Complementary Techniques NMR, ESR and μSR

Dr N J Clayden

School of Chemistry

University of East Anglia

University of East Anglia

Caveat

All depends on the actual chemical system under investigation

Starting point

- Muon is an extrinsic probe implanted into a material
- Magnetic properties like ^{1}H and e^{-1} , all S=1/2

- Muon implants as a diamagnetic muon think NMR
- Muon implants as muonium, or reacts to give a muoniated radical think ESR (spin label)

Diamagnetic muons and NMR Structure

- Unlike NMR, muons are NOT a structural tool
  - Cannot guide where the muon implants
  - Difficulty assigning the implantation site without assuming a structure
  - Short lifetime precludes any “chemical shift” information
  - Exception, the Knight shift in a metal, information on the electronic structure

Diamagnetic muons and NMR Dynamics

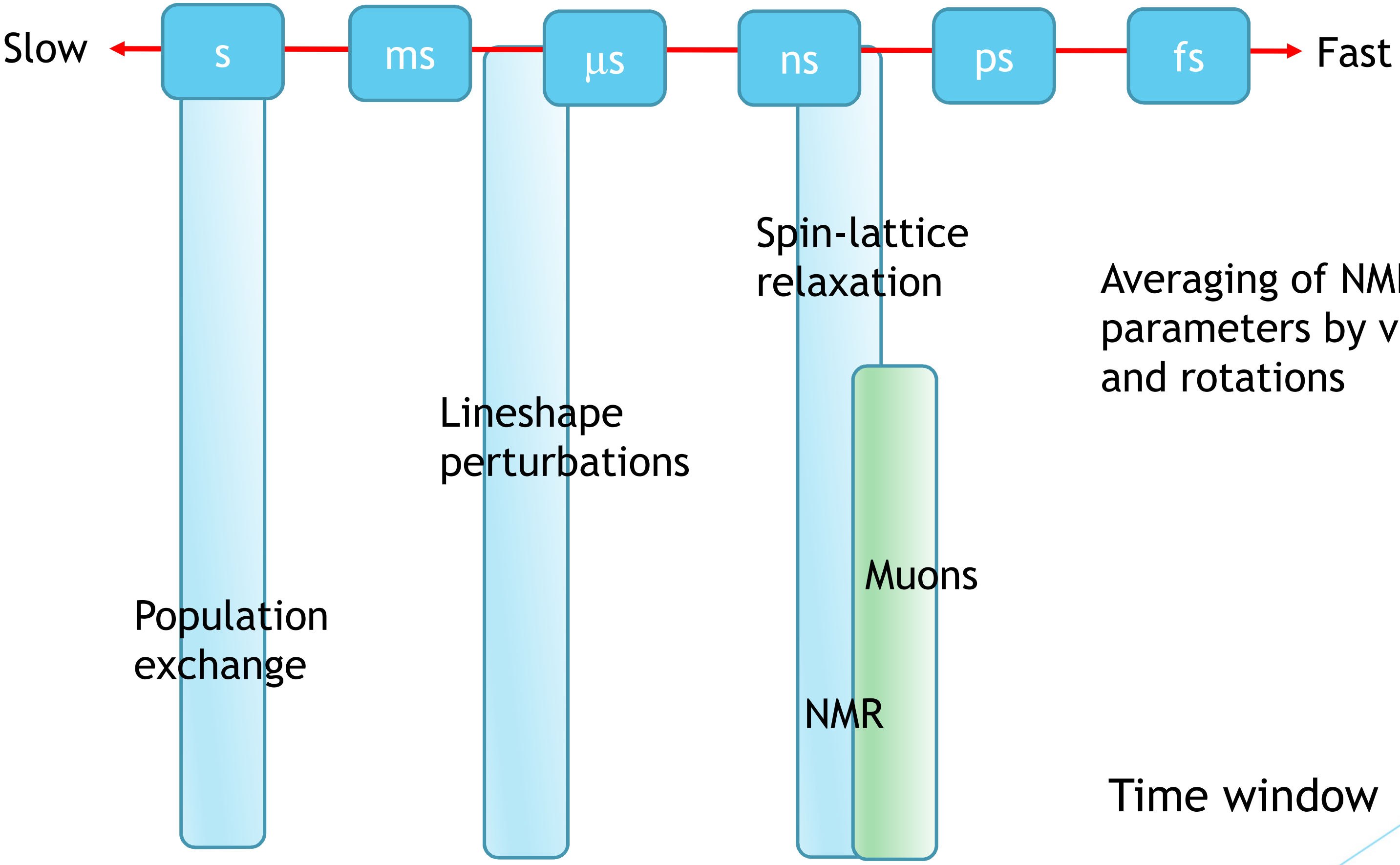
- Both NMR and muons can be used to study dynamic processes
- Timescales for both depend on parameter being observed
  - NMR: Population, chemical shift, J, T_1 and T_2
  - μSR: T_1 and T_2
- Averaging of dipolar interactions by the motion of the spin
  - Nuclear-nuclear dipole for NMR
  - Muon-nuclear dipole for μSR
  - Similar range of rates accessible ($\gamma_\mu \sim 3.184\gamma_H$)

