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ABSTRACT

Muonium (Mu = μ⁺e⁻) behaves like a light isotope of hydrogen, and adds to molecules with unsaturated bonds to form muoniated radicals. Muoniated radicals were observed by μSR (muon spin rotation, resonance, and relaxation spectroscopy). As an aid to spectral assignments, experimental hyperfine coupling constants (hfcs) were compared to values obtained from density functional theory computations. Detection and characterization of muoniated radicals were used to investigate, evaluate, and elucidate hydrogen atom chemical reaction mechanisms.

Instead of the anticipated silyl radicals, beta-muoniated disilanyl radicals were detected after reaction of Mu with stable singlet silylenes. A two-step reaction mechanism is proposed to explain the formation of muoniated disilanyl radicals.

For the double bond of a silene, it was determined experimentally that Mu adds preferentially to carbon over silicon with the ratio of 2.2 : 1 in THF. This is consistent with thermodynamic calculations and other considerations.

Reaction of muonium with germylidenes generated alpha-muoniated germyl radicals. The difference in reactivity of Mu with carbenes, silylenes, and germylidenes was explained in terms of the Lewis basicity of the ylidene (or ylidene analogue) and the Lewis acidity of the radical. The muon hfc in a germyl radical was found to have a linear relationship with the germylidene concentration, consistent with predictions of a dipole-dipole reaction field model.

Four of six possible radicals were observed from Mu addition to azulene. The ratios of observed products support a competition between two radical reaction mechanisms proposed by Alder et al. for the transformation of azulene into naphthalene.

While there are practical limitations to the μSR technique, it has been shown that it is a useful tool for investigation of hydrogen-atom reaction mechanisms. This is the first thesis to explore reaction mechanisms with the aid of μSR.
Keywords: Muonium; Silylene; Silene; Germylidene; Azulene; Free Radical

Subject Terms: Chemical structure; Radicals (Chemistry); Muons; Muonium; Silicon Compounds; Aromatic Compounds
DEDICATION

For Samantha, my best friend and eternal companion.
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# TABLE OF CONTENTS

Approval ................................................................................................................................. ii
Abstract ................................................................................................................................. iii
Dedication ............................................................................................................................... v
Acknowledgements ............................................................................................................... vi
Table of Contents ................................................................................................................ v
List of Figures ......................................................................................................................... xi
List of Tables ......................................................................................................................... xvii
List of Abbreviations ............................................................................................................. xx

## CHAPTER 1. INTRODUCTION:

*ODE ON A REACTION VESSEL* ........................................................................................... 1

1.1 The Importance of Reaction Mechanisms in Chemistry ................................................. 2
1.2 Hydrogen Atom Reactions ............................................................................................. 2
1.3 Chemistry and the Positive Muon ................................................................................... 3
1.4 Muonium Nomenclature ................................................................................................. 7
1.5 Formation of $\alpha$- and $\beta$-Muoniumated Radicals ...................................................... 8
1.6 Using Muonium to Study Reaction Mechanisms ............................................................ 9
1.7 Organization of the Thesis ............................................................................................. 10
1.8 Individual versus Collaborative Work .......................................................................... 10

## CHAPTER 2. THEORY OF MUONIUM SPECTROSCOPY:

*THE MUON, THE ELECTRON, AND THE MOLECULE* .................................................... 12

2.1 From Creation to Decay in 2.2 Microseconds ................................................................. 12

2.1.1 The Origin of the Muon ............................................................................................ 12
2.1.2 Diamagnetic and Paramagnetic Muon States ......................................................... 14
2.1.3 La Morte du Muon ................................................................................................ 15

2.2 Transverse Field Muon Spin Rotation ........................................................................... 17

2.2.1 Muons in a Transverse Field ................................................................................ 17
2.2.2 Muonium in a Transverse Field ........................................................................... 19
2.2.3 Muoniumated Free Radicals in a Transverse Field ............................................. 24

2.3 Muon Spin Polarization ................................................................................................ 27

2.3.1 Concentration, Kinetics, and Polarization ............................................................. 29

2.4 TF-$\mu$SR Asymmetry and Fourier Power Spectra ......................................................... 30
2.5 Avoided Muon Level Crossing Resonance ................................................................. 33

## CHAPTER 3. EXPERIMENTAL AND COMPUTATIONAL METHODS:

*POLARIZATION LOST* ......................................................................................................... 40

3.1 $\mu$SR Experiments ...................................................................................................... 40
LIST OF FIGURES

Figure 1.1: Indirect formation of an α-muoniated radical by muonium addition to trimethylsilyldiazomethane. ................................................................. 8

Figure 1.2: (a) Muonium addition to ketene to form the α-muoniated methyl radical, and (b) muonium addition to diazocyclopentadiene to generate the α-muoniated cyclopentadienyl radical. ........................................... 9

Figure 1.3: Direct formation of an α-muoniated radical by muonium addition to a carbene ........................................................................................................ 9

Figure 1.4: Keto–enol tautomerization of acetone and 2-hydroxy-1-propene. ................. 9

Figure 2.1: Positive pion decay in the rest frame of the pion. $P_X$ is the momentum vector and $S_X$ the spin vector of particle X. ........................................ 14

Figure 2.2: Positive muon decay. $P_X$ is the momentum vector and $S_X$ is the spin vector of particle X. ........................................................................... 16

Figure 2.3: Plot of the Zeeman energy splitting for the muon, a spin-1/2 particle. $\omega_0^{\mu}$ is the hyperfine frequency of Mu ($2.8 \times 10^{10}$ rad s$^{-1}$), and $B_0 = \left(\frac{\omega_0^{\mu}}{2\pi}\right)/\left(\gamma_e + \gamma_\mu\right) = 1585$ G. The scale was chosen for easy comparison of transition energies with Figure 2.4 ........................................ 19

Figure 2.4: Breit-Rabi diagram for muonium, a two spin-1/2 system. $\omega_0^{\mu}$ is the hyperfine frequency of Mu ($2.8 \times 10^{10}$ rad s$^{-1}$), and $B_0 = \left(\frac{\omega_0^{\mu}}{2\pi}\right)/\left(\gamma_e + \gamma_\mu\right) = 1585$ G. Of the four permitted transitions at low fields, only $\omega_{12}$ and $\omega_{34}$ are resolvable. ............................................. 23

Figure 2.5: (a) TF-μSR histogram of diamagnetic muons in an applied magnetic field of 400 Gauss, and (b) the corresponding asymmetry spectrum. The oscillation in each plot illustrates how the number of positrons striking a particular detector rise and fall as the spin of the muon precesses in the magnetic field. ........................................................................... 32

Figure 2.6: An example TF-μSR spectrum showing a pair of frequencies due to a muoniated radical symmetrically placed about the diamagnetic peak. This spectrum was collected at 14.5 kG from a 1.55 M solution of 1,3-bis(tert-butyl)silylimidazol-2-ylidene in tetrahydrofuran. ......................................................................................... 33

Figure 2.7: Energy level diagram for the three spin system consisting of an electron, a muon, and a magnetic nucleus. At an avoided level crossing resonance, $B_{1,LCR}$, the two states are nearly degenerate. The states mix, enabling a relaxation process in a longitudinal field. ......................... 35
Figure 2.8: The theoretical form for a $\mu$LCR spectrum resulting from a loss of muon polarization due to mixing of spin states in a longitudinal field.

Figure 2.9: Shifting of the asymmetry curve when the toggle field is applied (a) with the main magnetic field, and (b) when it is applied against the main field.

Figure 2.10: An example of a $\mu$LCR spectrum showing the differential shape of a resonance when field modulation is applied. This signal is attributed to a set of equivalent $^{14}\text{N}$ nuclei in a muoniated radical generated from a 1.55 M solution of 1,3-bis(tert-butyl)-silylimidazol-2-ylidene in tetrahydrofuran.

Figure 3.1: Beam line organization at TRIUMF. All of the experiments described in this thesis were performed on the M20 beam line, located in the Meson Hall.

Figure 3.2: Design of the sample cells used for the silylene, silene, germylidene, and azulene studies. Surface muons enter the cells through the thin stainless steel foil.

Figure 3.3: Schematic of a TF-$\mu$SR experiment. The spin and momentum of the muon are arranged perpendicular for this type of experiment. The muons pass though the muon detector (M), triggering a "start" input for the Time Digitizing Converter. The muon interacts with the sample (S), which is located within a magnetic field ($B_{\text{applied}}$). The daughter positron is detected, triggering a "stop" input. A $\mu$SR histogram is then generated by plotting the number of positrons detected by a particular detector as a function of time.

Figure 3.4: Flow diagram of the electronic setup for a TF-$\mu$SR experiment. A "start" input occurs when a muon passes through counter M, and a "stop" input is the result of positron detection at one of the four positron counters.

Figure 3.5: Schematic of a $\mu$LCR experiment. The spin and momentum of the muon are arranged anti-parallel for this type of experiment. The muon interacts with the sample (S), which is located within a magnetic field ($B_{\text{applied}}$). The daughter positron is detected in either the Forward (F) or Backward (B) counter. A $\mu$LCR spectrum is then generated by plotting the difference in the two asymmetries, which are distinguished by the phase of the toggle-field.

Figure 3.6: Two representations of the restricted model: (a) single-electron wavefunctions occur in degenerate pairs but have opposite spin labels; (b) orbitals can hold two spin-paired electrons.

Figure 3.7: Two types of models: (a) a restricted open-shell model where most wavefunctions are restricted, but a few contain only a single electron; (b) electron pairing is not required, and the single-electron wavefunctions do not occur in degenerate pairs.
Figure 3.8: Diagram illustrating the order of computed and “true” energies of a system ................................................................. 62
Figure 3.9: Competition of objectives in computational chemistry ......................... 64
Figure 4.1: Some of the first stable silylenes reported ............................................. 75
Figure 4.2: Radicals produced from these silylene molecules, 1,3-bis(tert-butyl)-silylimidazol-2-ylidene and 1,3-bis(tert-butyl)-silylimidazolin-2-ylidene, were studied by μSR techniques ........................................ 77
Figure 4.3: Relationship between an organosilane hydride and its corresponding radicals, ions, and radical ions ........................................... 78
Figure 4.4: Chain reaction mechanism for radical-based hydrosilylation ..................... 79
Figure 4.5: Chain reaction mechanism for radical promoted removal of a functional group by organosilicon hydrides ........................................ 80
Figure 4.6: Possible radicals from muonium addition to silylenes 4.4 and 4.5 ............. 82
Figure 4.7: TF-μSR spectrum from a 1.55 M solution of 4.4 (1,3-bis(tert-butyl)-silylimidazol-2-ylidene) in THF at 299 K in a transverse magnetic field of 14.5 kG ........................................ 83
Figure 4.8: TF-μSR spectrum from a 0.88 M solution of 4.5 (1,3-bis(tert-butyl)-silylimidazolin-2-ylidene) in THF at 313 K in a transverse magnetic field of 14.5 kG ........................................ 84
Figure 4.9: Temperature dependence of the muon hyperfine coupling constant in the muoniated radicals from unsaturated silylene 4.4 (○) and the saturated silylene 4.5 (□). The lines are only meant to serve as a guide for the eyes .............................................................. 85
Figure 4.10: μLCR spectrum from a 1.55 M solution of 4.4 (1,3-bis(tert-butyl)-silylimidazol-2-ylidene) in THF at 299 K ...................................................... 86
Figure 4.11: (a) and (b) are resonances detected in the μLCR spectrum from a 0.88 M solution of 4.5 (1,3-bis(tert-butyl)-silylimidazolin-2-ylidene) in THF at 313 K ...................................................... 87
Figure 4.12: μLCR percent signal amplitude as a function of magnetic field position for the radical from muonium addition to 4.5. Due to differing gyromagnetic ratios, the 14N and 1H have different amplitude curves. The dotted line (⋯⋯) is the 29Si amplitude curve, the solid line (—) is the 14N curve, the dashed line (- - -) is the 1H curve, and the circles (○) are the experimental data. The silicon curve is much lower in percent amplitude due to the low natural abundance of 29Si .............................................................. 91
Figure 4.13: Theoretical curve for the muon polarization transfer at 14.5 kG from the unsaturated silyl radical 4.4a to the unsaturated disilanyl radical 4.6 .............................................................. 98
Figure 4.14: Possible reaction mechanisms for formation of the muoniated disilanyl radical from 4.4: (a) by addition of muonium to the dimer; (b) by reaction of silyl radical 4.4a with an additional molecule of 4.4 .............................................................. 101
Figure 4.15: Disilanyl radical species detected by μSR studies .............................................102
Figure 4.16: An example of a 2:1 disilane product resulting from reaction of silylenes with halocarbons. .................................................................103
Figure 4.17: An example of a 1:1 silane product resulting from reaction of silylenes with halocarbons .................................................................103
Figure 4.18: A simplified representation of the optimized 3-dimensional structure of the unsaturated disilanyl radical 4.6 .........................................................105
Figure 4.19: A simplified representation of the optimized 3-dimensional structure of the saturated disilanyl radical 4.7 .........................................................105
Figure 5.1: Rearrangement of a dialkylsilylene into a cyclic silene .............................................112
Figure 5.2: Reaction mechanism suggested by Leigh for alcohol attack on a silene in tetrahydrofuran .................................................................114
Figure 5.3: Proposed reaction mechanism for muonium attack on a silene in tetrahydrofuran .................................................................114
Figure 5.4: TF-μSR spectrum from a 1.5 M solution of silene 5.2 in THF at 14.5 kG and 298 K. The signal near 400 MHz (labelled x) is an overtone of the diamagnetic signal .................................................................115
Figure 5.5: μLCR spectrum from a 1 M solution of 5.2 in THF at 312 K ..................................116
Figure 5.6: Radical products from Mu addition to silene 5.2 ..........................................................117
Figure 5.7: The optimized structure of 5.2-CMu with the methyl groups hidden ..........................119
Figure 5.8: The optimized structure of 5.2-SiMu with the methyl groups hidden ..........................119
Figure 6.1: Difference in reactivity of a dialkyl silylene and a dialkyl germylidene with TEMPO .................................................................125
Figure 6.2: 1,3-bis(tert-butyl)-germylimidazol-2-ylidene, whose reactions with large free radicals to form germyl radicals, were studied by Tumanskii et al .................................................................125
Figure 6.3: Additional germylidenes used in μSR experiments ......................................................126
Figure 6.4: TF-μSR spectra from a 1.1 M solution of germylidene 6.2 in THF at 272 K and 3.9 kG. At this magnetic field, the diamagnetic signal is near 52 MHz .................................................................127
Figure 6.5: TF-μSR spectrum from a 1.1 M solution of germylidene 6.2 in THF at 3.9 kG and 272 K. (a) Positive precession frequencies; (b) negative precession frequencies; (c) complete spectrum with negative precession frequency signals properly separated from the positive ones .................................................................129
Figure 6.6: Temperature dependence of the muon hyperfine coupling constant in the muoniated radical from unsaturated germylidene 6.2. The line is meant as a visual guide only. The error bars in $A_\mu$ are smaller than the shapes used to represent the data points .................................................................130
Figure 6.7: TF-μSR spectrum from a neat sample of acyclic germylidene 6.3 at 1.9 kG and 298 K, with the negative frequency signals properly separated from the positive ones .................................................................131
Figure 6.8: TF-μSR spectrum from a 1.56 M solution of germylidene 6.4 in THF at 14.5 kG and 298 K, with the negative frequency signals properly separated from the positive ones.  

Figure 6.9: TF-μSR spectrum from a 1.56 M solution of germylidene 6.4 in THF at 19.3 kG and 298 K, with the negative frequency signals properly separated from the positive ones.  

Figure 6.10: Attempts to model digermanyl radical 6.2c demonstrated that this species is not stable. The two germanium atoms were over 5.1 Å apart in the minimum energy structure.  

Figure 6.11: Germylidene 6.5 has been studied only by computational methods.  

Figure 6.12: Proton promoted dimerization of carbenes to form an ethene.  

Figure 6.13: Relative Lewis basicity of carbenes, silylenes, and germylidenes, and the relative Lewis acidity of their corresponding muoniated radicals.  

Figure 6.14: Temperature dependence of the muon hyperfine coupling constant in the muoniated radical from unsaturated germylidene 6.2, as a function of germylidene concentration in THF. The lines are meant as a visual guide only. The error bars in $A_\mu$ are smaller than the shapes used to represent the data points. 

Figure 6.15: Interpolated muon hyperfine coupling constant in the muoniated radical from unsaturated germylidene 6.2 at 310 K, as a function of germylidene mole fraction. The line represents the fit of Reddoch and Konishi's dipole-dipole reaction field model. The error bars in $A_\mu$ are smaller than the shapes used to represent the data points. 

Figure 7.1: Chemical structure of azulene, displaying the numbering system used in this thesis.  

Figure 7.2: (a) Mulliken atomic charges in azulene computed by DFT methods at the UB3LYP/6-31G(d) level; (b) azulene atomic charges with hydrogens summed into heavy atoms.  

Figure 7.3: Chemical structure of naphthalene. The numbering system used for naphthalene is not meant to directly relate to the system used for azulene.  

Figure 7.4: The Spiran mechanism.  

Figure 7.5: The Methylene Walk mechanism.  

Figure 7.6: TF-μSR spectrum from 1.5 M azulene in THF at 25°C in an applied magnetic field of 12.5 kG.  

Figure 7.7: TF-μSR spectrum from neat azulene at 109°C in an applied magnetic field of 12.5 kG.  

Figure 7.8: μLCR spectrum from 1.5 M azulene in THF at 25°C.  

Figure 7.9: Expansion of μLCR spectrum in the region of 2.9 kG for 1.5 M azulene in THF at 25°C.  

Figure 7.10: Expansion of μLCR spectrum in the region of 8.8 kG for 1.5 M azulene in THF at 25°C.
Figure 7.11: Expansion of μLCR spectrum in the region of 11.1 kG for 1.5 M azulene in THF at 25°C ..............................................................161

Figure 7.12: Expansion of μLCR spectrum in the region of 13.7 kG for 1.5 M azulene in THF at 25°C ..............................................................162

Figure 7.13: The symmetrically distinct reactive sites for: (a) pyrene; (b) fluoranthene; (c) triphenylene; (d) dodecahydrotriphenylene ..................166

Figure 7.14: LCR percent amplitude curves for the four detected radicals based on the measured $A_r$ values, along with the LCR experimental data. The experimental error bars are from the uncertainty in signal amplitude as determined during the fit of each signal. ........................................173

Figure 7.15: Temperature dependence of $A_r$ in 4-/5-Mu-azulyl (○), 6-Mu-azulyl (□), 2-Mu-azulyl (●), and 1-Mu-azulyl (■). The lines are a guide for the eyes only ..............................................................177
LIST OF TABLES

Table 1.1: Properties of the positive muon ................................................................. 4
Table 1.2: Properties of muonium .................................................................................. 6
Table 4.1: Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 4.4 ................................................................. 84
Table 4.2: Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 4.5 ................................................................. 84
Table 4.3: μLCR parameters for the muoniated radical from 4.4 as a function of temperature ........................................................................................................ 88
Table 4.4: μLCR parameters for the muoniated radical from 4.5 at 313 K ................. 88
Table 4.5: Potential nuclear hyperfine coupling constants based on a μLCR spectrum from a 1.55 M solution of 4.4 in THF at 299 K ........................................ 89
Table 4.6: Potential nuclear hyperfine coupling constants from a 0.88 M solution of 4.5 in THF at 313 K ................................................................................. 90
Table 4.7: Calculated and experimental silyl radical muon hyperfine coupling constants ................................................................................................................. 93
Table 4.8: Calculated and experimental disilanyl radical muon hyperfine coupling constants ........................................................................................................... 95
Table 4.9: Calculated nuclear hyperfine coupling constants for unsaturated disilanyl radical 4.6 ................................................................. 96
Table 4.10: Calculated nuclear hyperfine coupling constants for saturated disilanyl radical 4.7 ................................................................. 96
Table 4.11: Upper and lower limits for the second order rate constant for the N-heterocyclic silyl radicals 4.4a and 4.5a reacting with their silylene counterparts ......................................................................................... 100
Table 4.12: Second-order rate constants for the self-reaction of silyl radicals ............ 101
Table 4.13: Calculated and experimental dicarbenyl radical muon hyperfine coupling constants ........................................................................................................... 107
Table 5.1: Muon hfcs for the two radicals detected in TF-μSR experiments on silene 5.2 in a 1.5 M solution of THF at 14.5 kG ................................................. 116
Table 5.2: μLCR parameters for the muoniated radical from 5.2 at 312 K ................. 117
Table 5.3: Potential proton hyperfine coupling constants based on a μLCR spectrum from a 1 M solution of 5.2 in THF at 312 K ........................................... 117
Table 5.4: Computationally modelled muon hyperfine coupling constants for the radicals from silane 5.2 ........................................................................ 118
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Computationally modelled proton hyperfine coupling constants for Radical 5.2-SiMu.</td>
<td>119</td>
</tr>
<tr>
<td>5.6</td>
<td>Calculated heat of reaction for the radicals from silene 5.2.</td>
<td>120</td>
</tr>
<tr>
<td>6.1</td>
<td>Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.2 in THF at a concentration of 1.1 M.</td>
<td>129</td>
</tr>
<tr>
<td>6.2</td>
<td>Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.3.</td>
<td>131</td>
</tr>
<tr>
<td>6.3</td>
<td>Computational germyl, alkyl, and digermanyl radical muon hyperfine coupling constants for radicals from 6.2. The experimentally observed radical exhibits a muon hfc of 650 MHz at 298 K.</td>
<td>134</td>
</tr>
<tr>
<td>6.4</td>
<td>Computational germyl radical muon hyperfine coupling constant for the anticipated radical from 6.3. The experimentally determined muon hfc is 593 MHz at 298 K.</td>
<td>135</td>
</tr>
<tr>
<td>6.5</td>
<td>Computational muon hyperfine coupling constants from the germyl radicals of 6.4 and 6.5, and the digermanyl radical of 6.5. The experimental muon hfc for the radical from germylidene 6.4 is 947 MHz at 298 K.</td>
<td>137</td>
</tr>
<tr>
<td>6.6</td>
<td>Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.2 in THF at a concentration of 0.26 M.</td>
<td>141</td>
</tr>
<tr>
<td>6.7</td>
<td>Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.2 in THF at a concentration of 3.1 M.</td>
<td>141</td>
</tr>
<tr>
<td>7.1</td>
<td>Calculated energies of formation of the six hydrogen isotope adducts of azulene, with and without zero point energy corrections for hydrogen and its light “isotope”, Mu.</td>
<td>154</td>
</tr>
<tr>
<td>7.2</td>
<td>Energies of the transition states along the reaction coordinates for the six hydrogen isotope adducts of azulene, relative to the starting materials.</td>
<td>155</td>
</tr>
<tr>
<td>7.3</td>
<td>Muon hyperfine coupling constants of radicals detected in azulene.</td>
<td>157</td>
</tr>
<tr>
<td>7.4</td>
<td>Transverse field signal amplitudes relative to Radical A.</td>
<td>158</td>
</tr>
<tr>
<td>7.5</td>
<td>Resonant field positions for muoniated radicals in azulene.</td>
<td>162</td>
</tr>
<tr>
<td>7.6</td>
<td>Predicted muon hyperfine coupling constants, $A_\mu$/MHz, using the unrestricted Hartree-Fock method.</td>
<td>164</td>
</tr>
<tr>
<td>7.7</td>
<td>Predicted muon hyperfine coupling constants, $A_\mu$/MHz, using the unrestricted Becke and Lee-Yang-Parr hybrid functional.</td>
<td>164</td>
</tr>
<tr>
<td>7.8</td>
<td>TF-µSR radical assignments.</td>
<td>166</td>
</tr>
<tr>
<td>7.9</td>
<td>Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 1-Mu-azulyl.</td>
<td>168</td>
</tr>
<tr>
<td>7.10</td>
<td>Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 2-Mu-azulyl.</td>
<td>168</td>
</tr>
<tr>
<td>7.11</td>
<td>Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 4-Mu-azulyl.</td>
<td>169</td>
</tr>
</tbody>
</table>
Table 7.12: Calculated proton hyperfine coupling constants, \( A_p \)/MHz, using the UB3LYP functional for 5-Mu-azulyl. .............................................................169

Table 7.13: Calculated proton hyperfine coupling constants, \( A_p \)/MHz, using the UB3LYP functional for 6-Mu-azulyl. .............................................................170

Table 7.14: Calculated proton hyperfine coupling constants, \( A_p \)/MHz, using the UB3LYP functional for 9-Mu-azulyl. .............................................................170

Table 7.15: Ratio of calculated proton hyperfine coupling constants at the site of addition for the \( n-H \)-azulyl radicals using the UB3LYP functional........171

Table 7.16: Measured experimental proton hyperfine coupling constants in \( n-Mu \)-azulyl radicals.................................................................178

Table 7.17: Percentage of 1-, 2-, 9-Mu-azulyl and 4-, 5-, 6-Mu-azulyl radicals as a function of temperature. .................................................................180
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBS</td>
<td>complete basis set</td>
</tr>
<tr>
<td>c-GTO</td>
<td>contracted Gaussian-type orbital</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>FPT</td>
<td>freeze-pump-thaw</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian-type orbital</td>
</tr>
<tr>
<td>hfc(s)</td>
<td>hyperfine coupling constant(s)</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>SFU</td>
<td>Simon Fraser University</td>
</tr>
<tr>
<td>STO</td>
<td>Slater-type orbital</td>
</tr>
<tr>
<td>TDC</td>
<td>time digitizing converter</td>
</tr>
<tr>
<td>TF-μSR</td>
<td>transverse field muon spin rotation</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TRIUMF</td>
<td>Tri University Meson Facility</td>
</tr>
<tr>
<td>z.p.e.</td>
<td>zero point energy</td>
</tr>
<tr>
<td>μLCR</td>
<td>avoided muon level crossing resonance</td>
</tr>
<tr>
<td>μSR</td>
<td>muon spin rotation, resonance, relaxation spectroscopy</td>
</tr>
</tbody>
</table>
CHAPTER 1.
INTRODUCTION:
ODE ON A REACTION VESSEL

As I gaze upon your graceful neckline
transparent sand and robust stainless steel
I inwardly sigh and ask for a sign
if this one will work. It has a good seal.
Your unadorned frame, save some crude etching
“F14” scratched by metal on metal
reminds me to ask you, “What’s in a name?”
but silent you stand there, noble, fetching.
as secrets within, loud as a kettle,
whisperless tauntings, emerge from your frame.

What wondrous tales swim ‘round your belly?
Honeycomb nectar secure in your case.
I tickle your cheek, but ne’er a Nelly
no change appears on your resolute face.
Firmly I prod with vigorous muons.
Listen and hear how the silylene sings.
Reaction mysteries you will reveal
as positron daughters are granted wings.
Your silent plan I’ve finally ruined
and brought forth the truth. Oh, hear the bells peal.
1.1 The Importance of Reaction Mechanisms in Chemistry

In John Keats poem “Ode on a Grecian Urn” he expressed his theory of Negative Capability: that great people have the ability to accept that some things in life remain a mystery. While I agree that life is interesting with some of its permanent mysteries, I find it exciting that there are so many unknowns in our world which we can resolve. One type of unknown that chemists often plumb is reaction mechanisms describing how the reagents in a chemical reaction become product species. Understanding the individual steps involved in chemical reactions is important for controlling the outcome of known reactions and predicting the results of new reactions.

1.2 Hydrogen Atom Reactions

In this thesis, I explore reaction mechanisms involving the hydrogen atom. Reactions involving H atoms include:

- **Abstraction**
  \[ H + RX \rightarrow HX + R^\bullet, \quad (1.1) \]

- addition, e.g.
  \[ H + R_2C = CR_2 \rightarrow R_2\cdotCCR_2H, \quad (1.2) \]

- **substitution**
  \[ H + RX \rightarrow HR + X^\bullet, \quad (1.3) \]

- **radical combination,**
  \[ H + \cdot OH \rightarrow HOH, \quad (1.4) \]

- **electron transfer**
  \[ H + M^{n^\bullet} \rightarrow p^+ + M^{(n-1)^{\bullet}} \quad (1.5) \]
  \[ H + OH^- \rightarrow HOH + e_{aq}, \quad (1.6) \]

- and **spin exchange,**
  \[ H^\dagger + M^\dagger \rightarrow H^\dagger + M^\dagger. \quad (1.7) \]

The main method for generating H in liquids and solids is by radiolysis [1]. Unfortunately, complications arise from the large number of accompanying transient
species. Radiolysis of water yields $e^{-}$, $\cdot$OH, H$_2$, H$_2$O$_2$, and H$_3^+$ in addition to H [2]. Selective scavengers can be used to suppress the undesired transient species, but this greatly increases the complexity of the chemistry and often requires compromises. Acid can be added to convert $e^{-}$ into H, but this limits investigation of a reaction to acidic conditions. Photolysis is another method, but most solutes interfere with the reaction by light absorption. Photolysis is more limited in its applicability, and transient species still pose problems. Bond homolysis to create H also generates a radical R•. The only way to avoid competition from accompanying transient species completely is to inject H from outside the sample. This can be done by bubbling with a H + H$_2$ mixture formed by electric discharge in H$_2$ gas. This method, however, is unsuitable for direct study of kinetics and suffers from sample inhomogeneity.

1.3 Chemistry and the Positive Muon

Chemists are well acquainted with the three normal constituents of the atoms in a molecule, namely protons, neutrons, and electrons. Exotic atoms, such as positronium (Ps = e$^+$e$^-$) where the antimatter particle of the electron, the positron, behaves as a nucleus of a single electron atom, have been detected [3,4]. In a similar manner, the elementary particle called the muon has been used in chemistry to form an exotic atom called muonium (Mu = $\mu^+$e$^-$).

What is a muon? The muon is a lepton. In physics jargon, a lepton is a particle with spin 1/2. Leptons do not experience the strong nuclear force. They are members of

\[\text{t}^\text{While there is a level of particle physics involved in this research, it is not the focus. As such, for an overview of the strong nuclear force, the author points the reader to any of the many introductory texts on the subject, i.e. Tipler and Llewellyn's "Modern Physics" [5].}\]
the fermion family (particles with a half-integral spin), and they obey Fermi-Dirac statistics.

There are three known 'flavours' of lepton: the electronic, the muonic and the tauonic. For every flavour, there exists a massive particle (the electron, the muon, and the tau), and a massless particle (the corresponding neutrinos). Additionally, these six leptons each have an antiparticle. For example, the antiparticle of the electron is the positron. The classification of a muon as an elementary particle means that it cannot be broken down into smaller constituent parts.

Some properties of the positive muon are given in Table 1.1. Even though the average lifetime of a muon is only 2.2 microseconds, this time frame is sufficient for the

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>+e</td>
</tr>
<tr>
<td>Spin</td>
<td>1/2</td>
</tr>
<tr>
<td>Mass</td>
<td>$1.88353130(11) \times 10^{-28} \text{ kg}$</td>
</tr>
<tr>
<td></td>
<td>$= 0.1126095261(29) m_p$</td>
</tr>
<tr>
<td></td>
<td>$= 206.7682823(52) m_e$</td>
</tr>
<tr>
<td></td>
<td>$= 105.6583668(38) \text{ MeV } c^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$-4.49044786(16) \times 10^{-26} \text{ J } T^{-1}$</td>
</tr>
<tr>
<td>Magnetic moment ($\mu_\mu$)</td>
<td>$= -3.183345137(85) \mu_p$</td>
</tr>
<tr>
<td></td>
<td>$= 0.00483636199(12) \mu_e$</td>
</tr>
<tr>
<td>Magnetogyric ratio ($\gamma_\mu/2\pi$)</td>
<td>13.55388206(50) kHz $G^{-1}$</td>
</tr>
<tr>
<td>g-factor ($g_\mu$)</td>
<td>$= -2.0023318414(12)$</td>
</tr>
<tr>
<td>Decay scheme</td>
<td>$\mu^+ \rightarrow e^+ + v_e + \bar{\nu}_\mu$</td>
</tr>
<tr>
<td>Mean lifetime ($\tau_\mu$)</td>
<td>2.19714 $\mu$s</td>
</tr>
</tbody>
</table>

*References [6] and [7].
muon to participate in many fundamental chemical processes. As shown in the table, the muon has a mass of roughly one-ninth that of the proton. Since the muon has the same spin and charge as the proton, it behaves as a very light proton.

What use is an exotic atom like muonium? It certainly is not a standard reagent found in most chemical laboratories. In Table 1.1, the lifetime of the positive muon is given as only 2.2 microseconds, which is independent of the surrounding medium. The lifetime of $\mu^-$, on the other hand, is shorter in condensed matter than in vacuum; the negative muon can undergo nuclear capture. Just as the muon has a mass of roughly $1/9^{th}$ that of the proton, in Table 1.2 it is reported that muonium likewise has approximately $1/9^{th}$ the mass of a hydrogen atom. Despite this, the reduced masses of H and Mu are very similar. Consequently, the Bohr radii and ionization potentials of H and Mu differ by only about 0.5%. Thus, muonium can be treated as a light isotope of hydrogen.

