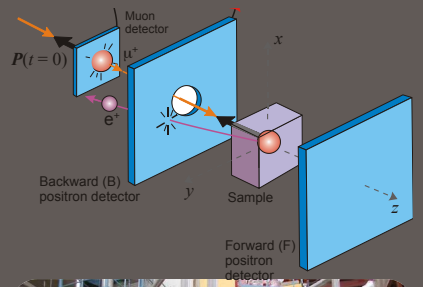
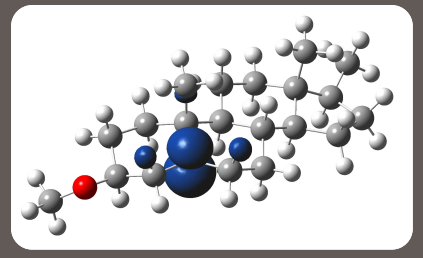
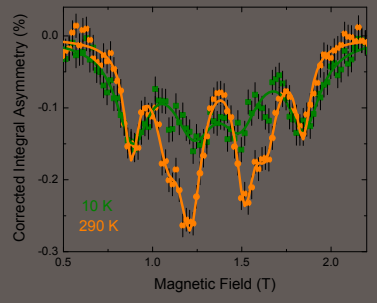
TRIUMF

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

μSR and βNMR of Soft Matter and Chemical Systems







Iain McKenzie

TRIUMF Centre for Molecular and Materials Science
Department of Chemistry, Simon Fraser University

Accelerating Science for Canada
Un accélérateur de la démarche scientifique canadienne

Muons and Chemistry

Mu^+

- Can't resolve chemical shifts so no structural information about diamagnetic muonated molecules.
- Mu^+ diffusion in materials.

Relaxation in WTF: Good for pulsed source

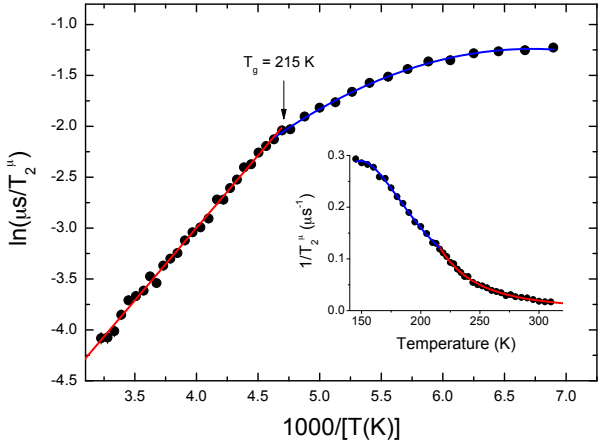
Muonium

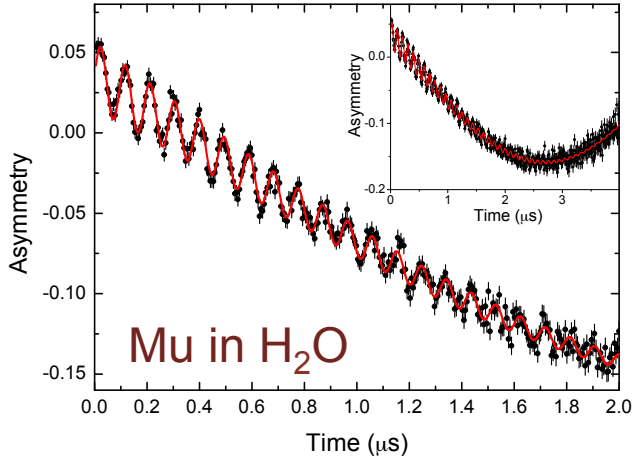
- Mu reaction kinetics in gases and liquids (isotope effect)

Relaxation in WTF: Good for pulsed source

- Interaction with environment

Mu^+ hopping in PEO

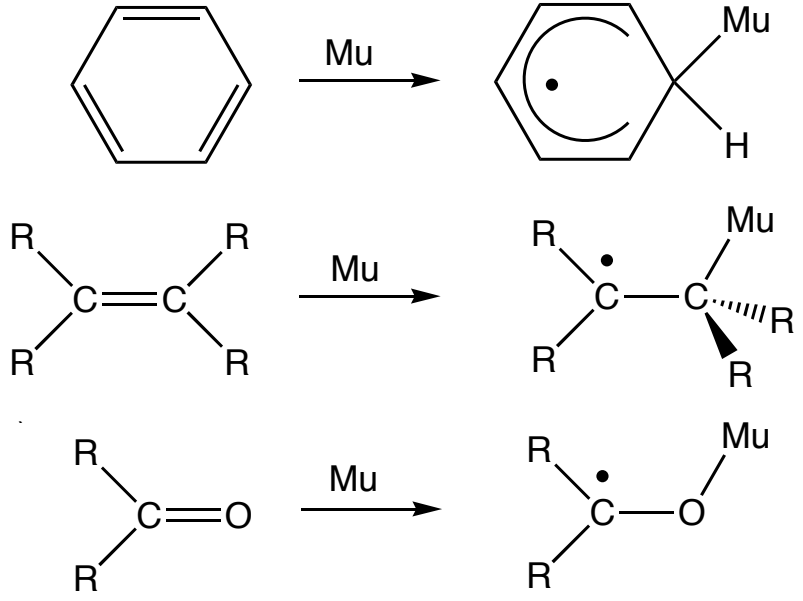




Muons and Chemistry

Muoniated Radicals

- Structure
- Molecular dynamics
- Reaction kinetics
- Spin labels



Identification of Muoniated Radicals

TF-μSR
Precession frequencies
(requires CW source)

ALC-μSR
Resonance fields

Solid

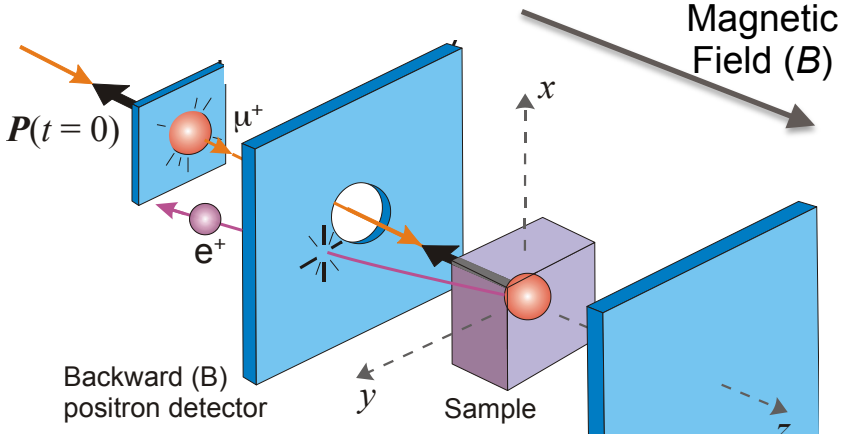
→ Muon hfcc (A_μ)

→ Nuclear hfccs
(H, D, ^{13}C, ^{14}N….)

