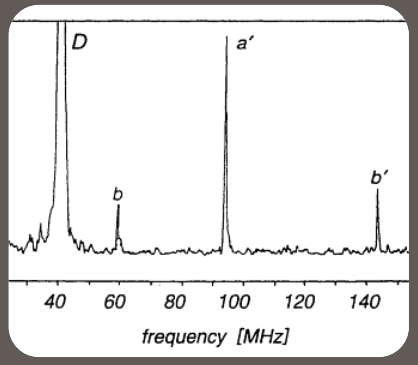
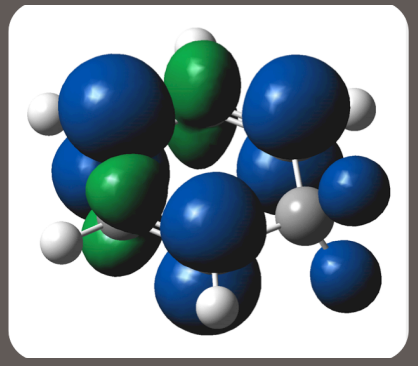
TRIUMF

Canada's national laboratory for particle and nuclear physics
Laboratoire national canadien pour la recherche en physique nucléaire
et en physique des particules

μSR of Free Radicals

Iain McKenzie | CMMS | TRIUMF



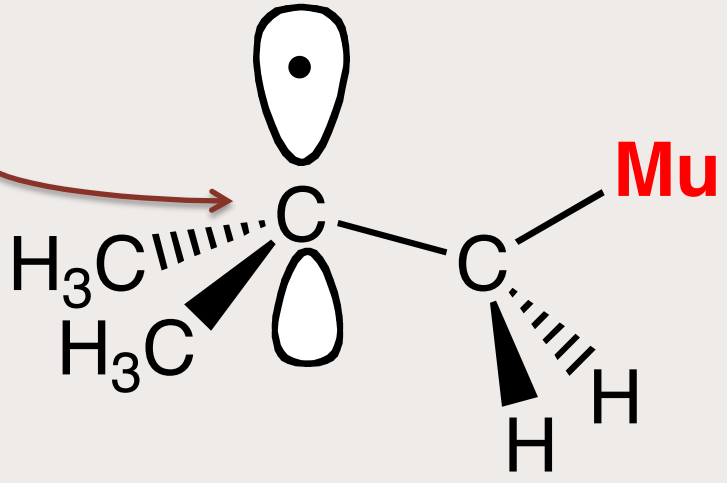


What is a Radical?

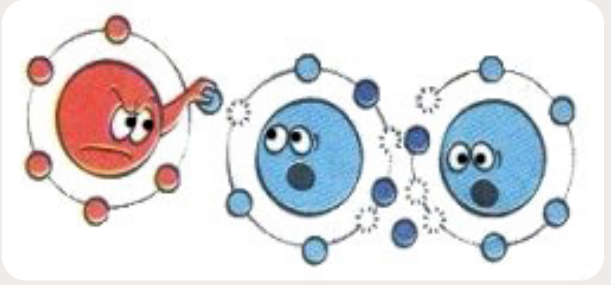
What is a Radical?

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

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"



Why Study Radicals?

$$\text{reactants} \rightarrow [\text{intermediates}] \rightarrow \text{products}$$

radicals
carbenes
carbocations
carbanions

- Through a better understanding of the properties of the intermediates, we can better control chemical reactions

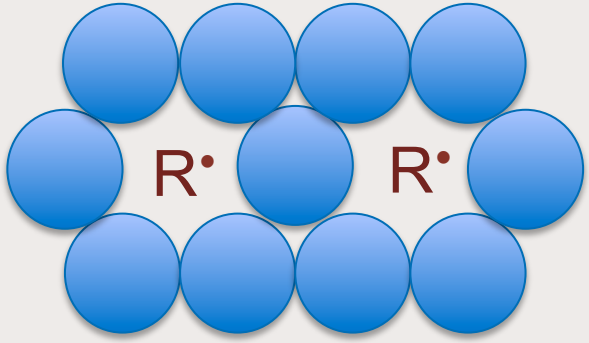
Difficulties in Studying Radicals

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

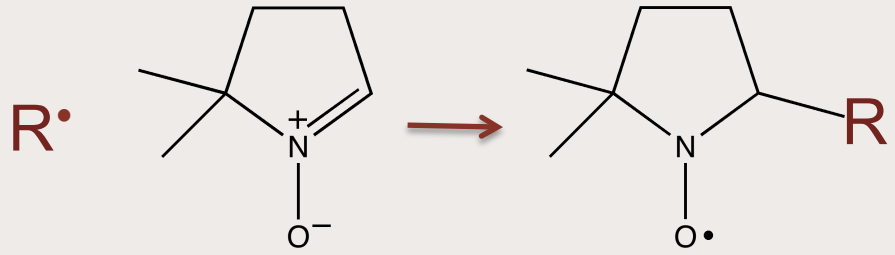
Signal ~ [R•]

Termination reaction

Matrix Isolation

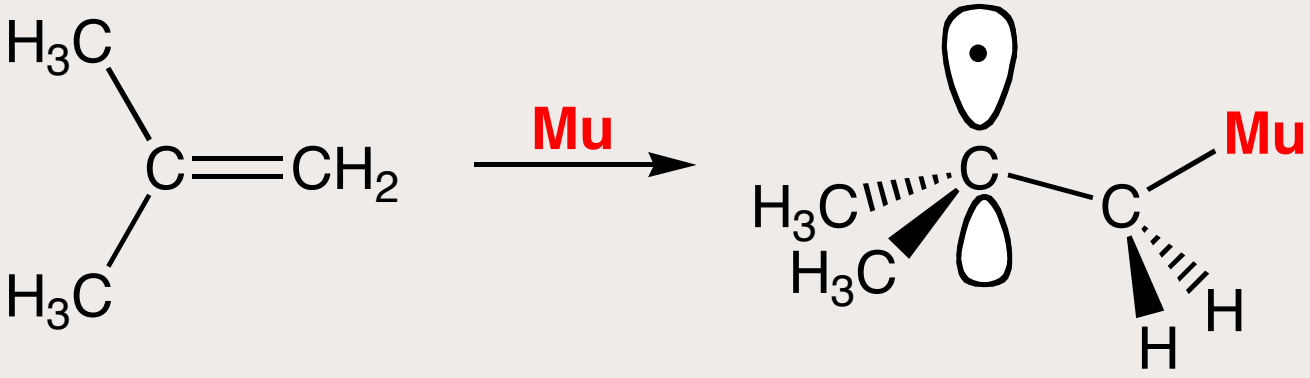


Spin Trapping



Muoniated Radicals

- Radicals produced by addition of Mu to an unsaturated bond



- Extremely dilute (no self termination reactions)
- Distribution of radicals depends on relative addition rates
  - Mu adds preferentially to less substituted end of C=C bond
  - Addition to isolated C=C bond faster than addition to phenyl ring
  - Addition to C=C ~100x faster than to C=O

Hfccs and 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

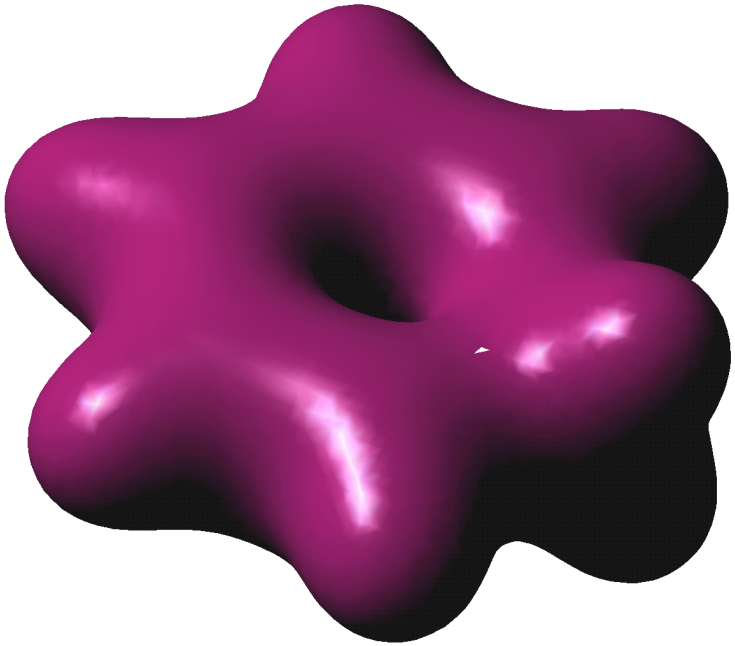
$$\rho^{SPIN}(\vec{r}) = \rho^{\alpha}(\vec{r}) - \rho^{\beta}(\vec{r})$$

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

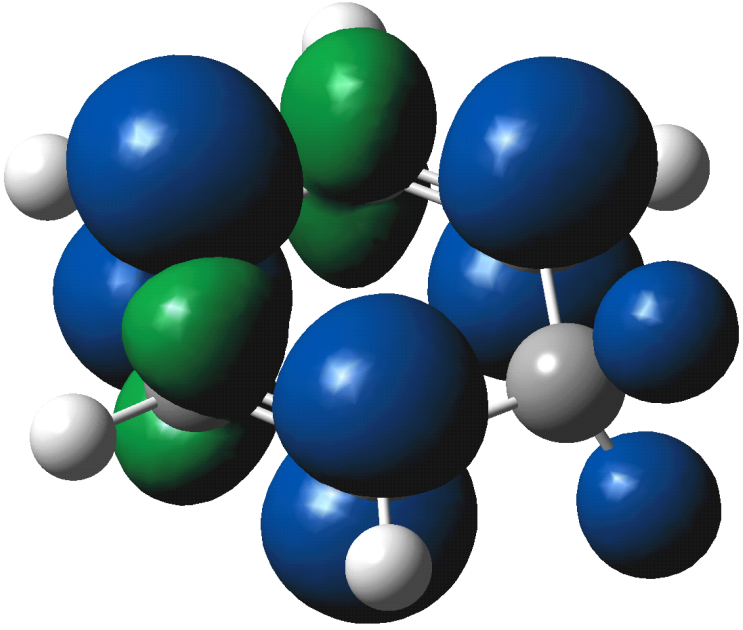
- The hfcc is directly proportional to the unpaired spin density at the nucleus

Electron and Spin Density in C_6H_6Mu

Electron density



Spin density

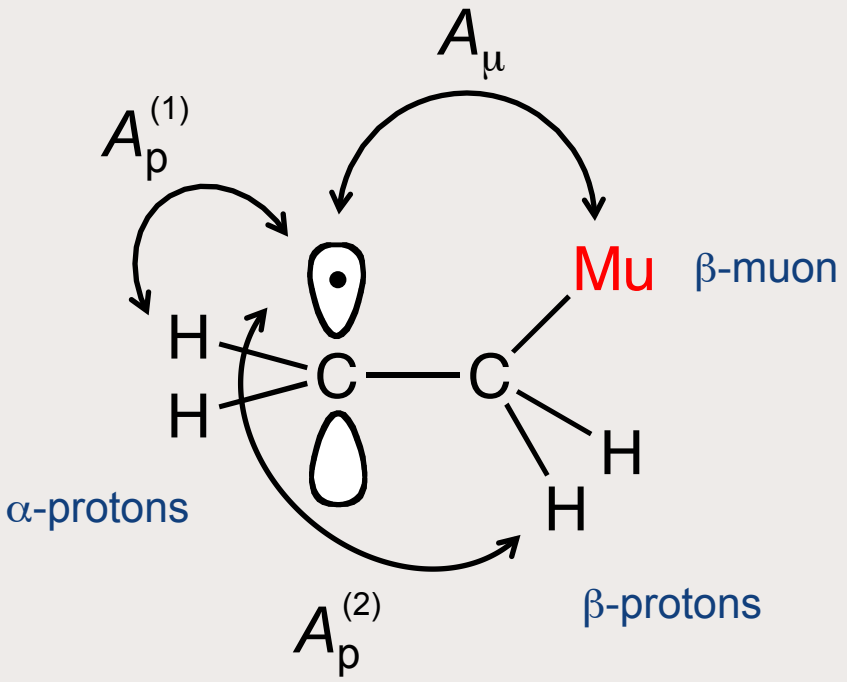


Blue: $\rho^{\alpha} > \rho^{\beta}$ Positive spin density

Green: $\rho^{\alpha} < \rho^{\beta}$ Negative spin density

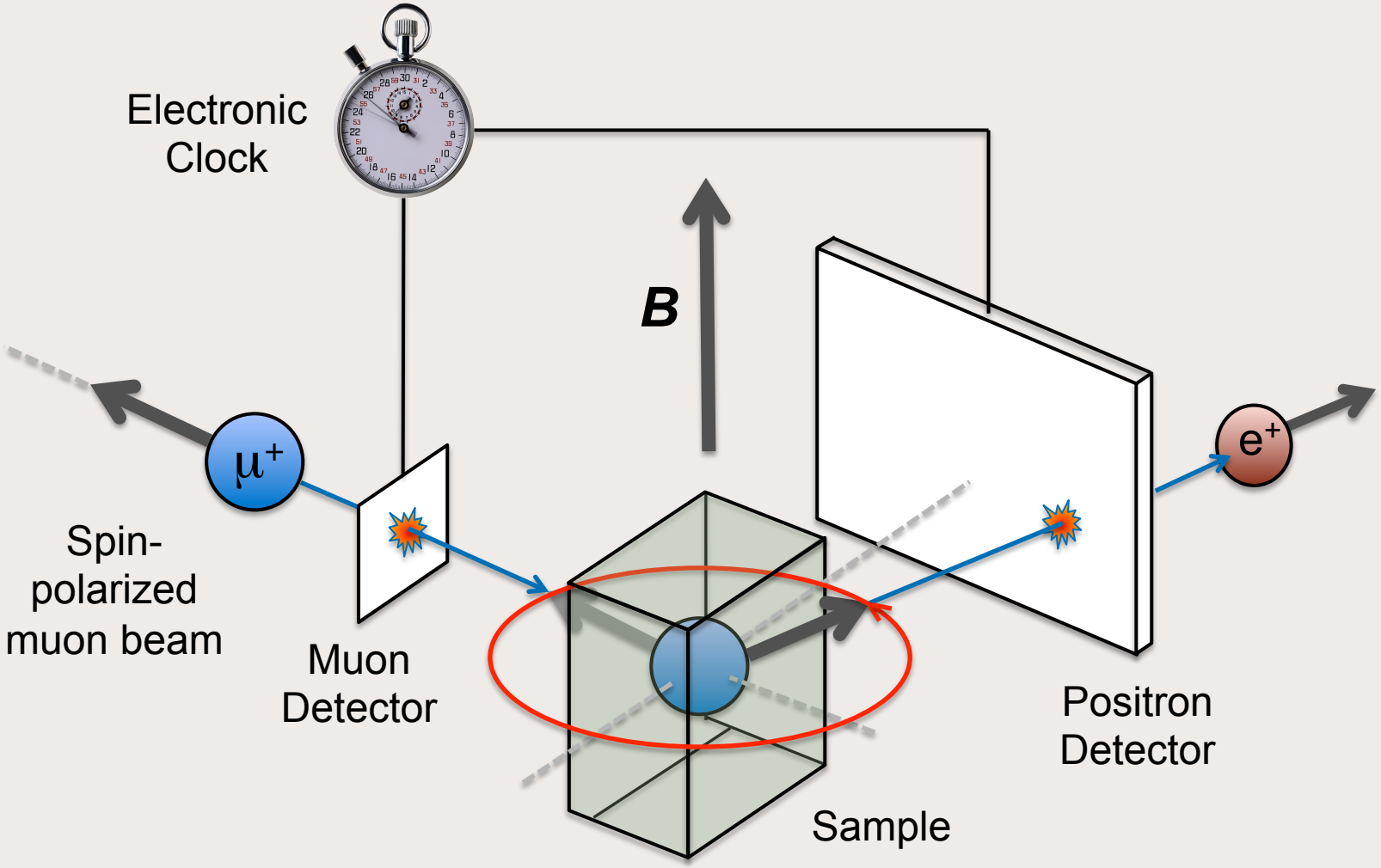
Hyperfine Coupling Constants

- A_X is the strength of the interaction between the spin of the electron and the magnetic dipole of the nucleus X
- Muon and nuclear hfccs provide information about the structure, configuration and conformation of the radical

