Muon Spectroscopy of Molecules

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Introduction

- **Muon states in matter**

Implanted positive muons may exist in any of the following forms.

a) Muon μ^+

b) Muonium μ^+e^-

c) Part of a radical

μSR

- **Properties of Muons?**

Mass = 0.11 proton

Charge = +e

Spin = 1/2

Magnetic moment = 3.18 x proton

μSR

- **Properties of Muonium** [μ^+e^-]

Isotope	Mass/m_e	Reduced mass/m_e	Bohr radius/nm	Ionisation energy/eV
Tritium (^3H)	5498	0.9998	0.05290	13.603
Deuterium (^2H)	3675	0.9997	0.05293	13.602
Protium (^1H)	1847	0.9995	0.05292	13.599
Muonium (Mu)	208	0.9952	0.05315	13.541

μSR

- **Molecules with Muonium** [μ^+e^-]

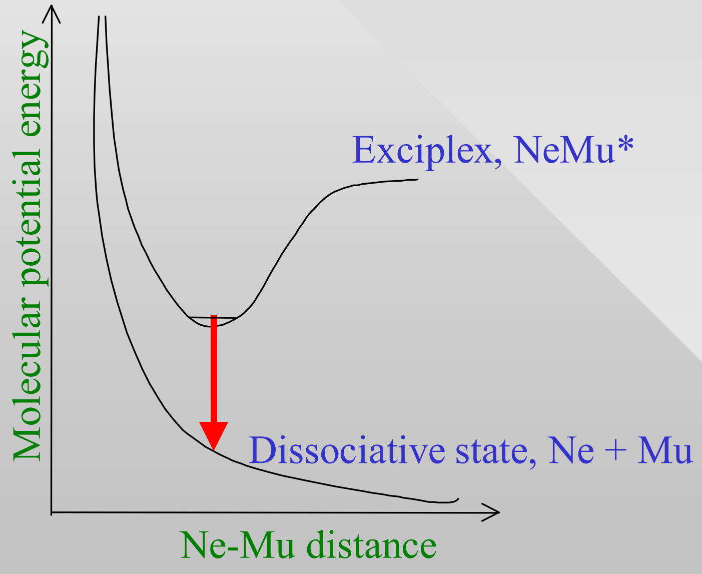
Some of the names to look out for

- ***Paul Percival***
- ***Emil Roduner***
- ***David Walker***
- ***Donald G. Fleming***
- ***Christopher Rhodes***
- ***Brian Webster***
- ***Rod Macrae***

μSR

- **Molecules with Muonium** $[\mu^+e^-]$

Chemiluminescence from the exiplex molecule NeMu*



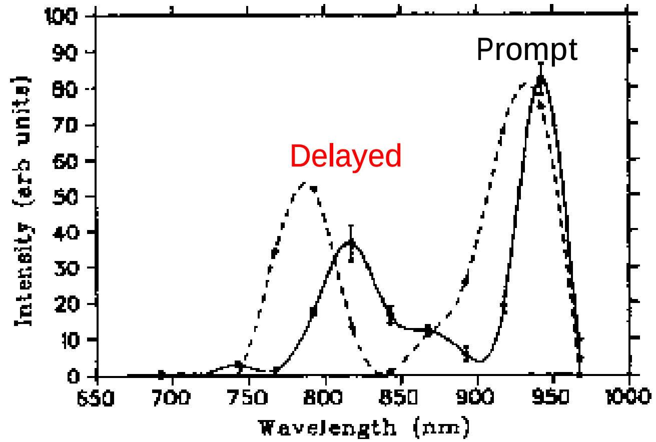
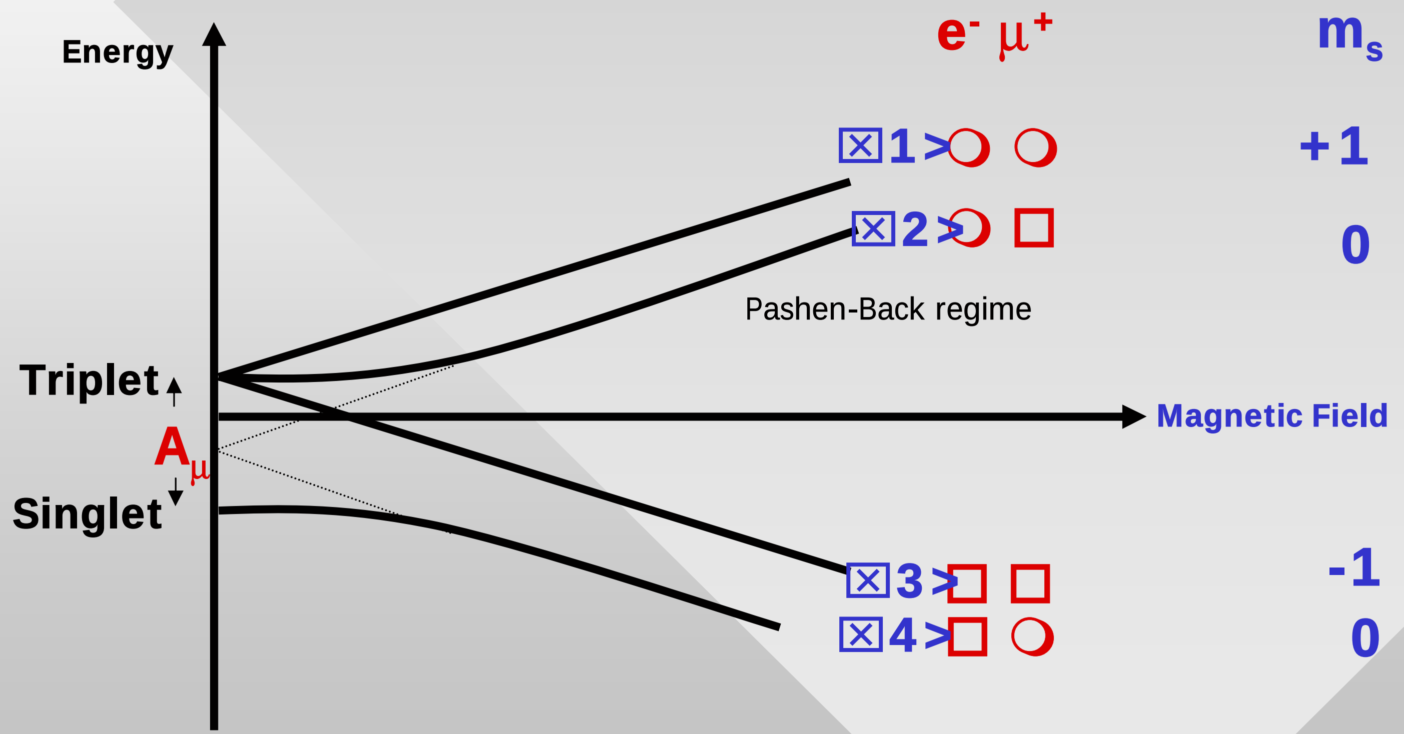


FIG. 15. A comparison of the CVF shoulder peak spectrum observed in 6 atm Ne and 1 Torr Ar (see Fig. 9) with simulated spectrum (dashed line), produced by *ab initio* calculations, as described in text. The calculated intensities are normalized to the experimental value (both in arbitrary units) in the region of the 943 nm peak.

