# Contents

Preface *ix* 

- **1** Perspective and Introductory Remarks 1
- 1.1 What Do Muons Bring to Chemistry? 1
- 1.2 Muon Facilities and Background to Experimental Muon Techniques 4

٧

1.3 The Development of Muonium Chemistry 5 References 8

# 2 Muon Beams and Spin Spectroscopy 11

- 2.1 Spin-Polarized Muon Beams 11
- 2.2 Muon Decay and Detection of Its Spin Polarization 13
- 2.3 Continuous Versus Pulsed Muon Beams 14
- 2.4 μSR Spectrometers 16
- 2.5 Spectroscopy of Muons in Diamagnetic Environments 18
- 2.5.1 Diamagnetic Muons in a Longitudinal Field 18
- 2.5.2 Diamagnetic Muons in a Transverse Field 19
- 2.5.3 Diamagnetic Muons in Zero Magnetic Field 22
- 2.6 Spectroscopy of Muonium 23
- 2.6.1 Muonium in a Transverse Field 24
- 2.6.2 Muonium in a Longitudinal Field 26
- 2.7 TF-μSR of Muoniated Radicals 28
- 2.7.1 Muoniated Radicals in Isotropic Environments 28
- 2.7.2 Muoniated Radicals in Anisotropic Environments 32
- 2.7.3 Polarization Transfer from Precursor to Radical 33
- 2.8 Avoided Level-Crossing Resonance of Muoniated Radicals 34
- 2.9 RF Muon Spin Resonance of Muoniated Radicals 39
- 2.10 Longitudinal-Field Repolarization Studies of Muoniated Radicals 40 References 43

# **3** Formation of Chemical States Incorporating Muons 45

- 3.1  $\mu^+$  Charge Exchange and Mu Formation in the Gas Phase 45
- 3.2 Mu Formation and Track Effects in Dense Media 49
- 3.3 Chemical Processes Forming Muoniated Molecules 53
- 3.4  $\mu^-$  Capture and Muonic Atoms 60
  - References 61

- vi Contents
  - 4 Chemical Reactivity and Dynamics in the Gas Phase 65
  - 4.1 Muon Spin Spectroscopy Applied to Chemical Kinetics 65
  - 4.2 Potential Energy Surfaces and Quantum Mass Effects 67
  - 4.3 Theoretical Background to Rate Calculations for Bimolecular Reactions *71*
  - 4.4 Early Experimental Studies: Mu + Halogens 73
  - 4.5 H Atom Abstraction Reactions 75
  - 4.6 State-selected Reactivity:  $Mu + H_2(v = 1)$  77
  - 4.7 Addition Reactions 79
  - 4.8 A New Type of Chemical Bond: Br—Mu—Br Vibrational Bonding 84 References 86
  - 5 Muonium Chemistry and Chemical Kinetics in Condensed Phases 89
  - 5.1 Setting the Stage: Chemical Reactivity in Liquids vs. Gases 89
  - 5.2 Muonium Diffusion in Water 90
  - 5.3 Pressure and Density Dependence 92
  - 5.4 Muon Spin Dephasing During Reaction 96
  - 5.5 Additional Effects on Mu and H Kinetics in the Liquid Phase 99
  - 5.6 Can Mu React by a Different Mechanism to H? 101
  - 5.7 A Case Study of a Complex Reaction System:  $Mu + H_2O_2$  102 References 105

# 6 Muoniated Free Radicals 107

- 6.1 Isotropic Hyperfine Coupling 107
- 6.1.1 Isotropic Hyperfine Coupling Constants of α Nuclei 108
- 6.1.2 Isotropic Hyperfine Coupling Constants of β Nuclei 110
- 6.2 Isotope Effects on Muoniated Radicals 111
- 6.2.1 Bond Length 111
- 6.2.2 Hyperfine Constants 113
- 6.2.3 Conformational Preference 114
- 6.3 Intramolecular Motion of Muoniated Radicals 116
- 6.3.1 The Muoniated *tert*-Butyl Radical *116*
- 6.3.2 Methyl Radicals 116
- 6.3.3 Other Alkyl Radicals *119*
- 6.3.4 Mu Adducts of Carbonyls 119
- 6.4 Reorientational Dynamics of Muoniated Radicals *120*
- 6.4.1 Dipolar Hyperfine Coupling Constants 120
- 6.4.2 Effect of Hyperfine Anisotropy on  $\Delta_1$  and  $\Delta_0$  Resonances 124
- 6.4.3 Anisotropic Motion of Muoniated Radicals in Solids 128
- 6.5 Solvent Effects on Hyperfine Coupling Constants 129
- 6.6 Kinetics of Reactions of Muoniated Radicals 131
- 6.6.1 Measuring Chemical Reaction Rates Using TF-µSR 131
- 6.6.2 Measuring Chemical Reaction Rates Using ALC-μSR 132