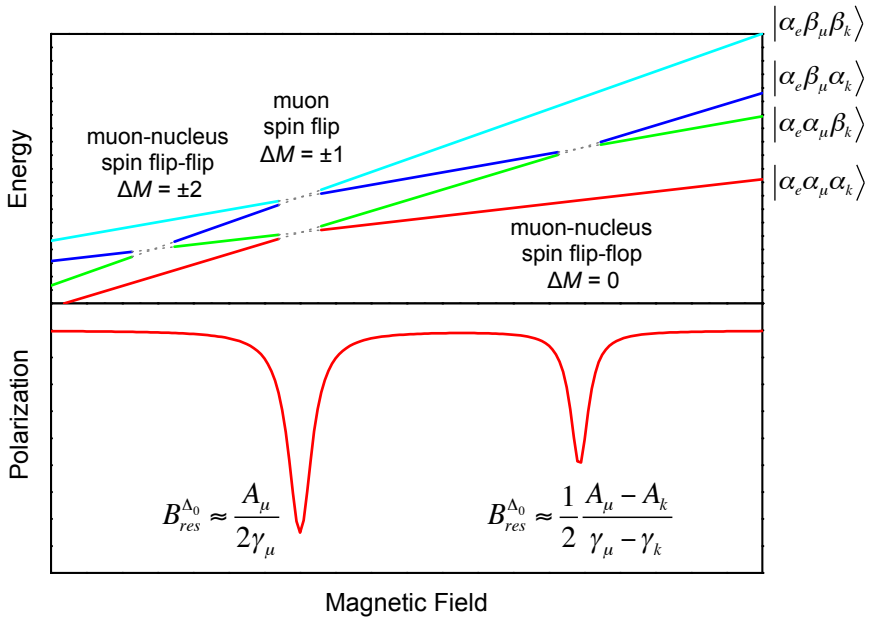
Hyperfine Coupling Constants → Distribution of unpaired electron

Temperature Dependence of HFCs →
- 3D structure
- Intramolecular motion

Level Crossing Resonance



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



Time integral measurement

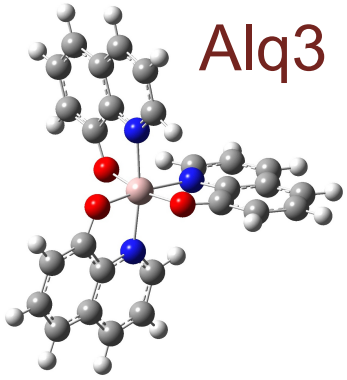
RATE IS CRITICAL!

HiFi @ ISIS: ~100 Mevents/hr

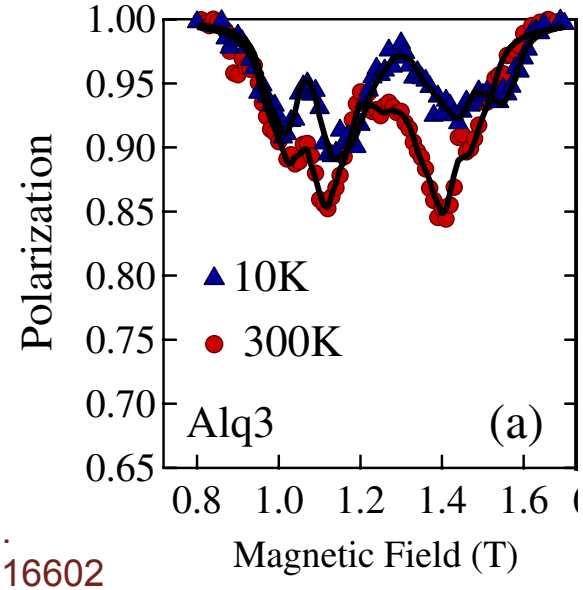
Helios @ TRIUMF: ~1800 Mevents/hr

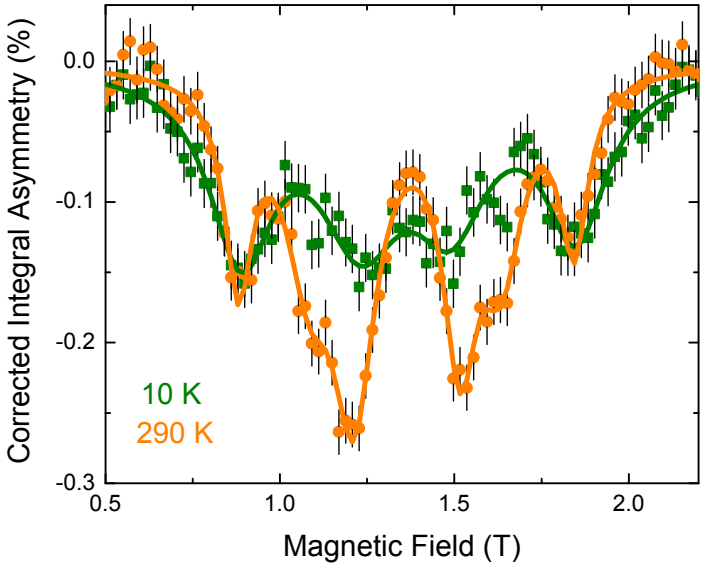
Why Rate is Important

- Ability to scan over wider field range. Find all resonances.



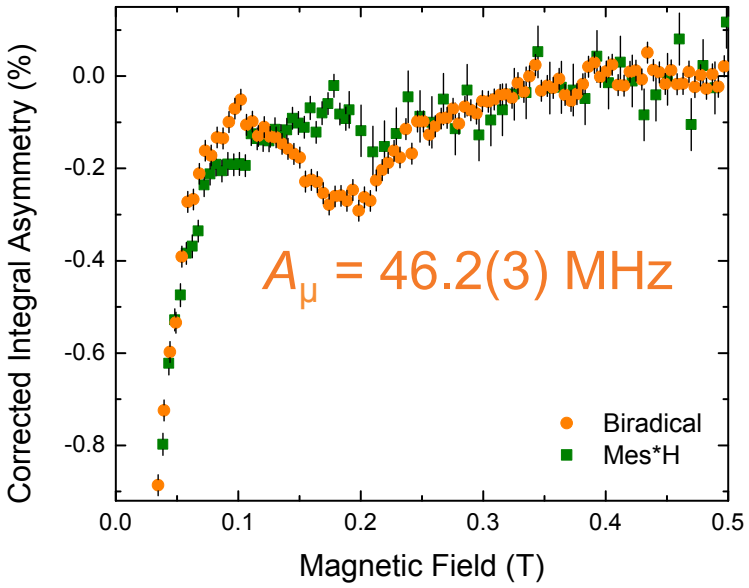
Nuccio et al.
PRL **2013**, *110*, 216602

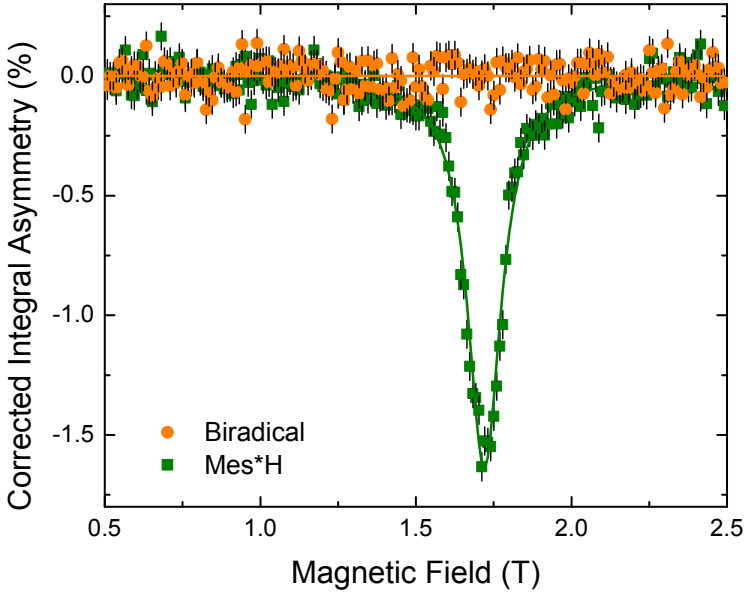




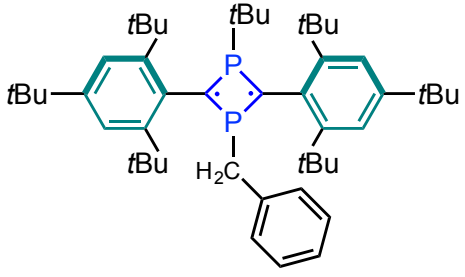
- Measure more samples, temperatures, field points, etc.
- Stability of beam over day. Can distort long ALC sweeps.