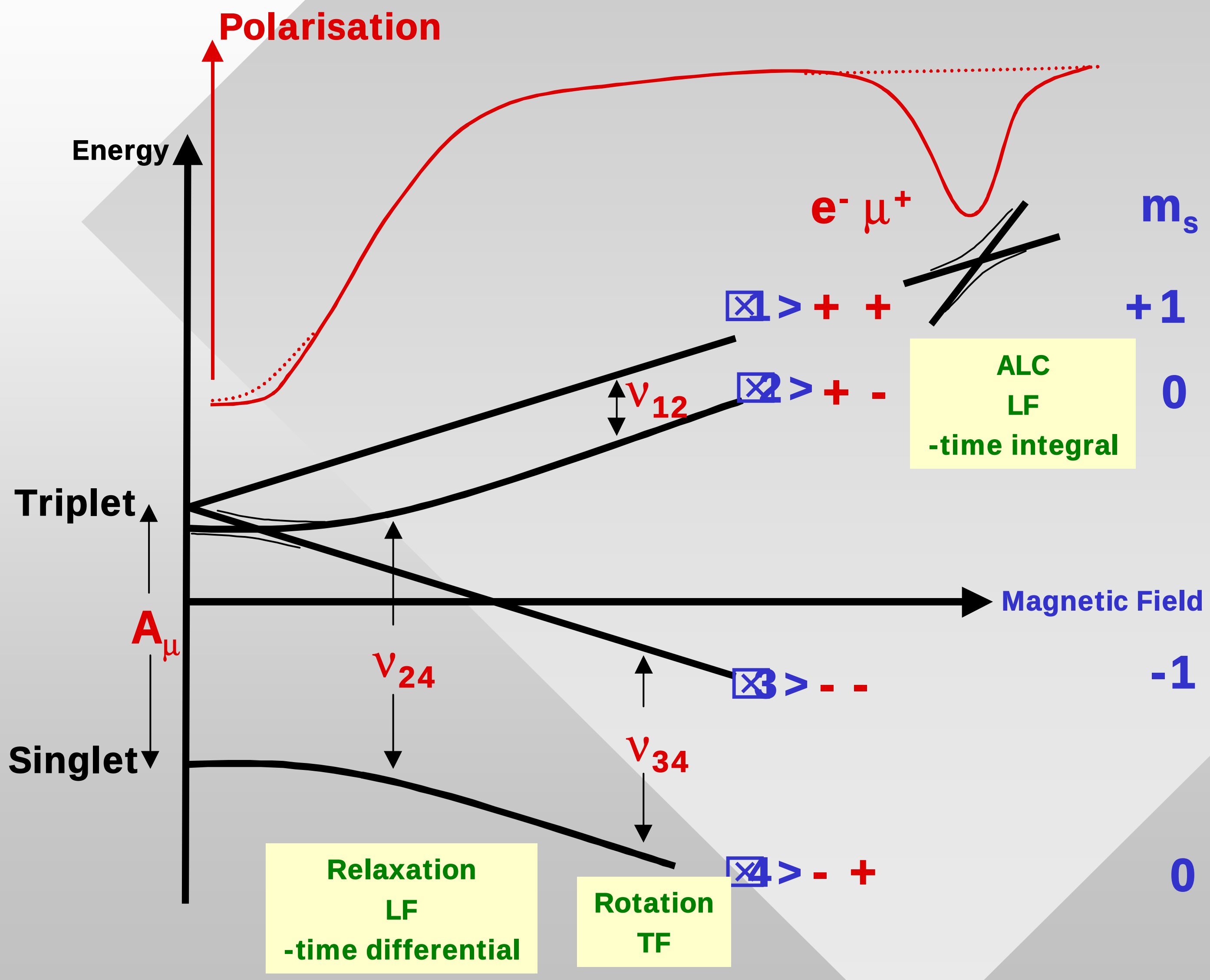
S. Baer et. al. J. Chem. Phys. 101 (1994) 1202

Muon - Electron system; *Breit - Rabi diagram*

$$H = hA_\mu\,\mathbf{S.I} + h\omega_e S_z + h\omega_\mu I_z$$



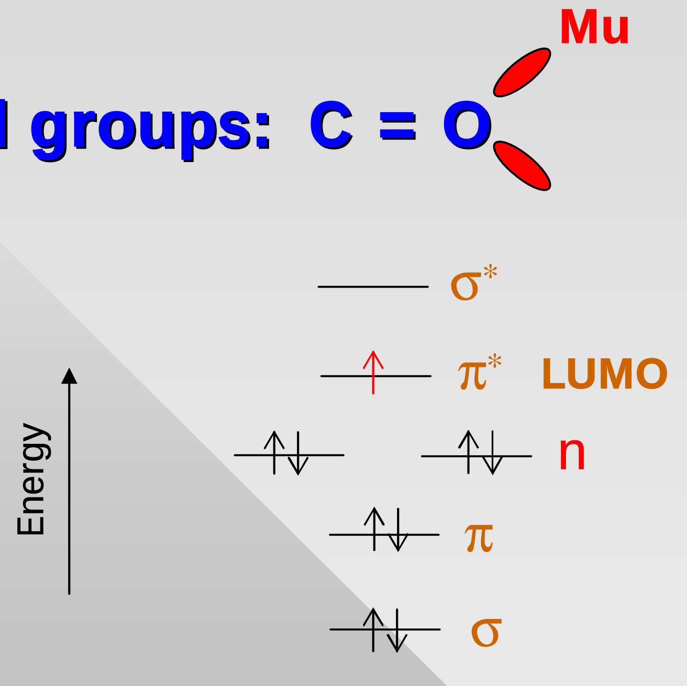
Muon - Electron system; *Breit - Rabi diagram*

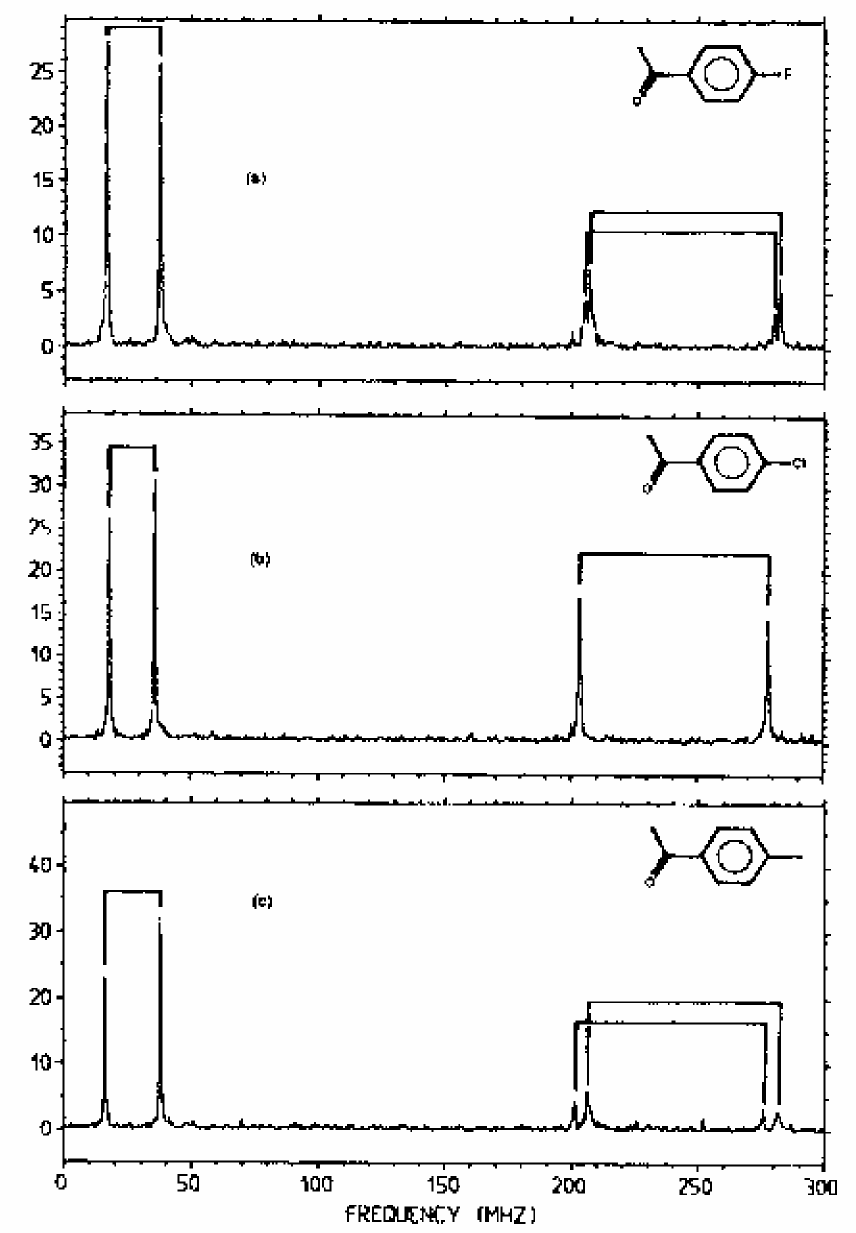


μSR

- **Molecules with Muonium** [μ^+e^-]

carbonyl groups: C = O





TF-MuSR spectra of
(a) 4-Fluoroacetophenone,
(b) 4-Chloroacetophenone
& (c) 4-Methylacetophenone
at 200 mT and 300 K

