CONTENTS

PREFACE ix
ACKNOWLEDGMENTS xiii
LIST OF SYMBOLS xv
CUMULATIVE LISTING OF VOLUMES IN SERIES xix

CHAPTER 1 INTRODUCTION AND SCOPE 1
1.1. History Preceding 1986 1
1.2. Technological Advances 5
1.3. Comparison to FTIR and NIR Absorption 10
1.4. Overview of the Book 12

CHAPTER 2 MAGNITUDE OF RAMAN SCATTERING 15
2.1. Theoretical Overview 15
2.2. Definition of Raman Cross Section 20
2.3. Magnitude of Raman Cross Sections 24
2.4. Raman Scattering Intensity 30

CHAPTER 3 COLLECTION AND DETECTION OF RAMAN SCATTERING 35
3.1. Signal Magnitude and Collection Function 35
3.2. Instrumental Variables Comprising the Collection Function 37
3.3. Spectrometer Response Function 41
3.4. Multiplex and Multichannel Spectrometers 43

CHAPTER 4 SIGNAL-TO-NOISE IN RAMAN SPECTROSCOPY 49
4.1. Definition and Measurement of SNR 49
4.2. Noise Sources 52
4.3. Signal-to-Noise Ratio Expressions 61
4.4. SNR Figure of Merit 65
4.5. SNR and Detection Limits 67
4.6. SNR for Multiplex Spectrometers 68

CHAPTER 5  INSTRUMENTATION OVERVIEW AND
SPECTROMETER PERFORMANCE 73

5.1. Major Spectrometer Components 74
5.2. Laser Wavelength 75
5.3. Dispersive vs. Nondispersive Spectrometers 78
5.4. Performance Criteria 79
5.5. Samples for Spectrometer Evaluation 83

CHAPTER 6  SAMPLING MODES IN RAMAN
SPECTROSCOPY 95

6.1. Sampling Overview 95
6.2. Performance Criteria 97
6.3. 180° Backscattering Geometry 99
6.4. 90° Sampling Geometry 114
6.5. Reducing the Laser Power Density at the Sample 118
6.6. Path Length Enhancement 120
6.7. Polarization Measurements 122

CHAPTER 7  LASERS FOR RAMAN SPECTROSCOPY 127

7.1. Overview 127
7.2. Ar⁺ and Kr⁺ Ion Lasers 130
7.3. Helium–Neon Lasers 133
7.4. Neodymium–YAG (Nd:YAG) 134
7.5. Diode Lasers 137
7.6. Laser Wavelength Filtering 142

CHAPTER 8  DISPERSIVE RAMAN SPECTROMETERS 149

8.1. Overview 149
8.2. Dispersive Spectrometer Configurations 155
8.3. Detector Considerations 179
8.4. Single-Channel Detectors 180
8.5. Multichannel Detectors and CCDs 183
8.6. Recording Methods for Dispersive Spectrometers 203
8.7. Examples of Dispersive Raman Applications 215

CHAPTER 9 NONDISPERSIVE RAMAN SPECTROMETERS 221
9.1. Tunable Bandpass Filters 221
9.2. Fourier Transform Raman Spectroscopy 225
9.3. Multichannel Fourier Transform Raman Spectroscopy 240
9.4. Extensions of FT-Raman for Longer Wavelength Operation 245
9.5. FT-Raman Examples 246

CHAPTER 10 CALIBRATION AND VALIDATION 251
10.1. Overview 251
10.2. Frequency and Raman Shift Calibration 251
10.3. Instrument Response Function Calibration 269
10.4. Absolute Response Calibration 288
10.5. Summary of Calibration and Validation Procedures 289

CHAPTER 11 RAMAN MICROSCOPY AND IMAGING 293
11.1. Overview of Raman Microscopy 293
11.2. Single-Point Raman Microspectroscopy 295
11.3. Line Imaging 309
11.4. Two-Dimensional Raman Imaging 316

CHAPTER 12 FIBER-OPTIC RAMAN SAMPLING 333
12.1. Overview of Fiber-Optic Sampling 333
12.2. Fiber-Optic Basics 334
12.3. Fiber–Spectrometer Interface 337
12.4. Fiber-Optic Probes 342
12.5. Comparisons of Fiber-Optic Sampling Probes 359
12.6. Waveguide Sampling for Analytical Raman Spectroscopy 364
12.7. Examples of Fiber-Optic Sampling 369

CHAPTER 13 RAMAN SPECTROSCOPY OF SURFACES 373
13.1. Overview 373
13.2. Surface Sensitivity 375
CONTENTS

13.3. Sampling Considerations 379
13.4. Surface Raman Spectroscopy without Field Enhancement 382
13.5. Electromagnetic Field Enhancement 390
13.6. Examples of Analytical Applications 409

INDEX 415