Short muon lifetime
2.2 μs

Slow chemical reactions

Conformational exchange

Molecular tumbling
Diffusion



Slow

s

ms

μs

ns

ps

fs

Fast

Spin-lattice relaxation

Averaging of NMR parameters by vibrations and rotations

Lineshape perturbations

Muons

Population exchange

NMR

Time window

(Magnitude of dependent interaction)$^{-1}$

Case study
Li$^+$ diffusion in Li-ion battery anodes

- Use the muon response as an indirect measurement of Li$^+$ diffusion

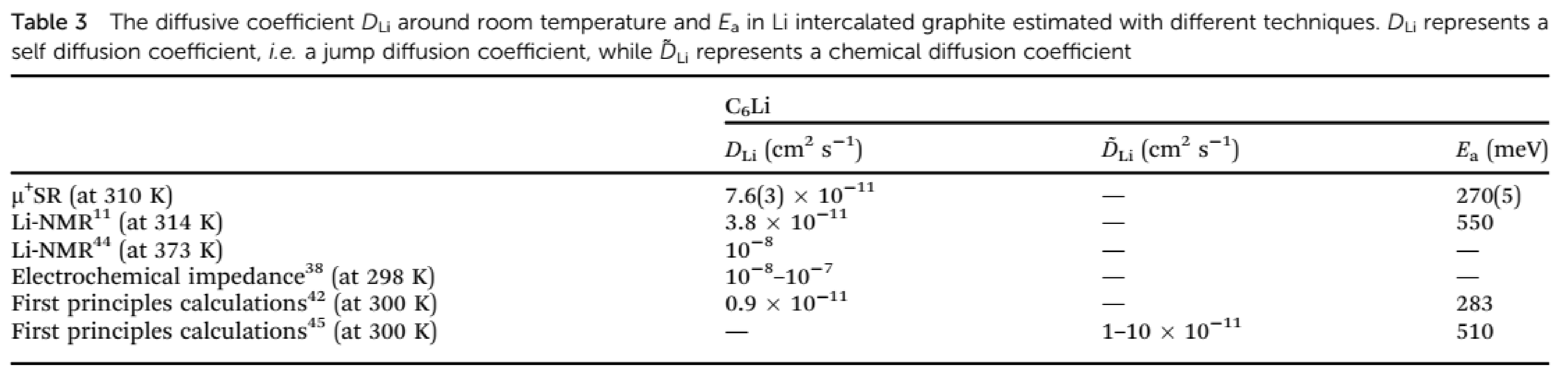
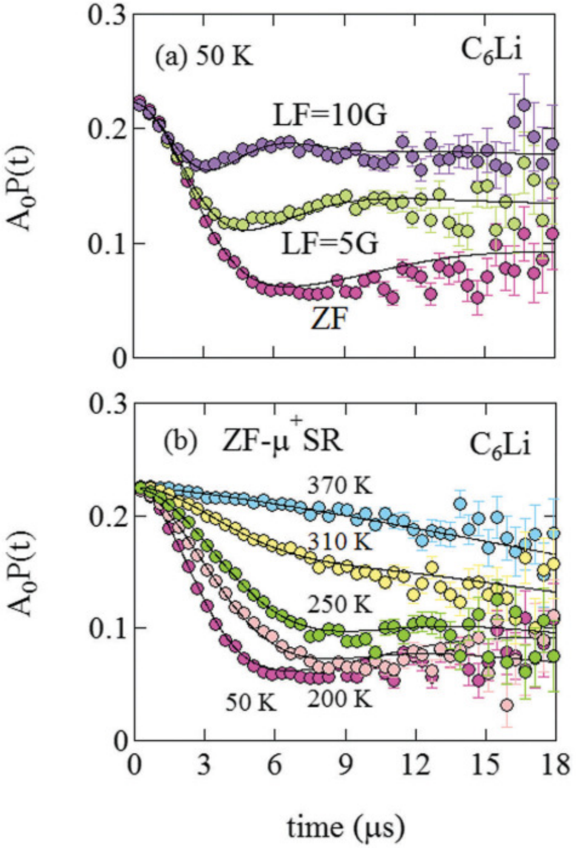