Probing Reactivity of Biradical

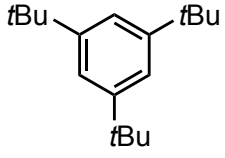




Biradical



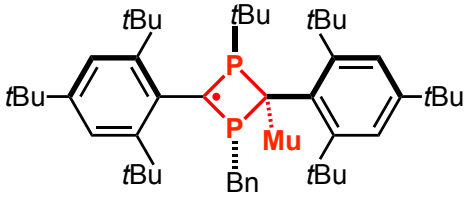
Mes*H



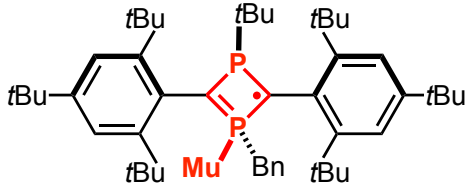
Ito et al. M1497 TRIUMF

Probing Reactivity of Biradical

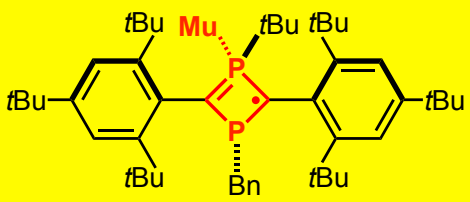
Possible Muonium Addition



C-attack



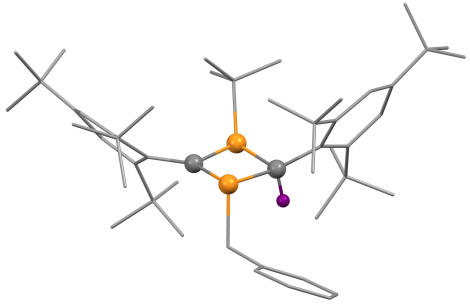
P-attack1

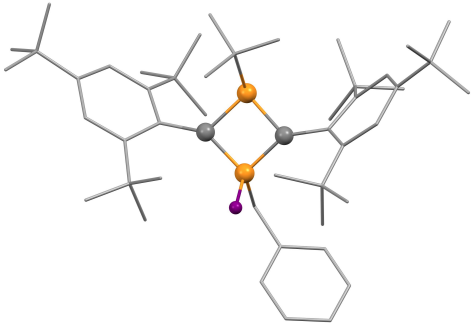


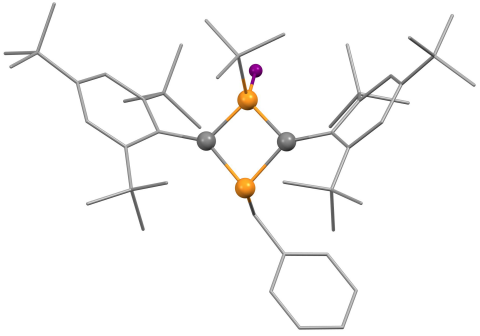
P-attack2

	C-attack	P-attack1	P-attack2
ΔE_{DFT} (Kcal/mol)	0.0	20.0	15.3
A_μ (MHz)	**6.4**	**394.4**	**51.5**

(UBP86-D/TZ2P)

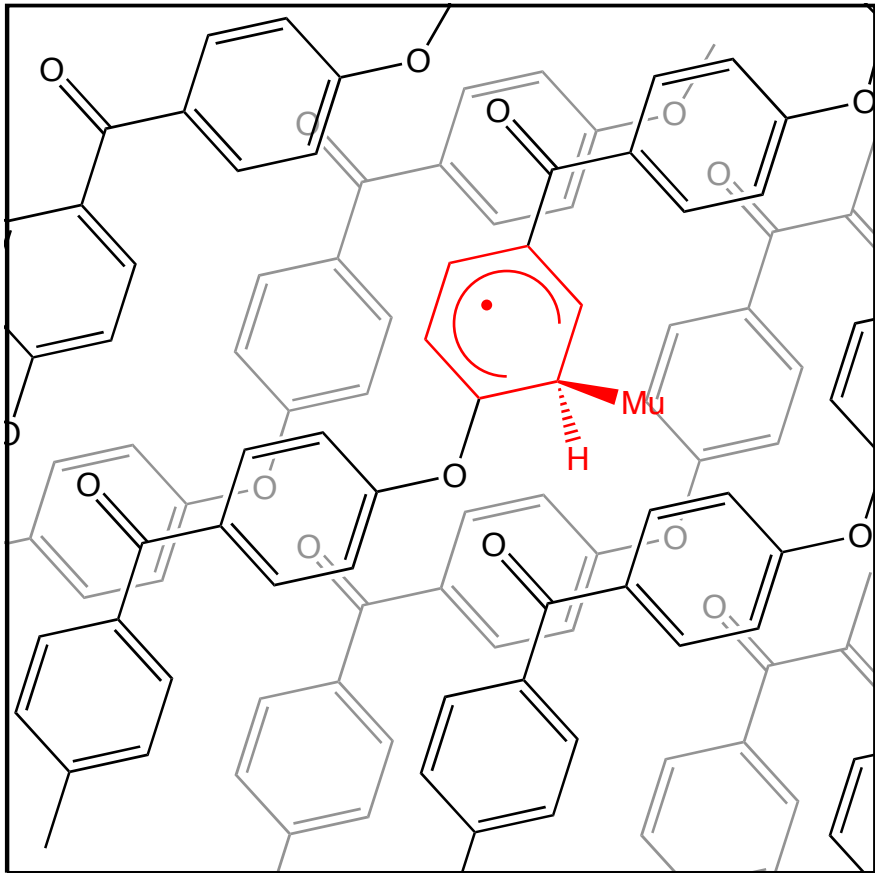






Ito et al. M1497 TRIUMF

Muoniated Probes in Soft Matter



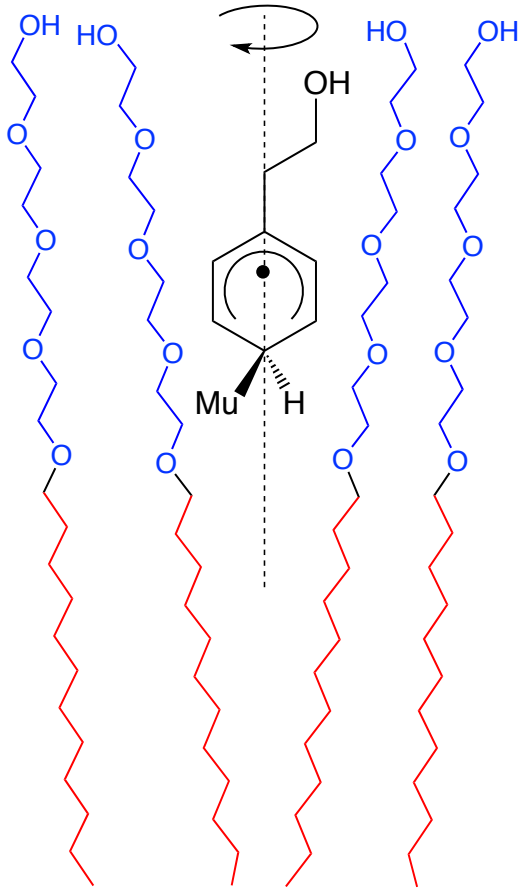
- Introduce spin label in soft matter system (liquid crystal, polymer)
- Similar to spin labeling with stable nitroxides *except smaller perturbation.*
- Radical sensitive to:
  - Orientation of probe
  - Polarity of local environment
  - Fluctuations on the ns to μs timescale