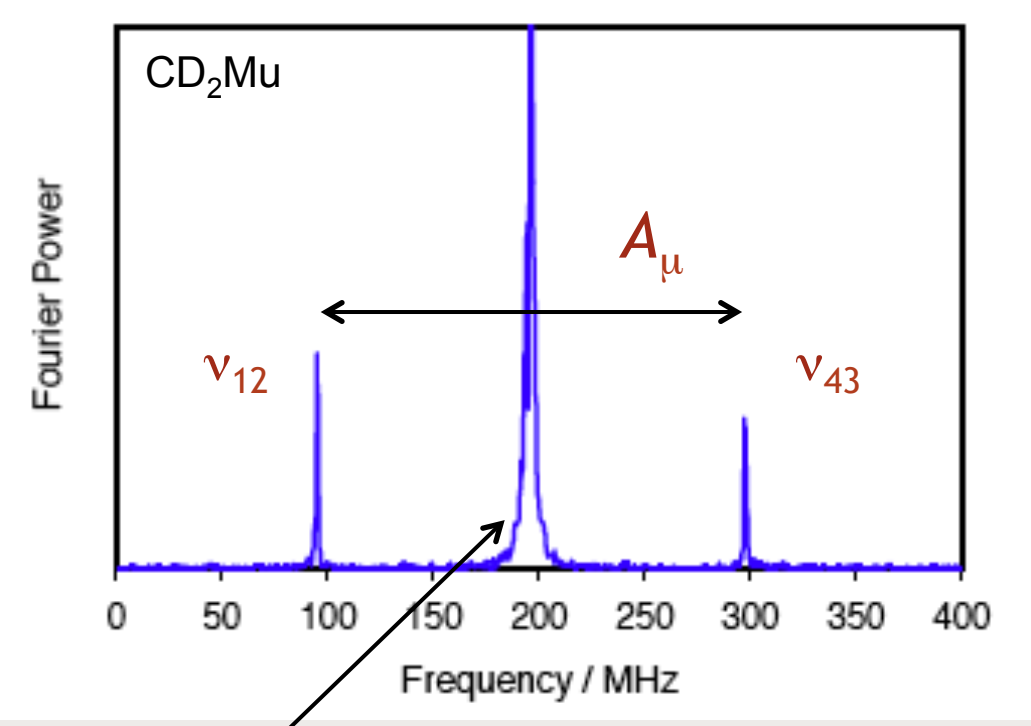


$$A_X = A_X^{(\text{isotropic})} + A_X^{(\text{dipole})}$$

Transverse Field Muon Spin Rotation



Transverse Field Muon Spin Rotation



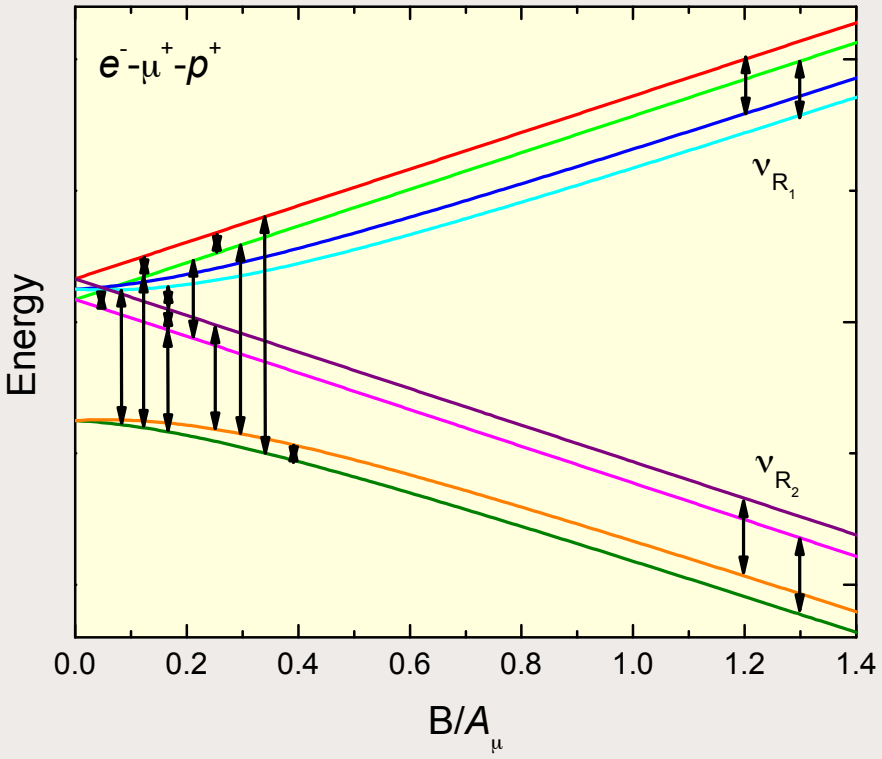
Diamagnetic frequency ν_D

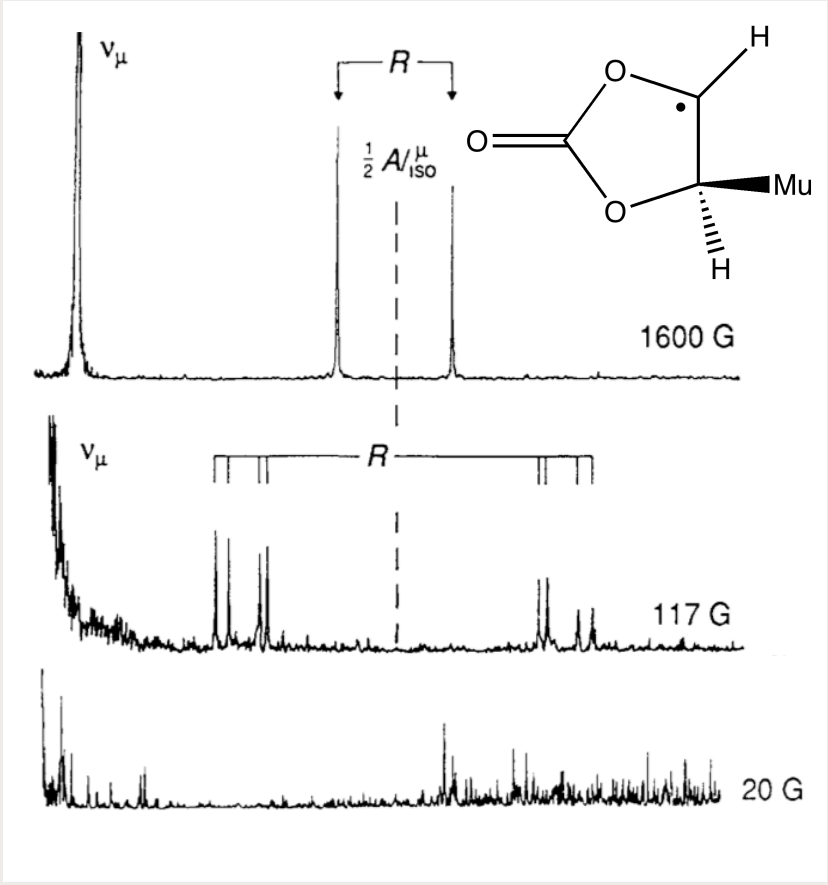
$$\nu_D = \gamma_\mu B$$

$$A_\mu(MHz) = \nu_{43} - \nu_{12}$$

Transverse Field Muon Spin Rotation

$$\nu_R = \nu_\mu \pm \tfrac{1}{2} A_\mu$$





Limitations of TF-μSR

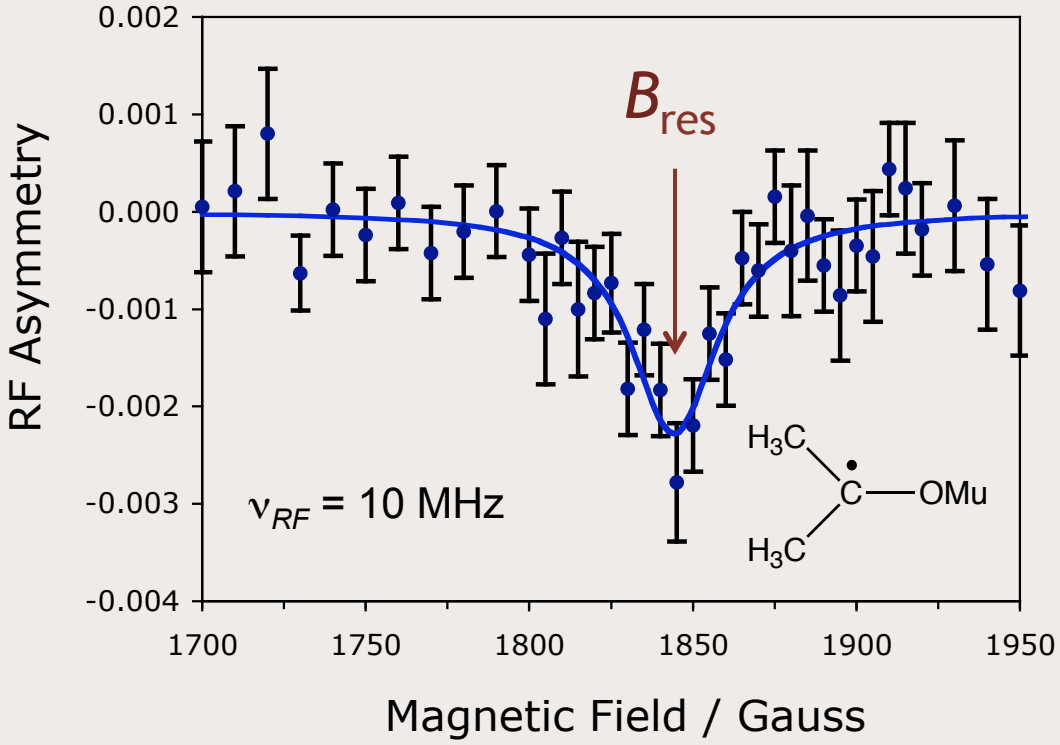
- Requires high concentration (~1 M) of precursor to prevent loss of polarization.

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

- 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

- You can't tell the muon where to go i.e. multiple muoniated radicals are formed, often ones you don't want

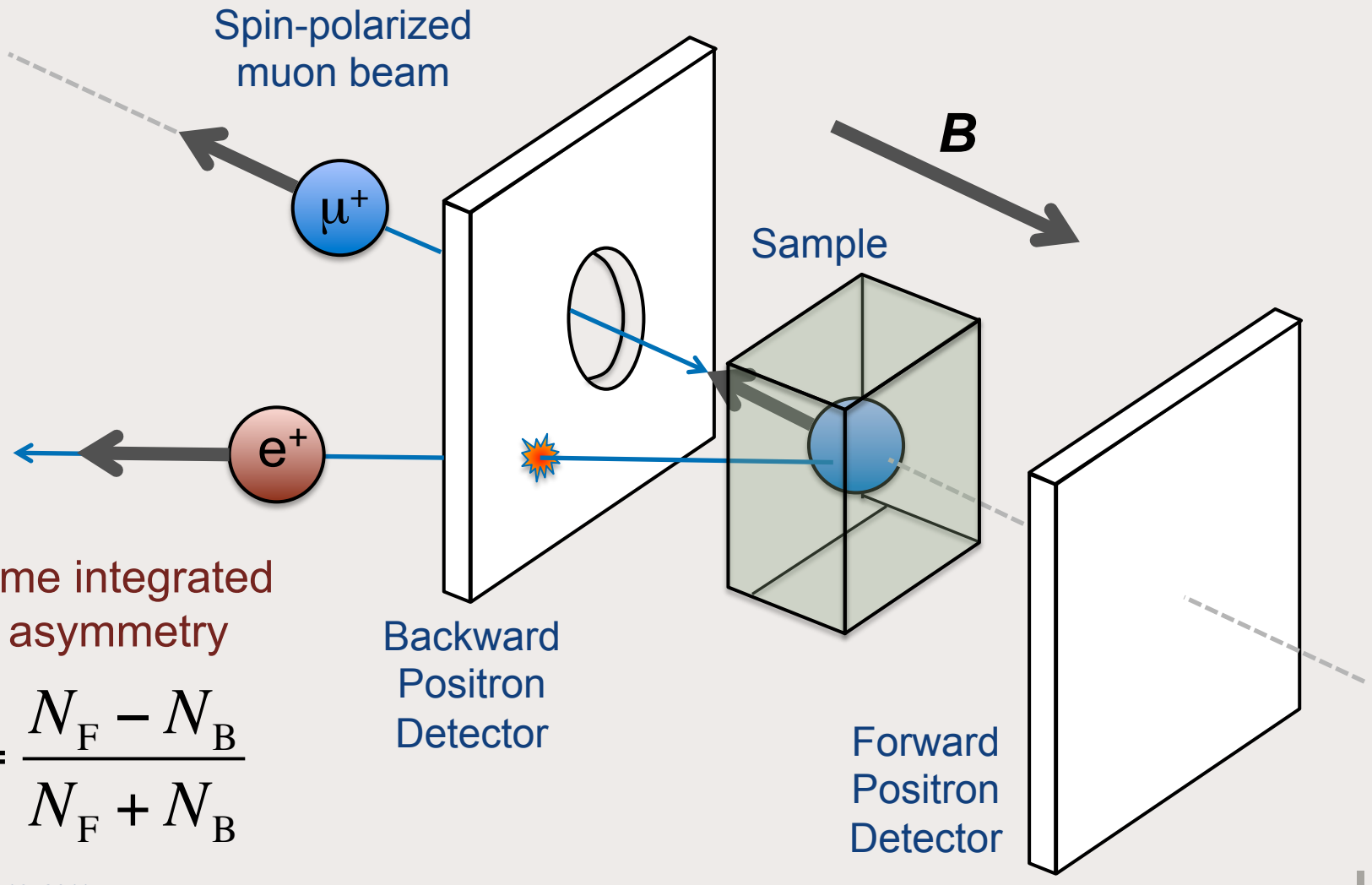
Radio Frequency Muon Spin Resonance



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

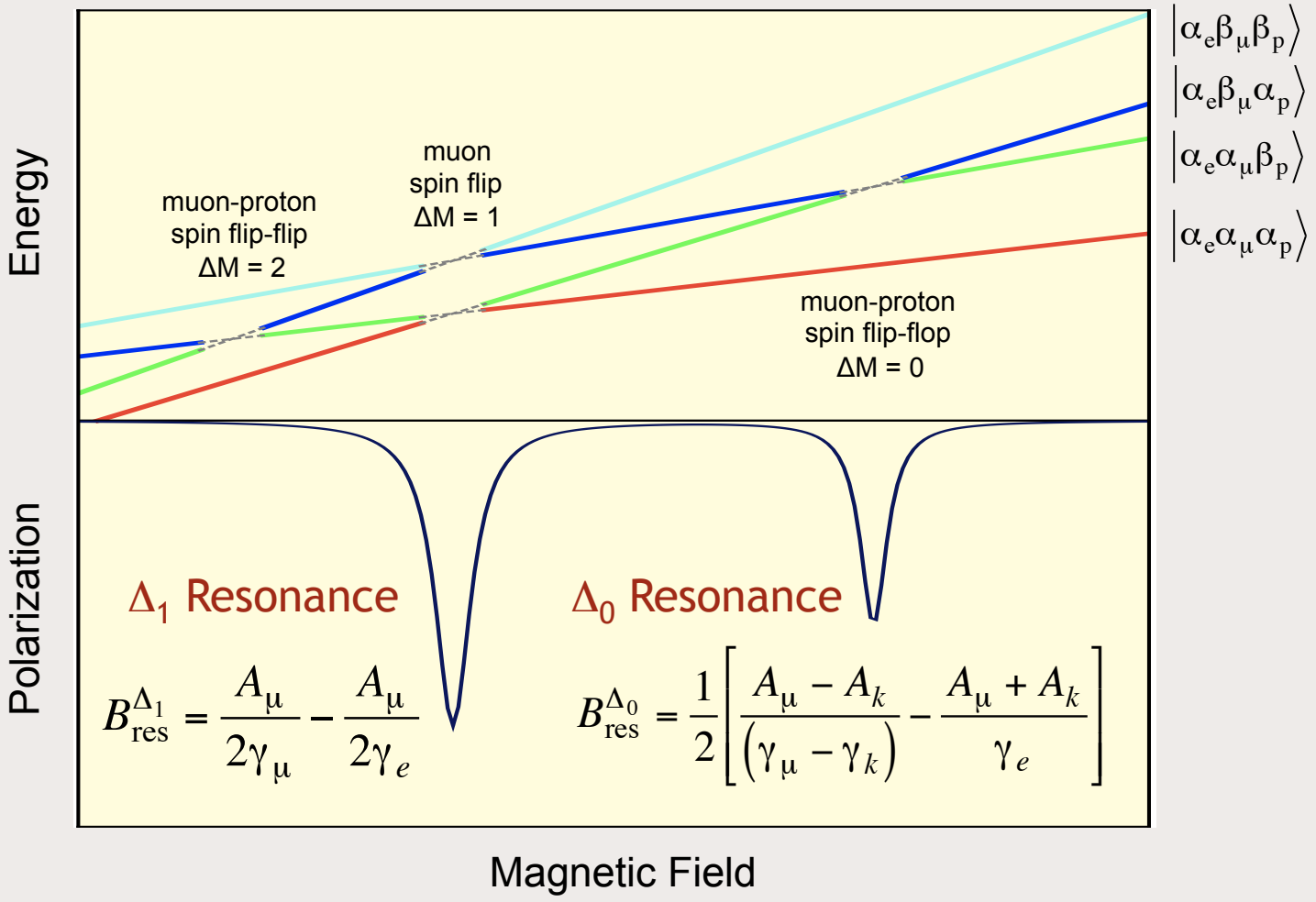
- Measure A_μ for slowly formed radicals (slow Mu addition or dilute solutions)