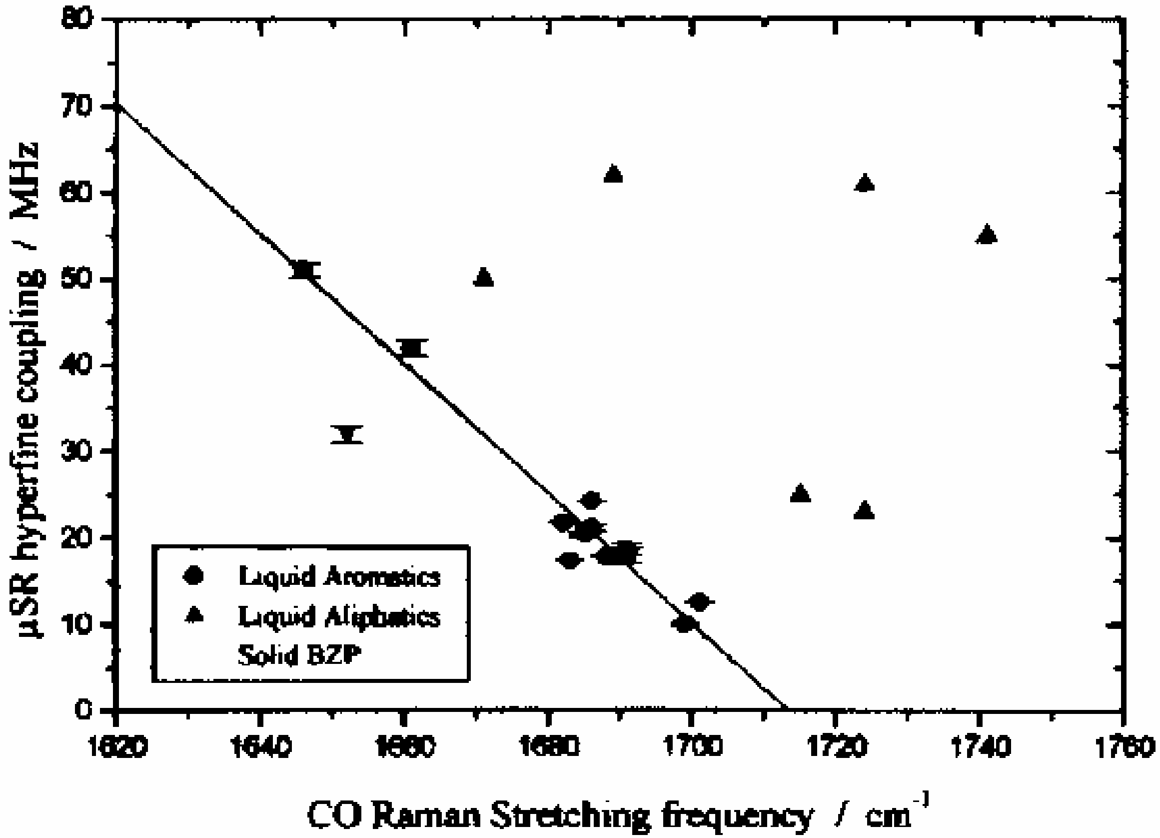
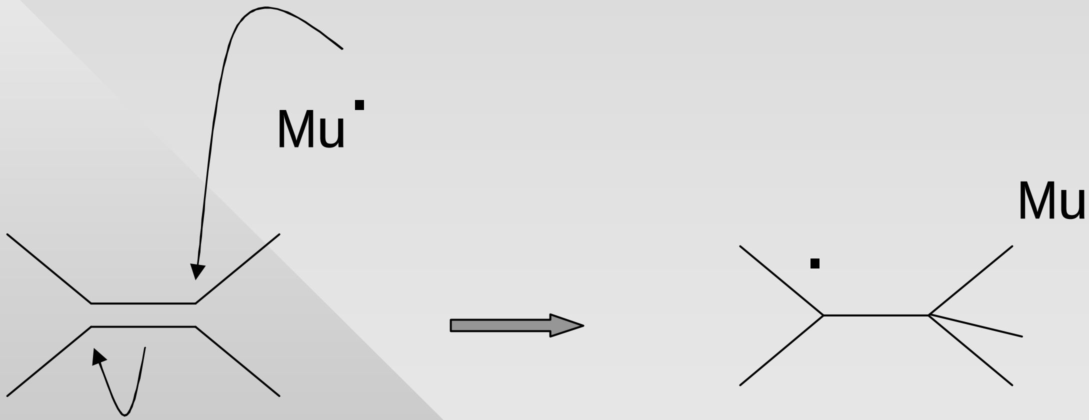


Figure 1. Correlation of closed-shell ν_{CO} with open-shell A_μ for various carbonyl species. Data of aliphatic species from ref 11. (Acetaldehylde: 23 MHz, 1724 cm^{-1}; acetone: 25 MHz, 1715 cm^{-1}; formamide: 50 MHz, 1671 cm^{-1}; ethyl acetate: 55 MHz, 1741 cm^{-1}; methylformate: 61 MHz, 1724 cm^{-1}; ditertiarybutyl ketone: 62 MHz, 1688 cm^{-1}.)

μSR

- **Molecules with Muonium** [μ^+e^-]



Ethene

$CH_2 = CH_2$

DNA

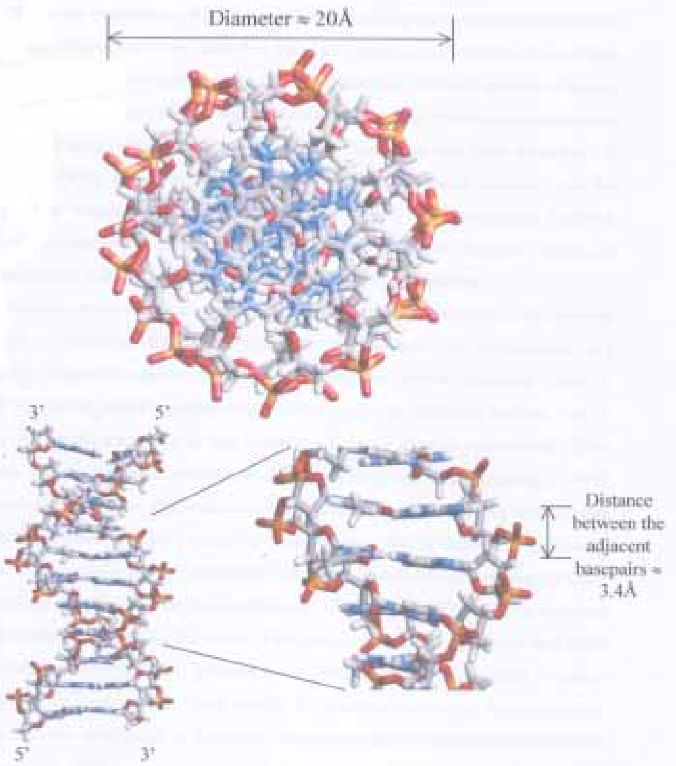
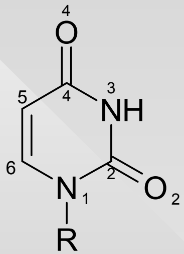


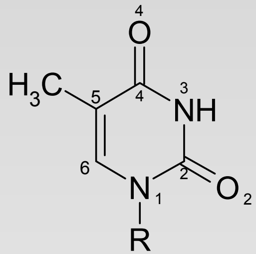
Illustration of B-form dsDNA. For this image, the original structure from Feng, B. and Stone, M. P., (1995), *Chem. Res. Toxicol.*, 8, 821, has been used (protein data bank entrance no. 1AGH). Colour code is as used in figure 1-1.

