The Positive Muon as a Probe in Chemistry
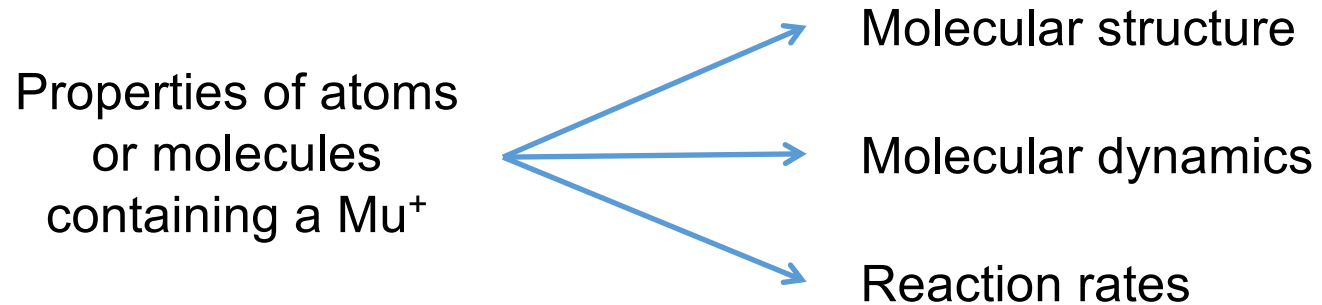
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Department of Chemistry, Simon Fraser University

μSR and Chemistry

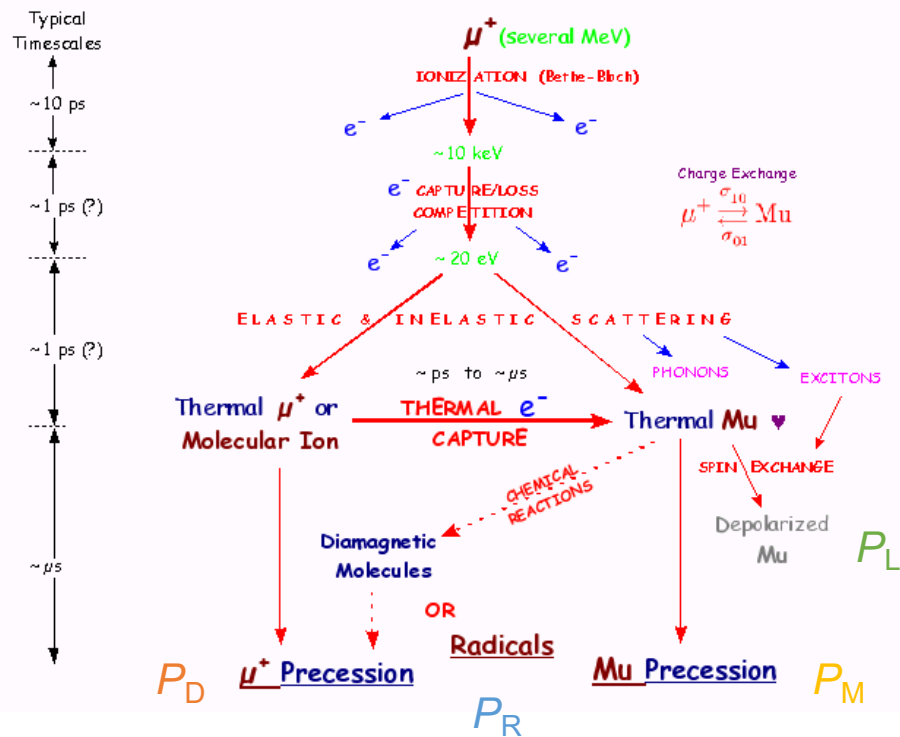Properties of atoms or molecules containing a Mu^+

→ Molecular structure

→ Molecular dynamics

→ Reaction rates

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
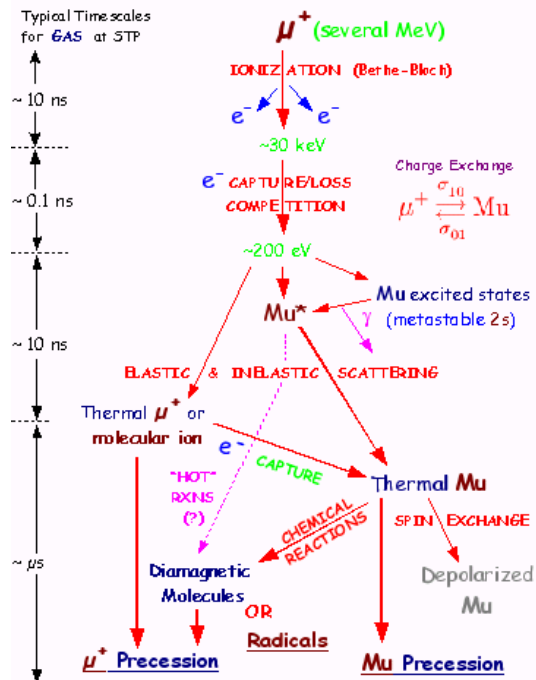

μ^+ & Mu in **Liquids** and **Solid** **Insulators** & **Semiconductors**

μ^+ & Mu in **Gases**

J. Brewer   http://musr.ca/intro/ppt/DMF/img5.html

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

Material	P_D	P_M	P_R	P_L
Ag $_{(s)}$	1.0	0	0	0
$CCl_{4\ (l)}$	1.0	0	0	0
$H_2O_{\ (l)}$	0.62	0.20	0	0.18
Ethanol $_{(l)}$	0.59	0.20	0	0.21
$SiH_{4\ (l)}$	0.53	0.21	0	0.26
$H_2C=CHCN_{\ (l)}$	0.28	0	>0	-
$C_6H_{6\ (l)}$	0.15	0	0.65	0.20

The amount of diamagnetic and paramagnetic muoniated species (Mu or radical) depends on the material and the radiolysis processes.
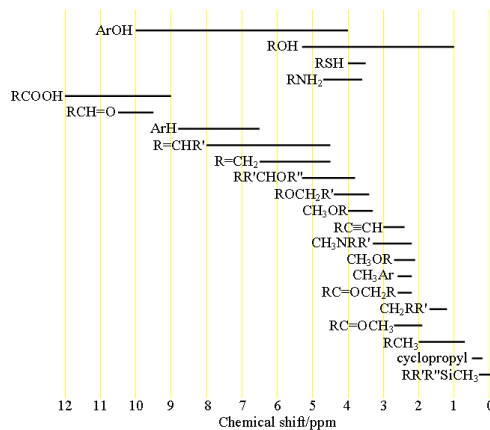
D. C. Walker, Muon and Muonium Chemistry, 1983

Diamagnetic Muons

Diagmagnetic states:
- Solvated muons (Mu^+)
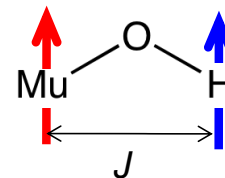- Molecular ions (N_2Mu^+)
- Compounds (MuOH)

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

ArOH
ROH
RSH
RNH$_2$
RCOOH
RCH=O
ArH
R=CHR'
R=CH$_2$
RR'CHOR''
ROCH$_2$R'
CH$_3$OR
RC≡CH
CH$_3$NRR'
CH$_3$OR
CH$_3$Ar
RC=OCH$_2$R
CH$_2$RR'
RC=OCH$_3$
RCH$_3$
cyclopropyl
RR'R''SiCH$_3$

12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical shift/ppm
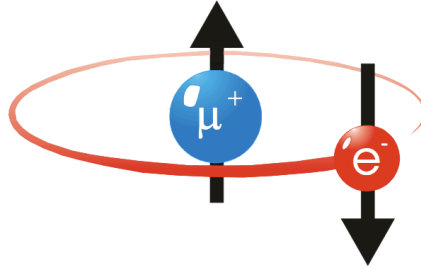
16 μs time window $\longrightarrow$ $\Delta\nu \cdot \Delta t \geq 1/4\pi$ $\longrightarrow$ $\Delta\nu_\mu \sim 5$ kHz

Different chemical states are *indistinguishable* for diamagnetic muons

Precess at ν_μ [MHz] = *135.5 B* [T]

Muonium – A Light Hydrogen Isotope

Muonium (Mu = [μ⁺,e⁻])

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

→
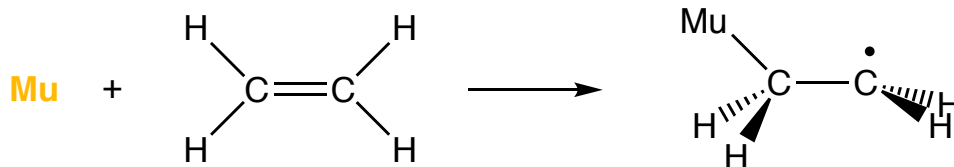
- Reduced mass = 0.995 m_r(H)
- Ionization energy = 0.9956 R_∞
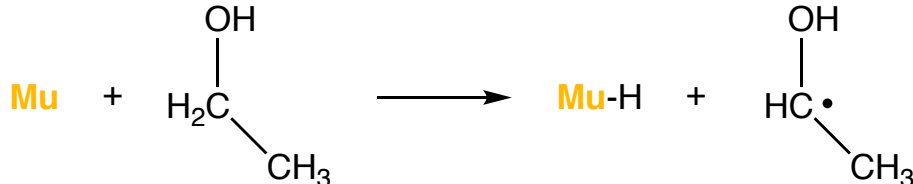- Bohr radius = 1.0044 a_0
- Mass Mu = 0.1131 Mass H

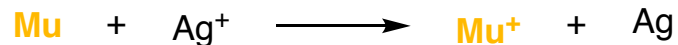**Chemically identical to H but has 1/9th the mass!**

Reactions of Muonium

Addition

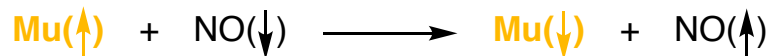$$\textbf{Mu} + \underset{\substack{H \\ \\ H}}{\overset{\substack{H \\ \\ H}}{C=C}} \longrightarrow$$

Abstraction

$$\textbf{Mu} + H_2C\underset{CH_3}{\overset{OH}{\Big\langle}} \longrightarrow \textbf{Mu}\text{-H} + HC\underset{CH_3}{\overset{OH}{\Big\langle}}\cdot$$

Oxidation - Reduction

$$\textbf{Mu} + Ag^+ \longrightarrow \textbf{Mu}^+ + Ag$$

Spin Exchange

$$\textbf{Mu}(\uparrow) + NO(\downarrow) \longrightarrow \textbf{Mu}(\downarrow) + NO(\uparrow)$$

Combination

$$\textbf{Mu} + \cdot OH \longrightarrow \textbf{Mu}\underset{}{\overset{O}{\diagup}}\diagdown_H$$

Acid-Base

$$\textbf{Mu} + {}^-OH \longrightarrow \textbf{Mu}\underset{}{\overset{O}{\diagup}}\diagdown_H + e^-_{solvated}$$
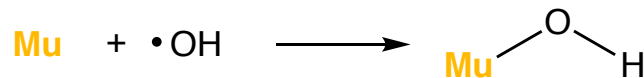
Problems Associated with Studying Atomic Hydrogen

Time (s)

Ionizing Radiation

H_2O

0

Physical stage

excitation   ionization

10^{-15} s

H_2O^* $H_2O^+ + e^-$

Physico-chemical stage

H_2O

$HO^\bullet + H^-$ H_2O^*

$H_2 + O(^1D)$ H_2O

H_2O H_2O

10^{-12} s

$H^\bullet + HO^\bullet$ $H_2 + 2\,HO^\bullet$ $HO^\bullet + H_3O^+$ $HO^\bullet + H_2 + OH^-$ e^-_{aq}

Chemical stage

10^{-6} s

e^-_{aq}, $H^\bullet$, $HO^\bullet$, $HO_2^\bullet$, OH^-, H_3O^+, H_2, H_2O_2
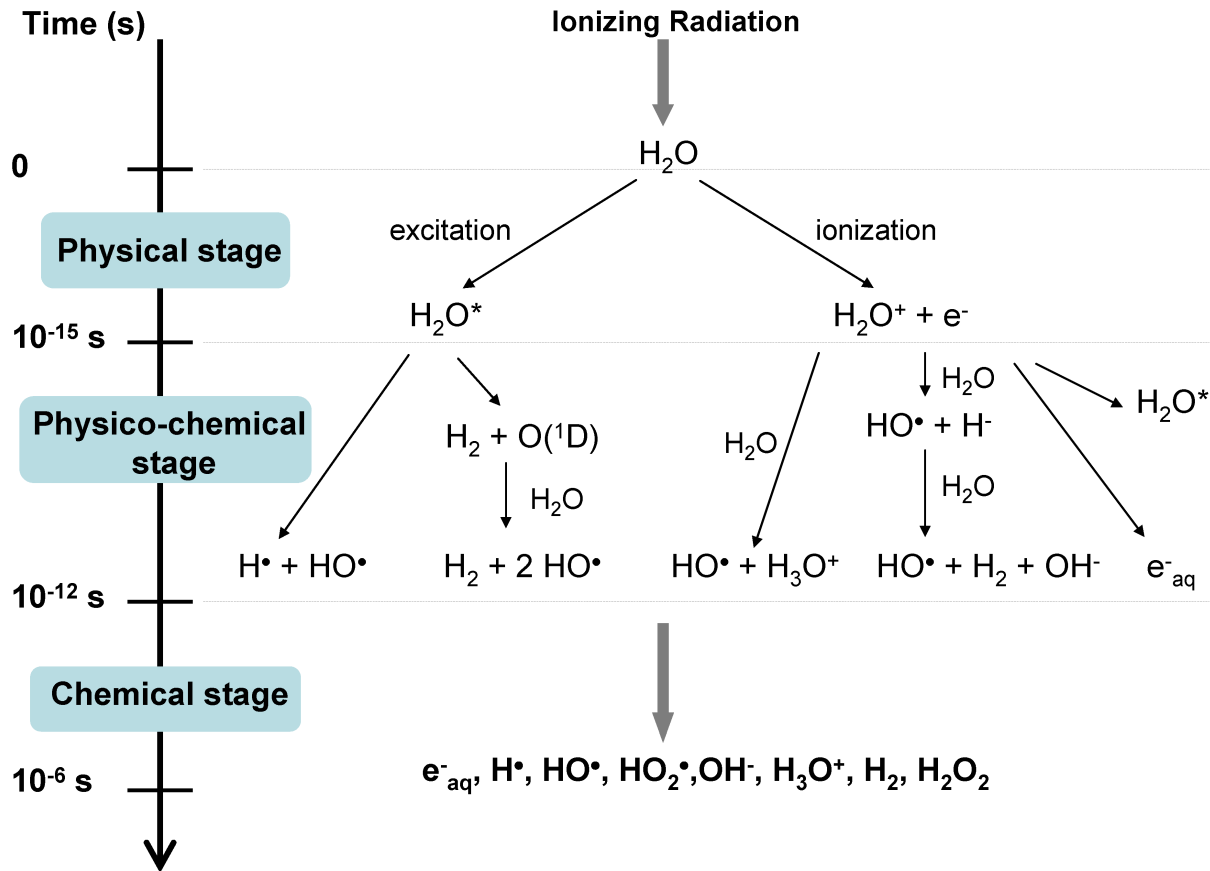
Multiple reactive species are formed with many possible reactions.

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

$$A_X = \frac{\mu_0 h}{3\pi} \gamma_e \gamma_X |\psi(0)|^2$$

Transmitted through bonds and proportional to unpaired electron spin density at nucleus
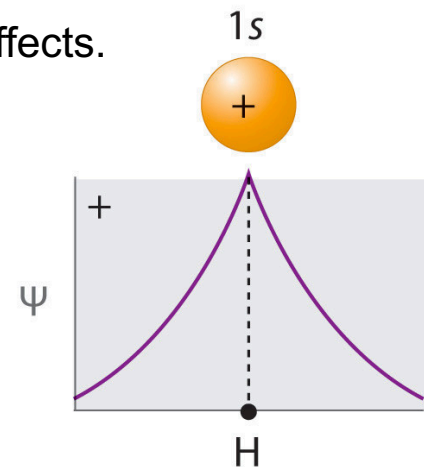
	Mu	H	D	T
Mass	0.1134	1.0073	2.0136	3.0155
Magnetic Moment (μp)	3.183	1	0.307	1.067
Larmor Frequency (MHz/T)	135.539	42.577	6.536	45.415
A_X (MHz)	4463.3	1420.4	218.3	1516

Transverse Field Muon Spin Rotation

Electronic Clock

B

Spin-polarized muon beam

μ⁺

Muon Detector

Sample

Positron Detector

e⁺
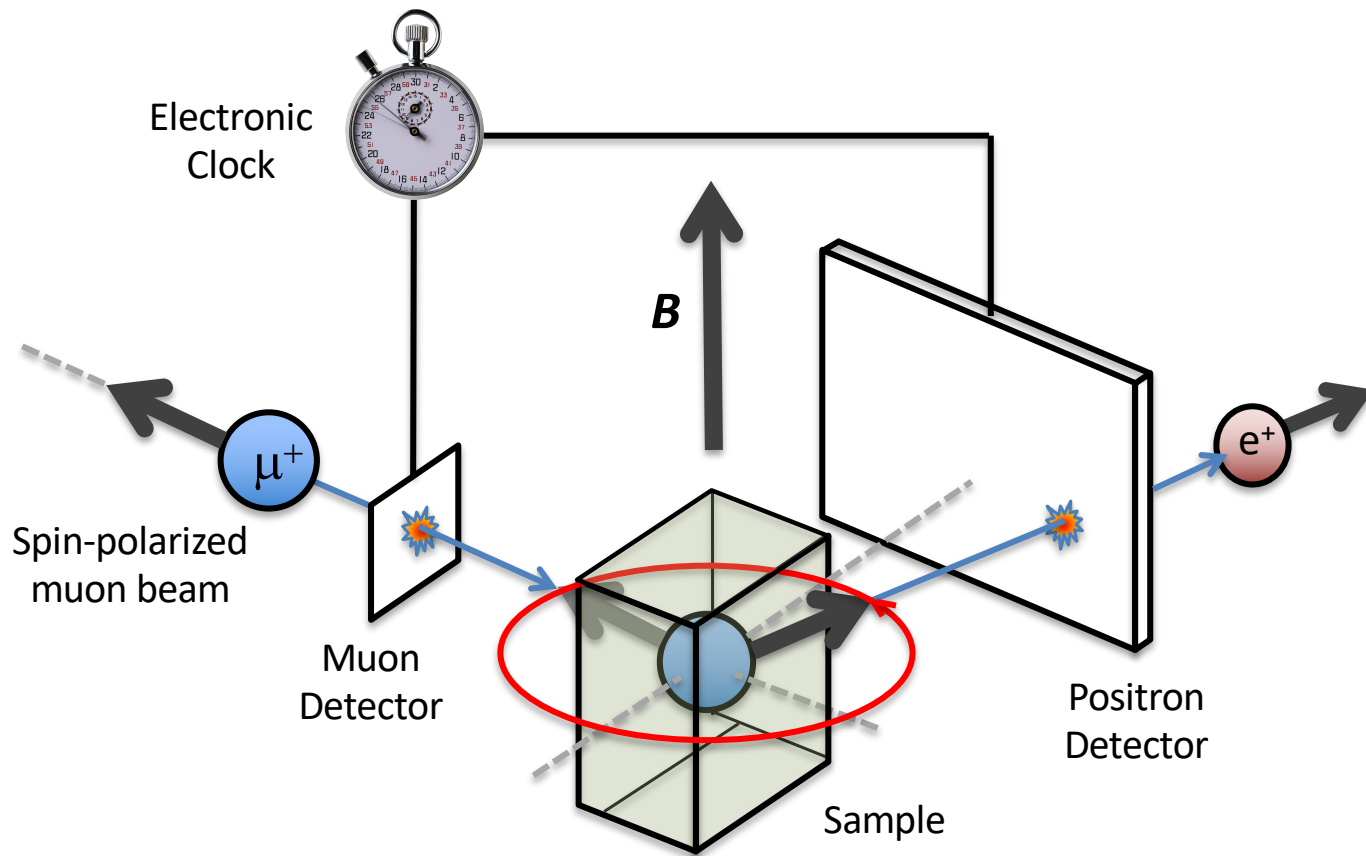
Spin States and Transitions in Muonium

$$|1\rangle = |\alpha^{e}\alpha^{\mu}\rangle \qquad E^{|1\rangle}/h = \tfrac{1}{4}A_{\mu} + \tfrac{1}{2}(\nu_{e} - \nu_{\mu})$$

$$|2\rangle = c\,|\alpha^{e}\beta^{\mu}\rangle + s\,|\beta^{e}\alpha^{\mu}\rangle \qquad E^{|2\rangle}/h = \tfrac{1}{4}A_{\mu} + \tfrac{1}{2}\left(\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}} - A_{\mu}\right)$$

$$|3\rangle = |\beta^{e}\beta^{\mu}\rangle \qquad E^{|3\rangle}/h = \tfrac{1}{4}A_{\mu} - \tfrac{1}{2}(\nu_{e} - \nu_{\mu})$$

$$|4\rangle = -s\,|\alpha^{e}\beta^{\mu}\rangle + c\,|\beta^{e}\alpha^{\mu}\rangle \qquad E^{|4\rangle}/h = -\tfrac{3}{4}A_{\mu} - \tfrac{1}{2}\left(\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}} - A_{\mu}\right)$$

$$c^{2} = \tfrac{1}{2} + \tfrac{1}{2}\frac{\nu_{e} + \nu_{\mu}}{\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}}};\ c = \tfrac{1}{\sqrt{2}} \text{ at } B = 0 \text{ and } 1 \text{ when } \nu_{e} + \nu_{\mu} \gg A_{\mu}$$

$$s^{2} = \tfrac{1}{2} - \tfrac{1}{2}\frac{\nu_{e} + \nu_{\mu}}{\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}}};\ s = \tfrac{1}{\sqrt{2}} \text{ at } B = 0 \text{ and } 0 \text{ when } \nu_{e} + \nu_{\mu} \gg A_{\mu}$$

Frequency	Amplitude
$\nu_{12} = \tfrac{1}{2}(\nu_{e} - \nu_{\mu}) - \tfrac{1}{2}\left[\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}} - A_{\mu}\right]$	$\propto c^{2}$
$\nu_{23} = \tfrac{1}{2}(\nu_{e} - \nu_{\mu}) + \tfrac{1}{2}\left[\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}} - A_{\mu}\right]$	$\propto s^{2}$
$\nu_{14} = \tfrac{1}{2}(\nu_{e} - \nu_{\mu}) + \tfrac{1}{2}\left[\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}} - A_{\mu}\right] + A_{\mu}$	$\propto s^{2}$
$\nu_{43} = \tfrac{1}{2}(\nu_{e} - \nu_{\mu}) - \tfrac{1}{2}\left[\sqrt{A_{\mu}^{2} + (\nu_{e} + \nu_{\mu})^{2}} - A_{\mu}\right] - A_{\mu}$	$\propto c^{2}$

α = spin up

β = spin down

Breit-Rabi Diagram
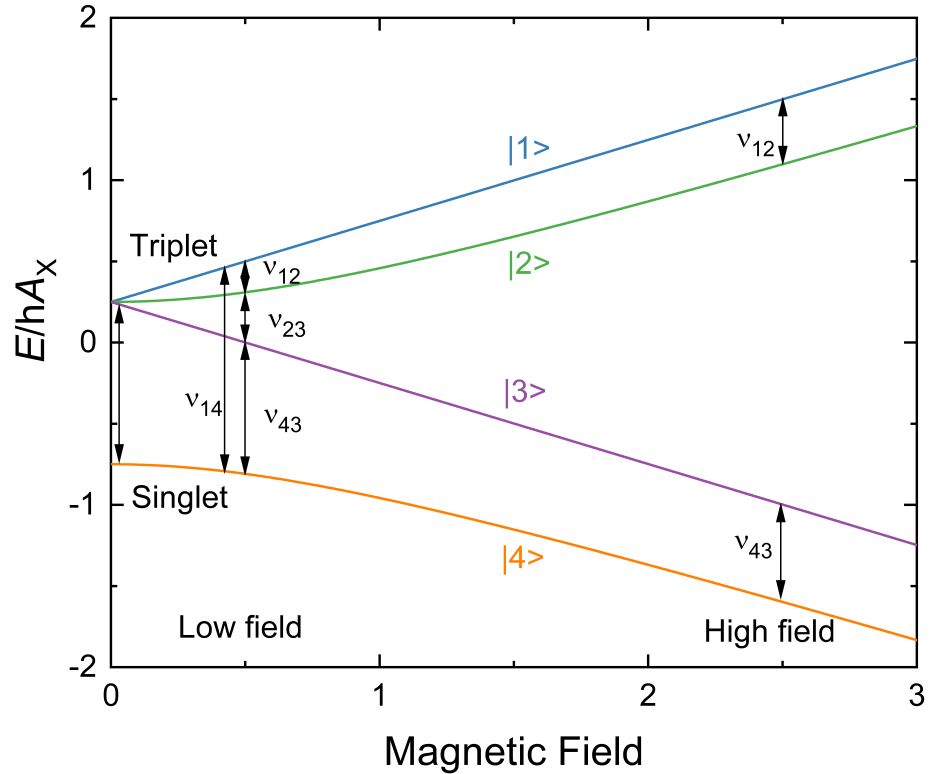
Intra-Triplet Transitions of Muonium

B = 2 G
A_μ = 4463 MHz
ν_e = 5.6 MHz

$A_\mu \gg (\nu_e + \nu_\mu)$

ν_{12} and ν_{23} are degenerate.

$\nu_{12} = \nu_{23} = \frac{1}{2}(\nu_e - \nu_\mu)$
$= \gamma_{Mu}/2\pi\ B$

$\gamma_{Mu}/2\pi = 102.88\ \gamma_\mu/2\pi$
(1.394 MHz G^{-1})
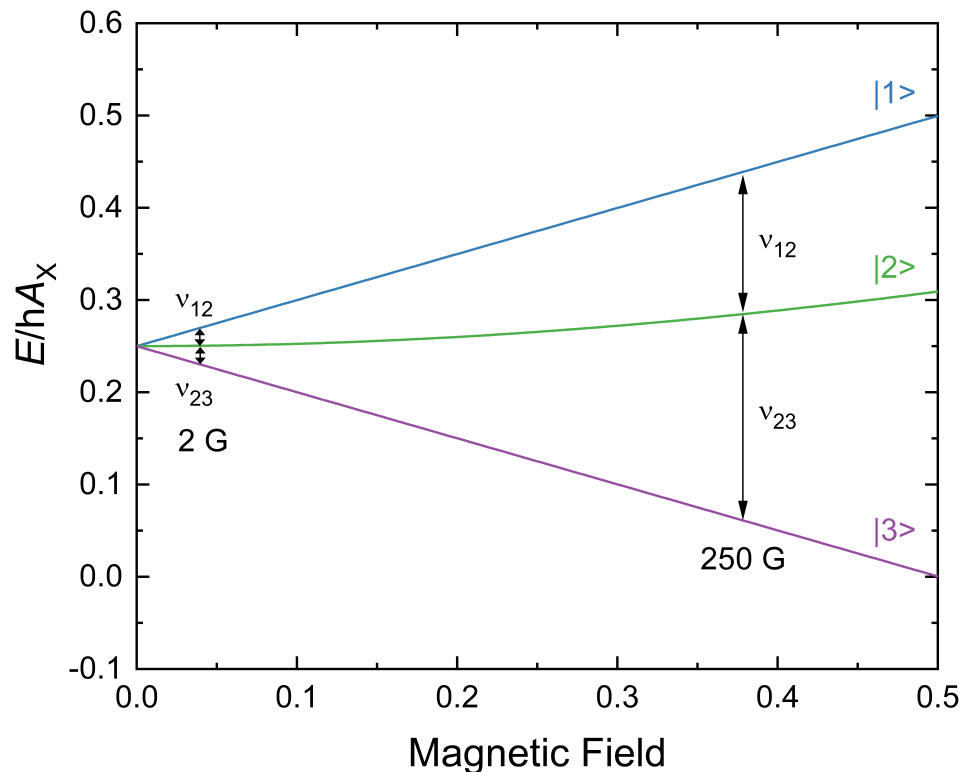
B = 250 G
ν_e = 701 MHz

ν_{12} and ν_{23} are NOT degenerate.