Approximating a chemical bond as a diatomic harmonic oscillator, we find that the fundamental vibrational frequency can be calculated as

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_{\text{reduced}}}},$$  \hspace{1cm} (1.8)

where $k$ is the force (or spring) constant of the bond, and $m_{\text{reduced}}$ is the reduced mass of the diatomic system. If a C-H bond is replaced by a C-D bond then $m_{\text{reduced}}$ increases by approximately a factor of 2, and the fundamental vibrational frequency decreases by a factor of $\sqrt{2}$. The energy of the $n^{th}$ vibrational level of a harmonic oscillator is given by

$$E_n = \hbar \nu \left( n + \frac{1}{2} \right),$$  \hspace{1cm} (1.9)
where $h$ is Planck’s constant. Thus, the zero-point energy ($E_n = 0$) would decrease by the same proportion as the fundamental vibrational frequency. Now consider replacing a C-H bond with a C-Mu bond. Since Mu has a mass $1/9^{\text{th}}$ that of the proton, the reduced mass of the C-Mu system is approximately $1/9^{\text{th}}$ that of C-H. This then corresponds to an increase in both the fundamental vibrational frequency and zero point energy by a factor of 3. This is important since comparisons of the hyperfine coupling constants of different isotopomers often show deviations not completely explained by the ratio of the magnetic moments. Due to the mass dependency of vibrational wavefunctions, these differences in hyperfine coupling constants can be explained as dynamic effects. Thus, muonium with its light mass relative to hydrogen can exhibit large isotope effects.

Table 1.2: Properties of muonium.$^a$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$0.1131 , m_H = 207.8 , m_e$</td>
</tr>
<tr>
<td>Reduced mass</td>
<td>$0.9956 , m_H$</td>
</tr>
<tr>
<td>Bohr radius</td>
<td>$0.5315 , \text{Å} = 1.0044 , a_0$</td>
</tr>
<tr>
<td>Ionization potential</td>
<td>$13.539 , \text{eV} = 0.9956 , I_H$</td>
</tr>
<tr>
<td>Magnetogyric ratio ($\gamma_{\text{Mu}}$)</td>
<td>$1.394 , \text{MHz G}^{-1}$</td>
</tr>
<tr>
<td>Hyperfine frequency</td>
<td>$4463 , \text{MHz in vacuum}$ (3.14 times that of H)</td>
</tr>
<tr>
<td>De Broglie wavelength (at 300 K)</td>
<td>$2.979 \times 10^{-8} , \text{cm} = 2.967 , \lambda_H$</td>
</tr>
<tr>
<td>Mean thermal velocity (at 300 K)</td>
<td>$0.75 \times 10^6 , \text{cm s}^{-1} = 2.967 , v_H$</td>
</tr>
</tbody>
</table>

$^a$ Reference [8].

Considering the difficulties outlined in Section 1.2, muonium has a number of significant advantages in studying H-atom reactions [9]. Muons can be implanted in any
sample, and in most substances muonium is formed. The detection techniques used in muonium chemistry are very specific, since only muoniated species are detected. Muons can be monitored one at a time, so that they each constitute an infinitely dilute probe of an essentially unperturbed system; an exception is the presence of radiolysis effects at the end of the muon track at short times [10]. Additionally, muonium has neutral charge, and as a single-atom radical it has no dipole moment. Therefore, it can be considered an unbiased probe of reactivity.

Research on muonium chemistry covers many aspects, including radical detection [11] and identification [12,13,14], substitution effects [15], kinetics and kinetic isotope effects [16,17,18], tunneling effects [19], and structure and dynamics [20,21,22,23,24]. A recent paper even describes how muonium can be used to study the partitioning of drug molecules between aqueous environments and lipid-like environments [25].

1.4 Muonium Nomenclature

As is typical at the birth of any field, the nomenclature of muonium chemistry at first was not standardized. In 2001, the International Union of Pure and Applied Chemistry (IUPAC) gave their recommendation for naming muonium and hydrogen atoms and their corresponding ions [26]. The author will endeavour to use proper nomenclature for the most part, but begs the understanding of the reader if slight deviations appear. Two examples are (1) the suggested chemical formula for the muonium atom is Mu·, but it is common place to drop the ‘dot’ and simply write Mu, and (2) the reaction of Mu with benzene can yield the muoniocyclohexadienyl radical, which is normally referred to as the muoniated cyclohexadienyl radical.
1.5 Formation of $\alpha$- and $\beta$-Muoniated Radicals

Muonium can add to an unsaturated bond, forming a muoniated radical, similar to the reaction shown in Equation (1.2). In the resulting species, the muon is adjacent to the radical center. This type of radical is called a $\beta$-muoniated radical. This class of species includes most of the radicals observed by $\mu$SR (muon spin rotation/resonance/relaxation).

Radicals with muonium attached directly to the radical center are referred to as $\alpha$-muoniated radicals. Very few species of this class have been observed, primarily due to the challenge in forming such a radical. The first reported $\alpha$-muoniated radical was the trimethylsilylmethyl radical, which was generated by the reaction of muonium with trimethylsilyldiazomethane [27]. Muonium addition to the carbon atom of the diazo functional group yields a nitrogen-centered-$\beta$-muoniated radical that rapidly decomposes into $N_2$ and the $\alpha$-muoniated radical. This is considered an indirection formation reaction, due to the involvement of an intermediate radical.

![Figure 1.1: Indirect formation of an $\alpha$-muoniated radical by muonium addition to trimethylsilyldiazomethane [27].](image)

More recently, two other $\alpha$-muoniated radicals were identified as forming by indirect mechanisms, namely the muoniated methyl radical from ketene [28], and the muoniated cyclopentadienyl radical from diazocyclopentadiene [29].
Figure 1.2: (a) Muonium addition to ketene to form the $\alpha$-muoniated methyl radical, and (b) muonium addition to diazocyclopentadiene to generate the $\alpha$-muoniated cyclopentadienyl radical.

The addition of muonium to stable singlet carbenes was investigated by McKenzie [29,30]. As there is no $\beta$-muoniated radical intermediate, this is referred to as a direct formation reaction.

Figure 1.3: Direct formation of an $\alpha$-muoniated radical by muonium addition to a carbene.

1.6 Using Muonium to Study Reaction Mechanisms

For all the research done using muonium as a hydrogen-like atom, including radical identification studies, little focus has been placed on using Mu to explore reaction mechanisms. I was involved with one of the few published examples of how muonium can provide information on a reaction mechanism that is not obtainable using the hydrogen atom, namely our study of the keto–enol tautomerization in near- and supercritical water [31].

Figure 1.4: Keto–enol tautomerization of acetone and 2-hydroxy-1-propene.
Under standard conditions the Mu adduct of the keto is detected, namely the 2-muoxy-2-propyl radical, \((\text{CH}_3)_2\text{COMu}\). Above 250°C, we observed a larger muon hyperfine coupling constant and an entirely different \(\mu\text{LCR}\) (muon level crossing resonance) spectrum. This was attributed to the formation of the Mu adduct of the enol, the 1-Mu-2-hydroxy-2-propyl radical, \(\text{CH}_3\text{C(OH)CH}_2\text{Mu}\). If the corresponding H-atom experiments had been performed, the two radicals would be indistinguishable.

### 1.7 Organization of the Thesis

In this thesis I describe case studies where muonium was used to explore, elucidate, or expand the understanding of reaction mechanisms. Chapters 2 and 3 introduce the theory and techniques of muonium chemistry. Chapter 4 focuses on hydrogen atom reactions with silylenes. Chapter 5 considers the relative reactivity of the carbon and silicon atoms in silenes. Chapter 6 compares the reactivity of germymldenes with the silylenes of Chapter 4. Chapter 7 is the last case study, and it considers proposed H-atom reaction mechanisms describing the rearrangement of azulene into naphthalene.

Muonium addition to silylenes and germymldenes was expected to yield \(\alpha\)-muoniated radicals, while it was anticipated that addition to silenes and azulene would generate \(\beta\)-muoniated radicals. Some of our results were very surprising!

### 1.8 Individual versus Collaborative Work

\(\mu\text{SR}\) experimental data collection was done in collaboration with other members of the SFU muonium chemistry group (SFUMU), with assistance from Dr. J.A.C.
Clyburne and Dr. R. West. The TRIUMF facility operates 24 hours a day, and research groups are allocated beam time in one-week periods. For this reason, the SFUMU group takes shifts to collect the μSR data. The silylenes, silenes, and germylidenes studied were provided by Dr. R. West or Dr. M. Kira. Beyond the assistance listed above, I performed all the work described in this thesis. I prepared the samples used for TRIUMF experiments, and participated in the data collection. I analyzed the spectra at SFU, using theoretical calculations I performed to interpret the results. I also wrote the first draft of papers based on this research, the details of which are presented in chapters 4 – 7.
2.1 From Creation to Decay in 2.2 Microseconds

2.1.1 The Origin of the Muon

The muon was first discovered in 1937 by Neddermeyer and Anderson [32] by its traces in photographic emulsions exposed to cosmic rays. When high energy protons in cosmic rays collide with molecules in the upper atmosphere production of new particles is initiated. One of these species is the positive pion, $\pi^+$, whose primary mode of decay (99.99%) [33] is into a positive muon and its neutrino with a mean lifetime of 26 nanoseconds, as shown below.

\[ \pi^+ \rightarrow \mu^+ + \nu_\mu \]  \hspace{1cm} (2.1)

To form the exotic muonium atom in quantities suitable for a chemical experiment, a more controllable source of muons is required. In the laboratory, muons are produced in a manner analogous to the reactions in the upper atmosphere. Protons or electrons are accelerated to an energy exceeding that corresponding to the charged pion rest mass (139.6 MeV/c$^2$) and collide with a pion production target, such as a sheet of copper or beryllium of suitable thickness. This reaction is expressed by

\[ p^+ + ^9\text{Be} \rightarrow ^{10}\text{Be} + \pi^+. \]  \hspace{1cm} (2.2)
Emitted pions with the desired charge and momentum are selected using a dipole magnet. These pions then decay in flight. Due to the nature of pion decay, momentum selection of the muons yields a spin polarized muon beam. Alternatively, muons obtained from pions which decay at rest at the surface of the production target produce a beam of polarized muons with energy of 4.1 MeV and momentum of 29.8 MeV/c. These latter muons are called surface muons. As the origin of the muon is the pion, which is classified as a meson (a composite particle with an integral spin), facilities which produce muons in copious quantities are referred to as meson factories.

In the rest-frame of the pion, when the decay occurs the product particles emerge in opposite directions to conserve linear momentum. Similarly, since the pion possesses spin 0 while the muon and its neutrino have spin 1/2, the spin vectors of the decay products must point in opposite directions to satisfy the conservation of angular momentum. Hence, the decay muon and its neutrino must have the same helicity.\footnote{Helicity $= m_s / s$, where $m_s$ is the $z$-component of the spin $s$, and the $z$-axis is in the direction of the particle's momentum. Since neutrinos have helicity -1, positive muons from positive pion decay must also have helicity -1. It then follows that muons, with spin of 1/2, have $m_s = -1/2$. Hence, muons produced in such a manner will always have their spin anti-parallel to their momentum.} For parity to be conserved there must be an equal probability for this helicity to be $\pm 1$. Experimentally, however, only neutrinos with negative helicity (and antineutrinos with positive helicity) have been observed. Thus, the muons emitted from the decay of pions at the production target are 100% polarized with negative helicity [34,35]. Thus, the decay scheme of Equation (2.1) violates parity, as illustrated in Figure 2.1.
2.1.2 Diamagnetic and Paramagnetic Muon States

Upon entering a medium, the muon loses kinetic energy through ionization and excitation of its surroundings. These processes occur in the first $10^{-12}$ s, which with our apparatus is before real time detection is possible. The exact process of thermalization is still under debate [10,36,37]. The number of muons in the sample at any time is very small and the total number in an experiment is typically on the order of $10^7 - 10^8$. Even after considering the $10^6$ ion pairs produced by each muon, relative to Avogadro's number the effect on the sample is insignificant. Hence, radiolysis damage to the sample is not considered.

The thermalized muon can exist in one of three different magnetic states: as a muon in a diamagnetic environment, as a free muonium atom, or as a muoniated radical. A muon in a diamagnetic environment can take many forms, namely free muons, solvated or trapped muons, or any diamagnetic molecule that has captured the muon, such as MuH, MuOH, etc. The common characteristic of these species is naturally the lack of unpaired electrons. Due to the short lifetime of the muon, the resolution of $\mu$SR experiments is insufficient to detect the small changes in the precession frequency between various diamagnetic environments. Hence, the identity of the diamagnetic environment cannot be determined, and is therefore uninformative to a chemist. Solid-state physicists, on the other hand, are able to utilize diamagnetic muons to probe local
magnetic field distributions. The more common Nuclear Magnetic Resonance (NMR) technique is useful for describing local magnetic fields in terms of chemical shifts.

In 1957, Friedman and Telegdi purported that the positive muon could form a bound state with an electron [38]. The first direct experimental observation of muonium in matter was reported in 1960 by Hughes et al. [39]. The capture of an electron by a muon from the surrounding medium can occur during the final stages of thermalization.

In 1963, Brodskii proposed that muoniated radicals could be formed by the addition of muonium to unsaturated molecules [40]. Muoniated radicals were first observed in the liquid phase by Roduner et al. in 1978 [12].

2.1.3 La Morte du Muon

The decay of the positive muon results in a positron, an electron neutrino, and an anti-muon neutrino, as shown in Equation (2.3) [41].

\[ \mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu \]  

(2.3)

Parity is also violated in this decay process. As a consequence of the conservation of energy, and linear and angular momentum in this three-body decay, the positron is emitted preferentially along the direction of the muon spin [42]. This provides an indirect measure of the muon polarization in a sample. Positrons produced from the decay of the positive muon can have a range of kinetic energies from 0 to \( E_{\text{max}} = 52.3 \) MeV.
Positive muon decay. $P_X$ is the momentum vector and $S_X$ is the spin vector of particle X.

The theory of the weak interaction can be used to generate a theoretical distribution of the decay positrons [43]:

$$\frac{dN}{d\varepsilon d\Omega} = \frac{C}{2\pi} [1 + A \cos \theta].$$

(2.4)

In this model, $N$ is the number of positrons with relative energy $\varepsilon = E/E_{max}$ emitted at the angle $\theta$ with respect to the initial spin polarization of the muon, $\Omega$ is the solid angle of the detector, $C = \varepsilon^2 (3 - 2\varepsilon)$, and the muon asymmetry $A = (2\varepsilon - 1)/(3 - 2\varepsilon)$. The muon asymmetry is maximal (unity) when decay positrons have energy $E_{max}$, and is minimal (-1/3) for low energy positrons. This means that low energy decay positrons are emitted in the direction opposite to the muon's spin. The average muon asymmetry over all positron energies is 1/3. This value can be increased by removing the low energy muons with a degrader. The total positron probability distribution can be obtained by integration of Equation (2.4) over energy and the detector solid angle. In the integrated form, $C$ and $A$ are replaced with their average values. In practice, the detection efficiency of positrons
depends on their energy and the experimental setup. Hence, in most muon experiments, an empirical muon asymmetry is used instead of the theoretical value.

Now that an overview of the production, reaction, and decay of the positive muon has been presented, the next few sections will describe how the muon and the decay positrons are used to collect information about the system of interest in various types of μSR spectroscopy.

2.2 Transverse Field Muon Spin Rotation

2.2.1 Muons in a Transverse Field

When a magnetic field, \( \vec{B} \), is applied transverse (perpendicular) to a magnetic moment, \( \vec{\mu} \), a torque is experienced, and the vector describing that moment begins to precess according to the 'right hand rule' associated with the vector equation describing this phenomenon.

\[
\vec{\tau} = \vec{\mu} \times \vec{B}
\]

The precession frequency of a magnetic moment is called the Larmor angular frequency, \( \omega \).

\[
\omega_k = 2\pi\gamma_k B
\]

In Equation (2.6), \( \gamma_k \) is the gyromagnetic ratio for species \( k \), and \( B \) is the net transverse magnetic field. Muons, with spin 1/2, have a magnetic moment, and hence precess in a transverse magnetic field.

A more complete explanation of this phenomenon utilizes the spin Hamiltonian of a muon:
\[ \hat{H} = g_\mu \beta_n \vec{B} \cdot \vec{I}^\mu, \]  
\hspace{1cm} (2.7)

where \( g_\mu \) is the muon g-value, \( \beta_n \) is the nuclear magneton, \( \vec{B} \) is the magnetic field vector, and \( \vec{I}^\mu \) is the muon spin operator. If the z-axis is defined as the direction of \( \vec{B} \), then Equation (2.7) can be simplified to

\[ \hat{H} = -\hbar \omega_\mu \hat{I}_z^\mu, \]  
\hspace{1cm} (2.8)

where \( \omega_\mu \) is the Zeeman angular frequency (Larmor angular frequency) of the muon. The corresponding eigenstates are

\[ |1\rangle = |\alpha_\mu \rangle = |1/2\rangle \quad \text{and} \quad |2\rangle = |\beta_\mu \rangle = |-1/2\rangle. \]  
\hspace{1cm} (2.9)

According to the time-independent non-relativistic Schrödinger wave equation,

\[ \hat{H} \psi = E \psi, \]  
\hspace{1cm} (2.10)

operating on these eigenstates yields the energy levels of the muon Zeeman interaction:

\[ \hat{H} |m_\mu \rangle = -\hbar \omega_\mu \hat{I}_z^\mu |m_\mu \rangle, \]  
\hspace{1cm} (2.11)

where

\[ \hat{I}_z^\mu |m_\mu \rangle = m_\mu |m_\mu \rangle. \]  
\hspace{1cm} (2.12)

Therefore,

\[ E_1 = -\frac{1}{2} \hbar \omega_\mu \]  
\hspace{1cm} (2.13)

\[ E_2 = \frac{1}{2} \hbar \omega_\mu. \]
Thus, the difference in energy between the two states is

$$\Delta E = E_2 - E_1 = h \omega_p .$$  

(2.14)

The variation of the two resulting energy levels as a function of magnetic field is displayed in Figure 2.3. In the absence of a magnetic field, the two energy levels are degenerate. When a magnetic field is applied, the degeneracy is lifted, and combining Equation (2.6) and Equation (2.14), we see that the energy required to induce a transition between the two states is directly proportional to the strength of the field:

$$\Delta E = h \gamma \mu B .$$

(2.15)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{zeeman_splitting}
\caption{Plot of the Zeeman energy splitting for the muon, a spin-1/2 particle. $\omega_0^{Mu}$ is the hyperfine frequency of Mu ($2.8 \times 10^{10}$ rad s$^{-1}$), and $B_0 = \left( \omega_0^{Mu} / 2\pi \right) / \left( \gamma_e + \gamma_\mu \right) = 1585$ G. The scale was chosen for easy comparison of transition energies with Figure 2.4.}
\end{figure}

2.2.2 Muonium in a Transverse Field

Let us now consider how muonium behaves in a transverse magnetic field. Muonium consists of two spin-1/2 particles, namely a muon and an electron. The muon spin not only interacts with the external magnetic field, but also the magnetic field
resulting from the electron spin. Similar to how a nuclear magnetic resonance (NMR) experiment is intended to detect transitions between different nuclear spin energy levels and electron paramagnetic resonance (EPR) is used to observe transitions between electron spin energy levels [44], muon spin spectroscopy is designed to monitor transitions between muon spin energy levels [45]. That said, the transitions studied by μSR must involve a change in the muon spin. The specific selection rules for each technique will be discussed as appropriate.

The spin Hamiltonian describing this system is given by

$$\hat{H} = \hbar \omega_e \hat{S}_e^z - \hbar \omega_\mu \hat{I}_\mu^z + \hbar \omega_0 \hat{S}_e^z \hat{I}_\mu^z,$$  \hspace{1cm} (2.16)

where $\hat{S}_e^z$ is the electron spin operator, $\hat{I}_\mu^z$ the muon spin operator, $\omega_e$ and $\omega_\mu$ the Zeeman angular frequencies, and $\omega_0$ the muon hyperfine coupling constant (hfc) in angular frequency units. Throughout this thesis, the muon hfc will be discussed in frequency units, and given the symbol $A_\mu$. An alternative representation of this constant is in energy units, $a_\mu$.

$$A_\mu = \frac{\omega_0}{2\pi} \hspace{1cm} (2.17)$$

$$a_\mu = \hbar \omega_0 \hspace{1cm} (2.18)$$

The magnitude of the hyperfine coupling constant is directly proportional to the unpaired electron spin density at the muon. Thus, any change in the distribution of electron spin density that affects the probability of the unpaired electron being located at the muon would be reflected in a change in the muon hfc.
To understand the connection between the transverse field μSR spectrum and the muon hfc, we must consider the energy levels of our two spin-1/2 system. The eigenstates corresponding to the spin Hamiltonian of Equation (2.16) are [8]

\[
\begin{align*}
|1\rangle &= |\alpha^e \alpha^e \rangle \\
|2\rangle &= s|\alpha^e \beta^e \rangle + c|\beta^e \alpha^e \rangle \\
|3\rangle &= |\beta^e \beta^e \rangle \\
|4\rangle &= c|\alpha^e \beta^e \rangle - s|\beta^e \alpha^e \rangle,
\end{align*}
\]

(2.19)

where

\[
c = \frac{1}{\sqrt{2}} \left(1 + \frac{\omega_e + \omega_\mu}{\sqrt{\omega_0^2 + (\omega_e + \omega_\mu)^2}}\right)^{1/2}
\]

(2.20)

\[
s = \frac{1}{\sqrt{2}} \left(1 - \frac{\omega_e + \omega_\mu}{\sqrt{\omega_0^2 + (\omega_e + \omega_\mu)^2}}\right)^{1/2}
\]

Applying the spin Hamiltonian of Equation (2.16) to these eigenstates yields the following energy levels:

\[
\begin{align*}
E_1 / h &= \frac{1}{4} \omega_0 + \omega_-
\\
E_2 / h &= \frac{1}{4} \omega_0 + \Omega
\\
E_3 / h &= \frac{1}{4} \omega_0 - \omega_-
\\
E_4 / h &= -\frac{3}{4} \omega_0 - \Omega,
\end{align*}
\]

(2.21)

where
Since the electron and muon Larmor frequencies are directly proportional to magnetic field strength, these energy levels vary with magnetic field. At zero magnetic field $E_1 = E_2 = E_3 = \frac{1}{4} \hbar \omega_0$ and $E_4 = -\frac{3}{4} \hbar \omega_0$, and thus we can identify the triplet and singlet states for this two spin system [46]. The magnetic field dependences of these eigenstates are illustrated in the Breit-Rabi diagram of Figure 2.4.

The $\mu$SR selection rules for this system are as follows:

$$\Delta m_\mu = \pm 1$$
$$\Delta m_\delta = 0.$$ (2.23)

Hence, there are four allowed transitions, as shown in Figure 2.4. It is instructive to note how much larger the energy separations between the various states are for Mu than for the isolated muon (Figure 2.3).

At low magnetic fields, the singlet state $|4\rangle$ is well separated from the triplet states, and thus two of the transitions, $\omega_{14}$ and $\omega_{34}$, are high in energy. In fact, they occur at a frequency on the order of $\omega_0 (~= 2.8 \times 10^{10} \text{ rad s}^{-1})$. Since the response time of a TF-$\mu$SR experiment with our apparatus is approximately 2 ns, these transitions are not observable. Thus, this half of the muonium ensemble appears to be completely depolarized. The other two transitions, $\omega_{12}$ and $\omega_{23}$, arise at the muonium Larmor
frequency, $\omega_{\text{Mu}} = 103 \omega_\mu$, but precess in the opposite direction to the free muon precession.

![Breit-Rabi diagram for muonium, a two spin-1/2 system.](image)

$\omega_{\text{Mu}}$ is the hyperfine frequency of Mu ($2.8 \times 10^{10}$ rad s$^{-1}$), and

$$B_0 = \left(\frac{\omega_{\text{Mu}}}{2\pi} / \left(\gamma_e + \gamma_\mu\right)\right) = 1585 \text{ G.}$$

Of the four permitted transitions at low fields, only $\omega_{12}$ and $\omega_{34}$ are resolvable.

At moderate fields, it follows from Equations (2.21) and (2.22) that the splitting of these two frequencies can be used to determine the muon hfc:

$$\omega_{12} = \omega_\perp - \Omega \quad (2.24)$$

$$\omega_{23} = \omega_\perp + \Omega \quad (2.25)$$

Then

$$\omega_{23} - \omega_{12} + \omega_0 = \sqrt{\omega_0^2 + (\omega_e + \omega_\mu)^2} \quad (2.26)$$

Solving for the muon hfc we obtain
Based on the algebraic manipulations involved, there is no concern of any extraneous roots arising when squaring both sides of Equation (2.26) to obtain Equation (2.27).

2.2.3 Muoniated Free Radicals in a Transverse Field

A radical is a molecular species with one (or more) unpaired electron(s), and hence is paramagnetic. Most radicals are very reactive. Muonium, having a single electron, is considered a radical. The more common isotopmer, the hydrogen atom, is often referred to as the simplest radical. The research discussed in this thesis is focused on radical species resulting from Mu addition to a molecule. Measurements of the electron-nuclear hfcs are useful in determining the identity of the species formed, but also provide information on the nature of the singly-occupied molecular orbital. This in turn yields details on molecular structure and dynamics.

Just as the unpaired electron couples to the muon in muonium, in a muoniated radical it also couples to any other magnetic nuclei. The spin Hamiltonian for such a multi-spin system in a gas or non-viscous liquid is given by

$$
\hat{H} = \hbar \omega_e \hat{S}_z^e - \hbar \omega_{\mu} \hat{I}_z^\mu + \hbar \omega_0 \hat{S}_y^e \hat{I}_y^\mu - \sum_k \hbar \omega_k \hat{I}_z^k + \sum_k \hbar \omega_0^k \hat{S}_y^k \hat{I}_y^k ,
$$  \hspace{1cm} (2.28)

where $\hat{S}_z^e$ is the electron spin operator, $\hat{I}_z^\mu$ the muon spin operator, $\omega_e$, $\omega_{\mu}$, and $\omega_k$, the Zeeman angular frequencies, and $\omega_0^\mu$ and $\omega_0^k$ the isotropic Fermi-contact hyperfine coupling constants (hfcs) in angular frequency units for the muon and the nuclei $k$, respectively.
respectively [47]. In liquids, the anisotropic contributions to the hfc arising from direct
dipole-dipole interactions are averaged to zero due to rapid tumbling of the radicals.

For \( N \) nuclei with spin quantum numbers \( I_k \) there are \( 4\prod_k(2I_k + 1) \) eigenstates
(the four eigenstates of muonium multiplied by the number of eigenstates from the
nuclei). In the high frequency limit, where \( \omega_e \gg \omega_0^\mu, \omega_0^k \), the eigenstates can be
expressed in terms of the basis of a product of the individual eigenkets:

\[
|m\rangle = \sum_j C_{m,j} |m_{s,j}\rangle \prod_k |m_{k,j}\rangle.
\]

For a set of equivalent nuclei with total angular momentum operator \( \hat{K} = \prod_k \hat{I}^k \) and
z-component of \( K \), represented by \( M \), the eigenstates take the form below:

\[
\begin{align*}
|1\rangle &= |\alpha^\mu \alpha^e\rangle \prod |K, M\rangle \\
|2\rangle &= \left(s |\alpha^\mu \beta^e\rangle + c |\beta^\mu \alpha^e\rangle\right) \prod |K, M\rangle \\
|3\rangle &= |\beta^\mu \beta^e\rangle \prod |K, M\rangle \\
|4\rangle &= \left(c |\alpha^\mu \beta^e\rangle - s |\beta^\mu \alpha^e\rangle\right) \prod |K, M\rangle.
\end{align*}
\]

The energies corresponding to these states can be determined in the same manner
as for the muonium two spin-1/2 system, this time applying the spin Hamiltonian of
Equation (2.28) to the eigenstates.

\[
\begin{align*}
E_1 / \hbar &= \frac{1}{4} \omega_0^\mu + \omega - \sum \omega_k M + \frac{1}{2} \sum \omega_0^k M \\
E_2 / \hbar &= \frac{1}{4} \omega_0^\mu + \omega + \sum \omega_k M + \frac{1}{2} \left(c^2 - s^2\right) \sum \omega_0^k M \\
E_3 / \hbar &= \frac{1}{4} \omega_0^\mu - \omega - \sum \omega_k M - \frac{1}{2} \sum \omega_0^k M \\
E_4 / \hbar &= -\frac{3}{4} \omega_0^\mu - \omega - \sum \omega_k M - \frac{1}{2} \left(c^2 - s^2\right) \sum \omega_0^k M \\
\end{align*}
\]
The selection rule for transitions between these states is

$$\Delta \left( m_s + m_\mu + \sum_k m_k \right) = \pm 1,$$  \hspace{1cm} (2.32)

where $m_i$ is the magnetic spin quantum number of particle $i$.

Due to the splitting brought about by the interaction with other magnetic nuclei, radical signals are rarely detectable at low fields. In sufficiently high fields, however, the electron Zeeman term is dominant and the energy levels of these states form two well-separated groups according to the sign of $m_k$. In the literature, this is sometimes referred to as decoupling, but the electron and nuclear spins never actually stop interacting so this terminology should be avoided. Observed transitions are due to the muon spin flip with no change in the electron spin. Under these conditions, the selection rule becomes

$$\Delta m_\mu = \pm 1, \quad \Delta m_s = 0, \quad \Delta m_k = 0 \text{ for all } k.$$  \hspace{1cm} (2.33)

The allowed transitions that are detectable at high fields form two degenerate groups, independent of the number of coupled nuclei [48]. Similar to the case of muonium in high transverse fields, these two sets of degenerate transitions correspond to the collection of transitions between the multitude of states referred to as $|1\rangle$ and $|2\rangle$ and those labelled $|3\rangle$ and $|4\rangle$ in Equation (2.30). These two frequencies are

$$\nu_{R1} = \nu_{mid} - \frac{1}{2} A_\mu,$$  \hspace{1cm} (2.34)

$$\nu_{R2} = \nu_{mid} + \frac{1}{2} A_\mu,$$  \hspace{1cm} (2.35)

where
In the high field limit, \( \nu_{\text{mid}} \) can be further approximated as \( \nu_D' \), where

\[
\nu_D' = \frac{\omega_\mu}{2\pi}.
\]  

(2.37)

Thus, the radical frequencies are approximately equally spaced about \( \nu_D \), the muon Larmor frequency. The muon hfc in frequency units, \( A_\mu \), is then calculated from the difference in the two radical precession frequencies.

### 2.3 Muon Spin Polarization

For a radical signal to be observed in a TF experiment the muons in that environment must have coherent spins. A density matrix description of muon spin polarization evolution in a magnetic field has been reported [49,50,51]. The observable muon polarization along a direction \( u \) is the sum of contributions \( P_u^X(t) \) from all species \( X \) containing muons,

\[
P_u(t) = \sum_X P_u^X(t). \tag{2.38}
\]

If a species \( X \) has been formed at a time \( t' \) and still exists at time \( t \) \((0 \leq t' \leq t)\) then its contribution is given by

\[
P_u^X(t) = \int_0^t p_u^X(t')q^X(t,t')\lambda_0 dt', \tag{2.39}
\]

where \( q^X(t,t') \) is the probability per unit time that \( X \) has been formed at time \( t' \) with a pseudo-first order rate constant \( \lambda_0 \) and that it still exists at time \( t \). \( p_u^X(t') \) is the
polarization of that fraction of the muon ensemble defined by \( q^X(t, t') \), and can be calculated as the expectation value of the \( u \)-component of the Pauli spin operator, \( \hat{\sigma}_u^X \).

The dimension of the matrix \( \hat{\sigma}_u^X \) is \( N = 4 \prod_k (2I^k + 1) \).

