Muons in Chemistry Training School 2014

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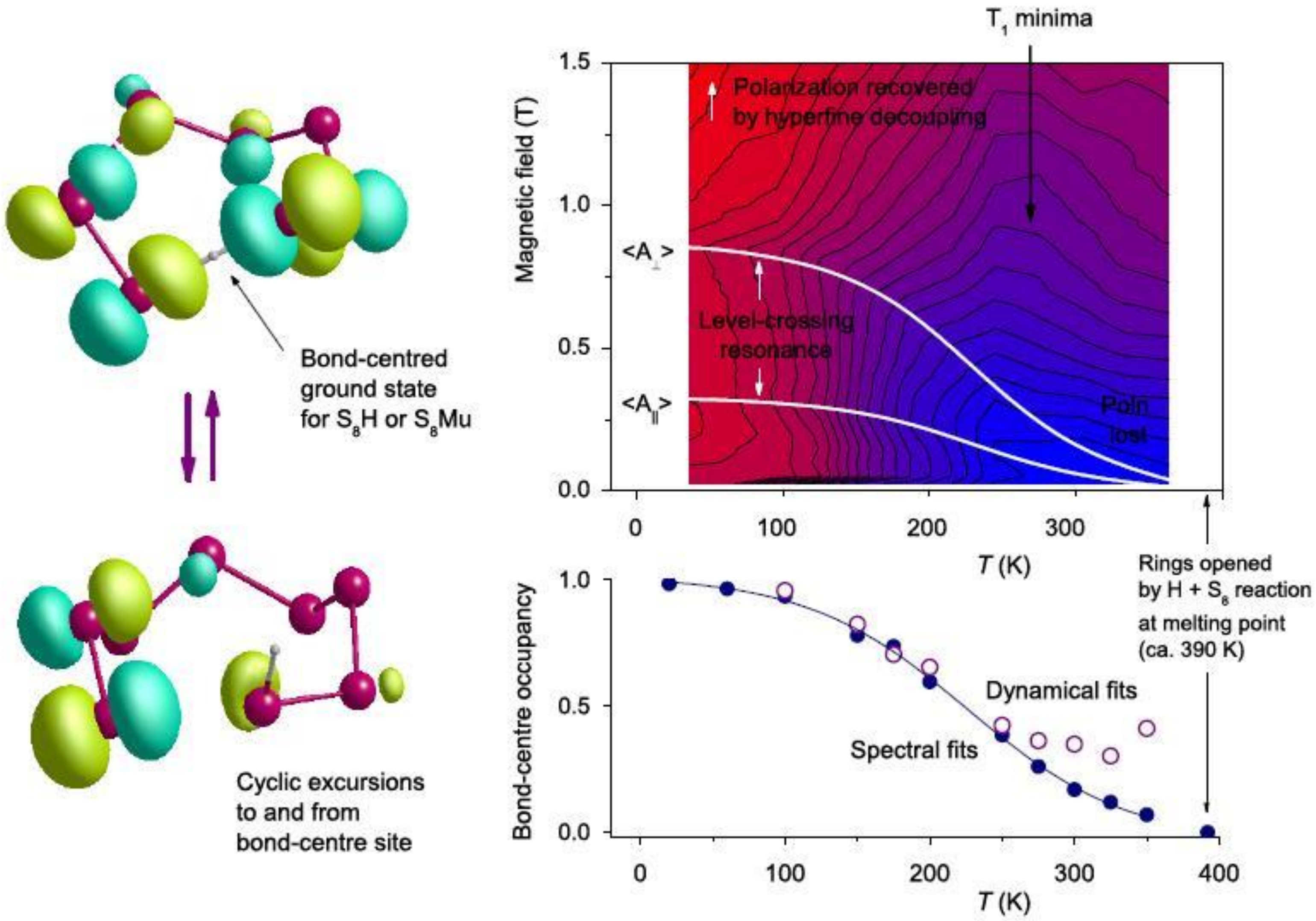
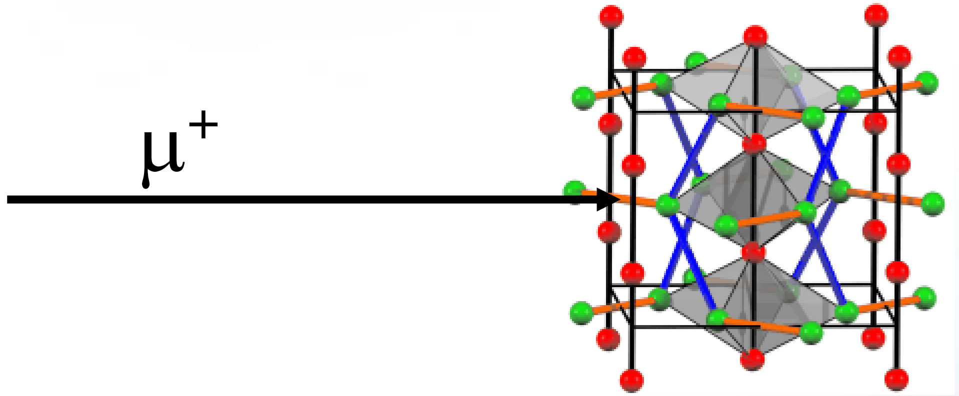
Why use muons?

- Extrinsic probe (Mu^+, $Mu^\bullet$, muoniated radical)
- Intrinsic interest
- Framing of the chemical problem
- Rationale
  - Muon as a light isotope of hydrogen
  - Magnetic moment
- Structure, dynamics and kinetics



S F J Cox *et al* 2011 *J. Phys.: Condens. Matter* **23** 315801 doi:10.1088/0953-8984/23/31/315801

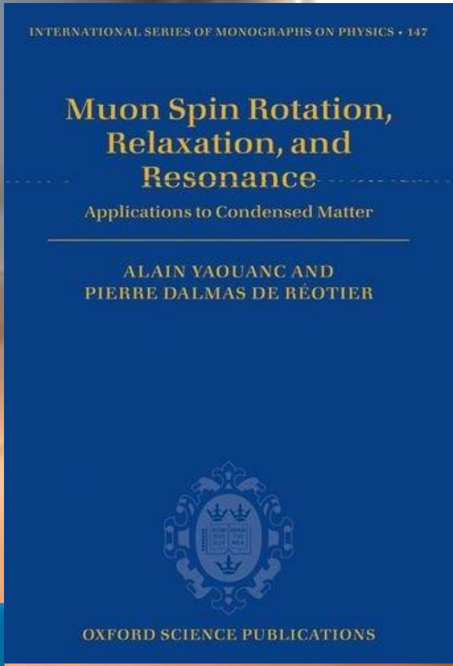
What happens?



Mu^+	diamagnetic
$\mathrm{Mu}^{\bullet}$	paramagnetic
$\mathrm{RMu}^{\bullet}$	paramagnetic

Muons in Chemistry

- Kinetic isotope effect in radical reactions
  - low mass of the muonium as an isotope of hydrogen,
- observation of hydrogen atom processes
- probing the local magnetic environment
- muons as an exotic particle.



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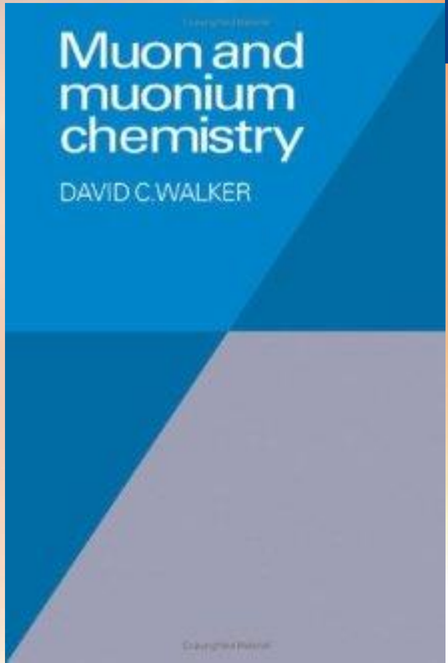
Muon Spin Rotation, Relaxation, and Resonance

Applications to Condensed Matter

ALAIN YAOUANC AND PIERRE DALMAS DE RÉOTIER

OXFORD SCIENCE PUBLICATIONS



Muon and muonium chemistry

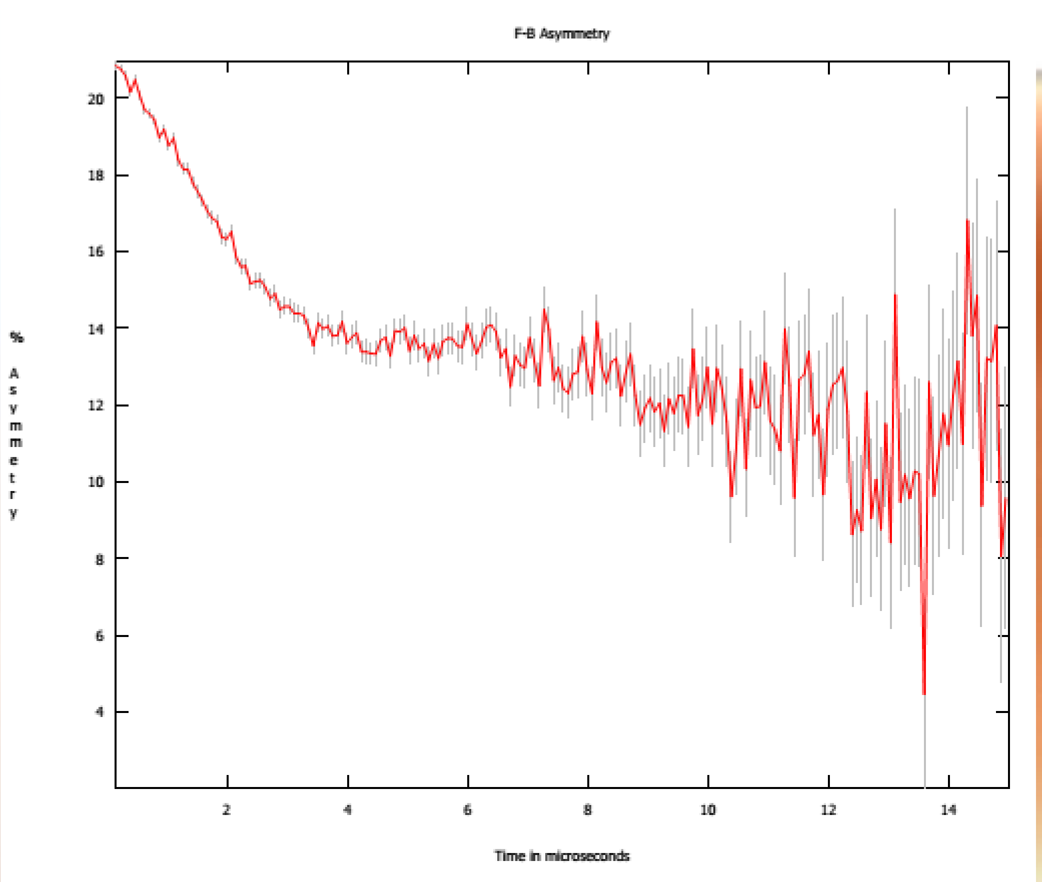
DAVID C. WALKER

New directions

- Surface studies
- Soft matter
- Combination experiments
  - Electric fields
  - Laser irradiation
- Extreme environments

What can be determined?

- Nature of the muon species
  - Mu^+, $Mu^\bullet$, muoniated radical
- Number of species
- Functional form of the decay
- Decay constant
- Hyperfine coupling constants
  - $Mu^\bullet$, muoniated radical



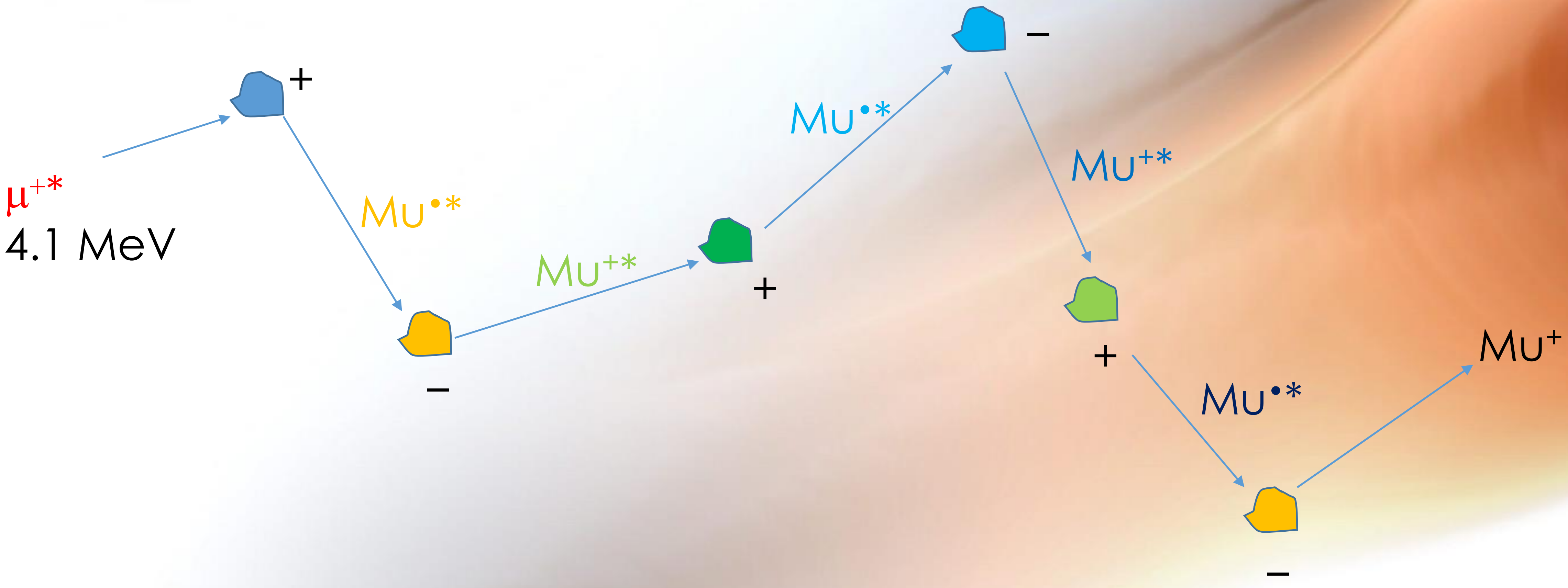
μ^+ implanted into $Zr(H_2PO_4)(PO_4).2H_2O$ at 10 K in zero external magnetic field

Illustrative example

- Sample: $Zr(H_2PO_4)(PO_4).2H_2O$
- Aim: study dynamics of implanted muon
- Expectation, diamagnetic muon
  - Insulator
  - Chemistry of similar systems
  - Bare Mu^+, trapped near O
  - Abstraction reaction, MuOH
  - Muon decay determined by field from local nuclear magnetic moments

Muon thermalisation

- But do we really know $Mu^\bullet$ wont be formed?