Determine A_μ by measuring ν_{12}, ν_{23} and ν_μ

$$A_\mu = \frac{(\nu_{23} - \nu_{12})^2 - (\nu_e + \nu_\mu)^2}{2(\nu_{23} - \nu_{12})}$$

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TF-μSR of Muonium

Low field $B \sim 2$ G
ν_{12} and ν_{23} are degenerate.
$\gamma_{Mu}/2\pi = 102.88\ \gamma_{\mu}/2\pi$
$(1.394$ MHz G$^{-1})$
Measure λ

Mu triplet precession
$\gamma_{Mu} \sim 1.4$ MHz/G

Diamagnetic Mu$^+$ precession
$\gamma_{\mu} = 0.01355$ MHz/G

Time (μs)
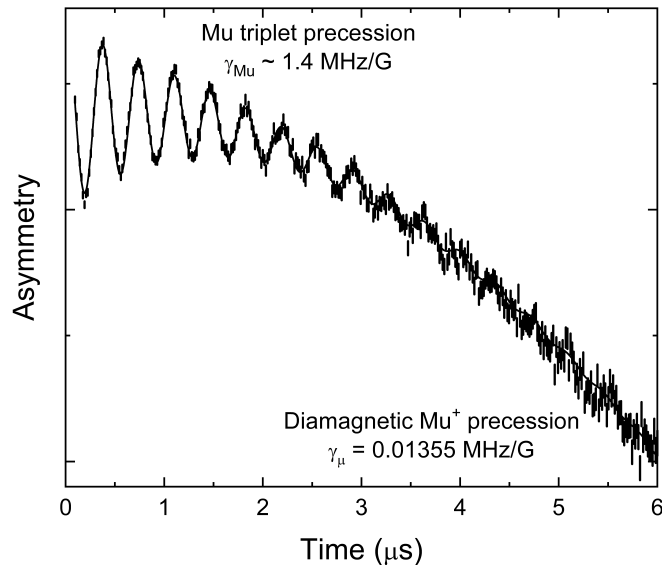
$$A(t) = A_D \cos(\omega_\mu t + \phi_D)$$
$$+ A_{Mu} \cos(\omega_{Mu} t + \phi_{Mu})\, e^{-\lambda_{Mu} t}$$

Intermediate field $B \sim 250$ G
ν_{12} and ν_{23} are <u>not</u> degenerate.
Measure A_μ

ν_{12}

ν_{23}

Frequency / MHz

Measuring Muonium Reaction Rate Constants
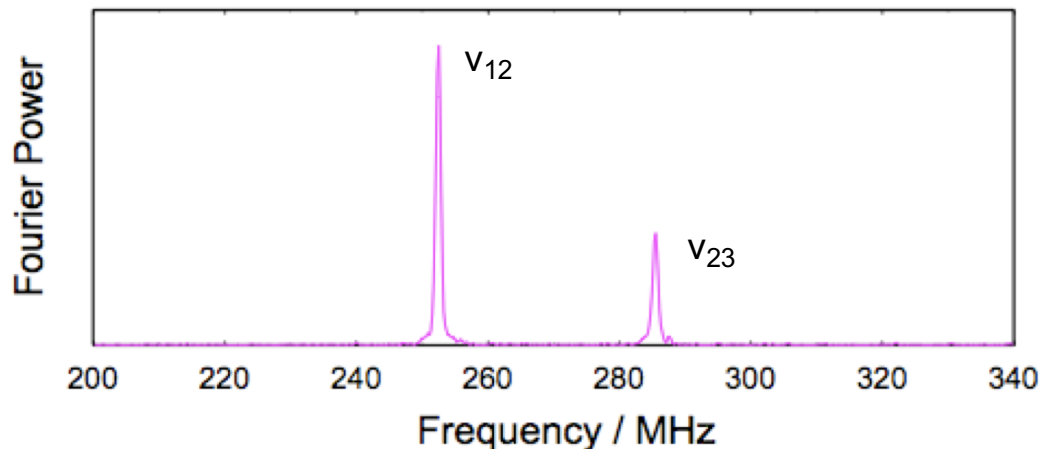
Increasing concentration of reactant

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

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Measuring Muonium Reaction Rate Constants

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

Relaxation in pure solvent

Pseudo-1st order rate constant

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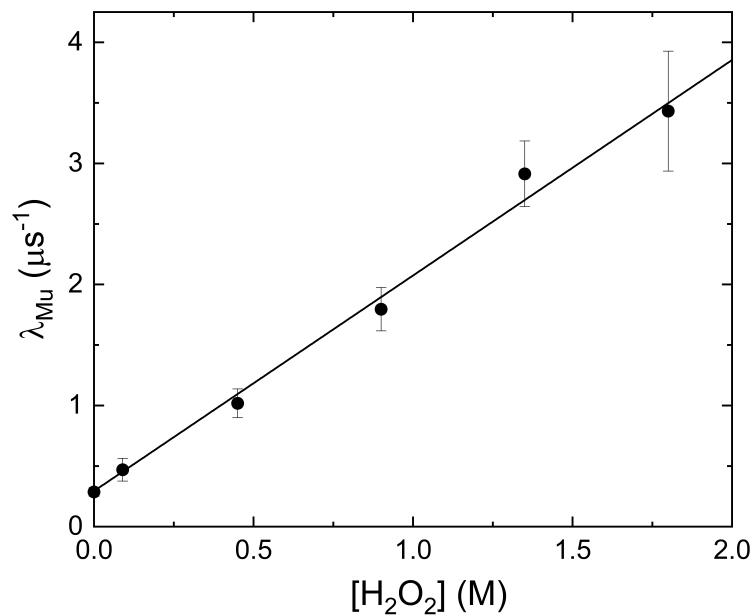
Ex) What is the rate constant for the reaction of Mu with hydrogen peroxide at 295 K and pH 7?

Plot λ versus $[H_2O_2]$

Slope = k_{Mu} = 1.8(1) $\times$ 10^6 M^{-1} s^{-1}

Kinetic Isotope Effects on Abstraction and Addition Reactions

Abstraction Reactions
$$k_{Mu} < k_H$$
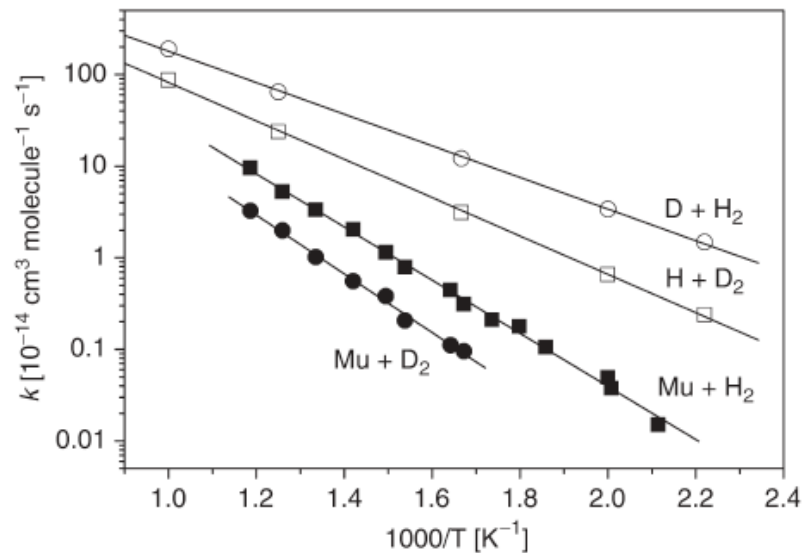
Addition Reactions
$$k_{Mu} > k_H$$
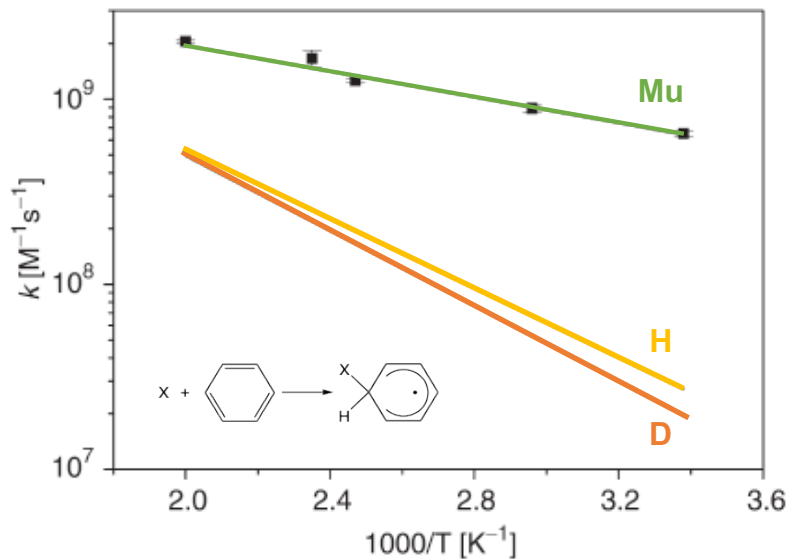
Isotope effect depends on the width and
height of the activation barrier

I. D. Reid et al. *J. Chem. Phys.* **86** (1987) 5578

E. Roduner et al. *Ber. Bunsenges. Phys. Chem.* **94** (1990) 1224

Muonium Kinetics in Extreme Environments
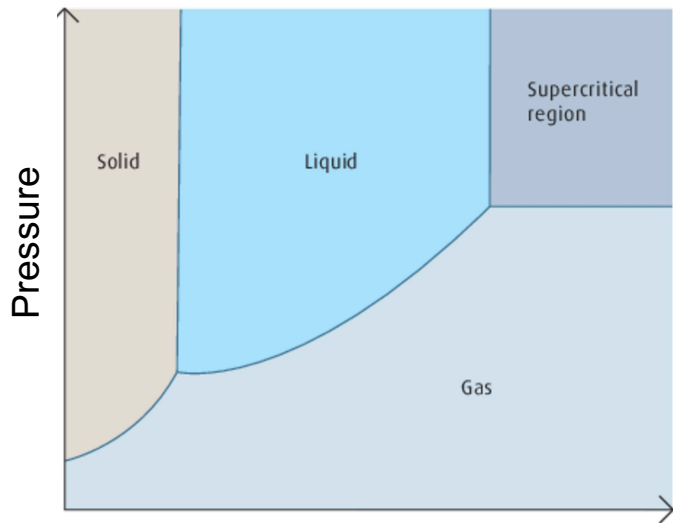
Supercritical water
P > 218 bar and
T > 647 K !

Mu + C_6H_6

Extrapolated from low temperature data
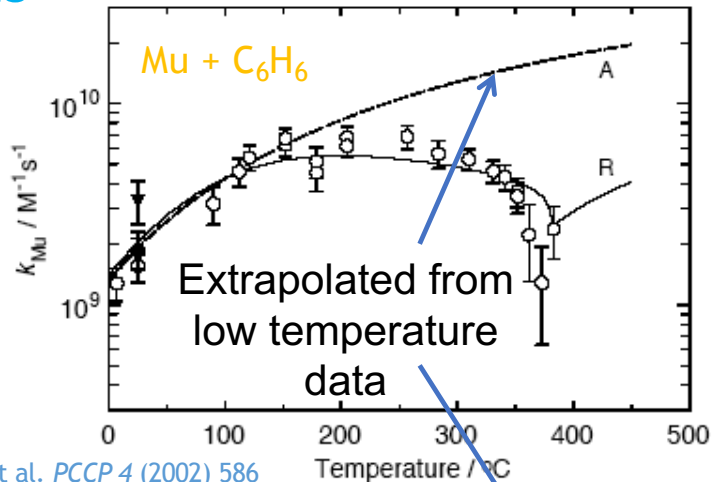
Ghandi et al. *PCCP 4* (2002) 586

Backward muons and decay positrons can get through pressure vessel

E_{max} = 52.8 MeV

e⁺

μ⁺

70 MeV/c

H + CH_3OH

Mu + CH_3OH
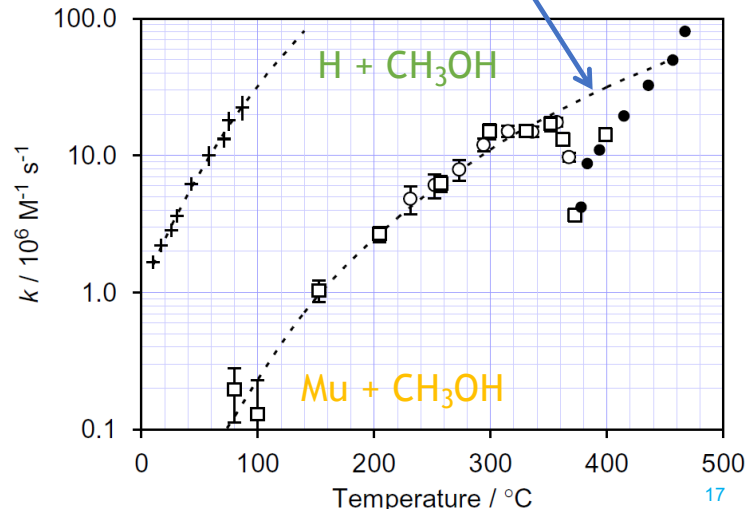
Percival et al. *Rad. Phys. Chem.* 76 (2007) 1231

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Muon detector

$P(t=0)$

$\vec{p}$

$e^{\tiny +}$

Backward (B) positron detector

Magnetic Field (B)

x

y

z

Sample

Forward (F) positron detector

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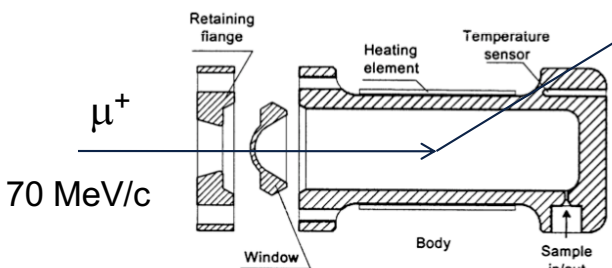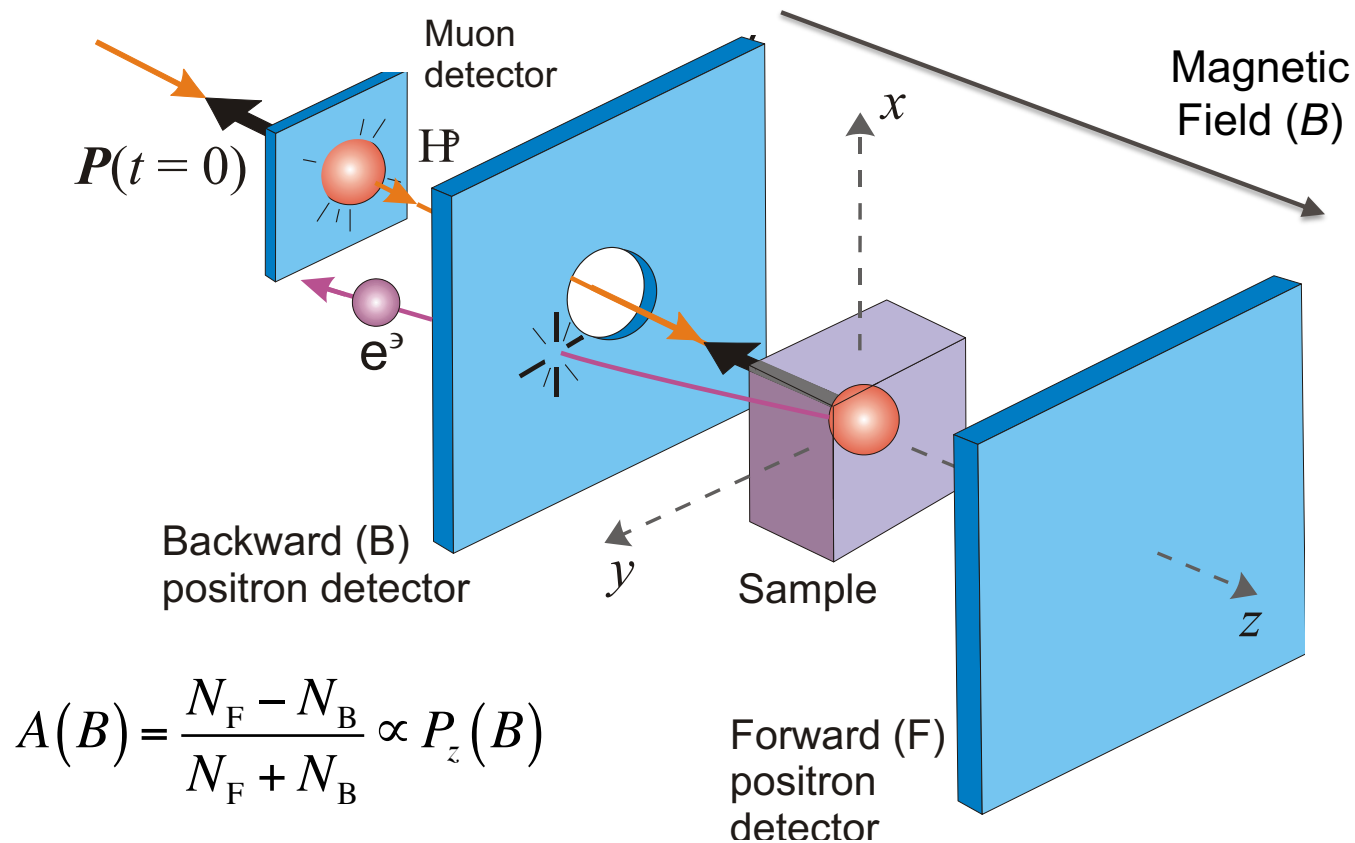
Repolarization of Muonium

- 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%.

Vacuum Mu
B_0 = 159.2 mT

N$_2$ gas

H$_2$O liquid

Normalized Mu Polarization

Magnetic Field (mT)
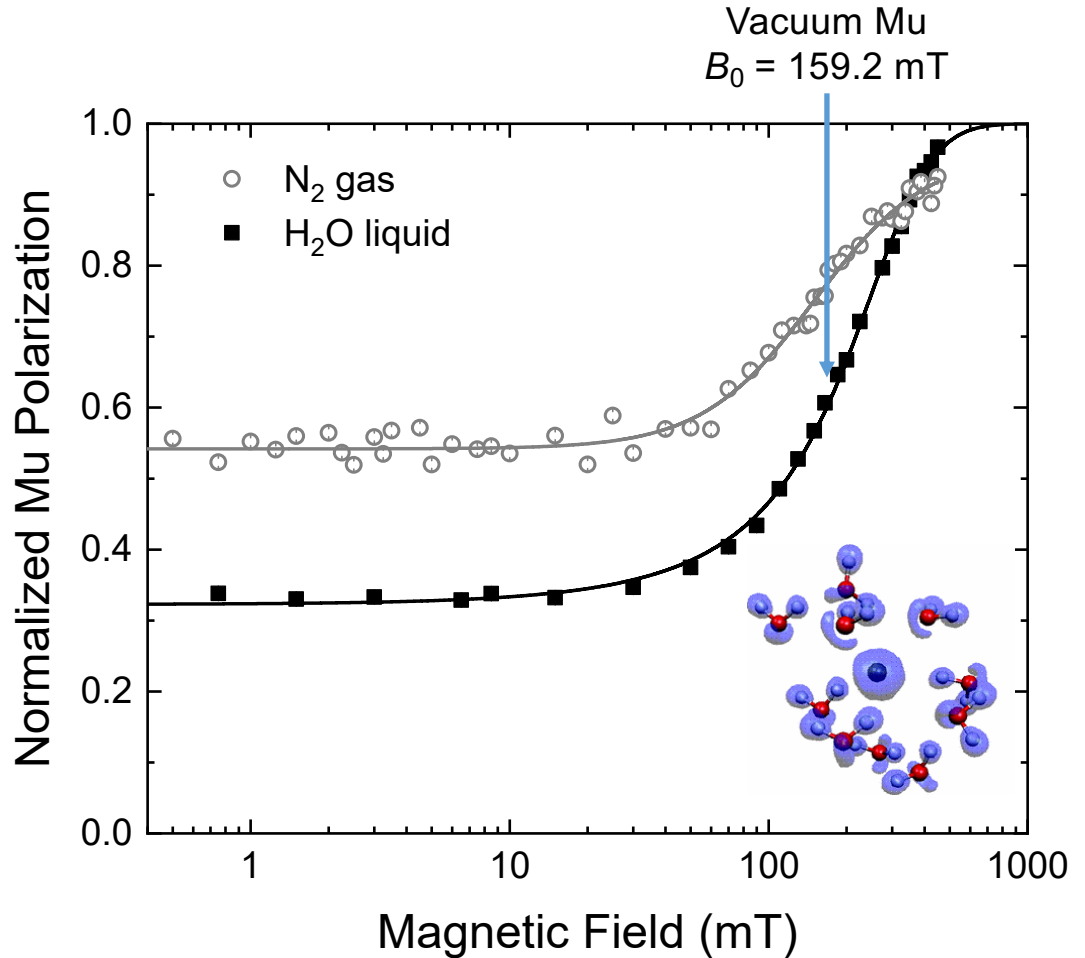
What Are Radicals?

- Radicals are atoms or molecules with one or more unpaired electrons.

  7 valence electrons
  (2 from each bond and
  1 unpaired electron)

  H_3C ⸻ C ⸻ C ⸻ Mu
  H_3C H
             H
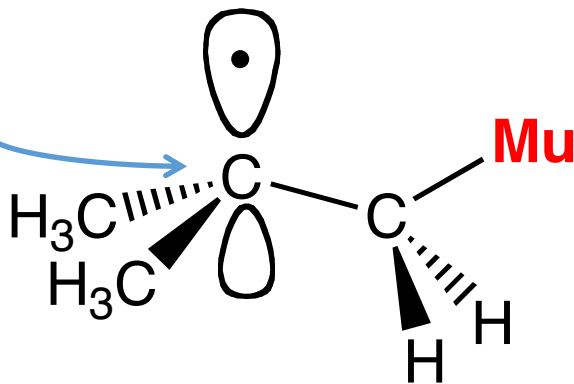
- Radicals are often highly reactive as it is usually energetically favorable for them to attain "closed shell configuration"
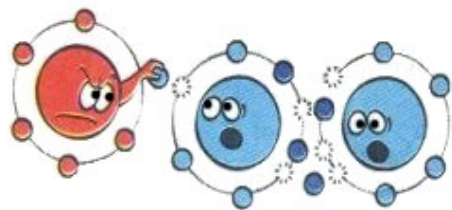
What are Free radicals ?

- Free radicals are like robbers which are deficient in energy.

- Free radicals attack and snatch energy from the other cells to satisfy themselves.

SAVE THE WHALES

DEFY THE LAWS OF GRAVITY

Free Radicals

VOTE EARLY & VOTE OFTEN

BAN PRO-TONS

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www.CartoonStock.com
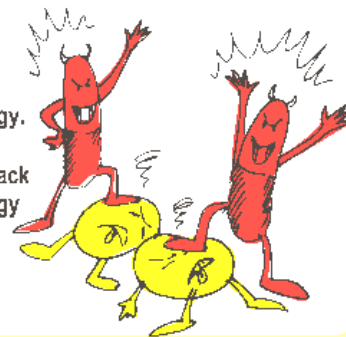
Difficulties of Studying Radicals

- Production of radicals often requires nasty mix of chemicals (e.g. Fenton's reagent) and/or irradiation (X-ray or e$^-$).

- Reactive radicals are difficult to study with traditional spectroscopic techniques (EPR, UV-Vis, IR)

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

$$R^\bullet + R^\bullet \longrightarrow R{-}R \qquad \textit{Termination reaction}$$

Matrix Isolation
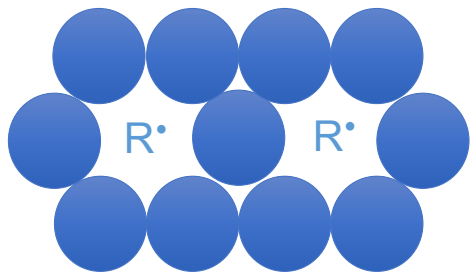
Prevent radical from reacting

Spin Trapping
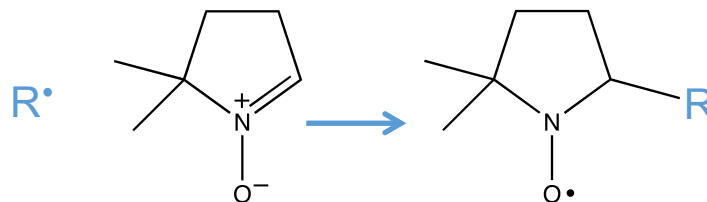
Convert initial radical to a less reactive radical

Formation of Muoniated Radicals

- Radicals produced by addition of Mu to an unsaturated bond.
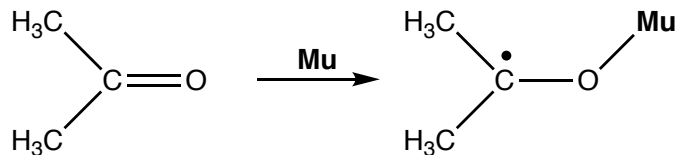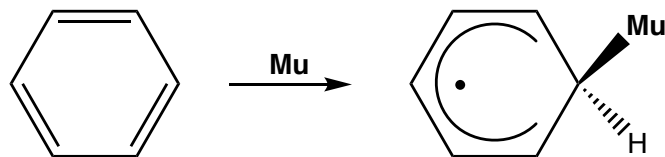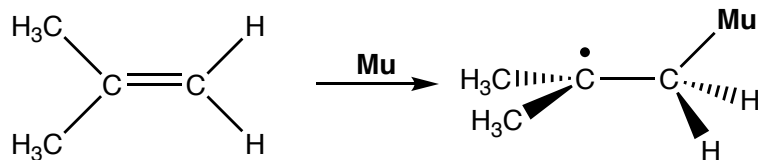
- Very few muons in the sample at one time, so no termination reactions.
- Radicals can be studied at any temperature and in any phase.

