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RAL-TR-2004-035

Presentations given as part of the radiofrequency collabaration project meeting

C. Johnson (Editor)

13 December 2004

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Presentations given as part of the

Radio Frequency Collaboration Project Meeting

C. Johnson (Editor)

October 2004

Overview

The Radio-Frequency collaboration project meeting brought together facility staff and visiting fellows who have contributed to the EPSRC Grant 'Development of Scientific Applications of Radio-Frequency Muon Spin Resonance' (GR/R53067/01). A variety of talks were presented on the day covering investigations using radio-frequency excitation and pulsed illumination techniques to study molecular systems and semiconductor materials. This document contains the slides that accompanied each of these presentations, a brief summary, written by the editor, provides a context for the talk.

RF Collaboration Project Meeting

10:30am, Friday 24th September 2004 Conference Room 3, R61, Rutherford Appleton Laboratory

A variety of talks on investigations using radio-frequency excitation and pulsed illumination to study molecular systems and semiconductor materials.

Meeting organiser: S.P. Cottrell and C. Johnson

Introduction

S.P. Cottrell (RAL)

Summary

In 1997, an EPSRC grant was awarded to RAL to enable the commissioning of an RF spectrometer on the DEVA beamline. In addition to allowing the construction of the instrument, funding was also provided for a cryo-furnace, special sample holders and the RF signal generator and amplifier kit still in use today.

The end of 2001 saw the award of a follow-up EPSRC grant to a collaboration comprising the Rutherford Appleton Laboratory (Cottrell, King, Cox, Lord) and the Universities of East Anglia (Jayasooriya, Clayden), Leicester (Davis) and Manchester (Conner). The emphasis of this new award was to enable the scientific commissioning of the RF spectrometer by funding 48 days of beamtime over three years, with work concentrated on four key areas, namely semiconductors, gas phase studies, radical chemistry and ionic materials. The grant provided a PDRA to support the experimental programme, funding for research fellows (Fleming, Macrae) to make extended visits to bring unique expertise to the project and money for publicising the RF technique at home and overseas conferences. Limited funds were also available for consumables to support the experimental programme.

Over the last three years the grant has provided new equipment that has facilitated experiments in the gas phase up to 50 bar and also liquid phase experiments where the degassing rig has been particularly important. Novel techniques have also been developed to study semi-conducting materials and RF methods have offered new insights into the shallow donor states recently discovered in II–VI materials.

Encouraged by these developments, interest in pulsed techniques from the wider user community has risen sharply over recent years, with a significant number of ISIS users now employing RF techniques in their own particular areas of research. The future for the RF-μSR technique at RAL, therefore, seems bright although further EPSRC funding, whether for technique development in general or focussed towards a particular theme, is clearly needed and was the subject of discussions during the meeting.

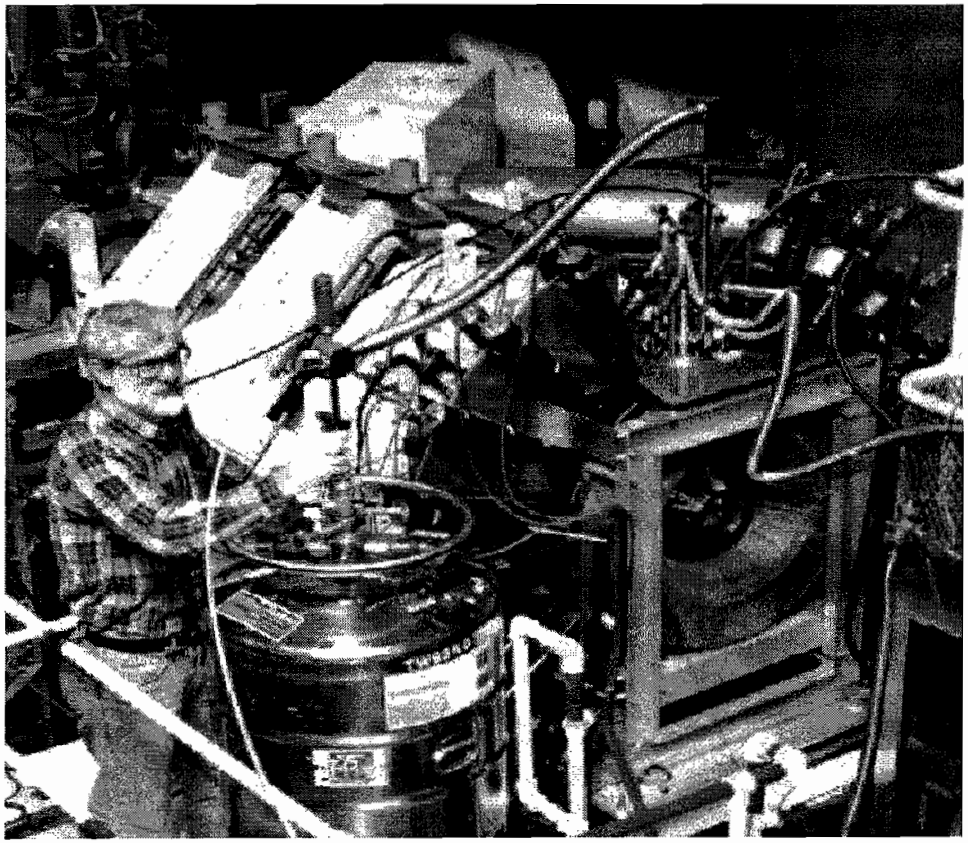
RF Collaboration Project Meeting

A variety of talks on investigations using
radio-frequency excitation and pulsed illumination
to study molecular systems and semiconductor materials

ISIS

Funding for RF-μSR (I)

EPSRC grant (~£270k) awarded 1997 to commission an RF spectrometer on the DEVA beamline.



The money also bought us a cryo-furnace, RF kit and special sample holders.

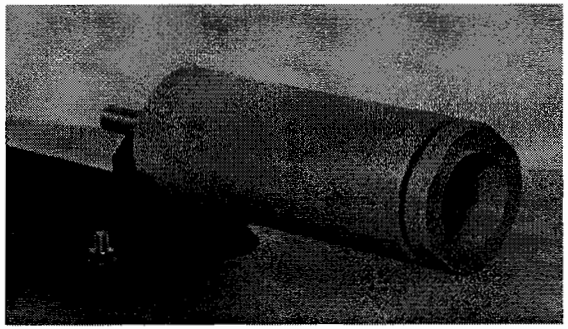
Funding for RF-μSR (II)

Follow-up EPSRC grant (~£800k) awarded December 2001(started 6th February 2002): scientific commissioning the RF spectrometer:

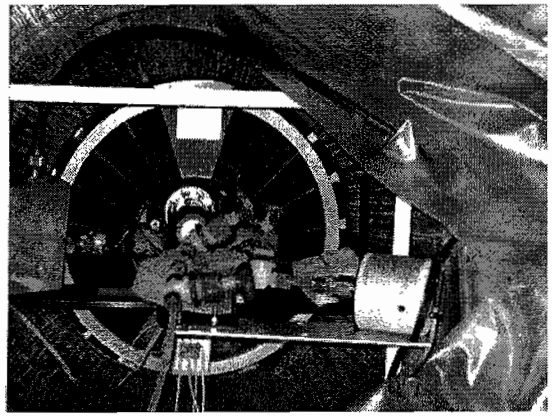
- Collaboration between RAL (Cottrell, King, Cox, Lord), UEA (Jayasooriya, Clayden), Leicester (Davis), Manchester (Connor).
- Funding for 48 days of beamtime over 3 years.
- Funding for a PDRA (Clive Johnson).
- Funding to bring two visiting fellows (Don Fleming and Rod Macrae) to the UK.
- Funding for consumables and kit to support experiments.
- Funding to attend conferences to publicise the technique.

New Equipment ...

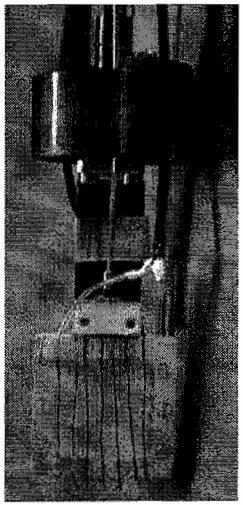
Gas cells and gas handling ...

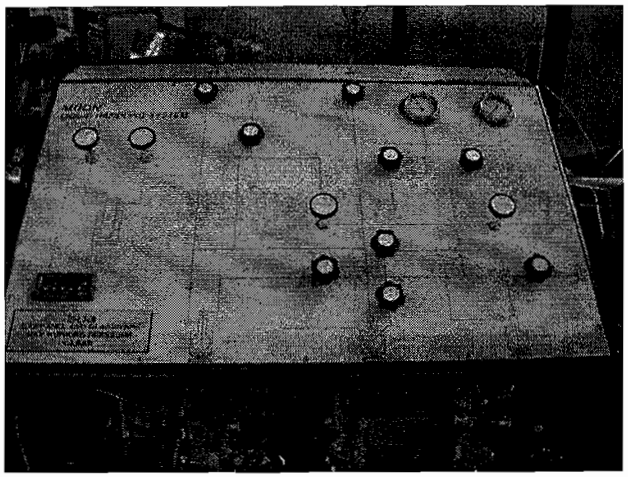


PEEK 10 - 50 bar



Liquid cells and liquid handling ...



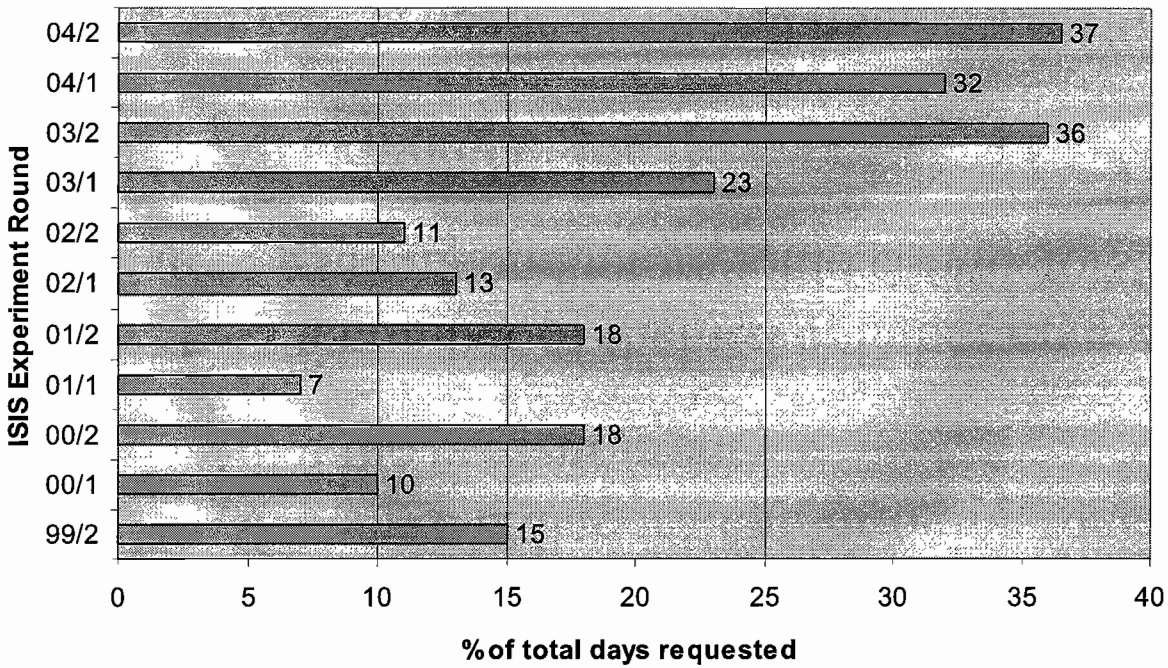


Deoxygenation of liquid by 'freeze-pump-thaw'

In-situ transfer and loading

New Interest in Pulsed techniques ...

Percentage of beamtime requests applying a pulsed stimulus ...



A Large fraction of these are RF experiments

Many groups are now using RF techniques:

Storchak/Eschencko (Russia/Switzerland), Carretta (Italy), Keren (Israel), Jayasooriya (UEA), Clayden (UEA), Yaouanc/Dalmas de Reotier (France), Lichti (USA), Ayres de Campos (Portugal), Fleming (Canada), Ghandi (Canada), Blundell (Oxford) and RAL (Cottrell/Cox/Johnson/King/Lord/Pratt).

Need to think about the future ...

... how to carry forward this work

A new EPSRC grant? If so, how should we structure it?

- As a large collaboration, bringing together all areas of work (like the present grant)
- As a number of themed collaborative grants (e.g. semiconductors/ionic conductors, chemistry/gases)
- As individual grants

A new grant is needed to bring manpower (PDRA) and money to the project, but it is now difficult for ISIS to apply for these things.

A new grant is probably best led by a University.

Mu reactions probed by RF-μSR

K. Ghandi (University of British Columbia)

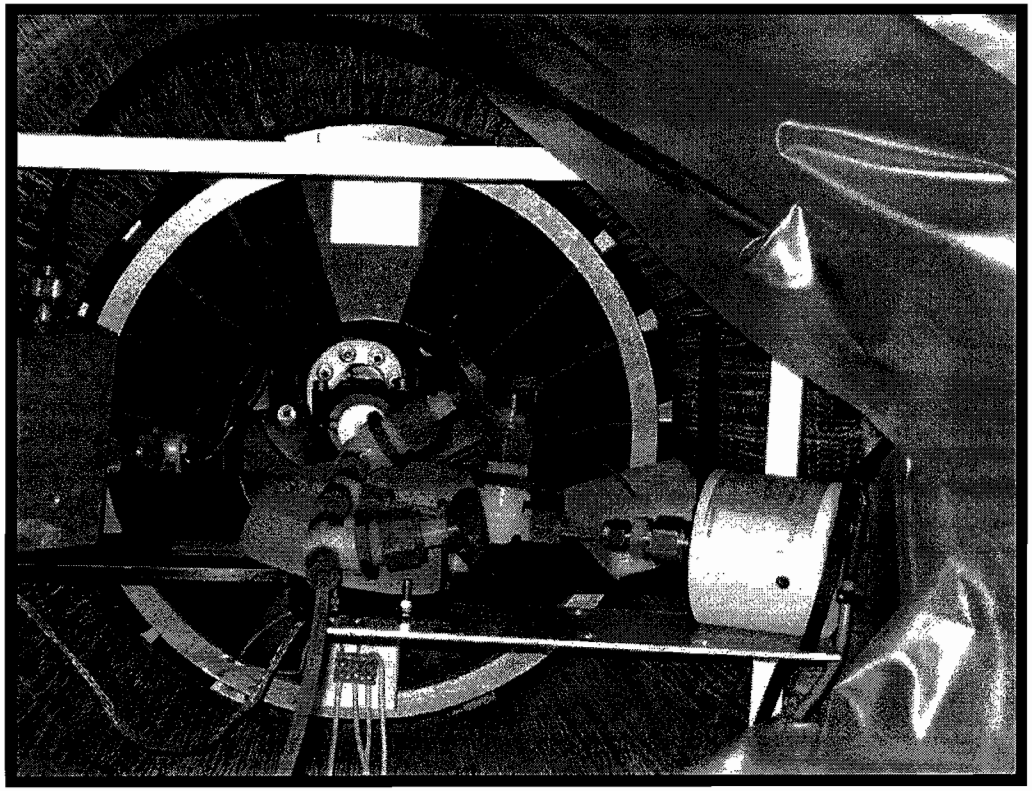
Summary

The study of muonium (Mu) chemistry has a long and distinguished past but there is still much which remains unknown. The mechanism of Mu formation, for example, along with its chemical dynamics relative to H and its chemistry in the excited state all present areas for future study.

Hydrogen abstraction reactions are important from both an industrial and mechanistic perspective and were the first examples of reaction dynamics chosen for investigation by RF-μSR in the present study. It was shown for the case of propane that Mu data obtained by either transverse field (TF) or RF measurements gave the same value for the rate constant. In addition, the application of the delayed RF technique allowed the build-up of the diamagnetic product of the reaction to be observed directly – its rate consistent with the Mu data. However, in the case of isobutane, delayed RF measurements showed no change in the diamagnetic signal over time even though the Mu data was consistent with that obtained by TF measurements showing that Mu was reacting. Such a result suggests that the Mu atom is selecting a different reaction channel to that of H.

Future directions for this work include the study of muonium with Br_2 (an initial TF-μSR experiment suggests the presence of a radical for which several structures can be proposed) along with a range of Mu/hydrocarbon and Mu/Halogen reactions.

Reactions Probed by RFμSR



Presented by: Khashayar Ghandi

Plan of the talk

- Gaps, where conventional Mu chemistry does not have a say
- RF-μSR: Results in the gas phase
- RF-μSR: Interesting(?) future experiments

Gaps in our knowledge about Mu chemistry

- Mu formation: mechanism mostly unknown

- Excited state Mu chemistry

- Chemical dynamics through different channels: Mu compared to H; different products?

1. Physical stage

Ionization, electronic Excitation and Hot reactions <10^{-14} sec

2. Physico-chemical stage

charge exchange depends on density:

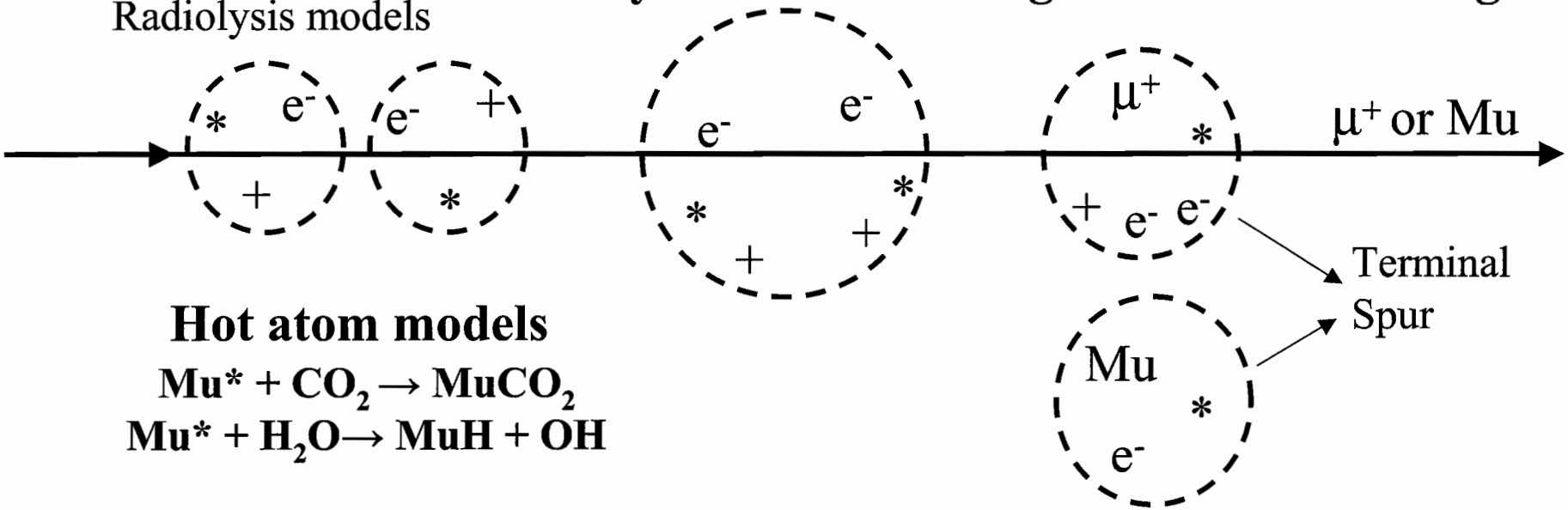
At density ~ 1 g/ml

$$\mu^+ + M \xrightarrow{\sigma 10} Mu + M^+$$
$$Mu + M \xrightarrow{\sigma 01} \mu^+ + M + e^-$$

< 1 ps

3. Physico-chemical stage and Chemical stage

3
Radiolysis models

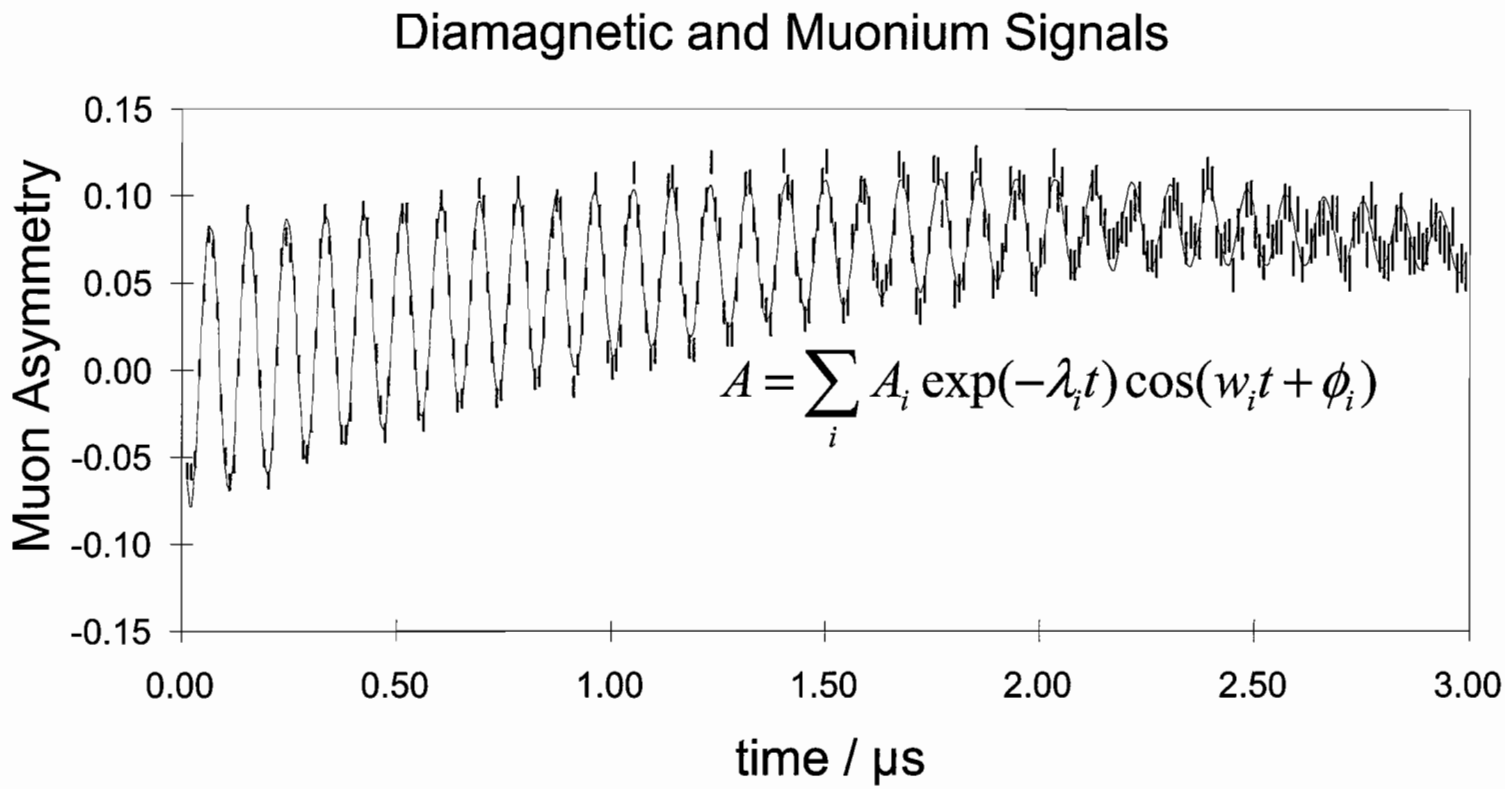


Hot atom models

$$Mu^* + CO_2 \rightarrow MuCO_2$$
$$Mu^* + H_2O \rightarrow MuH + OH$$

Mu + A → Product

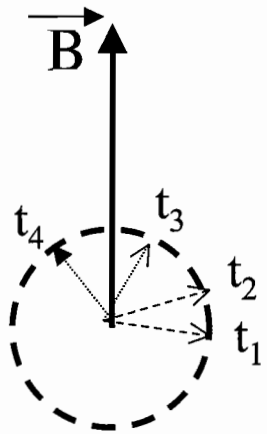
Can we assume the *same* reaction path for Mu and H ***always***?



We may **think** so, (same electronic PES), but we **DO NOT KNOW**

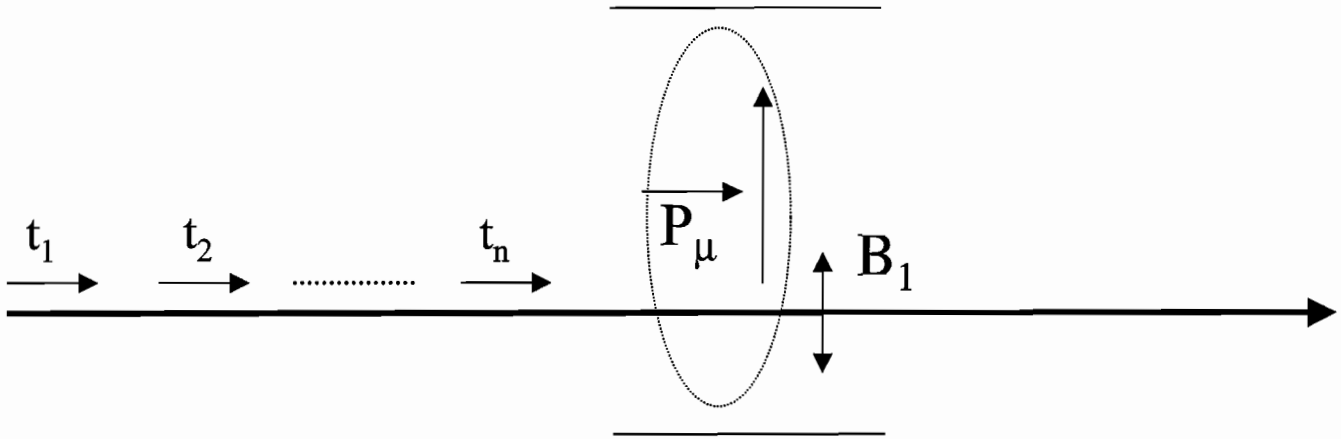
So far all information have been from TF experiments.

TF



Spin dephasing → Can't say what is the product

RF



No spin dephasing → Can determine **magnetic state** of the product, but can't characterize it at the molecular level: **Future: laser-RF-μSR**

Why did we choose 'hydrogen abstraction' reactions as our first examples of RF studies of reaction dynamics

- Important in cracking of alkenes & saturated hydrocarbons

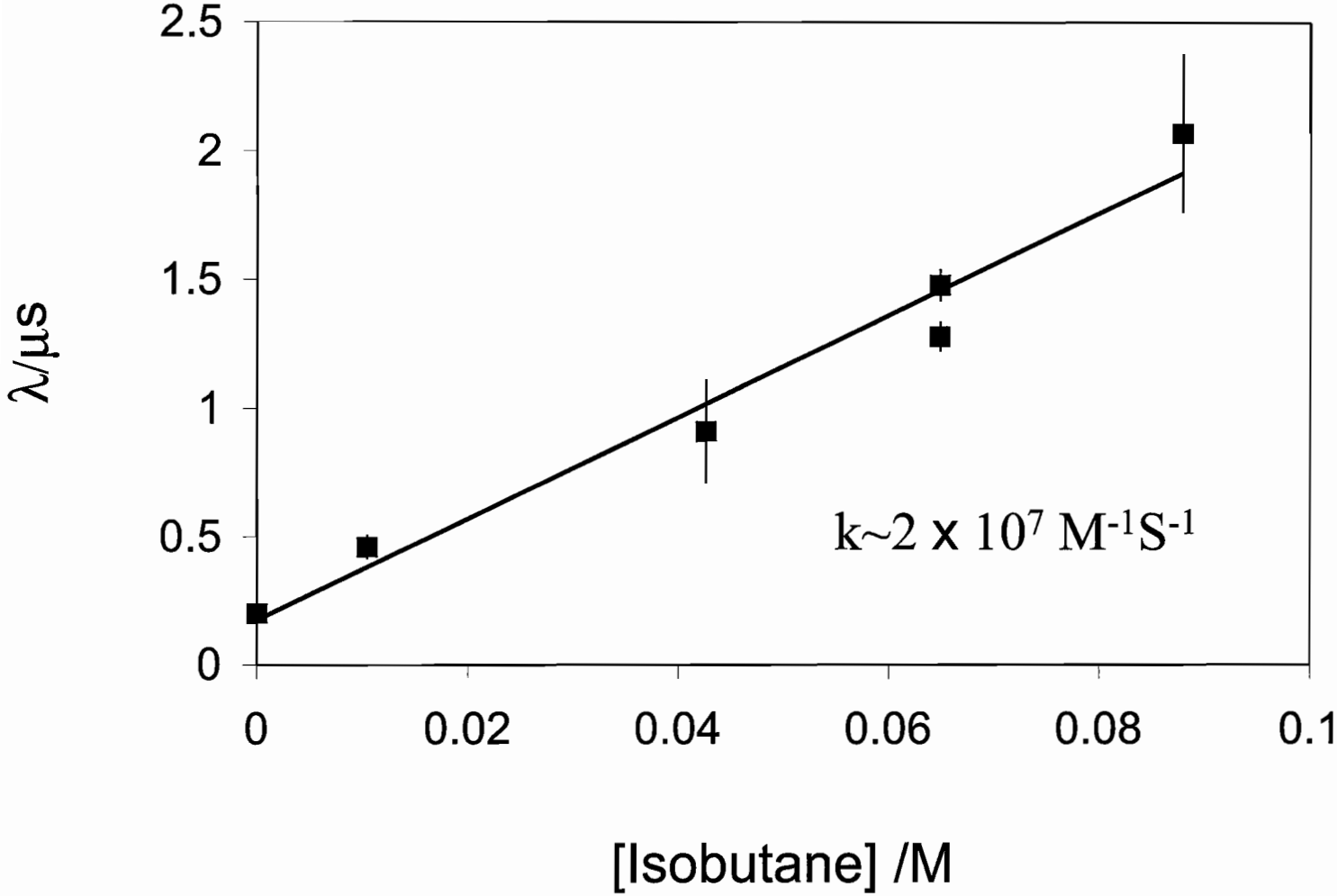
- Important in combustion

- We could select reactions with the same mechanisms but with orders of magnitudes different rate constants (HBr vs. propane)

- Involves multiple potential energy surfaces

$$Mu + RH \rightarrow MuH + R\bullet$$
$$Mu + RH \rightarrow MuR + H\bullet$$
$$Mu + RH \rightarrow MuRH\bullet \rightarrow Mu + RH$$
$$Mu + RH \rightarrow MuRH\bullet \rightarrow H + RMu$$

How do we measure rate constant in TF



Slope: rate constant

Offset: Back ground relaxation; field inhomogeneity

In our case R is Mu

$Mu + CH_4 \rightarrow MuH + CH_3^{\bullet}$ k_1

reaction rate only measurable at T>300°C

$Mu + C_2H_6 \rightarrow MuH + C_2H_5^{\bullet}$ k_2

reaction rate only measurable at T>200°C

~RT $k_2/k_1=10^5$

Primary reactions: all slow, longer chains, faster abstraction

$H + CH_3\text{-}CH_2\text{-}CH_3 \rightarrow H_2 + CH_3\text{-}CH\text{-}CH_3$

$Mu + CH_3\text{-}CH_2\text{-}CH_3 \rightarrow MuH + CH_3\text{-}CH\text{-}CH_3$

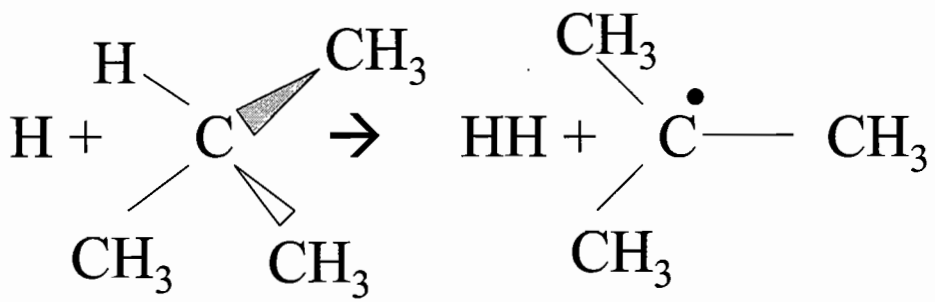
Secondary H-atom abstraction, should be faster than primary

TF for Mu $k \sim 1 \times 10^6\ M^{-1}S^{-1}$ (10^5 times faster than ethane) at RT

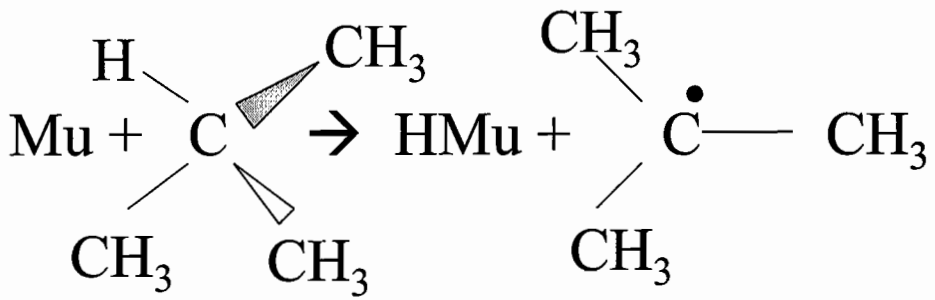
$$H + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow H_2 + CH_3\text{-}CH\text{-}CH_2\text{-}CH_3$$

$$Mu + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow MuH + CH_3\text{-}CH\text{-}CH_2\text{-}CH_3$$

TF & RF for Mu $k \sim 0.5 \times 10^7\ M^{-1}S^{-1}$ (5 times faster than propane) at RT



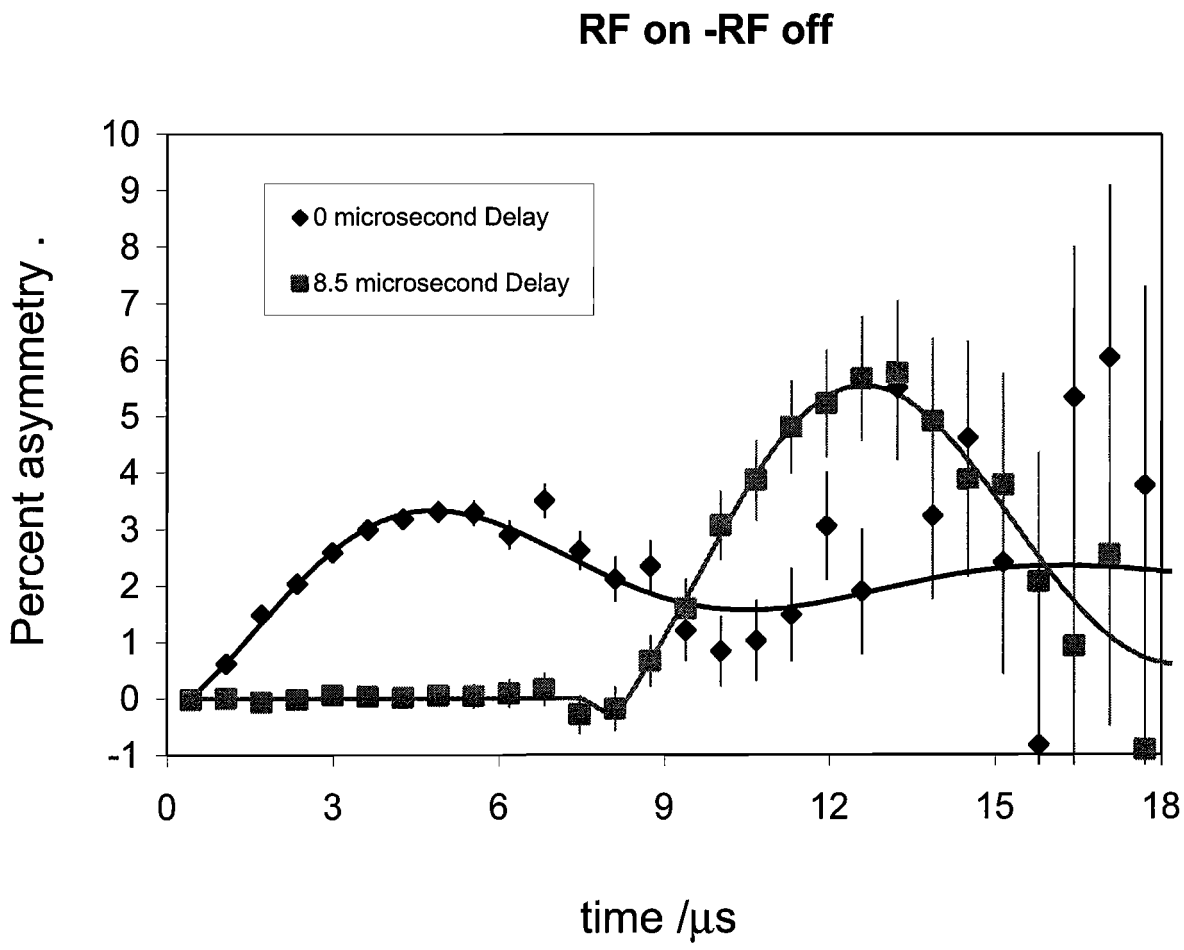
Tertiary H-atom abstraction, should be faster than secondary;



No experimental study, but theory predicts for H atom ~ 30 times faster than propane at RT

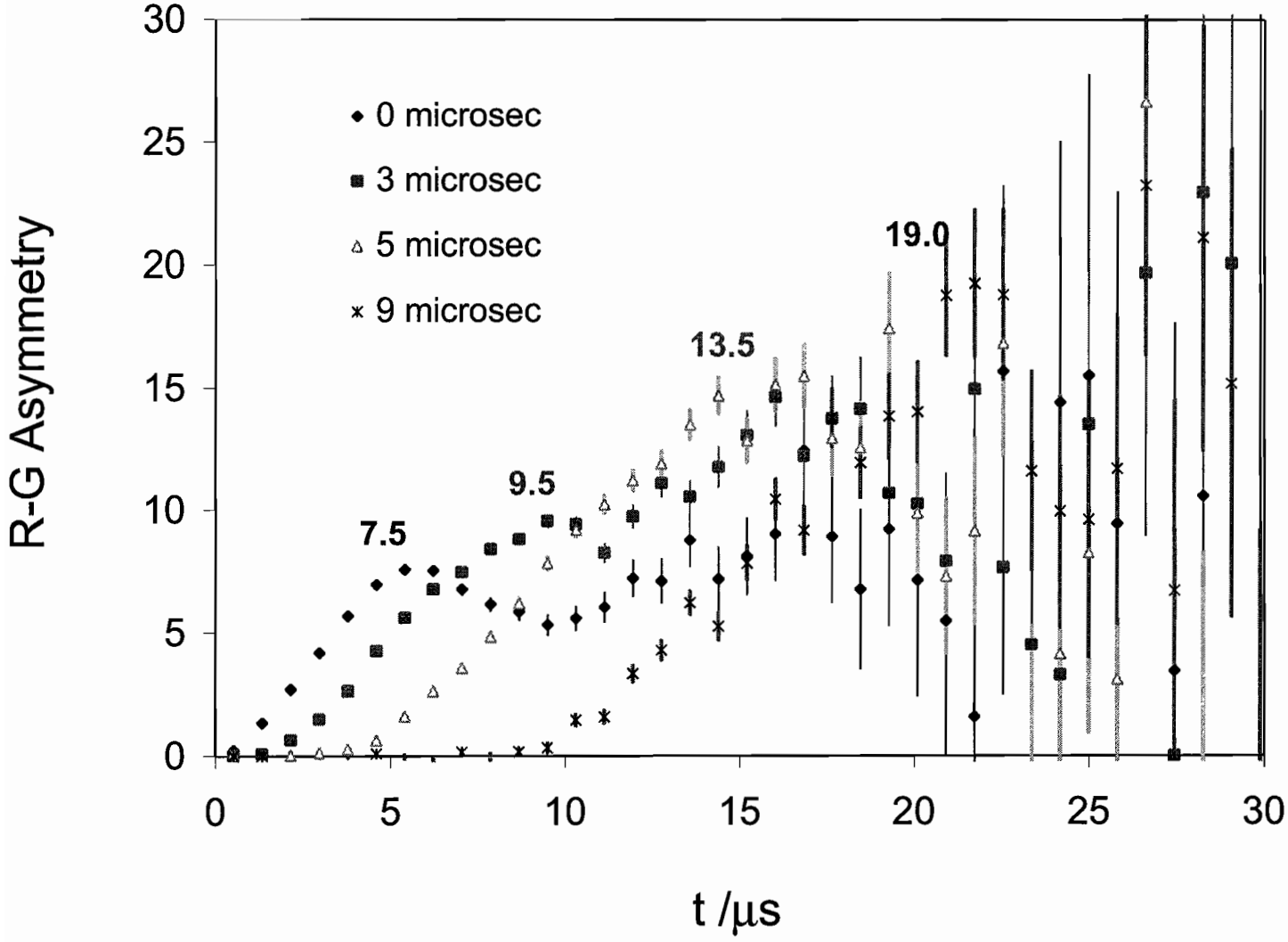
TF for Mu $k \sim 2 \times 10^7\ M^{-1}S^{-1}$ (~35 times faster than propane) at RT

Diamagnetic product?



