

# CONTENTS

|   |    |
|---|----|
| INTRODUCTION  | 1  |
| CHAPTER   |    |
| 1. INSTRUMENTS AND EXPERIMENTAL METHODS   | 5  |
| 1.1. TYPES OF MICROWAVE SPECTROGRAPHS   | 5  |
| 1.1 <i>a</i> . Fixed-Frequency Spectrometers  | 6  |
| 1.1 <i>b</i> . Frequency-Sweep Spectrometer with Crystal Video Receiver                 | 6  |
| 1.1 <i>c</i> . Frequency-Sweep Spectrometer with Radio-Frequency Receiver               | 7  |
| 1.1 <i>d</i> . Automatic Recording Spectrometers with Phase-Sensitive Lock-In Amplifier | 11 |
| 1.1 <i>e</i> . Atomic and Molecular Beam Methods  | 13 |
| 1.1 <i>f</i> . Paramagnetic Resonance Spectrographs                                     | 14 |
| 1.1 <i>g</i> . Zeeman Spectrograph for Gases  | 16 |
| 1.2. MICROWAVE COMPONENTS   | 18 |
| 1.2 <i>a</i> . Waveguide  | 20 |
| 1.2 <i>b</i> . Waveguide Bends, Connectors, and Tapers                                  | 23 |
| 1.2 <i>c</i> . Attenuators  | 24 |
| 1.2 <i>d</i> . Impedance-Matching Devices   | 25 |
| 1.2 <i>e</i> . Directional Couplers   | 25 |
| 1.2 <i>f</i> . The Magic Tee  | 29 |
| 1.2 <i>g</i> . Waveguide Mounts for Crystal Mixers and Detectors                        | 30 |
| 1.2 <i>h</i> . Detectors  | 33 |
| 1.2 <i>i</i> . Absorption Cells   | 37 |
| 1.2 <i>j</i> . Cavity Wavemeters  | 41 |
| 1.2 <i>k</i> . Sources of Radiation   | 44 |
| 1.3. ELECTRONIC COMPONENTS  | 53 |
| 1.3 <i>a</i> . Klystron Power Supplies  | 53 |
| 1.3 <i>b</i> . Pound Frequency Stabilizer for Klystrons                                 | 55 |
| 1.3 <i>c</i> . Stark-Modulation Oscillators   | 56 |
| 1.3 <i>d</i> . Low-Frequency Amplifier  | 57 |
| 1.3 <i>e</i> . Radio-Frequency Receivers  | 57 |
| 1.3 <i>f</i> . Phase-Sensitive Lock-In Amplifiers                                       | 60 |
| 1.4. SPECTROMETER SENSITIVITY   | 62 |
| 1.4 <i>a</i> . Minimum Detectable Signal  | 62 |
| 1.4 <i>b</i> . Nature of Over-All Noise Figure  | 64 |
| 1.4 <i>c</i> . Application to a Stark-Modulation Spectrograph                           | 67 |
| 1.4 <i>d</i> . Crystal Square-Law Detector  | 68 |
| 1.4 <i>e</i> . Thermal Detectors  | 71 |