- 6.6.3 Measuring Chemical Reaction Rates from the Transfer of Polarization from a Primary to a Secondary Radical *134*
- 6.7 Characterization of Novel Radicals by Muon Spin Spectroscopy 136
- 6.7.1 Radicals Containing Si or Ge 136
- 6.7.2 Radicals Containing P 137
- 6.7.3 Radicals Containing a Metal Atom 138
- 6.7.4 Muoniated Radicals Containing No Other Nuclear Moments *139* References *140*

# 7 Spin Relaxation Studies 143

- 7.1 Probing Spin Relaxation with Muons 143
- 7.2 Molecular Dynamics from Spin Relaxation 143
- 7.3 Muon Spin Relaxation Studies of Aqueous Solutions of Manganese(II) Ions 145
- 7.4 Muonium Spin Exchange with Paramagnetic Species 147
- 7.5 Spin Relaxation in Muoniated Radicals 150
- 7.6 Muon Spin Relaxation During Chemical Reaction 153 References 155

## 8 Aspects of Materials Chemistry 157

- 8.1 Muonium in Confined Spaces 157
- 8.2 Muonium and Muoniated Radicals in Fullerenes 160
- 8.3 Muonium and Radicals in Clathrates 164
- 8.4 Muoniated Radicals in Zeolites *167*
- 8.5 Muonium and Radicals on Surfaces *172* References *178*

## 9 Soft Matter, Organic Materials and Biological Systems 181

- 9.1 Soft Matter 181
- 9.2 Thermotropic Liquid Crystals 181
- 9.2.1 Orientational Ordering of MBBA 184
- 9.2.2 Fluctuations of 5CB 187
- 9.3 Cosurfactants in Bilayers and Micelles 190
- 9.4 Polymers 195
- 9.4.1 Dynamics in Non-conjugated Polymers 195
- 9.4.2 Electron Conduction in Conjugated Polymers *199*
- 9.5 Organic Materials 202
- 9.5.1 Magnetic Ordering in Organic Materials 202
- 9.5.2 Localized Defects in Organic Semiconductors 204
- 9.6 Biological Systems 207
- 9.6.1 µSR of DNA and Its Constituents 207
- 9.6.2 Muoniated Radicals Formed from Proteins 209
- 9.7 Concluding Thoughts 212 References 212

## **10** Future Developments and Outlook 215

- 10.1 Light Mass and Isotope Effects 215
- 10.2 Muon Spin Spectroscopy: Advantages and Limitations 216
- 10.3 New Methodologies 217
- 10.3.1 Transient Targets 217
- 10.3.2 Optical Spectroscopy 217
- 10.3.3 Spin Manipulation 218
- 10.4 Going Beyond Muon Spin Spectroscopy 218
- 10.4.1 Muon Tomography 218
- 10.4.2 Muon-Induced X-ray Emission 219
- 10.5 The Outlook for Muon Science 219
- 10.6 Conclusions 220
  - References 220

### Appendix A Derivation of Muon Polarization Expressions 223

- A.1 Polarization in a µSR Experiment 223
- A.2 Diamagnetic Muons in a Longitudinal Field 223
- A.3 Diamagnetic Muons in a Transverse Field 224
- A.4 Muonium in a Transverse Field 225
- A.5 Muonium in a Longitudinal Field 226
- A.6 Muoniated Radicals in Isotropic Environments 227
- A.7 Muoniated Radicals in High Transverse Fields 228
- A.8 Muoniated Radicals in Longitudinal Fields Outside Level Crossings 229
- A.9 Avoided Level-Crossing Muon Spin Resonance in Isotropic Environments 230
- A.10 Avoided Level-Crossing Muon Spin Resonance in Anisotropic Environments 232 References 234

#### Appendix B Muonium Rate Constants for Reactions in Solution 235

References 239

Index 241