μSR

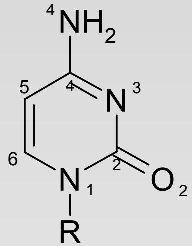
- **Molecules with Muonium** $[\mu^+ e^-]$



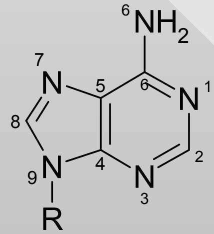
URACIL



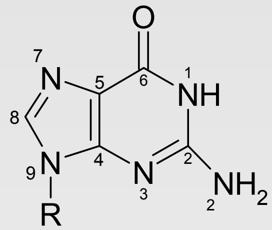
THYMINE



CYTOSINE



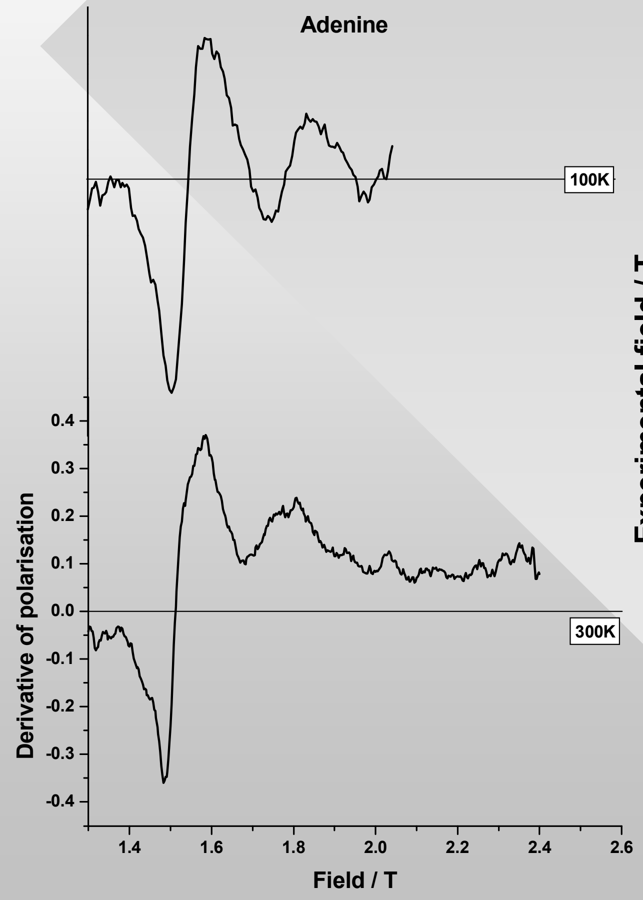
ADENINE

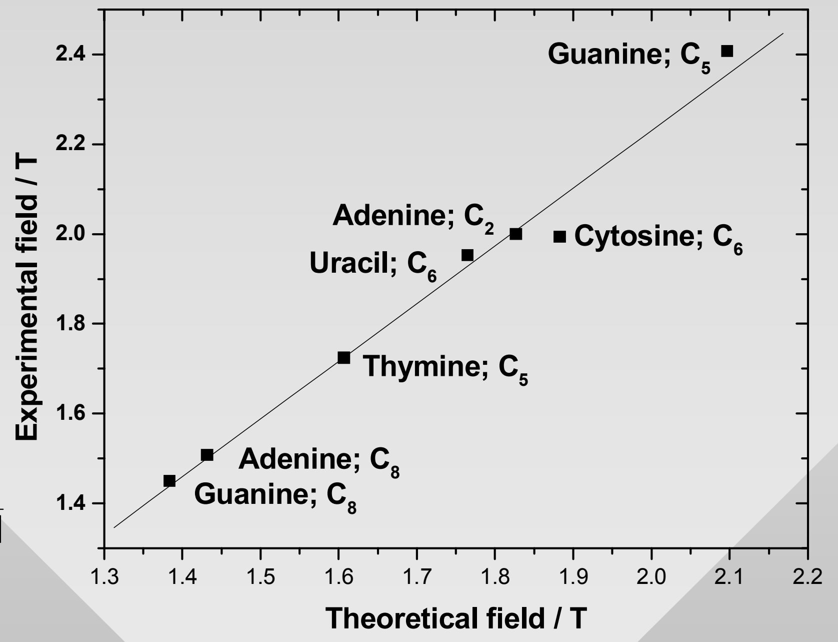


GUANINE

μSR

- **Molecules with Muonium** [μ^+e^-]