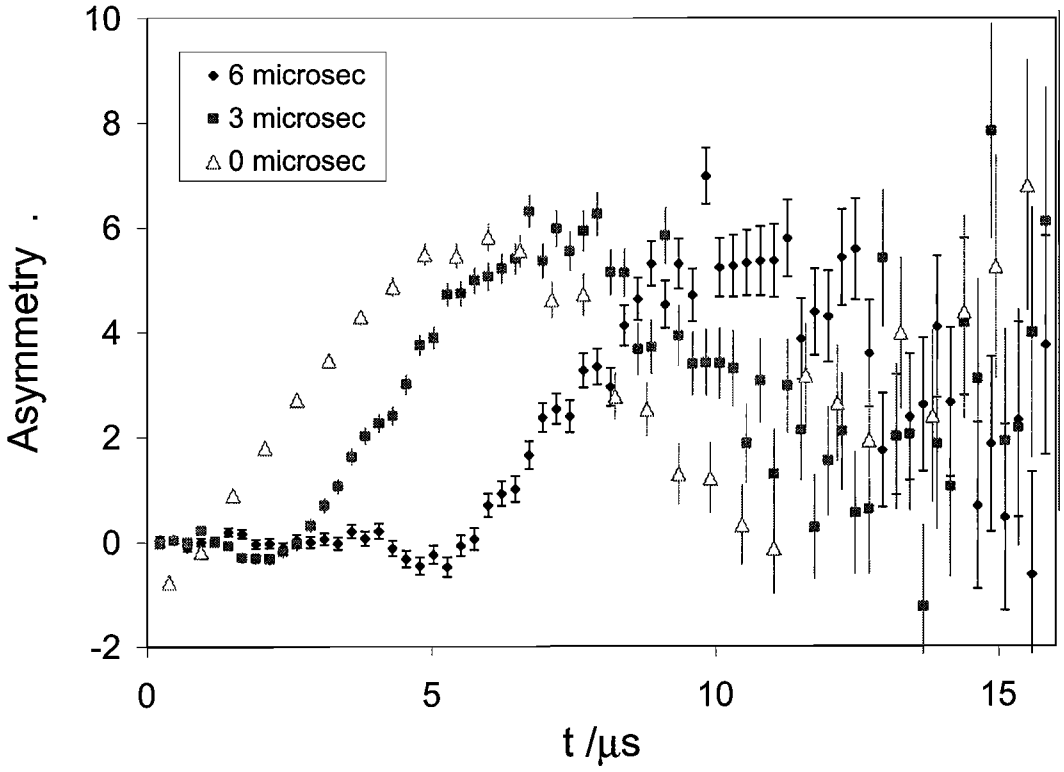
$$\mathbf{Mu + RH \rightarrow MuH + R}$$

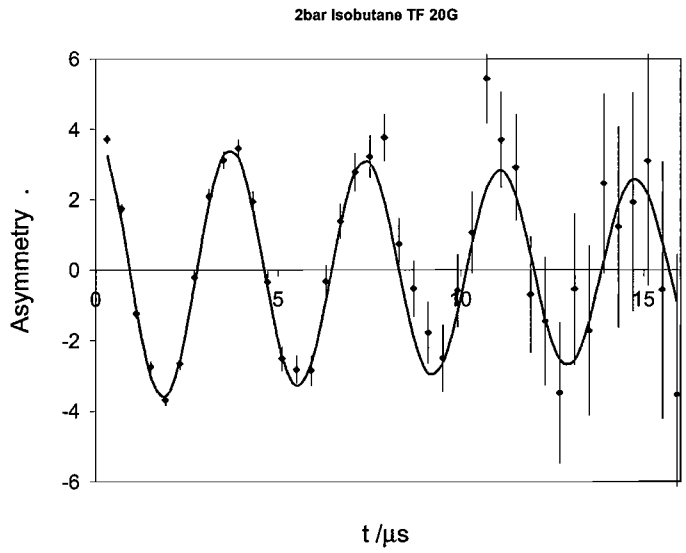
Diamagnetic product?



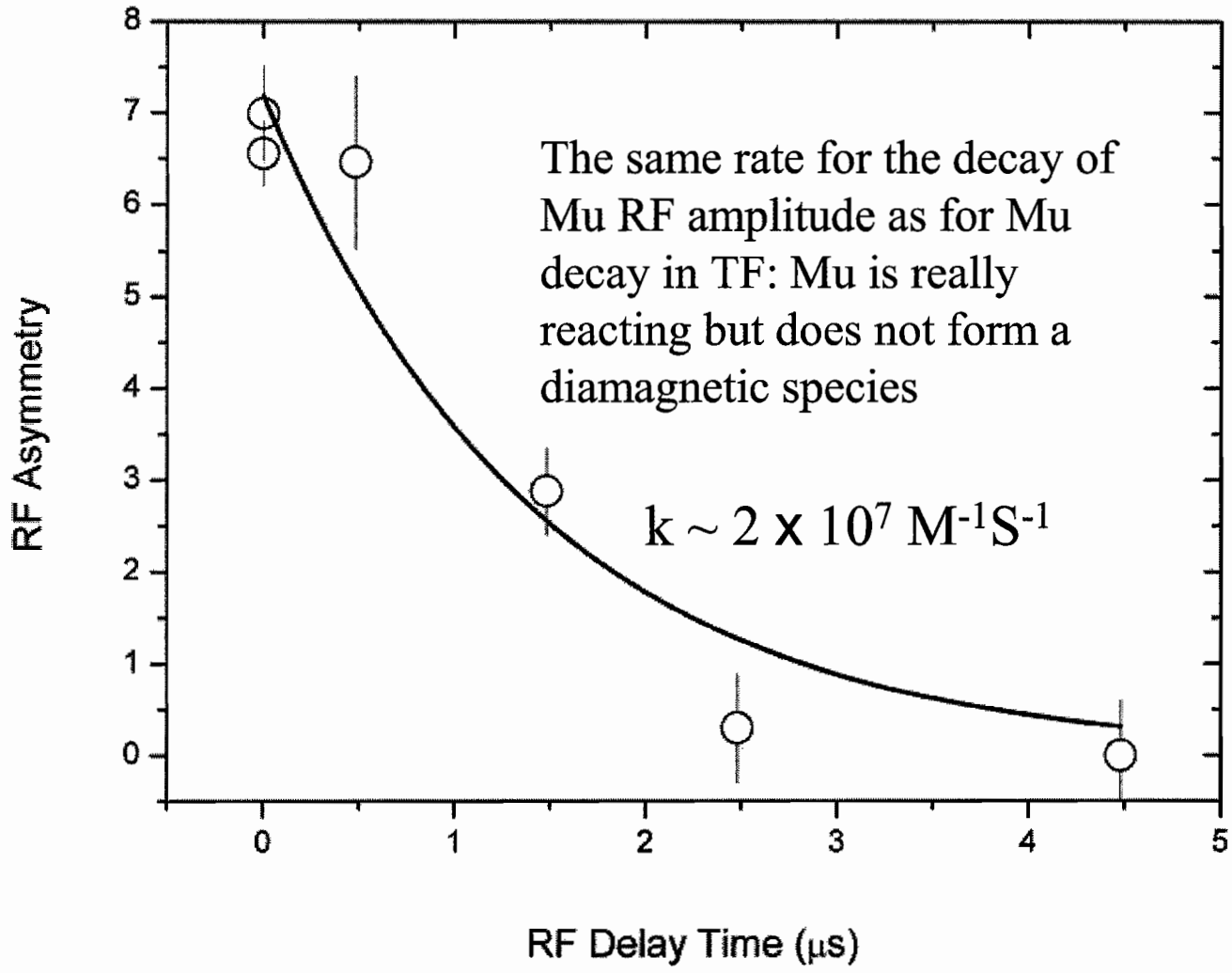
Mu + RH → MuH + R

Diamagnetic product?



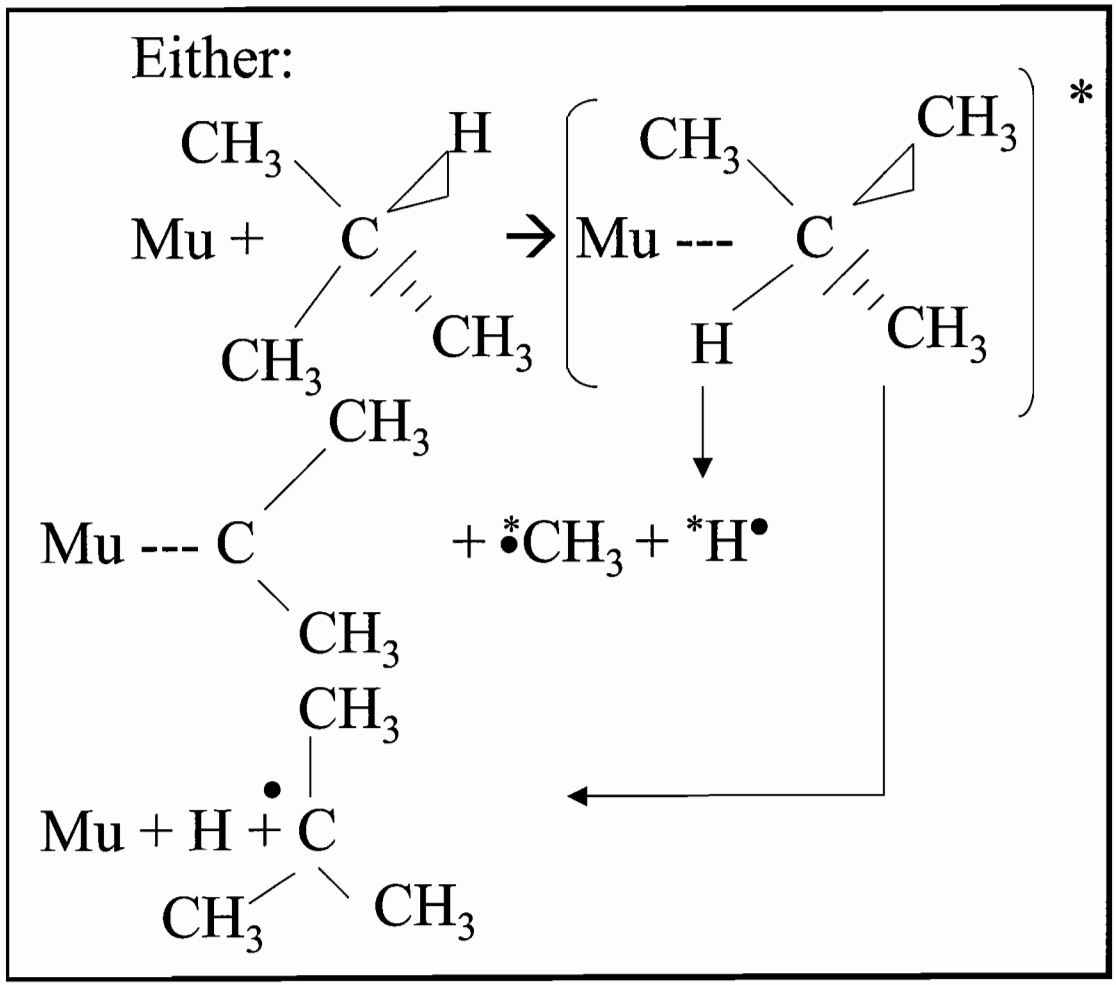


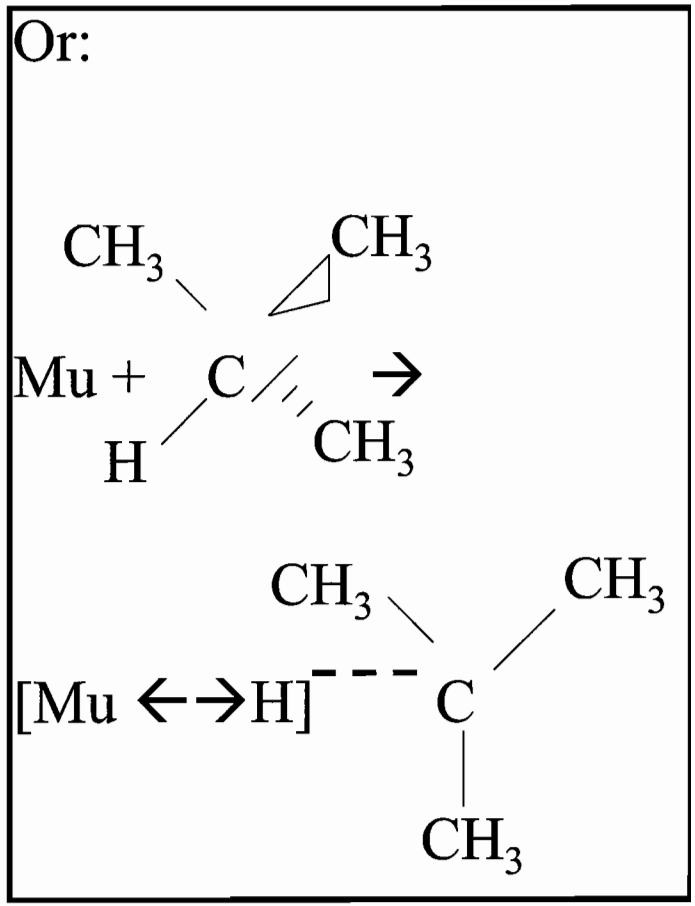
Is there any thing wrong with the RF system: RF Mu resonance



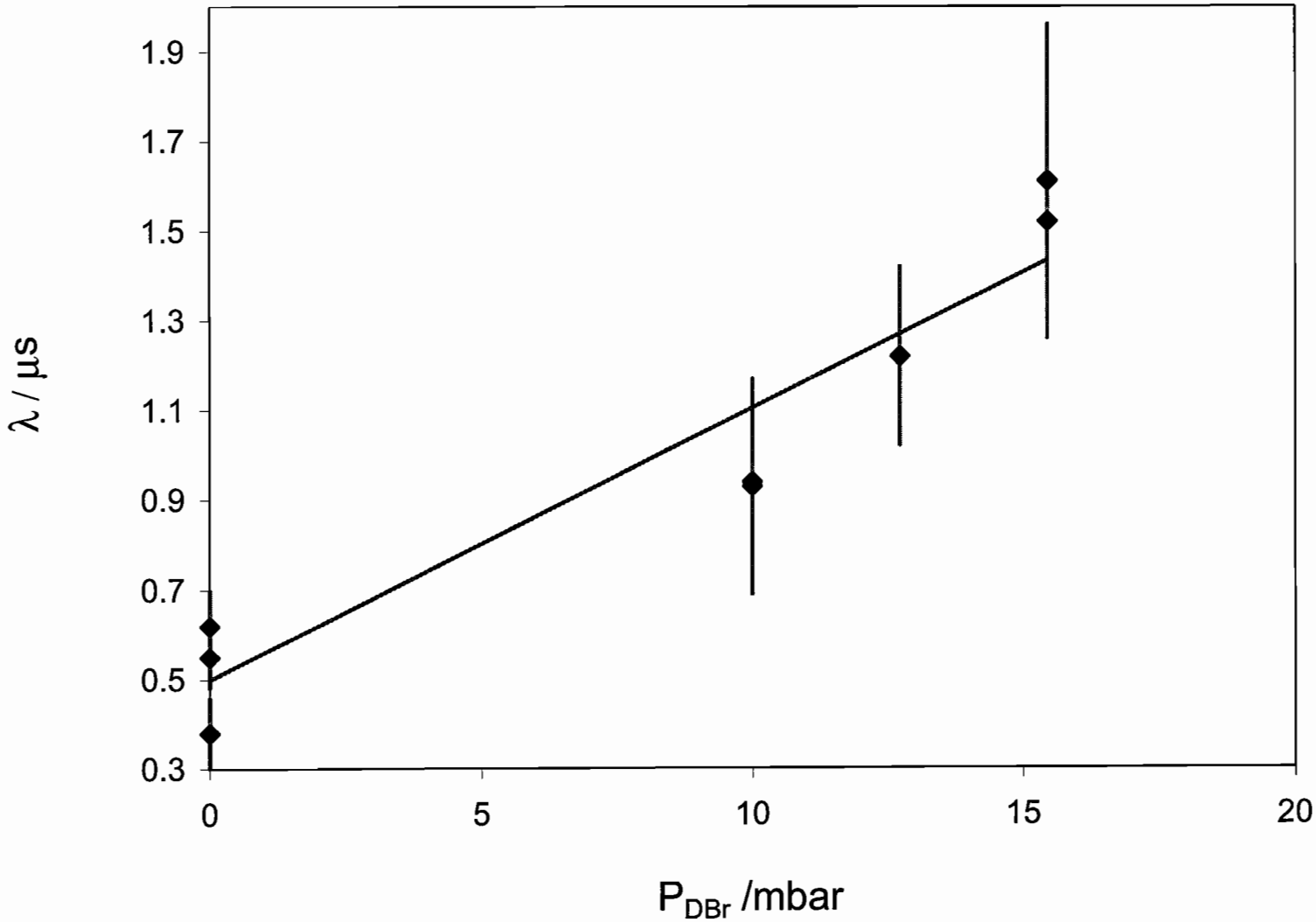
What is happening?

Mu is selecting a different channel compared to H => a dynamic effect or some channels are available to Mu via tunnelling

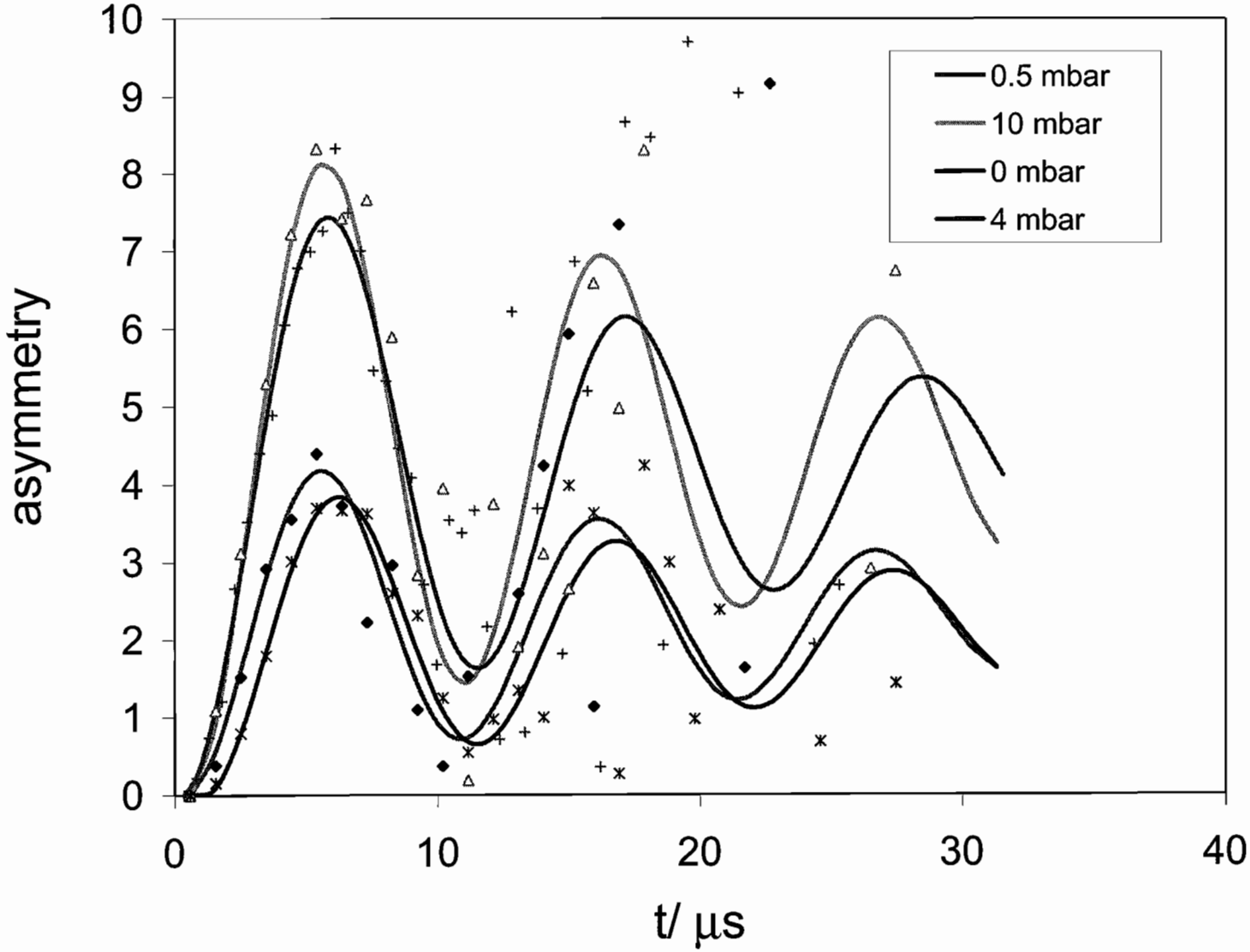




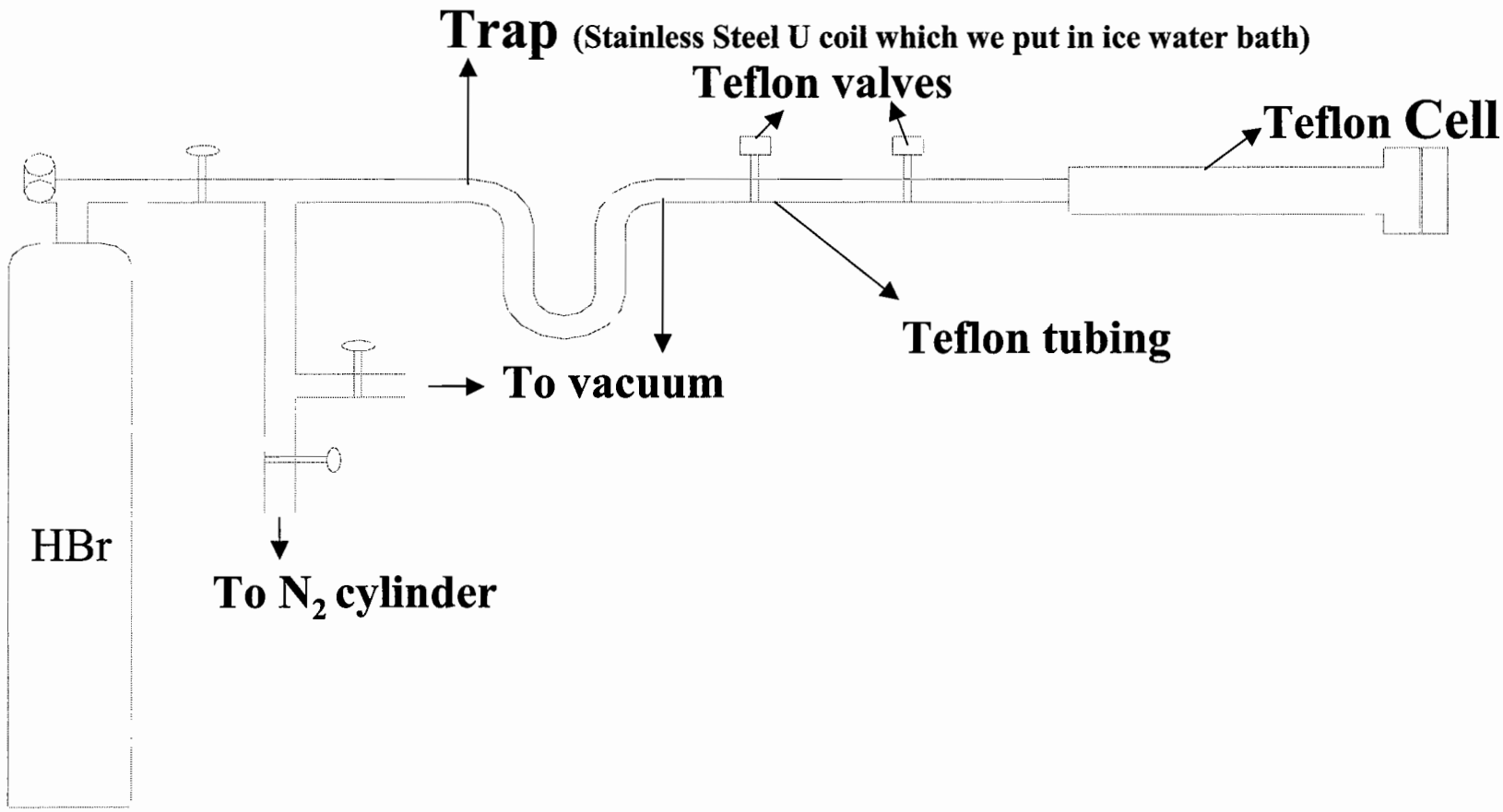
Mu + DBr → ?



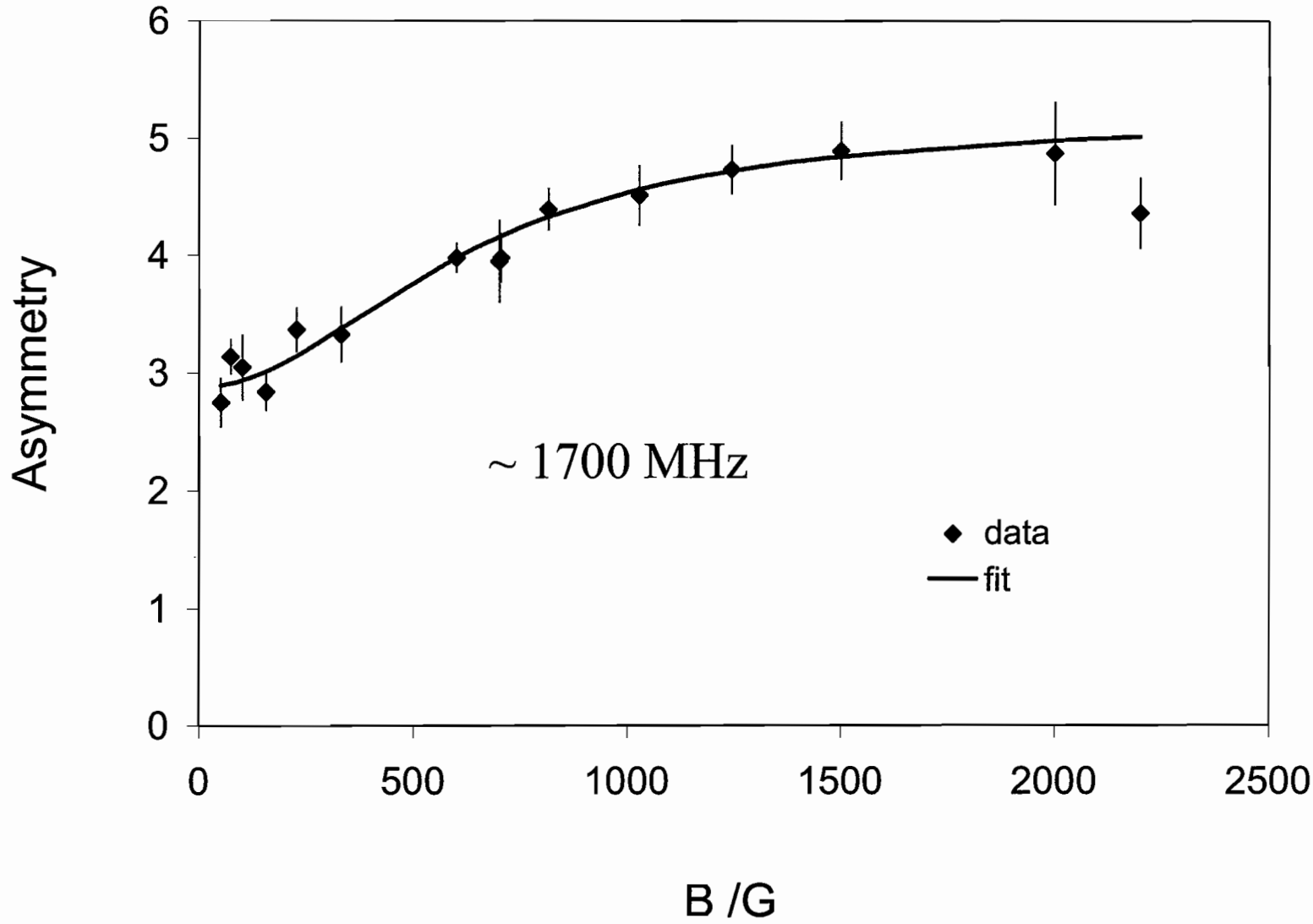
Diamagnetic product?



FUTURE: Specific examples of fundamental interest



FUTURE: Specific examples of fundamental interest



FUTURE: Specific examples of fundamental interest

Diamagnetic

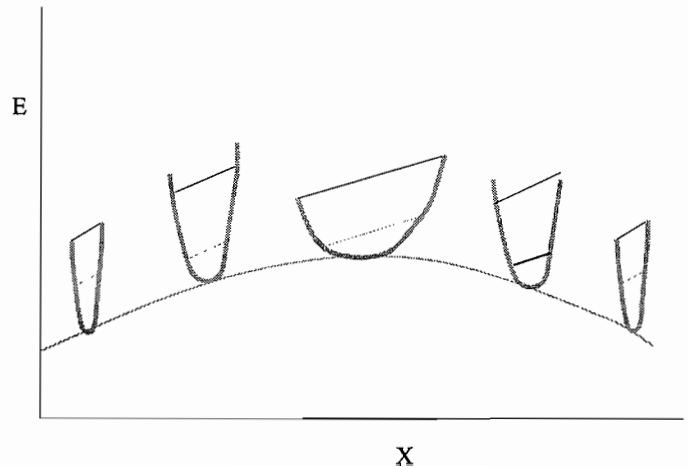
- $Mu + X_2$: Branching ratio for reactions: $Mu + X_2 \rightarrow MuX + X$

$Mu + X_2 \rightarrow MuX_2$ $\quad$ $Mu + X_2 \rightarrow XMuX$

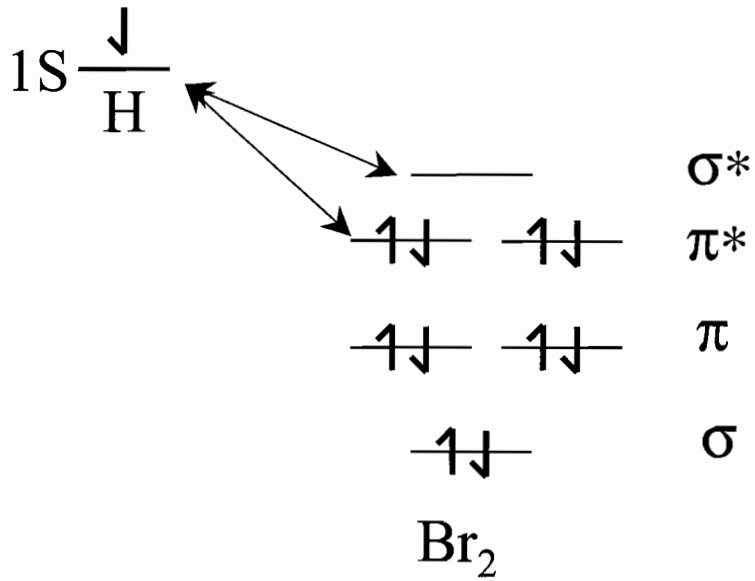
weak-complex free radicals

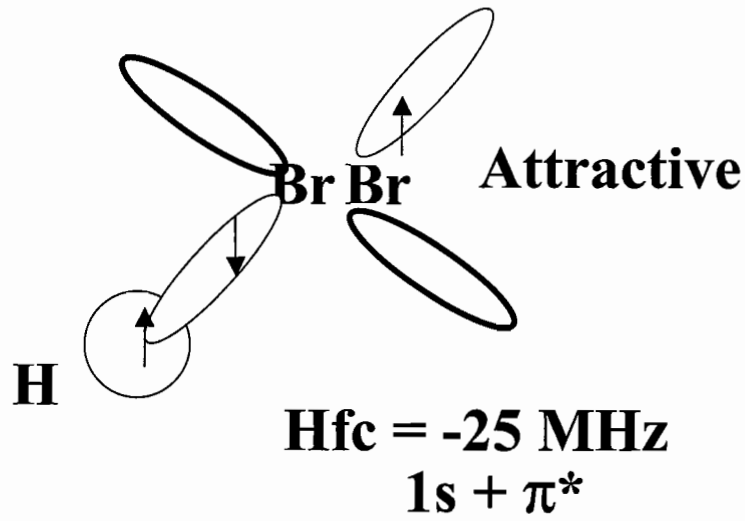
Vibrational bond: vibration of the nuclei in a system leads to a minimum (potential well) at a point where ***is not*** a minimum on an electronic potential energy surface

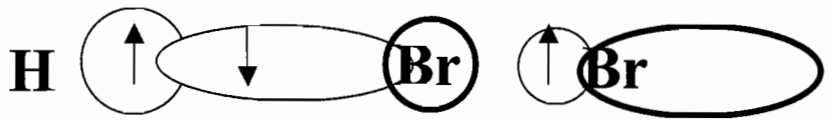
20 years ago predicted by Connor (U. of Manchester), Clary (Oxford),



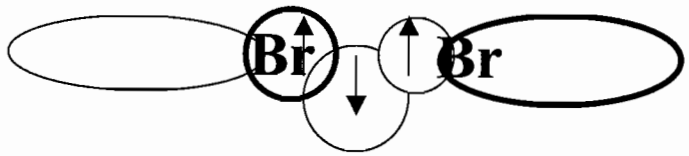
FUTURE: Specific examples of fundamental interest







Hfc = -450 MHz



Repulsive (not electronically bound)

H
1s + σ*

FUTURE: Specific examples of fundamental interest

- Would the 'to be formed' free radical linear, non linear or a vibrational bound
  vibrational bound => symmetric => one Br hfc
  => one coupling in RF, Also the Aμ should be large
  Aμ > 400 MHz
- Distinguish between the other two radicals by magnitude of the Aμ

The most stable

Aμ = –25.4 MHz

Mu

Br——Br

ΔE ~ 6.2 kcal/mol
~ 0.27 eV

Aμ = –3.07 MHz

Br —— Mu ——Br

ΔE ~ 13 kcal/mol
~ 0.55 eV

Aμ = –448 MHz

Br——Mu——Br

FUTURE

- Study H abstraction reactions at different temperatures

⇩

Activation energy

⇩

Comparison of activation energy with reactions of CH_4 and C_2H_6: another piece of information to distinguish different channels

- H-abstraction reactions from alkanes are late barrier reactions

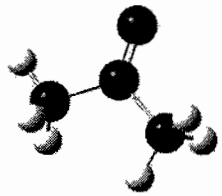
=> Study early barrier reactions

- Compare other branched and non-branched hydrocarbons: is it an effect of the branched chain?

- Other type of chemical reactions: should we rely on inferred mechanisms?

FUTURE: Specific examples related to environmental chemistry

- study of Mu+ CH_3-CH_2-CH_2-CH_2-CH_3, Mu+ CH_3-$CH(CH_3)$-CH_2-CH_3, CH_3-$C(CH_3)_2$-CH_3 and cyclic hydrocarbons

- study of the Mu +  reaction in the gas and liquid phase: Muoniated-radical forms; the hfcs ~ 30 MHz so it should be easy to measure the branching ratio of radical / MuH with delayed -RF measurement

FUTURE: Specific examples of fundamental interest

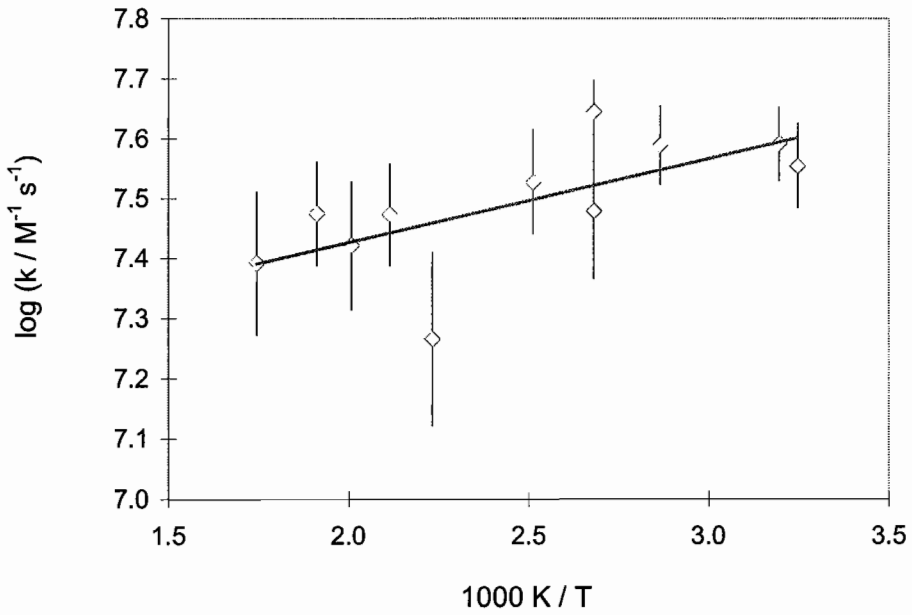


Figure Arrhenius plot for reaction of Mu and I in water obtained by measurement of reaction rates with TF μSR technique

The source of this negative temperature dependence cannot be completely understood by conventional continuous muon beam techniques due to complex mechanism (probably):

$$Mu + X^- \leftrightarrow \underset{\text{3400 MHz}}{Mu\,X^-} \rightarrow \underset{\text{Diamagnetic}}{\mu^+_{(aq)}} + X^- + e^-_{(aq)}$$

$$Mu\,X^- \rightarrow MuX + e^-_{(aq)}$$

Thanks

- Organizers of the workshop
- Dr. S. Cottrell, Dr. C. Johnson, Dr. J. Lord, Professor D. Fleming.
- Dr. P. King, Professor S. Cox
- **Centre for Molecular Structure and Dynamics $**
- Users support (J. Dreyer and his group)
- Sample safety support (Matthew Dickson)
- TRIUMF machine shop

Review of RF measurements in semiconductors

S.F.J. Cox (RAL)

Summary

Early TF-μSR work using muonium (Mu), a model for hydrogen, in semiconductors, has revealed the presence of an atomic-like state in quartz and two Mu species in silicon with very different hyperfine couplings. More recently, evidence for a shallow donor state in ZnO has been detected and subsequently confirmed for H by ENDOR.

The application of RF-μSR to the study of both quartz and silicon has confirmed the results of TF measurements. However, the power of this technique lies in its ability to analyse final state species providing new information on muonium dynamics in these materials. It can also been combined with the application of an electric field in order to analyse the resulting final state after initial state modification.

The development of a double-resonance ESR-μSR technique has allowed g-factors for the shallow-donor states in a range of semiconductors to be determined in good agreement with literature values. However, for a determination of the sign of this value a rotating RF field is required. Initial results of experiments using circular RF polarisation were presented.

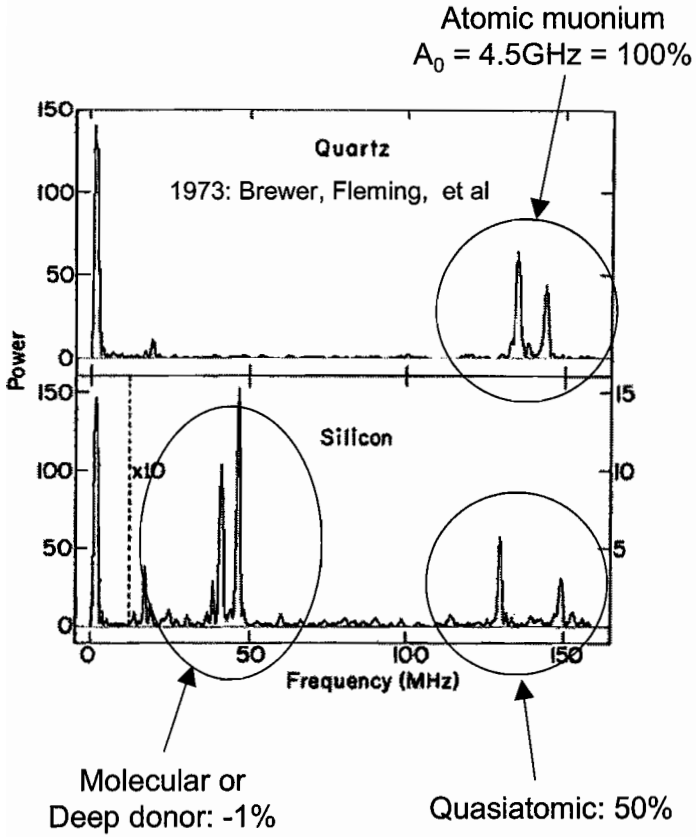
In addition, the double-resonance RF technique can decouple Mu from neighbouring spins allowing the study of diffusion, trapping and final state formation in a range of oxides and halides. Finally, the possibility of modifying the hyperfine coupling of interstitial Mu by lattice vibrations induced by acoustic resonance was introduced as an area for future work.

