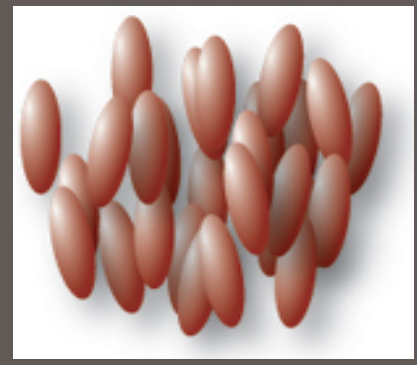
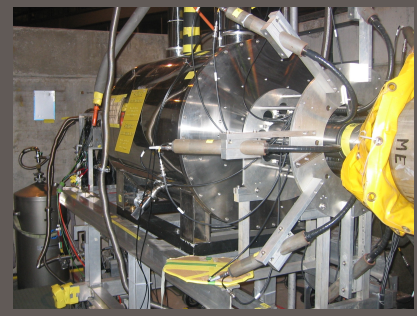
TRIUMF

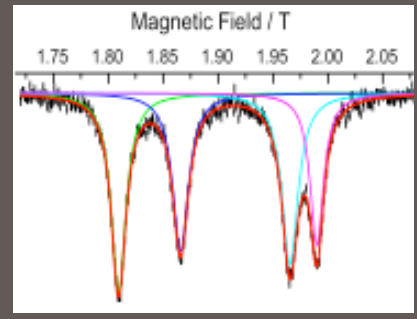
Canada's national laboratory for particle and nuclear physics
Laboratoire national canadien pour la recherche en physique nucléaire
et en physique des particules

μSR of Soft Matter:

Probing Dynamics in Complex Systems







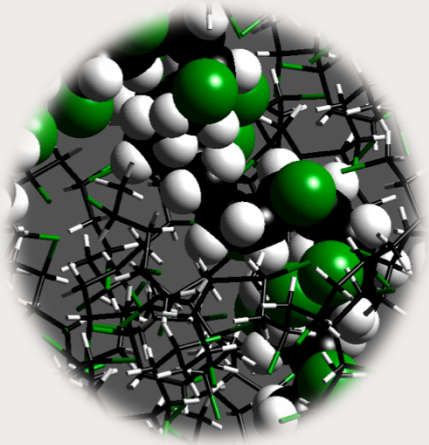
Iain McKenzie | CMMS | TRIUMF

Outline

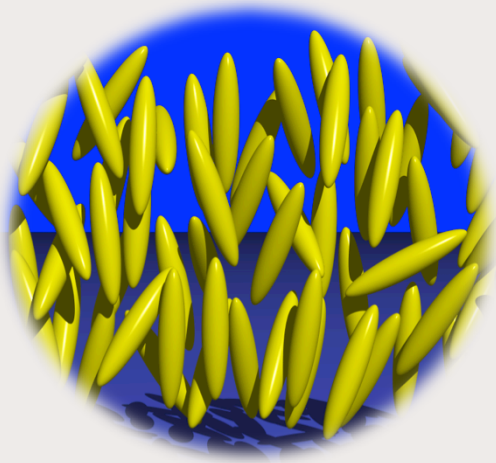
- Introduction to soft matter
- Rod-like liquid crystals
- Cosurfactant location in lyotropic liquid crystals
- Polymers
- Biological systems
- Conclusions

Soft Matter

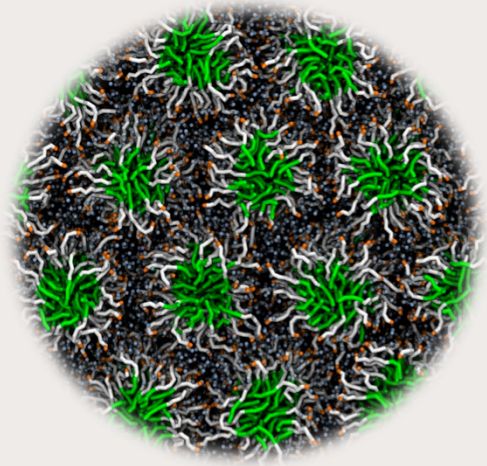
Polymers



Liquid Crystals

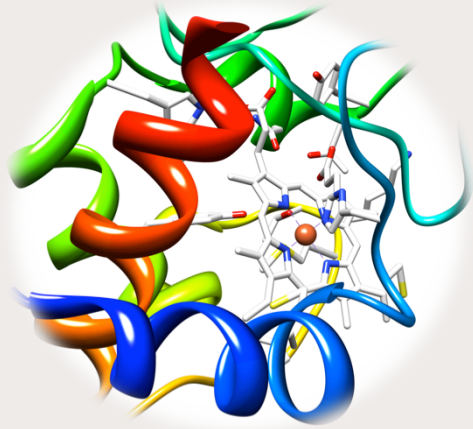


Surfactants



Colloids

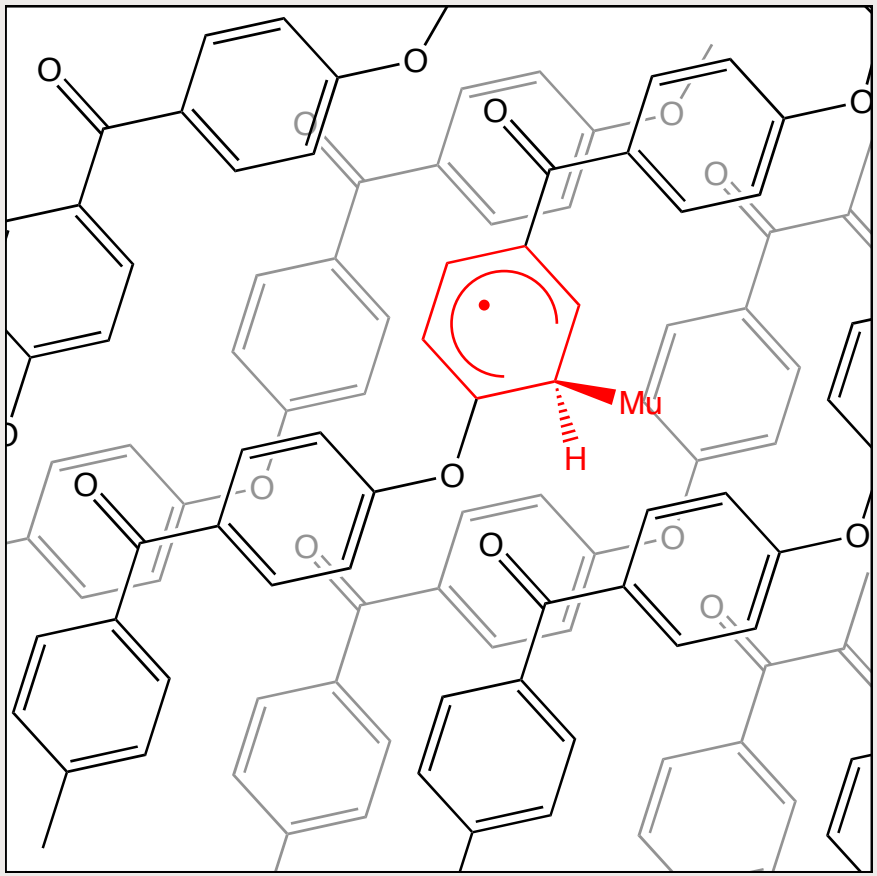
Biological

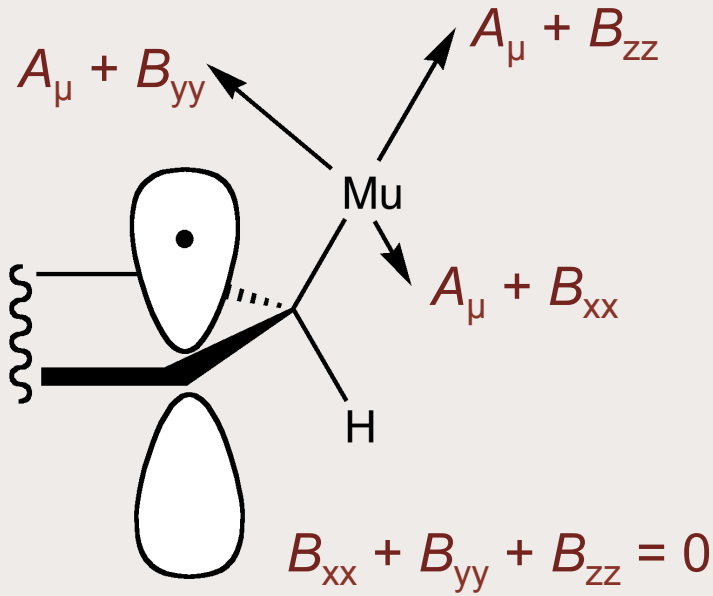


Characteristics of Soft Matter

- Predominant physical behaviors occur at an energy scale comparable with room temperature thermal energy
- Materials that are easily deformable by external stresses, electric or magnetic fields, or even by thermal fluctuations
- Soft matter can self-organize into mesoscopic physical structures; the structure and dynamics at the mesoscopic scales determine macroscopic physical properties

Muoniated Probes in Soft Matter

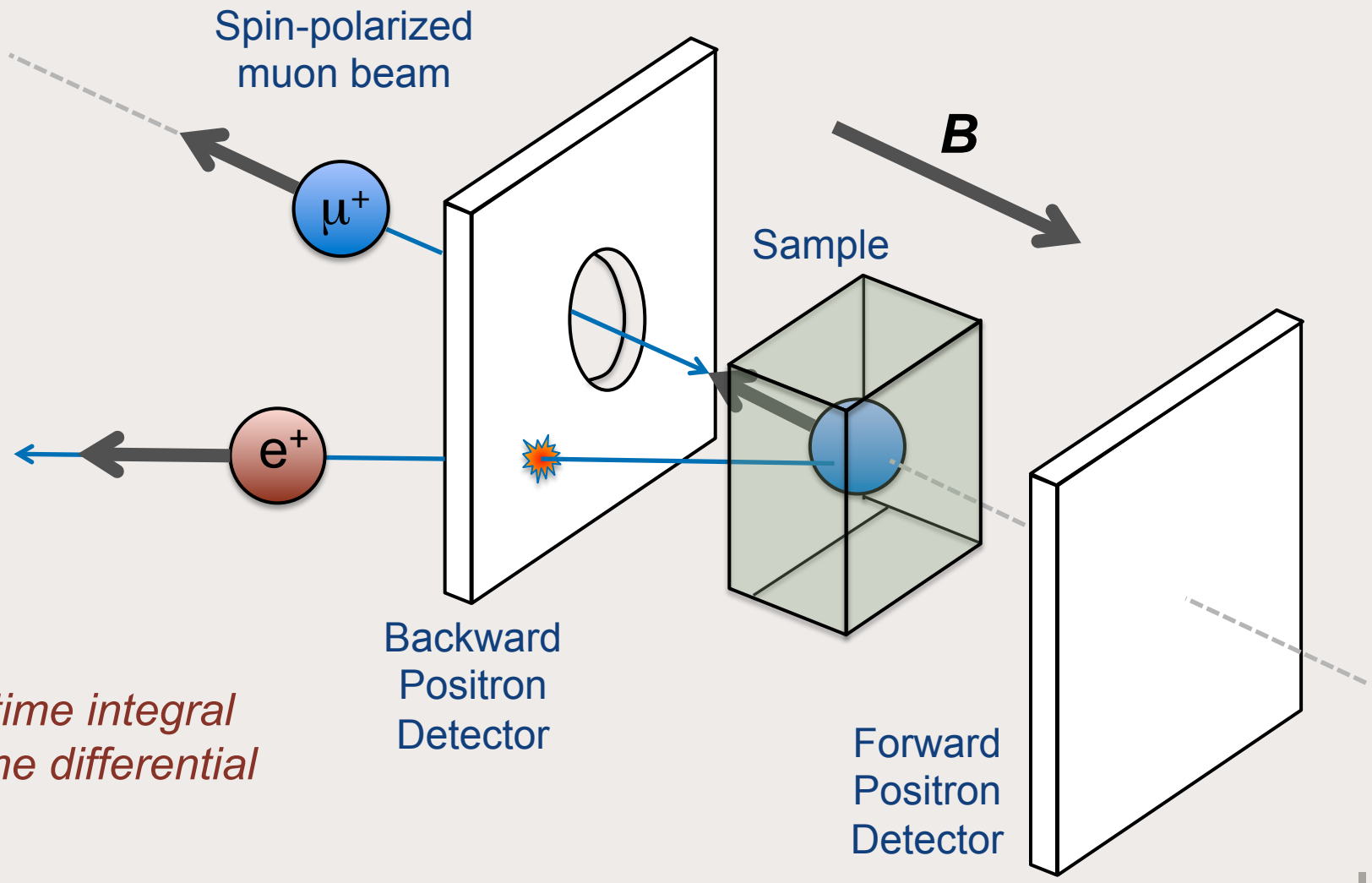




Sensitive to:

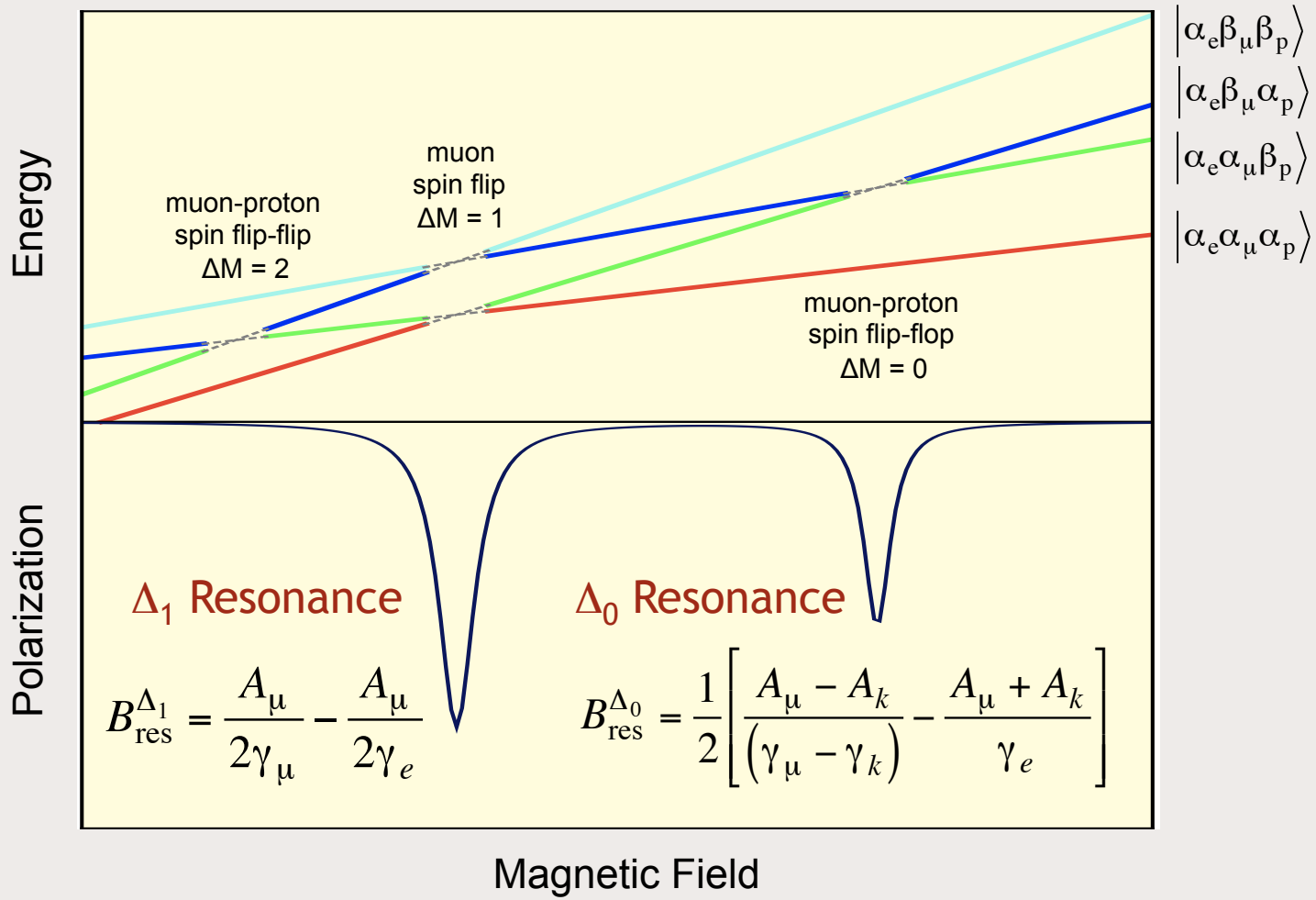
- Orientation of probe
- Local environment
- Fluctuations on the ns to μs timescale