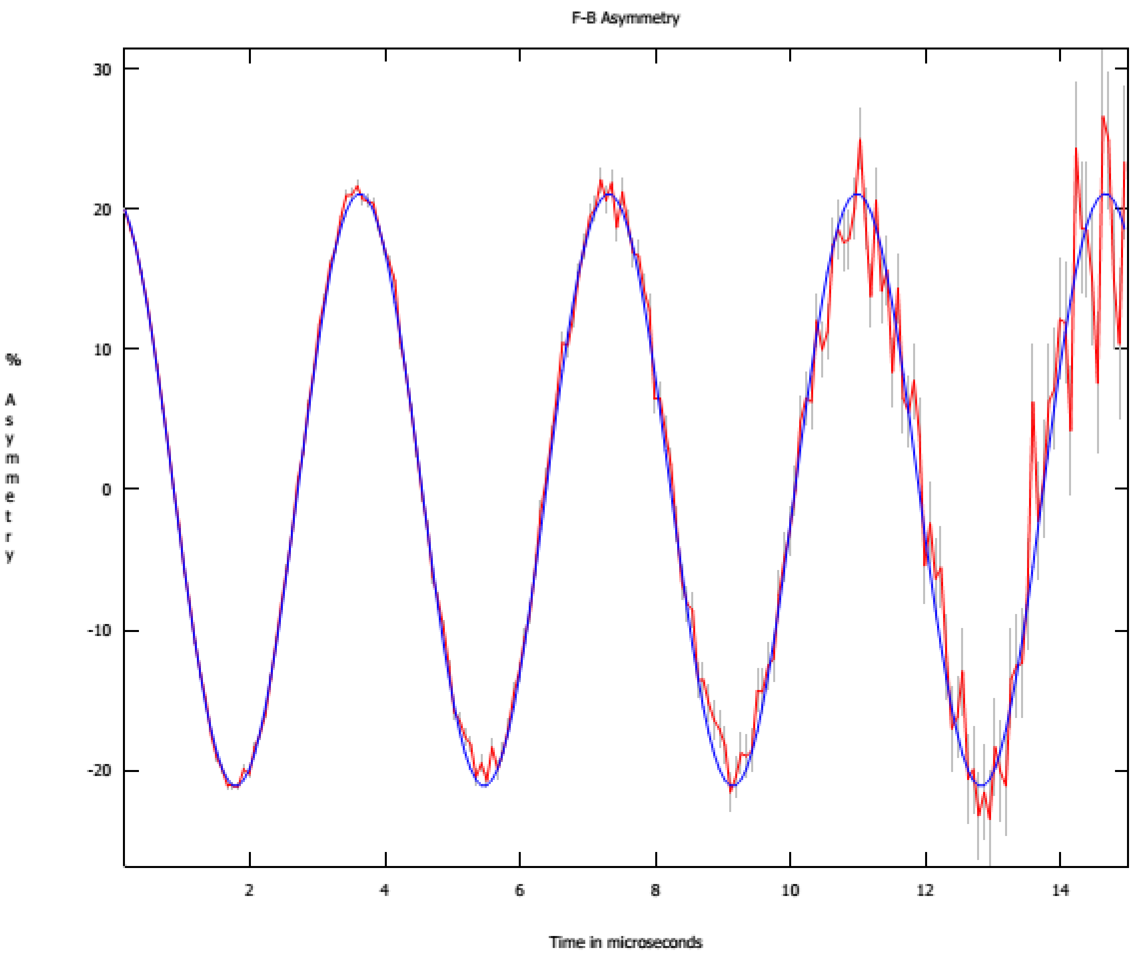


Check the asymmetry

Calibrate using Ag
Transverse field, 2 mT, 20 G

Fit to rotation frequency

$a_0 = 21.1\%$
0.271 MHz



Sample 20 G transverse field

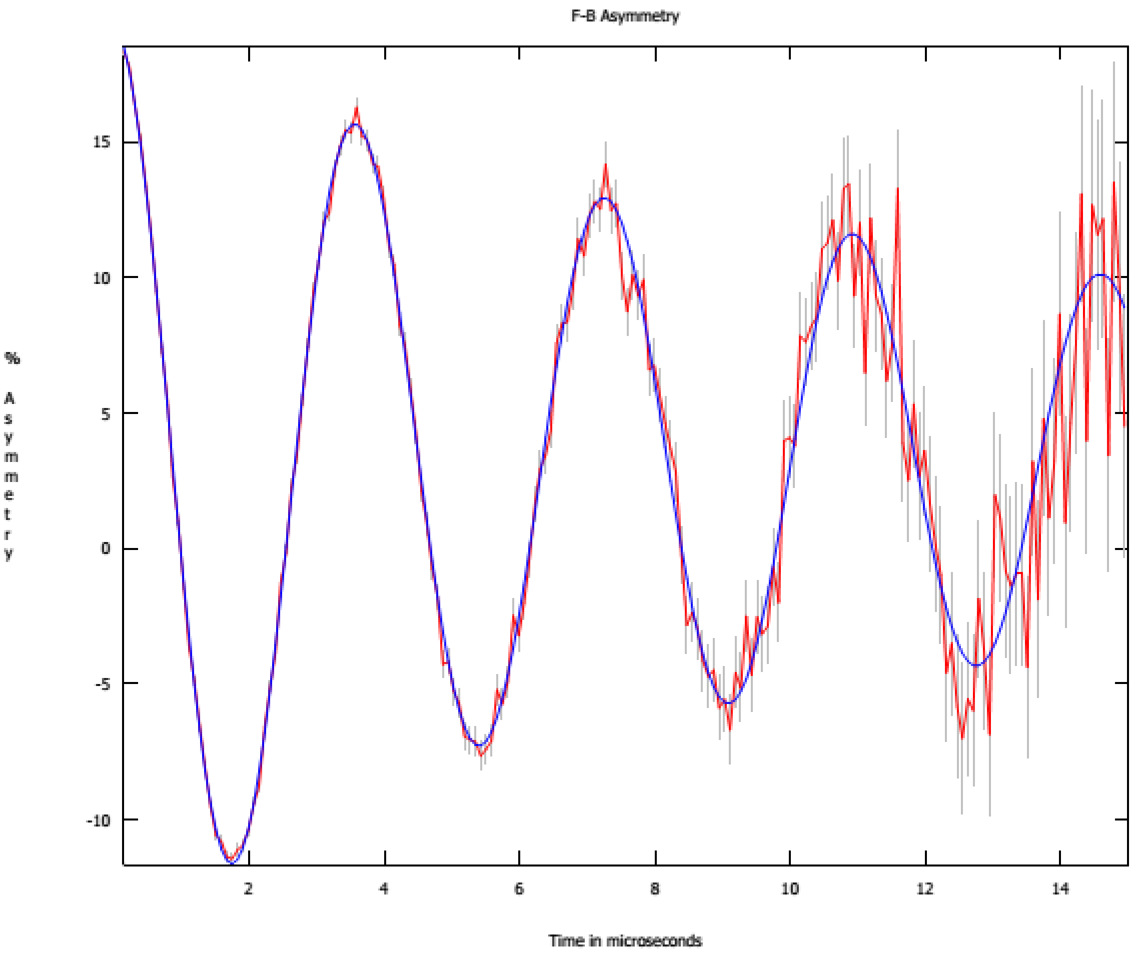
Transverse field, 20 G

Fit to rotation frequency
with Gaussian decay
Two components required

a_0 (1) = 16.23%
0.272 MHz
$\sigma = 0.04\ \mu s^{-1}$

a_0 (2) = 5.55%
0.276 MHz
$\sigma = 0.283\ \mu s^{-1}$

a_0 (T) = 21.8%



μ^+ implanted into $Zr(H_2PO_4)(PO_4).2H_2O$ at 10 K
in 2 mT, 20 G transverse magnetic field

Check the asymmetry

- Full asymmetry
- Rotation frequency typical of diamagnetic muon
- $P_D = 1.0$
- No evidence for muonium – repolarisation, $P_M = 0.0$
- No evidence for a “missing” fraction, $P_L = 0.0$
  - Hyperfine oscillations during thermalisation
  - Depolarising encounter with paramagnetic species (e_s^-)

Can we use the rotation frequency?

- Would be equivalent to the NMR chemical shift
- Severely limited by the muon lifetime

τ_{Mu} = 2.2 μs

Uncertainty Principle

$$\Delta\nu \cdot \Delta t = \frac{1}{4\pi}$$

$$\Delta\nu = \frac{10^6}{(4\pi \times 2.2)} = 0.036\ \text{MHz}$$

Typical ^{1}H chemical shifts ~ 10^{-5} MHz

How can we tell diamagnetic muons apart?

- Not through the rotation frequency!
- Size of local nuclear dipolar field
  - Obtain from the relaxation time constant
  - Propose structural model based on chemistry
  - Search crystal structure
- Evidence for two sites
  - Two different relaxation rates
  - Origin of multiple sites?

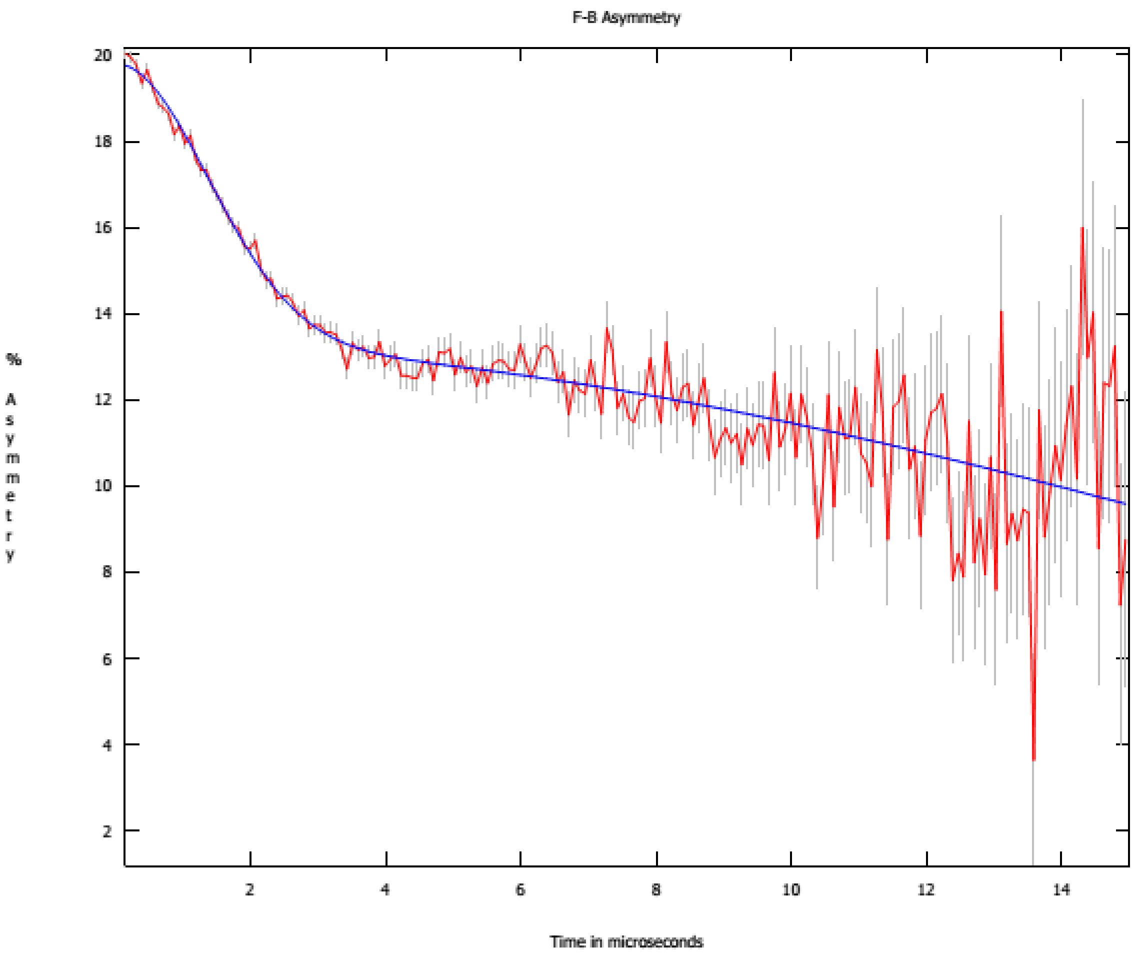
Zero-field MuSR

Fit to Gaussian decay
Two components required

a_0 (1) = 13.25%
σ = 0.038 μs^{-1}

a_0 (2) = 6.56%
σ = 0.522 μs^{-1}

Low temperature, no dynamics
Values for σ reflect local nuclear dipolar field



μ^+ implanted into $Zr(H_2PO_4)(PO_4).2H_2O$ at 10 K in zero external magnetic field

Zero-field MuSR

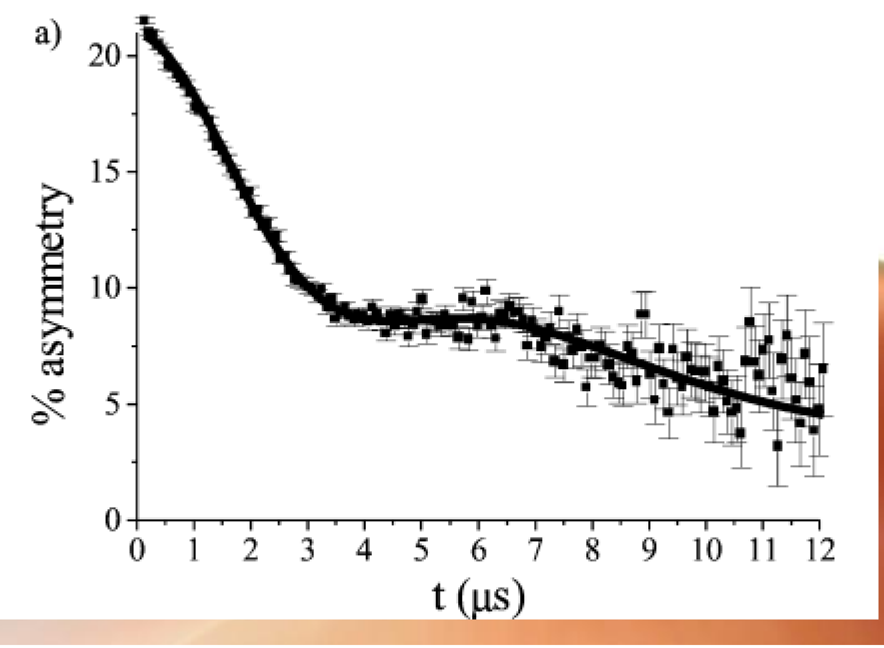
Fit to Gaussian Kubo-Toyabe decay
Two components required

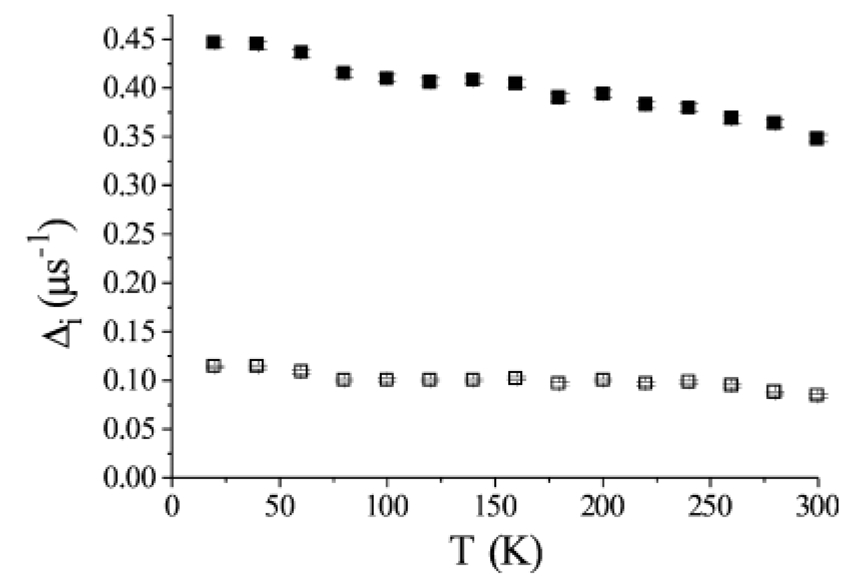
a_0 (1) ~ 10.5%
$\Delta = 0.12 \pm 0.005\ \mu s^{-1}$

a_0 (2) ~ 10.5%
$\Delta = 0.45 \pm 0.004\ \mu s^{-1}$

Little temperature dependence

Consistent with low proton conductivity
$10^{-3} - 10^{-4}$ S m^{-1} at 20° C





Evidence from $Zr(H_2PO_4)(PO_4)$

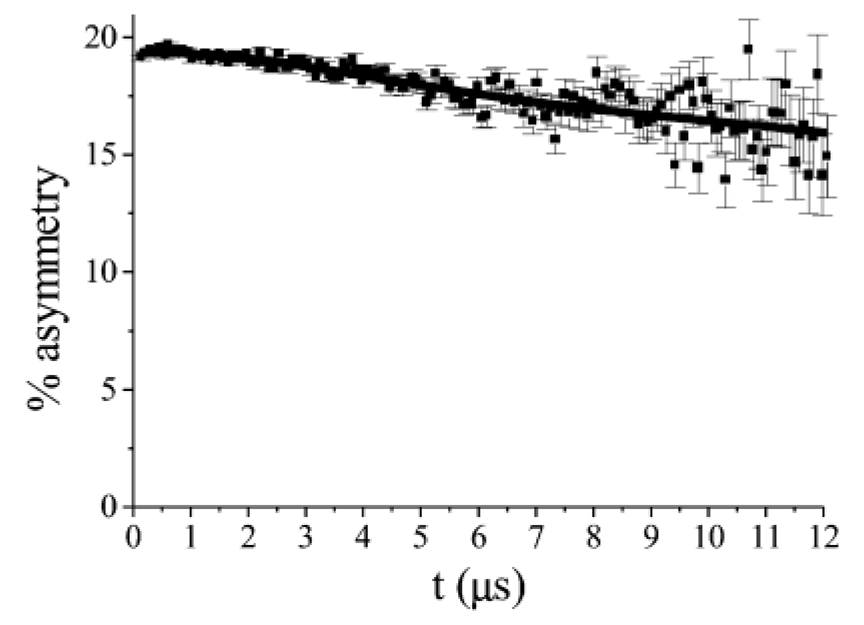
Fit to Gaussian Kubo-Toyabe decay
Two components required

a_0 (1) ~ 17.9%
$\Delta = 0.03 \pm 0.001\ \mu s^{-1}$

a_0 (2) ~ 1.5%
$\Delta = 0.202 \pm 0.01\ \mu s^{-1}$

Loss of faster decaying component
Associated with muon addition to H_2O

Slow decaying, Mu trapped by O-P



μ^+ implanted into $Zr(H_2PO_4)(PO_4)$ at 260 K
in zero external magnetic field

Interpretation of Δ

- Model reactions in ice

$$H_2O + \mu^+ = H_2OMu^+$$
$$H_2OMu^+ + L = HOMu + LH^+$$

- Hydrated crystals
  - Gypsum, 300 K HOMu
  - Oxalic acid dihydrate, H_2OMu^+

Calculation of Δ

- Related to the second moment, M_2

$$M_2 = 2\Delta^2$$

$$M_2 = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_S^2 \gamma_{Mu}^2 S(S+1)\sum_j r_j^{-6}$$

- Assume a substitution reaction
- Use H positions from neutron diffraction crystal structure

