CONTENTS

PREFACE xv

CHAPTER 1 INTRODUCTION TO VIBRATIONAL SPECTROSCOPY 1

1.1. Introduction 1
1.2. Molecular Vibrations 3
1.3. Vibration–Rotation Spectroscopy 6
1.4. Widths of Bands and Lines in Infrared Spectra 10
  1.4.1. Vibration–Rotation Spectra of Gases 10
  1.4.2. Spectra of Condensed-Phase Samples 11
1.5. Quantitative Considerations 12
  1.5.1. Beer’s Law 12
  1.5.2. Optical Constants 14
1.6. Polarized Radiation 15
1.7. Raman Spectrometry 16
1.8. Summary 18

CHAPTER 2 THEORETICAL BACKGROUND 19

2.1. Michelson Interferometer 19
2.2. Generation of an Interferogram 20
2.3. Effect of Finite Resolution 26
2.4. Apodization 30
2.5. Phase Effects 36
2.6. Effect of Beam Divergence 41
2.7. Effect of Mirror Misalignment 46
2.8. Effect of a Poor Mirror Drive 49
2.9. Rapid-Scan Interferometers 50
2.10. Step-Scan Interferometers 53
CHAPTER 3 SAMPLING THE INTERFEROGRAM

3.1. Sampling Frequency
   3.1.1. Nyquist Frequency
   3.1.2. Conceptual Discussion of Aliasing
   3.1.3. Mathematical Discussion of Aliasing

3.2. Aliasing

3.3. Dynamic Range
   3.3.1. ADC Specifications
   3.3.2. Digitization Noise
   3.3.3. Gain Ranging
   3.3.4. Chirping

3.4. Analog-to-Digital Converters

CHAPTER 4 FOURIER TRANSFORMS

4.1. Classical Fourier Transform
   4.1.1. Elementary Concepts
   4.1.2. Mathematical Basis

4.2. Fast Fourier Transform

4.3. Phase Correction

4.4. Fourier Transform: Pictorial Essay

4.5. Data Systems

CHAPTER 5 TWO-BEAM INTERFEROMETERS

5.1. Michelson-Type Interferometers
   5.1.1. Introduction
   5.1.2. Drive
   5.1.3. Bearings
   5.1.4. Fringe Referencing
   5.1.5. Dynamic Alignment

5.2. Tilt-Compensated Interferometers
   5.2.1. Cube-Corner Interferometers
   5.2.2. Other Designs

5.3. Refractively Scanned Interferometers

5.4. Polarization Interferometers

5.5. Step-Scan Interferometers

5.6. Stationary Interferometers

5.7. Beamsplitters
5.8. Lamellar Grating Interferometers 138
Appendix: Manufacturers of FT-IR Spectrometers 142

CHAPTER 6 OTHER COMPONENTS OF FT-IR SPECTROMETERS 143

6.1. Infrared Radiation Sources for Transmission and Reflection Spectrometry 143
  6.1.1. Mid-Infrared Sources 143
  6.1.2. Near-Infrared Sources 145
  6.1.3. Far-Infrared Sources 146

6.2. Detectors 146
  6.2.1. Thermal Detectors 146
  6.2.2. Quantum Detectors 148

6.3. Optics 152
  6.3.1. Paraboloidal Mirrors 152
  6.3.2. Plane Mirrors 155
  6.3.3. Ellipsoids, Toroids, and Other Aspherical Mirrors 155

6.4. Spectrometer Design 156

CHAPTER 7 SIGNAL-TO-NOISE RATIO 161

7.1. Detector Noise 161

7.2. Trading Rules in FT-IR Spectrometry 164
  7.2.1. Effect of Resolution and Throughput on SNR 164
  7.2.2. Effect of Apodization 165
  7.2.3. Effect of Changing Mirror Velocity 165

7.3. Digitization Noise 166

7.4. Other Sources of Noise 167
  7.4.1. Sampling Error 167
  7.4.2. Folding 168
  7.4.3. Fluctuation Noise 169
  7.4.4. Shot Noise 170

