The Positive Muon as a Probe in Chemistry

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We study Mu⁺ as a substitute for H⁺.

1. Because Mu⁺ is different from H⁺: isotope effects.

2. Because Mu⁺ is similar to H⁺: tracer, spin label
Radiolysis Processes and Chemical Environments

μ⁺ & Mu in Liquids and Solid Insulators & Semiconductors

μ⁺ (Several MeV)

Dissociation (Bethe-BlAck)

→ 10 keV

Charge Exchange

μ⁺ → Mu

→ 20 eV

ELASTIC & INELASTIC SCATTERING

~ p to ~ μs

THERMAL e⁻ CAPTURE

Thermal μ⁺ or Molecular Ion

μ⁺ Precession

P₀

ν⁺ Precession

P₁

Diamagnetic Molecules

Radicals

P₂

Chemical Reactions

Inelastic Reactions

P₃

Depolarized Mu

P₄

IUPAC: Use Mu⁺ instead of μ⁺ for thermalized muons.
Chemical States of Muons in Condensed Matter

1) Diamagnetic muons \(-P_D\)

2) Muonium \(-P_M\)

3) Muoniated Radicals \(-P_R\)

4) Missing Fraction \(-P_L\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(P_D)</th>
<th>(P_M)</th>
<th>(P_R)</th>
<th>(P_L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (s)</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CCl(_4) (l)</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)O (l)</td>
<td>0.62</td>
<td>0.20</td>
<td>0</td>
<td>0.18</td>
</tr>
<tr>
<td>Ethanol (l)</td>
<td>0.59</td>
<td>0.20</td>
<td>0</td>
<td>0.21</td>
</tr>
<tr>
<td>SiH(_4) (l)</td>
<td>0.53</td>
<td>0.21</td>
<td>0</td>
<td>0.26</td>
</tr>
<tr>
<td>H(_2)C=CHCN (l)</td>
<td>0.28</td>
<td>0</td>
<td>&gt;0</td>
<td>-</td>
</tr>
<tr>
<td>C(_6)H(_6) (l)</td>
<td>0.15</td>
<td>0</td>
<td>0.65</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The amount of diamagnetic and paramagnetic muoniated species (Mu or radical) depends on the material and the radiolysis processes.

D. C. Walker, Muon and Muonium Chemistry, 1983
Diamagnetic Muons

Diamagnetic states:

- Solvated muons (Mu$^+$)
- Molecular ions (N$_2$Mu$^+$)
- Compounds (MuOH)

No Unpaired Electrons

Chemical shift ranges similar for H, D and T.

- Suppose $\Delta \delta \sim 5$ ppm
  
  $B = 3$ T $\rightarrow \Delta \nu_\mu \sim 2$ kHz
  
  $B = 7$ T $\rightarrow \Delta \nu_\mu \sim 4.7$ kHz

Muon spin interacts with nuclear spins.

$J$ coupling $\sim$ Hz

16 $\mu$s time window $\Rightarrow \Delta \nu \cdot \Delta t \geq 1/4\pi$ $\Rightarrow \Delta \nu_\mu \sim 5$ kHz

Different chemical states are *indistinguishable* for diamagnetic muons

Precess at $\nu_\mu$ [MHz] = 135.5 $B$ [T]
Muonium – A Light Hydrogen Isotope

Chemically identical to H but has $1/9^{th}$ the mass!

The chemistry of an atom depends primarily on the ionization potential and the radius.

- Reduced mass = 0.995 $m_r(H)$
- Ionization energy = 0.9956 $R_{\infty}$
- Bohr radius = 1.0044 $a_0$
- Mass Mu = 0.1131 Mass H
Reactions of Muonium

Addition
\[
\text{Mu} + \text{CH}_2=\text{CH}_3 \rightarrow \text{Mu-H} + \text{CH}_2=\text{CH}_3
\]

Abstraction
\[
\text{Mu} + \text{CH}_3\text{OH} \rightarrow \text{Mu-H} + \text{CH}_3\text{O}^-
\]

Oxidation - Reduction
\[
\text{Mu} + \text{Ag}^+ \rightarrow \text{Mu}^+ + \text{Ag}
\]

Spin Exchange
\[
\text{Mu}(\uparrow) + \text{NO}(\downarrow) \rightarrow \text{Mu}(\downarrow) + \text{NO}(\uparrow)
\]

Combination
\[
\text{Mu} + \cdot\text{OH} \rightarrow \text{MuOH}
\]

Acid-Base
\[
\text{Mu} + \cdot\text{OH} \rightarrow \text{MuOH} + \text{e}^-_{\text{solvated}}
\]
Problems Associated with Studying Atomic Hydrogen

Multiple reactive species are formed with many possible reactions.
Hyperfine Coupling in Muonium

- Muon spin interacts with electron spin.
- The strength of the interaction is the hyperfine coupling constant (hfcc).
- Much larger than muon – nuclear interactions and leads to measurable effects.