If we assume that the observed species \( X \) is formed at \( t' = 0 \) with probability \( h_X \), and that it decays with a pseudo-first order rate constant \( \lambda_i \), then in a strong transverse field (\( u = x \)) where the eigenfunctions can be expressed in a basis of product functions (as shown in Equation (2.29)) the muon polarization for species \( X \) is

\[
P_x^X(t) = \frac{2h_X}{N} e^{-\lambda t} \sum_m \sum_{n \in m} |c^*_m c_n \langle \hat{\sigma}_x^\mu \mid m_{\mu,j} \rangle \times \delta_{yj} \prod_k \delta_k^{l_k} \cos(\omega_{nm}t)|^2,
\]

where the \( \delta \) are Kronecker delta functions and

\[
\omega_{nm} = \frac{1}{\hbar}(E_n - E_m).
\]

In low magnetic fields (e.g. 100 G), the muon polarization in radicals can be expressed as

\[
P(v_{12}) \equiv \frac{1}{2} \left[ \left\{ \frac{C_M^2 C_R^2 + C_M^2 S_M S_R - S_M^2 C_R^2 - C_M^2 S_M S_R}{1 + \Delta_{1212}^2} \right\}^2 + \right. \left. \left\{ \frac{C_M^2 C_R^2 + C_M^2 S_M S_R}{1 + \Delta_{1412}^2} \right\}^2 \right]^{1/2},
\]

where \( C_M, C_R, S_M, S_R \) are nuclear shielding constants.
where $\Delta_{1212} = (\omega_{12M} - \omega_{12R}) / \lambda$, $\Delta_{1214} = (\omega_{12M} - \omega_{14R}) / \lambda$, etc., M refers to muonium and R to the muoniated radical, and c and s are defined in Equation (2.20).

At high fields (e.g. 15 kG), $c_R \approx 1$ and $s_R \approx 0$. Then

$$P(v_{12}) = \frac{1}{2} \left[ \frac{c_M^2}{1 + \Delta_{1212}^2} + \frac{s_M^2}{1 + \Delta_{1412}^2} \right] + \left[ \frac{(c_M^2)\Delta_{1212}}{1 + \Delta_{1212}^2} + \frac{(s_M^2)\Delta_{1412}}{1 + \Delta_{1412}^2} \right]^{1/2}.$$  (2.44)

Given $s_M < c_M \approx 1$ and $\Delta_{1412} > \Delta_{1212}$,

$$P(v_{12}) = \frac{1}{2} \left[ \frac{1}{1 + \Delta_{1212}^2} \right]^{1/2}.$$  (2.45)

$$= \frac{1}{2} \left[ \frac{\lambda^2}{\lambda^2 + (\omega_{12M} - \omega_{12R})^2} \right]^{1/2}.$$  (2.45)

### 2.3.1 Concentration, Kinetics, and Polarization

The reaction of muonium addition to a molecule is a bimolecular process. Since the number of muons in the sample at a time is very small, the kinetics for these reactions follow pseudo-first order behaviour.

$$\text{rate} = k_1[Mu][Molecule] \approx \lambda_1[Mu], \text{ where } \lambda_1 = k_1[Molecule].$$  (2.46)
From Equation (2.45), the muon polarization in radicals depends on both the pseudo-first order rate constant, $\lambda_1$, and the difference in Larmor frequencies between the free muonium atom and the muoniated radical, $\Delta \omega_{mn}$. In high magnetic fields, the total muon polarization in a muoniated radical can be expressed as

$$P = \left[ \frac{\lambda^2}{\lambda^2 + (\Delta \omega_{12})^2} + \frac{\lambda^2}{\lambda^2 + (\Delta \omega_m)^2} \right]^{1/2}, \quad (2.47)$$

For a muoniated radical to be detected in a TF-$\mu$SR experiment there must be efficient transfer of spin polarization from Mu to the radical. If $k_1$ is on the order of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (diffusion-controlled limit) then solution concentrations near 1 M are appropriate for TF-$\mu$SR experiments, so that $\lambda_1$ is expected to be greater than $10^{10} \text{ s}^{-1}$. If a muoniated radical were to react and form a secondary radical, it is necessary that muon polarization again be transferred efficiently for the secondary radical to be detected. Both steps would follow Equation (2.47), with $\lambda$ representing the pseudo-first order rate constant in that step of the mechanism and $\Delta \omega_{mn}$ the difference in Larmor frequencies between the parent and daughter radical (Mu and the primary radical, or the primary and secondary radicals).

### 2.4 TF-$\mu$SR Asymmetry and Fourier Power Spectra

As will be explained in Chapter 3, muon spin rotation is a single-particle-counting technique. As such, in a transverse-field muon spin rotation (TF-$\mu$SR) experiment, data is only collected when a single muon is in the system at a time. However, we can utilize the concept of an ensemble of muons, understanding that in the case of muon spin rotation we are discussing a collection of data for many single-particle events.
As the Larmor frequency is dependent on the net transverse magnetic field experienced by the spin-polarized ensemble of muons, muons in different environments will precess at different frequencies. The time dependence of the muon asymmetry, as determined from angular distribution of the decay positrons, is used to extract the Larmor frequencies of muon spins in various magnetic environments, and this in turn provides information on the strength of the local magnetic fields in the system.

In the muon spin rotation technique, a beam of spin-polarized muons passes through a scintillation detector and into the sample of interest. When a muon moves through the detector an electronic pulse is generated, which starts a high precision clock. The muon then thermalizes in the sample, located in an external field transverse to the initial muon spin polarization. Precession of the muon spin occurs in a plane perpendicular to the applied magnetic field. Typically four positron detectors are arranged in this plane in orthogonal pairs (left-up and right-down, left-down and right-up). The electronic clock is stopped when the decay positron is detected. The data collected by each detector is reported in a histogram that has the following form:

\[ N(t) = N_0 e^{-t/\tau} \left[ 1 + A(t) \right] + B_g. \]  

(2.48)

In the above equation, \( t \) is time, \( N_0 \) is a normalization constant, \( B_g \) is the time-independent background, \( \tau_\mu \) is the muon lifetime (2.197 µs) and \( A(t) \) is the asymmetry spectrum. \( A(t) \) is extracted from the histogram. This parameter contains the information of the precession frequencies of the muon’s spin.

Under conditions where no muonium forms, the time dependence of the asymmetry is given by
where $A_D$ is the amplitude (related to the fraction of muon polarization in diamagnetic environments), $\lambda$ is the decay (relaxation) rate, $\omega_L$ is the muon Larmor angular frequency, and $\phi_0$ is the initial phase. Since the positron produced during the decay of a muon is preferentially emitted in the direction of the muon's spin, the asymmetry displays an oscillation as the number of positrons striking a particular detector rise and fall, illustrating the precession of the muon spin polarization. Example TF-μSR histogram and asymmetry plots are given in Figure 2.5.

\[ A(t) = A_0 e^{-\lambda t} \cos(\omega_L t + \phi_0), \]  

(2.49)

![Figure 2.5](image)

(a) TF-μSR histogram of diamagnetic muons in an applied magnetic field of 400 Gauss, and (b) the corresponding asymmetry spectrum. The oscillation in each plot illustrates how the number of positrons striking a particular detector rise and fall as the spin of the muon precesses in the magnetic field.
When muonium forms in low magnetic fields, the measured asymmetry is the sum of the muonium signal $A_{\text{Mu}}(t)$ and the diamagnetic signal $A_D(t)$:

$$A(t) = A_{\text{Mu}} e^{-\lambda_{\text{Mu}} t} \cos(\omega_{\text{Mu}} t + \phi_{\text{Mu}}) + A_D e^{-\lambda_D t} \cos(\omega_D t + \phi_D).$$  \hspace{1cm} (2.50)

The muonium decay rate, $\lambda_{\text{Mu}}$, can be used to determine the pseudo-first order decay rates for chemical reactions involving muonium [52,53].

In high magnetic fields, when muonium adds to a molecule generating a radical, Equations (2.34) and (2.35) predict the two radical frequencies are equidistant from the diamagnetic peak, as shown in the TF-$\mu$SR spectrum below:

![TF-$\mu$SR spectrum](image)

**Figure 2.6:** An example TF-$\mu$SR spectrum showing a pair of frequencies due to a muoniated radical symmetrically placed about the diamagnetic peak. This spectrum was collected at 14.5 kG from a 1.55 M solution of 1,3-bis(tert-butyl)-silylimidazol-2-ylidene in tetrahydrofuran.

### 2.5 Avoided Muon Level Crossing Resonance

An alternative arrangement for muon spin studies is with a magnetic field applied along the direction of the muon spin [54]. Experiments utilizing a field parallel to the muon spin are advantageous to slow reactions and/or dilute solutions as the problem of phase incoherence during the time of reaction is avoided since the processes that relax the
Muon spin do not occur. For the experiments discussed in this thesis, the longitudinal field avoided muon level crossing resonance (LF-AμLCR; also known as μLCR or LCR for short) technique was commonly employed.

Just as TF-μSR is used to determine the muon hyperfine coupling constant, μLCR provides a means of measuring both the magnitude and the sign (relative to the muon hfc) of other nuclear hyperfine interactions in free radicals. The phenomenon of μLCR was first proposed by Abragam in 1984 [54]. An avoided muon level crossing resonance occurs at specific applied magnetic fields where a muon transition frequency matches that of another magnetic nucleus in the coupled spin system. At the appropriate field, mixing of a pair of nearly degenerate levels, having different spin orientations for the muon and other nucleus, can occur by the hyperfine interaction. The resulting transfer of polarization from the muon to the other nucleus is detected as a resonant-like change in the spectrum as the magnetic field is swept through the LCR position.

The spin Hamiltonian for a muoniated radical in the gas phase or non-viscous fluid is given in Equation (2.28) (See Section 2.2.3). A full theoretical treatment of the μLCR technique applied to free radicals can be found elsewhere [55,56]. For our purposes, however, a simplified situation will suffice to illustrate the principles. Consider the scenario of a three spin-1/2 system, consisting of an electron, muon, and an appropriate magnetic nucleus (such as a proton). In the high field limit, off diagonal elements become negligible and eight product spin states \(|m_s\rangle|m_v\rangle|m_k\rangle\) satisfy the following spin Hamiltonian [57]:

\[
\hat{H} = \hbar \omega_e \hat{S}_z^e - \hbar \omega_\mu \hat{I}_z^\mu + \hbar \omega_0^k \hat{S}_z^k \hat{I}_z^k - \hbar \omega_\chi \hat{I}_z^k + \hbar \omega_0^k \hat{S}_z^k \hat{I}_z^k. \tag{2.51}
\]
Due to the dominance of the electron Zeeman term, the energy levels of these states form two well separated groups according to the sign of $m_s$. Thus, transitions involving a change in $m_s$ can be neglected. The selection rule for $\mu$LCR in isotropic systems then becomes

$$\Delta(m_\mu + m_k) = 0.$$  

(2.52)

These states can be accidentally degenerate depending on the relative values of $A_\mu$ and $A_k$. Near the field where these states approach degeneracy, the off-diagonal terms are no longer negligible and the two spin states mix. The result is a non-crossing (or avoided crossing) of the energy levels.

Figure 2.7: Energy level diagram for the three spin system consisting of an electron, a muon, and a magnetic nucleus. At an avoided level crossing resonance, $B_{LCR}$, the two states are nearly degenerate. The states mix, enabling a relaxation process in a longitudinal field.

In this first-order approximation, the energies of the states take the form
Thus, if two states, \( |m_s\rangle |\beta^+\rangle |\alpha^\pm\rangle \) and \( |m_s\rangle |\alpha^+\rangle |\beta^\pm\rangle \) have nearly degenerate energies then, using Equations (2.6) and (2.17), we obtain

\[
B = \frac{|A_u - A_k|}{2(\gamma_u - \gamma_k)}. \tag{2.54}
\]

Higher-order perturbation analysis yields [58]

\[
B = \left| \frac{A_u - A_k}{2(\gamma_u - \gamma_k)} - \frac{A_u^2 - 2MA_k^2}{2\gamma_k (A_u - A_k)} \right|. \tag{2.55}
\]

where

\[-I^z + 1 \leq M \leq I^z. \tag{2.56}\]

When \( A_u \) has been found using TF-\( \mu \)SR, measurement of the resonance field provides an accurate determination of the magnitude of the nuclear hfc as well as the sign relative to the muon hfc. This information cannot be easily obtained by EPR.

One of the benefits of \( \mu \)LCR is that at high fields the characteristics of each resonance are independent of the number of nuclei off resonance. Further information is also available from a \( \mu \)LCR spectrum, as the resonant lineshape is sensitive to the spin and number of nuclei on resonance [59,60]. Symmetrically equivalent nuclei have the same resonant field position. For systems with spin-1/2 nuclei, the Lorentzian lineshape has a full-width-at-half-maximum of
\[
\Delta B_{\text{FWHM}} = \left[ 1 + \left( \frac{2\pi \tau_m \nu_t}{\gamma_m - \gamma_e} \right)^2 \right]^{1/2},
\]

where

\[
\nu_t = \frac{c A_n A_k}{2B_{\text{LCR}} \gamma_e}
\]

is the small frequency splitting of the degenerate levels at resonance, \(c\) is a constant equal to 1 for a single spin-\(1/2\) nucleus and \(\sqrt{2}\) for two spin-\(1/2\) nuclei, determined by

\[
c = \sqrt{I^4 \left( I^4 + 1 \right) - M(M-1)},
\]

with \(M\) defined in Equation (2.56). Since a resonance is the result of a loss in muon polarization, the amplitude of a signal can be expressed as the reduction in muon polarization in the longitudinal direction at the resonance position. This is given by

\[
\Delta p_z = \frac{1}{4} \left[ \frac{(2\pi \tau_m \nu_t)^2}{\left(2\pi \tau_m \nu_t\right)^2 + 1} \right].
\]

Therefore, the \(\mu\)LCR spectrum consists of one resonance for each set of equivalent nuclei, and both the resonance width and amplitude are dependent on the number of nuclei in resonance.

The theoretical form for a \(\mu\)LCR spectrum resulting from a loss of muon polarization in the longitudinal field is shown in Figure 2.8. In a \(\mu\)LCR experiment, the spins of the muons do not precess in the longitudinal field, and so the distribution of decay positions should only vary when muon polarization is lost as the resonance field is approached. The asymmetry \((A)\) is then measured as the difference between the forward
(F) and backward (B) counts, divided by the total number of counts for each field position:

\[ A = \frac{(F - B)}{(F + B)} \]  

(2.61)

This approach is in contrast to the techniques of TF-μSR where only one muon is counted per time interval.

Figure 2.8: The theoretical form for a μLCR spectrum resulting from a loss of muon polarization due to mixing of spin states in a longitudinal field.

Without the need to associate each positron to its parent muon, this type of data collection utilizes higher beam currents, and thus counts are collected faster. A disadvantage is that the raw integrated asymmetry is sensitive to fluctuations in beam current and other systematic effects. To compensate for this effect, a small square-wave toggle field is introduced. As the main field is swept, this toggle field is applied parallel and anti-parallel to the main field direction. The resonance position then shifts downfield and upfield, correspondingly. The resulting asymmetries are referred to as \( A^- \) and \( A^+ \), respectively, and an example of each plot is shown below.
Figure 2.9:  Shifting of the asymmetry curve when the toggle field is applied (a) with the main magnetic field, and (b) when it is applied against the main field.

The $\mu$LCR spectrum is then plotted as the difference of these two sets of data, as shown in Figure 2.10. Details on the apparatus and facility used for these experiments will be provided in the next chapter.

Figure 2.10:  An example of a $\mu$LCR spectrum showing the differential shape of a resonance when field modulation is applied. This signal is attributed to a set of equivalent $^{14}\text{N}$ nuclei in a muoniated radical generated from a 1.55 M solution of 1,3-bis(tert-butyl)-silylimidazol-2-ylidene in tetrahydrofuran.
CHAPTER 3.
EXPERIMENTAL AND COMPUTATIONAL METHODS:
Polarization Lost

3.1 μSR Experiments

μSR researchers have four major facilities in the world where they can conduct their experiments. These centres can be divided into the two categories of CW (continuous wave) and pulsed muon facilities.

CW muon sources are ideal for time-differential μSR experiments requiring high time resolution. Better time resolution allows detection of higher frequencies and fast relaxing signals. One challenge of CW muon facilities is that the muon-stopping rate is limited by the muon lifetime, because consecutive muon decay events must be rejected over a time interval of many muon lifetimes to avoid ambiguity in relating a decay positron (electron from μ⁻) to its parent muon. This situation is called "pileup".

Pulsed muon facilities are superior for long time range experiments and those involving irradiation of the target with radio frequency or laser power during the muons’ short lifetime (on average 2.2 μs). The pulse structures of these muon beams imitate the pulse structures of the original proton beams, except that the pulses are further smeared out by the lifetime of the intermediate pions. A general requirement when utilizing a pulsed muon source for TF-μSR experiments is that the time width of the muon pulse must be considerably shorter than the muon lifetime and shorter than the period of any precession frequency to be observed, while the pulse repetition period must be longer than the muon lifetime. Since the muons do not all arrive simultaneously and all the
muons in a given pulse are counted together, the width of the muon pulse limits the time resolution of the experiment.

The principal CW muon sources are TRIUMF (the TRI-University Meson Facility in Vancouver, Canada) and the $\mu$SR facility at PSI (the Paul Scherrer Institut, near Zürich, Switzerland). At this time, the main centre for pulsed muon experiments is the $\mu$SR facility of ISIS with the associated RIKEN/RAL muon facility at the Rutherford Appleton Laboratory (near Oxford, England). Until its shutdown in 2006, the BOOM (BOOster Muon) facility and the associated Meson Science Laboratory of the KEK laboratory (near Tsukuba, Japan) also provided a pulsed muon beam. The closing of the source at Tsukuba is related to the construction of a new facility capable of pulsed muon experiments at MLF (Materials and Life Science Facility) within J-PARC (Japan Proton Accelerator Research Complex, near Tokai, Japan). It is anticipated that MLF will begin hosting $\mu$SR experiments shortly after the publication of this thesis.

All of the $\mu$SR experiments described in this thesis were conducted at TRIUMF. The original three universities from which the acronym stems are Simon Fraser University, the University of British Columbia, and the University of Victoria. Since its construction, four more universities have joined in managing the facility: the University of Alberta, Carleton University, the University of Toronto, and most recently, Université de Montréal. Six other Canadian universities also participate as associate members [61]. As a national facility, funding for TRIUMF is provided through the National Research Council of Canada.
3.1.1 TRIUMF Cyclotron

By applying an electrical current to a sample of hydrogen gas, the TRIUMF ion sources produce hydride ions, $\text{H}^-$. The electric charge of these negatively charged ions is used to steer them from the ion source to the cyclotron by use of electric and magnetic fields. The negative charge causes the ions to travel counter-clockwise in the magnetic field of the cyclotron, where they are accelerated in an expanding spiral between the two sets of magnets. The TRIUMF cyclotron can accelerate the hydride ions to a maximum energy of 520 MeV.

As an interesting piece of trivia, the cyclotron accelerates $10^{15}$ particles each second. When put in context with regard to Avogadro's number, less than a mole of $\text{H}_2$ gas has been used since 1974!

A thin material, called a stripping foil, is positioned in the cyclotron so that when the hydride ions attain the desired energy the ions strike the foil. This foil strips both electrons from the negatively charged species, with the heavier protons passing through the foil. Positively charged, the protons follow a clockwise path out of the cyclotron and into a beam line.

Four beams of protons can be extracted simultaneously [62]. As there is a separate stripping foil for each beam line, the energy of each line can be varied individually. BL1A (beam line 1A) delivers protons to the meson hall, and is the beam of interest to the work in this thesis. BL2A provides protons to the ISAC (Isotope Separator and Accelerator) facility. BL2C delivers a low-energy proton beam (70-100 MeV) for the production of radioisotopes and proton eye therapy. BL4 provides beam to experiments in the proton experimental hall.
Figure 3.1: Beam line organization at TRIUMF. All of the experiments described in this thesis were performed on the M20 beam line, located in the Meson Hall.

BL1A can deliver protons with energies between 183 and 520 MeV, and a maximum current of 200 µA at 500 MeV. In practice, it is rarely run above 100 µA. The extracted proton beam that passes down BL1A strikes two meson production targets. The first target, LAT1, supplies three secondary lines: M11 (a medium-energy, 80-300 MeV, pion channel), M13 (a low energy pion and surface muon channel), and M15 (a dedicated surface muon channel). The second production target, LAT2, feeds two secondary beam lines: M9B (a low energy pion and decay muon channel), and M20 (a dedicated surface muon channel). The experiments discussed in this thesis were exclusively performed on the M20 beam line.
3.1.2 Muon Beams

Three types of muon beam are available: forward, backward, and surface. A forward muon beam has higher energy than the other two, but it is rarely used due to the high stopping range (~35 g cm$^{-2}$) which gives rise to a large degree of range straggling if a thick degrader is used to reduce the muon momentum.

Beam line M9B provides a backward muon beam with polarization of 60-80%, and momentum that can be tuned between approximately 20 and 100 MeV/c. This beam has sufficient momentum to pass into the thick glass bulbs or high-pressure metal cells used for the hydrothermal experiments performed by the Simon Fraser University Muonium (SFUMU) research group [63]. The momentum used for these experiments typically ranges between 60 and 90 MeV/c. The sample sizes used for experiments discussed herein were much smaller than those used in our hydrothermal studies, and beam line M9B was not appropriate for this work.

Beam line M20 uses surface muons, which are produced from pions decaying at rest within a few $\mu$m of production target 1AT2 [64]. Surface muons are nearly monoenergetic (4.1 MeV) with a nominal momentum of 28.6 MeV/c. As discussed in Chapter 2, pion decay is a two-body process, resulting in a muon and a muon neutrino. The two particles are emitted collinearly to satisfy the conservation of momentum. Similarly, since the pion has zero spin, the total angular momentum of $\mu^+$ and $\nu_\mu$ must also be zero to satisfy the conservation of angular momentum. Since the spin of $\nu_\mu$ is antiparallel to its momentum, the muon spin must also be antiparallel to its momentum. Thus, if muons of a particular momentum direction are collected for the beam, a spin polarization of essentially 100% is possible.
Pion contamination of the muon beam is small. There are, however, roughly two orders of magnitude as many positrons as muons. Additionally, these surface muons in a strong transverse magnetic field have a radius of curvature of less than 1 m/kG. This would be inconvenient for transverse field experiments, as the muons would be deflected before even reaching the sample cell. A DC separator is employed to remove the positron contamination and to rotate the muon spin transverse to its momentum [65]. The spin rotator consists of a horizontally oriented magnetic field \( B_0 \) and a vertically oriented electric field \( E_0 \). The magnetic field of the rotator affects both the spin and momentum of the muons, while the electric field only influences the momentum. Thus, it is possible to tune \( B_0 \) and \( E_0 \) so that only particles with a certain mass are permitted to pass through the rotator without being deflected, and at the same time rotate the spin of those particles by 90°. Use of the rotator then allows injection of the surface muon beam into a strong magnetic field that is oriented longitudinally to the muon’s momentum, yet transverse to its spin. Keeping the applied field geometry constant, if the spin rotator is not used, the muon spin will then be longitudinal with the magnetic field. This makes it possible to use the same apparatus for both TF-\( \mu \)SR and LF-\( \mu \)LCR experiments.

3.1.3 Detectors

Plastic scintillators were used for particle detection. The incident muons and their decay positrons cause ionization within a scintillator, which then emits a flash of visible light. A light guide then transmits each quantum of light to a photomultiplier tube where the light package causes electron emission. Within the photomultiplier, this electron then promotes more electron emission, and each subsequent electron does the same. This cascade effect results in amplification of the signal. Finally, the signal is recorded.
electronically. The light guides are used to overcome the adverse effect of the high magnetic fields on the photomultiplier tubes; the light guides are designed specifically for each spectrometer, and are about 1 m in length so that the photomultiplier tubes can be positioned in low magnetic field regions. A consequence of the light guides, however, is a limitation on the time resolution of high magnetic field \( \mu \)SR experiments of 1 ns.

### 3.1.4 Magnets

All of the experiments described in this thesis employed the HELIOS spectrometer. The HELIOS superconducting magnet is capable of producing fields as high as 70 kG. Generally, fields between 3 and 20 kG were used; however, a few studies required magnetic fields as large as 36 kG.

It is important to have an accurate measure of the magnetic field for \( \mu \)SR experiments. In practice, the HELIOS superconducting magnet functions by having the operator select the current rather than magnetic field strength. To determine the relationship between the applied current and the resultant field, the diamagnetic frequency, \( \nu_D \), was measured for many TF-\( \mu \)SR spectra of varying applied currents. The corresponding magnetic field, \( B \), can then be determined for each experiment using

\[
\nu_D = \gamma_\mu B, \tag{3.1}
\]

where \( \gamma_\mu \) is the gyromagnetic ratio of the muon. The diamagnetic frequency for each histogram of each experimental run was determined separately, and the magnetic field found from the best-fit curve developed from the whole set of data. The modulation field (see Section 3.1.8) was calibrated in the same manner.
3.1.5 Temperature Control

Temperatures were controlled using a circulating fluid from a constant temperature bath. The circulating fluid was passed through copper coils attached to a copper plate that was in contact with the sample cell. The temperature of the cell was then measured using a platinum resistor that was embedded between the copper plate and the sample cell. As the sample cells contained less than 5 mL of compound, temperature gradients within the sample were considered insignificant. Uncertainties in the sample temperature were estimated to be less than 1 K.

3.1.6 Sample Cells

For the silylene, silene, germylidine, and azulene experiments, in all but one case the samples were either pure liquids or solids dissolved in tetrahydrofuran (THF); one sample of neat solid azulene was run above and below its melting point. As the muon will react with the paramagnetic oxygen gas molecule very quickly, it was of paramount importance that all oxygen be removed from the samples. The THF used as solvent was treated with three freeze-pump-thaw (FPT) cycles before being transferred to a nitrogen atmosphere glove box where all sample preparations were conducted.

Each sample cell is a cylindrical disk made of stainless steel fitted with a thin stainless steel foil to allow entry of the surface muons into the cell. At the opposite end of the cell, a stainless steel neck protrudes from the cylinder, with an attached glass neck. Sample is introduced into the cell through the neck slowly to avoid trapping gas bubbles, and tapping of the cell ensures filling is complete. A sketch of the sample cells used is shown in Figure 3.2.
Solid azulene was recrystallized from THF and then either transferred as a solid, or dissolved in THF and then transferred, into a sample cell. All silylene, silene, and germylidene samples were synthesized by either Dr. West's group at the Organosilicon Research Center based at the Madison campus of University of Wisconsin, or Dr. Kira's group from Tohoku University in Japan. As these compounds are air and moisture sensitive, they arrived at Simon Fraser University sealed under N₂. In the glove box, the solids were dissolved in THF and then the solutions and neat liquids were transferred to the same type of sample cells as used for azulene. Depending on the quantity of material available, the volume of the cell varied between 1 and 5 mL. An adapter and valve was used to transport the cell from the glove box to the vacuum line where the samples were frozen in liquid nitrogen and the nitrogen atmosphere removed before flame sealing the glass tube.

Figure 3.2: Design of the sample cells used for the silylene, silene, germylidene, and azulene studies. Surface muons enter the cells through the thin stainless steel foil.
3.1.7 TF-μSR

A schematic of the setup used for TF-μSR experiments is provided in Figure 3.3. The sample (S) is positioned in a magnetic field that is oriented parallel to the muon’s momentum, yet, by use of the spin rotator explained in Section 3.1.2, perpendicular to the muon’s spin. The incoming muons are detected by a thin scintillator counter (M), and the decay positrons are observed by one of four scintillator counters arranged in pairs around the cell: The left-up (LU) and right-down (RD) counters, and the left-down (LD) and right-up (RU) counters. For the sake of clarity, only the left-up and right-down counters are shown in Figure 3.3. Only two detectors, perpendicular to one another, are required for quadrature detection (to distinguish between positive and negative frequencies). However, using four counters with the stated geometry for TF-μSR increases the efficiency of signal detection.

The electronics room, with a multitude of wires weaving in and out of various time-delay circuits and discriminators, startled me when I first saw it. Fortunately, the principles upon which the electronics are designed are quite simple. When the electronics are in a “ready” state, an incident muon travelling through counter M triggers a “start” input of a Time Digitizing Converter (TDC). All pulses are routed through time-delay circuits to ensure time synchronisation. A “start” input begins a period of time called the data gate. The data gate typically is set to last several muon lifetimes. During the data gate, if a coincidence occurs in one of the four positron counters (LU, RD, LD, RU) then a “stop” input is sent to the TDC. The good count is then placed within the memory histogram corresponding to the counter that detected the positron. The time
between the "start" and "stop" input determines which channel within the histogram is incremented by one.

Figure 3.3: Schematic of a TF-\(\mu\)SR experiment. The spin and momentum of the muon are arranged perpendicular for this type of experiment. The muons pass though the muon detector (M), triggering a "start" input for the Time Digitizing Converter. The muon interacts with the sample (S), which is located within a magnetic field (\(B_{\text{applied}}\)). The daughter positron is detected, triggering a "stop" input. A \(\mu\)SR histogram is then generated by plotting the number of positrons detected by a particular detector as a function of time.
When correlation between muon and positron is required, precautions must be taken to ensure that only a single muon is in the sample during the data gate. If a second (or more) muon passes through the M counter during the data gate, any resulting positron cannot be unambiguously assigned to a parent muon. This is one of two situations referred to as pile-up. All pile-up events are rejected. The other source of pile-up occurs when a second muon is detected at counter M after the daughter positron has been observed, yet still during the data gate. Since the first source of pile-up is more common to arise for long-lived muons, a bias for events from short-lived muons could result if this second source of pile-up were not considered. Beam current is usually reduced with a set of collimators or slits to reduce the occurrence of muon pile-up.

Not every decay positron is detected. First, the detectors do not cover $4\pi$ radians, so some positrons escape without striking a detector. Second, positrons of low energy can be stopped in the sample or sample container. Third, if more than one positron strikes a particular detector at the same time (known as positron pile-up) then only one event is recorded. Finally, 100% efficiency of the positron detectors is not realistic, and some positrons will not be properly recorded as an event. If no positron is observed within the data gate, then the TDC is reset to the "ready" state. A flow diagram of the electronics is shown in Figure 3.4.

Determination of the muon's precession frequency requires correlation of muon and positron signals. When a magnetic field is applied, if muonium and any muonium-containing radicals form fast enough to maintain spin polarization then the number of decay positrons in any one of the four counters as a function of time helps us measure the
precession frequency of the muon's spin in the various environments. A typical TF-μSR histogram for this thesis has on the order of \(10^6-10^7\) events.

![Flow diagram of the electronic setup for a TF-μSR experiment. A “start” input occurs when a muon passes through counter M, and a “stop” input is the result of positron detection at one of the four positron counters.](image)

**Figure 3.4:** Flow diagram of the electronic setup for a TF-μSR experiment. A “start” input occurs when a muon passes through counter M, and a “stop” input is the result of positron detection at one of the four positron counters.

### 3.1.8 μLCR

For both TF-μSR and μLCR the field is oriented along the beam direction. The spin polarization is oriented transverse to the beam direction for TF-μSR using the spin rotator. For μLCR the spin polarization is aligned along the beam direction, and the spin rotator is used at a low voltage sufficient to separate positrons from muons. This simplifies the changes required to the apparatus when switching between the two modes of data collection. The primary adjustments to the spectrometer setup are the use of a square-wave field modulator, and the layout of the positron counters.
For this type of experiment, the four TF-μSR counters (LU, RD, LD, RU) are shifted forward with respect to the muon beam, and are collectively referred to as the forward counter (F). Another counter is positioned in the path of the incident muons, backwards (B) of the sample, with respect to the muon beam. Pile-up is not a concern, as the muon’s spin does not precess in the longitudinal field. Rather than sorting the data as a function of time (a time-differential experiment) the total muon decay asymmetry is sorted as a function of applied magnetic field (a time-integral experiment).

The number of counts in histograms $F$ and $B$, as a function of time, takes the form

$$F(t) = N_0 e^{-t/\tau_{\mu}} [1 + A(t)] + B_g$$

$$B(t) = N_0 e^{-t/\tau_{\mu}} [1 - A(t)] + B_g$$

where $t$ is time, $N_0$ is a normalization constant, $B_g$ is the time-independent background, $\tau_{\mu}$ is the muon lifetime, and $A(t)$ is the asymmetry spectrum. Ignoring the difference in background and normalization constants for the forward and backwards histograms, we can write

$$\frac{F - B}{F + B} = A(t).$$

The raw integrated asymmetry is sensitive to systematic errors. The effects of these errors are minimized through use of a small square-wave field modulation. The toggle field is applied parallel and anti-parallel to the main field direction and the data is then grouped into two data sets, corresponding to the two settings of the toggle field. Each of the two data sets is then used to calculate an asymmetry, either $A^+$ when the
toggle field is applied against the main magnetic field, or $A^-$ when the toggle is applied with the main field, where

$$A^+ = \sum_i A(t)_i$$

$$A^- = \sum_i A(t)_i.$$  \hspace{1cm} (3.5)

The $\mu$LCR spectrum is plotted as the difference of these two asymmetries:

$$A^+ - A^- = \frac{(F^+ - B^+)}{(F^+ + B^+)} - \frac{(F^- - B^-)}{(F^- + B^-)}.$$  \hspace{1cm} (3.6)

A field modulation of approximately 80 G was used for most of the $\mu$LCR experiments discussed in this thesis. If the resonance width is larger than the field modulation the lineshape appears to be approximately the differential of the loss of muon polarization curve (compare Figure 2.8 on page 38 with Figure 2.10 on page 39). This is called a field differential lineshape [66]. If the resonance width is substantially larger than the modulation the two asymmetry data sets may cancel each other out, while if the resonance width is significantly smaller than the modulation the two spin depolarization portraits will be separated, losing some of the benefit of the field modulation. Thus, it may be necessary to adjust the modulation for specific resonances. In practice, however, this is avoided when possible, as each adjustment of the modulation requires a new calibration of the modulation field.

