TEMPERATURE DEPENDENCE OF ISOTROPIC HYPERFINE COUPLING CONSTANTS OF THE MU-ETHYL RADICAL IN FAUJASITES

by

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Abstract

In this complete study of the isotropic hyperfine coupling constants (hfccs) of the Mu-ethyl radical in the NaY, HY and USY faujasites, across a temperature range of 5 to 500 K, the effects of changing the loading of guest molecules, and the type and number of cations in the zeolite was studied (while comparing the results to those of bulk ethene and silica-bound ethene), giving important information on the interactions of the radical with the faujasitic environments.

This is the first such report of a neutral alkyl free-radical in an unperturbed faujasite environment, and the first report of ethyl radical hfccs in any zeolite. This is also the first time that proton hfccs for an alkyl radical have been measured in zeolites. Apart from changes in the magnitude of the proton hfccs, their temperature trends are similar to those of the bulk.

At low temperatures, the muon hfccs values obtained were 10-15% higher than those observed in the bulk, an unprecedented hfcc shift for alkyl radicals and is the second largest environment-induced shift ever observed. Despite these shifts, the Mu-hfcc temperature-dependent trends follow the general shape of the bulk, indicating that intramolecular rotation about the Mu-ethyl radical’s C-C bond is not strongly influenced by binding within the faujasite.

Changing the loading of guest molecules in faujasites has a small, but present, effect on the Mu-ethyl radical’s muon hfccs. Strangely, increases in loading have the opposite effect in HY than in NaY, potential evidence that differing cation site locations in NaY and HY, relative
to the surrounding framework, cause microscopic differences in radical binding. By fitting an empirical equation offered by Roduner et al. to our data, we determined classical barriers to intramolecular rotation, which ranged from 1.16 to 1.36 (± 0.03 to 0.09) kJ mol$^{-1}$.

Temperature-independent $\mu$ALCR $\Delta_1$ linewidths help support our supposition that the Mu-radical binds within the zeolite framework. Also, loss of $\Delta_1$ peak intensity as temperature is increased indicates some sort of radical motion or isotropic averaging. This is the first case in which the $\Delta_1$ resonance has disappeared with temperature for a zeolite-bound Mu-radical.
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<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$A_\alpha$</td>
<td>$\alpha$-proton hyperfine coupling constant</td>
</tr>
<tr>
<td>$A_\beta$, $&lt;A&gt;$</td>
<td>$\beta$-proton hyperfine coupling constant, average $\beta$-proton hfcc</td>
</tr>
<tr>
<td>$A_\mu$, $A'_\mu$</td>
<td>Muon hyperfine coupling constant, reduced muon hfcc</td>
</tr>
<tr>
<td>$\alpha,\beta$-protons</td>
<td>Attached to, once removed from the radical-center carbon</td>
</tr>
<tr>
<td>$\alpha,\beta$-spin</td>
<td>$\frac{1}{2}, \frac{1}{2}$ states</td>
</tr>
<tr>
<td>$B(A_1)$</td>
<td>Field at which $A(m=1)$ resonance occurs</td>
</tr>
<tr>
<td>$B(A_0)$</td>
<td>Field at which $A(m=0)$ resonance occurs</td>
</tr>
<tr>
<td>$c^2$, $s^2$</td>
<td>Field-dependent amplitudes</td>
</tr>
<tr>
<td>$e^+$, $e^-$</td>
<td>Positron, electron</td>
</tr>
<tr>
<td>$E_a$(rot)</td>
<td>Classical barrier to intramolecular rotation</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite-type zeolite</td>
</tr>
<tr>
<td>FT-$\mu$SR</td>
<td>Fourier-Transform $\mu$SR</td>
</tr>
<tr>
<td>$\gamma_n$</td>
<td>Gyromagnetic ratio for particle ‘n’</td>
</tr>
<tr>
<td>hfcc</td>
<td>Hyperfine coupling constant</td>
</tr>
<tr>
<td>HY</td>
<td>Protonated ‘Y’ faujasite</td>
</tr>
<tr>
<td>$I_{s/2}$, $S_{s/2}$</td>
<td>Nuclear, electronic spin ladder operators</td>
</tr>
<tr>
<td>$L, M$</td>
<td>Constants for the McConnell equation: $L/r$ is polarization dependent and $M/r$ is hyperconjugation dependent, where $r = \text{spin density}$</td>
</tr>
<tr>
<td>LF</td>
<td>Longitudinal Field</td>
</tr>
<tr>
<td>LTA</td>
<td>Linde Type A zeolite</td>
</tr>
<tr>
<td>$m$</td>
<td>Magnetic spin quantum number</td>
</tr>
<tr>
<td>M20</td>
<td>Meson Hall’s research area #20</td>
</tr>
<tr>
<td>MFI</td>
<td>ZSM-5-type zeolite</td>
</tr>
<tr>
<td>MOR</td>
<td>Mordenite-type zeolite</td>
</tr>
<tr>
<td>Mu</td>
<td>Muonium ($\mu^e$)</td>
</tr>
<tr>
<td>NaY</td>
<td>Sodiated ‘Y’ faujasite</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NSERC</td>
<td>Natural Sciences and Engineering Research Council of Canada</td>
</tr>
<tr>
<td>$p^+$</td>
<td>Proton</td>
</tr>
<tr>
<td>$\pi^+$</td>
<td>Positive pion</td>
</tr>
<tr>
<td>PMT</td>
<td>PhotoMultipler Tube</td>
</tr>
<tr>
<td>SC</td>
<td>SuperCage site in a faujasite</td>
</tr>
<tr>
<td>SII</td>
<td>Octahedrally coordinated cation site found in a FAU SC</td>
</tr>
<tr>
<td>TF</td>
<td>Transverse-Field</td>
</tr>
<tr>
<td>TRIUMF</td>
<td>TRI-University Meson Facility</td>
</tr>
<tr>
<td>UBC</td>
<td>University of British Columbia</td>
</tr>
<tr>
<td>$\mu^+$</td>
<td>Positive muon</td>
</tr>
<tr>
<td>$\mu$ALCR</td>
<td>Muon Avoided Level Crossing Resonance</td>
</tr>
<tr>
<td>$\mu$SR</td>
<td>Muon Spin (Resonance, Relaxation, or Rotation)</td>
</tr>
<tr>
<td>USY</td>
<td>Protonated low-aluminum zeolite</td>
</tr>
<tr>
<td>$\nu_n$, $\bar{\nu}_n$</td>
<td>Neutrinos, antineutrinos, where $n = e, \mu, \tau$</td>
</tr>
<tr>
<td>$\nu^e$, $\nu^\mu$, $\nu^p$</td>
<td>Zeeman frequencies for electron, muon, proton</td>
</tr>
<tr>
<td>$\nu_{12}$, $\nu_{23}$, $\nu_{34}$</td>
<td>Frequencies of transition between the $</td>
</tr>
<tr>
<td>W</td>
<td>Window site in a faujasite</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Beat frequency</td>
</tr>
</tbody>
</table>
To my wife, Sarah, and my Father, Michael, whose patience and support through the course of this project helped me immensely
Acknowledgements

I would like to express my sincerest gratitude to my two supervisors at TRIUMF. To Dr. Don Fleming for his continual guidance, vast knowledge on the subjects of $\mu$SR and gas-phase physical chemistry, and his willingness and ability to teach me those subjects. To Dr. Kashayar Ghandi for his constant support and encouragement, his dedication to my success in this field, as well as his ability to always keep me grounded as a scientist.

I would also like to thank the other member of the UBC $\mu$SR gas chemistry group, Dr. Donald Arseneau for all of the time and attention that he devoted to our experimental success at TRIUMF. Also, the education that he provided to me on practical $\mu$SR technique was invaluable to my project. I acknowledge Drs. Syd Kreitzman and Bassam Hitti for technical assistance for the many times when the need arose.

This work was done during my 16-month stay as a Masters of Science student at the University of British Columbia, from May 2003 to July 2004.
Chapter 1 – Introduction

A. Organization of the Thesis

I first became involved with the UBC gas chemistry $\mu$SR group at TRIUMF during the last two years of my undergraduate study. The research focus at that time was primarily small molecule behaviour in supercritical carbon dioxide as probed by Muon ($\mu$) Spin Relaxation. Following this project, the topic of my undergraduate honours thesis was room-temperature hyperfine coupling constants of Mu-Alkyl radicals in faujasites [1]. For the past sixteen months, as my Masters Degree project, I have studied the hyperfine coupling constants of the Mu-ethyl radical in three faujasite environments as a function of temperature. The data for this project were obtained over three separate beam periods at the TRIUMF cyclotron.

This thesis consists of seven sections. The first and second sections give an introductory explanation of muons and the $\mu$SR technique, followed by how it can be used to probe hyperfine coupling constants of small molecules. The third section gives the results of relevant studies from the literature. The fourth section describes the role of zeolites in the petrochemical industry, goes into some detail on the topic of faujasites. Finally, the fifth, sixth and seventh sections give the results for the Mu-ethyl radical in the NaY, HY and USY faujasites as probed by $\mu$SR, a discussion of the data, followed by the conclusion.

B. Muonium Chemistry

Chemists who perform experiments using the positive muon, $\mu^+$, a physical-chemical probe, consider it an ultra-light isotope of the proton. The most important aspect of the use of this elementary particle in chemistry is that it has one-ninth the mass, but the same spin and charge as a proton. Despite the muon being a point charge, it behaves like a ‘hot’ hydrogen ion
upon injection into matter. For example, during its thermalization phase, a positive muon can capture an electron to form an atomic bound state, yielding muonium (Mu = \( \mu^+ e^- \)). Important properties of the positive muon and muonium are given in Table 1-1. Muonium and the hydrogen atom have almost the same reduced masses so their Bohr radii and ionization potentials are nearly identical, and as such they are considered isotopic analogues.

Muons are produced at a handful of facilities worldwide at present, including at the TRIUMF cyclotron near the campus of the University of British Columbia. The asymmetric decay of muons stopped in a sample, the result of its parity-violating decay [4], is the fundamental basis of the \( \mu \)SR (Muon Spin Relaxation, Rotation or Resonance) technique, allowing for investigation of muon-sample interactions. More specifically, the hyperfine interactions of the muon 'guest' in the sample 'host' can be probed, as described in the following sections.

Roduner *et al.* observed muoniated free radicals, formed by the addition of muonium to unsaturated molecules, for the first time in 1978 [5]. Since then, hyperfine coupling information, radical dynamics and reaction kinetics of many different muoniated free radicals have been reported [e.g., 6-9].
### Table 1-1
Properties of the Positive Muon and Muonium [2,3]

<table>
<thead>
<tr>
<th>Positive Muon – $\mu^+$</th>
<th>Muonium – Mu</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charge</strong></td>
<td>Mass</td>
</tr>
<tr>
<td>+e</td>
<td>106.19 MeV/c$^2$</td>
</tr>
<tr>
<td><strong>Spin, $S_\mu$</strong></td>
<td>Reduced Mass</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>0.9956 $\mu_\text{H}$</td>
</tr>
<tr>
<td><strong>Rest Mass, $m_\mu^+$</strong></td>
<td>First Bohr Radius</td>
</tr>
<tr>
<td>105.6584 MeV/c$^2$</td>
<td>0.5315 Å</td>
</tr>
<tr>
<td>0.11261 $m_\text{p}$</td>
<td>1.004 $a_0$</td>
</tr>
<tr>
<td><strong>Magnetic Moment, $\mu_\mu$</strong></td>
<td>First Ionization Potential</td>
</tr>
<tr>
<td>4.49048x10$^{-23}$ erg/G</td>
<td>13.54 eV</td>
</tr>
<tr>
<td>3.1833452 $\mu_\text{p}$</td>
<td>0.9956 (IP)$_\text{H}$</td>
</tr>
<tr>
<td><strong>g-factor, $g_\mu$</strong></td>
<td>Hyperfine Frequency</td>
</tr>
<tr>
<td>2.002331848</td>
<td>4463.34 MHz</td>
</tr>
<tr>
<td><strong>Gyromagnetic Ratio, $\gamma/2\pi$</strong></td>
<td></td>
</tr>
<tr>
<td>0.0135534 MHz/G</td>
<td></td>
</tr>
<tr>
<td><strong>Mean Lifetime, $\tau_\mu$</strong></td>
<td></td>
</tr>
<tr>
<td>2.197 $\mu$s</td>
<td></td>
</tr>
</tbody>
</table>
C. Production, Decay and Detection of the Positive Muon and Muonium

TRIUMF's cyclotron produces a proton beam of 500 MeV, which impinges on a production target (e.g., C or Be), generating positive pions (in our case) by the following nuclear reaction,

$$^{9}\text{Be} + p^+ \rightarrow ^{10}\text{Be} + \pi^+$$  \hspace{1cm} (1.1)

The pion has a mean lifetime of 26 ns, then decaying into a positive muon and a muon neutrino \[10\],

$$\pi^+ \rightarrow \mu^+ + \nu_\mu$$  \hspace{1cm} (1.2)

Because the muon and all neutrinos have spin \(\frac{1}{2}\), the muon neutrino has negative helicity (momentum opposite its spin direction), and the pion has zero spin, spin conservation demands that the muon is also produced with negative helicity (i.e., upon their formation via decay process (1.2) the muon spin vector points exactly opposite to its momentum direction). The immediate outcome of the muon's negative helicity is that all muons are produced 100% spin-polarized, i.e., a beam of positive muons injected into a sample or field is spin-oriented \[11\].

The muon's lifetime is \(\sim 2.2\ \mu s\), decaying to produce a positron and a neutrino-antineutrino pair \[12\],

$$\mu^* \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$$  \hspace{1cm} (1.3)

By similar arguments to those above, decay (1.3) also violates parity, and the muon decay positron in (1.3) is thus emitted preferentially in the direction of the muon spin \[13\]. It is the ability to detect this decay positron, and the predictability of its emission direction, along with the muon's initial 100% spin polarization that makes the \(\mu\)SR technique possible.
Muons implanted into a given environment, which will typically bear a magnetic field and/or contain nuclei with non-zero spin, interact with these surroundings, causing a change in their orientation and thus their anisotropic decay. Observation of this changing decay direction gives the asymmetry parameter, \( a \). If positrons of all energies were equally detectable, the observed asymmetry would be 1/3. However due to absorption of lower energy positrons and varying detector efficiencies, the empirically observed asymmetry, \( a_\mu \), is often lower, but can also be higher than 1/3 [6,14].

As a muon thermalizes in its environment and harnesses a nearby electron to form muonium, it not only interacts with the external and nearby nuclear magnetic environments, but also with its captured electron through the hyperfine interaction. Bare muonium has a “vacuum” hyperfine coupling constant, \( A_{\mu} = 4463 \text{ MHz} \) [15].

D. The \( \mu \)SR Technique at TRIUMF

TRIUMF is Canada’s national meson facility, which produces on average a 150 \( \mu \)A 500 MeV proton beam. Although the faculty of numerous universities throughout the world is represented by their research at TRIUMF, it is funded by the NRC and jointly operated by a consortium of Canadian universities, initially by the three British Columbian universities (hence “TRI-University Meson Facility” – TRIUMF), but joined soon thereafter by the University of Alberta. There are multiple beam lines at TRIUMF, allowing for simultaneous proton, pion, muon, radioisotope and rare particle studies. Figure 1-1 is a diagram of TRIUMF’s Meson Hall, where all \( \mu \)SR experiments take place [16].
Figure 1-1. Schematic of the TRIUMF meson hall. The high-energy proton beam is produced in the cyclotron, and then is distributed among the several beam lines for use in research. Used by permission of author [16].
i. Muon Production and Collection at TRIUMF [17]

As noted, intermediate-energy protons (~500 MeV) are directed down a principal beam line (BL1A), which has different muon production target stations ("T1" and "T2"). Upon proton bombardment, pions are produced by equation (1.1). The two types of muons most often used at TRIUMF are “surface” muons and “backward” muons, each being ideal for different target types. Surface muons are drawn from those pions decaying on (or within micrometers of) the pion production target, and their beams are highly monochromatic, with energies near 4.1 MeV and an average momentum of 29 MeV/c. As such these muons are ideal probes of gaseous, liquid, or powder samples. Contamination of these beams is high; there are approximately 100 positrons per surface muon, so DC separators are used to clear the contamination away, while spin rotating the muons such that their momentum vector is perpendicular to their spin. These DC separators use a combination of electric and magnetic fields to select muons of a certain momentum to be rotated and injected into a sample. Strong magnetic fields parallel to the muon’s spin and momentum can be set up easily, so that muons are injected into a spectrometer for longitudinal field (or LF) experiments. Using the DC separators on this setup spin rotates the muons, injecting them into the spectrometer in a transverse field (TF) fashion.

Backward muons are the decay products of in-flight pions. Since these pions decay while traveling forward, and muons can form with or against the direction of the pion’s momentum (forward or backward in the pion’s rest frame), the muon can either be formed with more or less momentum than original pion (forward or backward muons, respectively). Although production of ‘forward’ muons was the main mode of operation in the early days of
\(\mu SR\) at TRIUMF, such high energy muon beams are no longer needed. Note that a “backward” muon is only traveling backward in the pion’s *rest frame*; its net momentum vector still points forward. As such, the muons are formed with a high forward momentum in the *laboratory frame* and thus are ideal as dense media probes.

Regardless of what type of muon beam is formed, it is collected down different beam lines (or channels). There are three dedicated muon beam channels in use at TRIUMF today, M9, M15, and M20. M9 is a backward muon beam line, while M15 and M20 are surface muon beam lines. The M20 beam line was used for the work done in this thesis, and its schematic is shown in Figure 1-2. It consists of a series of bending magnets and quadrupoles for conditioning and directing, and focusing the beam, respectively. They are also tuned to select the momentum of the muons used.