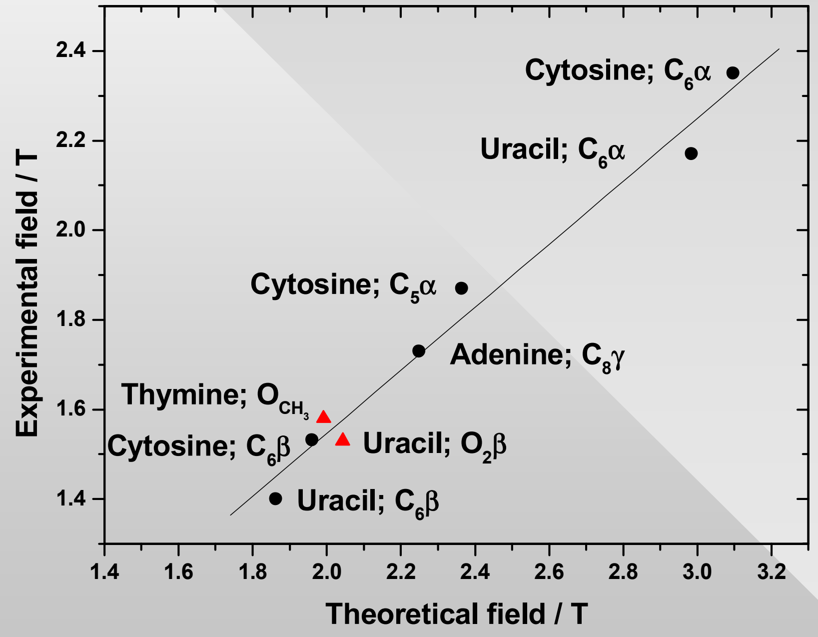




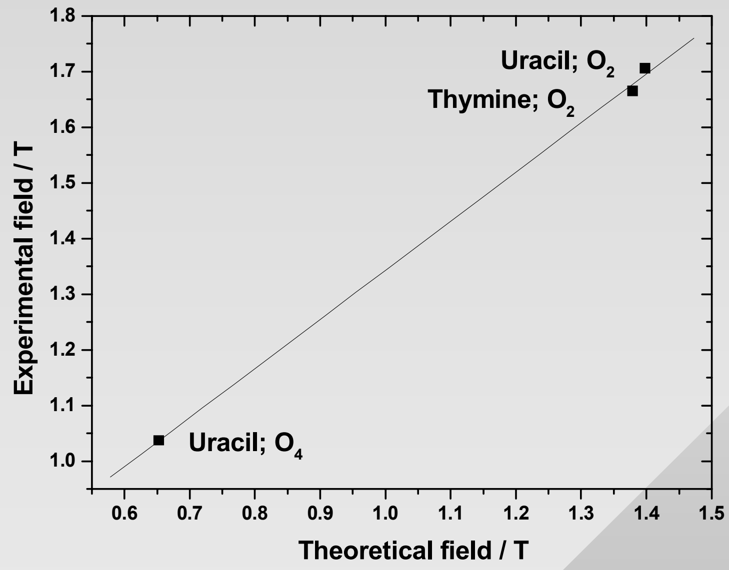
ALC |ΔM| = 1 resonance features

μSR

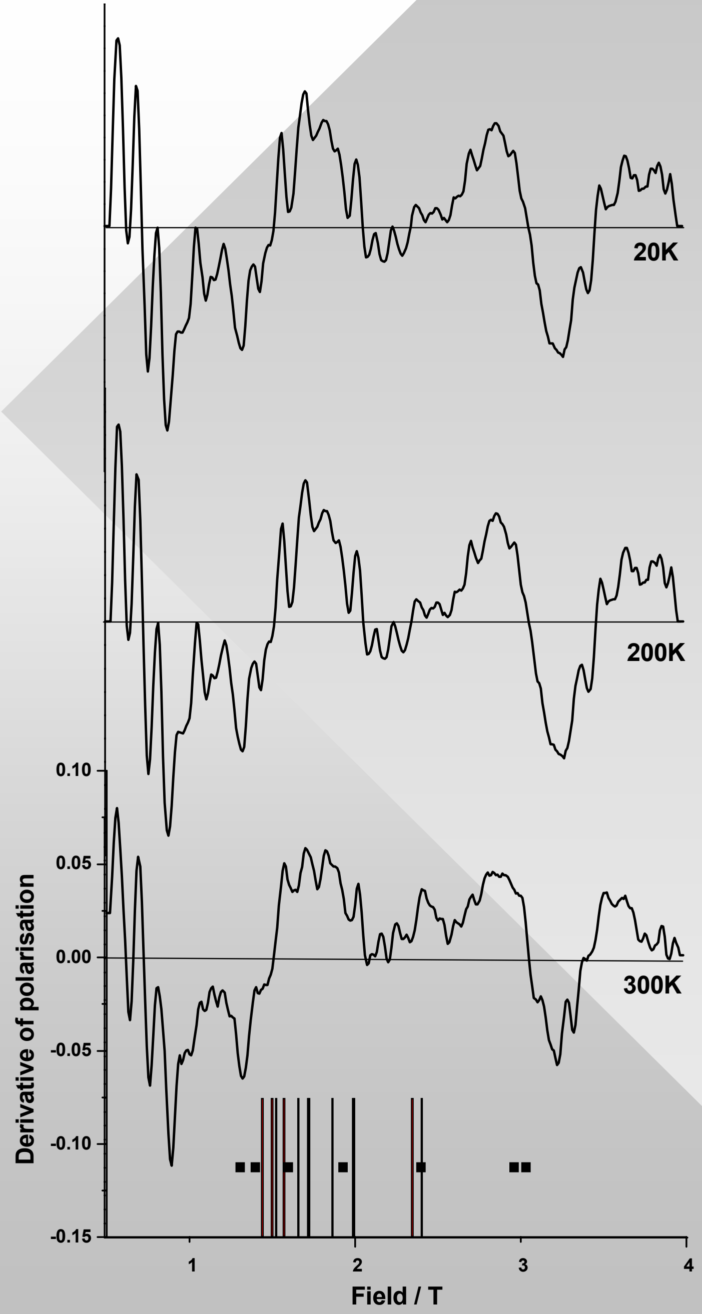
- **Molecules with Muonium** $[\mu^+ e^-]$



ALC |ΔM| = 0 resonance features



ALC |ΔM| = 1
O-Mu adduct resonance features



The ALC-μSR spectra of dsDNA (Herring testes).

The resonance signals observed and assigned for the different bases are indicated as a stick diagram for comparison.

The predicted positions, using the DFT results and the linear correlations, of the other possible addition sites on the bases for which no experimental ALC signals were observed are indicated as dark squares.

μSR

- **Molecules with Muonium** [μ^+e^-]

Two main types of measurement:

(a) Active observer of a process

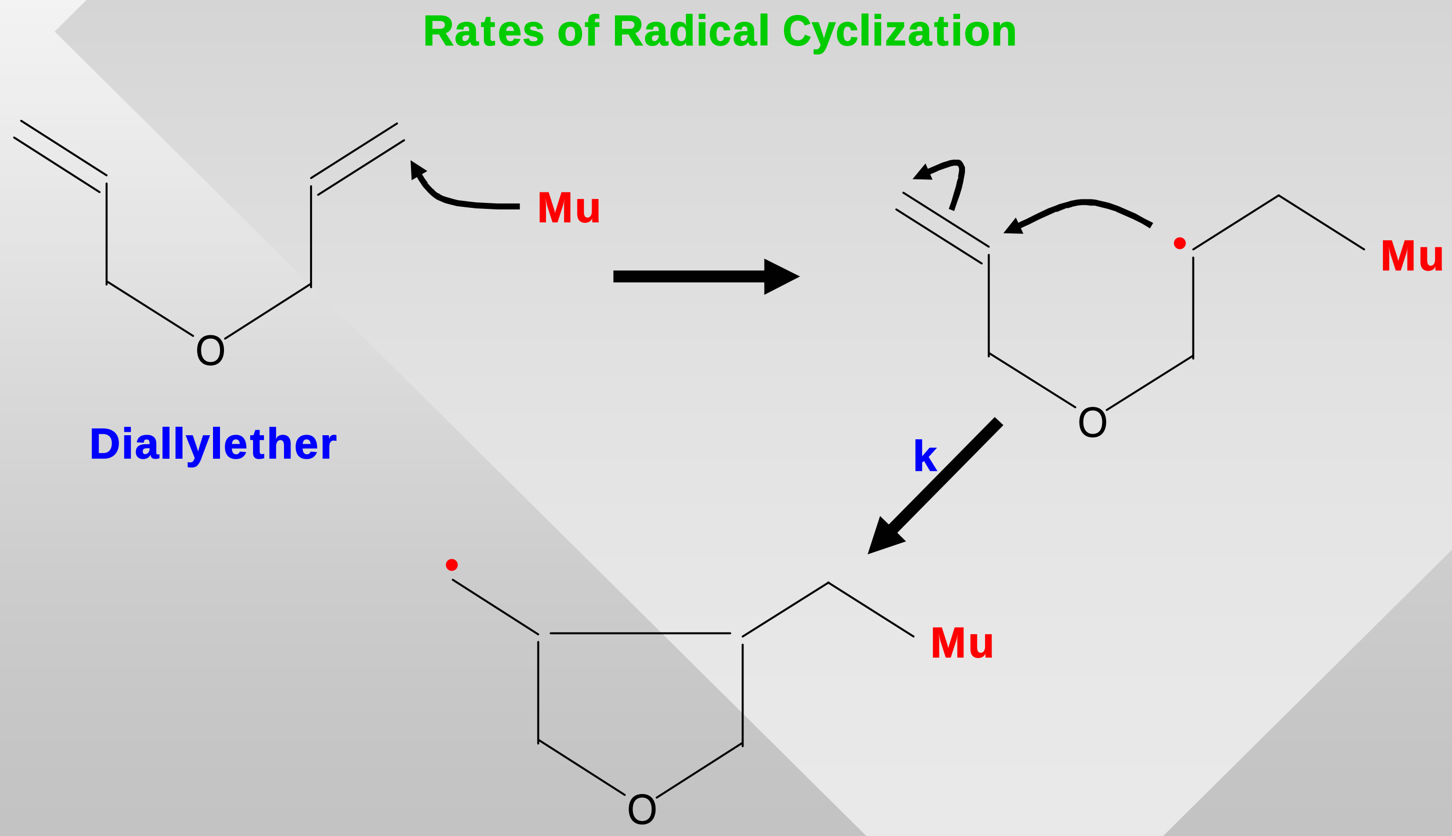
Radical formation modifies the process

(b) Passive observer of a process

Measured properties similar to close-shell compound

µSR

- **Molecules with Muonium** [µ⁺e⁻]



P. Burkhatd et. Al. J. Phys. Chem. 88 (1984) 773

μSR

- **Molecules with Muonium** [μ^+e^-]

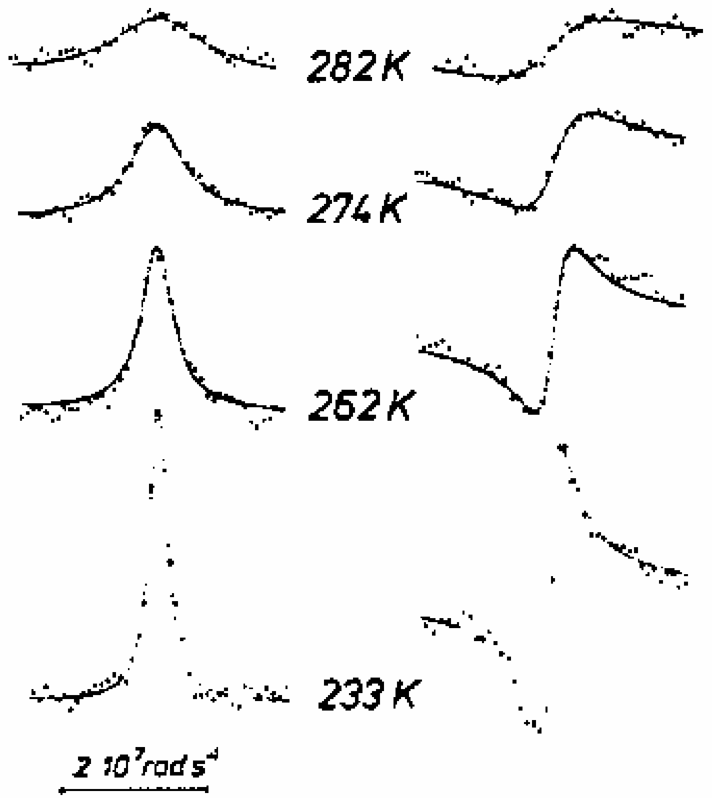


Figure 4. Absorption (left) and dispersion (right) profiles for one μSR line of Figure 2.