For each increment of main magnetic field, a preset count (on the order of $10^6$ events) is observed for the sum of the forward and backward counters, for each phase of the modulation field. Once the preset is achieved, the scalars are recorded by the data acquisition computer. After a predetermined number of presets have occurred, the main
magnetic field is increased or decreased, typically by an increment between 10 and 40 G. As an additional precaution to reduce the systemic error from inconsistent beam currents, data collection is automatically paused if the beam current fluctuates by more than 10 or 20 \%.

Figure 3.5: Schematic of a \mu LCR experiment. The spin and momentum of the muon are arranged anti-parallel for this type of experiment. The muon interacts with the sample (S), which is located within a magnetic field (B_{\text{applied}}). The daughter positron is detected in either the Forward (F) or Backward (B) counter. A \mu LCR spectrum is then generated by plotting the difference in the two asymmetries, which are distinguished by the phase of the toggle-field.
3.1.9 Data Analysis

Many "in-house" programs have been developed for analyzing μSR data. I will just provide an overview of the programs I have found particularly useful.

Since all data files are hosted on the TRIUMF server, it is necessary to either connect to the TRIUMF server, or to download the required data files from TRIUMF. Downloading is possible using a secure shell program such as the freeware WinSCP written by M. Prikryl. To connect to the TRIUMF server and analyze the data both a text-based and graphic interface are needed. Tera Term Secure Shell Extension (TTSSH) is a freeware open source terminal emulator (communication program) for MS-Windows, with the original code written by T. Teranishi and enhancements done by R. O'Callahan and E.A. Young. The X-Deep32 X-Server by P. Nambiar is one option for a display server, however the freeware version is no longer available.

Quick fits of the diamagnetic peak, and normalization and background constants were obtained using MUONFCN. MUONFCN was written as a subroutine of the MINUIT program [67] and was developed/improved by D. Garner, R. Keitel, I. Reid, and D.J. Arseneau.

TF-μSR spectra were analyzed using the program JOMU, written by a former SFUMU member, J. Schüth. This program can be used to analyze each of the four histograms separately, using a non-linear chi-squared minimization procedure to fit the data in the time domain, based on the four parameters of amplitude, frequency, relaxation, and phase angle. Up to ten signals can be fit at once. The visual output from JOMU can display the data both in the time domain, and in the frequency domain. The final parameters are then transferred to an EXCEL spreadsheet that I designed. In the
spreadsheet, the frequencies are used to determine the muon hyperfine coupling constant, $A_\mu$, for each radical on a histogram basis. A weighted least-squares fit of the four values of $A_\mu$ for each radical is then computed, and the final averaged values reported.

μLCR data can be viewed using the LCRPLOT program, written by J.H. Brewer and J.-C. Brodovitch, with revisions by D.J. Arseneau. The data is printed to a text file, and downloaded for fitting using an EXCEL spreadsheet designed by J.-C. Brodovitch. The fitting routine of the spreadsheet attempts to relate the data to a theoretical expression that is the difference of two Lorentzian functions corresponding to the two applications of the field modulation. The parameters for each resonance are field position, resonance amplitude, and resonance width. These fitted values are then transferred to another EXCEL spreadsheet written by J.-C. Brodovitch and converted to the hyperfine coupling constants of the other spin active nuclei.

3.2 Computational Experiments

For many of the experiments detailed in this thesis, the initial identity of the muoniated radicals was not clear, even with both TF-µSR and μLCR data. In these situations, the parent molecules, potential muoniated radicals and, in many cases, the transition states have been modelled mathematically to help discern the identity of the experimentally observed species. Computational approaches can elicit insights not available from standard experiments. For example, decades of experimentation left chemists puzzled over the reaction mechanism describing the azulene to naphthalene conversion. As will be described in Chapter 7, computational studies have revived the azulene to naphthalene discussion and presented new and exciting possible explanations.
Computational chemistry has grown in importance in the field of chemistry over the past few decades. Formal recognition of the influence computational techniques are having on chemical research came with the award of the 1998 Nobel Prize in Chemistry to W. Kohn (for his development of the density-functional theory) and J.A. Pople (for his significant contributions to computational methods in quantum chemistry).

In quantum chemistry, a chemical system is represented by its wavefunction, \( \psi \). Using the appropriate operator on the wavefunction, the desired property can be computed. For example, according to the Schrödinger wave equation, when the Hamiltonian operator, \( \hat{H} \), is applied to the wavefunction in the correct basis, the energy of the system, \( E \), is obtained.

\[
\hat{H} \psi = E \psi
\]  

(3.7)

A calculation of this type was provided in Chapter 2.

Unfortunately, except for the simplest of species, solving the Schrödinger wave equation exactly is impossible. The primary approximation of most computational methods uses the fact that the mass of even the lightest nuclei, the proton, is roughly 1800 times than of an electron. Therefore, to a decent approximation, we can take the extreme vantage of electrons moving in a field of fixed nuclei, and the nuclear and electron parts of the molecular wavefunction can be separated. This is referred to as the Born-Oppenheimer approximation, which expresses the Hamiltonian for a system with \( n \) electrons as

\[
\hat{H} = \left[ \sum_{i=1}^{n} \left( \frac{-\hbar^2}{2m} \nabla_i^2 + V_{\text{nuc}} (\vec{r}_i) \right) + \frac{1}{2} \sum_{i \neq j=1}^{n} \frac{e^2}{\vec{r}_{ij}} \right],
\]

(3.8)
where $V_{\text{nucl}}$ is the electrostatic potential produced by the nuclei, and $\nabla_i^2$ is the Laplacian, which in Cartesian coordinates takes the following form:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}. \quad (3.9)$$

Both summations in Equation (3.8) are over the electrons in the system. The terms in the first summation are related to the nuclei, while the term in the second is related to the electrons. Despite this simplification, solving Equation (3.7) for the Hamiltonian of Equation (3.8) can prove extremely difficult, and further approximations are made.

3.2.1 Methods

Two of the approaches for solving the Schrödinger wave equation are the semi-empirical technique and the ab initio approach [68]. Semi-empirical calculations are exactly as the name implies, partially based on experimental data; adjustable parameters whose values are determined by experimental data are used in conjunction with a simplified Hamiltonian. Due to the large degree of approximation, these calculations are considered computationally inexpensive so that complex systems can be investigated. The bias introduced by the dependency on experimental data, however, can lead to incorrect conclusions, depending on the appropriateness of using the parameters of one system to predict the behaviour of another. For this body of work, semi-empirical calculations were only used to generate the input structures for the ab initio calculations.

The Latin term ab initio means “from the beginning”, or “from first principles”. As such, this type of calculation does not depend on any experimental results, but rather the approximations depend on the physical interactions of the electrons and nuclei. For
example, the simplest type of *ab initio* calculation is the Hartree-Fock (HF) computation, in which the Coulombic electron-electron repulsion is replaced with its average effect. A consequence of such a simplification is that electrons in the HF model often get too close to each other, and thus the electron-electron repulsion term is too large. As a result, the HF energy is above (less negative than) the true ground state energy. *Ab initio* calculations are generally more reliable than semi-empirical computations; however, they typically also require more computing time.

Another important consideration is spin pairing, which leads to restricted and unrestricted variations of the methods. Compounds having an even number of electrons, all spin-paired, are called closed-shell systems. As shown in Figure 3.6, in such electronic singlet systems, the orbital solutions are produced in degenerate pairs; two single-electron wavefunctions (α and β) will have a common spatial description, but have opposite spin labels. Chemists more commonly subscribe to the description of two electrons that share an orbital, one spin up while the other is spin down. If the condition of double occupancy is imposed at the outset, the calculation is referred to as a restricted variation of the model.

![Figure 3.6](image)

*Figure 3.6:* Two representations of the restricted model: (a) single-electron wavefunctions occur in degenerate pairs but have opposite spin labels; (b) orbitals can hold two spin-paired electrons.
If we are dealing with species that contain an odd number of electrons, or systems such as triplet molecular oxygen where net zero spin does not occur, the restricted model is inappropriate. There are two options for dealing with these radical species. The first technique, referred to as the “restricted open-shell” scheme, restricts most, but not all, of the wavefunctions. The second method removes the constraint of double occupancy completely and allows each wavefunction to have its own spatial component (and energy). This is called the “unrestricted” variation. Unrestricted models are actually simpler and generally computationally cheaper than the corresponding restricted open-shell models, and hence are more widely used [69]. The majority of computations discussed in this body of work are on radicals, and so the unrestricted technique has been used.

(a) 
(b) \[\begin{array}{c}
\alpha \\
\beta
\end{array}\]

Figure 3.7: Two types of models: (a) a restricted open-shell model where most wavefunctions are restricted, but a few contain only a single electron; (b) electron pairing is not required, and the single-electron wavefunctions do not occur in degenerate pairs.

The primary focus of computational approaches for this thesis is the prediction of hyperfine coupling constants (hfcs) in radicals; however, determination of relative thermodynamic stability of radicals and transition states also plays a role in assigning
spectra. Calculating hfcs has proven to be a significant challenge for computational methods [70]. A review of ab initio approaches has demonstrated that electron correlation effects§ should not be neglected [71]. A diagram demonstrating the relationship between the various computed and "true" energies of a system is shown in Figure 3.8. For larger systems, density functional theory (DFT) calculations have proved to be less computationally strenuous than other ab initio techniques, and they inherently consider electron correlation. DFT calculations have become a popular choice for computational chemists [72,73], and have been demonstrated as effective for many radical systems [74,75].

Figure 3.8: Diagram illustrating the order of computed and "true" energies of a system.

§ One example of a contribution to electron correlation can be seen in the case of H₂. Near the ground state, an acceptable wavefunction can be represented by \( \left\{ H^+H^+ \right\} + \left\{ H^+H^+ \right\} + \left\{ H^-H^- \right\} + \left\{ H^+H^- \right\} \), where the superscript arrows denote the spins of the electrons formally assigned to the protons. As the bond is stretched and the system tends towards two separate hydrogen atoms, the third and fourth terms are not representative, and the energy of the system is incorrectly modeled.
3.2.2 Basis Sets

When a linear combination of a set of functions, $\phi_a$, is used to form a different set of functions, $\psi$, the original functions are called a basis set for the latter functions. Molecular orbitals can be expressed as linear combinations of atomic orbitals.

$$\psi = \sum_a c_a \phi_a$$  \hspace{1cm} (3.10)

In the above equation $\phi_a$ is an atomic orbital with $c_a$ as the coefficient in the linear combination. Thus, the atomic orbitals constitute a basis set for the molecular orbitals.

The true wavefunction of a system is usually unknown, and so another approximation occurs in selecting a basis set from which a trial wavefunction for the system is formed. The coefficients in the linear combinations are adjusted and the energy is recalculated in each iteration. According to the Variation Principle, the trial energy is reduced as the trial wavefunction approaches the true wavefunction. The coefficients of the atomic orbitals can be adjusted until the energies of two sequential iterations agree within a predetermined threshold.

In theory, the true wavefunction could always be obtained if an infinitely large basis set were used. This is often referred to as the complete basis set (CBS). Of course, this is unrealistic, and thus use of manageable basis sets always results in a basis set contraction error. The larger the basis set the smaller this error, but also the longer the computational requirements. Researchers seek a balance between the two opposing objectives of minimal error and minimal computation time.
### Figure 3.9: Competition of objectives in computational chemistry.

<table>
<thead>
<tr>
<th>Short Computational Time</th>
<th>Long Computational Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing Size of Basis Set</td>
<td></td>
</tr>
<tr>
<td>Large Basis Set Contraction Error</td>
<td>Small Basis Set Contraction Error</td>
</tr>
</tbody>
</table>

#### 3.2.2.1 Slater-type Orbitals and Gaussian-Type Orbitals

Now that a review of the role of basis sets in quantum calculations has been provided, it is necessary to consider what functions to use to represent the atomic orbitals that form the basis set. One option is to use a function called a Slater-type orbital (STO). STOs have a radical component of the form

\[
R(r) = N r^{n-1} e^{-\zeta r}
\]  

where \( r \) is the distance between the electron and the atomic nucleus, \( n \) is a natural number, \( \zeta \) is a constant related to the effective nuclear charge, and \( N \) is a normalization constant, given by

\[
N = (2\zeta)^n \frac{2^\zeta}{\sqrt{(2n)!}}.
\]

They are named after J.C. Slater, who proposed their use in 1930 [76]. STOs are useful for modelling atomic orbitals, and are used in the linear combination of atomic orbitals method. However, there are other, more efficient, methods for modelling chemical bonds.
The most commonly used type of function is a Gaussian-type orbital (GTO), as suggested by Boys [77]. A Gaussian function consists of an angular function multiplied by $e^{-r^2}$. Gaussian functions are favoured over other options, such as pure exponential functions and STOs, because of the relative ease to evaluate integrals containing such functions, and hence are computationally cheaper. Unfortunately, like some of the other options, these Gaussian functions tend to misrepresent the orbitals; specifically, they favour spherical environments. This hinders their ability to describe chemical bonds, the electronic distributions between nuclei. Also, GTOs do not have the correct shape at the nucleus (they are smooth curves), which reduces their effectiveness for calculating hyperfine coupling constants.

The first of these obstacles is surmounted by grouping several “primitive” Gaussian functions, $g$, together to form a contracted Gaussian-type orbital (cGTO), $G$.

$$G_i = \sum_i d_{i}g_i$$  \hspace{1cm} (3.13)

where $d_{i}$ are the contraction coefficients. The ease of working with these contracted Gaussian functions remains computationally favourable over other functions (such as STOs) even despite the larger number of basis functions generally required for comparable modelling.

The most straightforward basis set is one in which a single basis function is used for each atomic orbital. These minimal basis sets typically result in large basis set contraction errors. When two basis functions are used for each atomic orbital, the basis set is of type double-zeta (DZ). These represent a significant improvement over the minimal basis sets, but are computationally expensive. Since chemical bonding
predominantly is attributed to valence electrons, a reasonable compromise is to use a single contracted basis function for each core orbital and more than one contracted basis function for the valence orbitals. This is called a split-valence basis set.

The notation for the split-valence basis sets is attributed to J. Pople, and is typically of the form X-YZG. Here, the G informs us that this is a GTO. X represents the number of primitive Gaussian functions used for each core atomic orbital contracted basis function. The Y and Z denote that the valence atomic orbitals consist of two contracted basis functions comprising of Y and Z primitive Gaussian functions, respectively. The presence of two numbers after the hyphen implies that this is a split-valence double-zeta basis set. An example of a GTO of this form is 6-31G. Even more complex is 6-311G, which is a split-valence triple-zeta basis set whose valence atomic orbitals contain three contracted basis functions comprising of three, one, and one primitive Gaussian functions, respectively.

While it is important to have wavefunctions that properly model the bonding in a molecule to determine the optimal geometry of the species and the distribution of the unpaired electron in a radical, for the computation of hyperfine coupling constants it is also important to have accurate wavefunctions at the nucleus. Finding functions that satisfy both of these two requirements continues to be a challenge in the field of computational chemistry.

3.2.2.2 Polarization Functions

As discussed above, a shortcoming of a minimal (or even split-valence) basis set is that they represent atomic wavefunctions better than molecular wavefunctions. To overcoming this obstacle, d- or f-type functions can be issued to atoms where the valence
orbitals are of s- and p-type, and p-type functions to hydrogen where the valence orbital
is s-type. This permits displacement of electron density away from the nuclear centres.

These enhancement basis functions are called polarization functions. The
inclusion of polarization functions is represented in the notation by an addendum in
brackets of the form (a,b), where the first term describes the polarization functions added
to heavy atoms** and the second term denotes the extra polarization functions included
for any hydrogen atoms. An example of this type of basis set is 6-31G(2df,p), which has
two d-type and one f-type GTO included for each heavy atom and a single p-type orbital
added to each hydrogen atom.

An older notation for polarization functions that is encountered in the literature
takes the form 6-31G* (which is equivalent to 6-31G(d)) or 6-31G** (which means the
same as 6-31G(d,p)).

3.2.2.3 Diffuse Functions

Diffuse functions, GTOs with small exponents, are important in situations where
the electron density is spread out over the molecule. Inclusion of diffuse functions in a
basis set is represented in the notation by a + or ++ immediately before the G, i.e.
6-31+G. The single + denotes the addition of diffuse s-type and p-type functions to
heavy atoms, while ++ indicates additional s-type diffuse functions on hydrogen beyond
the diffuse functions described by +.

** Here, heavy atom is defined as an atom beyond helium, i.e., \( Z > 2 \).
3.2.2.4 Other Orbital Types of Interest

A few basis sets have been developed specifically for modelling systems that normally prove quite challenging. One such basis set is EPR-III. This basis set was specifically optimized for the calculation of isotropic hyperfine coupling constants [74]. It is a triple-zeta basis set including diffuse functions, two d-type and one f-type polarization functions, and the s-part is improved for a more appropriate description of the nuclear region.

While the EPR-III basis set may seem the ideal choice for calculating the hfcs of all radical species, unfortunately this basis set is only optimized for the H, B, C, N, O, and F atoms. Hence, while it has been utilized when permitted, another basis set was required for species containing atoms beyond fluorine.

The correlation-consistent polarized valence double-zeta basis set, cc-pVDZ, is the smallest in a series of “correlation consistent” basis sets developed by Dunning for high-level calculations [78]. This basis set applies to H-He, B-Ne, Al-Ar, Ga-Kr atoms, and includes polarization functions. These calculations are more intensive, but it has been noted that properties computed using successively larger basis sets of the Dunning series seem to converge exponentially, presumably to the corresponding complete basis set values.

3.2.3 Density Functional Theory

What is a functional? Essentially, a rule that maps a function to a number is considered a functional. For example, using the function $\psi(x) = x - 5$ in the functional $F$ defined below,
we obtain

\[ F[x-5] = \int_0^1 [x-5]^2 \, dx = \frac{61}{3} \quad (3.15) \]

In density functional theory, the energy is obtained from a functional of the electron density [79].

\[ E = E[\rho] \quad (3.16) \]

where the electron density of a system is determined by

\[ \rho(\vec{r}) = \sum_{i=1}^{n} |\psi_i(\vec{r})|^2 \quad (3.17) \]

meaning, the electron density at a position \( r \) can be found by summing up the probability of finding an electron at \( r \) in each of the \( n \) orbitals. Care is required when interpreting Equation (3.16). In the notation of Hohenberg and Kohn, the first \( E \) in Equation (3.16) is the energy (a number), while the second \( E \) is the energy functional (a functional which maps the electron density, \( \rho \), to a number).

In their 1964 publication, Hohenberg and Kohn were able to prove that a functional mapping the electron density to the energy exists, but could not elaborate on the exact form of the functional. In the following year, Kohn and Sham were able to provide some important insight on the functional of Equation (3.16) [80]. They demonstrated that the energy functional could be separated into multiple separate functionals of the electron density that can be individually evaluated.
\[ E[\rho] = T[\rho] + \int \rho(\vec{r}) V_{\text{nuc}}(\vec{r}) d\vec{r} + \frac{1}{2} \int \rho(\vec{r}) V_{\text{elec}}(\vec{r}) d\vec{r} + E_{\text{xc}}[\rho] \]  

The first functional, \( T[\rho] \), describes the kinetic energy of the system. The first of the two integral terms models the Coulomb interaction between the nuclei and the electron density, while the second represents the Coulomb interaction between the electrons and the electron density. Note how both of these two terms are also functionals of \( \rho \). The last term is called the exchange-correlation energy functional.

Kohn and Sham were unable to determine the form of this term, and it remains a challenge today. There are many different models for the exchange-correlation functional \([81]\), and there is no apparent agreement on which functional is best. The hybrid of the Becke exchange functional and the Lee-Yang-Parr correlation functional, known as B3LYP \([82]\), is very popular in the literature. The B3LYP method is actually a hybrid-HF-DFT (Hartree Fock - Density Functional Theory) method. For organic radicals, the unrestricted B3LYP functional tends to be the best option \([74]\). For this reason, it was used for all of the DFT calculations contained herein.

3.2.4 Computation Designation

When reporting a computation, it is standard practice to use the format of "Functional / Basis Set". An example would be UB3LYP/6-31G. If both a geometry optimization and a property calculation are to be performed, then the notation is "Functional for Property Calc. / Basis Set // Functional for Geometry Calc. / Basis Set" \([83]\). Unfortunately, this format does not appear to be uniform throughout the literature; in fact, in some cases, the same layout is used but the geometry optimization is given
before the property calculation. This could lead to serious misunderstandings, and so
great care should been taken to be explicit when discussing any calculations.

3.2.5 Programs

All structures were drawn, or imported using literature geometries, in Chem3D
Ultra 8.0, from CambridgeSoft Corporation [84]. Gaussian input files were then
generated using Chem3D, and run on the Simon Fraser University Bugaboo cluster using
Gaussian 98 [85,86]. In late 2007, all computations were moved over to the Lattice
server of the WestGrid cluster where Gaussian03 was employed [87].

3.3 Comparing Computations with Experimental Data

Muonium chemists will often divide the experimental muon hfc by 3.18, the ratio
of the muon and proton magnetic moments, to obtain a reduced muon hfc, $A_{\mu'}$. This
reduced muon hfc can then be compared with the corresponding proton hfc as determined
by EPR experiments. If muonium and the hydrogen atom behaved identically these two
values would match. However, that would not be very interesting! Muonium, which can
be considered a light isotope of hydrogen, often exhibits isotope effects. The primary
source of the hfc isotope effect for muonium is due to the difference in zero-point-
energies of the hydrogen and muonium atoms.

The C–Mu bond, with higher zero-point energy, is slightly longer than the C–H
bond. Roduner and Reid estimated the increase in bond length to be about 4.9 % for the
cyclohexadienyl radical [88], and that the C–H bond involving the same carbon atom was
about 0.3 % shorter than the other C–H bonds in the radical. Stretching of the C–Mu
bond can cause $A_{\mu'}$ to differ from $A_p$. 71
Conformational effects can also affect the muon hfc [89,90,91,92,93]. In a β-muoniated radical the C–Mu bond can be in a staggered or eclipsed orientation with respect to the orbital containing the unpaired electron. The observed muon hfc is the vibrational averaged value, as described by

$$A' = B_0 + B_1 \langle \cos^2 \theta \rangle,$$

where $\theta$ is the dihedral angle between the C–Mu bond and the orbital containing the unpaired electron. Claxton et al. compared the experimental proton hfcs in the ethyl radical with the muon hfcs for the corresponding muonium radical [94]. They observed an increase for $A'_{\mu}$ over $A'_{p}$ of 16 %. Buttar and Webster used a variation-perturbation approach to computationally model zero-point vibrational corrections to the $\beta$-hfc of the ethyl radical [95]. They found that the correction factors increase the non-corrected modelled hfc by 7 and 23 % for the protium- and muonium-substituted radicals, respectively. The increase of the muon hfc over the proton hfc matched with Claxton’s experimental findings, but also demonstrated that vibrationally averaging can significantly affect the muon hfc.

Isotope effects have been investigated in the muonium cyclohexadienyl [20], fullereryl [97,98], and carbenyl radicals [30], and factors between 10 – 30 % are common for these types of muonium radicals. Unless otherwise stated, for each of the calculations described in this thesis a hydrogen atom was used in place of muonium and the modelled hyperfine coupling constant was multiplied by a factor of 3.18 to compensate for the different magnetic moments. Without vibrational averaging corrections, the modelled muon hfcs were expected to differ from the experimental values. However, it was not clear at the outset what magnitude of correction factor might
be expected for the Si–Mu and Ge–Mu bonds, and if the primary isotope effect for the muon hfc found by Buttar and Webster would be appropriate for the muoniated radicals from azulene.
CHAPTER 4.
MUONIUM ADDITION TO
SILICON ANALOGUES OF CARBENES:
SILYLENES AND SONNETS

4.1 Carbene Chemistry

According to the IUPAC Gold Book, carbenes (R₂C:) are molecules containing neutral dicoordinate carbon atoms with six valence electrons [96]. Due to the resulting high reactivity, these species play key roles as intermediates in numerous thermal and photochemical reactions, and hence are extremely important in the field of synthetic chemistry [99]. Carbenes of the form (RR'N)₂C: have a singlet ground state rather than a highly reactive triplet state. This is the result of π-electron donation by the nitrogen atoms adjacent to the carbeneic center [100,101].

It has been shown that reaction of muonium with these compounds forms α-muoniated radicals, with the muonium atom adding exclusively to the carbeneic radical center [30,102].

\[
\begin{align*}
R_2C: + \text{Mu} & \rightarrow R_2C-\text{Mu} \\
\end{align*}
\]

The temperature dependence of the muon hyperfine coupling constants (hfcs), \( A_\mu \), in muoniated carbenyl radicals differs with the identity of the \(-R\) groups. The positive temperature dependence of \( A_\mu \) in 5-muono-1,3,4-triphenyl-1,2,4-triazol-5-yl has been explained by considering population of vibrational levels of the C-Mu out-of-plane mode
It has been suggested that the negative temperature dependence of $A_\mu$ observed for other carbenes studied by $\mu$SR might be the result of another vibrational mode, in particular inversion at the nitrogen atoms adjacent to the radical center [30].

Measurement of the $^{14}\text{N}$ hfcs for the same carbenes already investigated by TF-$\mu$SR could provide evidence that inversion at the nitrogen atoms does affect the muon hfc, or if some alternative mechanism is responsible. These experiments have been undertaken by the Simon Fraser University Muonium Chemistry (SFUMU) research group, and I will be a coauthor of the paper detailing our discoveries.

### 4.2 Silylene, Silyl, and Silane Chemistry

#### 4.2.1 Silylenes

Silylenes are similar to carbenes, but with the carbeneic carbon atom replaced with a silicon atom ($\text{R}_2\text{Si}:$). The $N$-heterocyclic silylenes 4.1 - 4.3 are silicon analogues of the Arduengo $N$-heterocyclic carbenes [103], and were first reported during the mid-1990s [104,105,106].

![Some of the first stable silylenes reported.](image)

Figure 4.1: Some of the first stable silylenes reported.
All three bis(aminosilylenes are stable at room temperature under anaerobic conditions. They benefit from electronic stabilization by the amino groups and from steric protection by the bulky alkyl groups. Further stability is afforded for 4.1 and 4.3 by aromatic π-electron delocalization over the silicon-containing ring. Reviews on the developments in stable silylene chemistry are available [107,108,109,110]. The most recent of these reviews stated the following:

“The radical chemistry of stable silylenes is just beginning to be investigated. ... Very little has yet been done to elucidate mechanisms of the many new reactions of these molecules. Thus a great deal remains for chemists to do in this area in the future.”

– Nicolas J. Hill & Robert West, 2004

When proposing a radical reaction mechanism it is useful to have an understanding of how the unpaired electron is distributed over the radical species. Electron paramagnetic resonance (EPR) experiments have been performed on the radical products of 4.4 with bulky free radicals [111], but there is no equivalent data for the reaction of the hydrogen atom with silylenes. Thus, the μSR experiments detailed herein complement the EPR work. Additionally, these measurements provide valuable insight into the fraction of spin density located on the hydrogen isotope attached to the radical center, and investigation of 4.5 by μSR allows comparison of electron density distribution between the saturated and unsaturated systems, something not explored previously.
Radicals produced from these silylene molecules, 1,3-bis(tert-butyl)-silylimidazol-2-ylidene and 1,3-bis(tert-butyl)-silylimidazolin-2-ylidene, were studied by μSR techniques.

The use of muonium to study silylenes was my inspiration for the short poem below, in homage to the sonnet “Break of Morning” by John Donne.

_Duty of Muonium_

Go, O sweet, and do react
no oxygen can hold you back
a double bond you might not see
but silicon will bind with thee
two point two, then thou are dead
and by thy spin your daughter’s lead.

4.2.2 The Chemistry of Silyl Radicals

The silyl radical is H₃Si·, however, the International Union of Pure and Applied Chemistry (IUPAC) has approved the use of the term silyl radical to refer to any R₃Si· species [96]. One of the most common methods used for generating silyl radicals is the reaction of atoms, radicals, or excited triplet states of some molecules with silicon hydrides [112,113].

\[
R_3SiH + X \cdot \longrightarrow R_3Si \cdot + XH
\]  

(4.2)

Several other techniques for producing silyl radicals from silanes exist, including the direct interaction of silanes with light [114].
In the gas phase the thermochemical properties of molecules are related to those of radicals by the corresponding homolytic bond dissociation enthalpies. Similarly, ionization potentials and electron affinities associate the thermochemistry of neutral and ionic species. The relationships between these types of manipulations are shown in Figure 4.3. In the liquid phase, electrochemical oxidation and reduction potentials serve as the equivalents of ionization potentials and electron affinities. Unfortunately, there is little experimental data on the oxidation and reduction potentials of silyl radicals.

![Figure 4.3: Relationship between an organosilane hydride and its corresponding radicals, ions, and radical ions.](image)

There is yet another process that can be used to obtain silyl radicals, namely the addition of free radicals to silylene molecules.

\[
R_2Si: + R'\cdot \longrightarrow R_2R'Si\cdot
\]  

(4.4)
The objective of the experiments detailed in this chapter is to determine if the muonium atom (acting as a light isotope of hydrogen) will add to the divalent silicon atom to produce a silyl radical. Silyl radicals play an important role in the radical-based hydrosilylation reaction shown below.

\[ \text{Y} + \text{R}_3\text{SiH} \rightarrow \text{R}_3\text{Si} \backslash \text{Y} \]  

(4.5)

A radical initiator, \( \text{In}^* \), can begin the process by abstracting a hydrogen atom from the silane, \( \text{R}_3\text{SiH} \), as shown below.

Termination Steps:
- \( 2\text{R}_3\text{Si}^* \rightarrow \) Decrease in \( \text{R}_3\text{SiCH}_2\text{CHY} \)
- \( \text{R}_3\text{SiCH}_2\text{CHY} + \text{R}_3\text{Si}^* \rightarrow \) Radical Concentration

Figure 4.4: Chain reaction mechanism for radical-based hydrosilylation.

If the kinetics of propagation outweighs those of termination, this can be viewed as a self-sustaining chain reaction. Examples of this type of reaction include \( \text{Et}_3\text{Si}^* \) addition to cyclohexene or propene, \( \text{Me}_3\text{SiSiMe}_2^* \) addition to 1-hexene, and \( [(\text{CH}_3)_3\text{Si}]_3\text{Si}^* \) addition to phenylethene [115,116,117].
Another chain reaction of interest is the removal of a functional group, \( Z \), by organosilicon hydrides [118].

\[
R'Z + R_3SiH \rightarrow R'H + R_3SiZ
\]  
(4.6)

The chain mechanism can be represented by the following flow diagram.

![Flow diagram](image)

Figure 4.5: Chain reaction mechanism for radical promoted removal of a functional group by organosilicon hydrides.

An excellent overview of silicon based radical reactions is provided in the text by Chatgilialoglu [119].

Silyl radicals are normally anticipated to deviate significantly from planarity, and thus are considered \( \sigma \)-type radicals [112]. It has been demonstrated that \( \alpha \)-substituents can have a profound influence on the geometry of silyl radicals. It is this reason that motivated our study of muoniated silicon-based radicals despite the EPR studies of Tumanskii et al. [111] on the formation of silyl radicals from silylenes. The muoniated
silyl radical is expected to mimic the hydrogen analogue better than the product of a bulky radical with a silylene. The geometry of the resulting silyl radical can then in turn affect its chemistry, including the kinetics of the different chain mechanisms just discussed.

The questions we had in mind throughout our experiments were:

(1) Does muonium react with silylenes sufficiently fast for a radical to be detected by the $\mu$SR technique?

(2) What species are produced by such a reaction?

(3) How do the characteristics of the parent silylene affect the distribution of unpaired electron spin density in the radical, particularly at the location of the hydrogen isotope?

4.3 $\mu$SR Experiments

For unsaturated silylene 4.4 (see Figure 4.2 on Page 77) there are two possible radical products from the addition of muonium: (a) Mu addition to the silicon atom forming a silyl radical, or (b) Mu addition to the C=C double bond. While Arduengo concluded that silylenes have significantly different electron-density distribution from carbenes [120], in our experiments, muonium addition to the ring C=C double bond was expected to be the less likely product. We anticipated that silylenes would react with muonium in a similar manner to carbenes, and that any species detected using the $\mu$SR techniques would be muoniated silyl radicals.