**ii. Detection of Muon Decay [18]**

Because they are forms of ionizing radiation, both incident muons and their decay positrons can induce scintillation (light emission) in certain materials. At TRIUMF, scintillator detectors are used to detect decay events by counting the individual photons produced, which are amplified by photomultiplier tubes (PMTs) that produce an analog voltage signal of approximately 300 mV. The PMTs are kept at a distance away from the experimental field by connecting the scintillators to long (\(-0.5-1.0\) m) light guides. These scintillation counters are often large “paddles”; their size, as well as the length of the light guides, can contribute to \(\mu SR\)'s \(-1\) ns time resolution.
Figure 1-2. Schematic diagram of the M20 beam line at TRIUMF. ‘M20B’ designates a bending magnet, and ‘M20Q’ stands for a quadrupole. ‘1AT2’ is the Beamline 1A Production Target 2. Jaws are used to help select muon intensity by collimating the beam. Used by permission of author [14].
The spectrometer used for this project is called Helios, which has a helium-cooled superconducting magnet capable of fields up to approximately 7 Tesla [19]. A schematic diagram of Helios and its counter setup is shown in Figure 1-3. A vast array of electronics is used to count incoming muons and detect their decay positrons. A muon traveling through the target cell window is detected by the backward (B) and the first muon (M1) counters. If the muon misses the cell window and hits the M2 counter, a kill signal is sent to the computer and the detectors are reset. Decay positrons are detected by coincidence either by the ‘Up’ U1 & U2 or the ‘Down’ D1 & D2 counters. The forward and backward counter arrangements are used for LF operation; while the up and down counter arrangements are used for TF operation.

The data from each counter are digitally recorded in a computer database and are binned in histograms of events (in the form of counts per unit time). The histogram sizes fortunately can be adjusted as desired, to observe different time-dependence aspects of the muons’ interactions with the given sample (described briefly in the following chapter).

iii. Muons and Muonium as Spin Probes

In research, muons and muonium are used as probes of kinetic isotope effects and of spin environments. This thesis focuses entirely upon the use of muons as spin probes of radicals, in particular Mu-radicals, by the addition of muonium to unsaturated organic molecules. Chemical kinetics will not be discussed here, rather the hyperfine coupling constants of the Mu-ethyl (C₂H₄Mu) and Mu-cyclohexadienyl (C₆H₆Mu) radicals in the bulk and zeolites will.
Figure 1-3. a) Schematic diagram of the Helios $\mu$SR Spectrometer (used by permission of author [19]), and b) the detector and cell orientations in Helios. The muon beam enters from the left. See text for explanation.
E. The Mu-ethyl and Mu-cyclohexadienyl Radicals

Muonium, as an H-atom analogue, can add across alkyl- or aryl-double bonds at thermal or epithermal (~eV) energies to form neutral Mu-alkyl or -aryl radicals [20]. As mentioned before, these radicals are the isotopic analogues of those radicals formed by addition of H-atoms to unsaturated molecules. Mu-radicals will be explained in more detail in the following chapter once Muonium has been better defined. The Mu-ethyl radical, shown in Figure 1-4, is formed via the addition of Mu to ethene. In terms of chemical environments, this radical has two types of protons, labelled α- and β-protons, indicating their proximity to the radical carbon center. These individual nuclei correspondingly have different hyperfine coupling constants (also explained later and abbreviated "hfccs"), labelled $A_{\alpha}$ and $A_{\beta}$; the muon’s hfcc is labelled $A_{\mu}$. Similarly, the Mu-cyclohexadienyl radical is formed by Mu addition to benzene, resulting in a partially-aromatic and partially-planar molecule with one sp$^3$ and five sp$^2$ hybridized carbon atoms.
Figure 1-4. The thermal addition of muonium to ethene, yielding the Mu-ethyl radical with the two chemically different $\alpha$- and $\beta$-protons, each having a different hyperfine coupling constant.
Chapter 2 – Mu-Radicals, Hyperfine Coupling Constants and their Detection

A. Muonium and Mu-radicals

i. Muonium

In zero magnetic field, the four basis spin states of muonium ($|m_e \mu \rangle = |\pm \frac{1}{2}, \pm \frac{1}{2}\rangle$) are split by the hyperfine interaction into a singlet state, $|S=0, M_s=0\rangle$, and a triplet state, $|S=1, M_s=(0,-1,1)\rangle$. When a magnetic field is applied, the degeneracy of the triplet state is lifted and four separate energy levels exist (in total), as shown by the Breit-Rabi diagram of Figure 2-1. In a transverse field the initial 100% muon polarization gives rise, theoretically, to the four transitions labelled in the figure as $v_{mn}$. At low fields ($\leq 10$G), the energy level differences $\Delta E_{12}$ and $\Delta E_{23}$ are approximately degenerate, so that $v_{12} = v_{23} = v_{Mu}$, giving a coherent precession frequency of triplet muonium. This characterizes many studies of Muonium kinetics, but is not of interest in the present study. At slightly higher fields, $\approx 10-20$G, the difference or "beat frequency", $\Omega = \frac{1}{2} (v_{23} - v_{12})$, gives a direct measure of the isotropic muon-electron hfcc, $A_{Mu}$ (which in a vacuum is 4463 MHz) [3]. In this field range energy eigenstates $|2\rangle$ and $|4\rangle$ are linear combinations of the $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ states, with field-dependent amplitudes, $c^2$ and $s^2$, as indicated in the figure. At the fields of interest in the present study ($B = 1-6$ kG), all transition frequencies, $v_{mn}$, are comparable to $A_{Mu}$ and cannot be resolved by the $\mu$SR technique, such that observation of muonium in TF is inherently limited to be a low-field technique.

In a longitudinal field there is no muon precession, but rather the muon spin in muonium is modulated at the modulation frequency $v_{24}$. The muon polarization is strongly field-dependent in longitudinal fields, for $B \gg A_{Mu}$ almost 100% of the initial polarization can be recovered. Though this thesis is not necessarily with muonium, it is the transfer of muon polarization to a
Figure 2-1. Breit-Rabi diagram of the energy levels of muonium as a function of applied field [58]. States $|2\rangle$ and $|4\rangle$ are mixed states with the field-dependent amplitudes $c^2$ and $s^2$. The hfcc of muonium, $A_{\mu\mu}$, is 4463 MHz (the splitting between the triplet and singlet states at zero field). X is the ratio of the applied field ("B") to the hyperfine field of muonium ("$B_0$" = 1585 G).

Transitions between energy levels m and n are labelled as $v_{mn}$. In the low field limit ($\leq 10$G for $B_0 = 1585$ G), the observed frequency is due to $v_{12}$ and $v_{23}$, which are approximately equal. In intermediate fields, $v_{12}$ and $v_{23}$ begin to differ and thus a 'beating' signal would be observed.
radical by Mu-addition that is important. The case of a muoniated radical can, in fact, be thought of as a 'scaled' Mu atom, in terms of hyperfine coupling.

### ii. Muonium Radicals

In muoniated radicals, the situation is similar insofar as a Mu-radical can be thought of as a pseudo-Mu atom. The magnetic field dependence of the Mu-radical’s energy level splitting is also dependent upon the muon-electron hfcc, but in this case it tends to be an order of magnitude smaller. This is because in Mu-radicals the muon-electron distance is greater since there are a number of nuclei around which the radical electron can propagate, giving rise to both a muon-electron hfcc, \( A_\mu \), and nuclear (proton) hfccs, \( A_p \) \([35,36]\). In the high-field limit, where \( X \geq 10 \) for the radical, \( s^2 \rightarrow 0 \) and \( c^2 \rightarrow 1 \), giving rise to the eigenstates shown in Figure 2-2. Two distinct frequencies can be detected, \( \nu_{12} \) and \( \nu_{34} \), which are then independent of field. The splitting between these energy levels is dependent upon the hyperfine coupling constant of the Mu-radical, \( A_{Mu}(R) \), which will now be referred to simply as ‘\( A_\mu \)’. In the first order, the simple calculation of the difference between \( \nu_{34} \) and \( \nu_{12} \) yields the radical’s muon hfcc (see Section 2.C.ii) to a high degree of accuracy (on the order of 0.1 to 1% error).

Figure 2-2 shows the Breit-Rabi diagram for a two-spin system with a hyperfine coupling constant of 330 MHz. Such a system, for example, could be the Mu-ethyl radical (\( \text{MuC}_2\text{H}_4 \)) in the gas phase in a transverse field, which has a muon-electron hyperfine coupling constant, \( A_\mu \), of approximately 330 MHz (\( A_\mu \) is the splitting between the triplet and singlet states at zero field) \([26]\). Again, in transverse fields, other nuclear spin interactions are not observed and thus the nearby proton energy levels are not included in the figure. The solid lines represent the exact
Figure 2-2. The Breit-Rabi diagram for a two-spin ($\mu^+e^-$) system with a hyperfine coupling, $A_\mu$, of 330 MHz (or $B_0 = 117$ G). States are labelled by their high-field values, which are not actually seen until fields corresponding to $X \geq 10$. The 330 MHz hyperfine coupling was observed for the Mu-ethyl radical in gaseous ethene at room temperature, which can be thought of as a pseudo Mu-atom and hence approximated as a two-spin system. The observed transition frequencies are $v_{12}$ and $v_{34}$, the difference between them giving a direct measure of the radical's muon hfcc. The dotted lines represent the field dependence of state $|2>$ and $|4>$'s energy levels in the high-field limit ($X \geq 10$), extrapolated to zero field. Taken and altered from Ref. 26 by permission of author.
energy eigenvalues of the muon-electron spin Hamiltonian in the absence of proton interactions, whereas the dashed lines are the high-field approximations for the second and fourth states.

Two radicals are discussed in this document, the Mu-ethyl radical, for which some bulk data is referenced (from previous studies [22,26,28,31,37-41]), and all zeolite data to date is reported (this work); and the Mu-cyclohexadienyl radical, the referenced data of which is from the bulk [8,23,32,42-44] and previous zeolite/silica studies [24,45-49]. Hyperfine couplings, Mu-radical detection methods and some results for the Mu-ethyl and Mu-cyclohexadienyl radicals will be discussed in the following sections.

B. Hyperfine Coupling Constants and $\mu$SR as a Hyperfine Coupling Probe [20,21]

Hyperfine coupling is a spin-spin interaction or coupling between a nucleus and a nearby, unpaired electron. It is generally a tensor, but can generally be broken down into two parts, anisotropic (direction dependent) and isotropic (direction independent) hyperfine coupling, both depending upon the population density of the electron around the nucleus. In the gas phase and most liquids, rapid tumbling averages the anisotropic hyperfine coupling constant (hfcc) to zero, leaving only the isotropic part, which have been determined by the UBC $\mu$SR gas chemistry group and others for alkenes [22], benzenes [23] and various other muoniated radicals [e.g.,30-33]. Isotropic hfccs, also known as Fermi contact terms, are studied in laser, ESR, and $\mu$SR-radical studies, or in any paramagnetic system with nonzero nuclear spins (e.g., certain inorganic or organometallic compounds with unpaired d-electrons).
The isotropic hfcc, $A$, gives a measure of the s-character of the orbital containing the radical electron *at the nucleus in question*, and is described by,

$$A = \frac{8\pi}{3} g_e g_N \mu_B \mu_N |\Psi(0)|^2$$  \hspace{1cm} (2.1)

where $g_e$ and $g_N$ are the electronic and nuclear g-factors, and $\mu_B$ and $\mu_N$ are the Bohr and nuclear magnetons, respectively ($\mu_n = \frac{e\hbar}{4\pi m_n}$, where in the Bohr magneton case, $m_n = m_e$) [20,53].

In order to compare the results from $\mu$SR and ESR studies, i.e., for $A_\mu$ to be compared to $A_p$ (where $p$ indicates ‘proton’; note, more specifically, $A_\alpha$ is the *alpha*-proton hfcc and $A_\beta$ is the *beta*-proton hfcc), it is sensible to correct for the mass difference between the two nuclei, so the muon hfcc is ‘reduced’ to $A'_\mu$ in terms of gyromagnetic ratios, that is,

$$A'_\mu = A_\mu \left( \frac{\gamma_p}{\gamma_\mu} \right) = 0.314 A_\mu$$  \hspace{1cm} (2.2)

This reduced muon hfcc can also be used in the determination of the average hyperfine coupling constant, $\langle A \rangle$, for direct comparisons of $\mu$SR and ESR results, where any significant differences between the two show “residual” or “secondary” isotope effects due to the muon. For example in ethene, when the Mu-ethyl radical is formed, at the beta-carbon (Figure 1-4) there are two protons and one muon bonded to the $sp^3$ carbon. This $-CH_2Mu$ group is considered an isotopomer of the $-CH_3$, or methyl, group and $\langle A \rangle$ is defined as,

$$\langle A \rangle_{CH_3} = \frac{1}{3} [A'_\mu(MuCH_2) + 2A_\beta(MuCH_2)]$$  \hspace{1cm} (2.3)
and is used to compare the two different $\mu$SR hfccs for the hydrogen/muonium atoms in -CH$_3$Mu to the one hfcc determined by ESR for the -CH$_3$ group [22]. Indeed, a residual isotope effect of $\sim$10% has been determined from studies in the gas and liquid phases [22,31,40,52,62].

C. Detection Methods

i. Synopsis of Detection Methods

Using the different techniques of $\mu$SR, muonium and muoniated alkyl radicals can be detected and characterized. Radical reaction kinetics, motional dynamics and hyperfine couplings can all be studied using a combination of longitudinal- and transverse-field $\mu$SR. In this research, the hyperfine couplings of the Mu-ethyl radical were determined using Transverse Field $\mu$SR (TF-$\mu$SR) and muon Avoided Level Crossing Resonance ($\mu$ALCR).

ii. The TF-$\mu$SR Technique and Detection of Mu-radicals

In transverse-field $\mu$SR (TF-$\mu$SR) experiments, muons enter a sample with their spins perpendicular to the applied DC-magnetic field. Since the muon decay is asymmetric, precessing muons give rise to an asymmetry which oscillates in time, and, combined with the decay lifetime of the muon (2.2 $\mu$s), to the raw $\mu$SR “signal” seen in Figure 2-3a.

The time histogram from a single counter of a TF-$\mu$SR run can be fit to the following equation:

$$N(t) = N_0 \exp(-t/\tau_0)[1 + A(t)] + N_B$$

(2.4)

where $N_0$ is a normalization factor, $N_B$ is a constant to account for time-independent background, and $A(t)$ is the muon decay asymmetry, having the form,

$$A(t) = \sum_i A_i e^{-\lambda_i t} \cos(\omega_i t + \phi_i)$$

(2.5)
Figure 2-3. Sample TF-μSR spectra for the Mu-ethyl radical in 10 bar ethene at 298K, 14.4 kG:

a) A raw spectrum of Mu-ethyl in the time domain ($N(t)$ as in Eqn (2.4)). In such a high field, oscillations are difficult to see, but are most noticeable at times before 0.2 μs.

b) The asymmetry spectrum of a), yielded when the raw spectrum is divided by $N_0 = \exp(-t/\tau_\mu)$, and the background term is subtracted. This is $A(t)$ from Equation (2.5). Oscillations are easier to see; it appears that two similar frequencies are present with opposite amplitudes.

c) An expanded portion of the asymmetry spectrum with a sinusoidal line (to guide the eye) showing two visible precession frequencies, determined to be at 31 and 195 MHz ($v_{12}$ and $v_D$, respectively). Note that this portion of the figure was taken from Ref. 28, although a), b), and d) are indeed from the same data. This spectrum shows the oscillating asymmetry of the Mu-ethyl radical. The higher radical frequency, $v_{34} = 359$ MHz, is not visible here.

d) The Fourier transform of b). The large peak dominating the spectrum at 195 MHz is due to muons in a diamagnetic environment, and the two smaller peaks at 31 and 359 MHz are the radical precession frequencies. The observed diamagnetic frequency (truncated by 100 times) corresponds to an applied field of ~14.4 kG, at which this spectrum was obtained.
where the subscript $i$ labels different possible magnetic environments that the muon may be found in (diamagnetic, muonium, Mu-radical), $A_i$ is the initial asymmetry, $\lambda_i$ is the relaxation rate, $\omega_i$ is the Larmor precession frequency, and $\phi_i$ is the initial phase of the muon spin polarization in that environment [29].

The $\mu$SR "signal" of interest is the asymmetry of Equation (2.5), easily obtained from (2.4), after correcting for the background, muon decay and normalization, as seen in Figure 2-3b. Grouping counts with similar times in the same 'bins', i.e., all counts from 0-5 ns are combined as one data point (plus errors), also with 5-10 ns, and so on, different aspects of the muons' oscillations can be seen. As an example, Figure 2-3c shows the same data as in Figure 2-3b, but it has been packed at 0.3125 ns/bin [28]. With this 'binning', two frequencies are clear – and these are determined from the fits to be at 31 and 195 MHz – from spin transitions in the muoniated ethyl radical and muons in a diamagnetic environment, respectively.

As one might guess, Fourier transform of an asymmetry spectrum leads to one like that shown in Figure 2-3d in frequency space, dubbed an 'FT-$\mu$SR' spectrum. Note that this is spectrum is from the same data as in Figure 2-3b and 2-3c, and that the height of the central peak (195 MHz -- due to diamagnetic environments) has been truncated because it is approximately 100 times taller than those of the muoniated radical. From these 'FT-$\mu$SR' spectra, Mu-ethyl radical hyperfine coupling constants can be determined, described in the following section, $A_\mu$ ($C_2H_4(g)$) $\approx 330$ MHz [28].
iii. Mu-radical Hyperfine Couplings as Measured by TF-μSR

In transverse field experiments, one can use the peak locations of frequency-space spectra to determine hfccs. Figure 2-4 shows an example FT-μSR spectrum for a sample of pure frozen benzene at 263 K in a field of approximately 22.5 kG [24]. Note the two peaks (38.5 and 563 MHz) symmetric about the central diamagnetic peak (300 MHz). The distance between these two peaks gives the muon’s hfcc (approximately 525 MHz). Relative peak heights are not indicative of populations of states, but reflect counter time resolution as well as this technique’s sampling time-window relative to the muon’s lifetime. The muon’s hfcc for the Mu-ethyl radical was also determined in this way in Ref. 28 (Figure 2-3); 359 – 31 MHz ≈ 330 MHz.

