

# Contents

List of Contributors	xv
Preface	xvii
Acknowledgements	xxiii

## 1 The Raman Effect *George Turrell*

I. Introduction	1
II. History of the Raman Effect	1
III. Mechanism of the Raman Effect	2
IV. Electromagnetic Radiation and Classical Light Scattering	5
V. Molecular Vibrations	8
VI. The Scattering Tensor	12
VII. Polarization in Gases and Liquids	15
VIII. Polarization in Crystals	16
IX. Raman Bandshapes	18
X. Resonance Raman Scattering and Fluorescence	20
XI. Postlog	23

## 2 Characteristics of Raman Microscopy *George Turrell, Michel Delhaye and Paul Dhamelincourt*

I. Introduction	27
II. Excitation Focusing	27
III. Collection Optics	29
IV. Absorbing Samples	33
V. Microscope-Spectrometer Coupling	37
A. Coupling Conditions	37
B. Design of Coupling Optics	38
VI. Confocal Raman Microscopy	39
A. Introduction	39

## vi Contents

B. The Confocal Effect	43
1. Raman light flux emitted by a thin slice of sample	43
2. Transmission of the Raman light flux through a confocal diaphragm	44
C. Conclusion	48

## 3 Instrumentation

***Michel Delhaye, Jacques Barbillat, Jean Aubard, Michel Bridoux and Edouard Da Silva***

I. Introduction	51
II. Characteristics of Laser Sources	52
A. Characteristics of a Gaussian Beam	52
B. Lens-focusing of a Gaussian Beam	53
C. Depth of Focus	54
D. Irradiance at the Image Waist	54
E. Exact Lens Relation for a Gaussian Beam	55
F. Laser Beam Quality	56
III. Microscope Objectives	57
A. Characteristics	57
B. Efficiency of Light Collection	58
1. Isotropic point source	59
2. Lambertian source	61
C. Lens Objectives	63
1. Spherical aberration	63
2. Immersion objectives	65
3. Metallurgical and biological objectives	66
4. Other aberrations	69
D. Mirror Objectives	70
1. Spherical mirrors	70
2. Aspherical mirrors	72
E. Comparison of Microscope Objectives with Camera Lenses	77
F. Determination of the Pupil Dimension of a Microscope Objective	78
IV. Spectral Analyzers	79
A. Introduction	79
1. Dispersive analyzers	80
2. Nondispersing analyzers	80
B. Geometrical Extent	81
C. Instrumental Spectral Profile and Bandpass	82
D. Stray Light Level	84
E. Dispersive Monochromators	87
F. Dispersive Spectrographs	90

G. The Fabry-Perot Interferometer	95
H. The Michelson Interferometer	97
I. Prefiltering Devices	100
1. Gratings	102
2. Interference filters	102
3. Bragg-diffraction filters	103
4. Holographic phase-grating filters	104
5. Optical coupling of spectral analyzers with a microscope	106
V. Photoelectric Detectors	106
A. Single-channel Detectors	107
1. Photomultiplier tubes	107
2. Silicon photodiodes	108
3. Germanium and InGaAs photodiodes	108
B. Multichannel Solid-state Detectors	109
1. Integration mode of solid-state detectors	109
2. Storage mode of solid-state detectors	110
C. Two-dimensional charge-transfer devices	110
1. CCD detectors	111
2. CID detectors	115
D. Self-scanned, Photodiode-array Detectors	116
1. Visible photodiode arrays (PDA)	116
2. Intensified photodiode arrays (IPDA)	118
3. Intensified photodiode-array detectors versus CCDs	118
E. NIR Photodiode Arrays and Solid-state Detectors	119
1. Germanium photodiode arrays	119
2. InGaAs photodiode linear arrays and two-dimensional matrices	119
F. Other Two-dimensional-imaging Detectors: PMTs	120
VI. Fluorescent Samples	121
A. Introduction	121
B. NIR Raman Microanalysis	122
C. FT Raman Spectroscopy	123
D. Conventional Dispersive Raman Spectroscopy	125
1. Single-channel technique	125
2. Multichannel technique	125
E. Conclusion	127
VII. Fiber Optics	128
A. Introduction	128
B. Characteristics of Optical Fiber Systems	128
C. Direct-coupled Raman Sensors	131
1. Coupling of the laser-excitation fiber to the sample medium	131
2. Raman light collection	133
3. Conclusion	140

