Contents

Preface xiii

Physical constants and conversion factors xv

About the author xvii

1 Introduction and review 1
- 1.1 Historical perspective 1
- 1.2 Definitions, derivations, and discovery 2
- 1.3 Review of quantum mechanics 3
  - 1.3.1 The particle in a box: A model for translational energies 5
  - 1.3.2 The rigid rotor: A model for rotational motion of diatomics 7
  - 1.3.3 The harmonic oscillator: Vibrational motion 10
    - 1.3.3.1 Classical mechanics of harmonic motion 10
    - 1.3.3.2 The quantum mechanical harmonic oscillator 12
    - 1.3.3.3 Harmonic oscillator raising and lowering operators 13
  - 1.3.4 The hydrogen atom 14
  - 1.3.5 General aspects of angular momentum in quantum mechanics 17
- 1.4 Approximate solutions to the Schrödinger equation: Variation and perturbation theory 18
  - 1.4.1 Variation method 18
  - 1.4.2 Perturbation theory 19
- 1.5 Statistical mechanics 21
- 1.6 Summary 26

Problems 26

References 27

2 The nature of electromagnetic radiation 29
- 2.1 Introduction 29
- 2.2 The classical description of electromagnetic radiation 30
  - 2.2.1 Maxwell's equations 30
  - 2.2.2 Polarization properties of light 34
  - 2.2.3 Electric dipole radiation 35
  - 2.2.4 Gaussian beams 37
- 2.3 Propagation of light in matter 38
  - 2.3.1 Refraction and reflection 38
  - 2.3.2 Absorption and emission of light 41
  - 2.3.3 Effect of an electromagnetic field on charged particles 42
- 2.4 Quantum mechanical aspects of light 43
  - 2.4.1 Quantization of the radiation field 43
  - 2.4.2 Blackbody radiation and the Planck distribution law 45
  - 2.4.3 The photoelectric effect and the discovery of photons 47
- 2.5 Summary 48

Problems 48

References 49

3 Electric and magnetic properties of molecules and bulk matter 51
3.1 Introduction 51
3.2 Electric properties of molecules 52
3.2.1 Review of electrostatics 52
3.2.2 Electric moments 54
3.2.3 Quantum mechanical calculation of multipole moments 56
3.2.4 Interaction of electric moments with the electric field 57
3.2.5 Polarizability and induced moments 58
3.2.6 Frequency dependence of polarizability 60
3.2.7 Quantum mechanical expression for the polarizability 62
3.3 Electric properties of bulk matter 62
3.3.1 Dielectric permittivity 62
3.3.2 Frequency dependence of permittivity 64
3.3.3 Relationships between macroscopic and microscopic properties 66
3.3.3.1 Nonpolar molecules in the gas phase 66
3.3.3.2 Nonpolar molecules in the condensed phase 67
3.3.3.3 Polar molecules in condensed phases 68
3.3.4 The local field problem: The Onsager and Kirkwood models 69
3.3.4.1 Onsager model 70
3.3.4.2 Kirkwood model 71
3.4 Magnetic properties of matter 72
3.4.1 Basic principles of magnetism 73
3.4.2 Magnetic properties of bulk matter 74
3.4.3 Magnetic moments and intrinsic angular momenta 75
3.4.4 Magnetic resonance phenomena 77
3.5 Summary 80
Problems 81
References 81
4 Time-dependent perturbation theory of spectroscopy 83
4.1 Introduction: Time dependence in quantum mechanics 83
4.2 Time-dependent perturbation theory 85
4.2.1 First-order solution to the time-dependent Schrödinger equation 85
4.2.2 Perturbation due to electromagnetic radiation: Momentum versus dipole operator 86
4.2.3 Fermi's Golden Rule and the time–energy uncertainty principle 89
4.2.3.1 Case 1. The limit $t \to \infty$ 89
4.2.3.2 Case 2. Exact resonance, monochromatic radiation 90
4.2.3.3 Case 3. Intermediate times and the time–energy uncertainty principle 90
4.2.3.4 Case 4. Accounting for the intensity distribution of the source 91
4.3 Rate expression for emission 91
4.3.1 Photon density of states 91
4.3.2 Fermi's Golden Rule for stimulated and spontaneous emission 92
4.4 Perturbation theory calculation of polarizability 93
4.4.1 Derivation of the Kramers–Heisenberg–Dirac equation 93
4.4.2 Finite state lifetimes and imaginary component of polarizability 97
4.4.3 Oscillator strength 98
4.5 Quantum mechanical expression for emission rate 98
4.6 Time dependence of the density matrix 100
4.7 Summary 105