Level Crossing Resonance

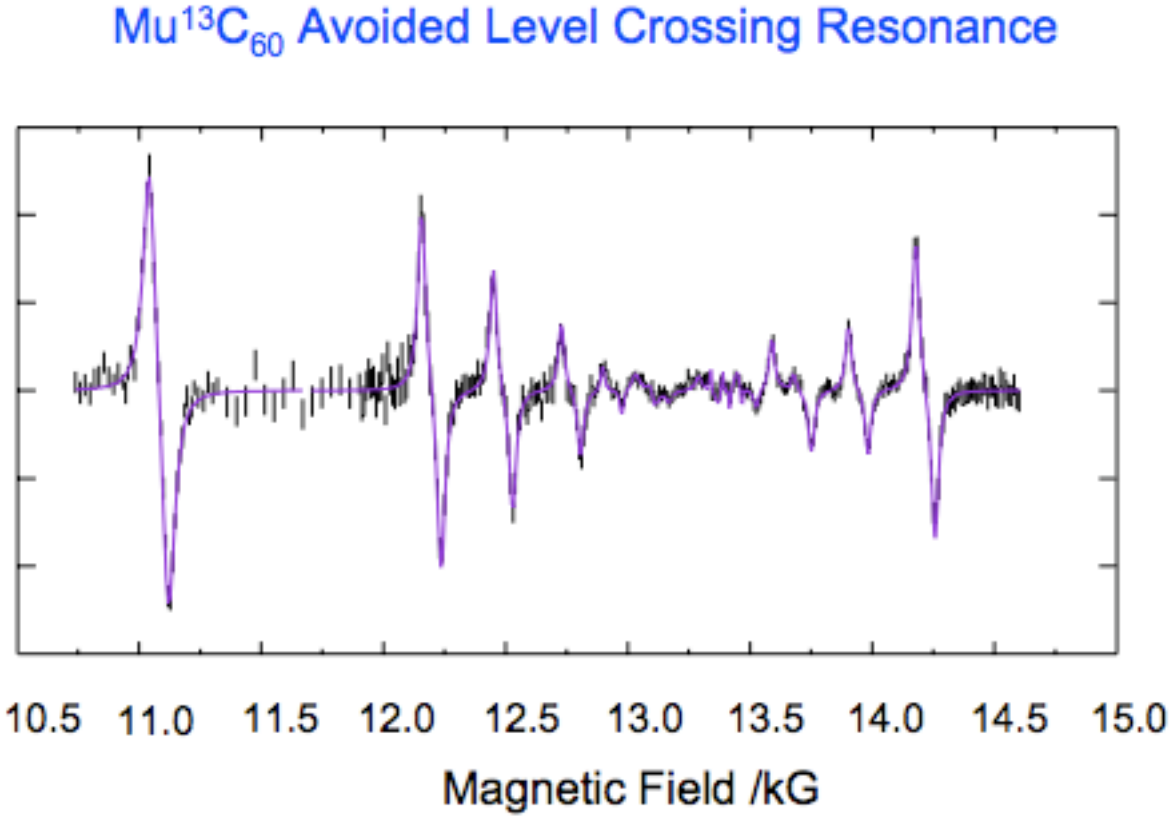


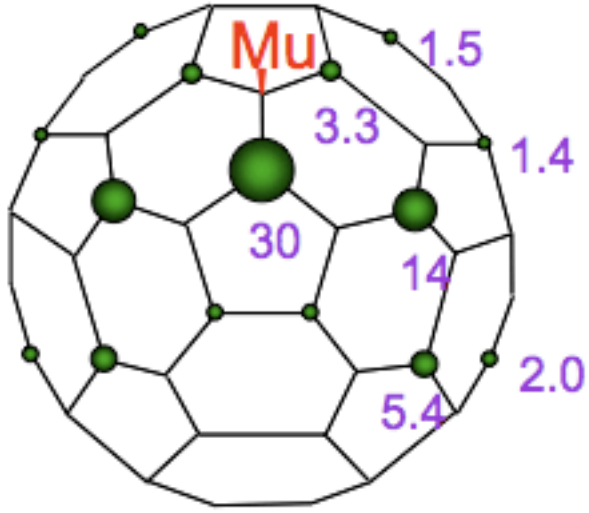
$$A = \frac{N_F - N_B}{N_F + N_B}$$

Level Crossing Resonance



ALC-μSR of $Mu^{13}C_{60}$

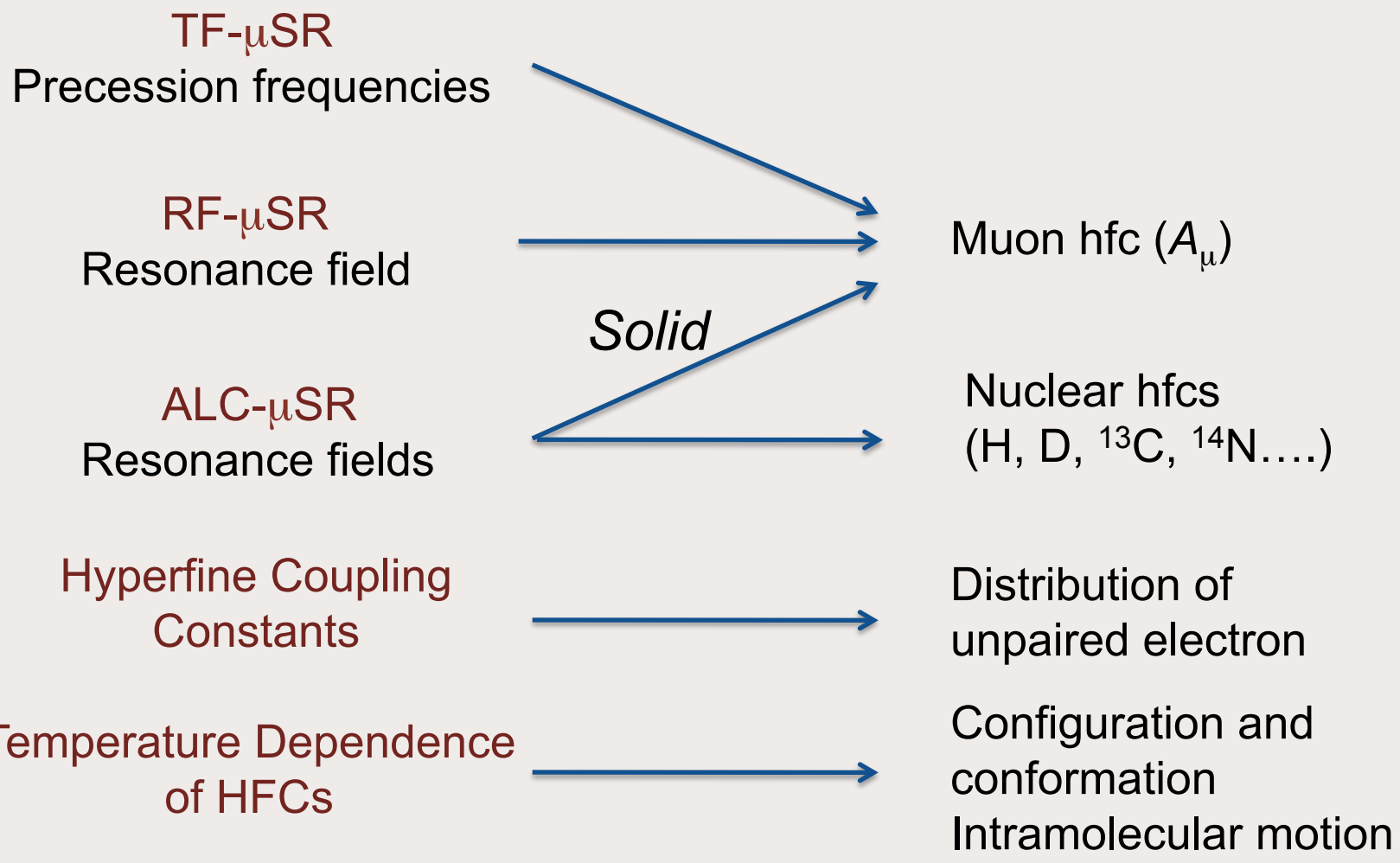




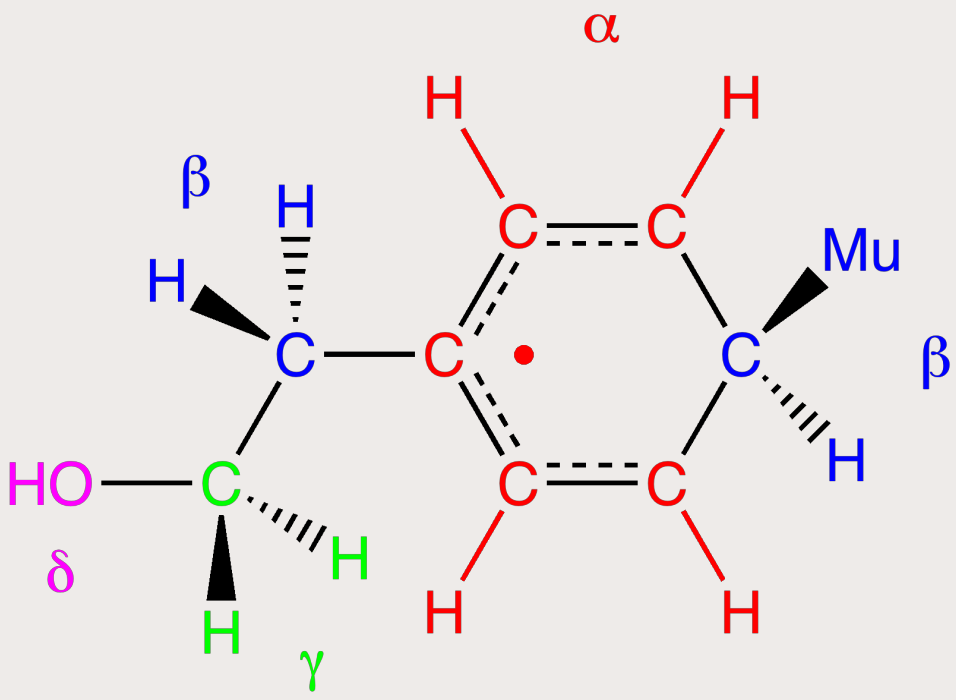
% Unpaired Spin Density

Percival *et al. Chem. Phys. Lett.* **1995**, *245*, 90

Identification of Muoniated Radicals



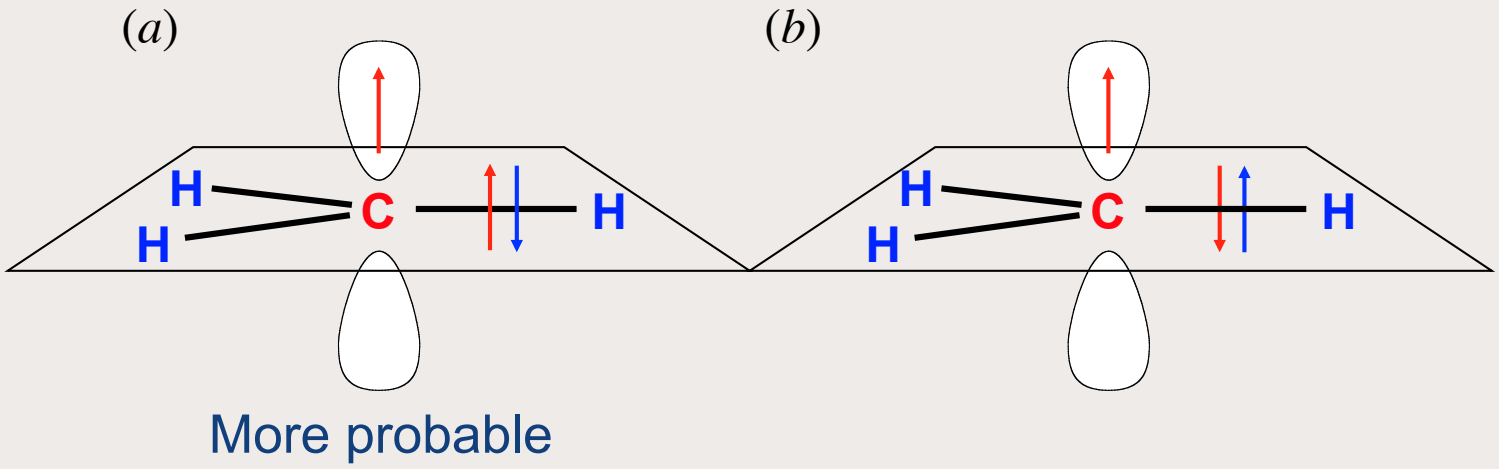
Nomenclature



- 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 Coupling of α-Nuclei

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



More probable

McConnell equation for α-nuclei

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

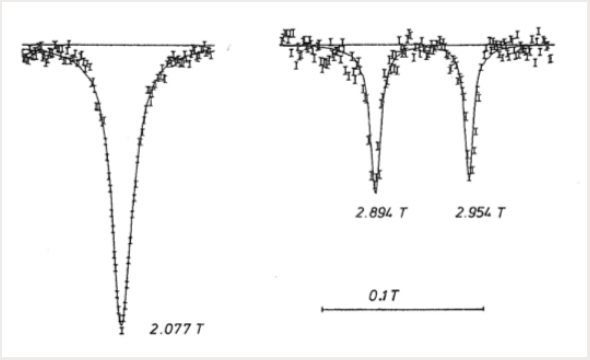
- ρ^{π} is the π-electron population at the adjacent carbon atom
- Q_p ~ -75 MHz

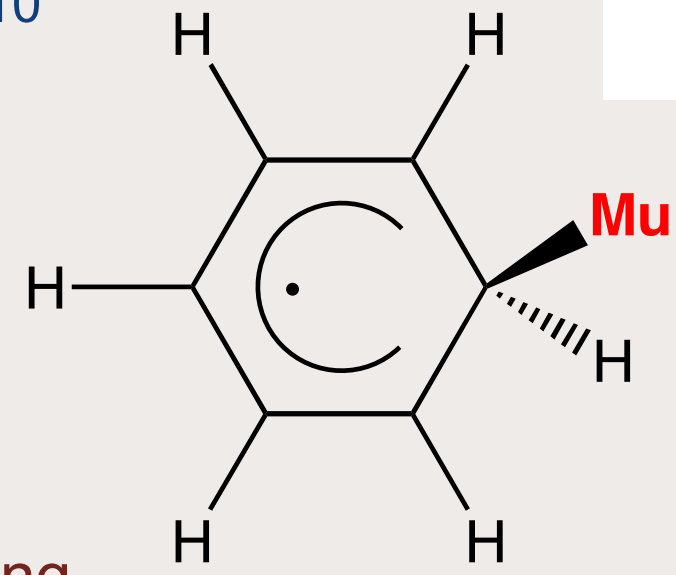
Muoniated Cyclohexadienyl Radical

Meta (2H α)

A_p = +7.5 MHz

ρ ~ -0.10





Para (1H α)

A_p = -36.8 MHz

ρ ~ +0.49

Muon (β)

A_μ = 514.6 MHz

Methylene (1H β)

A_p = 125 MHz

Ortho (2H α)

A_p = -25.5 MHz

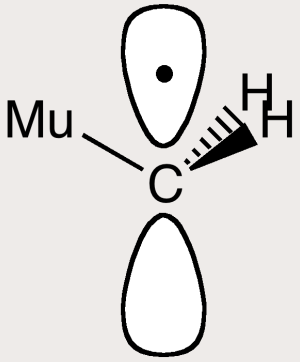
ρ ~ +0.35

Spin density around ring

2(0.35)+2(-0.10)+1(0.49)

~1

Out-of-plane Vibrations of α-Protons



- Direct overlap of nuclei with SOMO gives positive spin density contribution than partially counteracts negative spin density due to spin polarization

