D. I. BOWER
Reader in Polymer Spectroscopy
Interdisciplinary Research Centre in Polymer Science & Technology
Department of Physics, University of Leeds

W.F. MADDAMS
Senior Visiting Fellow
Department of Chemistry, University of Southampton

The vibrational spectroscopy of polymers
## Contents

**Preface**

1. **Introduction**
   1.1 Vibrational spectroscopy 1
      1.1.1 Molecular vibrations 1
      1.1.2 Infrared and Raman spectroscopy 1
   1.2 Fundamentals of polymers 2
      1.2.1 Addition polymers 3
      1.2.2 Step growth polymers 4
      1.2.3 Regular chains and defect structures 7
      1.2.4 Polymer morphology and crystallization 12
   1.3 The infrared and Raman spectra of polymers 14
   1.4 The electromagnetic spectrum – symbols and units 17
   1.5 Spectrometers and experimental methods in infrared spectroscopy 18
      1.5.1 Introduction 18
      1.5.2 The dispersive infrared spectrometer 21
      1.5.3 The Fourier transform spectrometer 24
      1.5.4 Sources, detectors and polarizers 27
      1.5.5 The preparation of samples for transmission spectroscopy 28
      1.5.6 Reflection spectroscopy 30
   1.6 Spectrometers and experimental methods in Raman spectroscopy 31
      1.6.1 Introduction 31
      1.6.2 Sources and optical systems 33
      1.6.3 Monochromators and detectors 34
      1.6.4 Sample preparation and mounting 36
   1.7 Mathematical techniques for processing spectra 38
   1.8 Further reading 41

2. **Symmetry and normal modes of vibration** 42
   2.1 Interatomic forces and molecular vibrations 42
      2.1.1 Interatomic forces 42
      2.1.2 Normal modes of vibration 44
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2 Symmetry and small molecules</td>
<td>47</td>
</tr>
<tr>
<td>2.2.1 Point symmetry operations and symmetry elements</td>
<td>47</td>
</tr>
<tr>
<td>2.2.2 Point groups</td>
<td>53</td>
</tr>
<tr>
<td>2.3 Group representations</td>
<td>57</td>
</tr>
<tr>
<td>2.3.1 Representation of groups by matrices</td>
<td>57</td>
</tr>
<tr>
<td>2.3.2 Reducible, irreducible and equivalent representations</td>
<td>60</td>
</tr>
<tr>
<td>2.3.3 Symmetry species and character tables</td>
<td>63</td>
</tr>
<tr>
<td>2.3.4 Notation for symmetry species</td>
<td>65</td>
</tr>
<tr>
<td>2.4 The number of normal modes of each symmetry species</td>
<td>66</td>
</tr>
<tr>
<td>2.4.1 A reducible 3N-dimensional representation of the point group</td>
<td>67</td>
</tr>
<tr>
<td>2.4.2 Reduction of the 3N-dimensional representation by the use of normal coordinates</td>
<td>69</td>
</tr>
<tr>
<td>2.4.3 The number of normal modes of each symmetry species</td>
<td>70</td>
</tr>
<tr>
<td>2.5 Symmetry coordinates and internal coordinates</td>
<td>74</td>
</tr>
<tr>
<td>2.6 Further reading</td>
<td>78</td>
</tr>
<tr>
<td>3 The vibrational modes of polymers</td>
<td>80</td>
</tr>
<tr>
<td>3.1 The vibrations of regular polymer chains</td>
<td>80</td>
</tr>
<tr>
<td>3.1.1 Introduction</td>
<td>80</td>
</tr>
<tr>
<td>3.1.2 Line group and factor group: polyethylene</td>
<td>81</td>
</tr>
<tr>
<td>3.1.3 Polyethylene and the vinyl polymers: descent in symmetry</td>
<td>89</td>
</tr>
<tr>
<td>3.1.4 Helical molecules</td>
<td>93</td>
</tr>
<tr>
<td>3.2 The vibrations of polymer crystals</td>
<td>97</td>
</tr>
<tr>
<td>3.2.1 The nature of the factor group modes</td>
<td>98</td>
</tr>
<tr>
<td>3.2.2 Factor group modes for crystalline PVC and polyethylene</td>
<td>100</td>
</tr>
<tr>
<td>3.3 Further reading</td>
<td>106</td>
</tr>
<tr>
<td>4 Infrared and Raman spectra</td>
<td>107</td>
</tr>
<tr>
<td>4.1 Semiclassical treatment of origins of spectra</td>
<td>107</td>
</tr>
<tr>
<td>4.1.1 Polarizability tensors and dipole moments</td>
<td>107</td>
</tr>
<tr>
<td>4.1.2 Infrared absorption – mechanism and selection rule</td>
<td>109</td>
</tr>
<tr>
<td>4.1.3 The origin of Raman scattering</td>
<td>111</td>
</tr>
<tr>
<td>4.1.4 Raman scattering and the rule of mutual exclusion</td>
<td>113</td>
</tr>
<tr>
<td>4.1.5 Selection rules for Raman activity: Raman tensors</td>
<td>117</td>
</tr>
</tbody>
</table>
Contents

