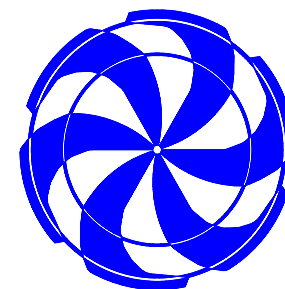


# Muon Spin Spectroscopy

Using the Positive Muon to Probe Matter

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Department of Chemistry  
Simon Fraser University  
and TRIUMF



# Muon and Muonium Properties

**Negative muon**  $\mu^-$  a heavy electron (mass =  $207 m_e$ )  
 $\tau = 2.2 \mu\text{s}$  in vacuum ...  
 ... less in matter because of nuclear capture  
 spin  $I = \frac{1}{2}$

**Positive muon**  $\mu^+$  a light proton (mass =  $0.11 m_p$ )  
 $\tau = 2.2 \mu\text{s}$  in vacuum *and* matter  
 spin  $I = \frac{1}{2}$

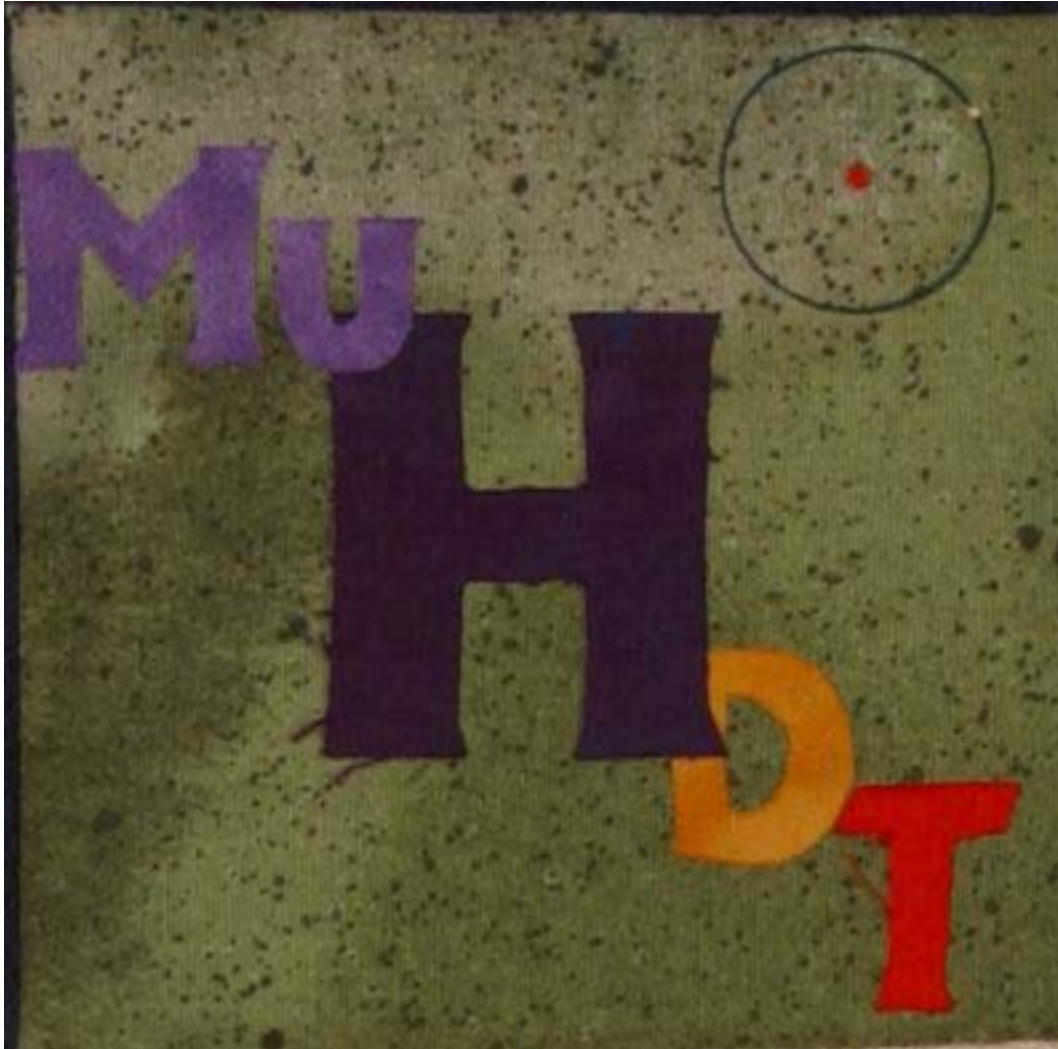
<b>Muonium</b> $\text{Mu} = \mu^+e^-$	a light hydrogen atom	$\text{Mu}^+ = \mu^+$
	Ionization Energy = 13.54 eV	H: 13.60 eV
	Bohr Radius = 0.532 Å	H: 0.529 Å

# The Periodic Table – Chemistry Department Quilt



[http://www.sfu.ca/chemistry/news/pt\\_quilt/index.htm](http://www.sfu.ca/chemistry/news/pt_quilt/index.htm)

# The Simplest Atom



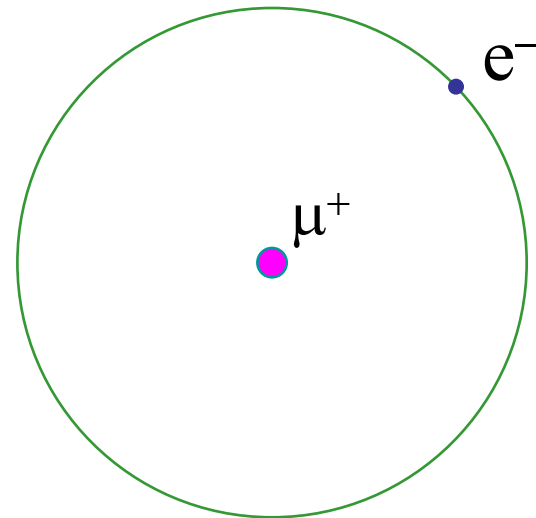
## Muonium – a light isotope of hydrogen

$$\text{Mu} \equiv \mu^+ e^-$$

The properties of a single electron atom are determined by the **reduced mass**

$$\frac{1}{m_r} = \frac{1}{m_N} + \frac{1}{m_e} \approx \frac{1}{m_e}$$

**i.e.**  $m_r \approx m_e$



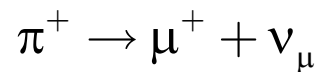
reduced mass of Mu = 0.995  $m_r(\text{H})$

ionization potential = 13.539 eV

Bohr radius = 0.532 Å

# Pions Decay to Give Muons

At TRIUMF, pions are produced by bombardment of a Be or C production target with 500 MeV protons. We take the positive pions, which decay to positive muons:



$$\tau = 26 \text{ ns}$$

In the pion rest frame:

Momentum is conserved:

Spin is conserved:

$$\overleftarrow{\nu} \quad \odot \quad \overrightarrow{\mu}$$

$$\overrightarrow{p}_\mu = -\overrightarrow{p}_\nu$$

$$\overrightarrow{\sigma}_\mu = -\overrightarrow{\sigma}_\nu$$

Spin and momentum are related through **helicity**:

$$\hat{h} = \frac{\vec{\sigma} \cdot \vec{p}}{|\vec{\sigma} \cdot \vec{p}|} \quad \hat{h}\psi = \pm 1\psi$$

For the neutrino,  $h = -1$ , i.e. the spin and momentum are anti-parallel.

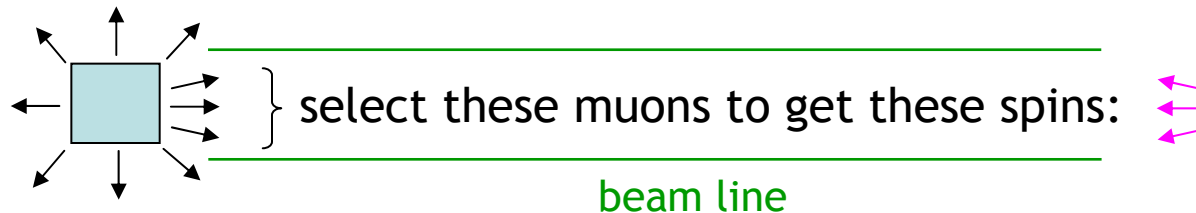
Therefore, muons are produced with  $\sigma$  and  $p$  anti-parallel.

$$\begin{array}{ccc} \overrightarrow{\sigma}_\nu & & \overleftarrow{\sigma}_\mu \\ \overleftarrow{p}_\nu & \odot & \overrightarrow{p}_\mu \end{array}$$

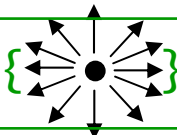
# Muon Beams are Spin Polarized

There are two commonly used types of muon beam:

**Surface Muon Beams** collect and transport muons which are created from the decay of pions at or near the surface of the pion production target.



**Decay Muon Beams** collect muons from pions which decay in flight.

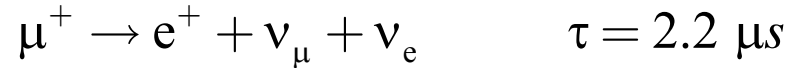
In the  $\pi$  rest frame only **backward**  and **forward** muons are transported.

The diagram shows a central black dot with arrows pointing outwards in all directions. A bracket on the left side of the dot points to the text "backward" and a bracket on the right side points to the text "forward".

In the laboratory frame, both momentum bites travel in the forward direction.

The **forward** (momentum) muons ( $p \sim 180$  MeV/c) have **backward** spin;  
the **backward** muons ( $p \sim 80$  MeV/c) have **forward** spin.

# Muon Decay



The 3 particle decay results in a spectrum of positron energies.