Isotropic Hyperfine Coupling

\[ A_X = \frac{\mu_0 \hbar}{3 \pi} \gamma_e \gamma_X |\psi(0)|^2 \]

Transmitted through bonds and proportional to unpaired electron spin density at nucleus

<table>
<thead>
<tr>
<th></th>
<th>Mu</th>
<th>H</th>
<th>D</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>0.1134</td>
<td>1.0073</td>
<td>2.0136</td>
<td>3.0155</td>
</tr>
<tr>
<td>Magnetic Moment ((\mu_p))</td>
<td>3.183</td>
<td>1</td>
<td>0.307</td>
<td>1.067</td>
</tr>
<tr>
<td>Larmor Frequency (MHz/T)</td>
<td>135.539</td>
<td>42.577</td>
<td>6.536</td>
<td>45.415</td>
</tr>
<tr>
<td>(A_X) (MHz)</td>
<td>4463.3</td>
<td>1420.4</td>
<td>218.3</td>
<td>1516</td>
</tr>
</tbody>
</table>
Transverse Field Muon Spin Rotation

- Spin-polarized muon beam
- Muon Detector
- Sample
- Positron Detector
- Electronic Clock
- Positron Detector
- B

Equations:

- $\mu^+$
- $e^+$
Spin States and Transitions in Muonium

\[ |1\rangle = |\alpha^e \alpha^\mu \rangle \]
\[ |2\rangle = c |\alpha^e \beta^\mu \rangle + s |\beta^e \alpha^\mu \rangle \]
\[ |3\rangle = |\beta^e \beta^\mu \rangle \]
\[ |4\rangle = -s |\alpha^e \beta^\mu \rangle + c |\beta^e \alpha^\mu \rangle \]

\[ E^{(1)} / h = \frac{1}{4} A^e + \frac{1}{2} (\nu_e - \nu_\mu) \]
\[ E^{(2)} / h = \frac{1}{4} A^e + \frac{1}{2} \left( \sqrt{A^2_\mu + (\nu_e + \nu_\mu)^2} - A_\mu \right) \]
\[ E^{(3)} / h = \frac{1}{4} A^e - \frac{1}{2} (\nu_e - \nu_\mu) \]
\[ E^{(4)} / h = -\frac{3}{4} A^e - \frac{1}{2} \left( \sqrt{A^2_\mu + (\nu_e + \nu_\mu)^2} - A_\mu \right) \]

\[ c^2 = \frac{1}{2} + \frac{1}{2} \sqrt{\nu_e + \nu_\mu / 2} ; \quad c = \frac{1}{\sqrt{2}} \text{ at } B = 0 \text{ and } 1 \text{ when } \nu_e + \nu_\mu \gg A_\mu \]
\[ s^2 = \frac{1}{2} - \frac{1}{2} \sqrt{\nu_e + \nu_\mu / 2} ; \quad s = \frac{1}{\sqrt{2}} \text{ at } B = 0 \text{ and } 0 \text{ when } \nu_e + \nu_\mu \gg A_\mu \]

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>\nu_{12} = \frac{1}{2} (\nu_e - \nu_\mu) - \frac{1}{2} \left( \sqrt{A^2_\mu + (\nu_e + \nu_\mu)^2} - A_\mu \right)</td>
<td>\propto c^2</td>
</tr>
<tr>
<td>\nu_{23} = \frac{1}{2} (\nu_e - \nu_\mu) + \frac{1}{2} \left( \sqrt{A^2_\mu + (\nu_e + \nu_\mu)^2} - A_\mu \right)</td>
<td>\propto s^2</td>
</tr>
<tr>
<td>\nu_{14} = \frac{1}{2} (\nu_e - \nu_\mu) + \frac{1}{2} \left( \sqrt{A^2_\mu + (\nu_e + \nu_\mu)^2} - A_\mu \right) + A_\mu</td>
<td>\propto s^2</td>
</tr>
<tr>
<td>\nu_{43} = \frac{1}{2} (\nu_e - \nu_\mu) - \frac{1}{2} \left( \sqrt{A^2_\mu + (\nu_e + \nu_\mu)^2} - A_\mu \right) - A_\mu</td>
<td>\propto c^2</td>
</tr>
</tbody>
</table>

\( \alpha = \text{spin up} \)
\( \beta = \text{spin down} \)
Intra-Triplet Transitions of Muonium

\[ B = 2 \, \text{G} \]
\[ A_\mu = 4463 \, \text{MHz} \]
\[ \nu_e = 5.6 \, \text{MHz} \]
\[ A_\mu \gg (\nu_e + \nu_\mu) \]
\[ \nu_{12} \text{ and } \nu_{23} \text{ are degenerate.} \]

\[ \nu_{12} = \nu_{23} = \frac{1}{2}(\nu_e - \nu_\mu) = \frac{\gamma_{\text{Mu}}}{2\pi} B \]

\[ \gamma_{\text{Mu}}/2\pi = 102.88 \, \gamma_\mu/2\pi \]
\[ (1.394 \, \text{MHz G}^{-1}) \]

\[ B = 250 \, \text{G} \]
\[ \nu_e = 701 \, \text{MHz} \]
\[ \nu_{12} \text{ and } \nu_{23} \text{ are NOT degenerate.} \]

Determine \( A_\mu \) by measuring \( \nu_{12}, \nu_{23} \) and \( \nu_\mu \)

\[ A_\mu = \frac{(\nu_{23} - \nu_{12})^2 - (\nu_e + \nu_\mu)^2}{2(\nu_{23} - \nu_{12})} \]
**TF-µSR of Muonium**

Low field $B \sim 2$ G

$v_{12}$ and $v_{23}$ are degenerate.