Radical Nomenclature
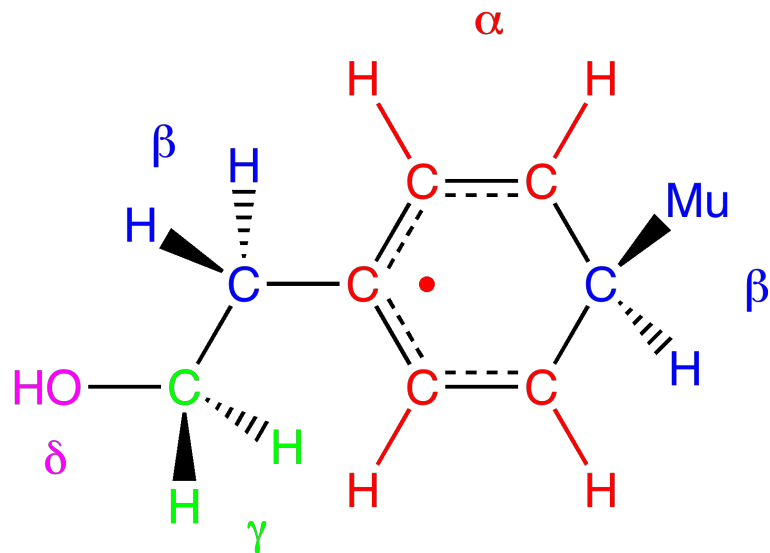
- **α carbon:** nucleus with significant unpaired electron spin density
- **α proton:** attached to an α carbon
- **β carbon:** one removed from α carbon
- **β proton:** attached to an β carbon
- **γ carbon:** one removed from β carbon
- ………….

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 ($I \geq \frac{1}{2}$).

$A_p^{(1)}$

A_μ

Mu   β-muon

α-protons

C — C

H

H

H

H   β-protons

$A_p^{(2)}$
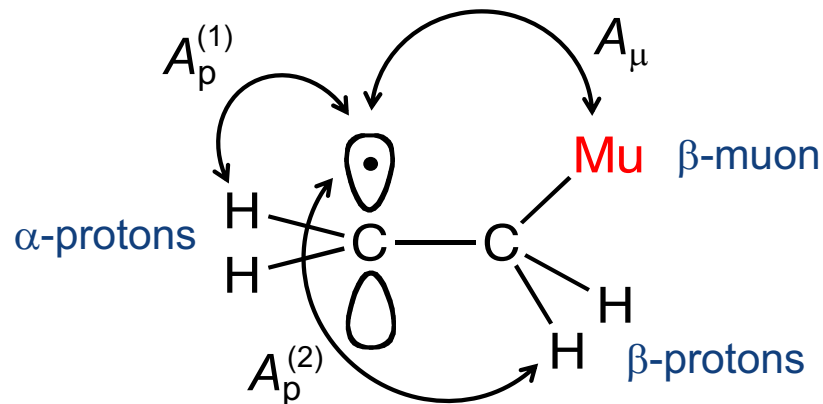
By measuring all of the hyperfine coupling constants one can map out the distribution of the unpaired electron and infer the structure of the radical.

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

$$\rho^{SPIN}(\vec{r}) = \rho^{\alpha}(\vec{r}) - \rho^{\beta}(\vec{r})$$

Blue: $\rho^{\alpha} > \rho^{\beta}$
Positive spin density`

Green: $\rho^{\alpha} < \rho^{\beta}$
Negative spin density
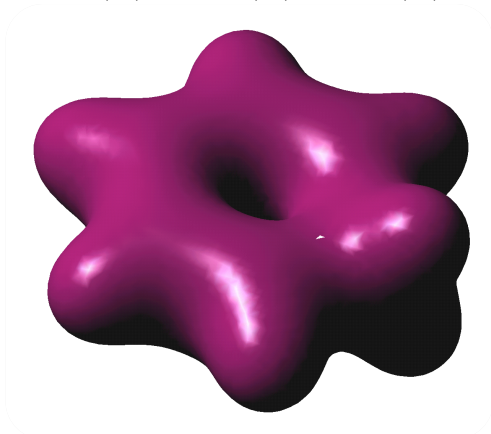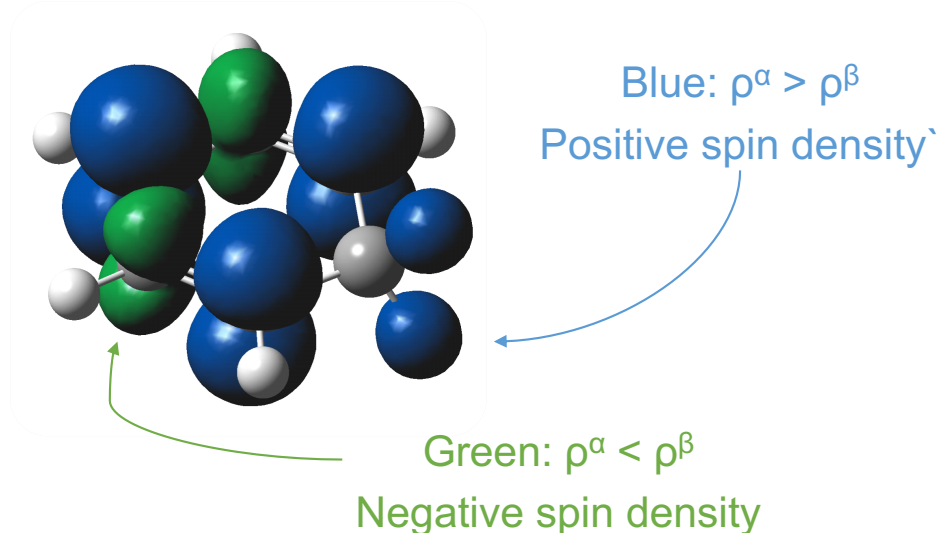
$$A_X = \left[\frac{2\mu_0}{3h} g_e \mu_B g_X \mu_X\right] \rho^{SPIN}(\vec{r} = 0)$$

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

Identification of Muoniated Radicals

TF-µSR
Precession frequencies $\longrightarrow$ Muon hfcc (A_m)

Δ_1 (solid)

ALC-µSR
Resonance fields $\longrightarrow$ Δ_0 $\longrightarrow$ Nuclear hfccs
(H, D, ^{13}C, ^{14}N….)

Hyperfine Coupling Constants $\longrightarrow$ Distribution of unpaired electron

Temperature Dependence of HFCs $\longrightarrow$ • 3D radical structure
• Intramolecular motion

TF-µSR of Muoniated Radicals

Allowed transitions

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

High field
$v_e > A_\mu$

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

Energy

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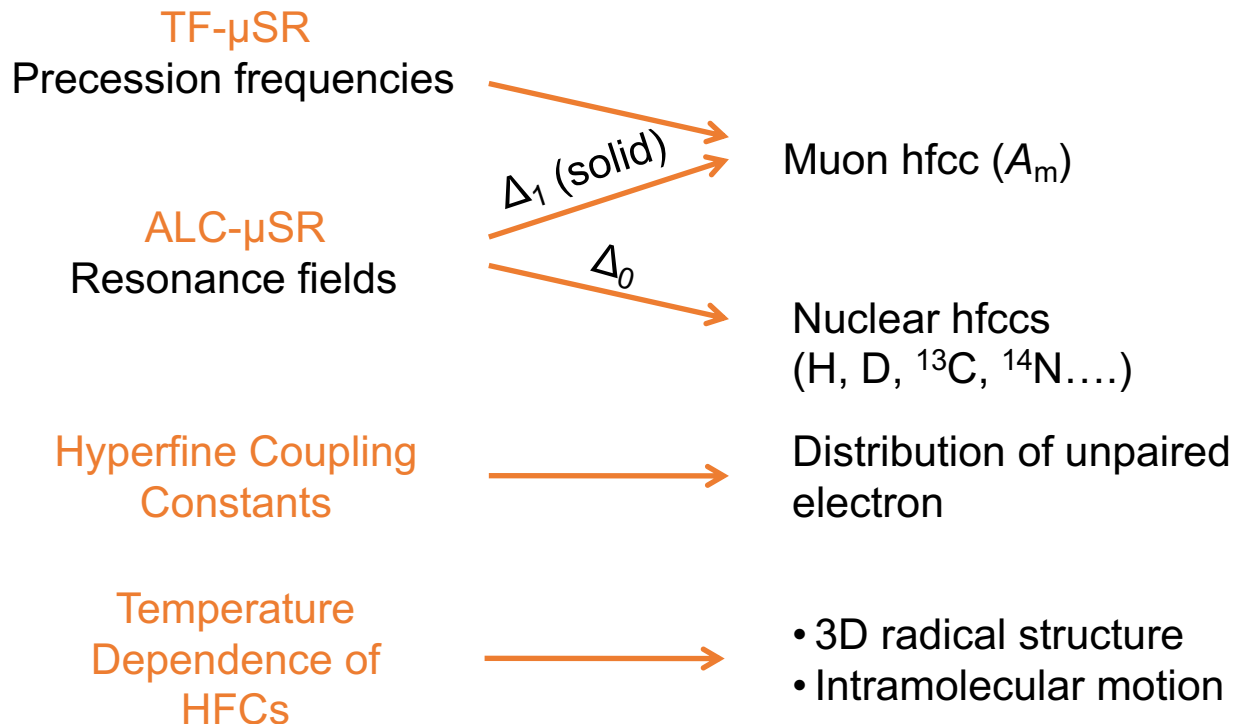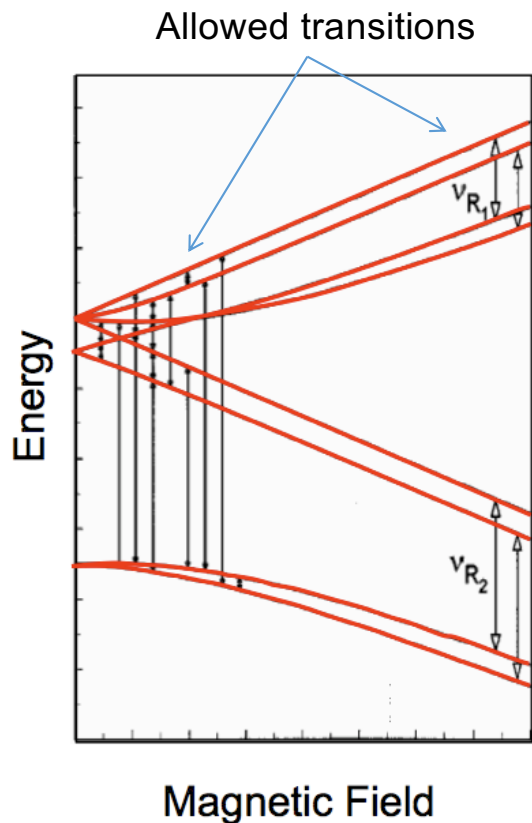
Breit-Rabi diagram for a
muon-electron-proton system

C_6H_6Mu

3000 G
1000 G
700 G
500 G

C_6D_6Mu

3000 G
1000 G
340 G

ν

200   240   280   320   MHz
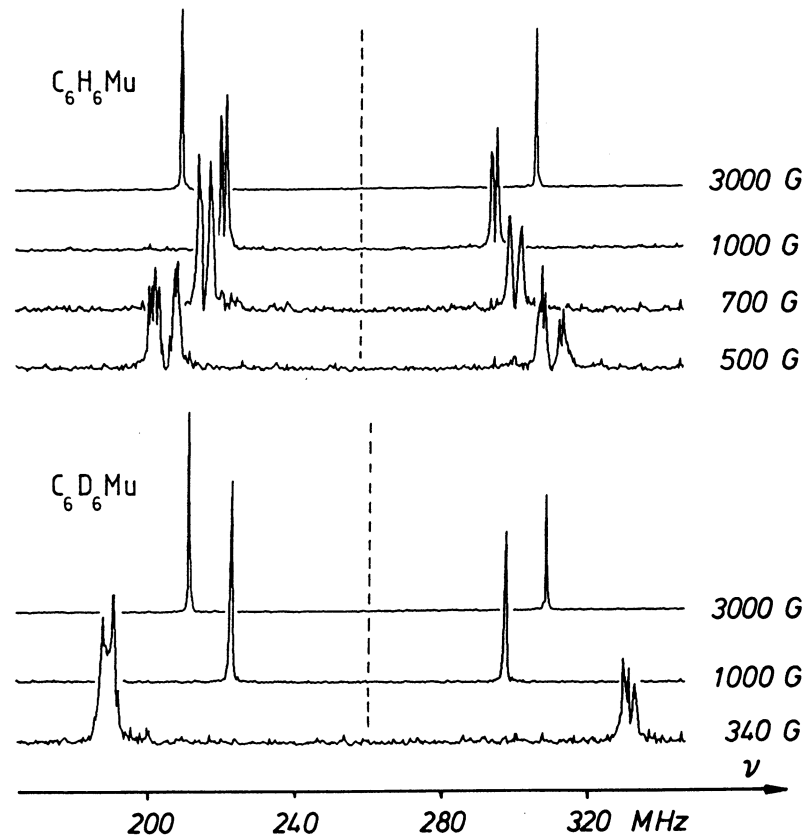
TF-μSR of C_6H_6Mu Radicals
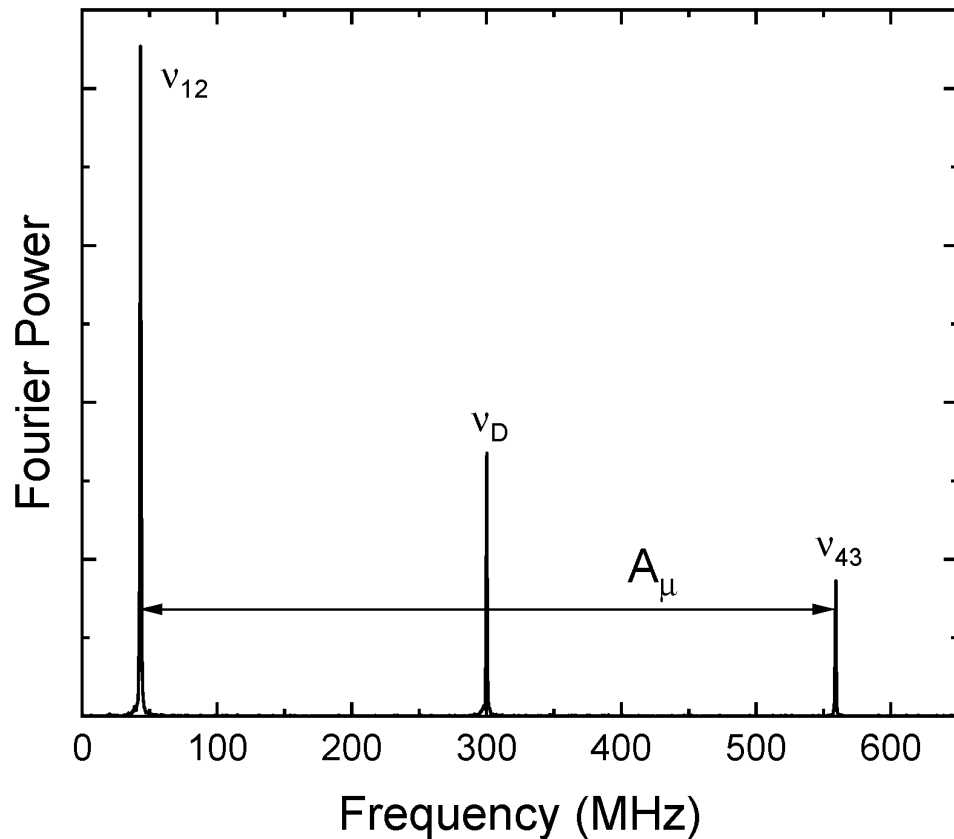
TF-μSR spectrum of benzene at 280 K and 2.2 T.

∴ v_D = 300.1 MHz

v_{43} = 559.1 MHz
v_{12} =   43.3 MHz

A_μ = 515.8 MHz

The lower amplitude of v_{43} compared with v_{12} is an artefact due to the time resolution of the spectrometer (0.39 ns).

TF-μSR of CH$_2$Mu Radicals
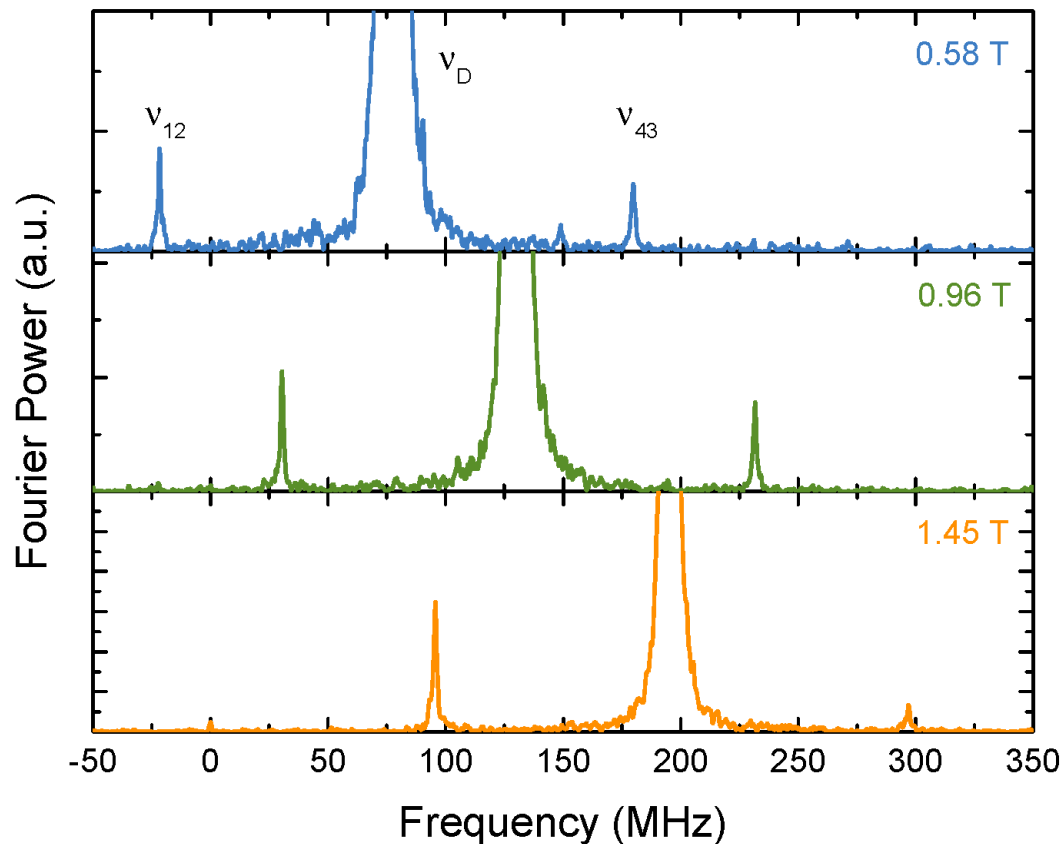
- The radical frequencies will shift position with magnetic field.

- Important check of whether signals are real or noise.

- Combination of low field and large A_μ can result in negative frequency (i.e. opposite direction to 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.

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

- h_M is the initial fraction of muon polarization in Mu
- λ is the first-order reaction rate
- $\Delta\omega_{12}$ is the change in precession frequency between Mu and the radical

Mu: A_μ = 4463 MHz
Radical: A_μ = 515 MHz
B = 1.5 T

ν_{12} ν_{43}

Radical Polarization (y-axis)
Mu $\to$ Radical 1st order rate (s^{-1}) (x-axis)
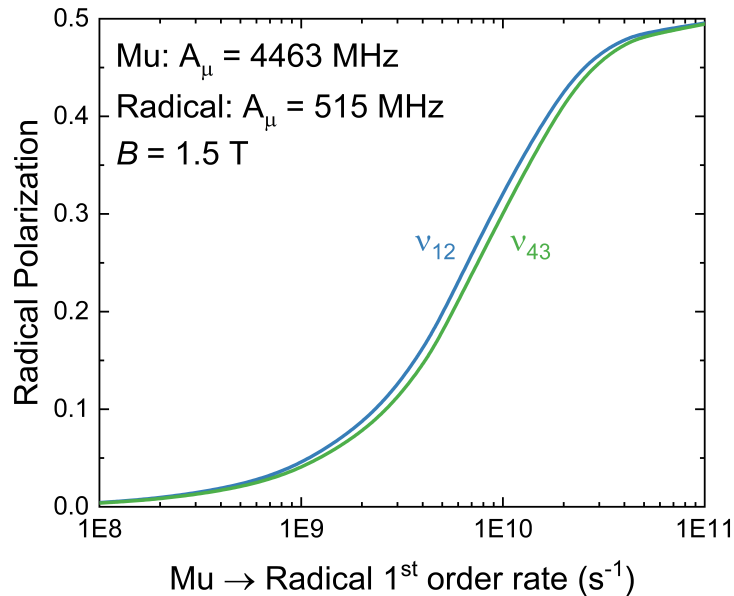
k_{Mu} = 10^{10} M^{-1} s^{-1}	0.01M	0.1 M	1 M	10 M
= 10^{8} M^{-1} s^{-1}	1 M	10 M	-	-

Repolarization of Muoniated Radicals
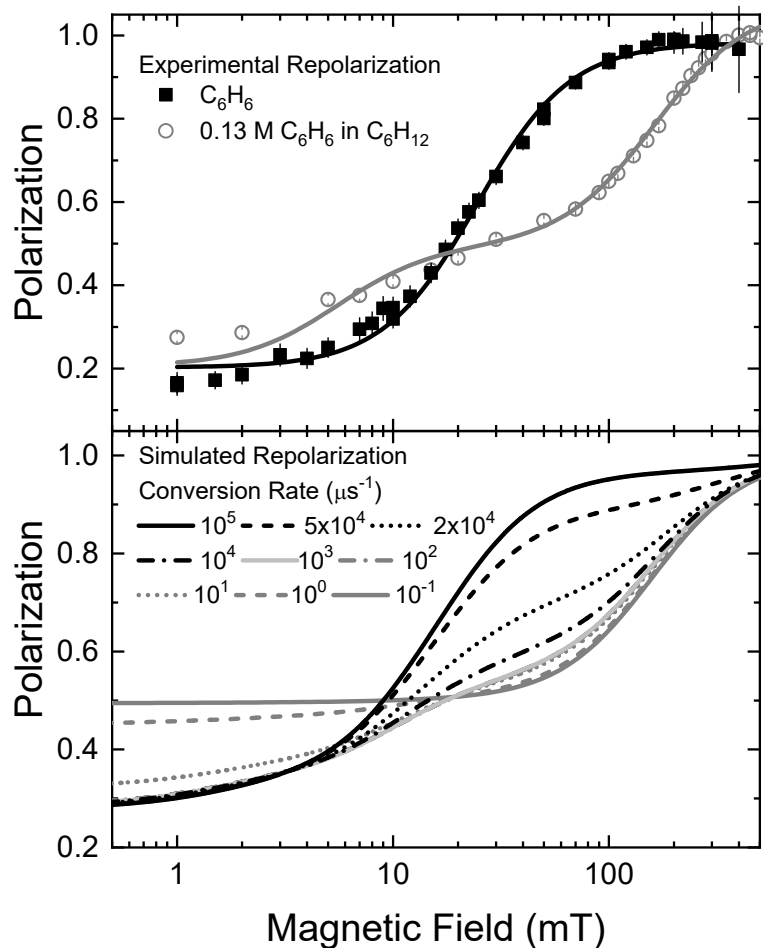
Prompt Formation

- Similar repolarization curve to Mu except with lower critical field due to smaller A_μ.
- 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

B_{res}

ν_{RF} = 10 MHz
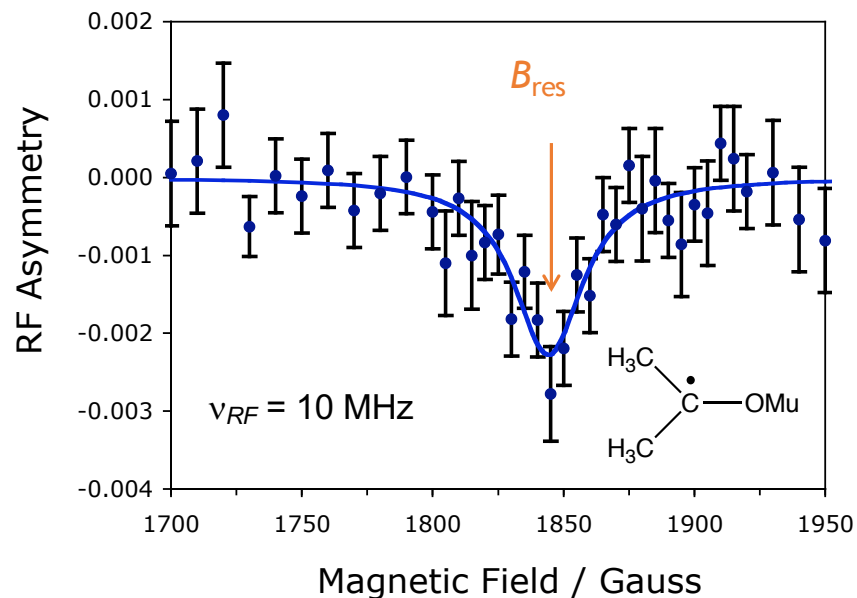
- Measure A_μ of slowly-formed muoniated radicals.
- Resonance when the RF frequency matches the ν_{12} or ν_{43} transitions (high field limit).

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

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

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

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

$$A_\mu = 30.0 \text{ MHz}$$

ALC-μSR of Muoniated Radicals
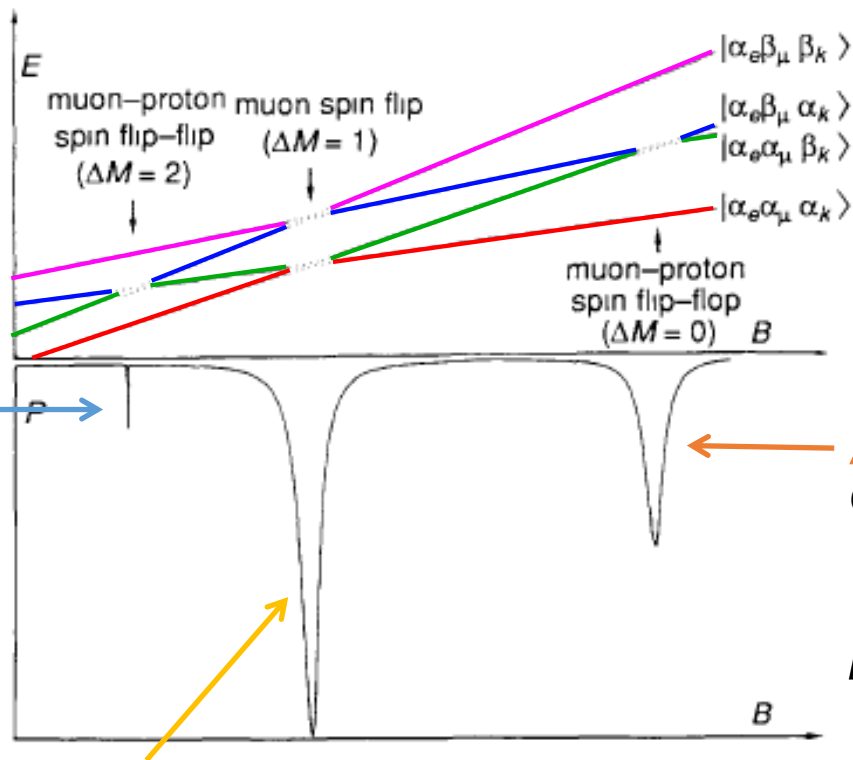
ΔM=2 Resonance
Narrow and weak.
Rarely observed.