Longitudinal Field μSR

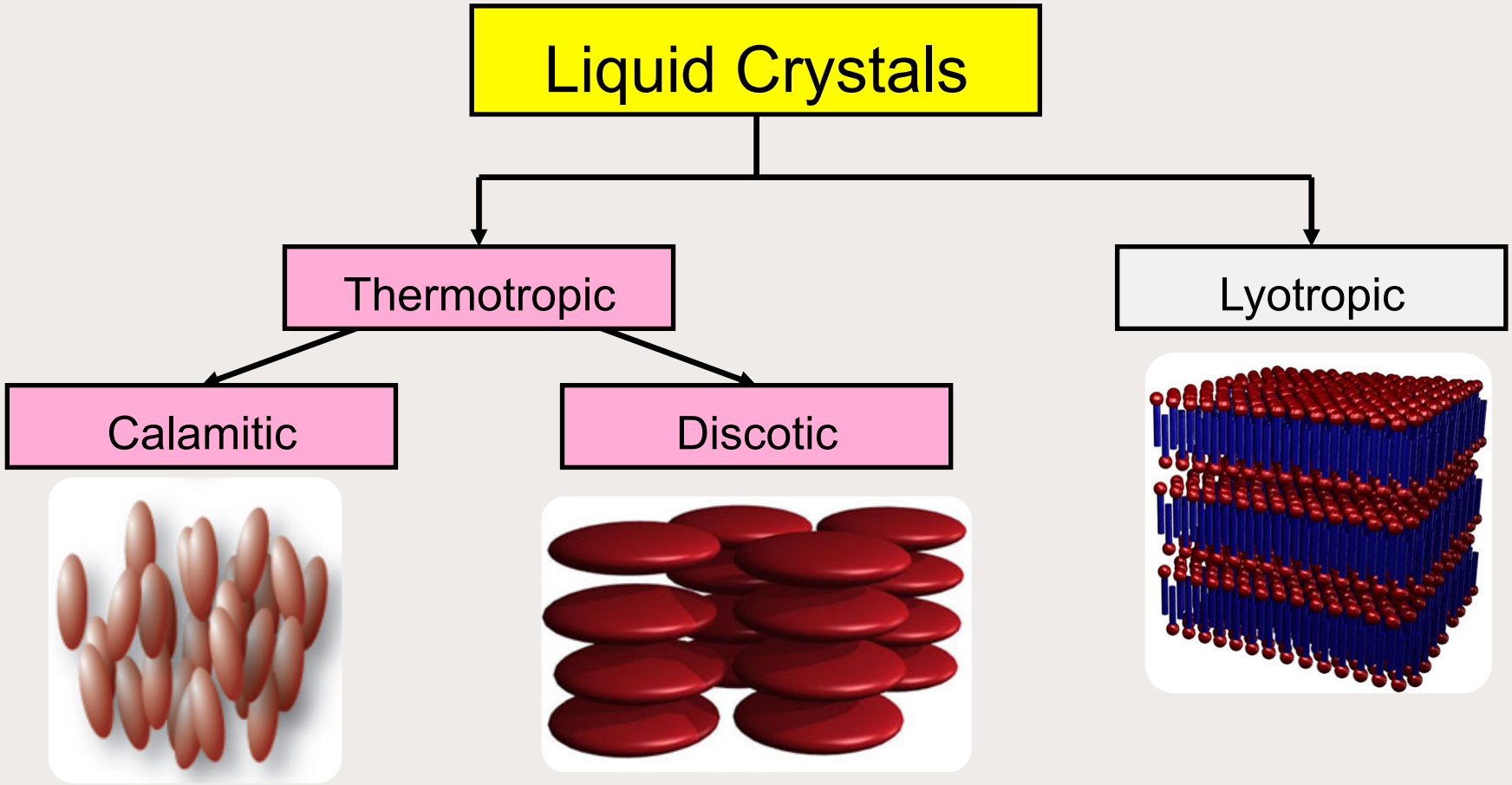


LCR: *time integral*
LF: *time differential*

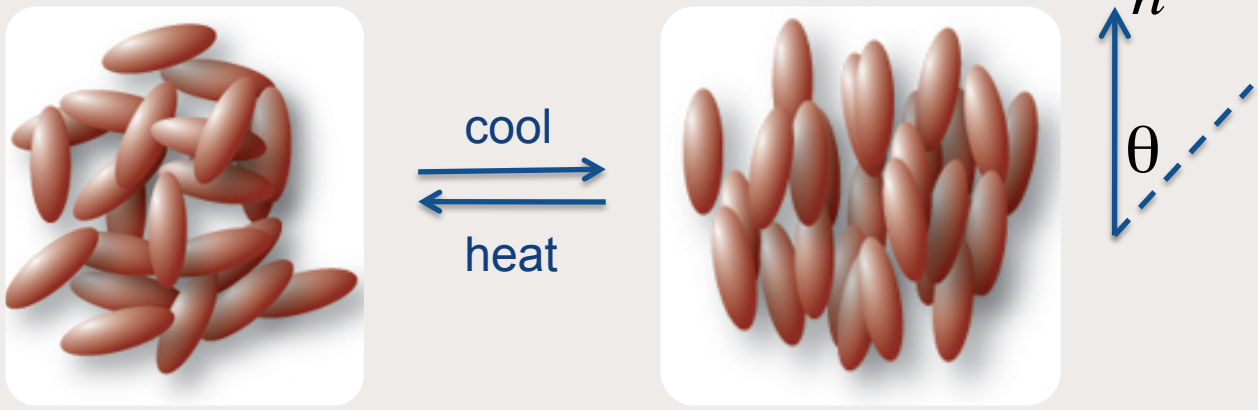
Level Crossing Resonance



Classification of Liquid Crystals



Rod-like Liquid Crystals

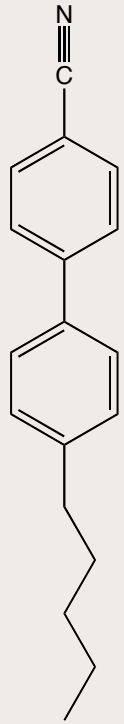


Isotropic Liquid

Nematic

$$S = \int_0^{\pi} \frac{1}{2}\left(3\cos^2\theta - 1\right) f(\theta) d\Omega$$

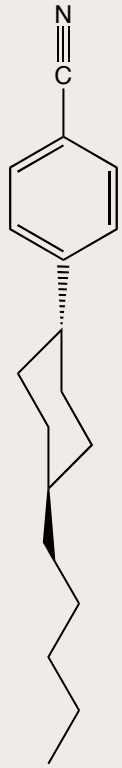
Rod-like Liquid Crystals



5CB

I-N 308 K

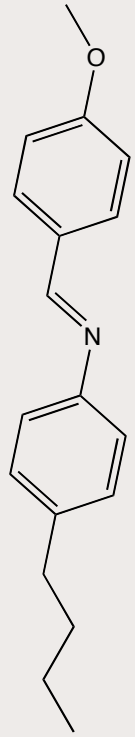
N-Cr 297 K



PCH5

I-N 328 K

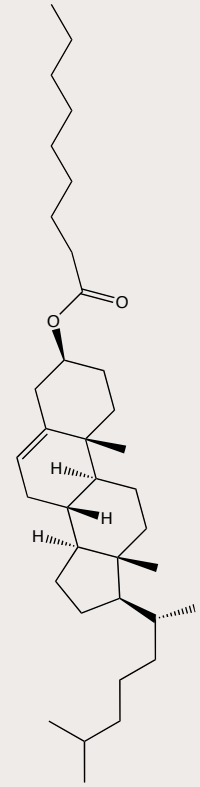
N-Cr 303 K



MBBA

I-N 314 K

N-Cr 290 K

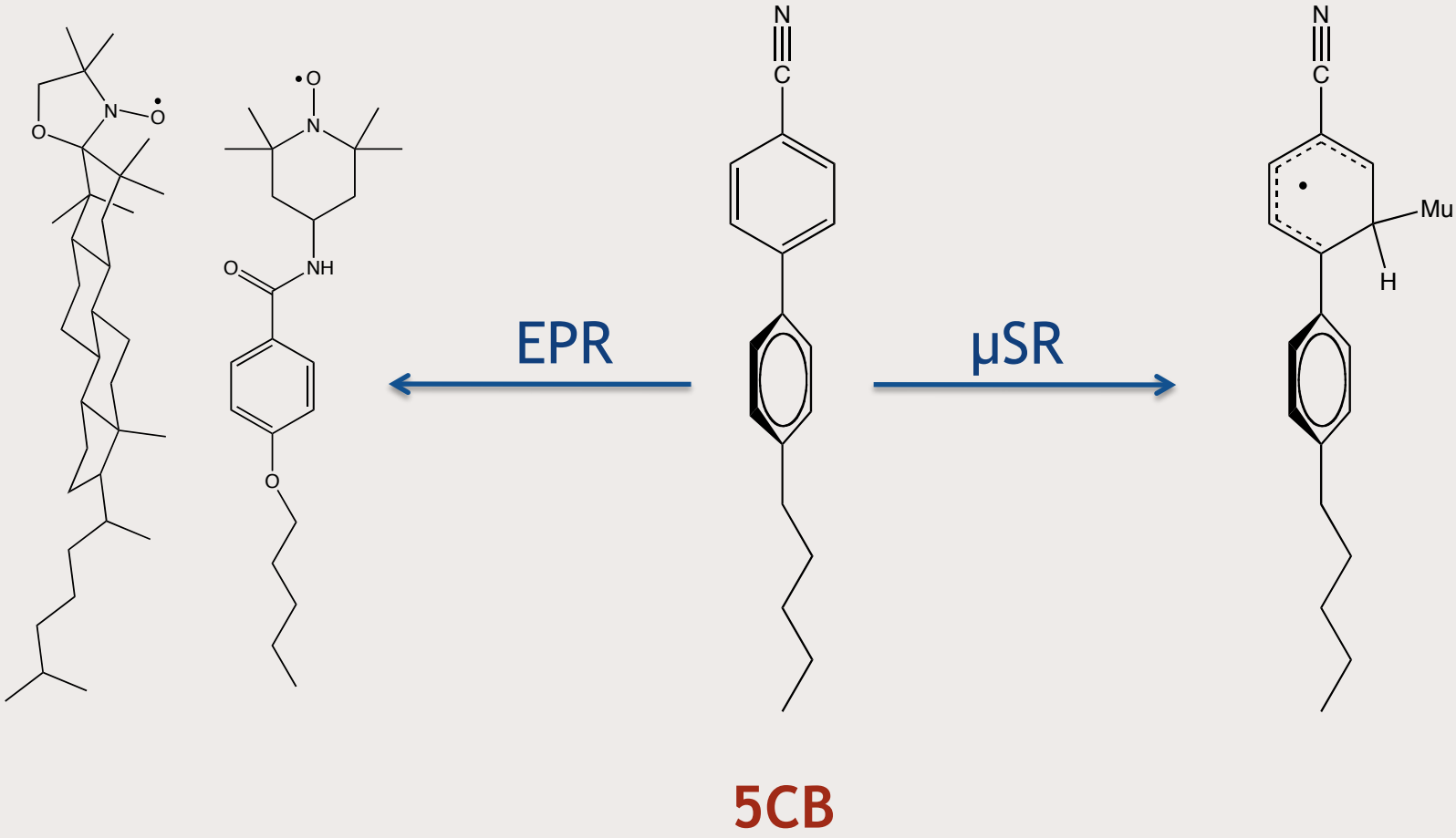


CN

I-N* 364 K

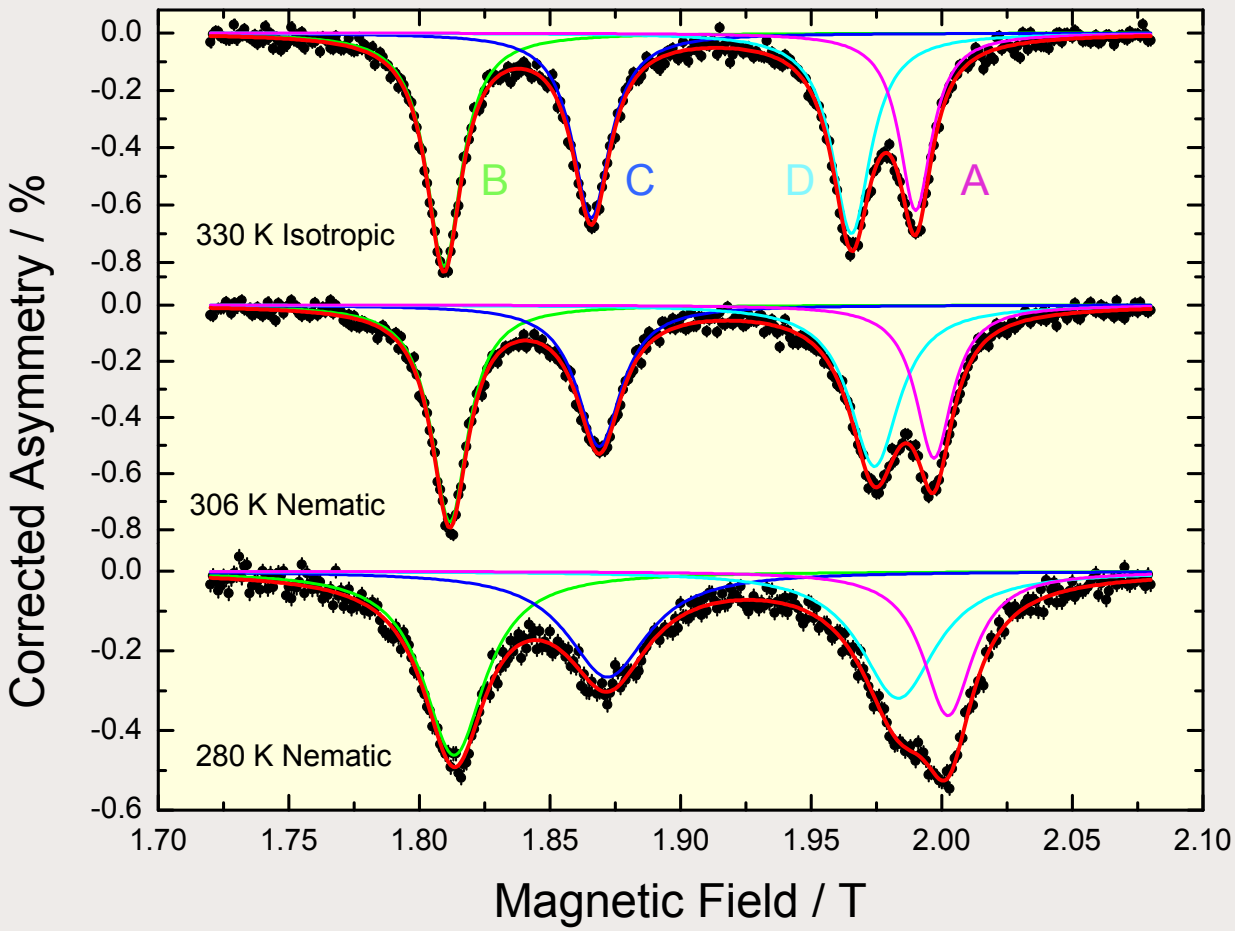
N*-SmA 348 K

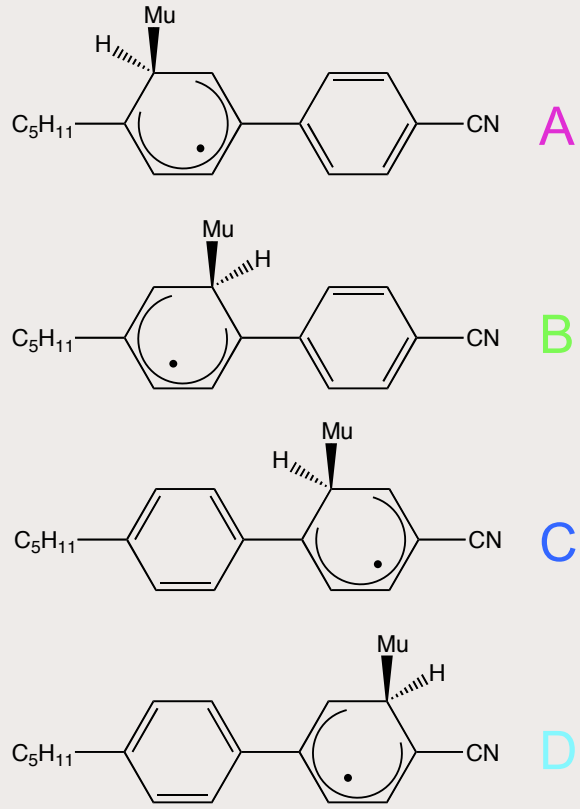
Spin Probes in Liquid Crystals



5CB

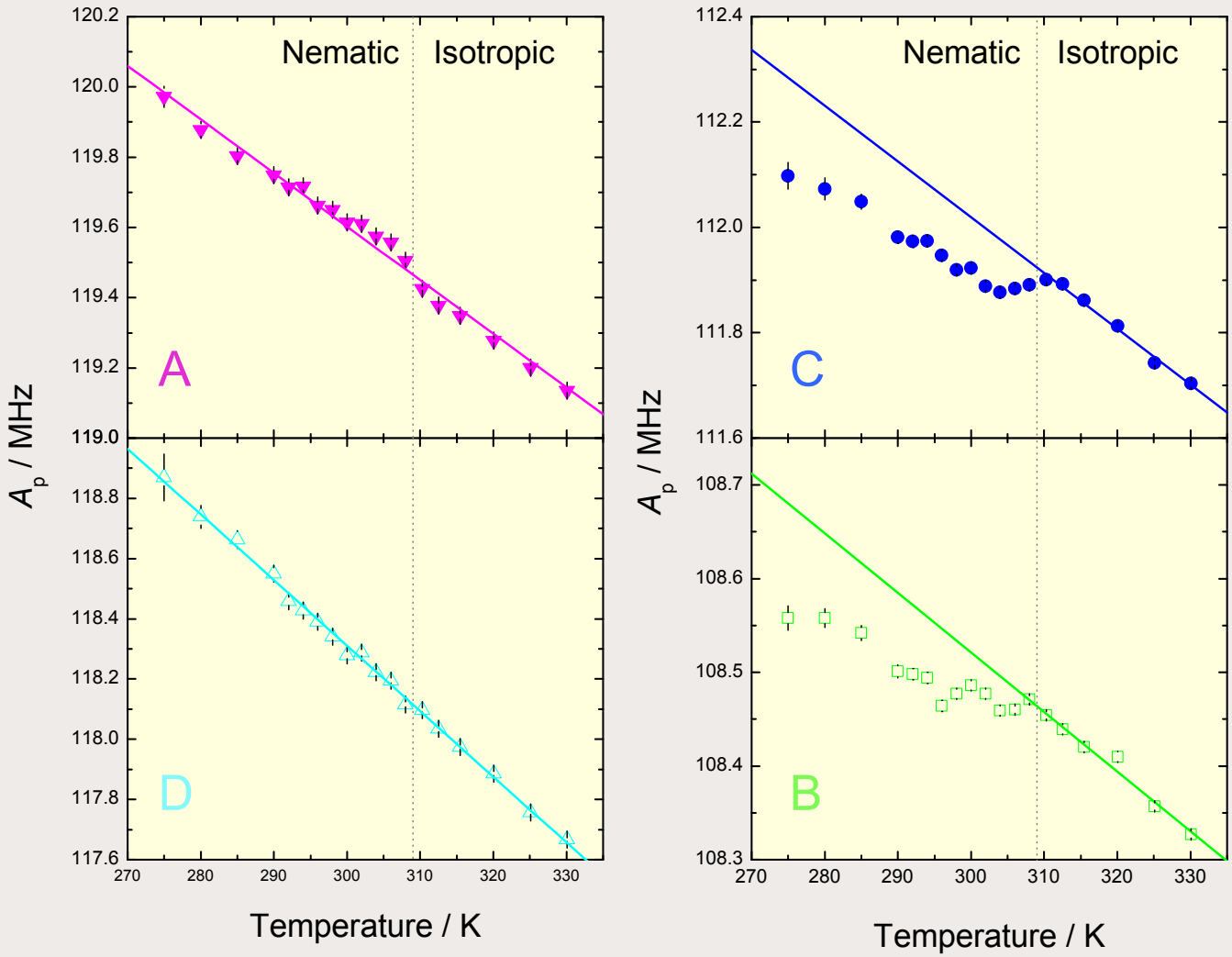
ALC-μSR of 5CB



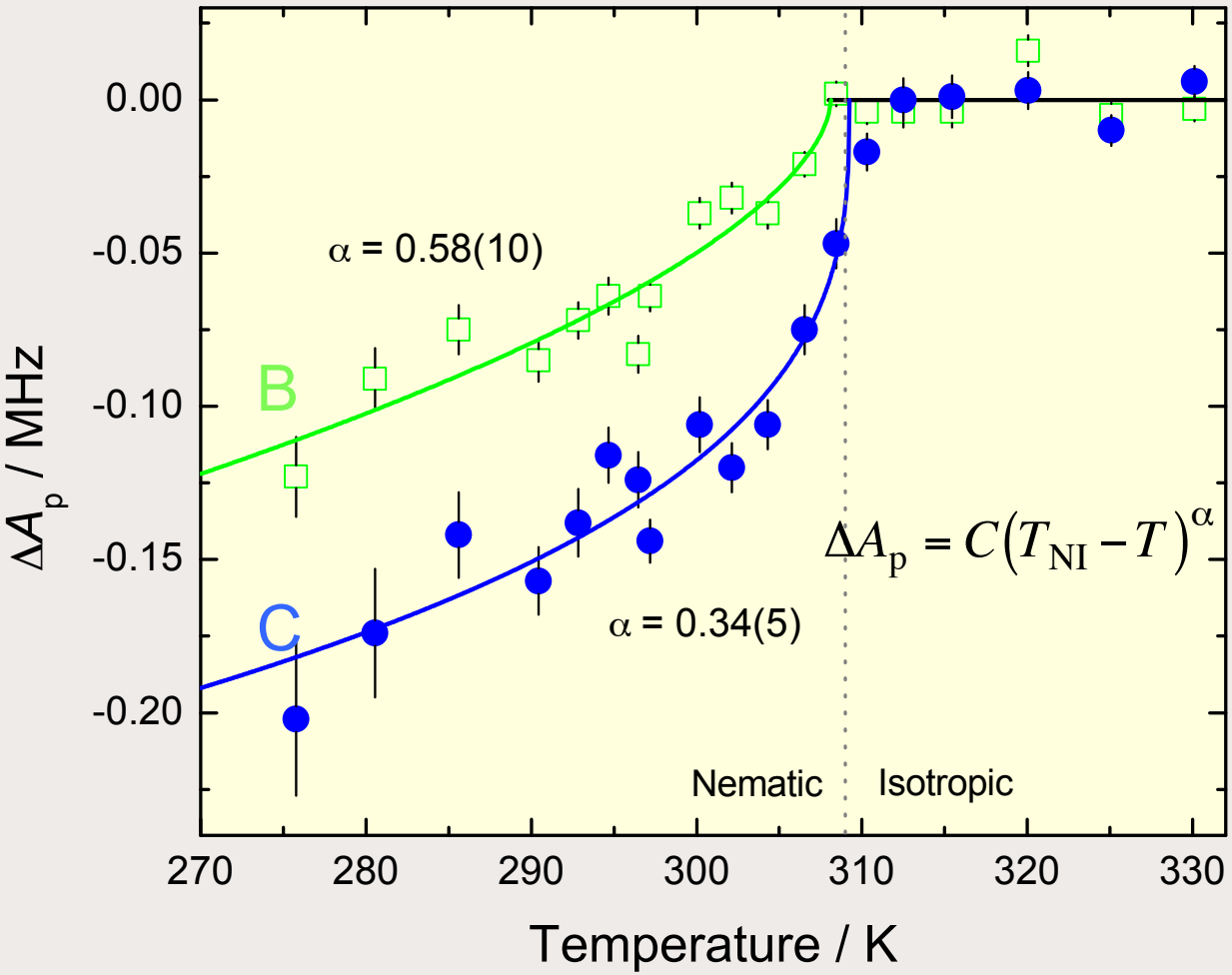


I. McKenzie et al. J. Phys. Chem. B **113**, 10135 (2009)

Temperature Dependence of Hfccs in 5CB



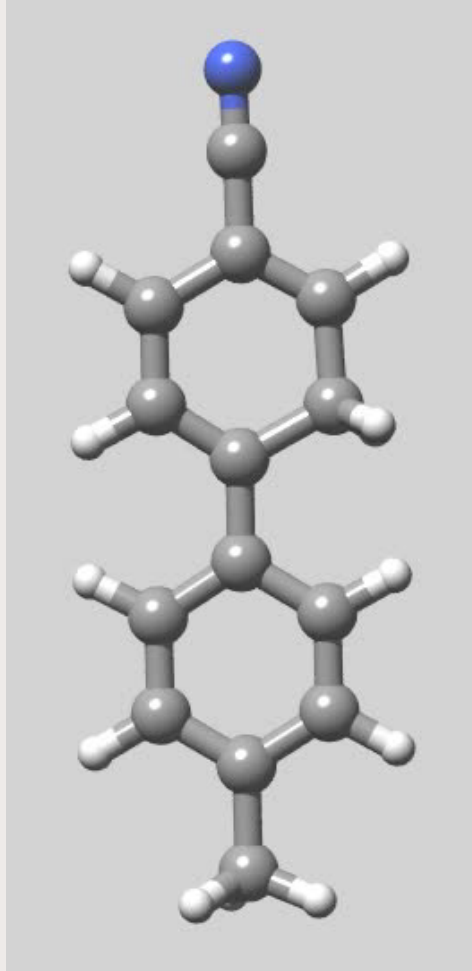
Hfcc Shifts in 5CB



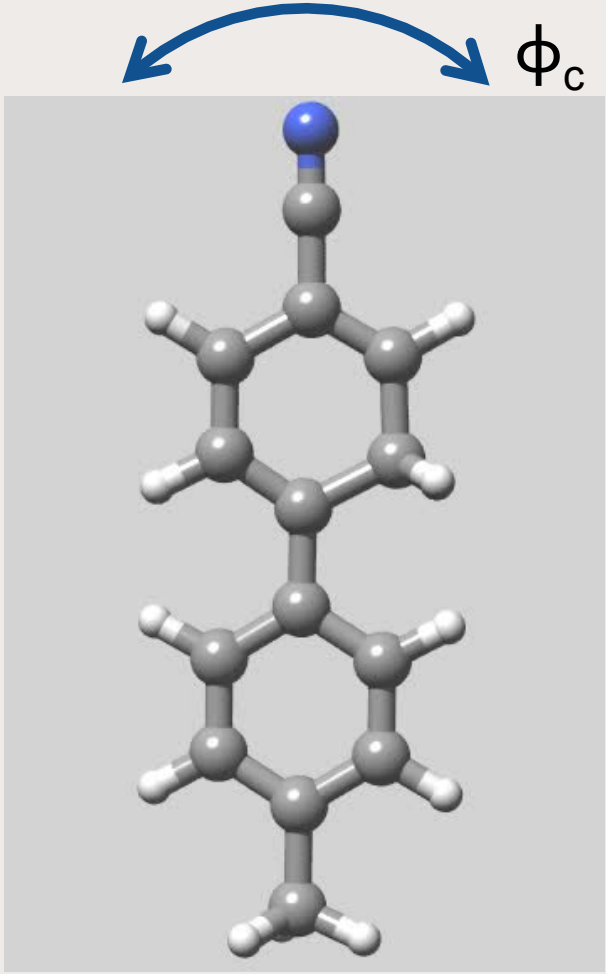
Molecular Motion and Dipolar Coupling

- Rapid uniaxial rotation produces axial hyperfine tensor ($D^{\parallel} = -2D^{\perp}$)
- Angle between rotation axis and the C−Mu bond results in small $D^{\parallel}$
- Hfccs depend on the angle between rotation axis and magnetic field (θ)