$\frac{\gamma_{\mu}}{2\pi} = 102.88 \frac{\gamma_{\mu}}{2\pi} (1.394 \text{ MHz G}^{-1})$

Measure $\lambda$.

Intermediate field $B \sim 250$ G

$v_{12}$ and $v_{23}$ are not degenerate.

Measure $A_{\mu}$

$$A(t) = A_D \cos(\omega_{\mu} t + \phi_D) + A_{Mu} \cos(\omega_{Mu} t + \phi_{Mu}) e^{-\lambda_{Mu} t}$$
Measuring Muonium Reaction Rate Constants

Chemical reaction causes dephasing and exponential damping of the Mu precession.

Increasing concentration of reactant
Measuring Muonium Reaction Rate Constants

\[ \lambda = \lambda_0 + k_{Mu}[X] \]

Relaxation in pure solvent  \[ \text{Pseudo-1}\text{st order rate constant} \]
Concentration of reactant X

Ex) What is the rate constant for the reaction of Mu with hydrogen peroxide at 295 K and pH 7?

Plot \( \lambda \) versus [\( \text{H}_2\text{O}_2 \)]

Slope = \( k_{Mu} = 1.8(1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \)
Kinetic Isotope Effects on Abstraction and Addition Reactions

**Abstraction Reactions**

\[ k_{\text{Mu}} < k_{\text{H}} \]

Isotope effect depends on the width and height of the activation barrier


**Addition Reactions**

\[ k_{\text{Mu}} > k_{\text{H}} \]

Muonium Kinetics in Extreme Environments

Supercritical water

$P > 218 \text{ bar}$ and $T > 647 \text{ K}$

Ghandi et al. PCCP 4 (2002) 586

$70 \text{ MeV/c} \ \mu^+$

$E_{\text{max}} = 52.8 \text{ MeV}$

Backward muons and decay positrons can get through pressure vessel

Extrapolated from low temperature data

Ghandi et al. PCCP 4 (2002) 586

Longitudinal Field Techniques – Repolarization / RF-μSR / ALC-μSR / LF-μSR

\[ A(B) = \frac{N_F - N_B}{N_F + N_B} \propto P_z(B) \]
Repolarization of Muonium

- Muons are spin polarized but electrons are not so equal probability of $|\alpha_\mu\alpha_e\rangle$ and $|\alpha_\mu\beta_e\rangle$.
- 50% of polarization lost in zero magnetic field.
- Magnetic field decouples muon and electron spins.

$$P_z(B) = \frac{1 + 2(B/B_0)^2}{2[1 + (B/B_0)^2]}$$

$$B_0 = \frac{A_\mu}{\gamma_e + \gamma_\mu}$$

- Hyperfine coupling to other nuclei results in the low-field Mu polarization being below 50%.

![Graph showing normalized Mu polarization against magnetic field](Vacuum_Mu_B0=159.2\ mT)
What Are Radicals?

- Radicals are atoms or molecules with one or more unpaired electrons.
  
  ![Radical Structure](image)
  
  7 valence electrons (2 from each bond and 1 unpaired electron)

- Radicals are often highly reactive as it is usually energetically favorable for them to attain “closed shell configuration”

What Are Free Radicals?

- Free radicals are like robbers which are deficient in energy.
- Free radicals attack and snatch energy from the other cells to satisfy themselves.
Difficulties of Studying Radicals

- Production of radicals often requires nasty mix of chemicals (e.g. Fenton’s reagent) and/or irradiation (X-ray or e\textsuperscript{-}).
- Reactive radicals are difficult to study with traditional spectroscopic techniques (EPR, UV-Vis, IR)

\[ \text{Signal} \sim [R^\bullet] \]

\[ R^\bullet + R^\bullet \rightarrow R-R \]  \textit{Termination reaction}

Matrix Isolation
- Prevent radical from reacting

Spin Trapping
- Convert initial radical to a less reactive radical
Formation of Muoniated Radicals

• Radicals produced by addition of Mu to an unsaturated bond.

- Very few muons in the sample at one time, so no termination reactions.
- Radicals can be studied at any temperature and in any phase.
Radical Nomenclature

- **α carbon**: nucleus with significant unpaired electron spin density
- **α proton**: attached to an α carbon
- **β carbon**: one removed from α carbon
- **β proton**: attached to an β carbon
- **γ carbon**: one removed from β carbon
- ................
Hyperfine Interactions in Muoniated Radicals

- Unpaired electron can interact with the muon and other nuclear spins.
- $A_X$ is the strength of the interaction between the spin of the electron and the magnetic dipole of the nucleus $X$ ($I \geq \frac{1}{2}$).