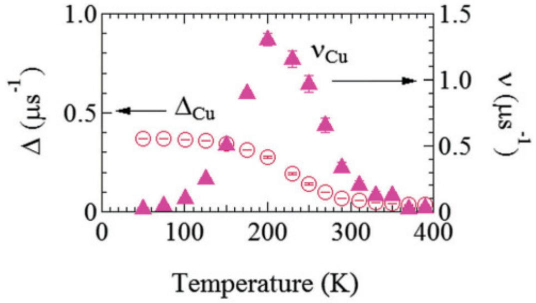
Table 3 The diffusive coefficient D_{Li} around room temperature and E_a in Li intercalated graphite estimated with different techniques. D_{Li} represents a self diffusion coefficient, *i.e.* a jump diffusion coefficient, while $\tilde{D}_{Li}$ represents a chemical diffusion coefficient

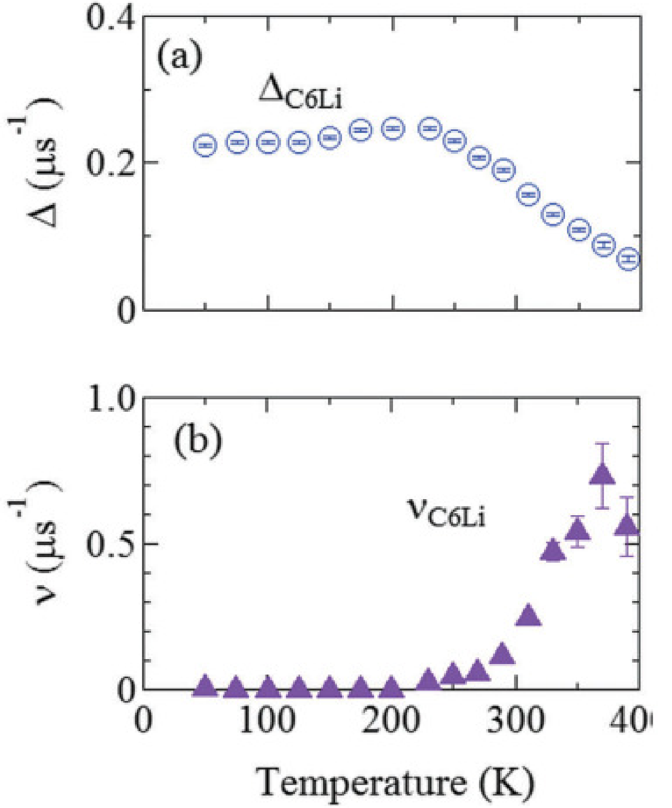
	C_6Li		
	D_{Li} ($cm^2\ s^{-1}$)	$\tilde{D}_{Li}$ ($cm^2\ s^{-1}$)	E_a (meV)
μ^+SR (at 310 K)	$7.6(3) \times 10^{-11}$	—	270(5)
Li-NMR[11] (at 314 K)	3.8×10^{-11}	—	550
Li-NMR[44] (at 373 K)	10^{-8}	—	—
Electrochemical impedance[38] (at 298 K)	10^{-8}–10^{-7}	—	—
First principles calculations[42] (at 300 K)	0.9×10^{-11}	—	283
First principles calculations[45] (at 300 K)	—	1–10×10^{-11}	510