7.5. Interferometers Versus Grating Spectrometers 171
  7.5.1. Fellgett's Advantage 171
  7.5.2. Jacquinot's Advantage 172
  7.5.3. Other Factors 173
CHAPTER 8  PHOTOMETRIC ACCURACY IN FT-IR SPECTROMETRY 177

8.1. Introduction 177
8.2. Effect of Spectral Resolution 177
8.3. Effect of Apodization 180
  8.3.1. Triangular Apodization 180
  8.3.2. Norton–Beer Apodization Functions 181
8.4. 100% Lines 181
  8.4.1. Short-Term Performance 181
  8.4.2. Glitches (Nonrandom Noise Sources) 184
  8.4.3. Long-Term Performance 185
  8.4.4. Effect of Sample Diameter and Thickness 186
8.5. Zero Energy Level 187
  8.5.1. Detector Response Nonlinearity 187
  8.5.2. Changes in Modulation Efficiency 191
  8.5.3. Sampling Effects 193
8.6. Linearity Between 100% and 0%T 194

CHAPTER 9  QUANTITATIVE ANALYSIS 197

9.1. Introduction 197
9.2. Beer’s Law 197
9.3. Spectral Subtraction 201
9.4. Linear Least-Squares Fitting Methods 204
9.5. Classical Least Squares 207
9.6. Inverse Least-Squares Regression 210
9.7. Principal Component Analysis 213
9.8. Principal Component Regression 215
9.9. Partial Least-Squares Regression 216
9.10. Validation 217
9.11. Multivariate Curve Resolution 218
9.13. Neural Networks 221

CHAPTER 10  DATA PROCESSING 225

10.1. Baseline Correction 225
10.2. Interpolation 227
10.3. Peak Picking 229
10.4. Spectral Smoothing 232
10.5. Band Fitting 235
10.6. Derivatives of Spectra 237
10.7. Fourier Self-Deconvolution 240
10.8. Spectral Searching 246

CHAPTER 11 CONVENTIONAL TRANSMISSION SPECTROMETRY 251
11.1. Condensed-Phase Samples 251
11.1.1 Window Materials 251
11.1.2 Band Intensities 251
11.1.3 Interference Fringes 253
11.1.4 Trace Analysis 255
11.2. Gas- and Vapor-Phase Samples 256

CHAPTER 12 POLARIZATION 261
12.1. Plane-Polarized Radiation 261
12.2. Circular Polarization 263
12.3. Polarization Modulation 264
12.4. Applications of Linear Dichroism 266
12.5. Vibrational Circular Dichroism 269

CHAPTER 13 SPECULAR REFLECTION 277
13.1. Introduction 277
13.2. Fresnel Reflection from Bulk Samples 277
13.2.1. Fresnel Equations 277
13.2.2. Nonabsorbing Materials 278
13.2.3. Absorbing Materials 279
13.3. Infrared Reflection–Absorption Spectrometry with Metal Substrates 282
13.3.1. Effect of Incidence Angle and Polarization 282
13.3.2. Polarization Modulation 287
13.3.3. Surface Selection Rule 290
13.4. IRRAS with Dielectric Substrates 293
13.5. Transflection 297
13.5.1. Thick Films on Metal Substrates 297
13.5.2. Liquid Sampling for Near-Infrared Spectrometry 300
13.6. Summary 300
CHAPTER 14 MICROSCOPES AND IMAGING 303
14.1. Microsampling with Beam Condensers 303
14.2. Microscopes 304
14.3. Diamond Anvil Cells 309
14.4. Reflection Microscopy 310
14.5. Hyperspectral FT-IR Imaging 312
  14.5.1. Hyperspectral Imaging with a Step-Scanning Interferometer 312
  14.5.2. Hyperspectral Imaging with a Continuous-Scanning Interferometer 314
  14.5.3. Signal-to-Noise Ratio 316
  14.5.4. Software 318
  14.5.5. Applications of Hyperspectral Imaging 319

CHAPTER 15 ATTENUATED TOTAL REFLECTION 321
15.1. Introduction 321
15.2. Theory 322
15.3. Practical Considerations 327
15.4. Accessories for Multiple Internal Reflection 329
15.5. Single-Reflection Accessories 336
15.6. Infrared Fibers 342
15.7. Summary 347

