- Preface to first edition p. xiii
- Preface to second edition p. xv
- Preface to third edition p. xvii
- Preface to fourth edition p. xix
- Units, dimensions and conventions p. xxi
- Fundamental constants p. xxiii
- Useful conversion factors p. xxv
- 1 Some important results in quantum mechanics p. 1
- 1.1 Spectroscopy and quantum mechanics p. 1
- 1.2 The evolution of quantum theory p. 2
- 1.3 The Schrodinger equation and some of its solutions p. 8
- 1.3.1 The Schrodinger equation p. 9
- 1.3.2 The hydrogen atom p. 11
- 1.3.3 Electron spin and nuclear spin angular momentum p. 17
- 1.3.4 The Born-Oppenheimer approximation p. 19
- 1.3.5 The rigid rotor p. 21
- 1.3.6 The harmonic oscillator p. 23
- Exercises p. 25
- Bibliography p. 26
- 2 Electromagnetic radiation and its interaction with atoms and molecules p. 27
- 2.1 Electromagnetic radiation p. 27
- 2.2 Absorption and emission of radiation p. 27
- 2.3 Line width p. 34
- 2.3.1 Natural line broadening p. 34
- 2.3.2 Doppler broadening p. 35
- 2.3.3 Pressure broadening p. 36
- 2.3.4 Power, or saturation, broadening p. 36
- 2.3.5 Removal of line broadening p. 37
- 2.3.5.1 Effusive atomic or molecular beams p. 37
- 2.3.5.2 Lamb dip spectroscopy p. 37
- Exercises p. 38
- Bibliography p. 39
- 3 General features of experimental methods p. 41
- 3.1 The electromagnetic spectrum p. 41
- 3.2 General components of an absorption experiment p. 42
- 3.3 Dispersing elements p. 43
- 3.3.1 Prisms p. 43
- 3.3.2 Diffraction gratings p. 45
- 3.3.3 Fourier transformation and interferometers p. 48
- 3.3.3.1 Radiofrequency radiation p. 49
- 3.3.3.2 Infrared, visible and ultraviolet radiation p. 55
- 3.4 Components of absorption experiments in various regions of the spectrum p. 59
- 3.4.1 Microwave and millimetre wave p. 59
- 3.4.2 Far-infrared p. 61

- 3.4.3 Near-infrared and mid-infrared p. 62
- 3.4.4 Visible and near-ultraviolet p. 62
- 3.4.5 Vacuum- or far-ultraviolet p. 63
- 3.5 Other experimental techniques p. 64
- 3.5.1 Attenuated total reflectance spectroscopy and reflection-absorption infrared spectroscopy p. 64
- 3.5.2 Atomic absorption spectroscopy p. 64
- 3.5.3 Inductively coupled plasma atomic emission spectroscopy p. 66
- 3.5.4 Flash photolysis p. 67
- 3.6 Typical recording spectrophotometers for the near-infrared, mid-infrared, visible and near-ultraviolet regions p. 68
- Exercise p. 70
- Bibliography p. 70
- 4 Molecular symmetry p. 73
- 4.1 Elements of symmetry p. 73
- 4.1.1 @n-Fold axis of symmetry, C[subscript n] p. 74
- 4.1.2 Plane of symmetry, [sigma] p. 75
- 4.1.3 Centre of inversion, i p. 76
- 4.1.4 @n-Fold rotation-reflection axis of symmetry, S[subscript n] p. 76
- 4.1.5 The identity element of symmetry, I (or E) p. 77
- 4.1.6 Generation of elements p. 77
- 4.1.7 Symmetry conditions for molecular chirality p. 78
- 4.2 Point groups p. 81
- 4.2.1 C[subscript n] point groups p. 82
- 4.2.2 S[subscript n] point groups p. 83
- 4.2.3 C[subscript nv] point groups p. 83
