CONTENTS

Preface v

1 Separation of Variables

1.1 The Schrödinger equation 2

1.2 Separation of the time-independent wave equation. Translational motion 4

1.3 Separation of the central-field equation 6

2 Nuclear Motion Separability in Diatomic Molecules

2.1 Experiment versus theory for the hydrogen molecule .. 9

2.2 Separation of the centre-of-mass motion 10

2.3 Adiabatic approximation 12

2.4 Separation of rotations and vibrations 16

2.5 Calculations for the H_2 molecule 17

2.6 Non-adiabatic effects 20

2.7 Potential energy curves.. 21

2.8 Generator coordinate theory of molecular spectra 24

3 Vibronic Coupling in Polyatomic Molecules

3.1 The Schrödinger equation 29

3.2 Adiabatic approximation 32

3.3 Corrections within adiabatic approximations 35

3.4 Breakdown of adiabatic approximations 39

3.5 Transition moments 44

4 Transition Intensity

4.1 Transition momentum versus transition length in computation of Herzberg–Teller induced intensity 47

4.2 Born–Oppenheimer approximation and calculation of vibrational transition intensities 50

5 Electronically Degenerate States
5.1 Resonance limit: Jahn–Teller and Renner–Teller effects .. 53
5.2 Pseudo Jahn–Teller effect .. 76

6 Vibronic Coupling Calculations
6.1 Approaches to calculations .. 88
6.2 *A priori* CNDO calculations .. 93
6.3 Quadratic and higher order coupling .. 95
6.4 Two-photon absorption .. 97
6.5 Breakdown of Born–Oppenheimer approximation .. 101

7 Anharmonicity
7.1 Occurrence and relevance .. 106
7.2 Anharmonicity and adiabatic wavefunctions .. 110
7.3 Local modes .. 115
7.4 Anharmonicity through nuclear kinetic energy operator .. 118

8 Implications and Manifestations in Molecular Spectroscopy
8.1 Absorption–emission mirror symmetry: transition moment interferences .. 120
8.2 Raman scattering .. 138
8.3 Circular dichroism (CD) .. 145
8.4 Multiphoton absorption .. 149

9 Molecular Dynamics
9.1 Radiationless transitions in isolated molecules .. 154
9.2 Intermolecular energy transfer .. 172
9.3 Unimolecular reactions .. 177

10 The Solid State
10.1 Nuclear motions .. 183
10.2 Frenkel exciton theory .. 184
10.3 Molecular vibrations .. 186
10.4 Exciton-phonon interactions .. 196

References .. 205
Further Reading .. 208
Appendices .. 210
Index .. 217