An argument given earlier in terms of a pseudo Mu-atom can be put in a more rigorous basis as follows: In high magnetic fields, the isotropic spin Hamiltonian for the Mu-ethyl radical is,

\[
\hat{H}/\hbar = v^e S_e - v^\mu I_{2\mu} - v^{A\alpha} I_{2\alpha} - v^\beta I_{2\beta} + A_\mu S \cdot I_\mu + A_\alpha S \cdot I_\alpha + A_\beta S \cdot I_\beta
\]  

(2.6)

Where \(v^e, v^\mu, v^{A\alpha}, v^\beta\) are Zeeman frequencies, and \(A_\mu, A_\alpha, A_\beta\) are the aforementioned hfccs [25-27]. The first four terms in (2.6) represent the Zeeman energies of the different spin-bearing particles in a magnetic field, neglecting \(^{13}\text{C}\) (of very minute natural abundance); the last three terms in the equation are the hyperfine contact interaction operators for the hyperfine interaction of the muon and other nuclei. Because four different Zeeman frequencies are involved here, and the allowed transitions should be \(\Delta M_{\text{tot}} = \pm 1\), detecting Mu-radicals at low fields is difficult. At high enough fields, where \(v^e \gg A_\mu, A_\alpha, A_\beta\), the selection rule becomes \(\Delta m_e = \Delta m_\alpha = \Delta m_\beta = 0\), and thus \(\Delta m_\mu = \Delta M_{\text{tot}} = \pm 1\). In these fields, only two transition frequencies show up in the radical spectrum, labelled in Figure 2-2 as “\(v_{12}\)”, “\(v_{34}\)”, corresponding to the transition lines in Figure 2-3d as peaks in Fourier space.
Upon muonium’s addition to benzene, the cyclohexadienyl radical, C₆H₆Mu, is formed. The two peaks identifying this radical are v₁₂ and v₃₄, at 38.5 and 563 MHz respectively. Their difference (~525 MHz) gives the isotropic muon hfcc, Aₓ. The central peak (v₀ = 300 MHz at this field) is due to muons in unknown diamagnetic environments. Used by permission of author [24].
Only muon hfccs can be determined in TF-/FT-\(\mu\)SR, calculated approximately from the two transition frequencies and the diamagnetic frequency, \(v_D\), as in equations (2.7) through (2.10),

\[
\begin{align*}
\nu_{\text{mid}} &= \frac{1}{2} \left[ \left( A^2 + (\nu_e + \nu_\mu)^2 \right)^{\frac{1}{2}} - \nu_e + \nu_\mu \right] \quad (2.7) \\
\nu_{12} &= \left| \nu_{\text{mid}} - \frac{1}{2} A_\mu \right| \quad \nu_{34} = \nu_{\text{mid}} + \frac{1}{2} A_\mu \quad (2.8)
\end{align*}
\]

To a good approximation \(\nu_{\text{mid}} \approx v_D\) at high fields, thus,

\[
\begin{align*}
\nu_{R1} &\approx \left| v_D - \frac{1}{2} A_\mu \right| \quad \nu_{R2} \approx v_D + \frac{1}{2} A_\mu \\
A_\mu &= \nu_{34} - \nu_{12} \quad (2.10)
\end{align*}
\]

Although the diamagnetic frequency arises from muons that decay while in unknown diamagnetic environments (and it has a well-known field dependence useful for field calibration), \(\nu_{\text{mid}}\) is the frequency exactly between the two transition frequencies, and is dependent on the applied field and the muon’s hfcc in the radical. The Breit-Rabi diagram for a three-spin system in the low and high-field limits is shown later in Figure 2-5a.

iv. Mu-radicals in LF and Muon Avoided Level Crossing Resonance [6,24]

As outlined earlier for the case of muonium, in a longitudinal field (LF) environment, where the initial muon polarization is parallel to the applied field, there is no dephasing (off of \(v_{24}\) resonance) and the muon decay asymmetry has the form,

\[
A(t) = \sum_i A_i e^{-\lambda_i t} \quad (2.11)
\]

where the symbols have the same meaning as in Equation 2.5 [26].
In our studies, muon Avoided Level Crossing Resonance, or $\mu$ALCR, was used to probe the Mu-ethyl radical in zeolites. $\mu$ALCR is a Longitudinal Field, Time Integral (LF-TI) technique by which muons are injected into a sample at varying fields, and the integrated forward and backward (F & B) positron rates are recorded. $\mu$ALCR was first employed to measure nuclear hyperfine interactions in the mid-1980s, after its application to $\mu$SR was proposed by Abragam [32,50,51]. It is much more sensitive to the detection of slowly formed radicals, on a time-scale comparable to the muon lifetime, than TF-$\mu$SR because of the conservation of phase in longitudinal fields noted above.

It is worth commenting that in probing dilute systems (as in the ethene-zeolite study in this thesis) using a combination of FT-$\mu$SR and $\mu$ALCR is ideal, for at conditions where one technique has hindered sensitivity, usually the other is superior, and *vice versa*. Another beneficial aspect of this technique, compared to FT-$\mu$SR, is that the hfccs of nearby (nonzero-spin) nuclei can be detected. For example, in MuC$_2$H$_4$ and MuC$_6$H$_6$, the non-equivalent protons present in the molecule have different, detectable hfccs. It is safe to assume that on the timescale of the muon’s lifetime, nearby protons do not significantly interact with one another, thus, Mu-alkyl or -aryl radicals can be treated as *separated* three-spin ($\frac{1}{2}$) systems.

Over the range of high fields used in $\mu$ALCR (5 - 40$^+$ kG), the energy eigenstates of these three-spin systems ($\mu^+, e^-, k_{\text{nuclear}}$) are approximately stationary Zeeman states. At certain magnetic fields, where two of these states approach degeneracy, their crossings are avoided by the isotropic Fermi contact and/or dipolar interaction of the spins. Around these fields, the eigenstates become linear combinations of pure Zeeman states, causing spontaneous spin-flips of
the muon alone, or the muon and a coupled proton. Muon spin-flips cause a reduction in the
detected decay asymmetry corresponding to a transfer of backward to forward counts as the
magnet is swept around these fields. It is at these points where 'avoided level crossings' (ALC)
occur. Figure 2-5 shows the Breit-Rabi diagram for a three-spin system at low and high
longitudinal fields.

Three different types of ALC resonances defined by $\Delta M$ are observable by $\mu$ALCR,
where $M = m^e + m^\mu + m^k$. The $\Delta_0$ ($\Delta M = 0$) resonance is driven by elements of the spin-
Hamiltonian matrix of the form $A^\mu k S^e \hat{J}^\mu k$ and $A^\mu k S^e \hat{J}^\mu k$, which are due to isotropic coupling
of the muon to a nuclear spin [24], and is sometimes referred to as the muon-proton spin “flip-
flop” resonance. Because this is the only ALC resonance due to isotropic couplings, it is the
only one observed in the gas or liquid phases, where rotational averaging eliminates dipolar
couplings.

The muon “flip” ($\Delta_1$ or $\Delta M = 1$) transition is a direct result of the dipolar (anisotropic)
part of the muon hyperfine interaction causing nearby Zeeman states to couple, and it arises from
spin-Hamiltonian matrix elements which contain $S^e \hat{J}^e$ [24]. This transition is dependent upon
the orientation of the hyperfine tensor's principal axes relative to the applied field [27]. Since
the tensor is fixed relative to the shape of the radical, and the radical reorients in space, this
transition serves as a sensitive probe to radical dynamics in ordered environments. The muon-
nuclear spin “flip-flip”, $\Delta_2$ ($\Delta M = 2$), transition occurs due to terms containing $S^e \hat{J}^e$, leading to
an ALC, like in the $\Delta_1$ case, also observed only in the presence of anisotropy [27].
Figure 2-5. The basis for avoided level crossing resonance:

a) The Breit-Rabi diagram for a three spin-$\frac{1}{2}$ system with a muon hfcc of 330 MHz (e.g., a muon, an electron and a nearby proton in the Mu-ethyl radical) in the low-field case. The transitions labelled $v_R$ and $v_{R1}$ are the same as $v_{12}$ and $v_{34}$ identified earlier, and can be seen in a TF-$\mu$SR experiment. Used by permission of author [26].

b) A sample $\mu$ALCR spectrum corresponding to the high-field energy level diagram for the above system [27]. Note that energy-levels that should cross as specific “resonant” fields are actually avoided crossings, due to off-diagonal matrix elements. At these resonances spontaneous spin-flips occur, labelled $\Delta M=0,1,2$. See discussion in text.
This resonance is usually weak and narrow, and is not pursued in this thesis. Because of the large energy gap between the electronic $\alpha$ and $\beta$ manifolds of states ($\sim 10^4$ MHz $T^{-1}$), usually transitions are only observed between states with the same $m_c$ (hyperfine energy level gaps for protons and muons are usually $\sim 100$ MHz), as shown in Figure 2-5.

\textbf{v. Mu-radical Hyperfine Couplings as Probed by $\mu$ALCR}

Measurements of the fields at which a particle resonance occurs gives the proton and muon hyperfine couplings accurately. The muon hfcc, $A_\mu$, can be determined from the field at which the $\Delta_1$ resonance (for the muon spin flip – where $\Delta m_\mu = 1$) occurs [24]:

$$B_r(\Delta_1) = \frac{1}{2} \left| \frac{A_\mu - A_\mu}{\gamma_\mu - \gamma_e} \right|$$

(2.12)

The selection rule for the muon-proton spin-flip-flop is $(\Delta m_\mu + \Delta m_p) = 0$, where both the muon and nuclear magnetic spin quantum numbers change. The proton hfccs, $A_p$ can be determined from the field at a $\Delta_0$ resonance and by knowing the value $A_\mu$ [24]:

$$B_r(\Delta_0) = \frac{1}{2} \left| \frac{A_\mu - A_k}{\gamma_\mu - \gamma_k} - \frac{A_\mu + A_k}{\gamma_e} \right|$$

(2.13)

It is worth noting that, unlike basic ESR techniques, the $\mu$ALCR technique is sensitive to the relative signs of the muon and coupled nucleus hfccs. The absolute magnitudes are also often well determined since errors in positions for both the $\Delta_0$ and $\Delta_1$ resonances can be as low as $\sim 0.1\%$ for well-resolved peaks. In some cases line-broadening, overlapping resonances and/or
weak amplitudes (particularly with $\Delta_1$ resonances) cause peaks to ‘sink’ into the baseline – with errors on the order of 5% (increasing the errors of $A_\mu$ accordingly). Since the proton hfccs are dependent upon $A_\mu$, when determined using only $\mu$ALCR data, errors in both the muon and proton hfccs tend to be high. Combining the data from FT-$\mu$SR and $\mu$ALCR compensates for this. Using the FT-$\mu$SR results for a muon hfcc with the $\Delta_0$ data from $\mu$ALCR runs yields good overall hfcc results with minimal uncertainty.

D. Experimental

Stainless steel cells (see Figure 2-6) of approximate outer diameter 4.5 cm, thickness of 1.5 cm, with a thin stainless steel muon entrance window of $\sim$50 $\mu$m thickness, were filled with known weights of one of three types of faujasite zeolite (NaY, HY or USY) obtained from Zeolyst International of Valley Forge, USA (Si/Al ratio = 2.5 for NaY and HY, and 15 for USY; average unit cell size = 24.45 Å) [66]. Filling the cells with the zeolite powder was done via one of the two small filling holes on the edge of the cell, which were then sealed with small copper gaskets and stainless steel screws. The cells were then connected to a diffusion pump via an annealed copper tube soldered to the back of the cell and were dehydrated at high temperature (450 – 500 degrees centigrade) under vacuum for over 5 hours each.

Following weighing of the dry, vacuum-tight cell, the zeolite was loaded with ethene gas, again via the copper tube attached to the cell. This was done in the following manner for all sample cells: Suppose a given cell was determined to contain 1.25 grams of the dry NaY faujasite (the unit cell formula weight of NaY is 12,805.6 g/mol) [66]. This corresponds to
Figure 2-6. Diagram of the zeolite-gas cell. The window at the front of the cell is made from stainless steel of approximately 50 $\mu$m thickness to allow passage of muons into the cell. The body of the cell is made from machined stainless steel. The filling holes are located on the sides of the cell; this part is sealed with copper gaskets under stainless steel screws. The gas-loading tube is a copper tube leading from a small hole in the back of the cell, and is crimped shut following zeolite drying and loading to ensure an airtight seal [1].
9.76x10^{-5} moles of NaY unit cells; because there are 8 supercages per unit cell, there are 7.81x10^{-4} moles of supercages [64,65]. This sample cell was then attached to an evacuated gas system having a total volume of 559 ml, monitored by a 10,000 torr “Baratron” pressure transducer (MKS Instruments, Andover, USA) with precision to 1 torr. The system was then filled with a known amount of ethene gas, usually on the order of 1000 to 1500 torr, and once a predetermined amount of gas was adsorbed into the zeolite (as indicated by a decrease in total system pressure) the remaining gas in the system was pumped out and the cell was sealed by using a “cold-weld” crimping tool (CHA Industries, USA) that produces a vacuum-tight seal. In the above example, if a loading of one ethene molecule per supercage (1/SC) was desired, 26 torr of gas would have to be adsorbed into the zeolite, at room temperature and assuming gas ideality. Samples were prepared at least a week ahead of data taking, to account for estimated molecular equilibration times at low loadings [24]. All data discussed herein was taken at loadings of 1, 3 or 5 gas molecule(s) per supercage. The estimated error on this loading technique is ±0.5/SC based on the combined errors associated with zeolite weighing and precision of allowed adsorption amounts (e.g., loading 26 torr, and not 20 or 30 torr before the remaining gas was pumped away).

Filled zeolite sample cells were mounted in a helium-flow cryostat for temperature control, and then placed in the “Helios” superconducting magnet. The temperature was varied in the range 5-500 K (allowed to equilibrate at each temperature for at least 20 minutes), and was monitored by two thermocouples attached to the target cell, typically giving consistent readings within 0.2 K. Being as the zeolite constitutes over 99% of the sample weight, essentially all muons stop in the faujasites and none in the gas between the minute grains. The muons are believed to diffuse to areas of ethene adsorption, where the muoniated ethyl radical forms by Mu addition.
FT-$\mu$SR and $\mu$ALCR experiments were carried out using TRIUMF's M20 surface muon beam line, running at nominal momentum over the course of three two-week beam periods. FT-data were taken at varying fields (1-6 kG) upon each cell's first use, to verify the identity of the $v_{12}$ and $v_{34}$ radical peaks (recall Figures 2-3 and 2-4), but typically a transverse field of 3.85 kG was used (at this field a diamagnetic peak is observed at 52.2 MHz). Field calibration was performed using the diamagnetic signal up to ~30 kG for more precise fitting of $\mu$ALCR spectra, since Helios' "applied current" to "field output" ratio is not constant.
Chapter 3 – Relevant Results from Past Mu-Radical Studies

A. The Mu-cyclohexadienyl Radical in Gaseous and Liquid Benzene

Percival et al. [32] and Yu et al. [43,52] reported the detection and hyperfine coupling constants of the Mu-cyclohexadienyl radical (and Mu-C₆D₆) in the liquid phase in two publications dating in the late 1980s. Fleming et al. published another study on MuC₆H₆ (and its D- and F-substituted forms) in gases at higher temperatures, in a 1997 article [23]. Their reported data for the MuC₆H₆ radical are compiled in Table 3-1, with Figure 3-1 showing the numbering scheme for the hydrogen atoms bound to the radical. Also included in the table are the temperature dependences of the hfccs; $A^\mu$ is the reduced muon hfcc (see Equation 2.2).

Percival et al. observed the Mu-cyclohexadienyl radical by $\mu$ALCR at 300K in liquid benzene; although TF-$\mu$SR was also employed, this was one of the first Mu-radical studies using $\mu$ALCR [32]. In this study, although no temperature dependence of hfccs was pursued, the muon and all six proton hfccs (only detectable by the $\mu$ALCR technique – seven total resonances were observed) were determined. Those seen for the H-atoms ortho and para to the muon, H(1,5) and H(3), are negative, an inherent trait of H-atoms with the same relative electron spin density as any H-atoms at the radical center, C(3) in this case. The meta and ipso H-atoms (H(2,4) and H(6)) and the muon (also at C(6)), have ‘negative’ spin densities at these positions (relative to the H(3) atom), and as such their hfccs have positive signs. The ability of the $\mu$ALCR technique to measure the relative signs of nuclear hfccs is an important benefit to classical single resonance ESR experiments, where they are impossible to determine [53]. In all $\mu$ALCR studies, the H-atom in the meta position was an extremely weak resonance, a consequence of its small nuclear hfcc.
Table 3-1

Reported Hyperfine Coupling Constants Observed in MuC₆H₆. The muon hfcc is given in "reduced units" (See Equation 2.2).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Nucleus</th>
<th>Hfcc (MHz)</th>
<th>( \frac{dA_i}{dT} ) (MHz K(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>27(1)</td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(1,5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(2,4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11(1)</td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25(1)</td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40(1)</td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54(1)</td>
<td>( \mu )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11(1)</td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25(1)</td>
<td>H(6)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>40(1)</td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54(1)</td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>H(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>H(1,5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>H(1,5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>H(2,4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>H(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>H(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( A'_{\mu} = 161.61(1) \)

\( A_p = -25.14(4) \)

\( A_p = 7.47(4) \)

\( A_p = -36.19(4) \)

\( A_p = 126.11(4) \)

\( A'_{\mu} = 161.940(4) \)

\( A'_{\mu} = 161.591(4) \)

\( A'_{\mu} = 161.228(4) \)

\( A'_{\mu} = 160.871(4) \)

\( A_p = 126.26(2) \)

\( A_p = 126.04(2) \)

\( A_p = 125.89(2) \)

\( A_p = 125.73(2) \)

\( A_p = 159.4(2) \)

\( A_p = 159.0(2) \)

\( A_p = 158.6(1) \)

\( A_p = 124.9(5) \)

\( A_p = 124.3(6) \)

\( A_p = 124.4(6) \)

\( A_p = -24.8(7) \)

\( A_p = -24.8(6) \)

\( A_p = 8.2(9) \)

\( A_p = -36.4(9) \)

\( A_p = -36.2(6) \)

\( \frac{dA'_{\mu}}{dT} = 0.025 \)

\( \frac{dA_p}{dT} = 0.012 \)

\( \frac{dA_p}{dT} = 0.020 \)

\( \frac{dA_p}{dT} \approx 0 \)

(due to large error bars)

N/A

[32]

[43,52]

[23]
Figure 3-1. The Mu-cyclohexadienyl (MuC₆H₆) radical, with the atomic numbering used in References 23, 32, 43 and 52.
In References 43 and 52 Yu et al. determined the muon and H(6) nuclear hfccs over a short range of temperatures in liquid benzene using μALCR, from 284 to 327 K, giving the temperature dependences of the two hfccs from linear fits to be \(-0.025\) MHz K\(^{-1}\) for the muon and \(-0.012\) MHz K\(^{-1}\) for the para-proton [43,52]. When averaging these two hfccs, and taking its derivative with respect to temperature, to determine isotopic substitution effects, a modified form of Equation 2.3 must be used,

\[
\langle A \rangle_{CH_{2}} = \frac{1}{2} \left[ A_{\mu}^\prime(MuCH) + A_{p-ipso}(MuCH) \right]
\]  

(3.1)

For these data, \(\frac{d\langle A \rangle_{CH_{2}}}{dT} = -0.0182\) MHz \(\cdot\) K\(^{-1}\), which is nearly identical to that for the methylene hfcc in \(C_{6}H_{7}\), \(-0.0180\) MHz \(\cdot\) K\(^{-1}\), indicating no noticeable isotopic substitution effects [43,54]. A slight negative slope in this hfcc-temperature dependence was suggested to be the direct result of out-of-plane bending by C(6) in \(C_{6}H_{7}\) and its derivatives [54,55].