$$A_X(\theta) = A_X^{iso} + \frac{1}{2} D_X^{\parallel}\left(3\cos^2\theta - 1\right)$$



Molecular Motion and Dipolar Coupling



- Fluctuations about director average the dipolar hfcc

$$\left\langle D_{\mathrm{X}}^{\parallel} \right\rangle = D_{\mathrm{X}}^{\parallel} \left(\frac{\cos\phi_c + \cos^2\phi_c}{2} \right)$$

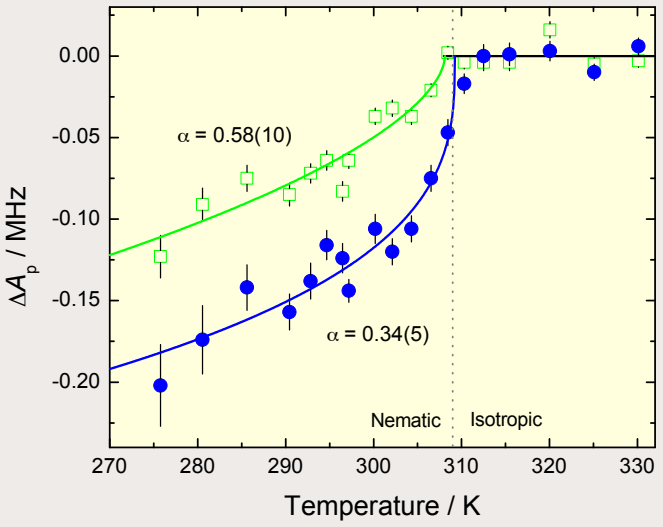
$$A_{\mathrm{X}}(\theta) = A_{\mathrm{X}}^{\mathrm{iso}} + \frac{1}{2}\left\langle D_{\mathrm{X}}^{\parallel} \right\rangle \left(3\cos^2\theta - 1 \right)$$

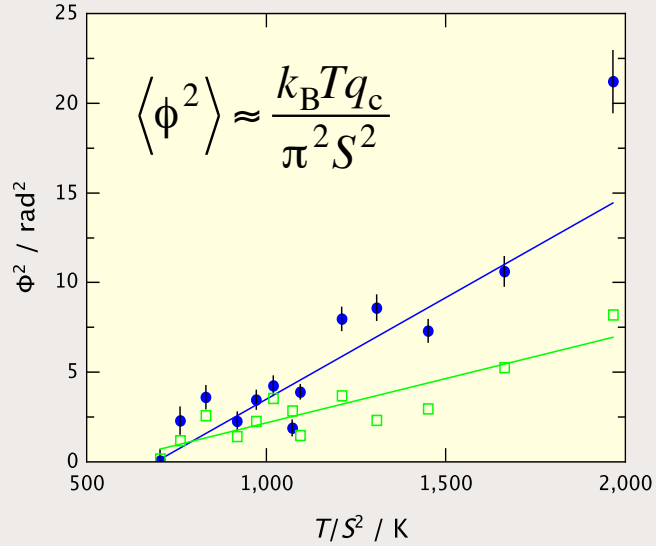
Motionally-Averaged Hfccs

- Sample aligned by magnetic field

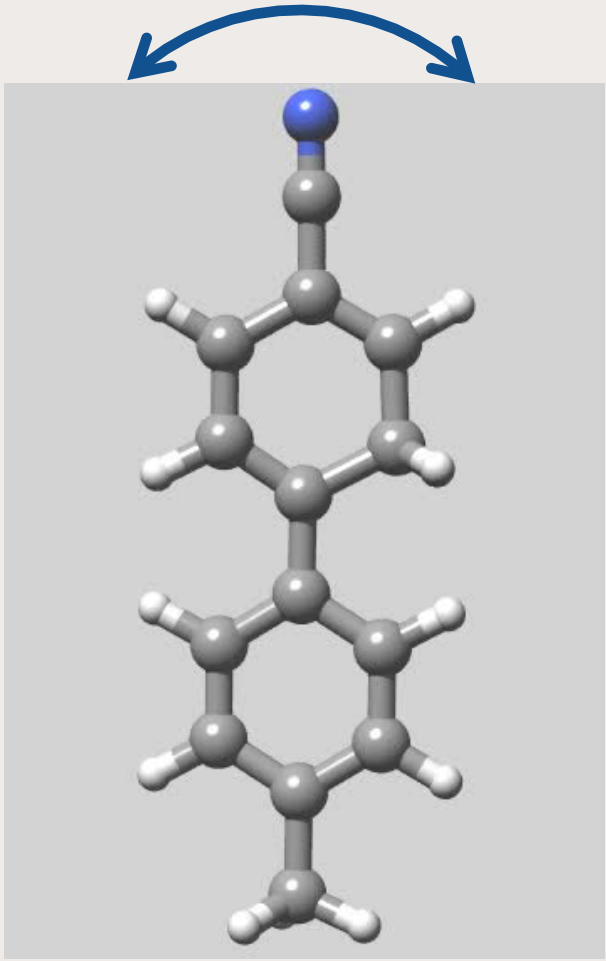
$$\langle A_X \rangle = \int_0^{\pi} \left[A_X^{iso} + \frac{1}{2} \left\langle D_X^{\parallel} \right\rangle \left(3\cos^2\theta - 1 \right) \right] f(\theta) d\Omega$$

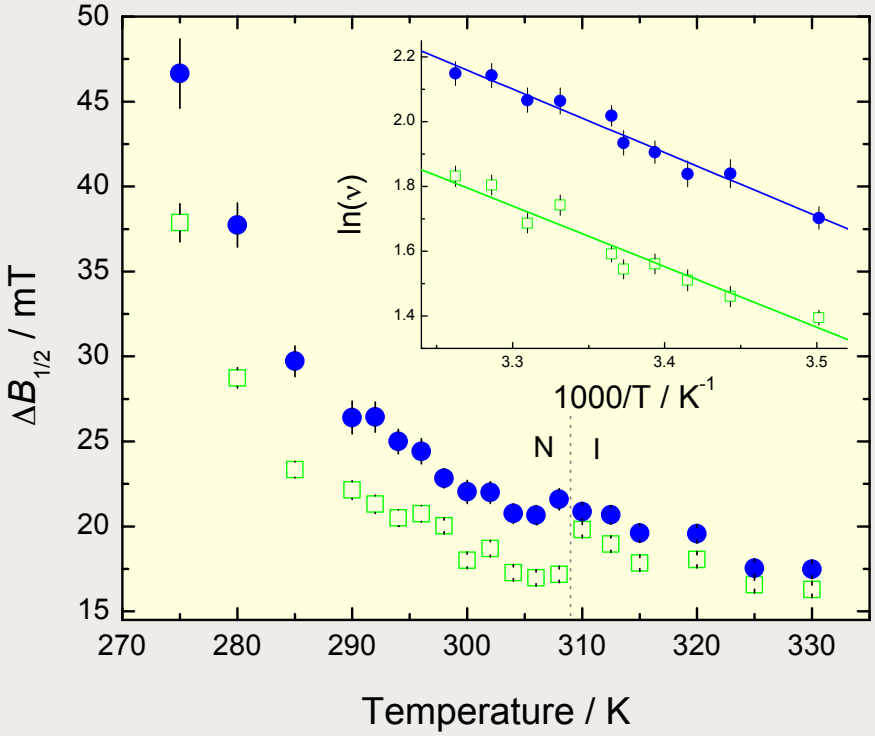
$$\Delta A_X = \langle A_X \rangle - A_X^{iso} = \left\langle D_X^{\parallel} \right\rangle S$$





Dynamics of Spin Probes in 5CB



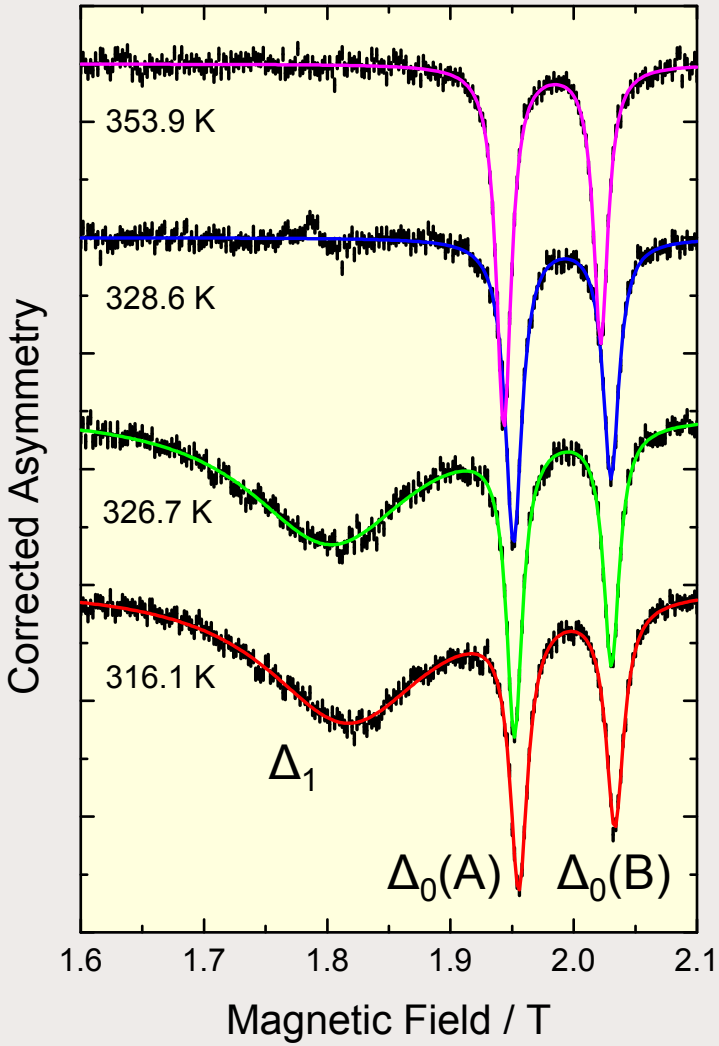


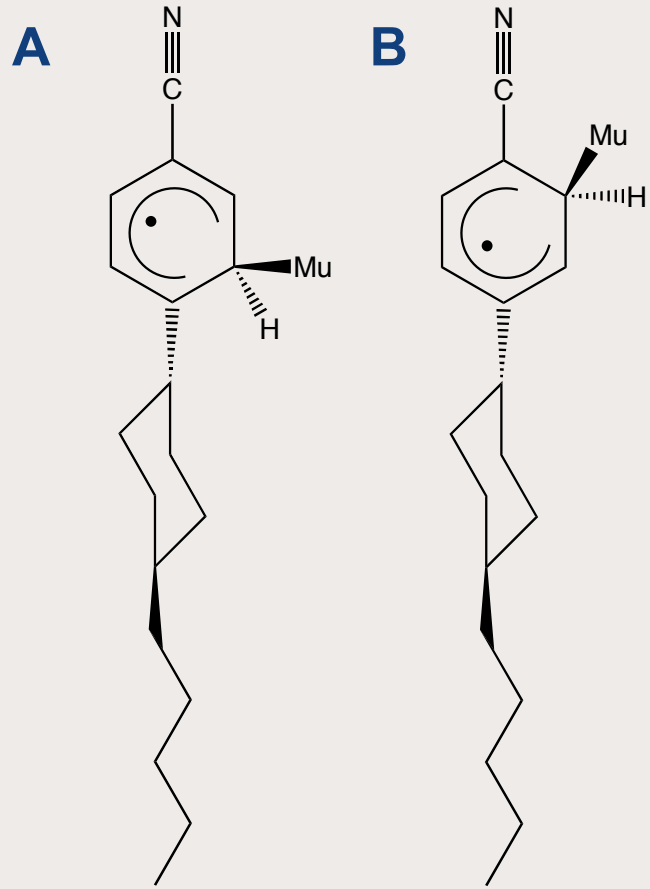
$$\nu \sim \frac{1}{\Delta B_{1/2}}$$

$$\ln \nu = A - \frac{\Delta E}{k_B T}$$

ΔE = 15.5 kJ mol^{-1}

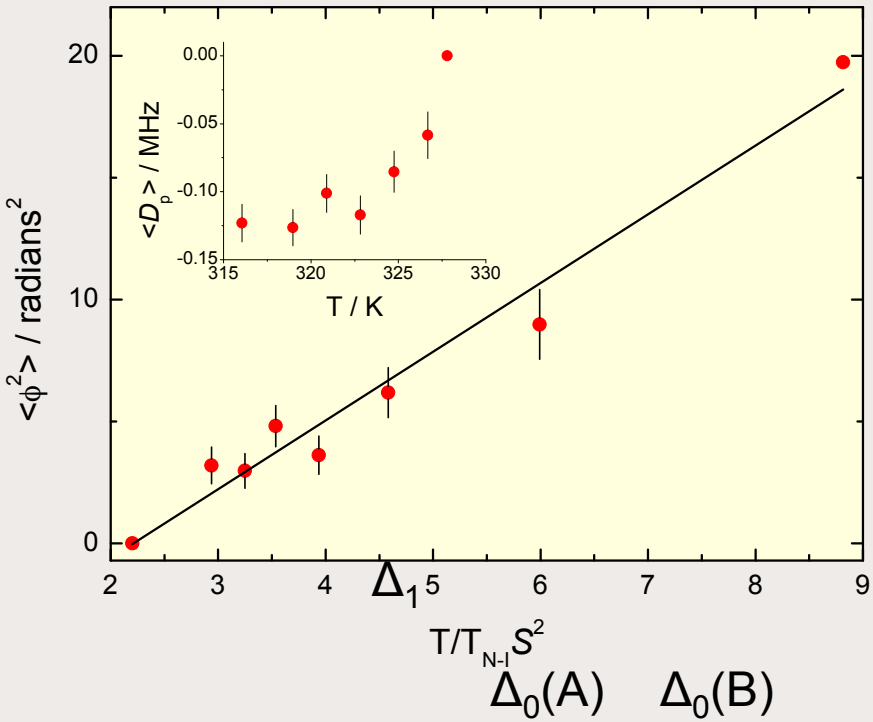
ALC-μSR of PCH5

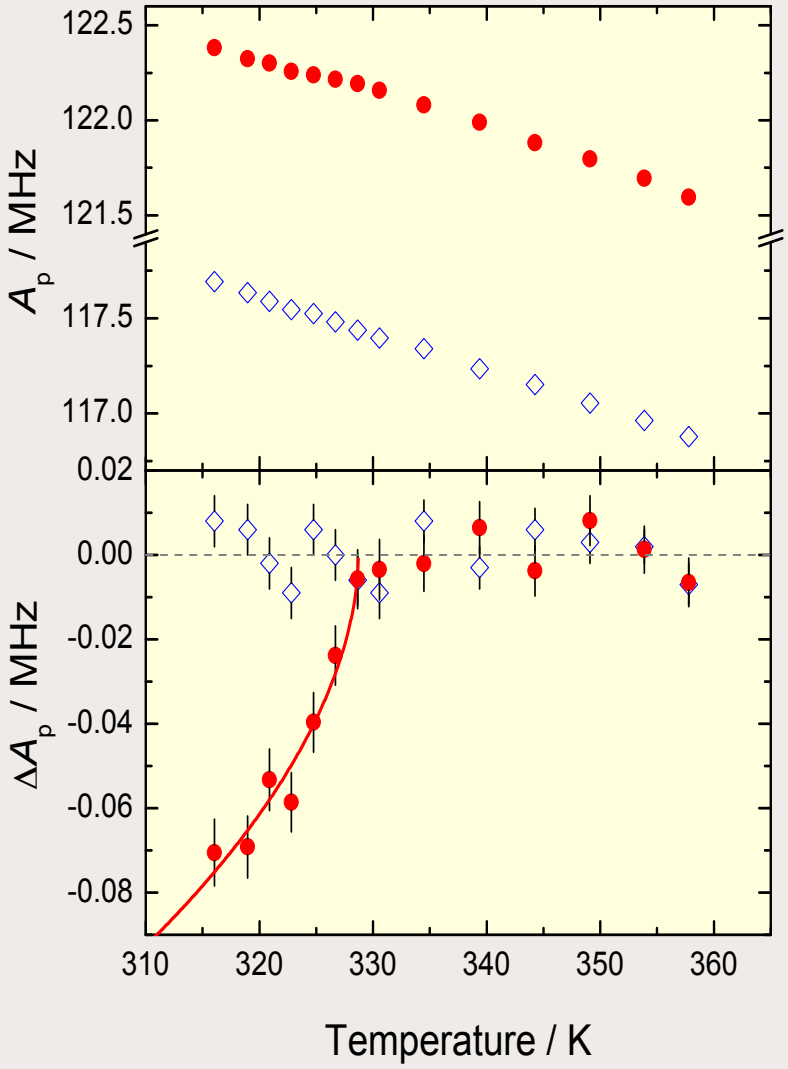




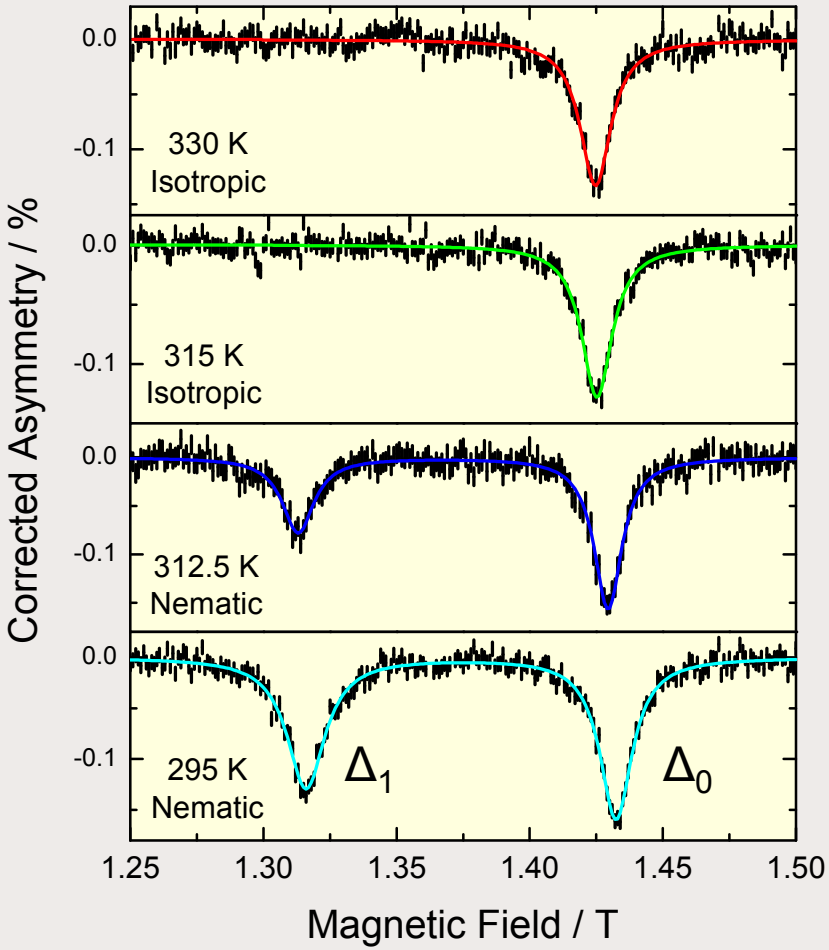
I. McKenzie et al. submitted Physics Procedia (2011)