4.2 Polarization effects 120
  4.2.1 Polarized infrared spectroscopy — dichroic ratios 120
  4.2.2 Polarized Raman spectroscopy — depolarization ratios 122

4.3 Vibrational assignments 125
  4.3.1 Introduction 125
  4.3.2 Factor group analysis — chain or local symmetry 126
  4.3.3 Group vibrations 131
  4.3.4 Model compounds 134
  4.3.5 Isotope substitution 134

4.4 Force fields and vibrational calculations 137
  4.4.1 The vibrational problem in Cartesian coordinates 138
  4.4.2 Generalized coordinates — the Wilson G and F matrices 139
  4.4.3 Mass-weighted Cartesian coordinates and normal coordinates 141
  4.4.4 The solution in principle; potential energy distributions 143
  4.4.5 Symmetry coordinates and internal symmetry coordinates 145
  4.4.6 Force fields and force constants 146
  4.4.7 Application to polymers 150

4.5 Finite chains 156

4.6 Overtone and combination frequencies; Fermi resonance 158

4.7 Further reading 161

5 The characterization of polymers 162
  5.1 Introduction 162
  5.2 The interpretation of polymer spectra: factor group analysis 163
    5.2.1 Polyethylene 163
    5.2.2 Poly(vinyl chloride) 173
    5.2.3 Poly(vinylidene chloride) 180
    5.2.4 Polytetrafluoroethylene 185
    5.2.5 Polystyrene 194
    5.2.6 Poly(ethylene terephthalate) 200
  5.3 The interpretation of polymer spectra: group frequencies 203
    5.3.1 Introduction 203
Contents

6.5.2 Vinyl polymers 254
6.5.3 Other polymers 255

6.6 Hydrogen bonding 256
6.6.1 Introduction 256
6.6.2 Polyamides 257
6.6.3 Polyurethanes 258
6.6.4 Biopolymers 262

6.7 Chain order and crystallinity 264
6.7.1 Introduction 264
6.7.2 Polyethylene 265
6.7.3 Polyoxymethylene 271
6.7.4 Poly(vinyl chloride) 274
6.7.5 Lattice modes in polyethylene and polytetrafluoroethylene 276
6.7.6 Differentiation between crystallinity and chain order 278

6.8 Chain folding in polyethylene 280
6.9 Longitudinal acoustic modes 286

6.10 Molecular orientation 292
6.10.1 Introduction 292
6.10.2 Theoretical background 293
6.10.3 Orientation in polyethylene and poly(ethylene terephthalate) 298

6.11 Further reading 301

References for chapters 5 and 6 303

A note on the use of the indexes 307

Index of spectra illustrated 308

Index of point groups 309

Index of group modes 309

Index of polymers 311

Main index 313