In the aforementioned work of Fleming et al., MuC\(_{6}\)H\(_{6}\), MuC\(_{6}\)D\(_{6}\), MuC\(_{6}\)F\(_{6}\) were studied by muonium addition to gaseous benzene and its derivatives using μALCR and TF-μSR. This study was performed from 40 to 80°C at two pressures, 1.4 and 15 atm, although hfccs were shown to be unaffected by these differing pressures [23]. For the Mu-cyclohexadienyl radical, hfcc temperature dependences for the Mu- and H(6)-atom was determinable, but only \(\frac{dA_{\mu}^\prime}{dT}\) was observed to be non-zero, having a value of \(-0.020\) MHz \(\cdot\) K\(^{-1}\) [23]. Further calculation of \(\frac{d\langle A \rangle_{CH_{2}}}{dT}\) using Equation 3.1 yields a value of \(-0.015\) MHz \(\cdot\) K\(^{-1}\), approximately 20% lower than that of the methylene hfcc in \(C_{6}H_{7}\), which represents condensed-phase data [54]. Despite the different phases involved in this comparison, only a ~1% shift is observed between liquid- and
gas-phase $\mu$SR data for $\text{MuC}_6\text{H}_7$ in the bulk [23], suggesting slightly more significant isotope
effects than seen in Reference 43. These isotope effects can be attributed to the differing H-C
and Mu-C bond lengths (in the cyclohexadienyl radical and its muoniated analogue,
respectively), likely being due to zero-point energy differences between the radicals [56,57].

B. The Mu-cyclohexadienyl Radical in the NaY Zeolite

Although zeolites will be discussed in detail in the next chapter, two important papers are
particularly relevant when reviewing the study of the Mu-cyclohexadienyl radical. Both of these
papers, from Fleming et al., discuss the guest-host interactions and hfccs of the radical in the
sodium cation form of the "Y" zeolite (with 2-3 benzene molecules per zeolite supercage)
[24,49]. Some data from the $\text{MuC}_6\text{H}_6$ radical observed in bulk solid benzene are also presented
for comparison, where at 263 K the muon hfcc is 525 MHz. Reference 49 (2000) first reports a
truly important aspect of radical study in zeolites, changes in molecular geometry (and likely
reactivity) due to interaction with the zeolite framework and/or extra-framework cations.

Two different orientations of the muoniated site on the Mu-cyclohexadienyl were
observed spectroscopically, characterized by two different hyperfine couplings for both the muon
and the proton of the C(6)HMu group. This result was in accord with the calculations of
Webster and Macrae at the time, suggesting that the aromatic electrons of the radical
(symbolized as the half-circle and dot on Figure 3-1) coordinate to a sodium cation of the zeolite,
making the two protons (or proton and muon in this case) at the radical carbon center
inequivalent [48]. This scenario is shown in Figure 3-2, which labels those two protons as $H_{\text{exo}}$
and $H_{\text{endo}}$, being as one is closer to (and the other farther away from) the sodium cation [adapted
Figure 3-2. The suggested geometry of the cyclohexadienyl radical when adsorbed to the $S_{II}$ cation site in the NaY zeolite. Because of the radical is coordinated to the cation, the two methylene protons are inequivalent and are labelled $H_{exo}$ and $H_{endo}$, as indicated. In the case of the Mu-cyclohexadienyl radical, the muon can occupy either orientation, thus leading to two different possible muon and H(6) hfccs. Taken from Ref. 24; used by permission of author.
from Ref. 48]. One notes in this figure that coordination of the radical to the cation causes a slightly distorted geometry at the para and ipso positions of the radical, which is more directly the cause of the two methylene protons being inequivalent; one is closer to the center of the π-electron density of the radical. Here, the hfccs for the orientations at 322K were reported as follows, and were in good agreement with calculations at that temperature [48,49]:

\[ A_{\mu}(exo) = 606 \pm 2 \text{ MHz} \quad \text{and} \quad A_{\mu}(endo) = 108 \pm 2 \text{ MHz} \quad \text{(muon farthest from the cation)} \]

\[ A_{\mu}(endo) = 430 \pm 2 \text{ MHz} \quad \text{and} \quad A_{\mu}(exo) = 70 \pm 5 \text{ MHz} \quad \text{(H(6) farthest from the cation)} \]

It is interesting to note here that the average muon hfcc from the two orientations, 518 MHz \((A_{\mu}' \approx 162 \text{ MHz})\), is essentially the same value as observed in the gas and liquid phases, within errors [23,32,43,49,52].

In addition to binding of the MuC₆H₆ radical to the Na\(S_{\Pi}\) cation site in NaY, it can also bind to the window (W) site, thus giving an additional, different, hfcc, rather close to that found in the bulk [24]. The W site is a constricted area (diameter \(\sim 7 \text{ Å}\)) connecting two adjacent supercages (diameter \(\sim 12 \text{ Å} \) – both explained in more detail in Chapter 4) in a faujasite. An in-depth study into the temperature dependence and possible existence of multiple binding sites and orientations was done here, with interesting results. Using a combination of FT-\(\mu\)SR and \(\mu\)ALCR (as was done in Reference 49), multiple muon and H(6) hfccs were determined, and an attempt was made to assign them to orientations and binding sites of the Mu-cyclohexadienyl radical. Figures 3-3 and 3-4 are example FT-\(\mu\)SR and \(\mu\)ALCR spectra, respectively of the
Figure 3-3. Fourier transform of the MuC₆H₆ radical in NaY at 322 K (2 per SC loading, 13.5 kG applied field). 'Dia' is the central diamagnetic frequency, and the three smaller peaks downfield at 32, 78 and 116 MHz are ν₁₂ transitions for three different radical orientations, named 'D', 'C', and 'B', respectively. See Figure 3-4 for the corresponding peaks on the μALCR spectrum. Taken from 24; used by permission of author.
Figure 3-4. $\mu$ALCR spectrum of the MuC$_6$H$_6$ radical for the same experimental conditions as stated in Figure 3-3. Top: the 'raw' spectrum. The dashed line represents a polynomial fit to the field-dependent background, with the solid curves being global Gaussian fits to the data. Bottom: the background-subtracted spectrum showing the peaks more clearly, with the same labelling as in Fig. 3-3. Peak A, is a $\Delta_0$ resonance of the CHMu group, whereas Peak B and D are different $\Delta_1$ resonances of this group for MuC$_6$H$_6$ bound at the cation site. Peak C is a $\Delta_1$ resonance due to the W site. Taken and altered from 24; used by permission of author.
radical in NaY; one can see the multiple peaks in both, representing different hfccs for the muon (in the FT spectrum) and both the muon and proton (in the μALCR spectrum), labelled in both spectra as A, B, C, and D (defined in Table 3-2) [24].

From these peaks, by attempting to correlate the results again to the calculations of Webster and Macrae, and by comparison to data from bulk spectra, the different possible orientations and sites were assigned as shown in Table 3-2 (taken and altered from Reference 24). Also included in the table are the hfccs as functions of temperature, plotted as Figure 3-5 (also taken from Reference 24). It is interesting to note that those radicals coordinating to the window site do not exhibit the same conformational change, and thus multiple hfccs, as seen in the cation-binding ones. Also, the slope of the muon hfcc at the window site is the steepest seen here, suggested by Fleming et al. to be linked to less restricted motion than seen for the cation-bound radical [24]. The trends seen for the endo proton and exo muon (Figure 3-5a,b) have opposite slopes, suggesting distortion of the Mu-cyclohexadienyl ring from planarity once the radical is bound to the SII cation site.
# Table 3-2

Hfecs Assignments for MuC₆H₆ in NaY: Theory and Experiment.
Taken and altered from Reference 24; used by permission of author.

<table>
<thead>
<tr>
<th>assignment</th>
<th>$A_{exp}$</th>
<th>$A_{theory}$</th>
<th>$dA_{exp}/dT$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[MHz]$^a$</td>
<td>[MHz]$^b$</td>
<td>[MHz K$^{-1}$]$^c$</td>
</tr>
<tr>
<td>A $\Delta_0(S_{</td>
<td></td>
<td>},H_{endo})$</td>
<td>108.1 ± 1.3</td>
</tr>
<tr>
<td>B $\Delta_1(S_{</td>
<td></td>
<td>},Mu_{exo})$</td>
<td>605.2 ± 0.4</td>
</tr>
<tr>
<td>D $\Delta_1(S_{</td>
<td></td>
<td>},Mu_{endo})$</td>
<td>430.7 ± 0.4</td>
</tr>
<tr>
<td>D $\Delta_0(S_{</td>
<td></td>
<td>},H_{exo})$</td>
<td>160 ± 5</td>
</tr>
<tr>
<td>C $\Delta_1(W,Mu)$</td>
<td>529.3 ± 0.4</td>
<td>507.4$^d$</td>
<td>−0.040±0.002</td>
</tr>
<tr>
<td>C $\Delta_0(W,H)$</td>
<td>≈130</td>
<td>124.9$^d$</td>
<td>−0.013±0.003$^d$</td>
</tr>
</tbody>
</table>

$^a$ hfecs from the experimental results at 322 K, and discussion in ref 24. $^b$ Calculated hfecs from the CIS calculations of Webster and Macrae, from ref 48, at 313 K. $^c$ Slope of the experimental hfecs with temperature, from ref 24, figures 2–10 therein. The muon hfecs are plotted in “reduced units”, $dA_{\mu}'/dT$, where $A_{\mu}' = A_{\mu}/3.184$. $^d$ Experimental results for gas-phase C₆H₆Mu at 313 K, from ref 23.
Figure 3-5. Temperature dependences of muon and H(6) hfccs for MuC₆H₆ in NaY for a) the endo proton at the Sᵥ cation site, b) the corresponding exo muon, and d) the endo muon at the Sᵥ site; c) shows the temperature trend for the muon hfcc for the window site-bound radicals. Note the difference in slopes of the muon and proton hfccs (b) and (a), a supporting indication of distortion of the Mu-cyclohexadienyl ring from planarity. Taken from Reference 24; used by permission of author.
C. The Mu-ethyl Radical in the Bulk and on Silica

Several papers on the Mu-ethyl radical's hyperfine coupling constants and molecular motion effects are particularly relevant to this thesis and are discussed here. The first article prepared by Roduner et al. is a general study of muoniated free radicals from Mu addition to liquid olefins and dienes [31]. In this paper only muon hfccs are presented, being as all data were obtained using FT-μSR. As mentioned before, only a single radical site is possible in the muoniated ethyl radical (MuC₂H₅) by Mu addition to ethene, and by looking at the difference between the reduced muon hfcc, \( A' \mu \), and the methyl proton hfccs, \( A_p \) determined with ESR data, for example, one can study the isotope effects caused by Mu-substitution in the radical. As Roduner et al. notes, unlike the ethyl radical's methyl proton hfccs, the muon hfcc in Mu-ethyl varies dramatically with temperature, as shown in Table 3-3 [31,59,60].

As seen in the table, \( A' \mu \) decreases as temperature is increased and is always much greater than \( A_p \); this is because of the radical's internal rotation. Alkyl radical β-proton (and isotopomer) hfccs obey the "McConnell" equation,

\[
A_{Hfcc} = L + M < \cos^2 \theta >
\]

(3.2)

where \( L \) and \( M \) are both constants, and \( M \) is much greater than \( L \) and \( 0 \leq \theta \leq 90^\circ \) is the angle between the alpha-carbon's (Cα) \( p_z \)-orbital ('inhabited' by the radical electron) and beta-carbon to H (or Mu) bond [53,61]. Experimentally, the observed hyperfine coupling in a μSR spectrum is the statistically-weighted average over all possible \( \theta \)'s, depending on a number of factors, including the potential barrier to internal rotation and the temperature [31].
Table 3-3

Ethyl Radical Hfccs as a Function of Temperature as Reported by Roduner et al. The muon hfcc is given in “reduced units” (See Equation 2.2), for comparison to the radical's proton hfccs as determined by ESR.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Temperature (K)</th>
<th>$A$ (MHz)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl ($C_2H_5$)</td>
<td>&quot;Invariant&quot;</td>
<td>75.3</td>
<td>[59,60]</td>
</tr>
<tr>
<td>Mu-ethyl ($\mu C_2H_4$)</td>
<td>111</td>
<td>130.8</td>
<td></td>
</tr>
<tr>
<td>Mu-ethyl (MuC$_2$H$_4$)</td>
<td>120</td>
<td>128.7</td>
<td></td>
</tr>
<tr>
<td>Mu-ethyl (MuC$_2$H$_4$)</td>
<td>140</td>
<td>124.2</td>
<td></td>
</tr>
<tr>
<td>Mu-ethyl (MuC$_2$H$_4$)</td>
<td>162</td>
<td>120.0</td>
<td>[31]</td>
</tr>
<tr>
<td>Mu-ethyl (MuC$_2$H$_4$)</td>
<td>182</td>
<td>116.7</td>
<td></td>
</tr>
<tr>
<td>Mu-ethyl (MuC$_2$H$_4$)</td>
<td>298</td>
<td>104.1</td>
<td></td>
</tr>
</tbody>
</table>
In the high temperature limit, unhindered rotation causes the <$\cos^2 \theta$> term to approach 0.5, and thus $A_{Hfcc}$ is equal to $L + \frac{1}{2}M$. For the Mu-ethyl radical, as its temperature is lowered its equilibrium conformation has $\theta < 45^\circ$, and the Mu-C bond begins to eclipse the C$_\alpha$ $p_z$-orbital. As such, the muon hfcc increases with decreasing temperature, with a maximal value at $\theta = 0$ degrees, $A_{Hfcc} = L + M$ (see Figure 3-6). Concomitantly the hfcc of the Mu-ethyl beta-protons decreases with temperature. In a regular ethyl radical, since the methyl group has threefold symmetry, and rotation is more free to lower temperatures, $\theta$ has little or no temperature dependence, thus neither does $A_{Hfcc}$ [22,31,37,52,59,60].

It is interesting to note that in the case of the Mu-tetramethylethyl radical (muoniated tetramethylethylene or 2,3-dimethylbut-2-ene, where in the place of alpha- and beta-protons in Mu-ethyl are methyl groups with their corresponding beta- and gamma-protons) the bulky methyl groups force the Mu atom to adopt a preferred conformation in the plane of the radical, $\theta \rightarrow 90^\circ$, causing its muon hfcc to increase with increasing temperature (Figure 3-6) [62].

Roduner et al. suggests that "an excellent fit" of their data to the empirical equation,

$$A'_\mu(T) = A'_\mu(T = \infty) + \left[A'_\mu(T = 0) - A'_\mu(T = \infty)\right] \times \left[1 - e^{-E_{\mu}/kT}\right] \quad (3.3)$$

was found, with $A'_\mu(T = \infty)$ set to the $A_{\mu}(\beta)$ for the ethyl radical, giving $A'_\mu(T = 0) = 154$ MHz and $E_{\mu}(\text{rot}) = 1.1$ kJ/mol, with this model describing classical rotation [31]. Later, this equation will be fit to the our data to determine $E_{\mu}(\text{rot})$ for the Mu-ethyl radical in different environments, though I will take each data set’s the lowest temperature point (~5K) as our $A'_\mu(T = 0)$.  