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

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

ΔM=1 Resonance

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

$$B_r = \left[\frac{A_\mu}{2\gamma_\mu} - \frac{A_\mu}{2\gamma_e} \right]$$

ALC-µSR of C_6H_6Mu and $^{13}C_6H_6Mu$
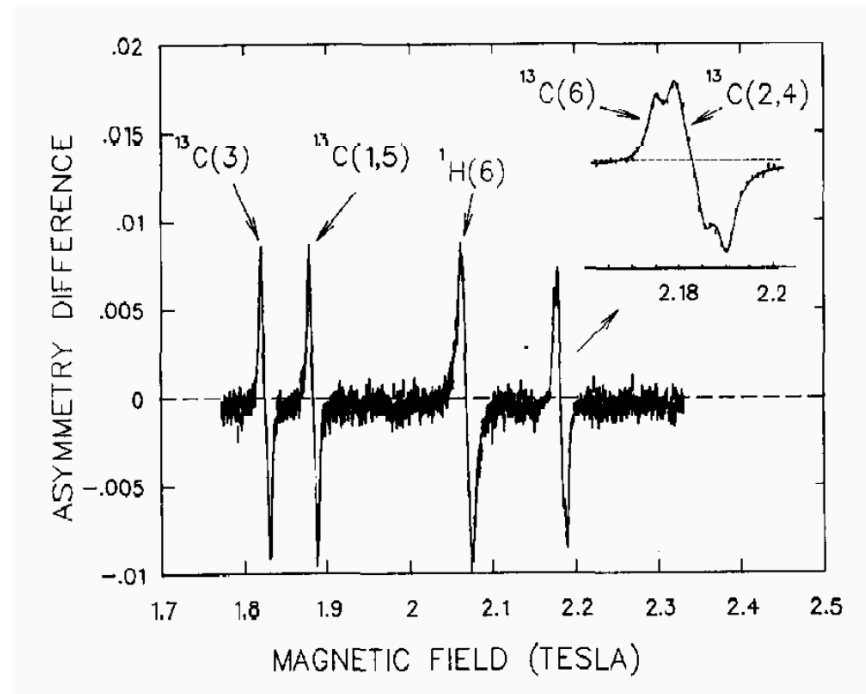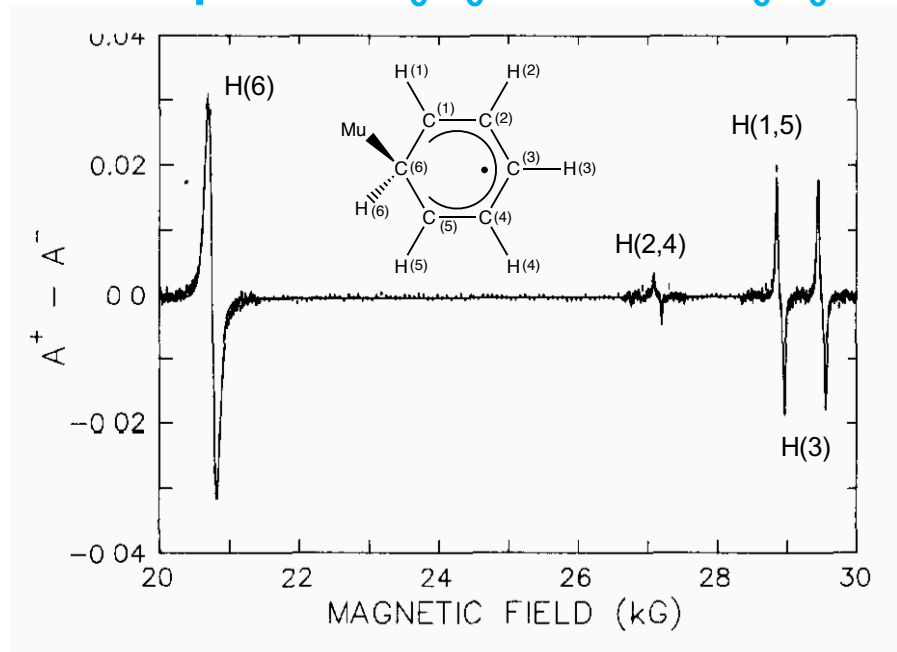
Nucleus	A_μ (MHz)	B_{res} (T)	A_p (MHz)
H(6)	514.47	2.0774	126.11
H(2,4)	514.47	2.7176	7.47
H(1,5)	514.47	2.8936	-25.14
H(3)	514.47	2.9532	-36.19

Nucleus	A_μ (MHz)	B_{res} (T)	A_C (MHz)
C(3)	512.28	1.8261	53.95
C(1,5)	512.28	1.8840	39.57
C(6)	512.28	2.1803	-34.08
C(2,4)	512.28	2.1849	-35.21

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*)   (*b*)
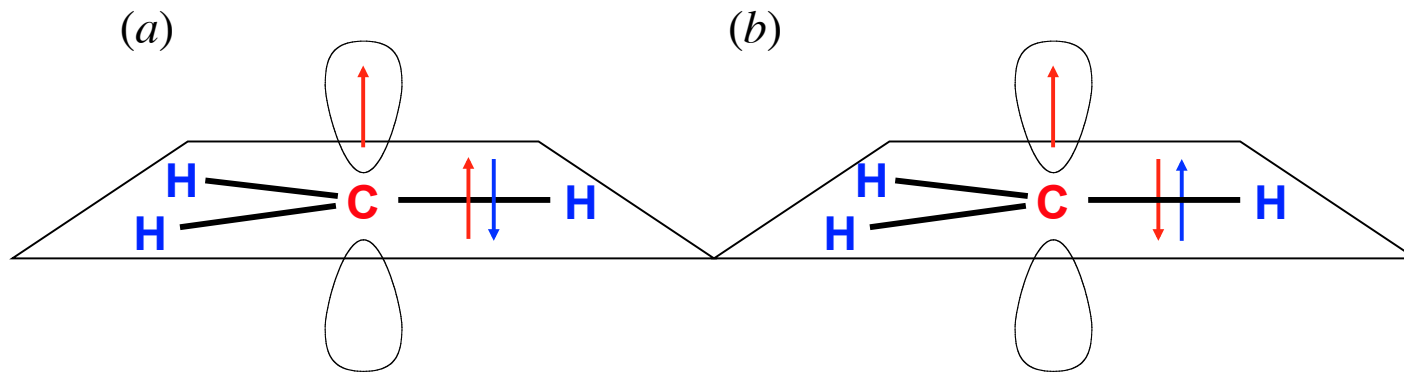
More probable

McConnell
equation
for α-nuclei

$$A_X = Q_X \rho^\pi$$

- ρ^π is the π-electron population at the adjacent carbon atom
- $Q_p \sim$ -75 MHz

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

Spin Density Distribution in the Muoniated Cyclohexadienyl Radical

Meta (2H α)

A_p = +7.5 MHz

ρ ~ -0.10

Muon (β)

$A_μ$ = 514.6 MHz

Methylene (1H β)

A_p = 125 MHz

Mu

H

Para (1H α)

A_p = -36.8 MHz

ρ ~ +0.49

Ortho (2H α)

A_p = -25.5 MHz

ρ ~ +0.35

Spin density around ring
2(0.35)+2(-0.10)+1(0.49)
~1
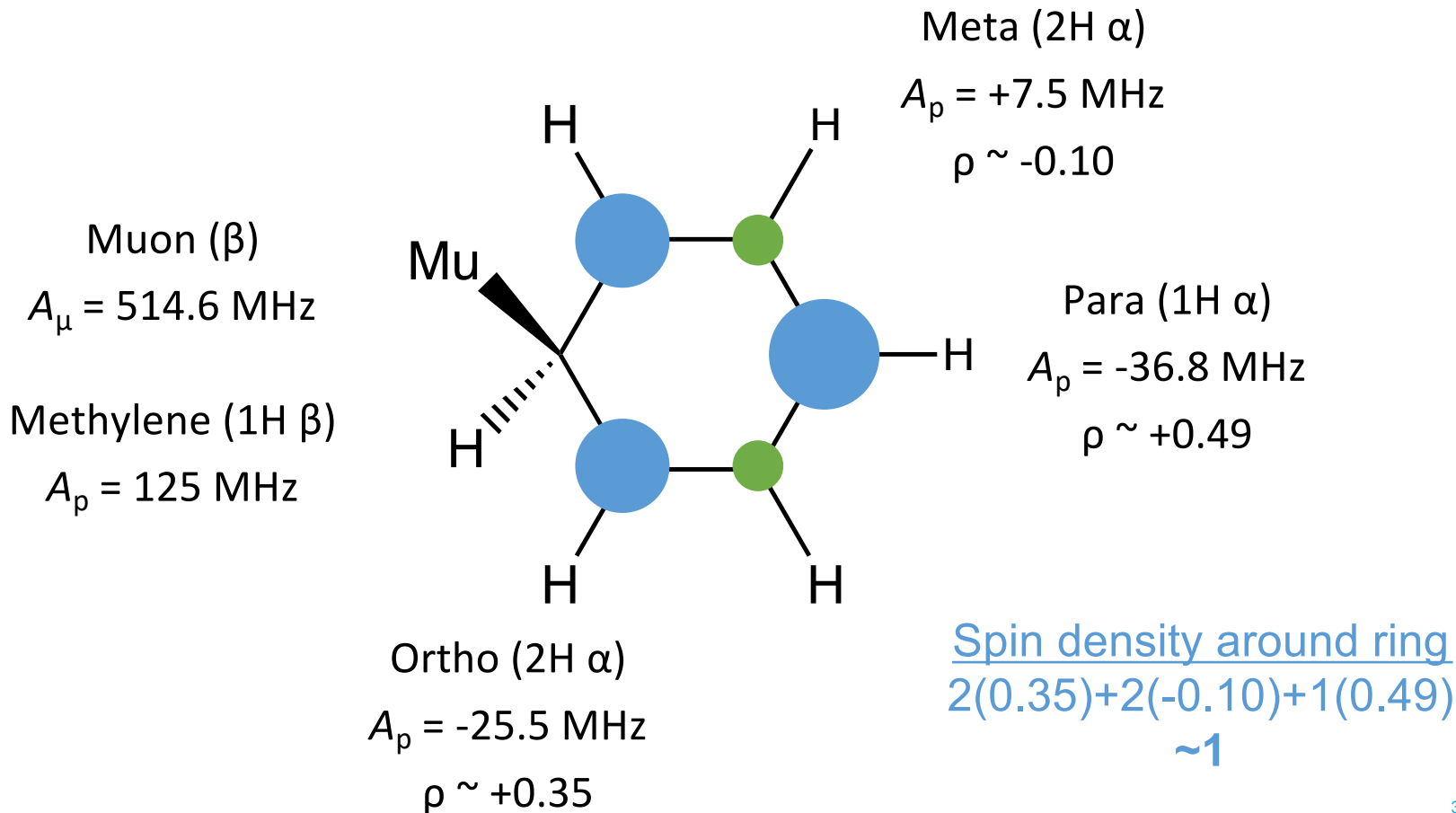
Spin Density Distribution in the MuC$_{60}$ Radical

Mu^{13}C$_{60}$ Avoided Level Crossing Resonance

Magnetic Field /kG

% Unpaired Spin Density

P. W. Percival *et al. Chem. Phys. Lett.* **1995**, *245*, 90
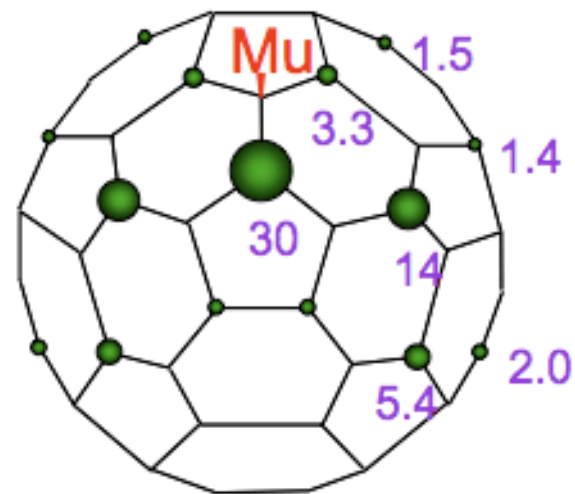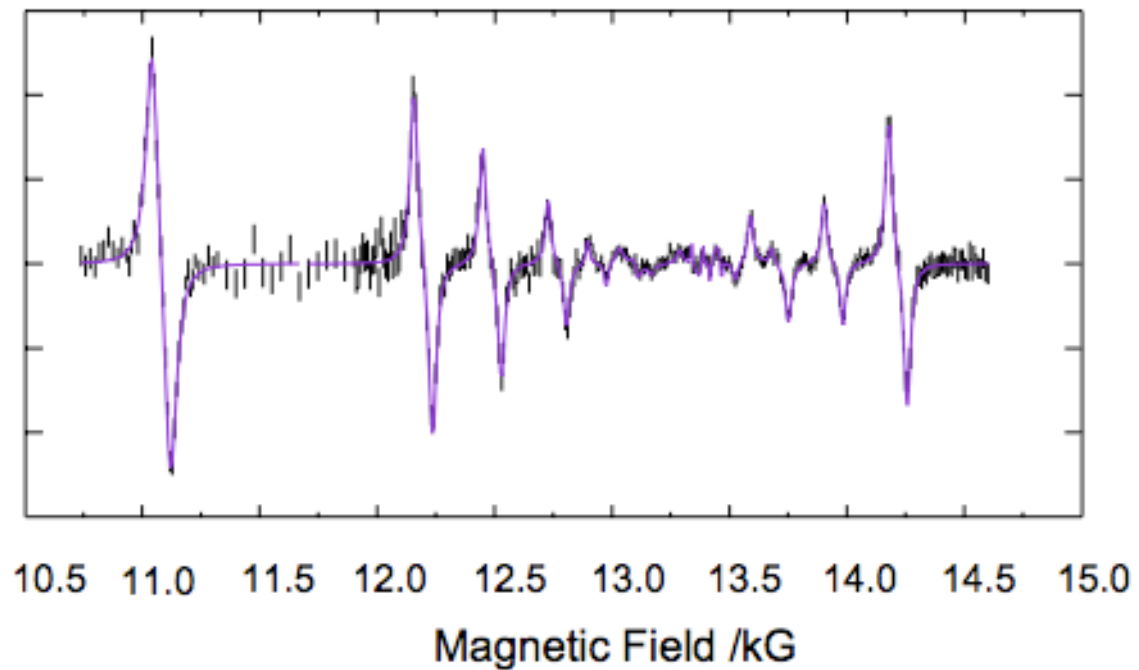
Identification of Radicals: Quantum Calculations

- 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?
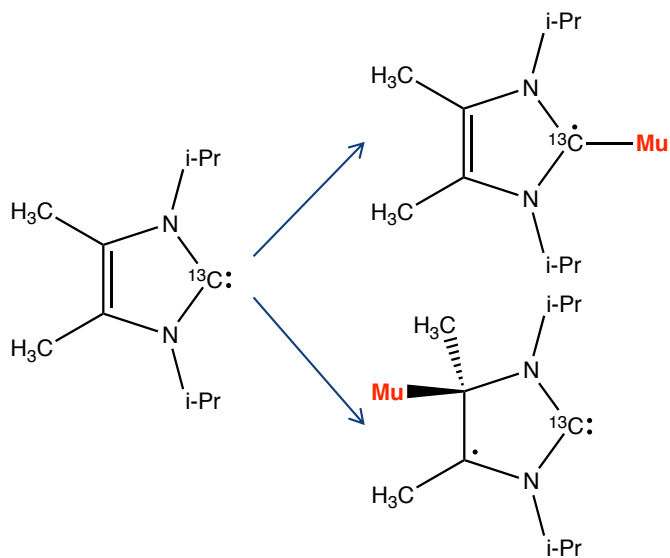
DFT Calculations

A_μ	278.8 MHz
$A_C(C2)$	136.0 MHz
$A_N(N1)$	8.3 MHz
$A_N(N3)$	8.3 MHz
$A_p(CH_3C5)$	-

B3LYP/6-311G**//B3LYP/EPR-III

A_μ	401.0 MHz
$A_C(C2)$	7.4 MHz
$A_N(N1)$	0.5 MHz
$A_N(N3)$	4.0 MHz
$A_p(CH_3C5)$	53.1 MHz

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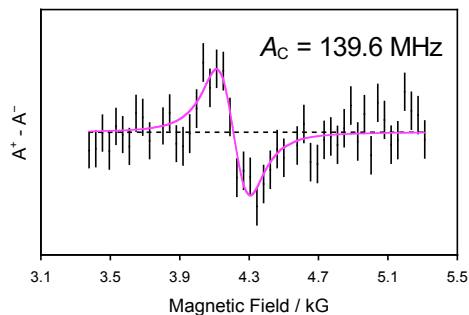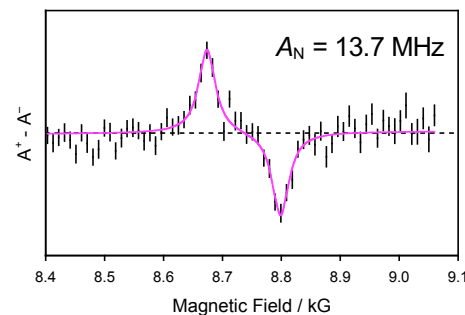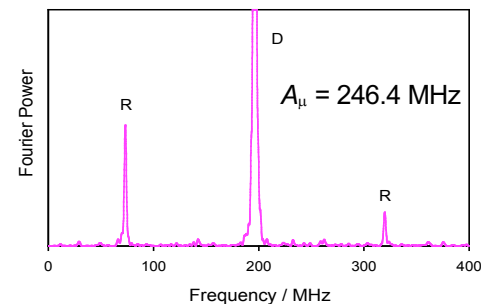
Similarities between measured and calculated hfccs suggests Mu adds to the carbeneic carbon.

I. McKenzie *et al. J. Am. Chem. Soc.* **2003**, *125*, 11565

Competing Reaction Pathways
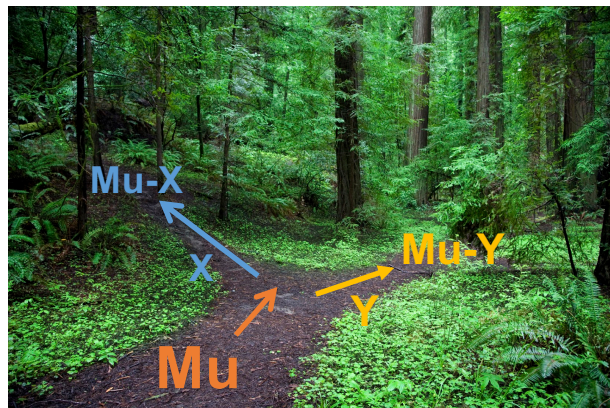
Mu can react in multiple ways. You can control where it ends up by altering the composition of the sample.

$$E_A^{(X)}$$

$$k_{Mu}^{(X)} = A^{(X)} e^{-\frac{E_A^{(X)}}{k_B T}}$$

Rate Mu-X formed
$$= k_{Mu}^{(X)}[X]$$

$$E_A^{(Y)}$$

Reactants

$$\Delta H^{(X)}$$

Mu-X

$$k_{Mu}^{(Y)} = A^{(Y)} e^{-\frac{E_A^{(Y)}}{k_B T}}$$

Rate Mu-Y formed
$$= k_{Mu}^{(Y)}[Y]$$

$$\Delta H^{(Y)}$$

Mu-Y

Products

Energy
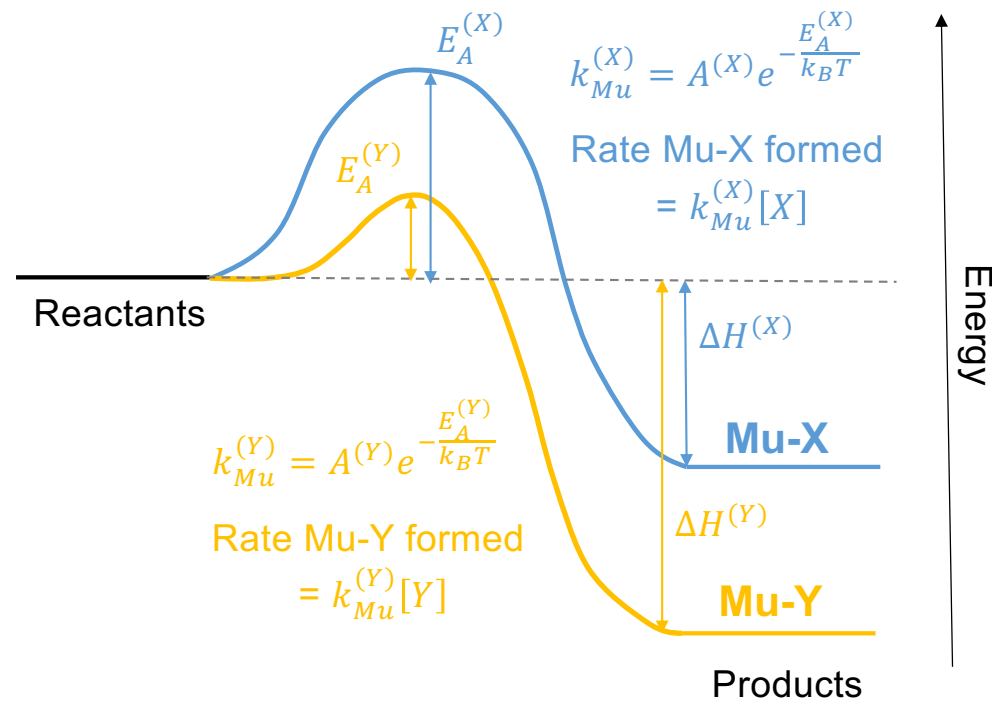
Relative yield of Mu-X $P_X = \dfrac{k_{Mu}^{(X)}[X]}{k_{Mu}^{(X)}[X] + k_{Mu}^{(Y)}[Y]}$

$k_{Mu}^{(X)} = 3\times10^8$ M^{-1} s^{-1}

$[X] = 2$ M

$P_X = 0.6$

Relative yield of Mu-Y $P_Y = \dfrac{k_{Mu}^{(Y)}[Y]}{k_{Mu}^{(X)}[X] + k_{Mu}^{(Y)}[Y]}$

$k_{Mu}^{(Y)} = 4\times10^9$ M^{-1} s^{-1}

$[Y] = 0.1$ M

$P_Y = 0.4$

Predicting Reaction Products: The Bell-Evans-Polanyi Theorem
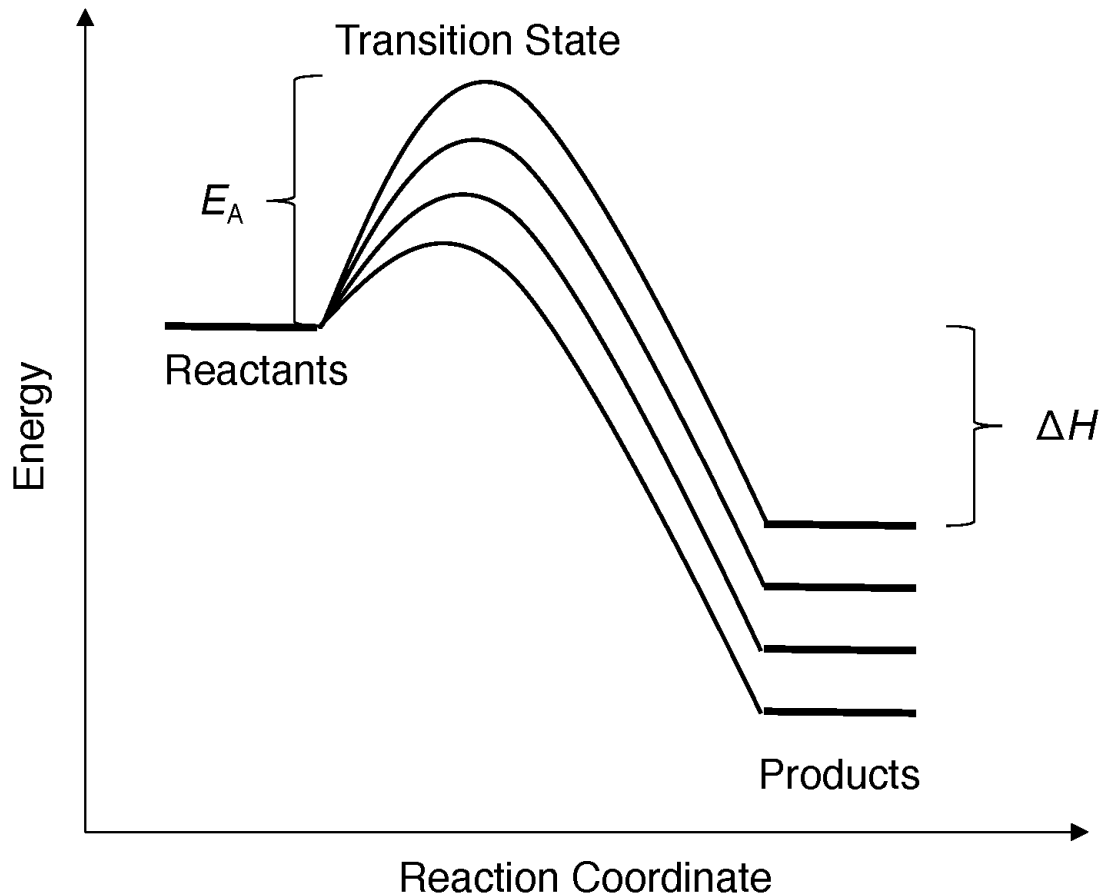
Addition reactions are exothermic, i.e. $\Delta H < 0$

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

$$E_A = E_0 + \alpha \Delta H$$

where α 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
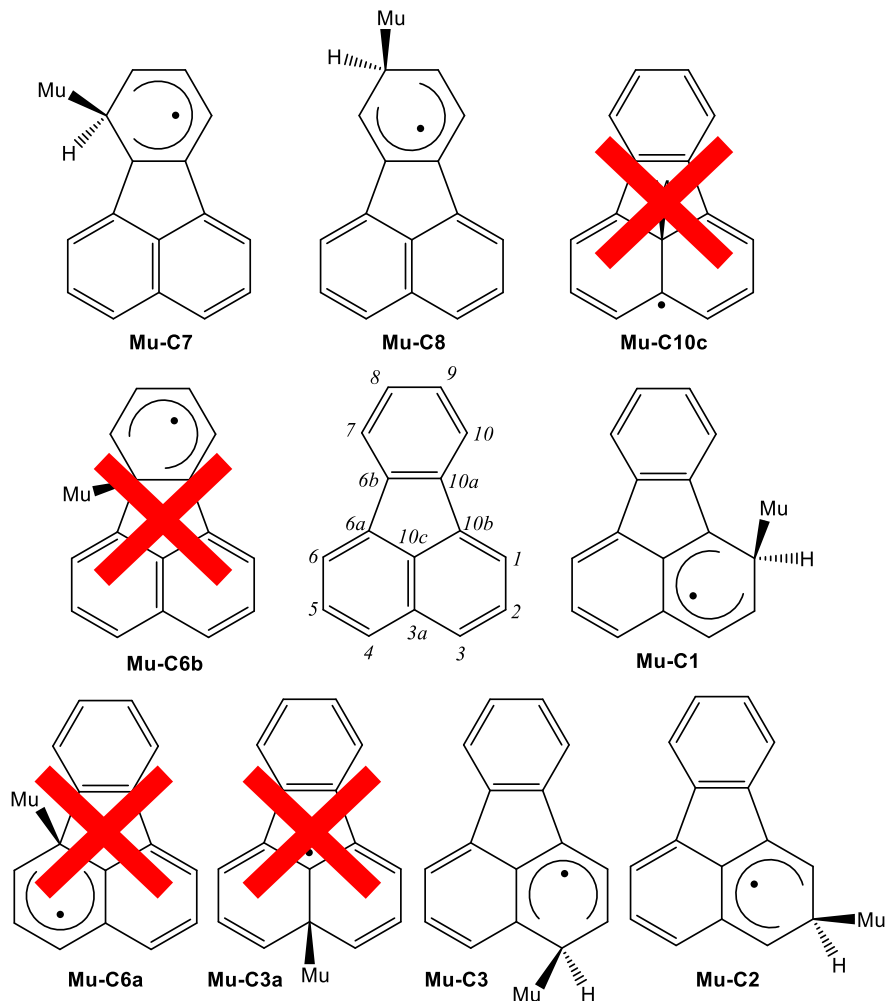
Radical	ΔH (kJ mol^{-1})	$\Delta\Delta H$ (kJ mol^{-1})
Mu-3a	-97	139
Mu-10c	-129	107
Mu-C6b	-164	72
Mu-C6a	-178	58
Mu-C7	-193	43
Mu-C2	-194	42
Mu-C8	-201	35
Mu-C1	-219	17
Mu-C3	-236	0