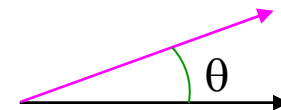
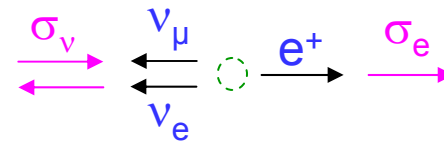
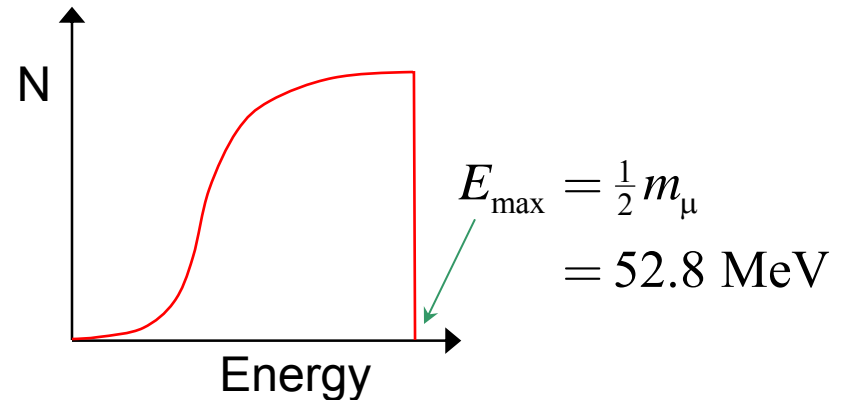
The spatial distribution of positrons is asymmetric and depends on the muon spin polarization.

Consider the decay pattern which results in the maximum positron energy:

The  $e^+$  is emitted in the direction of the muon spin at the moment of decay.

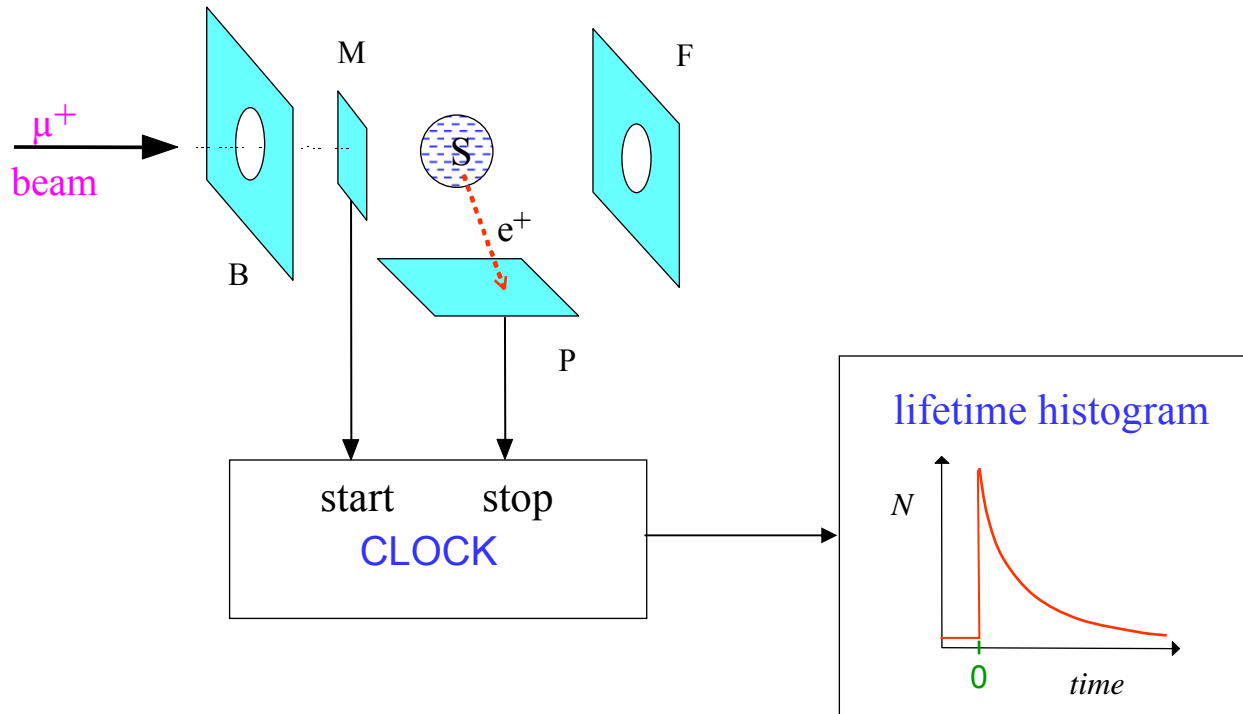
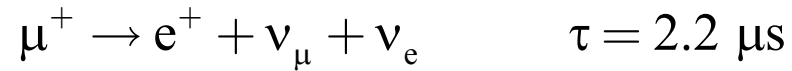
More generally,

$$\frac{dN(E, \theta)}{dE d\Omega} = C [1 + D(E) \cos \theta]$$



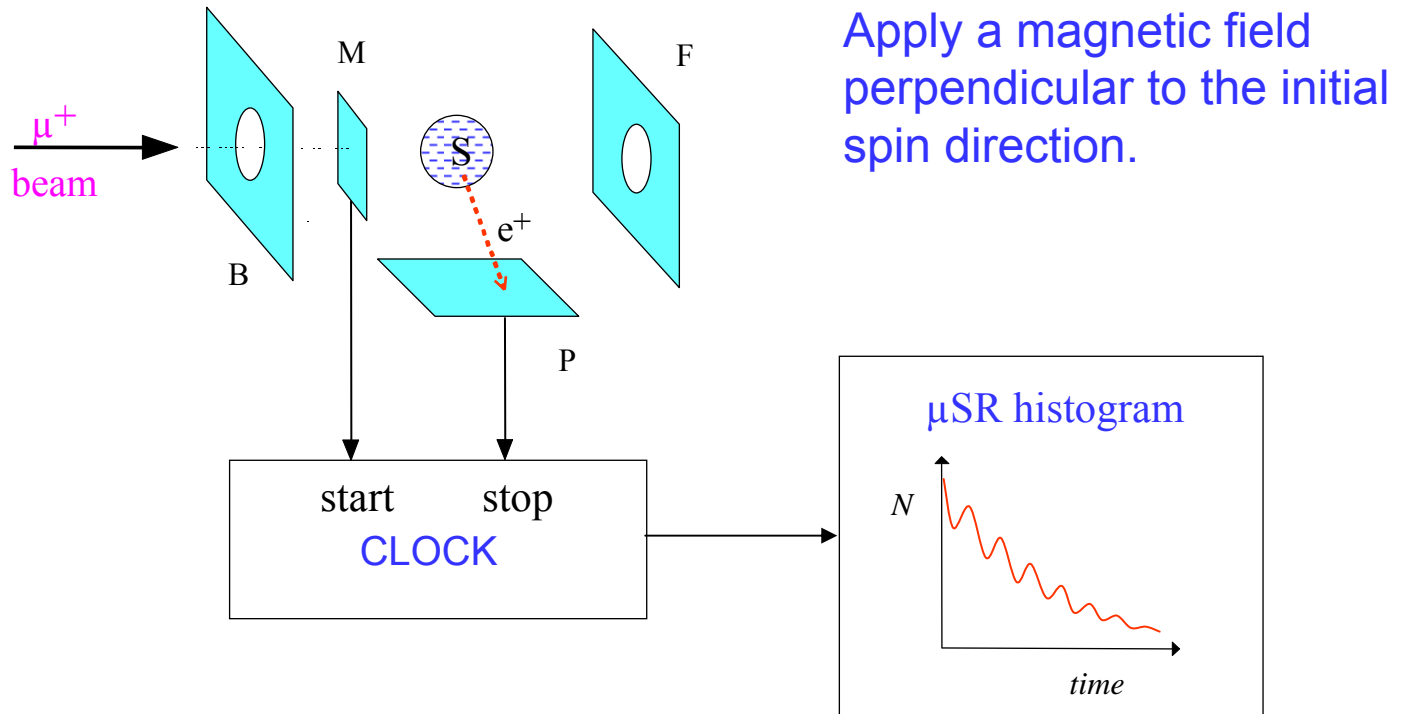


# The Muon Lifetime Experiment



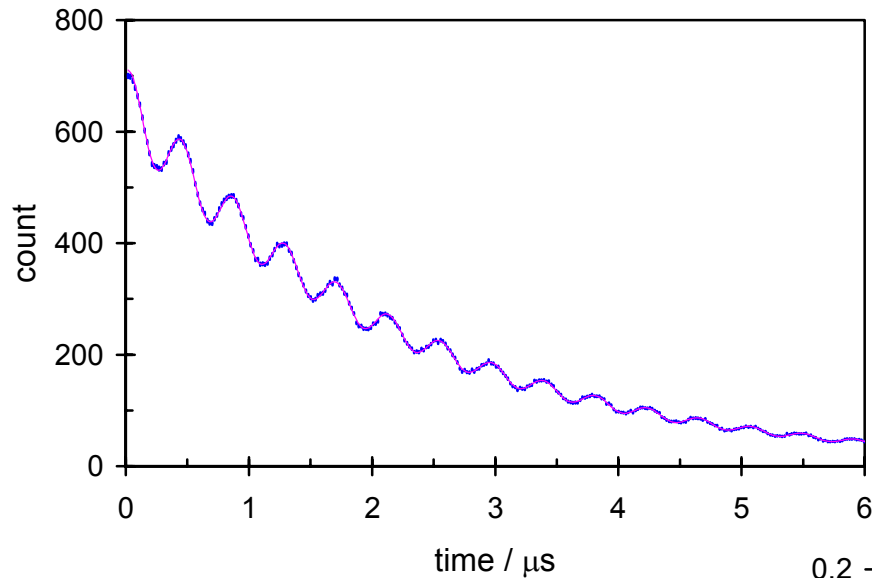
$$N = N_0 e^{-t/\tau} + \text{background}$$