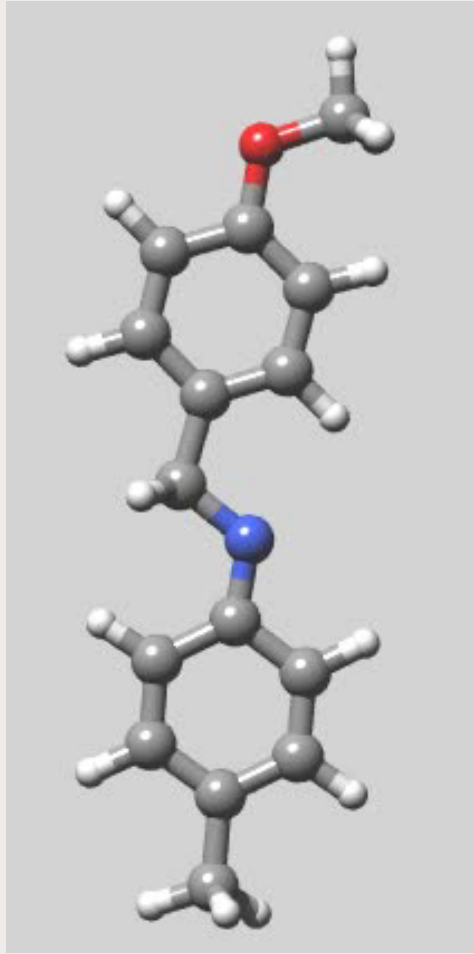
ALC-μSR of PCH5



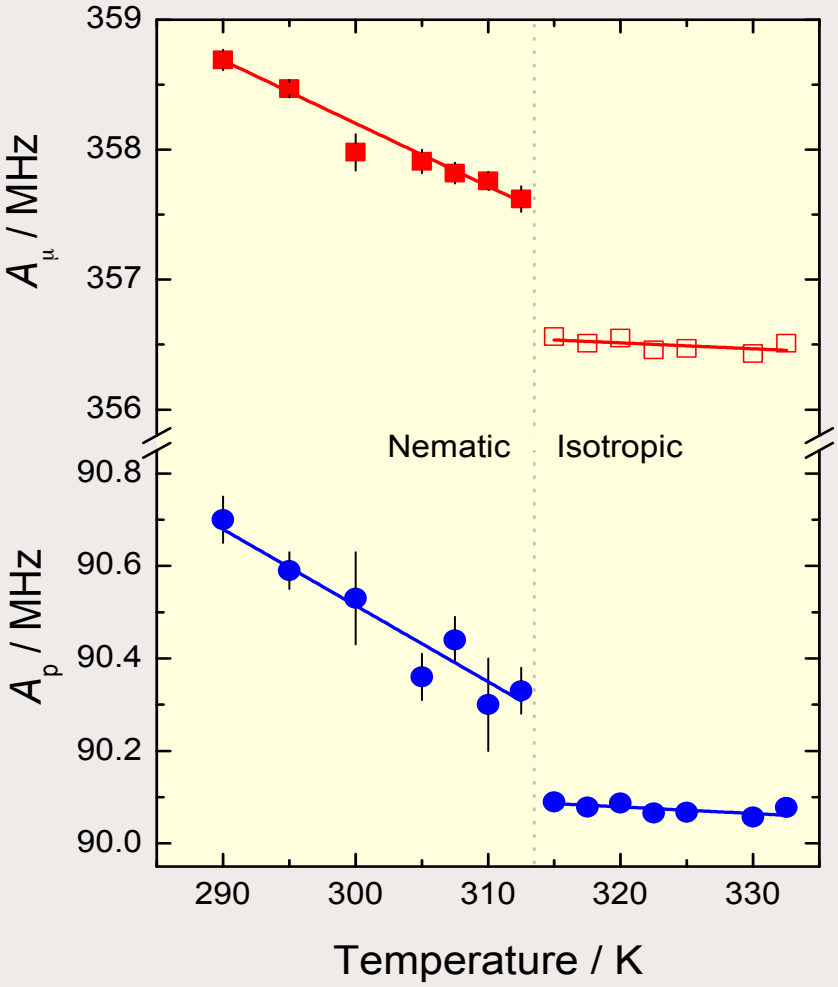


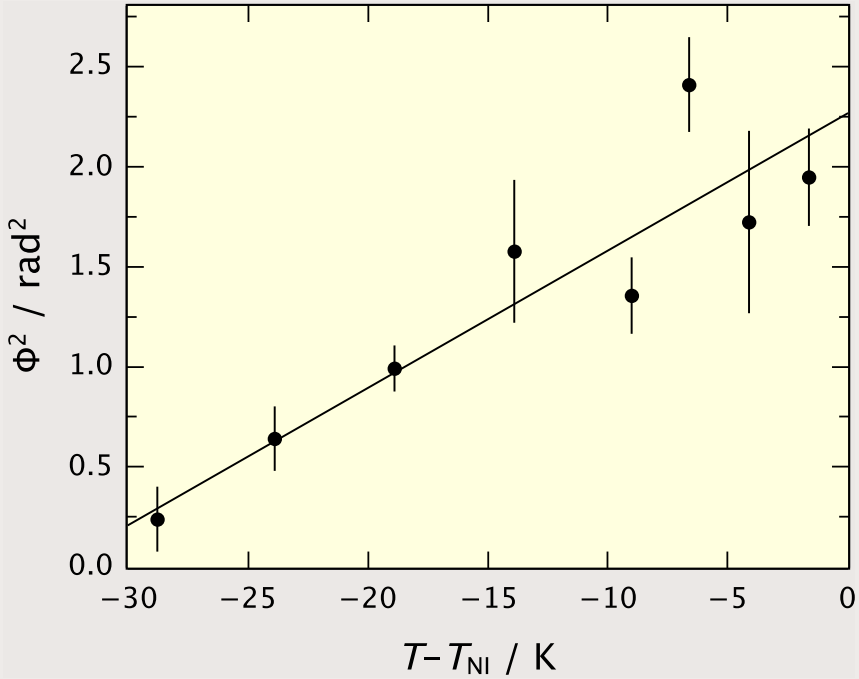
ALC-μSR of MBBA





Dynamics of Spin Probes in MBBA

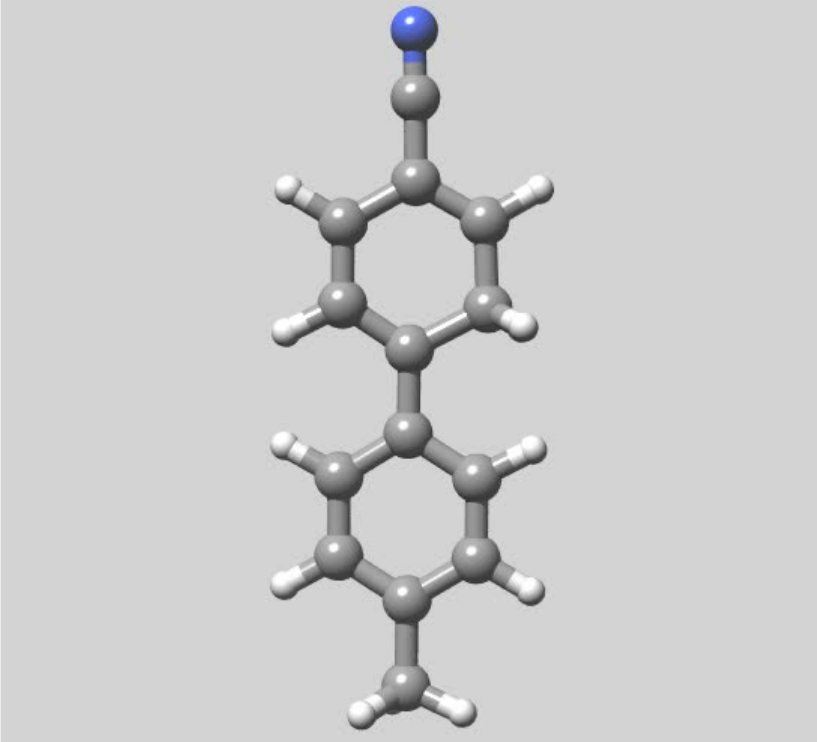




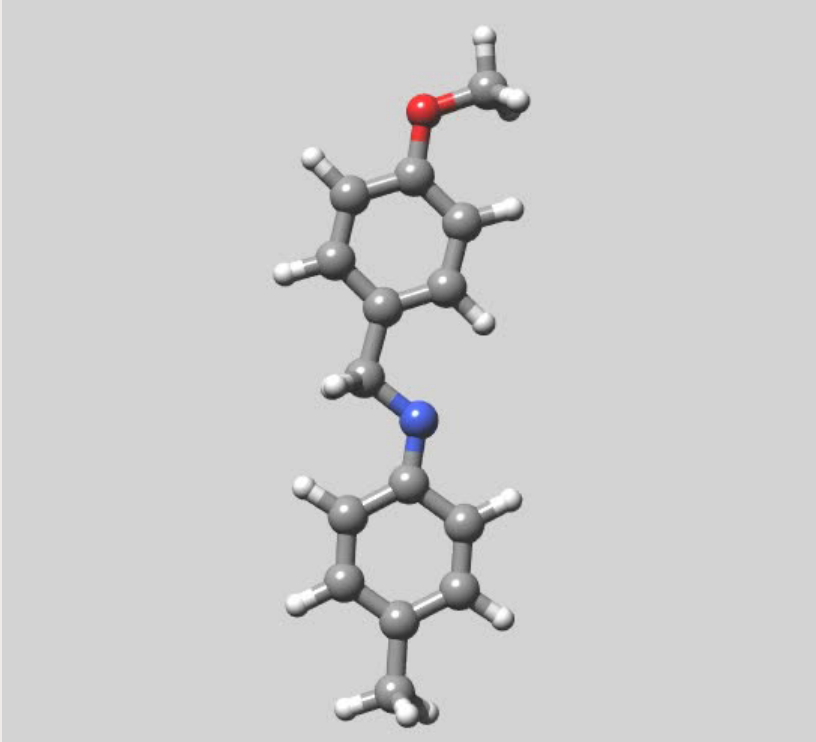
I. McKenzie et al. J. Phys. Chem. B (2011)

