Contents

Preface xiii
Units, dimensions, and conventions xv
Fundamental constants xix
Useful conversion factors xx

1 SOME IMPORTANT RESULTS IN QUANTUM MECHANICS

1.1 Spectroscopy and quantum mechanics 1
1.2 The evolution of quantum theory 2
1.3 The Schrödinger equation and some of its solutions 9
1.3.1 The Schrödinger equation 9
1.3.2 The hydrogen atom 11
1.3.3 Electron spin and nuclear spin angular momentum 18
1.3.4 The Born–Oppenheimer approximation 20
1.3.5 The rigid rotor 21
1.3.6 The harmonic oscillator 23
Questions 25
Bibliography 26

2 ELECTROMAGNETIC RADIATION AND ITS INTERACTION WITH ATOMS AND MOLECULES

2.1 Electromagnetic radiation 27
2.2 Absorption and emission of radiation 28
2.3 Line width 33
2.3.1 Natural line broadening 33
2.3.2 Doppler broadening 34
2.3.3 Pressure broadening 35
2.3.4 Removal of line broadening 35
2.3.4.1 Effusive atomic or molecular beams 36
2.3.4.2 Lamb dip spectroscopy 36

Questions 37
Bibliography 38

3 GENERAL FEATURES OF EXPERIMENTAL METHODS

3.1 The electromagnetic spectrum 39
3.2 General components of an absorption experiment 40
3.3 Dispersing elements 41
3.3.1 Prisms 41
3.3.2 Diffraction gratings 43
3.3.3 Interferometers 45
3.4 Components of absorption experiments in various regions of the spectrum 47
3.4.1 Microwave and millimetre wave 47
3.4.2 Far-infrared 49
3.4.3 Near- and mid-infrared 50
3.4.4 Visible and near-ultraviolet 50
3.4.5 Far-ultraviolet 51
3.5 Other experimental techniques 51
3.5.1 Attenuated total reflectance spectroscopy 51
3.5.2 Atomic absorption spectroscopy 52
3.5.3 Flash photolysis 53
3.6 Typical recording spectrophotometers for the near- and mid-infrared, visible, and near-ultraviolet regions 54
Questions 57
Bibliography 57

4 MOLECULAR SYMMETRY

4.1 Elements of symmetry 58
4.1.1 n-Fold axis of symmetry, C_n 59
4.1.2 Plane of symmetry, σ 60
4.1.3 Centre of inversion, i 62
4.1.4 n-Fold rotation–reflection axis of symmetry, S_n 62
4.1.5 The identity element of symmetry, I (or E) 63
4.1.6 Generation of elements 63
4.2 Point groups 64
4.2.1 C_n point groups 65
4.2.2 S_n point groups 65
4.2.3 C_{nv} point groups 66
4.2.4 D_n point groups 66
4.2.5 C_{nh} point groups 67
4.2.6 D_{nd} point groups 67
4.2.7 D_{nh} point groups 67

4.2.8 T_d point group 68
4.2.9 O_h point group 68
4.2.10 K_h point group 69
4.3 Point group character tables 69
4.3.1 C_{2v} character table 69
4.3.2 C_{3v} character table 73
4.3.3 $C_{\infty v}$ character table 77
Questions 78
Bibliography 79

5 ROTATIONAL SPECTROSCOPY

5.1 Linear, symmetric rotor, spherical rotor, and asymmetric rotor molecules 80
5.2 Rotational infrared, millimetre wave, and microwave spectra 82
5.2.1 Diatomic and linear polyatomic molecules 82
5.2.1.1 Transition frequencies or wavenumbers 82
5.2.1.2 Intensities 87
5.2.1.3 Centrifugal distortion 87
5.2.1.4 Diatomic molecules in excited vibrational states 88
5.2.2 Symmetric rotor molecules 89
5.2.3 Stark effect in diatomic, linear, and symmetric rotor molecules 92
5.2.4 Asymmetric rotor molecules 93
5.2.5 Spherical rotor molecules 94
5.2.6 Interstellar molecules detected by their radiofrequency, microwave, or millimetre wave spectra 95
5.3 Rotational Raman spectroscopy 98
5.3.1 Experimental methods 99
5.3.2 Theory of rotational Raman scattering 100
5.3.3 Rotational Raman spectra of diatomic and linear polyatomic molecules 102
5.3.4 Nuclear spin statistical weights 105
5.3.5 Rotational Raman spectra of symmetric and asymmetric rotor molecules 108
5.4 Structure determination from rotational constants 108
Questions 110
Bibliography 111

6 VIBRATIONAL SPECTROSCOPY

6.1 Diatomic molecules 112
6.1.1 Infrared spectra 113
6.1.2 Raman spectra 115

6.1.3 Anharmonicity 117
6.1.3.1 Electrical anharmonicity 117
6.1.3.2 Mechanical anharmonicity 117
6.1.4 Vibration–rotation spectroscopy 121
6.1.4.1 Infrared spectra 121
6.1.4.2 Raman spectra 126
6.2 Polyatomic molecules 128
6.2.1 Group vibrations 128
6.2.2 Vibrational selection rules 136
6.2.2.1 Infrared spectra 136
6.2.2.2 Raman spectra 142
6.2.3 Vibration–rotation spectroscopy 143
6.2.3.1 Infrared spectra of linear molecules 143
6.2.3.2 Infrared spectra of symmetric rotors 148
6.2.3.3 Infrared spectra of spherical rotors 149
6.2.3.4 Infrared spectra of asymmetric rotors 151
6.2.4 Anharmonicity 154
6.2.4.1 Potential energy surfaces 154
6.2.4.2 Vibrational term values 157
6.2.4.3 Local mode treatment of vibrations 157
6.2.4.4 Vibrational potential functions with more than one minimum 159
6.2.4.4(a) Inversion vibrations 159
6.2.4.4(b) Ring-puckering vibrations 161
6.2.4.4(c) Torsional vibrations 163
Questions 165
Bibliography 167