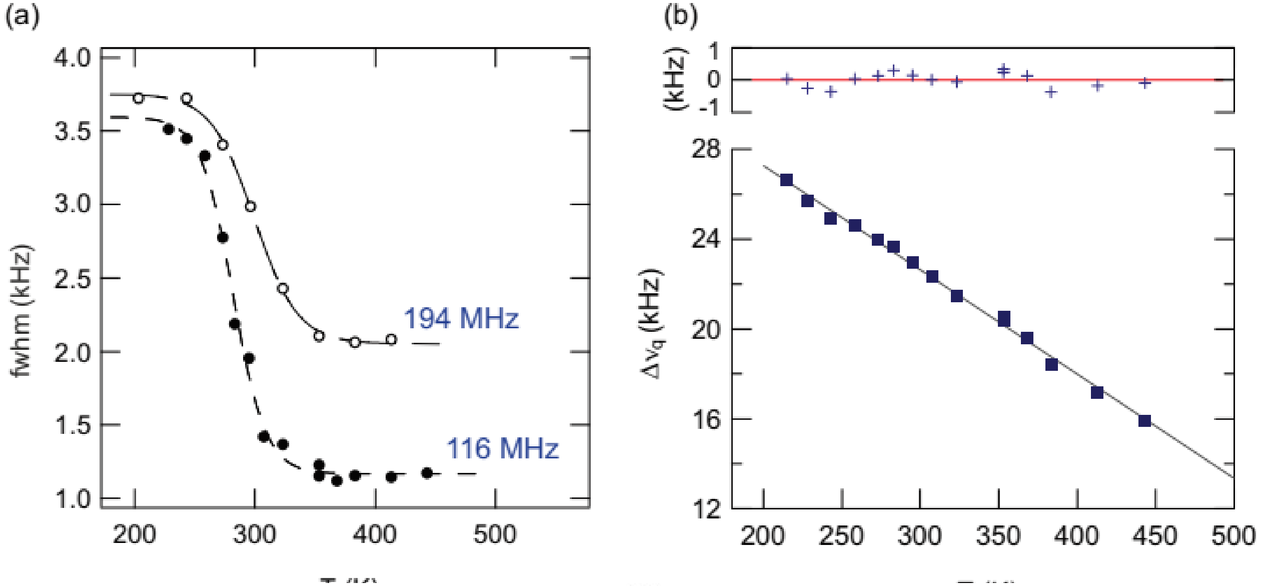
Izumi Umegaki et al *Phys.Chem.Chem.Phys.*, 2017, 19, 19058

Case study
Li$^+$ diffusion in Li-ion battery anodes



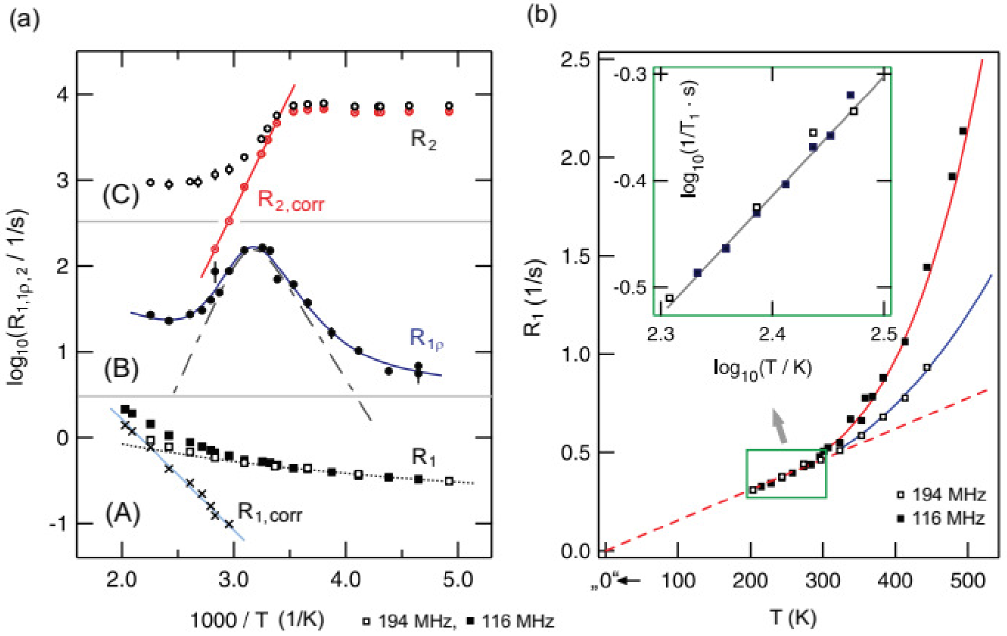






Motional narrowing from ^{7}Li NMR spectrum

NB Instrument used not optimal, too long pulse lengths 6-9 μs for $\pi/2$



^{7}Li NMR relaxation times T_1, $T_{1\rho}$ and T_2

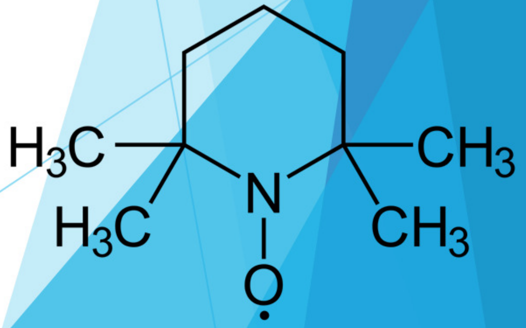
J Langer et al
PHYSICAL REVIEW B 88, 094304 (2013)