Silylenes 4.4 and 4.5 (see Figure 4.2 on Page 77) were synthesized, and purified in the solid state by Dr. R. West's team at the Organosilicon Research Center at the
University of Wisconsin, according to the published procedures [121,122]. A liquid sample was needed to ensure sharp spectral features by averaging anisotropic hyperfine parameters, and hence the samples used in the $\mu$SR experiments at TRIUMF were prepared by dissolving the solid compounds in tetrahydrofuran (THF). As silylenes are oxygen and moisture sensitive, these solutions were prepared in a nitrogen glove box using degassed THF and dry glassware. The solutions were sealed oxygen-free in stainless steel vessels fitted with a thin steel foil window. Transverse-field muon spin rotation (TF-$\mu$SR) and muon (avoided) level-crossing resonance ($\mu$LCR) experiments were performed at the M20 muon beam line at TRIUMF.

### 4.3.1 Transverse Field Muon Spin Rotation

TF-$\mu$SR spectra were collected at various magnetic fields and temperatures for the radicals formed by Mu addition to 4.4 and 4.5. Because muonium behaves chemically like a hydrogen atom, it readily adds to unsaturated bonds, or can form a bond with a lone-pair electron, forming a radical. In 4.4 there is both an unsaturated C=C bond and a lone pair of electrons formally drawn on the divalent silicon atom, and hence there are two possible products of muonium addition, as shown below.

Figure 4.6: Possible radicals from muonium addition to silylenes 4.4 and 4.5.
In the TF-μSR spectrum from 4.4 (Figure 4.7), two radical peaks are situated equidistant from the diamagnetic peak. The separation of these radical peaks is equal to the hfc of the muon in the associated radical. Since only one pair of peaks is present in the spectrum, clearly, only one radical product is detected. For 4.5, only one type of radical is expected, namely forming a new bond between the divalent silicon atom and muonium, 4.5a. Only one species was observed in the TF-μSR experiment, as shown in Figure 4.8, and thus it is tempting to attribute the detected radical to compound 4.5a.

The temperature dependence of the muon hfc was measured over a range of temperatures for the muoniated silyl radicals. In both cases, $A_\mu$ decreased with temperature. The measured $A_\mu$ values are reported in Table 4.1 and Table 4.2, with statistical uncertainties shown in parenthesis, and the trends are illustrated in Figure 4.9.

![Figure 4.7: TF-μSR spectrum from a 1.55 M solution of 4.4 (1,3-bis(tert-butyl)-silylimidazol-2-ylidene) in THF at 299 K in a transverse magnetic field of 14.5 kG.](image-url)
Figure 4.8:  TF-μSR spectrum from a 0.88 M solution of 4.5 (1,3-bis(tert-butyl)silylimidazolin-2-ylidene) in THF at 313 K in a transverse magnetic field of 14.5 kG.

Table 4.1:  Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 4.4.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$A_\mu$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>277</td>
<td>236.21 (3)</td>
</tr>
<tr>
<td>299</td>
<td>235.39 (2)</td>
</tr>
<tr>
<td>313</td>
<td>234.85 (5)</td>
</tr>
</tbody>
</table>

Statistical uncertainties are shown in parenthesis.

Table 4.2:  Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 4.5.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$A_\mu$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>277</td>
<td>155.46 (10)</td>
</tr>
<tr>
<td>299</td>
<td>155.06 (7)</td>
</tr>
<tr>
<td>313</td>
<td>154.87 (8)</td>
</tr>
</tbody>
</table>
Figure 4.9: Temperature dependence of the muon hyperfine coupling constant in the muoniated radicals from unsaturated silylene 4.4 (○) and the saturated silylene 4.5 (□). The lines are only meant to serve as a guide for the eyes.
4.3.2 Longitudinal Field Avoided Muon Level Crossing Resonance

To determine the hyperfine coupling constants for other spin-active nuclei in the radicals, these same samples were investigated by μLCR. The resulting spectra are displayed in Figure 4.10 and Figure 4.11. The μLCR spectra were fitted to Lorentzian line shapes. The simulated spectra are shown as continuous lines overlaid on the experimental data. The resonance parameters of field position and signal width (Full Width at Half Maximum, FWHM) for the radicals from 4.4 and 4.5 are given in Table 4.3 and Table 4.4, respectively. For 4.5, more than one type of nucleus in the radical is detected; to assist with the assignment of these signals the relative amplitudes are also reported.

![μLCR spectrum](image)

Figure 4.10: μLCR spectrum from a 1.55 M solution of 4.4 (1,3-bis(tert-butyl)-silylimidazol-2-ylidene) in THF at 299 K.
Figure 4.11: (a) and (b) are resonances detected in the μLCR spectrum from a 0.88 M solution of 4.5 (1,3-bis(tert-butyl)-silylimidazolin-2-ylidene) in THF at 313 K.
Table 4.3: \(\mu\text{LCR}\) parameters for the muoniated radical from 4.4 as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>(B_{\text{res}} /\text{G})</th>
<th>FWHM /G</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>8460.1 (1.0)</td>
<td>22.1 (1.1)</td>
</tr>
<tr>
<td>289</td>
<td>8408.4 (7)</td>
<td>24.1 (8)</td>
</tr>
<tr>
<td>299</td>
<td>8435.5 (7)</td>
<td>22.3 (8)</td>
</tr>
<tr>
<td>313</td>
<td>8452.3 (9)</td>
<td>21.2 (1.0)</td>
</tr>
</tbody>
</table>

Table 4.4: \(\mu\text{LCR}\) parameters for the muoniated radical from 4.5 at 313 K.

<table>
<thead>
<tr>
<th>(B_{\text{res}} /\text{G})</th>
<th>FWHM /G</th>
<th>Relative Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>5373 (2)</td>
<td>27 (3)</td>
<td>1.</td>
</tr>
<tr>
<td>5477 (4)</td>
<td>65 (9)</td>
<td>0.69 (6)</td>
</tr>
<tr>
<td>7784 (4)</td>
<td>29 (5)</td>
<td>0.45 (5)</td>
</tr>
<tr>
<td>7934 (7)</td>
<td>13 (6)</td>
<td>0.19 (7)</td>
</tr>
</tbody>
</table>

In the LCR spectrum of the muoniated radical from 4.4 (Figure 4.10) a single resonance is clearly visible. In Chapter 2 we introduced the equation relating a nuclear hyperfine coupling constant to the magnetic field where an avoided level crossing resonance would occur. Equation (2.55) is shown here again for reference.

\[ B = \left| \frac{A_n - A_k}{2(\gamma_n - \gamma_k)} - \frac{A_n^2 - 2MA_k^2}{2\gamma_n A_n - A_k} \right| \]  

(4.7)

The only types of nuclei in compound 4.4 are H, C, N, and Si. Since the silylene was prepared with the natural abundance of these elements (99.9% for \(^1\text{H}\), 1.1% for \(^{13}\text{C},\)
99.6% for $^{14}\text{N}$, 4.7% for $^{29}\text{Si}$), we can reject the carbon atoms as a potential source of this resonance, and doubt the silicon atom as a reasonable candidate. Inserting the various gyromagnetic ratios for $^1\text{H}$, $^{14}\text{N}$, and $^{29}\text{Si}$, and the muon hyperfine coupling constant obtained in the corresponding transverse field experiment, we can determine what the nuclear hfc would be (both magnitude and sign relative to $A_{\mu}$) for each type of nucleus if it had generated the signal. This information is collected in Table 4.5.

Table 4.5: Potential nuclear hyperfine coupling constants based on a \(\mu\)LCR spectrum from a 1.55 M solution of 4.4 in THF at 299 K.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>(A_k /\text{MHz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{H}$</td>
<td>77.55 (2)</td>
</tr>
<tr>
<td>$^{14}\text{N}$</td>
<td>10.78 (2)</td>
</tr>
<tr>
<td>$^{29}\text{Si}$</td>
<td>-8.69 (3)</td>
</tr>
</tbody>
</table>

In the work of Tumanskii et al., the identity of the attacking radical did not drastically change the hfc's of either the ring nitrogens or the backbone hydrogens [111]. They did not detect coupling to the silicon atom, but in a molecular modelling experiment they predicted a hyperfine value for this nucleus of 233.8 MHz. Comparing the potential \(A_k\) values in Table 4.5 with those reported by Tumanskii, I find $A_{\text{N-14}}$ of 10.78 MHz to be entirely reasonable. In contrast, the hydrogen hfc is too large when compared with Tumanskii's findings. While the electron density at the silicon atom will vary with the choice of attaching radical, I do not anticipate the magnitude of $A_{\text{Si-29}}$ to decrease from 233.8 to only 8.7 MHz when a smaller radical is used (Mu in place of CH\(_2\)Ph). Additionally, I do not expect the silicon atom with only 4.7% natural abundance would
generate a signal while the nitrogen and hydrogen atoms would not. For this reason, I argue that this lone resonance is due to a set of equivalent nitrogen atoms in the muoniated radical. Unless there is a reason why only one of the nitrogen atoms would have a detectable resonance, this suggests the radical is symmetric, supporting the case for radical 4.4a over radical 4.4b (see Figure 4.6 on Page 82).

For the muoniated radical resulting from silylene 4.5, four resonances are observed in the LCR spectrum as overlapping pairs. The potential nuclear hfcs are listed in Table 4.6. Comparing with the EPR results of Tumanskii, the most logical assignment is that two nitrogen atoms are responsible for the signals at 5373 and 5477 G, while the resonances at 7784 and 7934 G are due to protons.

Table 4.6: Potential nuclear hyperfine coupling constants from a 0.88 M solution of 4.5 in THF at 313 K.

<table>
<thead>
<tr>
<th>$B_{res}$/G</th>
<th>$A_{H-1}$/MHz</th>
<th>$A_{N-14}$/MHz</th>
<th>$A_{Si-29}$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>5373</td>
<td>54.30 (9)</td>
<td>11.75 (10)</td>
<td>-0.65 (10)</td>
</tr>
<tr>
<td>5477</td>
<td>52.37 (11)</td>
<td>9.01 (14)</td>
<td>-3.64 (15)</td>
</tr>
<tr>
<td>7784</td>
<td>9.63 (11)</td>
<td>-51.81 (13)</td>
<td>-69.73 (13)</td>
</tr>
<tr>
<td>7934</td>
<td>6.84 (15)</td>
<td>-55.77 (20)</td>
<td>-74.04 (21)</td>
</tr>
</tbody>
</table>

If the radical detected in the TF and LCR experiments from 4.5 is simply the species resulting from Mu addition to the silicon atom, then why do we not observe all four protons in the LCR spectrum? In fact, significant effort was required to generate a sufficient signal-to-noise ratio to detect any of the LCR signals. Why were these resonances so weak? These questions can be answered by considering the equations.
describing the amplitude of an LCR signal. As discussed in Chapter 2, the amplitude of an LCR line is proportional to the mean reduction in muon polarization, $\Delta P_z$ [123]. Equations (2.55) and (2.58) through (2.60) can provide a model for the signal amplitude. The result of such a model is illustrated in Figure 4.12. The curve for $^{29}$Si was adjusted by multiplying the calculated mean reduction in muon polarization by the natural abundance (0.047), since the polarization of the muon beam will only be reduced for the fraction of radicals containing the spin-active $^{29}$Si isotope.

![Diagram](image)

**Figure 4.12:** $\mu$LCR percent signal amplitude as a function of magnetic field position for the radical from muonium addition to 4.5. Due to differing gyromagnetic ratios, the $^{14}$N and $^1$H have different amplitude curves. The dotted line (· · ·) is the $^{29}$Si amplitude curve, the solid line (—) is the $^{14}$N curve, the dashed line (· - ·) is the $^1$H curve, and the circles (○) are the experimental data. The silicon curve is much lower in percent amplitude due to the low natural abundance of $^{29}$Si.

This plot demonstrates the dependence of LCR signal amplitude on the resonance field position, and that none of the LCR resonances are expected to have an amplitude...
greater than 10% of the maximum signal strength for an LCR experiment. Also apparent is that any proton with a smaller (in magnitude) hfc would have too weak a resonance to be detectable. Finally, this plot serves as a secondary confirmation that our \( \mu \text{LCR} \) assignments are correct, as the only amplitude curve that agrees with the experimental amplitudes within experimental error for the lower field signals is the nitrogen curve, and the only agreement for the higher field resonances is the proton curve. This assignment illustrates the inequivalent behaviour of both the nitrogens and the protons in the radical generated from 4.5, in contrast to the radical from 4.4.

### 4.4 Computational Models and Radical Assignments

While we have been successful at identifying the types of nuclei responsible for each resonance, at this point we have yet to confirm if the species detected by \( \mu \text{SR} \) techniques are indeed compounds 4.4a and 4.5a. Molecular modelling can aid in this endeavour.

#### 4.4.1 Silylene and Silyl Geometries and Hyperfine Coupling Constant Modelling

As a first step, the structures of silylenes 4.4 and 4.5 were modelled at the UB3LYP/6-31G(d) level, with the minor modification of replacing the \( \text{tert} \)-butyl ligands that are attached to the nitrogens with methyl groups. These output structures were then used as the starting point for the computation of optimal geometry of 4.4 and 4.5 with the \( \text{tert} \)-butyl ligands, performed with the same functional/basis set combination. In both cases, a hydrogen atom was then added to the resulting geometries in order to model the structures of the associated radicals, 4.4a, 4.4b, and 4.5a. The radical geometry optimization was followed by a hyperfine coupling constant calculation. The calculations
for the radical species were at the UB3LYP/cc-pVDZ//UB3LYP/6-31G(d) level. The muon hfcs computed in this fashion are summarized in Table 4.7. For comparison, the corresponding experimental results for the muon hfc are also listed beside each potential radical.

Table 4.7: Calculated and experimental silyl radical muon hyperfine coupling constants.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Label</th>
<th>Calc $A_{\mu}$/MHz (R = CH$_3$)</th>
<th>Calc $A_{\mu}$/MHz (R = t-Bu)</th>
<th>Expt $A_{\mu}$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image_url" alt="Image" /></td>
<td>4.4a</td>
<td>684</td>
<td>618</td>
<td>235</td>
</tr>
<tr>
<td><img src="image_url" alt="Image" /></td>
<td>4.4b</td>
<td>328</td>
<td>365</td>
<td>235</td>
</tr>
<tr>
<td><img src="image_url" alt="Image" /></td>
<td>4.5a</td>
<td>680</td>
<td>764</td>
<td>155</td>
</tr>
</tbody>
</table>

Clearly, the muon hfc calculations do not support the assignment of the two detected radicals as any of 4.4a, 4.4b, or 4.5a! To ensure that the choice of basis set is not the source of confusion, quick tests using 6-31G(d) in place of the cc-pVDZ basis set for the hfc calculation were performed. These computational experiments also suggest that the modelled species are not what we are observing experimentally.
It is very unlikely that an impurity is the cause of the μSR signals, as it would have to be in large concentration to complete with the reactive C=C and Si: centers. Dr. West’s group, who provided the silylenes, prepared fresh samples and checked them by NMR. The NMR experiments showed that the new samples were pure silylenes. Also, NMR data were collected for these silylenes in THF and benzene-d6, and there does not appear to be any solvent effect or complex formation. μSR experiments with silylenes 4.4 and 4.5 as solutions in THF were repeated. The experimental results were reproducible.

4.4.2 Dimerization: Are Two Rings Better Than One?

Based on the transverse field experiments it is clear that we are observing paramagnetic species, and based on the computational studies just discussed they are not the primary radicals due to muonium addition to the silylene molecules. At this point, I questioned if it were possible for the primary muoniated silyl radical to attack a neighbouring silylene molecule at the divalent silicon atom, producing a secondary radical. Such a species would be called a disilanyl radical.

A few considerations must be met before such a conclusion can be drawn. First, does molecular modelling of a disilanyl radical explain the experimental data; i.e. do the modelled hfcs match those from experiments? Second, is it kinetically feasible for a secondary radical to form within the brief existence of a muon, and can the muon polarization be transferred from the primary radical to the disilanyl radical? Finally, can we be sure that the disilanyl radical is forming in a two-step process where muonium adds to a silylene, followed by attack on another silylene molecule, rather than a dimer of the silylene molecule forming first and muonium adding to that species?
4.4.2.1 Computational Modelling of Disilanyl Radicals

Computational methods were again utilized, to model the anticipated disilanyl species. The previously calculated optimal geometries for both the silyl radicals and the corresponding silylene molecules were used together as a starting point for the disilanyl radical. The UB3LYP/cc-pVDZ//UB3LYP/6-31G(d) level of theory was used for these calculations. The disilanyl calculated muon hyperfine coupling constants are clearly a much better match than those of the silyl radicals.

Table 4.8: Calculated and experimental disilanyl radical muon hyperfine coupling constants.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Label</th>
<th>Calc $A_\mu$ /MHz (R = CH$_3$)</th>
<th>Calc $A_\mu$ /MHz (R = t-Bu)</th>
<th>Expt $A_\mu$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Disilanyl Radical" /></td>
<td>4.6</td>
<td>201</td>
<td>196</td>
<td>235</td>
</tr>
<tr>
<td><img src="image" alt="Disilanyl Radical" /></td>
<td>4.7</td>
<td>122</td>
<td>116</td>
<td>155</td>
</tr>
</tbody>
</table>

These are the first muoniated disilanyl radicals to be detected, and so there is no precedent with which to determine if a 20 % factor, presumably due to the zero-point vibrational averaging effects, is or is not appropriate. Despite the lack of information on the primary isotope effect, based on this modelling study, it is probable that the radicals
detected by μSR are the disilanyl radicals 4.6 and 4.7 shown in Table 4.8. Hyperfine coupling constants for other nuclei with significant spin density in the disilanyl radicals are reported in Table 4.9 and Table 4.10. For the ring protons in disilanyl radical 4.7, the two larger $A_k$ values are provided. The other pair of ring protons, as well as those in disilanyl radical 4.6, have hfcs of less than 3 MHz.

Table 4.9: Calculated nuclear hyperfine coupling constants for unsaturated disilanyl radical 4.6.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Location</th>
<th>Calc $A_k$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{14}$N</td>
<td>On the same ring as the unpaired e$^-$</td>
<td>13.3 &amp; 12.7</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>On the same ring as Mu</td>
<td>11.7 &amp; 8.9</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>On the same ring as the unpaired e$^-$</td>
<td>140.2</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>On the same ring as Mu</td>
<td>282.7</td>
</tr>
</tbody>
</table>

Table 4.10: Calculated nuclear hyperfine coupling constants for saturated disilanyl radical 4.7.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Location</th>
<th>Calc $A_k$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>On the same ring as the unpaired e$^-$</td>
<td>10.7 &amp; 9.6</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>On the same ring as the unpaired e$^-$</td>
<td>12.7 &amp; 5.7</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>On the same ring as Mu</td>
<td>9.5 &amp; 2.6</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>On the same ring as the unpaired e$^-$</td>
<td>322.7</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>On the same ring as Mu</td>
<td>232.4</td>
</tr>
</tbody>
</table>
Comparing the calculated hfcs in Table 4.9 for 4.6 with the potential hfcs based on experimental data, reported in Table 4.5, the molecular models agree with the $^{14}$N assignment for the $\mu$LCR resonance. For the saturated radical, 4.7, the calculated values listed in Table 4.10 support an assignment of $^{14}$N for the two resonances near 5400 G, and $^1$H for those near 7800 G, in agreement with my earlier conclusions.

### 4.4.2.2 Kinetics Considerations

My proposed reaction mechanism, formation of an $\alpha$-muoniated silyl radical followed by reaction with a silylene to generate a $\beta$-muoniated disilanyl radical, is an indirect formation reaction mechanism. It is important to consider if the muon spin polarization can be transferred from Mu to the $\beta$-muoniated disilanyl radical. The principles governing the transfer of muon spin polarization from free muonium to the primary radical, and from the primary radical to the secondary radical, are the same; the main factors are the pseudo-first order rate constants, $\lambda_1$ and $\lambda_2$, and the difference in Larmor frequencies.

The fact that we are able to observe a muoniated radical can provide us with a lower bound for the pseudo-first order rate constant $\lambda_2$. We can also obtain an upper bound for $\lambda_2$ from the signal amplitude. For any sample run in the same type of sample cell, the carbene 1,3-bis(isopropyl)-4,5-dimethylimidazol-2-ylidene has the largest radical signal amplitude. If we take the corresponding radical amplitude at the same temperature and magnetic field as a lower bound for the maximum polarization (hereafter referred to as the maximal polarization for simplicity), we see that the unsaturated disilanyl radical
amplitude is 50.7 % of this maximal value. The saturated disilanyl radical amplitude is 18.5 % of the maximum.

We use the DFT computed value for the silyl radical as reported in Table 4.7, 618 MHz, and the experimental value for the disilanyl radical, 235 MHz. From the muon hfc in the radicals, the radical precession frequencies can be determined. These values can then be used in Equation (2.47), and the muon polarization becomes a function of a single variable, $\lambda_2$. A plot of the muon polarization transfer from the silyl radical to the disilanyl radical at 14.5 kG, as a function of pseudo-first order rate constant, is given in Figure 4.13. A similarly shaped curve exists for the saturated silyl reaction (silyl $A_{\mu} = 764$ MHz, disilanyl $A_{\mu} = 155$ MHz).

![Figure 4.13: Theoretical curve for the muon polarization transfer at 14.5 kG from the unsaturated silyl radical 4.4a to the unsaturated disilanyl radical 4.6.](image)

---

\(^{22}\) The Fourier Transform Power Plot displays the square of the TF-\(\mu\)SR signal amplitude.
In the preceding discussion we ignored the changes in sensitivity of the detectors with frequency and assumed that there is full polarization transfer from Mu to silyl \((\lambda_1 > 10^{10} \text{ s}^{-1})\), so that the signal reduction to 50.7% is due to loss of polarization during the formation of the disilanyl radical. Muon polarization of 0.507 corresponds to a \(\lambda_2\) for the unsaturated silyl + silylene reaction of \(7.0 \times 10^8 \text{ s}^{-1}\). This value is an upper bound for the reaction rate, as the true maximum polarization may be larger than that observed for 1,3-bis(isopropyl)-4,5-dimethylimidazol-2-ylidene (meaning the polarization measured for the disilanyl radicals would be a smaller fraction of the maximum). If the same process is followed for the saturated system, we obtain an upper limit for \(\lambda_2\) of \(3.6 \times 10^8 \text{ s}^{-1}\).

Under optimal situations, all of the muon polarization is included in either the diamagnetic signal or the radical signals. However, there is typically some "lost" fraction (e.g. the detectors are not 100% efficient).

\[
P_{\text{Total}} = P_D + P_R + P_L
\]  

\((4.8)\)

Consider if the lost fraction in the spectrum from isopropyl carbene were attributed to the corresponding radicals (and not diamagnetic muons). The polarization observed for a disilanyl radical would then be a smaller fraction of the sum of \(P_R\) and \(P_L\) from 1,3-bis(isopropyl)-4,5-dimethylimidazol-2-ylidene than of the \(P_R\) value from the carbene alone. This smaller fraction can then be used in the same method as before to obtain a measure of the pseudo-first order rate constant, and would represent a lower bound. The lower limits for \(\lambda_2\) in the unsaturated and saturated systems are \(2.6 \times 10^8 \text{ s}^{-1}\) and \(1.5 \times 10^8 \text{ s}^{-1}\), respectively.
Finally, using these pseudo-first order rate constants along with the concentration of the silylene (1.55 M) in Equation (2.46), we can determine the upper and lower limits for the second-order rate constants. These are reported in Table 4.11.

<table>
<thead>
<tr>
<th></th>
<th>$k_2/10^8 \text{M}^{-1} \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4a + 4.4</td>
<td>1.7</td>
</tr>
<tr>
<td>4.5a + 4.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Upper Limit</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 4.11: Upper and lower limits for the second order rate constant for the $N$-heterocyclic silyl radicals 4.4a and 4.5a reacting with their silylene counterparts.

To my knowledge, this is the first determination of the rate constant for the reaction of an $N$-heterocyclic silyl radical with an $N$-heterocyclic silylene molecule, and apparently even for any silyl radical with a silylene. For comparison, the rate constants for self-reaction of various silyl radicals in the gas or liquid phase have been reported, and such data is provided in Table 4.12 [124,125,126,127].

Silyl radical addition to carbon-carbon double and triple bonds, carbon-oxygen double bonds, carbon-heteroatom multiple bonds, and heteroatom-heteroatom multiple bonds have also been studied, with second order rate constants ranging in orders of magnitude from $10^4$ to $10^9 \text{M}^{-1} \text{s}^{-1}$ [115,116,117,128,129]. Comparing our estimated rate constants with the reported values for similar reactions, we see that our values are entirely reasonable.
Table 4.12: Second-order rate constants for the self-reaction of silyl radicals.

<table>
<thead>
<tr>
<th></th>
<th>$k_2 / \text{M}^{-1} \text{s}^{-1}$</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{Si}^*$</td>
<td>$4.8 \times 10^{10}$</td>
<td>Gas</td>
</tr>
<tr>
<td>$\text{Et}_3\text{Si}^*$</td>
<td>$2 \times 10^{10}$</td>
<td>Liquid</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{Si}^*$</td>
<td>$5 \times 10^9$</td>
<td>Liquid</td>
</tr>
<tr>
<td>$\text{Me}_3\text{SiSi(#)Me}_2$</td>
<td>$1.4 \times 10^9$</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

### 4.4.2.3 Mechanistic Considerations

The last question posed on page 93 was if we could be certain that the disilanyl radical is forming in a two-step process where muonium adds to a silylene, followed by attack on another silylene molecule, rather than a dimer of the silylene molecule forming first and muonium adding to that species.

![Possible reaction mechanisms for formation of the muoniated disilanyl radical from 4.4](image)

**Figure 4.14:** Possible reaction mechanisms for formation of the muoniated disilanyl radical from 4.4: (a) by addition of muonium to the dimer; (b) by reaction of silyl radical 4.4a with an additional molecule of 4.4.
As stated earlier, NMR experiments on silylenes 4.4 and 4.5 in solutions of THF or benzene-d6 demonstrate that the silylenes exist in their monomeric state in solution. Additionally, if there were a mixture of monomer, dimer, or even more complex oligomers, then we would anticipate multiple pairs of signals in the TF-μSR spectrum.

4.4.3 Radical Assignments and Reaction Mechanisms

We conclude that since the only species present is the silylene as a monomer, the muonium atom adds to the silylene molecule forming the corresponding silyl radical, which then proceeds to react with another silylene molecule to generate a disilanyl radical. These reaction steps are illustrated in Figure 4.14b. The species detected in the TF-μSR spectra of Figure 4.7 and Figure 4.8 are compounds 4.6 and 4.7, respectively (both shown below).

![Diagram of disilanyl radicals 4.6 and 4.7]

Figure 4.15: Disilanyl radical species detected by μSR studies.

Moser et al. have studied the formation of disilanes from silylenes and halocarbons [130]. When silylene 4.4 reacts with CHCl₃, the disilane product shown in Figure 4.16 forms in greater than 98% yield. This species is called the 2:1 product, as it contains two silylenes per halocarbon.
Figure 4.16: An example of a 2:1 disilane product resulting from reaction of silylenes with halocarbons.

The saturated silylene 4.5 reacted similarly with CHCl₃, forming the 2:1 product in greater than 98% yield. However, reaction of either the unsaturated or saturated silylene react with isopropyl chloride yields a mixture of the 2:1 product and a 1:1 product (shown below).

Figure 4.17: An example of a 1:1 silane product resulting from reaction of silylenes with halocarbons.

Moser et al. attempted to rationalize their results by considering possible reaction mechanisms. One of the free-radical chain mechanisms proposed contains two steps where a silyl radical is formed by reaction of a silylene with an alkyl radical, followed by attack of the silyl radical on another silylene to form a disilanyl radical. The mechanism I have proposed in Figure 4.14 for the formation of the muoniated disilanyl radical corresponds to these steps of the free-radical chain mechanism, and hence our observation of the muoniated disilanyl radicals supports this reaction mechanism.

The process of investigation this project has taken served as inspiration for the following sonnet, which adheres to the traditional Italian form.
Ritual of a Scientist

When first I eyed the match I thought I knew,  
and celebrations in my mind were made.  
A thousand toasts from pen to paper played.  
But woe is me, and blackened was my view!  
My mind is torn for that bond can't be true,  
and in the endless mists I now must wade,  
the joy I once embraced did quickly fade.  
With rain upon my cheeks, my Lord, I sue  
that heaven send Kekulé's dream to me.  
Then in that place of solitude, a friend  
bows down and whispers to my shattered mind  
"The truth is there." The words, they set me free.  
Old models purged, I see a way to mend:  
Silyl and silylene together bind.

4.5 Disilanyl Geometry

A simplified representation of the optimized structure of the unsaturated disilanyl radical is shown in Figure 4.18, and the saturated in Figure 4.19. The methyl groups of the tert-butyl ligands have been hidden for clarity. Note the planarity of the rings in 4.6.

Geometry optimization calculations on the saturated disilanyl radical 4.7 and the unsaturated disilanyl radical 4.6 demonstrate that the saturated radical has a shorter Si-Si bond length (2.4415 Å versus 2.4875 Å). This trend agrees with the crystal structures of the related disilane molecules, where the bond lengths are 2.37 Å and 2.42 Å, respectively [130]. Moser explained the shorter Si-Si bond length in the crystal structure of a saturated disilane relative to that of an unsaturated disilane as the result of additional
twisting of the five-membered rings in the saturated compound, which reduces the steric repulsion between the two halves of the disilane molecule.

Figure 4.18: A simplified representation of the optimized 3-dimensional structure of the unsaturated disilanyl radical 4.6.

Figure 4.19: A simplified representation of the optimized 3-dimensional structure of the saturated disilanyl radical 4.7.

Since addition of a silyl radical (an $\alpha$-muoniated radical) to a silylene produces a disilanyl radical (a $\beta$-muoniated radical), increased dihedral angles result in decreased...
overlap between the muonium atom and the orbital containing the unpaired electron. This can explain why the radical from the saturated silylene has a lower hyperfine coupling constant than for the radical from the saturated silylene. The hyperfine coupling constant varies with $\cos^2 \theta$, where $\theta$ is the dihedral angle between the C–Mu bond and the orbital containing the unpaired electron. The geometry optimization calculations yield a value of $\theta$ for 4.7 of 76°, while for radical 4.6 the angle is 78.0°. Although this seems to suggest slightly greater twisting between the rings for the unsaturated radical, the errors of these calculations are likely greater than the difference between these two angles; the computed minimum energy structure generally is not the same as the vibrationally averaged structure.

We have already observed that a secondary isotope effect, related to the higher zero-point energy in the muoniated species, is required for correct modelling of the muon hfcs. The required vibrational averaging technique will affect this dihedral angle, and an increase in $\theta$ of approximately 2.5° for 4.7 accompanied by a similar decrease in $\theta$ for 4.6 would generate the expected ratio of $\cos^2 \theta$ terms. Due to the volume of calculations required, a vibrational averaging study for the muon hfcs was not undertaken. Such an endeavour is suggested for future research.

4.6 Dicarbenyl Radicals from Mu Addition to Carbenes?

Having concluded that the radicals produced by muonium addition to $N$-heterocyclic silylenes 4.4 and 4.5 yield disilanyl radicals and not the primary silyl radicals, it is worth reviewing the carbene $\mu$SR data. Some of the original attempts to generate carbenes failed due to the tendency of carbenes to dimerize [131,132,133]. The stability of unsaturated over saturated carbenes has been explained in terms of the singlet-
triplet gap [134]. In saturated carbenes, the five-center six-electron $\pi$ delocalization is no longer available as a stabilizing factor, so the singlet-triplet gap shrinks. For this reason, it proved more difficult to generate saturated $N$-heterocyclic singlet carbenes than unsaturated ones. In personal communications with Dr. Robert West of University of Wisconsin, a similar obstacle has been discussed for the preparation of the saturated, unsubstituted silylene. The saturated species tends to form the tetramer in the solid state, but the process is reversible for solutions.

Molecular modelling of the radicals 4.8 and 4.9 was done at the level of UB3LYP/EPR-III/UB3LYP/6-31G(d). This is the same level as used for the disilanyl radicals for the geometry optimization, but the EPR-III basis set was used in place of cc-pVDZ for the hyperfine coupling constant property calculation, since the EPR-III basis set was used for the carbenyl calculations. The results are collected below.