J.-C. Brodovitch et al. *Can. J. Chem.* 2003, 81, 1

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Competing Reaction Pathways: Reaction of Mu with Fluoranthene
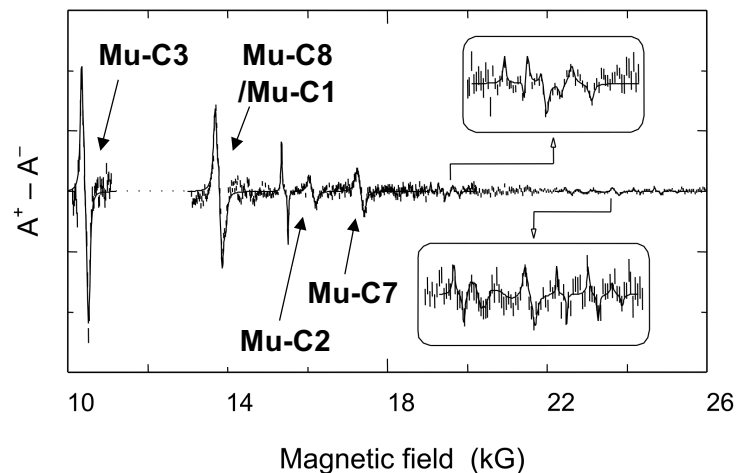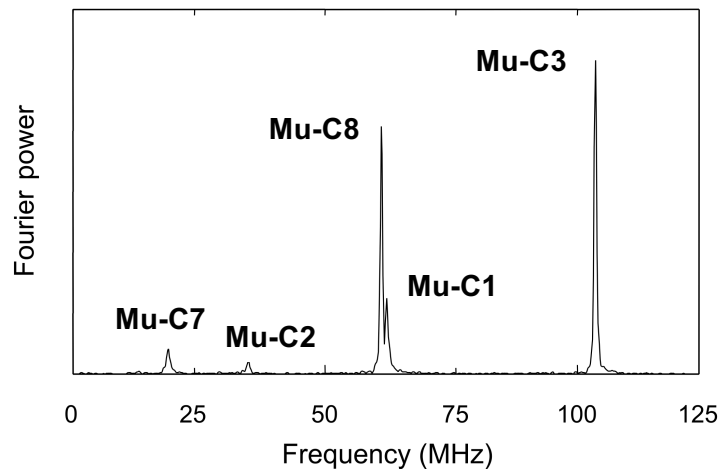
Radical	ΔH (kJ mol^{-1})	$\Delta\Delta H$ (kJ mol^{-1})	Yield
Mu-3a	-97	139	–
Mu-10c	-129	107	–
Mu-C6b	-164	72	–
Mu-C6a	-178	58	–
Mu-C7	-193	43	13.7
Mu-C2	-194	42	9.5
Mu-C8	-201	35	26.8
Mu-C1	-219	17	14.2
Mu-C3	-236	0	35.8

J.-C. Brodovitch et al. *Can. J. Chem.* 2003, 81, 1

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?

L. Chandrasena et al. *Angew. Chem. Int. Ed.* 2019, <u>131,</u> 303
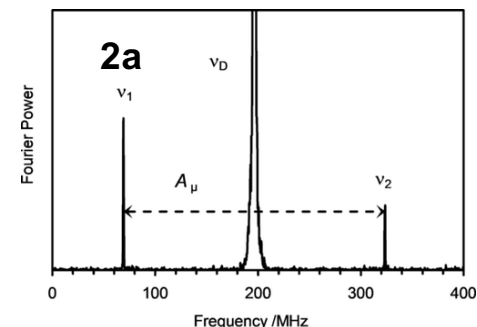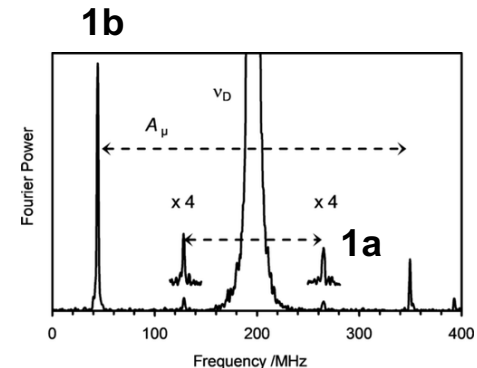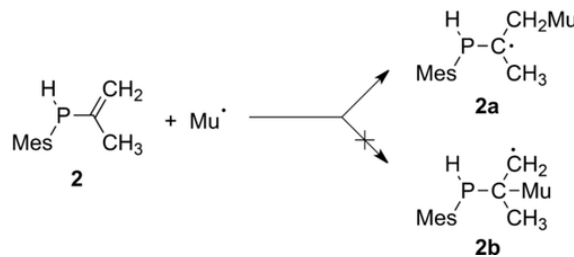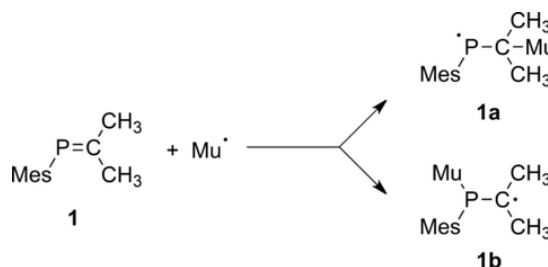
- Radicals **1b** and **2a** are isotopomers produced by different routes. Identity of radicals confirmed by comparing hyperfine coupling constants.

- Highly selective addition of radicals to the P-atom of the P=C bond gives a C-centered radical intermediate.

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Isotope Effect on Bond Stretching
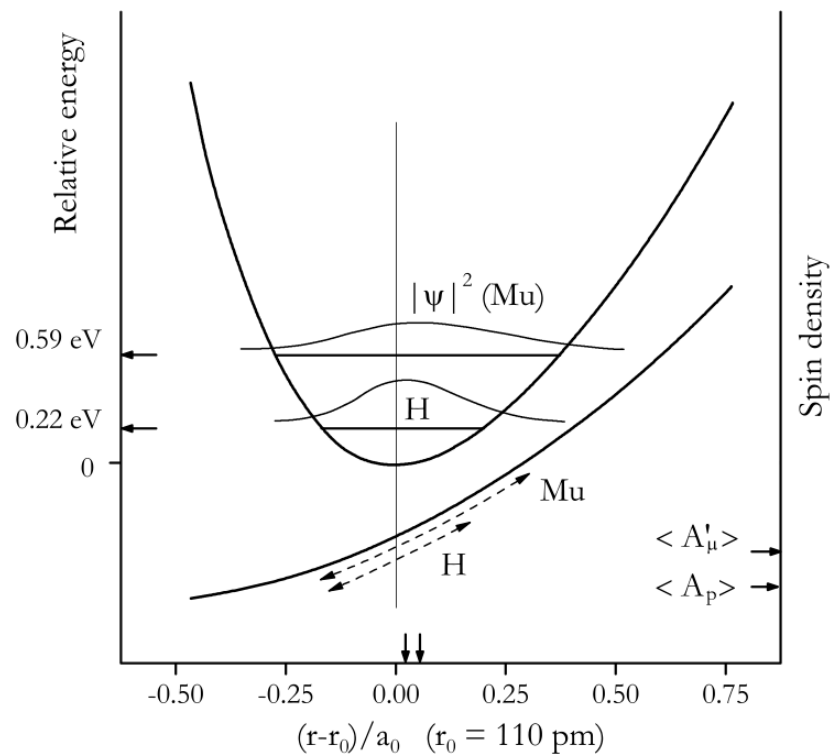
$$m_r = \frac{m_\mu m_x}{m_\mu + m_x} \approx m_\mu \qquad\qquad ZPE = \frac{1}{2}h\sqrt{\frac{k}{m_r}}$$

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_μ is negative).

E. Roduner and I. D. Reid, *Isr. J. Chem.* **1989**, *29*, 3

Hyperfine Coupling of β-Nuclei

$$A_P^\beta = \left[L + M \cos^2 \theta \right] \rho^\pi$$

More overlap with SOMO

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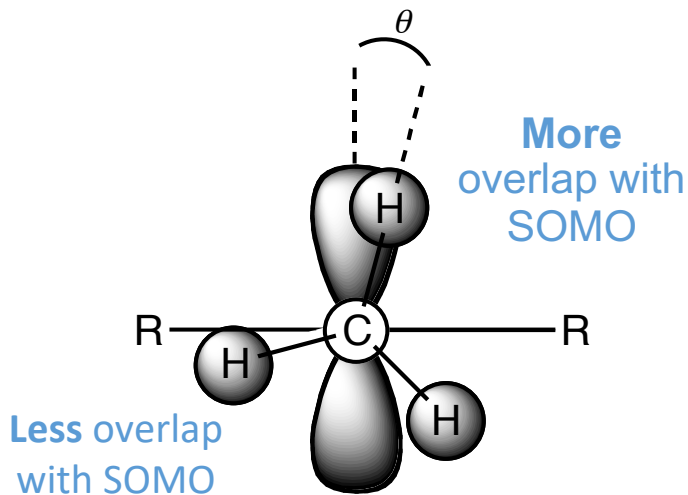
- *L*: orientation independent mechanisms (~0 – 10 MHz)
- *M*: spin density arising from hyperconjugation (~140 MHz)
- θ is the angle between C-X bond and SOMO
- ρ^π is the spin density on adjacent carbon

- 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: $A_R = \left(L + \tfrac{1}{2} M \right) \rho^\pi$
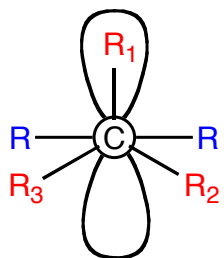
$$A_{R_1} = \left(L + M \right) \rho^\pi \qquad \frac{dA_{R_1}}{dT} < 0$$

$$A_{R_{2(3)}} = \left(L + \tfrac{1}{4} M \right) \rho^\pi \qquad \frac{dA_{R_{2(3)}}}{dT} > 0$$
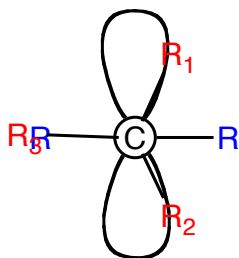
$$A_{R_{1(2)}} = \left(L + \tfrac{3}{4} M \right) \rho^\pi \qquad \frac{dA_{R_{1(2)}}}{dT} < 0$$

$$A_{R_3} = L \rho^\pi \qquad \frac{dA_{R_3}}{dT} > 0$$

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Isotope Effects on Intramolecular Dynamics
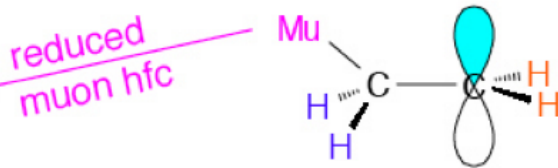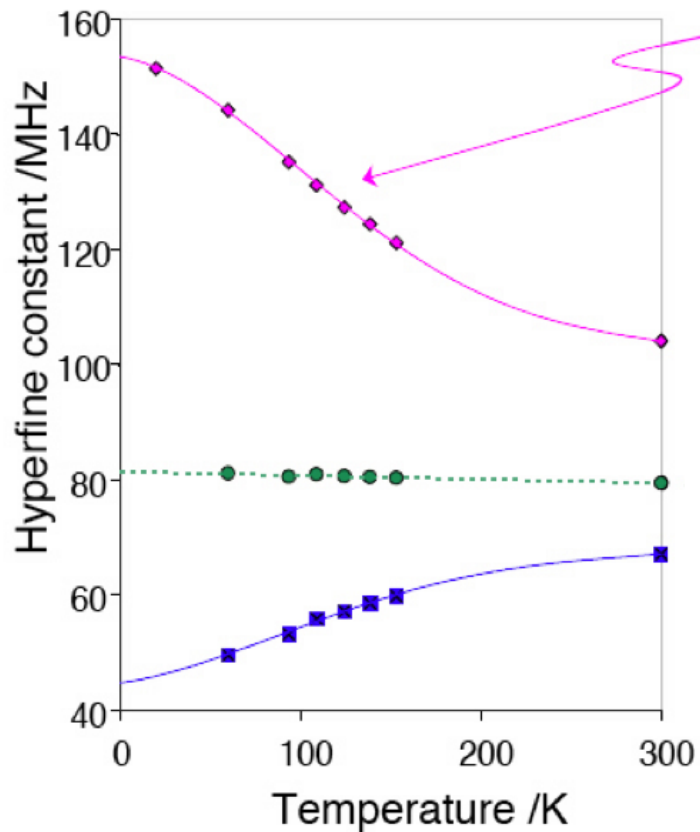
$$V(\varphi) = \frac{V_2}{2}\left(1 - \cos 2\varphi\right) + \frac{V_6}{2}\left(1 - \cos 6\varphi\right)$$

$$A_{\mu} = \left[L + M\left\langle \cos^2(\phi - \phi_0)\right\rangle\right]\rho$$

CH$_2$Mu

CH$_3$
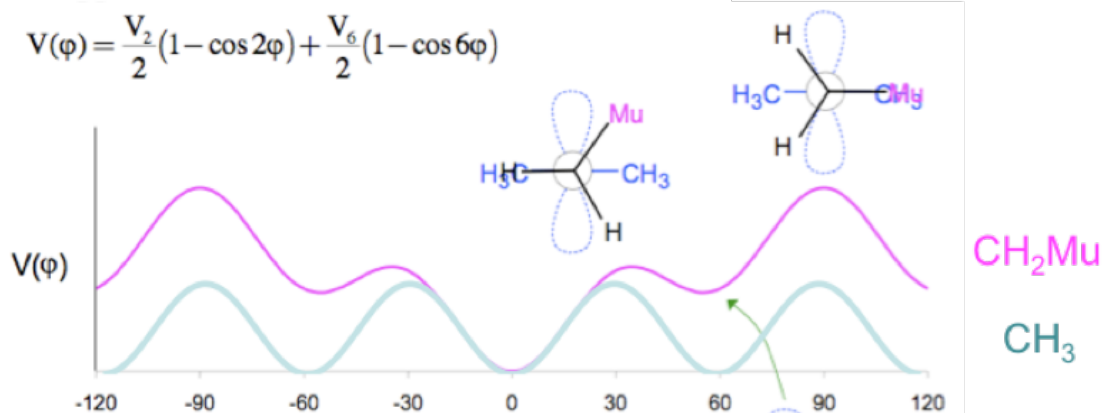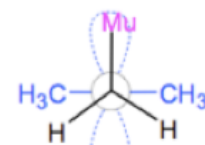
C-Mu bond aligns with SOMO at low temperatures

Measuring Radical Reaction Rates with ALC-µSR

Chemical reaction broadens ALC resonances.
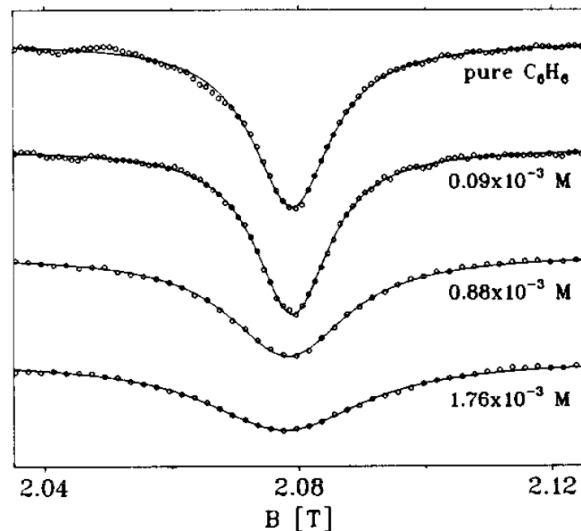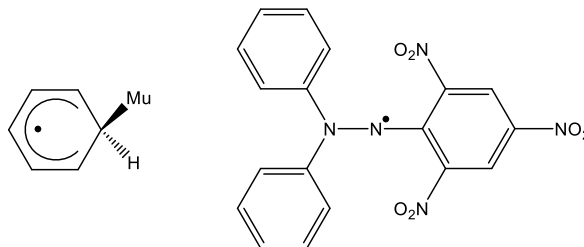
Δ_0 resonance width

$$\Delta B_{1/2} = \frac{\sqrt{\omega_{ALC}^2 + \lambda^2}}{2\pi(\gamma_\mu - \gamma_p)}$$

$$\lambda = \lambda_0 + k_R[X]$$

Slope = k_R
Units = $M^{-1}s^{-1}$

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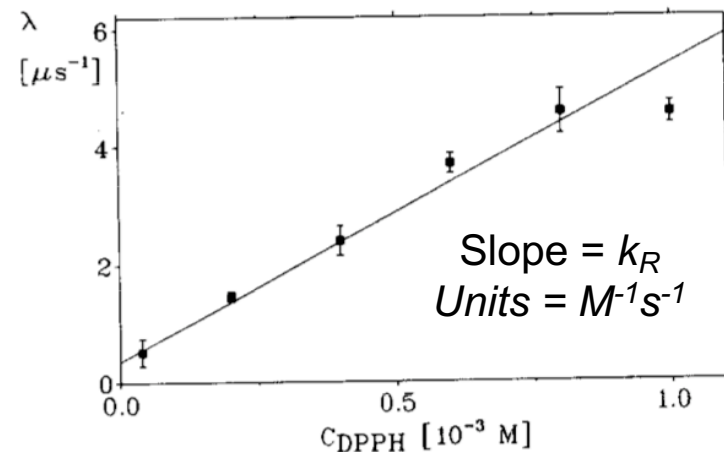
Dipolar Hyperfine Coupling

Point dipole

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

θ < 54.7°   Positive
θ = 54.7°   Zero
θ > 54.7°   Negative
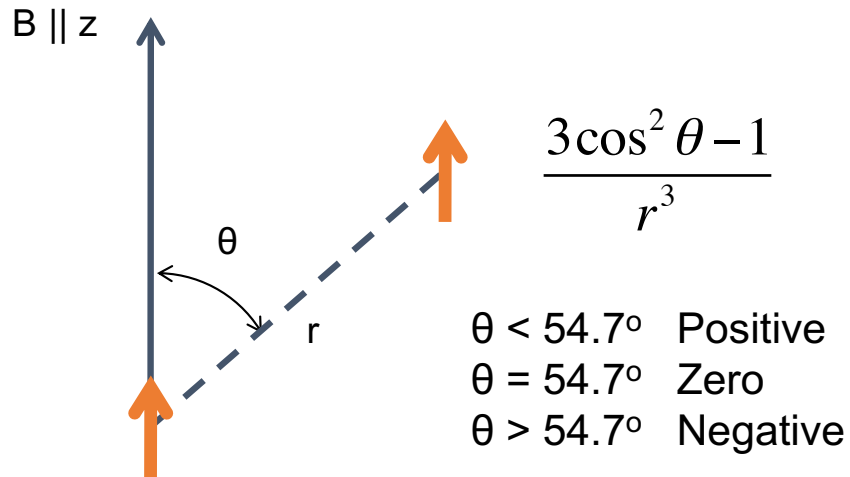
Delocalized electron
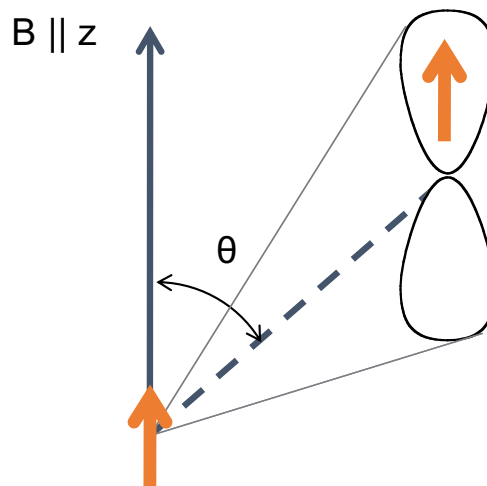
Integrate over the singly occupied molecular orbital (SOMO).

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

- Judge whether the unpaired electron (or SOMO) is mostly in the positive or the negative sector of a double cone with opening angle θ = 54.7°

Dipolar Hyperfine Coupling of α-Nuclei
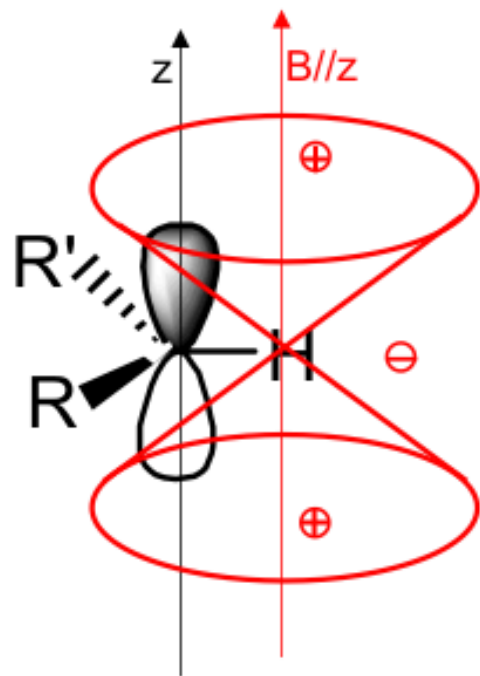
$B_{zz} \approx 0$
Orbital is partly in the positive and partly in the negative sector of the double cone
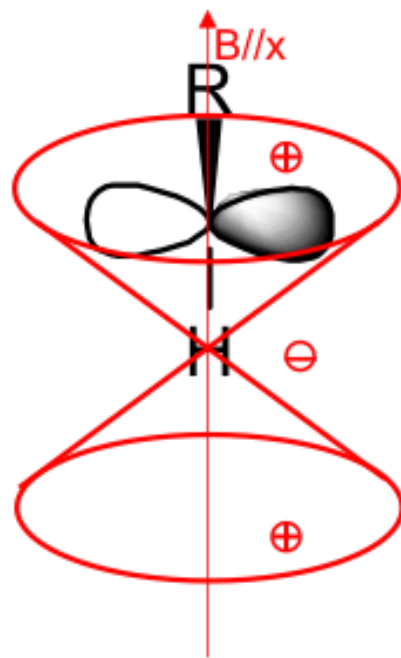
$B_{xx} > 0$
Orbital is essentially entirely in the positive sector of the double cone
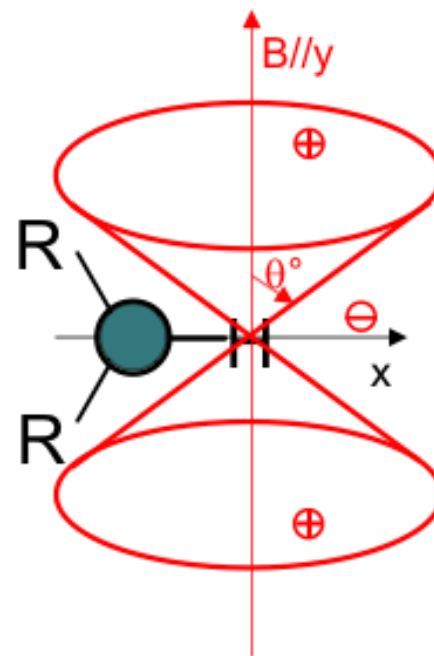
$B_{yy} < 0$
Orbital is essentially entirely in the negative sector of the double cone

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Dipolar Hyperfine Coupling of β-Nuclei

$B_{zz} < 0$

$B_{xx} > 0$

$B_{yy} < 0$
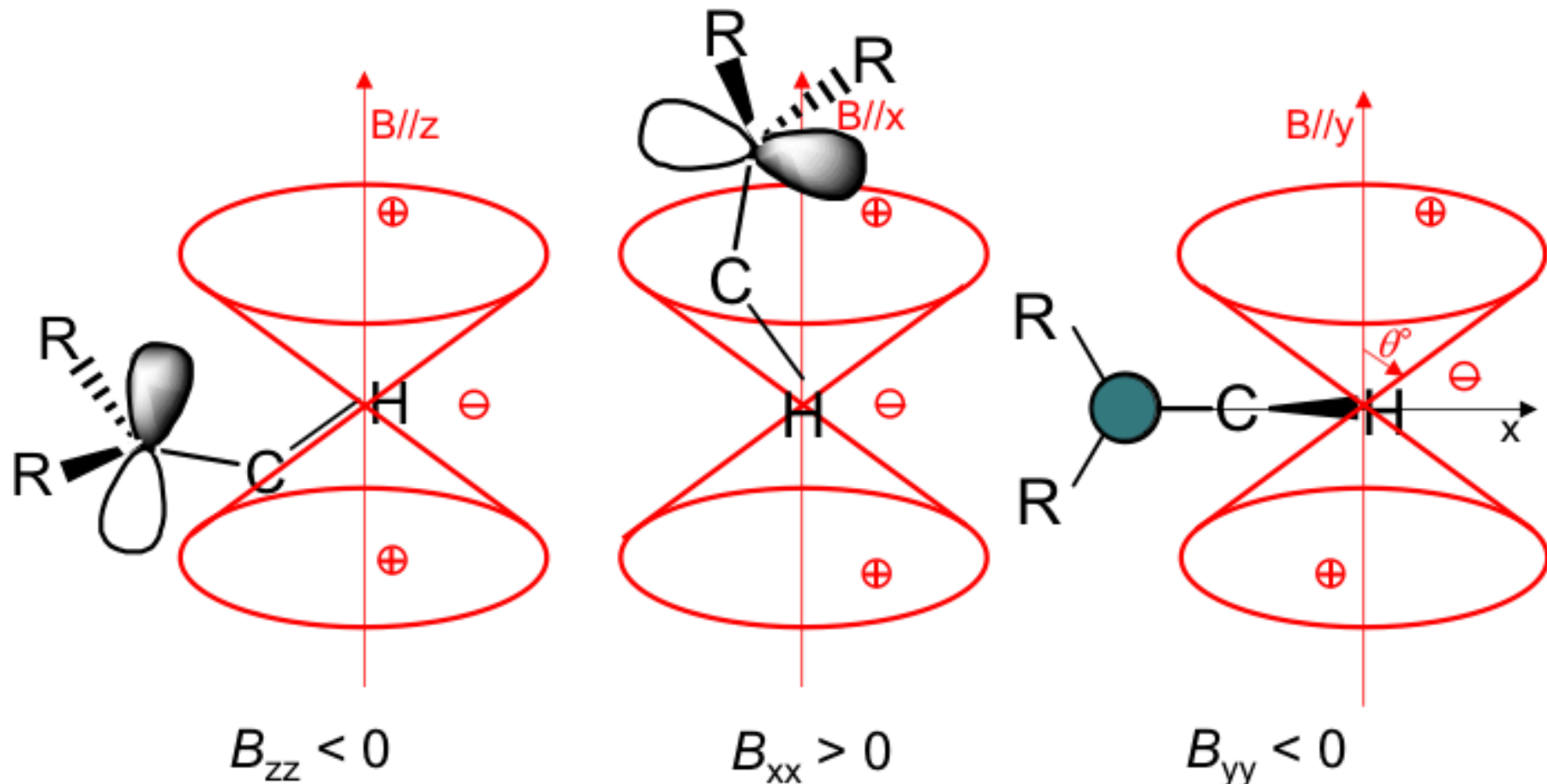
Motional Averaging of Hyperfine Tensors