Diamagnetic muons and NMR Reactions

- NMR extremely versatile
- μSR very limited
  - Movement from one trapped site to another is diffusion
  - Delayed formation of muonium
- Show as an “excess” relaxation rate

Muoniated radicals and ESR Structure

- Muoniated radicals are formed when muonium adds to a double bond
- ESR a probe for the local environment – spin labels
  - Solvation in membranes
  - Distance probes – separation between two labels
- (ESR can be used to study structure with unpaired electrons in general)
- μSR only used as a probe for the local environment
- Hyperfine couplings constants depend on the polarity of the medium


TEMPO

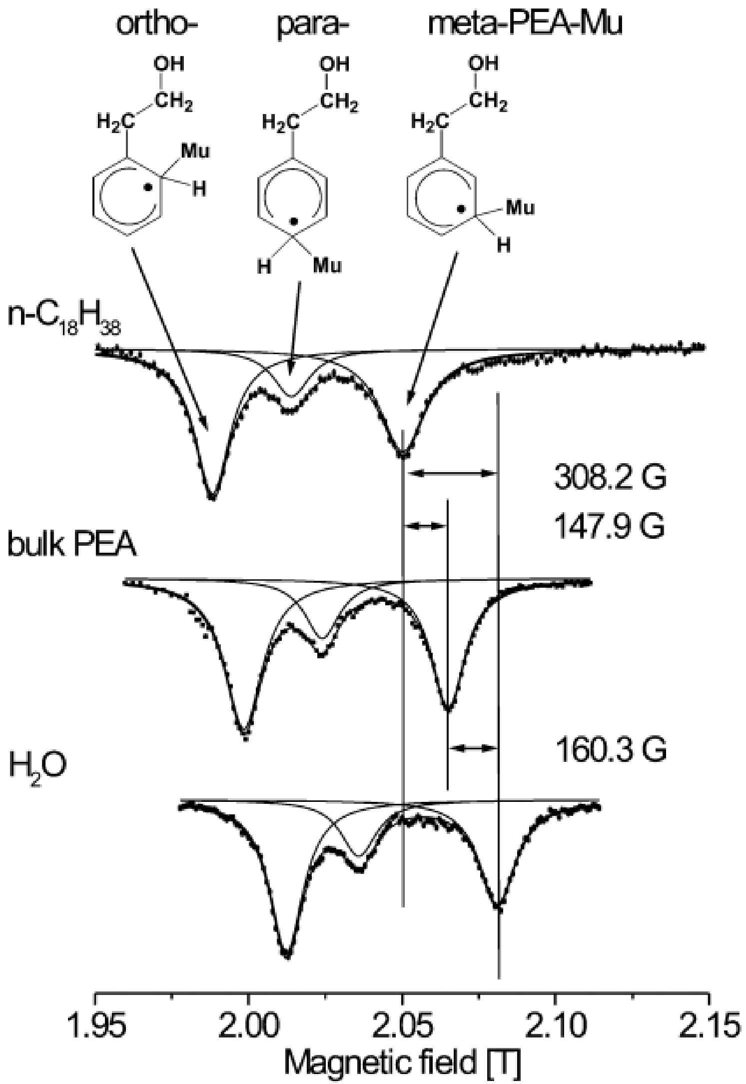
Muons or ESR spin labels

Muons

- Target molecule itself might be muoniated
- Insensitive
- Simple system (or complex without other muon targets)

ESR

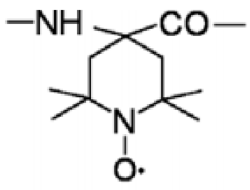
- Structure compromised by having spin label added
- Sensitive
- Complex systems



ALC-μSR
Resonant fields reflect differences in the hyperfine coupling constants A_H