By measuring all of the hyperfine coupling constants one can map out the distribution of the unpaired electron and infer the structure of the radical.
Electron Density Versus Spin Density

- Electron has a spin of 1/2
  \[ |\alpha\rangle: m_s = +1/2 \]
  \[ |\beta\rangle: m_s = -1/2 \]

**Electron density**

\[ \rho(\vec{r}) = \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r}) \]

**Spin density**

\[ \rho^{\text{SPIN}}(\vec{r}) = \rho^\alpha(\vec{r}) - \rho^\beta(\vec{r}) \]

The hfcc is directly proportional to the unpaired spin density at the nucleus

\[ A_X = \left[ \frac{2\mu_0}{3h} g_e \mu_B g_X \mu_X \right] \rho^{\text{SPIN}}(\vec{r} = 0) \]

- Blue: \( \rho^\alpha > \rho^\beta \)
  Positive spin density

- Green: \( \rho^\alpha < \rho^\beta \)
  Negative spin density
Identification of Muoniated Radicals

- TF-μSR
  - Precession frequencies
  - Δ₁ (solid)
  - Muon hfcc ($A_m$)

- ALC-μSR
  - Resonance fields
  - Δ₀
  - Nuclear hfccs (H, D, $^{13}$C, $^{14}$N….)

- Hyperfine Coupling Constants

- Temperature Dependence of HFCs
  - Distribution of unpaired electron
  - • 3D radical structure
  - • Intramolecular motion
TF-μSR of Muoniated Radicals

Allowed transitions

\[
\nu_{12} = \nu_D - \frac{1}{2}A_\mu
\]

High field
\(\nu_e > A_\mu\)

\[
\nu_{43} = \nu_D + \frac{1}{2}A_\mu
\]

Breit-Rabi diagram for a muon-electron-proton system

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E. Roduner *The Positive Muon as a Probe in Free Radical Chemistry* 1988
TF-μSR spectrum of benzene at 280 K and 2.2 T.
\[ \nu_D = 300.1 \text{ MHz} \]
\[ \nu_{43} = 559.1 \text{ MHz} \]
\[ \nu_{12} = 43.3 \text{ MHz} \]
\[ A_{\mu} = 515.8 \text{ MHz} \]

The lower amplitude of \( \nu_{43} \) compared with \( \nu_{12} \) is an artefact due to the time resolution of the spectrometer (0.39 ns).
The radical frequencies will shift position with magnetic field.

Important check of whether signals are real or noise.

Combination of low field and large $A_\mu$ can result in negative frequency (i.e. opposite direction to $\text{Mu}^+$).

Can be distinguished using two orthogonal pairs of detectors.
Limitations of TF-µSR

- Requires high concentration (~1 M) of precursor to prevent loss of polarization.

\[ P_{12}^R \approx \frac{1}{2} h_{\text{M}} \left[ \frac{\lambda^2}{\lambda^2 + \Delta \omega_{12}^2} \right]^{1/2} \]

- \( h_{\text{M}} \) is the initial fraction of muon polarization in Mu
- \( \lambda \) is the first-order reaction rate
- \( \Delta \omega_{12} \) is the change in precession frequency between Mu and the radical

### Table

<table>
<thead>
<tr>
<th>Precursor Concentration (M)</th>
<th>Mu → Radical 1st order rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M</td>
<td>0.1 M</td>
</tr>
<tr>
<td>0.1 M</td>
<td>1 M</td>
</tr>
<tr>
<td>1 M</td>
<td>10 M</td>
</tr>
<tr>
<td>10 M</td>
<td>-</td>
</tr>
<tr>
<td>10 M</td>
<td>-</td>
</tr>
</tbody>
</table>

\( k_{\text{Mu}} = 10^{10} \text{ M}^{-1} \text{ s}^{-1} \)
\( = 10^8 \text{ M}^{-1} \text{ s}^{-1} \)

Mu: \( A_{\mu} = 4463 \text{ MHz} \)
Radical: \( A_{\mu} = 515 \text{ MHz} \)
\( B = 1.5 \text{ T} \)
Repolarization of Muoniated Radicals

Prompt Formation
- Similar repolarization curve to Mu except with lower critical field due to smaller $A_\mu$.
- Lower polarization at low magnetic fields due to hyperfine coupling with other nuclei.

Slow Formation
- Two components in repolarization curve: low-field repolarization due to muoniated radical and high-field repolarization due to Mu.
- Does NOT indicate simultaneous presence of Mu and muoniated radical.
- Curve shape depends on conversion rate between Mu and muoniated radical.
RF-μSR of Muoniated Radicals

- Measure $A_\mu$ of slowly-formed muoniated radicals.
- Resonance when the RF frequency matches the $\nu_{12}$ or $\nu_{43}$ transitions (high field limit).

$$\nu_{RF} = \gamma_\mu B_{res} - \frac{1}{2} A_\mu$$

$$A_\mu = 2(\gamma_\mu B_{res} - \nu_{RF})$$

$$\gamma_\mu B_{res} = 25.0 \text{ MHz}$$

$$\nu_{RF} = 10.0 \text{ MHz}$$

$$A_\mu = 30.0 \text{ MHz}$$
**ALC-μSR of Muoniated Radicals**

- **ΔM=2 Resonance**
  - Narrow and weak.
  - Rarely observed.

- **ΔM=1 Resonance**
  - One ΔM = 1 resonance per radical
  - Sensitive indicator of reorientation dynamics on timescale of 20 - 50 ns.