- 4.2.4 D[subscript n] point groups p. 83
- 4.2.5 C[subscript nh] point groups p. 84
- 4.2.6 D[subscript nd] point groups p. 84
- 4.2.7 D[subscript nh] point groups p. 84
- 4.2.8 T[subscript d] point group p. 85
- 4.2.9 O[subscript h] point group p. 85
- 4.2.10 K[subscript h] point group p. 86
- 4.2.11 I[subscript h] point group p. 86
- 4.2.12 Other point groups p. 87
- 4.3 Point group character tables p. 87
- 4.3.1 C[subscript 2v] character table p. 87
- 4.3.2 C[subscript 3v] character table p. 92
- 4.3.3 C[subscript infinity]v] character table p. 96
- 4.3.4 I[subscript h] character table p. 97
- 4.4 Symmetry and dipole moments p. 97
- Exercises p. 102
- Bibliography p. 102
- 5 Rotational spectroscopy p. 103

- 5.1 Linear, symmetric rotor, spherical rotor and asymmetric rotor molecules p. 103
- 5.2 Rotational infrared, millimetre wave and microwave spectra p. 105
- 5.2.1 Diatomic and linear polyatomic molecules p. 105
- 5.2.1.1 Transition frequencies or wavenumbers p. 105
- 5.2.1.2 Intensities p. 110
- 5.2.1.3 Centrifugal distortion p. 111
- 5.2.1.4 Diatomic molecules in excited vibrational states p. 112
- 5.2.2 Symmetric rotor molecules p. 113
- 5.2.3 Stark effect in diatomic, linear and symmetric rotor molecules p. 115
- 5.2.4 Asymmetric rotor molecules p. 116
- 5.2.5 Spherical rotor molecules p. 117
- 5.2.6 Interstellar molecules detected by their radiofrequency, microwave or millimetre wave spectra p. 119
- 5.3 Rotational Raman spectroscopy p. 122
- 5.3.1 Experimental methods p. 122
- 5.3.2 Theory of rotational Raman scattering p. 124
- 5.3.3 Rotational Raman spectra of diatomic and linear polyatomic molecules p. 126
- 5.3.4 Nuclear spin statistical weights p. 128
- 5.3.5 Rotational Raman spectra of symmetric and asymmetric rotor molecules p. 131
- 5.4 Structure determination from rotational constants p. 131
- Exercises p. 134
- Bibliography p. 135
- 6 Vibrational spectroscopy p. 137
- 6.1 Diatomic molecules p. 137
- 6.1.1 Infrared spectra p. 138
- 6.1.2 Raman spectra p. 140
- 6.1.3 Anharmonicity p. 142
- 6.1.3.1 Electrical anharmonicity p. 142
- 6.1.3.2 Mechanical anharmonicity p. 142
- 6.1.4 Vibration-rotation spectroscopy p. 147
- 6.1.4.1 Infrared spectra p. 147
- 6.1.4.2 Raman spectra p. 151
- 6.2 Polyatomic molecules p. 154
- 6.2.1 Group vibrations p. 154
- 6.2.2 Number of normal vibrations of each symmetry species p. 162
- 6.2.2.1 Non-degenerate vibrations p. 163
- 6.2.2.2 Degenerate vibrations p. 165
- 6.2.3 Vibrational selection rules p. 166
- 6.2.3.1 Infrared spectra p. 166
- 6.2.3.2 Raman spectra p. 172
- 6.2.4 Vibration-rotation spectroscopy p. 173
- 6.2.4.1 Infrared spectra of linear molecules p. 174
- 6.2.4.2 Infrared spectra of symmetric rotors p. 178
- 6.2.4.3 Infrared spectra of spherical rotors p. 180

- 6.2.4.4 Infrared spectra of asymmetric rotors p. 181
- 6.2.5 Anharmonicity p. 184
- 6.2.5.1 Potential energy surfaces p. 184
- 6.2.5.2 Vibrational term values p. 186
- 6.2.5.3 Local mode treatment of vibrations p. 187