Comparison of 5CB and MBBA

$\Delta H_{NI} = 1.56$ J g^{-1}

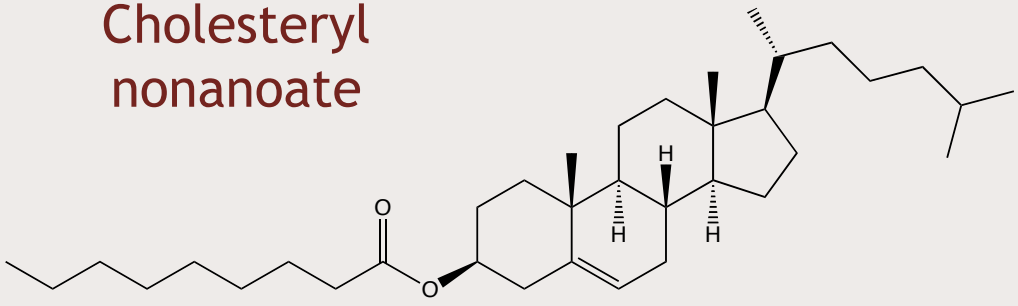


$\Delta H_{NI} = 0.92$ J g^{-1}

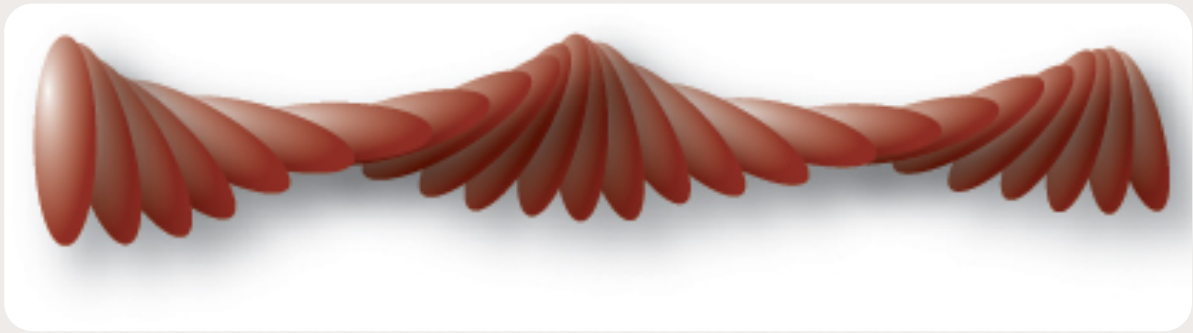


Cholesterolic Liquid Crystal

Cholesteryl nonanoate

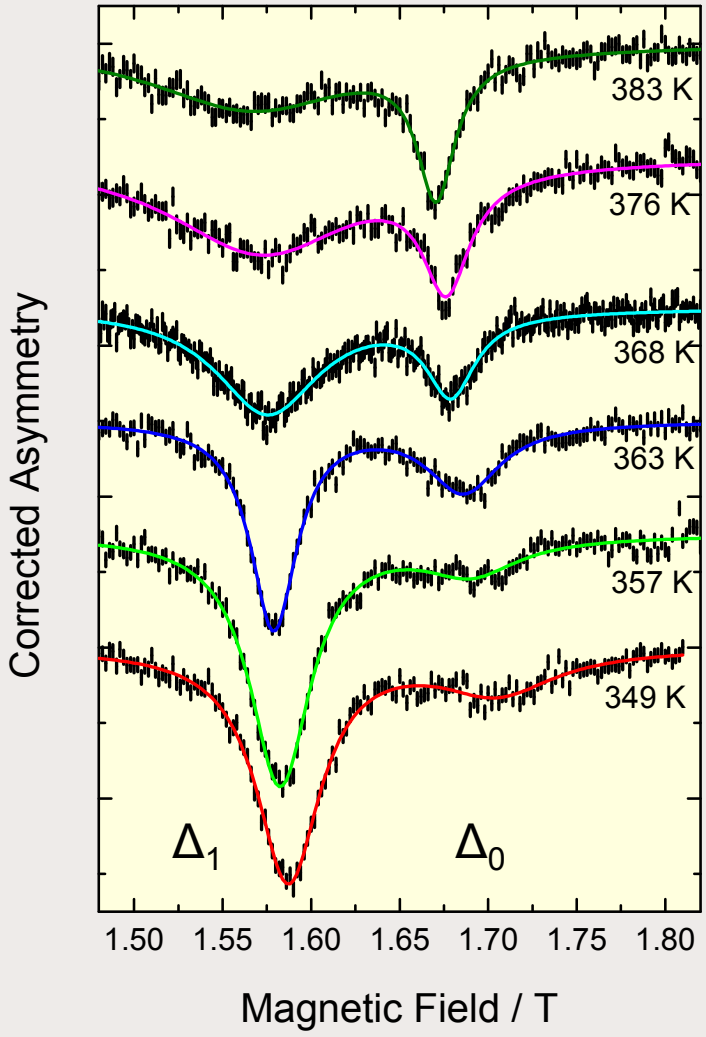


P/2

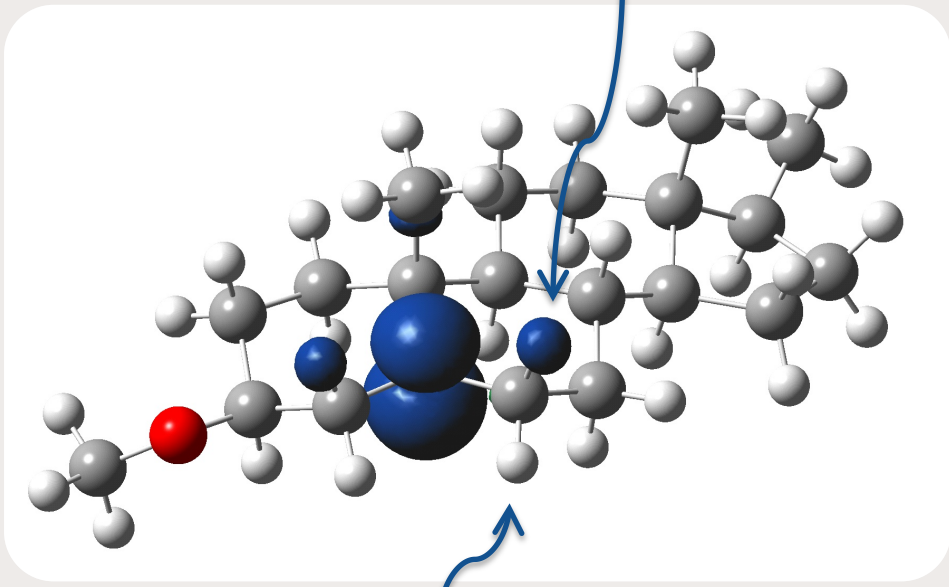


I. McKenzie et al. J. Phys. Chem. B (2011)

ALC-μSR of a Cholesterolic Liquid Crystal



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

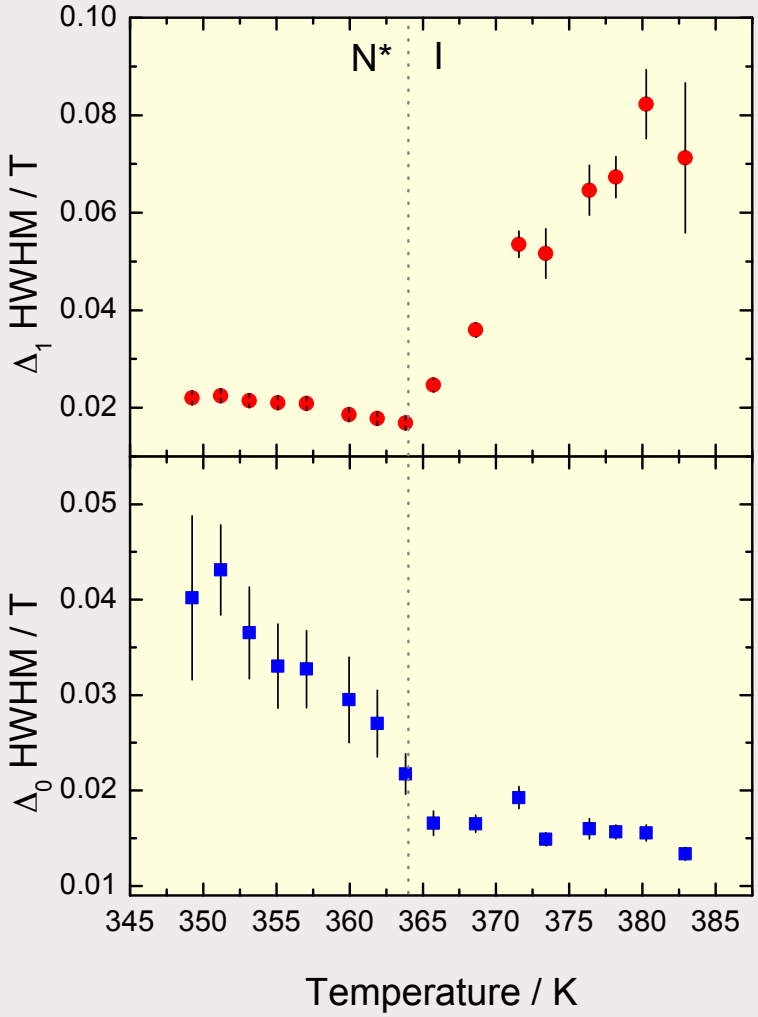


A_μ = 71.7 MHz
$B_{res}(\Delta_1)$ = 0.26 T

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

ALC-μSR of a Cholesterolic Liquid Crystal

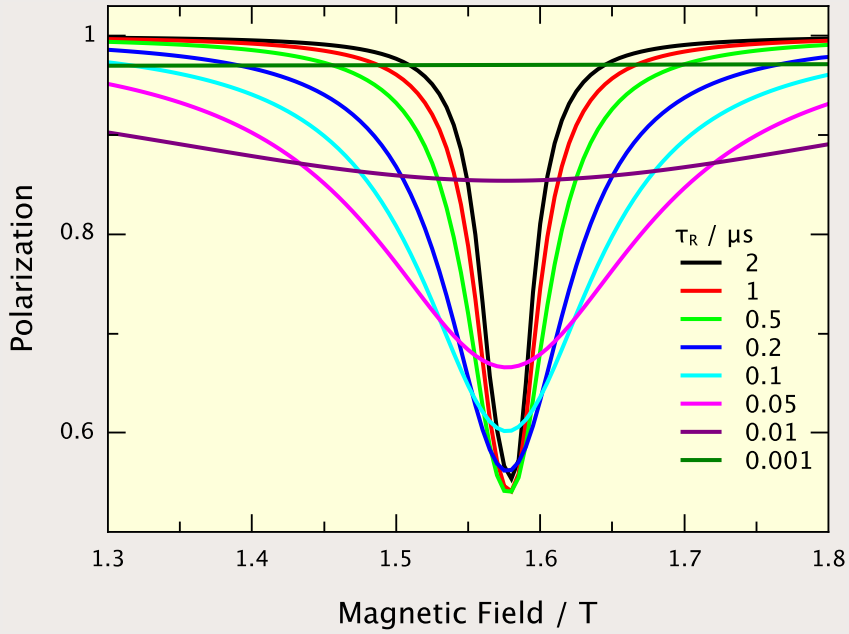
Below T_{N^*-I}
Δ_1 and Δ_0 narrow with increasing temperature



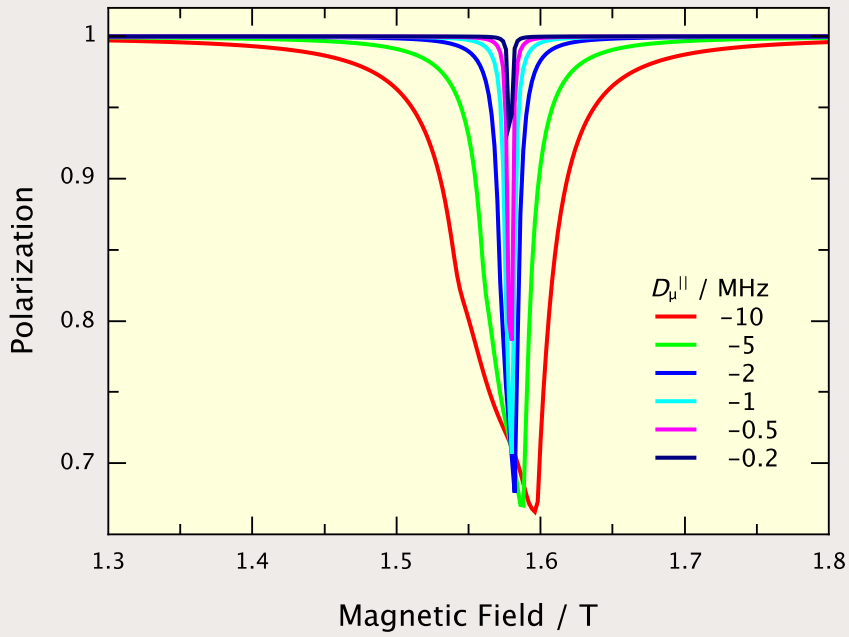
Above T_{N^*-I}
Δ_1 broadens and amplitude decreases and Δ_0 narrows with increasing temperature

ALC-μSR of a Cholesterolic Liquid Crystal

High Temperature (I phase)
Slow isotropic reorientation

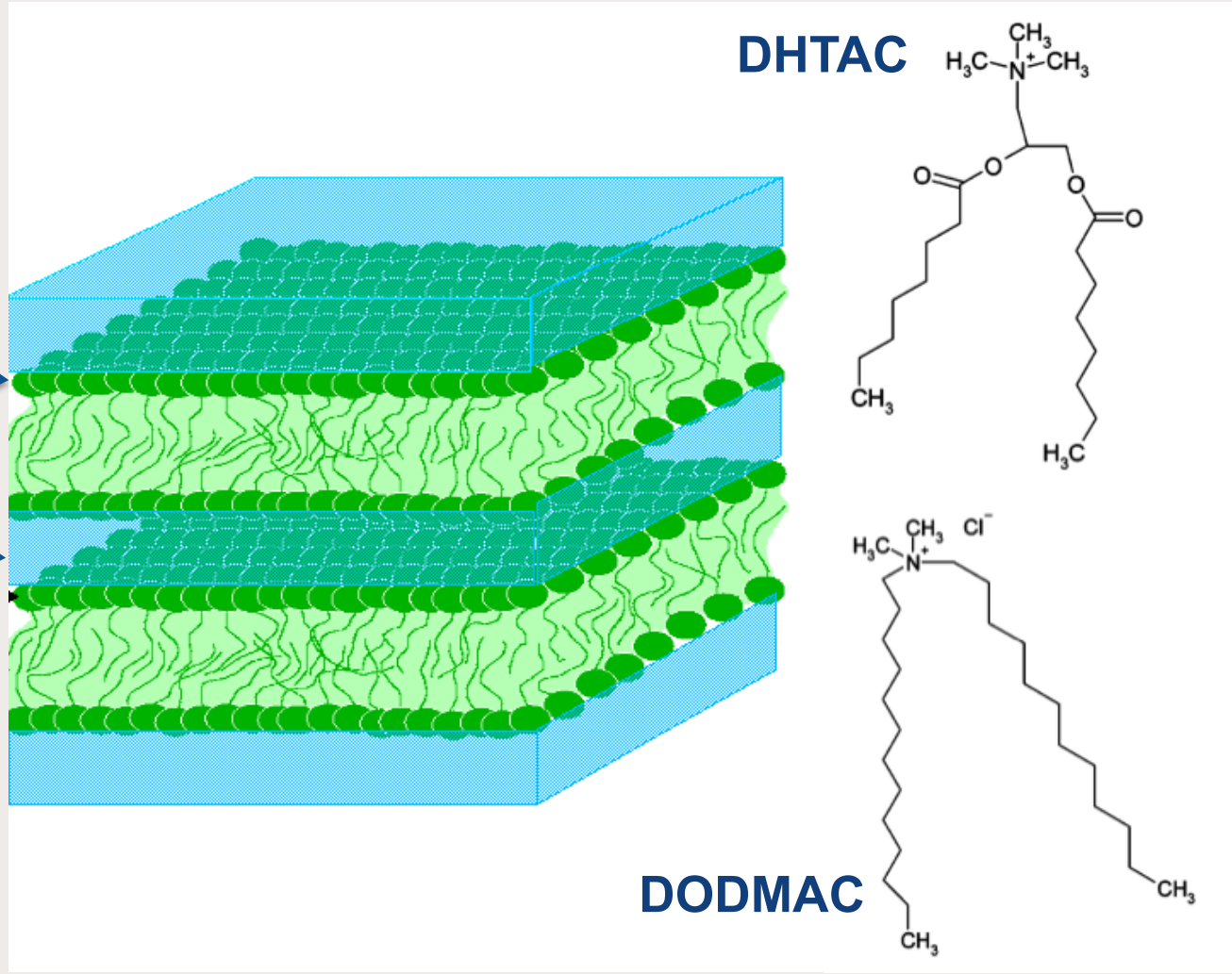


Low Temperature (N* phase)
Wobbling around preferred axis

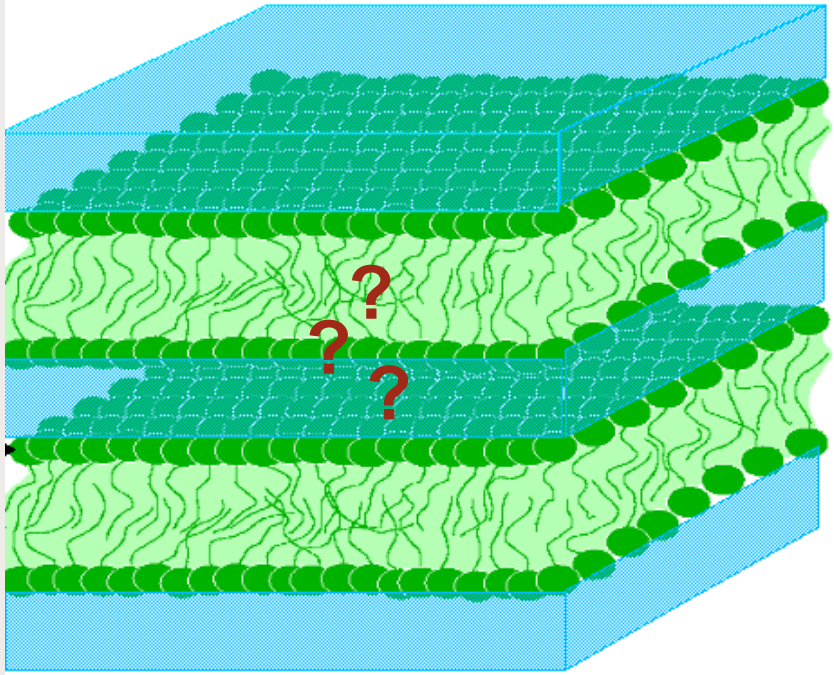


Fluctuation amplitude and τ_R determined from FWHM Δ_1

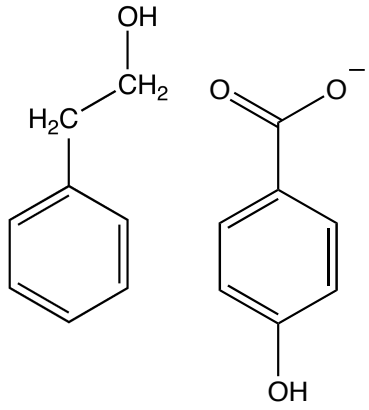
Lyotropic Liquid Crystals



Location of Cosurfactants?

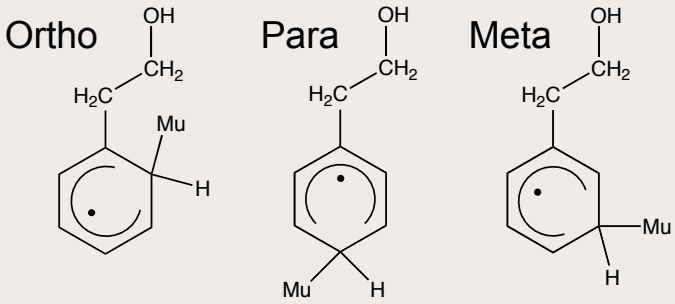


Cosurfactants

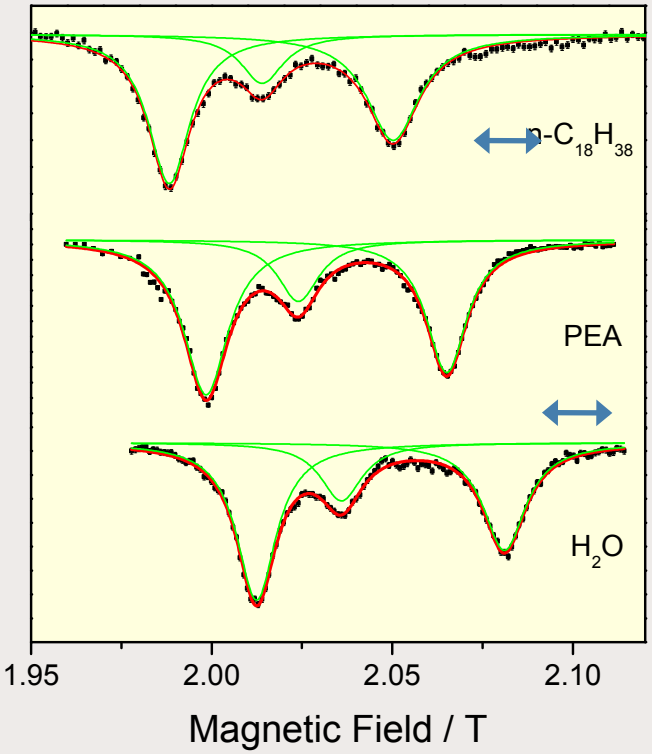


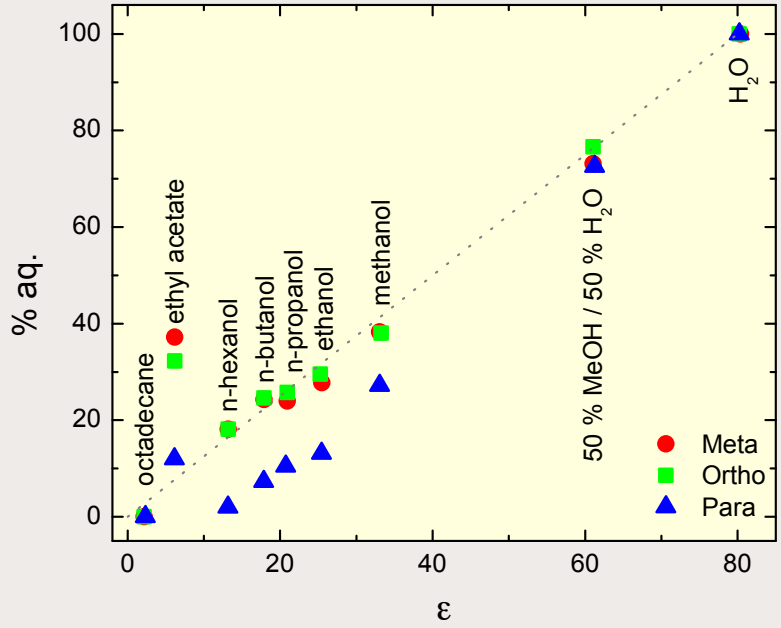
PEA **4HBA**

Mu Adducts of Phenylethanol



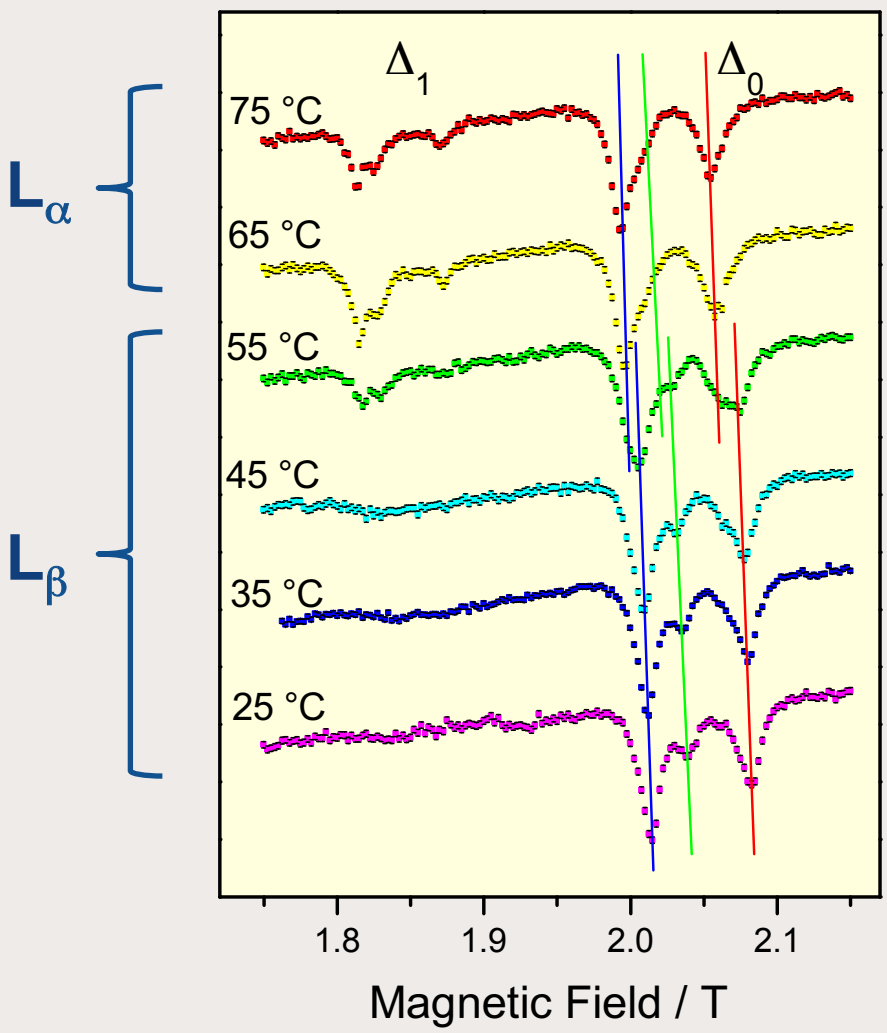
$$\%aq. = \frac{B_{res}^{X} - B_{res}^{C_{18}H_{38}}}{B_{res}^{H_2O} - B_{res}^{C_{18}H_{38}}}$$