RF resonance in electronic materials

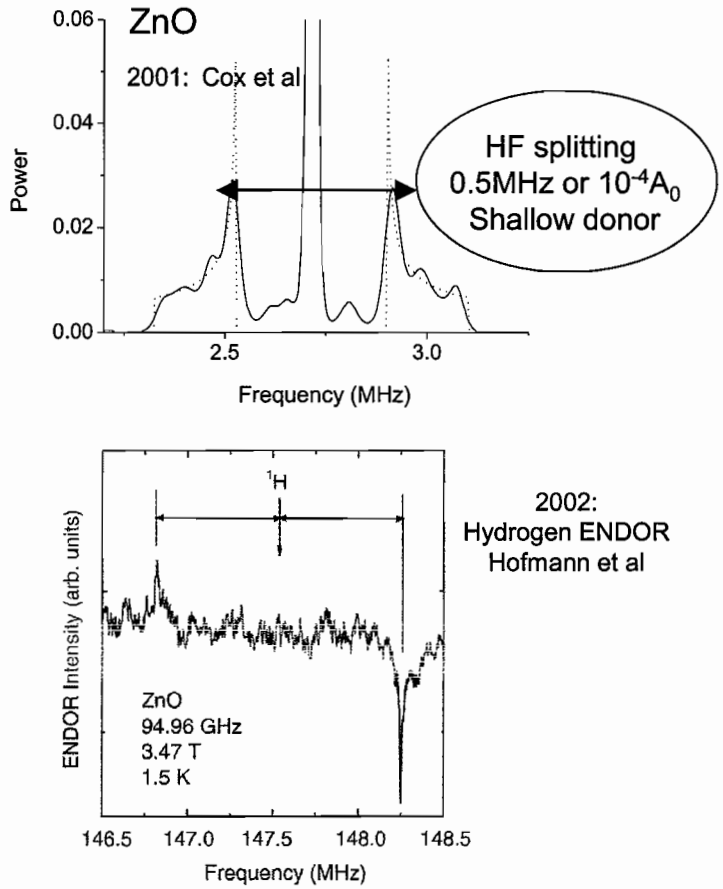
Muonium as a model for hydrogen in

- Semiconductors (Si, GaAs...)
- Widegaps (CdS, ZnO...)
- High-κ dielectrics (ZrO_2, HfO_2...)

Muonium spectroscopy

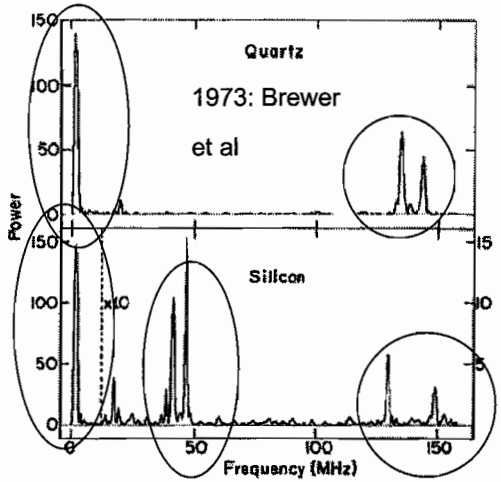


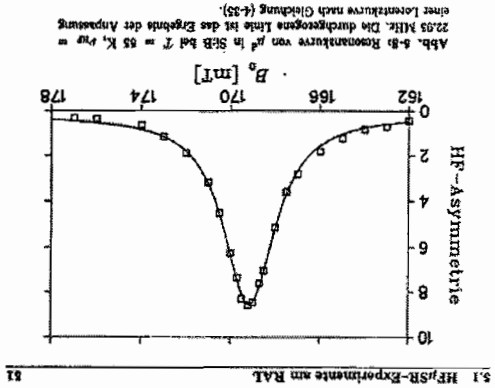
TF muon spin rotation

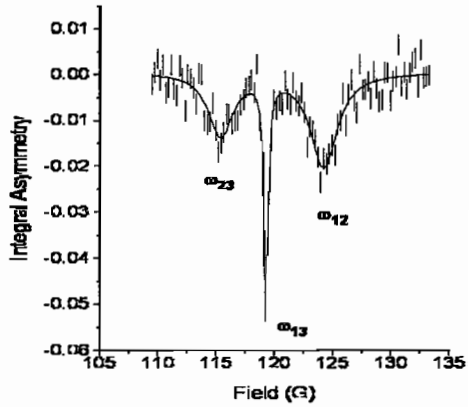


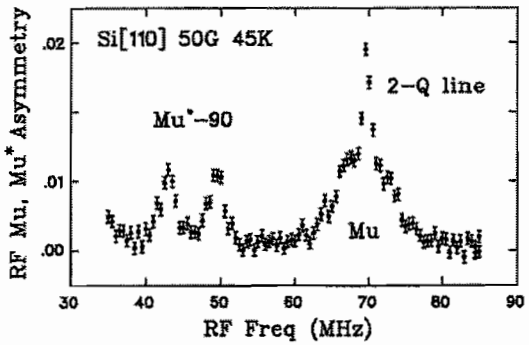
Muonium spectroscopy

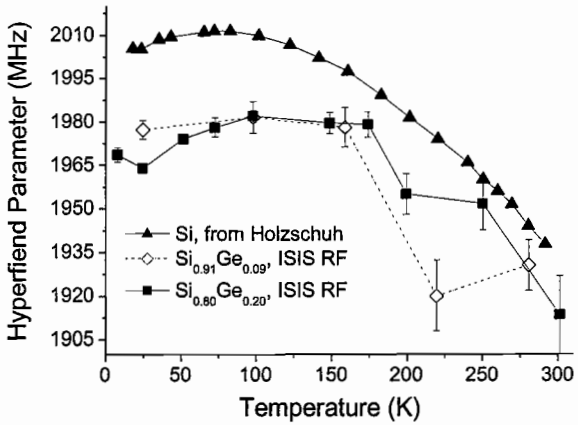
RF Resonance











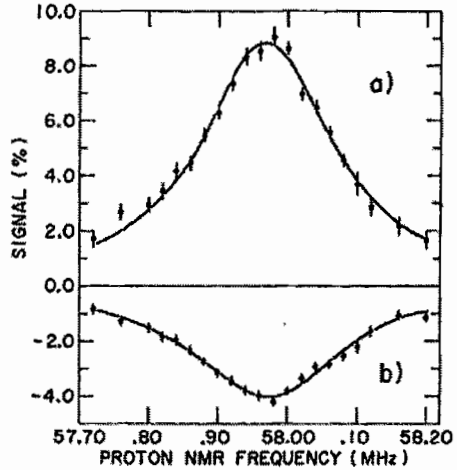


FIG. 2. A resonance line for transition ν_{12} in a 1.7-atm Kr target, for (a) backward and (b) forward positron decay. The solid line is a least-squares fit of a Lorentzian curve to the data. The linewidth is 55 G and arises from the muon decay and power broadening. The data shown were obtained in 11 h.

equation, $\nu(D)=\nu(0)(1+aD)$, after a small correction (2 parts in 10^7 at 5.3 atm) was made for the known quadratic density dependence.[7] The results of the density fits are

$$\begin{aligned} &\nu_{12}(0)=1917\,654.15(33)\ \text{kHz},\\ &a_{12}=-16.211(80)\ \text{kHz/atm (Kr, 0°C)};\\ &\nu_{34}(0)=2545\,648.20(36)\ \text{kHz},\\ &a_{34}=-19.779(86)\ \text{kHz/atm (Kr, 0°C)}. \end{aligned} \tag{5}$$

The zero-density values of ν_{12} and ν_{34} may be combined, with the use of Eqs. (3) and (4), to yield

$$\Delta\nu=4463\,302.35(52)\ \text{kHz (0.12 ppm)}, \tag{6}$$

$$\mu_\mu/\mu_p=3.183\,3403(44)\ \text{(1.4 ppm)}, \tag{7}$$

Muonium dynamics and electrical activity

Stuttgart at ISIS

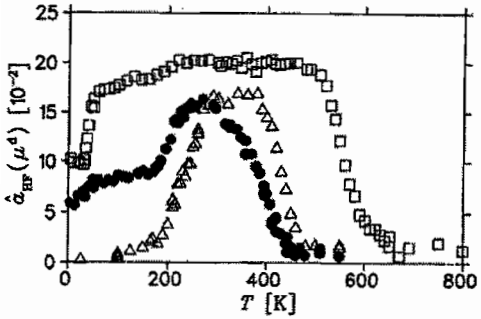
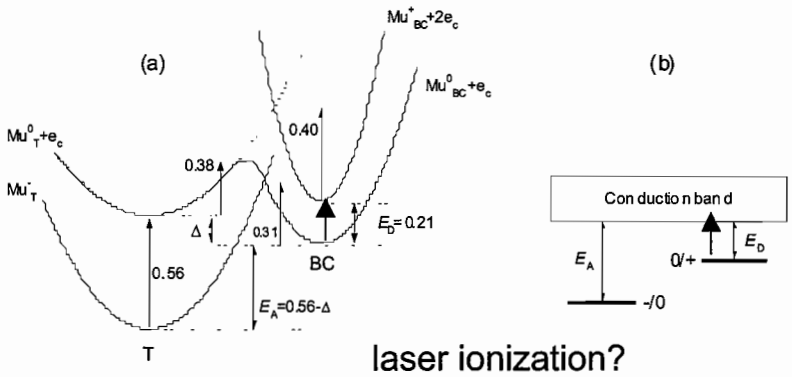


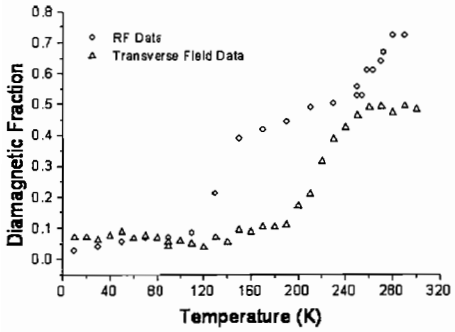
Abb. 6-1: Temperaturabhängigkeit der Resonanz-HF-Asymmetrie $\hat{a}_{RF}(T)$ von μ^4 in Silizium (ν_{HF} = 20.25 MHz, B_0 = 149.5 mT). Die volle Strahlasymmetrie beträgt a_{Strahl} = 0.24.
□: Si:B, $B_0 \parallel \langle 111 \rangle$.
•: Si:P(FZ), $B_0 \parallel \langle 111 \rangle$.
Δ: Si(I), $B_0 \parallel \langle 100 \rangle$.

TRIUMF 'standard model'

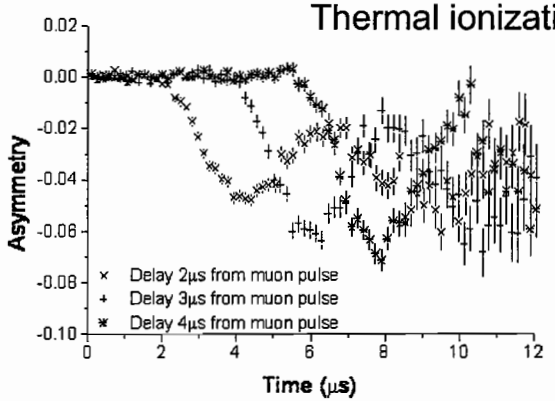


laser ionization?

ISIS at ISIS



Thermal ionization question



RF: analyses for final state
EF: modifies initial state!

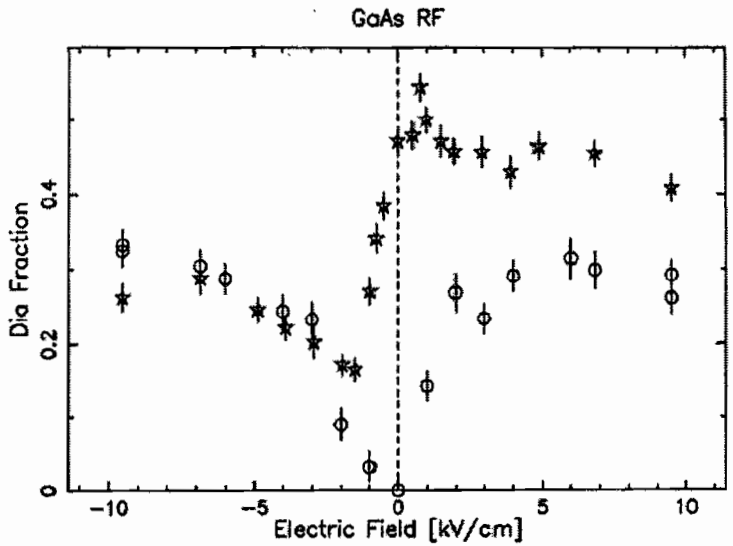
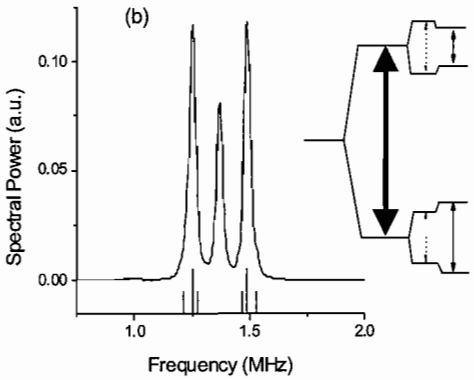
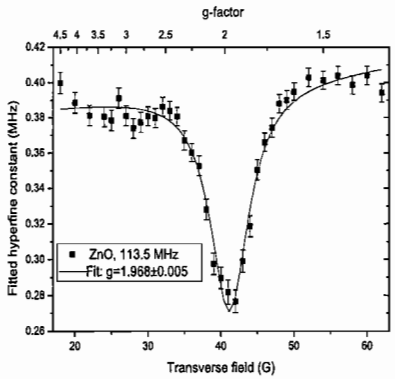
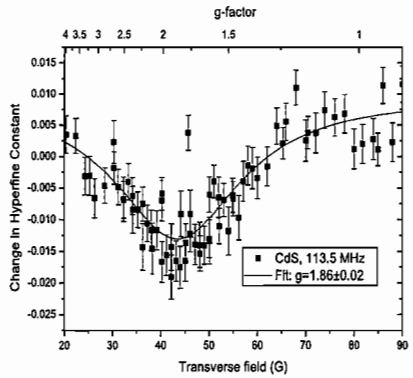


Fig. 2. Diamagnetic RF fraction in semi-insulating GaAs as a function of electric field. Circles: $T = 15$ K; stars: $T = 61.5$ K. Positive electric field is in the direction of the initial muon beam momentum.

ESR-μSR double resonance: g-factor determination

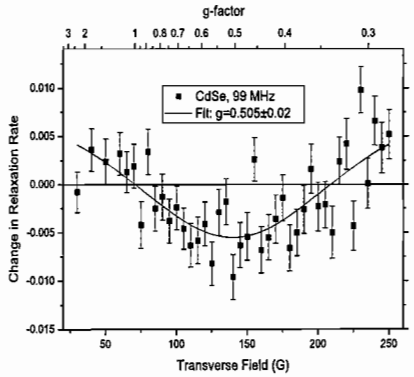


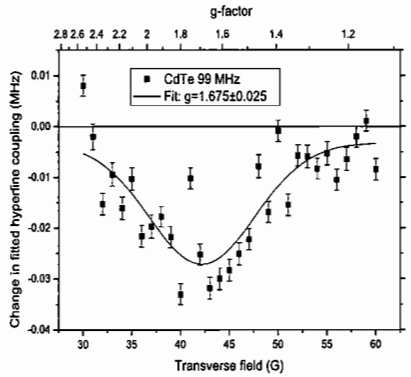




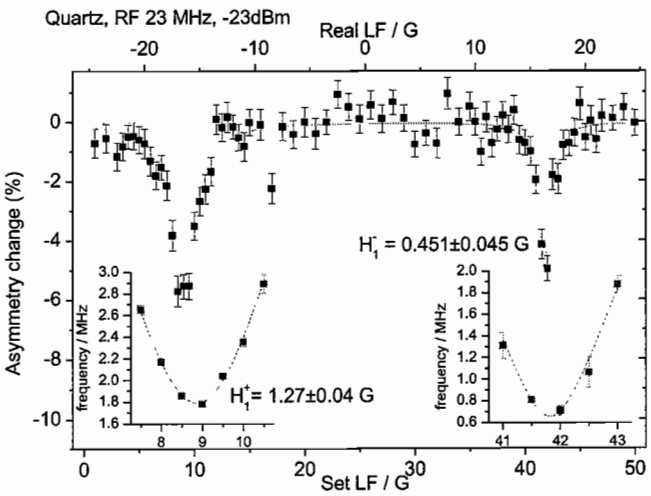
	ESR	μSR
ZnO	1.96	1.97(1)
CdS	1.78	1.86(2)
CdSe	0.67	0.51(2)
CdTe	-1.59	1.68(3)

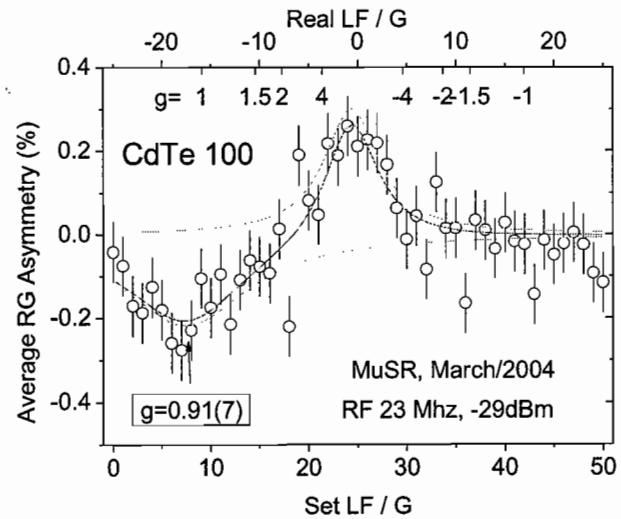
need rotating RF field!





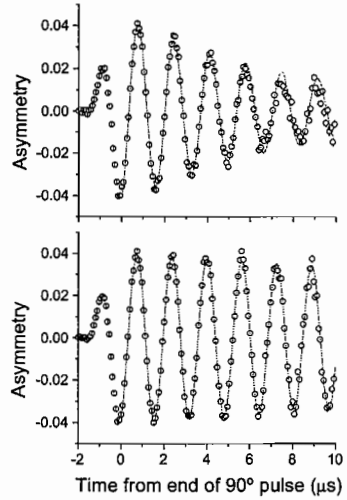
ESR-μSR double resonance: circular RF polarization tests





Decoupling

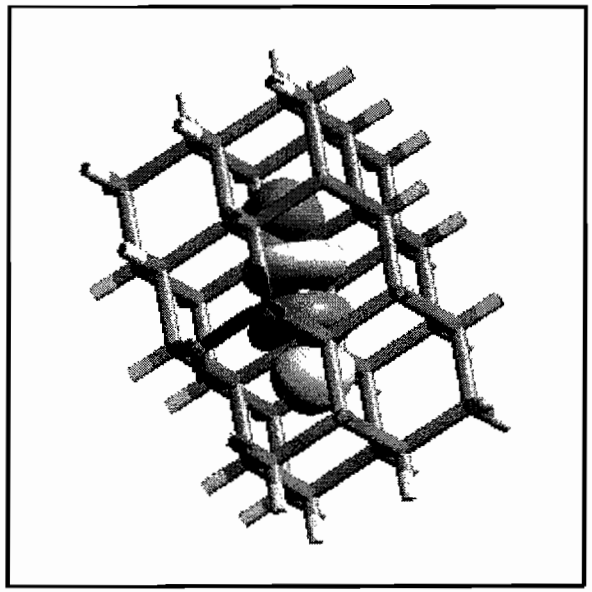
Search for Mu- via cation decoupling: (0/-) acceptor function

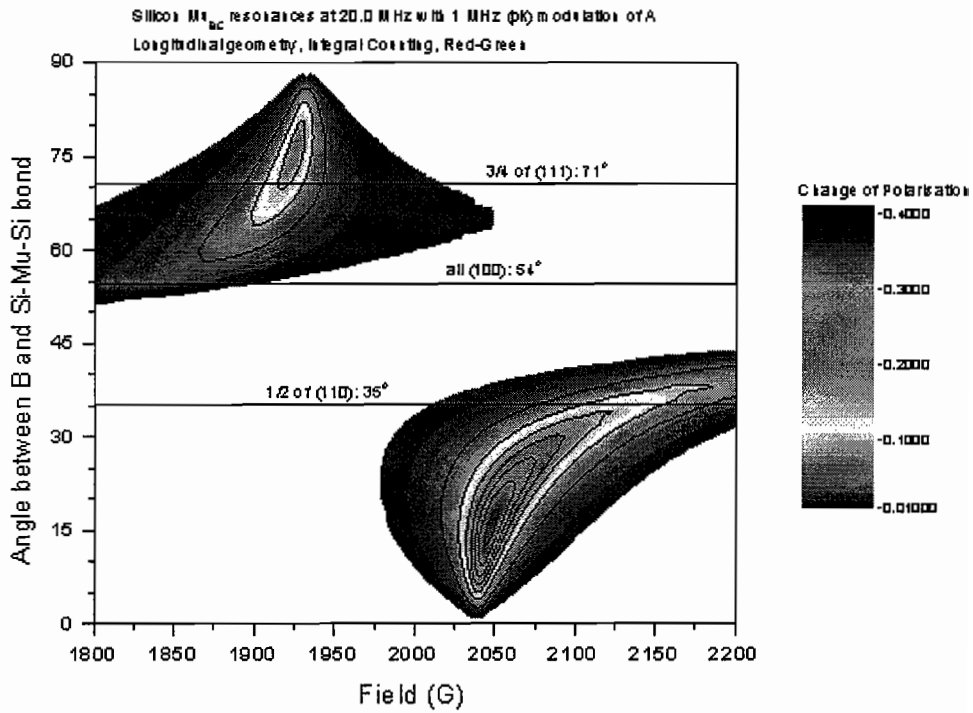


Diffusion / trapping / final states

Widegaps, oxides, halides

Acoustic resonance?





Muon implantation studies of organometallics: Ferrocene

U. Jayasooriya (University of East Anglia)

Summary

Unlike the muon study of organic compounds, that of metallocenes (an important class of polymerisation catalysts) has seen little development. Such compounds would seem ripe for study by μSR as correlation times for ring rotations, etc, are accessible and hydrogen addition to the metallocene is an important step in polymerisation termination.

Reaction of muonium with ferrocene may result in either addition to Fe or the cyclopentadiene (Cp) ring. Data obtained in the high temperature phase indicates the presence of both species with results for the Cp-Mu adduct in good agreement with previous measurements by NMR and QENS. In the case of muonium addition to a ring carbon it acts as a "passive observer" of the system since the extra electron enters a non-bonding orbital causing little effect on the electronic structure of the metallocene. However, if muonium adds to the iron atom the extra electron enters an anti-bonding orbital causing a weakening of the metal-organic bond. In such a case it is an "active observer" of the system.

If a number of assumptions are made regarding the electronic configuration of the Mu-Fe adduct (in particular the d-orbital angular momentum and spin orbit coupling) the level crossing data obtained for ferrocene can be interpreted. It was found that when no quenching of the orbital angular momentum was assumed the crystal field to spin-orbit ratio defined a unique set of level crossings for a particular temperature. Using this model, good agreement was found between experimental and calculated values for the fields at which level crossings were observed allowing interpretation of the zero-field splitting diagram. In addition, the presence of four peaks in the high-field region of the LC diagram suggests the presence of two Mu-Cp radicals, which are assigned to the Mu-endo and Mu-exo forms.

Future work in this area will be to use the combined μSR/pulsed illumination technique in order to measure the vibrational frequency of Mu-Fe and Mu-Cp in order to confirm the presence of these radicals.

MUON IMPLANTATION STUDIES OF ORGANOMETALLICS:

FERROCENE

Upali A. Jayasooriya, Roger Grinter, Penny L. Hubbard, Georgina M. Aston, John A. Stride, Gareth A. Hopkins, Laure Camus

School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, UK

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Paul Scherrer Institut, Villigen PSI, Switzerland

Stephen P. Cottrell, Stephen F.J. Cox

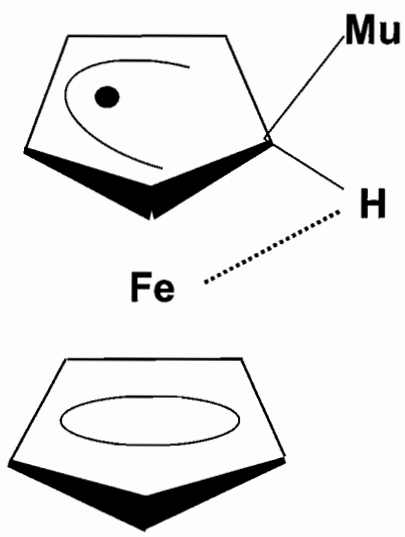
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, UK

Reasons

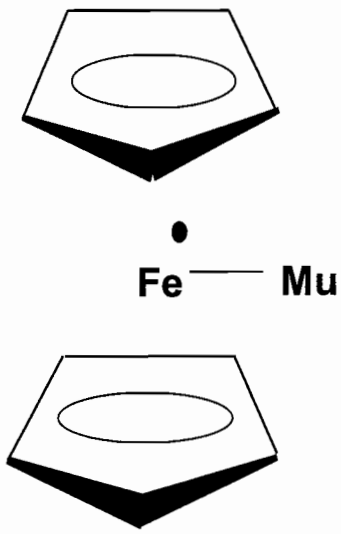
- Muon Spectroscopies of organic compounds are well developed, but no such studies of organometallics
- Metallocenes are very important catalysts for polymerisation reactions
- Ring dynamics of metallocenes are of importance to catalysis and the correlation times for such ring rotations at relevant temperatures happen to be accessible to μSR
- Hydrogen addition to metallocenes was found to be important for the termination of the polymerisation processes catalysed by metallocenes
- Spin-orbit coupling becomes important with molecules containing heavy atoms

FERROCENE

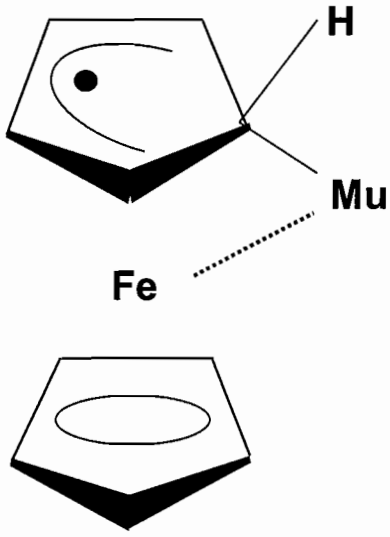
muoniated radicals



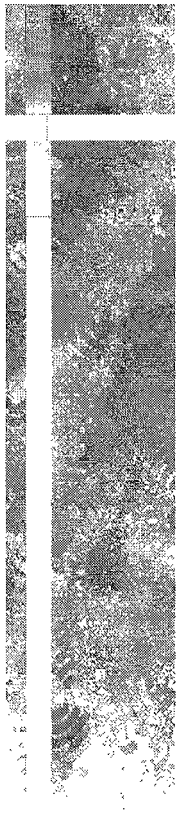
Mu - exo

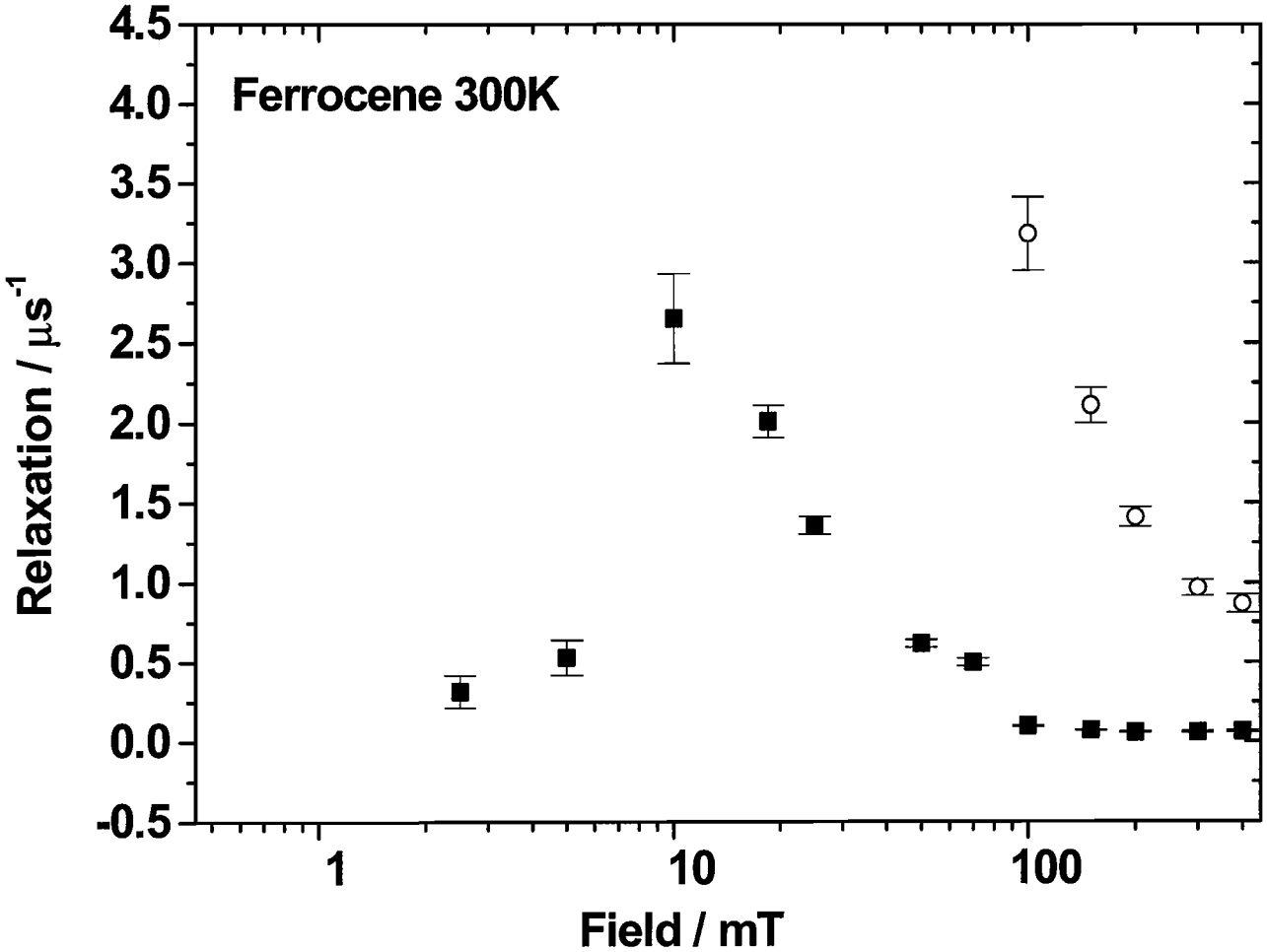


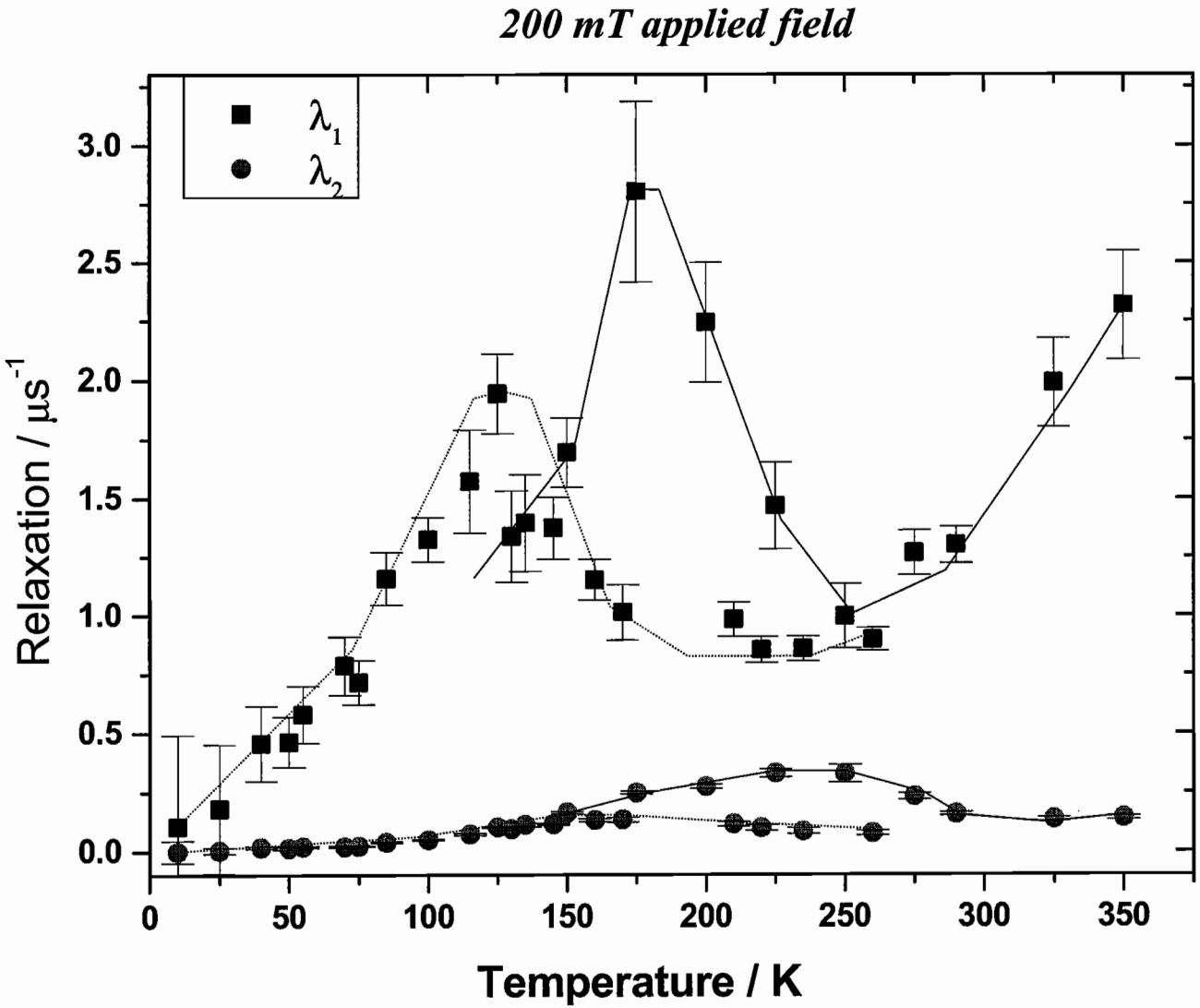
Fe - Mu

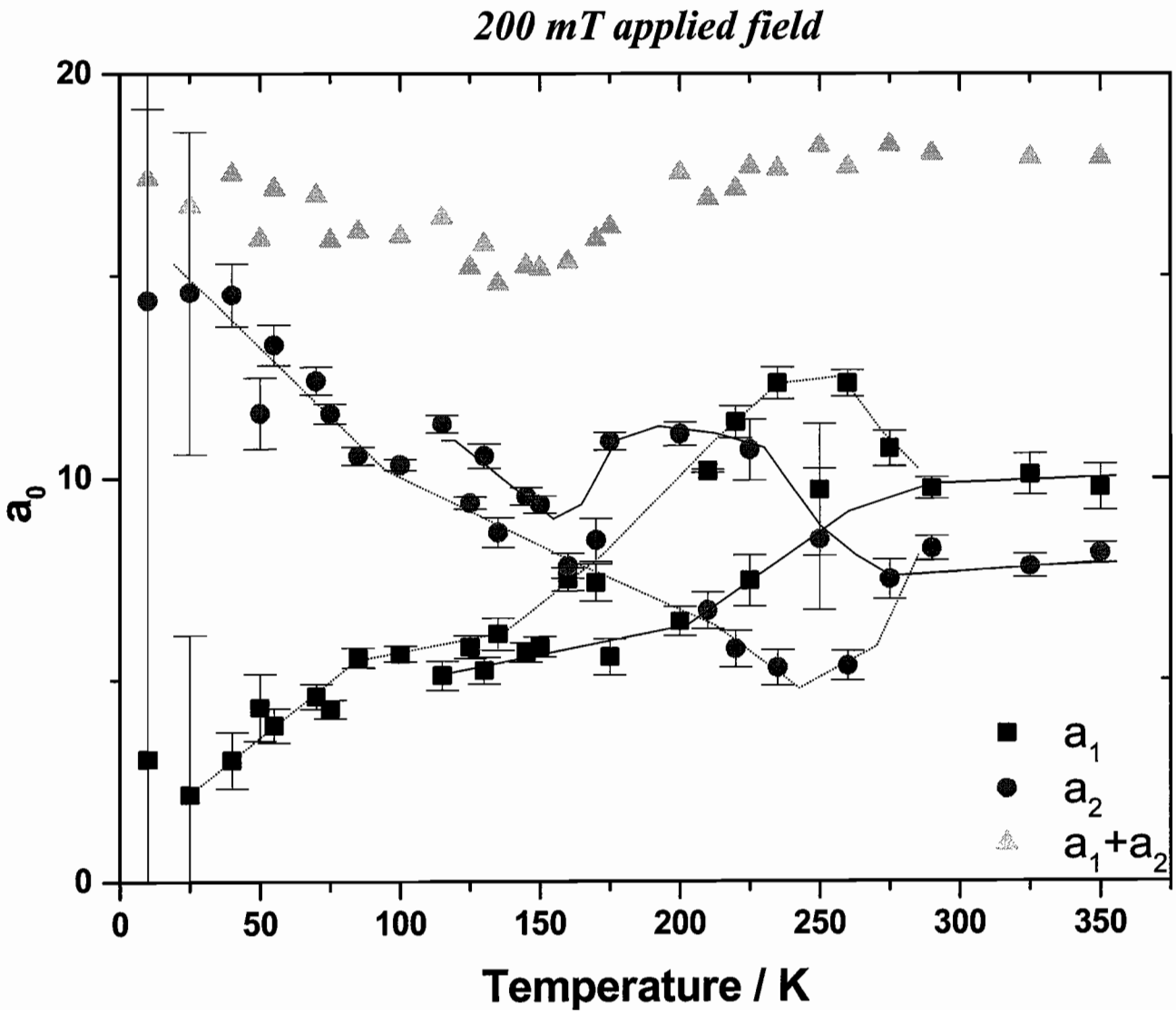


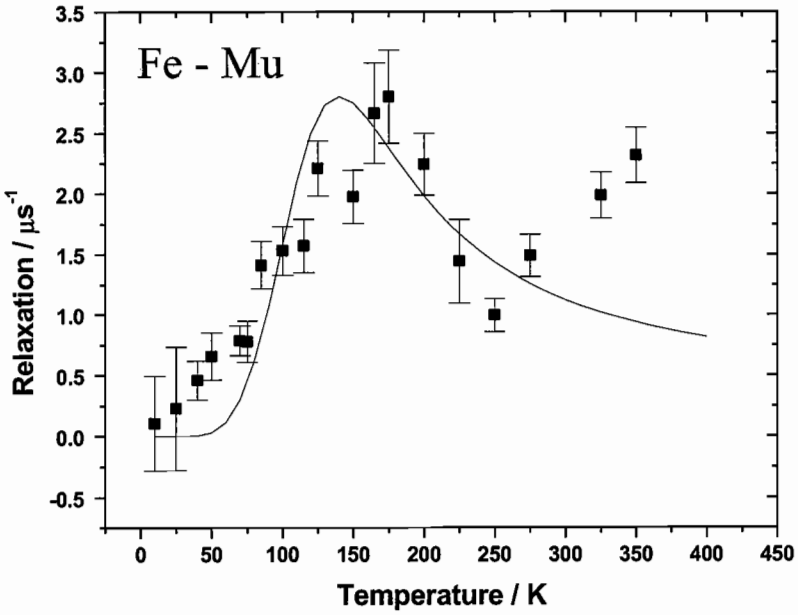
Mu - endo




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


200 mT applied field
λ1
λ2
Relaxation / μs-1
Temperature / K
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
50
100
150
200
250
300
350


200 mT applied field
20
10
0
a_0
0
50
100
150
200
250
300
350
Temperature / K
a_1
a_2
a_1+a_2



High Temperature Phase

at 200mT

$\Delta E = 3.41 \pm 0.42$ kJ mol^{-1}

$A = 6.3 \pm 1.7 \times 10^{11}$ s^{-1}

$\Delta E = 5.85 \pm 0.40$ kJ mol^{-1}

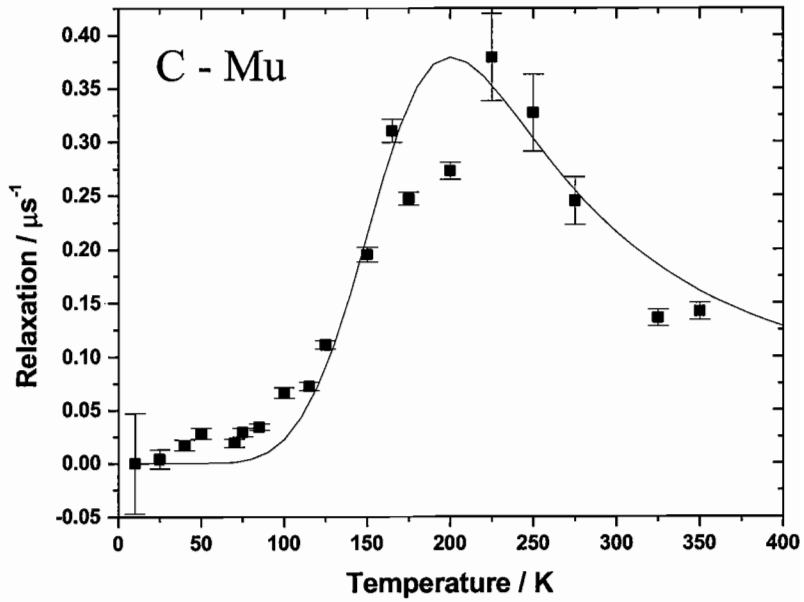
$A = 1.13 \pm 0.40 \times 10^{12}$ s^{-1}