Problems 106
References 107
5 The time-dependent approach to spectroscopy 109
5.1 Introduction 109
5.2 Time-correlation functions and spectra as Fourier transform pairs 110
5.3 Properties of time-correlation functions and spectral lineshapes 114
5.4 The Fluctuation–Dissipation Theorem 116
5.5 Rotational correlation functions and pure rotational spectra 117
5.5.1 Correlation functions for absorption and light scattering 118
5.5.2 Classical free–rotor correlation function and spectrum 119
5.6 Reorientational spectroscopy of liquids: Single-molecule and collective dynamics 120
5.6.1 Dielectric relaxation 120
5.6.2 Far-infrared absorption 123
5.6.3 Depolarized Rayleigh scattering 126
5.7 Vibration-rotation spectra 128
5.8 Spectral moments 130
5.9 Summary 131
Problems 132
References 132
6 Experimental considerations: Absorption, emission, and scattering 133
6.1 Introduction 133
6.2 Einstein *A* and *B* coefficients for absorption and emission 133
6.3 Absorption and stimulated emission 135
6.4 Electronic absorption and emission spectroscopy 137
6.4.1 Atomic spectra 140
6.4.2 Molecular electronic spectra 140
6.5 Measurement of light scattering: The Raman and Rayleigh effects 142
6.6 Spectral lineshapes 144
6.7 Summary 146
Problems 147
References 148
7 Atomic spectroscopy 149
7.1 Introduction 149
7.2 Good quantum numbers and not so good quantum numbers 149
7.2.1 The hydrogen atom: Energy levels and selection rules 150
7.2.2 Many-electron atoms 153
7.2.3 The Clebsch–Gordan series 157
7.2.4 Spin–orbit coupling 158
7.3 Selection rules for atomic absorption and emission 161
7.3.1 E1, M1, and E2 allowed transitions 161
7.3.2 Hyperfine structure 162
7.4 The effect of external fields 164
7.4.1 The Zeeman effect 164
7.4.2 The Stark effect 167
7.5 Atomic lasers and the principles of laser emission 167
7.6 Summary 171
Problems 172
References 172
8 Rotational spectroscopy 173
8.1 Introduction 173

8.2 Energy levels of free rigid rotors 173
8.2.1 Diatomics 173
8.2.2 Polyatomic rotations 175
8.2.2.1 Spherical tops 179
8.2.2.2 Prolate symmetric tops 179
8.2.2.3 Oblate symmetric tops 180
8.2.2.4 Asymmetric tops 180
8.2.2.5 Linear molecules 180
8.3 Angular momentum coupling in non-$^1\Sigma$ electronic states 181
8.4 Nuclear statistics and J states of homonuclear diatomics 183
8.5 Rotational absorption and emission spectroscopy 186
8.6 Rotational Raman spectroscopy 190
8.7 Corrections to the rigid-rotor approximation 195
8.8 Internal rotation 197
8.8.1 Free rotation limit, $k_BT >> V_0$ 198
8.8.2 Harmonic oscillator limit, $k_BT << V_0$ 199
8.9 Summary 200
Problems 201
References 202
9 Vibrational spectroscopy of diatomics 203
9.1 Introduction 203
9.2 The Born–Oppenheimer approximation and its consequences 203
9.3 The harmonic oscillator model 206
9.4 Selection rules for vibrational transitions 208
9.4.1 Infrared spectroscopy 208
9.4.2 Raman scattering 211
9.5 Beyond the rigid rotor-harmonic oscillator approximation 213
9.5.1 Perturbation theory of vibration–rotation energy 213
9.5.2 The Morse oscillator and other anharmonic potentials 216
9.6 Summary 218
Problems 218
References 219
10 Vibrational spectroscopy of polyatomic molecules 221
10.1 Introduction 221
10.2 Normal modes of vibration 222
10.2.1 Classical equations of motion for normal modes 223
10.2.2 Example: Normal modes of a linear triatomic 225
10.2.3 The Wilson F and G matrices 227
10.2.4 Group frequencies 228
10.3 Quantum mechanics of polyatomic vibrations 229
10.4 Group theoretical treatment of vibrations 230
10.4.1 Finding the symmetries of normal modes 230
10.4.2 Symmetries of vibrational wavefunctions 234
10.5 Selection rules for infrared absorption and Raman scattering: Group theoretical prediction of activity 236
10.6 Rotational structure 238
10.7 Anharmonicity 240
10.8 Selection rules at work: Benzene 243
10.9 Solvent effects on infrared spectra 244
10.10 Summary 246