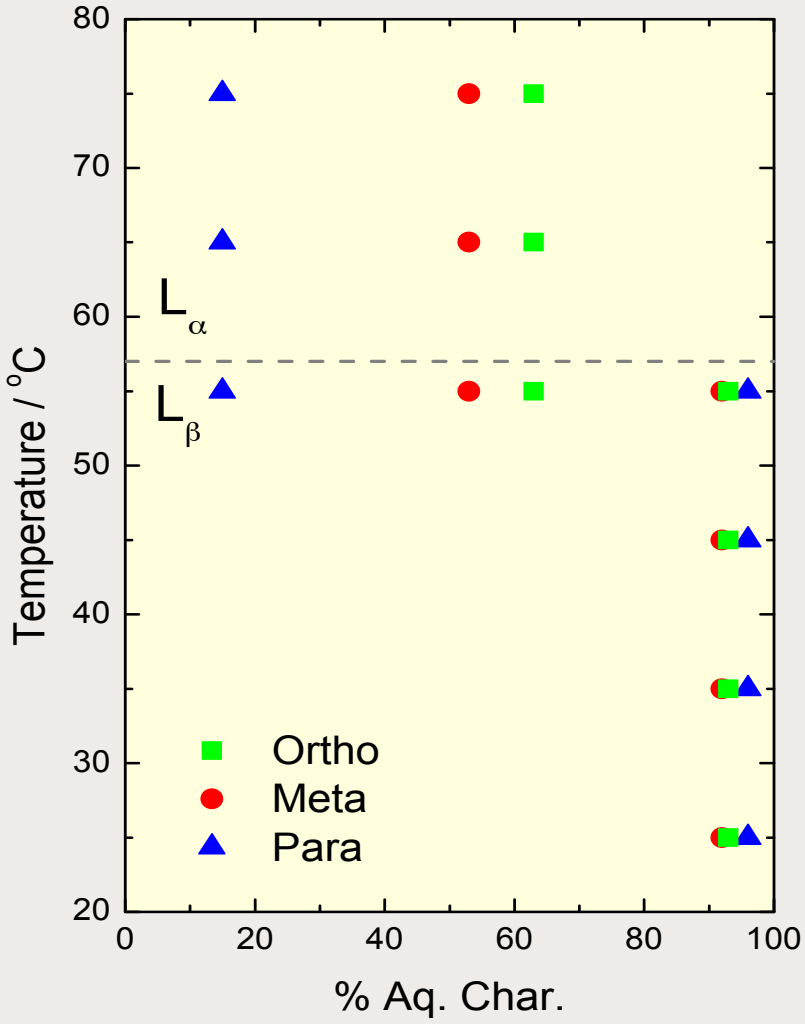




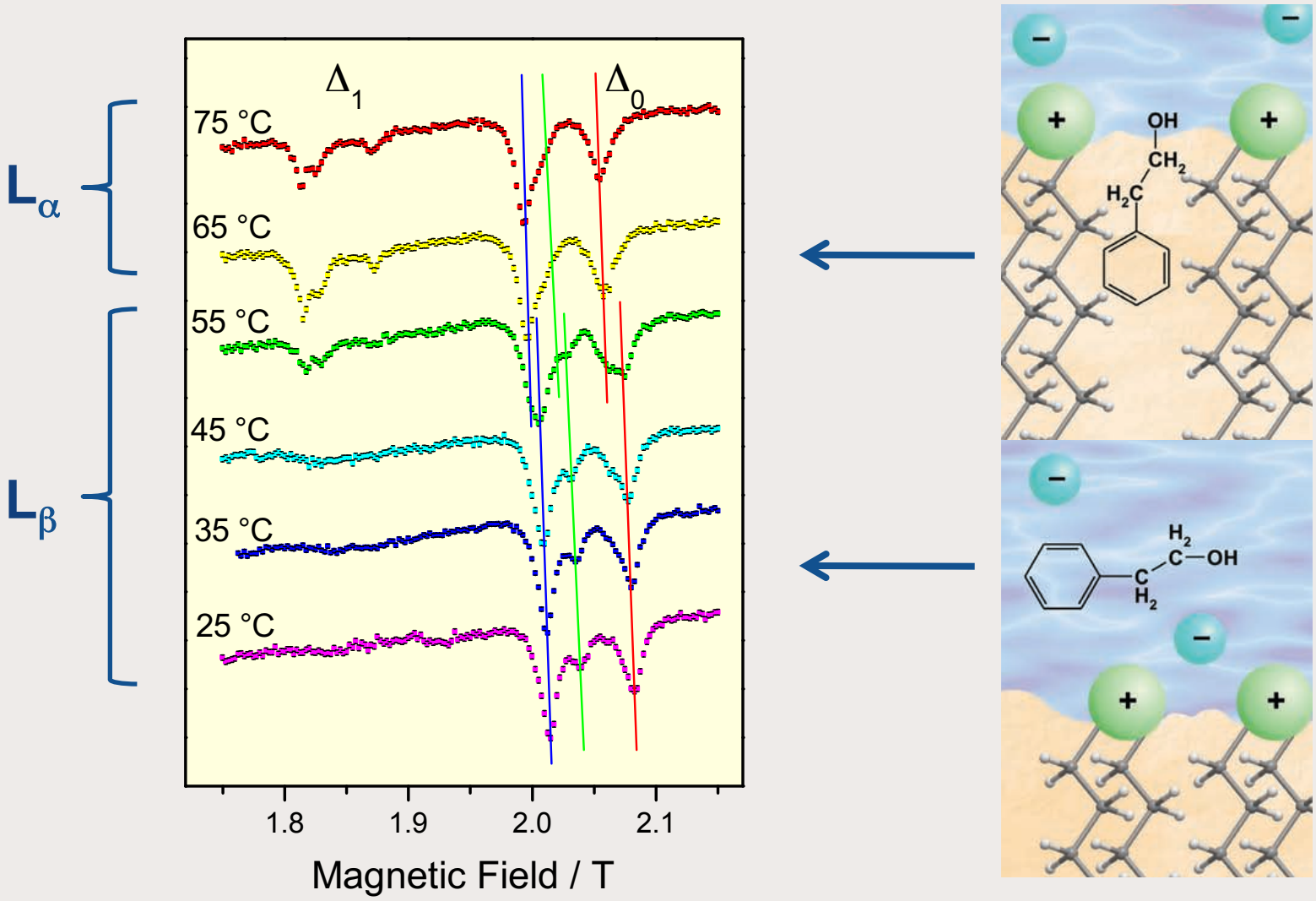
R. Scheuermann et al. PCCP, **4**, 1510 (2002)

Partitioning of Phenylethanol in DHTAC

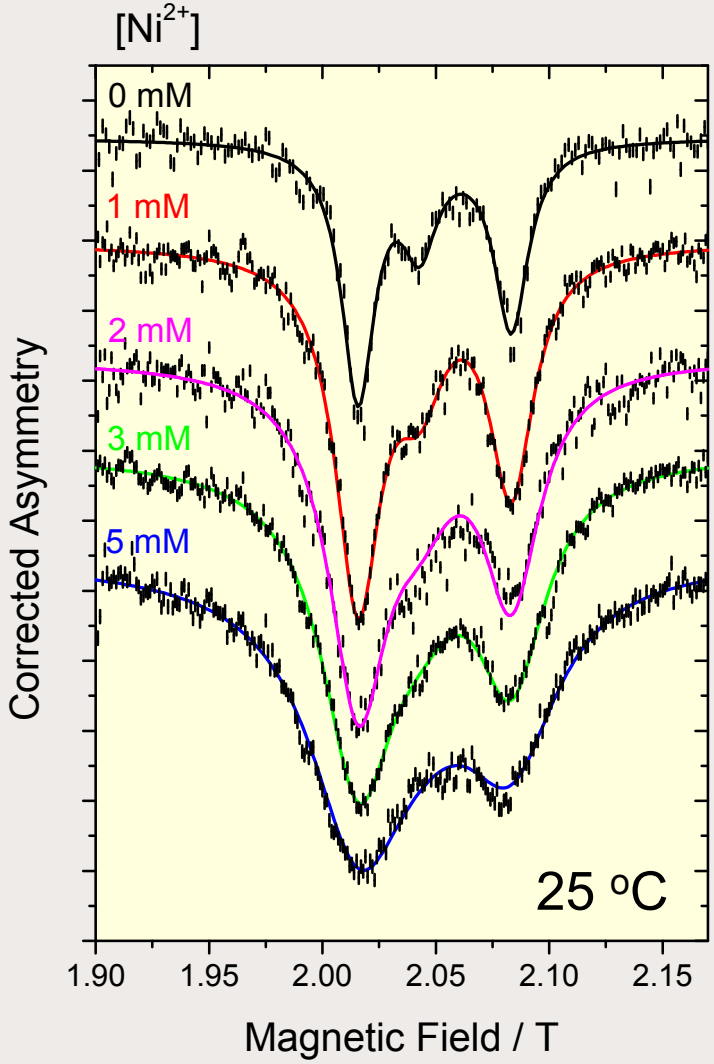




Partitioning of Phenylethanol in DHTAC



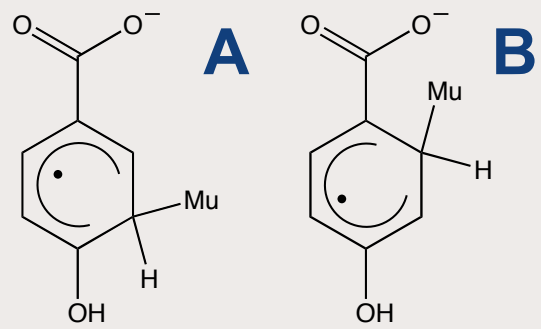
Spin Exchange Reactions in DHTAC

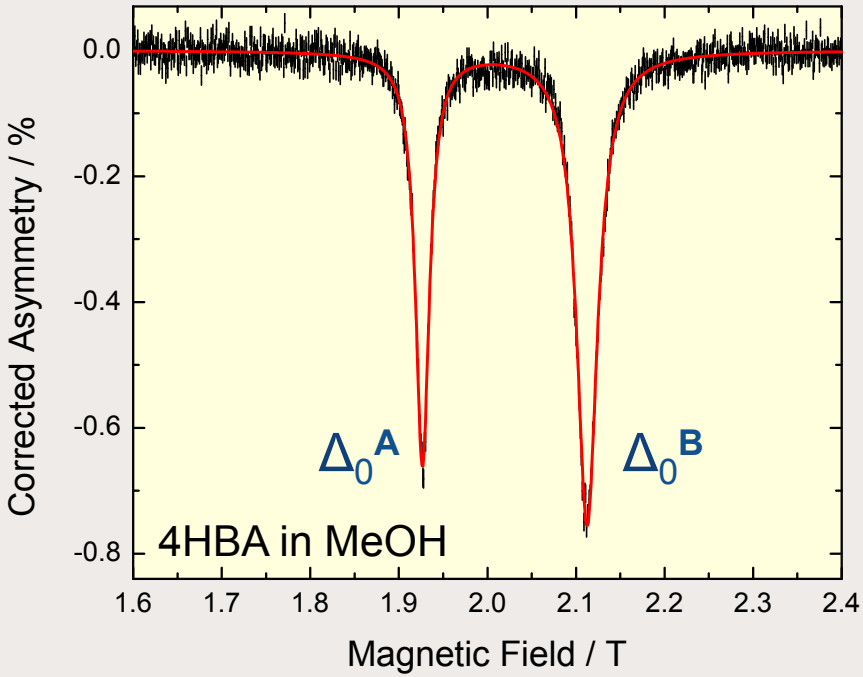


	T / °C	k_{ortho}	k_{meta}	k_{para}
		10^9 M^{-1} s^{-1}		
H_2O	25	1.90(3)	1.83(5)	1.4(1)
	75	4.44(5)	3.97(7)	4.0(1)
DHTAC	25	1.96(4)	1.86(6)	2.8(2)
	75	0.19(1)	0.21(1)	0.21(2)

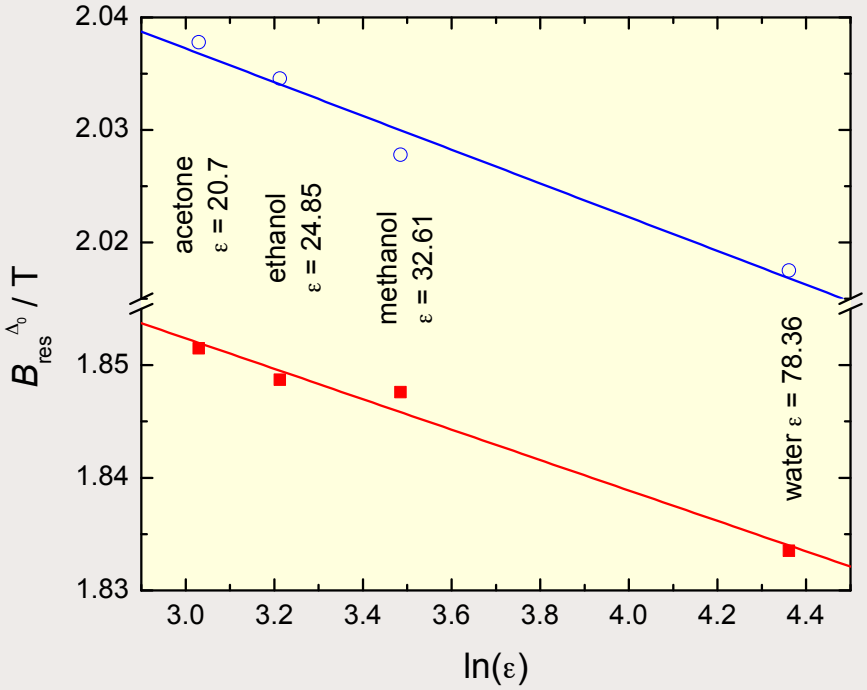
H. Dilger et al. Physica B **374-375**, 317 (2006)

Mu Adducts of 4HBA





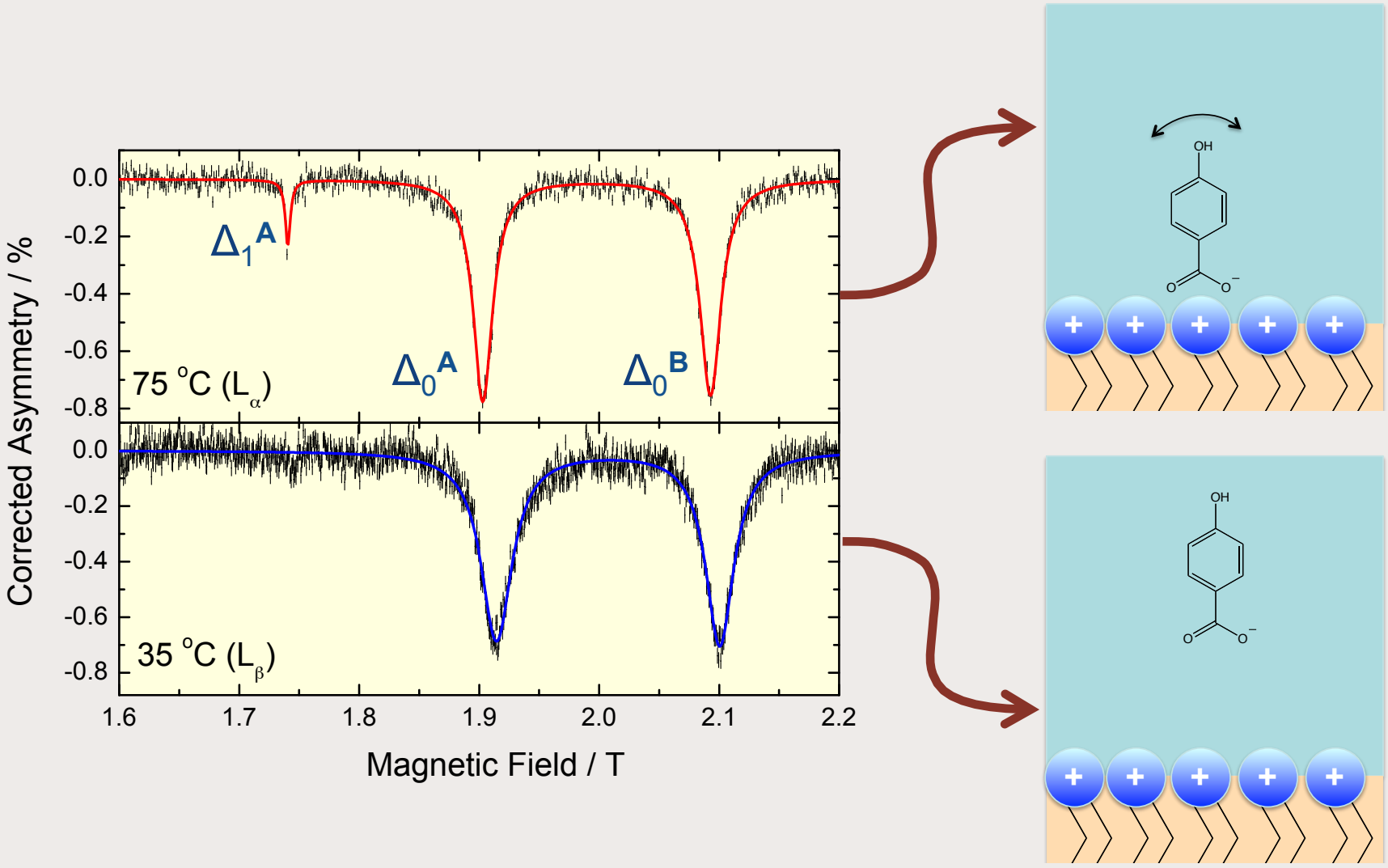
UB3LYP/6-311G**//UB3LYP/EPR-II with Polarized Continuum Model



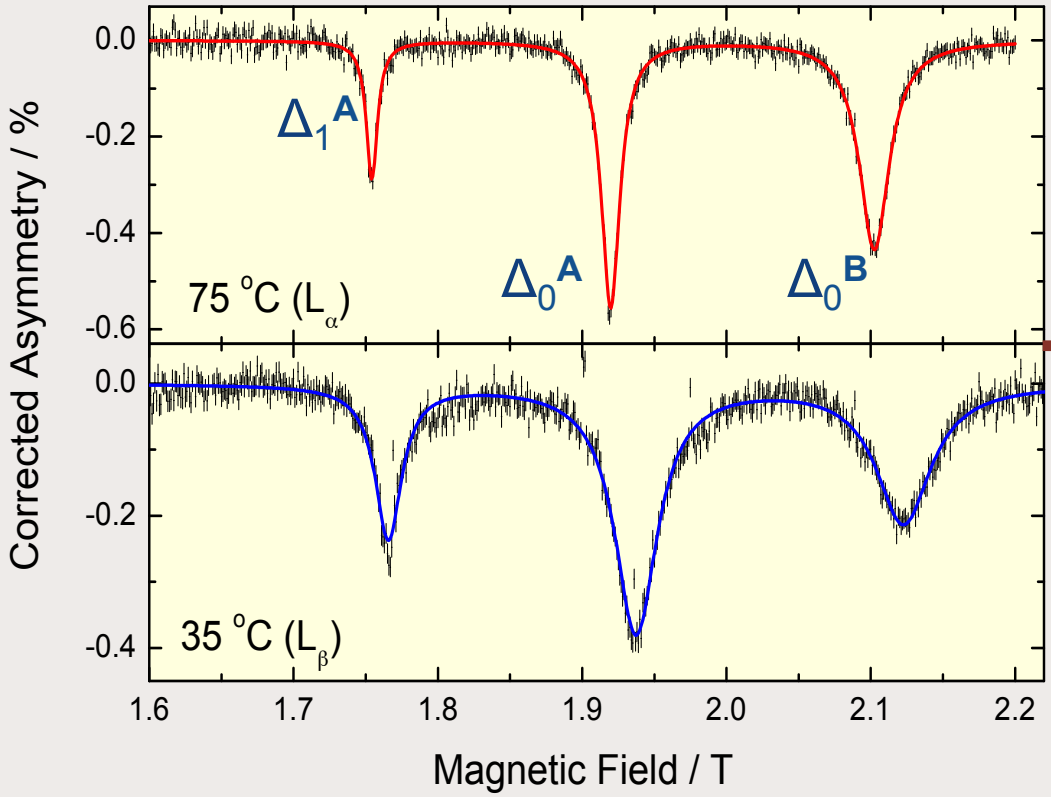
Wertheim reaction field model

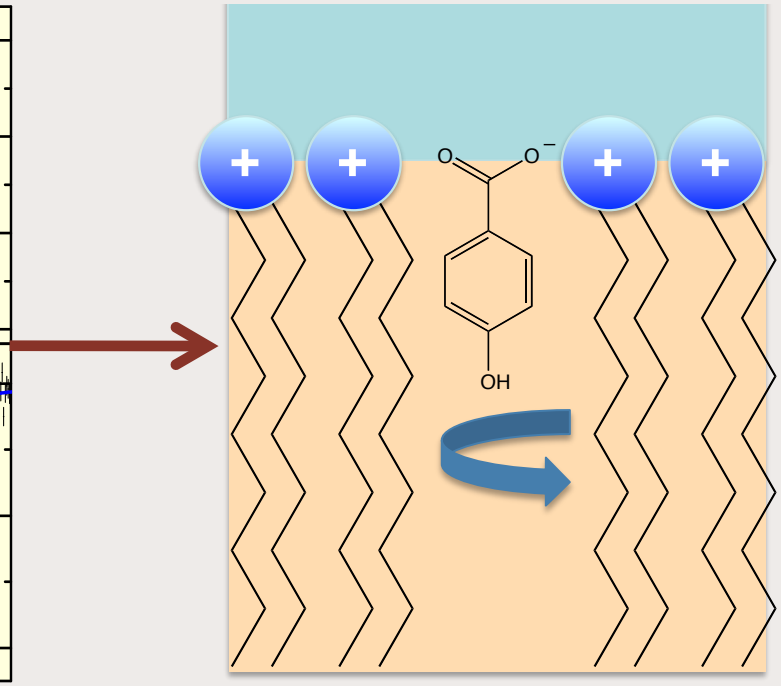
$$A_X(\varepsilon) = A_X^{vac} + k \ln(\varepsilon)$$