Table 4.13: Calculated and experimental dicarbenyl radical muon hyperfine coupling constants.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Label</th>
<th>Calc $A_\mu$ /MHz</th>
<th>Expt $A_\mu$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Radical 4.8" /></td>
<td>4.8</td>
<td>49.8</td>
<td>286.7</td>
</tr>
<tr>
<td><img src="image" alt="Radical 4.9" /></td>
<td>4.9</td>
<td>51.3</td>
<td>114.43</td>
</tr>
</tbody>
</table>

107
The predicted muon hfcs do not match with experiment in contrast to the carbenyl radical values [30], and so no change to the assignments is recommended.

4.7 Future Work

A small extension of this research project would be to study muonium addition to the derivative of silylene 4.5 where one of the hydrogen atoms on each of the ring carbons is replaced with a methyl group, such that the methyl groups are anti to each other. This silylene exists in its monomeric state in the pure liquid [135]. Preliminary studies of this species in THF at a concentration of 1 M detected four muoniated radicals. However, this sample was found to contain reagents used during the synthesis. Running a purified sample, both as a dilute solution and neat liquid, should clarify if additional radicals are being formed by muonium addition to the silylene. Comparing the experimental results with computational models, as done in this chapter, should allow assignment of the detected species. It is of particular interest to determine if muonium addition to the tetramer occurs.

Another avenue for future research is to determine the mode responsible for the temperature dependence of the muon hfcs in silylenes. It has been suggested that negative temperature dependence in carbenes may be due to a vibrational mode involving inversion at the nitrogen atoms [30]. A molecular modelling study of the vibrational motions in carbenes and silylenes may be able to determine if this mode is responsible, but such a project may have significant challenges due to the possible coupling between multiple vibrational modes that affect the hfcs. Computational approaches to such a problem have been made, but focus on fairly small radical species [136]. A vibrational averaging study of the two disilanyl radicals studied may also be of interest for future
work, to determine if the averaged geometries correctly model the ratio of muon hyperfine coupling constants.

Finally, it may be worth investigating muonium addition to the dimers of silylenes 4.4 and 4.5. Such species are known as disilenes, and in the subsequent chapter we look at a member of the closely related class of compounds called silenes. Muonium addition to the disilenes from 4.4 and 4.5 is expected to generate the same radicals as described herein. This experiment would be a useful check of our assignment.

4.8 Conclusions

The results detailed in this chapter illustrate the difference in reactivity of radical adducts of N-heterocyclic silylenes from the previously reported radical adducts of N-heterocyclic carbenes. While unexpected, formation of disilanyl radicals by muonium addition to a silylene and subsequent reaction with another silylene molecule provides an important model for silylene radical reactions. In addition, the hydrogen radical reaction model developed in this chapter is closely related to the silylene chain reaction mechanism of Moser et al., and hence provides explicit experimental evidence to support Moser’s argument. The use of muonium as a probe of H-atom reactions also proves that coupling of these silylenes occurs after Mu addition, and not before. This suggests that silylene dimerization can occur in the presence of hydrogen atoms, even in solutions where dimerization would otherwise not occur.
CHAPTER 5.
THE REACTIVITY OF A
CARBON–SILICON DOUBLE BOND:
ON THE SUBJECT OF SILENES

5.1 Silicon Analogues of Alkenes

When two silylenes come together such that the two lone pairs form a double bond between the two silicon atoms, then the resulting $R_2Si=SiR_2$ species is known as a disilene. This is a direct analogue of an alkene, $R_2C=CR_2$. If $\mu$SR studies were performed on a disilene, we would expect the muonium atom to add to one of the silicon atoms (the point of unsaturation), forming a disilanyl radical, the same type of species we obtained in our earlier silylene studies based on the mechanism shown in Figure 4.14.

In an alkene, if only one of the carbon atoms is replaced with a silicon atom, the $R_2C=SiR_2$ compound is referred to as a silene. The two reactive sites (the C and Si of the double bond) in this type of molecule might not be symmetrically reactive towards the muonium atom. If the hydrogen isotope is more likely to attach to one atom over the other, which site is preferred? Since this is a case of competition kinetics, we might ask if one rate constant is significantly larger than the other so that only one product is formed, or are the radicals generated in comparable quantities?

The early experimentalists working on forming a species with a doubly bonded silicon atom became familiar with frustration. Of particular note is Kipping, who at one point believed he had synthesized a disilene, $Ph(Et)Si=Si(Et)Ph$, but it was later determined to be a singly bonded compound [137,138]. After years without success,
Kipping eventually concluded that it was not possible to have multiple bonds to silicon [139].

Additional experimental work and ensuing theoretical studies led to the formulation of the ‘double bond rule’, which stated that elements with a principal quantum number greater than 2 do not form multiple bonds with themselves or with any other elements [140]. Clearly this rule referred to stable compounds, as transient species with doubly bonded silicon atoms were already being investigated. In fact, last year marked four decades since Gusel’nikov and Flowers pyrolyzed a silacyclobutane derivative to form the first transient silene [141]. In 1981, the ‘double bond rule’ was overturned when the first stable compounds containing Si=C and Si=Si bonds were reported [142,143].

Olefinic C=C bonds are roughly 15% shorter than related C-C single bonds, but Si=C bonds reduce by only about 10% from the single bond length. This is interpreted as weaker π-bonding due to overlap of a carbon 2p atomic orbital with a 3p silicon orbital. Additionally, because of the electronegativity difference between silicon and carbon, the Si=C bond is typically quite polar and strongly electrophilic. As a result, most silenes are highly reactive intermediates. Generally, the stable silenes that have been prepared exhibit some combination of steric and electronic effects to reduce their extreme reactivity; examples include the silylenes prepared by Brook [146].

Ever since Gusel’nikov and Flowers’ discovery, the synthesis and reactivity of multiply bonded silicon compounds, both transient and stable, have been a major focus of research, with many review articles published [144,145,146,147,148,149]. Despite the
level of activity in this field, there is little understanding of the radical chemistry of these compounds.

Dr. Kira of Tohoku University, Japan reported the first synthesis of an isolable dialkylsilylene in 1999 [150,151]. This species, compound 5.1, was distinct from previously prepared silylenes in that its stability was founded on steric protection of the divalent silicon atom by two trimethylsilyl groups attached to the α-carbons. While it is known to be monomeric in the solid state and stable at 0°C, the silylene slowly converts to the silacyclopentene, 5.2, in solution at room temperature. Compound 5.2 was the first example of a cyclic silene. Dr. Kira provided a purified sample of liquid silene 5.2 for our μSR studies, allowing us to begin our investigation of doubly bonded silicon species by considering the relative reactivity of the carbon and silicon atoms in the double bond.

![Figure 5.1: Rearrangement of a dialkylsilylene into a cyclic silene.](image)

**5.2 Silene Reaction Mechanisms**

Mechanisms have been proposed for many reactions of transient silenes, such as: with alkynes [152]; with alcohols, ketones, and carboxylic acids [153,154,155]; for substituent effects on the Si=C double bond [156]; to include solvent effects [157]. Of particular interest to our purposes is the last mechanism, which adjusts the model for transient silene reaction with nucleophilic reagents to take account of the environment of an ethereal solvent.
In the mechanism proposed by Leigh for the reaction of a transient silene with an aliphatic alcohol, shown in Figure 5.2, the nucleophilic oxygen atom attacks the silenic silicon atom, producing a zwitterionic complex [153]. This complex then yields an alkoxy silane by either proton transfer or stepwise deprotonation/protonation involving another alcohol molecule. An ethereal solvent, such as THF, is believed to behave like a nucleophile and complex with the silene at the silenic silicon [157]. Subsequent reaction with the alcohol then proceeds via protonation of the complex, either as a discrete step or in concert with the nucleophilic attack. This process can involve a single alcohol molecule, or a pair.

Muonium addition to silene 5.2 in THF was studied by μSR techniques. When the silene is complexed with THF, the muonium atom is expected to behave similarly to the electrophilic hydrogen nucleus in the above mechanism, as shown in Figure 5.3; the silenic silicon atom will complex with the oxygen of the ether solvent molecules, and the electrophilic hydrogen isotope will then add to the silenic carbon atom. In this case, however, the product species will be a muoniated radical, rather than an alkoxy silane molecule. For free silenes, the muonium atom can act as either an electrophile or a nucleophile, and might add to either the doubly bonded silicon or carbon atom, but not necessarily in equal proportions.
Figure 5.2: Reaction mechanism suggested by Leigh for alcohol attack on a silene in tetrahydrofuran [157].

Figure 5.3: Proposed reaction mechanism for muonium attack on a silene in tetrahydrofuran.
5.3 \( \mu \text{SR Experiments} \)

5.3.1 TF-\( \mu \text{SR} \)

A 1.5 M solution of silene 5.2 in THF was placed in a transverse magnetic field of 14.5 kG. TF-\( \mu \text{SR} \) data were collected at three temperatures: 283, 298, and 312 K. The TF-\( \mu \text{SR} \) spectrum for 298 K is shown in Figure 5.4. In the spectrum, two pairs of radical peaks are observed. This suggests that both radical products are forming. The unequal radical peak heights demonstrate that one radical is formed preferentially. The Fourier transform plot displays the squares of the radical amplitudes; the signal amplitudes were determined from fits to the data in time space (\( \mu \text{SR} \) histograms). The ratio of amplitudes for Radical B to Radical A is 2.2 : 1. The muon hfc's as a function of temperature are listed in Table 5.1 for both radicals.

![Fourier Transform Plot](image)

Figure 5.4: TF-\( \mu \text{SR} \) spectrum from a 1.5 M solution of silene 5.2 in THF at 14.5 kG and 298 K. The signal near 400 MHz (labelled \( \times \)) is an overtone of the diamagnetic signal.
Table 5.1: Muon hfcs for the two radicals detected in TF-μSR experiments on silene 5.2 in a 1.5 M solution of THF at 14.5 kG.

<table>
<thead>
<tr>
<th></th>
<th>( A_{\mu}(283 \text{ K}) )/MHz</th>
<th>( A_{\mu}(298 \text{ K}) )/MHz</th>
<th>( A_{\mu}(312 \text{ K}) )/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical A</td>
<td>184.91 (0.18)</td>
<td>186.88 (0.13)</td>
<td>189.60 (0.27)</td>
</tr>
<tr>
<td>Radical B</td>
<td>137.13 (0.06)</td>
<td>136.99 (0.05)</td>
<td>136.94 (0.05)</td>
</tr>
</tbody>
</table>

5.3.2 μLCR

The silene sample was placed in a longitudinal magnetic field, and μLCR data collected at 312 K. The resulting spectrum is shown in Figure 5.5. The two overlapping resonances in the spectrum are likely due to two nuclei of the same element with similar hfcs. To assign the signals we must determine which radical they are from (Radical A or Radical B), and the kind of nuclei responsible for the signals. The resonance parameters of field position and signal width for the radical are provided in Table 5.2.

![μLCR spectrum from a 1 M solution of 5.2 in THF at 312 K.](image)

Figure 5.5: μLCR spectrum from a 1 M solution of 5.2 in THF at 312 K.
Table 5.2: μLCR parameters for the muoniated radical from 5.2 at 312 K.

<table>
<thead>
<tr>
<th>$B_{res} / G$</th>
<th>FWHM / G</th>
</tr>
</thead>
<tbody>
<tr>
<td>5166 (7)</td>
<td>88 (13)</td>
</tr>
<tr>
<td>5424 (10)</td>
<td>127 (20)</td>
</tr>
</tbody>
</table>

Since protons are the only abundant spin active nuclei in radicals 5.2-CMu and 5.2-SiMu, and they must be in a suitable location to result in a significant hfc, the μLCR signal is assigned to the pair of inequivalent protons $\beta$ to the unpaired electron in radical 5.2-SiMu. At this point 5.2-SiMu still hasn’t been assigned as Radical A or Radical B. Using Equation (2.55) we can test what the nuclear hfc would be if the μLCR resonances are attributed to either Radical A or Radical B. The resulting values are listed in Table 5.3.

![Radical products from Mu addition to silene 5.2.](image)

Figure 5.6: Radical products from Mu addition to silene 5.2.

Table 5.3: Potential proton hyperfine coupling constants based on a μLCR spectrum from a 1 M solution of 5.2 in THF at 312 K.

<table>
<thead>
<tr>
<th>$B_{res} / G$</th>
<th>$A_p / MHz$</th>
<th>$A_p / MHz$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Radical A ($A_\mu \approx 190$ MHz)</td>
<td>Radical B ($A_\mu \approx 137$ MHz)</td>
</tr>
<tr>
<td>5166 (7)</td>
<td>92.63 (30)</td>
<td>40.32 (14)</td>
</tr>
<tr>
<td>5424 (10)</td>
<td>87.84 (33)</td>
<td>35.54 (19)</td>
</tr>
</tbody>
</table>
5.4 Analysis and Assignments

5.4.1 Computational Models

Geometry modelling computations were run at the UB3LYP/6-31G(d) level for simplified structures of silane 5.2 and its possible radicals, with the modification of replacing the trimethylsilyl (Me3Si-) ligands attached to the ring atoms with methyl groups. These output structures were then used as the starting point for the computation of optimal geometry of 5.2, 5.2-CMu and 5.2-SiMu with the trimethylsilyl ligands, performed at the same computation level. Each radical geometry optimization was followed by a hyperfine coupling constant calculation at the UB3LYP/cc-pVDZ level.

The muon hfcs from these computations are summarized in Table 5.4. Calculated hyperfine coupling constants for the β-protons in 5.2-SiMu are reported in Table 5.5. For both the methyl and the trimethylsilyl ligand calculations, the average β-proton hfc is calculated to be 76.5 MHz.

Table 5.4: Computationally modelled muon hyperfine coupling constants for the radicals from silane 5.2.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Calc (A_\mu) /MHz (R = CH₃)</th>
<th>Calc (A_\mu) /MHz (R = Si(CH₃)₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2-CMu</td>
<td>48</td>
<td>101</td>
</tr>
<tr>
<td>5.2-SiMu</td>
<td>178</td>
<td>226</td>
</tr>
</tbody>
</table>
Table 5.5: Computationally modelled proton hyperfine coupling constants for Radical 5.2-SiMu.

<table>
<thead>
<tr>
<th>Calc $A_p$/MHz (R = CH$_3$)</th>
<th>Calc $A_p$/MHz (R = Si(CH$_3$)$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99 &amp; 54 (Avg. 76.5)</td>
<td>113 &amp; 40 (Avg. 76.5)</td>
</tr>
</tbody>
</table>

5.4.2 Geometries and Thermodynamics

A simplified representation of the optimized 3-dimensional structure of Radical 5.2-CMu is shown in Figure 5.7, and of 5.2-SiMu in Figure 5.8. The methyl groups of the trimethylsilyl ligands have been removed for clarity.

Figure 5.7: The optimized structure of 5.2-CMu with the methyl groups hidden.

Figure 5.8: The optimized structure of 5.2-SiMu with the methyl groups hidden.
For each radical, the difference in the Hartree-Fock energy, $\Delta H$, for the radical and for the silene and hydrogen atom was computed and is given in Table 5.6. As shown in the table, hydrogen atom addition to the carbon atom is thermodynamically preferred by 17.9 kJ mol$^{-1}$. This piece of information also provides guidance on which radical we expect to form preferentially. However, the difference in heats of reaction should not be used to calculated the ratio of products that would form, as that neglects any difference in entropy and assumes thermodynamic control. The ratio of rate constants for the competing reaction channels governs the relative yields of the two radical products. Assuming that the pre-exponential factors are similar, the ratio will be dominated by the difference in activation barriers, which will be much smaller than the energy difference of the products.

Table 5.6: Calculated heat of reaction for the radicals from silene 5.2.

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\Delta H$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2-CMu</td>
<td>-340.2</td>
</tr>
<tr>
<td>5.2-SiMu</td>
<td>-322.3</td>
</tr>
</tbody>
</table>

5.4.3 Radical Assignments

The mechanism illustrated in Figure 5.3 suggests that the major radical (Radical B) should be 5.2-CMu (see Figure 5.6 on Page 117). The calculations reported in Table 5.6 support this assignment, since 5.2-CMu is thermodynamically more stable. Also, the computationally modelled muon hfc for 5.2-CMu, shown in Table 5.4, is smaller than the modelled muon hfc for 5.2-SiMu. This too agrees with the assignment.
of 5.2-CMu as Radical B and 5.2-SiMu as Radical A. As with Buttar and Webster's computational experiment [95], exact matches were not expected, as zero-point vibrational corrections for the radicals were not modelled.

The calculated β-proton hfcs can serve as a final check of our radical assignment. Only 5.2-SiMu has protons β to the unpaired electron, and hence is capable of generating μLCR resonances. Comparing the computed values in Table 5.5 with the possible β-proton hfcs from Table 5.3, we see that assigning 5.2-SiMu as Radical A is the better choice, and that the experimental proton hfcs are 92.63 ± 0.30 and 87.54 ± 0.33 MHz.

5.5 Future Work

This chapter describes an exploratory experiment on silenes. A follow-up experiment that comes immediately to mind is to investigate silene 5.2 by μSR in a non-ether type solvent, and check if the proportion of 5.2-C to 5.2-Si changes. This would be a simple test of the complexation between silene and solvent, and if the ligands that stabilize 5.2 hinder solvent-solute interactions.

A substantial expansion of this research would be to study additional silenes (R₂C=SiR₂), some disilenes, and related heteroatom double-bonded compounds. We have found that muonium addition to the carbon atom was dominant for the silene investigated. Is this typical of such species, and what factors (ligands, temperature, solvent, etc.) might affect the ratio of radical product yields? If one of the doubly-bonded atoms were a germanium or tin atom, would addition to this site be preferable over the carbon or silicon atom? To my knowledge, there have been no H-isotope radical studies
on heteroatom doubly bonded group-14 compounds, beyond those performed by the SFUMU group.

5.6 Conclusions

Muonium has been found to add to both the doubly-bonded carbon and silicon atoms in a silene. Addition to the silenic carbon atom is preferred over the silenic silicon atom by a factor of 2.2. The preference for muonium addition to carbon over silicon in THF supports the reaction mechanism proposed by Leigh, albeit there are differences between this radical reaction and his system.

Of additional interest, we have found that the muon hfcs for the Mu adducts of a silene are similar to the values found in the silylene experiments, supporting our assignment of those radicals as muoniated disilanyl radicals. For the disilanyl radicals, we found that a factor of 20 – 30% was appropriate to correlate the computationally modelled muon hfc with experiment. Like the disilanyl radicals, 5.2-CMu is a β-muoniated silicon-centered radical. However, the C-Mu bond relative to the orbital containing the unpaired electron is calculated to be in a more eclipsed conformation compared to the disilanyl radicals. It would appear that a factor of 35% is applicable for this silicon-based radical. This factor is expected to be due to zero-point vibrational averaging effects, which were not modelled.
CHAPTER 6.
MUONIUM ADDITION TO
GERMANIUM ANALOGUES OF CARBENES:
GERMYLIDENE’S TRAVELS

6.1 Germylidene Chemistry

H₃Ge• is known as the germyl radical. Proton and germanium coupling constants in H₃Ge• have been measured, and compared with the hyperfine coupling constants in the H₃C• and H₃Si• radicals [158,159]. For these small radicals, it was found that the magnitude of the proton hyperfine coupling constant decreased from the methyl radical to the silyl and then increased from the silyl radical to the germyl, as the sign of the hfc changed from negative (CH₃) to positive (SiH₃, GeH₃) [160,161]. The change in sign can be understood in terms of the optimal geometry; the methyl radical is planar, while the silyl and germyl radicals are non-planar. Each of these radicals was produced by hydrogen abstraction from the corresponding -ane.

It is now common to use the term germyl radical when discussing any species of the form R₃Ge•. Germyl radicals where R = Cl [162], CH₃ [163], and C₆H₅ [164], have also been studied by electron paramagnetic resonance (EPR) methods. Cl₃Ge• was obtained from γ radiation of a matrix of Cl₄Ge, while in the case of the alkyl ligands the radicals were generated by hydrogen abstraction from the R₃GeH germene. Since the germanium–hydrogen bond is the weakest in these alkane germanes, in order to create a R₂HGe• radical using this method the parent germene would need to contain two or more hydrogen atoms.
An alternative method of generating germyl radicals is radical addition to germylidenes. Formerly known as germylenes, germylidenes have the chemical structure \( R_2\text{Ge} \) and are germanium analogues of carbenes and silylenes [96]. Just as silyl radicals are important in silicon chemistry, likewise germyl radicals play an important role in synthetic germanium chemistry.

Understanding how the unpaired electron is distributed over the germyl radical is useful for proposing radical reaction mechanisms involving this species. We might expect the chemistry of these germanium compounds to be similar to that of the carbenes and silylenes. However, as we saw in Chapter 4, there is a significant difference in the chemistry of these two lighter group-14 elements: muoniated radicals from carbenes are stable within the \( \mu \text{SR} \) experimental time frame, while muoniated silyl radicals react with silylene molecules to form disilanyl radicals. Do germyl radicals behave more like the carbon or the silicon analogues, or do they behave in a unique manner?

When dialkyl silylene 5.1, is reacted with 2,2,6,6-tetramethylpiperidine-1-oxyl (commonly referred to as TEMPO), 1,3-disiladioxetane (6.1) is produced with 2,2,6,6-tetramethylpiperidine (TMP) as a side product, as shown in Figure 6.1 [165].

Compound 6.1 is referred to as a 1:1 product since the dialkyl silylene reacts with TEMPO in a 1:1 ratio. The analogous dialkyl germylidene, on the other hand, generates a 1:2 product upon reaction with TEMPO. Even the unsaturated silylene 4.4 has a different reactivity with TEMPO from either of these compounds [166]. Thus, there is precedence for silylene and germylidene molecules to behave differently in radical reactions.
EPR data has been collected on the radical products of 6.2 with bulky free-radicals [167], but there is no equivalent data for the reaction of the hydrogen atom with germylidenes. In the case of silylenes we saw that the species formed by hydrogen isotope addition quickly reacted further to form a disilanyl radical, while the addition of larger radicals produced silyl radicals stable on the EPR timescale [111]. Therefore, the germylidene EPR experiments using large free-radicals should not be assumed to predict the result of Mu addition.

Figure 6.1: Difference in reactivity of a dialkyl silylene and a dialkyl germylidene with TEMPO.

Figure 6.2: 1,3-bis(tert-butyl)-germylimidazol-2-ylidene, whose reactions with large free radicals to form germyl radicals, were studied by Tumanskii et al. [167].
6.2 μSR Experiments

Muoniated radicals from germylidene 6.2 and those illustrated in Figure 6.3 were investigated by μSR techniques. The germylidenes were synthesized and purified by Dr. R. West's team at the Organosilicon Research Center at the University of Wisconsin. Germylidene 6.2 was investigated in THF at concentrations of 0.26, 1.1, and 3.1 M; Compound 6.3 as a neat liquid sample; and 6.4 as a 1.56 M THF solution.

![Figure 6.3: Additional germylidenes used in μSR experiments.](image)

6.2.1 Transverse Field Muon Spin Rotation

Most of our TF-μSR experiments are run at high fields (ie. near 15 kG) to take advantage of on the focusing effect the field can have on the muon beam. However, to measure some muon hyperfine coupling constants lower fields may be more desirable. Specifically, if the value of $A_\mu$ is quite large, then the high frequency radical peak might be out of the range of detectable frequencies. Early experiments with germylidene 6.2 suggested the muon hfc was large enough to warrant repeating the experiment in a lower magnetic field.

A TF-μSR spectrum from germylidene 6.2 is shown in Figure 6.4. This spectrum was generated using the asymmetry data from a pair of positron detectors (e.g. LU and RD in Figure 3.3). When using only a pair of detectors arranged 180° relative to each
other with respect to the sample position, we are unable to differentiate positive and negative frequencies.

At a field of 3.9 kG, we expect the diamagnetic signal to appear near 52 MHz. The other two signals, near 264 and 389 MHz, do not appear to be on either side of the diamagnetic peak, as was the case for TF-μSR spectra in the earlier chapters. This is because one of the two peaks is due to a negative frequency. We can obtain the muon hfc from Figure 6.4 as the sum of the two radical frequencies, which is about 653 MHz. At a field of only 3.9 kG, the diamagnetic frequency is not equal to the average frequency of the two radical signals. However, we can still use this approximation to test our guess that the lower frequency radical peak is negative in sign. If the radical frequencies are –264 and +389 MHz, then the average value is 62.5 MHz. This isn’t far from the position of the diamagnetic peak, 52 MHz.

![Figure 6.4: TF-μSR spectra from a 1.1 M solution of germylidene 6.2 in THF at 272 K and 3.9 kG. At this magnetic field, the diamagnetic signal is near 52 MHz.](image)

To confirm our suspicions that one of these signals is a negative frequency, we can change the field and observe which direction the peaks move. When increasing the
field, the diamagnetic peak will shift toward more positive frequencies, as predicted by Equations (2.6) and (2.37). Both radical peaks will follow suit, as described by Equations (2.34) and (2.35), but the spacing between them will remain constant. Hence, the positive radical frequency will shift to the right of the spectrum, while the negative radical frequency will move toward the left end of the spectrum (less negative frequencies). As will be discussed later in this section, this procedure was used for germylidene 6.4.

Another method of confirming which signals are positive frequencies, and which are negative frequencies, is to use perpendicular detectors for quadrature detection and complex Fourier transformation. Positive frequencies are shown in Figure 6.5a, while negative plotted in Figure 6.5b. The entire spectrum, with positive and negative frequencies properly assigned, is displayed in Figure 6.5c. A small signal at -52 MHz, due to a reflection of the +52 MHz diamagnetic signal, has been suppressed for clarity.

The muon hfc values, as determined from TF-μSR spectra, are listed in Table 6.1 as a function of temperature. Since this data was collected in a relatively low magnetic field, $A_\mu$ should not be obtained by approximating Equation (2.36) with Equation (2.37), as this would introduce errors from second-order terms in the expressions for the energy level separations. A plot of the temperature dependence of this muon hfc is provided in Figure 6.6.
Figure 6.5: TF-μSR spectrum from a 1.1 M solution of germylidene 6.2 in THF at 3.9 kG and 272 K. (a) Positive precession frequencies; (b) negative precession frequencies; (c) complete spectrum with negative precession frequency signals properly separated from the positive ones.

Table 6.1: Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.2 in THF at a concentration of 1.1 M.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$A_{\mu}$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>272</td>
<td>653.08 (3)</td>
</tr>
<tr>
<td>298</td>
<td>650.39 (3)</td>
</tr>
<tr>
<td>299</td>
<td>650.18 (6)</td>
</tr>
<tr>
<td>309</td>
<td>649.11 (4)</td>
</tr>
<tr>
<td>323</td>
<td>647.70 (3)</td>
</tr>
<tr>
<td>351</td>
<td>644.80 (7)</td>
</tr>
</tbody>
</table>
Figure 6.6: Temperature dependence of the muon hyperfine coupling constant in the muoniated radical from unsaturated germylidene 6.2. The line is meant as a visual guide only. The error bars in $A_{\mu}$ are smaller than the shapes used to represent the data points.

Germylidene 6.3 (see Figure 6.3 on Page 126) is acyclic, and I was curious how this feature would affect the distribution of unpaired electron spin within the radical. The radical signals in the TF-\textmu SR spectrum were significantly weaker in a neat liquid sample of 6.3 than the 1.1 M THF solution of 6.2. The plot is shown in Figure 6.7, with the small signal at -26 MHz (a reflection of the +26 MHz diamagnetic signal) suppressed for clarity. Originally, I suspected that in the neat sample there was a larger fraction of muons which exist in a diamagnetic environment (and hence a smaller muonium fraction). However, the amplitude of the diamagnetic peak is actually larger in the spectrum from 6.2. It seems that there must be some other process occurring in the neat sample, resulting in a larger lost fraction than for the THF solution. Further investigation is warranted. The muon hfc for the radical from 6.3 was measured at two temperatures, and both values are reported in Table 6.2.
Figure 6.7: TF-μSR spectrum from a neat sample of acyclic germylidene 6.3 at 1.9 kG and 298 K, with the negative frequency signals properly separated from the positive ones.

Table 6.2: Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.3.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$A_\mu$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>284</td>
<td>598.0 (4)</td>
</tr>
<tr>
<td>298</td>
<td>593.3 (4)</td>
</tr>
</tbody>
</table>

Germylidene 6.4 (see Figure 6.3 on Page 126) was also studied by μSR methods as a 1.56 M THF solution. Initial studies on solutions of 6.4 suggested weak radical signals were present near the limit of our frequency detection range (~ 425 and 525 MHz). If these signals could be confirmed this was clearly going to be larger than the muon hfcs in the previously studied germylidene based radicals. In fact, to our knowledge, for a muoniated radical this would be the largest muon hyperfine coupling constant ever measured!
The spectrum was collected at a higher magnetic field (14.5 kG) to move the negative radical signal into a frequency region of better detector efficiency. Figure 6.8 shows the resulting spectrum, with positive and negative frequencies separated out, and the reflection of the diamagnetic signal removed. A weak radical peak appears near -275 MHz. To confirm this signal, the experiment was repeated at a magnetic field of 19.3 kG; the spectrum is given in Figure 6.9, again with the reflection of the diamagnetic signal hidden. Under these conditions the diamagnetic signal would move to higher frequencies by about 65 MHz, and the radical peak should behave similarly. The weak signal shifted appropriately, and is thus determined to be due to a muoniated radical. The corresponding $A_{\mu}$ is $(946.9 \pm 0.8)$ MHz.

Figure 6.8: TF-μSR spectrum from a 1.56 M solution of germylidene 6.4 in THF at 14.5 kG and 298 K, with the negative frequency signals properly separated from the positive ones.
6.3 Computational Models and Radical Assignments

While we have endeavoured to collect $\mu$LCR data on the radicals from 6.2, 6.3, and 6.4, so far we have not been successful. This forces us to rely more heavily on molecular modelling to determine our radical assignments.

6.3.1 Germylidene and Germyl Geometries and Hyperfine Coupling Constant Modelling

Initial calculations of 6.2 were run with a simplified structure where the tert-butyl ligands were replaced with methyl groups. Geometry optimization was done at the UB3LYP/6-31G(d) level. The output structure was then used as the starting point for the computation of optimal geometry of both the germyl and digermanyl radicals with H attached to the germanium atom, and the radical from H addition to a ring carbon atom of 6.2. The radical geometry optimization was followed by a hyperfine coupling constant calculation. As in previous chapters, the cc-pVDZ basis set was used in place of the
more commonly used EPR-III basis set because EPR-III is optimized for the H, B, C, N, O, and F atoms, which does not include the germanium atom found in these radicals. The predicted muon hfcs for the germyl and alkyl radicals are listed in Table 6.3.

Attempts at modelling the geometry of digermanyl radical 6.2c, shown in Figure 6.10, yielded a germyl radical and a separate germylidene molecule; the two germanium atoms were over 5.1 Å apart, and more than 97 % of the unpaired electron spin density was localized on the hydrogen–adduct ring. Therefore, the digermanyl radical is not stable. The $A_{\mu}$ corresponding to the attempts to model the digermanyl radical was similar to the value for the germyl radical, as it is representative of the germyl radical with minor distortions due to a neighbouring germylidene molecule.

Table 6.3: Computational germyl, alkyl, and digermanyl radical muon hyperfine coupling constants for radicals from 6.2. The experimentally observed radical exhibits a muon hfc of 650 MHz at 298 K.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Label</th>
<th>Calc $A_{\mu}$ /MHz (R = CH$_3$)</th>
<th>Calc $A_{\mu}$ /MHz (R = t-Bu)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Radical 6.2a" /></td>
<td>6.2a</td>
<td>485</td>
<td>542</td>
</tr>
<tr>
<td><img src="image" alt="Radical 6.2b" /></td>
<td>6.2b</td>
<td>326</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 6.10: Attempts to model digermanyl radical 6.2c demonstrated that this species is not stable. The two germanium atoms were over 5.1 Å apart in the minimum energy structure.

The acyclic germylidene geometry was optimized using the UB3LYP/6-31G(d) functional/basis set, and the expected radical from Mu addition to this species was modelled using the combination of UB3LYP/cc-pVDZ/UB3LYP/6-31G(d) calculations for hfc's and geometry. The computed muon hfc is reported in Table 6.4.

Table 6.4: Computational germyl radical muon hyperfine coupling constant for the anticipated radical from 6.3. The experimentally determined muon hfc is 593 MHz at 298 K.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Label</th>
<th>Calc $A_\mu$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{N} \cdot \text{Ge} \cdot \text{Mu}$</td>
<td>6.3a</td>
<td>482</td>
</tr>
</tbody>
</table>

Before modelling 6.4 and its potential radicals, the geometry for 6.5 and the corresponding radicals were computationally studied. Compounds 6.4 and 6.5 differ only in the additional tert-butyl group attached to the ring carbon in 6.4. The resulting muon hfc's are collected in Table 6.5.
Figure 6.11: Germylidene 6.5 has been studied only by computational methods.