Calculation of Δ

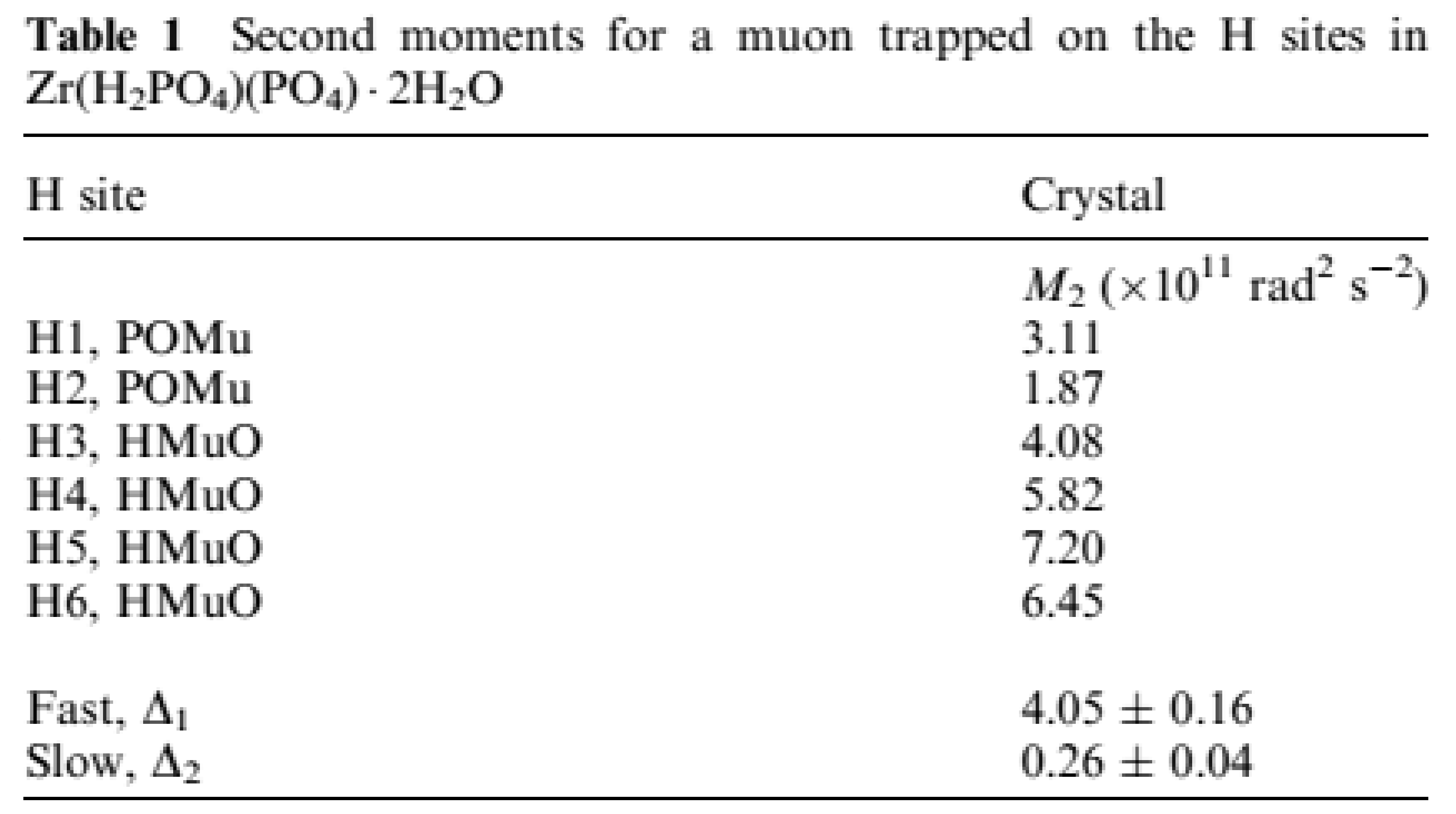


Table 1 Second moments for a muon trapped on the H sites in $Zr(H_2PO_4)(PO_4) \cdot 2H_2O$

H site	Crystal
	M_2 ($\times 10^{11}$ rad^2 s^{-2})
H1, POMu	3.11
H2, POMu	1.87
H3, HMuO	4.08
H4, HMuO	5.82
H5, HMuO	7.20
H6, HMuO	6.45
Fast, Δ_1	4.05 ± 0.16
Slow, Δ_2	0.26 ± 0.04

Isolated H_2OMu^+ $M_2 > 5.5 \times 10^{11}$ rad^{2}s^{-2}

Summary

- Diamagnetic muons, full asymmetry in any magnetic field
- Rotation frequency of 271 kHz in 2 mT (20 G) transverse field
- Relaxation rate from fit to time domain data
- Choose functional form e.g. gaussian, lorentzian on the basis of best fit χ^2
- Low temperature relaxation rate to assign muon site through M_2
- Temperature dependence indicative of muon dynamics

Muonium and muoniated radicals

- Paramagnetic: unpaired electron
- Strength of coupling between muon and electron given by the Hyperfine coupling constant

Isotropic hyperfine coupling

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

Unpaired electron density at nucleus
Transmitted through bonds

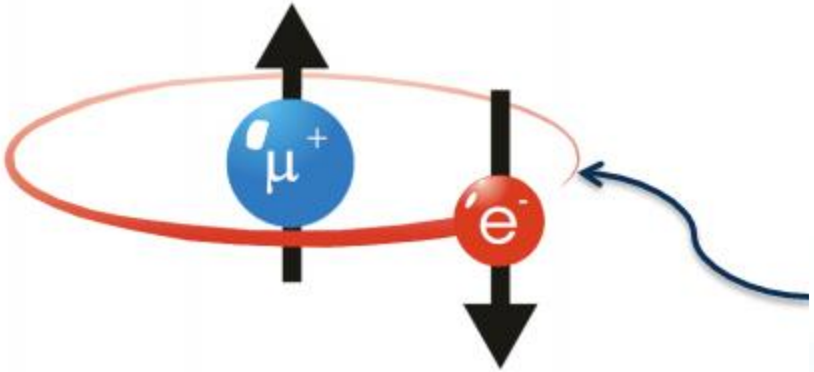
Anisotropic hyperfine coupling

$$D_X = \left(\frac{\mu_0 \gamma_e \gamma_X \hbar}{4\pi}\right) \left\langle \frac{1 - 3\cos^2\theta}{r^3} \right\rangle$$

Dipole-dipole
Through space
Averages to zero in solution

Order of 10-100's MHz

Muonium



Muonium, $Mu^\bullet$ (IUPAC)
μ^+, e^-

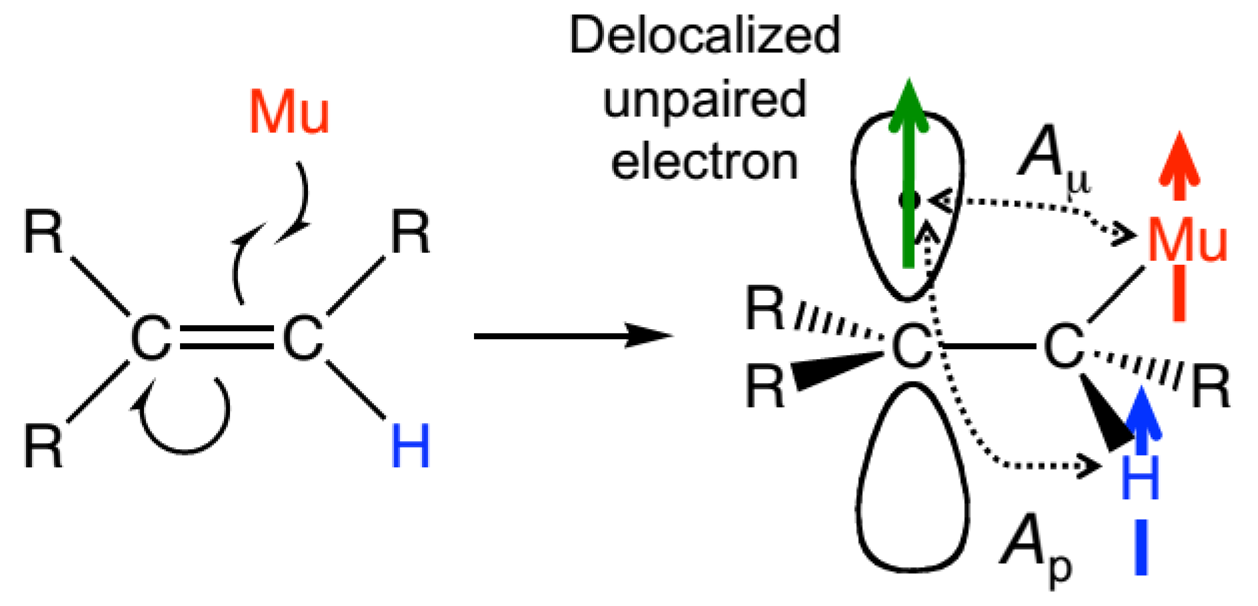
A_μ = 4.463 GHz

Reactive chemistry similar to $H^\bullet$

Ionisation energy 13.54 eV
Bohr radius 53.2 pm

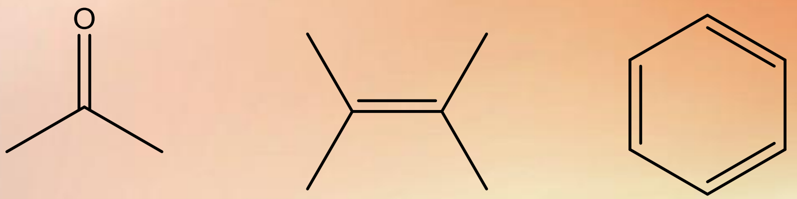
Muoniated radical

Muoniated = replacement of an H by muonium



Mu adds across
a double bond

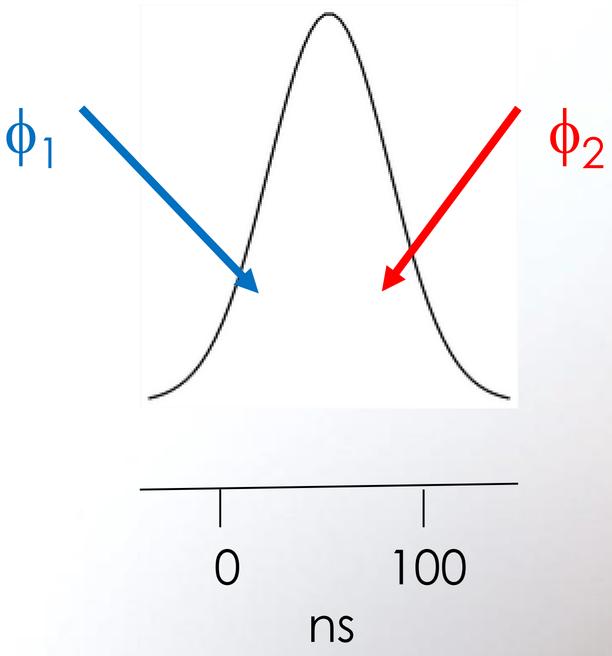
Range of hyperfine
coupling constants

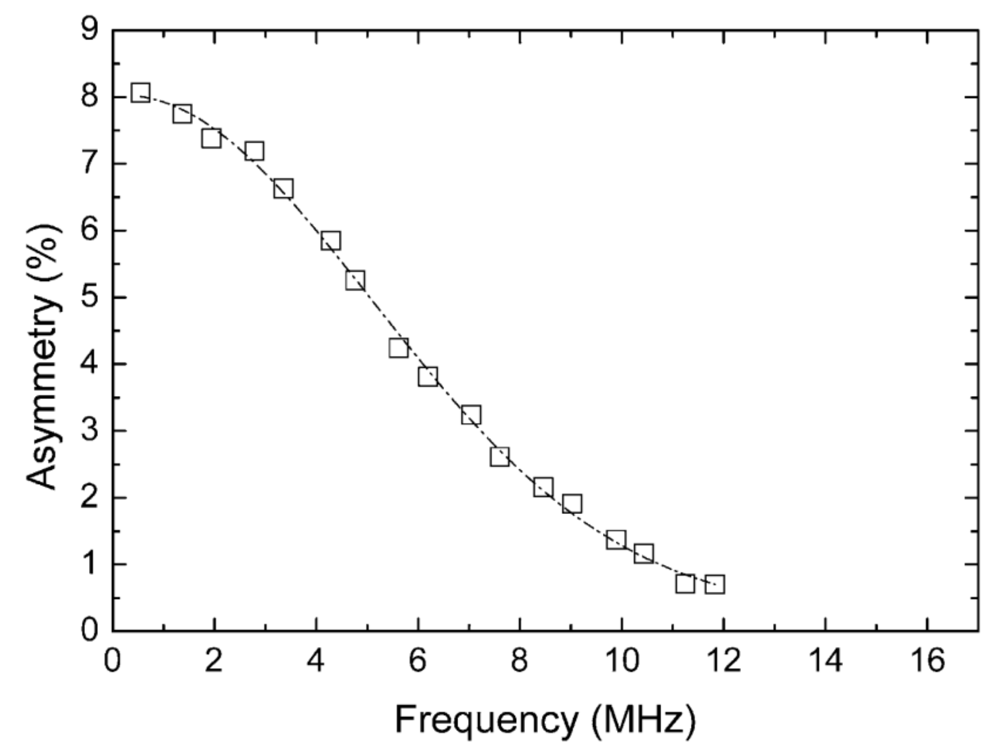


A_μ = 10 200 500 MHz

How do you know if you have a paramagnetic species?

- Full asymmetry not seen in a 2 mT TF experiment
- Finite width of muon pulse at ISIS





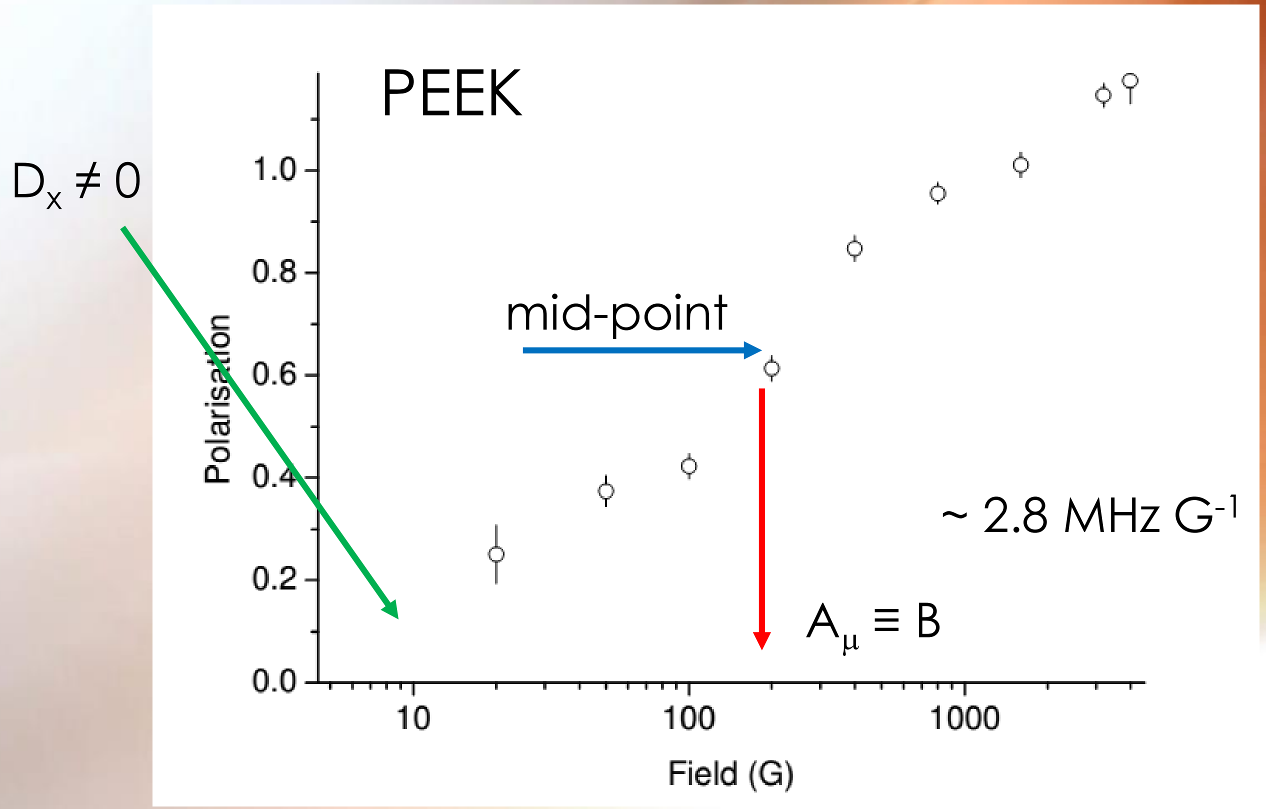
Triplet precession of muonium in quartz

Repolarisation

- Asymmetry increases with increasing longitudinal field

$$P = h_D + \frac{h_M}{2}\left[1 + \frac{x^2}{1+x^2}\right]$$

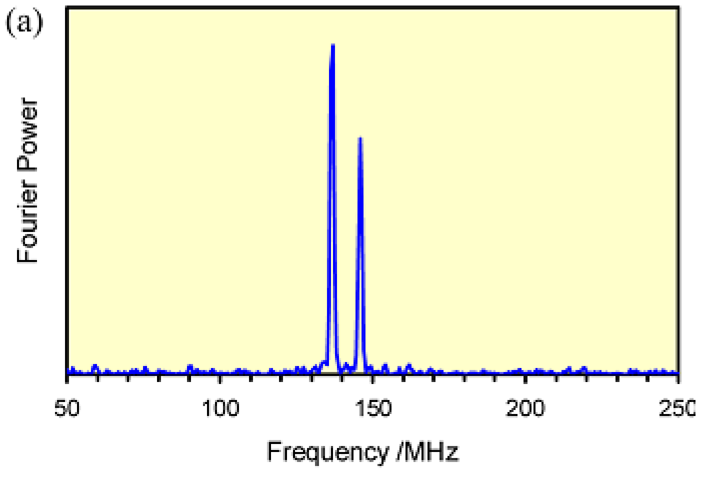
$$x = \frac{(\gamma_e + \gamma_\mu)B}{2\pi} \cdot \frac{1}{A_\mu}$$

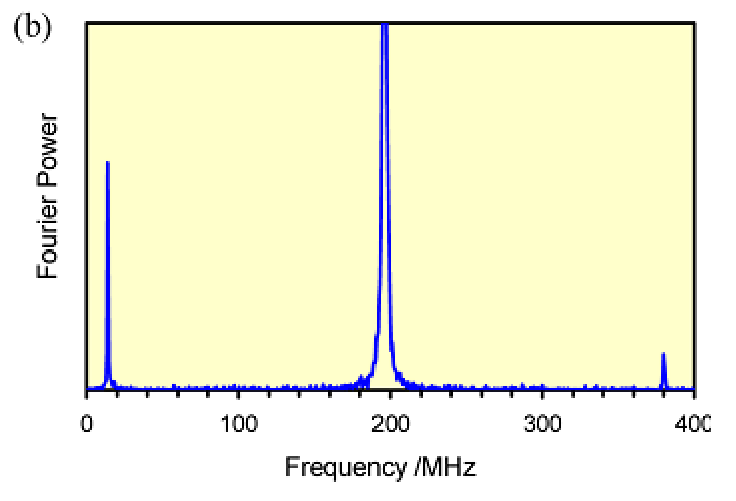


h_D = diamagnetic fraction
h_M = paramagnetic fraction
Aμ (MHz)

Muonium or muoniated radical?