NMR; $\Delta E = 5.4 \pm 0.5$ kJ mol^{-1}

$A = 2.2 \times 10^{12}$ s^{-1}

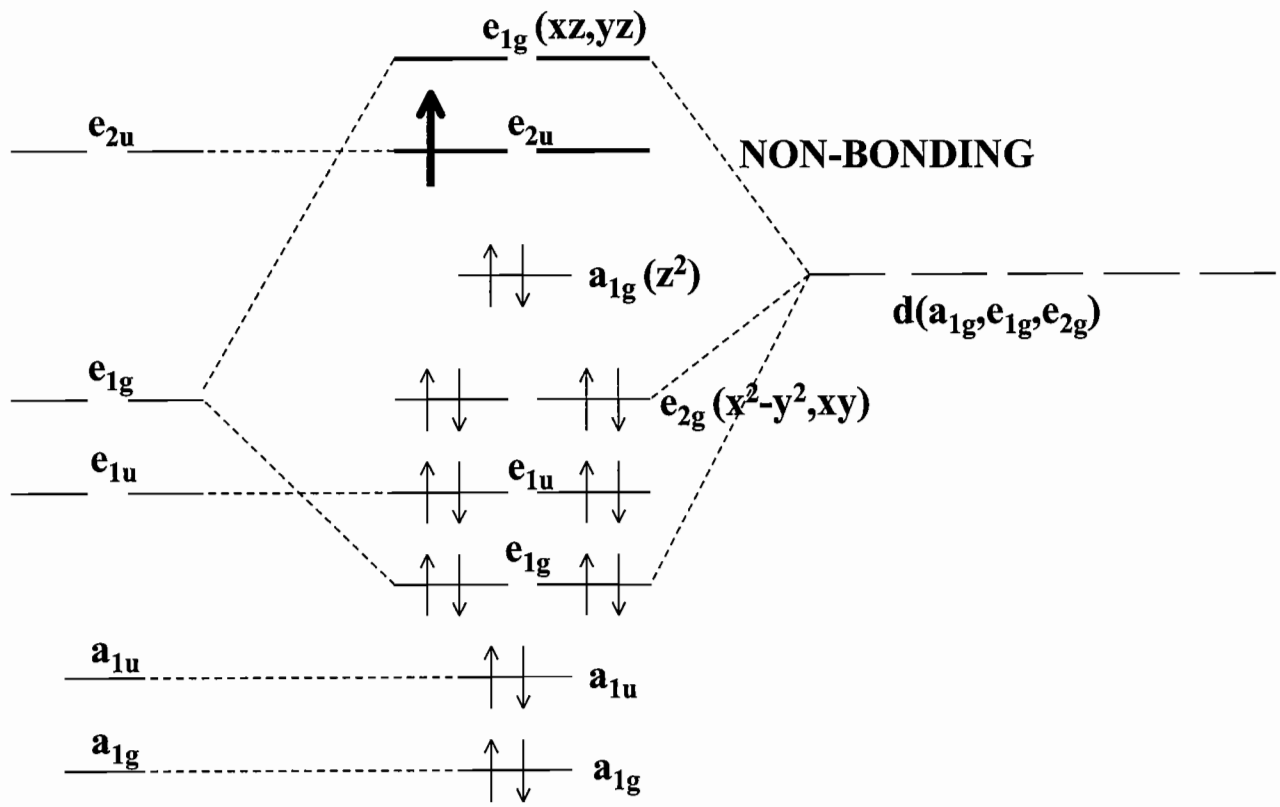
QENS; $\Delta E = 4.4 \pm 0.5$ kJ mol^{-1}

$A = 0.8 \times 10^{12}$ s^{-1}



C-Mu ring adduct MOs

Passive observer

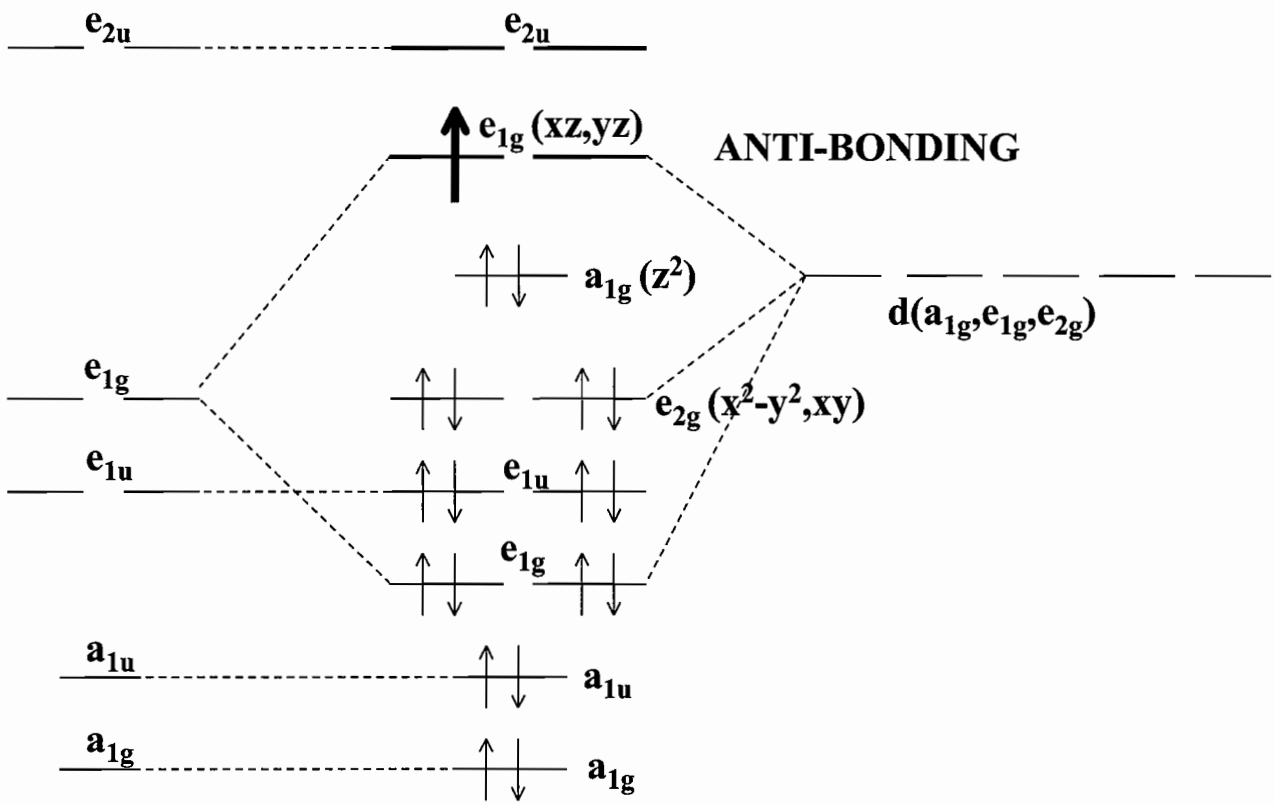


Cylopentadienyl ring MOs

Fe AOs

Fe-Mu adduct MOs

Active observer



Cylopentadienyl ring MOs

Fe AOs

Assumptions

1. A molecular orbital description of metallocenes is applicable and the electronic configuration of the muonium-metal adduct is similar to that of 'cobaltocene' in which the unpaired electron occupies one of a pair of degenerate orbitals designated e_{1g} in D_{5d} symmetry. This pair of orbitals is derived from the atomic 3d orbitals which have m_l values of ± 1 and may be expected to retain their orbital angular momentum under conditions of high axial symmetry.

2. The above electronic orbital angular momentum may be partially quenched by bonding, and this is allowed for in the present treatment by the introduction of a parameter γ; $0.0 \leq \gamma \leq 1.0$, where $\gamma = 1.0$ represents the unquenched situation.

3. The degeneracy of the 3d orbitals having $m_l = \pm 1$ may be lifted by forces in the solid state or by the formation of the muonium adduct. Following Ammeter and Swalen, [J.Chem.Phys.,**57**, 678 (1972)] we allow for this fact by introducing off-diagonal matrix elements $\pm iV$ ($i = \sqrt{-1}$) between states having $m_l = +1$ and those with $m_l = -1$ into the energy matrix. V is a crystal or ligand field parameter.

4. Significant spin-orbit coupling (spin-orbit coupling constant ζ) must also be allowed for. The effects of the parameters V, γ and ζ upon the electronic structure of the molecule have been discussed by Ammeter and Swalen,[23] in their detailed study of the electron paramagnetic resonance of cobaltocene. In this work we also observe a subtle interplay between them.

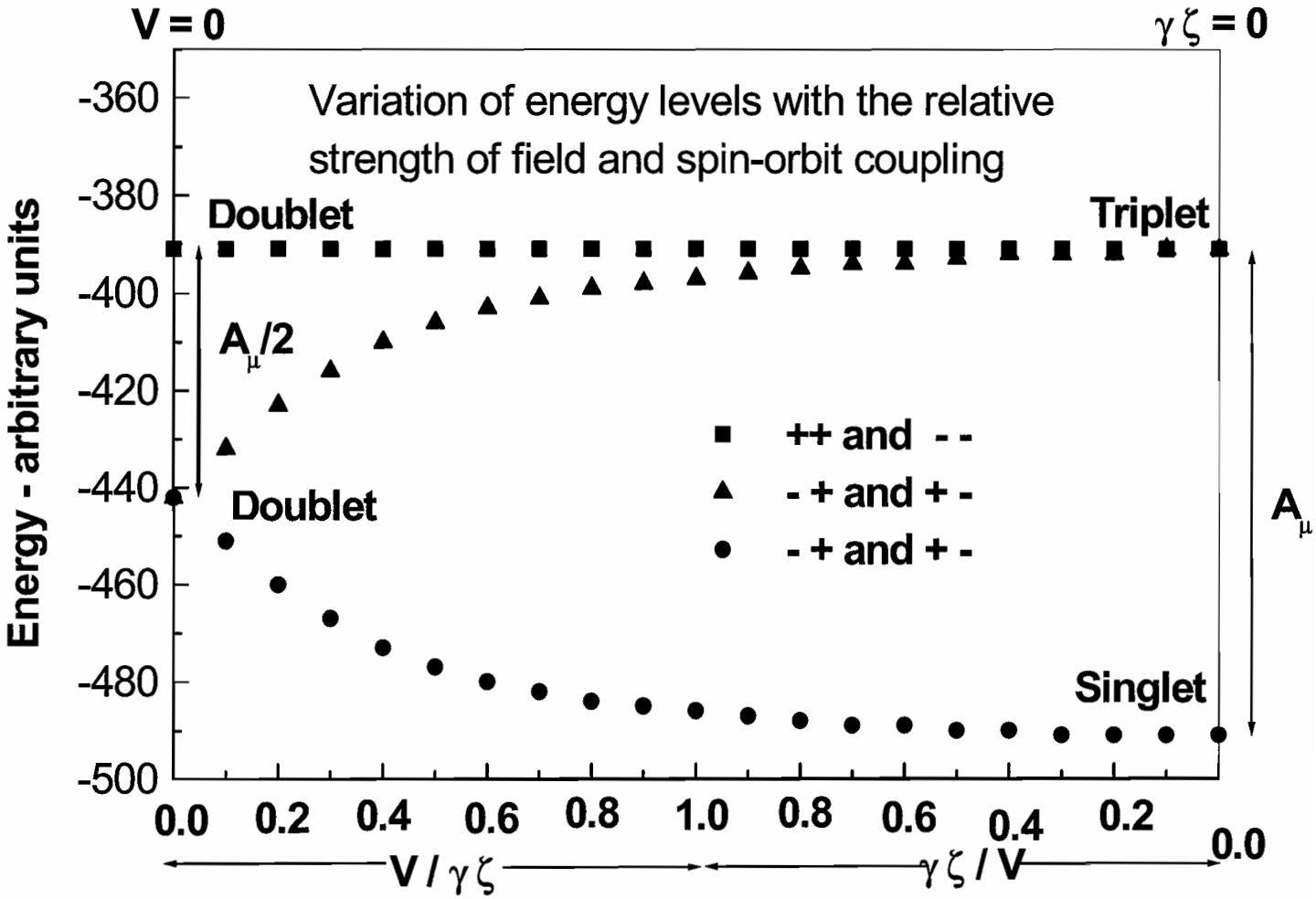
5. The system may be adequately described by a basis of eight microstates (| $m_l(e)$, $m_s(e)$, $m_s(\mu)$ >) consisting of two possible values of the z-component of the electronic orbital angular momentum, two possible spin orientations each of the unpaired electron and the muon. For a complete treatment many more states would be required since spin-orbit coupling connects microstates with $m_l = \pm 1$ with others having $m_l = 0$ and ± 2.

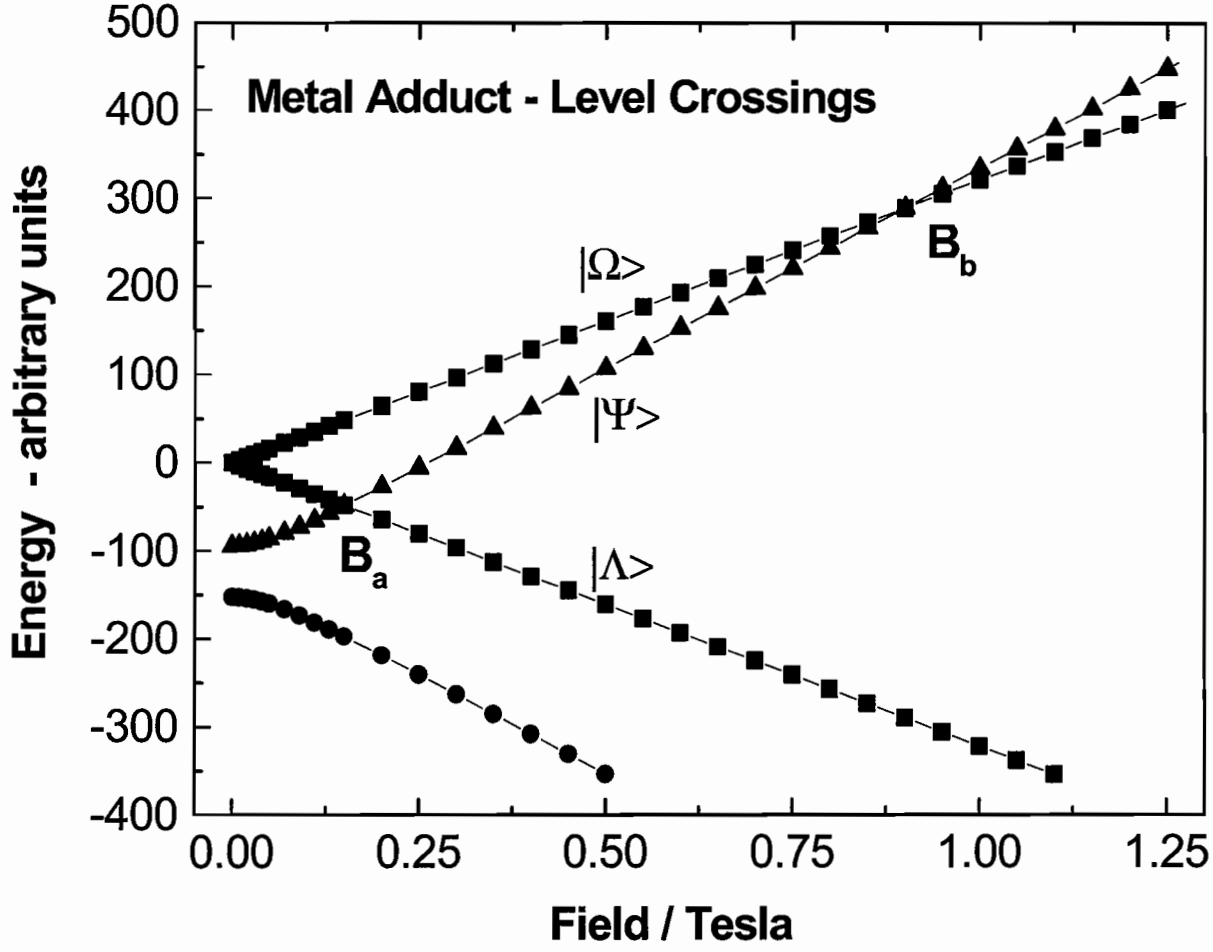
6. The magnetic interactions can be generated using the Hamiltonian:

$$\hat{H} = \gamma\varsigma \hat{l} \bullet \hat{S} + A_\mu \hat{I}_m \bullet \hat{S} + B\left[\left(\tfrac{1}{2}\gamma \hat{l}_z + \hat{S}_z\right)v_e - \hat{I}_{\mu z} v_\mu\right]$$

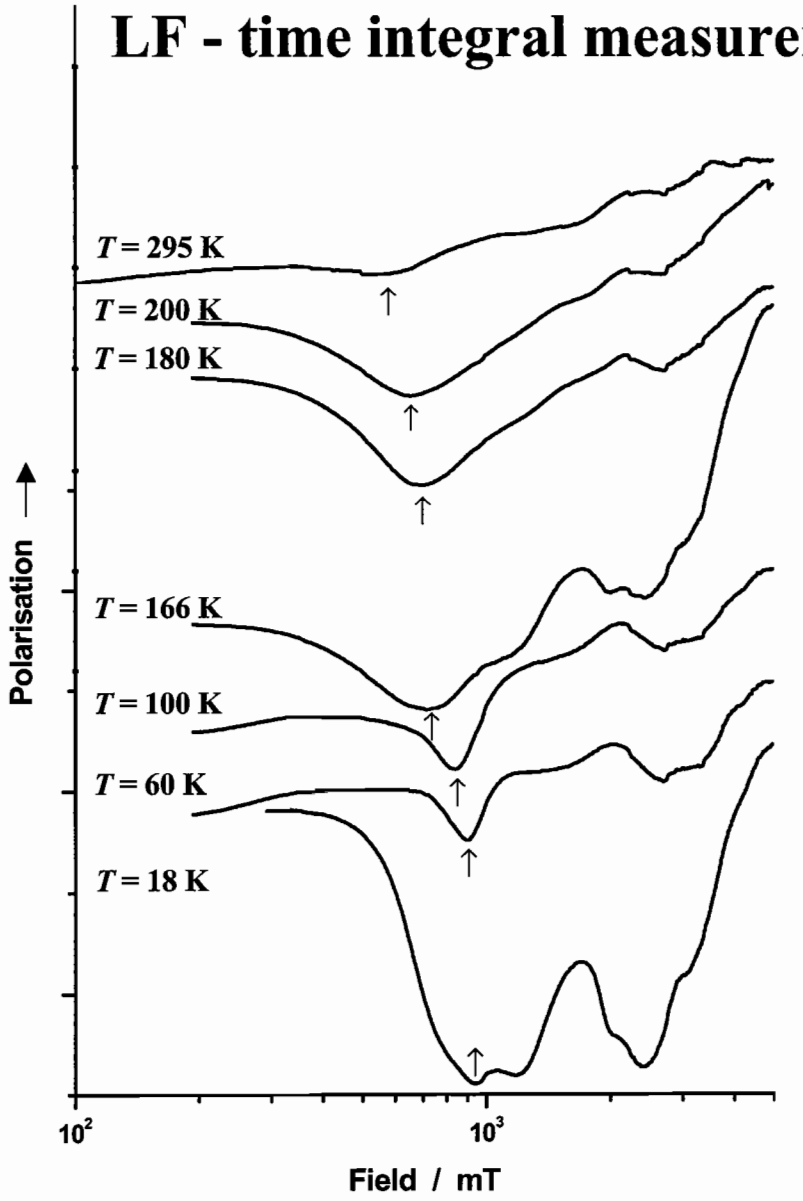
Where the familiar operators *s* for spin and *l* for angular momenta are used. A_μ is the muon coupling constant and V, γ and ζ have been defined above.

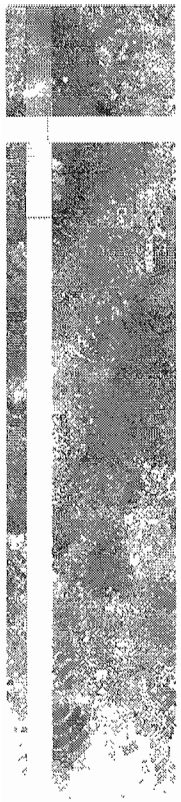
Zero-field splitting

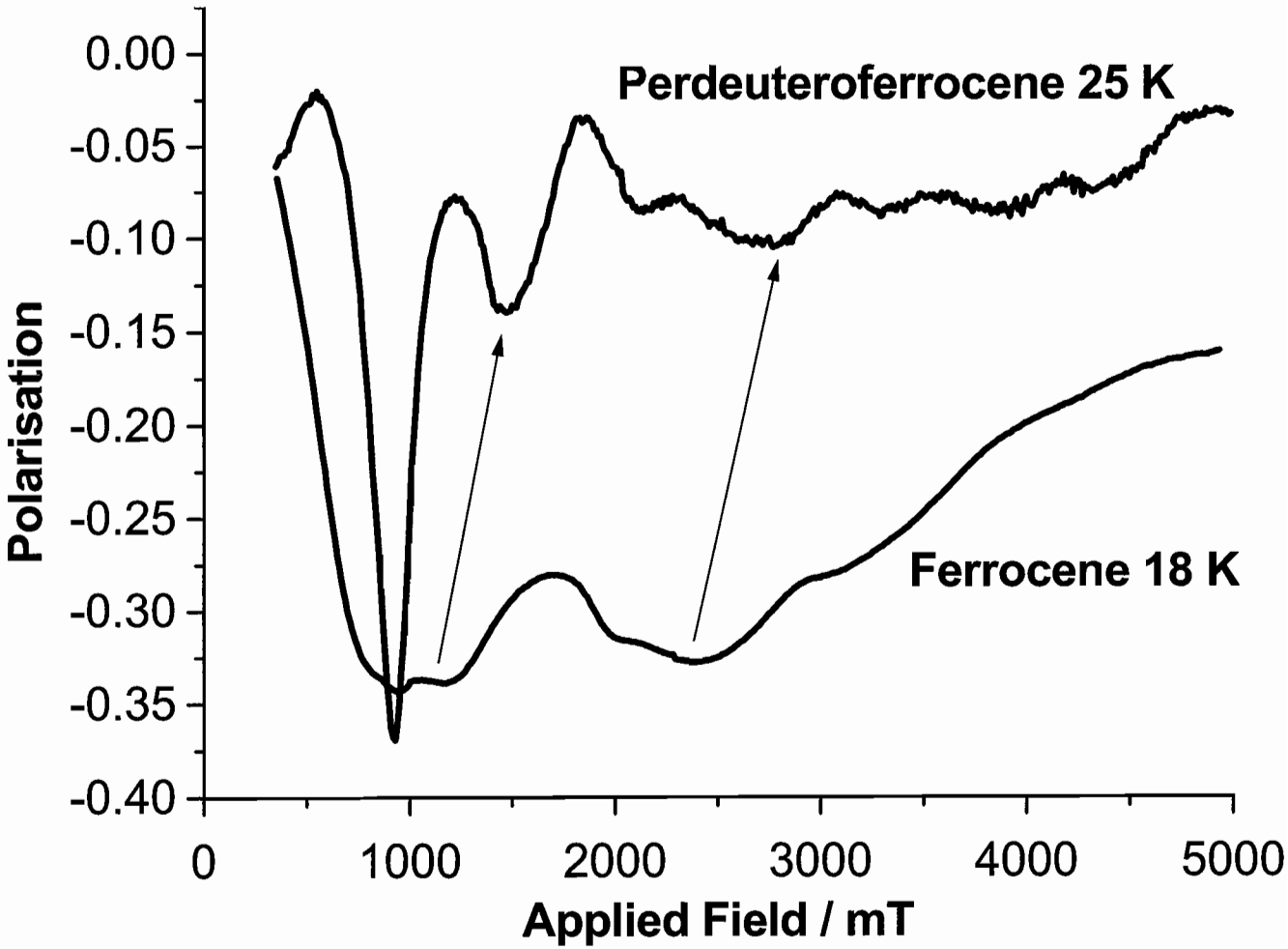



Metal Adduct - Level Crossings
Energy - arbitrary units
Field / Tesla
500
400
300
200
100
0
-100
-200
-300
-400
0.00
0.25
0.50
0.75
1.00
1.25
|Ω>
|Ψ>
|Λ>
B_a
B_b

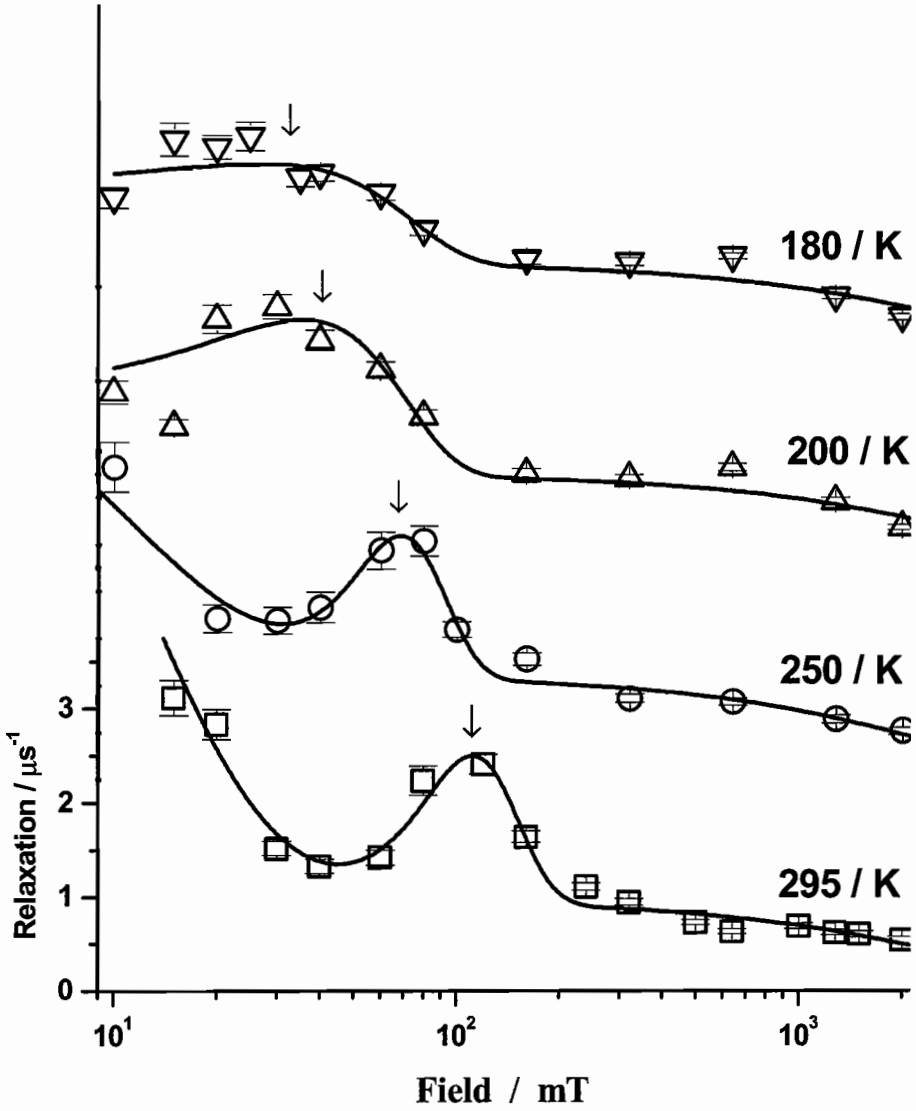
LF - time integral measurements

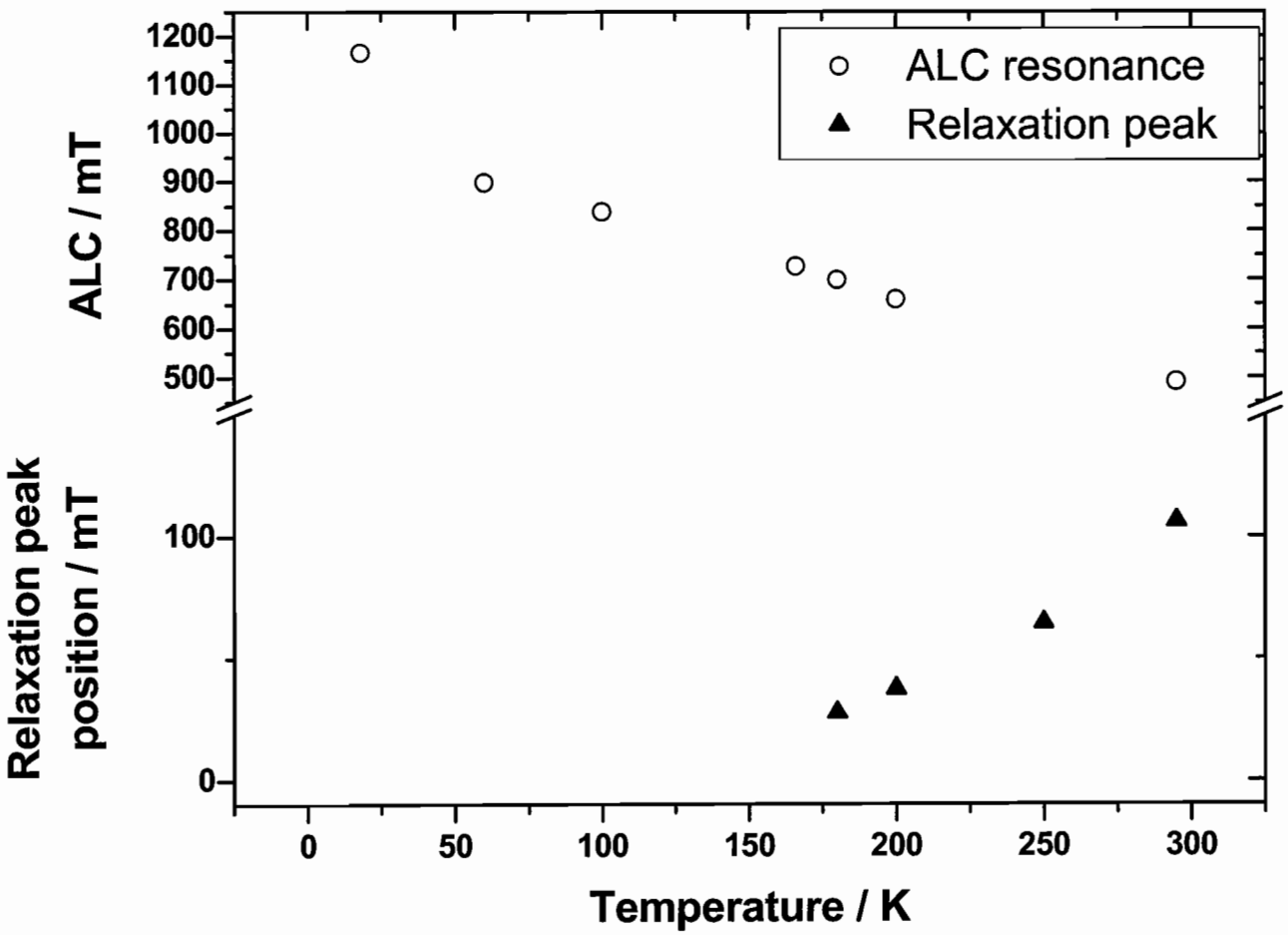





Perdeuteroferrocene 25 K
Ferrocene 18 K
Polarisation
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40
0
1000
2000
3000
4000
5000
Applied Field / mT

LF - time differential measurements



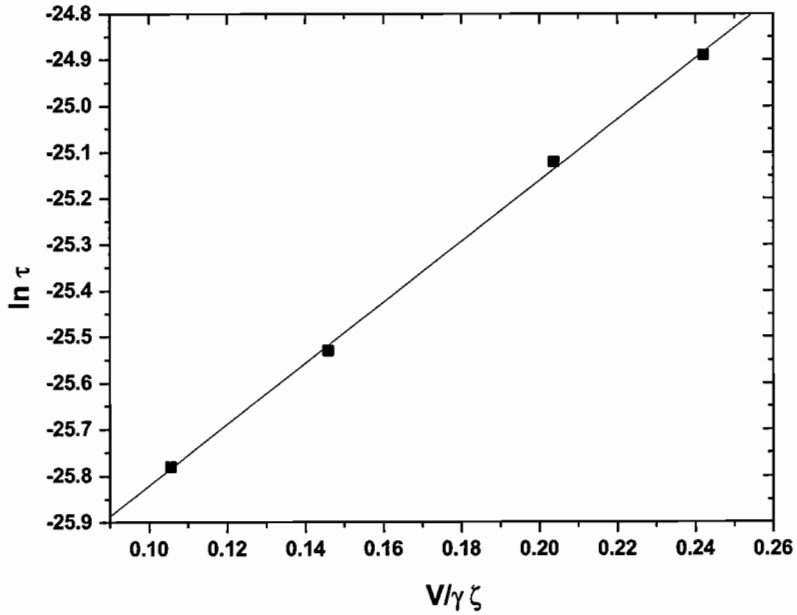

ALC resonance
Relaxation peak
ALC / mT
1200
1100
1000
900
800
700
600
500
Relaxation peak position / mT
100
0
0
50
100
150
200
250
300
Temperature / K

It is found that when the value of the quenching of the orbital motion, γ, is assumed to be 1, the ratio of crystal field to spin orbit coupling, $V/\gamma\xi$, is unique for a particular set of the level crossings B_a and B_b, and therefore is fixed for a given temperature. This therefore uniquely defines the state of the zero field splittings for this system at a particular temperature.

T / K	B_a / mT	B_b / mT	γ	$V \times 10^5$ / MHz	A_μ / MHz	B_a / mT	B_b / mT	Relative intensities B_b / B_a	$V/\gamma\xi$
	Exp.	*Exp.*	*Fixed*	*Calc*	*Calc.*	*Calc.*	*Calc.*	*Calc.*	*Calc.*
295	106	491	1.0	27.5	134	106	489	6.0	0.11
250	64	571*	1.0	38.0	156	64	569	4.1	0.15
200	37	659	1.0	53.1	180	37	657	3.0	0.20
180	28	699	1.0	63.2	191	28	697	2.6	0.24

* interpolation

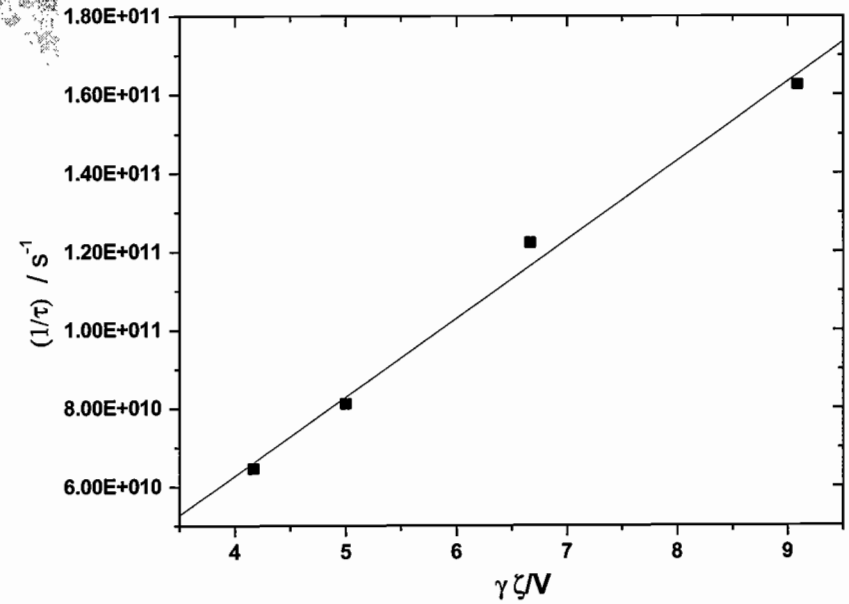
Explains why B_a is easier observed in relaxation.



$$\ln \tau = 6.61(0.14)\ V/\zeta - 26.48(0.03)$$

$\tau =$ 3.2 ps when V = 0

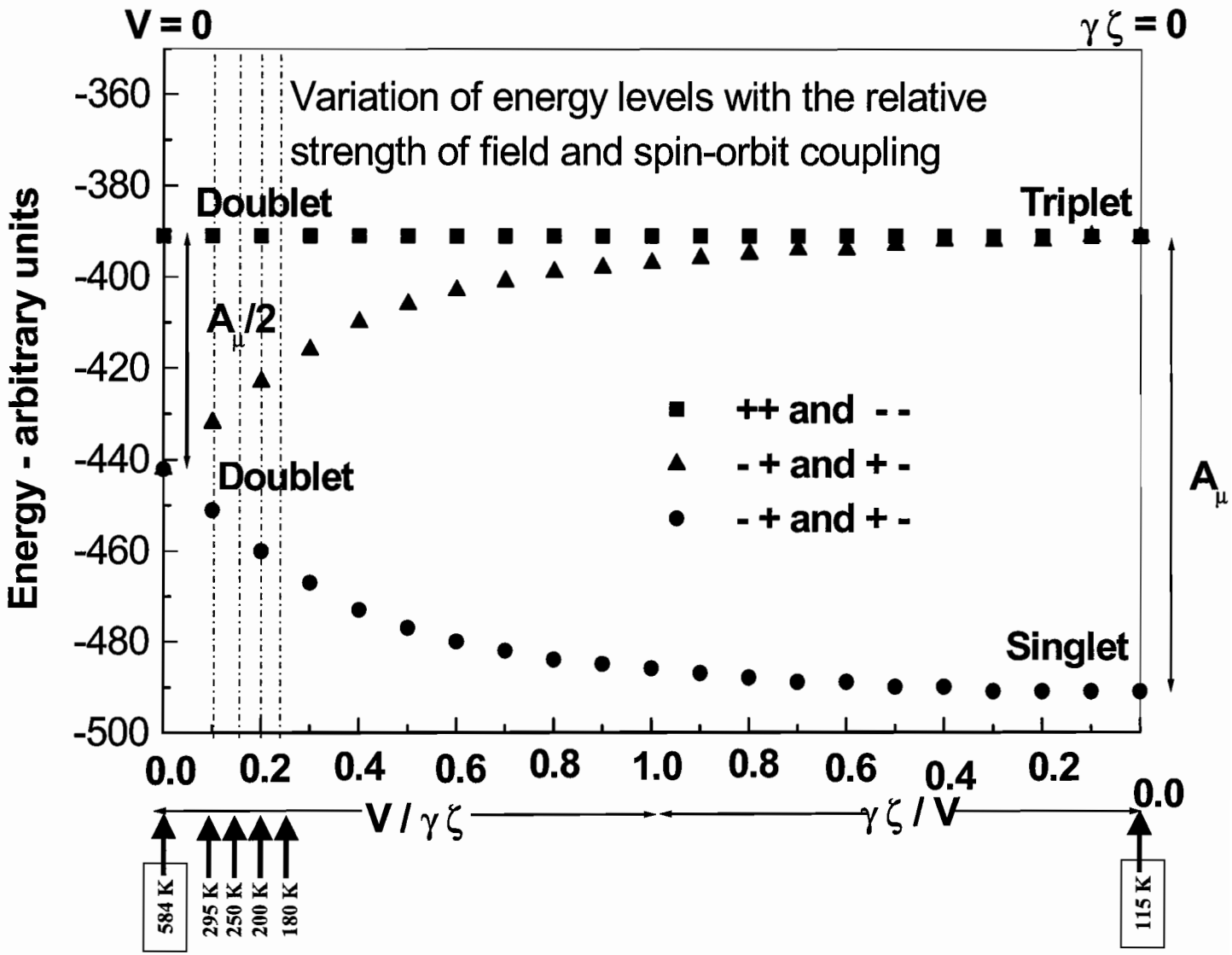
Temperature = 584 K



$$1/\tau = 2.01(0.13)\times10^{-10}\ (\zeta/V) - 1.77(0.84)\times10^{-10}$$

$\tau =$ 56.5 ps when $\gamma\zeta = 0$

Temperature = 115 K


V = 0
γζ = 0
Variation of energy levels with the relative strength of field and spin-orbit coupling
Doublet
Triplet
Doublet
Singlet
A_μ/2
A_μ
++ and - -
- + and + -
- + and + -
Energy - arbitrary units
-360
-380
-400
-420
-440
-460
-480
-500
0.0
0.2
0.4
0.6
0.8
1.0
0.8
0.6
0.4
0.2
0.0
V / γζ
γζ / V
584 K
295 K
250 K
200 K
180 K
115 K

C - Mu cyclopentadienyl ring adducts

We follow the treatment given by Roduner *et al.* [Nature, **345**, 328 (1990)] for ALCs.