- 6.2.5.4 Vibrational potential functions with more than one minimum p. 188
- 6.2.5.4(a) Inversion vibrations p. 189
- 6.2.5.4(b) Ring-puckering vibrations p. 191
- 6.2.5.4(c) Torsional vibrations p. 192
- Exercises p. 195
- Bibliography p. 196
- 7 Electronic spectroscopy p. 199
- 7.1 Atomic spectroscopy p. 199
- 7.1.1 The periodic table p. 199
- 7.1.2 Vector representation of momenta and vector coupling approximations p. 201
- 7.1.2.1 Angular momenta and magnetic moments p. 201
- 7.1.2.2 Coupling of angular momenta p. 205
- 7.1.2.3 Russell-Saunders coupling approximation p. 206
- 7.1.2.3(a) Non-equivalent electrons p. 206
- 7.1.2.3(b) Equivalent electrons p. 210
- 7.1.3 Spectra of alkali metal atoms p. 213
- 7.1.4 Spectrum of the hydrogen atom p. 216
- 7.1.5 Spectra of helium and the alkaline earth metal atoms p. 219
- 7.1.6 Spectra of other polyelectronic atoms p. 222
- 7.2 Electronic spectroscopy of diatomic molecules p. 225
- 7.2.1 Molecular orbitals p. 225
- 7.2.1.1 Homonuclear diatomic molecules p. 225
- 7.2.1.2 Heteronuclear diatomic molecules p. 232
- 7.2.2 Classification of electronic states p. 233
- 7.2.3 Electronic selection rules p. 236
- 7.2.4 Derivation of states arising from configurations p. 237
- 7.2.5 Vibrational coarse structure p. 240
- 7.2.5.1 Potential energy curves in excited electronic states p. 240
- 7.2.5.2 Progressions and sequences p. 242
- 7.2.5.3 The Franck-Condon principle p. 246
- 7.2.5.4 Deslandres tables p. 250
- 7.2.5.5 Dissociation energies p. 250
- 7.2.5.6 Repulsive states and continuous spectra p. 253
- 7.2.6 Rotational fine structure p. 254
- 7.2.6.1 [superscript 1 Sigma]-[superscript 1 Sigma] electronic and vibronic transitions p. 254
- 7.2.6.2 [superscript 1 Pi]-[superscript 1 Sigma] electronic and vibronic transitions p. 257
- 7.3 Electronic spectroscopy of polyatomic molecules p. 260
- 7.3.1 Molecular orbitals and electronic states p. 260
- 7.3.1.1 AH[subscript 2] molecules p. 261

- 7.3.1.1(a) [angle]HAN=180[degree] p. 261
- 7.3.1.1(b) [angle]HAH=90[degree] p. 263
- 7.3.1.2 Formaldehyde (H[subscript 2]CO) p. 265
- 7.3.1.3 Benzene p. 267
- 7.3.1.4 Crystal field and ligand field molecular orbitals p. 270
- 7.3.1.4(a) Crystal field theory p. 271
- 7.3.1.4(b) Ligand field theory p. 273
- 7.3.1.4(c) Electronic transitions p. 275
- 7.3.2 Electronic and vibronic selection rules p. 275
- 7.3.3 Chromophores p. 278
- 7.3.4 Vibrational coarse structure p. 278
- 7.3.4.1 Sequences p. 278
- 7.3.4.2 Progressions p. 279
- 7.3.4.2(a) Totally symmetric vibrations p. 279
- 7.3.4.2(b) Non-totally symmetric vibrations p. 279
- 7.3.5 Rotational fine structure p. 283
- 7.3.6 Diffuse spectra p. 284
- Exercises p. 287
- Bibliography p. 288
- 8 Photoelectron and related spectroscopies p. 289
- 8.1 Photoelectron spectroscopy p. 289
- 8.1.1 Experimental methods p. 291
- 8.1.1.1 Sources of monochromatic ionizing radiation p. 291
- 8.1.1.2 Electron velocity analysers p. 294
- 8.1.1.3 Electron detectors p. 294