- Muonium, large hyperfine coupling constant
    - ISIS: LF > 1 kG required for repolarisation
    - PSI/TRIUMF: High precession frequency at low TF





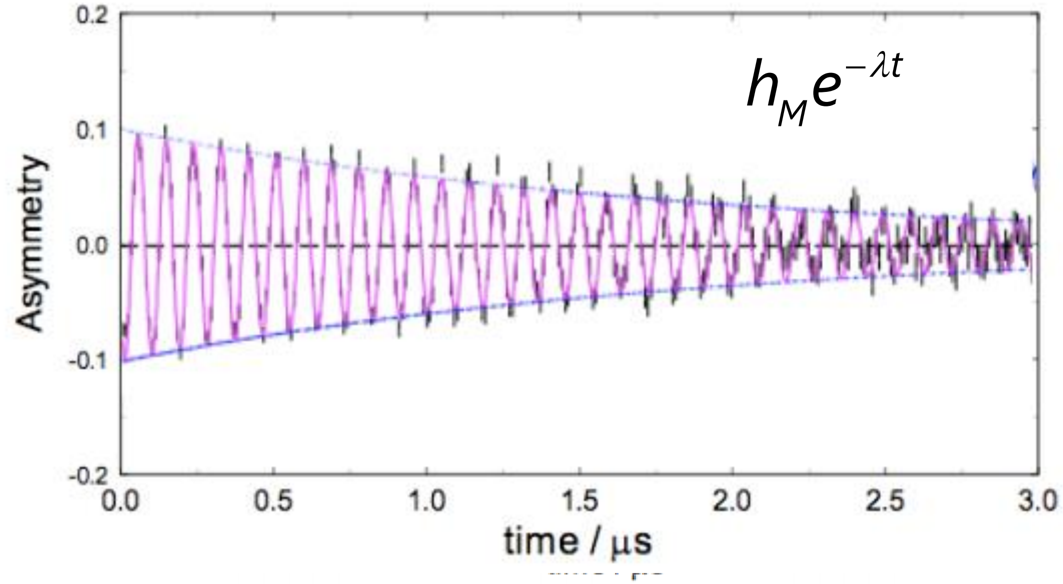
Cyclopentane hydrate -10° C in 100 G TF

2,5 -dihydrofuran hydrate -12° C in 14.46 kG TF

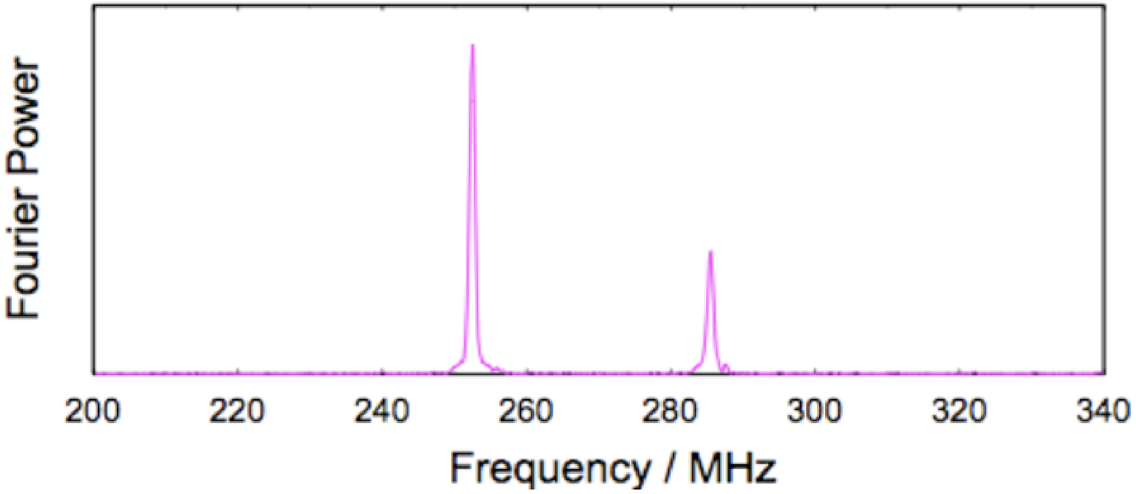
Percival et al J. Phys. Chem. A 2014, 118, 1162−1167

TF-MuSR of muonium

Low field < 10 G
Obtain the relaxation rate, λ
Kinetics



Intermediate field, 250 G
Measure A_μ
(Solvent dependent)



Measuring $Mu^{\bullet}$ reaction rates

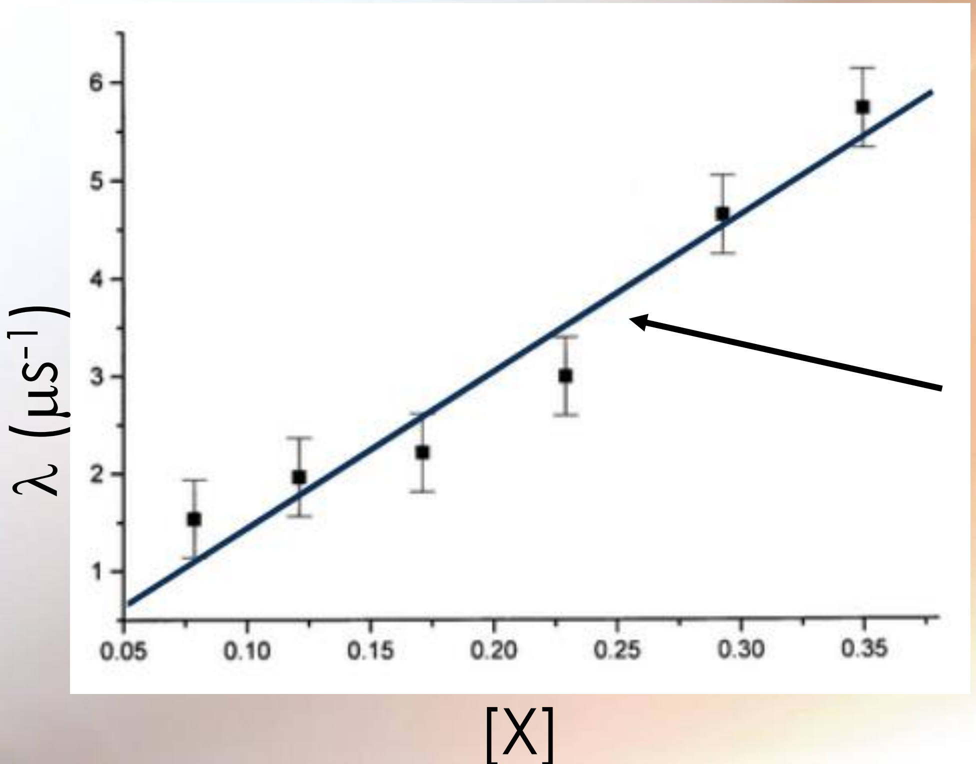
$$\lambda = \lambda_0 + k_{Mu}[X]$$

Concentration of reactant X

Relaxation rate
In pure solvent

Pseudo 1st order
Rate constant

Rate window
$10^5\ M^{-1}s^{-1} < k_{Mu} < 10^{10}\ M^{-1}s^{-1}$



Slope = k_{Mu} $(M^{-1}s^{-1})$

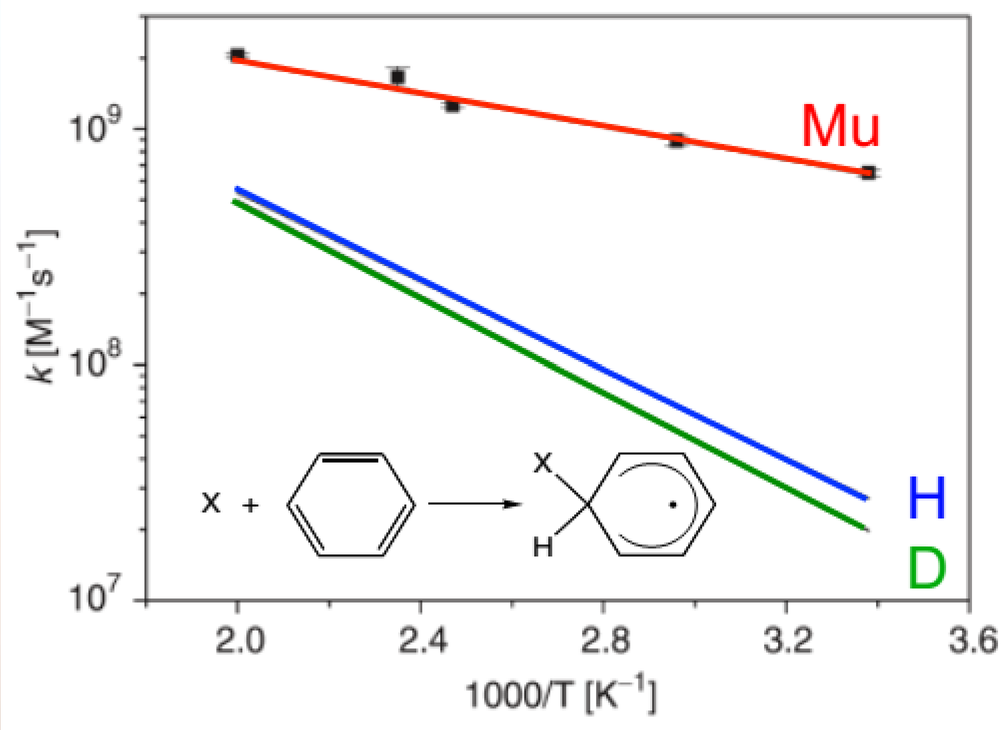
Muonium kinetics

Formation of muoniated radicals

Addition reactions
$k_{Mu} > k_H$

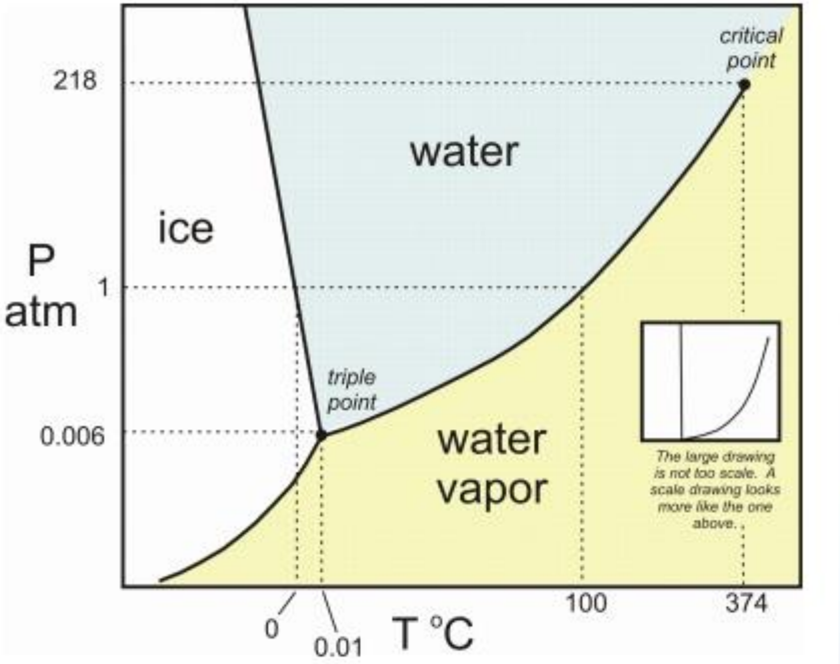
Diffusion controlled
Kinetic isotope effect

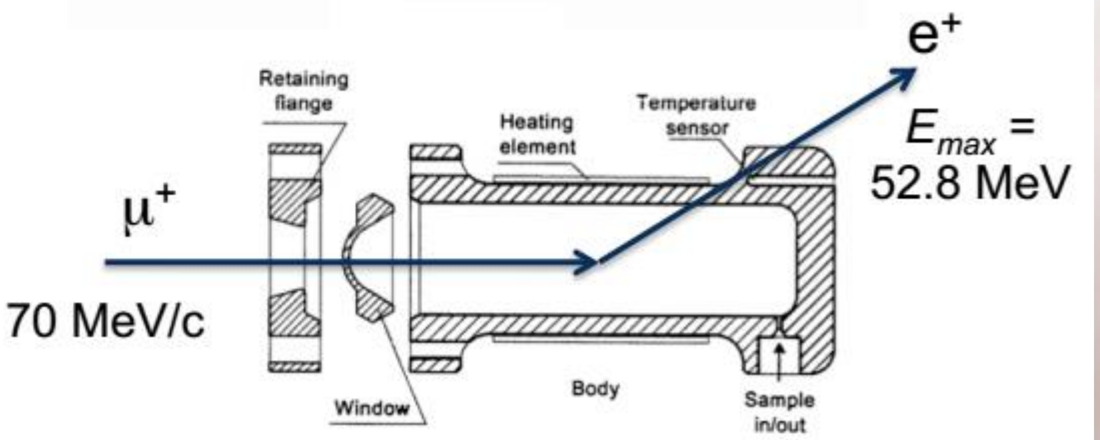
(Abstraction reactions
$H_2 + Mu^{\bullet} = MuH + H^{\bullet}$)



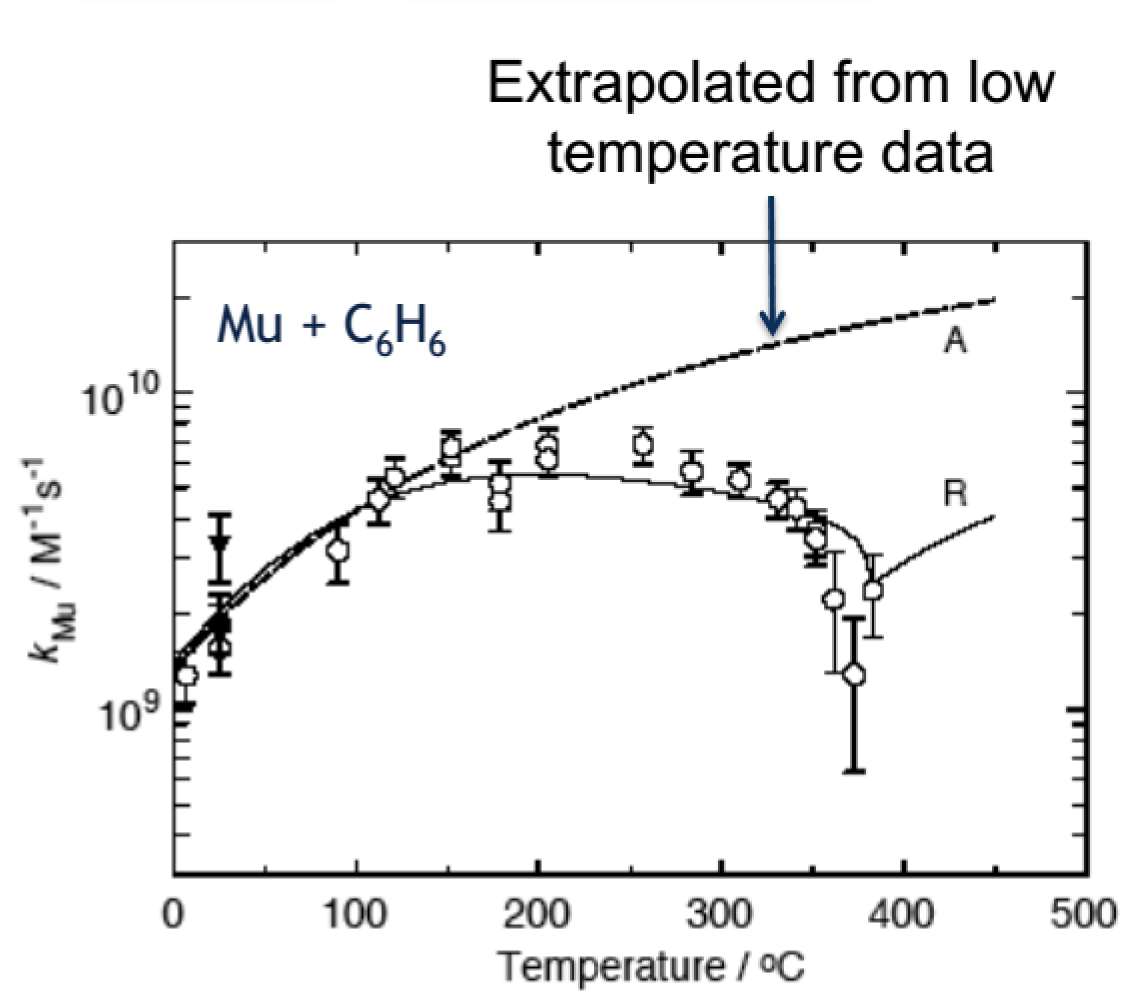
E. Roduner et al. Ber. Bunsenges. Phys. Chem. 94(1990) 1224