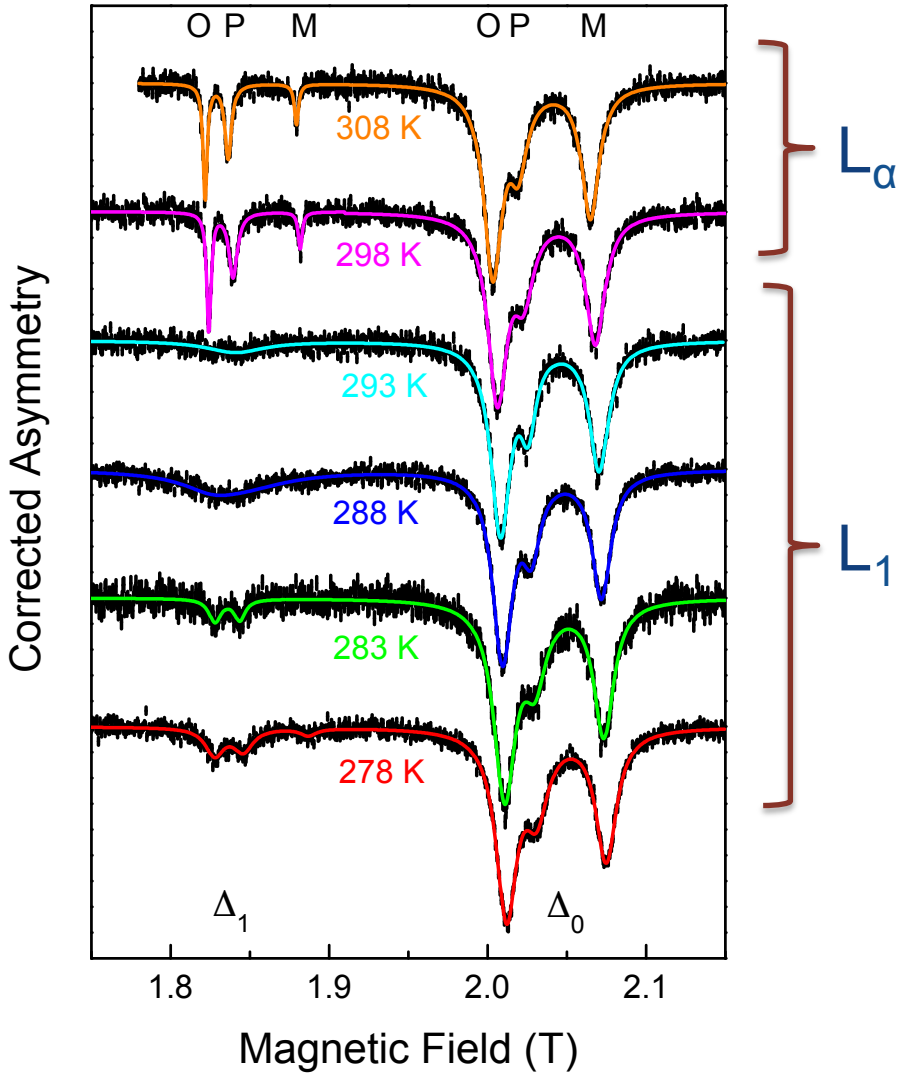
Cosurfactants in Bilayers and Micelles

$C_{12}E_4$

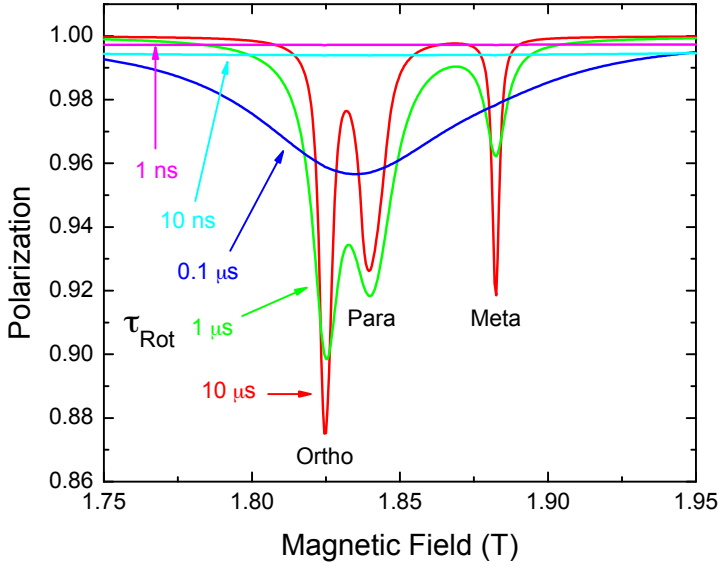
hydrophilic

hydrophobic



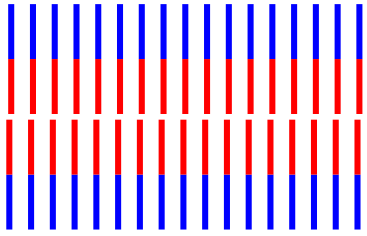


Cosurfactants in Bilayers and Micelles



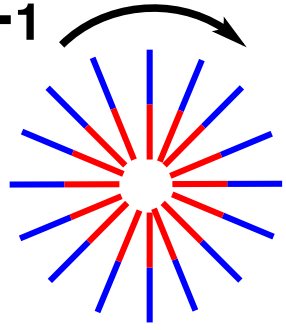
Bilayer doesn't rotate.
Rapid uniaxial rotation.