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

General $\quad B_{xx} + B_{yy} + B_{zz} = 0$

Axial symmetry $\quad D_{\parallel} + 2D_{\perp} = 0$

axial $\quad\longrightarrow\quad$ rotation $\quad\longrightarrow\quad$ new axial
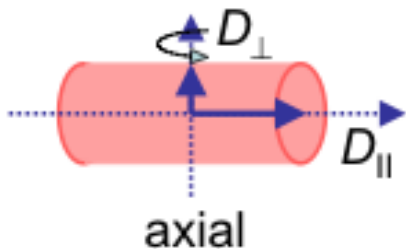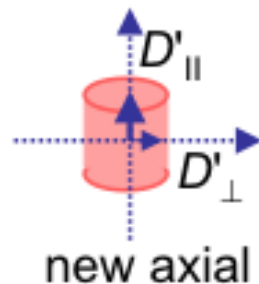
$$D_{\perp} = -\tfrac{1}{2}D_{\parallel}$$

$$D'_{\parallel} = D_{\perp} = -\tfrac{1}{2}D_{\parallel}$$
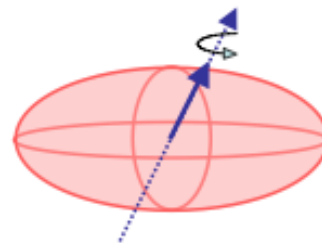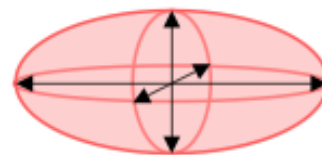
Rotational Averaging of Dipolar Hyperfine Coupling

Hyperfine Tensor

$B_{yy} \approx 0$
$B_{xx} = 8.6$ MHz
$B_{zz} = -8.6$ MHz
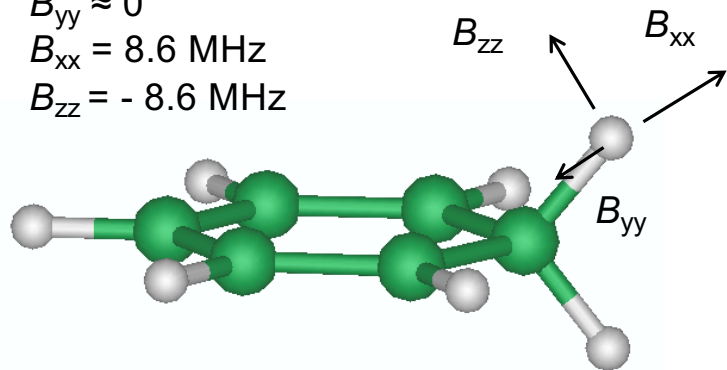
Hyperfine tensor is traceless so

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

Rapid rotation around an axis produces an axial hyperfine tensor

$$D_\mu^\| = -2D_\mu^\perp$$
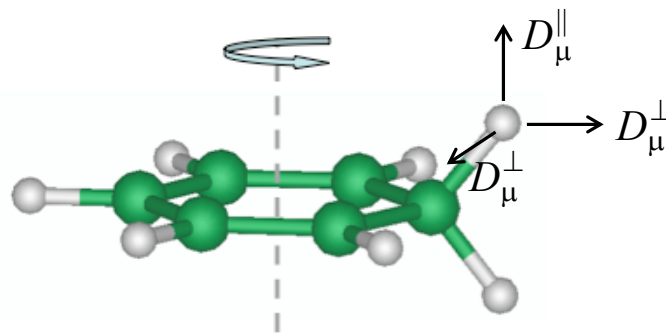
$D_\mu^\| = -6.8$ MHz

$D_\mu^\perp = +3.4$ MHz
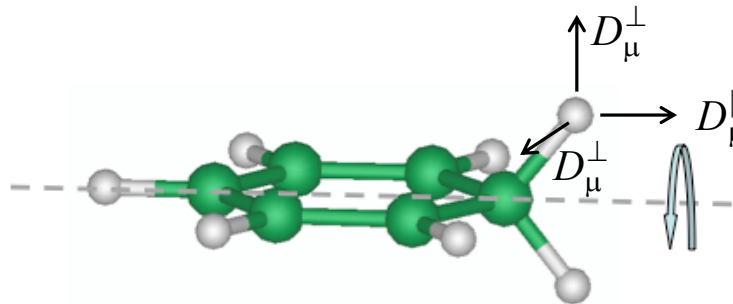
$D_\mu^\| = +5.8$ MHz

$D_\mu^\perp = -2.9$ MHz

ALC Lineshapes

Δ_1 lineshape depends on magnitude of dipolar hfc and the angle between unique axis and magnetic field (θ).

$$\overline{P}_z(B,\theta)=1-\frac{0.5q^2 P_z^0}{\left(\lambda/2\pi\right)^2+q^2+\gamma_\mu^2\left(B-B_{res}^{\Delta_1}\right)^2}$$

$$q=\frac{3}{2}D_\mu^\perp \sin\theta\cos\theta$$

In a powder the Δ_1 lineshape is obtained by integrating over all angles and weighting by the angular probability $f(\theta)$.

$$\overline{P}_z(B)=\int_0^\pi \overline{P}_z(B,\theta)f(\theta)2\pi\sin\theta d\theta$$
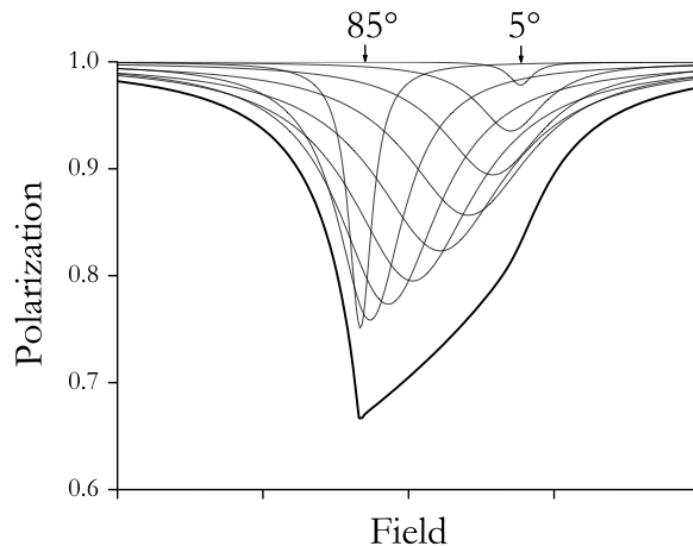
ALC Lineshapes

Preferred rotation axes can be determined
from the shape of ALC resonances.

$D_\mu^{\|} = -6.8$ MHz

$D_\mu^{\perp} = +3.4$ MHz
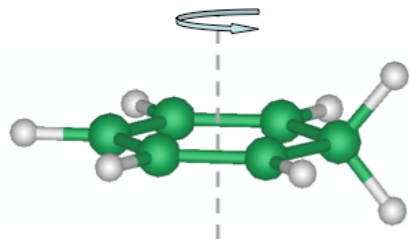
$D_\mu^{\|} = +5.8$ MHz

$D_\mu^{\perp} = -2.9$ MHz
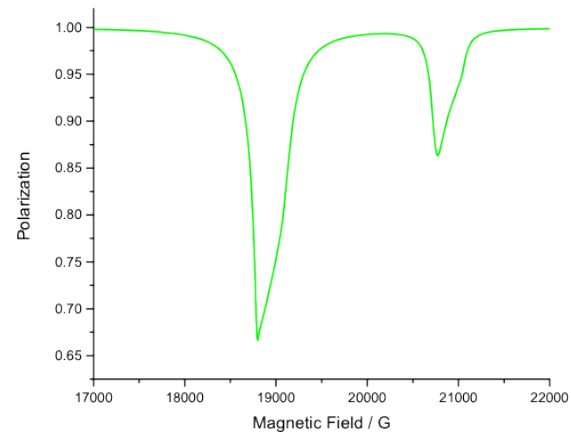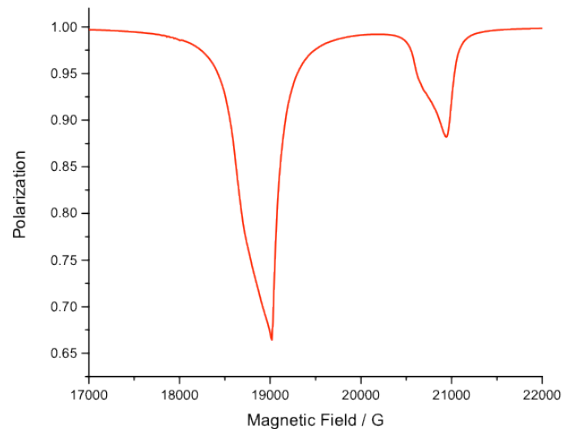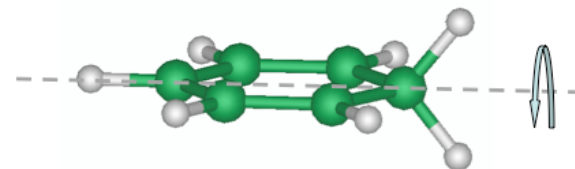
Dynamics of Mu Adduct of Norbornene
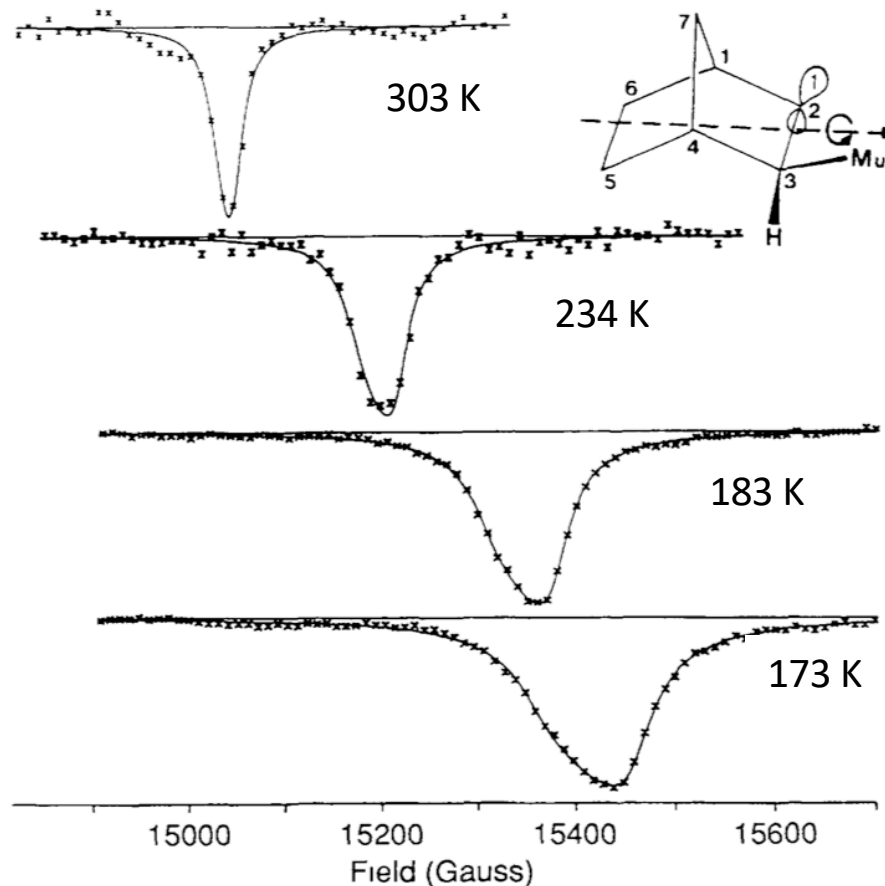
Δ_1 resonance

- Asymmetric lineshape indicates negative $D_\mu^{\parallel}$
- Preferred rotation around indicated axis.
- Decreasing $|D_\mu^{\parallel}|$ with increasing temperature due to wobbling of rotation axis.

E. Roduner *Chem. Soc. Rev.* **1993**, *29*, 337
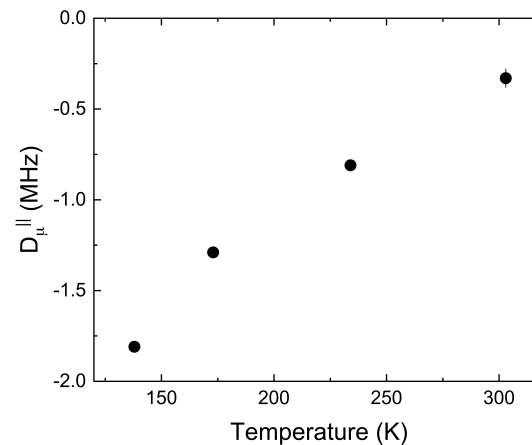
Dynamics of C$_{60}$ Versus C$_{70}$

C$_{60}$

Δ_1 broadens with increasing temperature

Isotropic rotation

C$_{70}$

Δ_1 narrows with increasing temperature
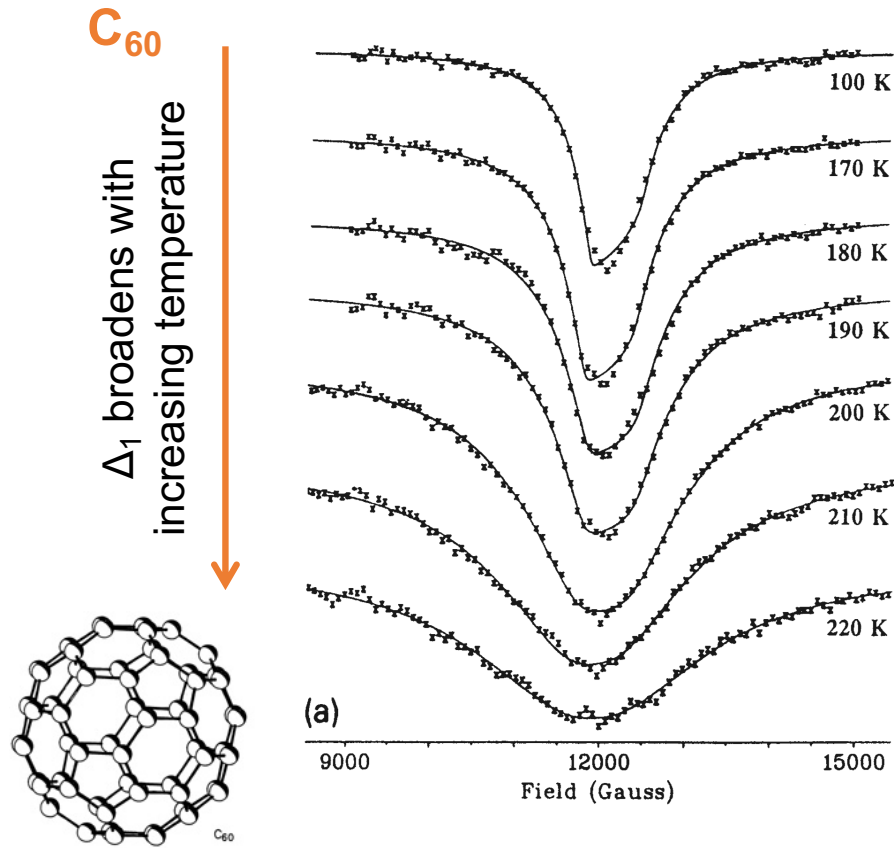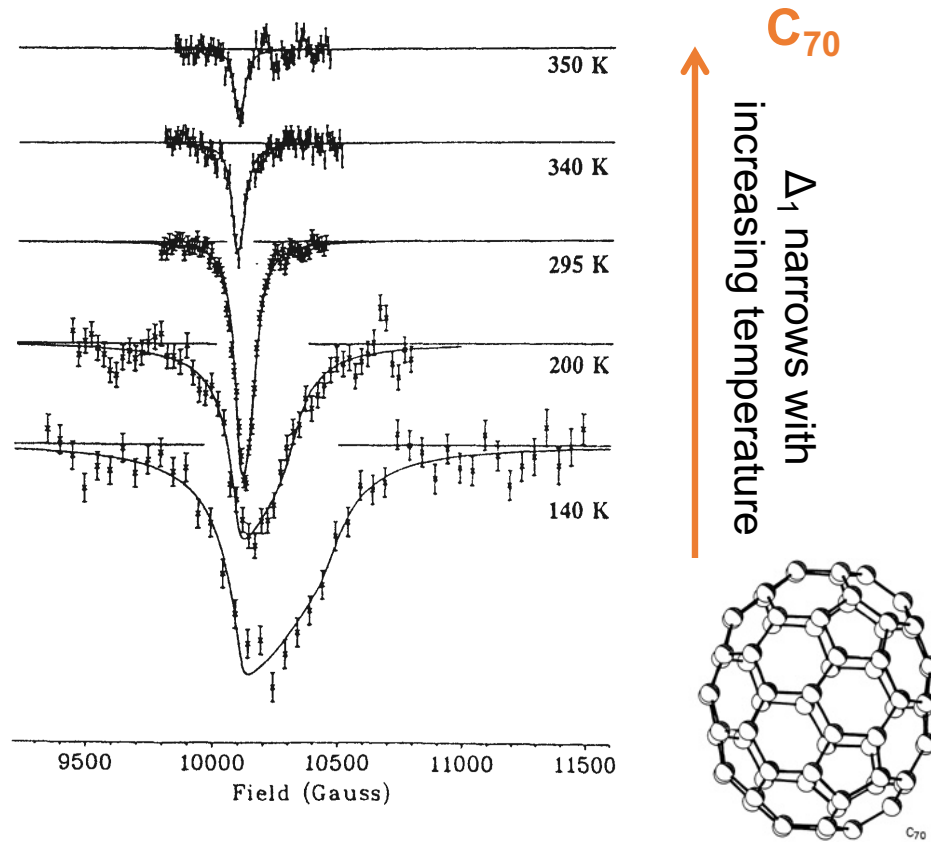
Wobbling around preferred axis

K. Prassides *Hyp. Int.* **1997**, *106*, 125

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:

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

C_6H_6Mu in benzene
300 K

1/T_1 / µs^{-1} vs Magnetic Field / G
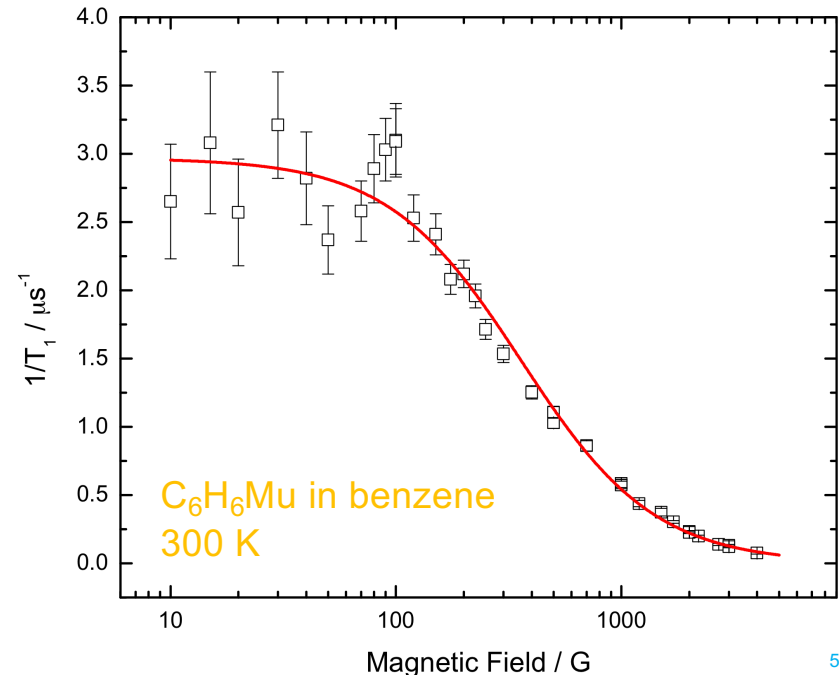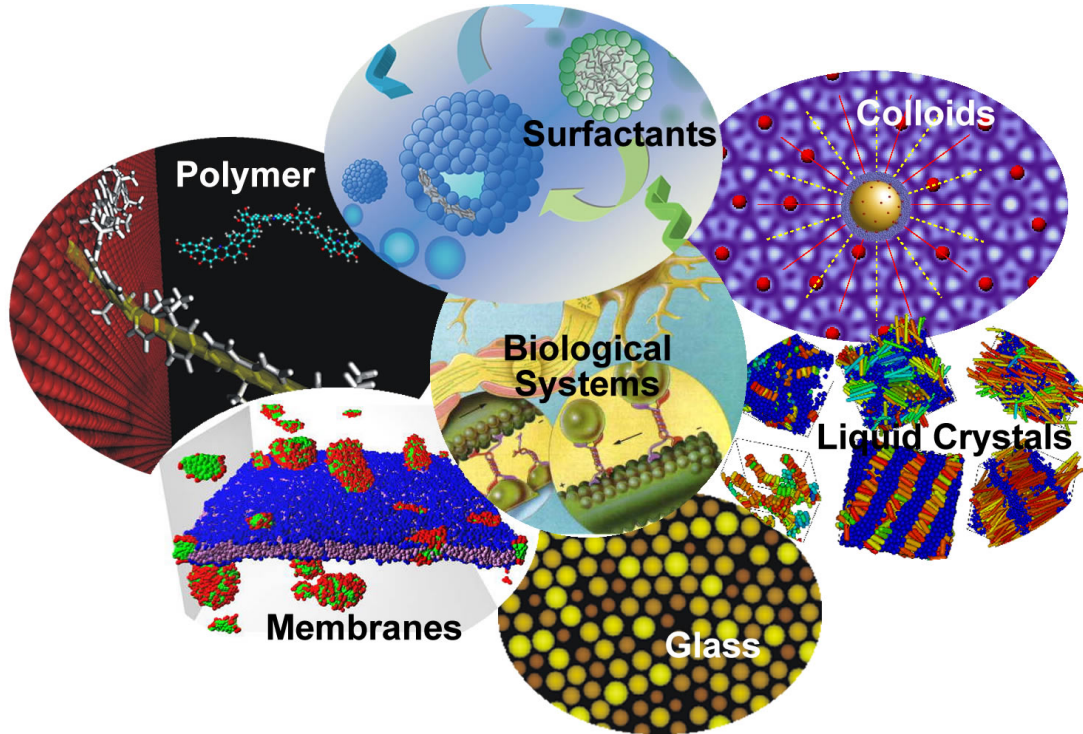
Soft Matter

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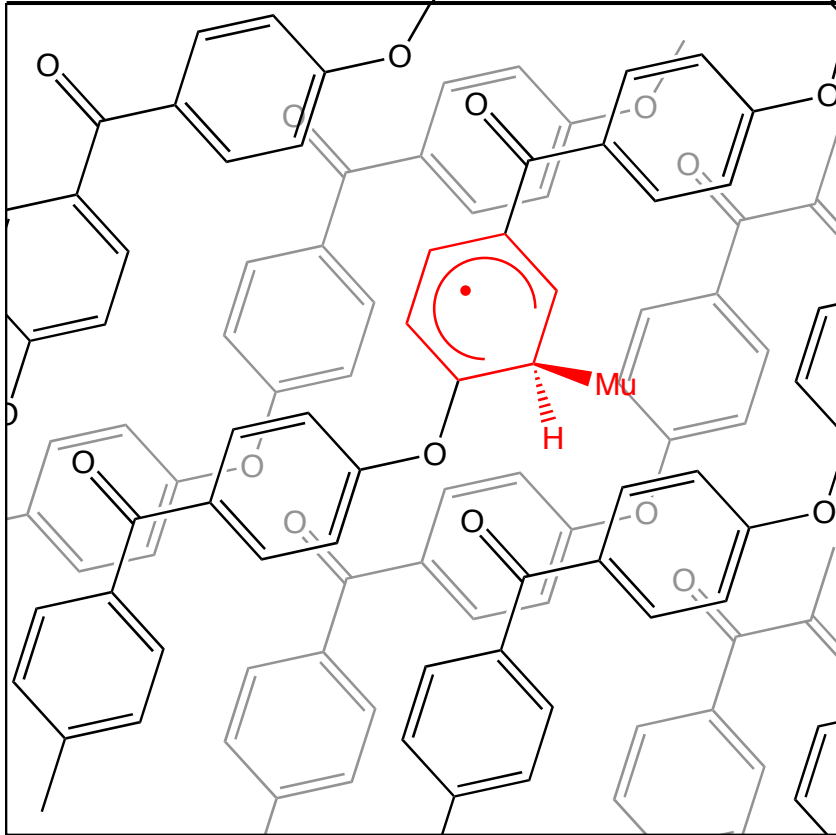
- Introduce spin label in soft matter system (liquid crystal, polymer)
- Similar to spin labeling with stable nitroxides *except smaller perturbation.*
- Radical sensitive to:
  - Orientation of probe
  - Polarity of local environment
  - Fluctuations on the ns to µs timescale