Extreme Environments



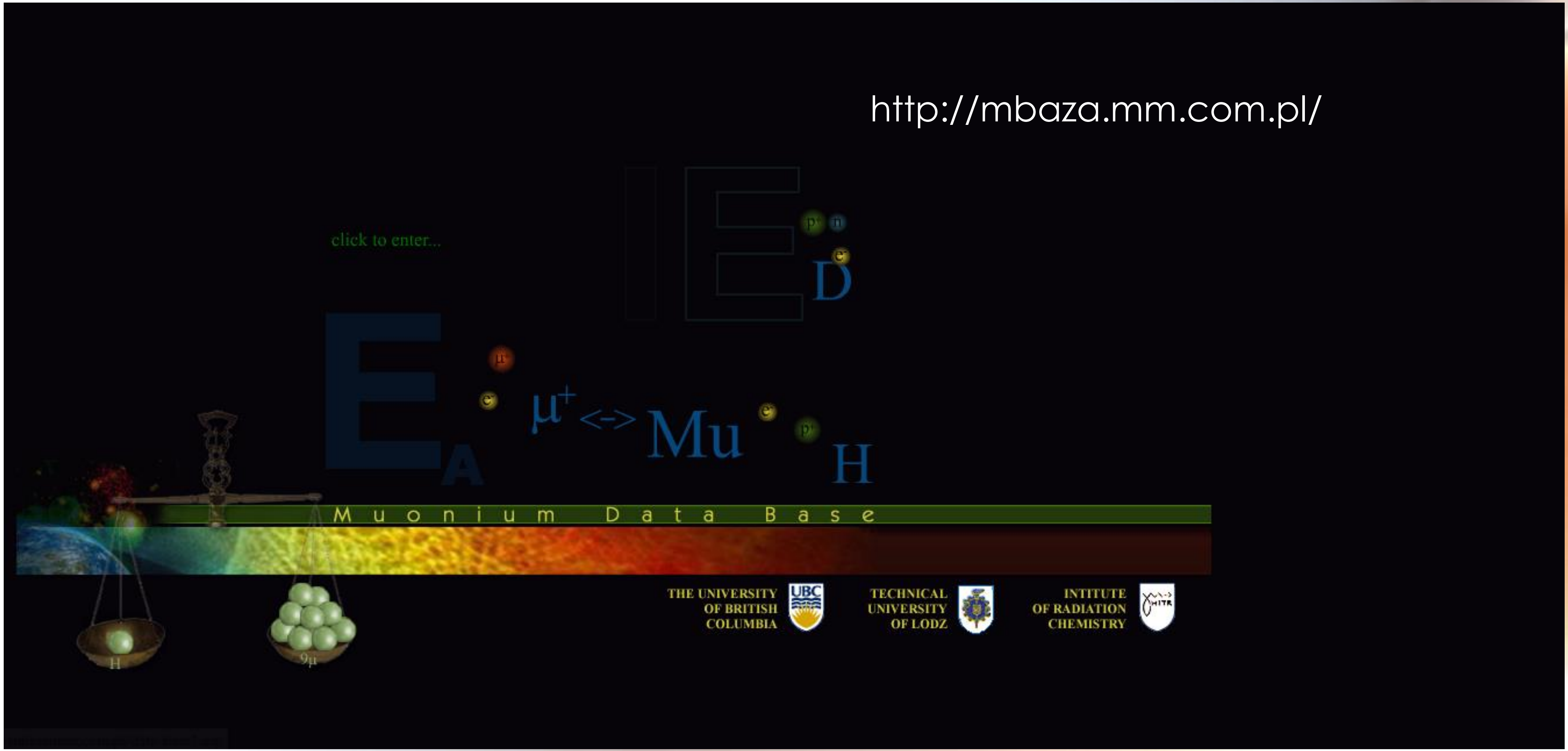


E_{max} = 52.8 MeV


Extrapolated from low temperature data

Phys. Chem. Chem. Phys., 2002, 4, 586–595

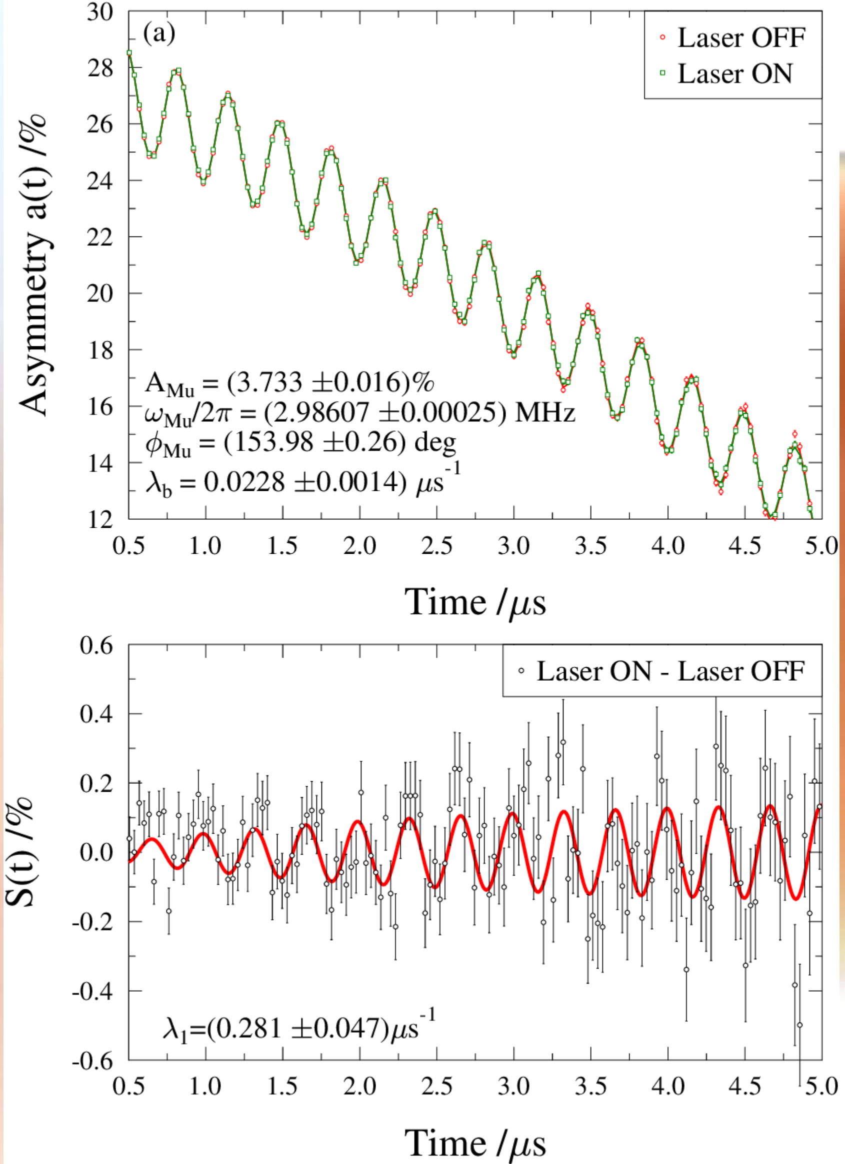
Compilation of muonium reaction rates



http://mbaza.mm.com.pl/

Combination experiments

- Combine muons with laser irradiation
- Excite H_2 to v=1
- H_2(v=1)+$Mu^\bullet$ reaction
- Explore reactivity in non-equilibrium states



Summary

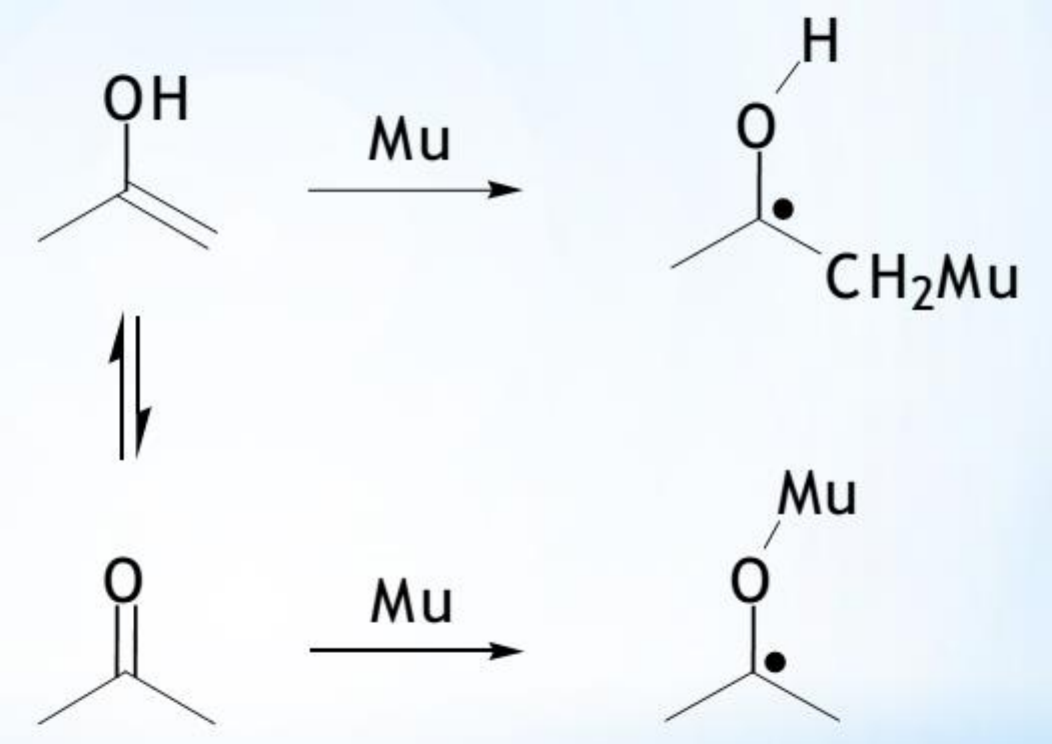
- Muoniums, low asymmetry in 20 G TF and LF
- Requires > kG for LF repolarisation (ISIS)
- High precession frequency (PSI/TRIUMF)
- Kinetics (dynamics/diffusion) from excess relaxation rate
- Reacts to give muoniated radicals
- Extensive database of muonium reaction rates
- Novelty, extreme conditions of temperature and pressure

Muoniated radicals

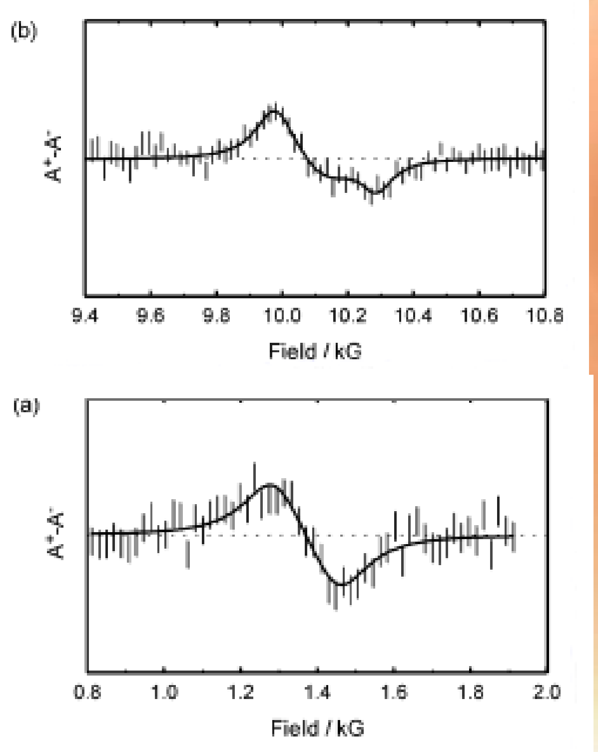
- System chosen to generate such species
- Presence of unsaturated carbon centre
  - Intrinsic
  - Target added, benzene will give muonio cyclohexyldienyl radical
- Hyperfine coupling constants sensitive to environment
- Chemical exchange/dynamics averages hyperfine coupling constants
- Kinetics and dynamics from excess relaxation rates

Extreme environments

Example of radical trapping to follow an equilibrium



Equilibrium in water

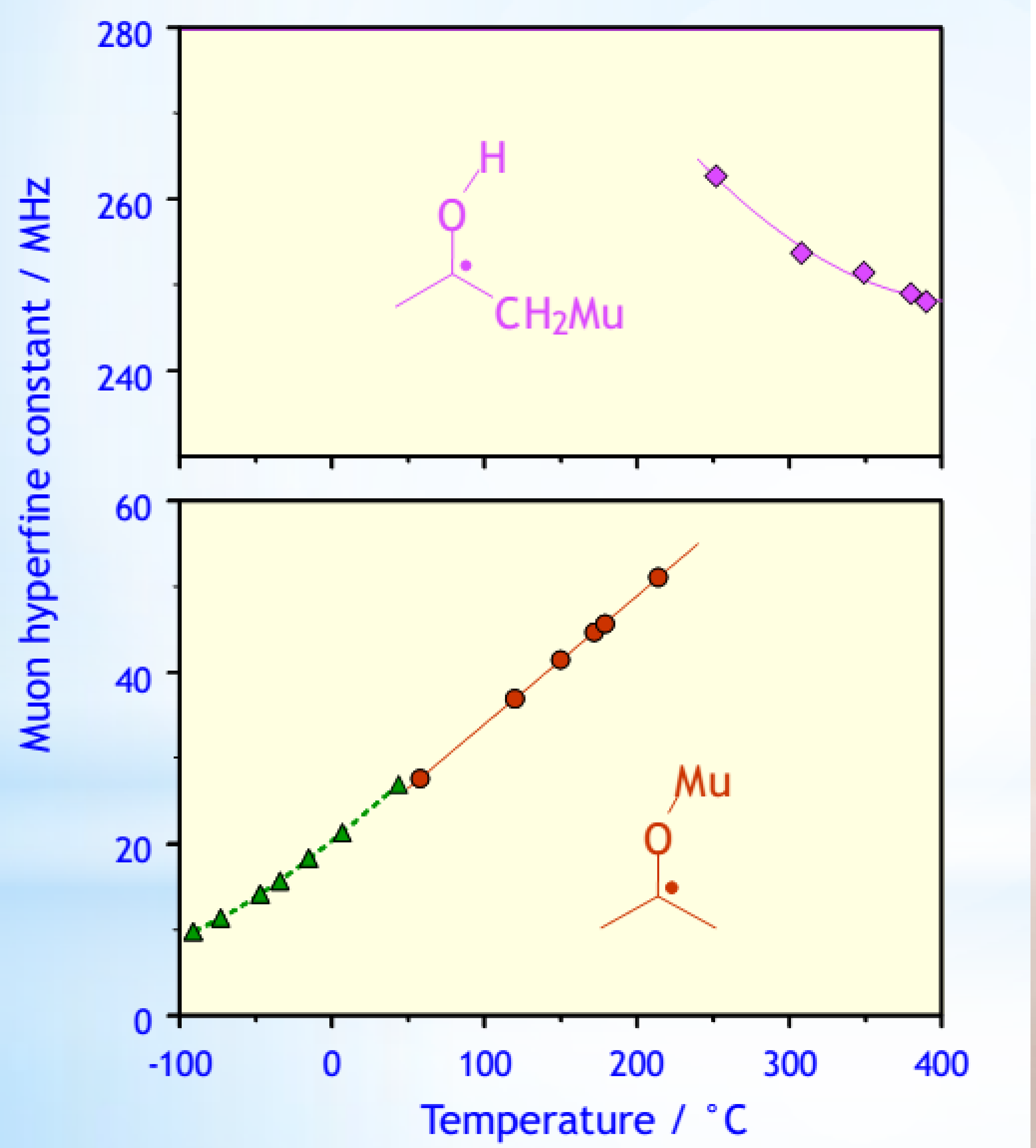


350° C 250 bar

92° C 136 bar

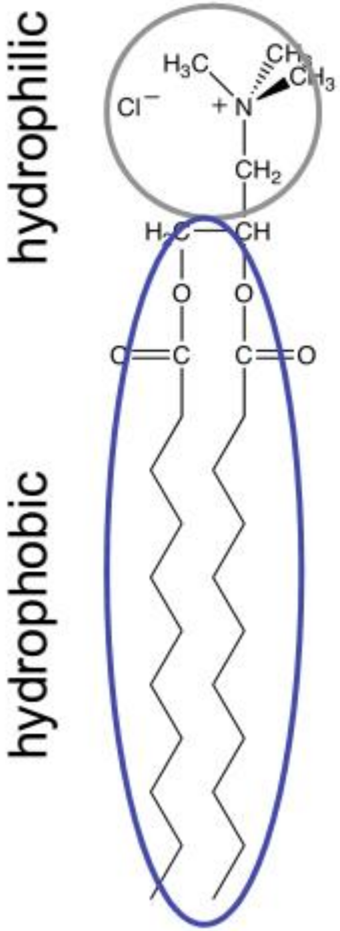
ALC-MuSR spectra of enol and keto radicals