TF-MuSR

μSR

- **Molecules with Muonium** [μ^+e^-]

k (338K) = 9.3 x 10^6 s^{-1}

and compares well with the literature estimates of

k (338K) = 8.8 x 10^6 s^{-1}

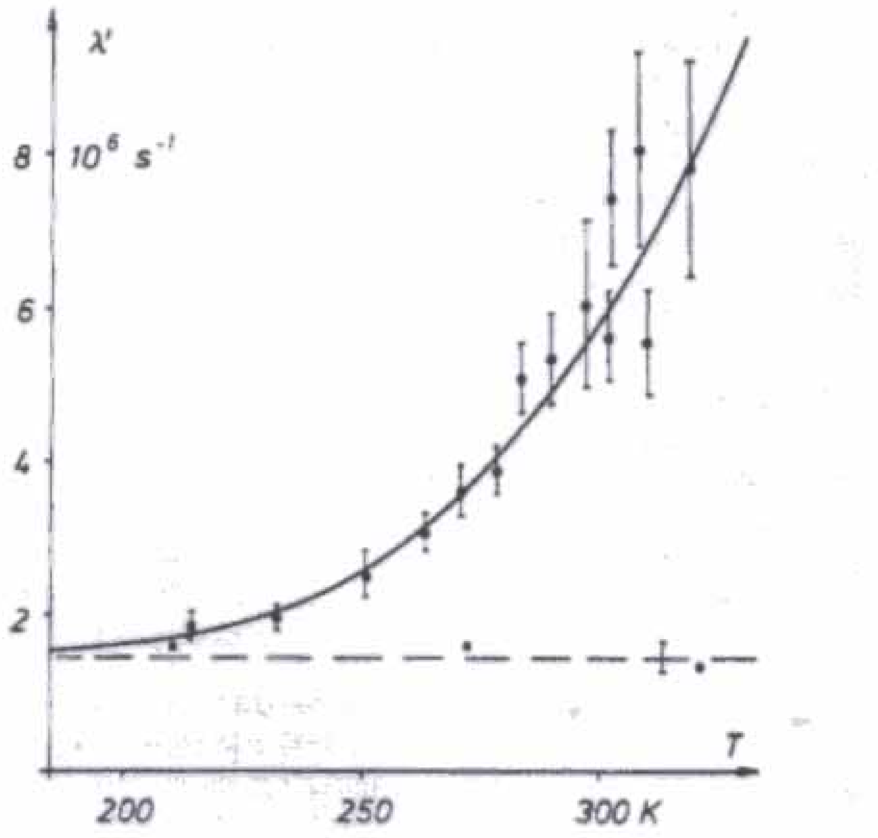
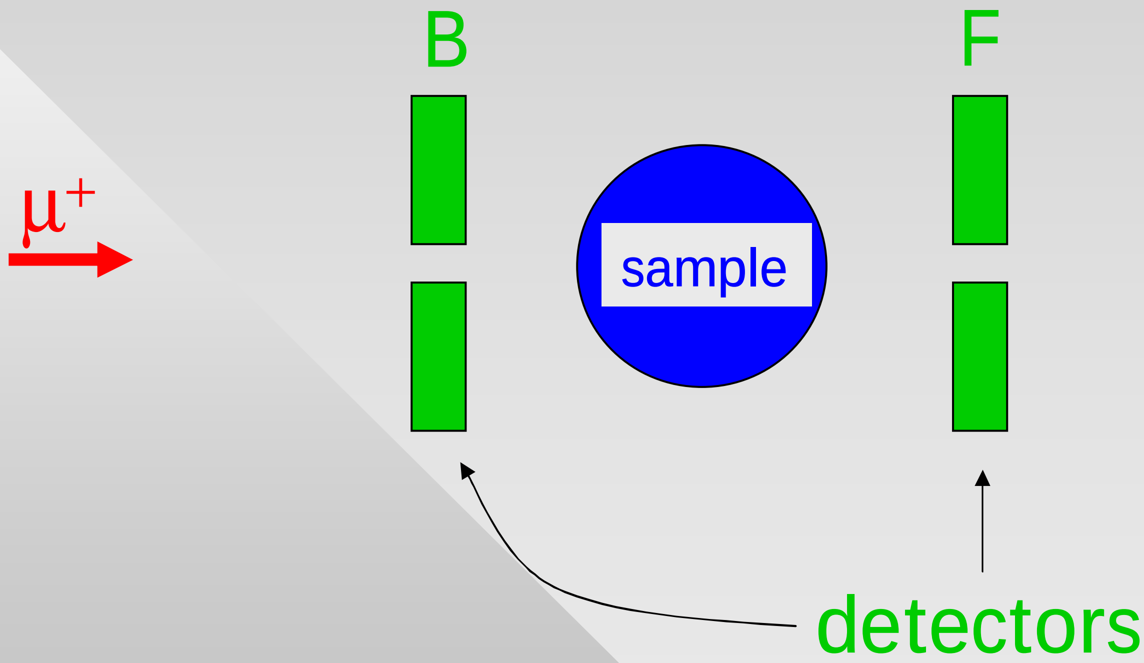


Figure 6. Line width parameters λ' for $CH_2{=}CHCH_2OCH_2\dot{C}HCH_2Mu$ (circles) and $CH_3CH_2CH_2OCH_2\dot{C}HCH_2Mu$ (squares) vs. temperature.

μSR

- **Muon Spin Relaxation**



Measure **(F - B) / (F + B)** vs **Time**

Molecular Dynamics

Theory

$$\lambda_{ij} = \left|M_{ij}\right|^2 . P_{ij} . \varphi\left(\omega_{ij}\right)$$

Coupling of perturbation

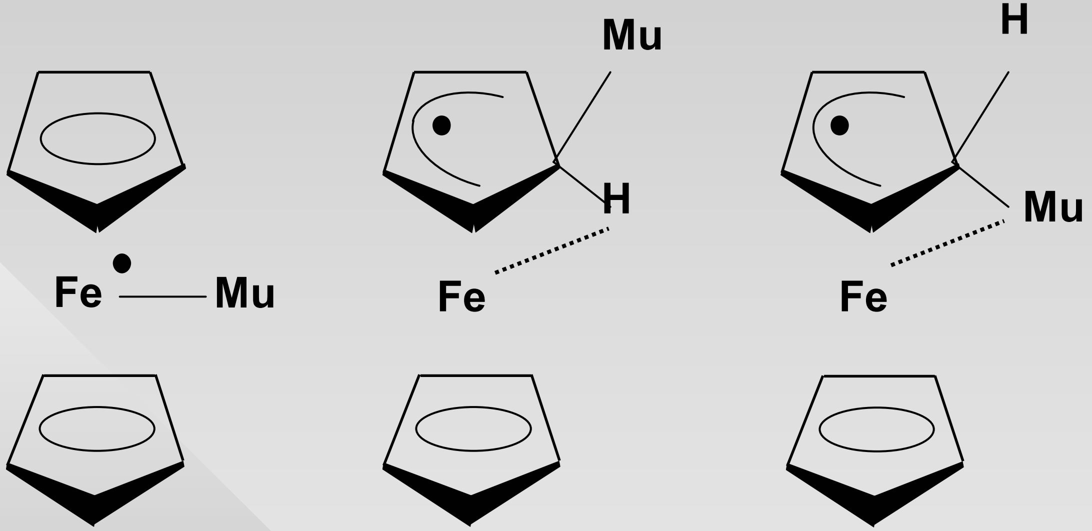
Change in muon polarisation

Spectral density of perturbation

$$\lambda = 2.\left(2\pi\delta A\right)^2 . \frac{x^2}{1+x^2} . \frac{\tau}{1+\tau^2\omega^2}$$