Typically > 100 MHz

E. Roduner et al
Phys. Chem. Chem. Phys., 2002, 4, 1510–1512

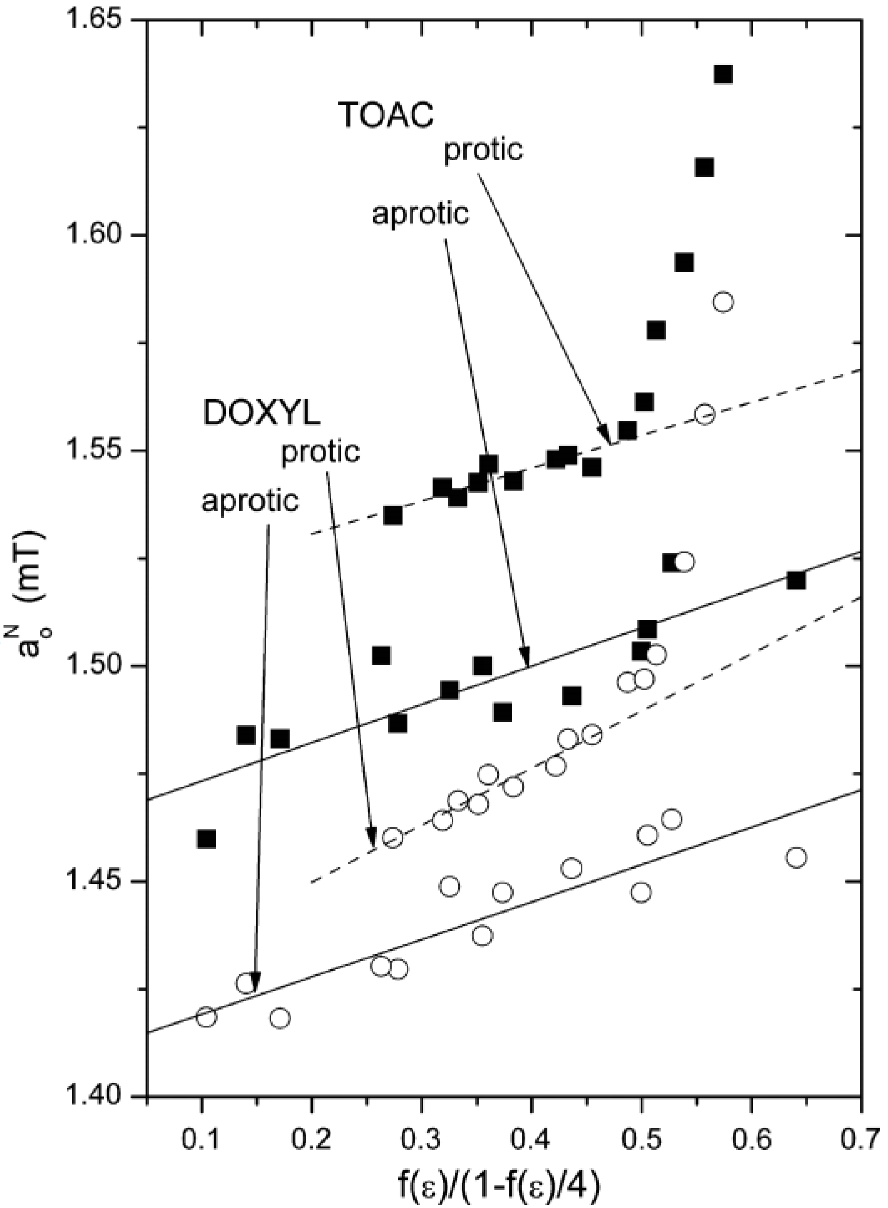


TOAC

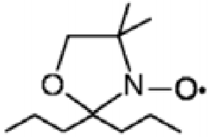
Hyperfine coupling between the electron and ^{14}N nuclear spin