- Out-of-plane vibrations cause the magnitude of α proton hfccs to decrease

$$A_{\mathrm{X}}(T) \approx \frac{\sum_{\nu=0}^{\infty} A_{\mathrm{X}}^{\nu} e^{-E_{\nu}/k_{\mathrm{B}}T}}{\sum_{\nu=0}^{\infty} e^{-E_{\nu}/k_{\mathrm{B}}T}}$$

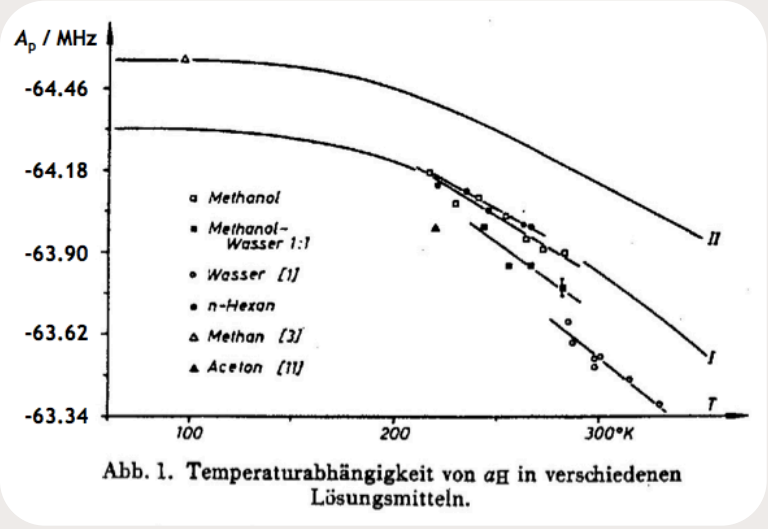
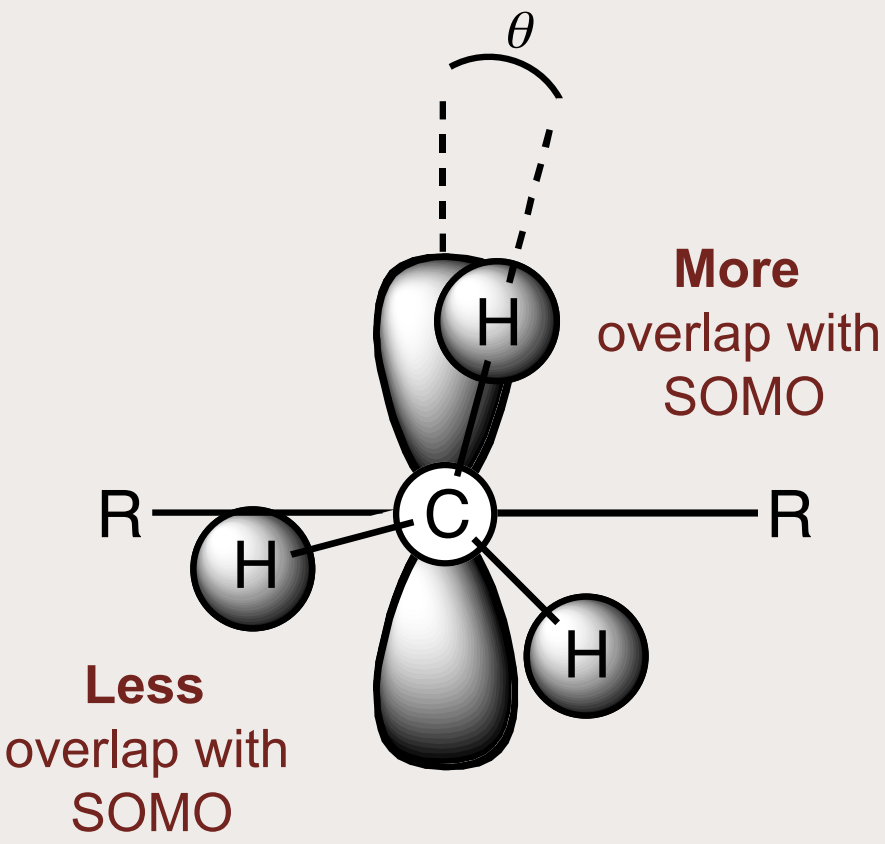


Abb. 1. Temperaturabhängigkeit von a_H in verschiedenen Lösungsmitteln.

Hyperfine Coupling of β-Nuclei



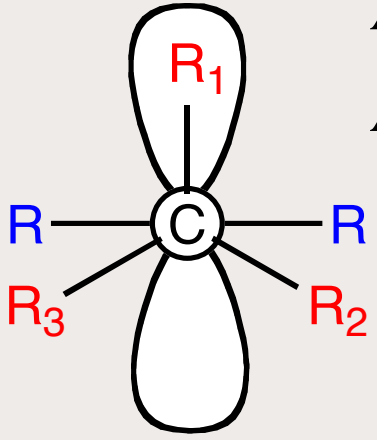
$$A_p^{\beta} = \left[L + M \cos^2 \theta \right] \rho^{\pi}$$

- *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
- ρ^{π} is the spin density on adjacent carbon

Pseudo-Methyl Groups

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

Freely rotating: $A_R = \left(L + \frac{1}{2}M\right)\rho^{\pi}$

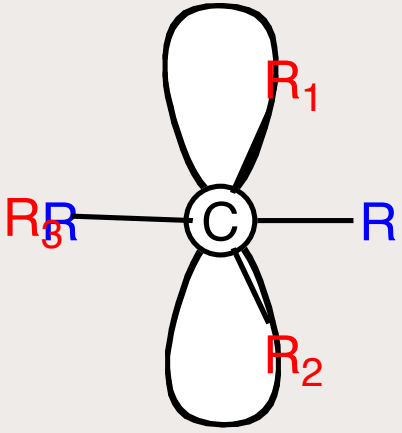


$$A_{R_1} = \left(L + M\right)\rho^{\pi}$$

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

$$\frac{dA_{R_1}}{dT} < 0$$

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



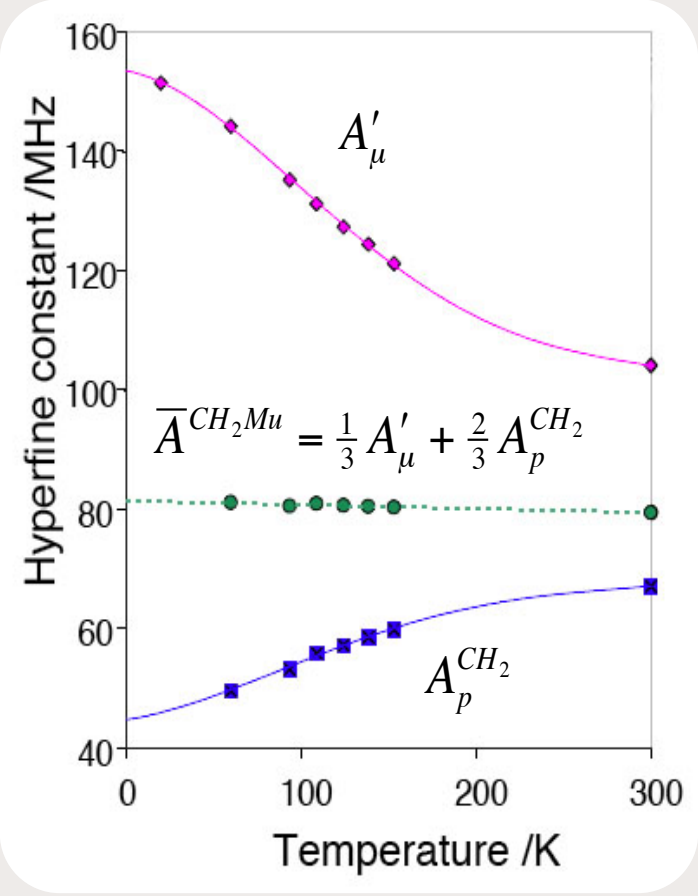
$$A_{R_{1(2)}} = \left(L + \frac{3}{4}M\right)\rho^{\pi}$$

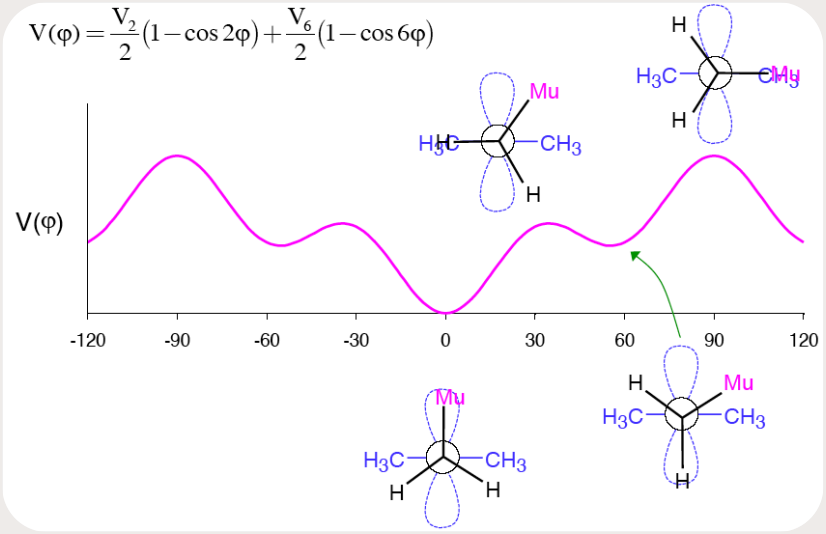
$$A_{R_3} = L\rho^{\pi}$$

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

$$\frac{dA_{R_3}}{dT} > 0$$

Temperature Dependence of β Hfccs

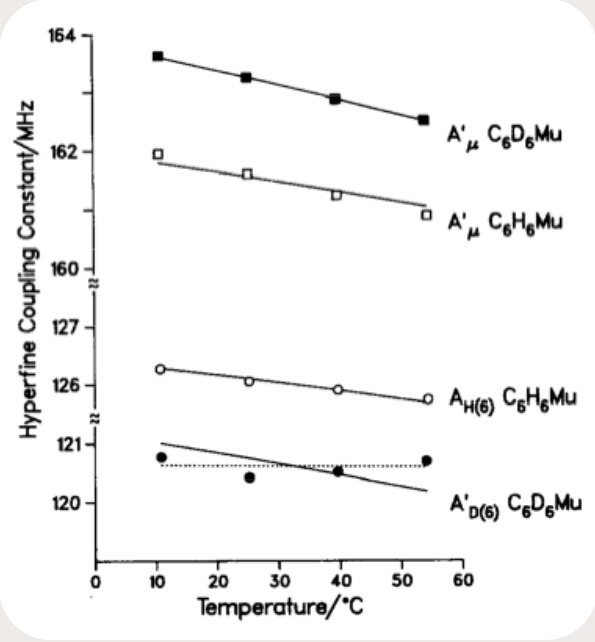




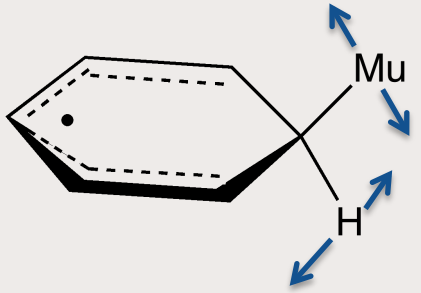
- C-Mu bond preferentially aligns with SOMO

Methylene Groups in C_6H_6Mu

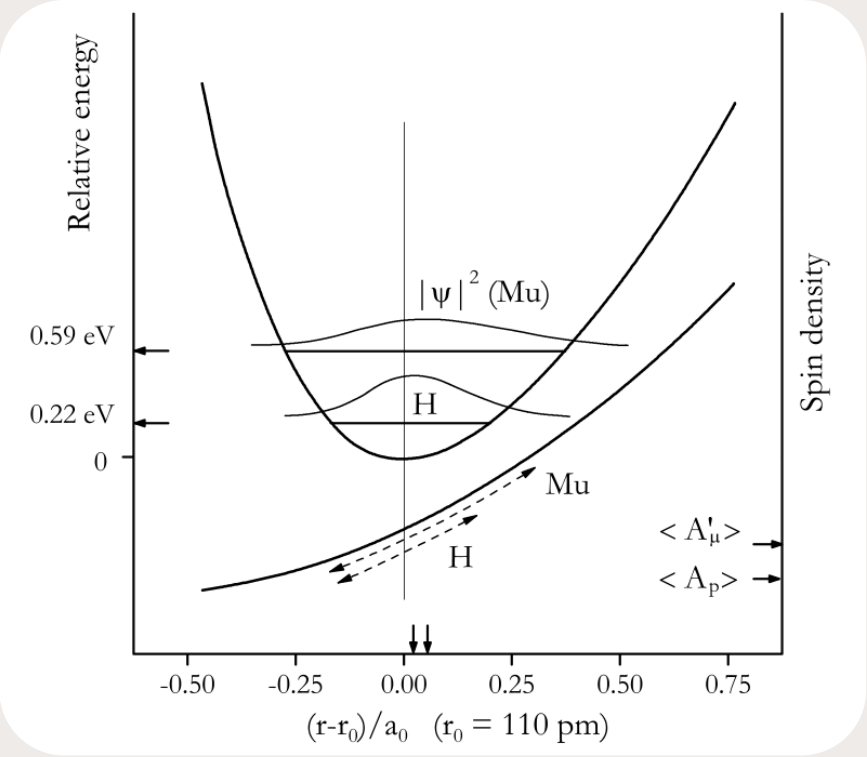
- Hfccs depend on spin density on *both* adjacent carbons
- Methylene (CHMu) group not free to rotate
- Reduction of β hfccs due to scissor motion of CHMu group (slightly increases θ)



$$A_{\mathrm{p}}^{\beta} = \left[L + M\cos^2\theta\right]\left(\sqrt{\rho_{C1}^{\pi}} + \sqrt{\rho_{C5}^{\pi}}\right)^2$$



Isotope Effects on Bond Length

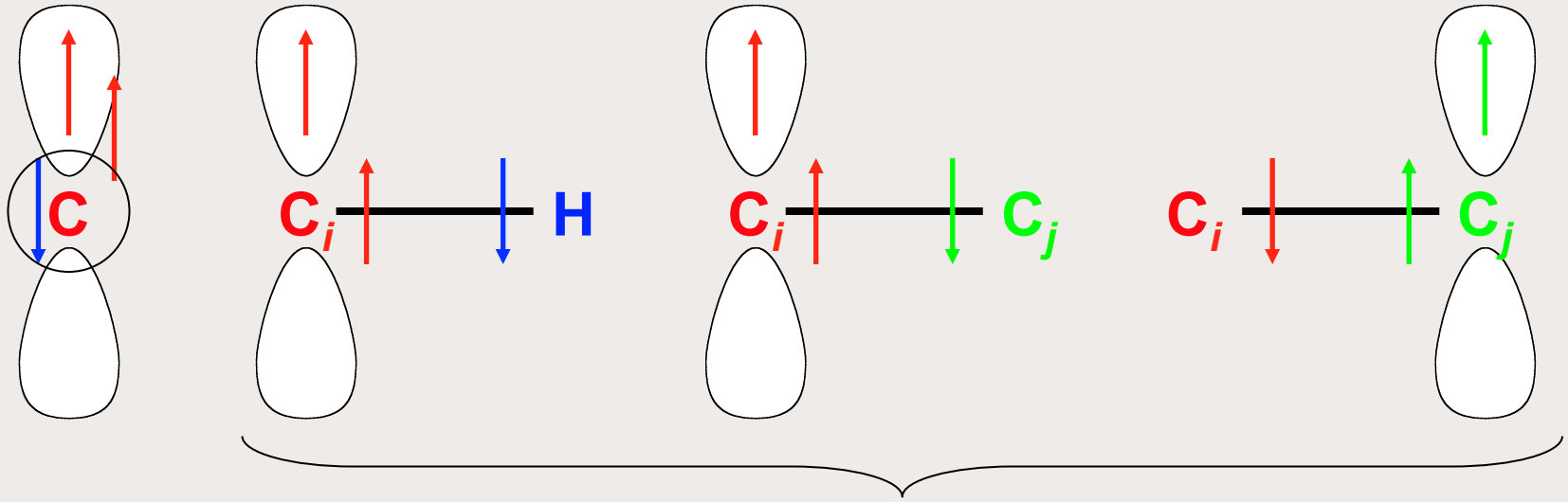


- Asymmetric bond stretching potential results in C-Mu bond being longer than C-H bond.