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Figure 3-6. Muon hfccs as a function of temperature for the Mu-ethyl (top) and Mu-tetramethylethyl (bottom) radicals. In the high temperature limit, the methyl group of Mu-ethyl rotates freely; as such the (reduced) muon hfcc approaches that of the beta-protons in the ethyl radical. As temperature is reduced, the methyl group’s orientation approaches the equilibrium conformation, where the muon eclipses the $C_\alpha p_z$-orbital (shown as upper Fischer projection). The opposite trend is seen for the Mu-tetramethylethyl radical, where steric hindrances more drastically control the behaviour (lower projection). Lines are to guide the eye. See text for discussion. Ethyl data from ethene loaded in NaY at 1/SC (see Chapter 5); tetramethylethyl data from Ref. 62.
Percival et al. and Dake Yu studied the Mu-ethyl radical in the bulk over a large range of temperatures, for the gas, liquid and solid phases using FT-\(\mu\)SR and \(\mu\)ALCR [22,52]. Because the \(\mu\)ALCR technique was employed, not only muon hfccs but also the alpha- and beta-proton hfccs were determinable. In particular, the muon and proton hfccs were measured at approximately 285 - 310K in gaseous ethene at pressures ranging from approximately 1 to 15 atm, and in solid and liquid ethene at temperatures of 20 to 153.4 K [22,52]. The results are given in Table 3-4, and shown in Figure 3-7. Noteworthy in the table and figure is the inclusion of the average hfcc, \(<A>\) (Equation 2.3), which in the absence of residual isotope effects should be identical to the ethyl radical's \(A_p(\beta)\) and constant [22,31,52,59,60]. Again, due to the observed temperature dependence, the main conclusion of the article is that the preferred conformation of the Mu-ethyl radical is one where the muon eclipses the \(C_a\) \(p_z\)-orbital, potentially arising from steric effects or enhanced hyperconjugation, both of which being due to the Mu-C bond, as it is slightly longer than H-C [52,62]. Fitting this data to Equation 3.3, and using \(A'_\mu(T = 0) = 152\) MHz, we determined \(E_a(\text{rot})\) for bulk ethene to be \(1.16 \pm 0.03\) kJ/mol (see Figure A.1 and discussion in Section 6.A.ii). Because this data set is far larger than that of Roduner et al., we consider the value determined from the fit of this data to be more reliable than reported in Reference 31.

Schwager et al. took the investigation of the Mu-ethyl radical a step further [37]. Using FT-\(\mu\)SR and \(\mu\)ALCR, Mu-ethyl's interaction with porous silica was studied at temperatures of 150 to 315 K. This environment is closest to that of zeolites studied in this thesis. Of main importance in this study were the temperature dependence of hfccs and the effects of molecular reorientation on the surface of the silica grains, determinable by \(\mu\)ALCR lineshapes. FT-\(\mu\)SR was performed across the above range of temperatures, whereas \(\mu\)ALCR measurements were
Muon and Proton Hfccs for the Mu-ethyl Radical in the bulk, as determined by TF-$\mu$SR and $\mu$ALCR [22,52]. Only one pressure (10 atm) represented by the higher temperature data, although was consistent to within 1 MHz for all pressures used (1-15 atm). Muon hfccs again in reduced units; typical uncertainty in hfcc 0.4 MHz, dominated by $A'_{\mu}$. Blank cells correspond to indeterminable values.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$A'_{\mu}$ (MHz)</th>
<th>$A_{\beta}$ (MHz)</th>
<th>$&lt;\Delta&gt;_{\text{CH}_2\text{Mu}}$ (MHz)</th>
<th>$A_{\alpha}$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0(1)</td>
<td>151.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.0(1)</td>
<td>144.2</td>
<td>49.6</td>
<td>81.1</td>
<td></td>
</tr>
<tr>
<td>93.6(1)</td>
<td>135.1</td>
<td>53.2</td>
<td>80.5</td>
<td></td>
</tr>
<tr>
<td>109.0(1)</td>
<td>131.1</td>
<td>55.8</td>
<td>80.9</td>
<td>-62.0</td>
</tr>
<tr>
<td>124.5(1)</td>
<td>127.3</td>
<td>57.3</td>
<td>80.6</td>
<td>-62.2</td>
</tr>
<tr>
<td>138.5(1)</td>
<td>124.4</td>
<td>58.7</td>
<td>80.6</td>
<td>-62.3</td>
</tr>
<tr>
<td>153.4(1)</td>
<td>121.2</td>
<td>59.8</td>
<td>80.3</td>
<td>-62.3</td>
</tr>
<tr>
<td>283.9(1)</td>
<td>104.8</td>
<td>66.8</td>
<td>79.4</td>
<td>-62.9</td>
</tr>
<tr>
<td>298.5(1)</td>
<td>103.6</td>
<td>66.8</td>
<td>79.1</td>
<td>-63.4</td>
</tr>
<tr>
<td>310.7(1)</td>
<td>102.8</td>
<td>67.2</td>
<td>79.0</td>
<td>-63.0</td>
</tr>
</tbody>
</table>
Figure 3-7. The temperature dependence of the muon and proton hfccs in the \( \text{MuC}_2\text{H}_4 \) radical. Hfccs are labelled as defined in the text. The solid lines are to guide the eye. Note the relatively constant values for both \(<A>\) and (negative) \( A_p(\alpha) \) with varying temperature. Data taken from Refs. 22 and 52; \(<A>\) interpolated from data for this work.
carried out from 190-298 K. Because a $\Delta_1$ resonance was only weakly observed at 247 K, all proton hfccs were determined using FT values of $A_{\mu}$. The (weak) presence of the 'muon flip' resonance is likely due to slightly anisotropic motion of the radical on silica surface – the linewidth of the $\Delta_1$ resonance is dependent upon the dipolar interaction, which averages to zero when free motion is permitted [37].

Figure 3-8 shows the hfccs determined for $\text{MuC}_2\text{H}_4$ on silica as a function of temperature. When compared to liquid or gas phase data the values only correspond to a 1.5% increase in muon hfcc, and a noticeably different temperature trend for the proton hfccs, consistent with a similar difference noted earlier for $\text{MuC}_6\text{H}_6$ (compare to Figure 3-7) [22,31,37,52]. Schwager et al. explain that the increasing trend of the proton hfccs is indicative of an increased 2s character of the radical electron-bearing atomic orbital, thus suggesting a bent radical when bound to silica [37]. This is compounded by the fact that reduced mobility due to the presence of strong-binding sites (with their estimated B.E. of 21.2 kJ/mol for ethene) further deviates the radical’s behaviour from that in the bulk at lower temperatures [37,63]. One must keep in mind, however, that at the temperatures at which these deviations are observed the hfcc errors are quite large, nearly negating this observation. For this reason, special care was taken to focus on the quality of the fit in the high-temperature end when applying this data to Equation 3.3 (estimating $A'_{\mu}(T = 0) = 150$ MHz), from which we determined $E_{\alpha}(\text{rot}) = 1.36 \pm 0.03$ kJ/mol for silica-bound ethene (see Figure A.2 and Section 6.A.ii).
Figure 3-8. The temperature dependence of the muon and proton hfccs in the MuC$_2$H$_4$ radical bound to a silica surface. Hfccs are labelled as defined in the text. The solid lines are to guide the eye. Comparison of proton hfccs shows some deviation of silica-bound Mu-ethyl from that in the bulk (Figure 3-7), though one must be cognizant of the errors involved. Data taken from Reference 37; $<\lambda>$ interpolated from data for this work.
Chapter 4 – Zeolites and their Use in Industry

A. Zeolites at a Glance

Although the first published discussion of zeolites was in 1756, and Zeolite A’s use as a molecular sieve has been known since the 1930’s, their potential use as catalysts was first announced in 1960 [67-69]. Paraffin isomerization and cracking using two particular types of the faujasite zeolite ("X" and "Y") were reported at that time in Ref. 69. Zeolites were rushed into industrial applications soon thereafter; their first role as agents in petroleum cracking was in 1962, which at present is the largest volume catalytic process (approximately 40 million barrels of oil produced per day by it) [68]. However, it is not the X and Y zeolites that are primarily used for this process on an industrial scale today; it was found that a zeolite called ZSM-5, particularly its acidic form, has far superior catalytic activity and wider applications in the petrochemical industry (as will be described later).

The term ‘zeolite’ originally only described porous aluminosilicates, but now also includes other crystalline inorganics with zeolitic frameworks (e.g., aluminophosphates, gallium phosphates) [67]. The general formula for zeolites is,

\[ M^{x+}_{\frac{a}{c}} [(SiO_2)_a (AlO_2)_b] \bullet (H_2O)_c \]  \hspace{1cm} (4.1)

showing the extra-framework charge-balancing cations \( M^{x+} \), the aluminosilicate framework, and the water of hydration [67]. For present purposes (i.e., for our faujasites), however, we will use more specifically,

\[ [(H^+, Na^+)_n][Al_{n}Si_{192-n}O_{284}]^{n-} \bullet (H_2O)_c \] \hspace{1cm} (4.2)

where the \( H^+ \) and \( Na^+ \) charge-balancing cations can be substituted with alkali, alkaline earth, or transition metal cations, as is seen in more unique zeolite types [70]. These cations are necessary due to the negative charges induced by the presence of Al atoms in the zeolite framework (i.e.,
SiO$_2$ is neutral, whereas AlO$_2$ has a -1 charge), and interact with this framework through the oxygen atoms adjacent to the framework aluminum atoms. Often, the cations originally present in the framework are large quaternary organic ammonium ions – remnants of the template-style syntheses of zeolites – which can block the zeolite pores and channels. ‘Calcination’, a process by which zeolites are heated to above 500° C in open air, combusts off these bulky molecules. More catalytically useful charge-balancing cations, such as H$^+$ or Na$^+$, are then introduced using an ion exchange column [67]. These new zeolites are usually written in the form Cat.Zeol., where “Cat.” is the cation type and “Zeol.” is the zeolite framework (e.g., “CaX” is the Ca$^{2+}$-bearing form of the X zeolite, “HZSM-5” is the protonated form of the ZSM-5 zeolite). Protonated zeolites (and some of those bearing lithium or sodium) are acidic, and basic zeolites can be made by the introduction of potassium, rubidium or cesium ions (the terms “solid acid” and “solid base” are often used for these types of zeolites), however some zeolites have amphoteric character (e.g., KY, NaX) [71]. The acid form of a zeolite can usually be acquired by ion exchange of the original cation with ammonium chloride, then by heating to drive off gaseous ammonia [67]. As of 1999, 103 industrial processes used solid acids, while 10 used solid bases and 14 used acid-base bifunctional catalysts; the focus of industry on the use of solid acids is likely because of the present lack of information on basic zeolites [72,73].

While the field was still in its infancy, zeolite synthesis required heat and water treatment of alumina and silica gels, but this was only able to yield zeolites with low silicon to aluminum ratios (“Si/Al”) [67]. Kerr, using varying quaternary organic ammonium cations, was able to gain minor control of the structure of the zeolite as it was being synthesized (a template reaction); this yielded new structures with larger Si/Al ratios than of those found in nature [67,68]. Because the catalytic ability and activity of a zeolite are clearly dependent upon the number of cation sites, which in itself is dependent on the Si/Al ratio, other techniques were
developed to raise the silicon content in zeolites. For example, steaming the protonated form of a zeolite at around 700°C drives off many of the H⁺ ions, and some of the framework aluminum in the process [67].

A number of techniques are used to characterize and study zeolite structure, but the most informative are electron microscopy, diffraction, and various forms of spectroscopy [67]. Traditionally, X-ray and neutron diffraction have been the workhorses for determination of molecular structure and atomic arrangement, requiring single crystals of relatively large size and good quality, but obtaining these is often difficult with zeolites. As noted in Ref. 67, new higher-intensity light sources (e.g., synchrotrons), capable of producing higher energy X-rays reduces the demand for large crystal size; however, Rietveld refinement – where a structure is proposed based on experimental data and then refined using bond angle and length constraints – is required for the most reliable results (Refs. 74 and 75 mentioned therein). Transmission and Scanning Electron Microscopies (TEM and SEM) as well as Vibrational, X-ray Fluorescence and Photoelectron Spectroscopies (IR/Raman, XRF and XPS) are extremely useful in probing the microstructures of zeolites, providing information on pore and channel sizes and orientations, as well as site symmetries and their interactions with “guest” molecules [67].

More recently Nuclear Magnetic Resonance (NMR) techniques have played roles in zeolites structure determination complimentary to diffraction techniques. In particular, the challenge of investigating of zeolite lattice structures has been eased through the use of $^{29}\text{Si}$, $^{27}\text{Al}$, $^1\text{H}$, $^2\text{H}$-NMR [67,110]. In addition, NMR and other magnetic resonance techniques, such as Electron Spin and Muon Spin Resonance (ESR and $\mu$SR), are ideal techniques for also
probing the orientations and interactions of zeolite "hosts" with their adsorbed "guests" because they can provide information about molecular structure, reaction kinetics and molecular dynamics, with small powder samples (i.e., large single crystals are not required) [e.g.,24,45,47,49,53,67,77,78].

Zeolites are ubiquitous in the chemical and petrochemical industries, with some more general roles including solvent drying, molecular sorting and selection, water softening, petroleum cracking, and gasoline production [67,68,76]. Four structure types will be discussed in detail herein, with mention of their specific roles in industry.

B. Framework Subunits

The microscopic frameworks of zeolites can have one, two or three-dimensional pores or channels (1-20 Å in diameter), which control their molecular selectivity [67,70,71]. Though the research in this thesis has utilized the faujasitic zeolites NaY, HY and USY only, it is of some interest to contrast their structure types with other commonly used zeolite forms. The following sections discuss in detail the structures and roles of the Mordenite, ZSM-5, Linde Type A (these three frameworks have been recently studied by µSR scientists [45-47,111,112]), and Faujasite zeolites, but first some common zeolite structure properties should be established.

Aluminosilicates consist of networks of TO₄ tetrahedra (where T = Al or Si); each pair of adjacent tetrahedra is linked by one oxygen atom [67,70,71]. In typical framework structure drawings (e.g., Figure 4-1), vertices represent the T atoms, and lines represent the T-O-T bonds. This can be misleading because although the lines are drawn straight, the bonds are never 180° (usually varying from 130 to 170°); these angles correlate the oxygen atoms’ electronic character (therefore their basicity), and can change with temperature [71].
Figure 4-1. Polyhedral cages that are observed in the Mordenite, ZSM-5, Linde Type A, and Faujasite zeolites. Vertices are occupied by T-atoms and the lines represent T-O-T bonds (see text). Under each structure is a topological descriptor (or best attempt at such) and its free volume in aluminosilicates (or an estimate of it). Reproduced following References 67 and 70.
The numerous geometric combinations of the T and O atoms are the building blocks of zeolite frameworks. Attaching polyhedra via shared faces or edges (e.g., a four-sided face of one polyhedral cage to the four-sided face of another cage) in some order yields many of the natural and synthetic zeolites used in industry today. Figure 4-1 shows the polyhedra used to construct the four zeolite types described in the following section. For example, the faujasite structure is made up of β-cages (or “sodalite cages” – [4^6^8]) connected by double 6-ring (or “hexagonal prism” – [4^6^2]) units.

C. Example Zeolite Frameworks

i. Mordenite (MOR)

Mordenite (given the structure code ‘MOR’ by the International Zeolite Association) is a channel-bearing zeolite made up of stacks of alternating units dubbed [4^1^5^6^1]a and [4^1^5^6^1]b in Figure 4-1. Zeolite channels are made of stacked rings and are defined by how many oxygen atoms (or T atoms) make up each ring. The framework structure of this naturally-occurring zeolite is shown in Figure 4-2. It has two channel types running along the z-axis; one is 12-ring and has a (elliptical) diameter of 6.5 x 7.0 Å, the other is 8-ring with a diameter of 2.6 x 5.7 Å. It also has 8-ring channels running along the y-axis with a diameter of 3.4 x 4.8 Å (these channels intersect both the 8- and 12-ring channels along the z-axis) [70,77]. A typical value for mordenite’s Si/Al ratio is 5 and it has 10 different types of oxygen atom (i.e., 10 different distinct T-O-T bond angles found in the framework – important in crystallography).

In industry, mordenite is used to a relatively small extent, with some mention of it being used to filter and treat water for the removal of heavy metal poisons [79,80]. More traditionally it has been used as a desiccant and in separation / purification applications, in particular for the
Figure 4-2. Framework representations for the Mordenite, ZSM-5, Linde Type A, and Faujasite zeolites (MOR, MFI, LTA, and FAU, respectively). These structures can be assembled using select combinations of the polyhedral cages given in Figure 4-1. Next to the three-letter designations are the coordinate axes. Taken and altered from Reference 70, permission to reproduce by Ch. Baerlocher (editor).
catalytic reduction of NO\textsubscript{x} and the removal of N\textsubscript{2}O (essentially for the drying and purification of acidic gases) [81,82]. Also, platinated mordenite (Pt-MOR) is used for the “Shell Hysomer” process of paraffin isomerization [68].

ii. ZSM-5 (MFI)

ZSM-5 (MFI) is another channel-bearing zeolite made up of stacks of the \([5^8]\) (pentasil) units seen in Figure 4-1. The MFI framework structure is shown in Figure 4-2. It has two perpendicular intersecting 10-ring channels, one along the x-axis with an elliptical diameter of 5.1 x 5.5 Å and the other ‘zigzagging’ along the y-axis with a diameter of 5.3 x 5.6 Å [70]. A typical value for ZSM-5’s Si/Al ratio is 10, although it can range from 5 to infinity, and it has 26 different oxygen types [77]. There are many industrial applications for ZSM-5, including petroleum cracking; aromatic syntheses, isomerization and disproportionation; olefin polymerization (including olefins to gasoline); methanol to gasoline; ester hydrolysis; and nitrogen exchange in heterocycles [68,83]. Interestingly, HZSM-5’s hexane cracking activity is proportional to its aluminum content, i.e., the rate at which hexane is broken down into smaller hydrocarbons is directly dependent on the number of cation sites (which is not the case in NaZSM-5) [68].

