tetrachloroethylene, C_2Cl_4 , 328-Cis and trans $C_2H_2Cl_2$, 329-CH ₃ CN and CH ₃ NC, 332-Methyl alcohol, CH ₃ OH and CH ₃ OD, 334-Other six-atomic molecules, 335	323
	(e)	Seven-atomic molecules. Sulfur hexafluoride, SF ₆ , 336—Methyl acetylene, CH ₃ —C \equiv CH, 337—Allene, CH ₂ $=$ C \equiv CH ₂ , 339—Ethylene oxide, C ₂ H ₄ O, 340—Other seven-atomic molecules, 342	336
	(f)	Eight-atomic molecules Ethane, C_2H_6 and C_2D_6 , 342 — $C_2H_4Cl_2$, $C_2H_2Cl_4$, and the question of rotational isomerism, 346 —Other eight-atomic molecules, 351	342

x

1	PAGE
(g) Nine-atomic molecules.	352
cyclopropane, C_3H_6 , 352—Dimetryl etner, $(CH_3)_2O$, 353—Pro- pylene, CH_3 — CH = CH_2 , 354—Other nine-atomic molecules, 356	
(h) Ten-atomic molecules	356
Dimethyl acetylene, CH_3 — $C\equiv C$ — CH_3 , 356—Azomethane, $(CH_3)_2N_2$, 357—Other ten-atomic molecules, 359	
(i) Eleven-atomic molecules	359
Propane, CH_3 — CH_2 — CH_3 , 359—Other eleven-atomic molecules, 362	1
(j) Twelve-atomic molecules	362
Benzene, C_6H_6 and C_6D_6 , 362—Other twelve-atomic molecules, 369	
CHAPTER IV: INTERACTION OF ROTATION AND VIBRATION, ROTATION-VIBRATION SPECTRA	370
1. LINEAR MOLECULES	370
(a) Energy levels.	370
Elementary treatment, 370—Symmetry properties of rotational	010
levels, 372—More detailed theory of the rotational constants α_i ;	
Coriolis interaction, 372—t-type doubling, 377—Perturbations, 378	
(b) Infrared spectrum	379
Selection rules, 379—Types of infrared bands, 380— Σ — Σ bands	
(3)], 389—Combination differences, evaluation of rotational con-	
stants, 390—Examples, 391—Determination of internuclear	
distances: isotope enect, 395	
(c) Raman spectrum	398
Raman bands, 399	
2. Symmetric Top Molecules	400
(a) Energy levels	400
Non-degenerate vibrational states, 400—Degenerate vibrational	100
states, 401—Symmetry properties of the rotational levels, 406—	
Inversion doubling, 411—Perturbations, 413	
(b) Infrared spectrum	414
Transitions between non-degenerate vibrational levels: parallel	
bands, 416—Transitions between non-degenerate vibrational	
evens: perpendicular and hybrid bands, 424—Transitions between a non-degenerate and a degenerate vibrational level: perpendicular	
bands, 428—Transitions between two degenerate vibrational	
levels, 433—Analysis of infrared bands, moments of inertia, and intermulation distances of grammatric ten malagular, 494	
internuclear distances of symmetric top molecules, 434	

xi .

		Р	AGE
	(c)	Raman spectrum	441
		Non-totally symmetric non-degenerate Raman bands, 442—De- generate Raman bands, 443—Unresolved Raman bands, 444	
3.	Sph	ERICAL TOP MOLECULES	446
	(a)	Energy levels Non-degenerate vibrational states, 446—Degenerate vibrational states, 447—Symmetry properties of the rotational levels, 449— Inversion doubling, 451—Coriolis splitting of the rotational levels, 451	446
	(b)	Infrared spectrum. Selection rules, $453 - F_2 - A_1$ transitions, 453 -Forbidden vibrational transitions, 456	453
	(c)	Raman spectrum Selection rules, $458 - A_1 - A_1$ transitions, $458 - E - A_1$ transitions, $458 - F_2 - A_1$ transitions, 458	458
4.	Asy	MMETRIC TOP MOLECULES	460
	(a)	Energy levels	460
		Unperturbed energy levels, 460—Symmetry properties, 462—Per- turbations, 466	
	(b)	Infrared spectrum	468
		Selection rules, 468—Type A bands, 469—Type B bands, 477— Type C bands, 480—Unresolved infrared bands, 482—Analysis of infrared bands of asymmetric top molecules, 484—Examples, moments of inertia and internuclear distances, 487	
	(c)	Raman spectrum	489
		Selection rules, 489—Unresolved Raman bands, 490	
5.	Mo	LECULES WITH FREE OR HINDERED INTERNAL ROTATION	491
	(a)	Energy levels Free rotation, 491—Hindered rotation, 494	491
	(b)	Infrared spectrum	496
		Symmetrical molecules, 496—Slightly asymmetric molecules, CH ₃ OH, 497	
	(c)	Raman spectrum	500
CHAP?	TEF	v: APPLICATIONS	501
1.	CAI	LCULATION OF THERMODYNAMIC QUANTITIES	501
		The partition function (state sum), 501—The vibrational partition function, 503—The rotational partition function, 505—Partition function for molecules with internal rotations, 510—Heat content and heat capacity, 512—Entropy and free energy, 519—Chemical equilibria, 526	
2.	NA	TURE OF LIQUID AND SOLID STATES: INTERMOLECULAR FORCES	531
		Rotation of molecules in liquids and solids, 531—Molecular vibra- tions in liquids and solids, 534	

xii

	PAGE
APPENDIX: PHYSICAL CONSTANTS AND	Conversion Factors 538
BIBLIOGRAPHY	539
AUTHOR INDEX	559
SUBJECT INDEX	