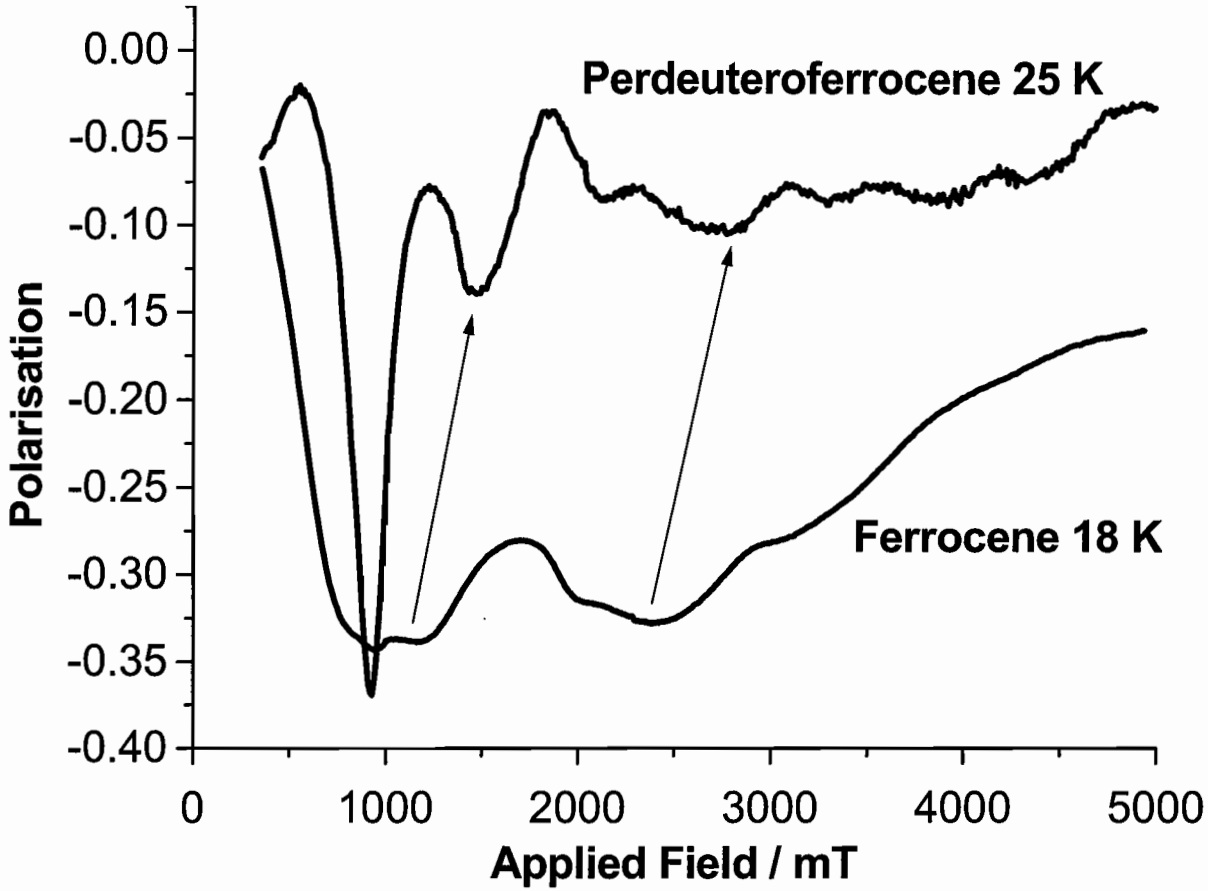
$$\hat{H} = A_\mu \hat{I}_\mu \bullet \hat{S} + A_p \hat{I}_p \bullet \hat{S} + B\left[\hat{S}_z v_e - \hat{I}_{pz} v_p - \hat{I}_{\mu z} v_\mu\right]$$

For the proton-muon spin flip-flop where ΔM = 0

$$B_0 = \left| \frac{A_\mu - A_p}{2(v_\mu - v_p)} \right|$$

and for the muon spin flip where ΔM = 1

$$B_1 = \left| \frac{A_\mu}{2 v_\mu} \right|$$



The presence of four rather than two peaks in the high-field region suggests the presence of two muonium-cyclopentadienyl ring-adduct radicals.

Examination of all the possible combination of assignments leads to the conclusion that

for one species $B_0 = 2.04$ T and $B_1 = 1.19$ T giving, using the above formulae,

A_μ = 322 MHz and A_p = –57 MHz, *[Mu - endo]*

while for the second species

$B_0 = 3.26$ T and $B_1 = 2.44$ T giving,

A_μ = 661 MHz and A_p = 55 MHz. *[Mu - exo]*

Where we have also assumed, in the light of earlier results, [Fleming *et al.* Physica **B**, **289-290**, 603 (2000)] that

A_μ is always positive in systems of this type.

Prospects for future Muon-Light experiments

- Measurement of Fe-Mu vibrational frequency and those of the C-Mu pair will be very characteristic of these bonds, and will confirm the presence of these radicals.

- A Muon-Light experiment where each of these vibrations in turn are excited while monitoring the μSR signals will provide the confirmation of the above assignments.

- This will then provide a general method of detecting and assigning μSR features to different radical species in a sample where there is a mix of several radicals

RF-μSR of the cyclohexadienyl radical

C. Johnson (RAL)

Summary

The presentation began with an outline of the equipment purchased under the Grant to allow the study of muon implantation in liquids using the RF-μSR technique. Dissolved oxygen is a particular problem in such studies leading to rapid depolarisation due to spin flips. A liquid handling system is now available allowing for the degassing of up to three samples by either freeze-pump-thaw of inert gas bubbling. In-situ loading of the clean liquids is also available using this system into a ceramic sample holder. Commissioning of the system was carried out using hexane where a decrease in the depolarisation rate of muonium, measured in 2 G transverse field (TF), was observed as more cleaning cycles were used. An RF field-sweep resonance curve for the diamagnetic component at 13 MHz was obtained. Delayed on resonance, 959 G, scans demonstrated no change in either the amplitude or depolarisation rate with time. An RF field-sweep resonance curve for muonium at 13 MHz showed a broad resonance consistent with the fast depolarisation rate observed in TF.

Following the successful commissioning experiments, an investigation of muoniated organic free radicals was undertaken starting with benzene. It was demonstrated that the RF-μSR technique was able to measure the isotropic hyperfine coupling, A_{Mu}, and splitting due to the 'ipso' proton, A_H, in excellent agreement with literature values.

Future developments of the RF-μSR technique will seek to improve the resolution of the resonance scans, in order to observe further splittings, by reduction of power broadening effects or by the use of a single 90° pulse.

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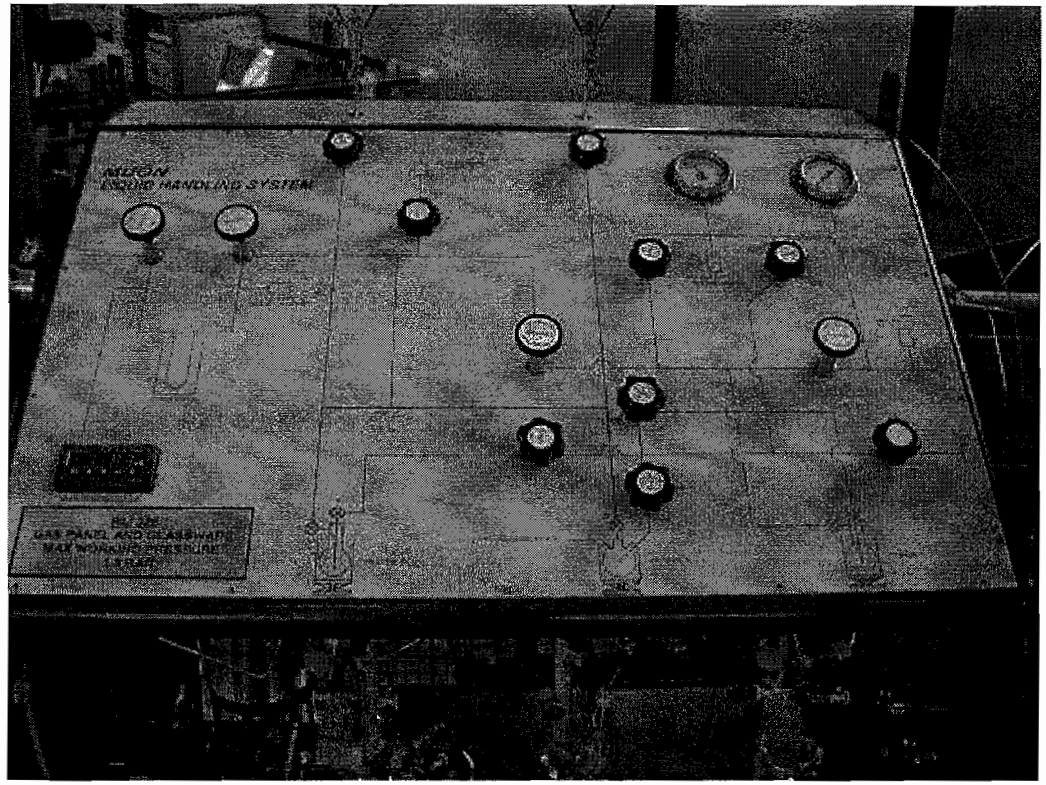
RF-μSR of the cyclohexadienyl radical

Clive Johnson
ISIS

Overview

- Experimental set-up
- Commissioning – Hexane
- Radical signal in Benzene
- Future prospects

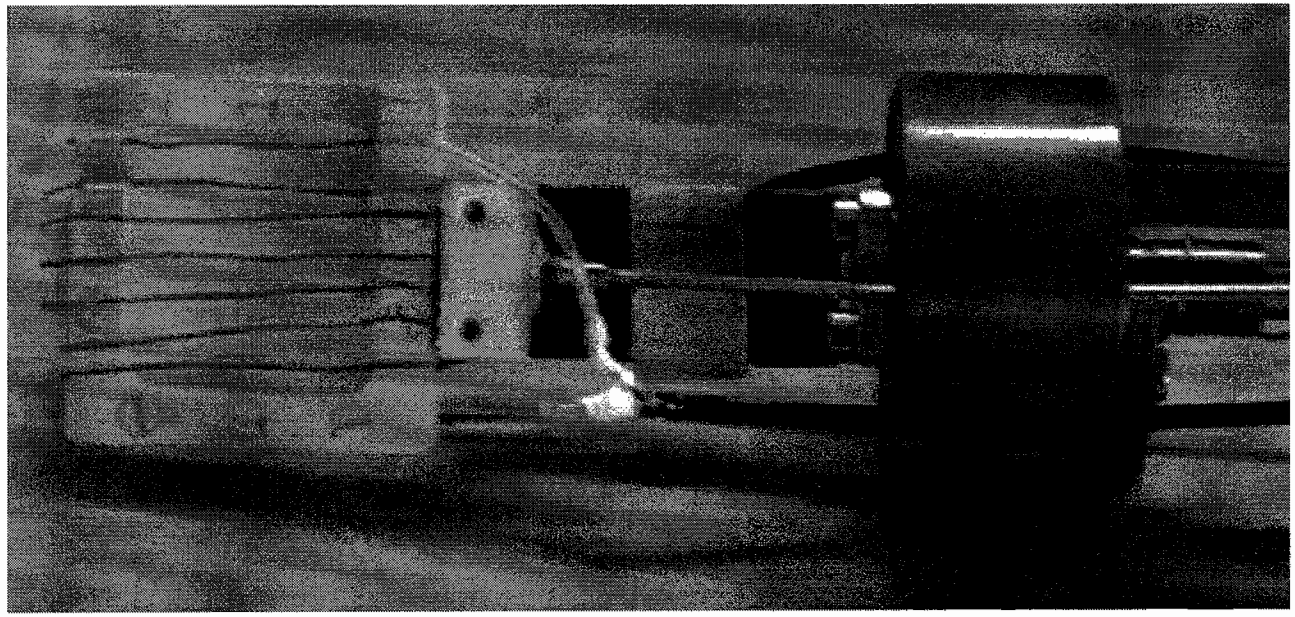
Experimental set-up



- Sample degassing

  The removal of oxygen by freeze-pump-thaw cycles.

Experimental set-up



- Sample holder

Commissioning – Hexane

- Simulation of muonium formation in liquid hydrocarbons
  (L.D.A. Siebbeles, S.M. Pimblott & S.F.J. Cox, *J. Chem Phys.*, **111**, 7493, 1999.)

  Prompt (epithermal) verses delayed muonium formation.

- No "delayed" muonium-formation in organic liquids
  (D.C. Walker, S. Karolczak, G.B. Porter & H.A. Gillis *J. Chem Phys.*, **118**, 7493, 2003.)

  Studies using added scavengers. Results consistent only with the "hot atom" model – prompt muonium formation.

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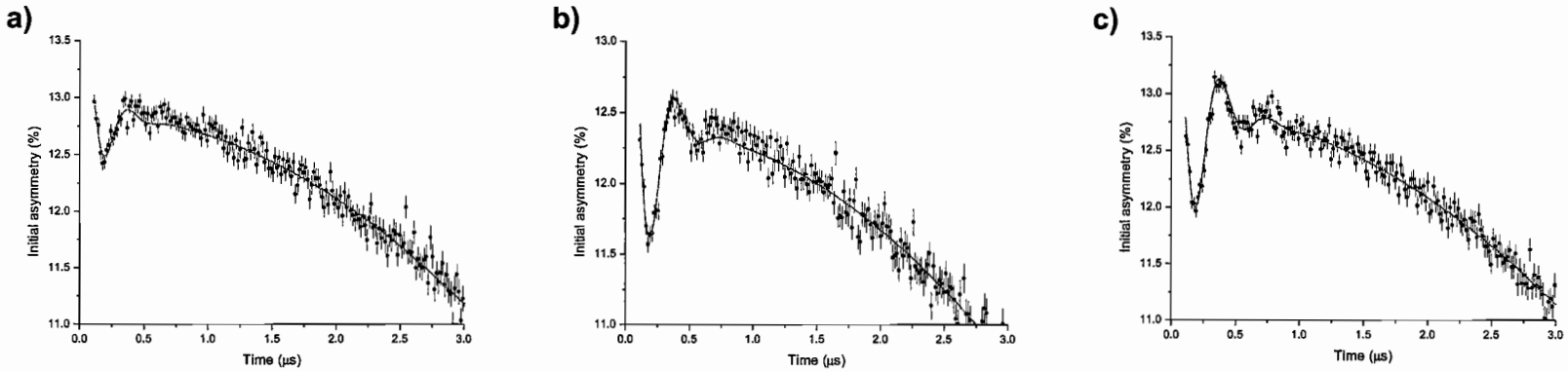
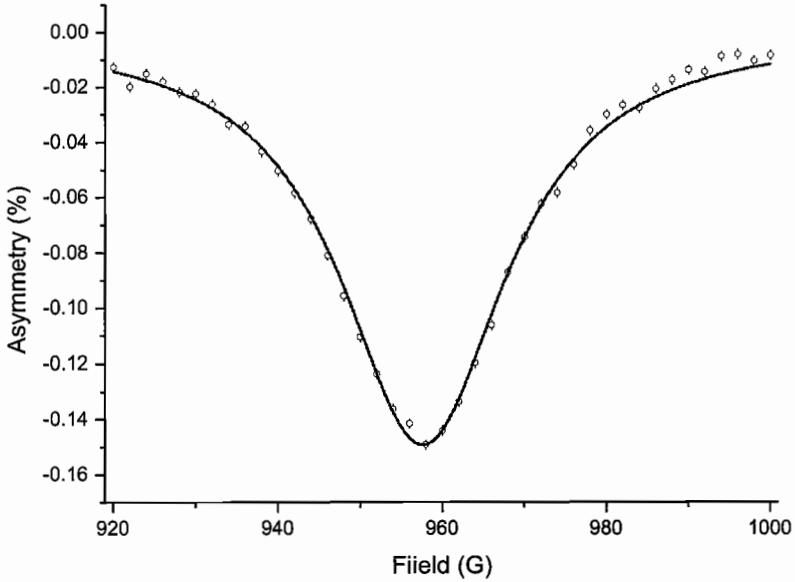
TF-μSR



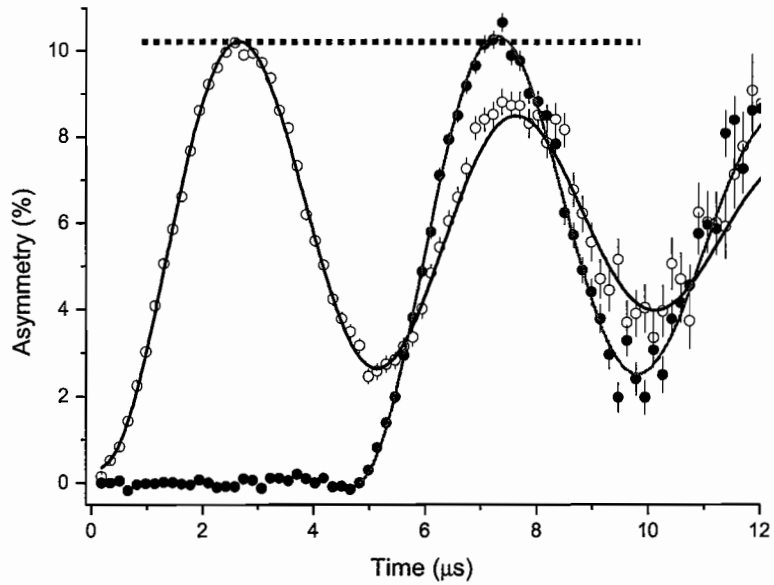
Muonium precession signal at 2 G in n-hexane after a) 4, b) 7 and c) 10 freeze-pump-thaw cycles.

Fpt cycles	Initial asymmetry (%)			Relaxation rate (μs-1)
	Diamagnetic	Paramagnetic	Missing	
4	12.87	3.41	6.72	7.96
7	12.41	5.86	4.73	6.66
10	12.86	4.90	5.24	5.45
6 + Na	12.59	4.39	6.02	5.20

RF-μSR - diamagnetic



Diamagnetic field-sweep resonance
13 MHz – 100 W



Diamagnetic on – resonance at 959 G
13 MHz – 100 W

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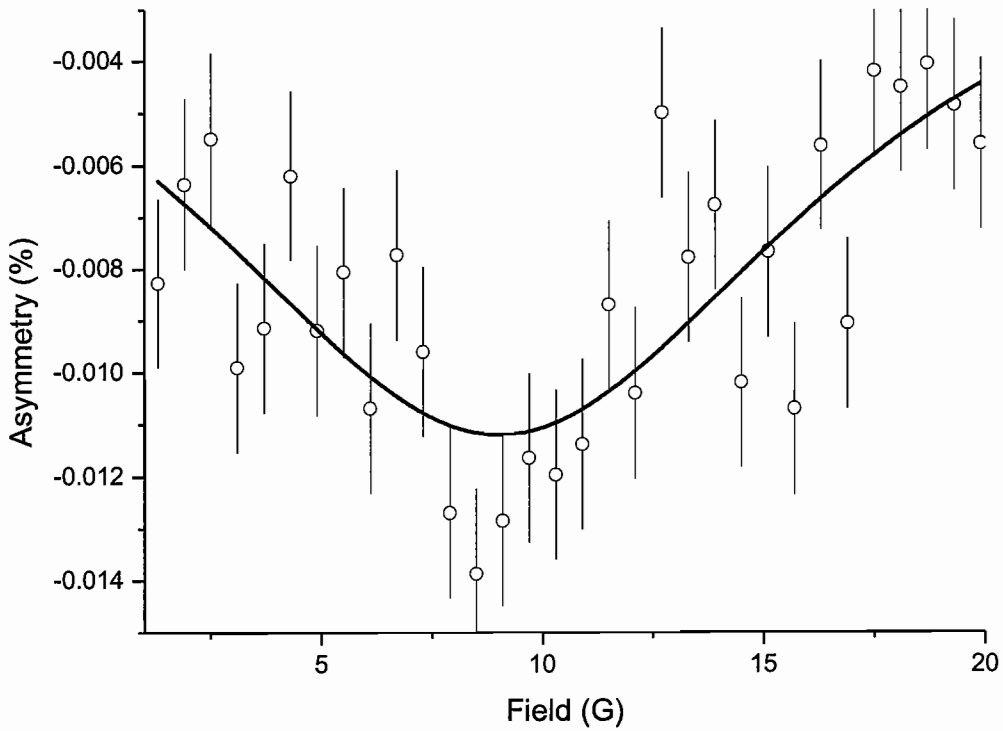
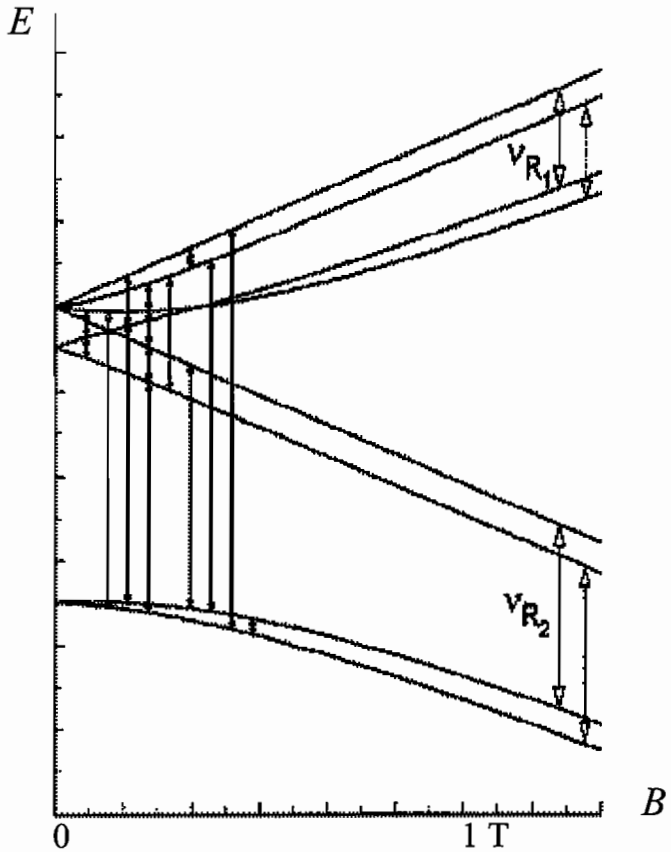
RF-μSR - paramagnetic



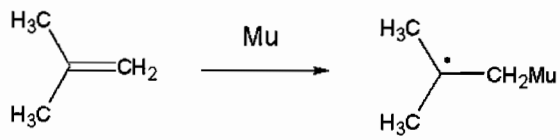
Field-sweep resonance

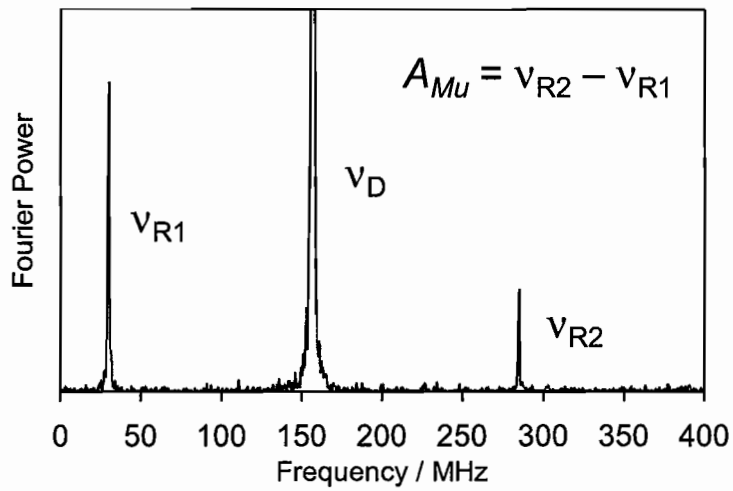
13 MHz – 5 W

Muoniated organic free radicals



Energy level diagram for a muonic radical with one proton coupling.





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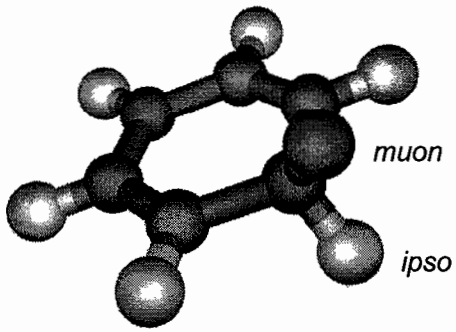
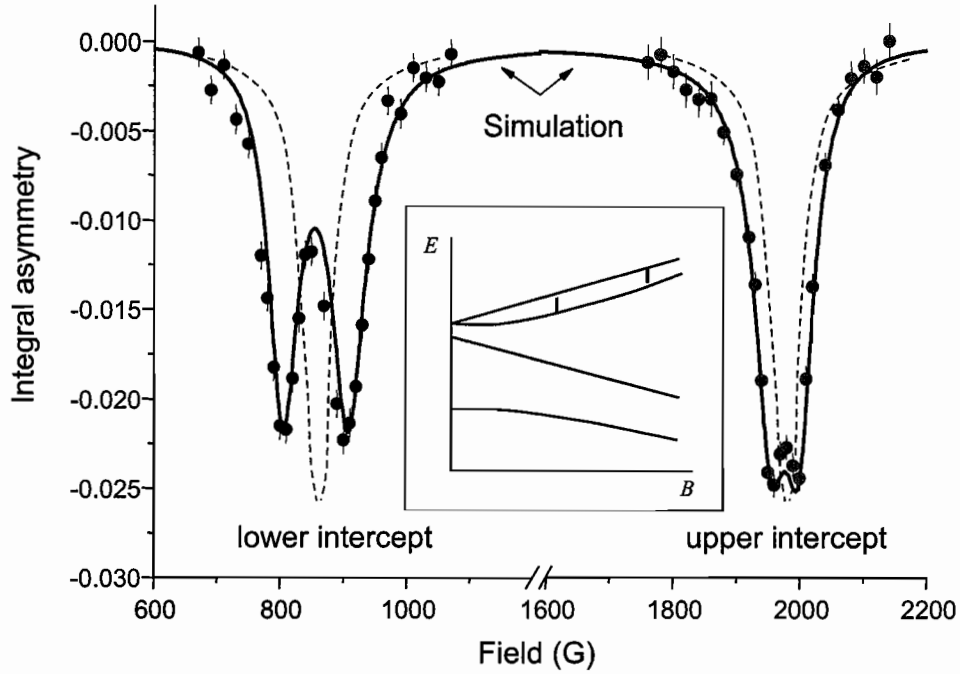
Cyclohexadienyl muoniated radical





RF-μSR signals for the ν_{12} transitions measured at 218.5 MHz

Isotropic hyperfine coupling:

A_{Mu} = 514.25(1) MHz at 298.0(3) K

= 514.41(1) MHz at 298.4 K [1]

A_H = 128.5(3) MHz 'ipso' proton

= 126.04(1) MHz at 298.4 K [1]

[1] D. Yu, P.W. Percival, J.-D. Brodovitch, S. –K. Leung, R. F. Kiefl, K. Venkateswaran and S.F.J. Cox, *Chem Phys.*, **142**, 229, 1990.

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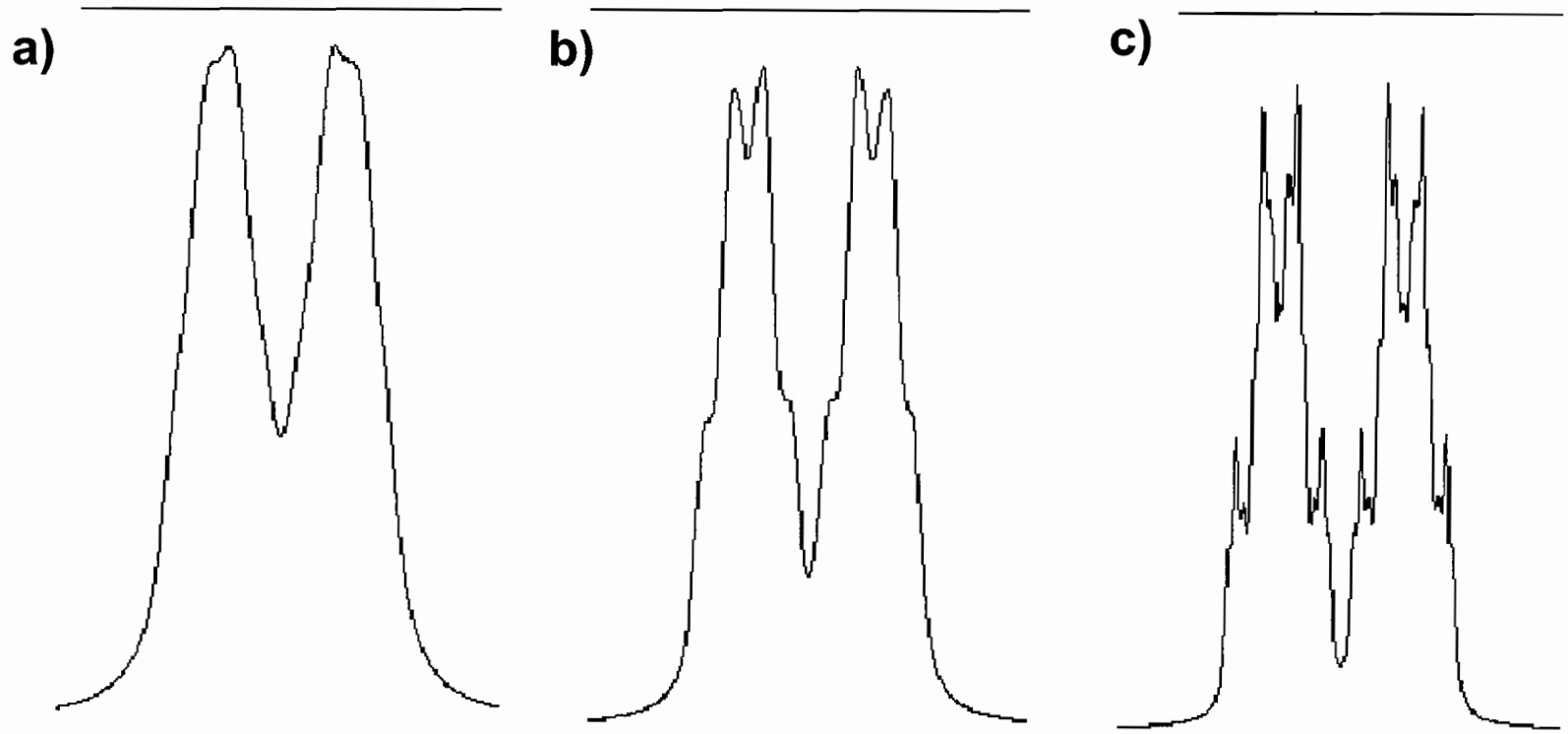
Continuous wave



A simulation of the effect on the observed resonance doublet in the cyclohexadienyl muoniated radical when the RF field is reduced from (a) 1 to (b) 0.5 and (c) 0.25.

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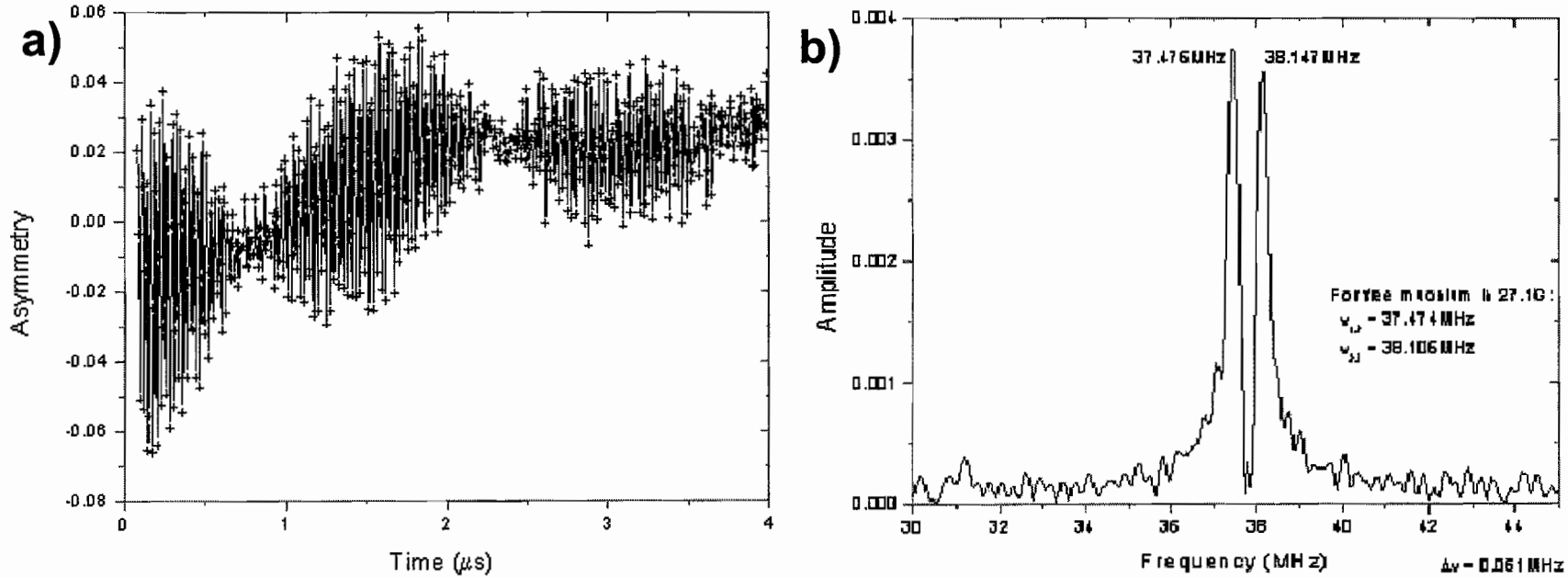
Single 90° pulse

200 ns RF pulse – 38 MHz 27.1 G



The time domain (a) and frequency domain (b) spectra for the muonium ν_{12} and ν_{23} transitions in quartz resulting from a single 90° RF pulse.

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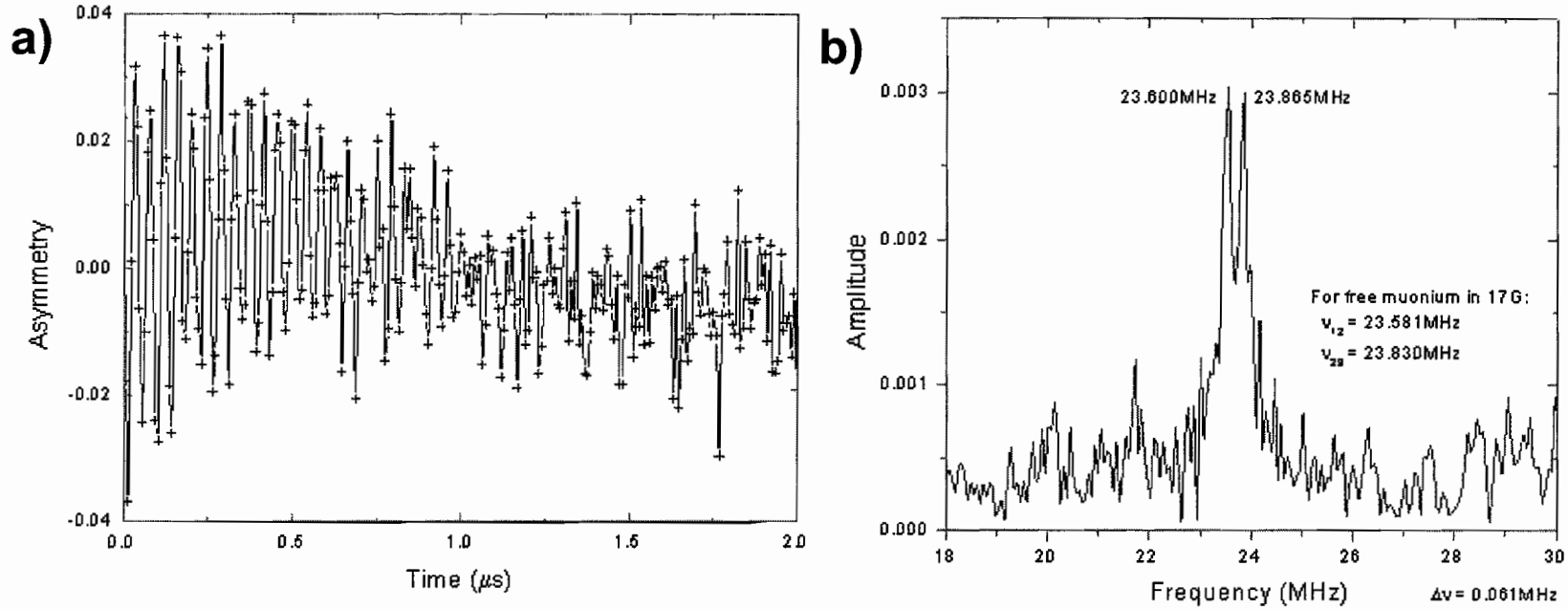
ISIS

Single 90° pulse

300 ns RF pulse – 23.5 MHz 17 G



The time domain (a) and frequency domain (b) spectra for the muonium ν_{12} and ν_{23} transitions in quartz resulting from a single 90° RF pulse.

Ferrocene, siloxanes and radicals – recent results from computational chemistry

R.M. Macrae (Marian College)

Summary

The cyclohexadienyl radical (C_6H_7) has often been used as a test case for the calculation of hyperfine coupling constants by open-shell *ab initio* computational techniques. The large amount of available experimental data on this radical makes detailed comparisons between different methods possible. From such studies it is found that, in general, for radicals, ROHF seriously underestimates spin polarisation effects, UHF overestimates them, Post-HF methods are costly, strongly basis set dependent and nontrivial to apply but hybrid DFT offers good results at reasonable computational cost.

For the free H case, calculation of the spin density using open-shell HF with a basis augmented with additional compact s-functions converges to the exact (Schrödinger) result whereas B3LYP tends to a higher limit. Comparison of HF and DFT methods as applied to the study of H trapping in octasilsesquioxanes shows that UHF methods lead to qualitatively incorrect spin density surfaces. Consequently, detrapping of H from the cage was found to be better modelled by hybrid DFT methods (subject to scaling) reproducing the qualitative behaviour of both the H isotropic hyperfine couplings and ^{29}Si superhyperfine couplings.

Computational chemists using different levels of theory have studied ferrocene, the prototypical metallocene, extensively over many years. However, H atom addition (in analogy of Mu) to the neutral species has not previously been treated. The results of recent DFT calculations suggest that although H/Mu addition to both Fe and cyclopentadiene (Cp) sites is predicted it is addition to Cp which is favoured. In addition, no evidence of an agostic species was found, in contrast with computations based on the protonated ferrocene cation. This can be attributed to the puckered-ring conformation adopted by the radical species. The effect of this ring puckering in the Cp adduct may be important for determining both the size of hyperfine coupling and the extent of its temperature dependence.

Ferrocene, siloxanes, and radicals - recent results from computational chemistry

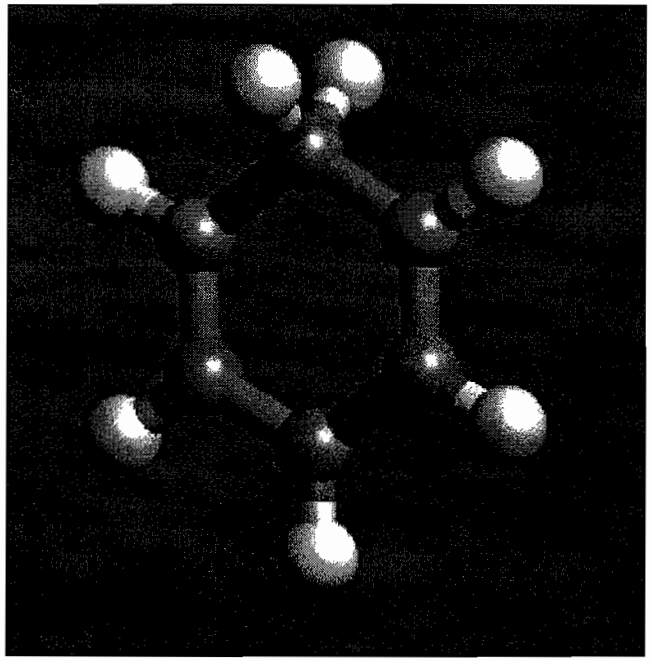
Roderick M. Macrae

Department of Natural and Behavioral Sciences,

Marian College, Indianapolis, IN

Calculation of hyperfine coupling constants

The cyclohexadienyl radical as a test case for open-shell computational techniques.

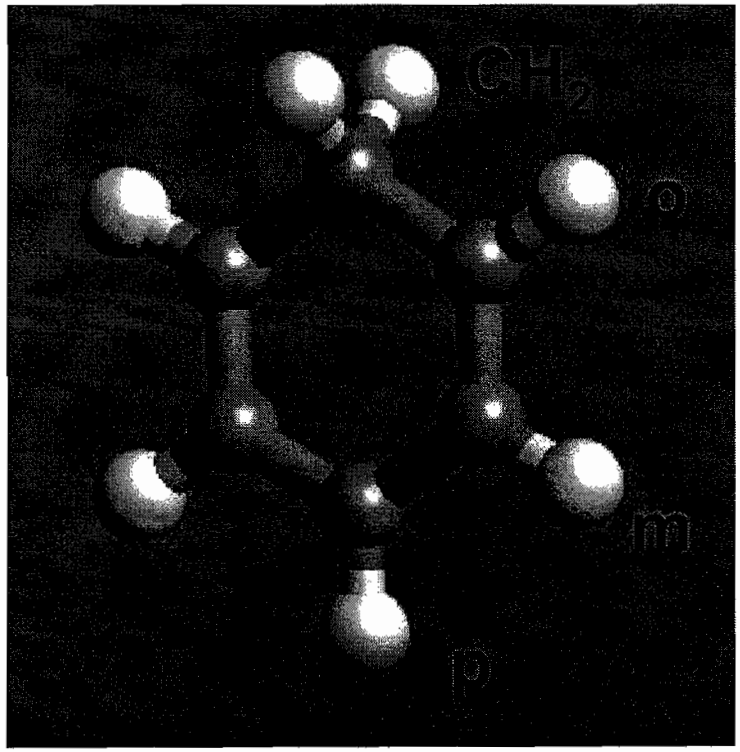


Stoichiometry:

C_6H_7

A simple, well-known radical.