The mechanism of monomolecular cracking in HZSM-5 is proposed in Reference 74 as follows, taking hexane as an example:

\[
\begin{align*}
CH_3(CH_2)_4CH_3 + ZOH & \rightleftharpoons CH_3CH_2CH_2CH_2CH_3 + ZO^- \quad (4.3) \\
CH_3CH_2CH_2CH_2CH_3 & \rightarrow H_2 + CH_3CH_2CH_2CH_2CH_3 \quad (4.4a)
\end{align*}
\]
\[ CH_3C^+H(CH_2)_3CH_3 \rightarrow CH_4 + C^+H_2(CH_2)_2CH_3 \]  
\[ (4.4b) \]

where both long-chain alkyl products in (4.4a) and (4.4b) are radical cations, and ZOH and ZO\(^-\) represent a small portion of the zeolite, protonated and deprotonated, respectively. It is likely that through proton abstraction by the zeolite framework, the cationic product in (4.4b) could become a secondary radical cation through intramolecular proton transfer, or it could undergo conversion to the more stable olefin, 1-pentene:

\[ ZO^- + C^+H_2(CH_2)_3CH_3 \rightarrow ZOH + CH_2=CH(CH_2)_2CH_3 \]  
\[ (4.5) \]

iii. Linde Type A (LTA)

The Linde Type A zeolite (LTA) is a cage-bearing zeolite, consisting of \([4^66^8]\) (sodalite) cages connected by \([4^6]\) (double 4-ring or "cubic prism") units as seen in Figure 4-1 [67]. The LTA framework structure is shown in Figure 4-2; note how the x, y and z-axes are indistinguishable. It has large spherical "\(\alpha\)-cages" (10 Å in diameter) repeating in all three dimensions, which are interconnected by circular 8-ring "windows" with a diameter of 4.1 Å [70]. Typically, Zeolite A has a 1 to 1 ratio of silicon to aluminum, and 3 different framework oxygen atom types [77]. NaA (or NaLTA) is used widely as a powerful desiccant in laboratories, as well as a water softener in detergents, efficiently removing calcium and magnesium cations from hard water without harming the environment [67,68]. CaA is used as a molecular sieve in separating nitrogen and oxygen gas
iv. Faujasite (FAU)

a. Framework

The faujasite zeolite (FAU) is also a cage-bearing zeolite, consisting of \([4^66^8]\) (sodalite) cages interconnected by \([4^62^2]\) (double 6-ring or hexagonal prism) units as seen in Figure 4-1 [67]. The FAU framework structure is shown in Figure 4-2, and the x, y and z-axes in this zeolite are also indistinguishable. Its “supercages” (SC, 12-13 Å in diameter) are larger than the \(\alpha\)-cages found in LTA, also repeating in all three dimensions, which are interconnected by circular 12-ring “windows” with a diameter of 7.4 Å [70]. All faujasites have only four types of oxygen atom, and there are two typical types of FAU with distinct ranges of Si/Al ratios [71]. The “X” zeolite tends to define those faujasites with Si/Al ratios below 2, whereas “Y” zeolites tend to have Si/Al ratios greater than 2, but below 5; the Y zeolite used by our group has an Si/Al ratio of 2.5 [66,71]. Another, more atypical type of faujasite used in our research, Ultra-Siliceous Y (USY), has a much less clear-cut definition. As suggested by its name, the sample of USY used in our research is a more de-aluminized form of HY, with a Si/Al ratio of 15 [66].

b. Industrial Uses of Faujasites

As mentioned earlier, although many industrial processes, such as olefin cracking and isomerization were first reported in the HX and HY zeolites, ZSM-5 has proven to be a far superior catalyst for these sorts of reactions. Faujasites still hold important roles in industry, however, the solid bases of (K, Rb, or Cs)-exchanged X are used to synthesize ethylbenzene and styrene, while Li- and Na-FAU are used in the production of other substituted benzenes (e.g., xylenes, toluene) [71]. NaY is also used in detergents as a water softener based on its ability to remove calcium and magnesium from water (like NaA) [68]. USY is used in gasoline and diesel production (cracking of crude oil), having a production efficiency close to that of ZSM-5 [93].
D. Guest Molecules in Faujasites

i. Oxygen Atom Types and Cation Sites

Figure 4-3 shows three views of the faujasite framework. Fig. 4-3a shows a FAU supercage with surrounding framework, identifying the four different oxygen atom types (designated O(1) through O(4)) and the possible cation positions. There are six major extra-framework cation sites in a hydrated zeolite, labelled with roman numerals I-V, and U (designated usually, for example, site I = “SI”), with slight variants of each location possible. Sites IV, V and U are referred to as “special cation positions” only found in the hydrated form of zeolite Y, and are thus unimportant to our studies since our samples were dried prior to use [84]. Asterisks and apostrophes following the SI, SII, and SIII site locations denote shifts of the cation from its original position.

SI cations are in the center of the hexagonal prisms of the faujasite and are octahedrally coordinated to six O(3) atoms; the SI’ site is shifted to just inside the adjacent sodalite cages, and the cation is only coordinated to three O(3) atoms [84,85]. The SII cation site is slightly inside the FAU SC, coordinated to three O(2) atoms of the hexagonal faces of adjacent sodalite cages; the SII’ and SII* sites are shifted away from and towards the center of the supercage, respectively, the former now coordinating to three O(4) atoms of the sodalite cage [84,85]. Finally, site III is along the edge of two adjacent four-member rings inside the supercage, coordinating to two O(1) and two O(4) atoms; SIII’ is shifted slightly towards the center of the SC [85]. Reference 85 comments that SIII and SIII’ are not occupied by cations in alkali forms of the Y zeolites with Si/Al = 2.5.
Figure 4-3. Detailed views of the faujasite framework:

a) The framework surrounding a FAU supercage, consisting of sodalite cages joined by hexagonal prisms. Different oxygen atoms (open circles) are labelled with Arabic numerals. Potential cation sites (filled circles) are labelled with Roman numerals, apostrophes and asterisks. Taken from Reference 84; used by permission of the American Chemical Society.

b) A closer view of the lower right section of the faujasite as seen in Figure 4-3a, showing the more relevant cation sites to our research (large black spheres), the different oxygen atom types (grey spheres), and T atoms (white spheres). Taken from Reference 85; Reproduced by permission of The Royal Society of Chemistry.

c) Internal details of a faujasite supercage. Note the four tetrahedrally oriented SII cations (gray spheres), and the windows, which connect adjacent supercages, opposite each cation site. Taken and altered from Reference 87 by permission of Elsevier.
In the dehydrated form of the NaY zeolite with a composition given in Eqn 4.2 where \( n = 56 \), the fractional occupancies of SII, SI’ and SI are 100%, 58% and 44%, respectively [85,86]. This zeolite composition matches that of the NaY sample used in our research (also, the acidic form of this zeolite is the HY sample that we studied). Because there are four SII sites per SC in our NaY and HY samples, and it can be assumed that they are 100% occupied by the corresponding sodium and hydrogen cations, there are 4 cations sites accessible to guests in the supercage. Figure 4-3b gives a closer look at two sodalite cages in the zeolite, also labelling the different oxygen types and the cation positions that are relevant to our research. Figure 4-3c shows the surrounding framework and SII cation sites of a supercage.

Also, as mentioned earlier, the USY sample that we studied has a Si/Al ratio of 15. This means that in USY there is only 16% of the number of cations per unit cell found in the Y zeolite. Due to the high occupancy of the SII site in the NaY zeolite, it is our estimate that the same occupancy ratios given earlier for NaY hold relatively closely for USY (translating to an average of \( \frac{1}{2} \) a cation per SC).

**ii. Binding of the Ethene Molecule in the Y Faujasite**

SI and SI’ sites are accessible to those molecules small enough to diffuse through the hexagonal face of the sodalite cage; however, in all publications we found regarding ethene-loaded Y zeolites, there is no mention of coordination to any cation site other than SII [85, 87-89]. Because of this, we assume the SI and SI’ cation sites are inaccessible to ethene. Henson *et al.* report a calculated binding energy for ethene to the SII sodium ion of 36.1 kJ mol\(^{-1}\). Another potential binding site for ethene in faujasites, apart from the aforementioned SII cation site, is the window site (with a calculated binding energy of 19.4 kJ mol\(^{-1}\)) [87].
In acidic faujasites, the protons found in the supercage are not called “SII protons”, being as they are not coordinated to the framework octahedrally. They do bind to single oxygen atoms in the vicinity of the SII sites, however, and will be referred to from now on as “supercage protons” or “supercage OH groups”. For ethene in acidic faujasites (H-FAU), bound to supercage protons, Limtrakul et al. calculated a binding energy of 34.3 kJ mol\(^{-1}\), which is comparable to the experimental estimate of 37.7 kJ mol\(^{-1}\) made by Cant and Hall using IR spectroscopy [88,91]. Figure 4-4 shows the preferred orientation of the ethene guest molecule at the SII and window sites in NaY, as calculated by Henson et al. and at the similar OH site in H-FAU as calculated by Limtrakul et al. [87,88]

### iii. Possible Mechanisms for H-atom Transfer in HY

Because the utility of the \(\mu\)SR technique employed (in this thesis) on ethene-loaded Y zeolites probes the interactions of the ethyl neutral free radical (as Mu-ethyl) with the zeolite, and not of ethene itself, it is important to provide some justification of the relevance of such a study to the field of zeolite catalysis. Although it has long been established that solid acid zeolites catalyze reactions through the protonation of guest molecules (e.g., hydrocarbons), those using spectroscopy rarely observe the carbocations (e.g., radical cations from protonation of alkenes) formed directly within the zeolite framework [90,92,94]. In fact, to date only three carbocations have been identified as persistent species in zeolites, thought to be because nearby framework oxygen atoms can bond covalently to these carbocations, forming what is called an “alkoxy intermediate” [90,92,113]. Although it is assumed that carbocations play the major role in hydrocarbon chemistry in zeolites, it is unclear what role is played by alkoxy intermediates, carbocations, radical cations and neutral free radicals inside the faujasite.

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Figure 4-4. Ethene in faujasites:

a) The two binding orientations for ethene in NaY as determined using Monte Carlo docking calculations coupled to neutron scattering results, from Henson et al. Taken from Reference 87; used by permission of Elsevier.

b) The optimized supercage proton binding orientation for ethene in H-FAU as determined by Limtrakul et al. using embedded cluster models in ab initio calculations. Optimized bond lengths (in picometers) are given in the figure. Taken from Reference 88; used by permission of Elsevier.
It has been suggested that some catalytic reactions may occur by the involvement of H-atoms adsorbed to the internal surfaces of zeolites; through addition of the H-atoms to unsaturated species, yielding neutral free radicals [76,77,95,96]. Figure 4-5a shows a possible mechanism by which either i) the ethyl free radical or ii) the zeolite-ethoxy reaction intermediate could be formed in an acidic zeolite environment, as hypothesized using information from References 90 and 92.

Werst et al., performing Electron Paramagnetic Resonance (EPR) studies on radiolyzed and photolyzed ZSM-5 and mordenite, observed the formation of six different neutral free radicals (including the ethyl radical), in addition to the expected radical cations [77]. They hypothesized that the H-atoms, formed through a photolytic process, add to the unsaturated guest molecules yielding neutral radicals [77]. Very little radiation chemistry on heterogeneous solids has been performed to date and it is unknown at present what the benefits would be of using ionizing radiation in zeolitic catalysis. Figure 4-5b shows a possible mechanism for the formation of the ethyl radical in an acidic zeolite in this process, followed by the radical’s migration to another cation site.

E. Why Use μSR to Study Guest-Host Interactions in Zeolites?

Electron Spin Resonance is the usual technique for free radical investigation; by this technique radical cations and a few neutral free radicals (by photolysis) have been reported in zeolites [77,97-101]. Study of neutral radicals in zeolites by ESR is hindered, however, because it is difficult to generate enough signal in dilute systems and, following photolysis, a high fraction of these formed radicals undergo geminate recombination (e.g., \( R^• + R^• \rightarrow R_2 \)), limiting signal amplitudes, though these recombination reactions can be mitigated by the restrictive
Figure 4-5. Possible mechanisms for H-atom transfer from the zeolite “host” framework (small section of framework shown) to guest ethene in H-FAU (HY)

a) Partial H-atom transfer from framework to adsorbed ethene resulting in formation of i) a neutral ethyl radical, or ii) an ethoxy intermediate bound to the framework. Due to its stability, the ethyl radical could migrate to a nearby cation site. Derived from information given in References 90 and 92.

b) Photolysis of a zeolite resulting in free H-atom, which then adds to adsorbed ethene. Derived from information given in Reference 77.
zeolite geometry [97,98,99]. μSR is a technique complimentary to ESR in the study of free radicals, and has a far greater sensitivity in studying radicals in dilute environments (e.g., low pressure gases, adsorbed gases in zeolites).

There are other studies of neutral free radicals generated in zeolites by photolysis of specific organic precursors, but it is unlikely that the radicals studied would bear relevance on catalytic processes in zeolites [97,98]. If the H-adducts of industrially-used molecules could be identified in zeolites, this could change. As such this is, in large part, the motivation of studying the Mu-radicals by μSR.

As mentioned, we studied the Mu-ethyl radical in the NaY, HY and USY faujasites to the extent discussed in the prior sections of this work. Present observations of the ethyl radical (as Mu-ethyl) in faujasites are the first of their kind, though the radical has been reported in NaZSM-5 as seen with EPR [77]. Also, prior to this work, there have been no detailed studies of any Mu-alkyl radicals in zeolites, and the Mu-ethyl radical in particular had never been seen in a zeolite environment, let alone in such a complete unique study, and is one of a few radicals to be observed in zeolites. The hfccs determined for the Mu-ethyl radical in NaY, HY and USY (presented in Chapter 5) are the basis for this thesis and are discussed in full in Chapter 6.
Chapter 5 – Results: Temperature Dependent Mu-ethyl Hfccs in Faujasites

A. Muon and Proton Hfccs as Determined by TF-$\mu$SR and $\mu$ALCR

Gaseous ethene was adsorbed in dehydrated and vacuum-pumped faujasite-filled sample cells by the technique described in Section 2.D. The ethene-loaded faujasites studied were NaY, at loadings of 1 and 3 ethene molecules per supercage ("1/SC" and "3/SC"); HY at 1/SC, 3/SC and 5/SC; and USY at 1/SC (all loadings with estimated errors of ±0.5/SC). We selected this sample combination because it would give us good insight into the effects of changing cation type (Na$^+$ versus H$^+$), the number of guests (1 vs. 3 vs. 5 per SC ethene loadings), and the number of cations available (HY versus USY). The isotropic muon and proton hfccs ($A_{\mu}$, $A_\alpha$ and $A_\beta$ in MHz) for the Mu-ethyl radical in these samples at different temperatures are given in Tables 5-1, 5-2 and 5-3.

B. Comparisons of Results

All results have been plotted against temperature in the figures to follow. For comparisons of the effects of cation type, cation number and loading number on muon hfccs, certain data have been plotted together (e.g., HY 1, 3 and 5/SC data on one graph to see loading dependence). Note that because we wish to understand the effects of changing the variables listed above, some data are repeated on different plots (e.g., NaY 1/SC data plotted on a loading dependence graph and on the cation type dependence graph). All $\alpha$- and $\beta$-proton hfccs have each been plotted on separate graphs. A graph of determined $<A>$ (average methyl proton hfccs, see Equation 2.3) data has also been included. For comparative purposes, included on all plots are data from $\mu$SR studies of bulk ethene and ethene adsorbed on silica [22,37,52] (see Tables 3-3, 3-4 and Figures 3-7 and 3-8 ).
Table 5-1

Muon and Proton Hfccs for the Mu-ethyl Radical in the a) NaY and b) HY faujasites at 1/SC loading, as determined by TF-μSR and μALCR. The muon hfcc is given in “reduced units” (See Equation 2.2). Italicized values for $A_\mu$ were those determined by TF-μSR data, non-italicized values are from μALCR data. Errors in the last digit for hfccs given in parenthesis; errors in temperature are less than 0.5 K. Blank areas correspond to undetermined values.

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Table 5-2

Muon and Proton Hfccs for the Mu-ethyl Radical in the a) NaY and b) HY faujasites at 3/SC loading, as determined by TF-μSR only. See caption for Table 5-1.

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Table 5-3

Muon and Proton Hfccs for the Mu-ethyl Radical in the a) HY faujasite at 5/SC loading and b) USY faujasite at 1/SC loading, as determined by TF-μSR and μALCR. See caption for Table 5-1.

