

## Contents

PREFACE . . . . .	vii
-------------------	-----

### **Characteristic Features of Polymer Spectra**

1. The Structure of Polymers . . . . .	1
2. Comparison of Spectra of Nonpolymeric and Polymeric Compounds . . . . .	3
<i>A. Nonpolymeric Compounds</i> . . . . .	3
<i>B. Polymeric Compounds</i> . . . . .	4
3. Orientation . . . . .	6
<i>A. General Principles of Infrared Dichroism</i> . . . . .	6
<i>B. Dichroism in Polymers</i> . . . . .	8
<i>C. Illustration</i> . . . . .	10
4. Crystallinity . . . . .	11
<i>A. Introduction</i> . . . . .	11
<i>B. Discussion of Observed Spectra</i> . . . . .	12
<i>C. Interpretation and Summary</i> . . . . .	16
5. Analytical Applications . . . . .	18
<i>A. Introduction</i> . . . . .	18
<i>B. Conventional Type of Infrared Analysis</i> . . . . .	19
<i>C. Chemical Reactions Involving Polymers</i> . . . . .	20
<i>D. End Group Analysis</i> . . . . .	20
<i>E. Unsaturation</i> . . . . .	24
<i>F. Configurational Isomers</i> . . . . .	27
References . . . . .	30

## II

### **Selection Rules for Chain Molecules**

1. Introduction . . . . .	33
2. Fundamentals of Group Theory . . . . .	33
<i>A. Definitions and Nomenclature</i> . . . . .	33
<i>B. Representation of a Group by Matrices</i> . . . . .	35
<i>C. Symmetry Groups</i> . . . . .	39
3. Normal Modes of Vibration . . . . .	50
<i>A. Simple Polyatomic Molecules</i> . . . . .	50
<i>B. Crystalline Systems</i> . . . . .	55
4. Selection Rules . . . . .	63
<i>A. General Selection Rules for Infrared and Raman Spectra</i> . . . . .	63

*Contents*

B.	<i>Symmetry Properties of Various Entities</i>	.	.	.	.	.	63
C.	<i>Specific Selection Rules</i>	.	.	.	.	.	65
D.	<i>Point Groups</i>	.	.	.	.	.	66
E.	<i>The Lattice Translation Group</i>	.	.	.	.	.	66
F.	<i>Space Groups</i>	.	.	.	.	.	74
G.	<i>Site Groups</i>	.	.	.	.	.	79
5.	Summary	.	.	.	.	.	80
6.	Illustrations	.	.	.	.	.	80
A.	<i>Polyethylene</i>	.	.	.	.	.	80
B.	<i>Polyhydroxymethylene</i>	.	.	.	.	.	91
	References	.	.	.	.	.	97

**III****Numerical Calculations of Vibrations in Chain Molecules**

1.	Introduction and Historical Background	.	.	.	.	.	98
2.	The Classical Example of Longitudinal Vibrations in a Monatomic Linear Lattice	.	.	.	.	.	98
A.	<i>Description of Model</i>	.	.	.	.	.	98
B.	<i>Equations of Motion</i>	.	.	.	.	.	99
C.	<i>Calculation of Vibrational Frequencies</i>	.	.	.	.	.	99
D.	<i>Geometrical Form of the Normal Vibrations</i>	.	.	.	.	.	101
E.	<i>Illustration</i>	.	.	.	.	.	102
F.	<i>Wavelength of Standing Waves and Phase Shift between Two Point Masses</i>	.	.	.	.	.	103
G.	<i>Frequency Branch</i>	.	.	.	.	.	105
3.	Diatomlic One-Dimensional Lattice	.	.	.	.	.	105
A.	<i>Longitudinal Vibrations</i>	.	.	.	.	.	105
B.	<i>Transverse Vibrations</i>	.	.	.	.	.	108
C.	<i>Summary</i>	.	.	.	.	.	109
4.	Chain Molecules with an <i>n</i> -Atomic Repeat Unit	.	.	.	.	.	109
5.	Planar Zig-Zag Chain	.	.	.	.	.	110
A.	<i>Introduction</i>	.	.	.	.	.	110
B.	<i>Equations of Motion for the In-Plane Vibrations</i>	.	.	.	.	.	111
C.	<i>Potentially Infrared-Active In-Plane Vibrations in an Infinitely Long Zig-Zag Chain</i>	.	.	.	.	.	114
D.	<i>In-Plane Vibrational Frequencies for a Chain with Equal Masses</i>	.	.	.	.	.	116
E.	<i>Out-of-Plane Vibrations</i>	.	.	.	.	.	118
F.	<i>Deviations from a Perfect Zig-Zag Chain</i>	.	.	.	.	.	119
G.	<i>Practical Calculations of Skeletal Vibrations</i>	.	.	.	.	.	120
	References	.	.	.	.	.	128