## CHAPTER

|   |     |
|---|-----|
| 1.5. MEASUREMENT OF LINE WIDTHS AND INTENSITIES                           | 71  |
| 1.5 <i>a</i> . Measurement of the Shapes of Narrow Lines                  | 71  |
| 1.5 <i>b</i> . Measurement of Relative Intensities                        | 74  |
| 1.5 <i>c</i> . Measurement of Absolute Intensities                        | 74  |
| 1.6. PRECISION FREQUENCY MEASUREMENTS                                     | 76  |
| 1.6 <i>a</i> . Measurement of Absolute Frequencies                        | 76  |
| 1.6 <i>b</i> . Measurement of Frequency Differences                       | 80  |
| 2. MICROWAVE SPECTRA OF GASES   | 84  |
| 2.1. ELECTRONIC SPECTRA   | 84  |
| 2.1 <i>a</i> . Atomic Spectra   | 84  |
| 2.1 <i>b</i> . Oxygen   | 86  |
| 2.2. MOLECULAR ROTATIONAL SPECTRA   | 89  |
| 2.2 <i>a</i> . Classical Description                                      | 90  |
| 2.2 <i>b</i> . Diatomic and Linear Molecules                              | 93  |
| 2.2 <i>c</i> . Symmetric-Top Molecules                                    | 97  |
| 2.2 <i>d</i> . Asymmetric-Top Molecules                                   | 108 |
| 2.3. TRANSITIONS BETWEEN <i>l</i> -TYPE DOUBLETS                          | 125 |
| 2.4. INVERSION SPECTRA  | 127 |
| 2.5. MAGNETIC RESONANCE SPECTRA OF GASES                                  | 132 |
| 2.6. HYPERFINE STRUCTURE  | 135 |
| 2.6 <i>a</i> . Nuclear Quadrupole Interactions                            | 136 |
| 2.6 <i>b</i> . Magnetic Hyperfine Structure                               | 147 |
| 2.6 <i>c</i> . Relative Intensities                                       | 149 |
| 3. STARK AND ZEEMAN EFFECTS   | 154 |
| 3.1. EFFECTS OF ELECTRIC FIELDS   | 156 |
| 3.1 <i>a</i> . Stark Effect of Molecules without Hyperfine Structure      | 156 |
| 3.1 <i>b</i> . Stark Effect of Molecules with Nuclear Quadrupole Coupling | 165 |
| 3.2. EFFECTS OF MAGNETIC FIELDS   | 173 |
| 3.2 <i>a</i> . Molecules in $^1\Sigma$ States                             | 173 |
| 3.2 <i>b</i> . Paramagnetic Molecules                                     | 180 |
| 3.2 <i>c</i> . Relative Intensities                                       | 183 |
| 4. SHAPES AND INTENSITIES OF ABSORPTION LINES OF GASES                    | 185 |
| 4.1. THE MICROWAVE ABSORPTION COEFFICIENT                                 | 185 |
| 4.2. LINE SHAPES  | 188 |
| 4.2 <i>a</i> . Doppler Broadening   | 188 |
| 4.2 <i>b</i> . Collision Broadening                                       | 188 |
| 4.3. SATURATION EFFECT  | 197 |
| 4.4. DIPOLE-MOMENT MATRIX ELEMENTS  | 199 |

## CONTENTS

xi

| CHAPTER   |     |
|---|-----|
| 4.5. POPULATION OF ENERGY STATES  | 203 |
| 4.5 <i>a.</i> The Partition Functions                                   | 205 |
| 4.5 <i>b.</i> Statistical Weights                                       | 206 |
| 4.6. INTENSITIES OF MOLECULAR ROTATIONAL LINES                          | 210 |
| 5. SPECTRA OF SOLIDS AND LIQUIDS  | 213 |
| 5.1. PARAMAGNETIC RESONANCE   | 213 |
| 5.1 <i>a.</i> Spectroscopic Splitting Factor                            | 213 |
| 5.1 <i>b.</i> Introduction to Crystalline Field Effects                 | 214 |
| 5.1 <i>c.</i> Characteristic Energies and Line Frequencies              | 216 |
| 5.1 <i>d.</i> Line Breadths   | 219 |
| 5.1 <i>e.</i> Salts of the Iron-Group Elements                          | 224 |
| 5.1 <i>f.</i> Rare Earths   | 234 |
| 5.1 <i>g.</i> Uranium Salts   | 235 |
| 5.1 <i>h.</i> Organic Free Radicals                                     | 236 |
| 5.1 <i>i.</i> Irradiated Crystals and Plastics                          | 237 |
| 5.1 <i>j.</i> Alkali Metals in Solution                                 | 239 |
| 5.1 <i>k.</i> Conduction Electrons in Metals                            | 240 |
| 5.1 <i>l.</i> Hyperfine Structure                                       | 240 |
| 5.2. FERROMAGNETIC RESONANCE  | 248 |
| 5.3. PURE NUCLEAR QUADRUPOLE SPECTRA                                    | 255 |
| 5.4. MICROWAVE ABSORPTION OF LIQUIDS                                    | 260 |
| 6. NUCLEAR PROPERTIES   | 265 |
| 6.1. SPINS  | 265 |
| 6.2. NUCLEAR QUADRUPOLE MOMENTS   | 267 |
| 6.3. NUCLEAR MAGNETIC MOMENTS   | 273 |
| 6.4. ATOMIC MASSES  | 275 |
| 7. ELECTRICAL PROPERTIES OF MOLECULES                                   | 279 |
| 7.1. NUCLEAR QUADRUPOLE COUPLINGS IN MOLECULES                          | 279 |
| 7.2. DIPOLE MOMENTS   | 287 |
| 7.2 <i>a.</i> Measured Values   | 288 |
| 7.2 <i>b.</i> Nature of Molecular Dipoles                               | 289 |
| 7.3. MOLECULAR QUADRUPOLE MOMENTS                                       | 294 |
| 7.4. MOLECULAR ROTATIONAL MAGNETIC MOMENTS                              | 296 |
| 8. MOLECULAR STRUCTURES   | 298 |
| 8.1. DETERMINATION OF MOLECULAR DIMENSIONS FROM ROTATIONAL<br>CONSTANTS | 298 |
| 8.1 <i>a.</i> Diatomic Molecules  | 300 |