~1540 MHz

Smaller then μSR
1mT = 10 G



D. Marsh, C. Toniolo
J. Magn. Reson. 190 (2008) 211–221

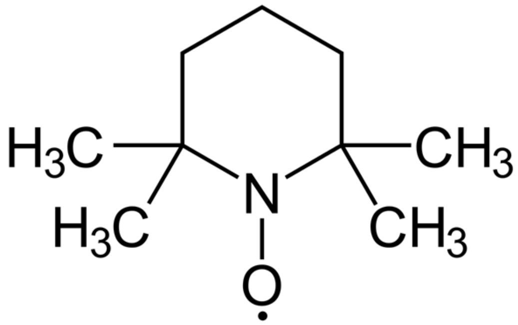


DOXYL

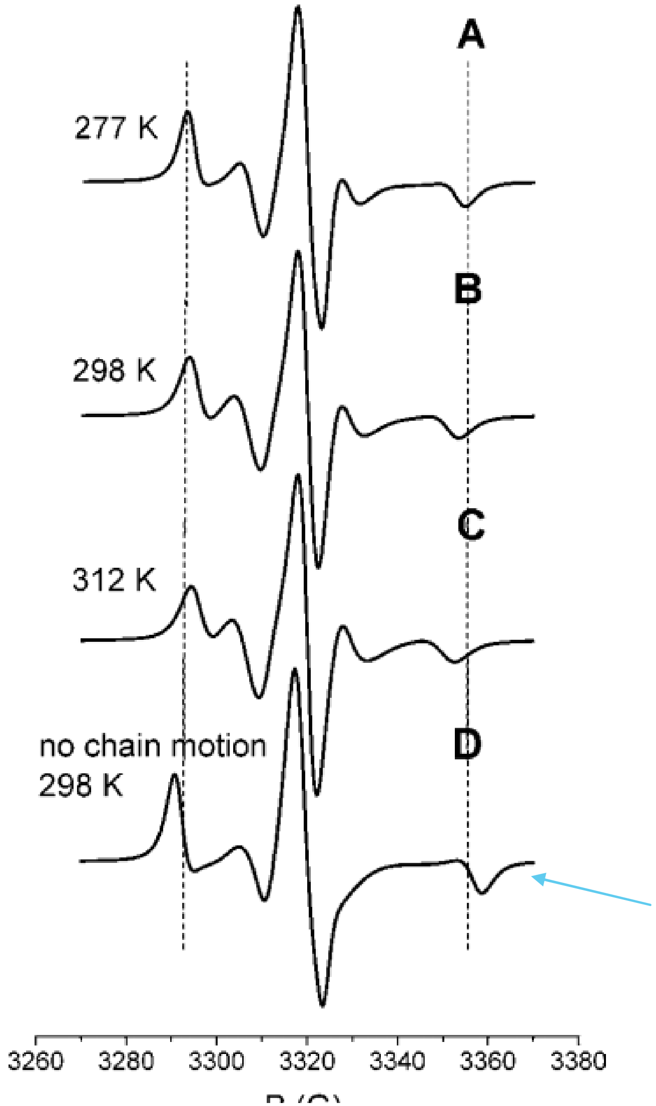
Strength of reaction field from the solvent

Muoniated radicals and ESR Dynamics

- Both ESR and μSR can be used to study dynamics
- ESR requires a spin label – nitroxide ions
- Both rely on averaging of hyperfine coupling constants
- Similar time window



ESR



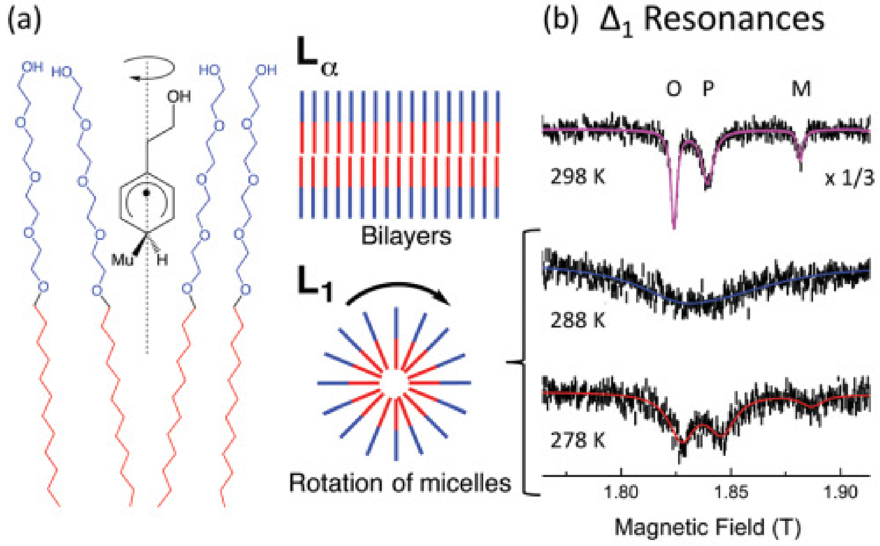
Complex analysis of conformers for a 72R2 mutant of T4L with torsional oscillations and conformational jumps

