

CONTENTS

Chapter 1

Introduction to Infrared Spectroscopy	1
1.1. Units	2
1.2. Regions of Electromagnetic Radiation	5
1.3. The Infrared Spectrum of a Compound	6
1.4. Atmospheric Absorptions	7

Chapter 2

Instruments	9
2.1. Description	9
2.2. Operating Variables	12
2.2A. Resolution	12
2.2B. Photometric Accuracy	15
2.2C. Quantitative Relations Between Operating Variables	18
2.3. Components of Infrared Spectrophotometers	20
2.3A. Sources	20
2.3B. Photometers and Photometric Systems	23
2.3C. Dispersing Elements	30
2.3D. Detectors	42
2.3E. Amplifiers and Recorders	46
2.3F. Polarizers	50
2.4. Special Operating Features	50
2.4A. Variation of Basic System Parameters	51
2.4B. Variation of Recording Parameters	52
2.4C. Optimization of Scan Time	53
2.4D. Compensation for Nonprogrammed Energy Losses	54
2.5. Available Instruments and Their Specifications	54
2.6. The Computer Revolution	63
References	63

Chapter 3

Accessories	65
3.1. Crystals	65
3.2. Gas Cells	66
3.3. Liquid Cells	68
3.4. KBr-Pellet Accessories	72

3.5. Beam Condensers	72
3.6. Polarizers	73
3.7. Specular Reflectance	73
3.8. ATR	74
3.9. Miscellany	75
References	76

Chapter 4

Theoretical Considerations in Infrared Spectroscopy	77
4.1. Notation	77
4.2. Diatomic Molecules	78
4.2A. Absorption of Infrared Radiation	78
4.2B. Relationship Between Band Contours and Vibrational-Rotational Energy	80
4.2C. Mathematical Relations for Rotational and Vibrational Energy	85
4.2D. The Intensity Distribution of a Band	95
4.3. Polyatomic Molecules	95
4.3A. The Relationship Between Observed Absorption Bands and Motions of the Atoms in a Molecule ..	95
4.3B. The Relationship Between Dipole Moment Changes and Infrared Absorption Bands	99
4.3C. Vibrations for Molecules Containing Four or More Atoms	102
4.4. The Relationship Between Symmetry of Molecules and Observed Absorption Bands	105
4.4A. Introduction	105
4.4B. Point Symmetry and Point Groups	106
4.4C. Point Groups for Various Molecules	107
4.5. Character Tables and Types (Species) of Vibrations	118
4.5A. Species for Point Groups C_1 , C_2 , C_s , and C_i	120
4.5B. Species for Point Groups C_{2v} , C_{2h} , and D_2	120
4.5C. Species of the D_{2h} Point Group	121
4.5D. Species of Vibration for C_{3v} and D_3 Groups	122
4.5E. Species of Vibration for Other C_{nv} Groups	124
4.5F. Species of Vibration of Other Groups	124
4.6. Molecules with Centers of Symmetry	125
4.7. Correlation of Species of Related Molecules	125
4.8. Calculation of Allowed Bands Using Group Theory	128
4.8A. Calculation of Allowed Fundamentals. The Character Table	130
4.8B. Calculation of the Allowed Combination Bands in the Infrared	133

4.8C. Calculation of the Allowed Overtone Bands in the Infrared	134
4.8D. Calculation of the Number of Allowed Infrared Fundamentals	137
4.9. Factors Influencing Band Positions and Band Contours in Polyatomic Molecules	138
4.9A. Fermi and Coriolis Perturbations	138
4.9B. Inversion Doubling	142
4.9C. Intensity Alternation of the Line Structure of Bands	145
4.9D. <i>l</i> -Type Doubling	145
4.10. Band Contours for Linear Molecules	146
4.11. The Method of Combination Differences Used to Obtain Rotational Constants of Diatomic and Linear Molecules	150
4.12. Vibrational–Rotational Energy Equations for the Symmetric Rotor	152
4.13. Analysis of the Ammonia Spectrum (Symmetric Rotor)	156
4.14. Spherical Rotor Molecules	157
4.15. The Asymmetric Rotor	157
4.16. Spectral Analysis of Formaldehyde (Near Symmetric Rotor)	158
4.16A. The 3–4 μ Region	172
4.16B. The 5.7 μ Region	174
4.16C. The 6–7 μ Region	175
4.16D. The 7.5–10 μ Region	175
4.17. Fundamental Frequencies of the Molecules $\text{CF}_2 = \text{CH}_2$, $\text{CF}_2 = \text{CHD}$, and $\text{CF}_2 = \text{CD}_2$	176
4.18. The Influence of Isotopic Substitution on Band Position	178
4.19. Conclusion	180
References	182