Partitioning of 4HBA in DHTAC

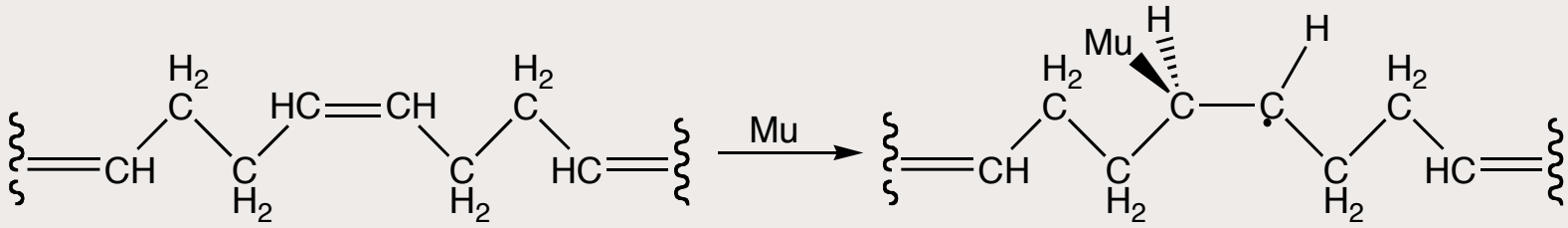


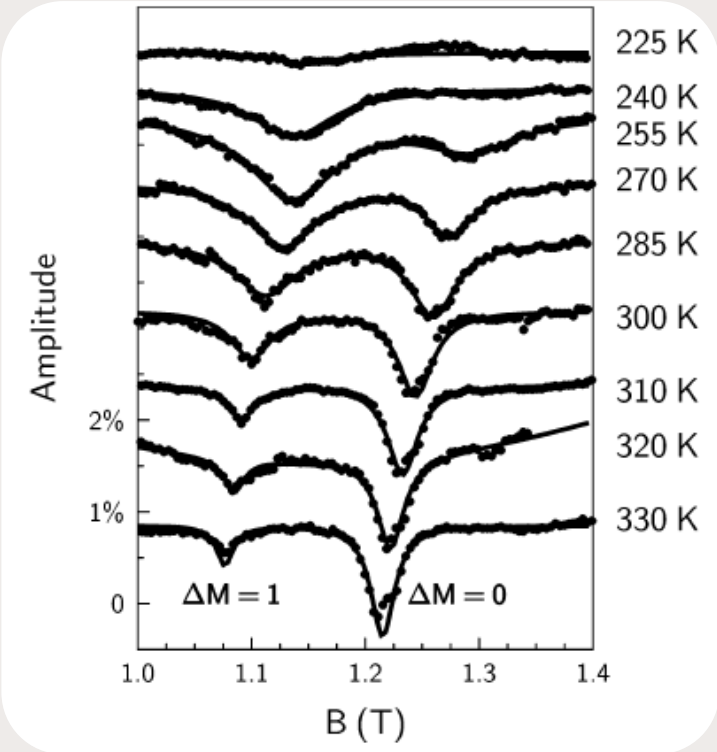
Partitioning of 4HBA in DODMAC





μSR of Non-Conducting Polymers



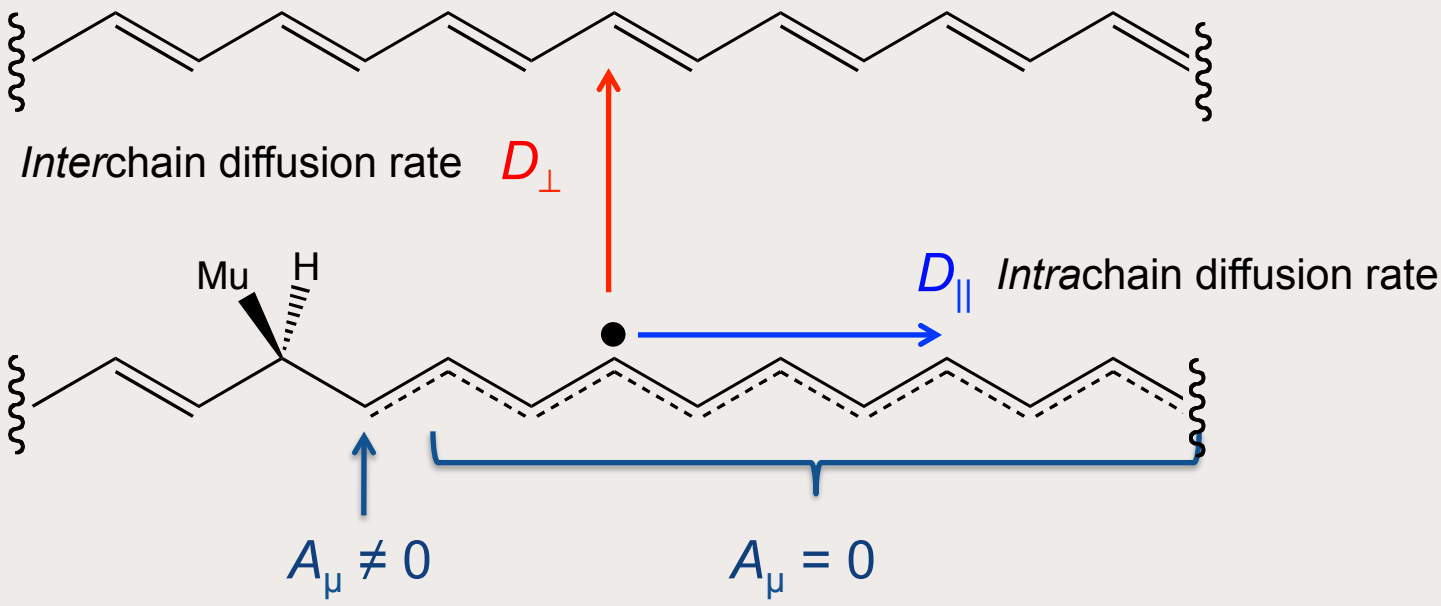


Polybutadiene

- Localized spin density due to isolated double bonds.
- Narrowing of resonances and shift of B_{res} due to rotation about the single bond.

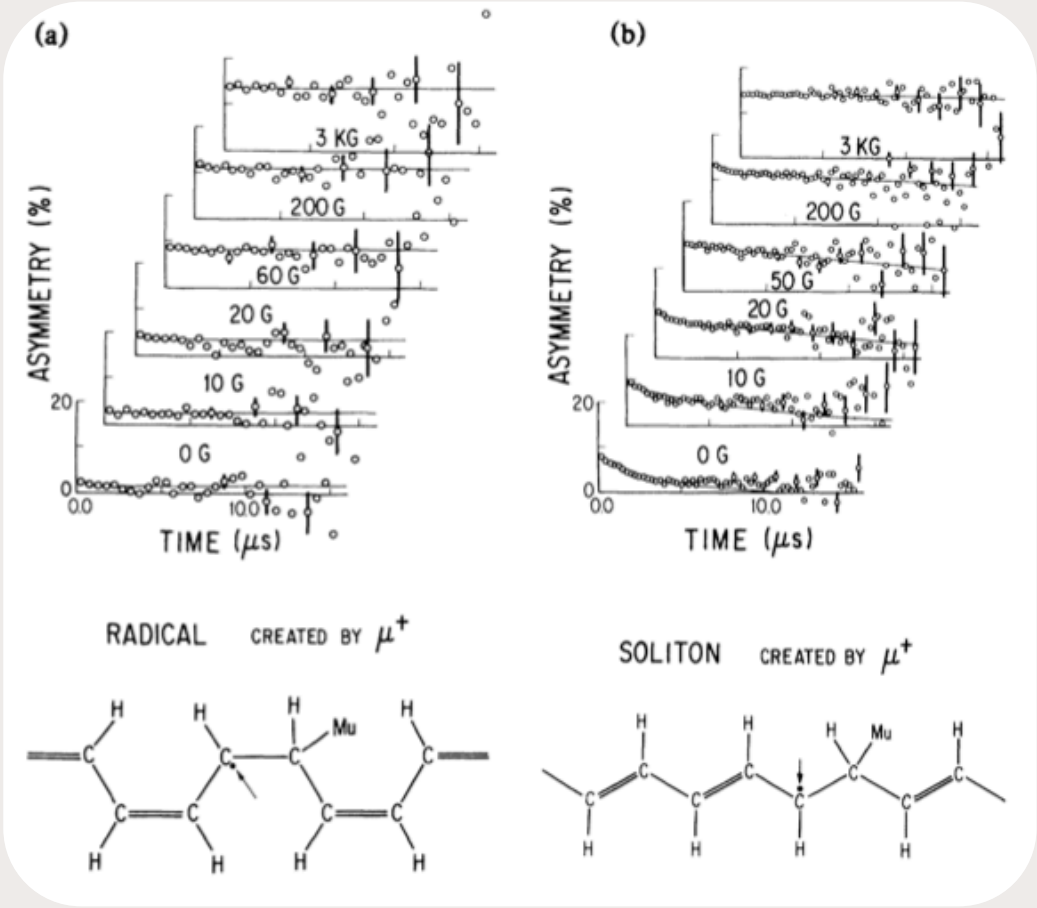
S. J. Blundell, Chem. Rev. **104**, 5717 (2004)

μSR of Conducting Polymers



Diffusion of the electron causes fluctuating spin density at the muon and relaxation of the muon's spin.

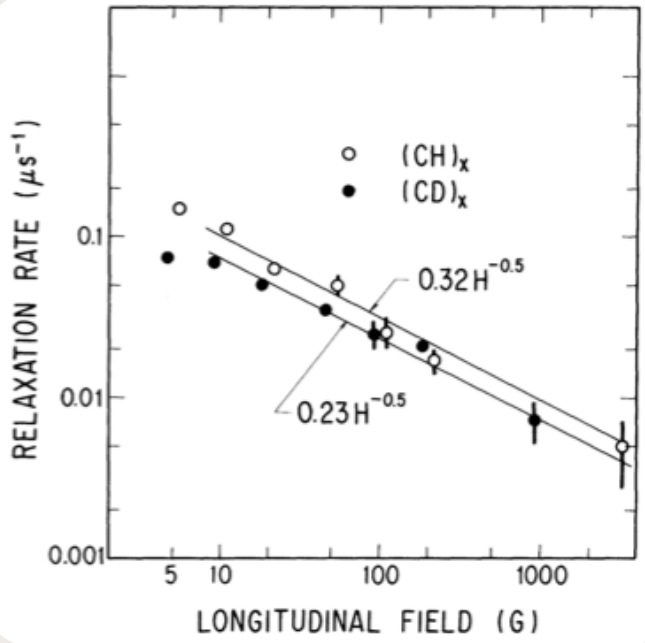
Polyacetylene



A_μ = 91 MHz

A_μ ~ 0

$$G_z(t) \approx Ae^{-t/T_1}$$



$$\frac{1}{T_1} \propto B^{-1/2}$$ 1-D diffusion

K. Nagamine et al., PRL **53**, 1763 (1984)

Risch-Kehr Model

$$G_z(t) = e^{\Gamma t}\mathrm{erfc}(\sqrt{\Gamma t}) \quad \text{when} \quad \lambda t_{exp} >> 1$$

Three parameters:

- Muon hfcc $\omega_0 = 2\pi A_\mu$
- Electron spin flip rate v
- Site-to-site hopping rate $D_{||}$

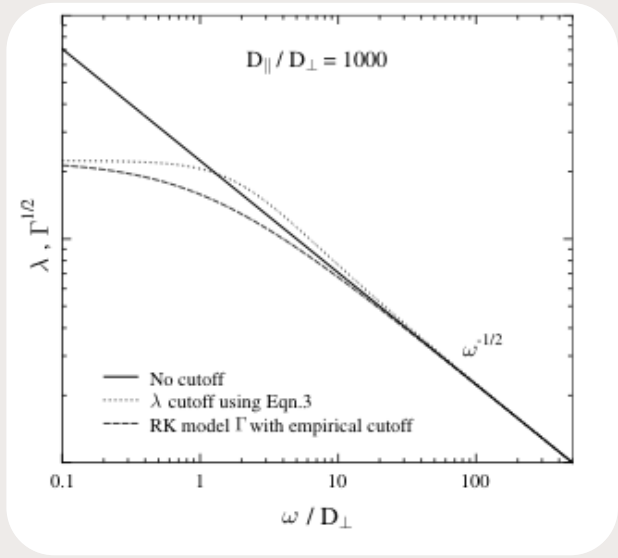
$$\Gamma = \frac{\nu}{\left(1 + 2D_{||}\frac{\sqrt{2\omega_e \nu}}{\omega_0^2}\right)^2}$$

Fast Diffusion Limit

$$\Gamma = \frac{\omega_0^4}{8\omega_e D_{||}^2}$$

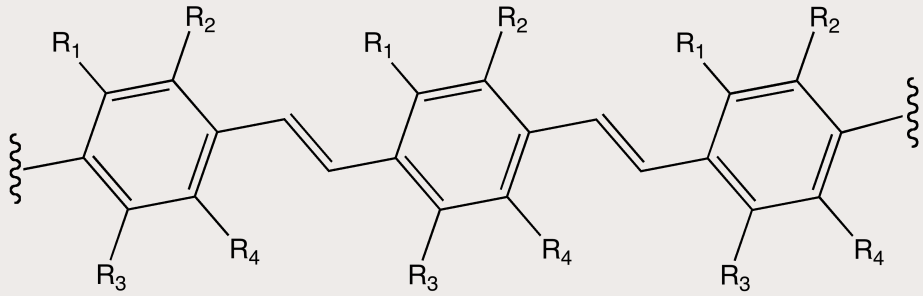
Interchain diffusion
Empirical cut-off

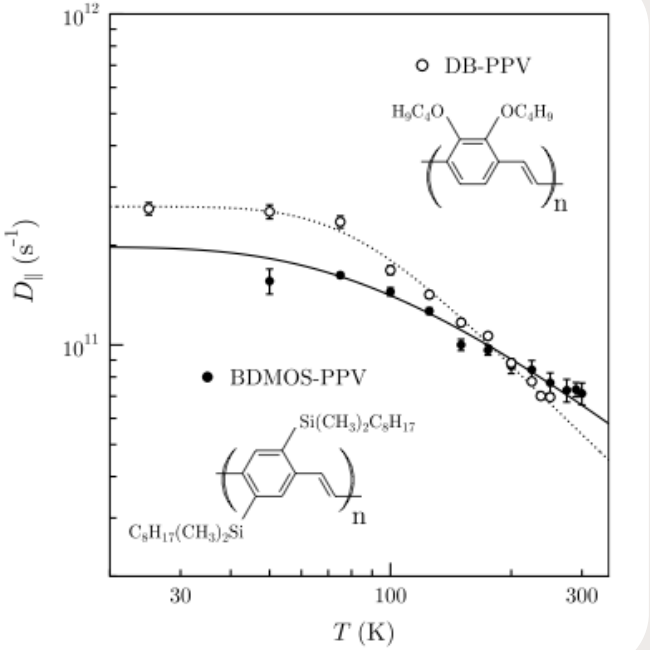
$$\Gamma = \frac{\Gamma_0}{(1 + \omega_e / D_\perp)}$$