Lyotropic Liquid Crystals with Cosurfactants

DHTAC
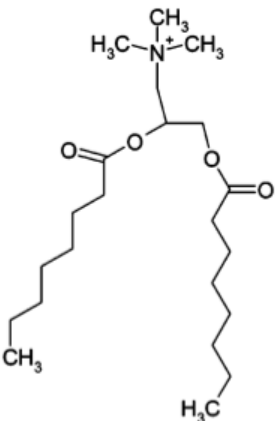
polar head groups

non-polar alkyl chains

aqueous layer
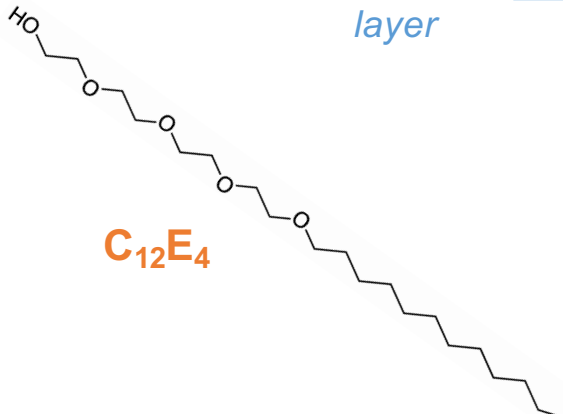
C$_{12}$E$_4$
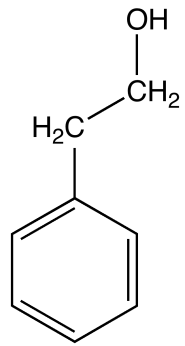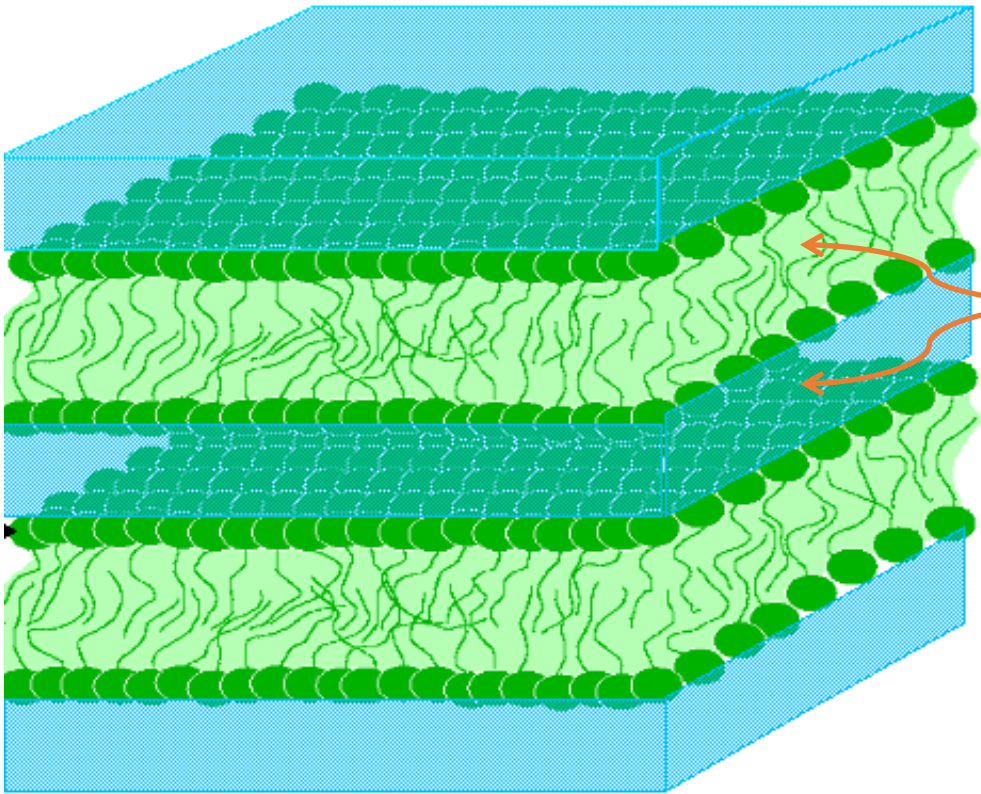
Phenylethanol Cosurfactant

ALC-µSR of Phenylethanol Cosurfactant
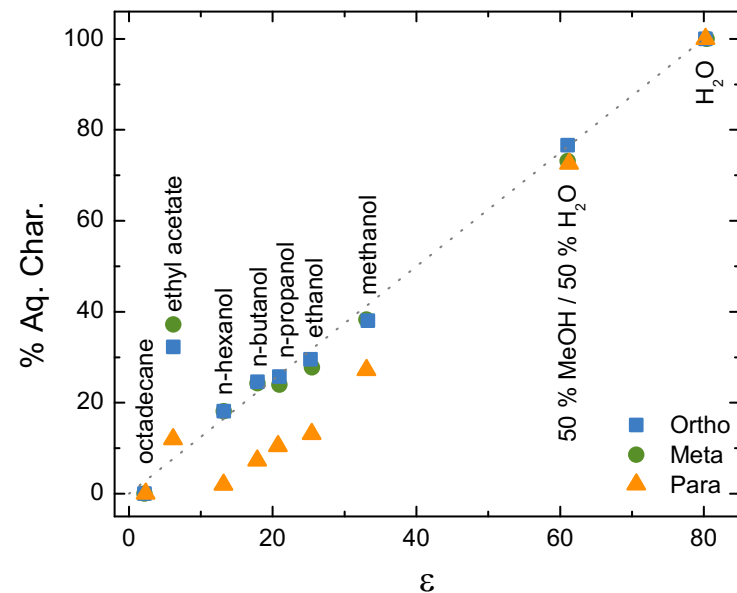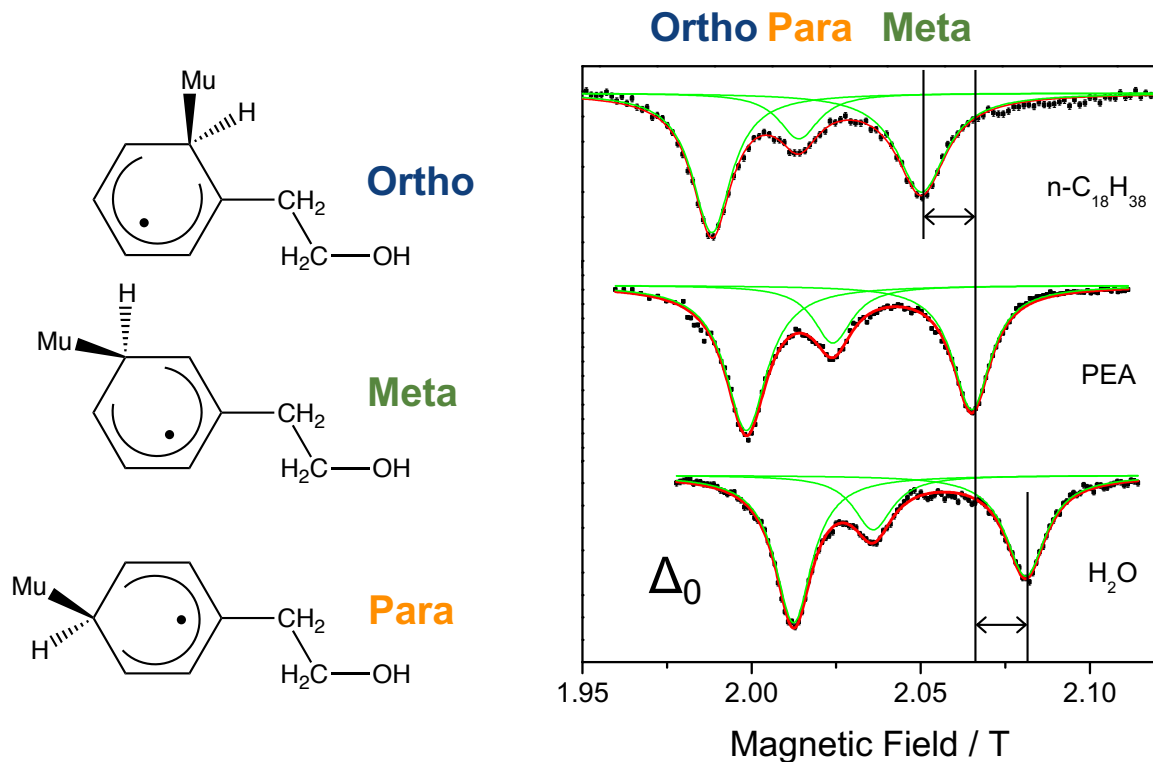
Hfccs are sensitive to the polarity of the local environment

ALC-μSR of Phenylethanol Cosurfactant in DHTAC Bilayer

A. Martyniak et al., *Phys. Chem. Chem. Phys.* **8**, 4723 (2006)
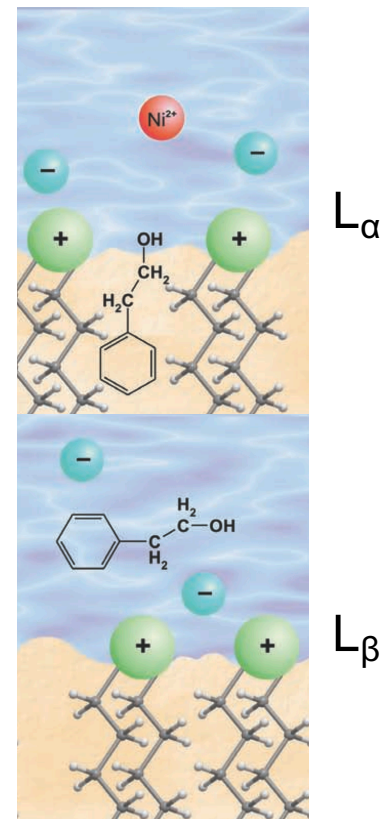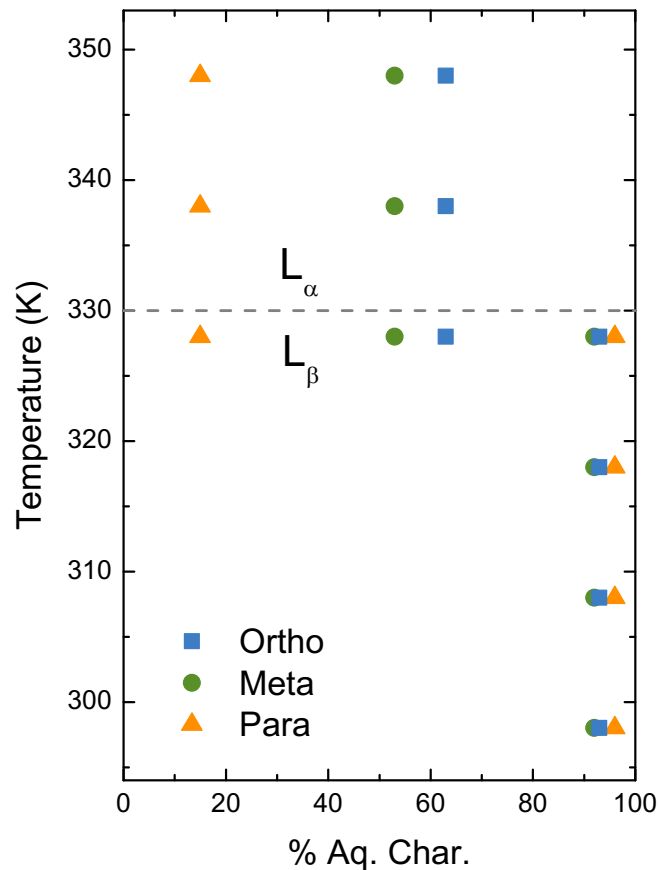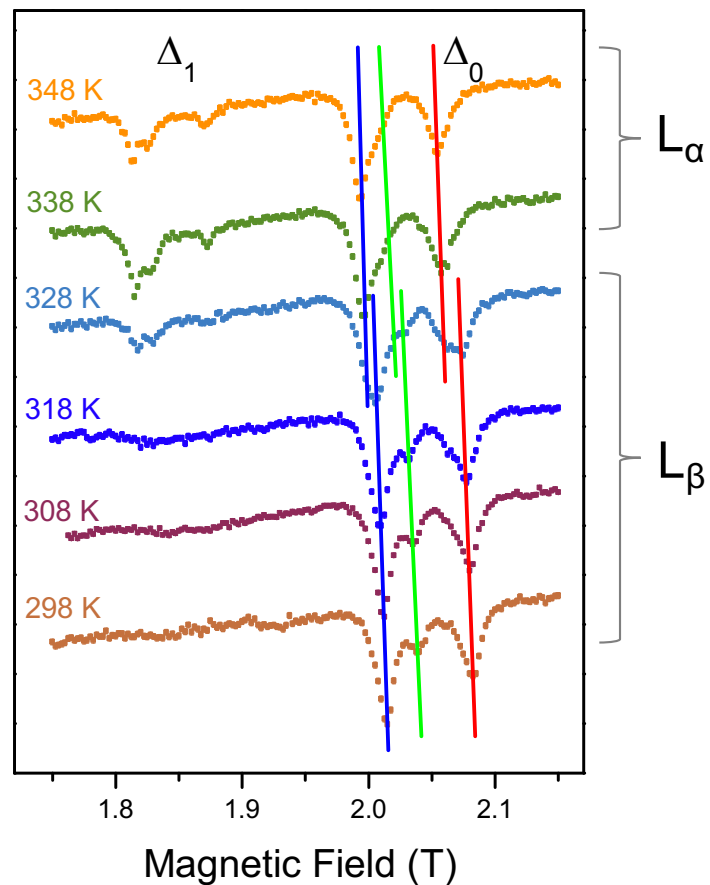
Spin-Exchange Reaction Between Mu Adducts of PEA and Ni^{2+}
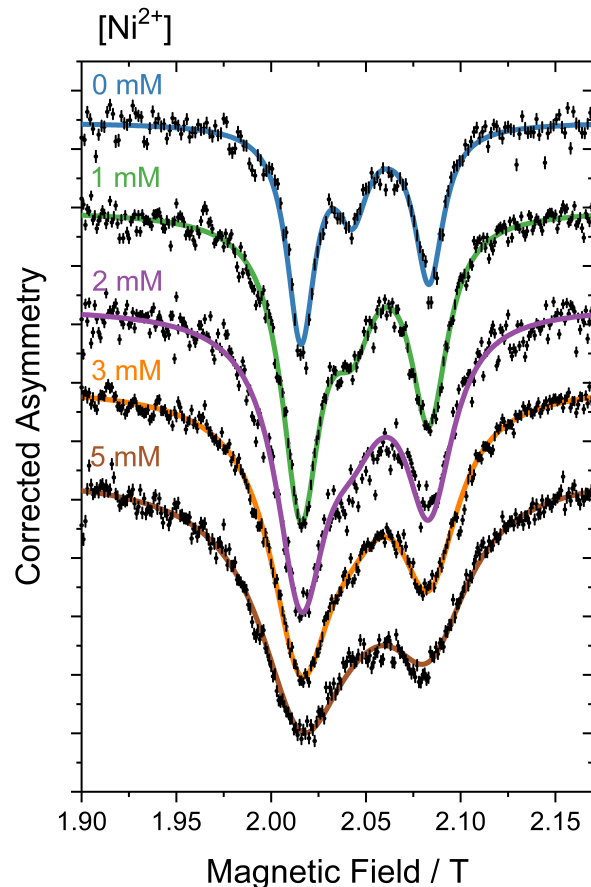
	T / K	k_{ortho}	k_{meta}	k_{para}
		10^9 M^{-1} s^{-1}		
H$_2$O	298	1.90(3)	1.83(5)	1.4(1)
	348	4.44(5)	3.97(7)	4.0(1)
DHTAC	298	1.96(4)	1.86(6)	2.8(2)
	348	0.19(1)	0.21(1)	0.21(2)
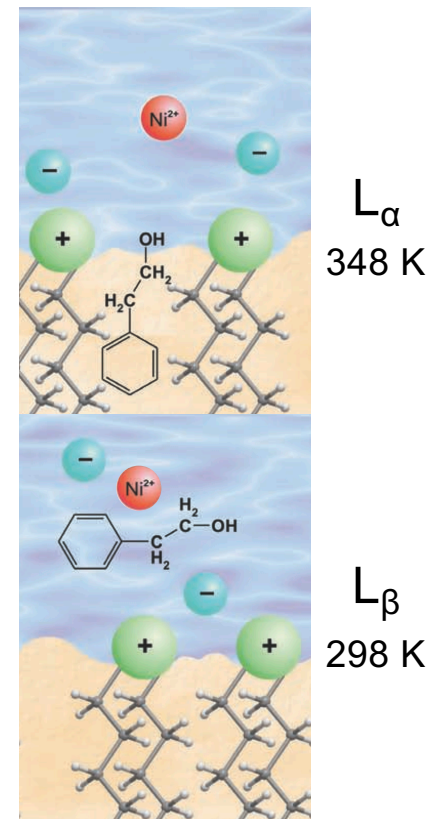
L$_\alpha$
348 K

L$_\beta$
298 K

H. Dilger et al. Physica B **374-375**, 317 (2006)

ALC-µSR of Phenylethanol Cosurfactant in $C_{12}E_4$

(a)

(b) Δ_1 Resonances

I. McKenzie et al., *Phys. Chem. Chem. Phys.* 19, 9551 (2017)

Crystalline Solid — Temperature — Liquid Crystal — Isotropic Liquid

φ

Mu-2-PCH5   Mu-3-PCH5

353.9 K
328.6 K
326.7 K
316.1 K

Overlapping Δ_1

Corrected Asymmetry

Magnetic Field (T)

Magnetic field aligns director in nematic phase, which shifts the Δ_0 resonance.

Mu-3-PCH5

T_{NI}

$$\Delta B_{res} = K \langle D_X^{\parallel} \rangle S$$

Mu-2-PCH5

ΔB_{res} (mT)

Temperature (K)
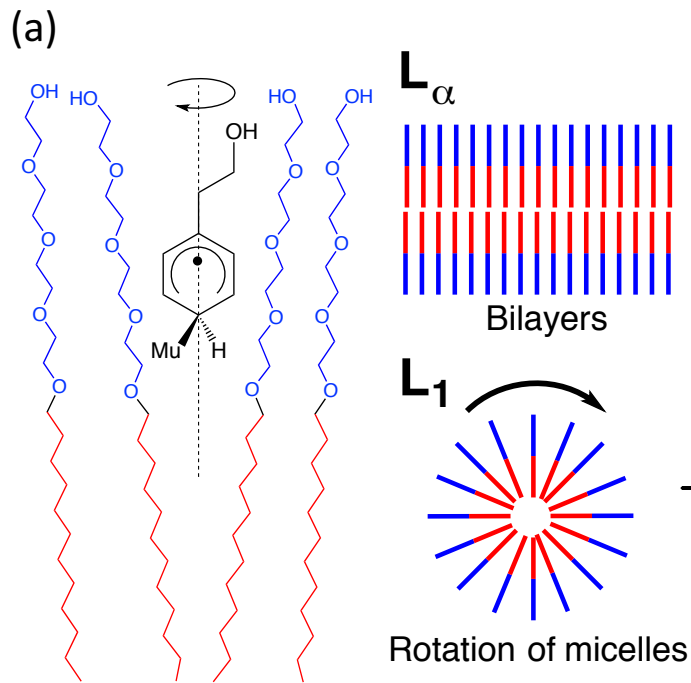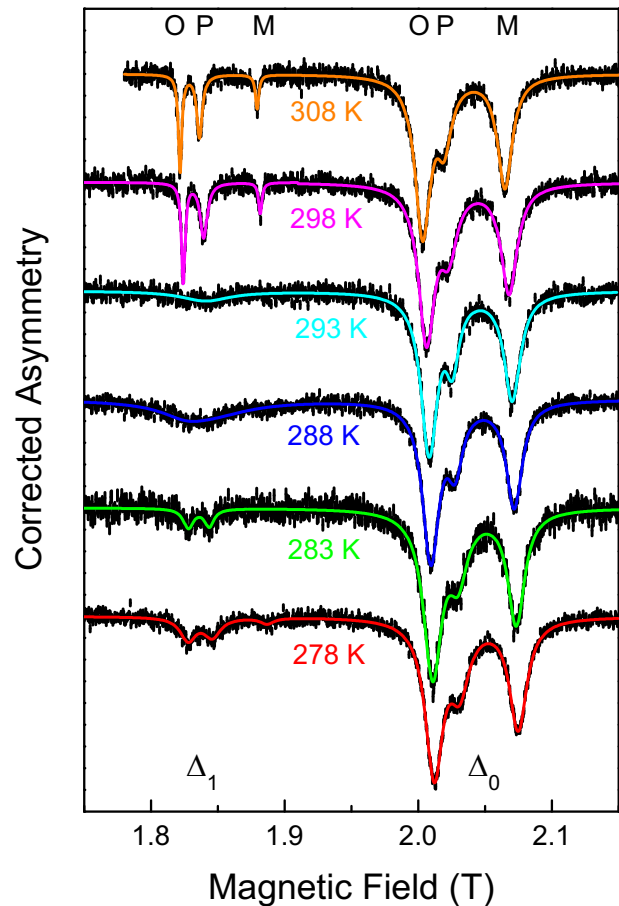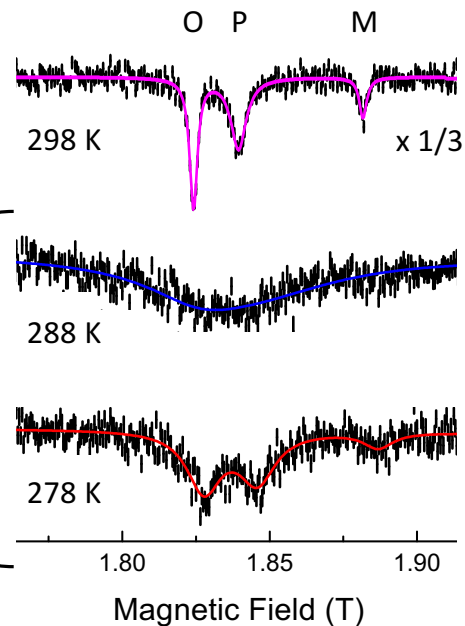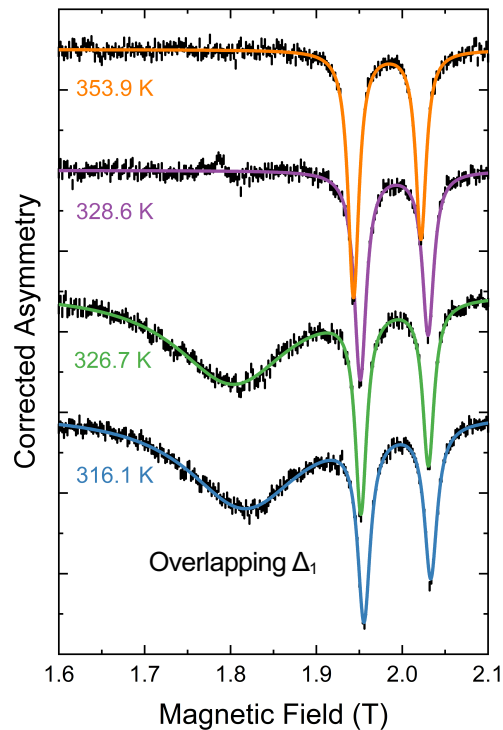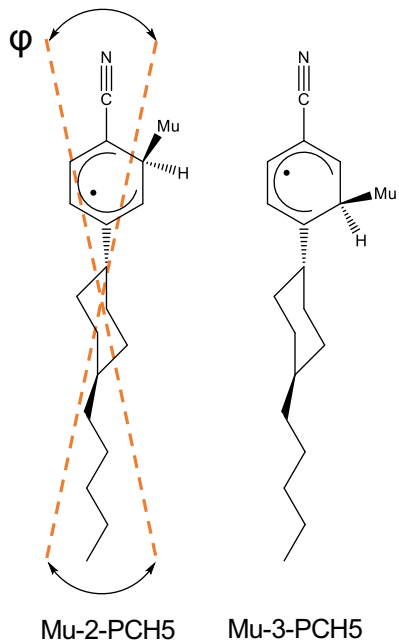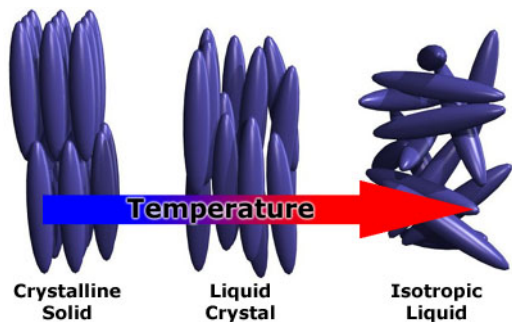
Wobbling within a cone of angle φ

$$\langle D_X^{\parallel} \rangle = \tfrac{1}{2} D_X^{\parallel} (\cos \varphi + \cos^2 \varphi)$$

$$\langle \varphi^2 \rangle \approx \frac{k_B q_c}{\pi} \left(\frac{T}{S^2} \right)$$

$\langle \varphi^2 \rangle$ (radians²)

$T/(T_{NI} S^2)$
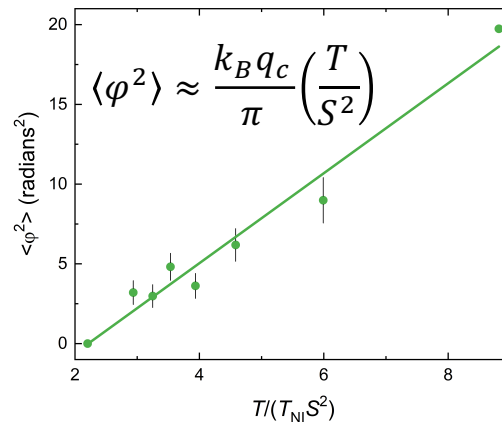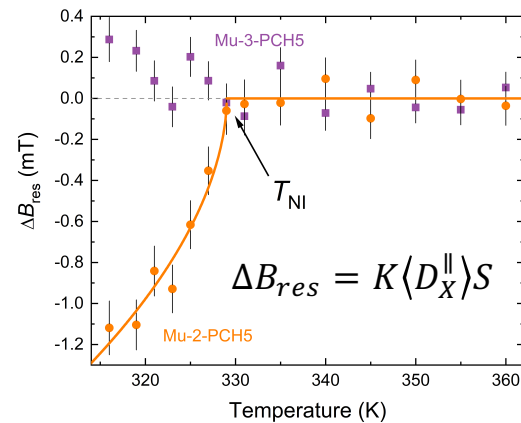
Muoniated Spin Probes in a Cholesterolic Liquid Crystal

Cholesteryl nonanoate

helical axis

Mu

Chiral nematic phase (N*)

pitch p

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

$A_\mu = 442$ MHz
$B_{res}(\Delta_1) = 1.62$ T
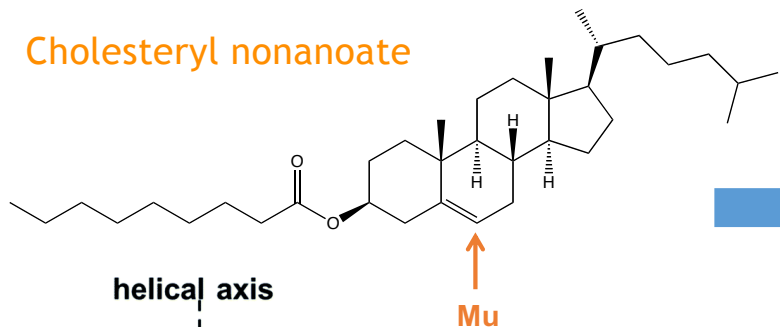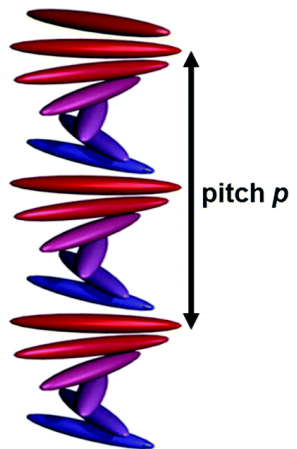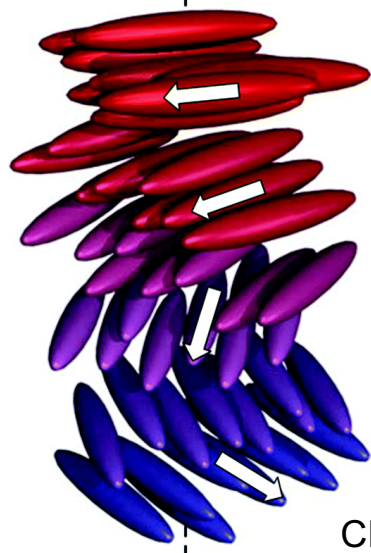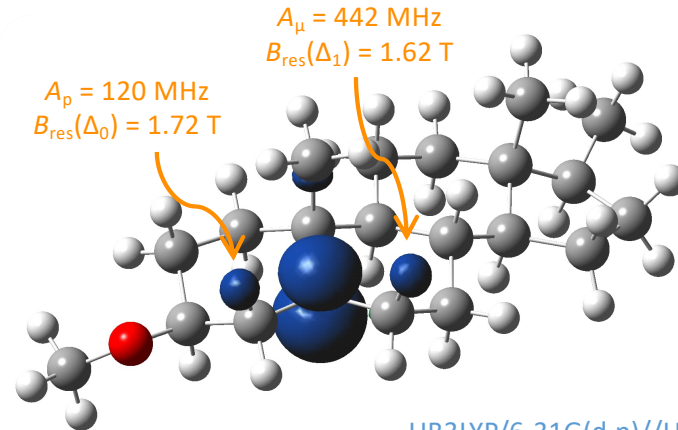
UB3LYP/6-31G(d,p)//UPBE0/EPR-II