|                |   |     |
|----------------|---|-----|
| CHAPTER        |   |     |
| 8.1 <i>b</i> . | Linear Polyatomic Molecules   | 301 |
| 8.1 <i>c</i> . | Symmetric-Top Molecules   | 304 |
| 8.1 <i>d</i> . | Asymmetric-Top Molecules  | 306 |
| 8.2.           | FACTORS AFFECTING BOND LENGTHS AND BOND ANGLES                                  | 308 |
| 8.2 <i>a</i> . | Covalent Resonance or Bond Conjugation  | 310 |
| 8.2 <i>b</i> . | Ionic Character   | 313 |
| 8.2 <i>c</i> . | Bond-Orbital Hybridization  | 314 |
| 8.3.           | CONSIDERATION OF PARTICULAR STRUCTURES  | 316 |
| 8.3 <i>a</i> . | Bonds to Hydrogen   | 316 |
| 8.3 <i>b</i> . | Halogen Bonds to C, Si, and Ge  | 318 |
| 8.3 <i>c</i> . | Hydrides and Halides of N, P, As, and Sb  | 319 |
| 8.3 <i>d</i> . | Inter-Halogens  | 321 |
| 8.3 <i>e</i> . | Boron Compounds   | 321 |
| 8.3 <i>f</i> . | Interaction of Single and Triple Bonds  | 322 |
| 8.3 <i>g</i> . | Nature of Bonding of Zn, Cd, and Hg   | 323 |
| 9.             | APPLICATIONS IN OTHER FIELDS  | 325 |
| 9.1.           | ELECTRONIC APPLICATIONS   | 325 |
| 9.1 <i>a</i> . | Spectrum-Line Frequency Stabilization of Oscillators                            | 325 |
| 9.1 <i>b</i> . | Spectrum Lines as Primary Frequency Standards: the Atomic or<br>Molecular Clock | 328 |
| 9.1 <i>c</i> . | Absorption Lines as Secondary Frequency Standards                               | 329 |
| 9.1 <i>d</i> . | The Stabilization of Magnetic Fields  | 329 |
| 9.2.           | APPLICATIONS TO ASTRONOMY   | 330 |
| 9.3.           | ANALYSES  | 332 |
| 9.3 <i>a</i> . | Isotopic Analysis   | 332 |
| 9.3 <i>b</i> . | Chemical Analysis   | 333 |
| APPENDIX       |   | 337 |
| BIBLIOGRAPHY   |   | 407 |
| NAME INDEX     |   | 435 |
| SUBJECT INDEX  |   | 441 |