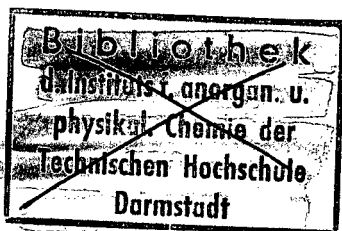


# Infrared and Raman Spectra of Crystals

GEORGE TURRELL

*Professeur Associé,  
Laboratoire de Spectroscopie Infrarouge,  
Faculté des Sciences de Bordeaux,  
France*

Tür 2



1972

Inventar Nr. 243 / PC



ACADEMIC PRESS · LONDON AND NEW YORK

~~Inv. Nr.~~ 3910

## CONTENTS

PREFACE	v
ACKNOWLEDGEMENTS	vii

### CHAPTER 1

#### Molecular Vibrations

I. INTRODUCTION	1
II. KINETIC ENERGY	2
III. INTERNAL COORDINATES	5
IV. POTENTIAL ENERGY	7
V. NORMAL VIBRATIONS	9
VI. QUANTUM-MECHANICAL VIEWPOINT	15
VII. SELECTION RULES	15
VIII. ABSOLUTE INTENSITIES	19
REFERENCES	21

### CHAPTER 2

#### Molecular Symmetry

I. SYMMETRY OPERATIONS	22
II. ALGEBRA OF SYMMETRY OPERATIONS	25
III. POINT GROUPS	27
IV. EQUIVALENT ATOMS AND SUBGROUPS	28
V. COORDINATE TRANSFORMATIONS	29
VI. CONJUGATE OPERATIONS AND CLASSES	32
VII. IRREDUCIBLE REPRESENTATIONS	33
VIII. CHARACTER TABLES	35
IX. "MAGIC FORMULA"	37
X. CLASSIFICATION OF MOLECULAR MOTIONS	38
XI. INTERNAL COORDINATES AND REDUNDANCY	41
XII. SYMMETRY COORDINATES	44
XIII. VIBRATIONAL SELECTION RULES	48
XIV. SUBGROUPS AND CORRELATION DIAGRAMS	56
REFERENCES	59

**CHAPTER 3****Lattice Dynamics**

I. INFINITE MONATOMIC CHAIN . . . . .	60
II. BOUNDARY CONDITIONS . . . . .	67
III. DIATOMIC CHAIN . . . . .	69
IV. DISTRIBUTION OF LATTICE FREQUENCIES . . . . .	73
V. VIBRATIONS OF THREE-DIMENSIONAL LATTICES . . . . .	75
VI. PHONONS . . . . .	77
VII. RECIPROCAL LATTICE AND BRILLOUIN ZONES . . . . .	79
VIII. DYNAMICAL MATRIX . . . . .	82
REFERENCES . . . . .	86

**CHAPTER 4****Crystal Symmetry**

I. CRYSTAL CLASSES . . . . .	87
II. PROPERTIES OF SPACE GROUPS . . . . .	89
III. SCREW AXES AND GLIDE PLANES . . . . .	94
IV. SITE SYMMETRY . . . . .	99
V. PRIMITIVE CELLS . . . . .	99
VI. IRREDUCIBLE REPRESENTATIONS OF THE TRANSLATION GROUP . . . . .	103
VII. FACTOR-GROUP ANALYSIS . . . . .	107
VIII. MOLECULAR AND COMPLEX IONIC CRYSTALS . . . . .	111
IX. FACTOR-GROUP ANALYSIS OF MOLECULAR CRYSTALS: EXAMPLES . . . . .	113
X. FACTOR-GROUP ANALYSIS OF COMPLEX IONIC CRYSTALS: EXAMPLES . . . . .	122
REFERENCES . . . . .	135