383 K
376 K
369 K
364 K
357 K
349 K

Corrected Asymmetry

Magnetic Field (T)

Δ_1 Δ_0

1.5   1.6   1.7   1.8

I. McKenzie et al., *J. Phys. Chem. B* 115, 9360 (2011)

68
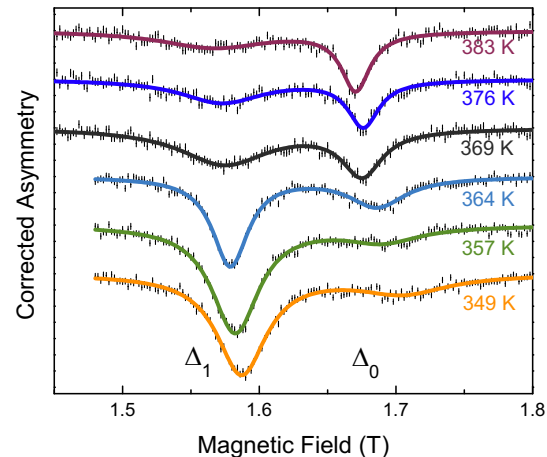
Muoniated Spin Probes in a Cholesterolic Liquid Crystal
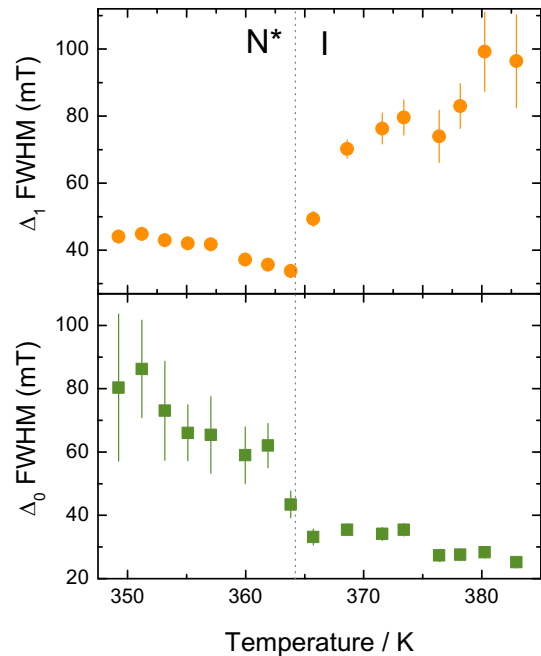
N*: *Wobbling around a preferred axis*
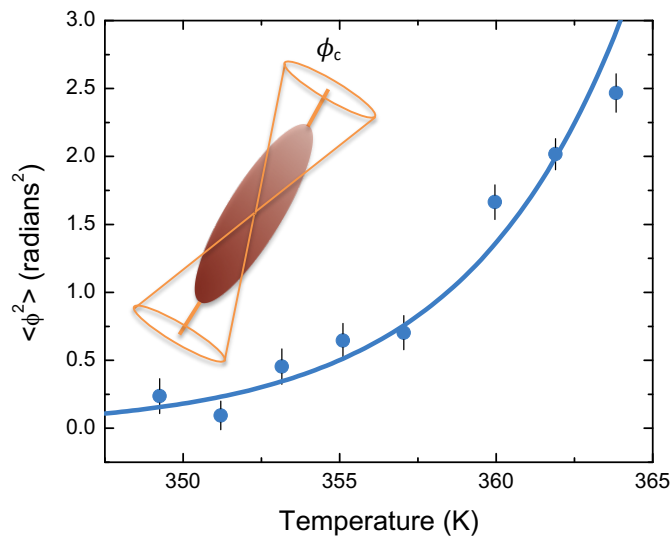
I: *Slow Isotropic Reorientation*
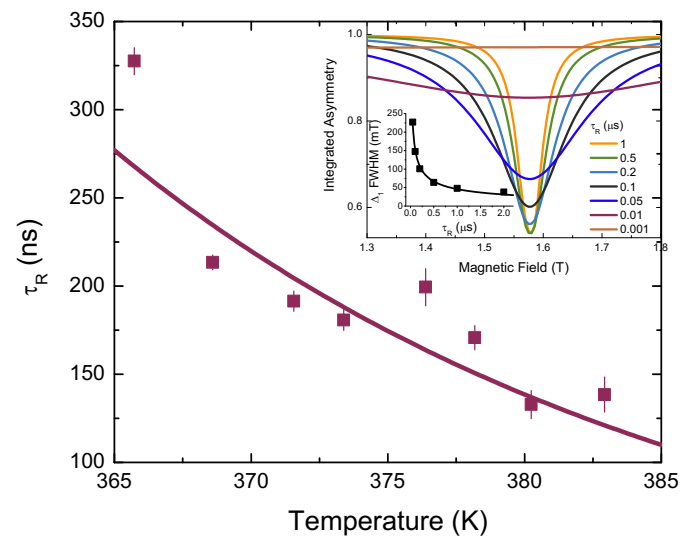
LF-µSR Studies of Phenyl Ring Dynamics in Polystyrene

Spin relaxation due to muoniated cyclohexadienyl radicals formed by Mu addition to phenyl side chains.
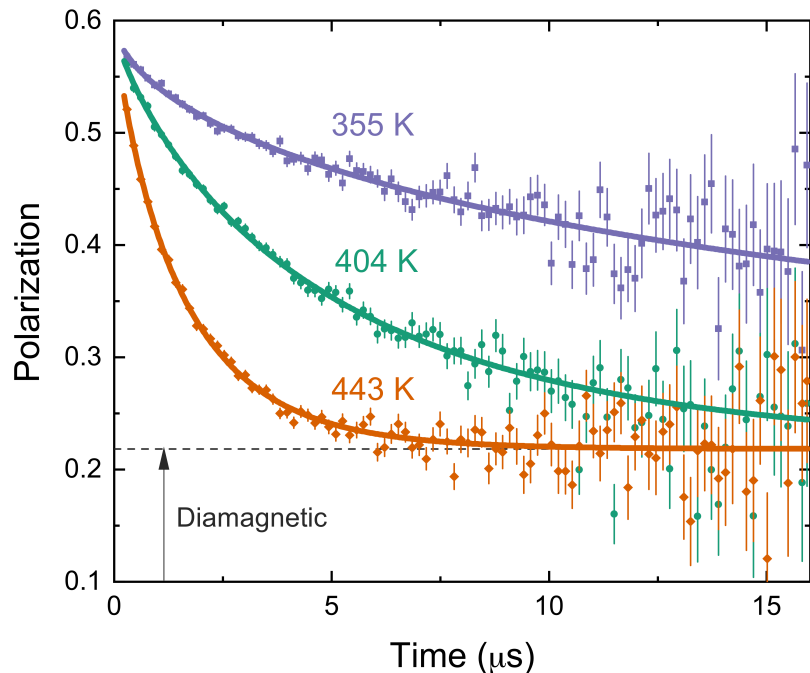
Distribution of local environments

Rapid backbone motion leads to uniform environment

Change at T_g

$$P(t) = P_D + P_R e^{-(t/T_1^\mu)^\kappa}$$
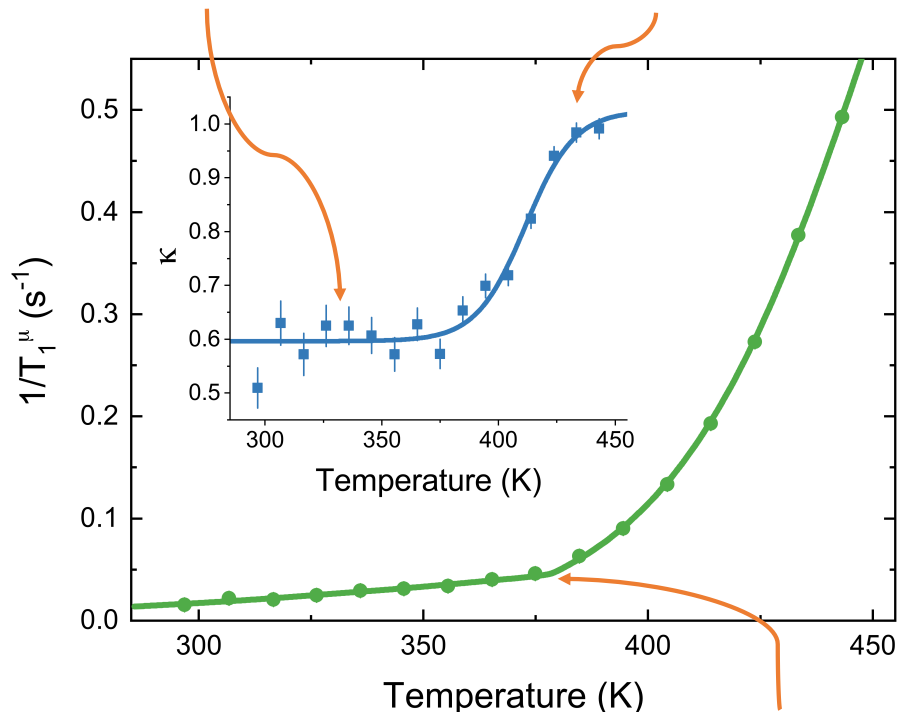
LF-μSR Studies of Phenyl Ring Dynamics in Polystyrene

Change in phenyl ring dynamics at the glass transition.

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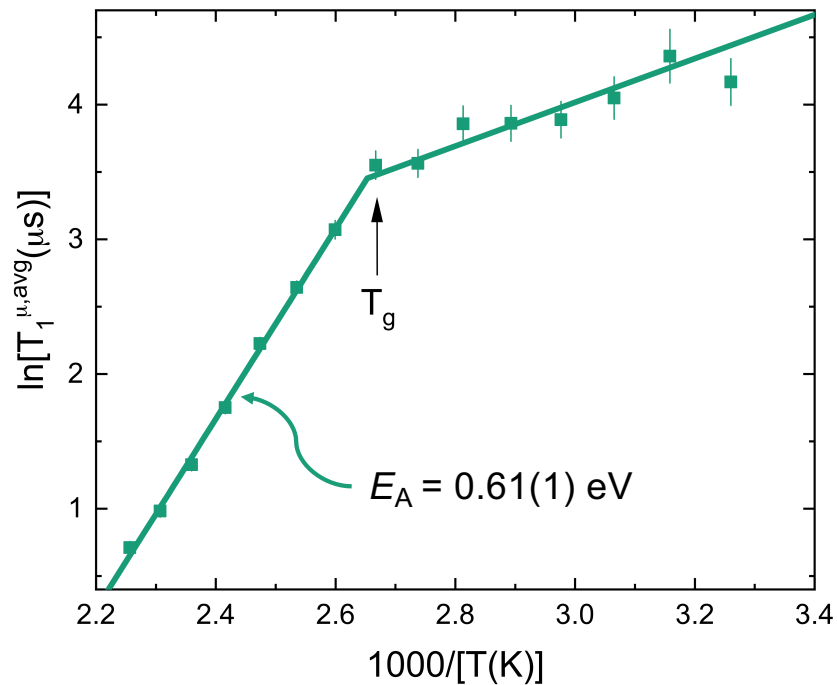
$$\ln\left[T_1^{\mu,\mathrm{avg}}\right] = \ln\left[\frac{\omega_e^2 \tau_0}{0.14[A_\mu : A_\mu]}\right] + \left(\frac{E_A}{k_B}\right) T^{-1}$$
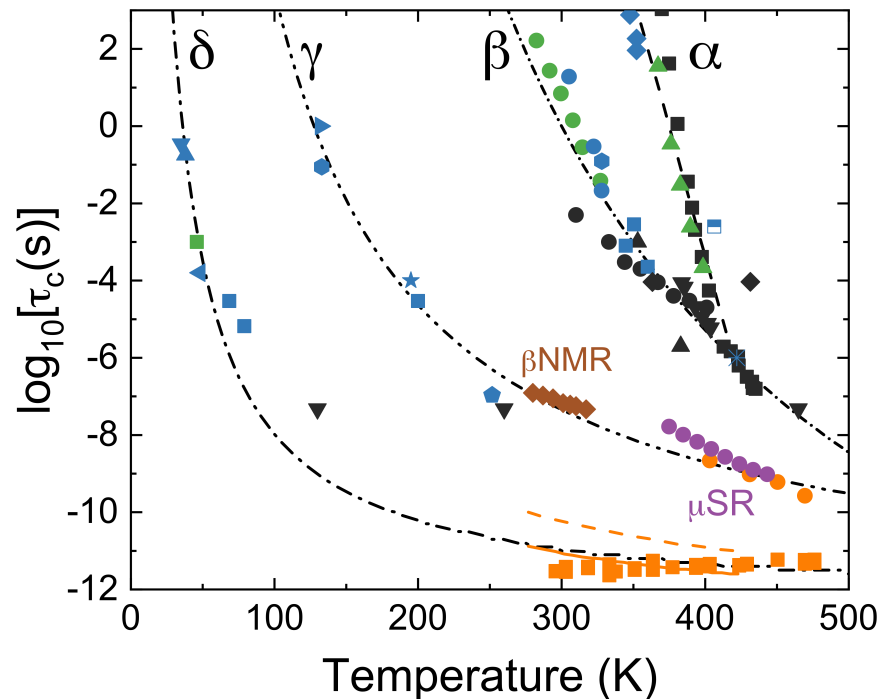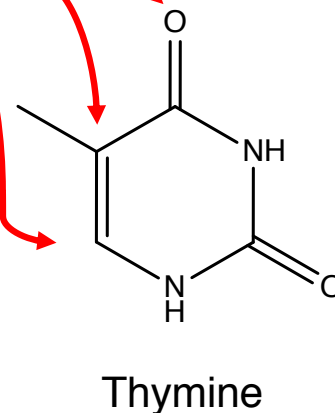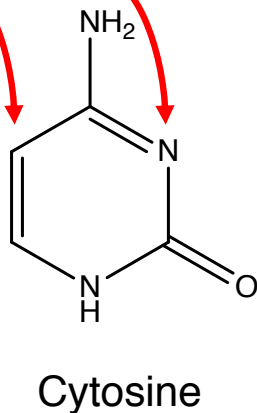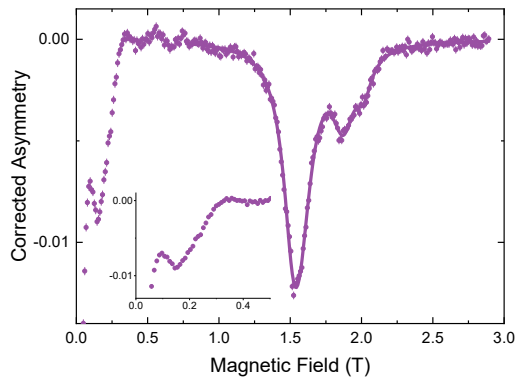
Biological Systems: Mu Addition to Nucleobases

Adenine

Guanine

Cytosine

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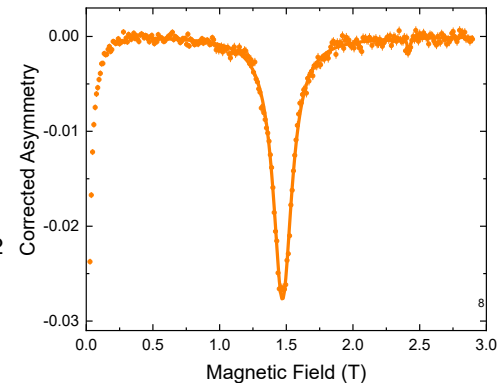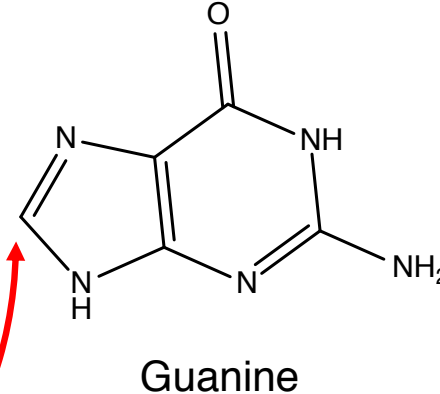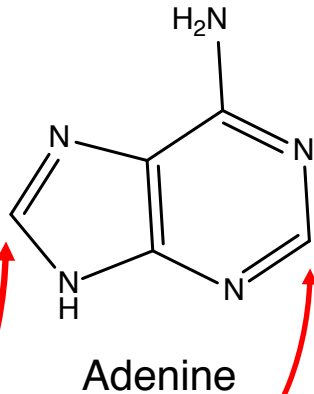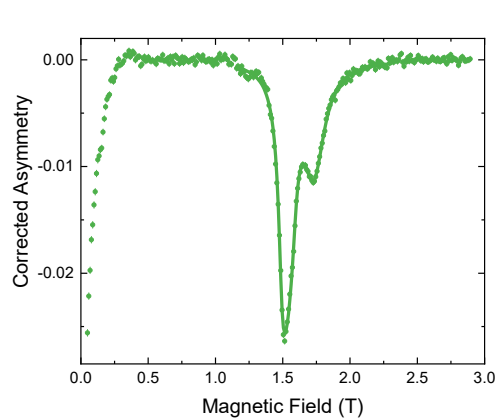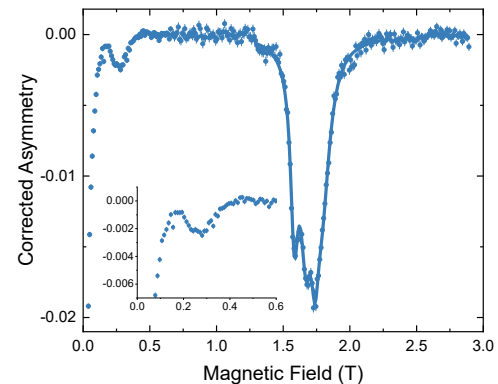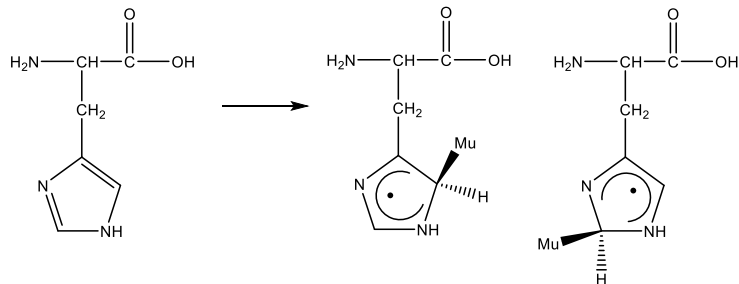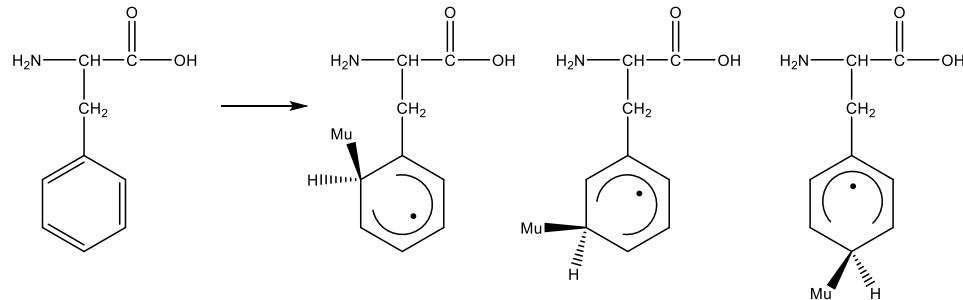
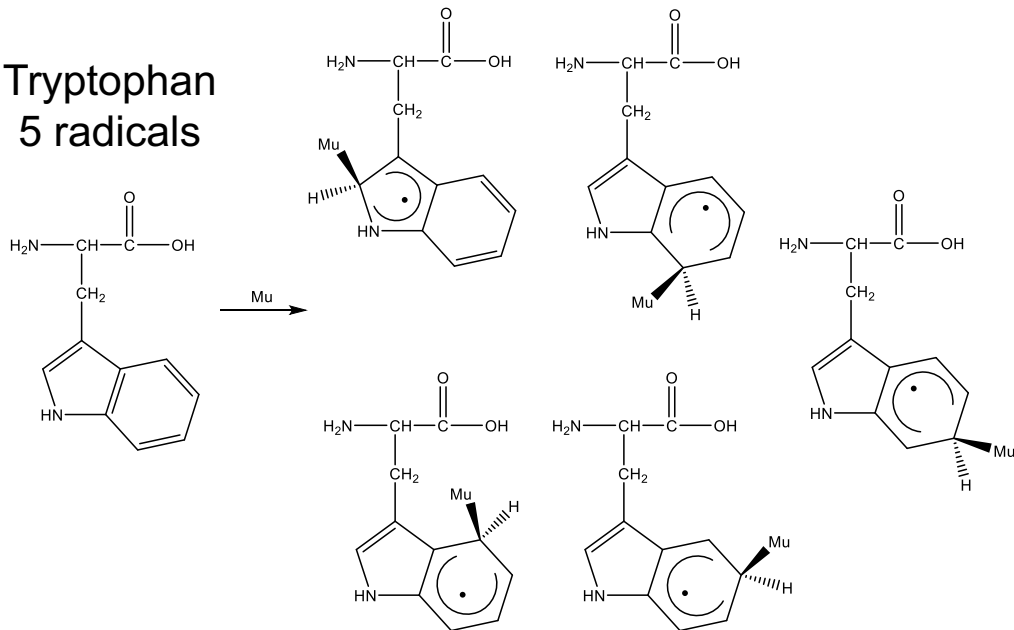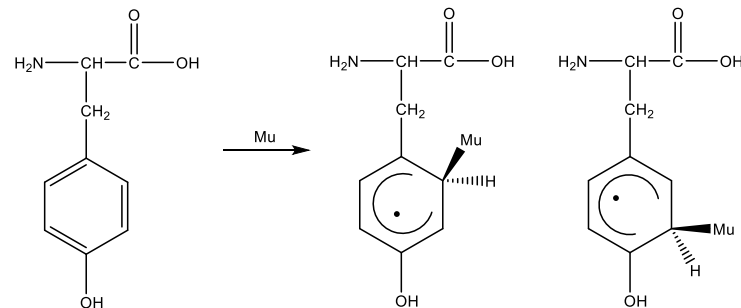# Biological Systems: 4 of 21 Amino Acids Have Unsaturated Side Groups

Histidine – 2 radicals

Phenylalanine – 3 radicals
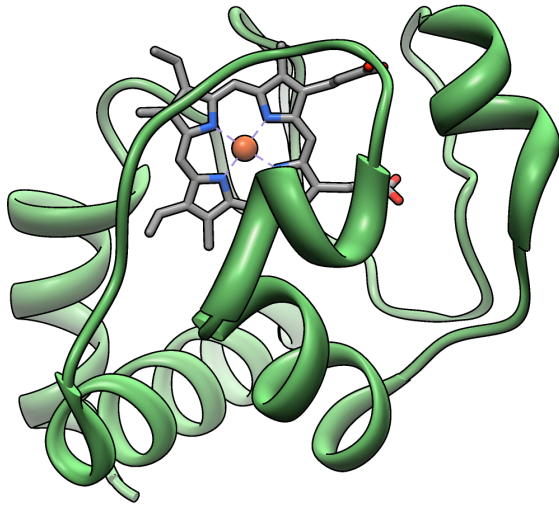
Tryptophan
5 radicals

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.

K. Nagamine, Eur. Phys. J. A **13**, 189 (2002)
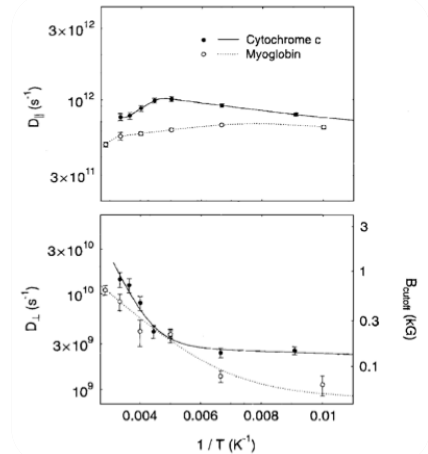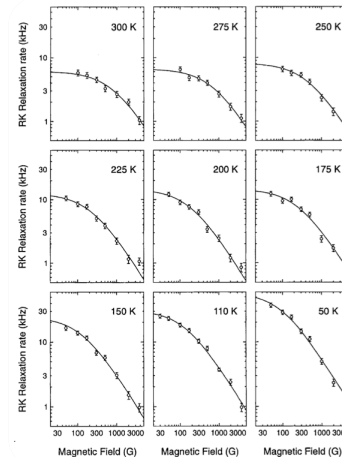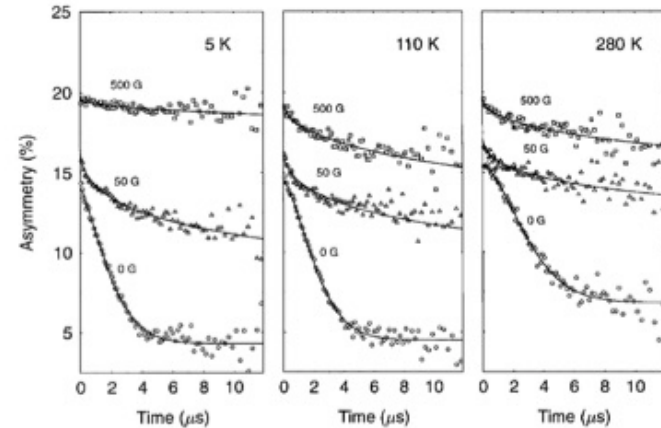
Conclusions

- 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

- E. Roduner, *The Positive Muon as a Probe in Free Radical Chemistry: Potential and Limitations of the µSR Techniques*, (Springer-Verlag, Berlin, Heidelberg 1988).

- D. C. Walker, *Muon and Muonium Chemistry*, (Cambridge University Press, U.K. 1983).

- I. McKenzie and E. Roduner, Naturwissenschaften 96, 873, (2009).

- I. McKenzie, Annual Reports Section C (Physical Chemistry) 109, 65, (2013).