Experimental results



	o	m	p	CH_2
A_p C_6H_7	25.22	7.54	36.83	134.61
A_p C_6H_6Mu	-25.14	7.47	36.19	126.11
A_C C_6H_6Mu	39.57	-35.21	53.95	-34.08
A'_μ C_6H_6Mu				161.61

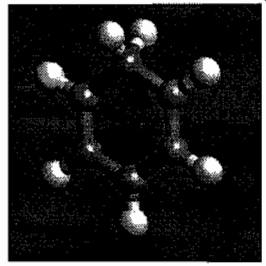
/MHz

References:

ESR (^1H): M. B. Yim, D. E. Wood, *J. Amer. Chem. Soc.* **97**, (1975), 1004.

ALC-μSR: R. F. Kiefl, P. W. Percival, J. C. Brodovitch, S. K. Leung, D. Yu, K. Venkateswaran, S. F. J. Cox, *Chem. Phys. Letters* **143**, (1988), 613.

Ab initio coupling constants vs experiment



In atomic units, $A_{iso} = \frac{8\pi}{3}\alpha^2 \frac{g_{el} g_I}{4m_I} \rho(\mathbf{r})$

	ROHF	ROHF-SCI	MR-SCI	INDO	SCF	CCSD	CCSD(T)
$A_p(CH_2)$	47.4	96.7	100.3	193.9 Ref. 1	142.2	116.6	112.0 Ref. 2

Recent work:

Method	Basis	$A_p(CH_2)$	$A_p(o)$	$A_p(m)$	$A_p(p)$
UB-PW91	6-31G(d,p)	141.8	-28.3	7.8	-37.0
UB-PW91	6-311G(d,p)	139.2	-24.2	6.4	-31.9
UB3-LYP	6-311G(d,p)	137.6	-26.7	9.3	-35.2
UHF	6-311G(d,p)	141.6	-83.4	62.4	-87.3
UCISD	6-31G(d,p)	132.2	-49.8	26.0	-65.2
CIS	6-311G(p)	96.0	-23.7	6.4	-52.0
Exp	-	134.6	-25.2	7.5	36.8

/MHz

Refs.

1. D. M. Chipman, *J. Phys. Chem.* **96**, (1992), 3294.

2. S. A. Perera, L. N. Salemi, R. J. Bartlett, *J. Chem. Phys.* **106**, (1997), 4061.

Story so far:

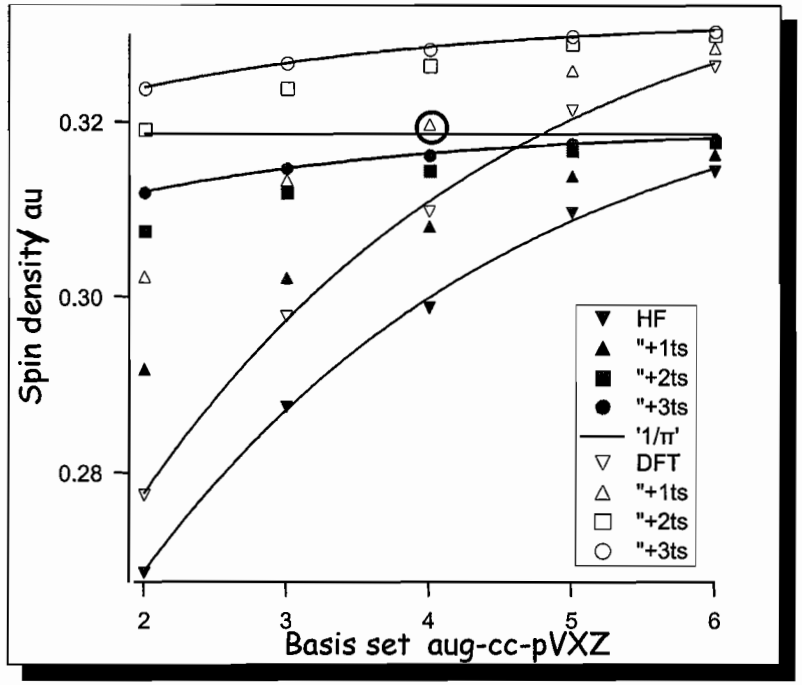
ROHF puts all spin density in SOMO and seriously underestimates spin polarization effects.

UHF suffers from spin contamination - wavefunction is not an eigenfunction of $\langle S^2 \rangle$ - overestimates spin polarization.

Post-HF methods are costly and bear traces of weaknesses of reference function.

Density functional methods give good results at very reasonable computational cost.

Calculated spin density in the free H atom



- Correlation consistent bases
  - Additional compact *s*-functions
    - Inward geometric progression
  - DFT = B3LYP

- Exact result is π^{-1}
  - UHF exact
    - Convergence (from below) is very slow without tight *s*-functions
  - B3LYP limit too large
    - aug-cc-pVQZ + 1 tight *s* (denoted **O**) accidentally matches π^{-1}

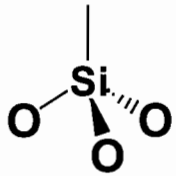
Figure: I. Carmichael

Relevance - H trapping/detrapping in octasilsesquioxanes

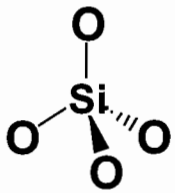
Stoichiometry:

$RSiO_{3/2}$

Nomenclature:

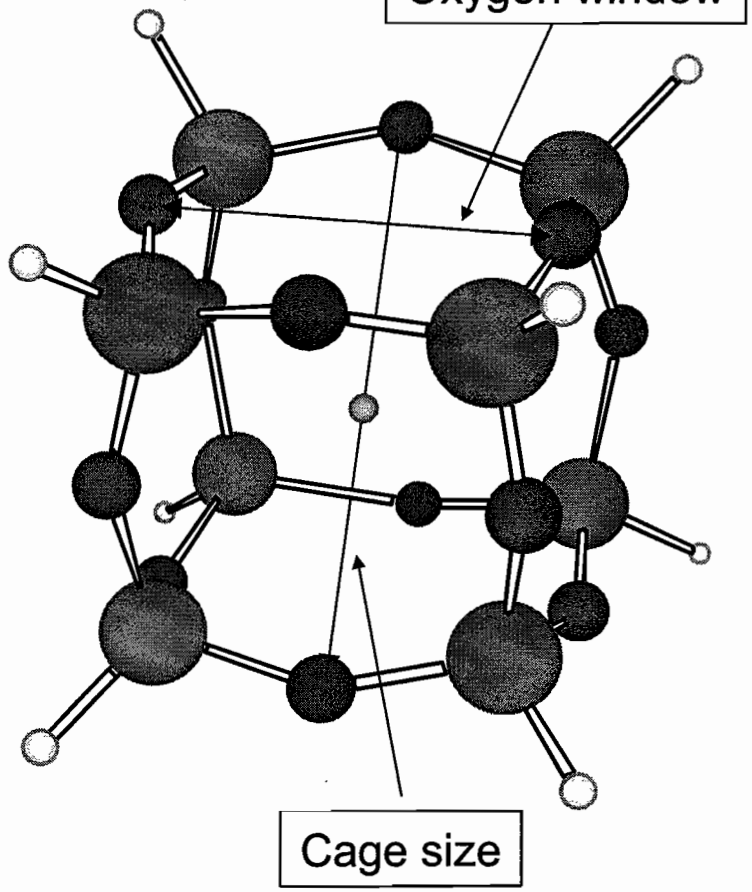


T_8

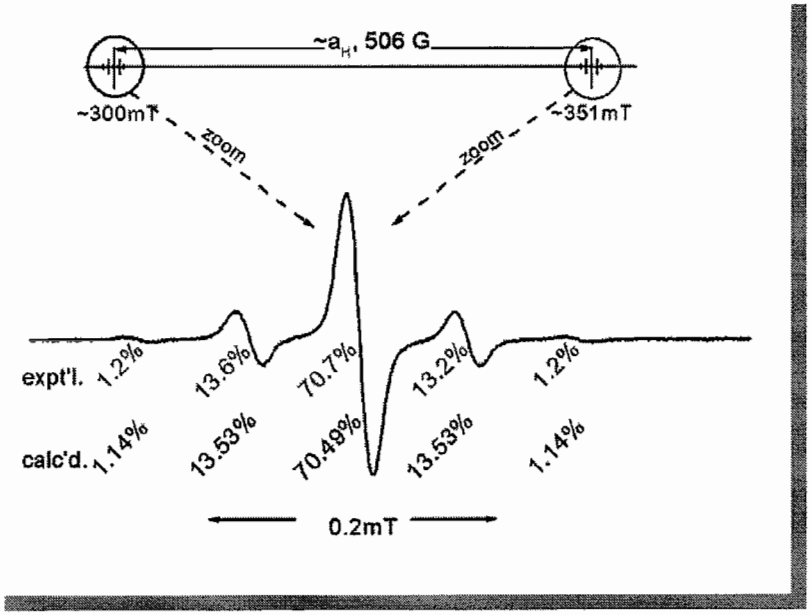


Q_8

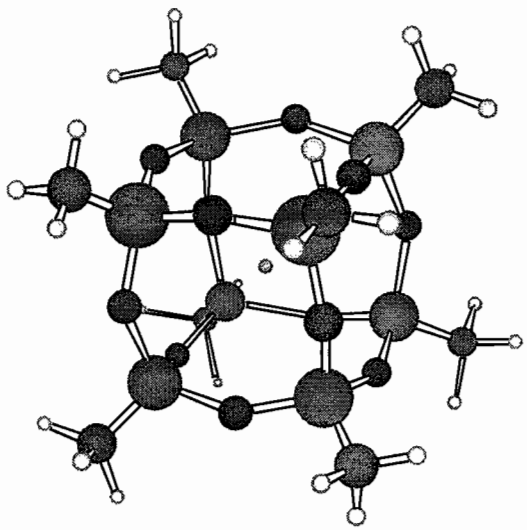
$H@HT_8$



Experimental signature:



H@MeT$_8$



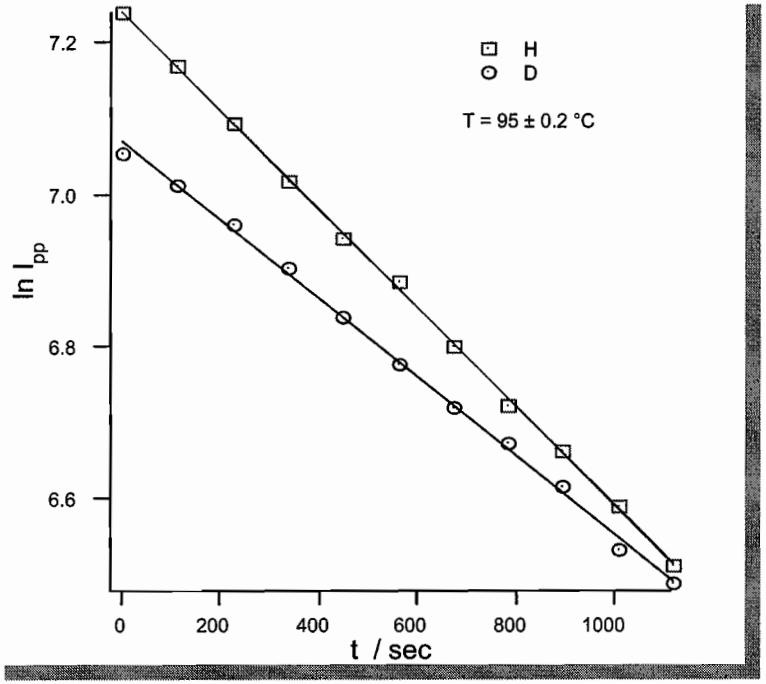
^{29}Si superhyperfine coupling of proton hyperfine doublet.

Intensity pattern consistent with eight I=1/2 ^{29}Si nuclei at 4.9% natural abundance.

H is trapped in the cage!

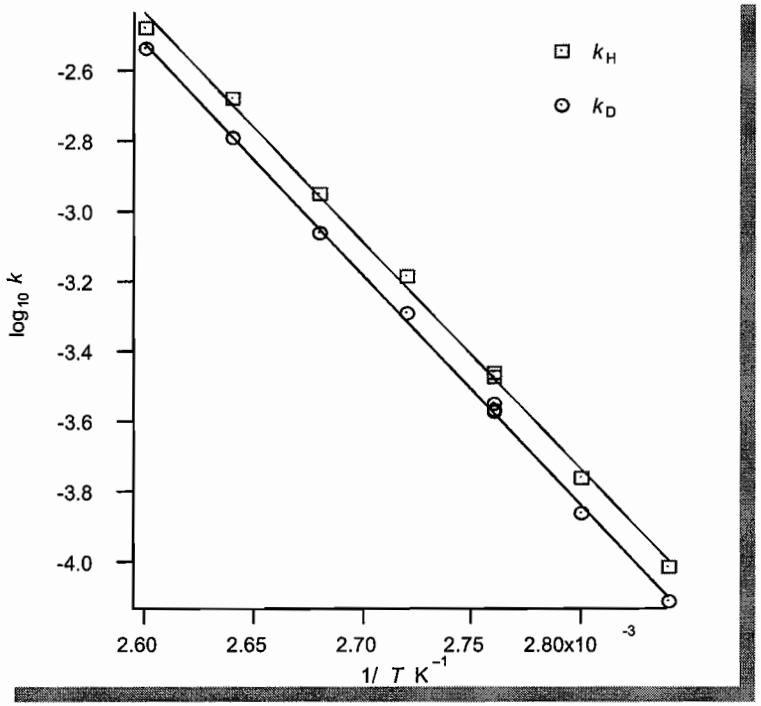
Escape from the cage - H and D atoms

Decay of ESR signal at 95°C
H@MeT_8 in toluene



- H· leaves faster than D·
  - Thermal escape over a barrier

Temperature dependence of H· and D· detrapping from MeT_8

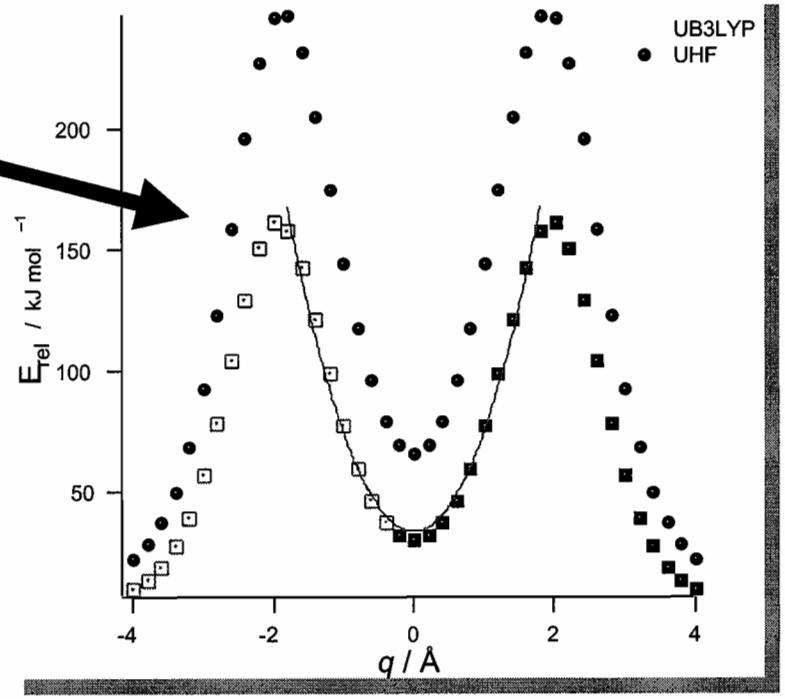


- Activation parameters

	H□	D□
E / kJ mol^{Š1}	126.7	127.4
$\log_{10} A$	14.8	14.8

Rigid trapping potential

Asymptotically matched rigid potentials in $H@HT_8$



- Basis is 6-311G(d,p) on Si, O, and H but cc-pVQZ for H_t
  - 502 basis functions

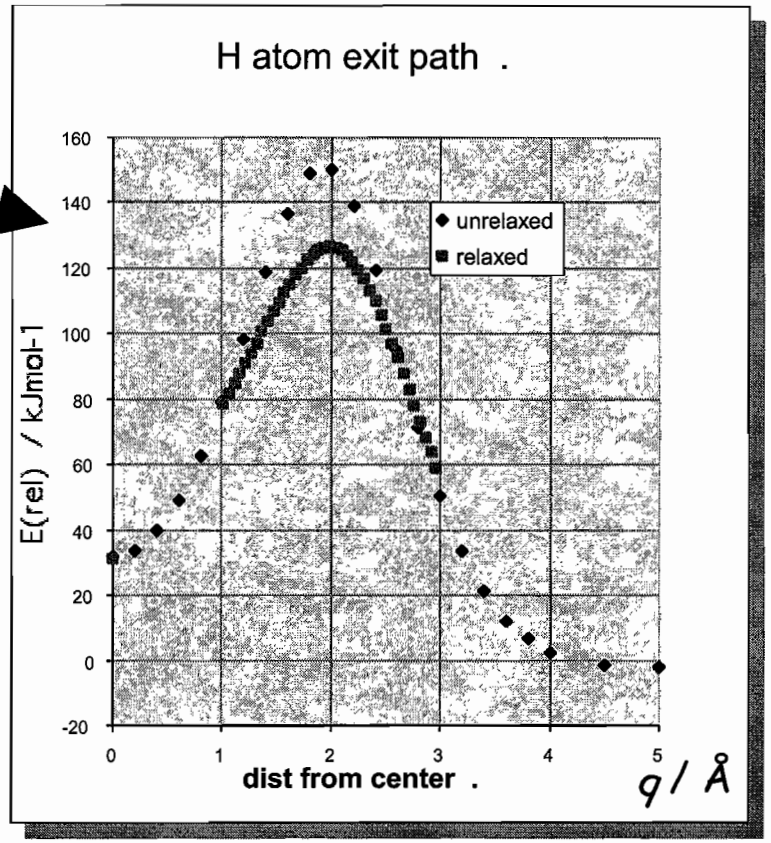
- DFT predicts lower barrier
  - Shallower well
  - Harmonic potential fits well

H· exit path

Comparison of rigid and relaxed trapping potentials in $H@HT_8$

- Escape barrier (kJ mol^{-1})
  - Basis 6-311G(d,p)

	rigid	*relaxed*
UHF	169	158
UB3LYP	132	105
UMP2	125	101
Expt.	127	



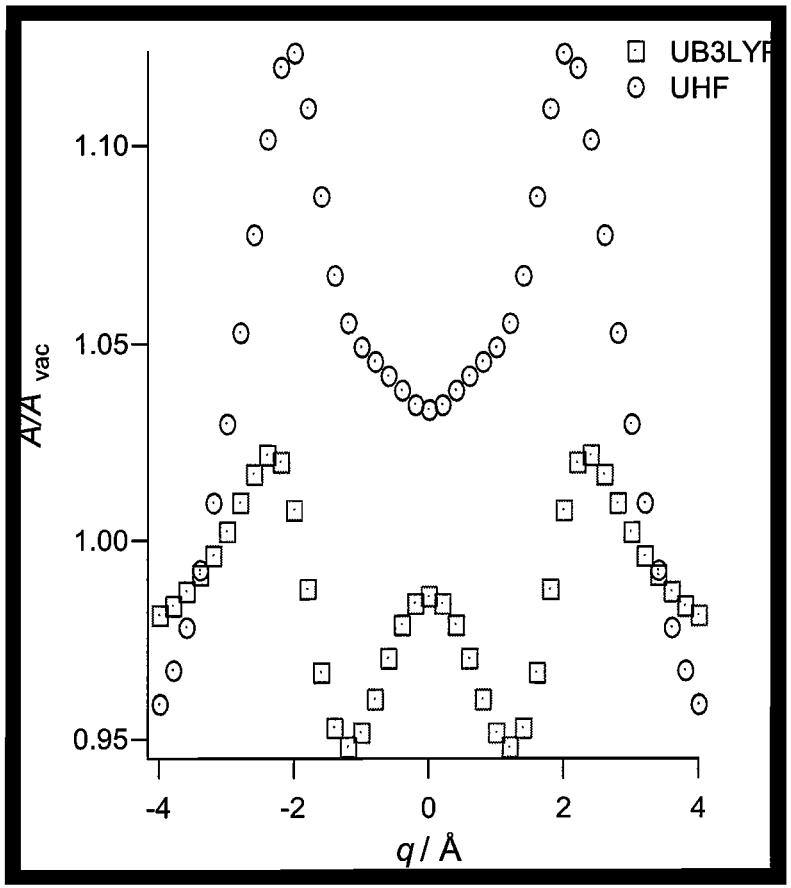
- Rigid cage approximation holds for q < 100 pm

Hyperfine coupling vs displacement from cage center

Scaled hyperfine coupling in rigid cage potential

Basis is 6-311G(d,p) on Si, O, and H but cc-*p*VQZ for H_t

Cage boundary ~ 200 pm



- Dramatic differences in coupling behavior between UHF and UB3LYP
  - UMP2 agrees with DFT

Calculating the ^{1}H hyperfine coupling eigenvalues

$$V(r) = V_0 + \frac{1}{2}kr^2$$

$$A_p = a_0 + \sum_i a_i r^{2i}$$

$$= a_0 + \sum_i a_i \sum_{\lambda+\mu+\nu=1} (i;\lambda,\mu,\nu) x^{2\lambda} y^{2\mu} z^{2\nu}$$

$$\langle A_p \rangle_{n_x n_y n_z} = a_0 + \sum_i a_i \beta^{2i} \sum_{\lambda+\mu+\nu=1} (i;\lambda,\mu,\nu) K^{(2\lambda)}_{n_x n_x} K^{(2\mu)}_{n_y n_y} K^{(2\nu)}_{n_z n_z}$$

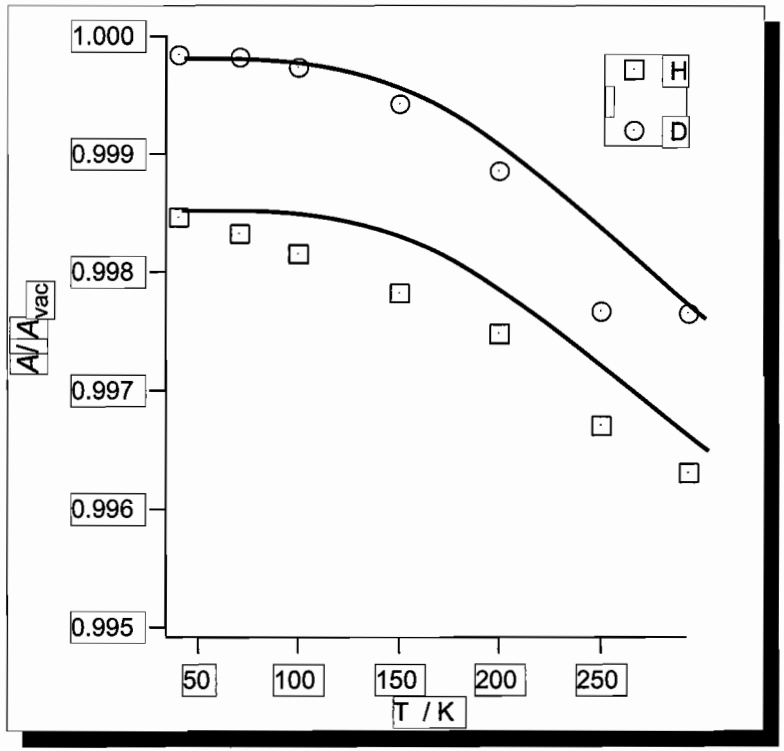
- Assume harmonic potential
  - and local isotropicity
- Expand coupling at H_+ in an *even* power series in *r*
  - $(i;\lambda,\mu,\nu)$ are multinomial coefficients
    - $i!/(\lambda!\mu!\nu!)$
- Expectation value
  - K are Hermite polynomial matrix elements
    - From recursion relation
  - β depends on mode frequency
    - and on effective mass
- Temperature dependence from Boltzmann averaging

Temperature-dependence of A_p

Experimental results A = $a(^nH)$ scaled against vacuum values

H 1420.4057 MHz
D 218.2563 MHz

Computed values scaled to A_H at low T



- Isotope effects recovered — even for muonium(~0.986)
- Trends qualitatively correct but temperature dependence too weak
  - Need to consider cage nonrigidity?

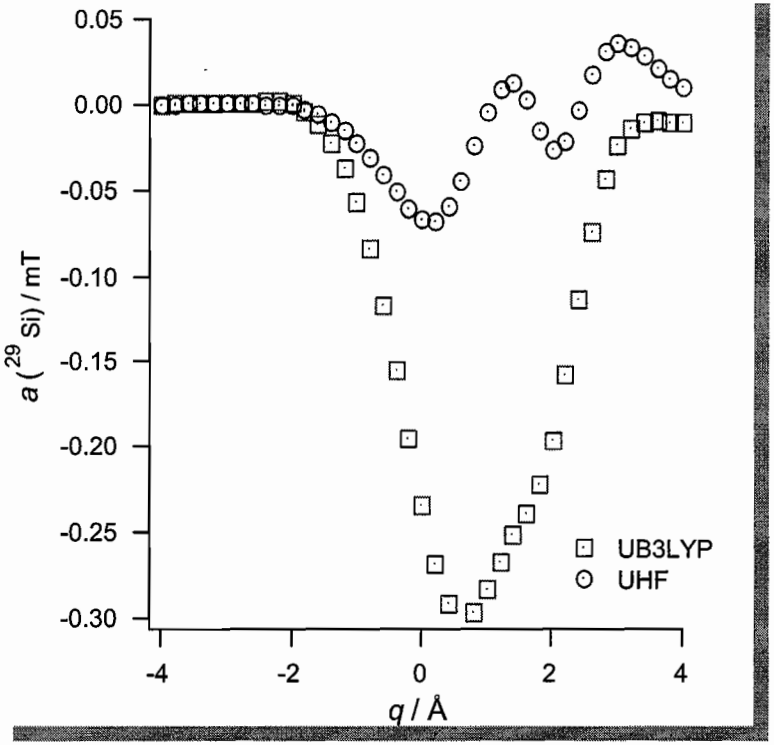
Experiment — Dilger *et al.*, *Physica B* **289** 482 (2000)

^{29}Si superhyperfine couplings

Basis is 6-311G(d,p) on Si, O, and H but cc-pVQZ for H_t

Coupling asymmetric w.r.t. H displacement

- Dramatic differences in coupling behavior between UHF and UB3LYP
- UMP2 agrees with DFT



Expectation values of superhyperfine coupling

$$V(r) = V_0 + \frac{1}{2}kr^2$$

$$A_{Si} = a_0 + \sum_i a_i q^i$$

$$\langle A_{Si} \rangle_n = a_0 + \sum_i a_i \beta^i K_{nn}^{(i)}$$

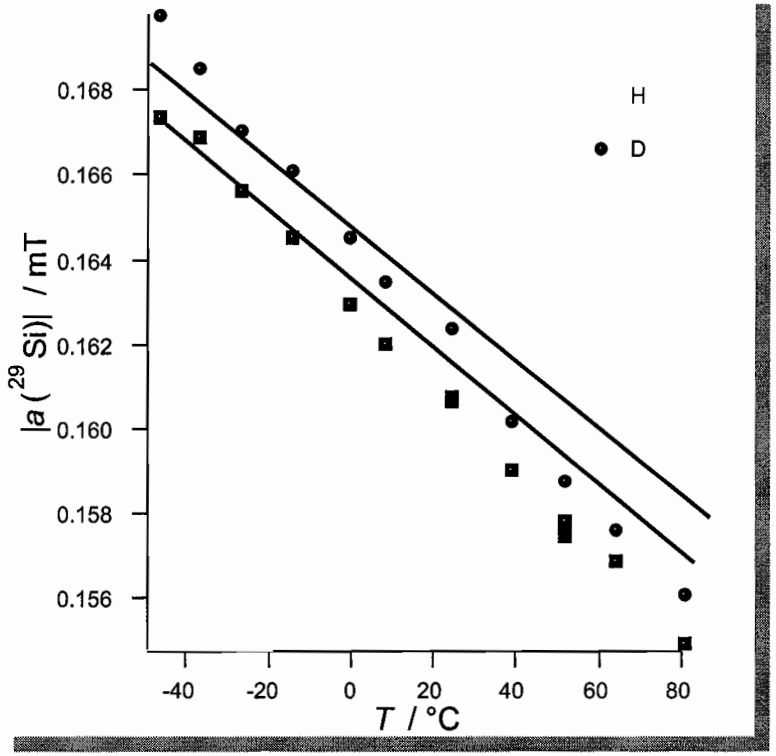
- Assume motion along three orthogonal channels
  - each in a harmonic potential
- Expand coupling at Si in an *odd* power series in *q*
- Expectation value
  - β depends on frequency
- Temperature dependence from Boltzmann averaging

T-dependence of superhyperfine coupling

Calculated T-dependence based on B3LYP data

$$a_N = \frac{8\pi}{3} g_e \beta_e g_N \beta_N Q_N(0) / n_e$$

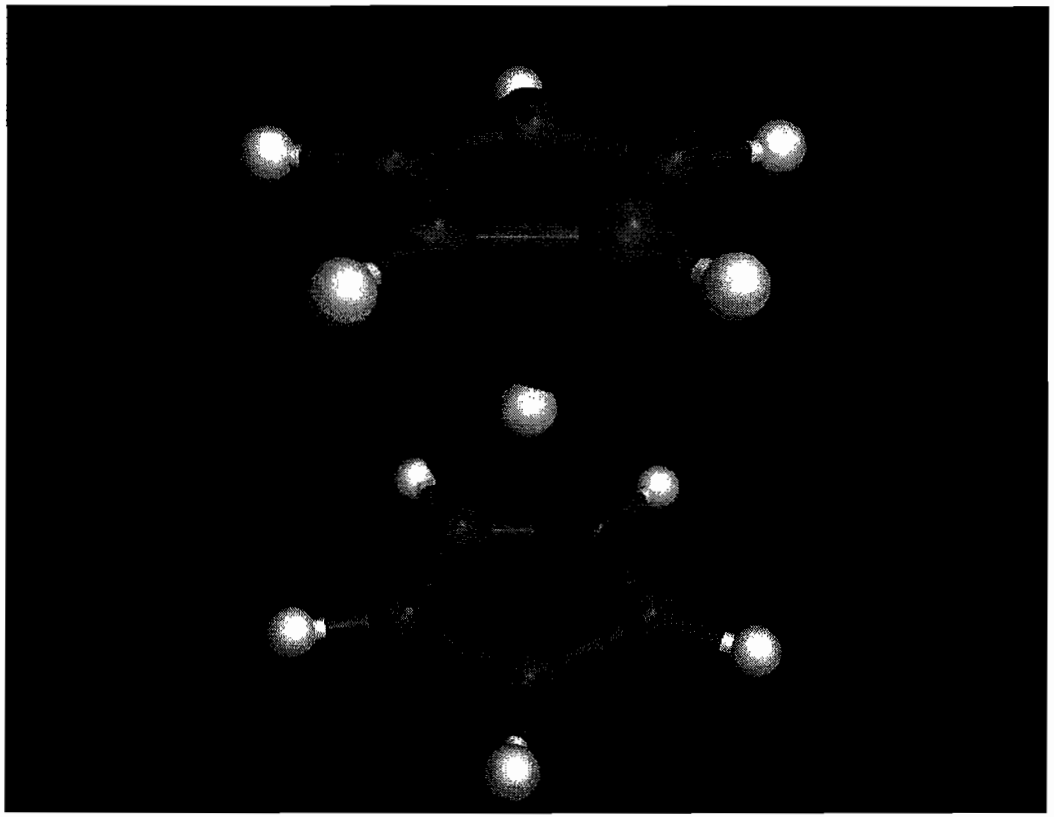
$$Q_N(0)/n_e = \frac{\langle \psi | \sum_i \delta(\mathbf{r}_i - \mathbf{r}_N) 2\hat{S}_{z_i} | \psi \rangle}{\langle \psi | \sum_i 2\hat{S}_{z_i} | \psi \rangle}$$



- Slopes qualitatively correct but temperature dependence too weak
  - Need to consider nonrigid cages
- Isotope ordering correct, but results scaled to match low-T data for H·
  - Si basis set inadequacies

Ferrocene

$C_{10}H_{10}Fe$ or $Fe(cp)_2$



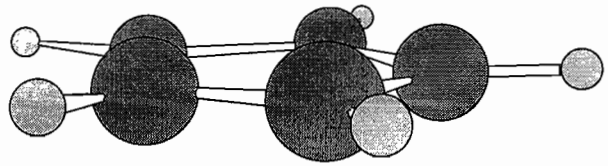
The prototypical metallocene.

A notoriously problematic system for computational chemistry.

Ferrocene - theory vs experiment

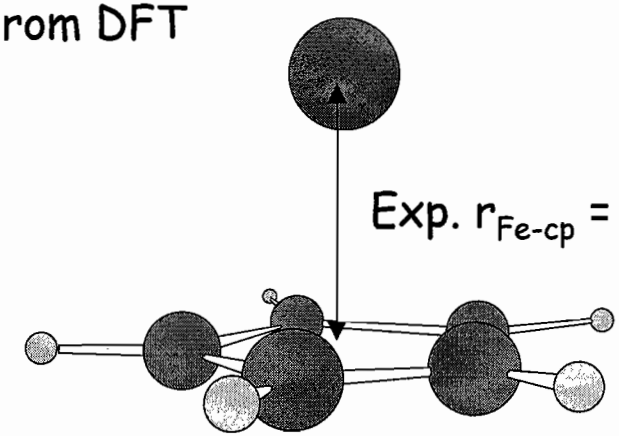
Unusual symmetry - D_{5d} in crystal, D_{5h} in gas phase. Singlet spin state.

Metal-ring distance:



Method	Basis functions	$r_{Fe\text{-}cp}$/Å
HF[1]	351 GTO	1.88
MP2[2]	510 GTO	1.58
MCPF[2]	510 GTO	1.68
CASPT2[3]	255 GTO	1.64
LDA/NL[4]	TZ/DZ STO	1.64

Good results from DFT



Exp. $r_{Fe\text{-}cp}$ = 1.65Å

Refs.

1. H. P. Lüthi et al., *J. Chem. Phys.* **77** (1982) 2002
2. C. Park, J. Almlöf, *J. Chem. Phys.* **95** (1991) 1829
3. K. Perloot et al., *J. Phys. Chem.* **99** (1995) 3465
4. A. Bérces et al., *J. Phys. Chem.* **98** (1994) 1584

μSR Experiments

(U. Jayasooriya et al.)

LF-μSR and ALC-μSR results interpreted in terms of *three* radicals:

Fe adduct - model incorporates spin-orbit coupling:

Fe adduct

A'_μ(166 K) = 60 MHz

$$\hat{H} = \gamma\zeta\hat{\mathbf{l}} \bullet \hat{\mathbf{S}} + A_\mu \hat{\mathbf{I}}_\mu \bullet \hat{\mathbf{S}} + B\left[\left(\frac{1}{2}\gamma\hat{l}_z + \hat{S}_z\right)\nu_e - \hat{I}_{\mu z}\nu_\mu\right]$$

Cp ring adducts:

"agostic Mu"

"agostic H"

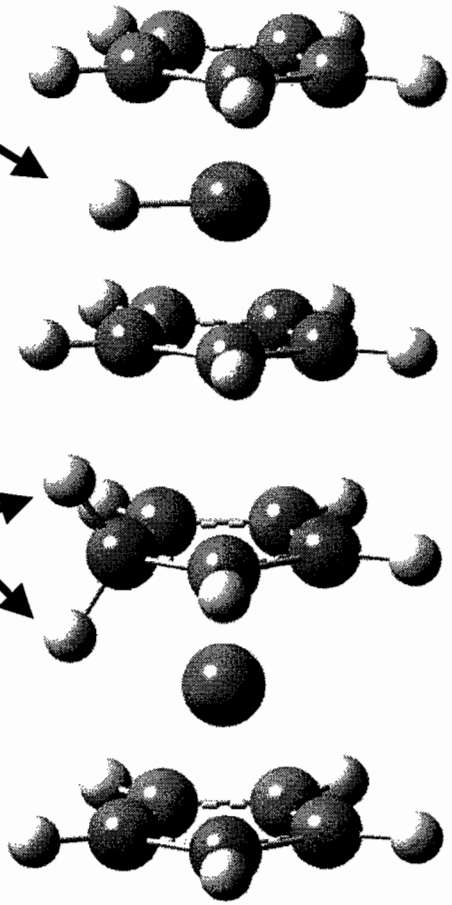
(shared between ring and Fe)

Cp adducts

A'_μ = 101 MHz, A_H = -57 MHz*

or

A'_μ = 209 MHz, A_H = 56.5 MHz*

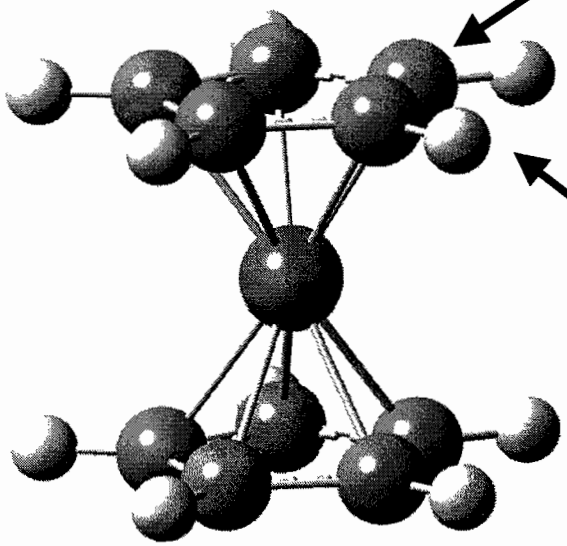


* model-dependent

Protonated Ferrocene

No calculations in the literature on neutral ferrocene H adducts.

Protonated (cation) species has been considered in context of electropilic attack on $Fe(cp)_2$.



Exo attack (hard electrophiles) leads to Cp adduct

Endo attack (soft electrophiles) leads to Fe adduct or "agostic" species

Theory:

DFT (B-PW91) and CCSD

M. J. Máyor-Lopez et al., *J. Chem. Phys.* **113** (2000) 8009

Agostic species seems to be global minimum by ~8 kJ mol^{-1}

Probable rapid interchange between ring and metal-protonated forms (supported by HPMS)

DFT results

Method/basis: B3LYP/6-31G(d) and B3LYP/6-311+G(d,p)

196 symmetry-adapted GTOs	344 symmetry-adapted GTOs
428 primitives	542 primitives

Benchmark calculation: ferrocene

$r_{Fe\text{-}cp}$ = 1.656Å prismatic (eclipsed geometry - minimum)

$r_{Fe\text{-}cp}$ = 1.657Å antiprismatic (staggered - saddle point)

ΔE = 0.656 kJ mol^{-1} (6-31G(d)), 7.59 kJ mol^{-1} (6-311+G(d,p))

Experiment (gas-phase electron diffraction) 3.8±1.3 kJ mol^{-1}.

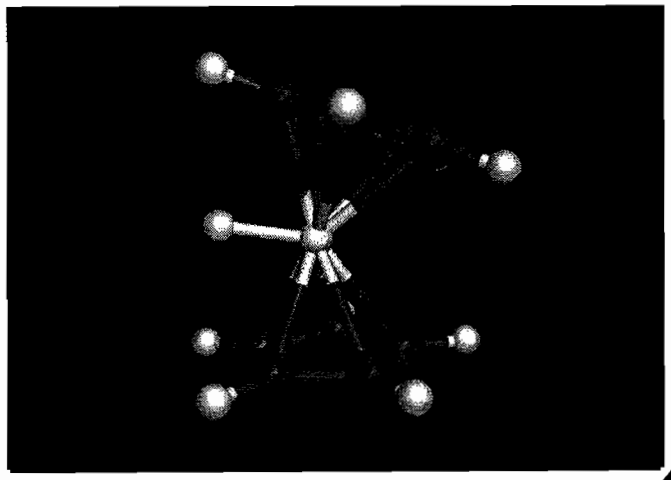
H(Mu) adducts

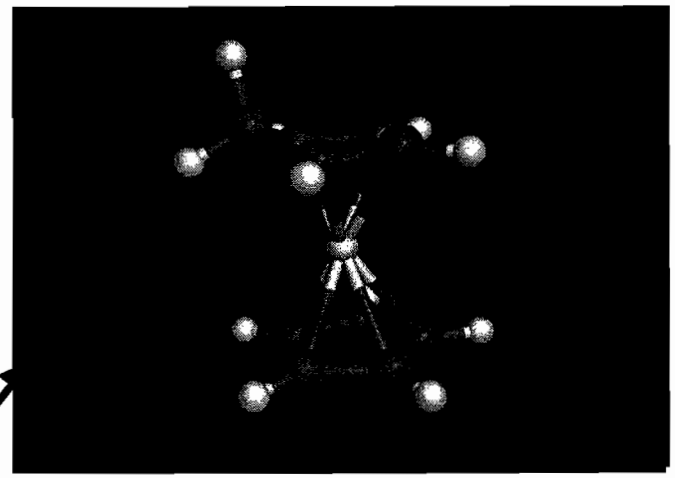
B3LYP/6-311+G(d,p)

Both adducts optimize to *staggered* ring geometry (eclipsed is saddle-point).

Cp adduct favored by ~100kJ mol^{-1}.

No evidence of stable agostic species.