L_α

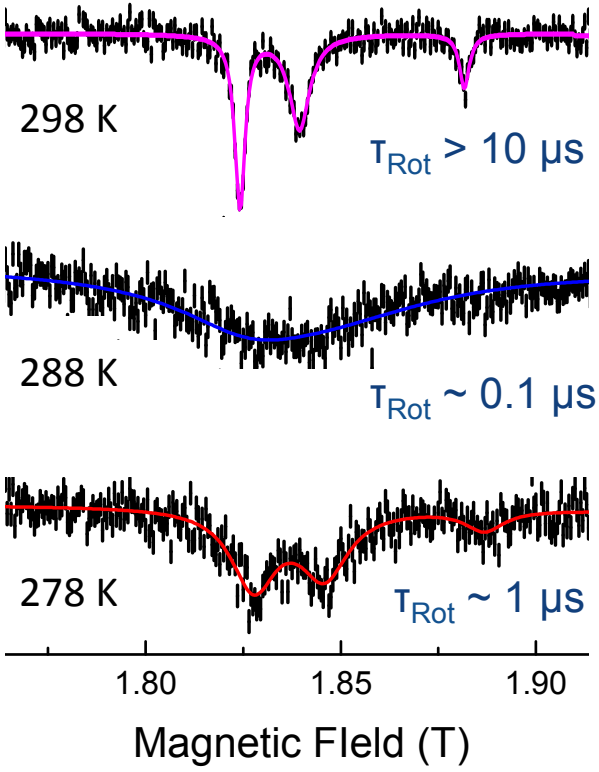


Bilayers

L_1



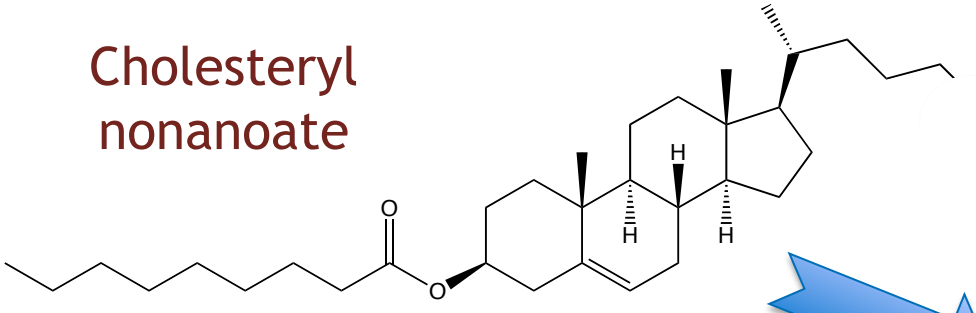
Rotation of micelles



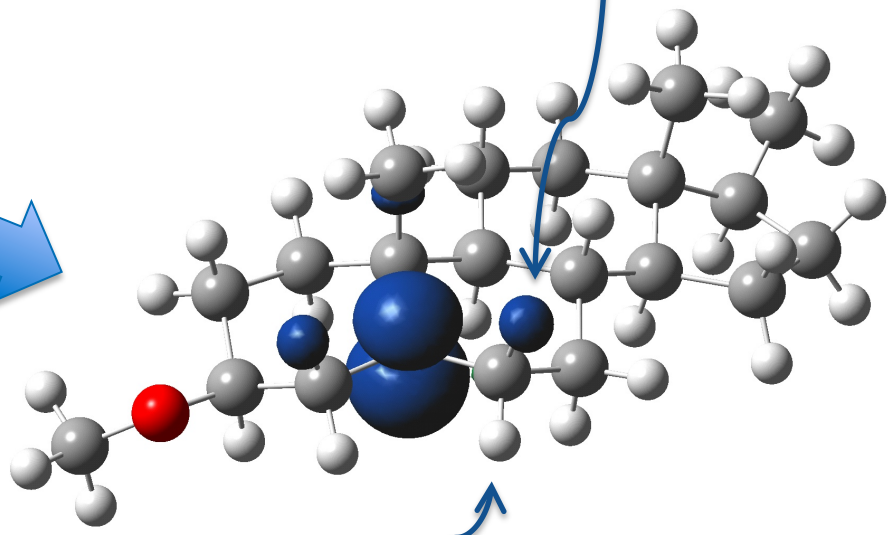
Slow rotation of micelle broadens Δ_1

Cholesterolic Liquid Crystal

Cholesteryl nonanoate



A_μ = 441.9 MHz
$B_{res}(\Delta_1)$ = 1.62 T



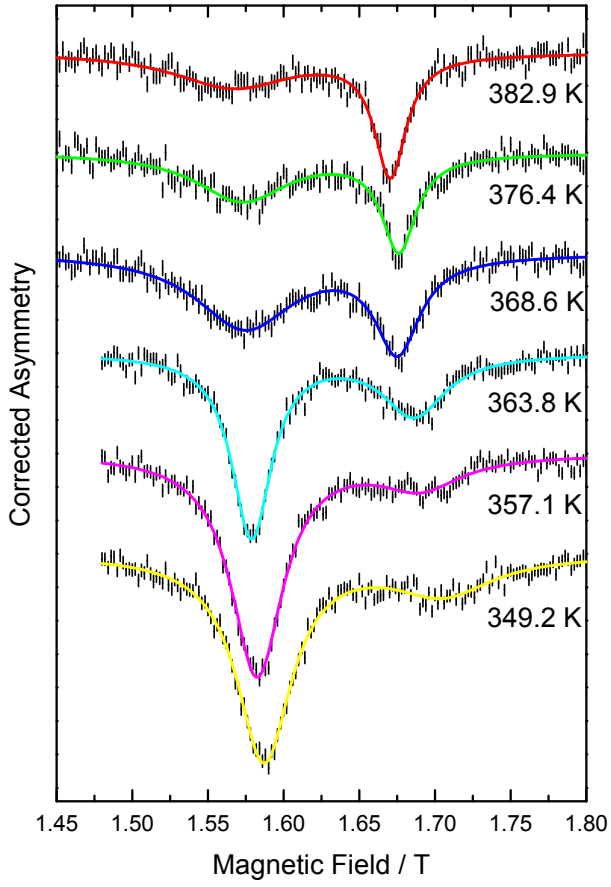
P/2

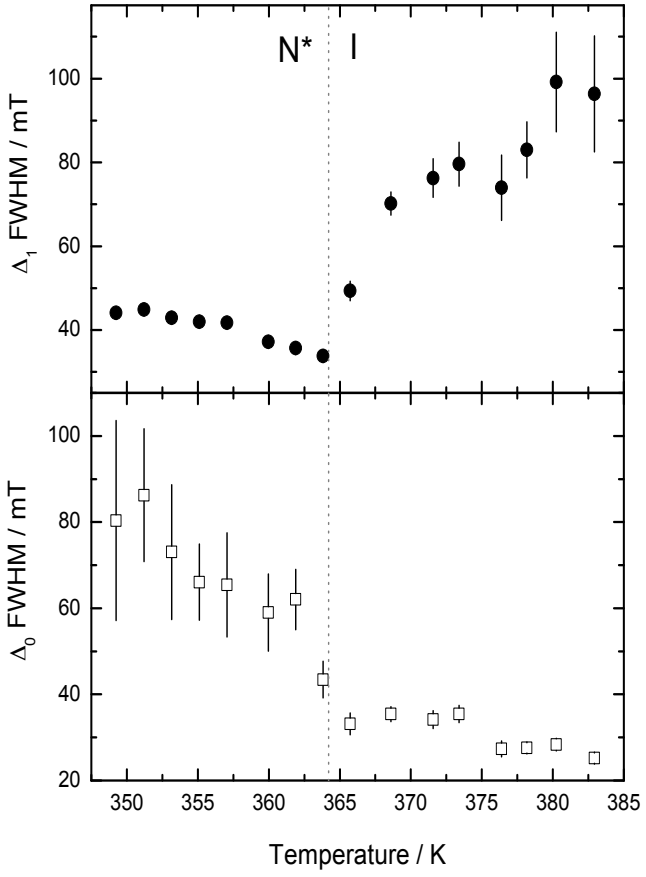
A_μ = 71.7 MHz
$B_{res}(\Delta_1)$ = 0.26 T

McKenzie et al. *JPCB* **2011**, *115*, 9360

UB3LYP/6-31G(d,p)//
UPBE0/EPR-II

Cholesterolic Liquid Crystal





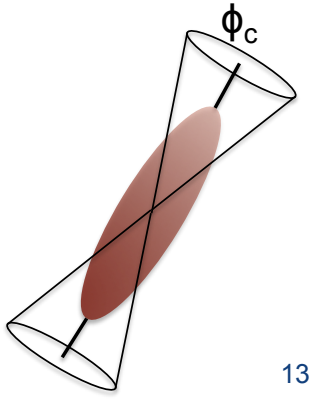
Isotropic phase

Slow isotropic reorientation broadens Δ_1

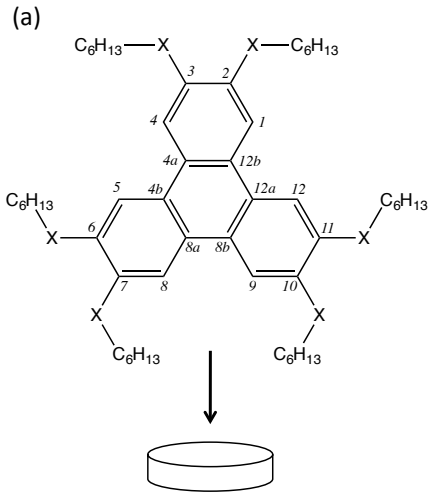
N* phase

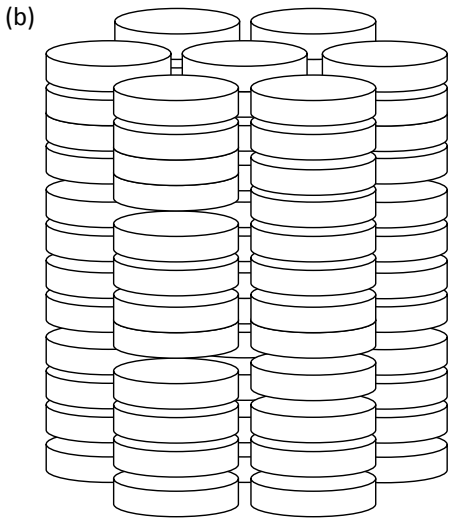
Wobbling within a cone averages dipolar hyperfine coupling