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

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

^{13}C Hfccs



π,σ spin polarization

Karplus Fraenkel equation for planar radicals

$$a_{C_i} = \left(S^{C_i} + \sum_{j=1}^{3} Q_{CX}^{X} \right) \rho_{C_i} + \sum_{j=1}^{3} Q_{XC}^{C} \rho_{C_j}$$

S^{C_i} = -12.7 G

Q_{CH}^{C} = +19.5 G

$Q_{C_iC_j}^{C}$ = +14.4 G

$Q_{C_jC_i}^{C}$ = -13.9 G

Quantum Calculations

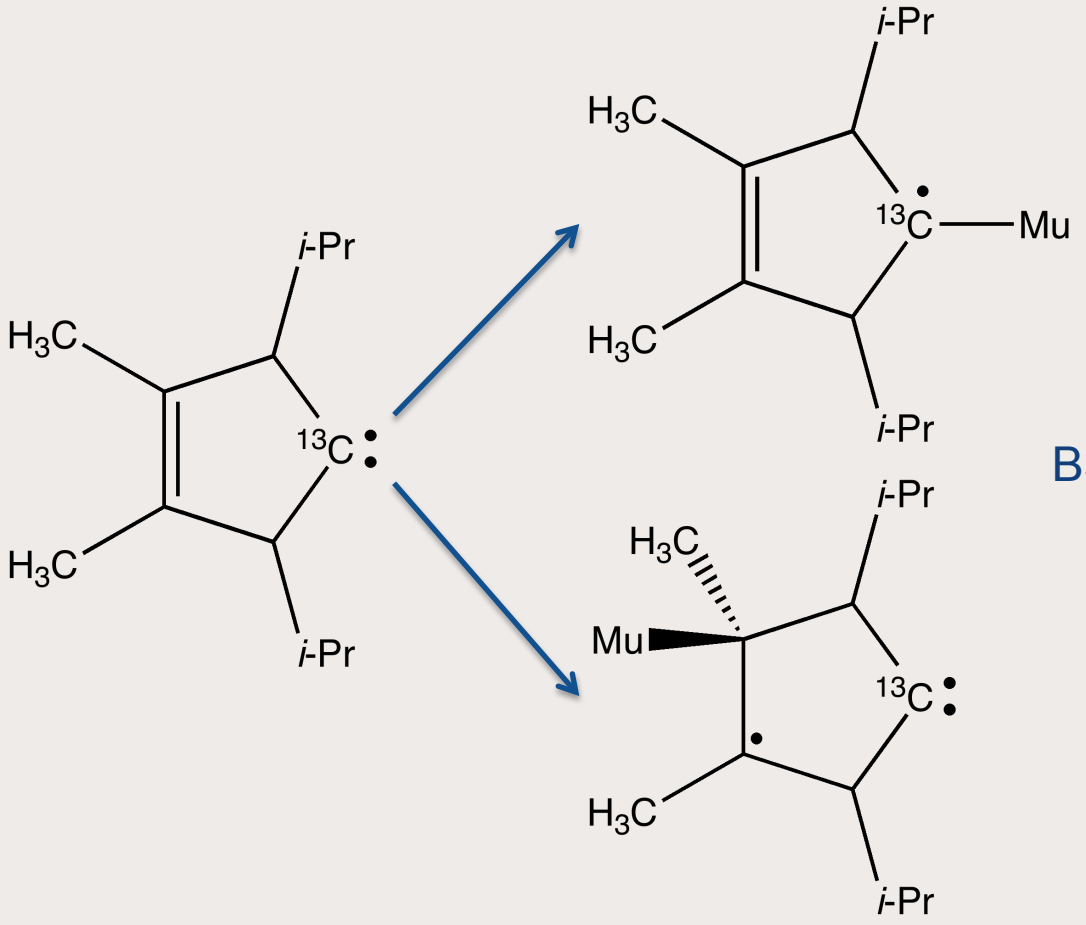
- μSR spectra do not give direct access to the radical structure. This must be inferred.
- Magnetic properties of a radical often depend on the subtle interplay of several different effects.(e.g. vibrational averaging, solvent effects, substituent effects….)
- Quantum calculations are used to
  - support 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 determining the magnetic properties of a radical

Ab Initio Calculations

- Use unrestricted method (treats α and β electrons separately) to correctly account for spin polarization.
- Density functional methods (such as B3LYP) 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
- Benchmark your calculations against closely related known systems

Mu Adducts of Carbenes

- How do stable carbenes react with a simple free radical?

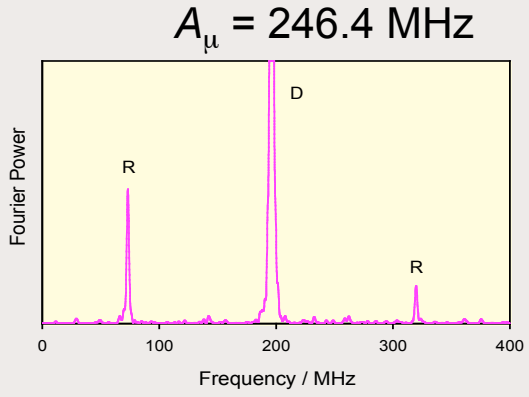


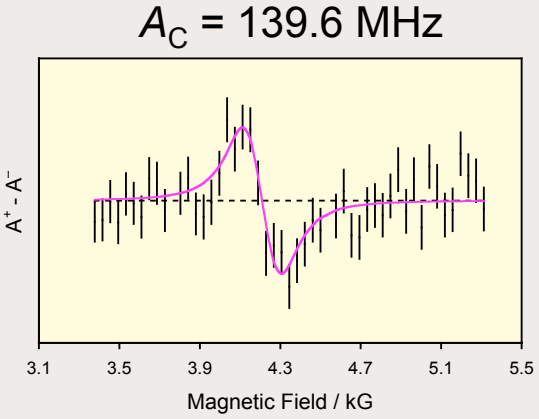
A_μ	278.8 MHz
A_C(C2)	136.0 MHz
A_N(N1)	8.3 MHz
A_N(N3)	8.3 MHz
A_p(CH_3C5)	-

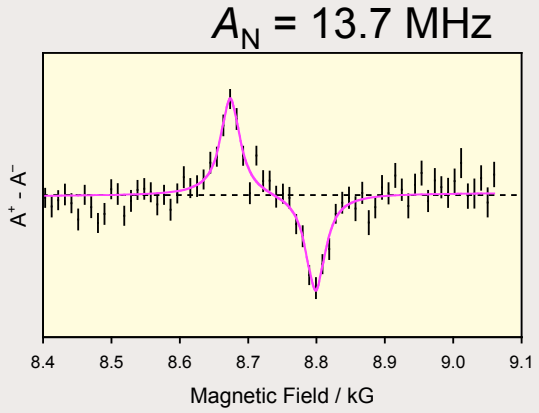
B3LYP/6-311G**//B3LYP/EPR-III

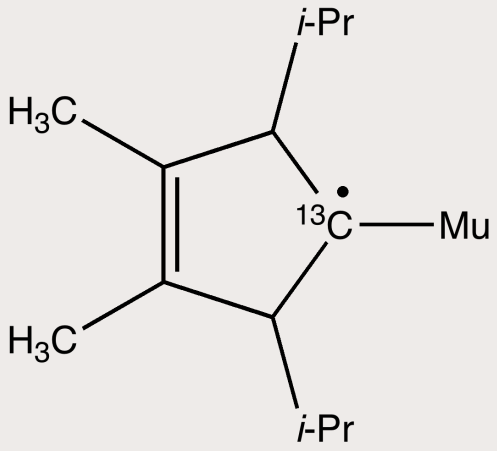
A_μ	401.0 MHz
A_C(C2)	7.4 MHz
A_N(N1)	0.5 MHz
A_N(N3)	4.0 MHz
A_p(CH_3C5)	53.1 MHz

Mu Adducts of Carbenes





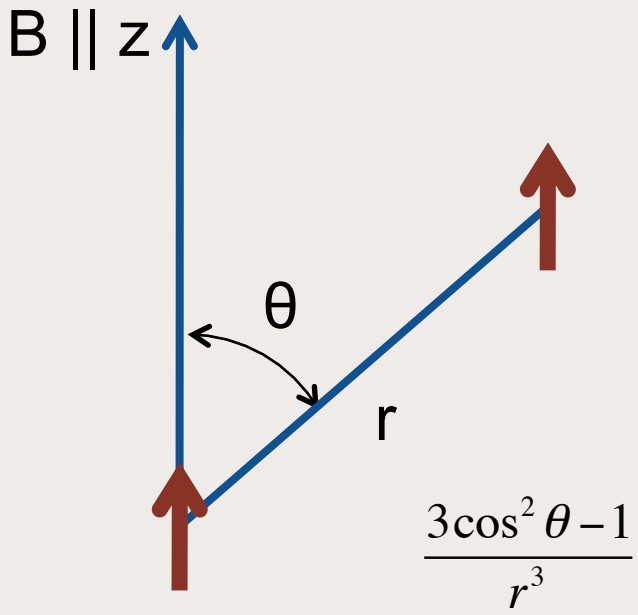




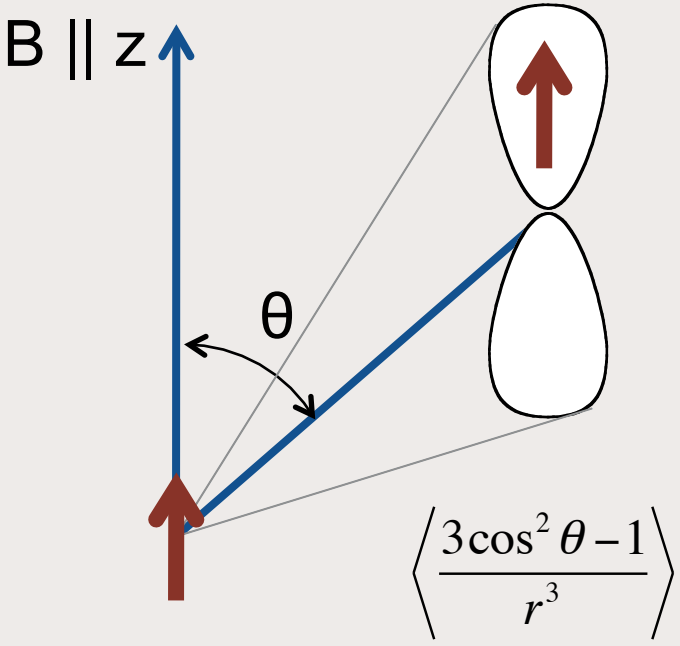
- Structure assigned by comparing hfccs with DFT calculations of possible radicals.

Dipolar Coupling

Point dipole

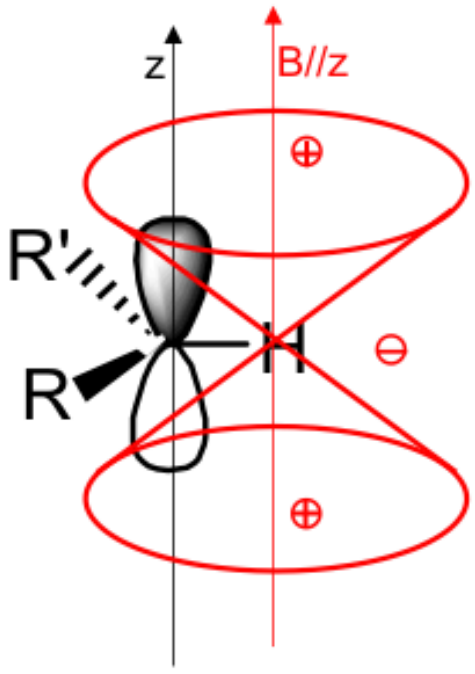


Delocalized electron



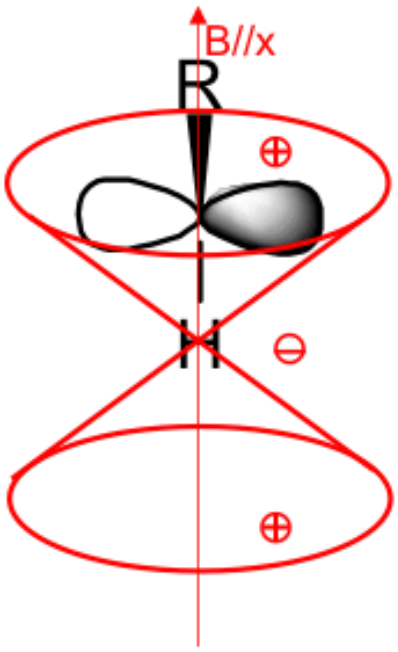
- Judge whether the unpaired electron is mostly in the positive or the negative sector of a double cone with opening angle θ = 54.7°

Dipolar Coupling of α-Nuclei



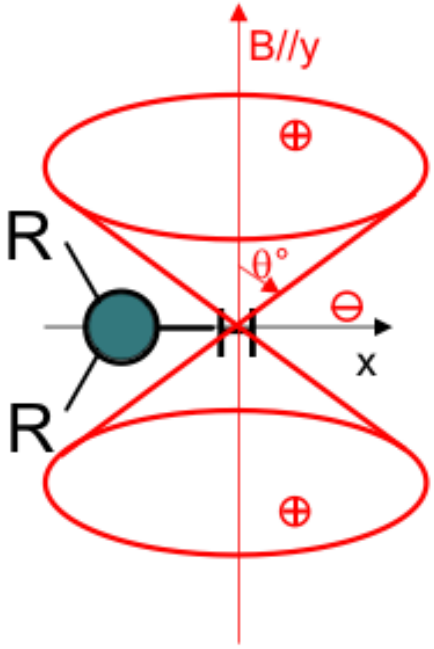
$B_{zz} \approx 0$

Orbital is partly in the positive and partly in the negative sector of the double cone



$B_{xx} > 0$

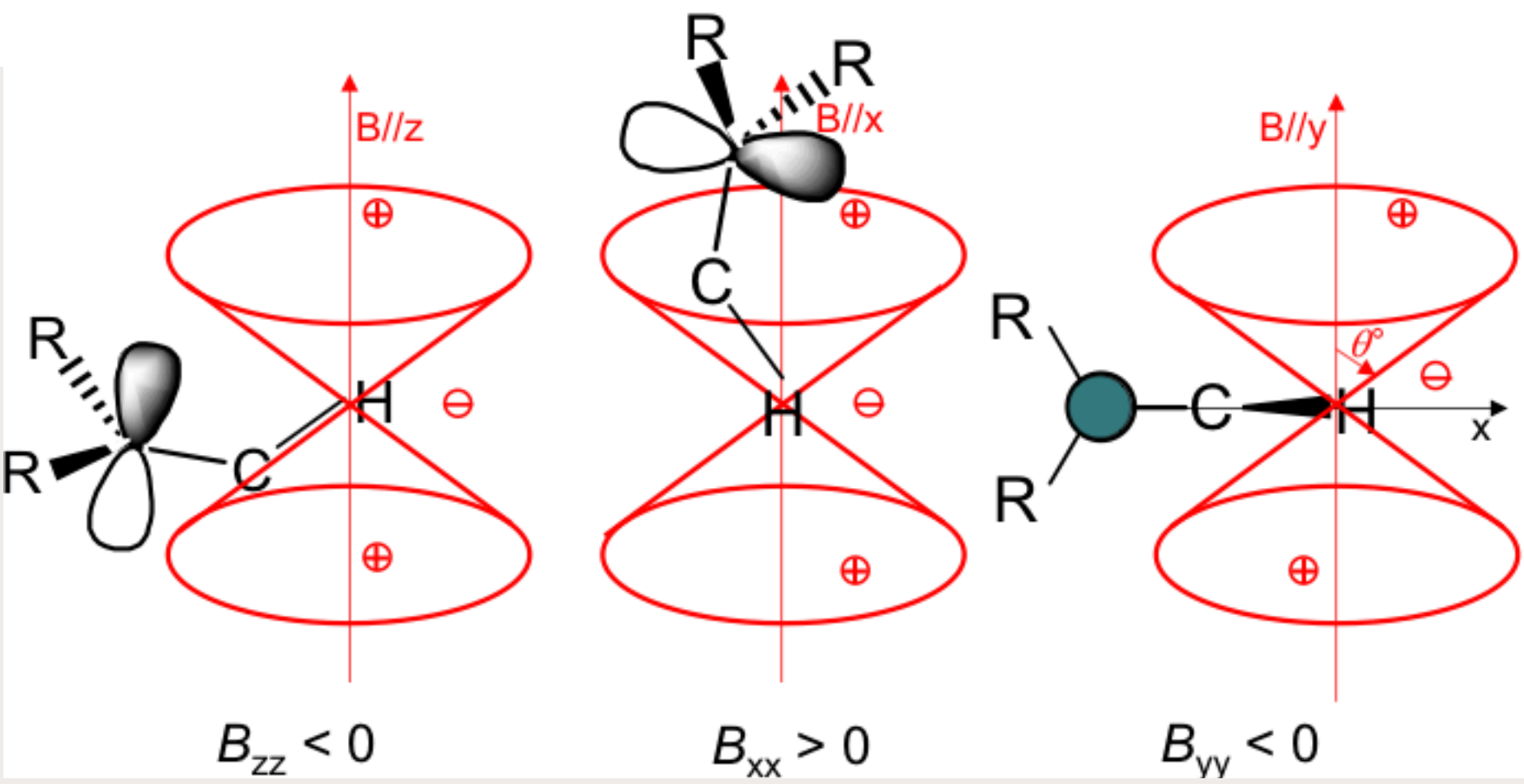
Orbital is essentially entirely in the positive sector of the double cone