Problems 247
References 247
11 Electronic spectroscopy 249
11.1 Introduction 249
11.2 Diatomic molecules: Electronic states and selection rules 250
11.2.1 Molecular orbitals and electronic configurations for diatomics 251
11.2.2 Term symbols for diatomics 254
11.2.3 Selection rules 257
11.2.3.1 Electric dipole transitions (E1) 257
11.2.3.2 Electric quadrupole transitions (E2) 258
11.2.3.3 Magnetic dipole transitions (M1) 258
11.2.3.4 Examples of selection rules at work: O_2 and I_2 258
11.3 Vibrational structure in electronic spectra of diatomics 259
11.3.1 Absorption spectra 259
11.3.2 Emission spectra 262
11.3.3 Dissociation and predissociation 263
11.4 Born–Oppenheimer breakdown in diatomic molecules 265
11.5 Polyatomic molecules: Electronic states and selection rules 266
11.5.1 Molecular orbitals and electronic states of H_2O 267
11.5.2 Franck–Condon progressions in electronic spectra of polyatomics 268
11.5.3 Benzene: Electronic spectra and vibronic activity of nontotally symmetric modes 270
11.6 Transition metal complexes: Forbidden transitions and the Jahn–Teller effect 273
11.7 Emission spectroscopy of polyatomic molecules 277
11.8 Nonradiative relaxation of polyatomic molecules 280
11.9 Chromophores 283
11.10 Solvent effects in electronic spectroscopy 284
11.11 Summary 287
Problems 288
References 289
12 Raman and resonance Raman spectroscopy 291
12.1 Introduction 291
12.2 Selection rules in Raman scattering 292
12.2.1 Off-resonance Raman scattering 294
12.2.2 Resonance Raman scattering 296
12.3 Polarization in Raman scattering 299
12.3.1 Polarization in off-resonance Raman scattering 300
12.3.2 Polarization in resonance Raman scattering 302
12.4 Rotational and vibrational dynamics in Raman scattering 304
12.5 Analysis of Raman excitation profiles 309
12.5.1 Transform theory of Raman intensity 310
12.5.2 Time-dependent theory of resonance Raman and electronic spectra 312
12.6 Surface-enhanced Raman scattering 319
12.7 Summary 323
Problems 323
References 324
13 Nonlinear optical spectroscopy 327
13.1 Introduction 327
13.2 Classical approaches to nonlinear optical processes 329
13.2.1 Polarization as an expansion in powers of the incident field 329

13.2.2 Three-wave mixing (TWM) 330
13.2.3 Four-wave mixing (FWM) 335
13.2.4 Classical calculation of $\chi^{(2)}$ and $\chi^{(3)}$ 336
13.2.5 Second-order frequency conversion in the small signal limit 339
13.3 Quantum mechanical approach to nonlinear optical processes 343
13.3.1 Time-dependent perturbation theory approach 343
13.3.2 Density matrix calculation of $\chi^{(2)}$ and $\chi^{(3)}$ 346
13.4 Feynman diagrams and calculation of time-dependent response functions 352
13.5 Experimental applications of nonlinear processes 359
13.5.1 Examples of $\chi^{(2)}$ experiments 359
13.5.2 Examples of $\chi^{(3)}$ experiments 362
13.5.2.1 Two-photon and multiphoton absorption 362
13.5.2.2 Coherent Raman spectroscopy 365
13.5.2.3 Spontaneous Raman scattering as a third-order nonlinear process 368
13.5.2.4 Femtosecond stimulated Raman spectroscopy 371
13.6 Summary 373
Problems 373
References 374
14 Time-resolved spectroscopy 377
14.1 Introduction 377
14.2 Time-resolved fluorescence spectroscopy 378
14.2.1 Polarization in time-resolved fluorescence spectroscopy 379
14.2.2 Time-resolved fluorescence Stokes shift 381
14.3 Time-resolved four-wave mixing experiments 385
14.3.1 Third-order nonlinear response function 387
14.3.2 Pump-probe spectroscopy 388
14.3.2.1 Transient absorption spectra of excited electronic states 392
14.3.2.2 Time-resolved vibrational spectroscopy 396
14.4 Transient grating and photon echo experiments 399
14.4.1 Transient grating spectroscopy 401
14.4.2 Photon echo spectroscopy 403
14.5 Two-dimensional spectroscopy 408
14.6 Summary 412
Problems 412
References 413
Appendix A: Math review 415
Appendix B: Principles of electrostatics 427
Appendix C: Group theory 433
Index 445