S.F.J. Cox and D.S. Sivia, Hyperfine Interactions 87 (1994) 971

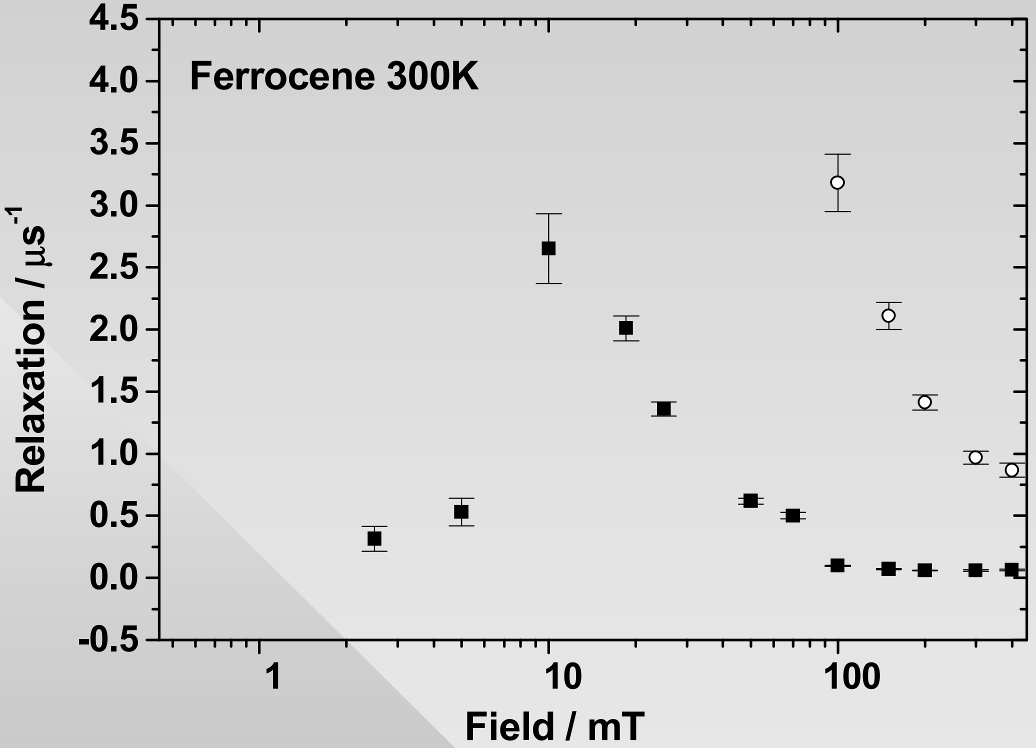
FERROCENE

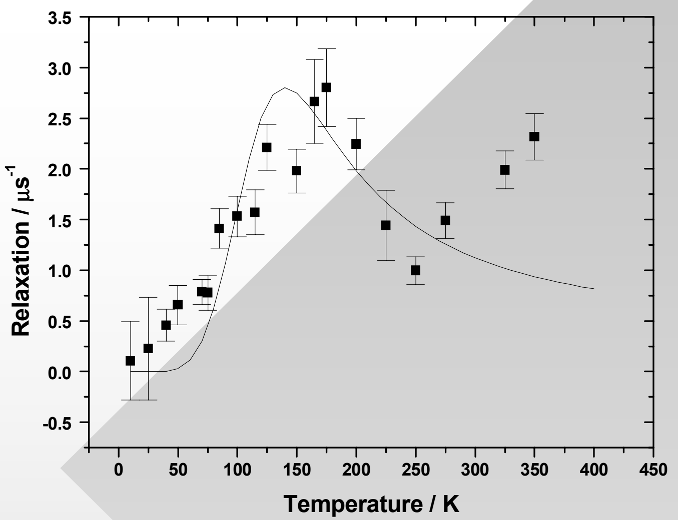


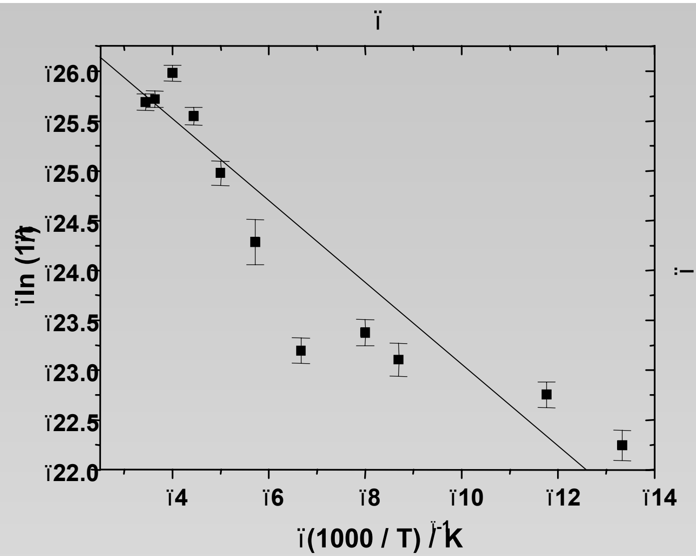
Fe-Mu radical

cp-Mu exo-radical

cp-Mu endo-radical


Ferrocene 300K
Relaxation / μs-1
Field / mT
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1
10
100