$B_{yy} < 0$

Orbital is essentially entirely in the negative sector of the double cone

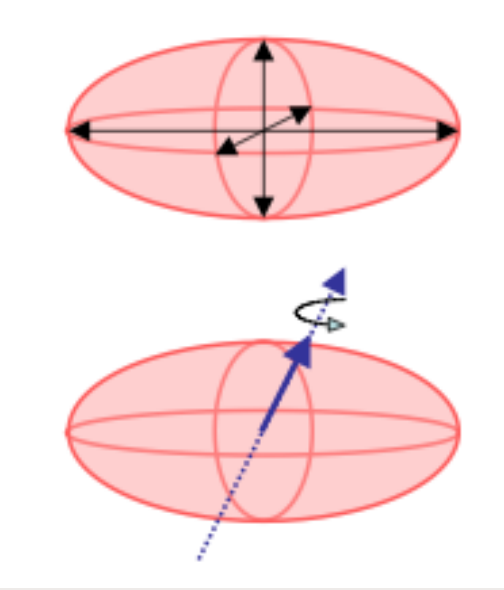
Dipolar Coupling of β-Nuclei

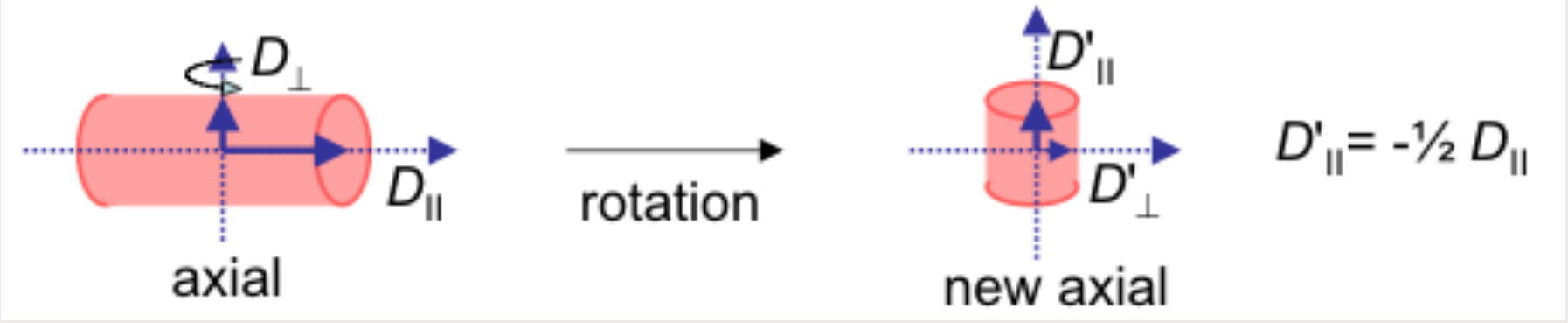


Motional Averaging

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

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





ALC Lineshapes

D_μ: magnitude of dipolar hfcc
θ: angle between unique axis and magnetic field.

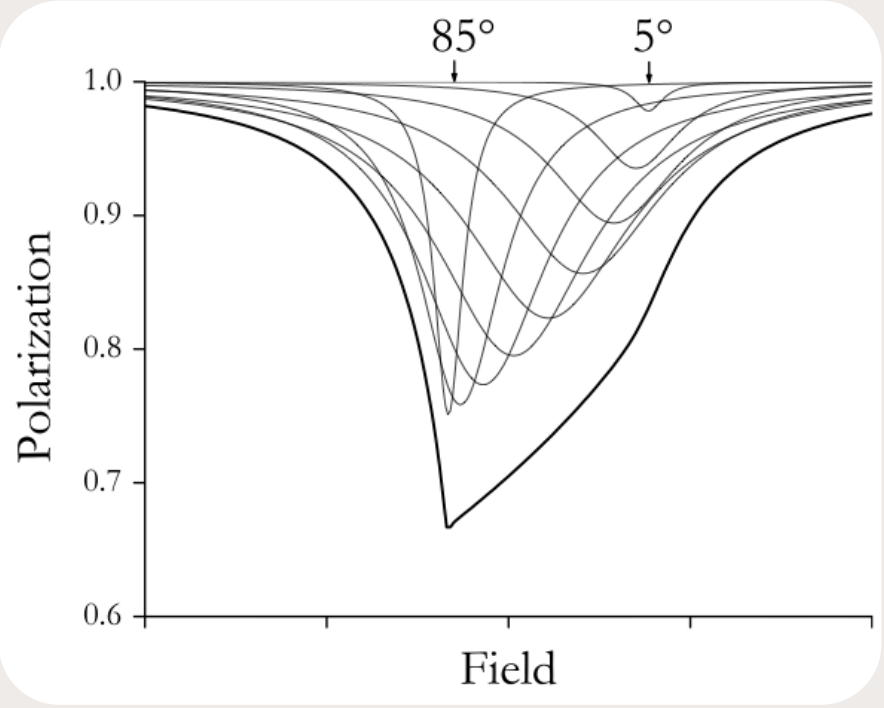
$$\overline{P}_z(B,\theta) = 1 - \frac{0.5q^2 P_z^0}{(\lambda/2\pi)^2 + q^2 + \gamma_\mu^2 \left(B - B_{res}^{\Delta_1}\right)^2}$$

$$q = -\frac{3}{4} D_\mu^{\parallel} \sin\theta\cos\theta$$

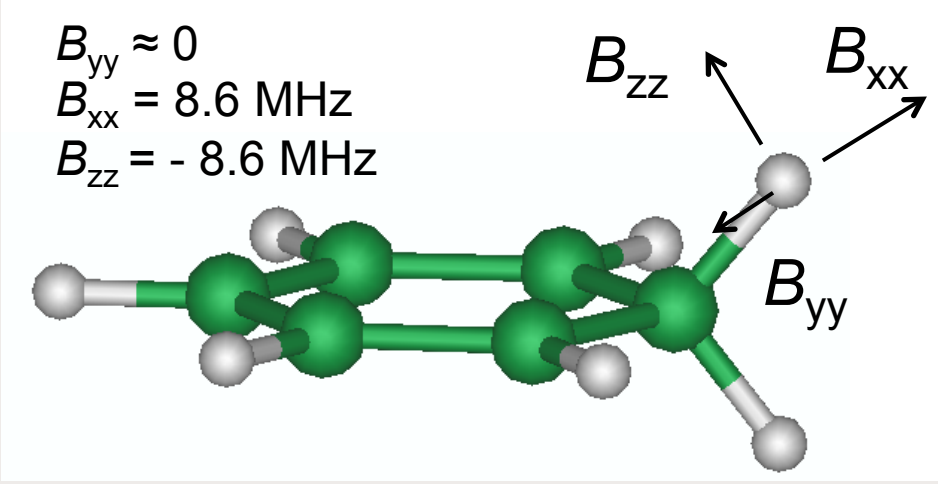
$$B_{res}^{\Delta_1} = \left(\frac{1}{2\gamma_\mu} - \frac{1}{2\gamma_e}\right)\left[A_\mu^{iso} + \tfrac{1}{2} D_\mu^{\parallel}\left(3\cos^2\theta - 1\right)\right]$$

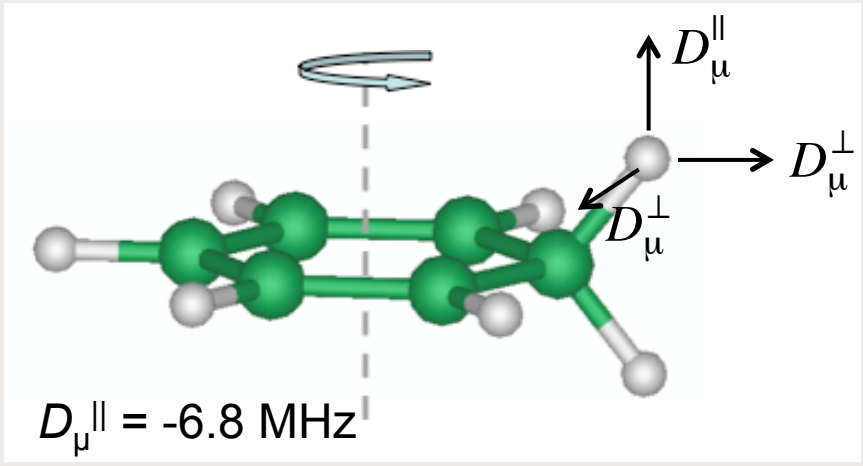
Powder Δ_1 shape obtained by integrating over all θ and weighting by probability $f(\theta)$.

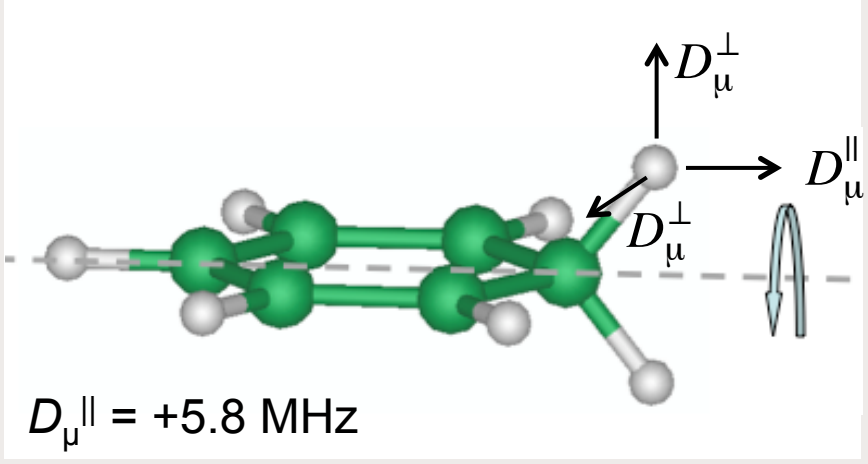
$$\overline{P}_z(B) = \int_0^{\pi} \overline{P}_z(B,\theta) f(\theta) 2\pi \sin\theta d\theta$$