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i. Muon Hfcc Loading Dependence

Figure 5-1 shows the reduced muon hfccs for the Mu-ethyl radical in ethene-loaded NaY faujasite at 1 and 3 per supercage loadings as a function of temperature, compared with Mu-ethyl data for the bulk and on silica. Figure 5-2 shows similar plots in HY at 1, 3 and 5 loadings per supercage. These plots are assembled to show the effect of increasing the number of guest molecules in the zeolite. Using these data, the effects of interaction between ethene molecules ("guest-guest interactions") should be determinable and separable from those of ethene with the framework ("guest-host interactions").

ii. Muon Hfcc Cation-Type Dependence

Figure 5-3 is a comparison of the reduced muon hfccs for the Mu-ethyl radical at ethene loadings of 1 per supercage in NaY and HY, again compared with bulk and silica data. This graph is intended to show the effect of replacing the SII sodium cations with protons, in the absence of guest-guest interactions, due to the low loading.

iii. Muon Hfcc Dependence on Number of Cation Sites

Figure 5-4 is a comparison of the reduced muon hfccs for the Mu-ethyl radical in HY and USY (both at 1/SC ethene loading). As described in Section 4.D.i, although both HY and the form of USY that we used are acidic, they differ significantly in the number of cation sites present per supercage. Because each supercage in USY is estimated to have 0 or 1 extra-framework cations, there are no other cation sites for adsorbed species (i.e., the Mu-ethyl radical) to migrate to, unlike in HY which would have 3 other cation sites available. Differences in results in this case could also be attributed to slight changes in framework structure (i.e., bond angles), due to the differing Al content between HY and USY.
Figure 5-1. Comparison of the reduced muon hfccs (see Equation 2.2) for the Mu-ethyl radical in the NaY faujasite at 1/SC (open triangles) and 3/SC (open diamonds) ethene loadings. Data from bulk (filled diamonds) and silica-adsorbed (filled triangles) ethene have been included for comparative purposes [22,37,52]. Solid and dashed lines are to guide the eye. Error bars that are smaller than the size of the points have been omitted and only represent statistical errors.
Figure 5-2. Comparison of the reduced muon hfccs (see Equation 2.2) for the Mu-ethyl radical in the HY faujasite at 1/SC (open circles), 3/SC (open diamonds), and 5/SC (open squares) ethene loadings. See the caption for Figure 5-1 for details.
Figure 5-3. Comparison of the reduced muon hfccs (see Equation 2.2) for the Mu-ethyl radical at 1/SC ethene loadings in NaY (open triangles) and HY (open circles). See the caption for Figure 5-1 for details.
Figure 5-4. Comparison of the reduced muon hfccs (see Equation 2.2) for the Mu-ethyl radical at 1/SC ethene loadings in HY (open circles) and USY (crosses). See the caption for Figure 5-1 for details. It is again noted that the error bars are the size of the points unless specifically indicated to be otherwise.
iv. Proton Hfccs

Figures 5-5 and 5-6 are comparisons of the hfccs for $\alpha$- and $\beta$-protons, respectively, of the Mu-ethyl radical at ethene loadings of 1 per supercage in NaY, HY and USY, as well as 5 per supercage in HY. Comparisons to the bulk and silica powder are also provided.

v. Average Methyl Proton Hfccs, $<\Delta>_\text{CH}_2$

As discussed in Section 2.B and given by Equation 2.3, the average methyl proton hfcc, $<\Delta>_\text{CH}_2$ or "$<\Delta>$" from herein, is used to compare hfccs determined by $\mu$SR to those reported in the ESR literature (see Equation 2.3). Any differences in these data are attributed to secondary isotope effects, that is, minute changes in bond lengths and angles due to isotopic substitution that can affect either or both of "$L$" and "$M$" as discussed in Chapter 6. Figure 5-7 compares the determined values of $<\Delta>$ for the Mu-ethyl radical at ethene loadings of 1 per supercage in NaY, HY and USY, and 5 per supercage in HY. Also included on the graph are (methyl) $\beta$-proton hfccs determined by ESR spectroscopy (in solid argon, benzene-diethyl ether mixtures, and pure liquid ethene) [59,60,102-104]. Note that these values are approximately temperature-independent, as indicated by the solid line seen in Figure 5-7. Unfortunately, the only ESR study that mentions the ethyl radical in a zeolite, Reference 77, does not report the hfccs for the radical, possibly due to inability to resolve the spectrum sufficiently.

vi. $\mu$ALCR Lineshapes

Figures 5-8 to 5-10 show the temperature dependence of the $\mu$ALCR lineshapes for the Mu-ethyl radical's $\Delta_1$ resonance at a loading of 1 ethene molecule per supercage in NaY, HY and USY, respectively. Comparisons of this linewidth to those seen in bulk phase data help to provide us with basic information on dynamics.
Figure 5-5. Comparison of the α-proton hfccs for the Mu-ethyl radical at 1/SC ethene loadings in NaY (open triangles), HY (open circles) and USY (crosses), and in 5/SC HY (open squares). See the caption for Figure 5-1 for details. Note the non-linear trend for silica-bound ethene, likely attributed to erroneous data points for this sample below 240 K.
Figure 5-6. Comparison of the $\beta$-proton hfccs for the Mu-ethyl radical at 1/SC ethene loadings in NaY (open triangles), HY (open circles) and USY (crosses), and in 5/SC HY (open squares). See the caption for Figure 5-1 for details. In this case, for reasons described in Sections 2.B and 3.C, a decrease in $\beta$-proton hfcc should be expected with decreasing temperature, reflecting the upwards trend of the muon hfccs.
Figure 5-7. Comparison of the average methyl proton hfccs (see Equation 2.3) for the Mu-ethyl radical at 1/SC ethene loadings in NaY (open triangles), HY (open circles) and USY (crosses), and in 5/SC HY (open squares). See the caption for Figure 5-1 for details. In addition to bulk and silica data, also included here are methyl proton hfccs for the Ethyl (C\textsubscript{2}H\textsubscript{5}) radical as determined by ESR (bold dash-lines at \textasciitilde75.2 MHz) [59,60,102-104].
Figure 5-8. Sections of the $\mu$ALCR spectra obtained for NaY at a loading of 1/SC over the range of temperatures at which the $\Delta_1$ resonance was seen. Note the narrowest peaks observed at 60 and 90 K, broadening when temperature is increased or decreased.
Figure 5-9. Sections of the \(\mu\)ALCR spectra obtained for HY at a loading of 1/SC over the range of temperatures at which the \(\Delta_1\) resonance was seen. Note the different scale than in Figure 5-8, and the relatively constant linewidth over all temperatures.
Figure 5-10. Sections of the $\mu$ALCR spectra obtained for USY at a loading of 1/SC over the range of temperatures at which the $\Delta_1$ resonance was seen. Note the constant linewidth, and the sharper, higher-field $\Delta_0$ resonance is also seen on this plot for temperatures above 90K.
Chapter 6 – Discussion of Results

A. Overview of the Data

i. Important Aspects of Our Results

Upon completion of this study, several important results emerge; they are:

➢ This complete study of the hyperfine coupling constants of the Mu-ethyl radical in faujasites is the first such example of a neutral alkyl free-radical in an unperturbed faujasite environment, and the first report of ethyl radical hfccs in any zeolite.

➢ At lower temperatures, the muon hfccs reach values 10-15% higher than those observed in the bulk. This large a shift is unprecedented for alkyl radicals (see Figures 5-1 through 5-4 with regards to bulk and silica values), and is the second largest environment-induced shift ever observed (20% shift for Mu-cyclohexadienyl in NaY) [22,24,37,49,52]. Such a shift is experimentally indicative of a localized dipolar interaction, as the result of cation binding [108].

➢ Such shifts are clear indications of interaction with and binding to the zeolite extraframework cations, in turn suggesting strong binding to the cation site. This suggestion is supported by computational results, which indicate Mu-ethyl radical binding energies to the sodium cation in NaY of ~120 kJ mol$^{-1}$, and of ~100 kJ mol$^{-1}$ when bound to the supercage OH group in HY [108], three to four times the result calculated for the binding of ethene [87,88]. This result gives important information on the types of reactive intermediates possible in ethene-loaded faujasites, namely, that a bound neutral free-radical remains bound until it reacts. Such high binding energies are also indicative of there being a large dipolar component to the Mu-ethyl radical [108].
Despite the shifts, the Mu-hfcc temperature-dependent trends follow the general shape of the bulk (Figures 5-1 to 5-4), indicating that intramolecular rotation about the Mu-ethyl radical's C-C bond is not strongly influenced by binding within the faujasite, which is not surprising.

The effect of increasing the number of guests in faujasites (loading) has a small effect on the muon hfccs for the Mu-ethyl radical, although it is observed. Particularly strange is that increases in loading have the opposite effect in HY than in NaY; convincing evidence that the location of the cation site (i.e., relative to surrounding framework) in the Y faujasite causes microscopic differences in radical binding.

For the first time, proton hfccs for alkyl radical have been measured in zeolites. Apart from changes in the magnitude of these hfccs, their temperature trends tend to be similar to those of bulk.

The relatively constant linewidths of the $\mu$ALCR $\Delta_1$ resonances as functions of temperature (see Figures 5-8 to 5-10) support our supposition that the Mu-radical is bound inside the zeolite supercages (most likely to the cations), and not between the grains of zeolite powder. This is because the $\mu$ALCR linewidths would narrow through to a minimum width matching that observed for liquid ethene at the condensation point of $\sim$169.5 K [52,109].

Loss of $\Delta_1$ peak intensity for the Mu-ethyl radical as temperature is increased, which was not observed for the Mu-cyclohexadienyl radical, indicates some sort of radical motion or isotropic averaging [24,49]. This is the first case in which the $\Delta_1$ resonance has disappeared with temperature for a zeolite-bound Mu-radical.
**ii. The Energetic Barrier to Internal Rotation (Equation 3.3)**

Using Equation 3.3, a simple Arrhenius model, an empirical relation given by Roduner et al., one can describe the Mu-ethyl radical’s muon and β-proton hfccs as functions of the temperature, their low- and high-temperature limit hfccs, and the classical energy barrier to internal rotation [31]. Because of our ample amounts of muon hfcc data, we can determine the Mu-ethyl radical’s internal rotational barrier, $E_{a\text{,rot}}$, in each environment studied. Plots showing each of these empirical fits are given in the Appendix (Figures A-1 to A-8).

In all cases, $A'_\mu(T=\infty)$ was set to the $A_\beta$ for the ethyl radical (75.3 MHz, invariant with temperature), and $A'_\mu(T=0)$ for a particular data was set to the estimated y-intercept (based on the low temperature data, if it exists),

$$A'_\mu(T) = A'_\mu(T=\infty) + [A'_\mu(T=0) - A'_\mu(T=\infty)] \times \left[ 1 - e^{-E_{a\text{,rot}}/RT} \right]$$  (3.3)

The figures in the Appendix show the attempted best fits of the above equation for the Mu-ethyl radical in bulk ethene, on silica gel, in NaY, HY, and USY at the 1/SC loading, and also in HY at the 3/SC and 5/SC loadings. As discussed below in Section 6.E, the muon hfcc temperature trend for Mu-ethyl in ethene-loaded USY appears to have two separable parts, as such the data points equal to or greater than 180 K have been fit separately ("High Temp") than those below 180 K ("Low Temp"). It is important to note that this empirical equation fits the bulk data nicely, but not well for zeolite-loaded radical data, as such the ‘best fits’ pass through the middle of each curve, following as closely as the variable fitting parameters would allow. A noteworthy result of this task is that all rotational barrier energies (for our samples, the bulk and on silica) were determined to range from 1.16 – 1.36 kJ mol$^{-1}$ (with errors of 0.03 kJ mol$^{-1}$ for the bulk and
silica, and 0.09 kJ mol\(^{-1}\) for our zeolite samples, estimated in *purely subjective terms* based on ease of fitting). The small differences in these values suggest that binding within the zeolite has only a minor impact on the intra-molecular rotational motion of the Mu-ethyl radical.

**B. Ethene Loaded in the NaY Faujasite**

The muon hfccs for the Mu-ethyl radical in the NaY zeolite loaded at 1 and 3 ethene molecules per supercage are very similar, both being 8-10% higher than observed in the bulk and 5-7% higher than on silica at the moderate-to-high temperatures studied (see Figure 5-1). At low temperatures, the trend deviates more from the bulk, increasing to 10-15% higher hfcc values, with the low temperature (or “McConnell”) plateau at around 170 MHz. Although there was insufficient data to determine the 3/SC trend at low temperatures, it seems reasonable to assume that it plateaus at approximately the same temperature.

The marked difference in \(A^\mu\) in NaY from values seen for the radical in the bulk or bound to silica could be due to many contributors, for example, molecular distortion associated with binding to the SII sodium cation. The bent Mu-ethyl radical’s shape, caused by cation binding, could cause increased muon hfccs if the molecule became situated such that the molecular orbital containing the radical electron had more overlap with the muon’s atomic orbitals. The overall shape of the trend is likely due to the preferred conformation of the radical being where the muon eclipses the radical electron’s \(p_z\)-orbital at the lowest temperatures, as described in Section 3.C. The 8-15% shifts in hfccs seen in Figure 5-1 (and subsequent figures) are the second largest shifts seen for Mu-radicals in surface environments, after the Mu-cyclohexadienyl radical in NaY, where these shifts (also due to cation binding) were twice as large [24,49].
For the 1 per supercage data (and matched by the 3/SC set), the high-temperature end appears to be gradually approaching a second plateau indicative of the free rotation limit. It is assumed that this value is that determined by ESR for the methyl proton hfcc in bulk ethene, $A_\mu^{(T=\infty)} = A_p(\text{CH}_3) = 75.3\text{MHz}$, which is almost invariant for all temperatures reported [59,60,102-104]. Using the McConnell Equation, 3.2, and values for $A_\mu$ in the high- and low-temperature limit, we can solve for the constants $L$ and $M$, found to be $L = -20\text{ MHz}$ and $M = 190\text{ MHz}$ (with estimated errors of 1 MHz). The $L$ and $M$ values are defined, in this case, for the muon bound to the $\beta$-carbon of the Mu-ethyl radical, and a comment on the origin of these two terms is in order here. The Beta-hfccs depend on the interactions about the C-C bond, described by the dihedral angle, $\theta$, and the out-of-plane bend at the $-\text{CH}_2$ group, described by the angle $\phi$. Expansion in $\theta$ and $\phi$ leads to a series of different terms, the leading order of which is a $\cos^2\theta$ dependence, for the case where $\phi = 0$. Since $\theta$ changes with temperature, this can be described empirically in the McConnell equation by $<\cos^2\theta>$ [44,53]. Both $L$ and $M$ values are proportional to the spin density, $r = |\Psi^2_{1s}(0)|$ at the adjacent carbon ($C_\beta$) nucleus, and both are thus environment dependent. $M/r$ is hyperconjugation-dependent – remember it depends on the dihedral angle between the Mu-C bond and the radical electron’s $p_z$-orbital, $\theta$ – whereas $L/r$ is polarization-dependent, i.e., it depends on the electron spin polarization due to the radical electron at the $C_\beta$ [52,53,105]. The bulk values for $L$ and $M$, as calculated from Reference 52, are -2 and 154 MHz, respectively [52]. The differences in $L$ and $M$ values determined for the NaY-loaded Mu-ethyl radical, relative to the bulk, leads us to believe that adsorption of the radical into the internal voids of NaY faujasite results in relatively significant molecular deformation. Apart from decreases in spin-density due to the zeolite environment, leading to overall scaled increases in $L$ and $M$, molecular deformation leading to increased
hyperconjugation between the radical electron to the Mu-C bond could explain the significantly higher $M$ value.

As seen in Figure 5-1, the only region where the data for the 1 and 3 per supercage loadings disagree is in the moderate temperature-range, between 120 and 300 K. In this region, the maximum difference between the two loading's hfccs is ~2%. This small divergence due to loading also appears to be the case with the HY loading comparisons (in the following section). Unfortunately, the reason for this trend is not yet understood.

C. Ethene Loaded in the HY Faujasite

The muon hfccs for the Mu-ethyl radical in the HY zeolite loaded at 1, 3 and 5 ethene molecules per supercage are not as similar as in the previous case, with the shapes of their temperature trends varying more with respect to one another at moderate temperatures (see Figure 5-2). Here the trend is clearest, and, surprisingly the higher loadings have the lower muon hfccs, seemingly in contrast with the NaY results. The hfccs range from 2-5% higher than bulk and silica results at high temperatures, to 10-15% higher than the bulk at low temperatures for the same reasons described in Section 6.A.i.

The McConnell plateaus here are estimated to intercept the $y$-axis of Figure 5-2 from 165 to 168 MHz, corresponding to $L = -18$ MHz and $M = 186$ MHz (with estimated errors of 2 MHz), averaged over all loadings. These values are quite similar to those seen in NaY, suggesting similar effects influencing the molecular shape in the two faujasites. These data also appear to be gradually approaching the aforementioned ESR plateau of ~75 MHz at high temperatures.
Despite the apparent scatter of the data at some points, a trend is evident, particularly at temperatures near or above 120 K: as loading is increased, hfccs decrease, approaching those values of ethene-adsorbed silica more clearly than seen in the NaY case. This could be because, as more guests are introduced into the zeolite, the framework plays a bigger role in binding. Although this is the by-product of an enhanced guest-guest interaction, this suggests that guest-host interactions are dominant in the HY environment. Again, it is important to remind the reader here that the important \( \text{H}^+ \) binding site in faujasites, dubbed the ‘supercage OH group’, is not in the center of the hexagonal face of a sodalite cage, but is found extremely close to one particular oxygen atom of that face, bringing any OH-bound guests closer to nearby framework than in NaY (see Figure 4-3b). Apart from the obvious interpretation that increasing loading decreases the number of available binding sites and thus more Mu-ethyl radical-framework interaction is necessary, the reasons for this trend are also unclear. Perhaps steric repulsion from other guests forces Mu-ethyl to be bound more closely to the framework, and farther away from the center of the supercage and other guests. The more guests per supercage, the stronger the steric repulsion, and thus the Mu-ethyl radical is more tightly bound to the framework. On the other hand, the Mu-ethyl radical is small enough to “fit” easily within the supercage (see Figure 4-4) so additional experiments which study guests with more bulky substituents (e.g., isobutene, tetramethyl-ethylene) are needed to be able to support this conclusion. Such experiments are currently underway at TRIUMF.

D. Cation Type Dependence – A Direct Comparison of Na\(^+\) and H\(^+\)

Apart from the aforementioned opposing trends seen with increasing ethene loading, there appears to be little to no cation dependence at 1/SC loading, as shown in Figure 5-3, although the more obvious difference is seen in the low temperature plateau region. Taking into account that the hfcc trend for the 3/SC loading at intermediate temperatures is above the 1/SC
trend for NaY and below it for HY, one can deduce that at a loading for 3/SC, *HY-loaded* Mu-ethyl had hfccs closer to that of ethene-adsorbed silica. At low temperatures in the 1/SC loading, one can note, however, different values for the McConnell plateau, where the Na\(^+\)-bound radical has \( A'_{\mu}(T=0) = 170 \text{ MHz} \) and the H\(^+\)-bound radical has \( A'_{\mu}(T=0) = 168 \text{ MHz} \). The potential dependence of muon hfccs on cation type is slightly underrepresented here, however, at temperatures from 20 to 100 K the two hfcc trends seem quite different (~3%), implying a less restricted C-C bond rotation for HY at these temperatures under the assumption that Equation 3.3 is correct.

The differences in \( L \) and \( M \) for the two cation types are quite small, the more significant of the two being that \( M \) is higher by ~3% in NaY. In qualitative terms this suggests that the shapes of the Mu-ethyl radical in NaY and HY are quite similar. Remember, however, that in both faujasites (and in USY) the radical has far higher \( M \) values than seen when in the bulk, leading us to believe that adsorption of the radical into the internal voids of faujasites results in relatively significant molecular deformation.

**E. Ethene Loaded in the USY Faujasite and Cation Number Dependence**

The first point of note with this sample is that the USY (1/SC) temperature trend’s plateaus closely match those of HY at 1/SC loading, both intercepting the y-axis of Figure 5-4 at ~168 MHz (1 MHz estimated error), thus giving the USY-bound radical the same \( L \) and \( M \) values of -18 and 186 MHz, respectively. Despite there being one or fewer cation sites per supercage in USY but 4 per SC in HY, this is not surprising since both faujasites are charge-balanced with protons at the sites dubbed earlier as “supercage OH” groups [66,85,86]. The similar plateau energies for the two faujasites support the idea that, regardless of minor
differences in framework structure due to differing aluminum content, the nature of binding of the Mu-ethyl radical to USY and HY is identical at low temperatures.