Chapter 5

The Use of Characteristic Group Frequencies in Structural Analysis	184
5.1. General Objectives	184
5.2. Definition of Group Frequencies	184
5.3. Group Frequencies and the Vibrational Analysis of a Molecule	186
5.3A. The Constancy of Spectral Positions of Group Frequencies	188
5.3B. Group Frequencies of M—H Structural Units	189
5.3C. Terminal Structural Groups such as C=O and Multiple-Bond Groups	189
5.3D. Group Frequencies of Units Where the Mass Factor Is Important	190

5.3E.	Ring and Other Group Vibrations	190
5.3F.	The Influence of Symmetry on Group Frequencies ..	190
5.3G.	Summary	191
5.4.	Group Frequencies of the CH ₃ , CH ₂ , and CH Structural Units	193
5.4A.	Alkanes Containing the CH ₃ and CH ₂ Units	193
5.4B.	Branched-Chain Hydrocarbons	196
5.4C.	CH ₃ Groups Adjacent to Atoms Other than Saturated Carbon	197
5.4D.	CH ₂ Groups Adjacent to Atoms Other than Saturated Carbon	218
5.4E.	Saturated Ring Systems	222
5.4F.	Groups Having Absorption Bands Which Interfere with Group Frequency Assignments of CH ₃ and CH ₂ Groups	230
5.4G.	The Spectra of Compounds with CH ₃ and CH ₂ Groups	231
5.4H.	CH ₃ and CH ₂ Group Frequencies in Alkenes	235
5.4I.	CH ₃ and CH ₂ Group Frequencies in Aromatic Compounds	239
5.5.	Group Frequencies Associated with Alkenes	249
5.5A.	1680–1580 cm ⁻¹ Region for Alkenes	252
5.5B.	970–660 cm ⁻¹ Region for Alkenes	254
5.5C.	3100–3000 cm ⁻¹ Region for the —C=C—H Group	255
5.5D.	Interpretation of Spectra of Alkenes	255
5.6.	Group Frequencies Associated with Alkynes	259
5.6A.	Group Frequencies Associated with the Unit C≡C—H	260
5.7.	Characteristic Group Frequencies for Benzene Derivatives	261
5.7A.	Aromatic CH Stretching Frequencies	261
5.7B.	Benzene Ring Vibrations in the 2000–1660 cm ⁻¹ Region	262
5.7C.	Aromatic Ring Frequencies in the 1600–1450 cm ⁻¹ Region	263
5.7D.	Benzene Ring Vibrations in the 1225–950 cm ⁻¹ Region	264
5.7E.	Group Frequencies of Benzene Derivatives in the 950–650 cm ⁻¹ Region	265
5.7F.	Summary of Benzene Ring Group Frequencies	266
5.8.	Vibrations of Pyridine and Its Derivatives	268

5.9. Group Frequencies Associated with the C = O Structural Unit	268
5.10. Group Frequencies Associated with the C — O — C and C — O — H Structural Units	277
5.11. Group Frequencies Associated with NH and CN Structural Units	277
5.12. Amide I Band	281
5.13. Amide II Band	282
5.14. Amide III, IV, V, and VI Bands	282
5.15. Group Frequencies for Fluorocarbons	283
5.16. Group Frequencies for the C=N, N=O, C≡N, and Other Structural Units	283
5.17. Organic Molecules Coordinated to Inorganic Salts	290
5.18. Practice Interpretation of Spectra	292
References	300

Chapter 6

Quantitative Analysis	303
6.1. Beer's Law	303
6.2. Analysis of a Series of Samples	305
6.3. Multicomponent Analysis	309
6.4. Solid Samples	310
6.5. Gas Samples	311
6.6. "One-Time" Analysis	312
6.7. Sources of Error	312
6.8. Noninterchangeability of Data	316
6.9. Measuring Absorbance	316
6.10. Accuracy	319
6.11. Other Techniques	320
6.12. Literature	321
Reference	321

Chapter 7

Sample-Handling Techniques	322
7.1. Gases	323
7.2. Liquids	324
7.3. Solids	329
7.4. Miscellany	339
7.5. Microsampling	341
7.6. Conclusions	341
References	342

Chapter 8

Spectra and Reference Library	343
8.1. General References to Infrared Spectroscopy	343
8.2. Government Publications	346
8.3. House Organs of Various Companies and Laboratories	346
8.4. Reference Spectrograms and Spectral Retrieval Systems	347
8.5. Abstracting Services and Bibliographies	357
Appendixes	
Appendix 1. Additional References	359
Appendix 2. Character Tables of the Most Important Point Groups	362
Index	373