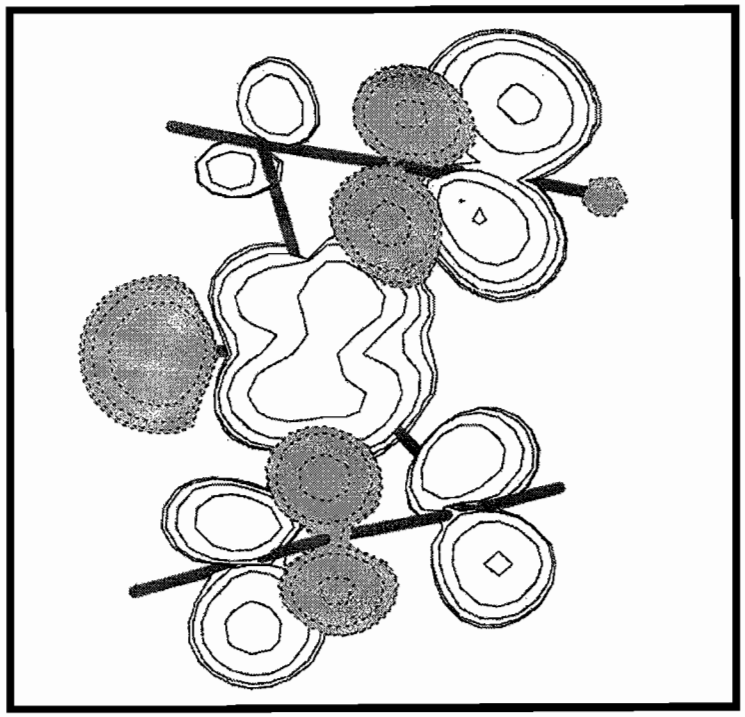


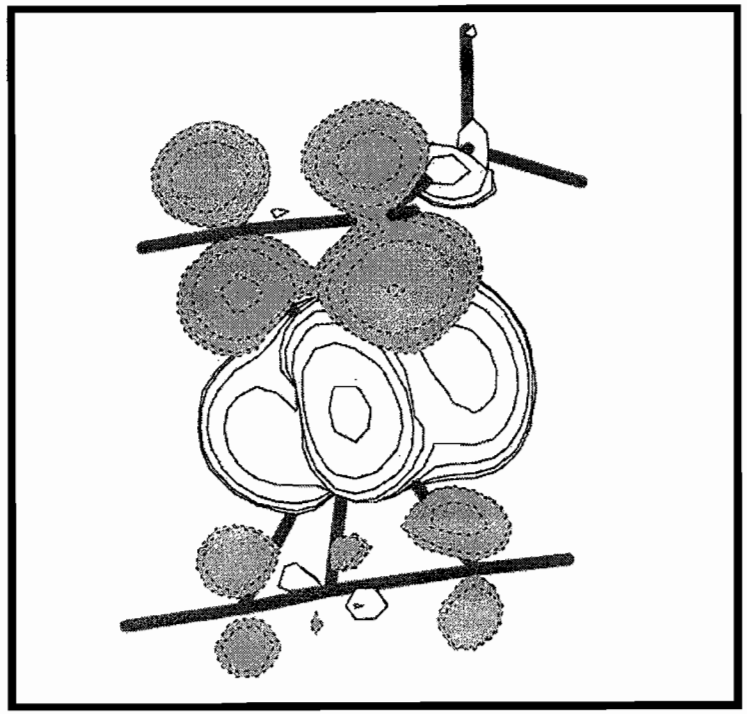


Out-of-plane distortion

6-31G(d) values consistent with these. Little staggered-eclipsed dependence of couplings.

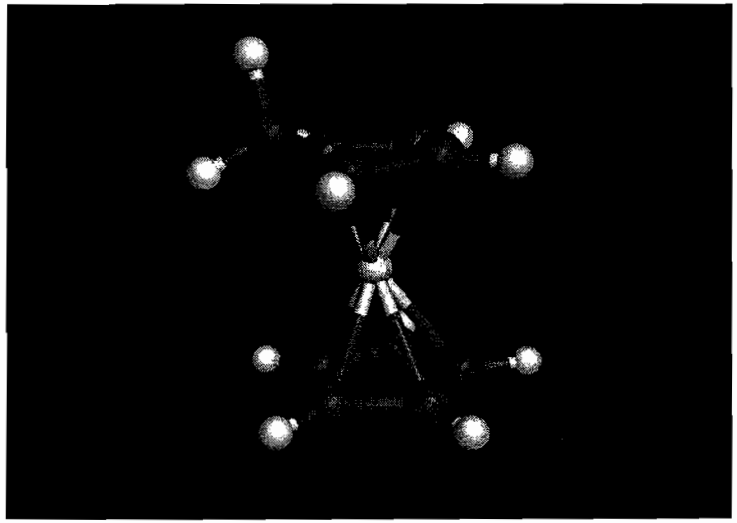
Spin density distributions in Fe and Cp adducts



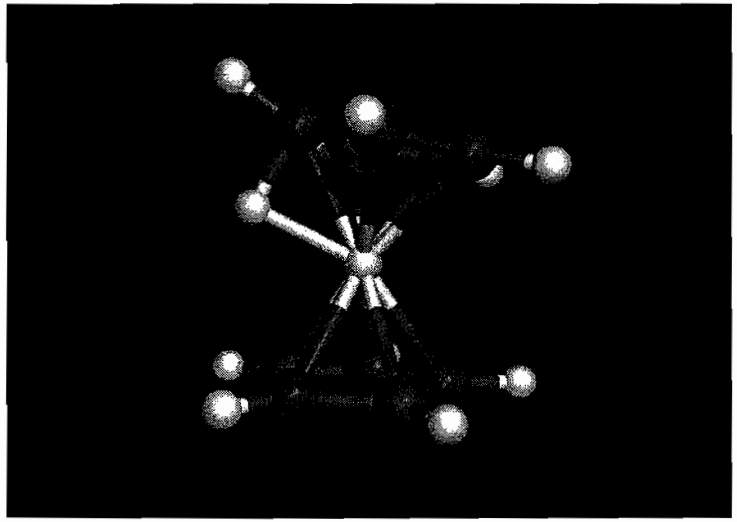


Relative stabilization of Cp adduct w.r.t. Fe adduct comes mainly from 89.3 kJ mol^{-1} energy difference between SOMOs.

Radical vs cation



Puckered ring - conventional C-H bond lengths



Near-planar ring - truly agostic (in agreement with CISD result).

Ring puckering effect on hfcc?

Cp adduct - effect of puckering (6-31G(d))

Initial geom. (planar ring)	→	Optimum geom. (puckered)
A_H = 176.1 MHz (exo)		A_H = 6.3 MHz (exo)
A_H = 97.7 MHz (endo)		A_H = -0.9 MHz (endo)

Dramatic effect on coupling.

Important to determine if puckering reproducible with other methods (MP2).

Cf. Mayór-Lopez et al. (*JCP* **113** (2000) 8009) - different degrees of puckering obtained for cation using different methods - lowest with DFT, highest with MP2.

Importance of *vibrations* - under investigation.

Conclusions

1. Hybrid density functional theory gives results comparable with high-level post-HF methods for radicals and (subject to scaling) H atoms.

2. Experimental results on cyclohexadienyl radical (simple model system) reproduced with good accuracy.

3. Siloxane cages - qualitative behavior of H isotope hyperfine couplings and Si superhyperfine couplings is reproduced.

4. Ferrocene H/Mu adducts - high-(-ve)-coupling Fe adduct species and low-coupling Cp adduct species identified. No evidence of an agostic species, in contrast with the protonated ferrocene cation.

5. Ring puckering effects in Cp adduct may be important for determining both size of coupling and extent of T-dependence.

Collaborators:

Radicals: Dr. B. Webster (Glasgow)

Siloxanes: Dr. Ian Carmichael, Dr. Michael Paech (NDRL)

Ferrocene: Dr. Upali Jayasooriya, Dr. Penny Hubbard, Dr. Roger Grinter (UEA) - thanks to Prof. John Plane (UEA) for computational facilities.

Financial support:

Siloxanes: Basic Energy Sciences, USDOE

Ferrocene: RF project, EPSRC

A strategy for the measurement of the vibrations of a muoniated radical centre: Experimental evidence

F.L. Pratt (RAL)

Summary

The combination of pulsed illumination and μSR offers a new way to spectroscopically identify muoniated radical states by utilising the vast database of hydrogenic vibrational frequencies. The anharmonicity of the vibrational potential leads to a difference in the hyperfine tensor between excited vibrational states and the ground state. Long lifetimes for excited states make detection by light emission very difficult but studies become feasible using absorption combined with state detection via the muon polarization.

An initial experiment was carried out using an oriented single crystal of benzophenone in which a single type of muoniated radical could be formed with a unique orientation of its hyperfine tensor (previously determined to be 19° to the c-axis). Pulsed illumination at $\lambda > 850$ nm resulted in a light-induced asymmetry change being observed in the repolarisation data; the magnitude of which was in agreement with a theoretical calculation based on ethanal.

Having demonstrated the principle of the technique, further work is planned but will require a high-power, tuneable source of illumination and finer control of field and sample orientations.

A Strategy for the Measurement of the Vibrations of a Muoniated Radical Centre: Experimental Evidence

Francis Pratt
ISIS

Upali A. Jayasooriya, Georgina Aston, Susan Hall, Penny Hubbard
UEA

Martin McCoustra
Nottingham

ChemPhysChem 5, 257 (2004)

ISIS

Motivation

New way to spectroscopically identify muoniated radical states, based on the vast database of hydrogenic vibrational frequencies

Anharmonicity of the vibrational potential leads to a difference in hyperfine tensor between excited vibrational states and the ground state

Could also be useful for gaining information about anharmonicity in molecular vibrational potentials at large displacement

Long lifetimes for excited states (e.g. fraction of a ms in MuF*) make detection by light emission very difficult, but studies becomes feasible using absorption combined with state detection via the muon polarisation

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Demonstration Experiment

Requirements:

Relatively high vibrational frequency, compatible with available tunable sources

O-Mu stretch: 1μm or 10,000 cm^{-1}

Slowest possible vibrational relaxation rate

Solid phase at low temperature

System with one type of radical and one orientation of the hyperfine tensor

Possibility to grow large single crystals

→ **Benzophenone**

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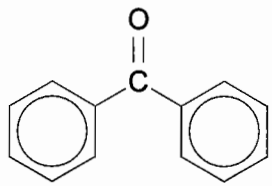
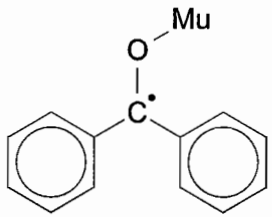
Benzophenone and its Muoniated Radicals

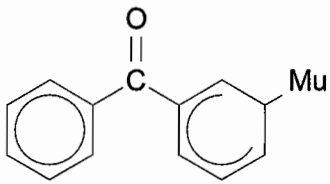
Benzophenone



Carbonyl radical (muon analogue of diphenylhydroxymethyl radical)



Phenyl or Ring radical



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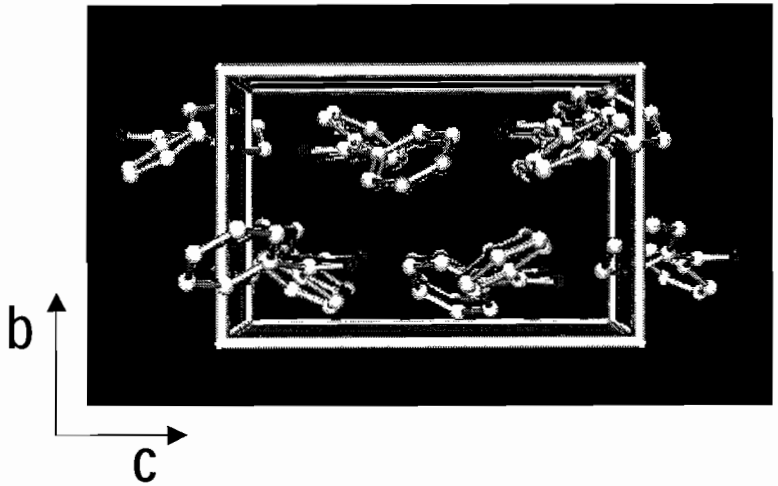
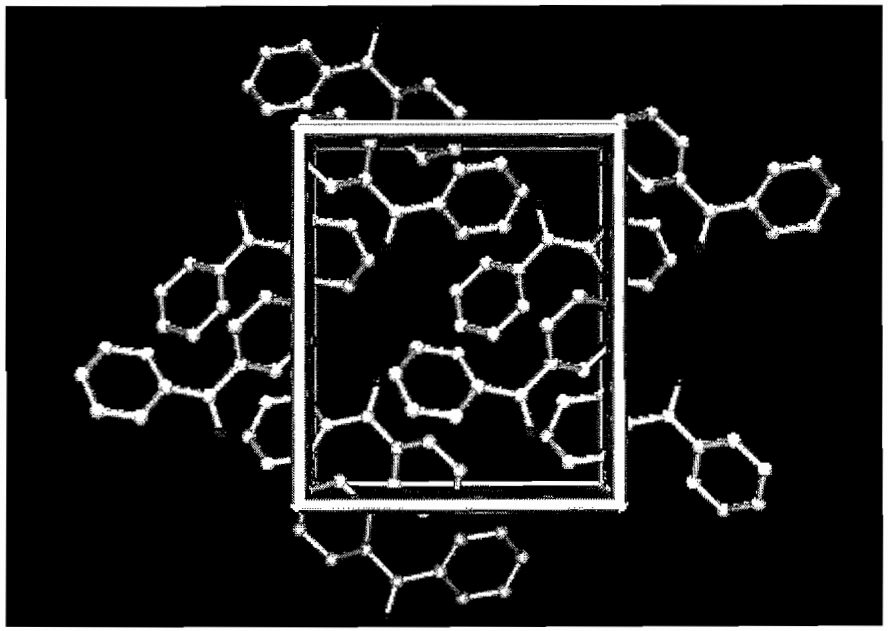
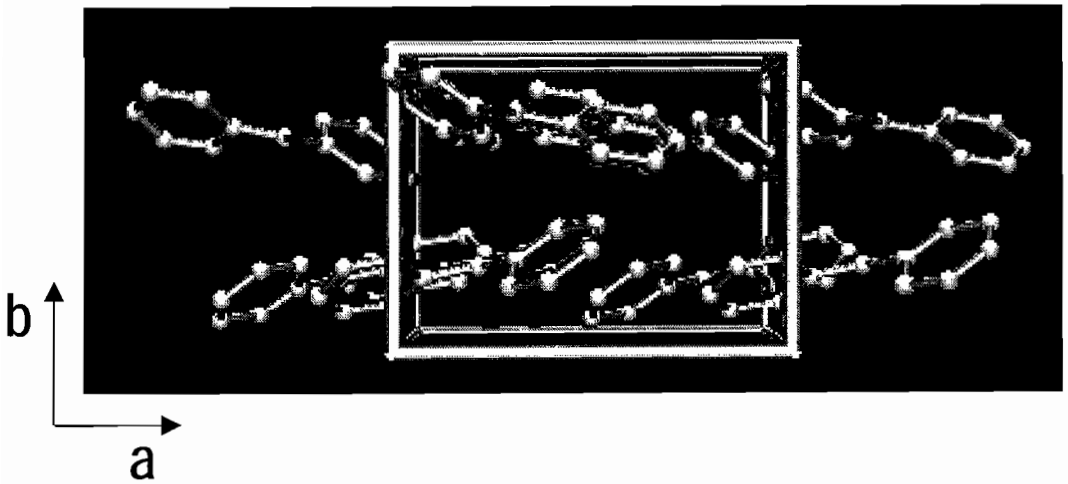
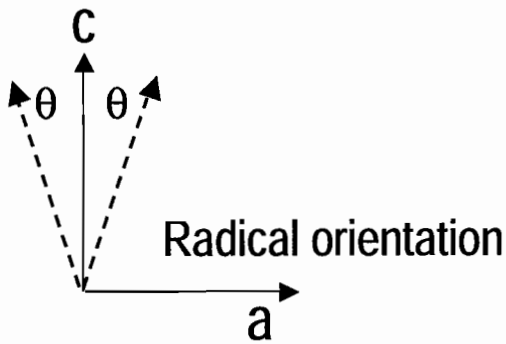
Benzophenone Crystal Structure



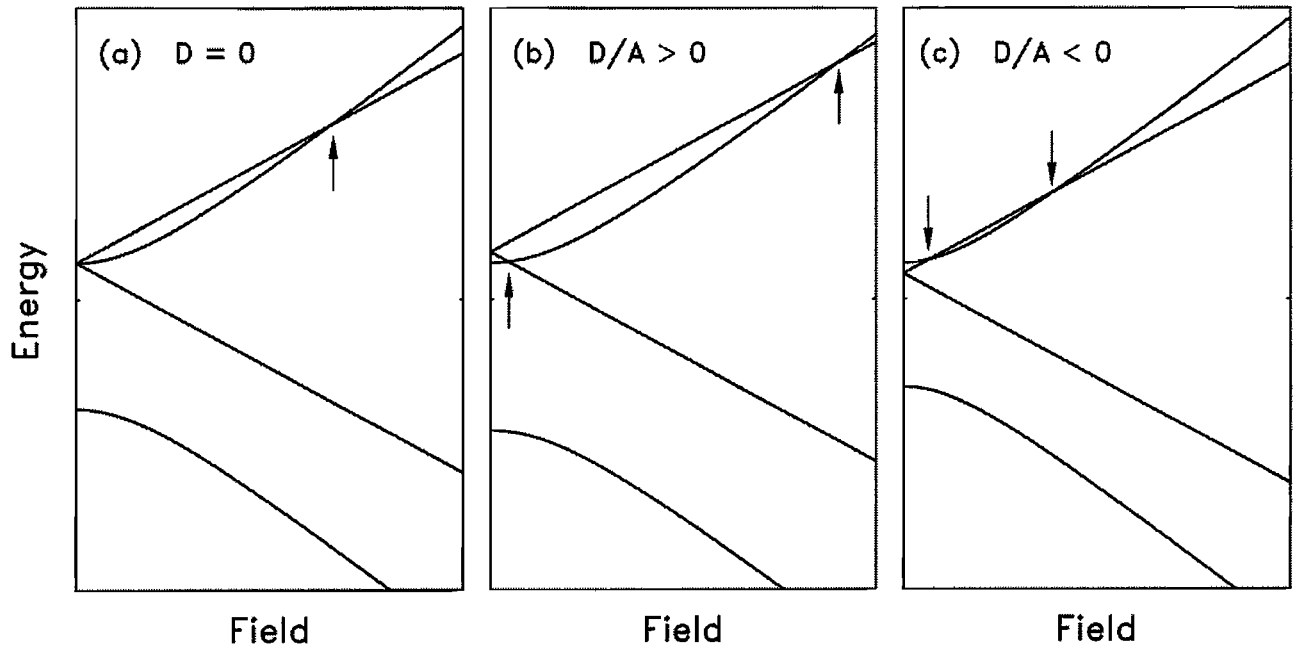






Level Crossing Resonance (LCR)

$\Delta M=1$ resonances (muon spin flip)



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Previous Angle-Dependent Muon Spin Rotation Studies at PSI

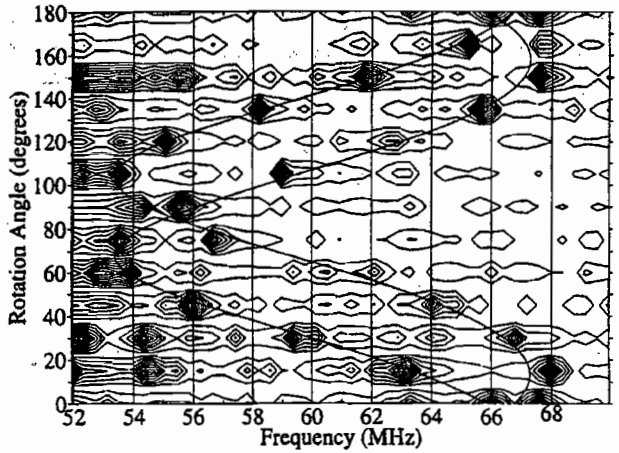


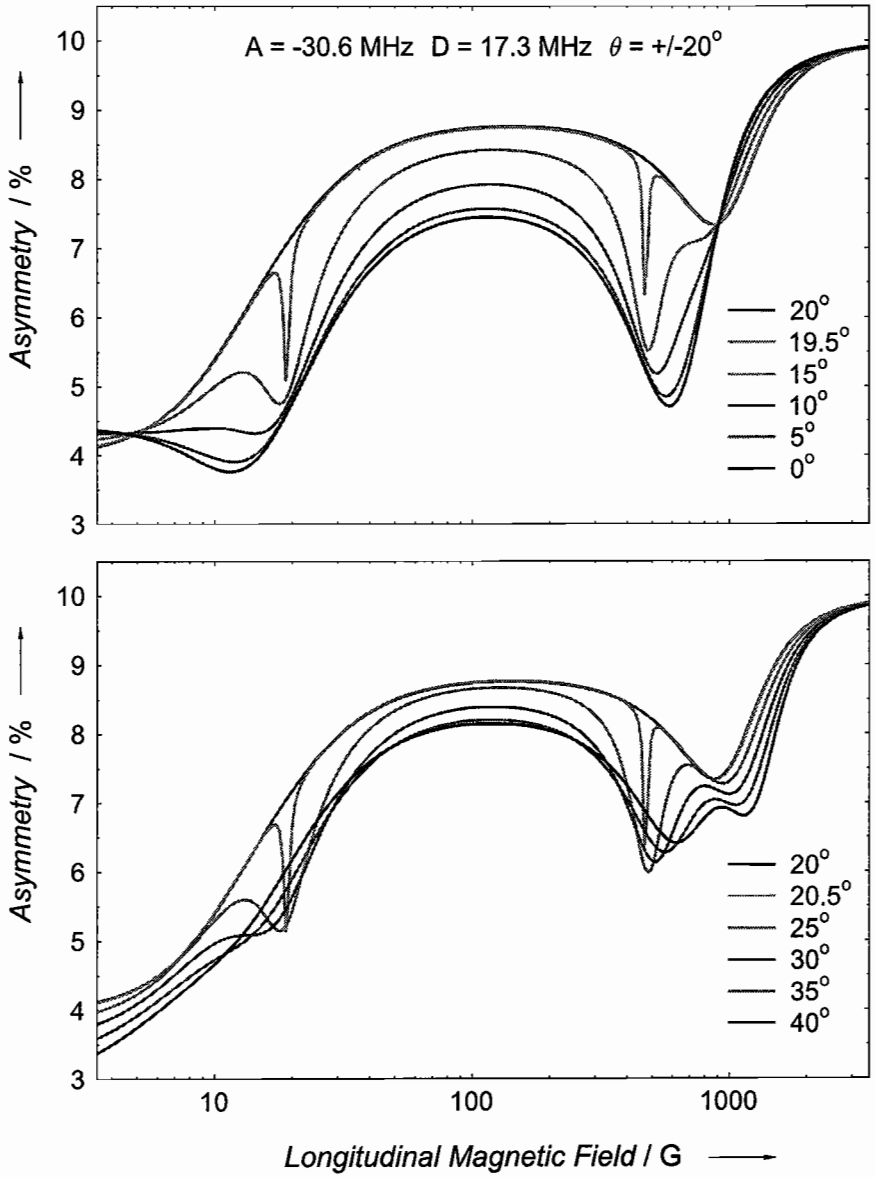
Fig. 1. Variation in the upper radical frequency ν_+ as the crystal was rotated about the b axis. The a axis is parallel to the 3 kG field at 176° and the c axis is at 86°. The lines show the values from the fitted hyperfine tensor.

$|A| = 31.8$ MHz; $|D| = 21.0$ MHz
Oriented at 19° to the c axis
(room temperature study)

Aston et al, HFI 106, 157 (1997)

ISIS

LCR Simulation for a Benzophenone-like System



Pair of radicals at +/-20°

When the field direction becomes close to the principal axis, the resonances sharpen up and then vanish for exact alignment

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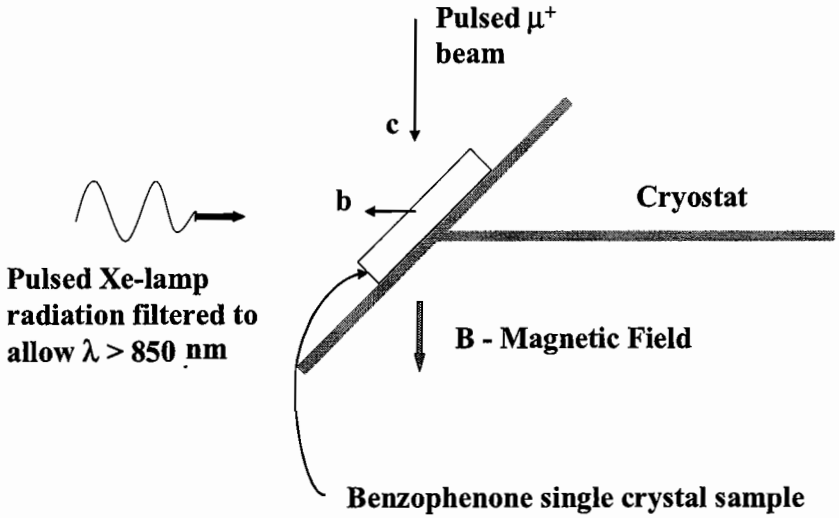
Experimental Setup

Experimental setup: Light pulse synchronized to every other muon pulse.



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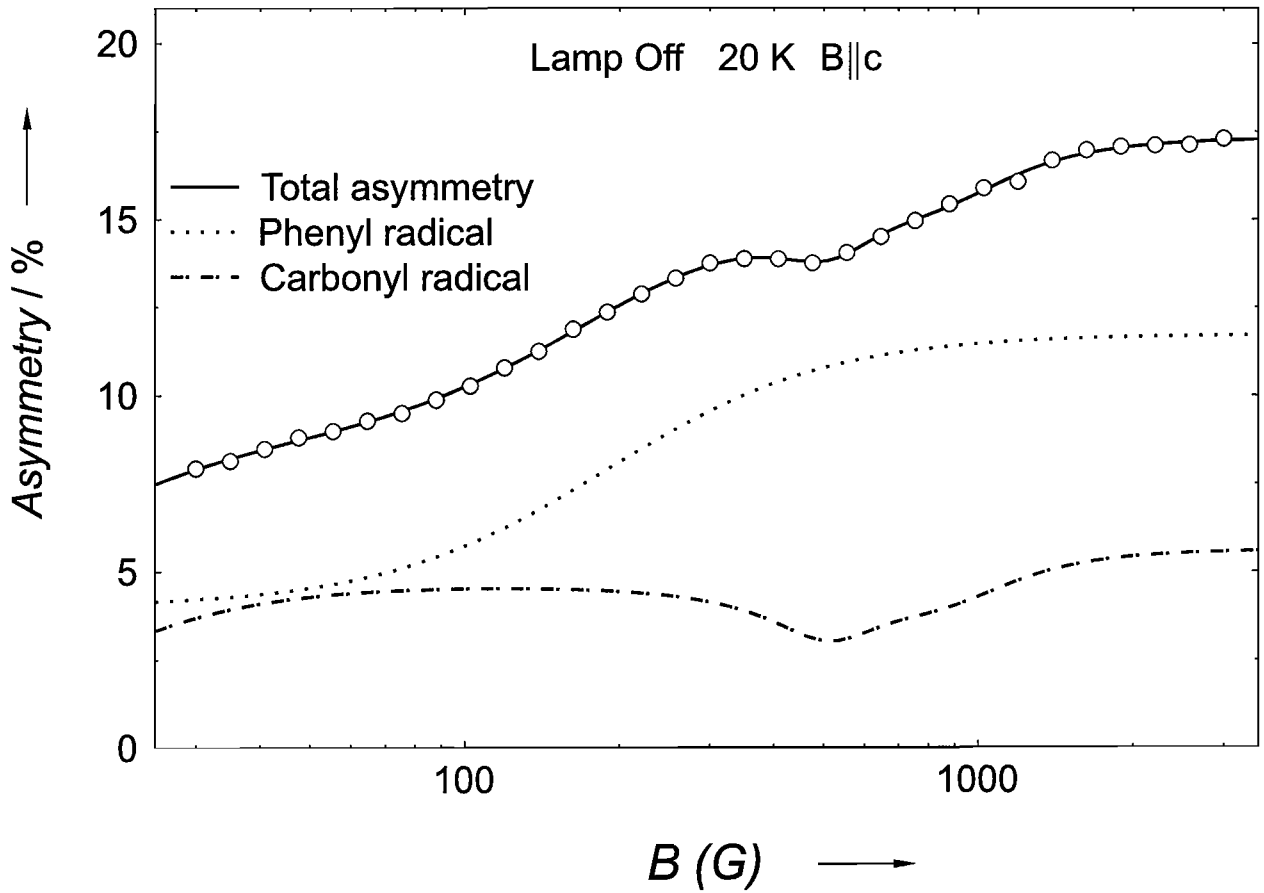
Measurement – Repolarisation and Level Crossing



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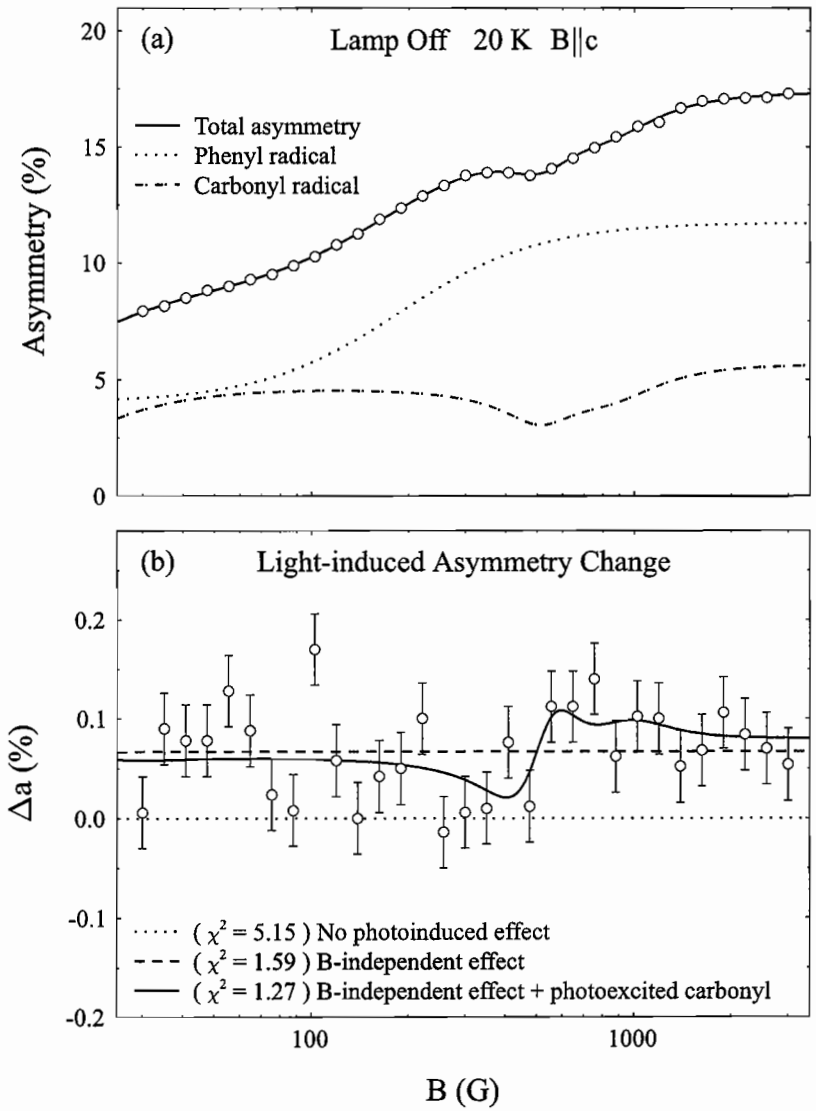
Measurement – Light Effect



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Fitted Parameters

Ground State (light off):

Carbonyl adduct			Ring adduct
A_{CO} (MHz)	D_{CO} (MHz)	θ (°)	A_{ring} (GHz)
-30.6(8)	17.3(5)	22(1)	0.53(1)

Excited State (light on):

ΔA_{CO} = +0.21(5) MHz

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Expected Size of the Photoinduced Effect

Calculation of A_{CO} for the *trans* O-Mu state in ethanal

Probert and Fisher JPCM 9, 3241 (1997)

Calculated Hyperfine Coupling

Ground state:	A_{CO} = -25.1(4) MHz
First excited state:	A_{CO} = +44.9(8) MHz
Difference:	ΔA_{CO} = +70.0(9) MHz

Experiment

Observed change:	ΔA_{CO}^{obs} = +0.21(5) MHz
Excited state fraction:	0.2 MHz / 70 MHz = 0.3 %
	(Assuming ΔA_{CO} is similar between benzophenone and ethanal)

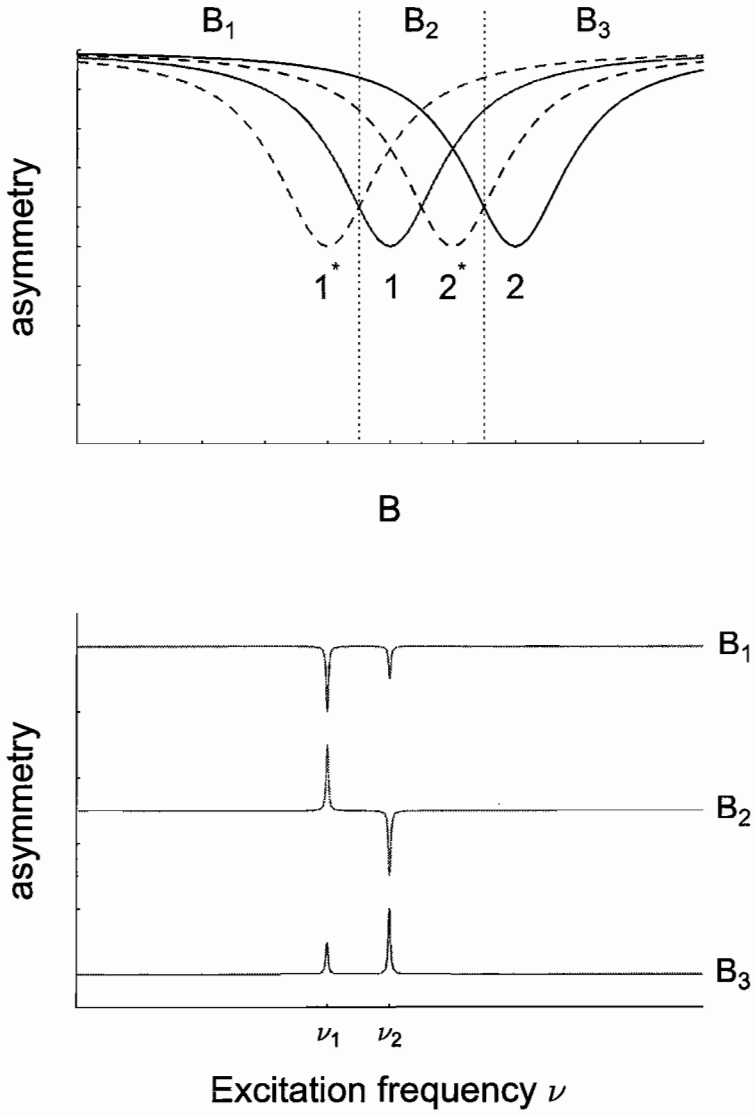
Power Spectral Density

P_{calc} = 0.6 W $nm^{-1}cm^{-2}$ (for 0.3% population of the excited state)

P_{est} = 0.3 W $nm^{-1}cm^{-2}$ (estimated power used in actual experimental setup)

ISIS

Muonium Vibrational Spectroscopy with Tunable Lasers



ISIS

Conclusion

The test experiment has demonstrated the principle of the technique

Further work will require:

- A high power tunable source for the 1000nm region
- Fine control of the orientation of the field and the sample

ISIS

Muonium laser chemistry: Some experimental results

K. Ghandi (University of British Columbia)

Summary

The combination of laser light and RF-μSR holds the possibility for a better understanding of muonium (Mu) formation and its reaction dynamics, reaction selectivity and the transient chemistry involved in Photodynamic Therapy (PDT). In PDT, oxygen radicals are used to cause death in cells (cancerous or bacterial) previously treated with a photosensitiser.

The first step in demonstrating the new technique is the construction of a sample cell capable of bring laser light into "contact" with the muoniated sample and the observation of a Mu/laser interaction. Preliminary experiments using such a cell without laser illumination have demonstrated the formation of muonium within the cell volume at the low pressures required. In addition, separate experiments suggest that laser excitation at 532 nm in water has a marked effect on Mu formation. A possible explanation for this observation is the quenching of an important Mu formation pathway due to optical absorption by the hydrated electron. Further avenues of research were also suggested.

For application to PDT studies, the reaction of Mu with O_2 is important and results suggest that laser illumination can bring about a reduction in the rate of this reaction either by direct perturbation of the H_2O molecule or by solvent fluctuations.

In a final study, the interaction of laser light with the muoniated Rose Bengal molecule was investigated. Zero field data suggests that the signal coherent with delayed laser excitation was detected. If confirmed, this would allow a wide range of physical and chemical parameters to be determined and an outline strategy for the characterisation of diamagnetic molecules is presented.

In the future, this combination of techniques could lead to the study of radical dynamics and kinetics in the excited state and that of free radicals and other transients associated with PDT.

Results from Laser μSR Experiments

a start

Presented by: Khashayar Ghandi

Plan of the talk

- Why?
- Laser-μSR or Laser Pump Muon Probe Results
- Future experiments

RF-μSR Can characterize the magnetic states of products of the process of muon thermalization, but can`t characterize them at the molecular level completely

Future: laser-RF-μSR

Why?
laser μSR

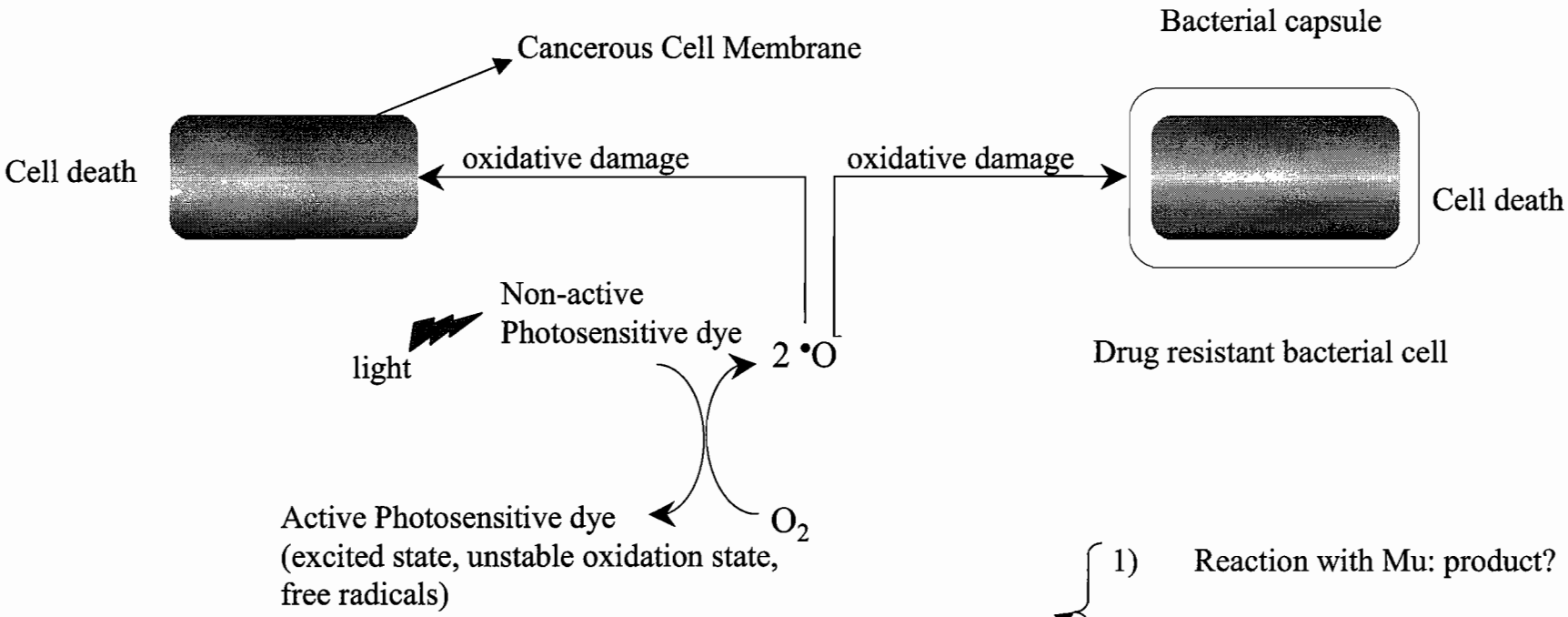
1) Better understanding of the process of Mu formation

2) Better understanding of PES, effects of zero point energy along the reaction path and tunnelling on excited state reactivity and product excitation.

3) Combining laser control (selective reactions of excited states) and mass control.
Can we use the large k_{Mu}/k_H and large difference in reaction rates of different excited states to provide information on production of isotope enriched products?

4) Study Transient chemistry involved in Photo Dynamic Therapy (PDT)

Photodynamic therapy: what is it?