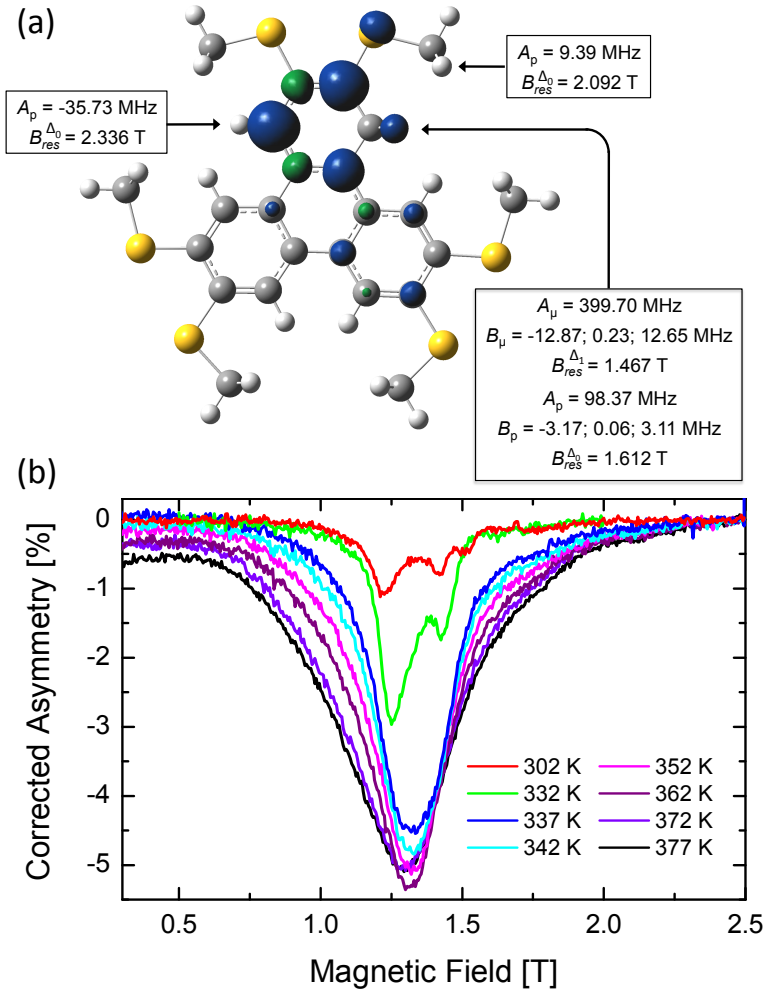
Narrows Δ_1



Discotic Liquid Crystals



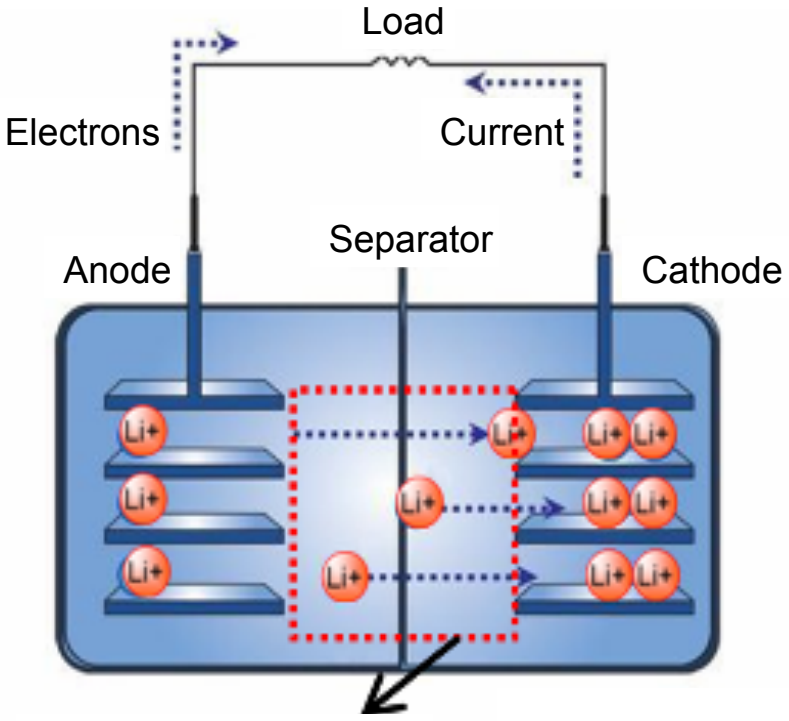




- Formation of 1D "molecular wires" in Col_h and H phases.
- λ_e ~ 100's of μs^{-1} in Col_h and H phases of HHTT. Mechanism unknown.

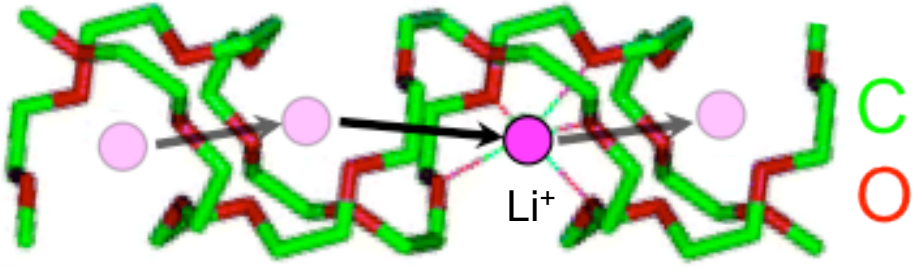
McKenzie et al. *PRE* **2013**, *87*, 012504

Polymer Electrolytes



Solid Polymer Electrolyte

Polyethylene oxide (PEO) or $(CH_2\text{-}CH_2\text{-}O)_n$ is used as electrolyte in lithium-ion batteries.

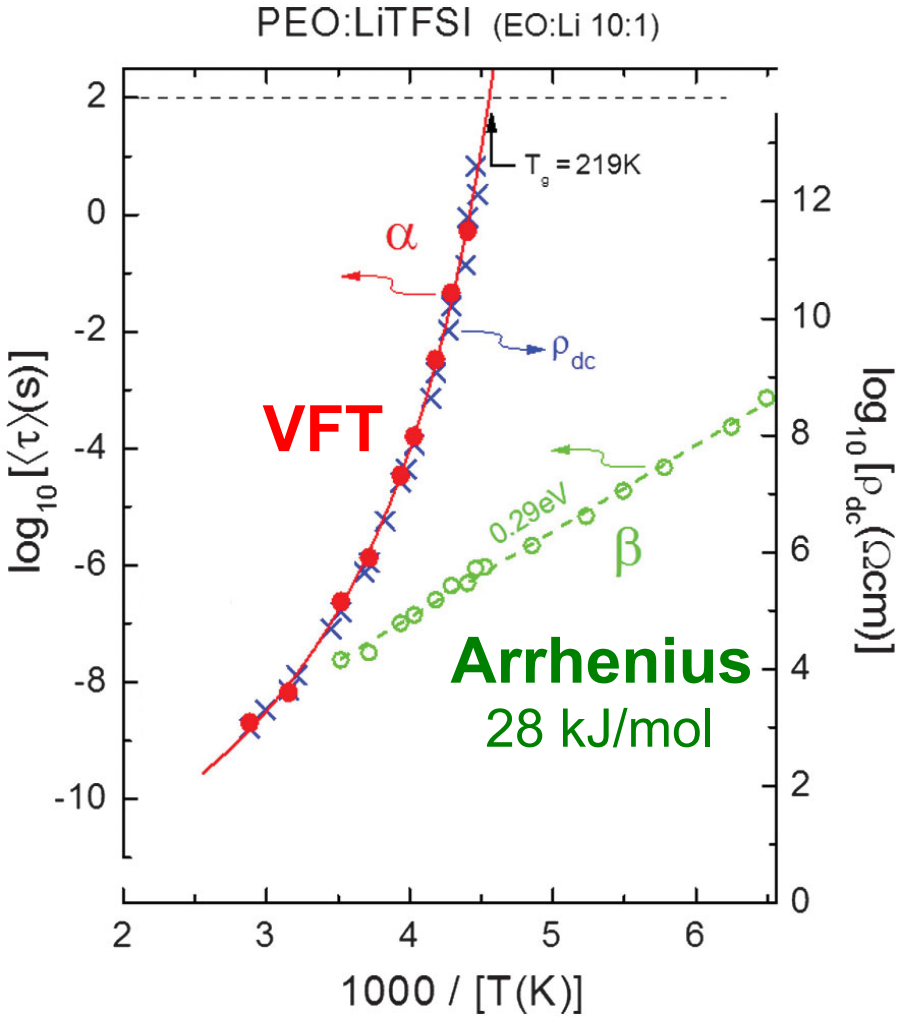


Understanding microscopic dynamics of Li^+ in polymer electrolyte essential to optimize materials.