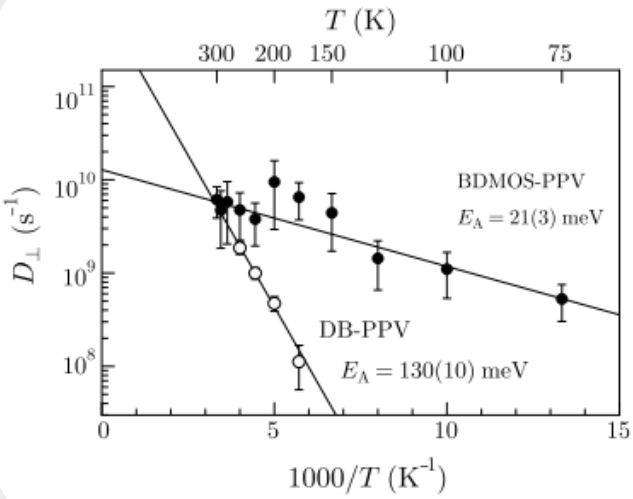


F. L. Pratt, J. Phys. Condens. Matter **16**, S4779 (2004)

Polyphenylenevinylene

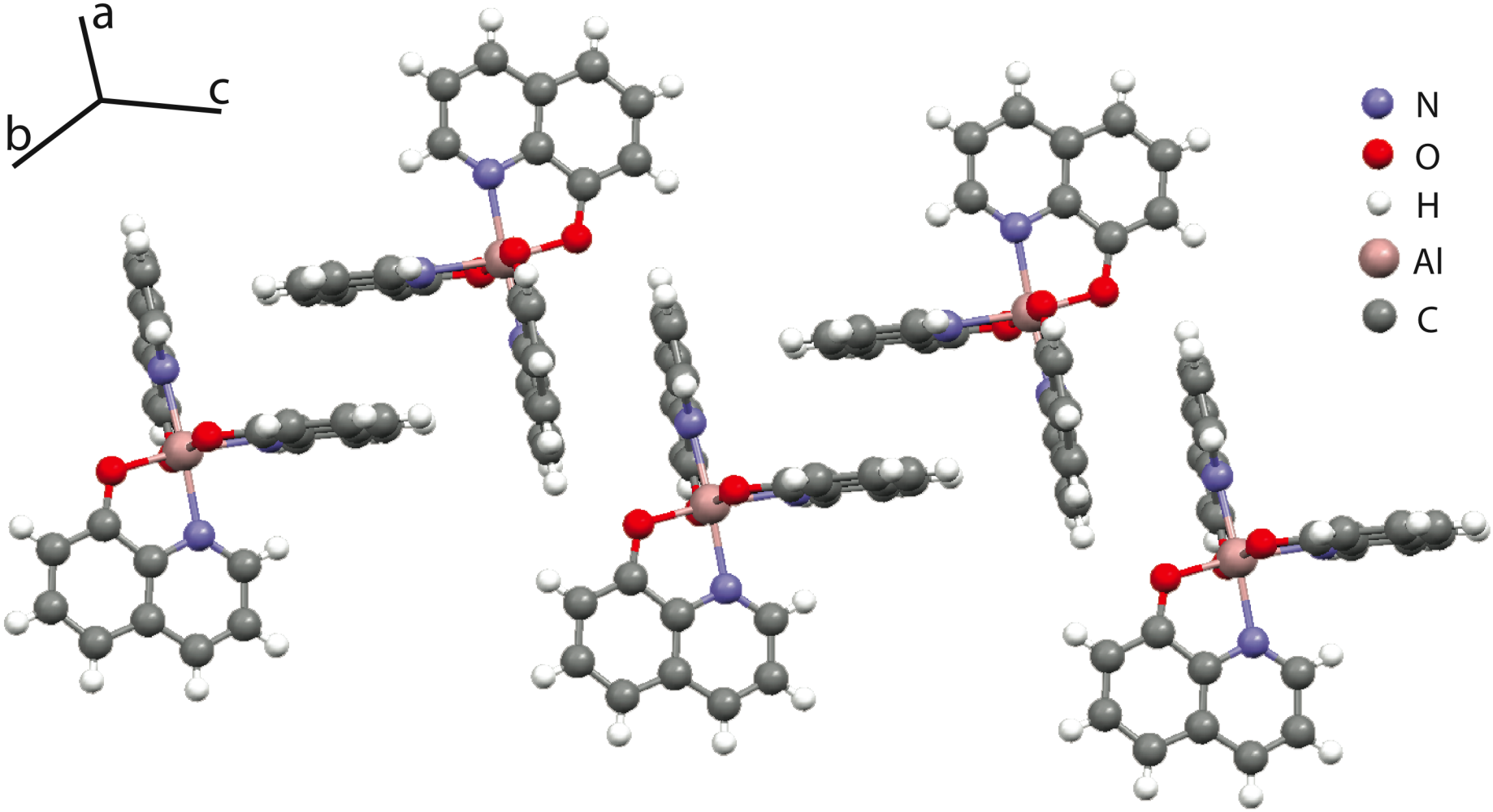




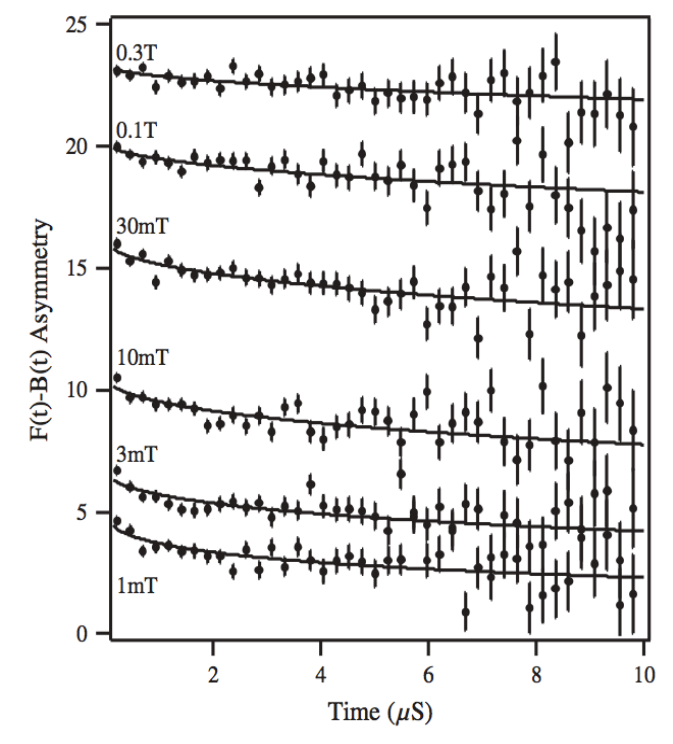


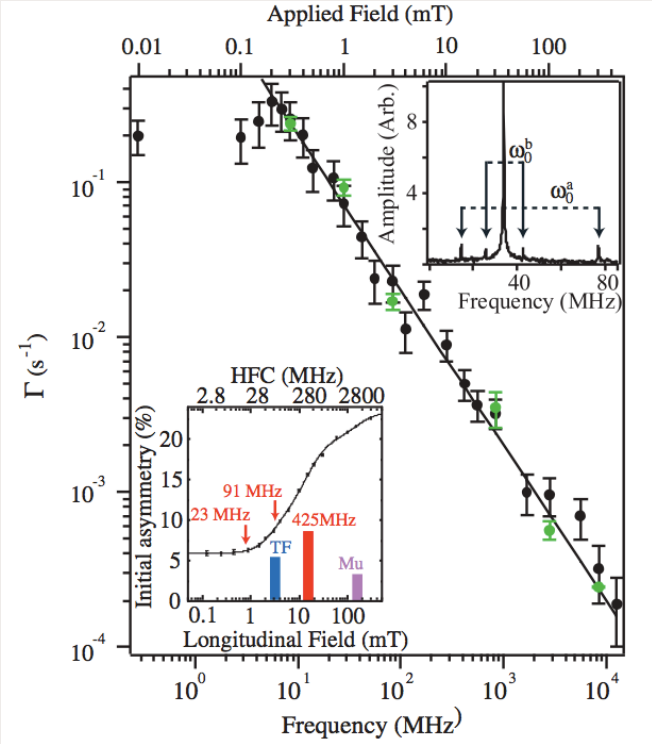
F. L. Pratt et al. Physica B **326**, 34 (2003)

A Cautionary Tale: Alq_3



A Cautionary Tale: Alq_3

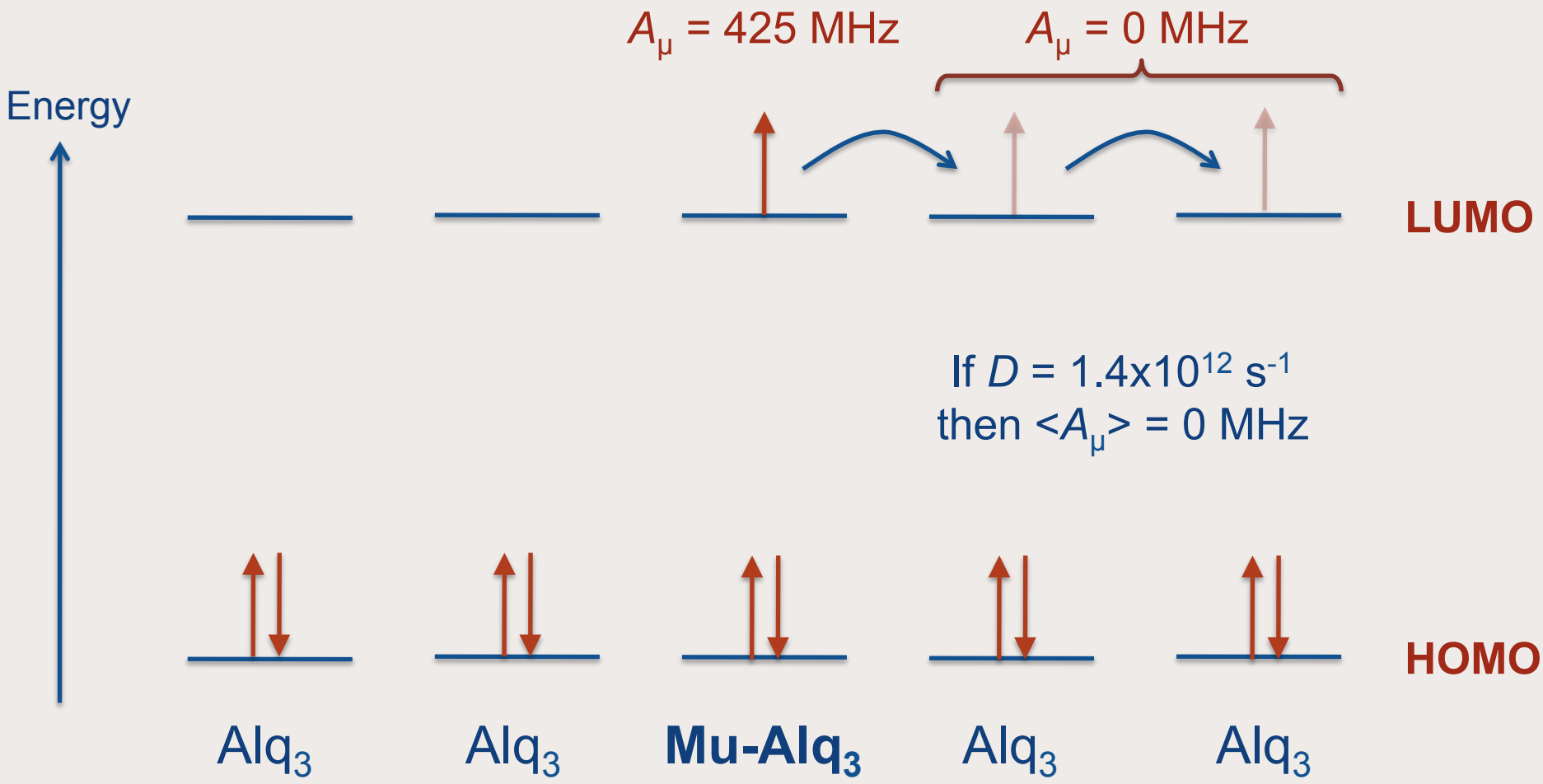




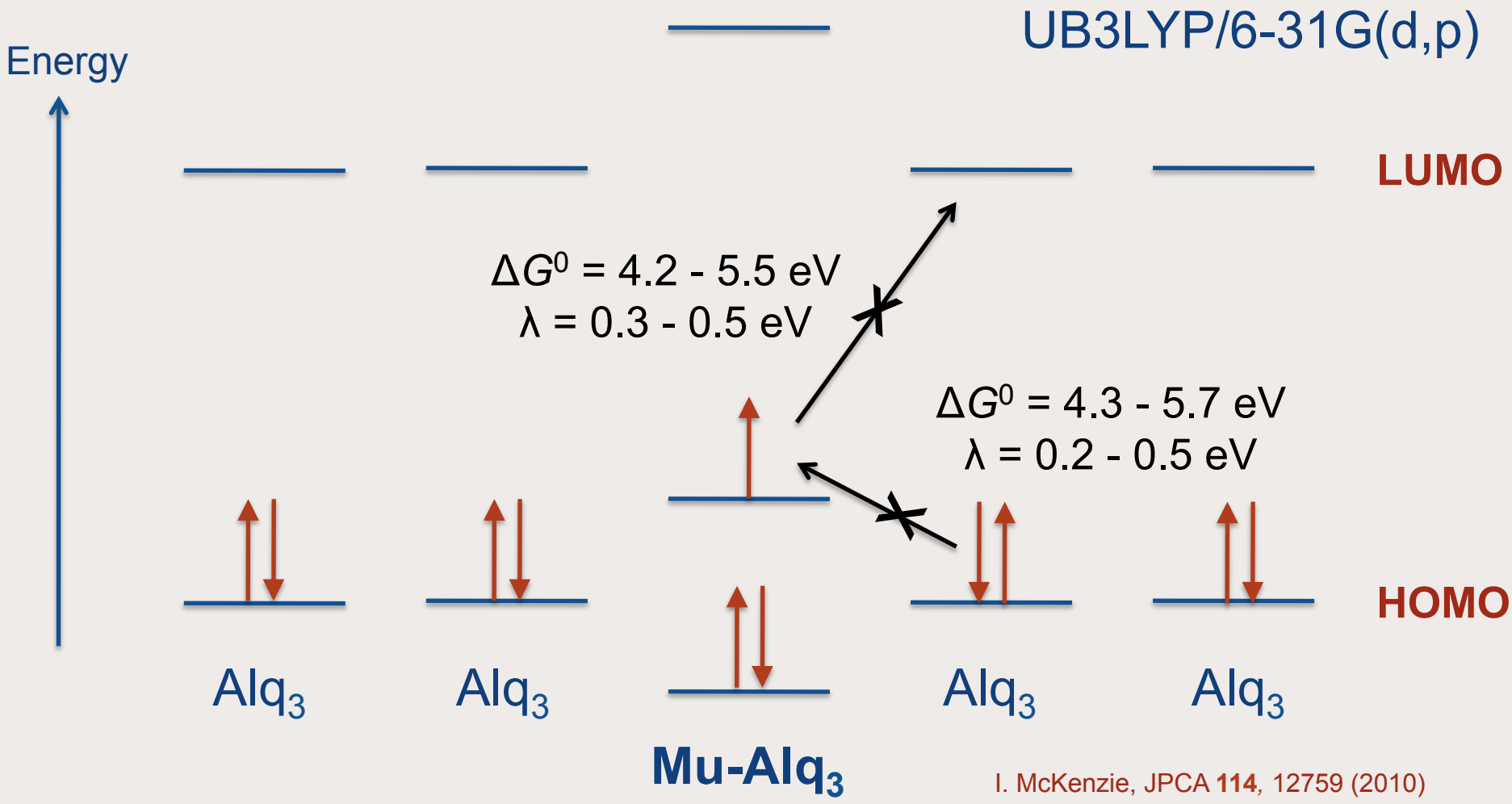
$$D = 1.4 \pm 0.2 \times 10^{12}\ s^{-1}$$

A. J. Drew et al., PRL **100**, 116601 (2008)

Assumed Behaviour in Alq_3



Actual Behaviour in Alq_3

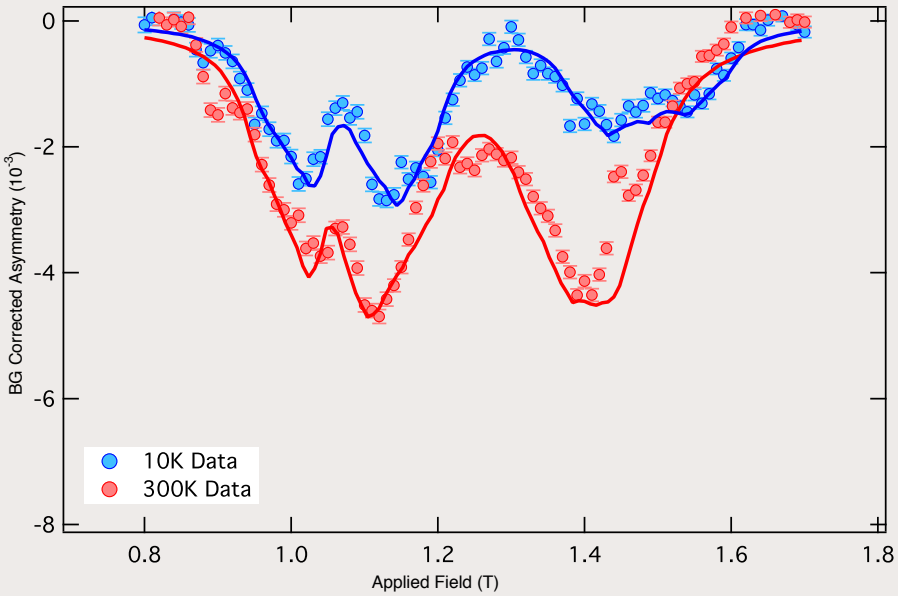


I. McKenzie, JPCA **114**, 12759 (2010)

ALC-μSR of Alq_3

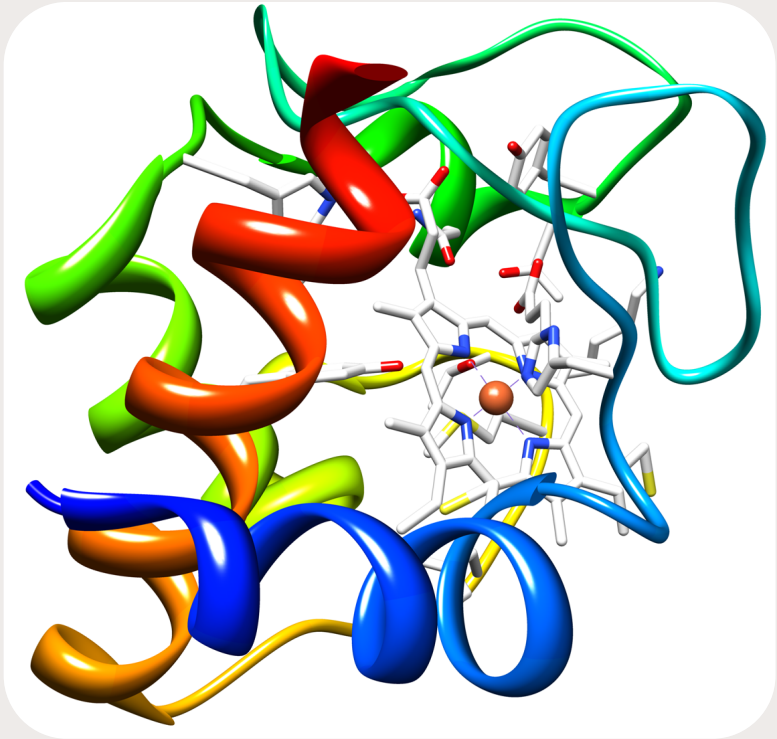
UB3LYP/6-31G(d,p)

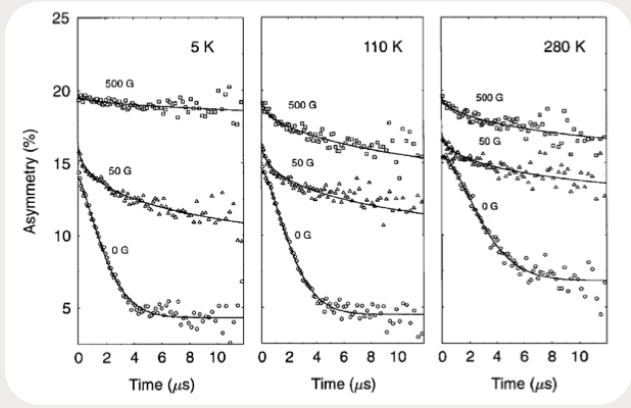
Position	$B_{res}(\Delta_1)$ / T	$B_{res}(\Delta_0)$ / T
2	1.26	1.37
3	1.65	1.80
4	1.15	1.26
5	0.82	0.90
6	1.72	1.88
7	1.02	1.11

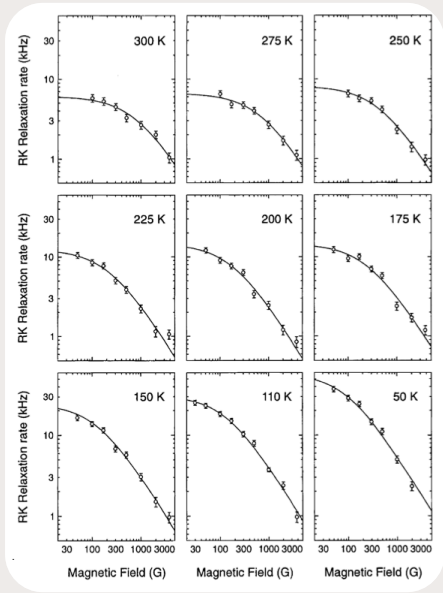


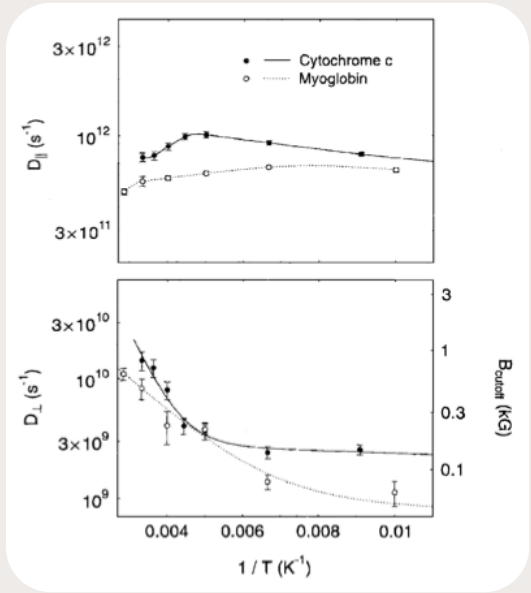
ALC resonances → Localized electron spin density

Cytochrome C



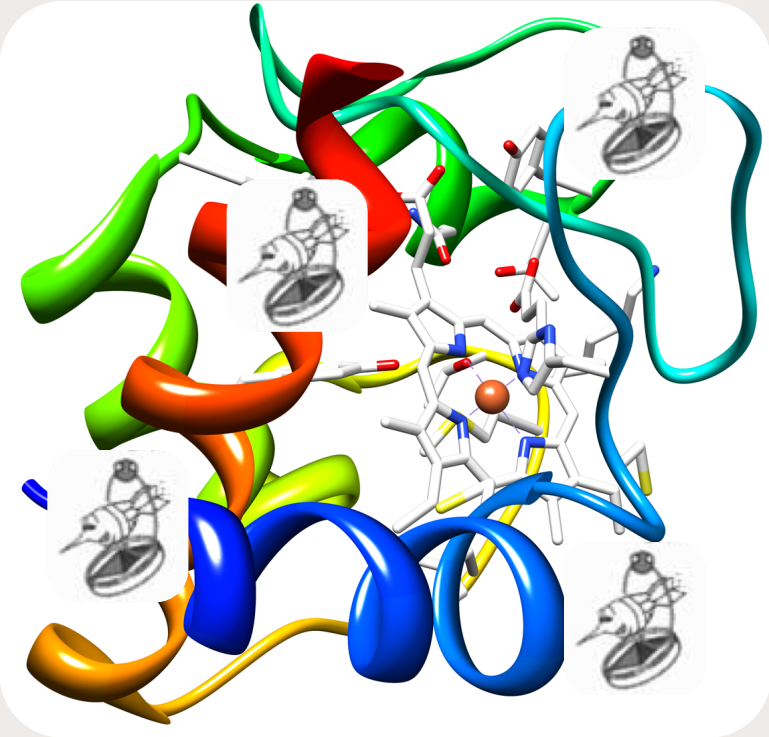






K. Nagamine, Eur. Phys. J. A **13**, 189 (2002)

Cytochrome C



Muons can be used to spin label biological molecules

But

- Many sites for Mu addition
- Many types of radicals with very different hyperfine parameters

What is the physical meaning of Γ?

K. Nagamine, Eur. Phys. J. A **13**, 189 (2002)

Conclusion

The muon is a local probe; you need to understand it's local environment before you draw conclusions about material properties