

Contents

| | |
|---|-----------|
| Preface | v |
| Foreword | vii |
| 1. Molecules, Isomerism and Large Amplitude Vibrations | 1 |
| 1.1 Introduction | 1 |
| 1.2 Isomerism | 3 |
| 1.3 Potential Energies Associated with Internal Rotation | 5 |
| 1.4 The Experimental Approach | 11 |
| 1.4.1 Spectroscopic methods | 11 |
| 1.4.2 Diffraction methods | 14 |
| 1.4.3 Relaxation methods | 15 |
| 1.4.4 Classical methods | 19 |
| 2. Molecular Energy Levels | 21 |
| 2.1 Introduction | 21 |
| 2.2 Solution of the Schrödinger Equation | 21 |
| 2.3 The Molecular Hamiltonian Operator and Energy Levels | 26 |
| 2.4 Electronic States and Potential Energy Surfaces | 29 |
| 2.5 Molecular Vibrations | 30 |
| 2.5.1 Introduction | 30 |
| 2.5.2 Small amplitude molecular vibrations and classical mechanics | 30 |
| 2.5.3 Small amplitude molecular vibrations and quantum mechanics | 35 |
| 2.5.4 The separation of molecular vibrations | 36 |
| 2.6 The Mathematical Representation of Potential Energy Curves for Large Amplitude Vibrations | 38 |
| 2.6.1 Periodic potential functions | 39 |

| | |
|---|----|
| 2.6.2 Non-periodic potential functions | 40 |
| 2.7 Calculation of the Energy Levels associated with One-dimensional Potential Functions | 42 |
| 2.7.1 Internal rotation hindered by a symmetrical twofold barrier | 42 |
| 2.7.2 The energy levels associated with a simple non-periodic potential function | 47 |
| 2.8 Molecular Rotation | 51 |
| 2.8.1 Rotation in classical mechanics | 51 |
| 2.8.2 Inertial classification of molecules | 52 |
| 2.8.3 Rigid rotor energy levels | 53 |
| 2.8.4 Effective rigid rotor energy levels and rotational constants | 57 |
| 2.8.5 Centrifugal distortion | 60 |
| 2.9 Vibration Rotation Interactions | 61 |

3. Experimental Methods of Studying Large Amplitude Internal Motions in Molecules **66**

| | |
|---|----|
| 3.1 Introduction | 66 |
| 3.2 Microwave Spectroscopy | 66 |
| 3.3 Infrared and Raman Spectroscopy | 73 |
| 3.4 Nuclear Magnetic Resonance Spectroscopy | 77 |
| 3.5 Gas Phase Electron Diffraction | 81 |

4. The Origin of Potential Barriers **86**

| | |
|--|-----|
| 4.1 Introduction | 86 |
| 4.2 Ethane and Early Theories of the Origin of Barriers | 87 |
| 4.3 Barriers and Conformational Energy Differences Dominated by Specific Interactions | 87 |
| 4.3.1 Different types of intramolecular forces | 87 |
| 4.3.2 Double bond character due to resonance | 88 |
| 4.3.3 Hydrogen bonding | 89 |
| 4.3.4 Steric effects | 91 |
| 4.4 The Derivation of Information about Intramolecular Forces from Experimental Potential Functions | 92 |
| 4.5 The Empirical Approach to the Computation of Conformational Energies and Barriers | 94 |
| 4.6 Ab Initio Computations of Conformational Energies and Barrier Heights | 96 |
| 4.6.1 Ab initio molecular orbital computations | 97 |
| 4.6.2 Energy component analysis of rotational barriers | 99 |
| 4.6.3 Charge distribution analysis of rotational barriers | 101 |
| 4.7 Conclusion | 101 |