# Muon Spin Rotation, $\mu$ SR



$$N = N_0 e^{-t/\tau} [1 + aP(t) \cos(\omega t + \phi)] + \text{background}$$

# The $\mu$ SR Histogram

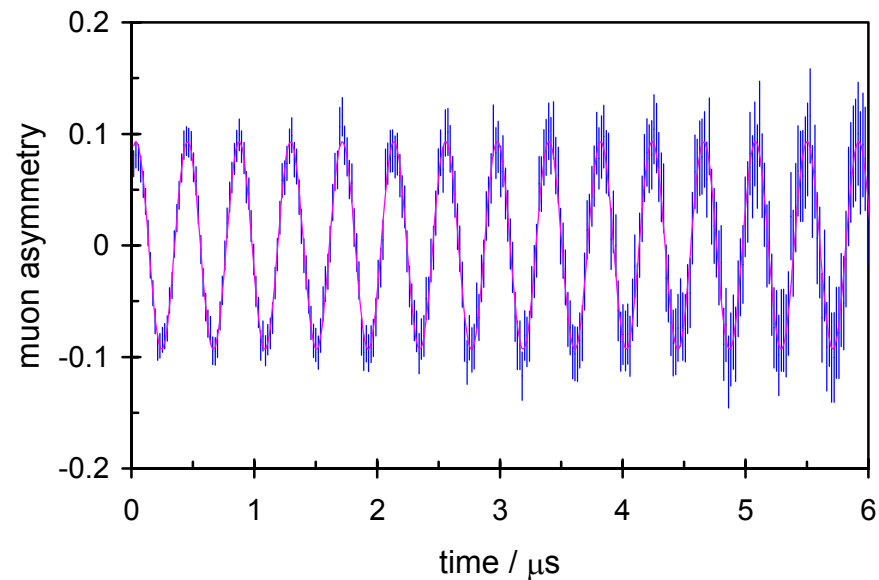


$$N_0 e^{-t/\tau} [1 + aP(t) \cos(\omega t + \phi)] + B$$

Subtract the constant background and divide out the exponential decay ...

... to get the muon asymmetry, which represents the time dependence of the muon spin polarization.

$$aP(t) \cos(\omega t + \phi)$$



# $\mu$ SR: Muon Spectroscopy

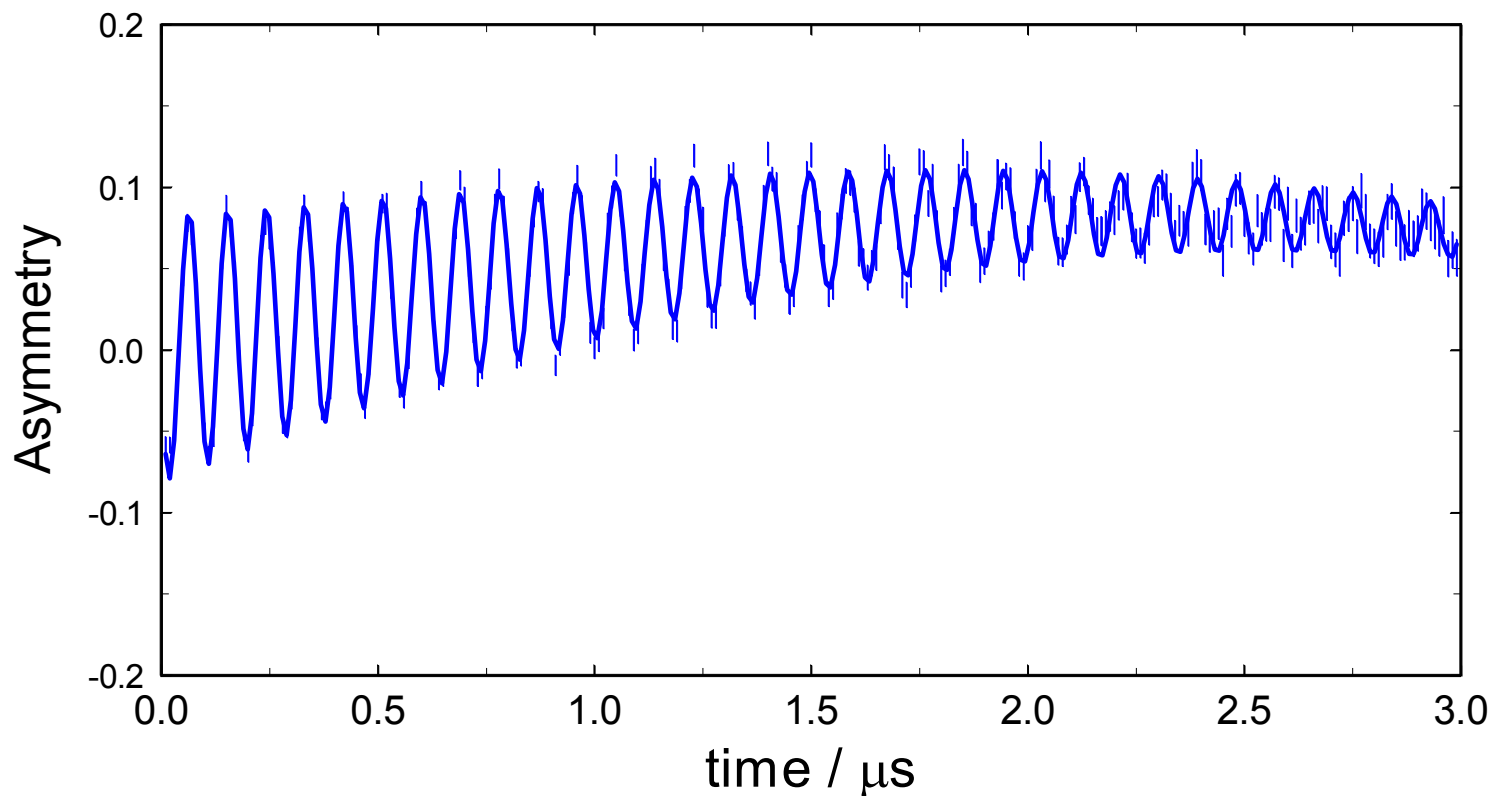
## Muon Spin Rotation

- spin polarized muon beam
- muons are implanted in the sample
- muons decay:  $\mu^+ \rightarrow e^+ + \nu_\mu + \nu_e$   $\tau = 2.2 \mu\text{s}$
- angular distribution of  $e^+$  has maximum in muon spin direction
- precession of muon spins in transverse magnetic field
- equivalent to free induction decay in pulsed NMR or ESR