Extreme environments



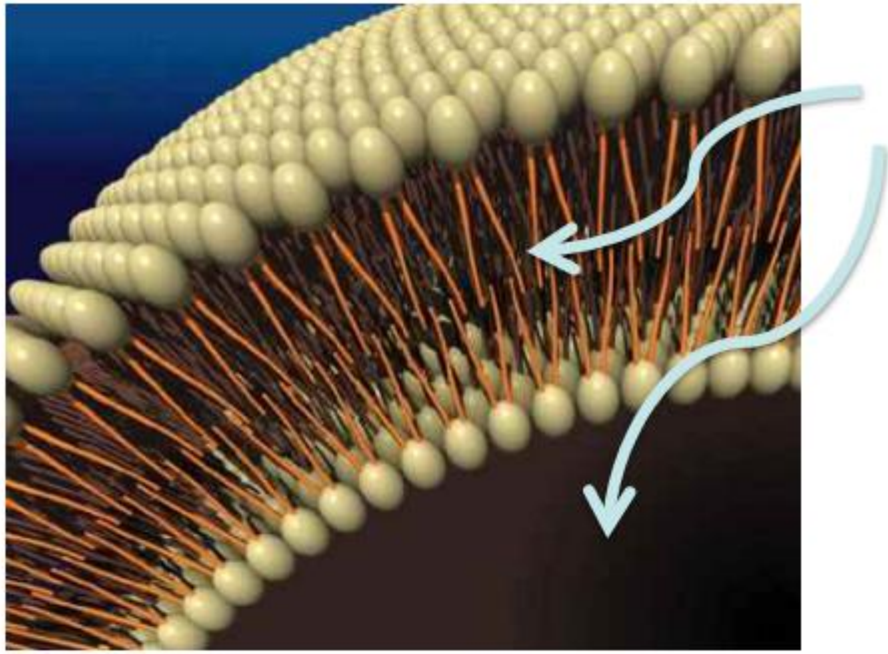
Ghandi, Addison-Jones, Brodovitch, McCollum, McKenzie, and Percival, JACS 125 (2003) 9594.

Soft Matter



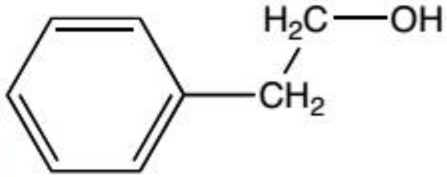
Surfactant

DHTAC



Surfactants can form bilayers, micelles, vesicles, etc.

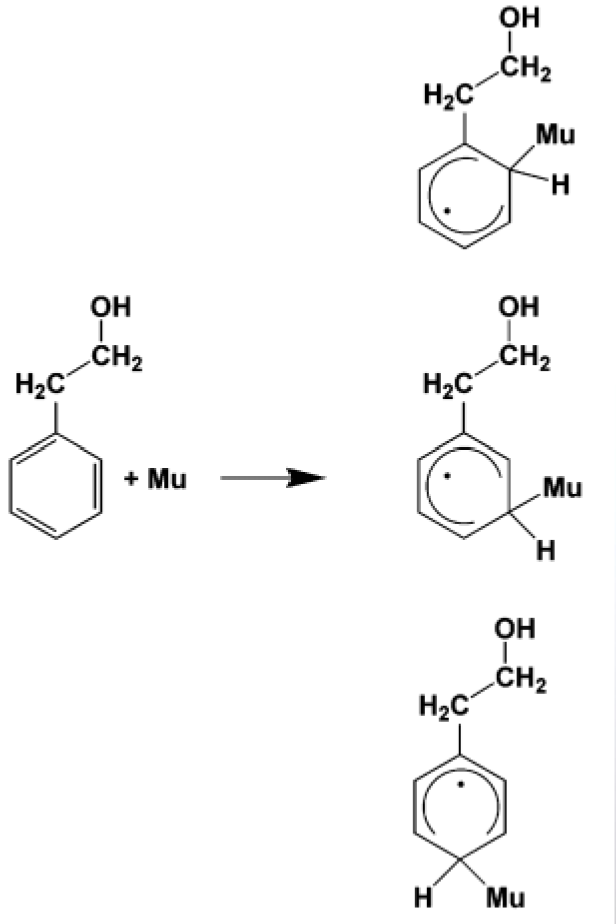
Co-surfactant

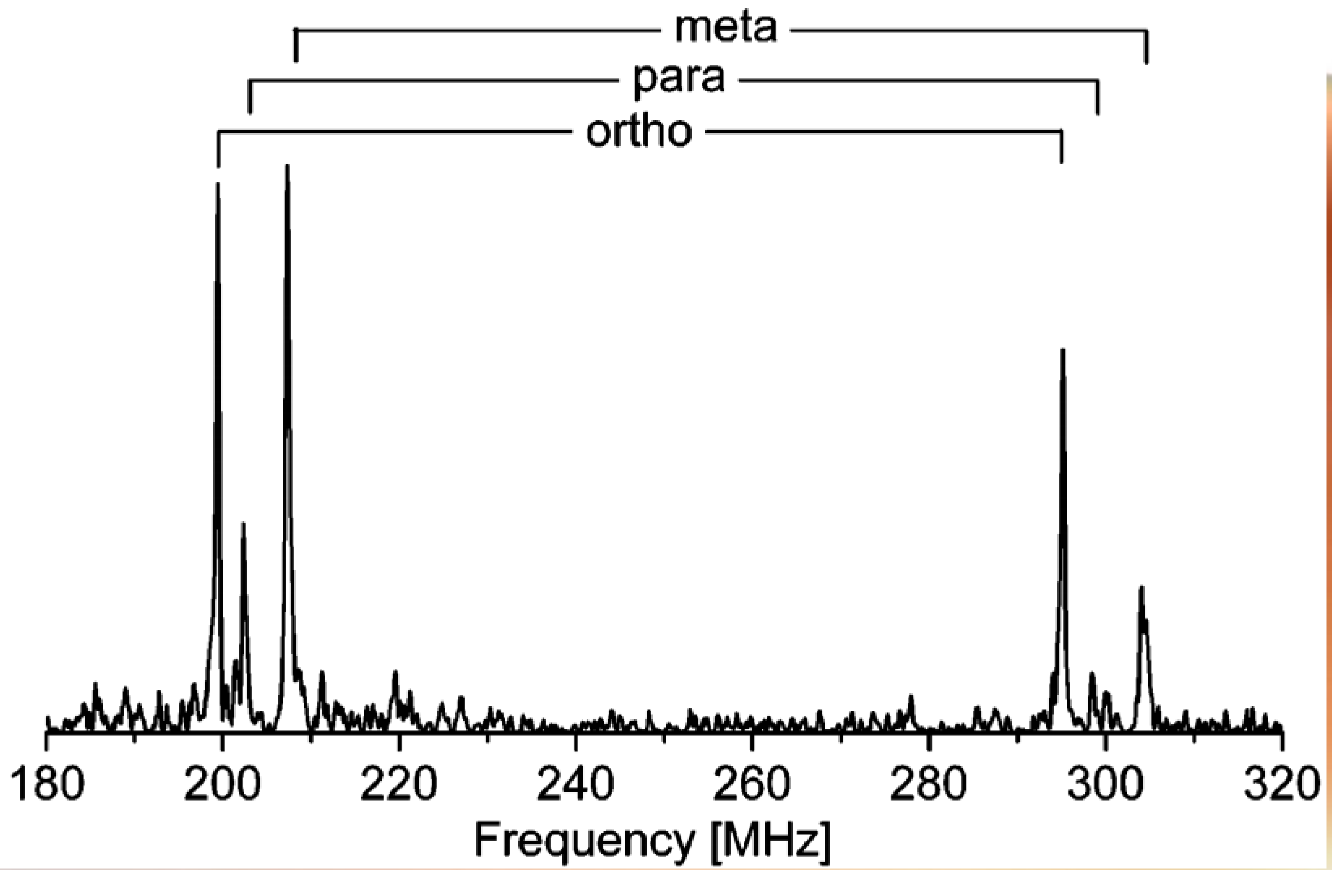


2-phenylethanol

- Fragrances
- Food additives.
- Drug delivery

TF-MuSR, A_μ

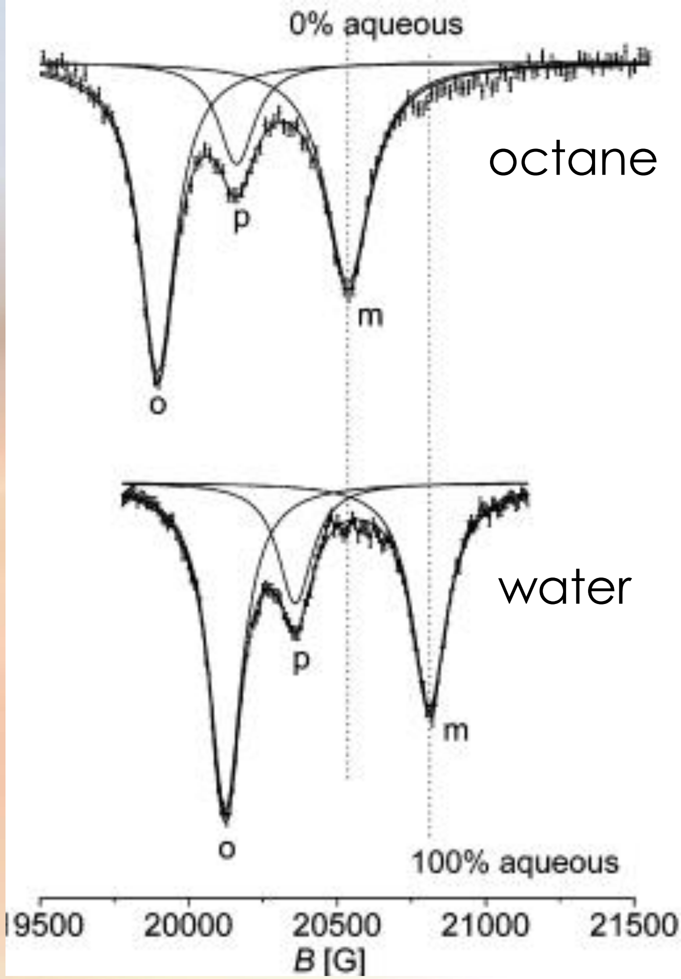




Langmuir 2004,20,2652-2659

ALC-MuSR, A_H

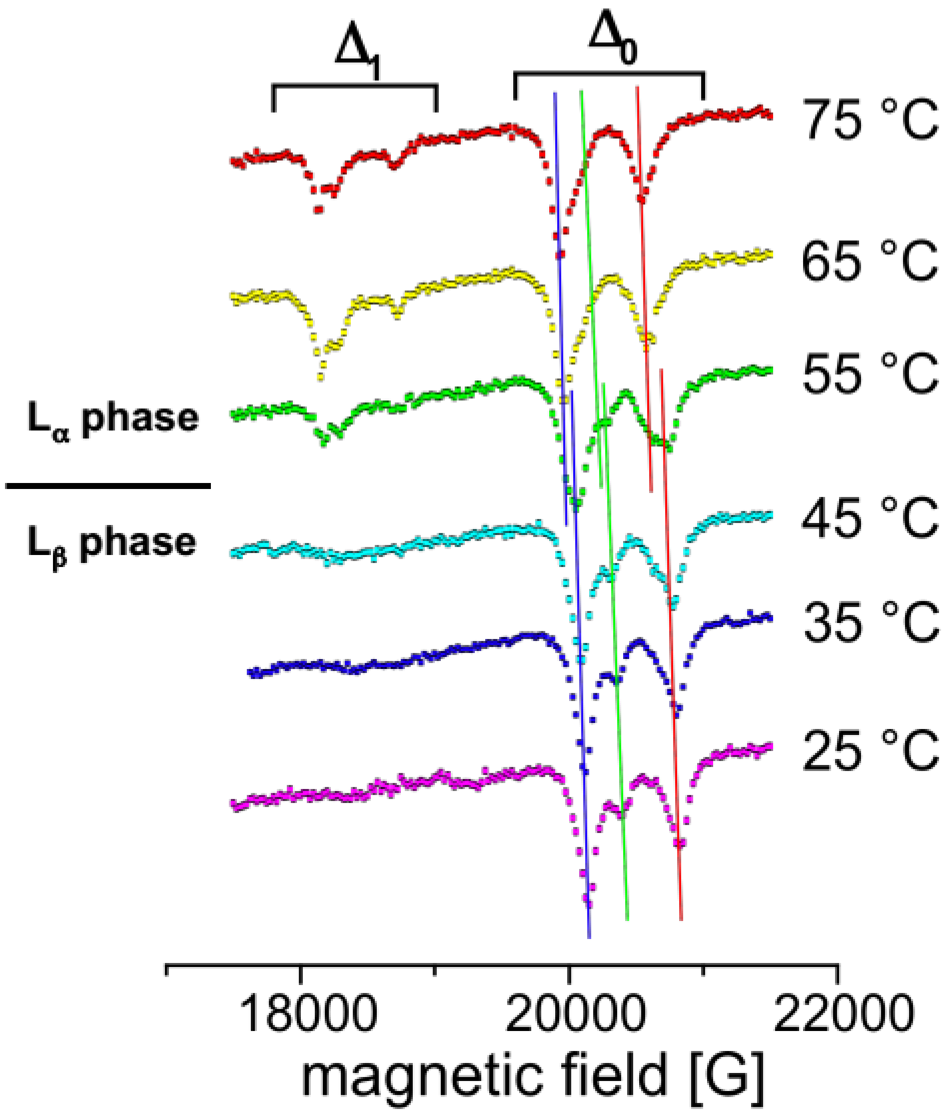
- Generally better signal-to-noise
  - Improved count rates
  - No dephasing problem with slow forming radicals
- Avoided-Level-Crossing
  - Mu, e and H energy levels
  - Depolarisation at the ALC
- Gives A_H rather than A_μ
- Initial problem, defining range of the magnetic field swept