- **ΔM=0 Resonance**
  - Observed in solids, liquids and gases.

\[ B_r \approx \left| \frac{A_u - A_k}{2(\gamma_\mu - \gamma_k)} - \frac{A_u + A_k}{2\gamma_e} \right| \]

\[ B_r = \left[ \frac{A_u}{2\gamma_\mu} - \frac{A_u}{2\gamma_e} \right] \]
### ALC-μSR of C₆H₆Mu and ¹³C₆H₆Mu

#### Table 1: Magnetic Field Differences and Nucleus Parameters

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$A_\mu$ (MHz)</th>
<th>$B_{res}$ (T)</th>
<th>$A_p$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(6)</td>
<td>514.47</td>
<td>2.0774</td>
<td>126.11</td>
</tr>
<tr>
<td>H(2,4)</td>
<td>514.47</td>
<td>2.7176</td>
<td>7.47</td>
</tr>
<tr>
<td>H(1,5)</td>
<td>514.47</td>
<td>2.8936</td>
<td>-25.14</td>
</tr>
<tr>
<td>H(3)</td>
<td>514.47</td>
<td>2.9532</td>
<td>-36.19</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$A_\mu$ (MHz)</th>
<th>$B_{res}$ (T)</th>
<th>$A_C$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(3)</td>
<td>512.28</td>
<td>1.8261</td>
<td>53.95</td>
</tr>
<tr>
<td>C(1,5)</td>
<td>512.28</td>
<td>1.8840</td>
<td>39.57</td>
</tr>
<tr>
<td>C(6)</td>
<td>512.28</td>
<td>2.1803</td>
<td>-34.08</td>
</tr>
<tr>
<td>C(2,4)</td>
<td>512.28</td>
<td>2.1849</td>
<td>-35.21</td>
</tr>
</tbody>
</table>
McConnell’s Law for α-Hydrogens

- α-nuclei lie in nodal plane but have negative spin density due to spin polarization of the bond

\[ A_X = Q_X \rho^\pi \]

- \( \rho^\pi \) is the π-electron population at the adjacent carbon atom
- \( Q_p \sim -75 \text{ MHz} \)

- The hfccs of the α-hydrogens are used to determine the spin density distribution in the π system.

More probable

McConnell equation for α-nuclei
Spin Density Distribution in the Muoniated Cyclohexadienyl Radical

Muon (β)
$A_\mu = 514.6$ MHz

Methylene (1H β)
$A_p = 125$ MHz

Ortho (2H α)
$A_p = -25.5$ MHz
$\rho \sim +0.35$

Meta (2H α)
$A_p = +7.5$ MHz
$\rho \sim -0.10$

Para (1H α)
$A_p = -36.8$ MHz
$\rho \sim +0.49$

Spin density around ring
$2(0.35) + 2(-0.10) + 1(0.49) \sim 1$
Spin Density Distribution in the \( \text{MuC}_6 \) Radical

\[ \text{Mu}^{13}\text{C}_6 \] Avoided Level Crossing Resonance

% Unpaired Spin Density

Identification of Radicals: Quantum Calculations

• μSR spectra do not give direct access to the radical structure. This must be inferred from the magnitude and temperature dependence of hfccs.

• Magnetic properties of a radical often depend on the subtle interplay of several different effects. (e.g. conformation, vibrational averaging, solvent effects, substituent effects….)

• Quantum calculations are used to:
  • Support and compliment the experimental results to determine the electronic and geometric structure of the radical starting from its spectral properties.
  • Evaluate the role of different effects on the magnetic properties of a radical.
  • Eliminate possible structures that have different hfccs than experimental values.
  • Calculate relative energies of possible structures. Lower energy structures are more likely to form.
How to Perform Quantum Calculations on Radicals

• Commercial ab initio packages such as Gaussian 16 or Amsterdam Density Functional.
• Use unrestricted method (treats α and β electrons separately) to correctly account for spin polarization.
• Density functional methods (such as B3LYP or PBE0) give isotropic hfcc that are in good agreement with experimental values and are practical for larger radicals.
• The larger the basis set, the more accurate the wavefunction but the computational time is much longer. EPR-II and EPR-III basis sets optimized for calculating hfccs.
• Benchmark your calculations against closely-related, known systems.
• Include vibrational averaging effects.
  • Gaussian includes vibrational averaging (Fermi keyword).
  • Empirical treatment in cyclohexadienyl radicals: increase C-Mu bond length by 4.9% and decrease the methylene C-H bond length by 0.3%.
How Does a Radical React with a Carbene?

DFT Calculations

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\mu}$</td>
<td>278.8 MHz</td>
</tr>
<tr>
<td>$A_C(C2)$</td>
<td>136.0 MHz</td>
</tr>
<tr>
<td>$A_N(N1)$</td>
<td>8.3 MHz</td>
</tr>
<tr>
<td>$A_N(N3)$</td>
<td>8.3 MHz</td>
</tr>
<tr>
<td>$A_{\mu}(\text{CH}_3\text{C}5)$</td>
<td>-</td>
</tr>
</tbody>
</table>

μSR Measurements

- $A_{\mu} = 246.4$ MHz
- $A_N = 13.7$ MHz
- $A_C = 139.6$ MHz

Similarities between measured and calculated hfccs suggests Mu adds to the carbeneic carbon.