However, acknowledging the earlier point about natural scatter in the data, it appears that the muon hfcc temperature trend is not as smoothly structured for USY as with NaY and HY at this loading (Figure 5-3). In fact, the data set appears to be separable into two parts: hfccs for temperatures below 180 K, and those for temperatures equal to or greater than 180 K, which will be investigated with respect to rotational barriers in the following section.

F. Internal Rotational Barriers in NaY, HY and USY

For NaY, using $A'_\mu (T = \infty) = 75.3$ MHz and the lowest temperature point of the McConnell plateau, $A'_\mu (T = 0) = 170$ MHz, to fit Equation 3.3 with our data, we determine an internal rotation energy barrier, $E_a(\text{rot}) = 1240\pm90$ J mol$^{-1}$ (See Figure A-3). This is 140 J mol$^{-1}$ higher than the energy reported by Roduner et al. for Mu-ethyl in the bulk phase, 90 J mol$^{-1}$ higher than calculated for Percival et al.’s bulk data, and 120 J mol$^{-1}$ lower than calculated for Schwager et al.’s silica-bound data [22,31,37]. This indicates the cation binding in NaY hinders rotation of the radical, but not as significantly as the type of binding present in silica [22,31,37,52].

In HY, fitting Equation 3.3 to our data using $A'_\mu (T = \infty) = 75.3$ MHz and the lowest temperature points of the McConnell plateaus, $(A'_\mu (T = 0) = 167, 168$ and 165 MHz, for 1, 3 and 5 per SC loadings, respectively), we determine an internal rotation energy barrier, $E_a(\text{rot}) = 1260\pm90$ J mol$^{-1}$ for all three separate data sets, as shown in Figures A-4 though A-6 (See Appendix). This value is very similar to that of NaY, likely because, although the major
contributors to binding (e.g., cation, framework interactions) may differ between the two faujasite types, the net result on the rotational energy barrier of the Mu-ethyl radical is the same; it is again increased with respect to the bulk.

For the USY 1/SC data at temperatures below 180 K, when using $A'_\mu(T = \infty) = 75.3$ MHz and $A'_\mu(T = 0) = 167$ MHz, the best fit for Equation 3.3 gives an $E_a$(rot) of $1360 \pm 90$ J mol$^{-1}$, equal to that of silica (see Figures A-2 and A-7). This high rotational energy barrier relative to those calculated in NaY and HY suggests that in USY (at low temperatures) and silica the Mu-ethyl radical is bound more tightly than in HY. However, their similarity to one another in rotational energy barriers suggests that, to the Mu-ethyl radical, the silica surface is very similar to that of the internal surface of USY. This is not surprising considering that the surface of all silica powders produced by the CO$_2$ drying process are “almost exclusively covered with hydroxyl groups”, in the words of the author of Reference 106. In some cases, the -OH groups found on these silica gels can be converted to hydrophobic (-OR) groups, such as the trimethylsilyl-group [106]. Although the framework surrounding the OH-binding sites in USY is significantly different from that on silica (explaining the differences in hfccs between the two samples), OH-binding might well play a primary role in setting the rotational energy barrier.

In USY 1/SC at temperatures of 180 K or higher, when using $A'_\mu(T = \infty) = 75.3$ MHz and $A'_\mu(T = 0) = 162$ MHz, Equation 3.3 fits differently, giving for an $E_a$(rot) of $1160 \pm 90$ J mol$^{-1}$, a $A'_\mu(T = 0) = 162$ MHz (see Figure A.8). In this case, the rotational energy barrier was fixed to that of the bulk, as the muon hfcc trend in this temperature range indicates that the Mu-ethyl radical in USY has more “bulk character” than in HY and NaY at 1/SC. This could be explained by the suggestion that each USY-loaded radical spends more time unbound from the cation than...
in HY or NaY at higher temperatures. This could in turn be for reasons related to the number of cations present in the supercage that are available to the ethene molecule (prior to muoniation). Thus, following an appreciable “dwell time” bound to a cation, the ethene molecule spontaneously leaves the site, or “jumps”. In NaY or HY, this alkene has four cation sites (or more, considering adjacent supercages connected by large windows) available to which it can bind again. In USY however, there is at most only one cation site in each supercage, causing the jumping molecule to remain unbound for significantly longer times than it would in NaY or HY. Although this time the molecule spends “free” of a binding site would be short relative to its time spent bound, it could conceivably be long enough to give the Mu-ethyl radical, upon muoniation of unbound ethene, more ‘bulk-like’ character, thus lowering its muon hfcc and energetic barrier to internal rotation.

Another more likely explanation is that since there are some supercages that have no cation, at a loading of one ethene molecule per SC there may be some supercages in which the only binding possible is that to the framework, which would be relatively weak. Ethene molecules bound in this state, having shorter “dwell times”, have more gas-like character, thus averaging the sample’s muon hfccs (upon muoniation of ethene) closer to that of the bulk.

It should be emphasized that it is not the Mu-ethyl radical that is jumping in these pictures, but the ethene molecule itself. This is because ab initio calculations for this system made by a member of our group show the binding energy of the Mu-ethyl radical to the supercage -OH group to be approximately 100 kJ mol\(^{-1}\) [108], which is over three times the binding energy of ethene to H-FAU as calculated by Limtrakul et al. (34.3 kJ mol\(^{-1}\)), and renders the jumping of the Mu-ethyl radical much less likely than of ethene alone [88,108].
G. α-Proton Hfcc Comparison

For the α-protons of the Mu-ethyl radical, determined from the $\Delta_0$ resonances of the $\mu$ALCR spectrum (Equation 2.13), the α-proton hfcc trend for NaY (1/SC) seems to follow most closely that of bulk ethene in the region around 200 K (see Figure 5-5), but less so at the 150 K temperature point, which could be erroneous – usually $\Delta_0$ resonances at lower temperatures are less trustworthy since their $\mu$ALCR intensity drops to zero near these temperatures). Both the higher temperature NaY data and the α-proton hfccs for Mu-ethyl in HY at loadings of 1 and 5 ethene molecules per supercage tend to be more trustworthy, since their temperature-trends are less erratic. The hfccs seen in HY at a loading of 1/SC exhibit deviations from both the bulk and silica data, being as much as 15% higher in magnitude (less negative) than in the bulk, and at 5/SC 10% lower, similar to the higher temperature NaY data. Slopes on average are slightly negative, more so than in the bulk, with proton hfccs increasing in magnitude with decreasing temperature. The α-proton hfcc data for USY (1/SC) is similar to that of HY, and with a similar slope.

These facts suggest a bending of the radical with increasing temperature, such that the radical electron-bearing atomic orbital gains more $2s$ character, reflected by the alpha protons, which are in contact with $C_\alpha$ by a $sp^2$ hybridized orbital, experiencing an increase in hfcc [37].
H. \( \beta \)-Proton Hfcc Comparison

As would be expected from arguments given in sections 2.B and 3.C, \textit{vis-à-vis} rotation about the C-C bond axis (Equation 3.2), all \( \beta \)-proton hfccs are expected to increase with increasing temperature (Figure 5-6 – the trend opposite to that exhibited for the Mu-hfccs). This is because with increasing temperature, as the muon rotates away from its preferred conformation of eclipsing the \( p_z \) orbital of the unpaired electron, the \( \beta \)-protons move closer to this orientation [114]. For this reason, the \( \beta \)-proton hfccs reported for silica-bound ethene by Schwager \textit{et al.} seem suspect at the lowest temperatures. Again, the hfccs for NaY loaded with 1 per supercage of ethene follows most closely to the trend seen in the bulk, though there appears to be some scatter in the data near 200 K. The slopes are comparable to the bulk data, though again the large error bars and erratic behaviour of the USY data suggest the 270 K data point to be less reliable. The \( \beta \)-proton hfcc trends for the HY samples (1/SC and 5/SC) mimic this corrected trend for NaY, but have roughly the same slope as the bulk data. As with the muon hfccs discussed earlier, these \( \beta \)-proton hfccs are also generally about 5\% higher with the exception of the NaY data, which falls below the bulk data at intermediate temperatures. This is not understood at present.

It is interesting to note that, despite being bound quite strongly to the SII cation or supercage OH sites, the conformational changes due to C-C rotation mirror quite closely those in the bulk. These motional dynamic effects appear to offer little guidance as to the temperature dependence of the binding of the radical to the cation site, something that is likely better resolved by the complete analysis of the \( \mu \)ALCR lineshapes.
I. \(<A>\) – Average Methyl Proton Hfcc Comparison

As mentioned before, \(<A>\) values determined from \(\mu\)SR data are used for comparison to ESR-determined methyl proton hfccs, and are plotted in Figure 5-7. Deviations from the ESR results are indicative of secondary isotope effects. Unfortunately, the relatively large error bars, a result of adding those from muon and proton hfccs (Equation 2.3) in quadrature, precludes drawing detailed conclusions. Nevertheless, the trend is towards increasing values at the lower temperatures, as well there is a general shift to values higher than in the bulk for temperatures below 200 K, where the bulk data also lay roughly parallel to and approximately 7% above the ESR-determined values of \(A_\beta\) for the ethyl radical. All three faujasite data sets likely exhibit the same trends for the following reasons: As one decreases temperature, the secondary isotope effects (the inherent effects of altered vibrational modes due to isotopic substitution) rise dramatically due to increased hyperconjugation of the C-Mu (C-H) bond (i.e., as one 'cools' the radical, vibrational stretching modes decrease in amplitude, leading to a greater C-Mu (C-H) orbital overlap) [40,52].
J. Linewidths as Qualitative Indicators of Binding and Motion

As shown in Figures 5-8 to 5-10, $\mu$ALCR $\Delta_1$ resonances, the width of which being dependent upon hyperfine anisotropy, have relatively constant linewidths as functions of temperature ($\sim$500 G FWHM for NaY and HY, $\sim$1000G FWHM for USY). This supports the suggestion that the Mu-radical is bound inside the zeolite supercages (most likely to the cations), and not between the grains of zeolite powder. Schwager et al. only observed a $\Delta_1$ resonance at one temperature for the Mu-ethyl radical in silica (explained to be due to motion of the radical on the surface), and they are not observed in gas- or liquid-phase data [32,37,52]. We suspect that if ethene was only binding to the external surface of the zeolite, and not to the internal framework, the $\mu$ALCR linewidths would narrow with decreasing temperature through to a width matching that observed for liquid ethene at the condensation point of $\sim$169.5 K, and then to a minimum width similar to that seen for solid benzene at $\sim$104.0 K [52,109], which they do not. Why USY has linewidths approximately twice those seen in NaY and HY is unclear at present, although it is indicative of increased radical mobility [115].

$\Delta_1$ peak intensity for the Mu-ethyl radical in faujasites also decreases as temperature is increased, disappearing at approximately 240 K for HY and USY by "sinking" into the baseline, and at 150 K for NaY by "broadening" into the baseline. These behaviours were not observed for the Mu-cyclohexadienyl radical, and indicate some sort of radical motion or isotropic averaging in the case of NaY [24,49,115]. For HY and USY, however, a loss of peak intensity while linewidths remain constant has yet to be described in the literature with a theoretical model, and as such it is difficult to construct an simple explanation. These are the first cases in which $\Delta_1$ resonances have disappeared into the baseline with an increase in temperature for a zeolite-bound Mu-radical.
Chapter 7 – Summary

As a uniquely-endowed spin probe, muonium and the µSR technique have been used to form and study neutral free radicals for the past two decades. This is the first time, however, that the neutral Mu-ethyl radical has been observed in zeolites. Most previous studies of neutral free radicals in zeolites have been facilitated by photolysis reactions of organic precursors, which are likely not as representative of those select radical formation mechanisms in zeolites that are expected to involve H-atom transfer reactions. In the only published article that mentions observation of the ethyl radical in a zeolite (in particular NaZSM-5), the hyperfine coupling constants were not included [77]. Because the µSR technique produces a neutral free radical using a hydrogen atom isotope, studies of this radical give good insight into possible mechanisms occurring inside the zeolite during its catalytic cycles. The very fact that both the Mu-ethyl radical’s muon and proton hfcc’s are noticeably affected when ethene is loaded in zeolites is a clear indication of the interaction of the radical with the zeolite, an important first step in understanding any catalytic mechanism.

Correlation of the results from the study of Mu-ethyl radical-loaded zeolites to those of theoretical calculations helps one obtain information on framework, cation and loading-dependent interactions. The study of the temperature dependence of the muon and proton hfccs can even give unique insight into the spin density, polarization and hyperconjugation effects exhibited for the Mu-ethyl radical. This research, as a follow-up to previous work reported in my B.Sc. thesis (room temperature hfccs of the Mu-ethyl and the Mu-t-butyl radicals in the Y faujasite) [1], and with the Mu-cyclohexadienyl radical in NaY [24,49], demonstrates the usefulness and power of the FT-µSR and µALCR in the study of organic free radicals in closed environments.
In the future, studies of the $\mu$ALCR line-widths, not discussed here, will allow us to understand motional dynamics of the radical while it is coordinated to the zeolite, as well as help us determine the radicals’ anisotropic hyperfine coupling constants. Also, experiments taking advantage of the $\mu$SR technique’s ability to probe kinetic addition and molecular relaxation rates will provide the next step in mapping the nature of catalytic activity in faujasites. Studies with a highly-dealuminized zeolite (essentially no cations), called “DAY”, will also provide valuable information to the differences between extra framework cation binding and to the framework itself.
References

3. Dr. Jeff Sonier’s MSc thesis, UBC, Department of Physics (1994).
14. Taken from online source: [http://musr.triumf.ca/intro/musr/muSRBrochure.pdf](http://musr.triumf.ca/intro/musr/muSRBrochure.pdf)
16. Taken from online source at: [http://www.triumf.ca/tourmap.pdf](http://www.triumf.ca/tourmap.pdf)
19. Taken from online source: [http://musr.triumf.ca/equip/helios.html](http://musr.triumf.ca/equip/helios.html)
20. Dr. M.C.L. Gerry’s MSc thesis, UBC, Department of Chemistry (1962).


34. Patterson, B.D., Rev. Mod. Phys. 60 (1988) 69.


52. Dr. Dake Yu’s PhD thesis, SFU, Department of Chemistry (1989).


66. Taken from online source: http://www.zeolyst.com/html/zeoly.html
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107. Taken from online source: http://chemdat.merck.de/en/analysis/index.html
Appendix – Determination of Barriers to Internal Rotation from Hfccs

As discussed in Section 6.A.ii, by using Equation 3.3, the empirical relation of a system based on an Arrhenius function given by Roduner et al., one can describe the Mu-ethyl radical’s muon and β-proton hfccs as functions of the temperature, their low- and high-temperature limit hfccs, and the energy barrier to internal rotation. The following plots, Figures A-1 to A-8, show the fits of the equation to our data. As time did not permit a correct ‘least-squares’ analysis of the data, the errors supplied were estimated in purely subjective terms, based on ease and flexibility of fitting.
Figure A-1. Best-fit of Equation 3.3 (filled triangles) of the muon hfccs for the Mu-ethyl radical in bulk ethene, overlapping experimental data (open triangles) [22,52]. Variables used for this fit are $A'_\mu(T=0) = 152 \text{ MHz}$ and $E_a(\text{rot}) = 1.16\pm0.03 \text{ kJ mol}^{-1}$. Note the fit's overlap to the data.
Figure A-2. Best-fit of Equation 3.3 (filled triangles) of the muon hfccs for the Mu-ethyl radical in silica-bound ethene, overlapping experimental data (open triangles) [37]. Variables used for this fit are \( A'_\mu(T=0) = 150 \text{ MHz} \) and \( E_{\mu(\text{rot})} = 1.36\pm0.03 \text{ kJ mol}^{-1} \).
Figure A-3. Best-fit of Equation 3.3 (filled triangles) of the muon hfccs for the Mu-ethyl radical in NaY 1/SC loading, overlapping experimental data (open triangles). Variables used for this fit are $A'_\mu(T=0) = 170$ MHz and $E_d(\text{rot}) = 1.24 \pm 0.09$ kJ mol$^{-1}$. 
Figure A-4. Best-fit of Equation 3.3 (filled triangles) of the muon hfccs for the Mu-ethyl radical in HY 1/SC loading, overlapping experimental data (open triangles). Variables used for this fit are $A'_\mu(T=0) = 167$ MHz and $E_d(\text{rot}) = 1.26 \pm 0.09$ kJ mol$^{-1}$. 
Fit of Equation 3.3 to HY Loaded Data - 3/SC

Figure A-5. Best-fit of Equation 3.3 (filled triangles) of the muon hfccs for the Mu-ethyl radical in HY 3/SC loading, overlapping experimental data (open triangles). Variables used for this fit are $A'_\mu(T=0) = 168$ MHz and $E_d$(rot) = $1.26\pm0.09$ kJ mol$^{-1}$.
Figure A-6. Best-fit of Equation 3.3 (filled triangles) of the muon hfccs for the Mu-ethyl radical in HY 5/SC loading, overlapping experimental data (open triangles). Variables used for this fit are $A'_\mu(T=0) = 165$ MHz and $E_a$(rot) = 1.26±0.09 kJ mol$^{-1}$. 
Figure A-7. Best-fit of Equation 3.3 (filled triangles) of the *LOW TEMPERATURE* muon hfccs for the Mu-ethyl radical in USY 1/SC loading, overlapping experimental data (open triangles).

Variables used for this fit are $A'_{\mu}(T=0) = 167$ MHz and $E_a(\text{rot}) = 1.36\pm0.09$ kJ mol$^{-1}$.
Figure A-8. Best-fit of Equation 3.3 (filled triangles) of the \textit{HIGH TEMPERATURE} muon hfccs for the Mu-ethyl radical in USY 1/SC loading, overlapping experimental data (open triangles). Variables used for this fit are $A'_\mu(T=0) = 162 \text{ MHz}$ and $E_a(\text{rot}) = 1.16\pm0.09 \text{ kJ mol}^{-1}$. 