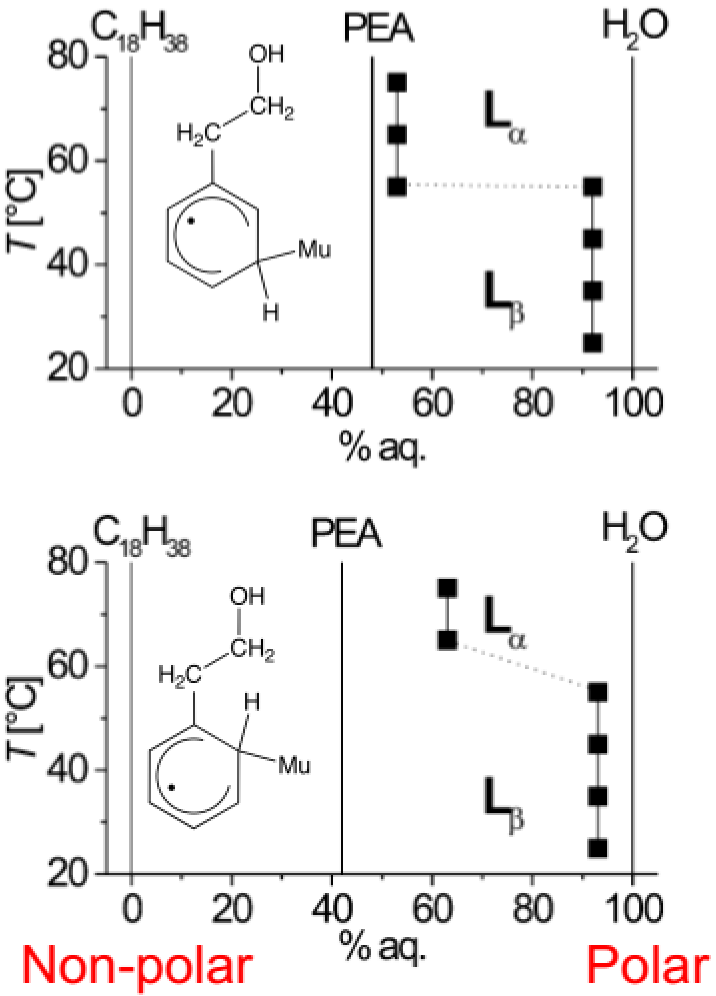


ALC-MuSR at 35° C

Partitioning of co-surfactant

40 mM Phenylethanol in DHTAC



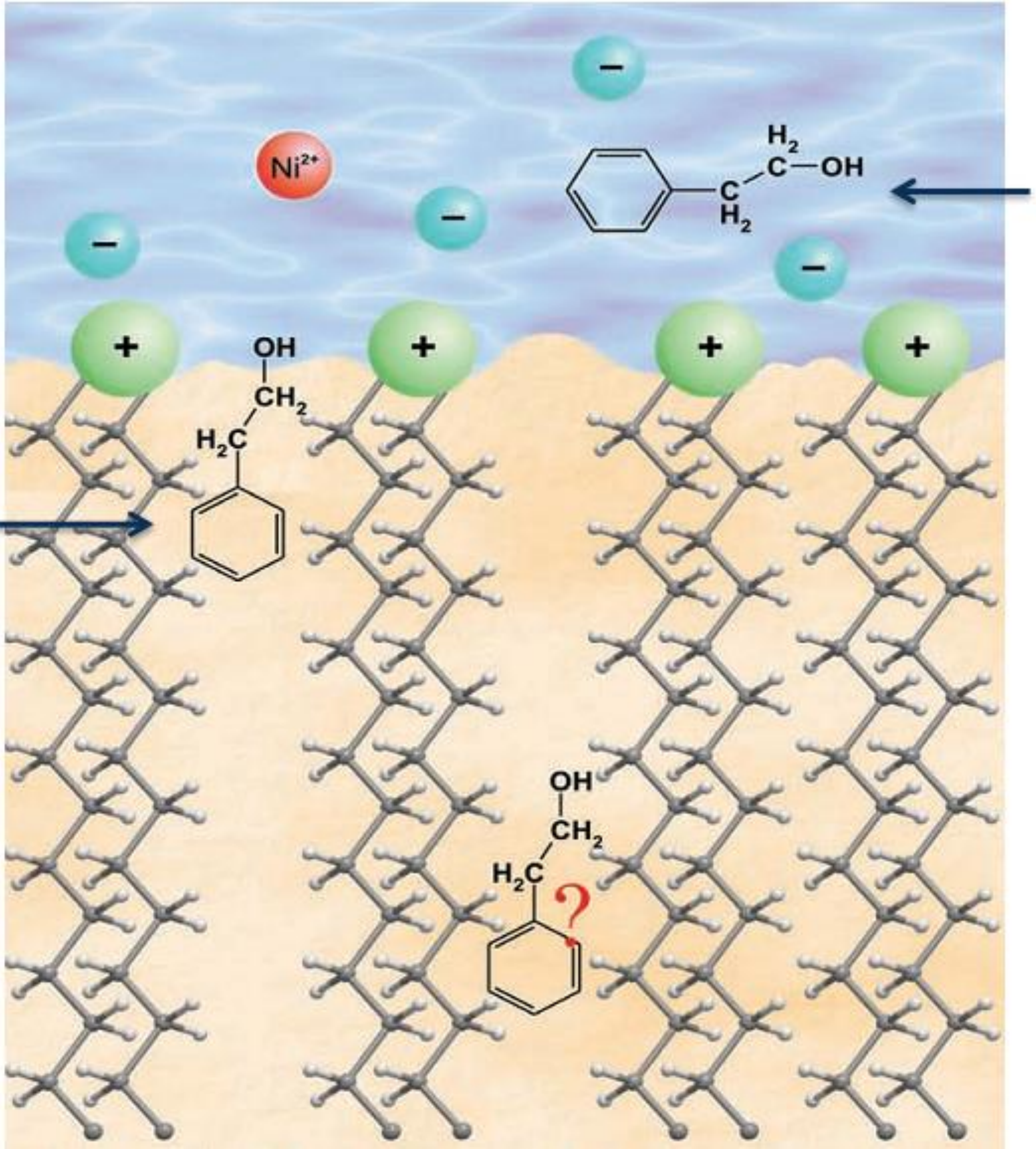


Scheuermann *et al. PCCP* **2002**, *4*, 1510

Partitioning of co-surfactant

L_α Phase

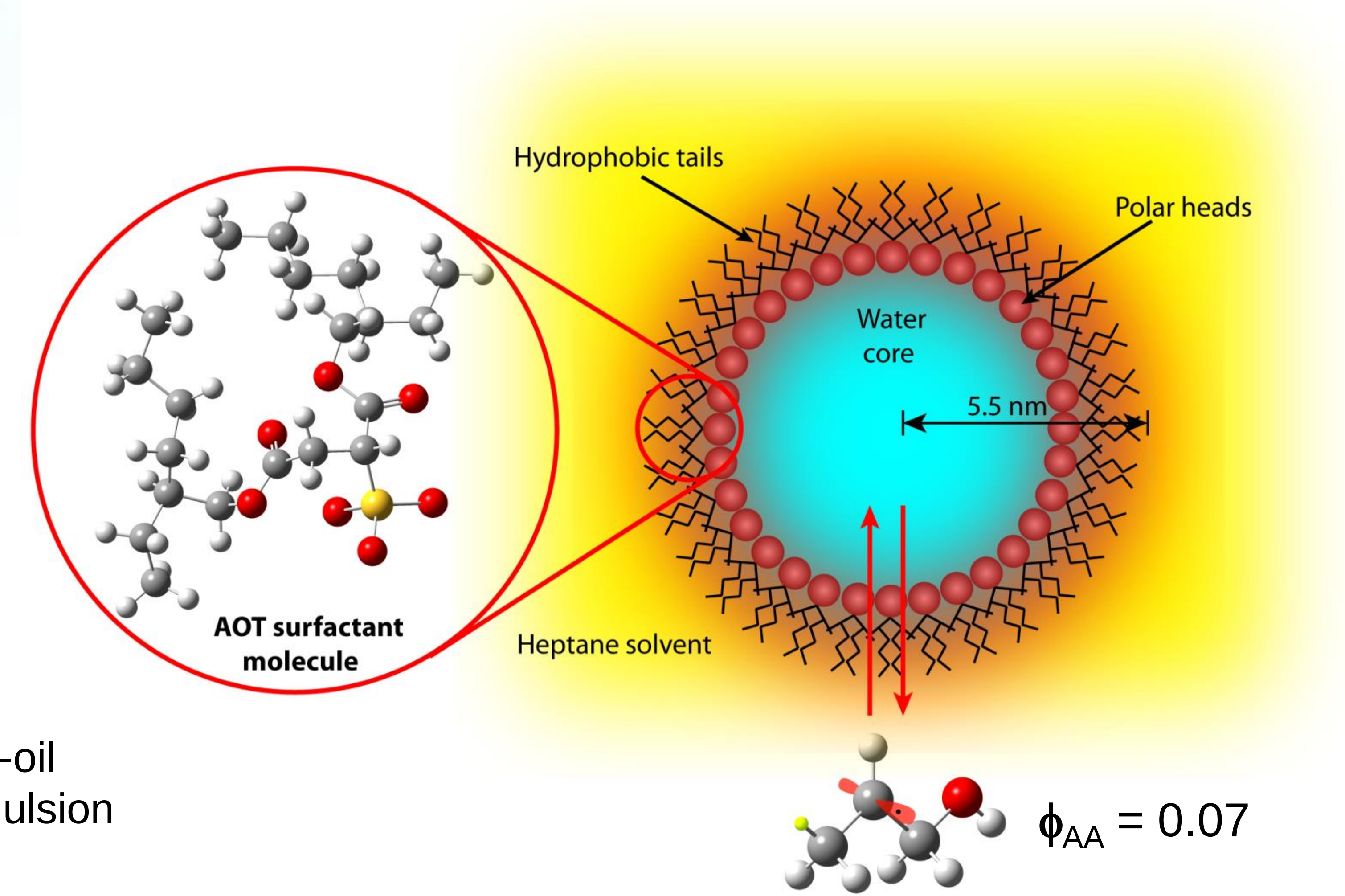
- Δ_1 resonances indicate anisotropic motion with $\tau_c >$ ~50 ns.
- *%aq.char* similar to that of PEA in ethyl acetate.
- PEA resides at the interface of the DHTAC bilayer.



L_β Phase

- No Δ_1 resonances indicates rapid isotropic rotation.
- *%aq.char* indicates highly aqueous environment.
- PEA expelled from the DHTAC bilayer.

Interfacial transfer

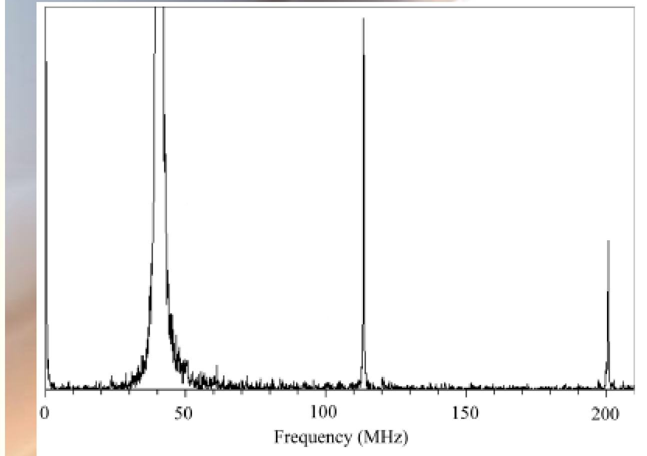


$\phi_{AA} = 0.07$

Water-in-oil
Microemulsion

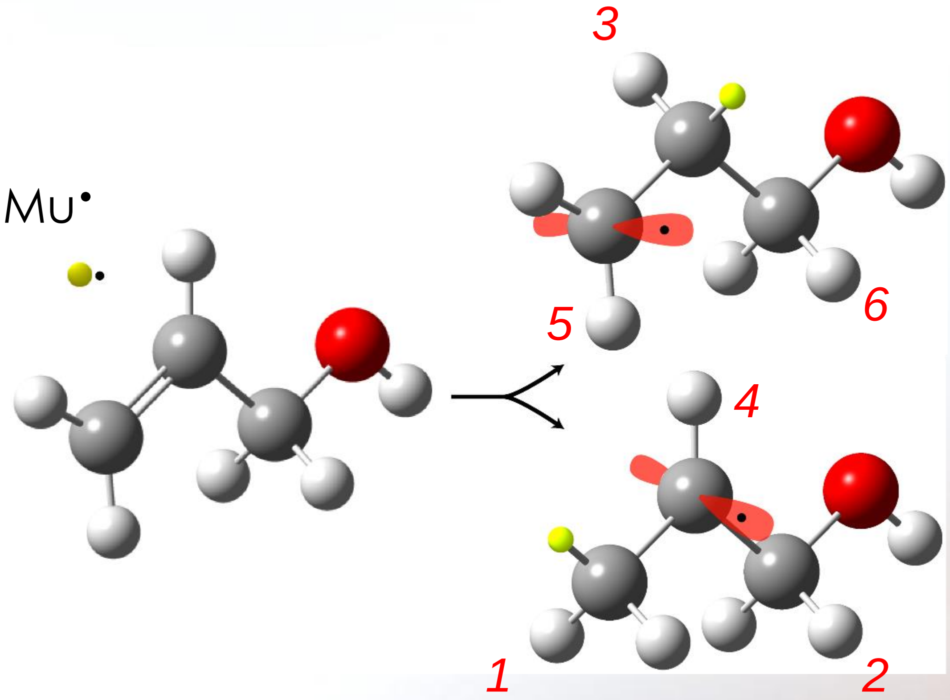
Muoniated Allyl Alcohol (AA) Radical

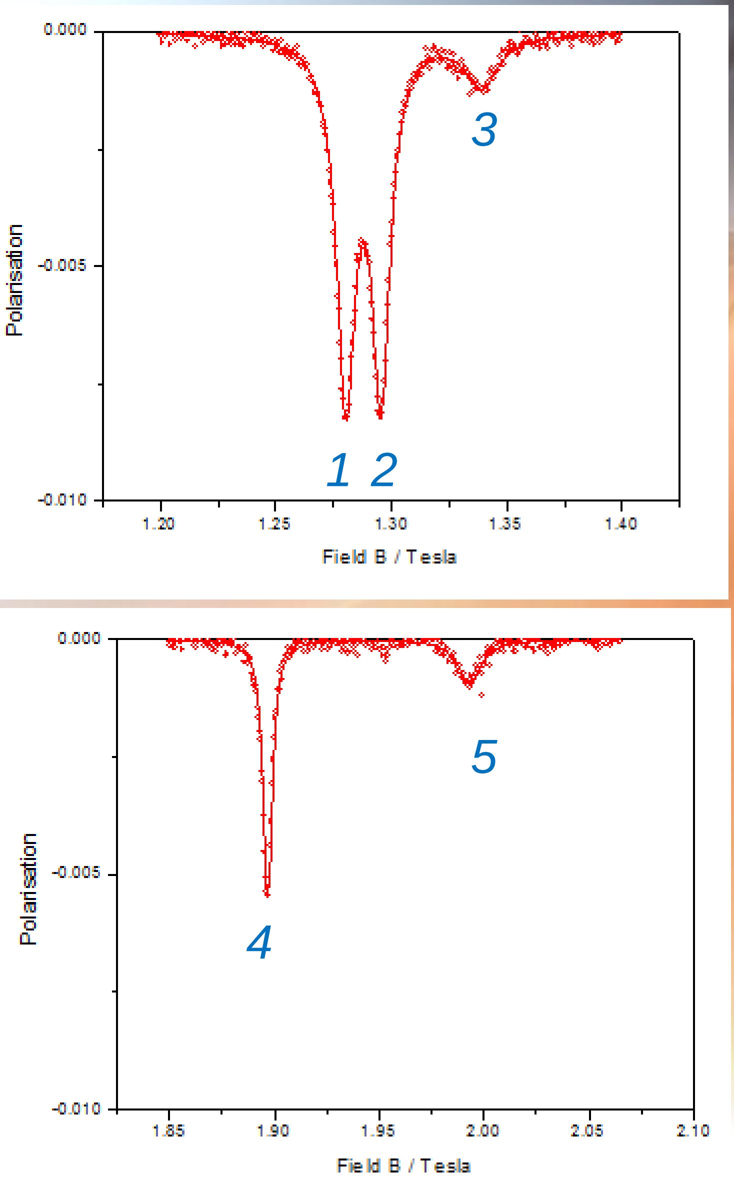
(AA is CH_2=CH-CH_2-OH)



TF-MuSR of AA in Heptane

Interfacial transfer

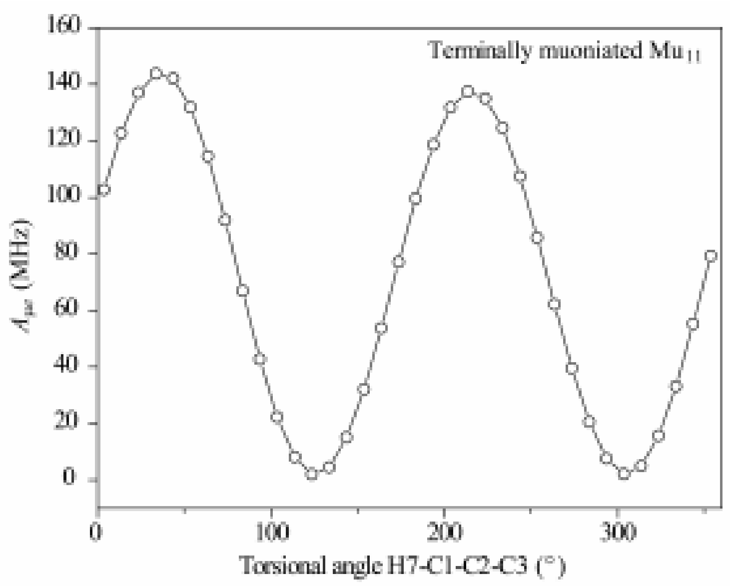


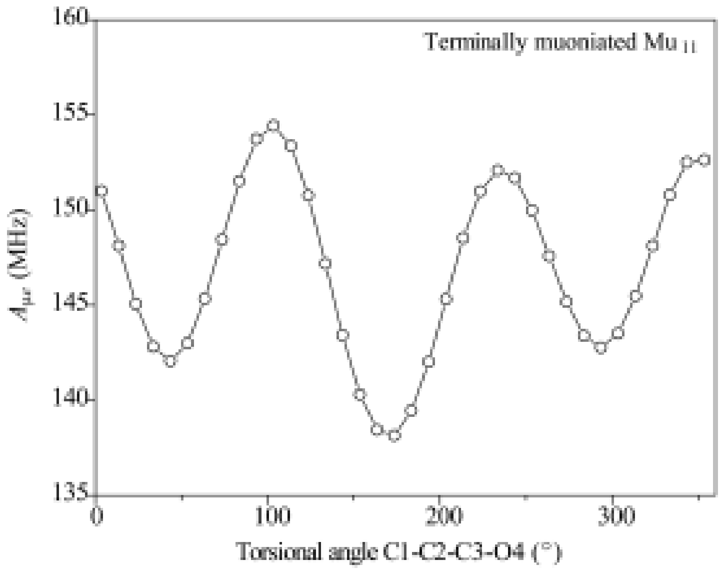


ALC-MuSR of AA in heptane

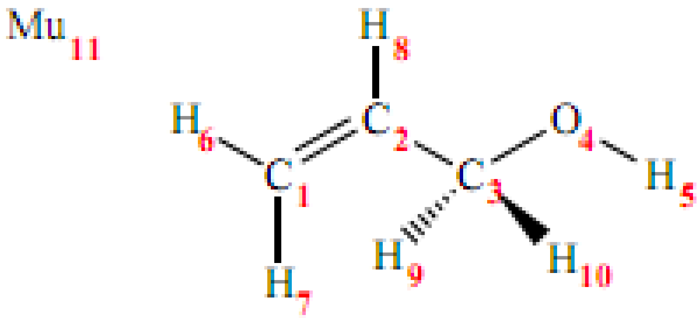
DFT calculation of hyperfine coupling constants

