# Contents

Preface ............................................. ix  
Acknowledgements ............................ xi  

## CHAPTER 1  INTRODUCTION, BASIC THEORY AND PRINCIPLES  
1.1 Introduction ................................. 1  
1.2 History ....................................... 2  
1.3 Basic Theory .................................. 2  
1.4 Molecular Vibrations ....................... 8  
1.5 Group Vibrations ............................. 11  
1.6 Basic Interpretation of a Spectrum ....... 13  
1.7 Summary ...................................... 19  

## CHAPTER 2  THE RAMAN EXPERIMENT – RAMAN INSTRUMENTATION, SAMPLE PRESENTATION, DATA HANDLING AND PRACTICAL ASPECTS OF INTERPRETATION  
2.1 Introduction .................................. 21  
2.2 Choice of Instrument ......................... 22  
2.3 Transmission Raman Scattering and Spatially Offset Raman Scattering .................. 29  
2.4 Raman Sample Preparation and Handling 30  

2.4.1 Sample Mounting – Optical Considerations ................................................... 31  
2.4.2 Raman Sample Handling .................. 34  
2.5 Sample Mounting Accessories ............. 40  

2.5.1 Small Fibres, Films, Liquids and Powders ................................................... 40  
2.5.2 Variable Temperature and Pressure Cells ................................................... 40  
2.5.3 Special Applications – Thin Films, Surfaces and Catalysts ......................... 42  
2.5.4 Reaction Cells, Flow Through Cells, Sample Changers and Automated Mounts 44  
2.6 Fibre-Optic Coupling and Wave Guides 45  
2.7 Microscopy .................................... 49  

2.7.1 Raman Microscopes ....................... 49  
2.7.2 Depth Profiling .......................... 51  
2.7.3 Imaging and Mapping .................... 51
Contents

2.8 Calibration 56
2.9 Data Manipulation, Presentation and Quantitation 59
  2.9.1 Manipulation of Spectra for Presentation 59
  2.9.2 Presentation of Spectra 63
  2.9.3 Quantitation 64
2.10 An Approach to Qualitative Interpretation 66
  2.10.1 Factors to Consider in the Interpretation of a Raman Spectrum of an Unknown Sample 67
    2.10.1.1 Knowledge of the Sample and Sample Preparation Effects 68
    2.10.1.2 Instrument and Software Effects 69
    2.10.1.3 The Spectrum 69
  2.10.2 Computer-Aided Spectrum Interpretation 70
  2.10.3 Spectra Formats for Transfer and Exchange of Data 73
2.11 Summary 74

CHAPTER 3 THE THEORY OF RAMAN SPECTROSCOPY 77
  3.1 Introduction 77
  3.2 Absorption and Scattering 78
  3.3 States of a System and Hooke’s Law 79
  3.4 The Basic Selection Rule 82
  3.5 Number and Symmetry of Vibrations 83
  3.6 The Mutual Exclusion Rule 84
  3.7 Understanding Polarizability 85
  3.8 Polarizability and the Measurement of Polarization 89
  3.9 Symmetry Elements and Point Groups 93
  3.10 Lattice Modes 97
  3.11 Summary 98

CHAPTER 4 RESONANCE RAMAN SCATTERING 101
  4.1 Introduction 101
  4.2 The Basic Process 102
  4.3 Key Differences Between Resonance and Normal Raman Scattering 102
    4.3.1 Intensity Increase 103
    4.3.2 Franck Condon and Herzberg Teller Scattering 105
    4.3.3 Overtones 108
    4.3.4 Wavelength Dependence 109
    4.3.5 Electronic Information 111
  4.4 Practical Aspects 113
  4.5 Summary 116
CHAPTER 5  SURFACE ENHANCED RAMAN SCATTERING
AND SURFACE ENHANCED RESONANCE RAMAN
SCATTERING
5.1 Introduction 119
5.2 Electromagnetic and Charge Transfer Enhancement 123
  5.2.1 Electromagnetic Enhancement 124
  5.2.2 Charge Transfer or Chemical Enhancement 128
  5.2.3 Stages in the SERS Process 133
5.3 Surface Enhanced Resonance Raman
  Scattering (SERRS) 134
5.4 Selection Rules 135
5.5 Surface Chemistry 137
5.6 Substrates 139
5.7 Quantitation and Multiplex Detection 145
5.8 Summary 147

CHAPTER 6  APPLICATIONS
6.1 Introduction 151
6.2 Inorganics and Minerals and Environmental Analysis 151
6.3 Art and Archaeology 156
6.4 Polymers and Emulsions 158
  6.4.1 Overview 158
  6.4.2 Simple Qualitative Polymer Studies 158
  6.4.3 Quantitative Polymer Studies 162
6.5 Dyes and Pigments 163
  6.5.1 Raman Colour Probes 163
  6.5.2 In Situ Analysis 164
  6.5.3 Raman Studies of Tautomerism in Azo Dyes 167
  6.5.4 Polymorphism in Dyes 168
6.6 Electronics Applications 169
6.7 Biological and Clinical Applications 174
  6.7.1 Introduction 174
6.8 Pharmaceuticals 176
6.9 Forensic Applications 180
6.10 Process Analysis and Reaction Following 183
  6.10.1 Introduction 183
  6.10.2 Electronics and Semiconductors 183
  6.10.3 PCl₃ Production Monitoring 184
  6.10.4 Anatase and Rutile Forms of Titanium Dioxide 184
  6.10.5 Polymers and Emulsions 185
  6.10.6 Pharmaceutical Industry 186
  6.10.7 Solid-Phase Organic Synthesis/Combinatorial Chemistry 186
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.10.8</td>
<td>Fermentations</td>
<td>188</td>
</tr>
<tr>
<td>6.10.9</td>
<td>Gases</td>
<td>188</td>
</tr>
<tr>
<td>6.10.10</td>
<td>Catalysts</td>
<td>188</td>
</tr>
<tr>
<td>6.10.11</td>
<td>Nuclear Industry</td>
<td>191</td>
</tr>
<tr>
<td>6.11</td>
<td>Summary</td>
<td>191</td>
</tr>
<tr>
<td>7</td>
<td>MORE ADVANCED RAMAN SCATTERING TECHNIQUES</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>199</td>
</tr>
<tr>
<td>7.2</td>
<td>Flexible Optics</td>
<td>200</td>
</tr>
<tr>
<td>7.3</td>
<td>Spatial Resolution</td>
<td>204</td>
</tr>
<tr>
<td>7.4</td>
<td>Pulsed and Tunable Lasers</td>
<td>207</td>
</tr>
<tr>
<td>7.5</td>
<td>Tip-Enhanced Raman Scattering and SNOM</td>
<td>214</td>
</tr>
<tr>
<td>7.6</td>
<td>Single-Molecule Detection</td>
<td>216</td>
</tr>
<tr>
<td>7.7</td>
<td>Time-Resolved Scattering</td>
<td>218</td>
</tr>
<tr>
<td>7.8</td>
<td>Fluorescence Rejection</td>
<td>222</td>
</tr>
<tr>
<td>7.9</td>
<td>Raman Optical Activity</td>
<td>222</td>
</tr>
<tr>
<td>7.10</td>
<td>UV Excitation</td>
<td>223</td>
</tr>
<tr>
<td>7.11</td>
<td>Summary</td>
<td>227</td>
</tr>
<tr>
<td>Appendix A</td>
<td>Table of Inorganic Band Positions</td>
<td></td>
</tr>
<tr>
<td>Index</td>
<td></td>
<td>233</td>
</tr>
</tbody>
</table>