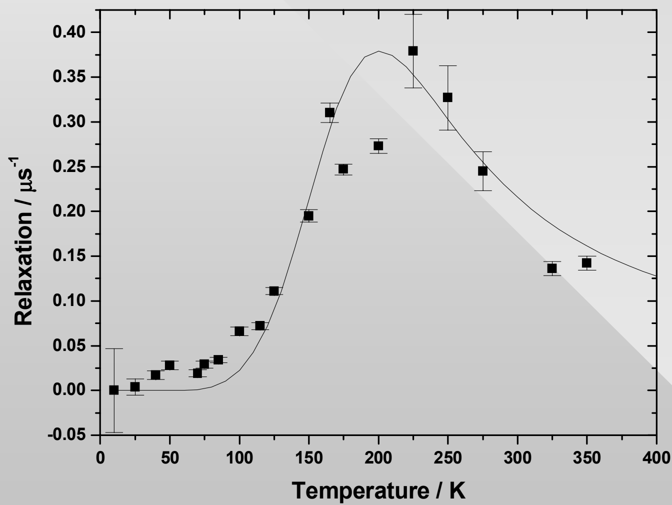


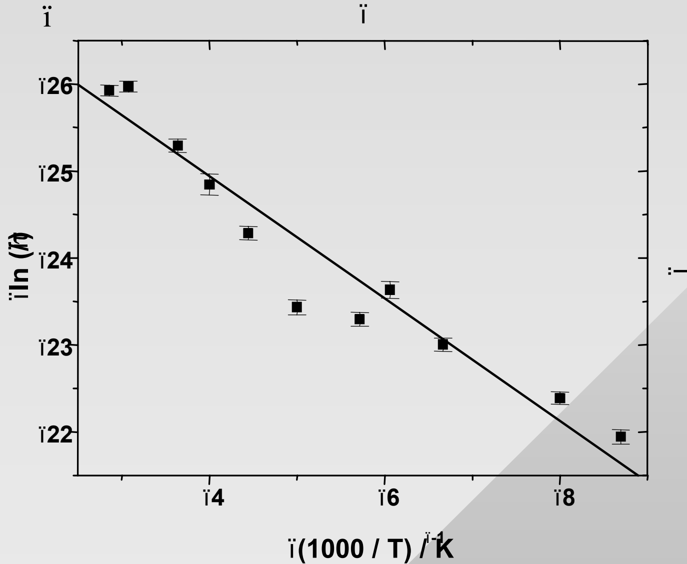
Fe-Mu

ΔE = 3.4(0.4) kJ mol^{-1}

A = 6.3(1.7)x10^{11} s^{-1}

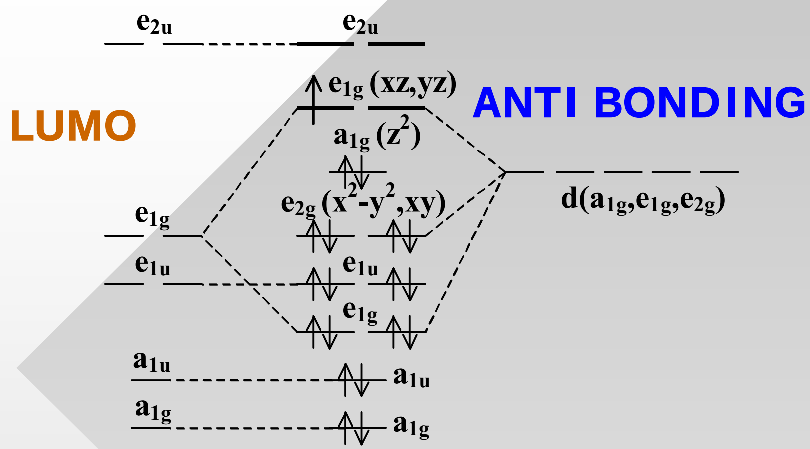
Cp-Mu repolarises like benzene





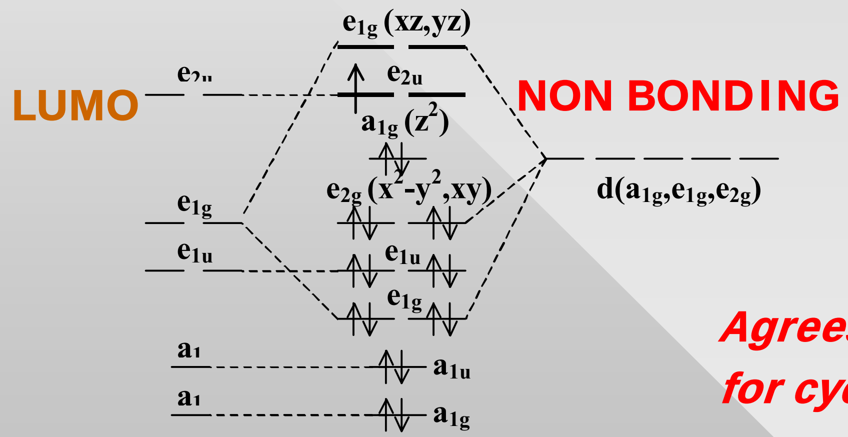
ΔE = 5.8(0.4) kJ mol^{-1}

A = 1.1(0.4)x10^{12} s^{-1}



ΔE = 3.4(0.4) kJ mol^{-1}

A = 6.3x10^{11}(1.7) s^{-1}



ΔE = 5.8(0.4) kJ mol^{-1}

A = 1.1x10^{12}(0.4) s^{-1}

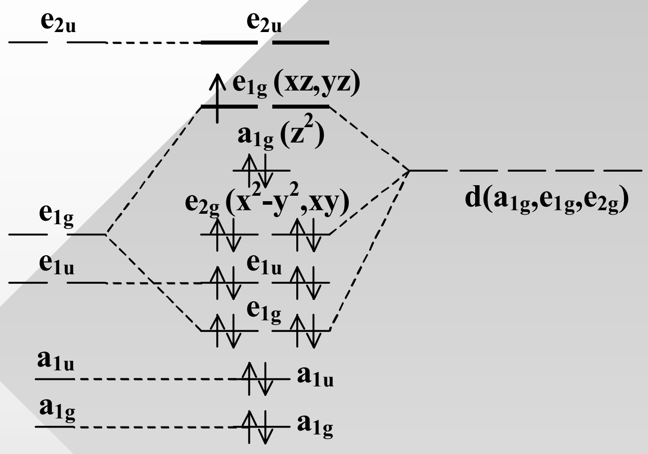
Agrees with NMR & QENS values for cyclopentadienyl ring rotation

I	II	IIIb	IVb	Vb	VIb	VIIb	VIIIb			Ib	IIb	III	IV	V	VI	VII	0
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
H												LUMO anti-bonding					He
Li	Be											B	C	N	O	F	Ne
Na	Mg	LUMO non-bonding ←						→				Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		Uuo
Lanthanides *			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides **			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Benzene chromium tricarbonyl
Cyclopentadienyl manganese tricarbonyl → **Agree with NMR and QENS**

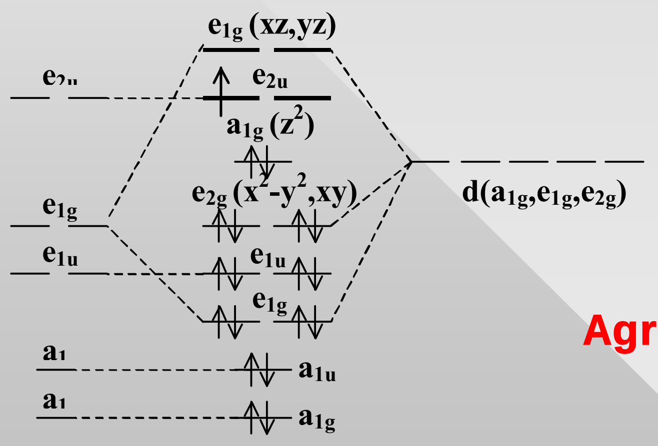
Ferrocene → **Both types**

Ruthenocene
Osmocene → **Do not agree with NMR and QENS**



ΔE = 3.4(0.4) kJ mol^{-1}

A = 6.3(1.7) s^{-1}



ΔE = 5.8(0.4) kJ mol^{-1}

A = 1.1(0.4) s^{-1}

Agrees with NMR & QENS values

Photoelectron spectroscopic evidence to show the drop in energy of the d-orbitals across the Periodic Table.

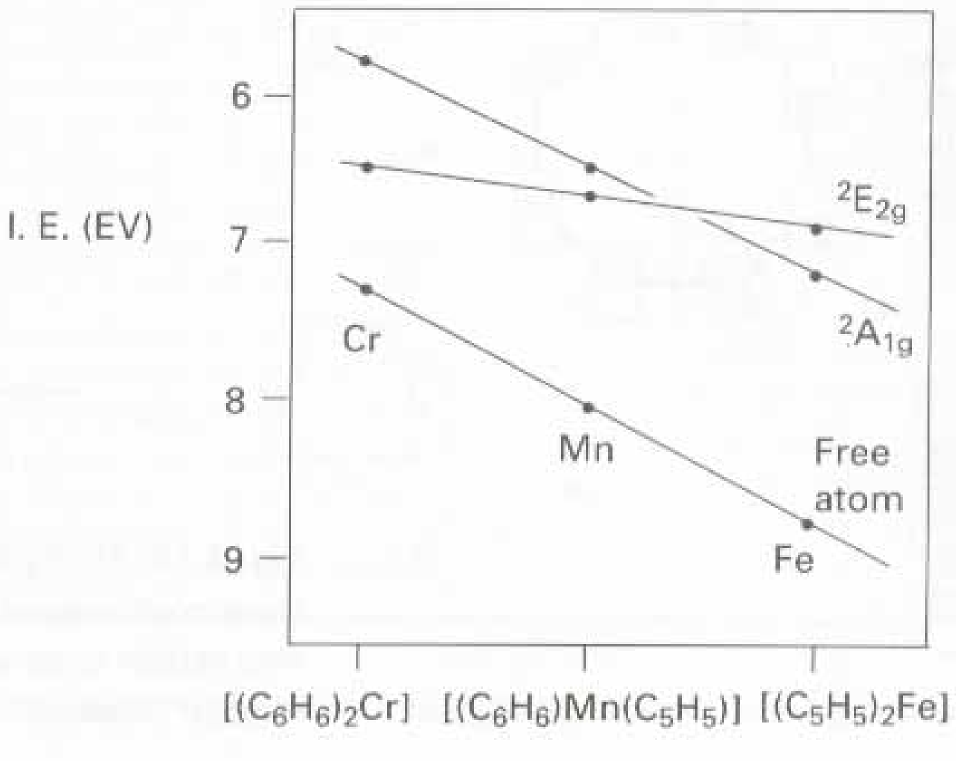


Fig. 3.14 A plot of the energies of the $^2A_{1g}$ amd $^2E_{2g}$ ion states for isoelectronic metallocenes derived from UV photoelectron spectral studies.

Acknowledgements

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Roger Grinter	UEA

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