Since the germyl radical from 6.5 is close to the experimental muon hfc from the solution of 6.4 (if a multiplication factor to represent vibrational averaging effects of roughly 20% is applied), the germyl radical from 6.4 was modelled. The germyl radicals from 6.4 and 6.5 have similar $A_\mu$ values, so it seems that the tert-butyl ligand on the ring carbon does not drastically affect the muon hfcs. The digermanyl radical of 6.5, on the other hand, has a significantly different muon hfc from the germyl radical, and so it was expected that the $A_\mu$ value for the digermanyl radical of 6.4 would also be far removed from the germyl radical muon hfc. As such, the digermanyl radical of 6.4 was not modelled.

Muonium can add on the same side (syn) or the opposite side (anti) of the ring with respect to the tert-butyl ligand. These two structures were modelled. $6.4a$-anti was calculated to be 45.7 kJ mol$^{-1}$ more stable than the -syn conformer.
Table 6.5: Computational muon hyperfine coupling constants from the germyl radicals of 6.4 and 6.5, and the digermanyl radical of 6.5. The experimental muon hfc for the radical from germylidene 6.4 is 947 MHz at 298 K.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Label</th>
<th>Calc $A_{\mu}$/MHz (R = CH$_3$)</th>
<th>Calc $A_{\mu}$/MHz (R = t-Bu)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Germyl Radical" /></td>
<td>6.4a-syn</td>
<td>-</td>
<td>820</td>
</tr>
<tr>
<td><img src="image" alt="Germyl Radical" /></td>
<td>6.4a-anti</td>
<td>-</td>
<td>771</td>
</tr>
<tr>
<td><img src="image" alt="Germyl Radical" /></td>
<td>6.5a</td>
<td>906</td>
<td>839</td>
</tr>
<tr>
<td><img src="image" alt="Germyl Radical" /></td>
<td>6.5b</td>
<td>256</td>
<td>-</td>
</tr>
</tbody>
</table>

6.3.2 Radical Assignments

For germylidene 6.2, muonium adds to the germanium atom and the resulting germyl radical does not react with another germylidene molecule within the time window of the TF-μSR experiment. The ratio of the experimental and computationally modelled $A_{\mu}$ is about 1.20. A factor of 20%, presumably due to vibrational averaging effects, is
not unreasonable. Germylidene 6.3 also reacts with muonium to form a germyl radical, and the ratio of experimental and modelled muon hfcs is 23 %.

The TF-μSR spectra from germylidene 6.4 have weak radical signals. The ratio for the experimental and calculated muon hfcs ranges from 15 % for the less stable -syn conformer and 23 % for the preferred -anti conformer. Since the 6.4a-syn radical is significantly less stable than the 6.4a-anti radical, this cannot be attributed to reversible interconversion between the two radical conformations. However, if the rate of formation of 6.4a-syn is fast enough to compete with 6.4a-anti formation then there may be some dephasing of the muon polarization as the syn conformer converts to the anti structure. To test for this, I transformed the time-spectrum over different time ranges, looking for changes in the shape of the radical peak. I found that if very early data ($t < 0.1 \, \mu s$) are excluded the radical peak disappears, either meaning that the radical species is very short-lived or that dephasing of the muon polarization happens very quickly. It is unclear whether interconversion is happening and is responsible for the loss of muon polarization, or if there is a secondary reaction consuming the germyl radical.

6.4 Alkyl, Silyl, and Germyl Reactivities

In Chapter 4 we noted that in μSR studies on carbenes we detect radicals from Mu addition to the carbeneic carbon atom. In the same chapter, we found that Mu adds to the silenic silicon atom in silylenes, and the resulting radical reacts further to form a disilanyl radical. In this chapter, we found that germylidenes behave more like carbenes than silylenes, with the germyl radical from Mu addition to a germylidene not reacting further with another germylidene molecule in the μSR experimental time window.
To understand why silicon is the ‘odd man out’ we began by considering the equilibrium between triaminoethene and two separate carbene molecules, which is called the Wanzlick Equilibrium [131]. In the 1960s Lemal et al. and Winberg et al. performed experiments on ethenes, and Lemal suggested that electrophiles cleave the carbon–carbon double bond forming carbenes [168,169].

Alder has furthered the understanding of Wanzlick-type equilibria using electrophiles [170,171]. He found that some persistent carbenes readily dimerize in the presence of a source of protons, and that the reaction is not second-, but first-order in carbene. The proposed mechanism is shown in Figure 6.12. Proton transfer to the carbene, generating a formamidinium ion, is a similar process to the radical reaction of Mu addition to a carbene. The subsequent reaction of the formamidinium ion with a carbene molecule depends on the Lewis acidity of the ion and the Lewis basicity of the carbene. If the combination reaction occurs, the substituted ethane ion can then be deprotonated by a carbene, regenerating the formamidinium ion.

\[
\begin{align*}
\text{Et}_2\text{N} & \quad + \quad \text{H}^+ \\
\text{Et}_2\text{N} & \quad \text{Et}_2\text{N}^+ \\
\text{Et}_2\text{N} & \quad \text{Et}_2\text{N} \\
\text{Et}_2\text{N} & \quad \text{Et}_2\text{N} \\
\text{Et}_2\text{N} & \quad \text{Et}_2\text{N} \\
\text{Et}_2\text{N} & \quad \text{Et}_2\text{N} \\
\text{Et}_2\text{N} & \quad \text{Et}_2\text{N} \\
\end{align*}
\]

Figure 6.12: Proton promoted dimerization of carbenes to form an ethene.
As a qualitative argument, moving down column 14 in the periodic table the non-bonding electrons of the silylene molecule are more loosely held (more reactive) than for the carbene since they are further from the nucleus. Based on this we might expect that the silylene molecules are better Lewis bases than carbene molecules. The silyl radical, however, would be a worse Lewis acid than the corresponding alkyl radical as the silicon atom is less electronegative than the carbon atom. While the radical’s acidity may have decreased, the increased basicity of the parent molecule shifts the combination equilibrium toward the disilanyl radical.

This argument can be carried over to the germyl-germylidene combination reaction (see Figure 6.13). A germylidene molecule may have an increased basic nature relative to the silylene and carbene analogues. A germyl radical, on the other hand, would then be a worse Lewis acid than the silyl or alkyl analogues. This could explain why the disilanyl radical readily forms while the dialkyl and digermanyl radicals do not; the silicon case is at the balance point of optimal Lewis acidity and basicity of reactants.

![Figure 6.13: Relative Lewis basicity of carbenes, silylenes, and germylidenes, and the relative Lewis acidity of their corresponding muoniated radicals.](image)

140
6.5 Concentration effects on Germyl Hyperfine Coupling Constants

Germyl radical 6.2a was detected by TF-μSR in solutions of 6.2 in THF at concentrations of 0.26 M, 1.1 M, and 3.1 M. The muon hfc was measured as a function of temperature for each of the three samples, and the results are reported in Table 6.6, Table 6.1, and Table 6.7, respectively. Figure 6.14 shows that the temperature dependence of $A_\mu$ is essentially parallel for these three solutions, but that there is also distinct concentration dependence.

Table 6.6: Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.2 in THF at a concentration of 0.26 M.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$A_\mu$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>277</td>
<td>651.33 (5)</td>
</tr>
<tr>
<td>299</td>
<td>649.25 (5)</td>
</tr>
<tr>
<td>312</td>
<td>647.85 (3)</td>
</tr>
</tbody>
</table>

Table 6.7: Muon hyperfine coupling constant as a function of temperature in the muoniated radical from 6.2 in THF at a concentration of 3.1 M.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$A_\mu$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>654.34 (5)</td>
</tr>
<tr>
<td>281</td>
<td>653.21 (5)</td>
</tr>
<tr>
<td>290</td>
<td>652.51 (4)</td>
</tr>
<tr>
<td>310</td>
<td>650.65 (6)</td>
</tr>
<tr>
<td>322</td>
<td>649.59 (6)</td>
</tr>
<tr>
<td>332</td>
<td>648.45 (4)</td>
</tr>
</tbody>
</table>
Reddoch and Konishi have developed a dipole–dipole reaction field model to explain solvent dependency of the $^{14}\text{N}$ hfcs in di-tert-butyl-nitroxide (DTBN) [172]. They computed the additional electric field at the center of the NO group that is due to the dipole moment of the nearest neighbour solvent molecule, and concluded that $A_{\text{N-14}}$ exhibits linear dependency on the solvent dipole moment concentration, defined as

$$[\mu] = \mu \frac{\rho}{M},$$

(6.1)

where $\mu$ is the dipole moment of the solvent, $\rho$ is the solvent density, and $M$ the molecular weight of the solvent. The linear dependency of the nuclear hfc can be expressed as

$$A = C_1 + C_2 [\mu],$$

(6.2)
where \( C_1 \) and \( C_2 \) are empirical constants that depend on the type of radical under consideration.

If the solute is of sufficient concentration and has a dipole moment, the solute itself can also influence the unpaired electron spin density in the radical species. Under these conditions, the overall dipole moment concentration would be used in Equation (6.2), and is calculated as

\[
[L_{\text{Overall}}] = [L_{\text{Solvent}}] \chi_{\text{Solvent}} + [L_{\text{Solute}}] \chi_{\text{Solute}},
\]

(6.3)

where \( \chi \) represents mole fractions.

In the gas phase, THF has a dipole moment of 1.63 D. The density of THF is 0.8892 g cm\(^{-3}\) at 20\(^\circ\)C, and this value was used to determine a solvent dipole moment concentration of 20.1 D mol dm\(^{-3}\). The calculated dipole moment for germylidene 6.2 is 1.81 D. The density of the germylidene is approximately 1.9 g cm\(^{-3}\), and we calculate a solvent dipole moment concentration of 14.3 D mol dm\(^{-3}\).

TF-\(\mu\)SR spectra were collected over a range of temperatures from 270 K to 351 K, and for each concentration a spectrum was collected near 310 K. The value of \( A_{\mu} \) at 310 K in each solution was interpolated from the linear fits of the experimental data. These values were then fit to Equation (6.2), yielding

\[
A_{\mu} (T = 310 \text{ K}) = 694.1(6) \text{ MHz} - 2.29(3) \frac{\text{MHz dm}^3}{\text{D mol}} \left[ L_{\text{Overall}} \right],
\]

(6.4)

Since the two mole fractions must sum to unity, inserting Equation (6.3) into Equation (6.4) yields an expression for the muon hfc as a function of mole fraction of germylidene. The fit of Equation (6.4), expressed as a function of \( \chi_{\text{Germylidene}} \), is displayed in Figure 6.15.
along with the interpolated muon hfc's at 310 K. The concentration dependence of $A_\mu$ is consistent with the linear dependence predicted by Equation (6.2).

![Graph](image)

Figure 6.15: Interpolated muon hyperfine coupling constant in the muoniated radical from unsaturated germlylidene 6.2 at 310 K, as a function of germlylidene mole fraction. The line represents the fit of Reddoch and Konishi's dipole–dipole reaction field model. The error bars in $A_\mu$ are smaller than the shapes used to represent the data points.

### 6.6 Future Work

To date no LCR resonances have been observed for muoniated radicals from germlyidenes. Measurement of the ring $^{14}$N hfc's, and the ring protons in appropriate radicals, would provide insight into the fraction of the unpaired electron spin density that is dispersed away from the germanium atom, relative to the silicon and carbon analogues.

As new germlyidenes become available, it will be interesting to check if variation of ligands alters the reactivity of the germyl radical with neighbouring germlylidene molecules. With carbenes, silylenes, and germlyidenes now investigated by $\mu$SR techniques, it seems natural that future studies will include the tin analogue, stannylidenes.
6.7 Conclusions

Muonium adds to germylidenes at the germanium atom, generating germyl radicals. These species are stable on the $\mu$SR time scale, and do not react further like the silicon analogues. A factor of roughly 20 – 23 %, due to vibrational averaging effects not considered in my models, appears to be appropriate for germyl radicals. The germylidene concentration dependence of the muon hfc in 6.2 was successfully explained in terms of Reddoch and Konishi's dipole–dipole reaction field model.
CHAPTER 7.
THE REARRANGEMENT OF AZULENE TO NAPHTHALENE:
A TALE OF TWO CHEMICALS

“Clearly, further experimental evidence is necessary to make definite conclusions about the most likely mechanism.”
– Dr. A. Stirling, on the rearrangement of azulene to naphthalene [173].

7.1 The History of Azulene

As early as the 15th century an azure-blue extract was produced by steam distillation of chamomile. It was not until 1863, however, that Septimus Piesse discovered the compound responsible for the colouration from distillates of yarrow and wormwood, and named it azulene [174]. The structure of azulene remained a mystery until Lavoslav (Leopold) Ružička, winner of the 1939 Nobel Prize in Chemistry, suggested the linked 5- and 7-membered rings that we recognize today [175]. Figure 7.1 shows the numbering system I will use when discussing azulene.

![Figure 7.1: Chemical structure of azulene, displaying the numbering system used in this thesis.](image)

Placidus Plattner performed the first organic synthesis of azulene in 1937 [176] (coincidently the same year that Neddermeyer and Anderson discovered the muon). A nuclear magnetic resonance spectrum of azulene was published in 1958 by Schneider et
This work was followed up in 1961 by a study of π-electron densities in azulene from \(^{13}\)C and \(^1\)H nuclear magnetic resonance shifts [178]. Historically, azulene has been a relatively expensive material. In 2005, it cost roughly $500 to purchase just a few grams. Proponents of a novel synthetic method for preparing azulene from cycloheptatriene suggest it will help to make azulene and its derivatives more affordable [179].

7.2 The Naphthalene Connection

7.2.1 Experimental Methods

Naphthalene, well known for its use in mothballs, is a chemical isomer of azulene. While naphthalene is non-polar, azulene has a permanent dipole moment of 0.80 ± 0.02 D, with the smaller of the two rings being the negative end of the molecule [180].

![Figure 7.2: (a) Mulliken atomic charges in azulene computed by DFT methods at the UB3LYP/6-31G(d) level; (b) azulene atomic charges with hydrogens summed into heavy atoms.](image)

Comparing the structures of azulene and naphthalene, shown in Figure 7.1 and Figure 7.3, one can imagine a structural rearrangement occurring where azulene is...
transformed into the more thermodynamically stable naphthalene. Heilbronner et al. reported such a conversion in 1947 [181], and since that time both experimentalists and theoreticians have endeavoured to elicit the reaction pathway. Traditionally, the experiments have focused on end-product analysis from samples of $^{13}$C labelled azulenes or substituted azulenes.

Figure 7.3: Chemical structure of naphthalene. The numbering system used for naphthalene is not meant to directly relate to the system used for azulene.

Becker et al. subjected 4-$^{13}$C-azulene to photolysis and to flash thermolysis, and were unable to explain the distribution of resulting napthalenes [182]. Zeller and Wentrup investigated the flash thermolysis of 4,7-$^{13}$C$_2$-azulene and formulated their norcaradiene-vinylidene mechanism. However, three of the observed products could not be explained by this mechanism [183]. Scott and Kirms approached the challenge using 1-$^{13}$C-azulene and 9-$^{13}$C-azulene [184,185]. They were unsuccessful at explaining their results in terms of a mechanism as well. In addition to these carbon-labelling techniques, deuterium labelling at carbons 2 and 4 of azulene have also been studied in an attempt to elicit better understand of the reactions involved in the transformation [182,186].

Use of substituent groups in place of the hydrogen atoms has also been a popular method for garnering experimental data on the azulene-to-naphthalene rearrangement. Methyl, dimethyl, and trimethyl substitutions have been carried out [186,187,188,189,190]. Similarly, cyano groups have been attached to carbons 1 and 2.
of azulene, dicarbomethoxy substitutions performed at carbons 4 and 5, and other functional groups have been employed [186,187,191].

Additional methods and types of spectroscopy have also been used in an effort to uncover the process of this rearrangement [192,193]. Based on these results reaction models have been discussed, but no single model has proven completely adequate [194,195,196,197].

7.2.2 Computational Approaches

Recently, computational studies have proposed competition between two different radical-promoted reaction mechanisms as the process responsible for the thermal rearrangement of azulene into naphthalene [173,198]. The activation energies for all intramolecular pathways considered are between 19.5 and 23.6 kJ mol$^{-1}$, while the radical routes have activation barriers of only 5.7 to 9.3 kJ mol$^{-1}$.

In describing possible mechanisms, I will follow Alder's convention [198]; the species formed by the addition of a free radical to azulene will be referred to as an $n$-$X$-azulyl radical, where $n$ denotes the site of addition (based on Figure 7.1) and $X$ is the attacking radical. One of the radical mechanisms is called the Spiran Pathway [198], and is shown in Figure 7.4. This conversion process begins with hydrogen atom transfer to a carbon in the five membered ring of azulene, producing one of the three possible radicals: 1-, 2-, or 9-$H$-azulyl. The other two radicals, 3- and 10-$H$-azulyl are equivalent to one of the three species just discussed. The Methylene Walk is the other radical mechanism used to describe the rearrangement [198], and is provided in Figure 7.5. This route is initiated by H-atom addition to a carbon in the seven membered ring of azulene, not
counting the two bridging atoms. The potential species are the 4-, 5-, and 6-$H$-azulyl radicals. Again, due to symmetry, the 7- and 8-$H$-azulyl radicals are already considered.

Figure 7.4: The Spiran mechanism [198].
Figure 7.5: The Methylene Walk mechanism [198].
7.3 Using Muonium to Investigate Azulene

Both of the radical-promoted pathways proposed involve an azulene intermediate with an •H (or •CH$_2$–) unit attached to carbon-9. Our experience with radical adducts of polycyclic hydrocarbons [199,200,201] made us question the likelihood of detecting hydrogen atom addition at the bridgehead carbons (Sites 9/10 in azulene) due to the thermodynamic preference for addition to other sites [198].

For the radical promoted pathways to be serious contenders in this debate, as Stirling pointed out, experimental data on hydrogen radical adducts of azulene is required. Using the light isotope of hydrogen, muonium, we set out to investigate which of the six possible radicals would form by muonium addition.

Due to the symmetry of azulene, sites 2 and 6 are singly degenerate, while the other four sites are doubly degenerate, so if all other things are equal it may be expected that 2-Mu-azu1yl and 6-Mu-azulyl would form in half the proportion of the other radicals. However, there are other factors affecting the distribution of radicals, including charge distribution and relative reactivity of sites, the thermodynamic stability of the radical products, and transition-state barrier heights.

The most thermodynamically stable radicals are the 1-H and 2-H adducts. It should be noted that both of these radicals are invoked by the Spiran mechanism for rearrangement to naphthalene. Thus, if no other hydrogen isotope radicals were observed during the time domain of the μSR technique then this would provide experimental evidence to seriously question if the Methylene Walk pathway is involved in the thermal rearrangement of azulene to naphthalene. Conversely, if additional radicals were
detected then this data could substantiate the proposed competition between the Spiran
and Methylene-Walk mechanisms.

7.4 Muoniated Azulyl Radical Experiments

7.4.1 DFT Calculations for Muoniated Azulyl Radicals

Rudimentary calculations on the hfcs in azulene anion radicals and cation radicals
exist [202,203]. These methods, however, are generally outdated, and the geometry of
the charged azulene radicals should not be expected to describe the structure of a neutral
n-H-azulyl radical. No calculations for the hfcs in an n-H-azulyl radical can be found in
the literature. For this reason, it was important for us to run DFT calculations on the
n-H-azulyl radicals to compare with our experimental data.

7.4.1.1 Geometry Optimization Calculations

First, the structures of azulene and its six hydrogen adducts must be modelled. DFT
calculations were performed using the same functional/basis set pair as Alder,
UB3LYP/6-31G(d), to test the reproducibility of the relative energies of formation, and
additional computations were run to determine the zero-point energy corrections to the
ergies for muonium. The computed values are listed in Table 7.1, and are reported
relative to the most stable of the six radicals. All of these hydrogen addition reactions are
calculated to be exothermic, with reaction enthalpies ranging from -152 kJ mol$^{-1}$ for
9-H-azulyl to -189 kJ mol$^{-1}$ for 1-H-azulyl.

Other basis sets yielded similar relative energies. While the relative energies did
not change significantly, the modelled geometry of some of the radicals was highly
dependent on the choice of basis set. The predicted geometry then has an effect on the
anticipated muon and proton hfcs in the radical. A more detailed discussion on this topic is given in Section 7.5.

Table 7.1: Calculated energies of formation of the six hydrogen isotope adducts of azulene, with and without zero point energy corrections for hydrogen and its light “isotope”, Mu.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Without z.p.e. correction</th>
<th>With z.p.e. correction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alder†ΔE/kJ mol⁻¹</td>
<td>McCollumΔE/kJ mol⁻¹</td>
</tr>
<tr>
<td>1-H-azulyl</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2-H-azulyl</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>6-H-azulyl</td>
<td>24.1</td>
<td>24.3</td>
</tr>
<tr>
<td>4-H-azulyl</td>
<td>30.7</td>
<td>30.8</td>
</tr>
<tr>
<td>5-H-azulyl</td>
<td>30.9</td>
<td>31.0</td>
</tr>
<tr>
<td>9-H-azulyl</td>
<td>37.5</td>
<td>37.6</td>
</tr>
</tbody>
</table>

† See Reference [198].

7.4.1.2 Transition State Calculations for Muoniated Azulyl Radicals

The transition states for the formation of each of the six n-H-azulyl radicals were computationally modelled. The QST2 option was used in conjunction with UB3LYP/6-31G(d). This option calls on the Synchronous Transit-Guided Quasi-Newton (STQN) Method, developed by C. Peng and H. B. Schlegel [204]. QST2 uses the input of reagent and product geometries to predict the transition structure. The calculated energy barriers, relative to the starting materials of azulene and the hydrogen atom, are tallied in Table 7.2.

1-H-azulyl is the only reaction that was predicted to have no formation reaction barrier. The QST3 option, similar to QST2, invokes the STQN Method, but it requires an
approximate transition state geometry as well as input structures for the reactants and products. QST3 was used with UB3LYP/6-31G(d) to confirm that formation of 1-$H$-azulyl has no reaction barrier.

In terms of increasing reaction barrier, the radicals follow the same order as in Table 7.1. The largest barrier to reaction is for 9-$H$-azulyl. Combining this with the fact that it is predicted to be the least thermodynamically stable of the six radicals, strongly suggests that it is the least likely to be observed.

Table 7.2: Energies of the transition states along the reaction coordinates for the six hydrogen isotope adducts of azulene, relative to the starting materials.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Transition State Barrier Height /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-$H$-azulyl</td>
<td>No Barrier</td>
</tr>
<tr>
<td>2-$H$-azulyl</td>
<td>2.6</td>
</tr>
<tr>
<td>6-$H$-azulyl</td>
<td>6.2</td>
</tr>
<tr>
<td>4-$H$-azulyl</td>
<td>7.9</td>
</tr>
<tr>
<td>5-$H$-azulyl</td>
<td>5.2</td>
</tr>
<tr>
<td>9-$H$-azulyl</td>
<td>14.1</td>
</tr>
</tbody>
</table>

7.4.2 TF-μSR Experiments with Azulene

TF-μSR data was collected on radicals produced from azulene dissolved in tetrahydrofuran (THF) at temperatures of 2 and 25°C at concentrations of 0.4 and 1.5 M, respectively. Additionally, neat azulene (recrystallized from THF) was studied above its melting point, at 109°C. All samples were sealed oxygen-free in stainless steel vessels
fitted with a thin steel foil window. Sample temperatures were maintained by passing fluid from a constant temperature bath through the sample mount, which was surrounded by vacuum.

An example of a TF-μSR spectrum from azulene in THF is given in Figure 7.6, and another of azulene melt in Figure 7.7. For each spectrum, the large truncated peak is due to muons in a diamagnetic environment. The radical signals appear as pairs spaced approximately evenly about the diamagnetic peak, each pair representing one radical species. The resulting hfcs are collected in Table 7.3.

Figure 7.6: TF-μSR spectrum from 1.5 M azulene in THF at 25°C in an applied magnetic field of 12.5 kG.
Figure 7.7: TF-μSR spectrum from neat azulene at 109°C in an applied magnetic field of 12.5 kG.

Table 7.3: Muon hyperfine coupling constants of radicals detected in azulene.

<table>
<thead>
<tr>
<th>Radical</th>
<th>$A_\mu(2^\circ C)$ /MHz</th>
<th>$A_\mu(25^\circ C)$ /MHz</th>
<th>$A_\mu(109^\circ C)$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical A</td>
<td>73.42 (2)</td>
<td>74.86 (2)</td>
<td>79.58 (2)</td>
</tr>
<tr>
<td>Radical B</td>
<td>205.00 (4)</td>
<td>201.14 (3)</td>
<td>192.40 (2)</td>
</tr>
<tr>
<td>Radical C</td>
<td>226.89 (2)</td>
<td>226.37 (3)</td>
<td>225.12 (2)</td>
</tr>
<tr>
<td>Radical D</td>
<td>270.89 (4)</td>
<td>268.58 (3)</td>
<td>259.66 (5)</td>
</tr>
</tbody>
</table>
Table 7.4: Transverse field signal amplitudes relative to Radical A.

<table>
<thead>
<tr>
<th></th>
<th>Amplitude (2°C)</th>
<th>Amplitude (25°C)</th>
<th>Amplitude (109°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical A</td>
<td>1.00 (6)</td>
<td>1.00 (5)</td>
<td>1.00 (4)</td>
</tr>
<tr>
<td>Radical B</td>
<td>0.86 (3)</td>
<td>0.92 (3)</td>
<td>0.91 (2)</td>
</tr>
<tr>
<td>Radical C</td>
<td>0.52 (3)</td>
<td>0.46 (2)</td>
<td>0.32 (3)</td>
</tr>
<tr>
<td>Radical D</td>
<td>0.34 (3)</td>
<td>0.23 (5)</td>
<td>0.24 (4)</td>
</tr>
</tbody>
</table>

The peak heights displayed in the Fourier Transform power plots are the squares of the signal amplitudes. Table 7.4 lists the signal amplitudes at each temperature, relative to Radical A. A possible, weak signal was found near the low frequency peak for Radical B. However, the inconsistency of its presence and the signal-to-noise ratio for this peak was too poor to properly identify it as a radical.

Additional studies were attempted using alternative solvents in hopes of detecting the fifth and sixth radical from Mu addition to azulene. The challenge is finding a liquid with good solvating properties for azulene, and which results in a high fraction of muons that form muonium, yet does not react with muonium itself. While benzene clearly reacts with muonium, the muonium fraction is large in this liquid and it readily dissolves azulene. Thus, a sample of azulene in benzene was investigated, but it proved less efficient than the THF samples in terms of the signal-to-noise ratio for time spent; the radicals were shorter lived in benzene, probably due to reaction with benzene. A ‘deep-eutectic’ mixture of choline chloride and urea was also considered as a possible solvent for azulene, but like benzene, it was not an effective choice.
7.4.3 μLCR Experiments with Azulene

μLCR data was collected on radicals produced from azulene under the same conditions as the TF-μSR experiments. Since azulene has eight protons, each muoniated radical could potentially give rise to as many as eight resonances, with the signals from different radicals possibly distributed in overlapping field regions. In practice, only the proton couplings with the largest magnitude are likely to give detectable signals, and the resonance amplitudes are scaled by the radical abundances as determined in the TF experiment.

The μLCR spectrum from 1.5 M azulene in THF at 25°C is given in Figure 7.8. Expansion of the μLCR spectrum around each assigned resonance is provided in Figure 7.9 through Figure 7.12. Each vertical line in the spectrum represents a data point and its error bars. The curve running through the data points is obtained by fitting the spectra to the standard equations described in Chapter 2. A minimization process is utilized to ensure the curve is the best fit. It may appear difficult to distinguish some of the weak resonances from the background noise. One important tool for identifying weak signals is our use of a square-wave toggle field, as described in Chapters 2 and 3. The modulation results in a specific lineshape for the resonance, which has a maximum and a minimum separated by twice the modulation amplitude. Any fortuitous ‘hills’ or ‘valleys’ in the data that do not exhibit this field separation are not assigned as a resonance.
Figure 7.8: \( \mu \)LCR spectrum from 1.5 M azulene in THF at 25°C.

Figure 7.9: Expansion of \( \mu \)LCR spectrum in the region of 2.9 kG for 1.5 M azulene in THF at 25°C.
Figure 7.10: Expansion of $\mu$LCR spectrum in the region of 8.8 kG for 1.5 M azulene in THF at 25°C.

Figure 7.11: Expansion of $\mu$LCR spectrum in the region of 11.1 kG for 1.5 M azulene in THF at 25°C.
Figure 7.12: Expansion of μLCR spectrum in the region of 13.7 kG for 1.5 M azulene in THF at 25°C.

Table 7.5: Resonant field positions for muoniated radicals in azulene.

<table>
<thead>
<tr>
<th>$B_{\text{res}}$ (2°C)/kG</th>
<th>$B_{\text{res}}$ (25°C)/kG</th>
<th>$B_{\text{res}}$ (109°C)/kG</th>
<th>Percent Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.848 (6)</td>
<td>2.917 (3)</td>
<td>3.068 (8)</td>
<td>15 (5)</td>
</tr>
<tr>
<td>8.822 (3)</td>
<td>8.800 (4)</td>
<td>8.721 (4)</td>
<td>24 (7)</td>
</tr>
<tr>
<td>11.239 (12)</td>
<td>11.123 (11)</td>
<td>11.120 (16)</td>
<td>11 (5)</td>
</tr>
<tr>
<td>13.741 (5)</td>
<td>13.705 (3) -</td>
<td>11 (5)</td>
<td></td>
</tr>
</tbody>
</table>

Amplitude as a percent of maximum possible signal amplitude based on the 25°C data.

The resonance field positions, obtained from the fitting routine, are reported in Table 7.5. There are three other field positions at which there appears to be a resonance, approximately 3.5, 4.7, and 5.6 kG. Unfortunately, the signal-to-noise ratio is too low to be positive the signal is real.
7.5 Radical Identification

Assigning each of the four observed radicals in the TF spectrum to one of the six possible n-Mu-azulyl radicals is not a trivial process. Even more challenging is the association of each LCR signal to one of these radicals, and if possible, to a particular proton in the designated species.

7.5.1 Density Functional Theory Calculations for $A_\mu$

Using the geometries for the six n-H-azulyl radicals reported by Alder, hyperfine coupling constants were modelled using both the UHF method and the UB3LYP function, along with a wide variety of basis sets. The resulting hfcs for the hydrogen isotope in each radical was multiplied by the ratio of the muon and proton magnetic moments (a factor of 3.18), and are reported in Table 7.6 and Table 7.7. The titles of the columns detail the basis set used. The radicals are listed in order of increasing hyperfine constant.

Unfortunately, no set of calculations performed well at matching the experimental data. Even implementation of an adjustment factor to a set of predictions was not successful in determining an ideal functional/basis set combination. What did become apparent, however, is that the various basis sets agree about the order of the radicals in terms of increasing muon hfc, when the choice of method is consistent. The order, however, does change with the method. The UB3LYP functional predicts the hyperfine coupling constant for 4-Mu-azulyl to be larger than the 2- and 6-Mu adducts, which is opposite to the UHF method.
Table 7.6: Predicted muon hyperfine coupling constants, $A_\mu$ /MHz, using the unrestricted Hartree-Fock method.

<table>
<thead>
<tr>
<th></th>
<th>STO-3G</th>
<th>3-21G</th>
<th>6-31G</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Mu-azulyl</td>
<td>73</td>
<td>97</td>
<td>112</td>
</tr>
<tr>
<td>9-Mu-azulyl</td>
<td>268</td>
<td>245</td>
<td>281</td>
</tr>
<tr>
<td>4-Mu-azulyl</td>
<td>305</td>
<td>308</td>
<td>363</td>
</tr>
<tr>
<td>2-Mu-azulyl</td>
<td>391</td>
<td>349</td>
<td>415</td>
</tr>
<tr>
<td>6-Mu-azulyl</td>
<td>430</td>
<td>374</td>
<td>442</td>
</tr>
<tr>
<td>5-Mu-azulyl</td>
<td>503</td>
<td>441</td>
<td>523</td>
</tr>
</tbody>
</table>

Table 7.7: Predicted muon hyperfine coupling constants, $A_\mu$ /MHz, using the unrestricted Becke and Lee-Yang-Parr hybrid functional.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Mu-azulyl</td>
<td>110</td>
<td>129</td>
<td>125</td>
<td>122</td>
<td>135</td>
</tr>
<tr>
<td>9-Mu-azulyl</td>
<td>188</td>
<td>219</td>
<td>209</td>
<td>199</td>
<td>219</td>
</tr>
<tr>
<td>2-Mu-azulyl</td>
<td>214</td>
<td>252</td>
<td>239</td>
<td>239</td>
<td>264</td>
</tr>
<tr>
<td>6-Mu-azulyl</td>
<td>245</td>
<td>288</td>
<td>265</td>
<td>272</td>
<td>301</td>
</tr>
<tr>
<td>4-Mu-azulyl</td>
<td>251</td>
<td>293</td>
<td>279</td>
<td>276</td>
<td>308</td>
</tr>
<tr>
<td>5-Mu-azulyl</td>
<td>261</td>
<td>306</td>
<td>288</td>
<td>283</td>
<td>320</td>
</tr>
</tbody>
</table>

7.5.2 Assigning the TF spectrum

From geometry optimization and hfc DFT calculations, I anticipate the 1-Mu-azulyl radical to be the most commonly formed and to have the lowest muon hfc. For most TF spectra from azulene, the strongest radical signal is Radical A, which also has the smallest hfc. Thus, I assign 1-Mu-azulyl to Radical A.
Clearly, the second most stable radical is predicted to be 2-Mu-azulyl. The calculated muon hfcs using the UB3LYP functional agree that the 2-Mu-azulyl radical has the next smallest value for $A_\mu$, other than the 9-Mu-azulyl radical, which if it even forms at all would be in very small quantities considering its relative instability. However, all other factors being equal, 1-Mu-azulyl should be twice as abundant as 2-Mu-azulyl. Radical B is produced in relatively similar proportions as Radical A. It is unclear why the quantity of 2-Mu-azulyl rivals that of 1-Mu-azulyl, but it is suspected that the dipole moment of the azulene molecule may play a role.