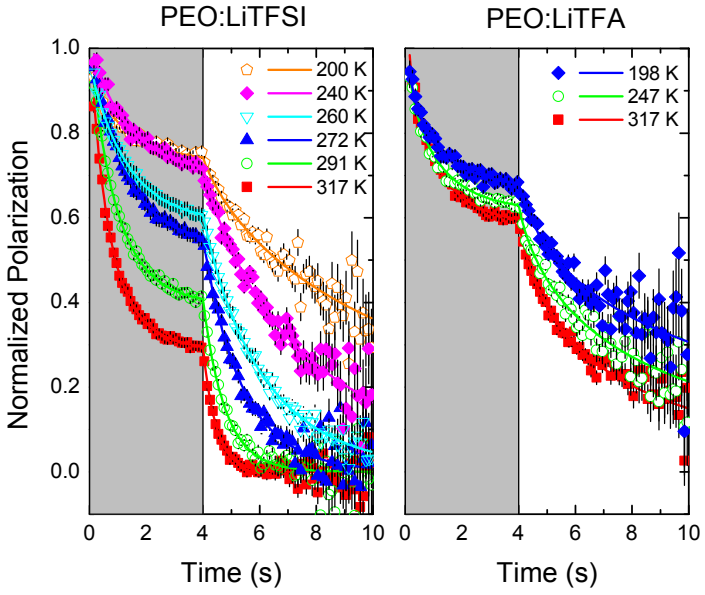
Bulk Measurements Versus Local Probes?

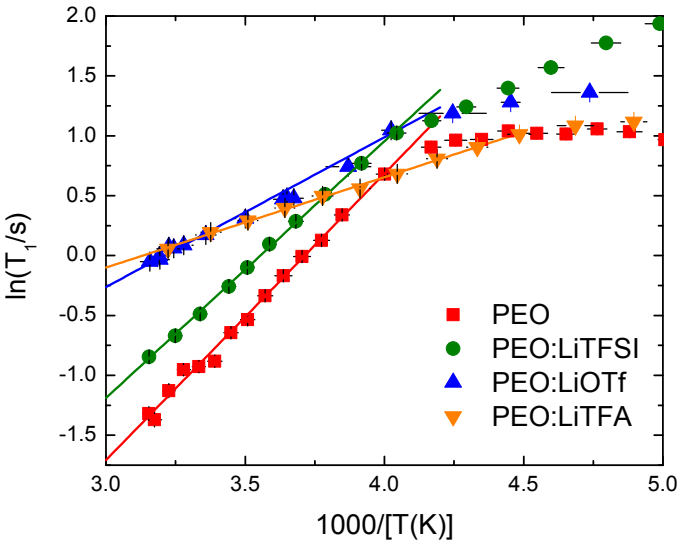
- α-relaxation (main chain motion) and DC conductivity have identical temperature dependence (VFT).
- Implication is that the α-relaxation plays an important role in long range Li^+ transport.

C. Do et al. *PRL.* **2013**, *111,* 018301

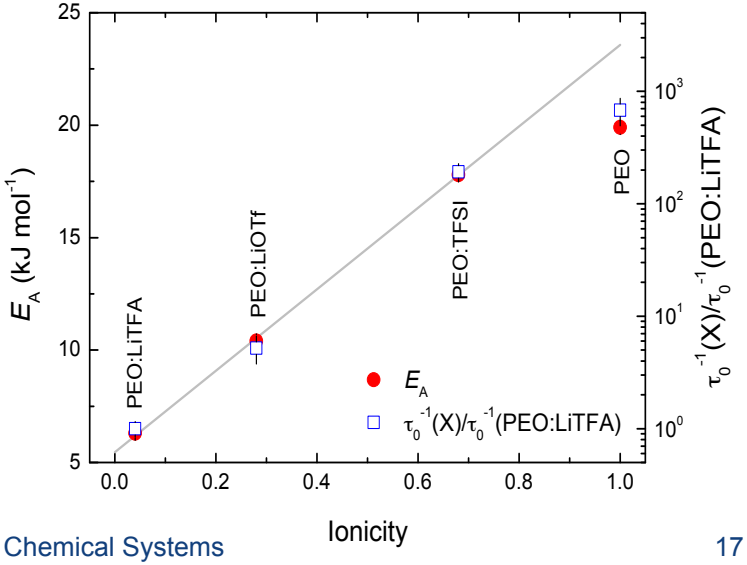


β-NMR of Lithium Diffusion in PEO

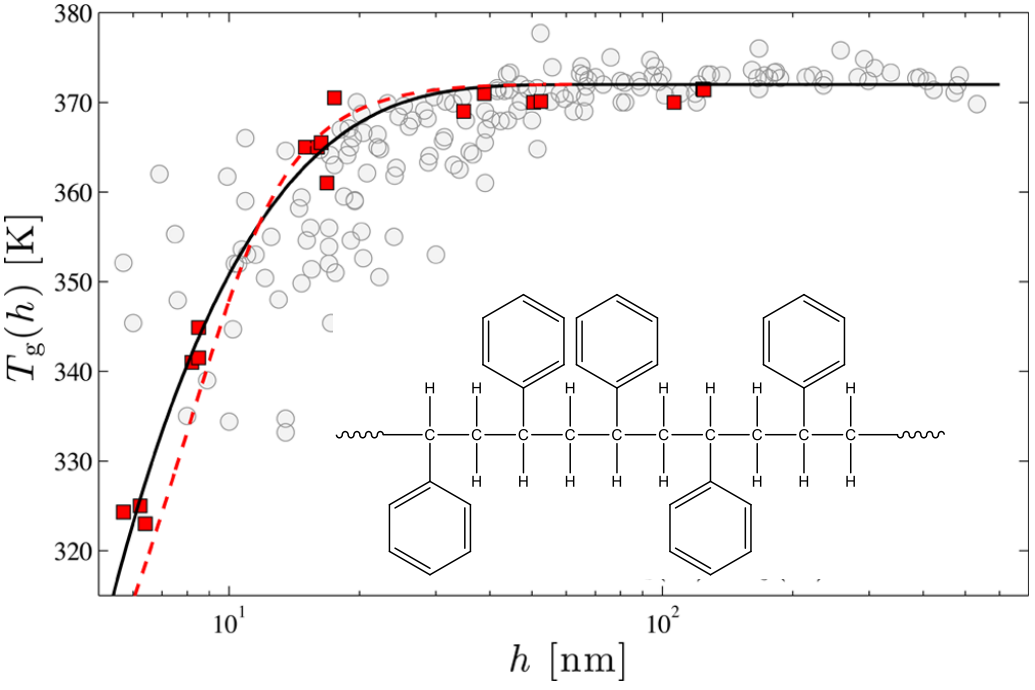




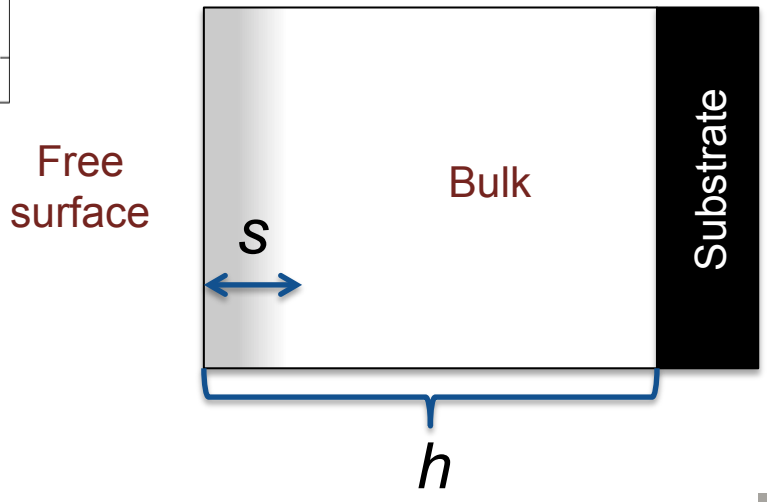
- Hopping of $^{8}Li^{+}$ appears to be an Arrhenius process.
- Diffusion parameters depend strongly on the ionicity of the lithium salt.