# Muonium in supercritical water

400°C, 245 bar

8 G

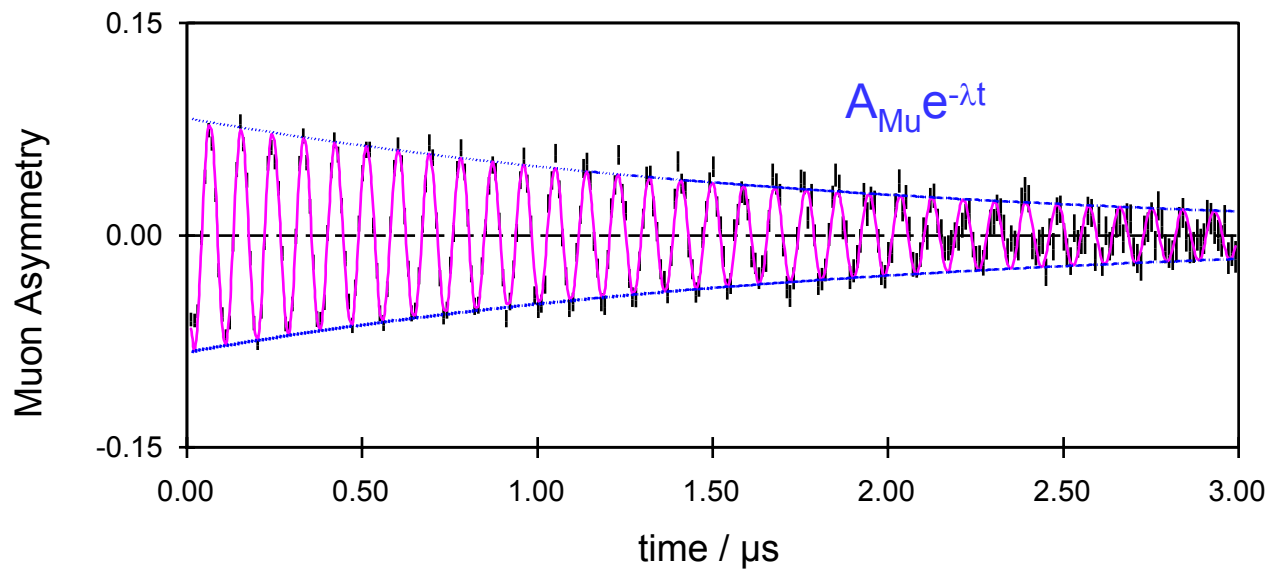


Percival, Brodovitch, Ghandi et al., Phys. Chem. Chem. Phys. 1 (1999) 4999

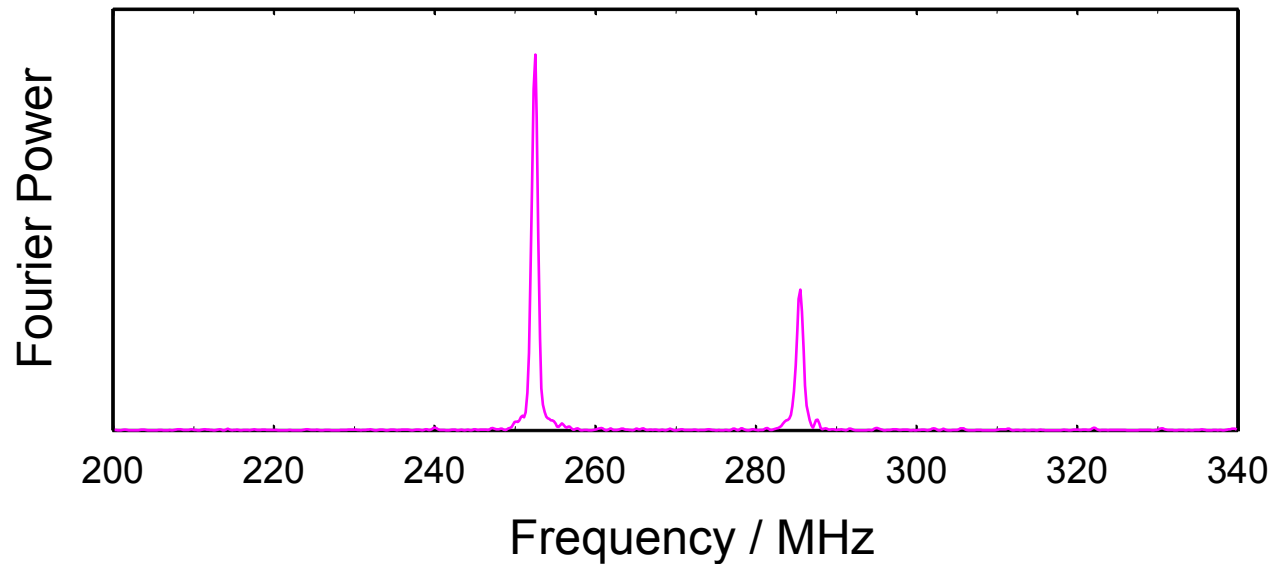
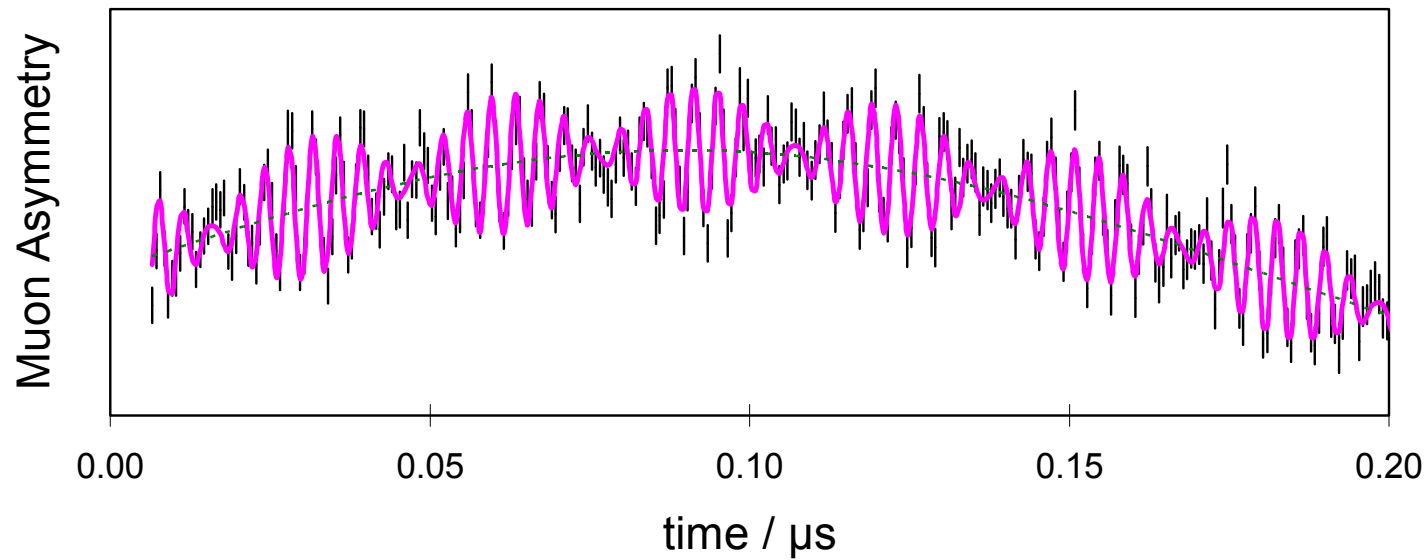
# Muonium in supercritical water

400°C, 245 bar, 8 G

Diamagnetic signal subtracted



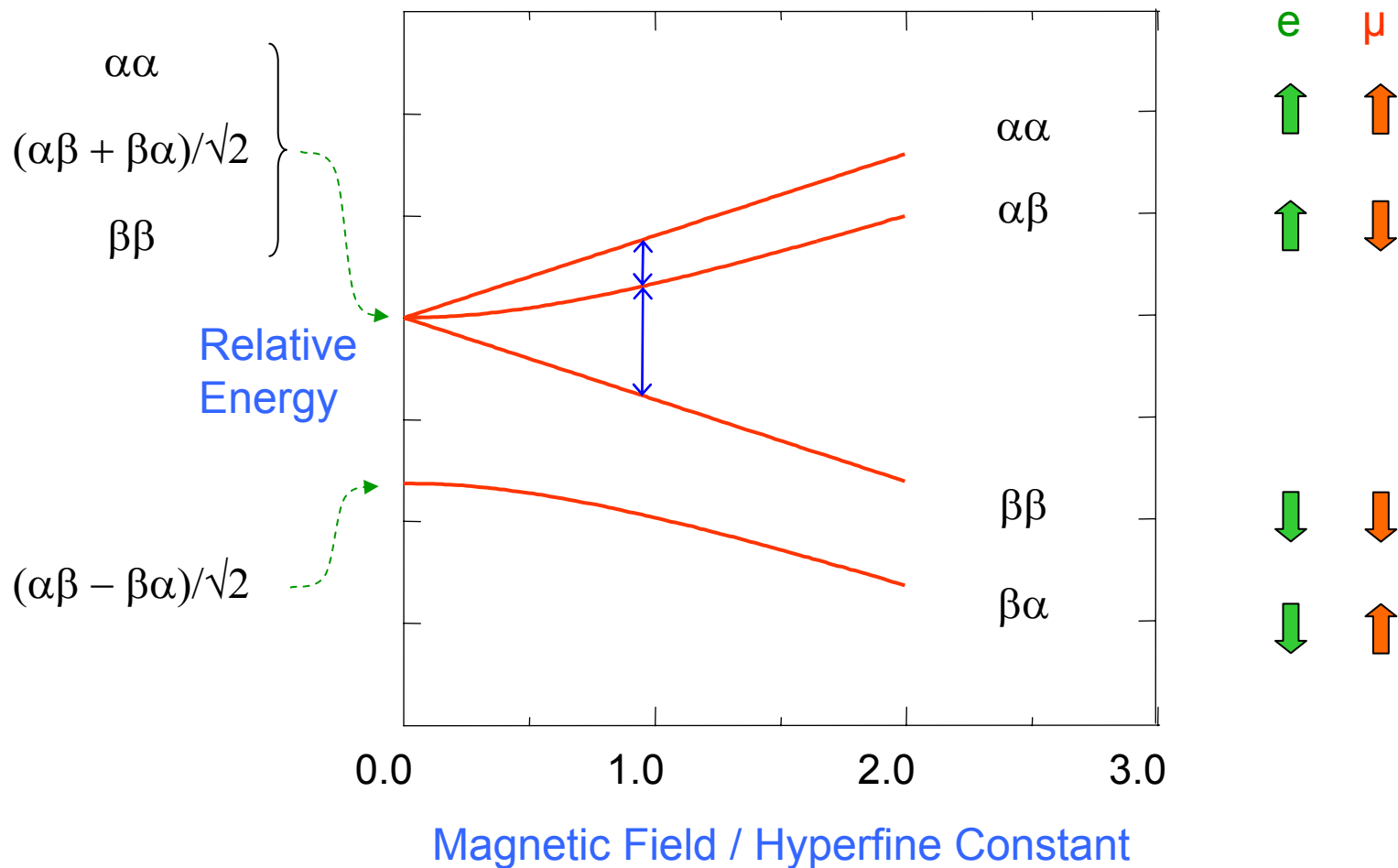
# Muonium in supercritical water at 196 G