## viii Contents

D. Indirect-coupled Raman Sensors	141
E. Conclusions	148
VIII. A Brief Survey of Digital Signal Processing	152
A. Introduction	152
B. Mathematical Background	152
1. The impulse and sampling functions	152
2. Convolution	154
3. The Fourier transform	155
C. Measurement and Sampling of Analog Signals	158
1. Generalities and initial hypotheses	158
2. Applications of the sampling theorem	158
3. Sampling of analog signals	161
D. Practical Considerations in the Digitizing of Raman Spectra	161
1. Slit function and lineshape	161
2. The sampling steps as functions of spectral lineshape and width	162
E. Digital Data Methods for Improving the Signal-to-Noise Ratio	165
1. Signal averaging	165
2. Filtering and windowing	166
3. Data smoothing	169
F. Conclusion	171

## 4 Raman Imaging

**Jacques Barbillat**

I. Introduction	175
II. Direct Imaging	176
A. Global Sample Illumination	176
B. Spectral Filtering	177
C. Characteristics of Direct Imaging Techniques	180
1. Advantages	180
2. Disadvantages	181
III. Series Imaging	182
A. Laser Scanning Methods	182
1. Point illumination	182
2. Line illumination	182
3. Confocal line scanning	185
4. Common characteristics of scanning imaging techniques	187
B. Encoding Techniques	188
IV. Signal-to-Noise Ratio (S/N) and Collection Time	189
A. Line Illumination versus Global Illumination	190
1. The same total laser power used in both measurements	190

2. Each pixel of the sample receives the maximum allowable power in both measurements	191
V. Hadamard Imaging versus Global Illumination and Line Scanning	191
VI. Examples of Applications	192
VII. Conclusion	196

## **5 Raman Microscopy and Other Local-analysis Techniques**

***Michel Truchet, Jean-Claude Merlin and George Turrell***

I. Introduction	201
II. Electron Microscopy	202
A. Illuminating Column	202
1. Upper portion of the electron microscope	202
2. Radiation-matter interaction at the sample	204
3. The image	206
III. Coupling of Raman and Electron Microscopies	210
A. General Considerations	210
B. Photon Optics Collection	212
C. Transfer Optics	215
1. Column output	215
2. Column, laser and Raman spectrometer connection	217
D. Analysis Conditions	219
1. Efficiency	219
2. Samples under vacuum	219
3. Sample size and analytical efficiency	219
E. Conclusion	220
Raman	220
A. Fundamental Principles	220
B. Coupling Conditions	222
C. Applications	223
Raman Spectroscopies	224
A. Introduction	224
B. Principles of Instrumentation	224
C. Coupling Conditions	226
D. Applications	227
with the Raman Microprobe	228
A. General Considerations	228
B. Instrumental Configurations	229
C. Coupling Conditions	230
D. Applications	230
VI. Microscopies	231

## **x Contents**

VIII.	Microchromatography and Other Separation Methods	231
A.	Thin-layer Chromatography	231
B.	High-performance Liquid Chromatography	233
IX.	Optical Waveguides: Raman Spectra of Films and Adsorbed Species	234
A.	Introduction	234
B.	Integrated Optics	236
C.	Applications	239

## **6 Applications to Materials Science**

***Paul Dhamelincourt and Shin-ichi Nakashima***

I.	Introduction	243
II.	Inorganic Solids	244
A.	Catalysts	244
1.	Introduction	244
2.	Characterization by vibrational spectroscopy	245
3.	Raman spectroscopic analysis of precursor oxides	245
4.	Brönsted acidity of supported oxides	247
5.	Sulfidation of precursor oxides	248
6.	Conclusion	250
B.	Ceramics	250
1.	Introduction	250
2.	Polyphase ceramics	250
3.	High-T <sub>c</sub> ceramics	252
C.	Protective Coatings	255
1.	Polycrystalline diamond coatings	255
2.	Silica coatings	257
III.	Microelectronics and Semiconductors	258
A.	Introduction	258
B.	Raman Microprobe Measurements	259
1.	Heating effects	259
2.	Oblique incidence	260
3.	Depth profiling	260
C.	Ion Implantation and Annealing	260
D.	Determination of Crystallographic Orientation	267
E.	Distribution of Free Carriers	273
F.	Strain in Materials	275
G.	Thermal Conversion of SiC Polytypes	277
H.	Raman Microprobe Measurements of Inorganic Conducting Materials	278

IV. Polymers and Fibers	279
A. Introduction	279
B. Identification of Defects	279
C. Analysis of Chemical Composition	280
D. Analysis of Morphology in Polyester Fibers	280
E. Conclusion	284
V. General Conclusions	285