7 ELECTRONIC SPECTROSCOPY

7.1 Atomic spectroscopy 168
7.1.1 The periodic table 168
7.1.2 Vector representation of momenta and vector coupling approximations 173
7.1.2.1 Angular momenta and magnetic moments 173
7.1.2.2 Coupling of angular momenta 174
7.1.2.3 Russell–Saunders coupling approximation 175
7.1.2.3(a) Non-equivalent electrons 175
7.1.2.3(b) Equivalent electrons 180
7.1.3 Spectra of alkali metal atoms 183
7.1.4 Spectrum of the hydrogen atom 187
7.1.5 Spectra of helium and the alkaline earth metal atoms 189
7.1.6 Spectra of other polyelectronic atoms 192

7.2 Electronic spectroscopy of diatomic molecules 194
7.2.1 Molecular orbitals 194
7.2.1.1 Homonuclear diatomic molecules 194
7.2.1.2 Heteronuclear diatomic molecules 201
7.2.2 Classification of electronic states 202
7.2.3 Electronic selection rules 205
7.2.4 Derivation of states arising from configurations 206
7.2.5 Vibrational coarse structure 208
7.2.5.1 Potential energy curves in excited electronic states 208
7.2.5.2 Progressions and sequences 211
7.2.5.3 The Franck–Condon principle 213
7.2.5.4 Deslandres tables 218
7.2.5.5 Dissociation energies 220
7.2.5.6 Repulsive states and continuous spectra 221
7.2.6 Rotational fine structure 222
7.2.6.1 $^1\Sigma - {}^1\Sigma$ electronic and vibronic transitions 222
7.2.6.2 $^1\Pi - {}^1\Sigma$ electronic and vibronic transitions 226
7.3 Electronic spectroscopy of polyatomic molecules 229
7.3.1 Molecular orbitals and electronic states 229
7.3.1.1 AH_2 molecules 230
7.3.1.1(a) $\angle$ HAH = 180° 230
7.3.1.1(b) $\angle$ HAH = 90° 231
7.3.1.2 Formaldehyde (H_2CO) 234
7.3.1.3 Benzene 236
7.3.1.4 Crystal field and ligand field molecular orbitals 239
7.3.1.4(a) Crystal field theory 240
7.3.1.4(b) Ligand field theory 243
7.3.1.4(c) Electronic transitions 244
7.3.2 Electronic and vibronic selection rules 244
7.3.3 Chromophores 247
7.3.4 Vibrational coarse structure 248
7.3.4.1 Sequences 248
7.3.4.2 Progressions 248
7.3.4.2(a) Totally symmetric vibrations 248
7.3.4.2(b) Non-totally symmetric vibrations 250
7.3.5 Rotational fine structure 252
7.3.6 Diffuse spectra 254
Questions 257
Bibliography 258

8 PHOTOELECTRON AND RELATED SPECTROSCOPIES

8.1 Photoelectron spectroscopy 260
8.1.1 Experimental methods 262

8.1.1.1 Sources of monochromatic ionizing radiation 262
8.1.1.2 Electron velocity analysers 265
8.1.1.3 Electron detectors 265
8.1.1.4 Resolution 267
8.1.2 Ionization processes and Koopmans' theorem 267
8.1.3 Photoelectron spectra and their interpretation 268
8.1.3.1 Ultraviolet photoelectron spectra of atoms 269
8.1.3.2 Ultraviolet photoelectron spectra of molecules 270
8.1.3.2(a) Hydrogen 270
8.1.3.2(b) Nitrogen 272
8.1.3.2(c) Hydrogen bromide 274
8.1.3.2(d) Water 275
8.1.3.2(e) Benzene 276
8.1.3.3 X-ray photoelectron spectra of gases 277
8.1.3.4 X-ray photoelectron spectra of solids 283
8.2 Auger electron spectroscopy 285
8.2.1 Experimental method 287
8.2.2 Processes in Auger electron ejection 287
8.2.3 Examples of Auger electron spectra 289
8.3 Extended X-ray absorption fine structure 293
Questions 300
Bibliography 301

9 LASERS AND LASER SPECTROSCOPY

9.1 General discussion of lasers 302
9.1.1 General features and properties 302
9.1.2 Methods of obtaining population inversion 304
9.1.3 Laser cavity modes 306
9.1.4 Q-switching 307
9.1.5 Mode locking 308
9.1.6 Harmonic generation 310
9.2 Examples of lasers 310
9.2.1 The ruby laser 310
9.2.2 The neodymium–YAG laser 312
9.2.3 The diode or semiconductor laser 313
9.2.4 The helium–neon laser 316
9.2.5 The argon ion and krypton ion lasers 318
9.2.6 The nitrogen (N_2) laser 319
9.2.7 The excimer and exciplex lasers 320
9.2.8 The carbon dioxide laser 322
9.2.9 The dye lasers 323
9.2.10 Laser materials in general 326

9.3 Uses of lasers in spectroscopy 327
9.3.1 Hyper Raman spectroscopy 328
9.3.2 Stimulated Raman spectroscopy 330
9.3.3 Coherent anti-Stokes Raman scattering spectroscopy 332
9.3.4 Laser Stark (or laser electric resonance) spectroscopy 333
9.3.5 Two-photon and multiphoton absorption 336
9.3.6 Multiphoton dissociation and laser separation of isotopes 339
9.3.7 Single vibronic level fluorescence 342
9.3.8 Spectroscopy of molecules in supersonic jets 345
Questions 349
Bibliography 350
Appendix 351
Character tables 351
Index 369