400°C  
245 bar

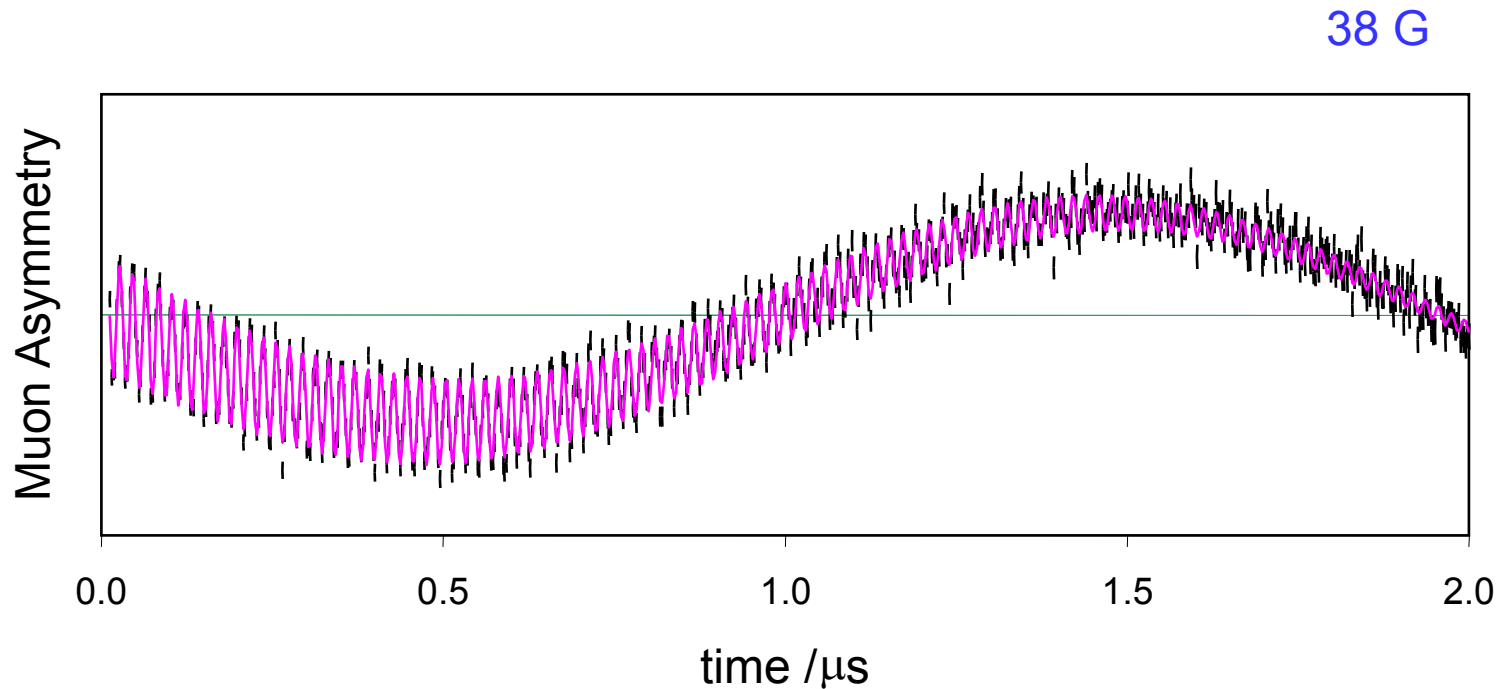
# Energy levels of a two spin- $\frac{1}{2}$ system

## Breit-Rabi diagram





# Muon spin precession in D<sub>2</sub>O crystal at 227 K

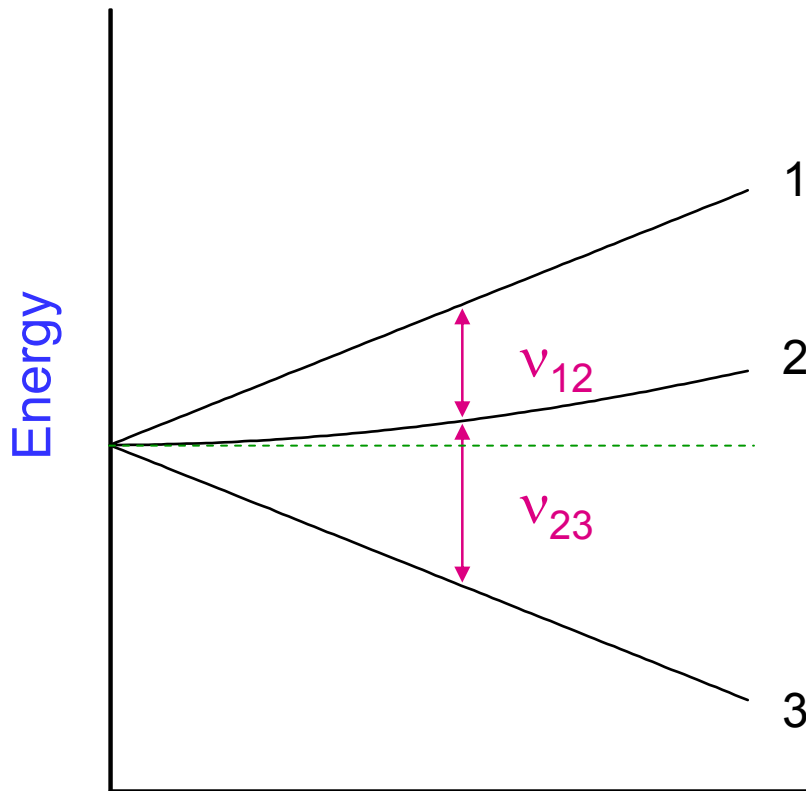


The high frequency precession is due to “triplet” ( $F=1$ ) muonium.

The low frequency is due to muons in diamagnetic environments, such as  $\text{MuOD}$  and  $\text{MuOD}_2^+$

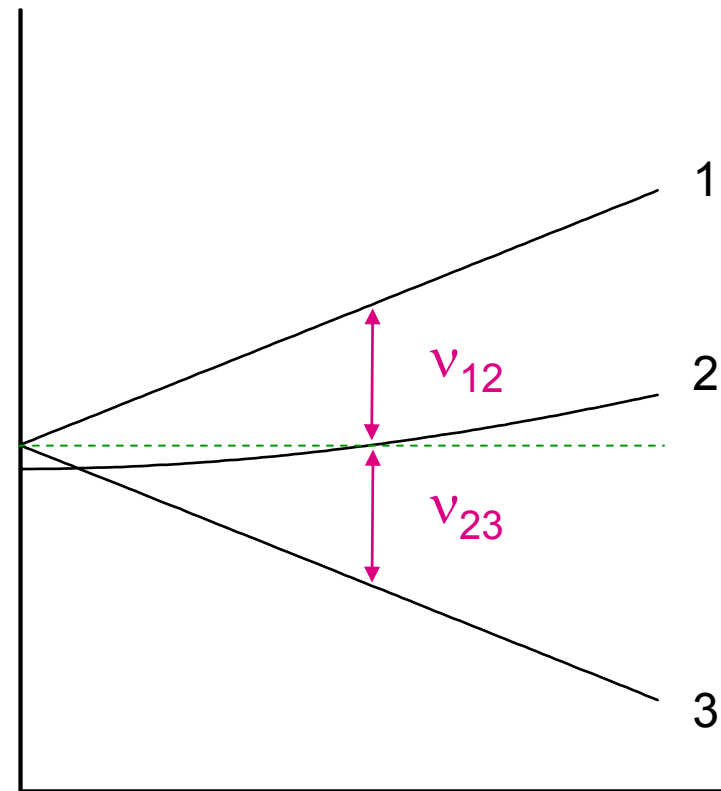
# Muonium precession frequencies in low magnetic field

isotropic hyperfine case



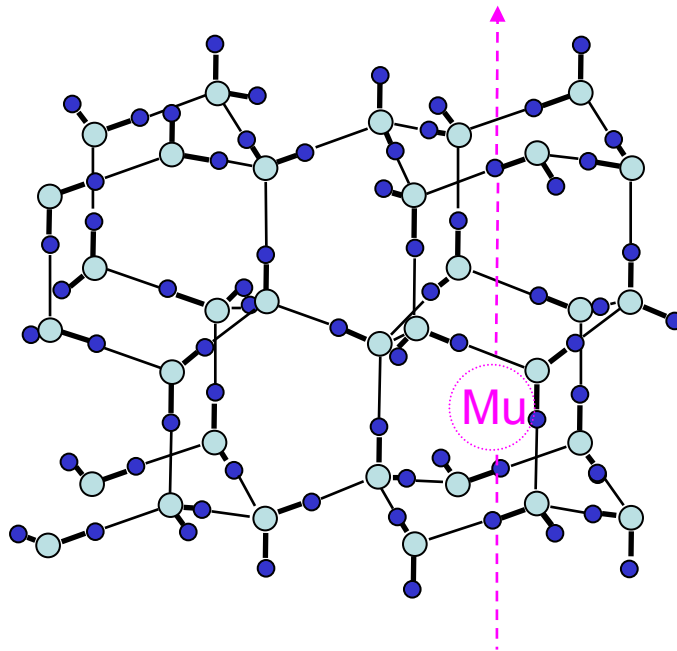
Magnetic Field

axial anisotropy

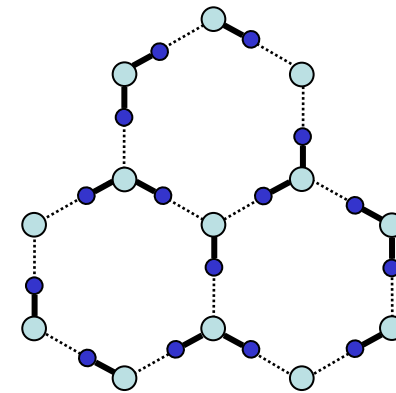


Magnetic Field

# Muonium diffuses along the c-axis channels of ice-Ih



side view



view along  $c$  channel

# $\mu$ SR: Muon spectroscopic methods

## Common features:

- spin polarized muon beam
- muons are implanted in the sample
- muons decay:  $\mu^+ \rightarrow e^+ + \nu_\mu + \nu_e$   $\tau = 2.2 \mu\text{s}$
- angular distribution of  $e^+$  has maximum in muon spin direction

## Muon Spin Rotation $\mu$ SR (TF- $\mu$ SR)

- precession of muon spins in transverse magnetic field
- equivalent to free induction decay in pulsed NMR or ESR