## 7 Applications in Earth, Planetary and Environmental Sciences

***Paul F. McMillan, Jean Dubessy and Russell Hemley***

I. Introduction	289
II. Practical Aspects	290
III. Mineralogy and Petrology	293
A. Phase Identification in Natural and Synthetic Samples	293
1. Identification of crystalline polymorphs	293
2. Shocked phases and meteorites	296
3. Mineral inclusions	299
B. Phase Identification in the Environmental Sciences	299
1. Aerosols	299
2. Airborne urban particles and pollution studies	300
C. Establishment of Mineralogical Phase Diagrams	301
1. Structural characterization of phases by high-pressure, high-temperature experiments	301
2. High-pressure and high-temperature <i>in situ</i> studies	304
3. Calculation of thermodynamic properties	307
D. Phase Transitions in Minerals	310
1. Displacive phase transitions	310
2. Order-disorder transitions	312
3. Pressure-induced amorphization	315
E. Micro-Raman Studies of Condensed Gases	316
IV. Geochemistry	320
A. Fluid Inclusions	320
1. Cations and anions in the aqueous phase	321
2. Hydrocarbon-fluid inclusions and diagenetic fluids	325
3. Fluid inclusions in the C-O-H-N-S system	329
B. Glasses and Melts	343
1. Compositional studies of glasses	344
2. Structural studies of silicate glasses at high pressures	347
3. Silicate liquids at high temperatures	349
4. Interaction of volatile species with melts and glasses	351

**8 Biological Applications*****Michel Truchet***

I.	Introduction	367
II.	From Histology to Cytology	368
III.	From Morphology to Analysis	369
IV.	Raman Microanalysis Applied to Bioaccumulations	370
	A. Lysosomes	370
	B. Spherocrystals	372
	C. Secretion Products (Chitin)	373
V.	Trends in Raman Microscopy as Applied to Cells and Tissues	373
	A. Living Samples	373
	B. Ultrastructures	374
VI.	Conclusion	375

**9 Applications in Medicine*****Michel Manfait and Igor Nabiev***

I.	Introduction	379
	A. Conventional Raman Microscopy	379
	B. Surface-enhanced Raman Scattering and the SERS Microprobe	381
II.	Experimental Conditions for the Raman Microprobe Analysis of Biomedical Samples	384
	A. Conventional Raman Microprobe Technique	385
	B. SERS Microprobe Technique	387
III.	Raman Microscopy of Single Living Cells and Chromosomes	389
IV.	Raman Microscopy of Ocular Lenses	391
V.	Surface-enhanced Raman Scattering (SERS) Microscopy	392
	A. Substrates for SERS Microscopy of Biomedical Samples	392
	1. Hydrosols	394
	2. Vacuum-deposited metal island films	399
	3. Nuclear pores	402
	B. SERS Microscopy of Living Cells and Drug Pharmacokinetics	403
	1. SERS microprobe analysis of intact biological organisms	403
	2. SERS microprobe studies of dimethylcrocin and ellipticine in single living cells on silver island films and hydrosols	405
	3. Doxorubicin pharmacokinetics probed by SERS microspectroscopy of a living cell	409
	4. Micro-SERS analysis of topotecan in a living cell and <b><i>in vitro</i></b> modeling of its intracellular interactions	411

5. SERS microprobe detection of sialic residues on the membrane of a living cell	412
VI. Summary	415

## 10 Applications in Art, Jewelry and Forensic Science

***Claude Coupry and Didier Brissaud***

I. Introduction	421
II. Art objects	422
A. Experimental Procedures	422
1. Identification <i>in situ</i>	422
2. Microscopic sampling	423
B. Application to the Study of Pigments	425
1. The use of the resonance Raman effect	425
2. Reference data bank	426
3. Some examples	427
C. Dye Studies	436
D. Supports for Restoration and Conservation	437
E. Conclusion	438
III. Jewellery	438
A. Experimental Procedures	439
1. Samples	439
2. Spectra	439
B. Analysis of Inclusions	440
1. Natural minerals	440
2. Synthetic gems	441
IV. Forensic Science	442
A. Introduction	442
B. Methodology	443
C. Instrumentation	445
D. Some Examples of the Use of Raman Spectra as Juridic Evidence	446
1. Paintings	446
2. Paints	447
3. Polymers	447
4. Minerals	449
E. Quality Control	449
F. New Areas of Application	449
1. Drugs	449
2. Propellants and explosives	450
G. Conclusions	450
- Index	455