I. McKenzie et al. J. Am. Chem. Soc. 2003, 125, 11565
Mu can react in multiple ways. You can control where it ends up by altering the composition of the sample.

Relative yield of Mu-X

\[ P_X = \frac{k_{Mu}^{(X)} [X]}{k_{Mu}^{(X)} [X] + k_{Mu}^{(Y)} [Y]} \]

Relative yield of Mu-Y

\[ P_Y = \frac{k_{Mu}^{(Y)} [Y]}{k_{Mu}^{(X)} [X] + k_{Mu}^{(Y)} [Y]} \]

\[ k_{Mu}^{(X)} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \]
\[ k_{Mu}^{(Y)} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \]

\[ [X] = 2 \text{ M} \]
\[ [Y] = 0.1 \text{ M} \]

\[ P_X = 0.6 \]
\[ P_Y = 0.4 \]
Predicting Reaction Products: The Bell-Evans-Polanyi Theorem

Addition reactions are exothermic, i.e. \( \Delta H < 0 \)

The activation energy \( E_A \) is linearly related to the reaction enthalpy \( \Delta H \) for a series of related single-step reactions.

\[ E_A = E_0 + \alpha \Delta H \]

where \( \alpha \) is a measure of “lateness” of the transition state \( (0 > > 1) \).

More exothermic reactions are generally faster.
Competing Reaction Pathways: Reaction of Mu with Fluoranthene

<table>
<thead>
<tr>
<th>Radical</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>ΔΔH (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mu-3a</td>
<td>-97</td>
<td>139</td>
</tr>
<tr>
<td>Mu-10c</td>
<td>-129</td>
<td>107</td>
</tr>
<tr>
<td>Mu-C6b</td>
<td>-164</td>
<td>72</td>
</tr>
<tr>
<td>Mu-C6a</td>
<td>-178</td>
<td>58</td>
</tr>
<tr>
<td>Mu-C7</td>
<td>-193</td>
<td>43</td>
</tr>
<tr>
<td>Mu-C2</td>
<td>-194</td>
<td>42</td>
</tr>
<tr>
<td>Mu-C8</td>
<td>-201</td>
<td>35</td>
</tr>
<tr>
<td>Mu-C1</td>
<td>-219</td>
<td>17</td>
</tr>
<tr>
<td>Mu-C3</td>
<td>-236</td>
<td>0</td>
</tr>
</tbody>
</table>

Competing Reaction Pathways: Reaction of Mu with Fluoranthene

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta \Delta H$ (kJ mol$^{-1}$)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mu-3a</td>
<td>-97</td>
<td>139</td>
<td>–</td>
</tr>
<tr>
<td>Mu-10c</td>
<td>-129</td>
<td>107</td>
<td>–</td>
</tr>
<tr>
<td>Mu-C6b</td>
<td>-164</td>
<td>72</td>
<td>–</td>
</tr>
<tr>
<td>Mu-C6a</td>
<td>-178</td>
<td>58</td>
<td>–</td>
</tr>
<tr>
<td>Mu-C7</td>
<td>-193</td>
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<tr>
<td>Mu-C3</td>
<td>-236</td>
<td>0</td>
<td>35.8</td>
</tr>
</tbody>
</table>

Free Radical Reactivity of a Phosphaalkene

- Free radical polymerization of phosphaalkenes (P=C) to produce new functional polymers.
- Initiation step of polymerization involves radical addition to phosphaalkenes.

**How does a simple free radical, muonium (Mu), react with phosphaalkenes?**

- Radicals 1b and 2a are isotopomers produced by different routes. Identity of radicals confirmed by comparing hyperfine coupling constants.
- Highly selective addition of radicals to the P-atom of the P=C bond gives a C-centered radical intermediate.

Isotope Effect on Bond Stretching

Asymmetric bond stretching potential results in C-Mu bond being longer than C-H bond.

$$r_{\text{C-Mu}} \approx 1.049 \, r_{\text{C-H}}$$

Hfccs becomes increasingly positive with increasing bond length (although $|A_\mu|$ decreases if $A_\mu$ is negative).


$$m_\mu = \frac{m_\mu m_\chi}{m_\mu + m_\chi} \approx m_\mu \quad \text{ZPE} = \frac{1}{2} \hbar \sqrt{\frac{k}{m_\mu}}$$
Hyperfine Coupling of β-Nuclei

\[ A^\beta_p = \left[ L + M \cos^2 \theta \right] \rho^\pi \]

- **L**: orientation independent mechanisms (~0 – 10 MHz)
- **M**: spin density arising from hyperconjugation (~140 MHz)
- **θ** is the angle between C-X bond and SOMO
- **\( \rho^\pi \)** is the spin density on adjacent carbon

• The preferred configuration of the radical can be determined from measuring the magnitude and temperature dependence of the hfcc.