Thermodynamically, muonium addition to carbon-6 in azulene is the next most stable scenario. The DFT calculations using the UB3LYP functional predict the muon hfc of the 6-Mu-azulyl to be roughly 150 MHz larger than $A_\mu$ for 1-Mu-azulyl and about 30 MHz larger than for 2-Mu-azulyl. This matches the muon hfc for Radical C, which over the three temperature sets is on average 150 MHz larger than that for Radical A and 27 MHz larger than for Radical B. Additionally, Radical C is the next strongest signal. Based on these arguments, I assign Radical C as 6-Mu-azulyl.

Based on the geometry optimization the next most stable species are the 4-Mu and 5-Mu adducts. Unfortunately, the muon hfcs for these species are difficult to model since the geometry at these sites is substantially more distorted than any of the other Mu adducts of azulene. The predicted $A_\mu$ values for these two radicals are consistently similar across all the basis sets used with the UB3LYP functional. Thus, at this time we cannot unambiguously assign Radical D to a specific muoniated azulyl radical, but the models do support an argument that this unknown species is either 4- or 5-Mu-azulyl.
Table 7.8: TF-μSR radical assignments.

<table>
<thead>
<tr>
<th>Expt $A_\mu$ /MHz</th>
<th>Signal</th>
<th>Assignment</th>
<th>$6-31++G(2df,p)$ $A_\mu$ /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>A</td>
<td>1-Mu-azulyl</td>
<td>122</td>
</tr>
<tr>
<td>201</td>
<td>B</td>
<td>2-Mu-azulyl</td>
<td>239</td>
</tr>
<tr>
<td>226</td>
<td>C</td>
<td>6-Mu-azulyl</td>
<td>272</td>
</tr>
<tr>
<td>268</td>
<td>D</td>
<td>4- or 5-Mu-azulyl</td>
<td>276 or 283</td>
</tr>
</tbody>
</table>

It is instructive to compare this assignment with other polyaromatic ring systems studied by μSR techniques. Based on symmetry, pyrene (shown in Figure 7.13) has five different sites for muonium addition. Muonium addition was observed for three of the carbons (C1, C2, and C3), but there was no evidence for addition to the bridgehead carbons (C4 and C5) [199].

![Figure 7.13: The symmetrically distinct reactive sites for: (a) pyrene; (b) fluoranthene; (c) triphenylene; (d) dodecahydrotriphenylene.](image)

As shown in Figure 7.13, fluoranthene has nine symmetrically distinct reactive sites. Five muoniated radicals from fluoranthene have been detected [200]. The signals in the spectrum were assigned to radicals from Mu addition to C1, C2, C3, C4, and C5; again, there was no evidence for addition to the bridgehead carbons. More recently,
triphenylene and dodecahydrotriphenylene were both investigated by μSR methods (also shown in Figure 7.13) [201]. For triphenylene, Mu addition to C1 and C2 were observed, but not to the bridgehead carbons. Muonium only adds to the bridgehead carbons when there is no other site for Mu addition, namely if all the C1 and C2 type carbons are saturated. This is the case in dodecahydrotriphenylene. C9 in azulene is a bridgehead carbon, and matching our experience with other polyaromatic ring systems, the 9-Mu-azulyl radical was not observed in the TF-μSR spectra.

7.6 Assigning the LCR Spectrum

7.6.1 Density Functional Theory Calculations for \( A_p \)

Both the UHF and UB3LYP functionals, along with various basis sets, were used to model the proton hfcs for the six possible radical species. The resulting values are reported in Table 7.9 through Table 7.14, where the proton numbering corresponds to the related carbon atom. For most protons, the various modelling approaches yield hfcs that agree within 5-10 MHz. The only exceptions are proton-2 in 2-Mu-azulyl, and proton-6 in 6-Mu-azulyl. In both cases, the 3-21G basis set predicts a proton hfc lower than average, and the EPR-III basis set predicts a value above the average.
Table 7.9: Calculated proton hyperfine coupling constants, $A_p$ /MHz, using the UB3LYP functional for 1-Mu-azulyl.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton-1</td>
<td>35</td>
<td>41</td>
<td>39</td>
<td>38</td>
<td>42</td>
</tr>
<tr>
<td>Proton-2</td>
<td>-23</td>
<td>-28</td>
<td>-25</td>
<td>-23</td>
<td>-25</td>
</tr>
<tr>
<td>Proton-3</td>
<td>9</td>
<td>11</td>
<td>9</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Proton-4</td>
<td>10</td>
<td>12</td>
<td>11</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Proton-5</td>
<td>-24</td>
<td>-29</td>
<td>-27</td>
<td>-24</td>
<td>-26</td>
</tr>
<tr>
<td>Proton-6</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>Proton-7</td>
<td>-10</td>
<td>-13</td>
<td>-12</td>
<td>-11</td>
<td>-12</td>
</tr>
<tr>
<td>Proton-8</td>
<td>-16</td>
<td>-20</td>
<td>-18</td>
<td>-16</td>
<td>-17</td>
</tr>
</tbody>
</table>

Table 7.10: Calculated proton hyperfine coupling constants, $A_p$ /MHz, using the UB3LYP functional for 2-Mu-azulyl.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton-1</td>
<td>-14</td>
<td>-18</td>
<td>-16</td>
<td>-14</td>
<td>-16</td>
</tr>
<tr>
<td>Proton-2</td>
<td>67</td>
<td>79</td>
<td>75</td>
<td>75</td>
<td>83</td>
</tr>
<tr>
<td>Proton-3</td>
<td>-14</td>
<td>-18</td>
<td>-16</td>
<td>-14</td>
<td>-16</td>
</tr>
<tr>
<td>Proton-4</td>
<td>-25</td>
<td>-30</td>
<td>-27</td>
<td>-25</td>
<td>-28</td>
</tr>
<tr>
<td>Proton-5</td>
<td>13</td>
<td>16</td>
<td>14</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>Proton-6</td>
<td>-29</td>
<td>-35</td>
<td>-32</td>
<td>-30</td>
<td>-33</td>
</tr>
<tr>
<td>Proton-7</td>
<td>13</td>
<td>16</td>
<td>14</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>Proton-8</td>
<td>-25</td>
<td>-30</td>
<td>-27</td>
<td>-25</td>
<td>-28</td>
</tr>
</tbody>
</table>
Table 7.11: Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 4-Mu-azulyl.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton-1</td>
<td>7</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>8</td>
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<tr>
<td>Proton-2</td>
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<td>-22</td>
<td>-20</td>
<td>-17</td>
<td>-20</td>
</tr>
<tr>
<td>Proton-3</td>
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<td>-5</td>
<td>-5</td>
<td>-4</td>
<td>-6</td>
</tr>
<tr>
<td>Proton-4</td>
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<td>32</td>
<td>30</td>
<td>29</td>
<td>33</td>
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<tr>
<td>Proton-5</td>
<td>-22</td>
<td>-27</td>
<td>-24</td>
<td>-20</td>
<td>-24</td>
</tr>
<tr>
<td>Proton-6</td>
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<td>12</td>
<td>11</td>
<td>9</td>
<td>12</td>
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<tr>
<td>Proton-7</td>
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<td>-34</td>
<td>-31</td>
<td>-27</td>
<td>-31</td>
</tr>
<tr>
<td>Proton-8</td>
<td>11</td>
<td>14</td>
<td>13</td>
<td>11</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 7.12: Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 5-Mu-azulyl.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
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<tr>
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<td>-30</td>
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<td>-31</td>
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<tr>
<td>Proton-2</td>
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<td>12</td>
<td>11</td>
<td>14</td>
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<tr>
<td>Proton-3</td>
<td>-25</td>
<td>-31</td>
<td>-28</td>
<td>-25</td>
<td>-29</td>
</tr>
<tr>
<td>Proton-4</td>
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<td>-13</td>
<td>-11</td>
<td>-10</td>
<td>-11</td>
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<tr>
<td>Proton-5</td>
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<td>18</td>
<td>21</td>
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<td>Proton-7</td>
<td>11</td>
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<td>11</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Proton-8</td>
<td>-24</td>
<td>-29</td>
<td>-25</td>
<td>-22</td>
<td>-26</td>
</tr>
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</table>
Table 7.13: Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 6-Mu-azulyl.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton-1</td>
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<td>11</td>
<td>9</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Proton-2</td>
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<td>-29</td>
<td>-27</td>
<td>-30</td>
</tr>
<tr>
<td>Proton-3</td>
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<td>9</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Proton-4</td>
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<td>6</td>
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<td>8</td>
</tr>
<tr>
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<td>-19</td>
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<td>Proton-6</td>
<td>77</td>
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<td>-21</td>
</tr>
<tr>
<td>Proton-8</td>
<td>6</td>
<td>8</td>
<td>6</td>
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<td>8</td>
</tr>
</tbody>
</table>

Table 7.14: Calculated proton hyperfine coupling constants, $A_p$/MHz, using the UB3LYP functional for 9-Mu-azulyl.

<table>
<thead>
<tr>
<th></th>
<th>3-21G</th>
<th>6-31G</th>
<th>6-31G(d)</th>
<th>6-31++G(2df,p)</th>
<th>EPR-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton-1</td>
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<td>-27</td>
<td>-25</td>
<td>-21</td>
<td>-24</td>
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<tr>
<td>Proton-2</td>
<td>9</td>
<td>11</td>
<td>10</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Proton-3</td>
<td>-24</td>
<td>-29</td>
<td>-27</td>
<td>-22</td>
<td>-25</td>
</tr>
<tr>
<td>Proton-4</td>
<td>-26</td>
<td>-31</td>
<td>-28</td>
<td>-23</td>
<td>-26</td>
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<tr>
<td>Proton-5</td>
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<td>16</td>
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<td>15</td>
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<tr>
<td>Proton-6</td>
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<td>-28</td>
<td>-26</td>
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<td>-24</td>
</tr>
<tr>
<td>Proton-7</td>
<td>11</td>
<td>14</td>
<td>13</td>
<td>10</td>
<td>12</td>
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<tr>
<td>Proton-8</td>
<td>-18</td>
<td>-22</td>
<td>-20</td>
<td>-17</td>
<td>-19</td>
</tr>
</tbody>
</table>
7.6.2 Methods Used to Assign the LCR spectrum

Determining what proton in which radical is responsible for each resonance in this system is a challenging puzzle. Two important pieces that helped us arrive at a solution are the predicted isotope effect between the proton and muon attached to the same carbon in an \( n\text{-Mu-azulyl} \) radical, and the experimental resonance amplitudes. Since the geometries used for the hfc calculations was for \( n\text{-H-azulyl} \) and not \( n\text{-Mu-azulyl} \) radicals, the ratio of \( A_p \) values for protons attached to the same carbon only provides a guide for the experimental secondary isotope effects. The true values will vary from those reported in Table 7.15, due to the difference in the zero-point energy of muonium and the hydrogen atom. Since carbon-9 does not have an attached proton, no ratio is reported for \( 9\text{-H-azulyl} \).

Table 7.15: Ratio of calculated proton hyperfine coupling constants at the site of addition for the \( n\text{-H-azulyl} \) radicals using the UB3LYP functional.

<table>
<thead>
<tr>
<th>( n\text{-Mu-azulyl} )</th>
<th>Ratio of ( A_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-( Mu\text{-azulyl} )</td>
<td>1.0</td>
</tr>
<tr>
<td>2-( Mu\text{-azulyl} )</td>
<td>1.0</td>
</tr>
<tr>
<td>6-( Mu\text{-azulyl} )</td>
<td>1.0</td>
</tr>
<tr>
<td>4-( Mu\text{-azulyl} )</td>
<td>2.9</td>
</tr>
<tr>
<td>5-( Mu\text{-azulyl} )</td>
<td>4.8</td>
</tr>
</tbody>
</table>

If the carbon framework of an \( n\text{-Mu-azulyl} \) radical is planar, and the muon and proton lie in mirror positions above and below this plane, then for protons on the same
carbon the computations generate a ratio of unity between the proton hfcs. It has been shown that an effective method for predicting the muon hfc in conjugated carbon systems, such as azulene, is to lengthen the bond corresponding to C-Mu by 4.3% in these calculations to model the known vibrational averaging effects [88]. Generally, an increase in the predicted isotope effect results. The predicted primary isotope effects from this method for 1-, 2-, and 6-Mu-azulyl were all about 11%. The other radicals are non-planar, with the hydrogen isotope s-orbital bonding with a nearly non-hybridized \( p_z \) carbon orbital. Thus, substantially larger proton hfc ratios are predicted for these species.

The remaining resonances prove to be more difficult to pin down. One technique that was used was to consider the experimental signal amplitude percent, as reported in Table 7.5, and compare these to the predicted amplitudes. These expected LCR amplitudes are generated using the standard equations describing a resonance in an LCR experiment, as given in Chapter 2. The anticipated amplitudes are dependent on the height of the corresponding TF-\( \mu \)SR signal. A plot of the predicted amplitudes, along with the experimental data, is given in Figure 7.14.
Figure 7.14: LCR percent amplitude curves for the four detected radicals based on the measured $A_\mu$ values, along with the LCR experimental data. The experimental error bars are from the uncertainty in signal amplitude as determined during the fit of each signal.

7.6.3 Resonance at 2.9 kG

Using the predicted isotope effects, we can propose possible resonance positions. Take 1-Mu-azulyl for example. At 25°C, experimentally $A_\mu = 75$ MHz for this radical and the expected isotope effect is 1.11. Thus, we anticipate a value for $A_p$ of about $\frac{1}{1.11} \left( \frac{75 \text{ MHz}}{3.18} \right)$, which is 21 MHz. Using the standard equations for μLCR given in Chapter 2, we find this corresponds to a magnetic field of 2.9 kG. When we consider the LCR data presented in Section 7.4.3, we see that there is, in fact, a signal at 2.917 kG. Assigning this resonance to any other radical would result in an $A_p$ of over 145 MHz. Therefore, we can clearly see that the resonance shown in Figure 7.9 is due to Radical A, which was assigned to the structure 1-Mu-azulyl. Since these calculation methods have predicted a value for $A_\mu$ that is 1.6 times too large, likely the same can be said for the proton on the same carbon, and the only positive $A_p$ larger than 21 MHz is for proton-1.
In fact, reducing the average predicted $A_p$ for proton-1 by a factor of 1.6 yields 23 MHz, so the calculations at least have inflated the predicted the hfcs for these two nuclei by a similar factor.

7.6.4 Resonance at 8.8 kG

The resonance at 8.800 kG is not due to muonium addition to carbon-1 nor carbon-4/carbon-5 of azulene, since the resulting proton hfc would be too large in magnitude, negative for the former while positive for the latter. This leaves us with two options: the 2-Mu or the 6-Mu adduct. If this resonance is attributed to 2-Mu-azulyl then $A_p = 36.5$ MHz. Since the computations tend to predict higher hfcs than observed experimentally, only proton-2 could be responsible if this species generated the signal. The secondary isotope effect that would then result is 1.7, which is significantly larger than expected.

The other radical to consider is 6-Mu-azulyl, which would result in $A_p = 61.8$ MHz. The only proton in this radical that could have a coupling constant this large is proton-6. The resulting isotope effect is 1.15, which is very close to the computationally predicted value of 1.11.

To make a decision regarding this resonance, its percent amplitude and the predicted percent amplitude curves for these two radicals are considered. The amplitude at this field position is 35 % of the maximum possible for 2-Mu-azulyl, or 22 % for 6-Mu-azulyl. As reported in Table 7.5, the resonance has percent amplitude of $(24 \pm 7)$ %. This information, together with the considerations regarding isotope effects, leads to the conclusion that this resonance is due to proton-6 in 6-Mu-azulyl.
7.6.5 Resonance at 11.1 kG

The next resonance is situated at a magnetic field of 11.124 kG. Muonium addition to carbon-1 cannot be responsible for this signal; otherwise, it would describe a proton with a negative hfc of magnitude over 130 MHz. If the resonance were due to 2-, 4-/5-, or 6-Mu-azulyl it would correspond to a proton coupling constant of -6.5, 60.1, or 18.8 MHz, respectively. The percent amplitude of this signal is (11 ± 5) %. 2-Mu-azulyl is predicted to have percent amplitude of only 1% at this field position, and such a weak signal is normally not detectable above the background noise in the spectrum. The 4-/5- and 6-Mu adducts of azulene are expected to have percent amplitudes of 9 % and 7 %, respectively.

One challenge of assigning this resonance to 4- or 5-Mu-azulyl is trying to determine which proton in the radical could be responsible. Proton-4 in 4-Mu-azulyl has the largest positive hfc from the DFT calculations (see Table 7.11). Unfortunately, the computed values for $A_p$ are well below the 60 MHz this field position corresponds to if the $A_p$ in this radical is $\sim 269$ MHz. Predictions for $A_p$ in 5-Mu-azulyl are also too small.

Considering 6-Mu-azulyl, in terms of hfc, this resonance could be due to proton-1 (or equivalently proton-3). Provided that the assignment of the resonance at 8.800 kG to proton-6 in 6-Mu-azulyl is correct, however, then this resonance should have a width that is less than that of the 8.800 kG signal; instead, it has a width close to double that of the 8.800 kG resonance.

Given the current information, it would be rash to assign this resonance to either radical definitively. We wait until considering the temperature dependence of the data, as will be done in Section 7.7, before deciding on which assignment is correct.
7.6.6  Resonance at 13.7 kG

The final resonance to consider occurs at 13.705 kG. As for the previous signal, 1-Mu-azulyl can immediately be rejected based on the $A_p$ that would be required. Using the same argument, 2- and 5-Mu-azulyl can also be counted out. At this field position, a signal from 4-Mu-azulyl is predicted to have percent amplitude of 0.5 %, so it is clearly not responsible for this resonance. That only leaves 6-Mu-azulyl. The experimental amplitude percent is $(11 \pm 5) \%$, which agrees with the predicted value of 10 %. The corresponding proton hfc is -29.5 MHz, which is close to the predicted value for proton-2 in this radical. Another option is proton-5 (or equivalently, proton-7).

7.7  Temperature Dependence of the Hyperfine Coupling Constants in Muoniated Azulyl Radicals

7.7.1  Temperature Dependence of the Muon Hyperfine Coupling Constants

In Table 7.3, the measured muon hfcs were reported as a function of temperature. It is interesting to note that $A_\mu$ for 1-Mu-azulyl increases with temperature, while it decreases (or is approximately constant) with temperature for the other three observed species. A plot of the temperature dependences is given in Figure 7.15.

Negative temperature gradients of the muon and proton hfcs have been successfully interpreted in a study of Mu-substituted cyclohexadienyl radicals [20]. This was accomplished by attributing the temperature dependence to a vibrational mode in the molecule where the carbon at the site of addition remains in the plane of the molecule, while the two attached protons (or one proton and one muon) “wag” such that their out of plane angle $\beta$ varies. Such a motion is a reasonable option, at least partially, for explaining the behaviour of radicals 2-, 4-/5-, and 6-Mu-azulyl. An alternative is a
change in the geometry of the molecule about the site of addition. Based on the geometry minimization calculations performed on radical 4-Mu-azulyl it was determined that as the distortion of the carbon framework from planarity increases, the value of $A_\mu$ decreases. One could imagine that higher temperatures may result in greater flexibility of the carbon framework, and thus a smaller $A_\mu$.

Figure 7.15: Temperature dependence of $A_\mu$ in 4-/5-Mu-azulyl (○), 6-Mu-azulyl (□), 2-Mu-azulyl (●), and 1-Mu-azulyl (■). The lines are a guide for the eyes only.
1-H-azulyl, however, showed a positive temperature dependence. A vibrational mode that has been found to generate a positive temperature gradient for planar molecules involves the entire CHMu group moving out of the plane defined by the rest of the molecule [20]. A possible alternate explanation is C-H wagging in an anharmonic potential well.

### 7.7.2 Temperature Dependence of the Proton Hyperfine Coupling Constants

Table 7.16 lists the values of $A_p$ for the observed resonances as a function of temperature. For the signal assigned to 1-Mu-azulyl, $A_p$ shifts towards more positive values with increasing temperature, just as $A_{fl}$ does. For the two resonances attributed to 6-Mu-azulyl, $A_p$ behaves in a manner similar to $A_{fl}$ for that radical as well; they remain roughly constant with temperature. Only one resonance has not yet been attributed to a particular radical.

<table>
<thead>
<tr>
<th>Field /kG</th>
<th>Radical</th>
<th>$A_p$ (2°C) /MHz</th>
<th>$A_p$ (25°C) /MHz</th>
<th>$A_p$ (109°C) /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.917</td>
<td>1-Mu-azulyl</td>
<td>20.16 (11)</td>
<td>20.72 (5)</td>
<td>22.22 (15)</td>
</tr>
<tr>
<td>8.800</td>
<td>6-Mu-azulyl</td>
<td>61.94 (5)</td>
<td>61.84 (7)</td>
<td>62.06 (8)</td>
</tr>
<tr>
<td>11.124</td>
<td>6-Mu-azulyl</td>
<td>17.2 (2)</td>
<td>18.8 (2)</td>
<td>17.6 (3)</td>
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<tr>
<td></td>
<td>4-/5-Mu-azulyl</td>
<td>60.9 (2)</td>
<td>60.8 (2)</td>
<td>51.9 (3)</td>
</tr>
<tr>
<td>13.705</td>
<td>6-Mu-azulyl</td>
<td>-29.20 (9)</td>
<td>-29.05 (5)</td>
<td>-</td>
</tr>
</tbody>
</table>
If the resonance at 11.124 kG is the result of proton-1 and proton-3 in
6-Mu-azulyl, we again expect the resulting $A_p$ value to be almost temperature
independent. While the result for 25°C is a little high compared to the other two
temperatures, the data seems to support this theory. Interpreting this resonance as due to
a proton in 4-/5-Mu-azulyl, on the other hand, illustrates a proton that has a constant $A_p$
between 2 and 25°C, and then a drastic drop of about 9 MHz for the highest temperature.
It seems unlikely that the muon and proton hfc's would both undergo significant change
and yet remain in the same proportion to keep the position of the resonance virtually
constant at 11.1 kG. Thus, detecting this signal over several temperatures proved pivotal
in assigning this resonance as due to proton-1 and proton-3, in 6-Mu-azulyl.

Interpretation of the muon and proton hfc dependencies on temperature may yield
further understanding of this system. A future in-depth computational study is warranted
to identify the intramolecular motions responsible for the varying temperature effects.

7.8  **Spiran Pathway vs. Methylene-walk Mechanism**

According to the reaction model of Alder et al., the 1-, 2-, and 9-Mu-azulyl
radicals rearrange to naphthalene via the Spiran Pathway, while 4-, 5-, 6-Mu-azulyl
radicals follow the Methylene Walk. The methylation of azulene at 165°C by Alder et al.
yielded primarily 1- and 2-methylazulene: 87.0 % of the products were from addition to
carbons 1, 2, or 9, and the remaining 13.0 % were from addition to carbons 4, 5, or 6
[187]. As discussed earlier, thermolysis experiments where $^{13}$C-labelled azulene was
used generated ratios for the two mechanisms in favour of the Spiran Pathway ranging
from 79:21 to 64:36. An interpretation in terms of these radical-promoted pathways was
that higher temperatures would shift this competition towards an increased preference for the Methylene Walk [198].

Transverse field $\mu$SR amplitudes are related to the radical yields by the degree of polarization that is transferred from free Mu to the Mu-containing radical. As described in Chapter 2, this polarization is proportional to

$$P(v_{12}) = \frac{1}{2} \left[ \frac{\lambda^2}{\lambda^2 + (\omega_{12M} - \omega_{12R})^2} \right]^{1/2},$$

(7.1)

where $\lambda$ is the pseudo-first order rate constant, $\omega_{12M}$ is the lowest precession frequency of muonium, and $\omega_{12R}$ is the corresponding radical precession frequency. As long as the difference between the radical precession frequencies and $\omega_{12M}$ is relatively constant ($\omega_{12M} \sim 1900$ MHz for 12.5 kG), we can use the transverse field amplitudes as a measure of the radical yields. The observed fraction of radicals corresponding to each mechanism, for each temperature studied, is reported in Table 7.17. All three spectra were collected at lower temperatures than Alder's methylation experiment.

Table 7.17: Percentage of 1-, 2-, 9-Mu-azulyl and 4-, 5-, 6-Mu-azulyl radicals as a function of temperature.

<table>
<thead>
<tr>
<th>Site of Mu Addition</th>
<th>Fraction of Products (2°C)</th>
<th>Fraction of Products (25°C)</th>
<th>Fraction of Products (109°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-, 2-, 9-</td>
<td>68 (3)</td>
<td>74 (3)</td>
<td>77 (3)</td>
</tr>
<tr>
<td>4-, 5-, 6-</td>
<td>32 (2)</td>
<td>26 (2)</td>
<td>23 (2)</td>
</tr>
</tbody>
</table>
Similar to the methylation of azulene, radical addition to carbon-1 and -2 is most common, and both of these products follow the Spiran Pathway. This is to be expected considering the relative thermal stability of these radicals, as reported in Table 7.1. A few important differences, however, are apparent. The amount of 4-, 5-, and 6-Mu-azulyl radicals produced at these low temperatures is larger than would be expected based on the methylation experiment; our experimental ratios are closer to the thermolysis experiments where hydrogen radicals presumably initiate the rearrangement, demonstrating the value of muonium as an isotope of hydrogen.

One interpretation for the difference between the muonium and methyl experiments is that the •CH$_3$ group, at lower temperatures, has a greater preference over hydrogen isotopes for addition to the 5-membered ring, due to the lesser degree of carbon plane distortion resulting from addition. An alternative explanation is that in the time window of the μSR technique we observe the kinetically favoured products due to the initial radical addition step rather than the thermally preferred species.

The kinetic bottleneck for the radical promoted mechanisms is the formation of the required H-azulyl structure from more stable H-azulyl species (9-H-azulyl and 4-H-azulyl for the Spiran and the Methylene Walk mechanisms, respectively) [173]. 4-Mu-azulyl might have been detected in the TF-μSR experiments (as Radical D). 9-Mu-azulyl, on the other hand, was not detected within the time domain of the TF-μSR experiment. Similarly, the end-product analysis of benzyl [205] or methyl adducts of azulene did not reveal any addition to carbon-9.

Despite not observing the 9-Mu adduct, our experimental data supports the argument of the proposed model of competing Spiran and Methylene Walk mechanisms.
Perhaps this radical is primarily formed by rearrangement from the more stable 1-Mu and 2-Mu-azulyl radicals. Before the Spiran Pathway can definitively be accepted as contributing to the rearrangement process, the elusive 9-H-azulyl intermediate (or the muoniated version) needs to be detected.

7.9 Future Work

A limiting factor in assigning many of the LCR signals to a unique proton is the deviation of the DFT calculations from the experimental results. This is the first report of an n-H-azulyl type radical, and thus, before now there has been no experimental data with which to compare the computational methods. Exploration of the current computational techniques or development of a more appropriate functional/basis set would be an ideal next step for this research program. Once a choice computational method has been identified, investigation can be undertaken on the molecular motions possibly governing the temperature dependent variation of the muon and proton hfcs.

In terms of future experimental work, testing additional solvents to obtain viable options for μSR studies may prove fruitful. Restraints on the available beam time limit the signal/noise ratio we are able to obtain for a given spectrum. The TF spectra used in this study ran for roughly forty million decay positron counts. If a liquid with good solvating properties for azulene, and which results in a high fraction of muons that form muonium, yet does not react with muonium itself, can be found then it would be worth the time to leave a sample running for significantly longer to determine if any 9-Mu-azulyl is formed during the μSR experiment.
7.10 Conclusions

Four of the six possible muonium adducts of azulene are observable by TF-μSR. This is the first report of detection of a radical adduct of azulene, and more importantly of n-H-azulyl type radicals. The TF signals were matched to the radicals using density functional theory calculations of the thermodynamic stability and hyperfine coupling constants. Assignment of the LCR proton resonances required computation of the proton hyperfine coupling constants, modelling of the resonance amplitudes as a function of field position, and consideration of temperature effects on the resonance position. While addition to carbon-9 of azulene was not detected, rearrangement to such a species, as described by the Spiran Pathway and Methylene Walk mechanisms seems reasonable. Evaluation of the radical fractions in terms of the Spiran Pathway : Methylene Walk ratio demonstrates that the proposed mechanistic competition for the rearrangement of azulene into naphthalene is probable.
CHAPTER 8.
SUMMARY AND CONCLUSIONS:
MUCH ADO ABOUT MECHANISMS

In other works, muonium has been used to detect and identify radical species, to study substitution effects, to measure reaction kinetics and kinetic isotope effects, to explore tunneling effects, and to investigate chemical structures and dynamics. This is the first thesis to use muonium to investigate radical reaction mechanisms. Case studies explored in this thesis include the reactions of H with silylenes, silenes, germylidenes, and azulene.

Using Mu as a probe of H-atom reactions with silylenes illustrated an interesting departure from the chemistry previously explored with bulky free radicals; unlike the reaction of TEMPO with silylenes, which generated a silyl radical, muonium addition to silylenes resulted in the formation of disilanyl radicals. This is the first detection of a secondary radical by μSR techniques. While the detection of these β-muoniated radicals was unexpected, this discovery lead to the formulation of the two-step mechanism I proposed. Independently developed, my reaction mechanism provides experimental support for a mechanism proposed to explain the formation of halodisilanes from the reactions of silylenes with halocarbons [130].

Reaction of muonium with a silene yielded two different radical species; one due to Mu addition to the doubly-bonded carbon atom and the other from Mu addition to the unsaturated silicon atom. Muonium, acting as an unbiased probe, demonstrated that the
carbon has greater reactivity toward H atoms than the silicon, so that the \( \beta \)-muoniated silyl radical forms preferentially by a factor of 2.2 : 1.

It was found that germylidenes react with muonium in a manner similar to carbenes; Mu adds to the germanium atom, producing an \( \alpha \)-muoniumated radical. The germyl radical does not react further during the time window of a \( \mu \)SR experiment, a clear distinction between the reactivity of the germanium compounds and the silicon species. The difference in reaction mechanisms was explained in terms of the Lewis basicity of the ylidene and the Lewis acidity of the radical.

In the case of azulene, \( \mu \)SR experiments provide the first direct experimental evidence of transient azulyl radicals. The observed ratio of radical abundances supports the proposed model for a competition between the Spiran Pathway and Methylene Walk mechanisms.

Could the use of muonium ever become as common as EPR or even NMR? As with all great scientific techniques, challenges arise, limiting the use of our methods. First, and foremost, \( \mu \)SR studies require a particle accelerator. The muon, as a radioactive particle, has a lifetime that limits the spectral information that can be obtained; the signals in a TF-\( \mu \)SR spectrum are too broad to determine chemical shifts, which is why we only study paramagnetic compounds. For muoniated radicals to be detected the rate of reaction must be sufficient for spin polarization transfer to occur. This limits us to solutions of relatively high concentrations when compared to other techniques like NMR or EPR. Since the radicals under investigation contain muonium in place of hydrogen, generally experimental data cannot be directly compared with computational models due to an unknown scaling factor from primary isotope effects.
One other complication is that some systems such as azulene yield multiple radicals, and it can be a significant challenge to assign the spectrum.

Despite the obstacles, these case studies successfully demonstrate the utility of muonium in eliciting H-atom reaction mechanisms. Muonium can be used to study analogues of H-adduct radicals not previously characterized, and with the synthesis of novel compounds, there will always be more to explore.
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