**IV****Vibrational Interaction in Chain Molecules**

<b>1.</b> The Coupled Oscillator Model . . . . .	129
<b>2.</b> Normal Vibrations in a Chain of $N$ Coupled Oscillators . . . . .	131
<i>A. Introduction</i> . . . . .	131
<i>B. Chain of Parallel Dipoles</i> . . . . .	132
<i>C. Chain of Antiparallel Dipoles</i> . . . . .	135
<i>D. Magnitude of Expected Splitting in the Spectrum</i> . . . . .	136
<i>E. Geometrical Form of Normal Vibrations</i> . . . . .	136
<b>3.</b> Infrared Spectra of a Finite Chain of Coupled Oscillators, Selection Rules, and Expected Intensity Distribution in Progression Band Series . . . . .	141
<i>A. General Discussion</i> . . . . .	141
<i>B. Total Dipole Moment Change for a Normal Vibration</i> . . . . .	142
<i>C. Absorption Intensity Distribution in Band Series</i> . . . . .	143
<b>4.</b> Comparison of Theory with Observed Spectra . . . . .	146
<i>A. Limitations of the Theoretical Treatment</i> . . . . .	146
<i>B. Hydrocarbon Zig-Zag Chains</i> . . . . .	148
<i>C. Carbonyl Absorption Band in 1-Nylon Chains</i> . . . . .	162
<i>D. Outlook</i> . . . . .	163
<b>References</b> . . . . .	163

**V****Orientation Measurements**

<b>1.</b> Introduction . . . . .	166
<b>2.</b> Experimental Techniques and Dichroic Ratio Measurements . . . . .	166
<i>A. Sample Preparation</i> . . . . .	166
<i>B. Polarizer and Instrument Polarization</i> . . . . .	167
<i>C. The Infrared Microspectrometer</i> . . . . .	169
<i>D. Sources for Errors in Dichroic Ratio Measurements</i> . . . . .	172
<i>E. Measurement of Dichroic Ratios Close to Unity</i> . . . . .	179
<b>3.</b> Orientation and Infrared Dichroism . . . . .	180
<i>A. Introductory Remarks</i> . . . . .	180
<i>B. Coordinate Transformations</i> . . . . .	181
<i>C. The Absorption Intensity Ellipsoid</i> . . . . .	182
<i>D. Dichroic Ratios, General Definitions</i> . . . . .	185
<b>4.</b> Dichroic Behavior of Individual Types of Orientation . . . . .	189
<i>A. General Discussion</i> . . . . .	189
<i>B. Perfect Axial Orientation</i> . . . . .	195

<i>C. Partial Axial Orientation . . . . .</i>	198
<i>D. Perfect Symmetrical Planar Orientation . . . . .</i>	213
<i>E. Partial Symmetrical Planar Orientation . . . . .</i>	215
<i>F. Preferred Planar Orientation . . . . .</i>	217
<i>G. Uniaxial and Uniplanar Orientation . . . . .</i>	222
<b>5. Examples . . . . .</b>	<b>225</b>
<i>A. Linear Polyethylene . . . . .</i>	225
<i>B. Isotactic Polystyrene . . . . .</i>	228
<b>References . . . . .</b>	<b>232</b>

## **Appendix**

<b>Guide to the Literature of Individual Polymers . . . . .</b>	<b>234</b>
<b>References . . . . .</b>	<b>244</b>
<b>AUTHOR INDEX . . . . .</b>	<b>253</b>
<b>SUBJECT INDEX . . . . .</b>	<b>261</b>