At high temperatures the methyl group is freely rotating:

\[ A_R = \left( L + \frac{1}{2} M \right) \rho^\pi \]

\[ \frac{dA_{R_1}}{dT} < 0 \]

\[ \frac{dA_{R_{2(3)}}}{dT} > 0 \]

\[ A_{R_{1(2)}} = \left( L + \frac{3}{4} M \right) \rho^\pi \]

\[ \frac{dA_{R_{1(2)}}}{dT} < 0 \]

\[ A_{R_3} = L \rho^\pi \]

\[ \frac{dA_{R_3}}{dT} > 0 \]
Isotope Effects on Intramolecular Dynamics

C-Mu bond aligns with SOMO at low temperatures
Measuring Radical Reaction Rates with ALC-µSR

Chemical reaction broadens ALC resonances.

\[ \Delta_0 \text{ resonance width} \]
\[ \Delta B_{1/2} = \frac{\sqrt{\omega_{ALC}^2 + \lambda^2}}{2\pi(\gamma_\mu - \gamma_p)} \]
\[ \lambda = \lambda_0 + k_R [X] \]

Slope = \( k_R \)

Units = M\(^{-1}\)s\(^{-1}\)

E. Roduner The Positive Muon as a Probe in Free Radical Chemistry 1988
Dipolar Hyperfine Coupling

Point dipole

\[ \frac{3 \cos^2 \theta - 1}{r^3} \]

- \( \theta < 54.7^\circ \) Positive
- \( \theta = 54.7^\circ \) Zero
- \( \theta > 54.7^\circ \) Negative

Delocalized electron

Integrate over the singly occupied molecular orbital (SOMO).

\[ \left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle \]

- Judge whether the unpaired electron (or SOMO) is mostly in the positive or the negative sector of a double cone with opening angle \( \theta = 54.7^\circ \)
Dipolar Hyperfine Coupling of $\alpha$-Nuclei

$B_{zz} \approx 0$
Orbital is partly in the positive and partly in the negative sector of the double cone

$B_{xx} > 0$
Orbital is essentially entirely in the positive sector of the double cone

$B_{yy} < 0$
Orbital is essentially entirely in the negative sector of the double cone
Dipolar Hyperfine Coupling of β-Nuclei

\[ B_{zz} < 0 \quad B_{xx} > 0 \quad B_{yy} < 0 \]
Motional Averaging of Hyperfine Tensors

- Hyperfine tensor can be represented as an ellipsoid
- Dipolar coupling is traceless

General: \[ B_{xx} + B_{yy} + B_{zz} = 0 \]
Axial symmetry: \[ D_{\parallel} + 2D_{\perp} = 0 \]

\[ D_{\perp} = -\frac{1}{2} D_{\parallel} \]
\[ D'_{\parallel} = D_{\perp} = -\frac{1}{2} D_{\parallel} \]
Rotational Averaging of Dipolar Hyperfine Coupling

Hyperfine Tensor

- $B_{yy} \approx 0$
- $B_{xx} = 8.6$ MHz
- $B_{zz} = -8.6$ MHz

Hyperfine tensor is traceless so

$$B_{xx} + B_{yy} + B_{zz} = 0$$

Rapid rotation around an axis produces an axial hyperfine tensor

$$D_{\mu}^\parallel = -2D_{\mu}^\perp$$

- $D_{\mu}^\parallel = -6.8$ MHz
- $D_{\mu}^\perp = +3.4$ MHz

- $D_{\mu}^\parallel = +5.8$ MHz
- $D_{\mu}^\perp = -2.9$ MHz
**ALC Lineshapes**

\( \Delta_1 \) lineshape depends on magnitude of dipolar hfc and the angle between unique axis and magnetic field (\( \theta \)).

\[
\bar{P}_z(B, \theta) = 1 - \frac{0.5q^2 P^0_z}{\left(\frac{\lambda}{2\pi}\right)^2 + q^2 + \gamma^2 \mu \left(B - B_{\text{res}}^{\Delta_1}\right)^2}
\]

\[q = \frac{3}{2} D^\perp \mu \sin \theta \cos \theta\]

In a powder the \( \Delta_1 \) lineshape is obtained by integrating over all angles and weighting by the angular probability \( f(\theta) \).

\[
\bar{P}_z(B) = \int_0^{\pi} \bar{P}_z(B, \theta) f(\theta) 2\pi \sin \theta d\theta
\]
Preferred rotation axes can be determined from the shape of ALC resonances.

\[ D_{\parallel}^{\mu} = -6.8 \text{ MHz} \]
\[ D_{\perp}^{\mu} = +3.4 \text{ MHz} \]

\[ D_{\parallel}^{\mu} = +5.8 \text{ MHz} \]
\[ D_{\perp}^{\mu} = -2.9 \text{ MHz} \]
Dynamics of Mu Adduct of Norbornene

Δ₁ resonance
- Asymmetric lineshape indicates negative $D_μ^{||}$
- Preferred rotation around indicated axis.
- Decreasing $|D_μ^{||}|$ with increasing temperature due to wobbling of rotation axis.

Dynamics of $C_{60}$ Versus $C_{70}$

$C_{60}$

$\Delta_1$ broadens with increasing temperature

$C_{70}$

$\Delta_1$ narrows with increasing temperature

Isotropic rotation

Wobbling around preferred axis

**LF-μSR Studies of Dynamics**

Provides information about motion of free radicals.
Measure time dependence of muon spin polarization.
Relaxation of the diamagnetic muons in longitudinal fields is negligible on the μSR time scale.
Relaxation of the muon spin in radicals may be caused by:
- fluctuating isotropic hyperfine interactions
- fluctuating anisotropic hyperfine interactions
- the spin–rotation interactions of the electron and the muon
Dominant mechanism depends on the magnetic field.