Glass Transition in Polystyrene Thin Films

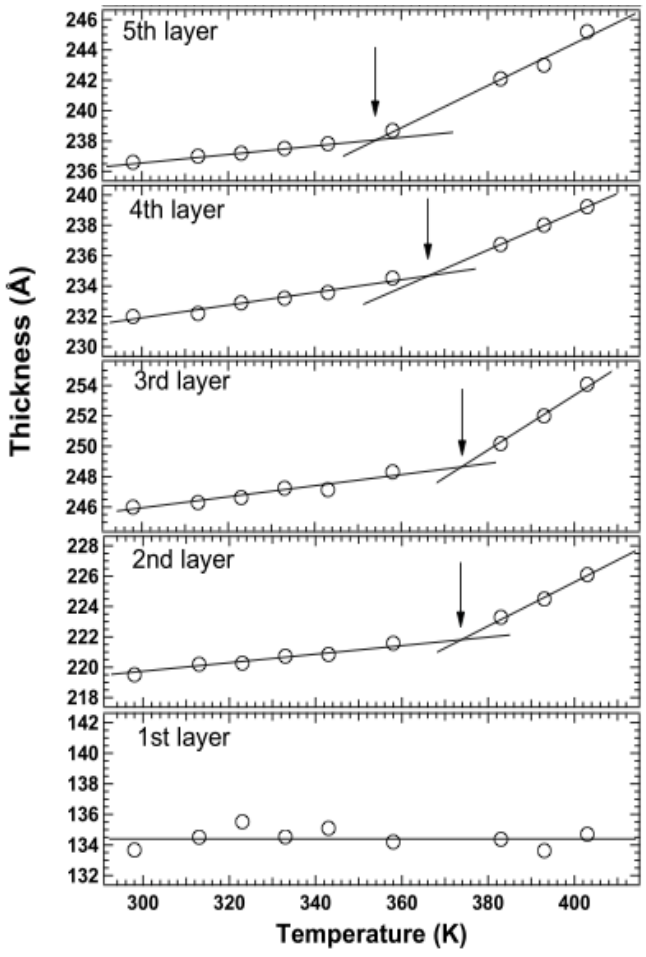


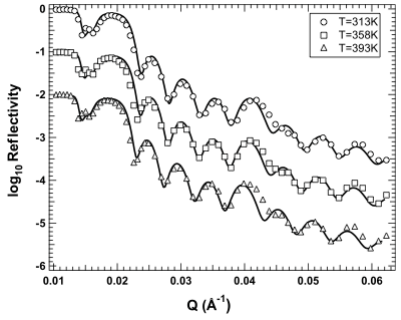
- Reduction of T_g for thin, supported PS films
- Results suggest region near the surface with enhanced dynamics



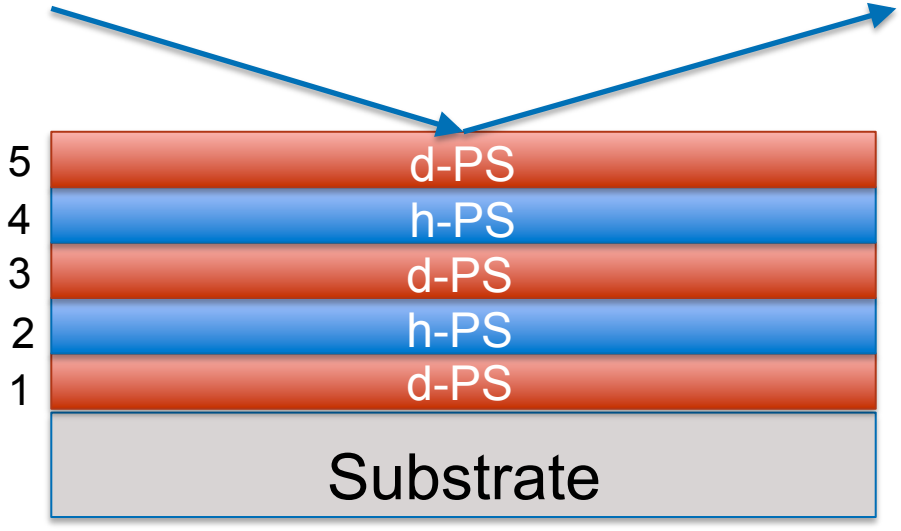
J.A. Forrest and K. Dalnoki-Veress
Adv. Colloid Interface Sci. **2001**, *94*, 167

Evidence for Lower T_g Near the Surface



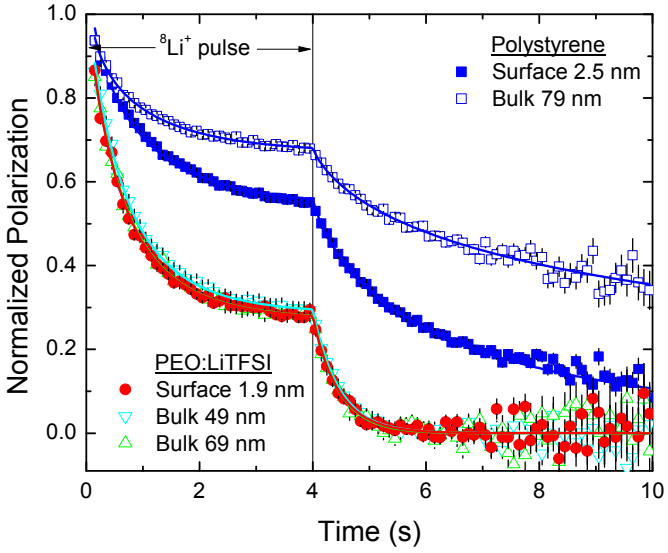


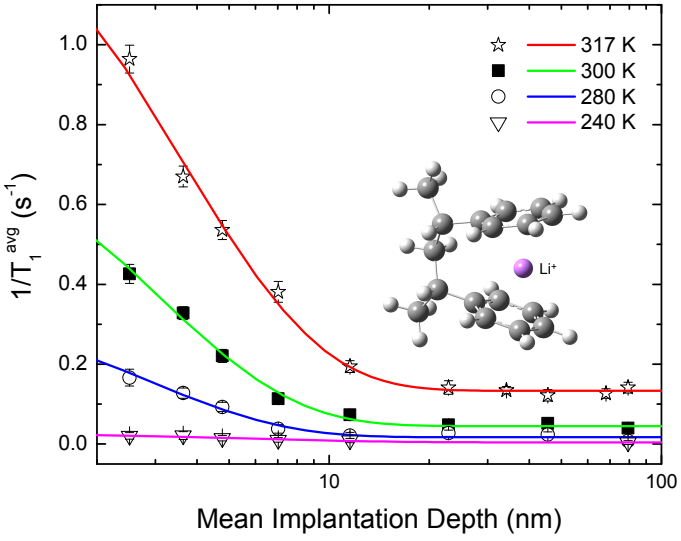
Neutron reflectometry on 100 nm thick multilayer film



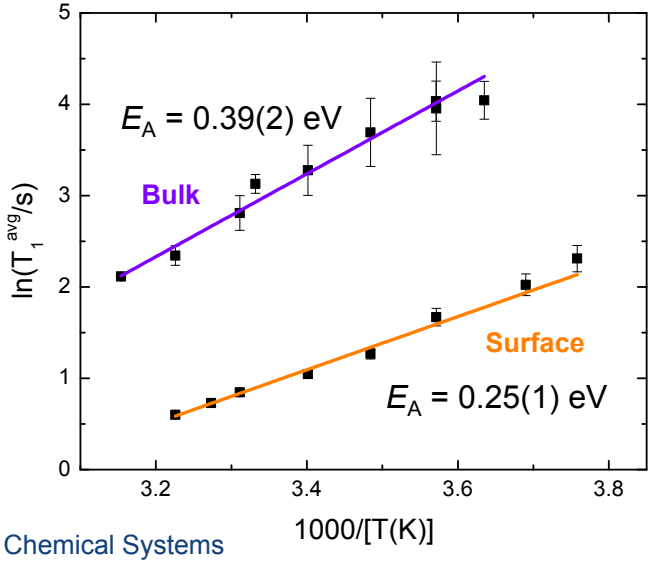
R. Inoue et al.
Phys. Rev. E **2011**, *83*, 021801

β-NMR of Polystyrene





- Spin relaxation due to torsional motion of phenyl rings.
- Enhanced dynamics and lower torsional barrier within ~10 nm of free surface.



Thank you!
Merci

iain.mckenzie@triumf.ca
http://www.musr.ca

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