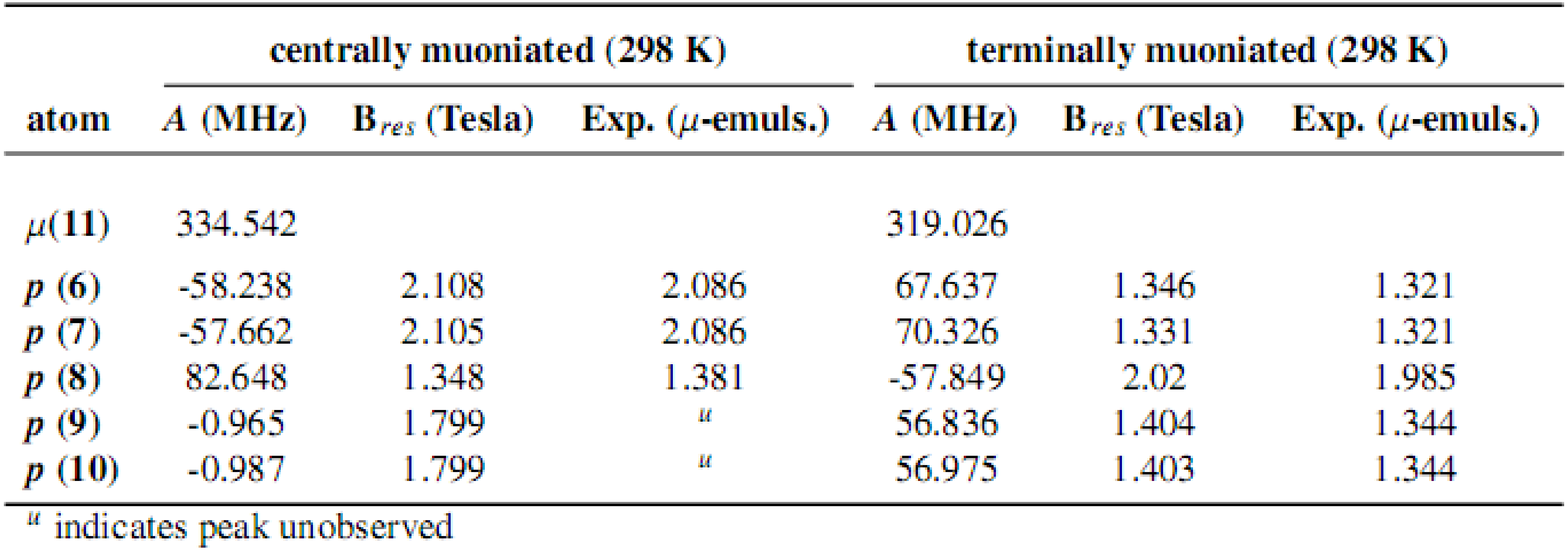
- B3LYP hydrid GGA functional : EPR-III basis set (triple zeta)
- Gaussian 03
- Gas phase calculation, averaging over two torsional oscillations ca 100 cm^{-1} required





DFT calculations

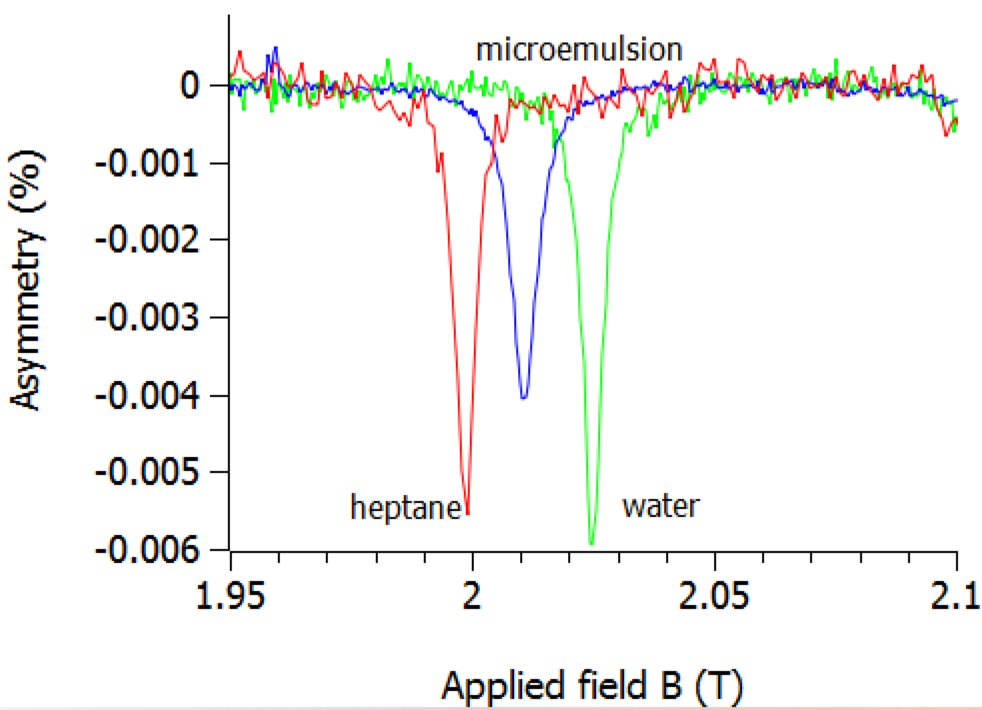




	centrally muoniated (298 K)			terminally muoniated (298 K)		
atom	**A (MHz)**	**B_{res} (Tesla)**	**Exp. (μ-emuls.)**	**A (MHz)**	**B_{res} (Tesla)**	**Exp. (μ-emuls.)**
μ(11)	334.542			319.026		
p (6)	-58.238	2.108	2.086	67.637	1.346	1.321
p (7)	-57.662	2.105	2.086	70.326	1.331	1.321
p (8)	82.648	1.348	1.381	-57.849	2.02	1.985
p (9)	-0.965	1.799	^{u}	56.836	1.404	1.344
p (10)	-0.987	1.799	^{u}	56.975	1.403	1.344

^{u} indicates peak unobserved

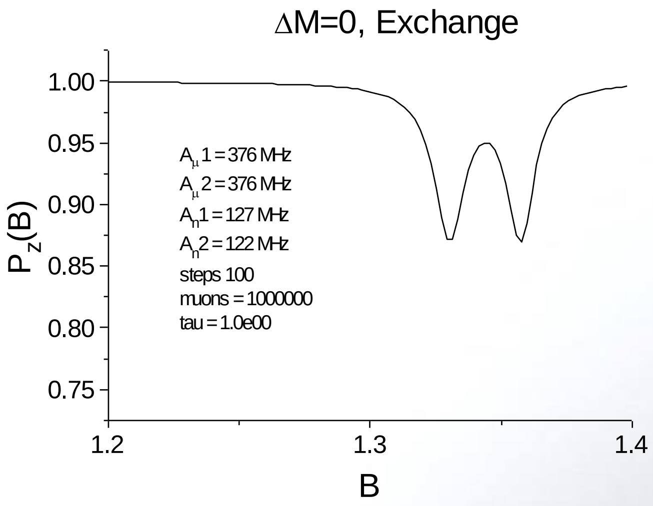
Chemical exchange

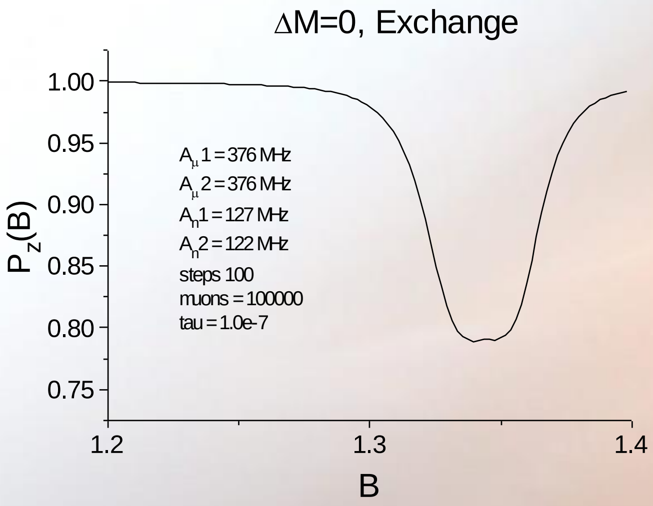


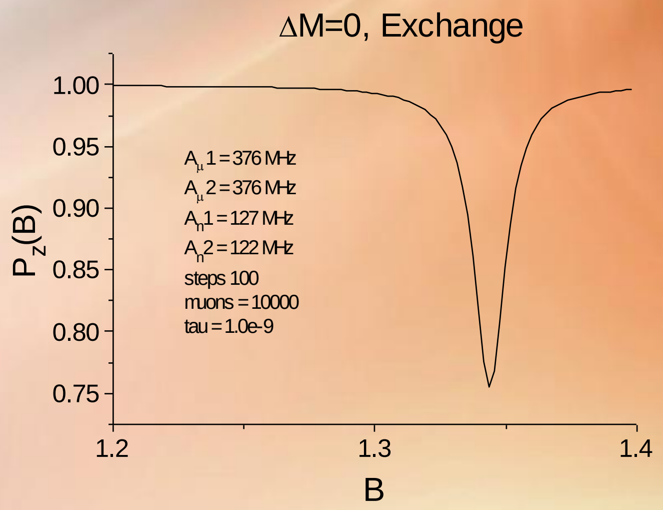
ALC-MuSR spectrum at 280 K
showing peak 4

Simulation of ALC spectra

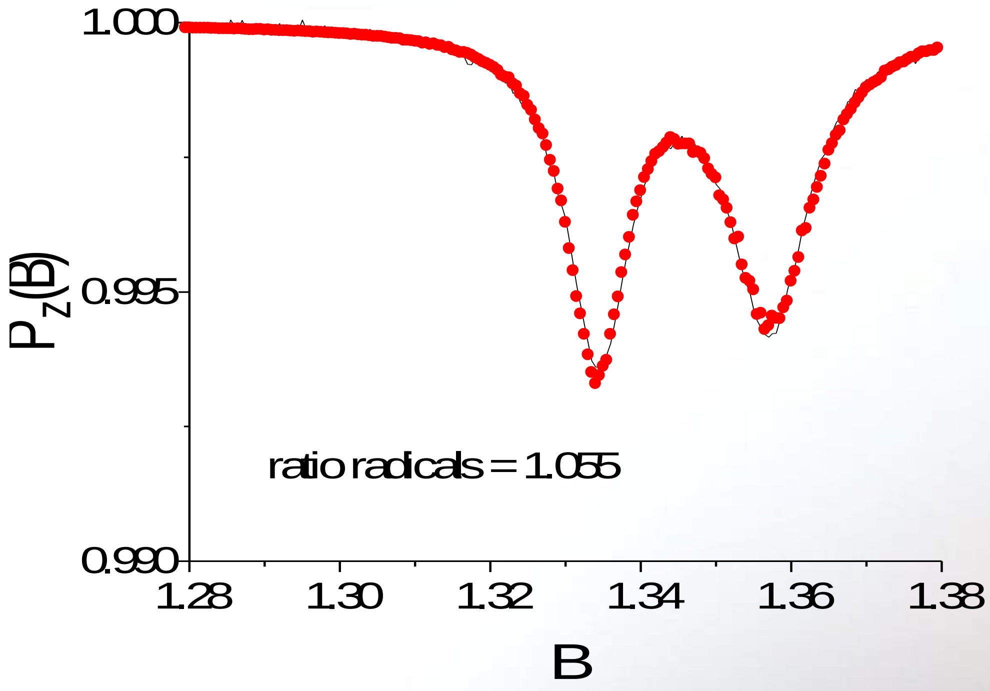
- Monte-Carlo (Tregenna-Piggott, Roduner)
- QUANTUM (Lord)


ΔM=0, Exchange


ΔM=0, Exchange


ΔM=0, Exchange

Simulation of ALC spectrum



τ = 6.5 x 10^{-9} s

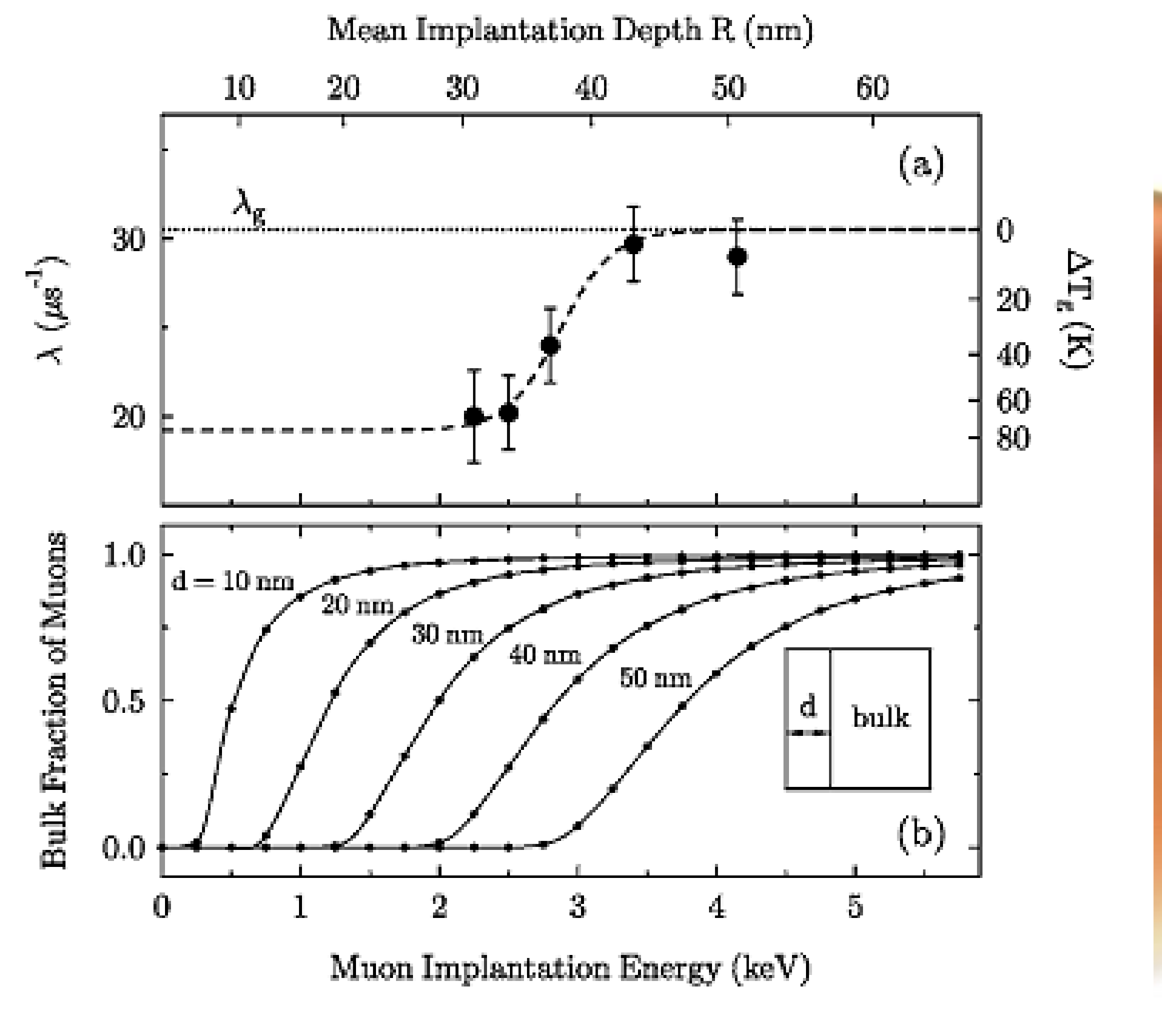
(153.4 MHz)

For the process

RMu•$_{oil}$: Mi = {RMu•$_{water}$:Mi}

Surface dynamics

- Typical penetration depth, 4.1 MeV, mm’s
- Slow muons, moderator
  - Only at PSI
  - Ag foil 125 mm, layer of van der Waal gas N_2 on Ar at 20 K
- Polystyrene
  - Muniocyclohexadienyl radical
  - Bulk T_g, more static λ_g
  - Surface, more mobile



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Summary

- Muoniated radicals formed by reactions between muonium and unsaturated centres
- Intrinsic or added target molecules
- Identify through repolarisation and hyperfine coupling constant
- Monitor radical kinetics and dynamics through λ
- Hyperfine coupling constants sensitive to environment
- Location and exchange between sites
- ALC Δ_1 shapes sensitive to dynamics