In low magnetic fields:

\[
\frac{1}{T_1^\mu} \text{ (indirect)} = \frac{1}{1 + X^2} \frac{1}{T_1^e} = \frac{\Delta_E^2}{1 + X^2} \left( \frac{2 \tau_e}{1 + \omega_e^2 \tau_e^2} \right)
\]

![Graph](image.png)
• Predominant physical behaviors occur at an energy scale comparable with room temperature thermal energy

• Materials that are easily deformable by external stresses, electric or magnetic fields, or even by thermal fluctuations

• Soft matter can self-organize into mesoscopic physical structures; the structure and dynamics at the mesoscopic scales determine macroscopic physical properties
Muoniated Probes in Soft Matter

- Introduce spin label in soft matter system (liquid crystal, polymer)
- Similar to spin labeling with stable nitroxides except smaller perturbation.
- Radical sensitive to:
  - Orientation of probe
  - Polarity of local environment
  - Fluctuations on the ns to µs timescale
Lyotropic Liquid Crystals with Cosurfactants

DHTAC

$C_{12}E_4$

polar head groups

non-polar alkyl chains

aqueous layer

Phenylethanol Cosurfactant
**ALC-μSR of Phenylethanol Cosurfactant**

Hfccs are sensitive to the polarity of the local environment

ALC-μSR of Phenylethanol Cosurfactant in DHTAC Bilayer

Spin-Exchange Reaction Between Mu Adducts of PEA and Ni$^{2+}$

<table>
<thead>
<tr>
<th></th>
<th>T / K</th>
<th>$k_{\text{ortho}}$</th>
<th>$k_{\text{meta}}$</th>
<th>$k_{\text{para}}$</th>
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<tr>
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<td>H$_2$O</td>
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<tr>
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<td>DHTAC</td>
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</tbody>
</table>

ALC-μSR of Phenylethanol Cosurfactant in C$_{12}$E$_4$

ALC-µSR of the Nematic Liquid Crystal PCH5

Magnetic field aligns director in nematic phase, which shifts the Δ₀ resonance.

Wobbling within a cone of angle φ

\[ \langle D_x^\parallel \rangle = \frac{1}{2} T_x^\parallel (\cos φ + \cos^2 φ) \]
Muoniated Spin Probes in a Cholesterolic Liquid Crystal

Cholesteryl nonanoate

Helical axis

Pitch $p$

Chiral nematic phase ($N^*$)

UB3LYP/6-31G(d,p)//UBPBE0/EPR-II

$A_e = 442$ MHz
$B_{res}(\Delta_1) = 1.62$ T

$A_p = 120$ MHz
$B_{res}(\Delta_0) = 1.72$ T

Muoniated Spin Probes in a Cholesterolic Liquid Crystal

N*: Wobbling around a preferred axis

I: Slow Isotropic Reorientation

LF-μSR Studies of Phenyl Ring Dynamics in Polystyrene

Spin relaxation due to muoniated cyclohexadienyl radicals formed by Mu addition to phenyl side chains.

\[ P(t) = P_D + P_R e^{-(t/T_1^\mu)^\kappa} \]

Distribution of local environments

Rapid backbone motion leads to uniform environment

Change at \( T_g \)
LF-μSR Studies of Phenyl Ring Dynamics in Polystyrene

Change in phenyl ring dynamics at the glass transition.

Relaxation map of polystyrene.

\[ \ln[T_1^{\mu,avg}(\mu s)] = \ln \left[ \frac{\omega_e^2 \tau_0}{0.14[A_\mu : A_\mu]} \right] + \left( \frac{E_A}{k_B} \right) T^{-1} \]
Biological Systems: Mu Addition to Nucleobases

Biological Systems: 4 of 21 Amino Acids Have Unsaturated Side Groups

- **Histidine – 2 radicals**

- **Phenylalanine – 3 radicals**

- **Tryptophan – 5 radicals**

- **Tyrosine – 2 radicals**
Biological Systems: µSR of Cytochrome C Protein

12 kDa protein consisting of a single 104 amino acid peptide with a heme group

- Temperature and field dependent muon spin relaxation.
- Spin relaxation due to multiple types of radical (Mu addition to amino acids and heme group).
- Localized spin density: fitting with Risch-Kehr not meaningful.
- Nearly impossible to deconvolute.

Conclusions

- Muonium is a light hydrogen of hydrogen. Kinetics studies of Mu are performed to learn about isotope effects or to study reactions under conditions not amenable to other techniques.
- The structure, conformation and dynamics of muoniated radicals can be determined by measuring the magnitude and temperature dependence of the muon and nuclear hfccs using techniques such as TF-µSR, RF-µSR, ALC-µSR and repolarization.
- Muoniated radicals can be used as local probes in soft matter. They provide information about the local environment and dynamics on timescales between that accessible by NMR and neutron scattering.

Literature