| | |
|---|------------|
| 5. Internal Rotation of Symmetric Groups | 103 |
| 5.1 Introduction | 103 |
| 5.2 Ethane | 103 |
| 5.3 Torsional Energy Levels | 104 |
| 5.3.1 Symmetry considerations | 105 |
| 5.3.2 Spin statistical weights and absorption line intensities | 107 |
| 5.4 The Calculation of Potential Barriers | 109 |
| 5.4.1 Torsional frequency method | 109 |
| 5.4.2 High barriers | 110 |
| 5.4.3 Intermediate barriers | 111 |
| 5.4.4 Assessment of the torsional frequency method | 112 |
| 5.5 Splittings Method | 112 |
| 5.5.1 Principal axis method | 114 |
| 5.5.2 Internal axis method | 120 |
| 5.6 Comparison of Torsional Frequency and Splittings Method | 123 |
| 5.7 Internal Rotation in Symmetric Rotors | 124 |
| 5.8 NMR Methods | 125 |
| 5.9 Some Selected Methyl and other Symmetric Barriers | 127 |
| 5.9.1 Barriers about C—C bonds in substituted ethanes | 127 |
| 5.9.2 Other symmetric barriers | 130 |
| 5.10 Low Potential Barriers | 133 |
| 5.11 Multiple Symmetric Groups | 136 |
| 5.12 Internal Rotation in Methanol and Acetaldehyde | 140 |
| 5.12.1 Methyl alcohol | 141 |
| 5.12.2 Acetaldehyde | 141 |
| 6. Internal Rotation of Asymmetric Groups | 145 |
| 6.1 Introduction | 145 |
| 6.2 Asymmetric Potential Functions | 148 |
| 6.3 Internal Rotation in Completely Asymmetric Molecules | 153 |
| 6.3.1 The torsional equation | 155 |
| 6.3.2 Rotational energy levels and torsion-rotation interactions | 156 |
| 6.3.3 The Hamiltonian in the instantaneous principal axis system of the molecule | 157 |
| 6.3.4 The reduced potential | 158 |
| 6.3.5 Internal rotation in 3-fluoropropene | 158 |
| 6.4 Internal Rotation in some Selected Molecules | 162 |
| 6.4.1 Molecules with predominantly twofold barriers | 162 |
| 6.4.2 Molecules with a predominantly threefold potential function | 166 |
| 7. Inversion | 171 |
| 7.1 Introduction | 171 |

| | |
|---|------------|
| 7.2 Quantum Mechanical Characteristics of the Inversion Vibration | 173 |
| 7.2.1 Properties of molecular wave functions for an inverting molecule | 174 |
| 7.2.2 Potential functions for the inversion mode | 180 |
| 7.2.2.1 Harmonic oscillator perturbed by a Gaussian barrier | 180 |
| 7.2.2.2 Quadratic-quartic potential function | 182 |
| 7.2.2.3 Manning potential function | 183 |
| 7.2.3 Rotation-inversion spectrum of the XY_3 symmetric top | 183 |
| 7.3 Inversion in Asymmetric Rotors | 185 |
| 7.3.1 Rotation-inversion spectrum of an inverting asymmetric top molecule | 186 |
| 7.3.2 Vibration-rotation interactions | 189 |
| 7.3.3 Inverting molecules | 191 |
| 7.4 Inversion in Molecules containing more than One Large Amplitude Vibration | 193 |
| 7.5 Inversion in Excited Electronic States | 194 |
| 7.6 Molecules with High Barriers to Inversion | 195 |
| 8. Large Amplitude Vibrations in Ring Compounds | 197 |
| 8.1 Introduction | 197 |
| 8.2 Strain in Ring Compounds | 200 |
| 8.3 Four-Membered Rings | 203 |
| 8.3.1 Coordinates and potential functions for four-membered rings | 203 |
| 8.3.2 Examples of ring puckering | 206 |
| 8.4 Five-Membered Rings | 208 |
| 8.4.1 Pseudorotation | 209 |
| 8.4.2. The Hamiltonian operator and energy levels for pseudorotation | 213 |
| 8.4.3. Examples of pseudorotation | 215 |
| 8.4.4 Five-membered rings with one or two double bonds | 218 |
| 8.5 Six-Membered and Larger Rings | 219 |
| 8.5.1 Cyclohexane and its derivatives | 219 |
| 8.5.2 Six-membered rings with one and two double bonds | 220 |
| 8.6 Fused and Bridged Ring Systems | 222 |
| 9. Internal Rotation and Conformational Flexibility in Macromolecules | 226 |
| 9.1 Introduction | 226 |
| 9.2 Proteins | 227 |
| 9.3 Nucleic acids | 233 |
| 9.4 Carbohydrates | 235 |
| 9.5 Conclusion | 239 |
| Index | 241 |