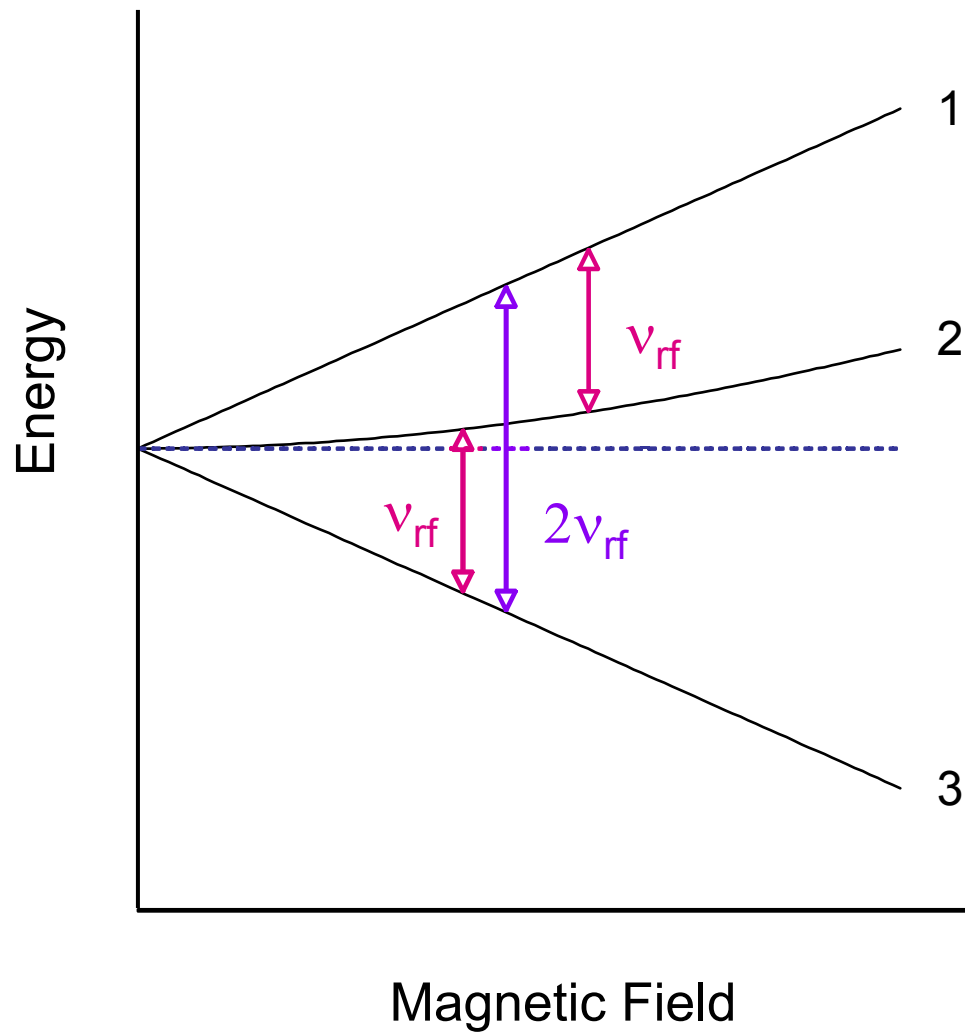
## Muon Spin Resonance RF- $\mu$ SR

- muon spin polarization *along* magnetic field
- transitions induced by rf field as in conventional NMR

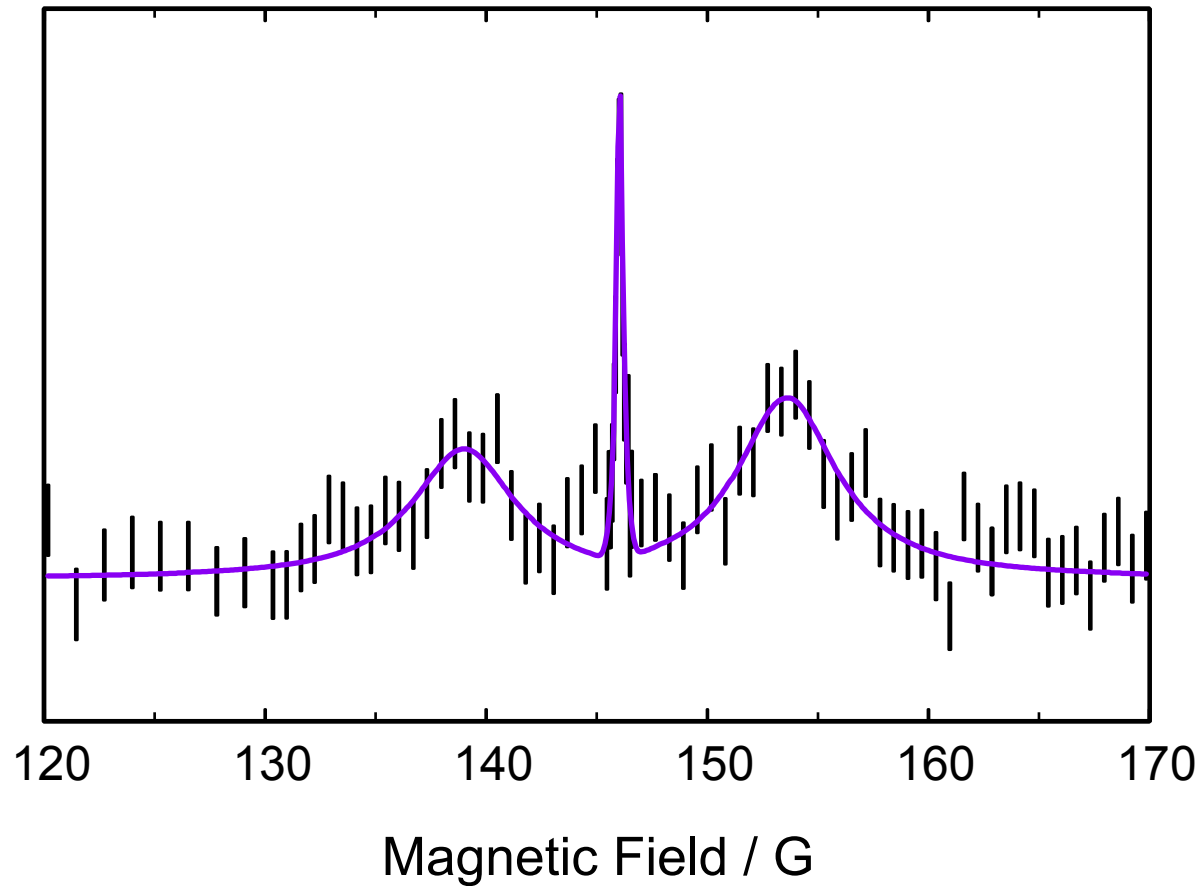
## Muon Level Crossing Resonance $\mu$ LCR (ALCR)

- mixing of spin levels causes *avoided* level crossing
- polarization is lost at magnetic fields where level crossing occurs

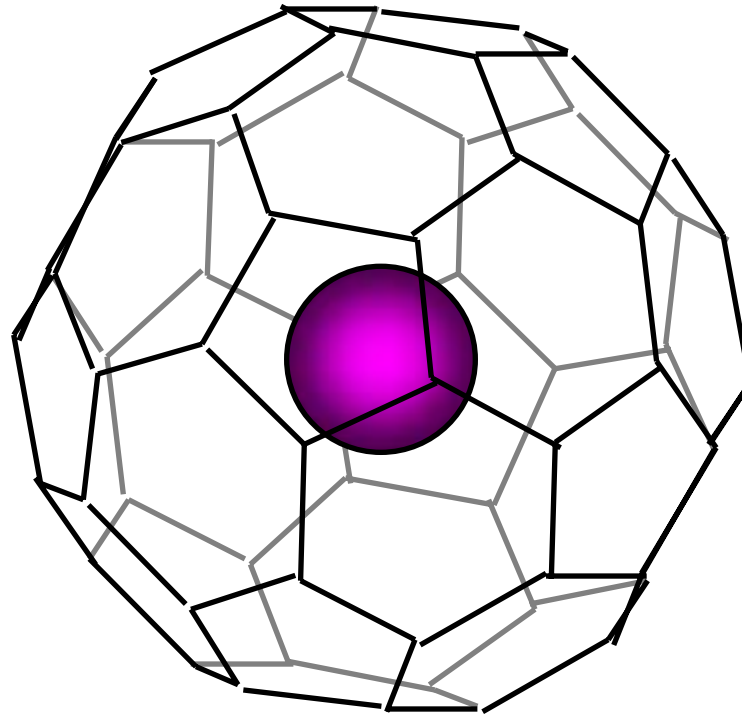
# RF Transitions in Muonium at Low Magnetic Field



# RF $\mu$ SR Spectrum of Mu@C<sub>60</sub> in C<sub>60</sub> Powder

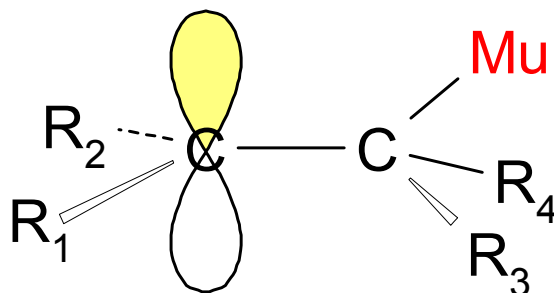


# Endohedral Muonium $\text{Mu@C}_{60}$



Muonium in a universe of its own

# Muoniated free radicals



$\mu$ SR:

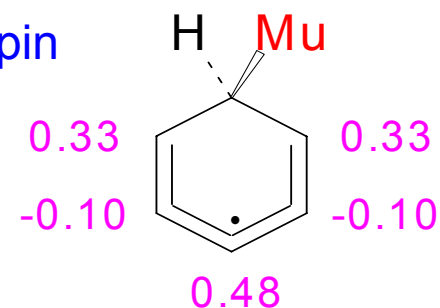
precession frequencies  $\Rightarrow$  muon hyperfine coupling