CHAPTER 16 DIFFUSE REFLECTION 349
16.1. Theory of Diffuse Reflection 349
16.2. Accessories for Diffuse Reflection 353
16.3. Applications of Mid-Infrared Diffuse Reflection Spectrometry 355
16.4. Applications of Near-Infrared Diffuse Reflection Spectrometry 358
16.5. Reference Materials for Diffuse Reflection Spectrometry 361

CHAPTER 17 EMISSION 363
17.1. Introduction 363
17.2. Infrared Emission Spectra of Gases 363
CHAPTER 18  FOURIER TRANSFORM RAMAN SPECTROMETRY  375

18.1. Introduction  375
18.2. Instrumentation  378
  18.2.1. Nd: YAG Laser  378
  18.2.2. Filters  380
  18.2.3. Collection Optics  381
  18.2.4. Interferometer  382
  18.2.5. Detector  382
  18.2.6. Spectrometer  384
18.3. FT Raman Versus CCD Raman Spectrometry  385
18.4. Applications of FT-Raman Spectrometry  387
  18.4.1. Standard Raman Spectroscopy  387
  18.4.2. Surface-Enhanced Raman Spectroscopy  389
18.5. Summary  391

CHAPTER 19  TIME-RESOLVED SPECTROMETRY  395

19.1. Continuous-Scanning Interferometers  395
  19.1.1. Instrumental Considerations  395
  19.1.2. Applications  397
19.2. Time-Resolved Measurements Using Step-Scan Interferometers  400
  19.2.1. Instrumental Considerations  400
  19.2.2. Applications of Time-Resolved Spectroscopy with a Step-Scan Interferometer  402
19.3. Stroboscopic Spectrometry  407
19.4. Asynchronous Time-Resolved FT-IR Spectrometry  408
  19.4.1. Instrumental Considerations  408
  19.4.2. Application to Liquid-Crystal Orientation Dynamics  412
CHAPTER 20 PHOTOACOUSTIC SPECTROMETRY

20.1. Photoacoustic Spectroscopy of Gases 415
20.2. Photoacoustic Spectroscopy of Solids with a Rapid-Scanning Interferometer 417
20.3. Photoacoustic Spectroscopy of Solids with a Step-Scan Interferometer 425
  20.3.1. Phase Modulation 425
  20.3.2. Depth Profiling by Varying the Photoacoustic Phase 428
  20.3.3. Multifrequency Measurements 431

CHAPTER 21 SAMPLE MODULATION SPECTROMETRY WITH A STEP-SCAN INTERFEROMETER

21.1. Dynamic Infrared Linear Dichroism Measured with a Monochromator 435
21.2. DIRLD Spectrometry with a Step-Scan Fourier Transform Spectrometer 440
21.3. Two-Dimensional Correlation Plots 448
21.4. DIRLD Spectrometry with a FT-IR Spectrometry and Digital Signal Processing 454
21.5. Other Sample Modulation Measurements with Step-Scan Interferometers 458
  21.5.1. Liquid-Crystal Electroreorientation 458
  21.5.2. Infrared Spectroelectrochemistry 460

CHAPTER 22 ATMOSPHERIC MONITORING

22.1. Extractive Atmospheric Monitoring 463
22.2. Open-Path Atmospheric Monitoring 466

CHAPTER 23 COUPLED TECHNIQUES

23.1. Introduction 481
23.2. Light-Pipe-Based GC/FT-IR Interfaces 482
  23.2.1. Instrumental Considerations 482
  23.2.2. Spectroscopic Considerations 485
  23.2.3. Chromatogram Construction 486
  23.2.4. Example of GC/FT-IR 490
23.3. Mobile-Phase Elimination Approaches for GC/FT-IR 491
CONTENTS

23.3.1. Introduction 491
23.3.2. Matrix Isolation GC/FT-IR 491
23.3.3. Direct Deposition GC/FT-IR 493

23.4. HPLC/FT-IR Interface 495
23.4.1. Measurements Made with Flow Cells 495
23.4.2. Mobile-Phase Examination Techniques for HPLC/FT-IR 496

23.5. SFC/FT-IR Interface 500
23.6. TGA/FT-IR 502

23.7. Other Coupled Techniques 504

INDEX 509