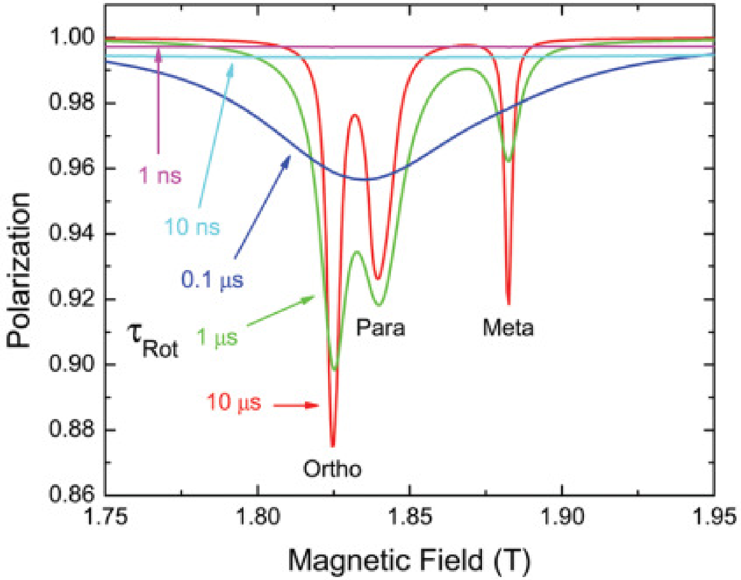
Alberta Ferrarini et al
J. Phys. Chem. B **2006,** *110,* 26260-26271

No side chain motion

Muons

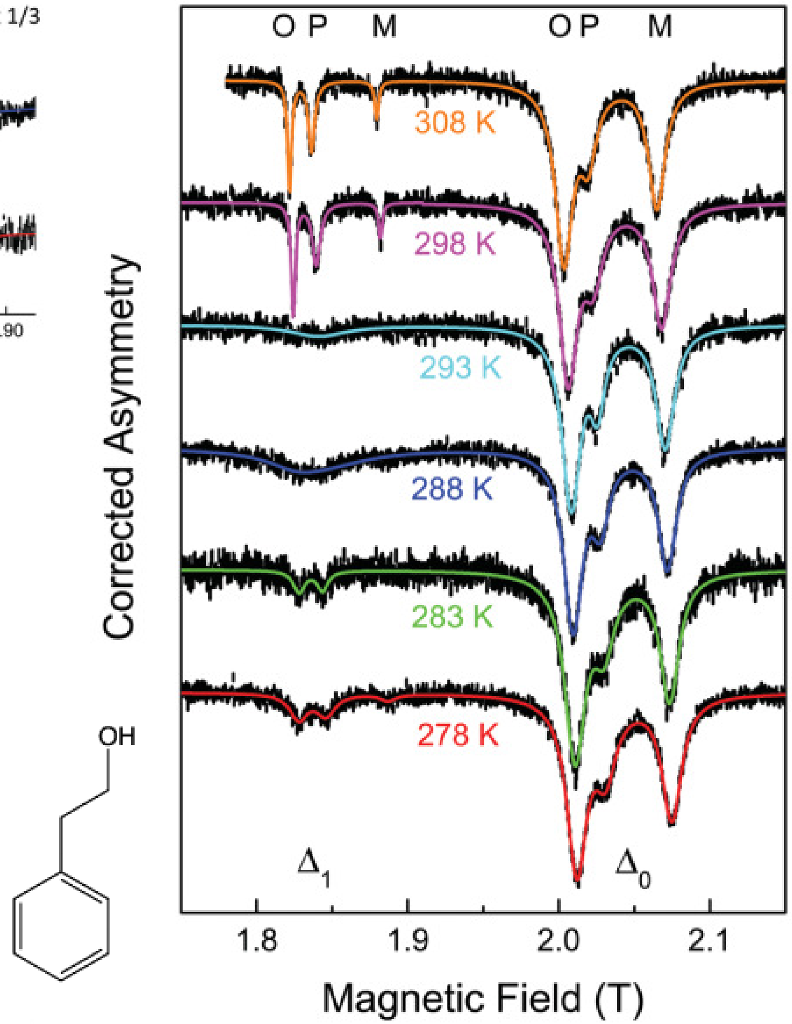
MCKenzie et al Phys.Chem.Chem.Phys., 2017, 19, 9551





2-phenyl ethanol in 35% wt $C_{12}E_4$

Probe is the molecule partitioning



General comparison

NMR

- Target
  - Intrinsic NMR active nucleus e.g. ^{13}C
- Detection
  - Induced voltage in a coil
- Phase
  - Solid, liquid, rarely gas
- Sensitivity
  - Depends on nucleus but < 10 mg

µSR

- Target
  - Implanted muon, muonium or muoniated radical,
- Detection
  - Positron decay product, scintillator/PMT
- Phase
  - Solid, liquid, gas
- Sensitivity
  - Typically 1-2 g