- 8.1.1.4 Resolution p. 294
- 8.1.2 Ionization processes and Koopmans' theorem p. 295
- 8.1.3 Photoelectron spectra and their interpretation p. 297
- 8.1.3.1 Ultraviolet photoelectron spectra of atoms p. 297
- 8.1.3.2 Ultraviolet photoelectron spectra of molecules p. 298
- 8.1.3.2(a) Hydrogen p. 298
- 8.1.3.2(b) Nitrogen p. 300
- 8.1.3.2(c) Hydrogen bromide p. 302
- 8.1.3.2(d) Water p. 305
- 8.1.3.2(e) Benzene p. 305
- 8.1.3.3 X-ray photoelectron spectra of gases p. 307
- 8.1.3.4 X-ray photoelectron spectra of solids p. 313
- 8.2 Auger electronand X-ray fluorescence spectroscopy p. 315
- 8.2.1 Auger electron spectroscopy p. 317
- 8.2.1.1 Experimental method p. 317
- 8.2.1.2 Processes in Auger electron ejection p. 318
- 8.2.1.3 Examples of Auger electron spectra p. 319
- 8.2.2 X-ray fluorescence spectroscopy p. 322
- 8.2.2.1 Experimental method p. 322

- 8.2.2.2 Processes in X-ray fluorescence p. 324
- 8.2.2.3 Examples of X-ray fluorescence spectra p. 325
- 8.3 Extended X-ray absorption fine structure p. 327
- Exercises p. 334
- Bibliography p. 335
- 9 Lasers and laser spectroscopy p. 337
- 9.1 General discussion of lasers p. 337
- 9.1.1 General features and properties p. 337
- 9.1.2 Methods of obtaining population inversion p. 340
- 9.1.3 Laser cavity modes p. 341
- 9.1.4 Q-switching p. 342
- 9.1.5 Mode locking p. 344
- 9.1.6 Harmonic generation p. 345
- 9.2 Examples of lasers p. 346
- 9.2.1 The ruby and alexandrite lasers p. 346
- 9.2.2 The titanium-sapphire laser p. 348
- 9.2.3 The neodymium-YAG laser p. 349
- 9.2.4 The diode or semiconductor laser p. 350
- 9.2.5 The helium-neon laser p. 352
- 9.2.6 The argon ion and krypton ion lasers p. 354
- 9.2.7 The nitrogen (N[subscript 2]) laser p. 355
- 9.2.8 The excimer and exciplex lasers p. 356
- 9.2.9 The carbon dioxide laser p. 358
- 9.2.10 The dye lasers p. 359
- 9.2.11 Laser materials in general p. 362
- 9.3 Uses of lasers in spectroscopy p. 362
- 9.3.1 Hyper Raman spectroscopy p. 363
- 9.3.2 Stimulated Raman spectroscopy p. 365
- 9.3.3 Coherent anti-Stokes Raman scattering spectroscopy p. 367
- 9.3.4 Laser Stark (or laser electron resonance) spectroscopy p. 368
- 9.3.5 Two-photon and multiphoton absorption p. 371
- 9.3.6 Multiphoton dissociation and laser separation of isotopes p. 374
- 9.3.7 Single vibronic level, or dispersed, fluorescence p. 377
- 9.3.8 Light detection and ranging (LIDAR) p. 379
- 9.3.9 Cavity ring-down spectroscopy p. 382
- 9.3.10 Femtosecond spectroscopy p. 387
- 9.3.11 Spectroscopy of molecules in supersonic jets p. 393
- 9.3.11.1 Properties of a supersonic jet p. 393
- 9.3.11.2 Fluorescence excitation spectroscopy p. 396
- 9.3.11.3 Single vibronic level, or dispersed, fluorescence spectroscopy p. 400
- 9.3.11.4 Zero kinetic energy photoelectron spectroscopy p. 402
- Exercises p. 404
- Bibliography p. 405
- Appendix

- A Character tables p. 407
- B Symmetry species of vibrations p. 423
- Index of Atoms and Molecules p. 429
- Subject Index p. 439