**CHAPTER 5****Optical Properties of Crystals**

I. ELECTROMAGNETIC BASIS . . . . .	136
II. ABSORPTION AND REFLECTION OF RADIATION . . . . .	138
III. DIELECTRIC DISPERSION . . . . .	141
IV. EFFECTIVE FIELD AND ABSORPTION INTENSITIES . . . . .	147
V. WAVE PROPAGATION IN ANISOTROPIC MEDIA . . . . .	150
VI. INFRARED DICHROISM . . . . .	153
VII. RAMAN SCATTERING . . . . .	158
VIII. RAMAN SPECTRA OF NAPHTHALENE SINGLE CRYSTALS . . . . .	164
IX. COMBINATIONS AND OVERTONES: MULTIPHONON PROCESSES . . . . .	169
X. INTERACTION OF ELECTROMAGNETIC RADIATION . . . . .	172
REFERENCES . . . . .	176

## CHAPTER 6

## Determination of Force Fields and Structures

I. INTERATOMIC FORCES IN SOLIDS . . . . .	178
II. F-G Method at $k=0$ . . . . .	180
III. FORCE CONSTANTS OF PEROVSKITE FLUORIDES . . . . .	186
IV. SEPARATION OF INTERNAL AND EXTERNAL VIBRATIONS . . . . .	193
V. LATTICE VIBRATIONS OF BENZENE AND NAPHTHALENE . . . . .	199
VI. SPECTROSCOPIC PROPERTIES OF HYDROGEN BONDS . . . . .	207
VII. STRUCTURES OF CALCIUM AMIDES . . . . .	214
VIII. STRUCTURE OF CRYSTALLINE TRIFLUOROACETONITRILE . . . . .	219
REFERENCES . . . . .	222

## CHAPTER 7

## Infrared and Raman Spectra of Polymers

I. COUPLED-OSCILLATOR MODEL . . . . .	224
II. COUPLING OF NITRATE AND CARBONATE IONS IN ARAGONITES . . . . .	226
III. CHAIN SYMMETRY AND LINE GROUPS: POLYETHYLENE . . . . .	232
IV. FINITE CHAINS: <i>n</i> -PARAFFINS . . . . .	236
V. CRYSTALLINE POLYMERS AND CHAIN INTERACTIONS . . . . .	247
VI. INTRACHAIN FORCES IN <i>n</i> -PARAFFINS . . . . .	254
VII. INTERCHAIN COUPLING IN CRYSTALLINE POLYETHYLENE . . . . .	259
VIII. VIBRATIONS OF HELICAL CHAINS . . . . .	262
REFERENCES . . . . .	266

## CHAPTER 8

## Spectra of Impure Crystals

I. INFRARED SPECTRA AND ANHARMONICITY OF THE CYANATE ION . . . . .	267
II. IMPURITY-LATTICE INTERACTION . . . . .	272
III. INFRARED SPECTRA OF THE AZIDE ION IN ALKALI-HALIDE LATTICES . . . . .	277
IV. DYNAMICS OF IMPERFECT LATTICES . . . . .	285
V. INFRARED SPECTRA OF LOCALIZED IMPURITY MODES . . . . .	292
VI. VIBRATIONAL SELECTION RULES FOR IMPURE CRYSTALS . . . . .	294
VII. COMBINATION SPECTRA: CYANATE ION IN KBr . . . . .	299
VIII. SPECTRA OF RARE-GAS MATRIX-ISOLATED SPECIES . . . . .	301
IX. EXTERNAL MOTIONS OF TRAPPED HYDROGEN HALIDES . . . . .	304
REFERENCES . . . . .	313

**Appendices**

A. G-MATRIX ELEMENTS FOR STRETCHING AND BENDING COORDINATES . . . . .	315
B. CALCULATION OF FORCE CONSTANTS . . . . .	319
C. CHARACTER TABLES . . . . .	324
D. SUBGROUPS OF THE CRYSTALLOGRAPHIC POINT GROUPS . . . . .	338
E. SPACE GROUPS AND CRYSTALLOGRAPHIC SITES . . . . .	340
F. BRAVAIS LATTICES AND PRIMITIVE CELLS . . . . .	350
G. POLARIZABILITY TENSORS FOR THE 32 CRYSTAL CLASSES . . . . .	358
H. LINEAR-RESPONSE THEORY AND THE KRAMERS-KRONIG RELATIONS . . . . .	362
REFERENCES . . . . .	364
AUTHOR INDEX . . . . .	367
SUBJECT INDEX . . . . .	373