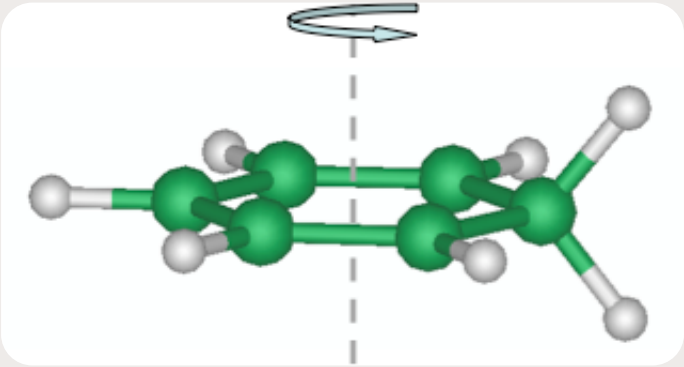
Motional Averaging of C_6H_6Mu

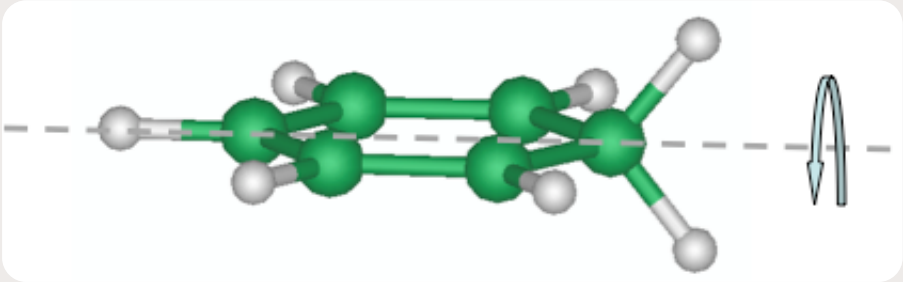


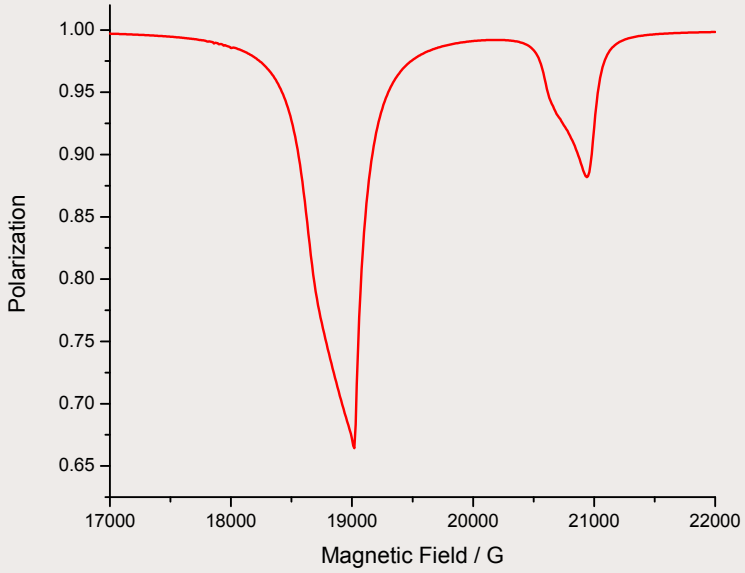


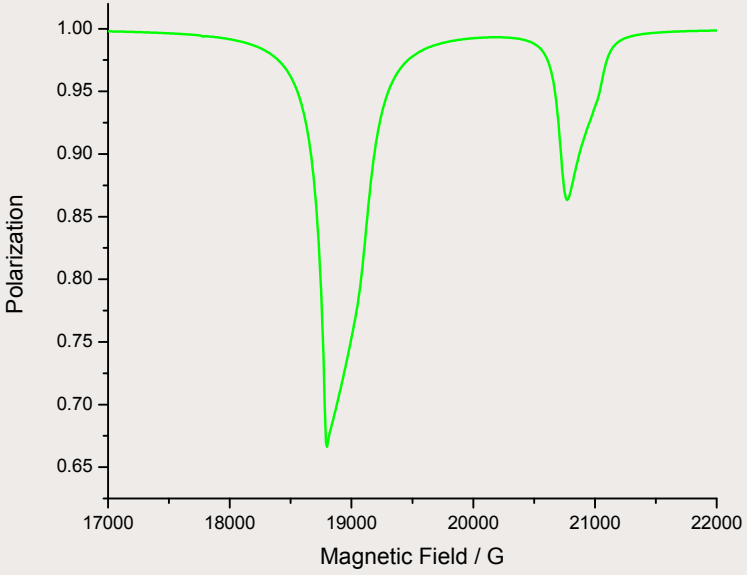


ALC Lineshapes

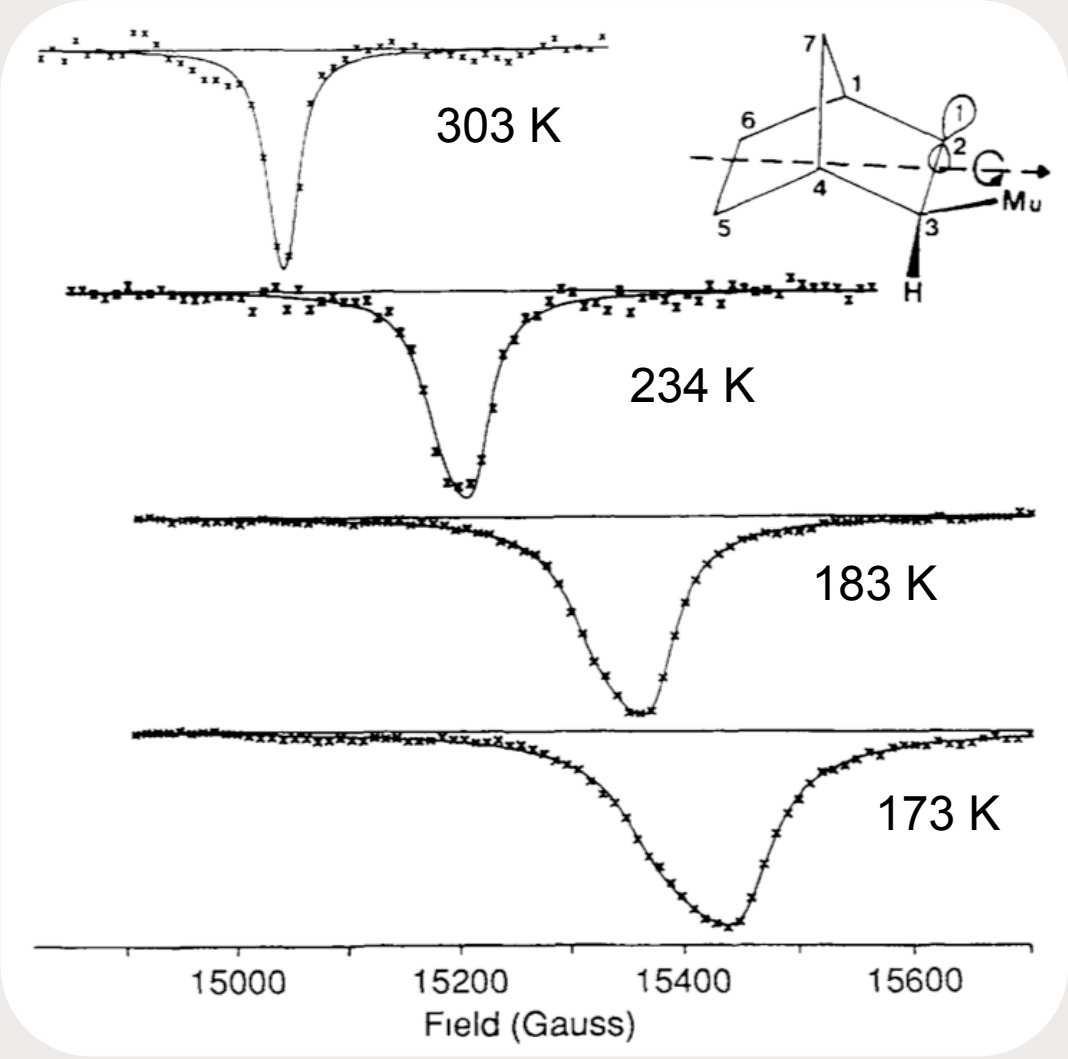






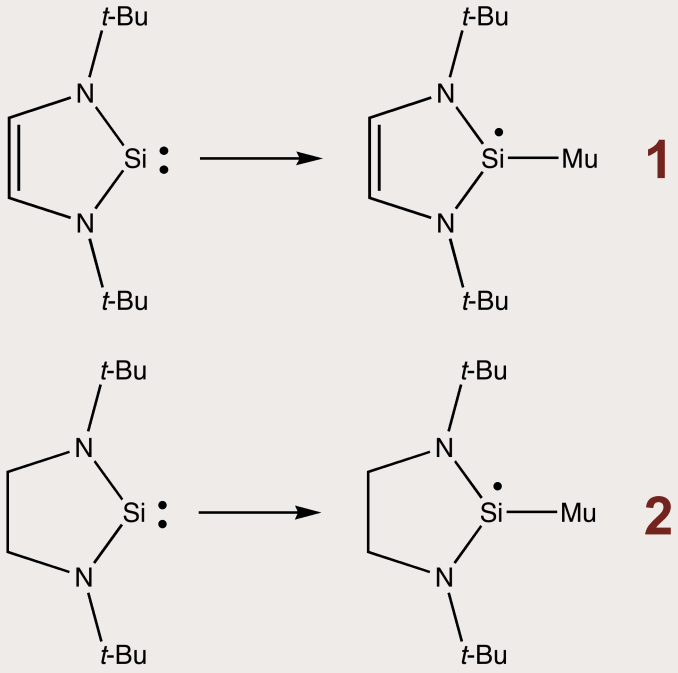


Dynamics of Muoniated Norbornyl Radical



- Asymmetric shape indicates $D_\mu^{\parallel} < 0$
- Preferred rotation around indicated axis.
- Decreasing $|D_\mu^{\parallel}|$ with increasing temperature due to wobbling of rotation axis.

Organosilicon Radicals

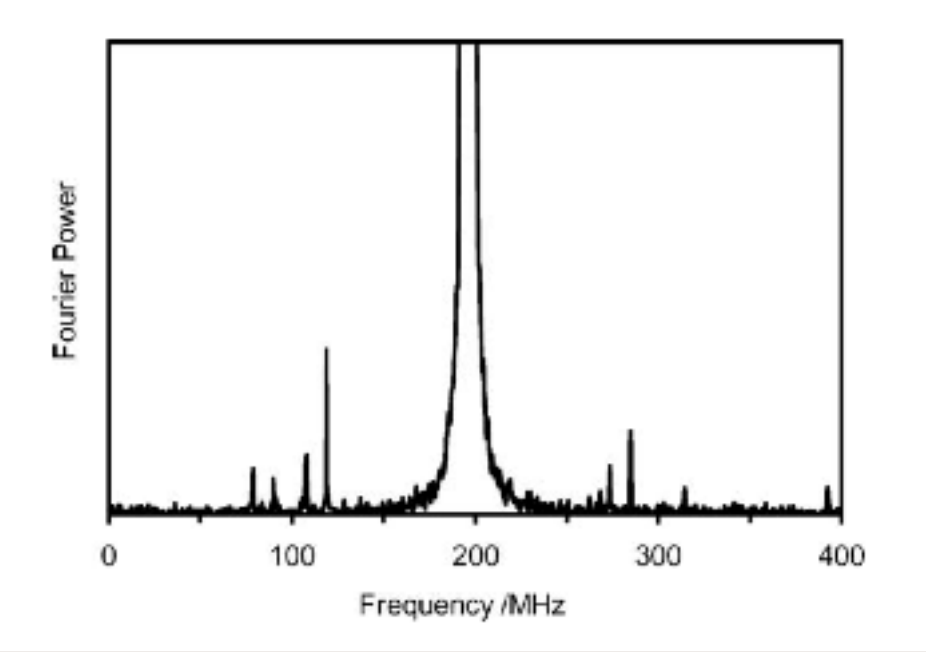


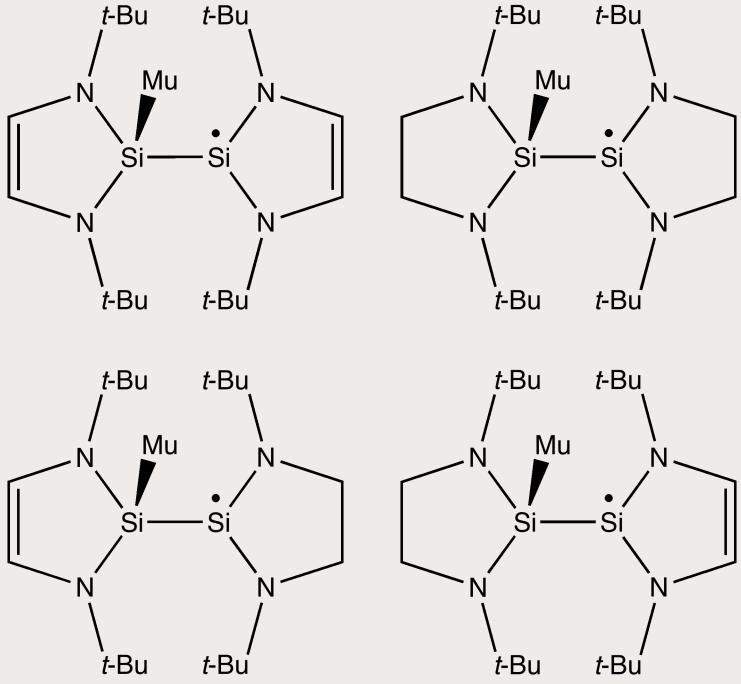
	Calculated A_μ	Exp. A_μ
1	618	235.4
2	764	154.9

Difference between calculated and experimental A_μ values means these are not the radicals are formed.

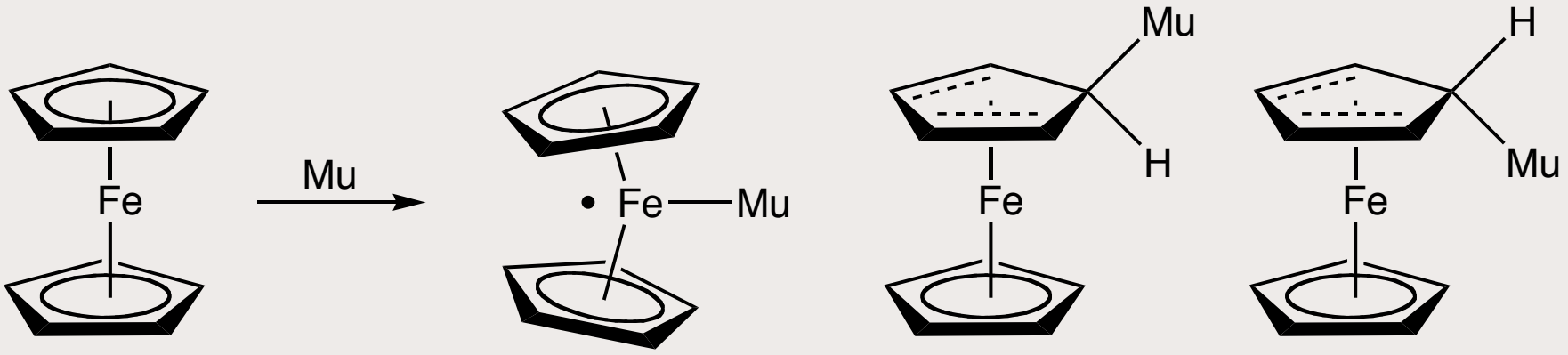
Organosilicon Radicals

- Observation of secondary radical formed by radical addition to silylene
- Confirmed by observing products of equimolar **1** and **2**





Organometallic Radicals



Ferrocene

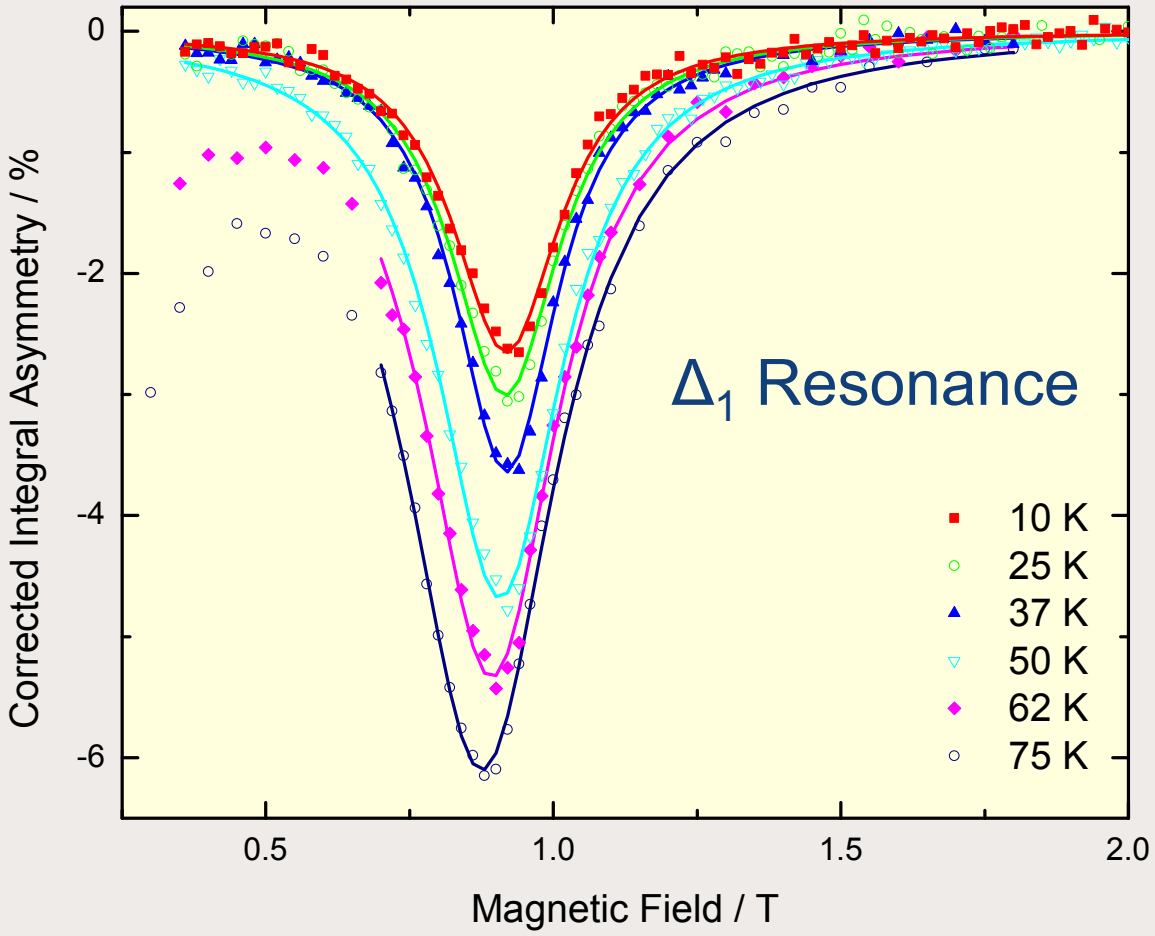
Fe Adduct
19 electrons

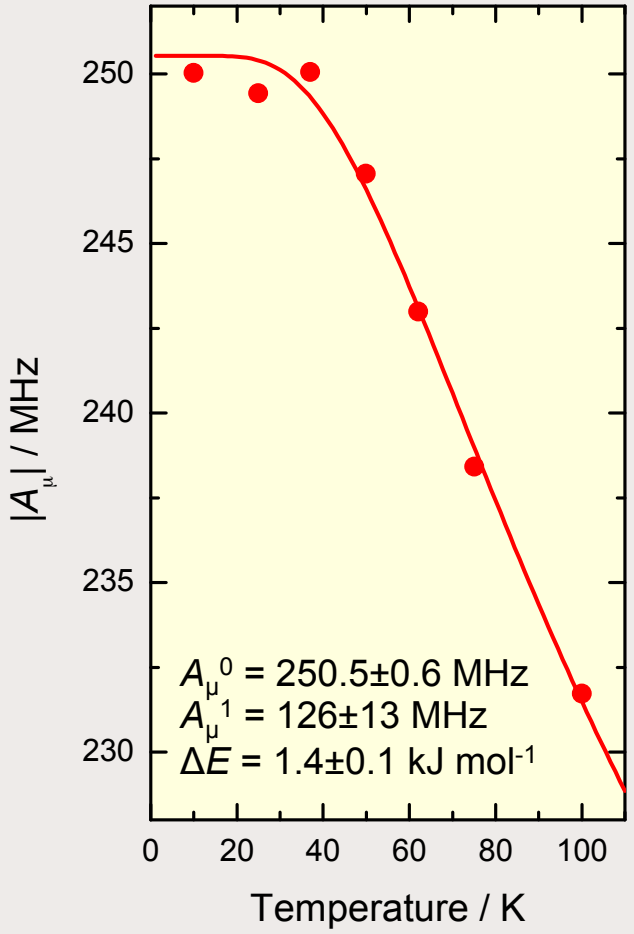
exo *endo*

Cp Adducts
17 electrons

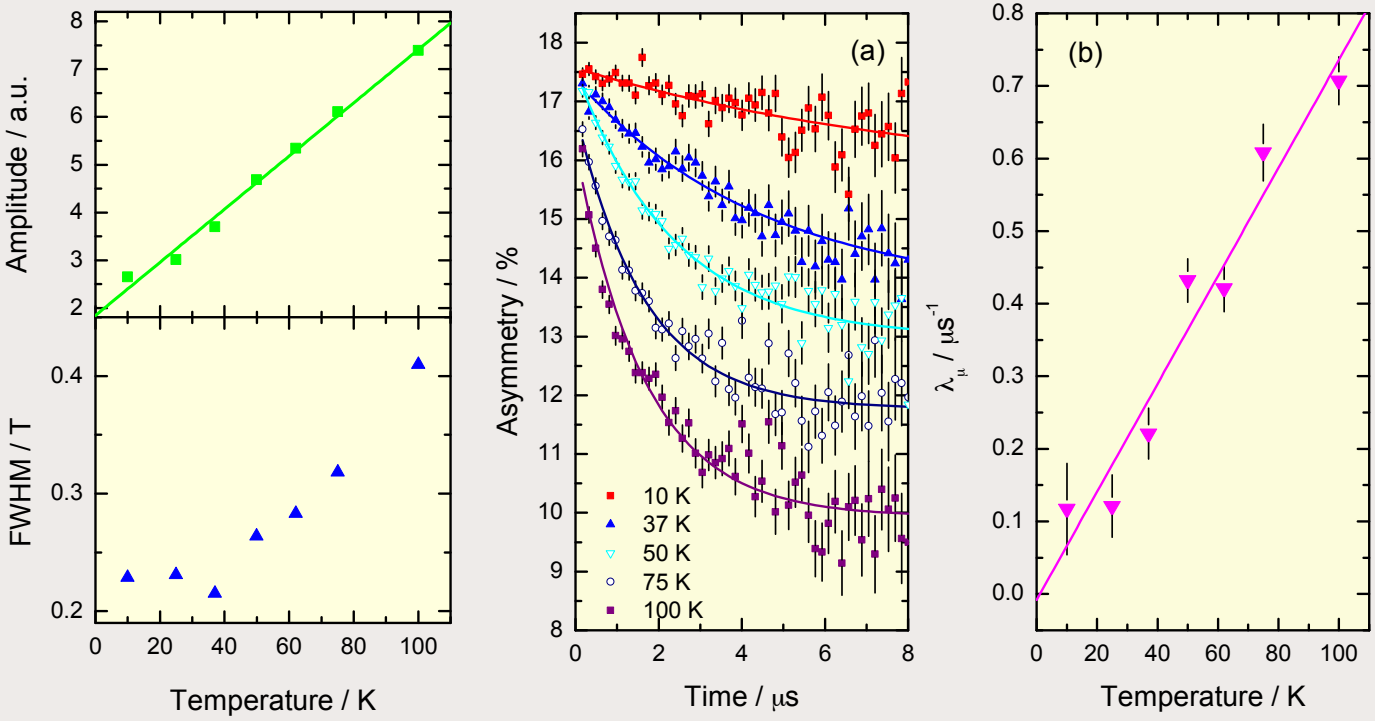
- How does H/Mu react with ferrocene?
- What are the structures of the resulting radicals?