$\mu$ LCR:

resonance fields  $\Rightarrow$  other nuclear hyperfine couplings

hyperfine couplings  $\Rightarrow$  distribution of unpaired electron spin

e.g. cyclohexadienyl

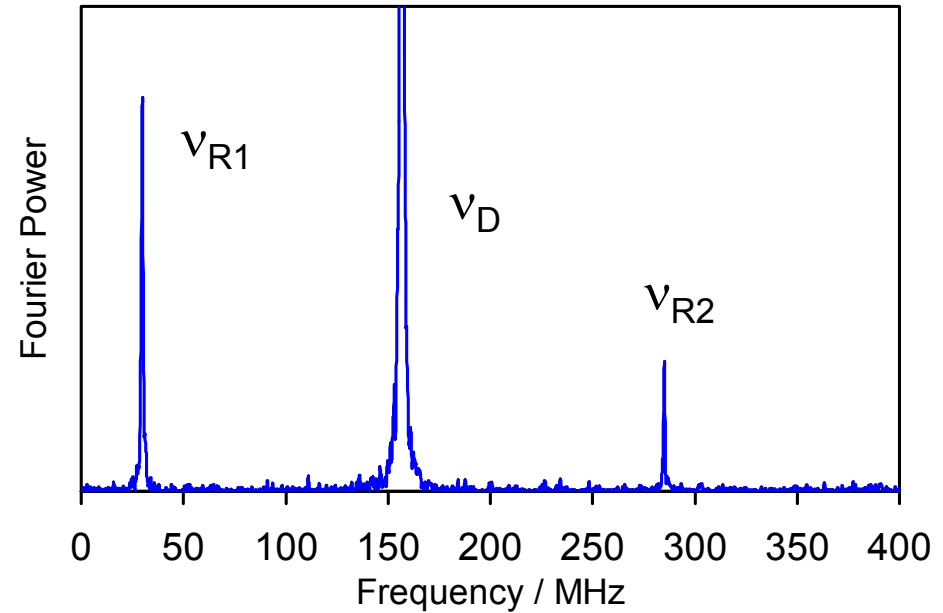
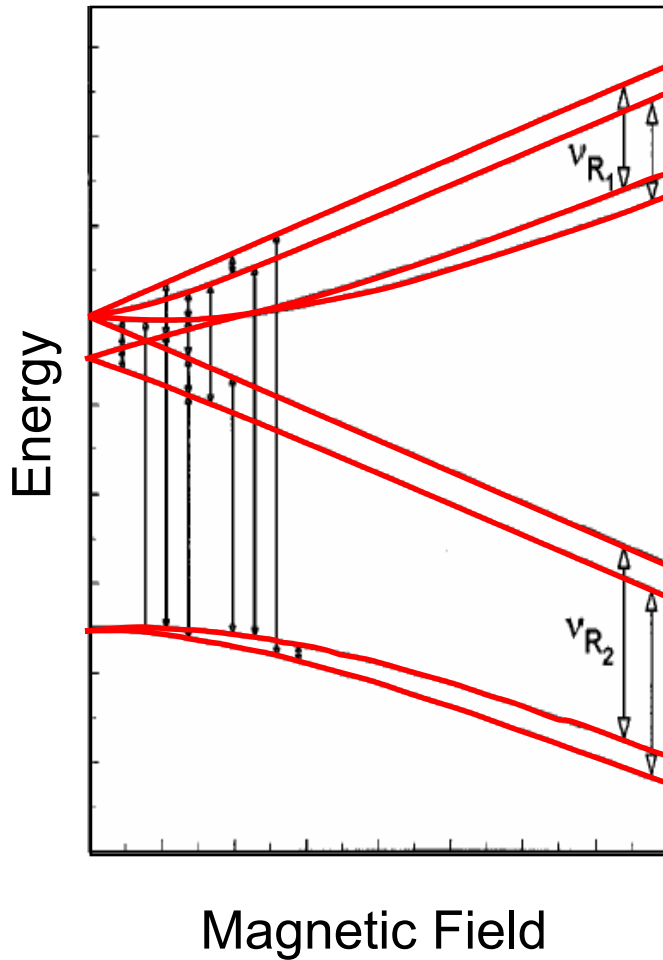


Temperature dependence of hyperfine couplings

$\Rightarrow$  intramolecular motion



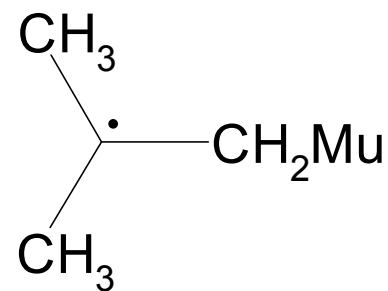
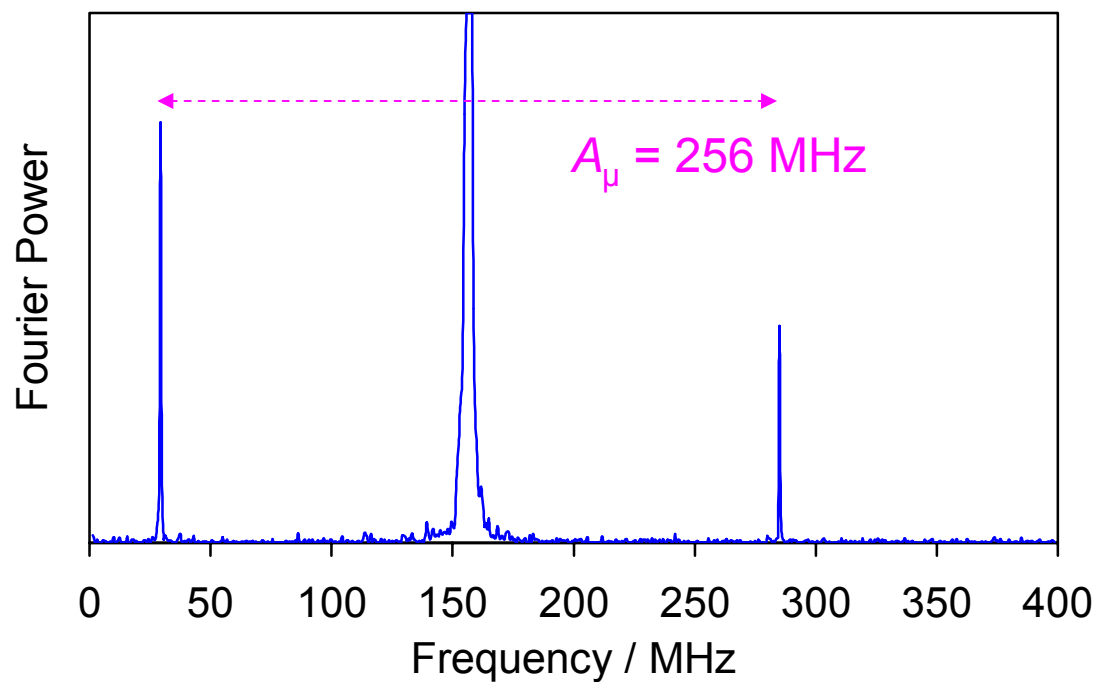
# Transverse field muon spin rotation of radicals



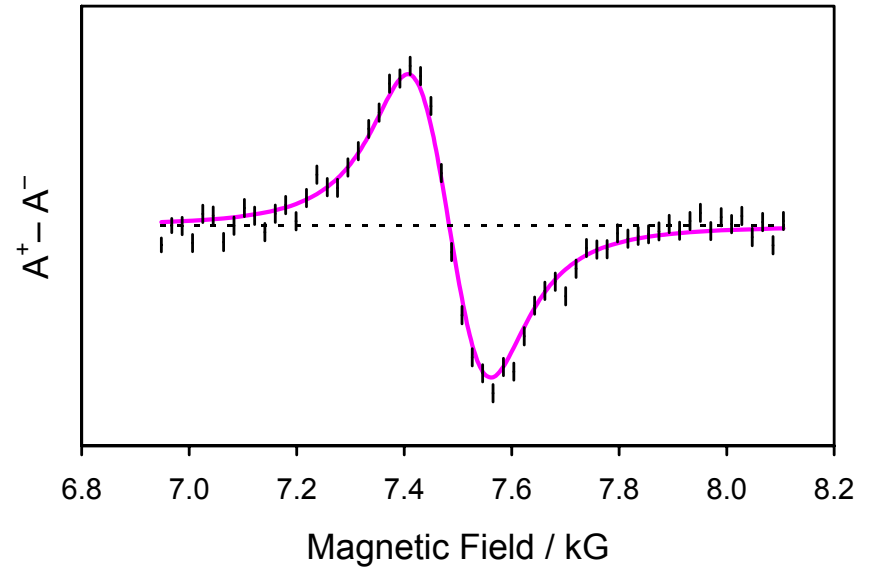
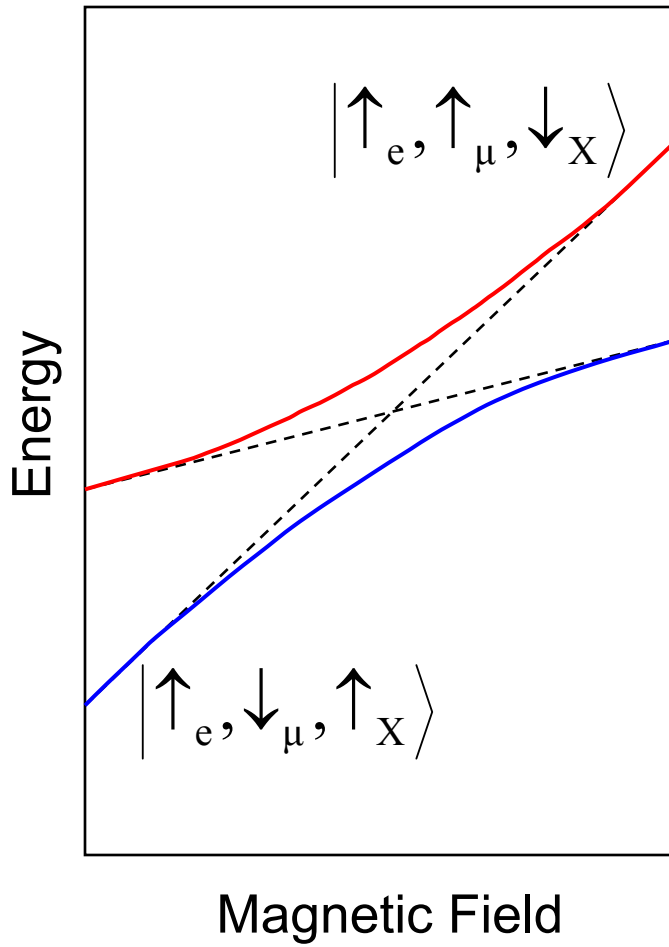
$$A_{\mu} = \nu_{R2} - \nu_{R1}$$