ALC-μSR of Ferrocene





ALC-μSR of Ferrocene

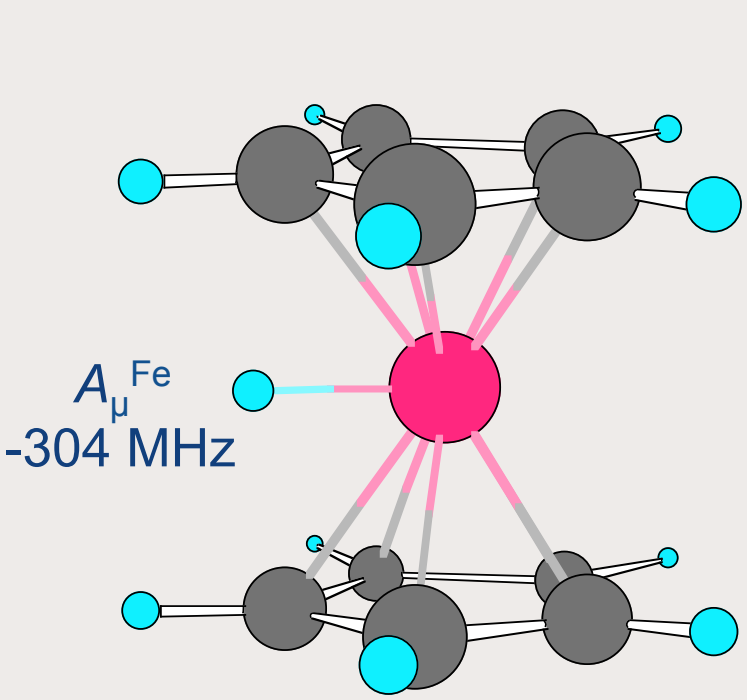


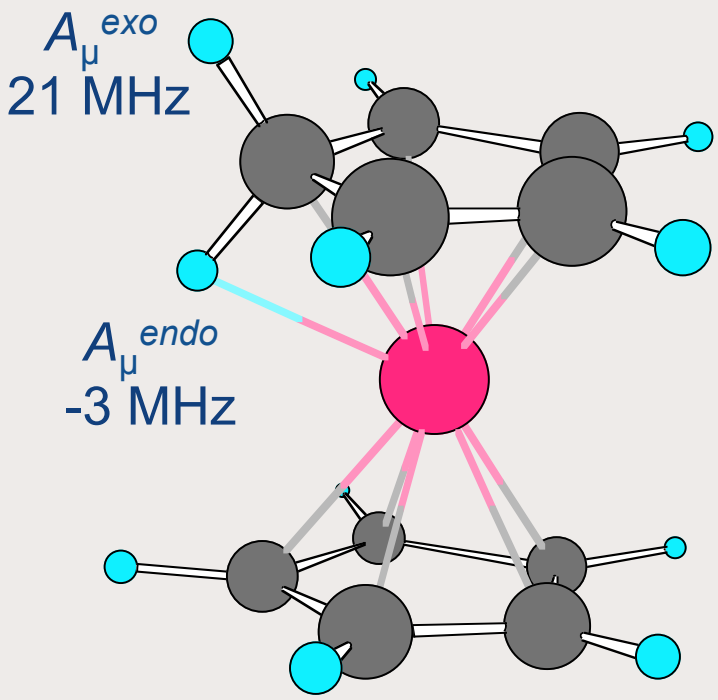
λ_e and λ_μ increasing with temperature

Chemical reaction?

DFT Calculations of Mu Adducts of Ferrocene

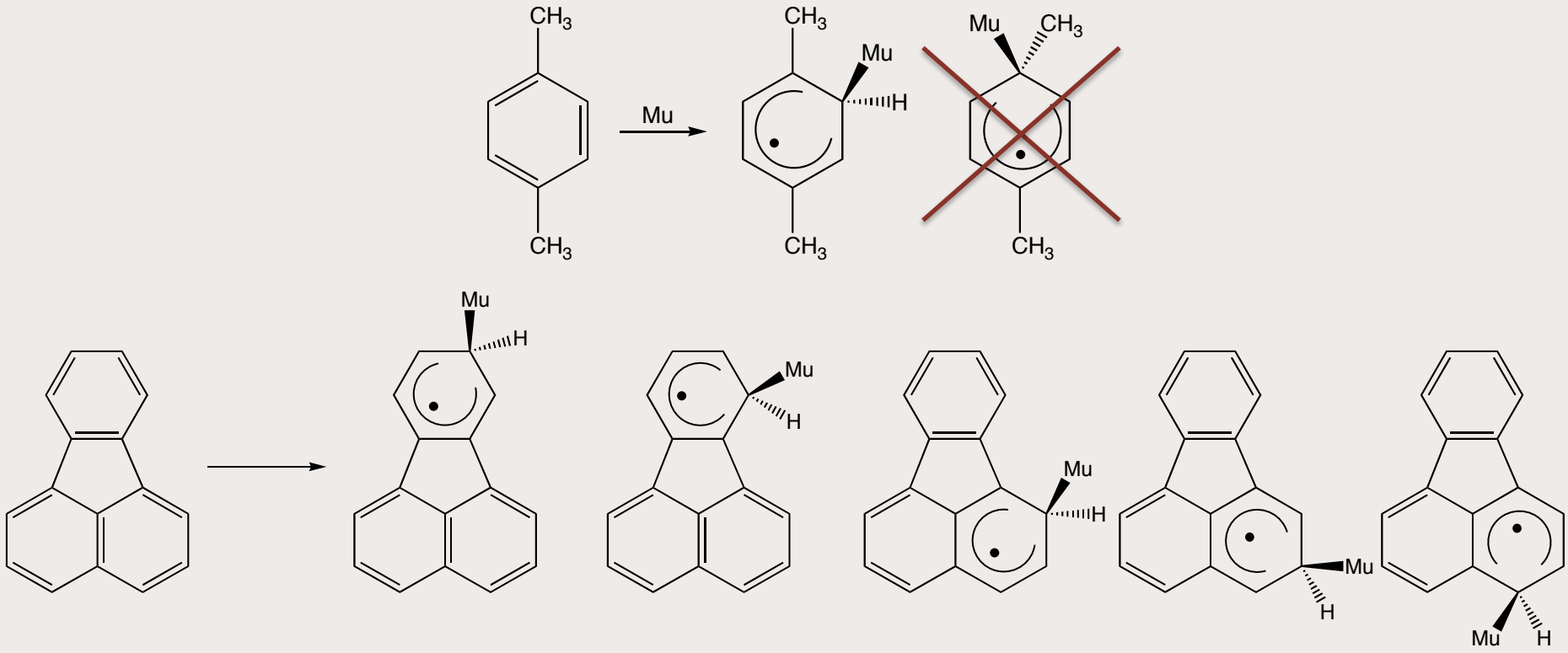
R. M. Macrae, Physica B **374-375**, 307 (2006) UB3LYP/6-311+G(d,p)





more stable by 79.8 kJ mol^{-1}

Reaction of Mu with Aromatic Compounds

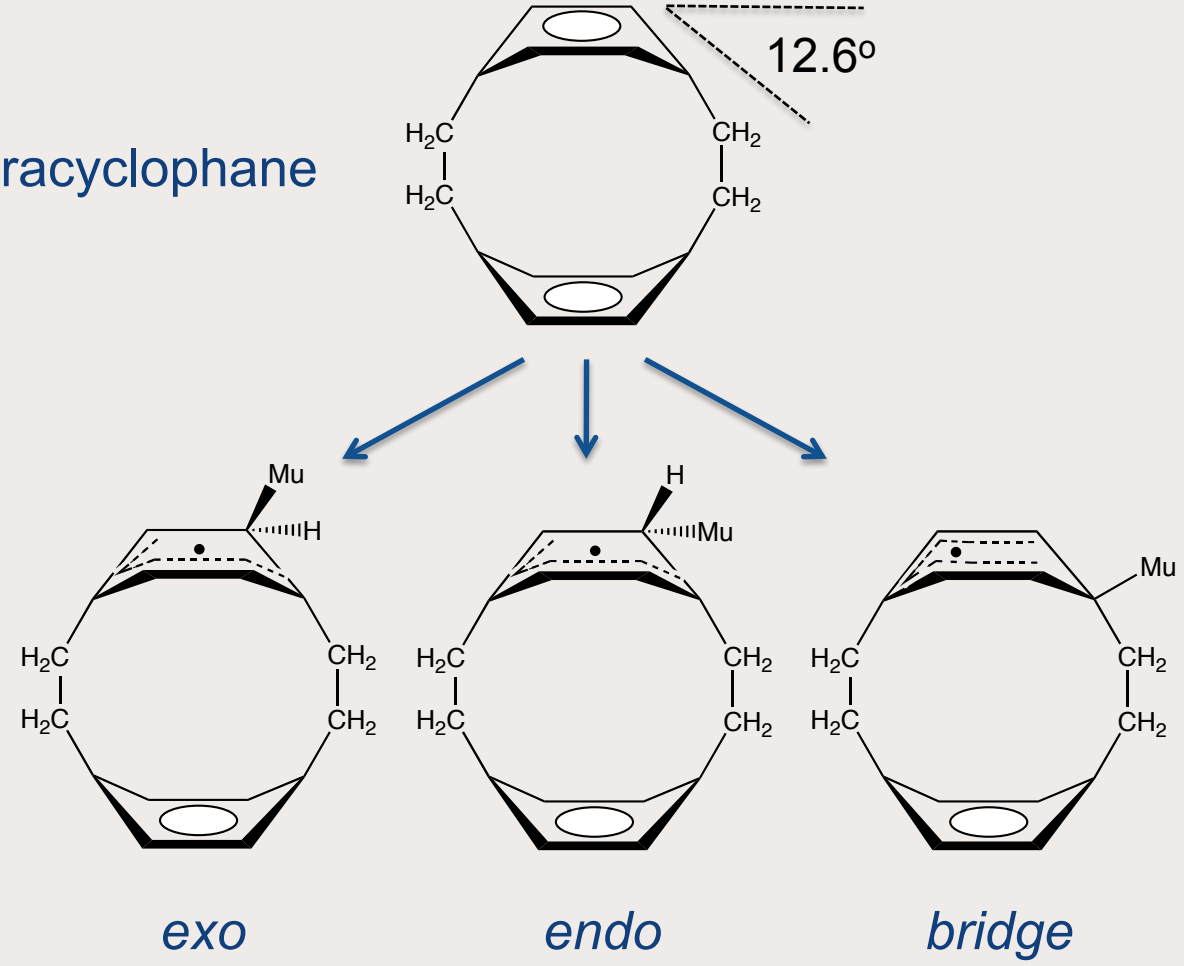


Brodovitch et al. Can. J. Chem. **81**, 1 (2003)

No addition at tertiary carbons*

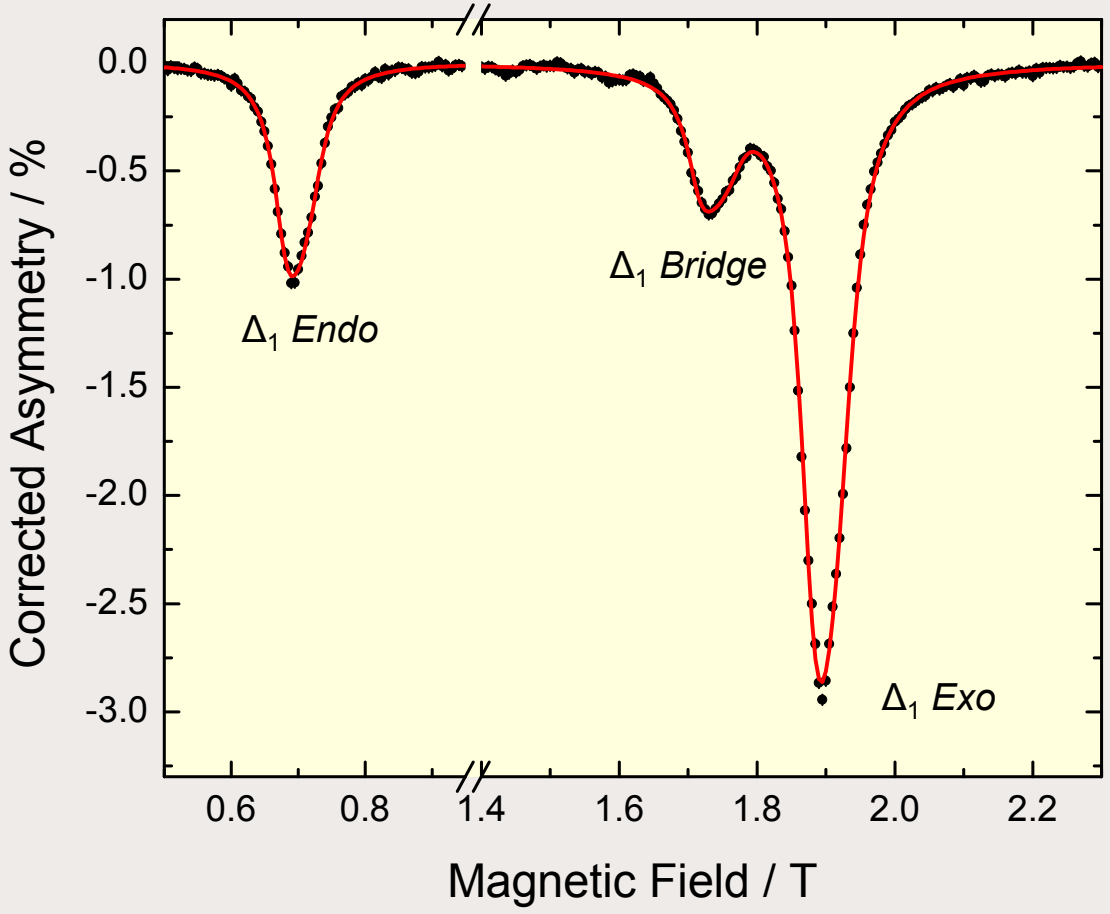
Strained Aromatic Compounds

[2.2]paracyclophane



ALC-μSR of [2.2]Paracyclophane

UB3LYP/6-311G(d,p)//UPBE0/EPR-II



Exo

A_μ = 530.9 MHz

Δ_1 = 1.95 T

67±1 %

Endo

A_μ = 169.9 MHz

Δ_1 = 0.62 T

22±1 %

Bridge

A_μ = 469.0 MHz

Δ_1 = 1.72 T

11±1 %

Conclusions and References

- μSR is a powerful technique for characterizing free radicals in the solid, liquid or gas phases

References

- E. Roduner, Chem. Soc. Rev. **22**, 337 (1993)
- C. J. Rhodes, J. Chem. Soc. Perkin Trans. **2**, 1379 (2002)
- I. McKenzie and E. Roduner, Naturwissenschaften **96**, 873 (2009)