# Fourier power $\mu$ SR spectrum of tert-butyl

1 M *tert*-Butanol 280°C 250 bar 11.5 kG

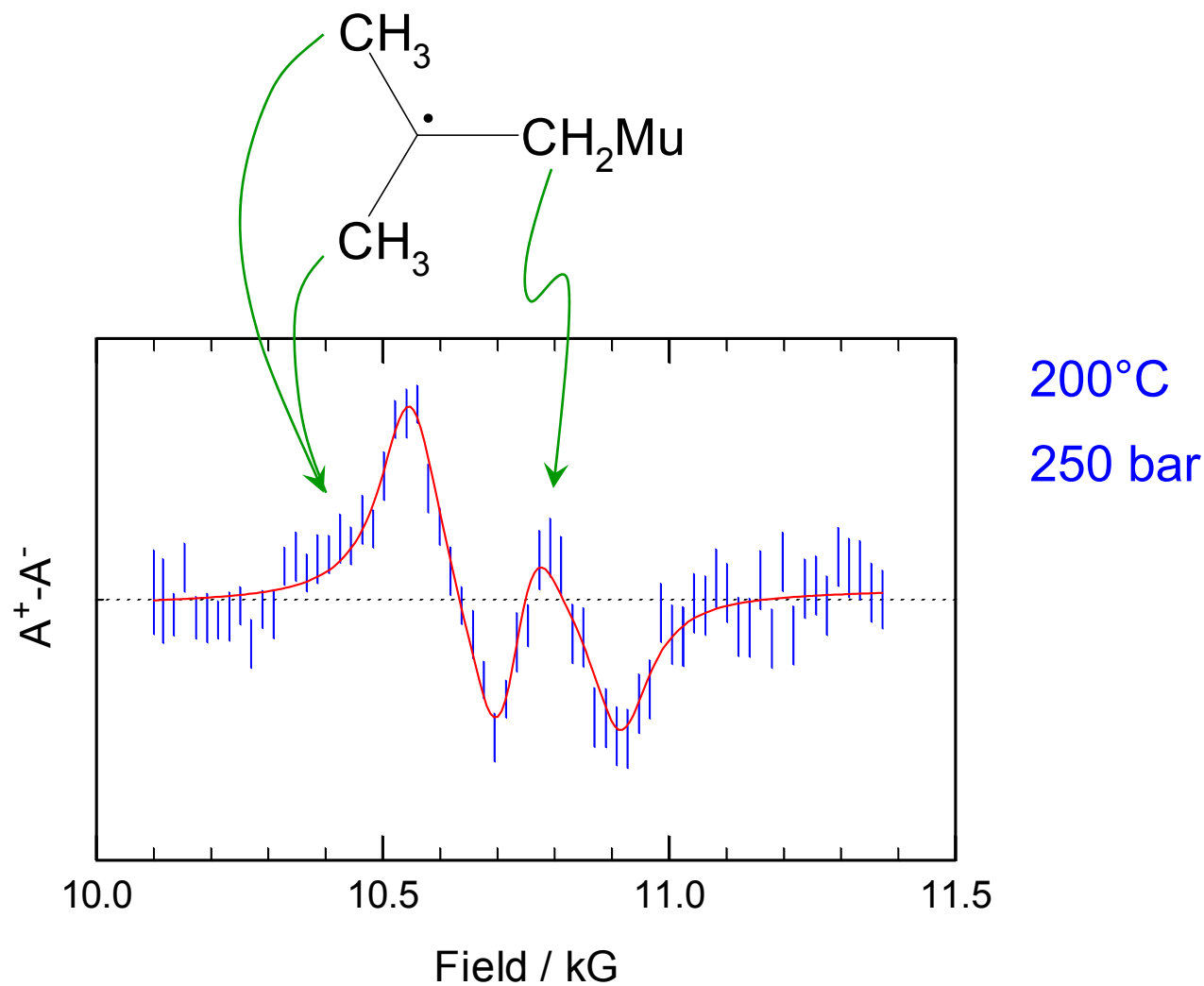


# Avoided Muon Level Crossing Resonance



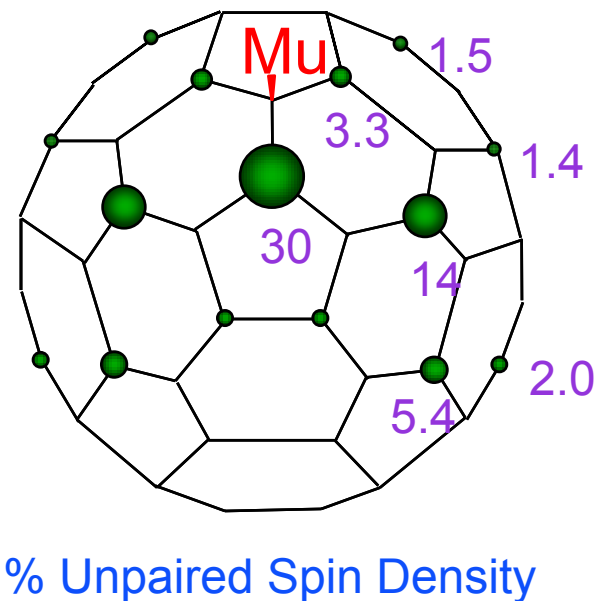
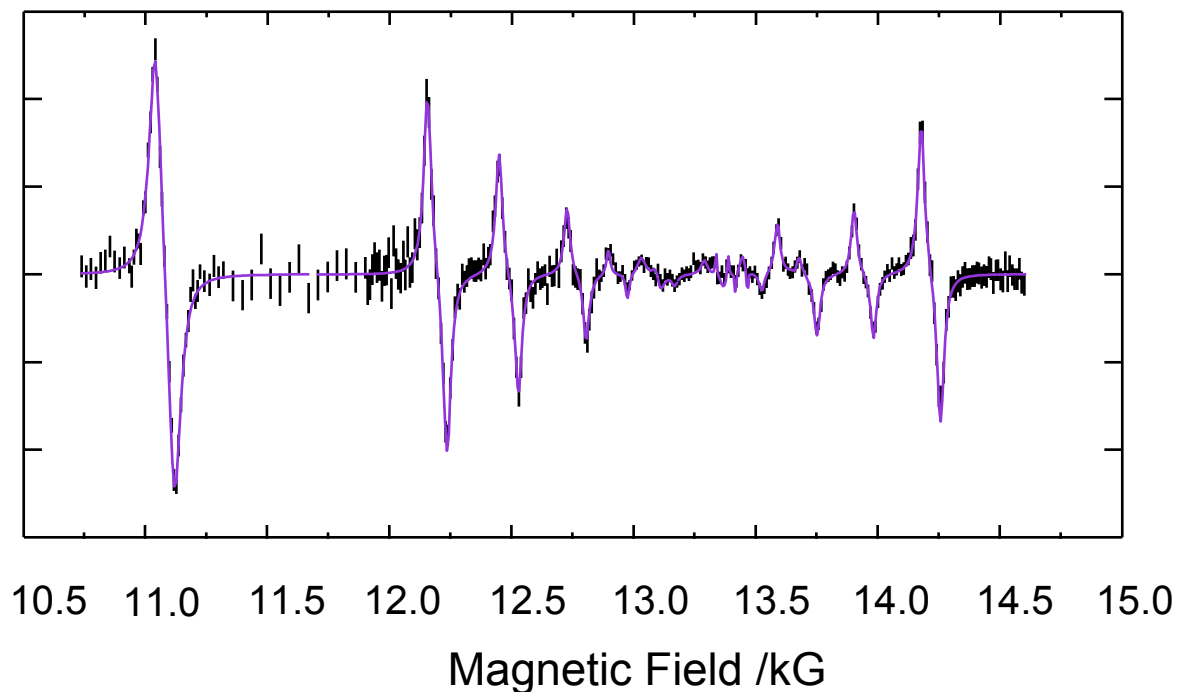
$$B_{\text{res}} \approx \frac{1}{2} \frac{A_\mu - A_X}{\gamma_\mu - \gamma_X}$$

# tert-Butyl radical in water



# Hyperfine constants are used to map unpaired spin in radicals

## Mu<sup>13</sup>C<sub>60</sub> Avoided Level Crossing Resonance



Percival, Addison-Jones, Brodovitch, Ji, et al., Chem. Phys. Lett., 245 (1995) 90

# H atoms and free radicals in liquids

H is the simplest atom

⇒ fundamental chemistry

H is a constituent of water, hydrocarbons, carbohydrates

⇒ essential chemistry

Chemically speaking, Mu  $\equiv$  H

We study Mu as a substitute for H

because it is **similar**: tracer, spin label

because it is **different** : isotope effects

# Muonium Chemistry – areas of application

Muonium (caged)	Mu as probe of local environment Fixed cage: fullerenes, silsesquioxanes partial: ice transient: water
Kinetics	How fast does it go? in gases: reaction dynamics liquids: solvent effects; diffusion vs. activation control
Structure (needs e-spin)	Where does it end up? Free radicals: unpaired spin distribution
Mechanism	How does it get there? Identification of radical products Transfer of muon polarization
Dynamics intramolecular intermolecular	Nature is floppy! Temperature dependence of hyperfine constants LCR lineshape analysis

## Further Reading

[http://www.sfu.ca/chemistry/news/pt\\_quilt/index.htm](http://www.sfu.ca/chemistry/news/pt_quilt/index.htm)

<http://musr.org/cmms.php>

<http://musr.org/intro/musr/muSRBrochure.pdf>