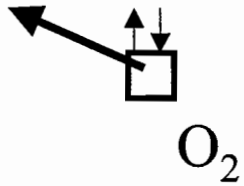


Questions we will answer:

- Reactivity of singlet O with free radicals
  - 1) Reaction with Mu: product?
  - 2) Reaction with organic free radicals
- Study mechanism of singlet O using photosensitizers. Are there free radical intermediates? Are electronic excited states involved? How are their reactions different in the bulk and at membranes?
- Is the main reaction of the triplet states spin exchange or redox?

Probing science involved in PDT with muon

Ground state photosensitizer



Eventual goal:

excite ↑↓□ to ↑↑△ at a wavelength that O_2 doesn`t absorb

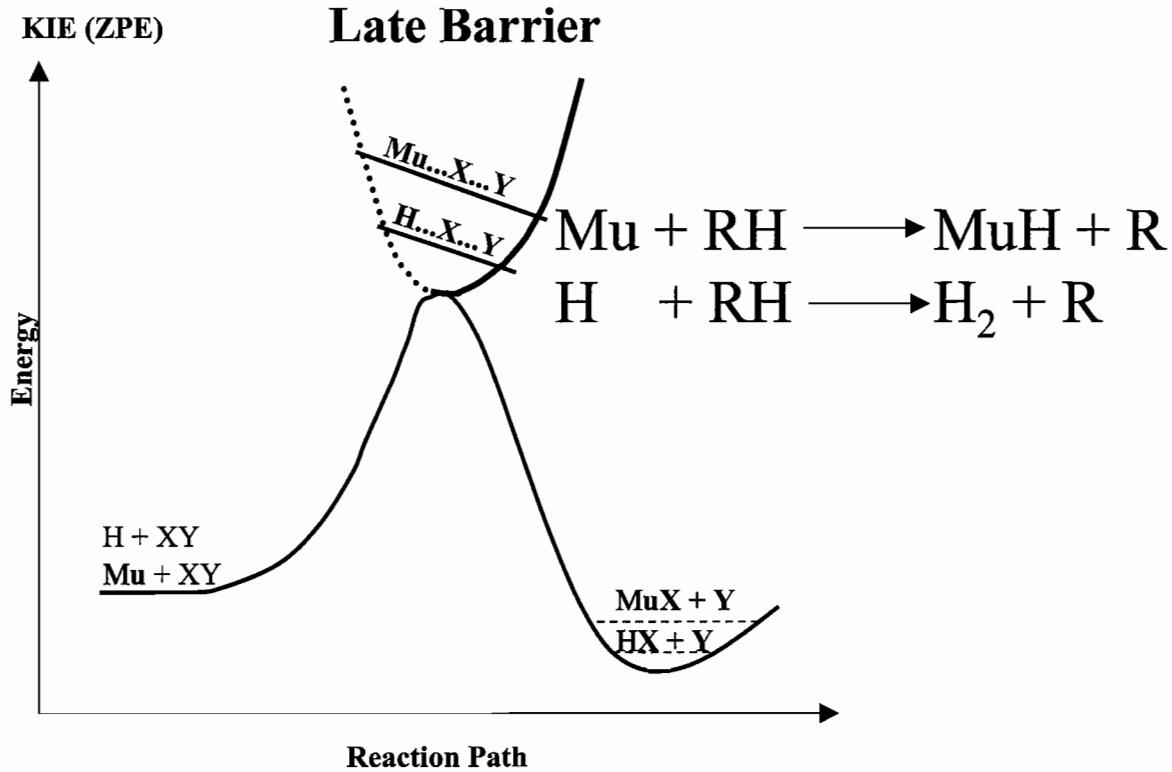
study reactions of ↑↑△ with Mu and free radical (muoniated)

Mu or ↑↑△ + ↑↑O_2 → ↑↓□ + ↑↓O_2

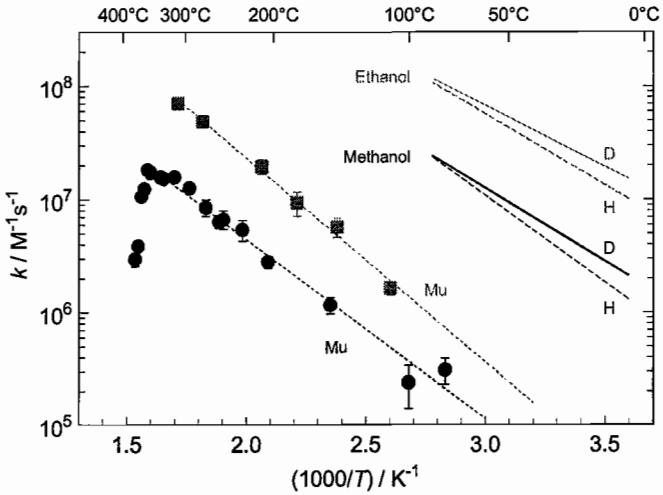
1. Does laser irradiation affect Mu formation?
2. We have to check if reaction of O_2 and Mu is or is not affected in the absence of ↑↓□
3. Study effect of laser light on muoniated species of ↑↓□

Role of Mu/H in probing PES first indicated by Connor *et al.* in 1978

Further info on PES and ZPE by study reactions with exited state molecules

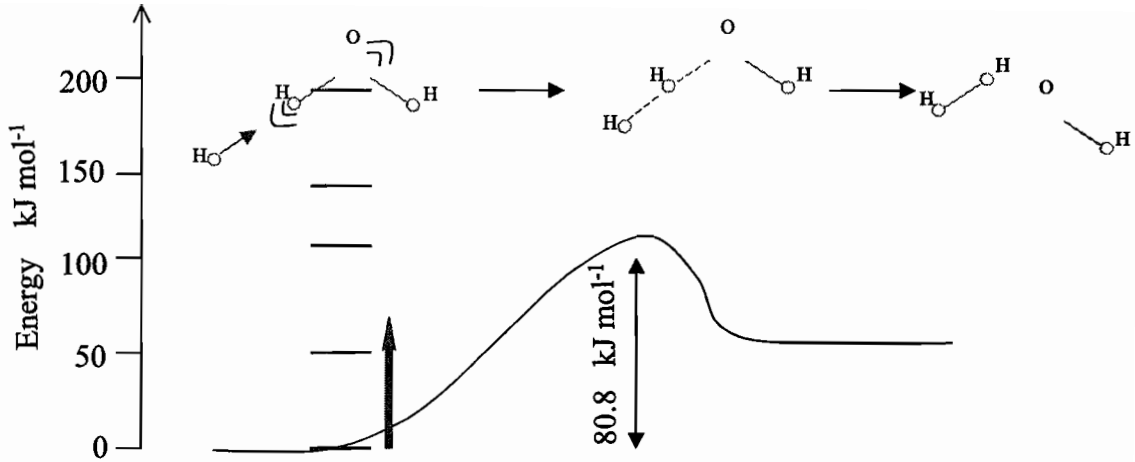


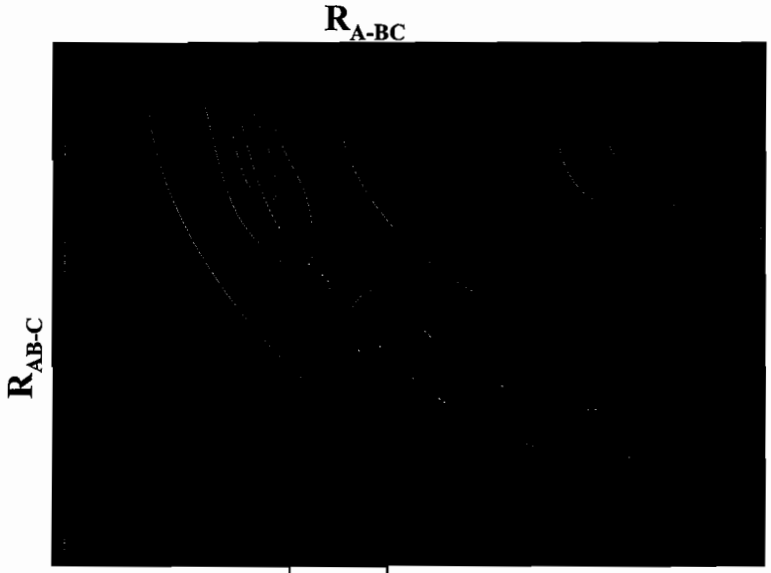
Work of K. Ghandi and PW Percival in SCW →



Late Barrier (endothermic reactions)

Vibrational excitation in reactants help





$k_{04} \sim 2k_{03} \sim 10k_{02}$ for $H + H_2O^*$

What would be the source of KIE?

Probably $\boxed{k_{04}^{Mu}, k_{03}^{Mu}} > \boxed{k_{04}^{H}, k_{03}^{H}}$

but how much faster?

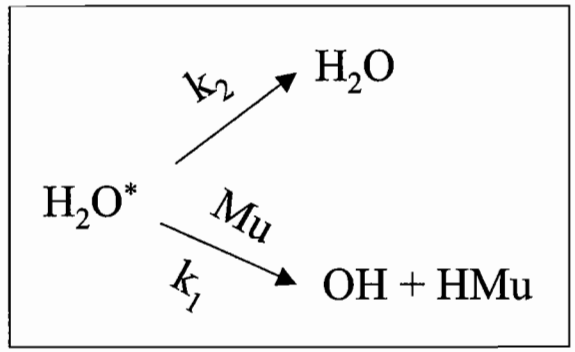
How about $\boxed{k_{02}^{Mu}}$?

Larger? How important is tunnelling on excited state reactions, for energies ~ Ea?

Slower? ZPE effect: would ZPE be important when there is significant vibrational energy along reaction coordinate?

Difficulties

Must be: $k_1 > k_2$
No data on k_1 - very little data on k_2



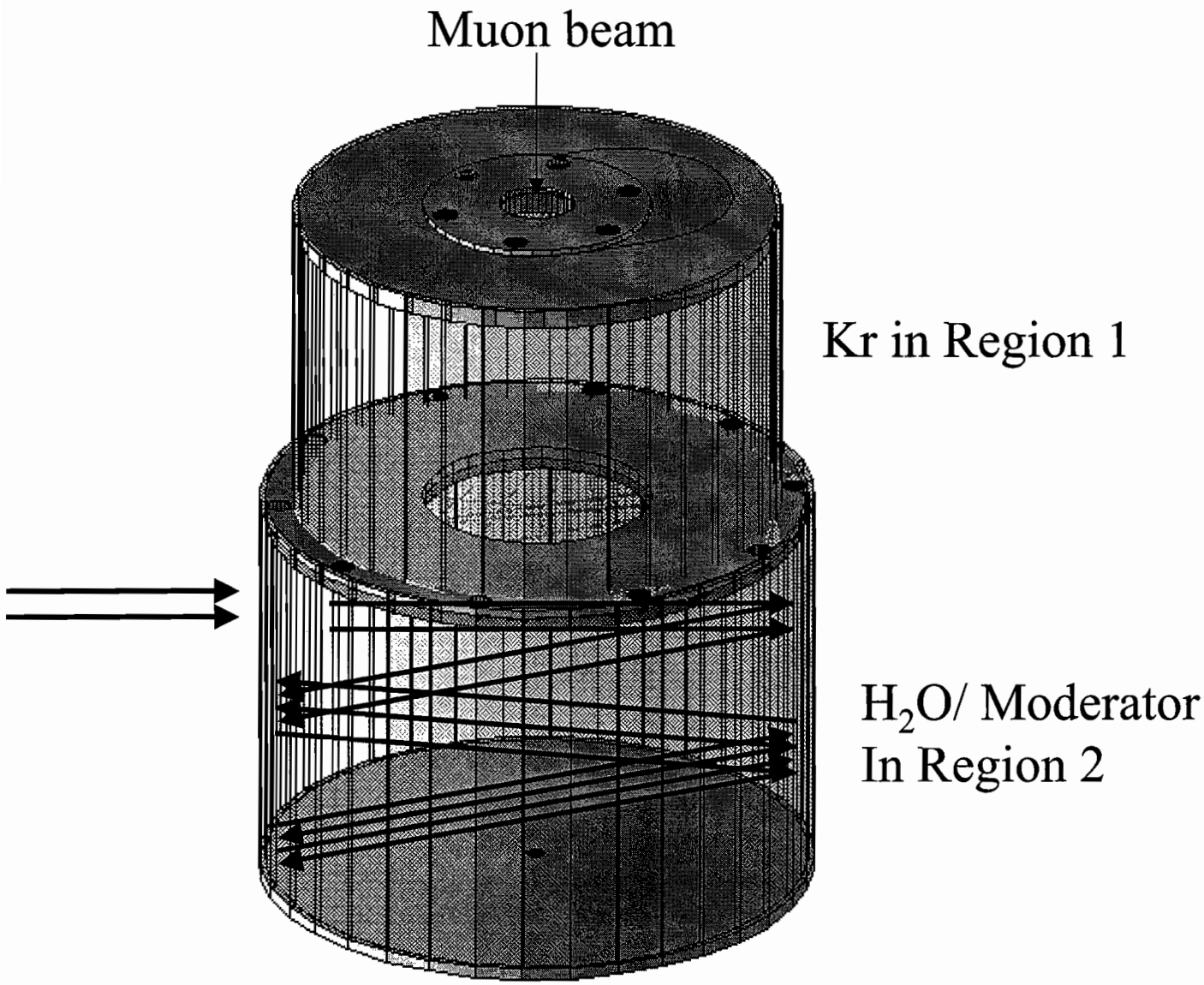
Based on data on vibrational relaxation in H_2O for $|04\rangle^-$ state and in He for $|2\rangle_b$ $|02\rangle^-$ state:

- $[H_2O] < 100$ mtorr
- At 1 atm He $\Longrightarrow$ 1 % of $[H_2O]$ remains excited $\Longrightarrow$ $\lambda \sim 0.05 / \mu s$ if $\frac{k_{Mu}}{k_H} \sim 3$

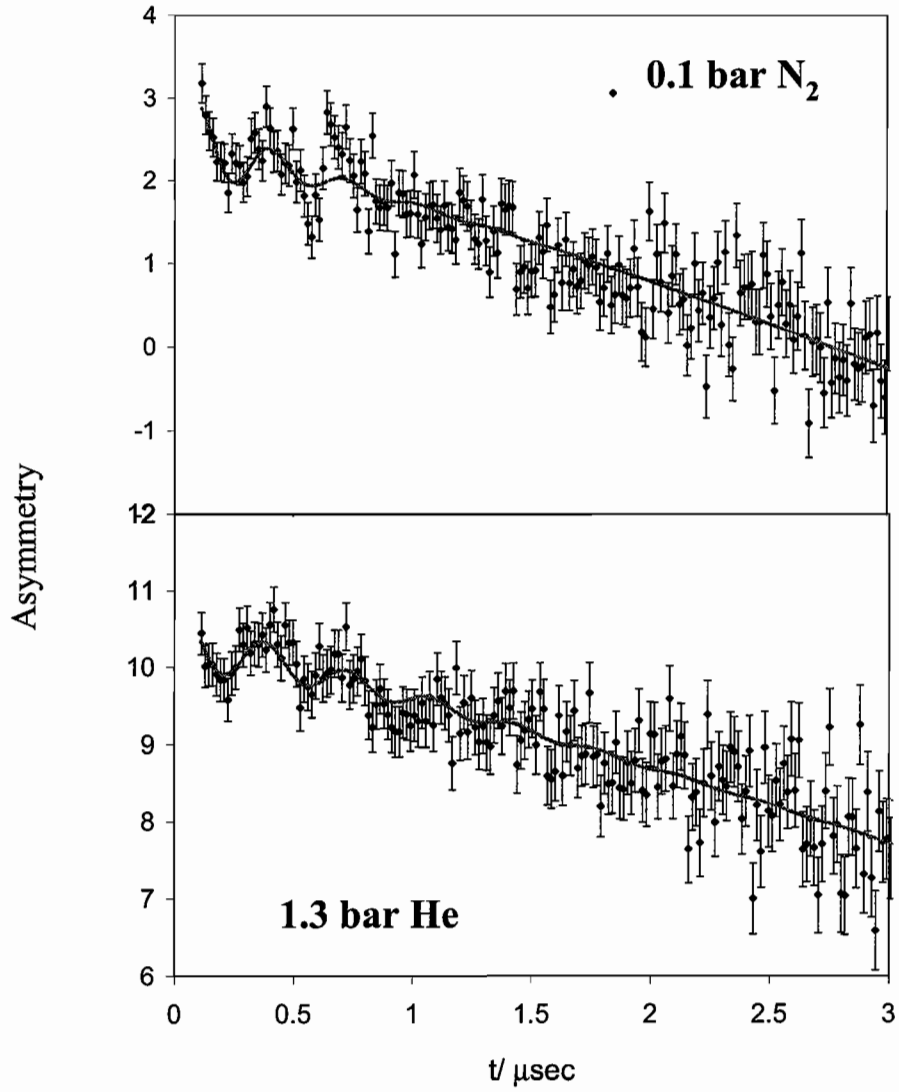
- Mu should be produced and stopped in ~ 100 mtorr H_2O

1 atm He

Laser cell



Does it work?


0.1 bar N_2
1.3 bar He
Asymmetry
t/ µsec
4
3
2
1
0
-1
-2
11
10
9
8
7
6
0
0.5
1
1.5
2
2.5
3

Next steps in this direction

- Optimize the cell to stop muon and form Mu at even lower densities
- Install the optical windows and internal mirrors
- Get a Pumped-Dye-laser so that we can study Mu reactions with vibrationally excited state molecules in the gas phase
- Combine this with optical probes to gain information as well on the fluorescence of the muoniated products: complete state to state dynamics

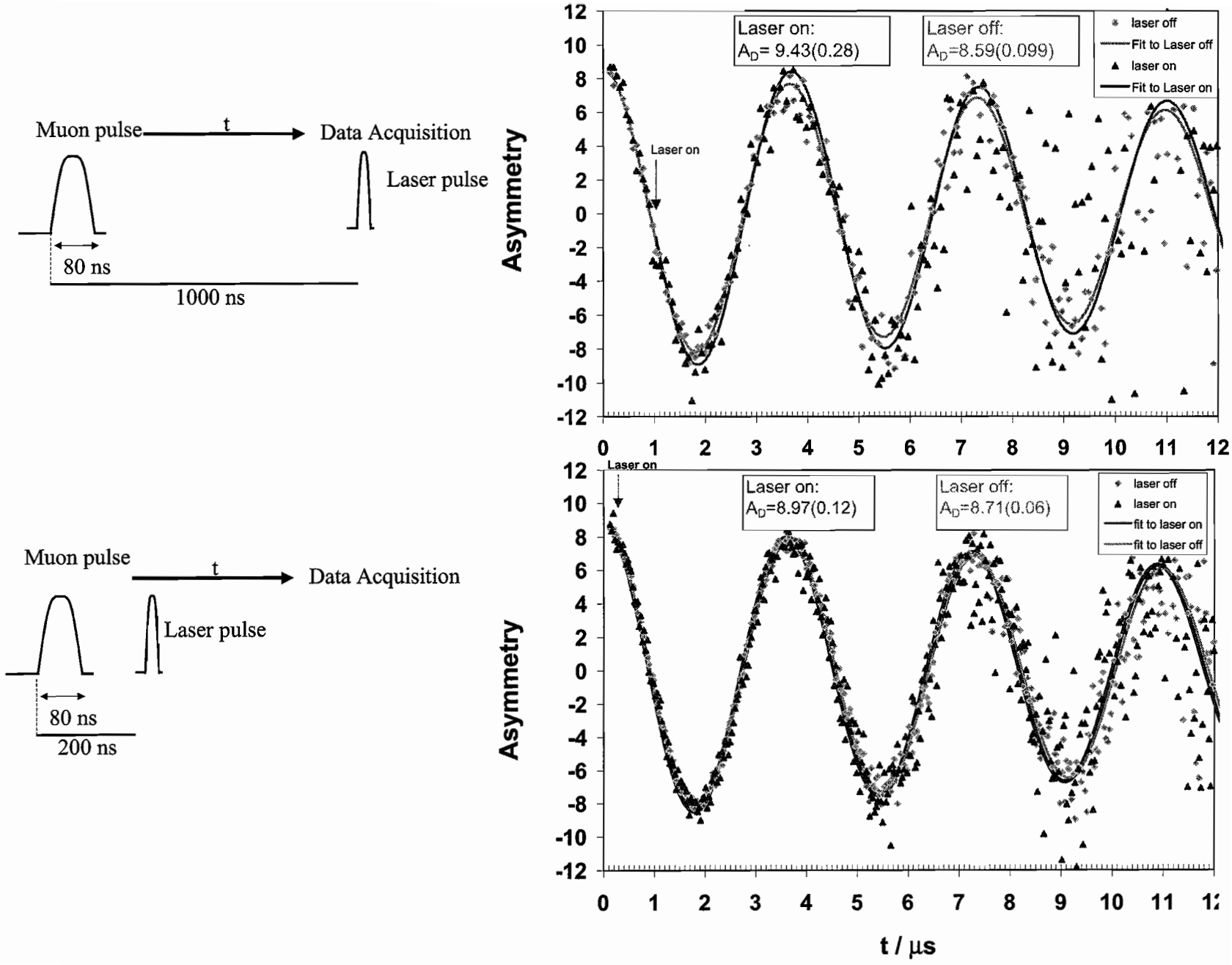
Effect of Laser excitation at 532 nm on Mu formation in water, why?

Water chosen for many reasons:

- The most important solvent, due to its outstanding role in nature and particularly in our body and therefore understanding its radiation chemistry is related to our plans to study free radical processes involved in PDT

- Water significantly affect the outcome of many chemical reactions: Large dipole moment and unique hydrogen bonding network

- The mechanism of Mu formation in water is well studied as compared to that in other solvents: Mu formation in liquid water is believed to be entirely through radiolysis processes , in which a significant role is played by hydrated electrons that absorb light in the visible region including at 532 nm, the second harmonic of the Nd: YAG laser available to us.


Muon pulse
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Data Acquisition
Laser pulse
80 ns
1000 ns
Laser on:
A_D= 9.43(0.28)
Laser off:
A_D=8.59(0.099)
laser off
Fit to Laser off
laser on
Fit to Laser on
Laser on
Asymmetry
Muon pulse
t
Data Acquisition
Laser pulse
80 ns
200 ns
Laser on
Laser on:
A_D=8.97(0.12)
Laser off:
A_D=8.71(0.06)
laser off
laser on
fit to laser on
fit to laser off
Asymmetry
t / μs

Results

1) The asymmetry is shifted by 10% at 1 μs delay and by 2.7% at 0.2 μs delay

2) With laser irradiation of water we can manipulate the processes that determine the distribution of muon spin polarization among different muon fractions

3) These studies can shed light on the end of track radiolysis effects in intermediate linear energy transfer (LET) region, a unique contribution of laser-μSR to the field of radiolysis processes

4) Laser irradiation has the maximum effect at 1μs delay after muon implantation

Optical absorption of the *hydrated electron*

The hydrated electron plays a significant role in the process of Mu formation in water.

$\mu^+ + e^- \rightarrow Mu$

$\mu^+ + RH \rightarrow RHMu^{+*}$

$RHMu^{+*} + RH \rightarrow RHMu^+ + RH$

$RHMu^+ + e^- \rightarrow Mu + RH$

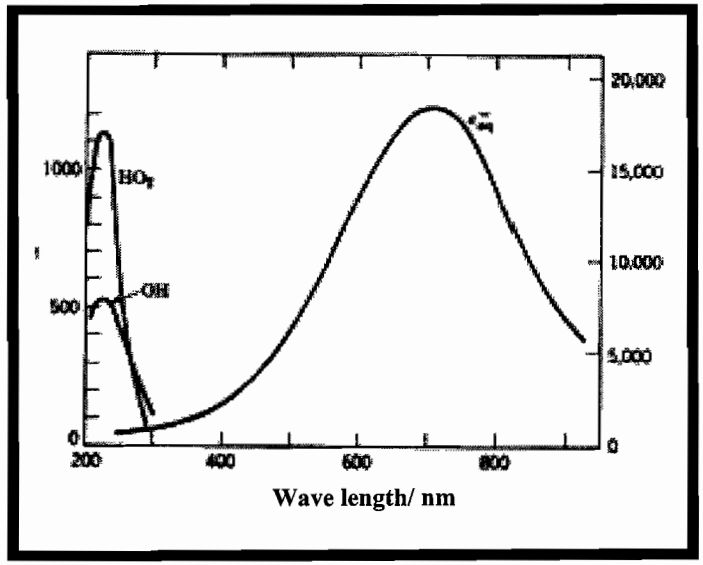
$RHMu^+ + RH \rightarrow RMu + RH_2^+$

$Mu + e_{sol}^- \rightarrow$ spin depolarized Mu

$Mu + e_{sol}^- \rightarrow MuH + OH^-$

$Mu + (R^\bullet) \rightarrow$ spin depolarized

$Mu + (R^\bullet) \rightarrow MuR$ (R = OH, H)



J.W.T. Spinks and R.J. Woods, "An Introduction to Radiation Chemistry", John Wiley & Sons, New York, 1976

A small fraction in ~ μs

Mostly but not completely in < ps

What does it mean?

$$Mu^{+}OH_2 + e^{-}_{(aq)} \rightarrow Mu + H_2O \qquad 1\mu S$$

quench this

- e^- in the **gas phase**: plane wave, no interaction with the radiation field.
- e^- in the **water**: trapped (solvated) => bound states, modulated by water movement of the solvent cage => broad spectra
- ground state of e^- in the **water** : spherical charge distribution localized in a cavity of ~ 4 Å
- excitation of e^- in the **water** : 1) non-symmetrical (p-like) charge distribution and , 2) at lower wavelengths partial delocalisation (escape) of charge
- changes in solvent structure from the relaxation of the hydrated electron

Where do we go in this direction?

Long term:

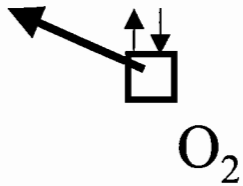
- Study the effect of excitation or photochemical transformation of transients involved in Mu formation on diamagnetic, Mu, muoniated radical and missing fractions. This along with RF studies will eventually allow us to sort out real mechanism of Mu formation; provide unique information on the dynamics of the end of track radiolysis processes in high LET radiation

Short term:

- Study the effect of laser excitation (different powers) of hydrated electrons at early times, i.e. during muon pulse; can we gain information on faster processes in radiolysis of water?
- Study the effect of excitation at larger wavelengths (when we have accesses to pumped-dye-laser) of hydrated electrons where there is less electron delocalisation but more change in the shape of electron distribution from spherical.
- Study the effects on other solvents, novel chemical mediums e.g. green solvents such as SCFs and ionic liquids

Probing science involved in PDT with muon

Ground state photosensitizer



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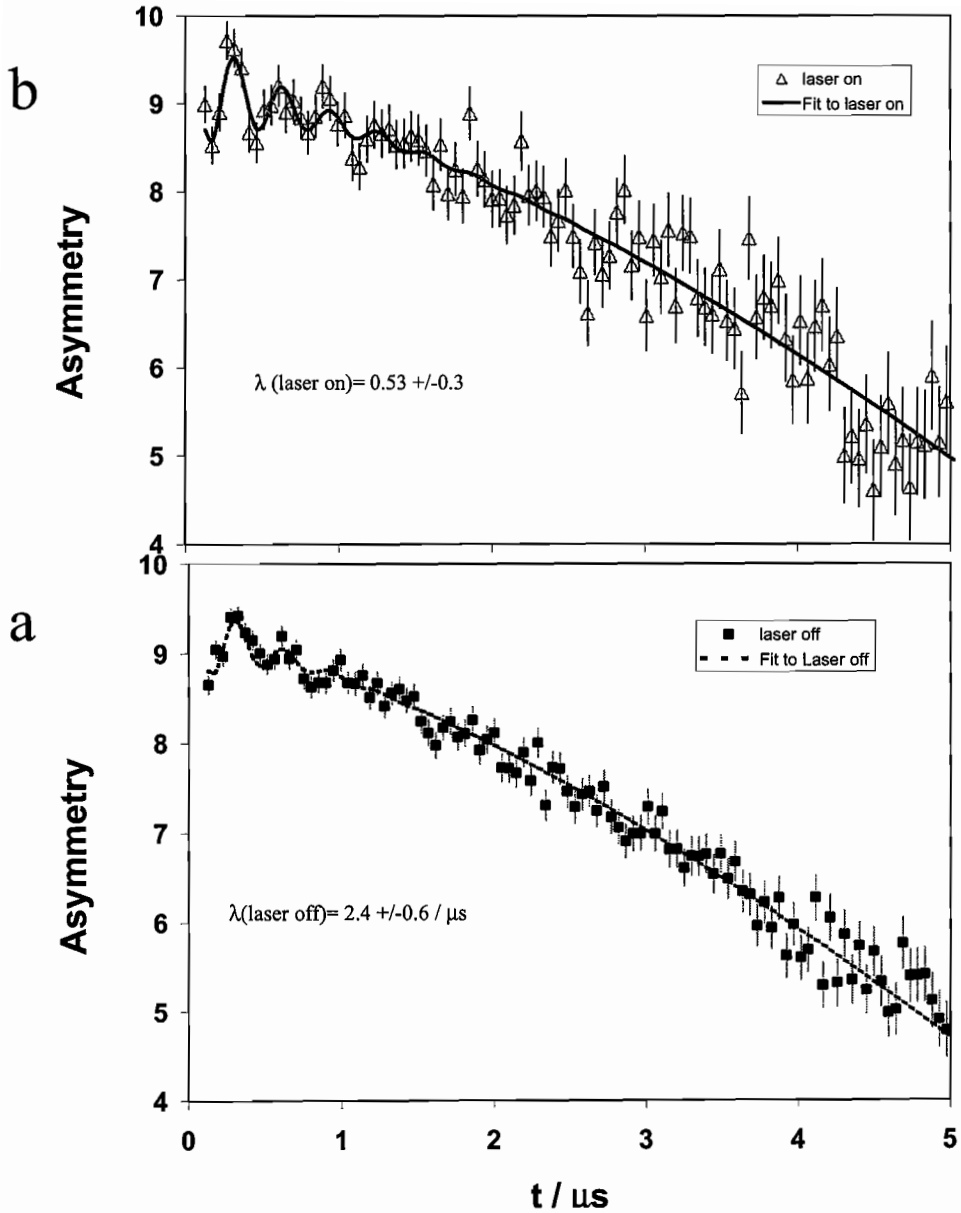
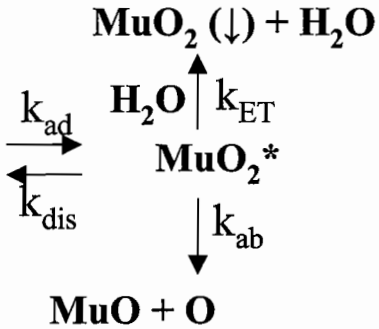


$Mu + O_2$ reaction

1) $Mu (\uparrow) + O_2 (\downarrow\downarrow) \rightarrow Mu (\downarrow) + O_2 (\uparrow\downarrow)$

Exothermic with a high density of states at threshold (high pressure limit)

2) $Mu (\uparrow) + O_2 (\downarrow\downarrow)$



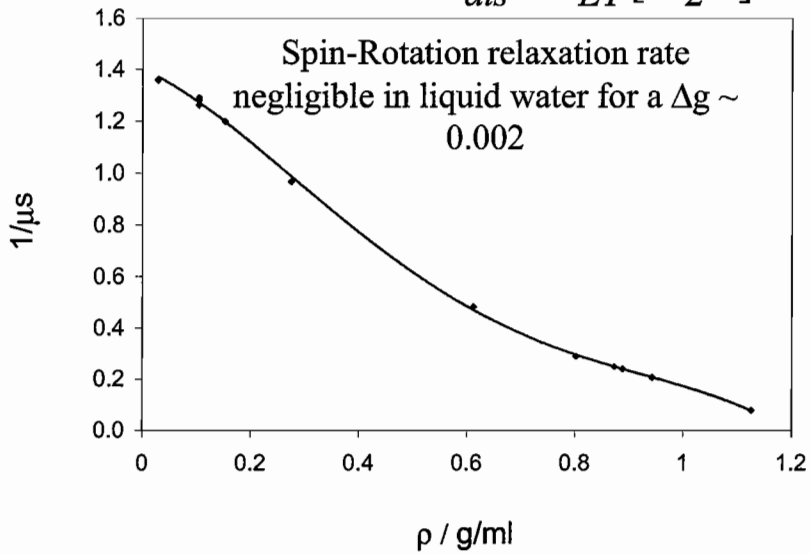
a) The asymmetry in 10^{-4} M O_2 aqueous solution; fast relaxing signal with a decay rate ~ 2.4 /μs **b)** The asymmetry in 10^{-4} M O_2 aqueous solution when the 532nm laser pulse without any delay relative to the muon pulse; slow relaxing signal with a decay rate ~ 0.5 /μs

Decay rate at 2G TF for Mu + O_2 reaction depends on:

1) Spin Exchange
2) Chemical reactions
   (addition & dissociation & abstraction)
3) The rate of Energy Transfer
4) Spin Rotation of MuO_2^* $\lambda = \lambda_{SR} + k_{SE}[O_2] + (k_{ch}[O_2] = \frac{k_{ad}(k_{ET}[H_2O] + k_{ab})}{k_{dis} + k_{ET}[H_2O] + k_{ab}}[O_2])$

$k_{ab} << k_{ET}[H_2O]$ and $k_{ab} << k_{dis}$

$$\Longrightarrow \quad \lambda = \lambda_{SR} + k_{SE}[O_2] + (k_{ch}[O_2] = \frac{k_{ad}(k_{ET}[H_2O])}{k_{dis} + k_{ET}[H_2O]}[O_2])$$



$k_{dis} >> k_{ET}[H_2O] \longrightarrow \lambda = k_{SE}[O_2] + k[H_2O][O_2]$

$k[H_2O] = 5.4\times10^{-11} cm^3 molecule^{-1} s^{-1}$ at 300 bar $N_2 \longrightarrow$ 0.15 g/ml

At 1 g/ml $k[H_2O] \approx 4\times10^{-10} cm^3 molecule^{-1} s^{-1}$

$k_{obs} \approx 0.6\times10^{-10} cm^3 molecule^{-1} s^{-1}$

$\longrightarrow$ Either at 1 g/ml in water, the addition reaction is close to high pressure limit or addition reaction is as important as SE

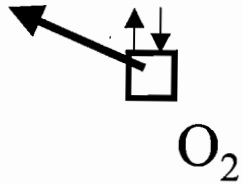
The most probable causes of laser induced low reaction rate:

1) Perturbation of orientation of water molecules along addition reaction coordinate (note that the reaction is early, without electronic barrier, and MuO_2 has a dipole but Mu and O_2 do not have)

2) Solvent fluctuations, Mu in low density environment (clathrate like – repulsive water-Mu interaction) and O_2 in high density environment (attractive water- O_2 interaction)

Probing science involved in PDT with muon

Ground state photosensitizer



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study reactions of ↑↑△ with Mu and free radical (muoniated)

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1. Does laser irradiation affect Mu formation?
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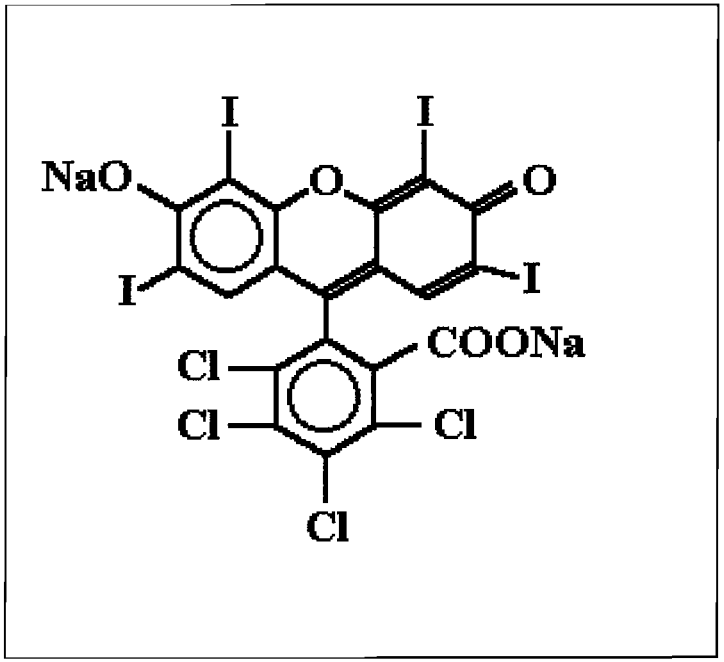
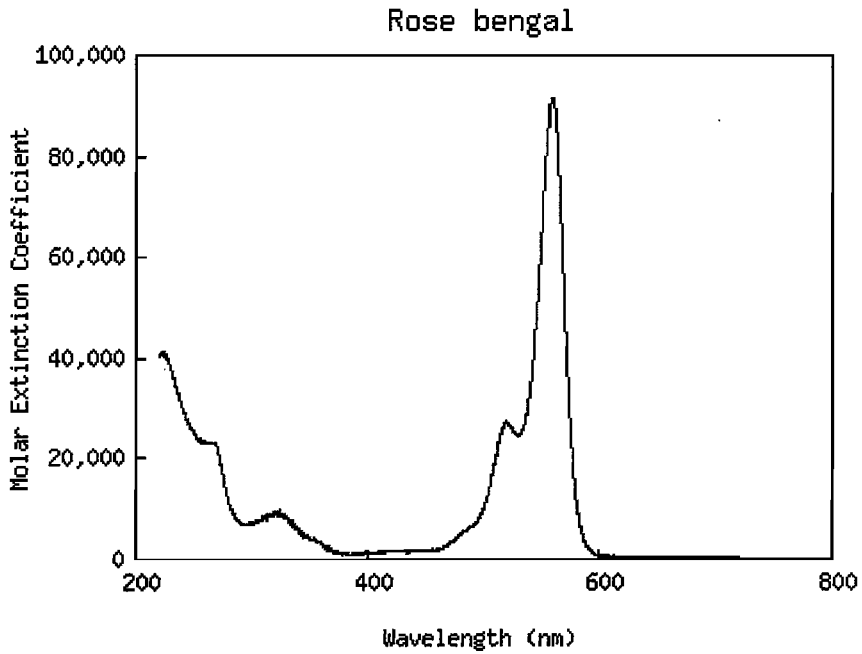
3. Study effect of laser light on muoniated species of ↑↓□

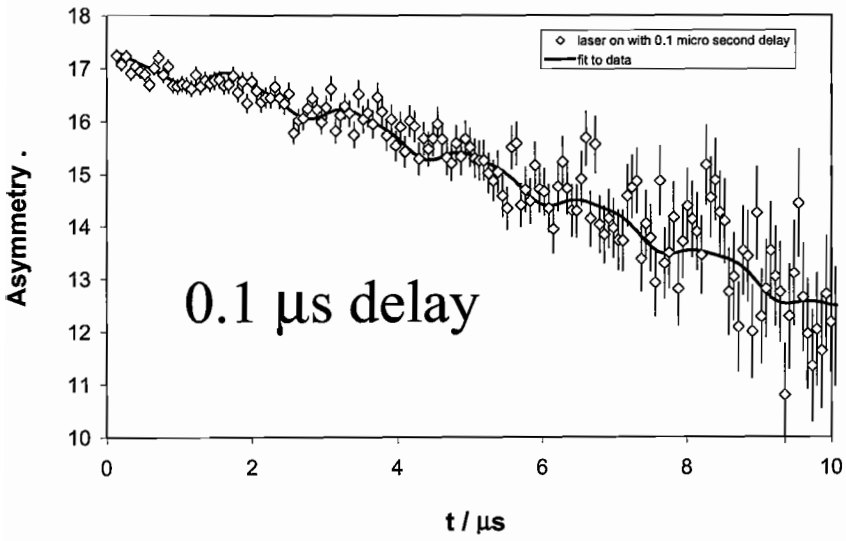
The chemistry of possible transients involved in PDT;
First step: characterization

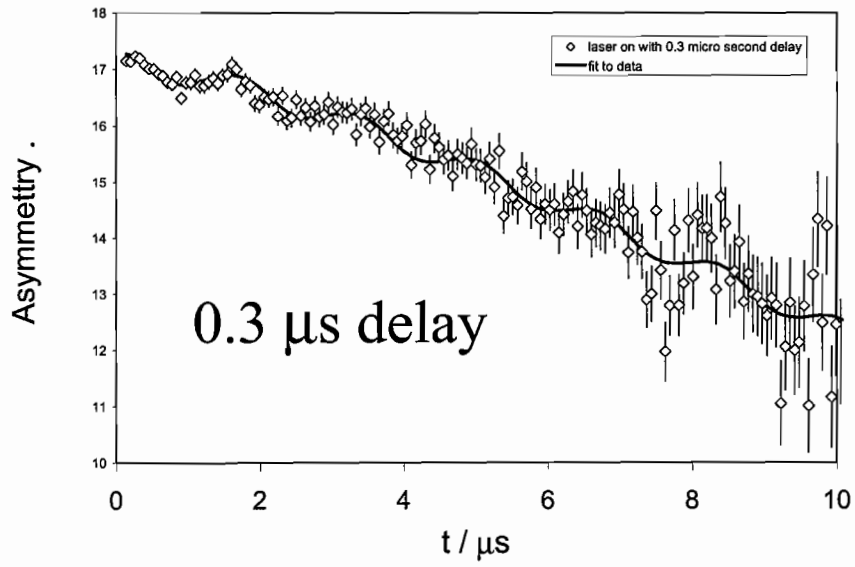
Rose Bengal: A photosensitizer that absorbs significantly at 532 nm (second harmonic of Nd:YAG)

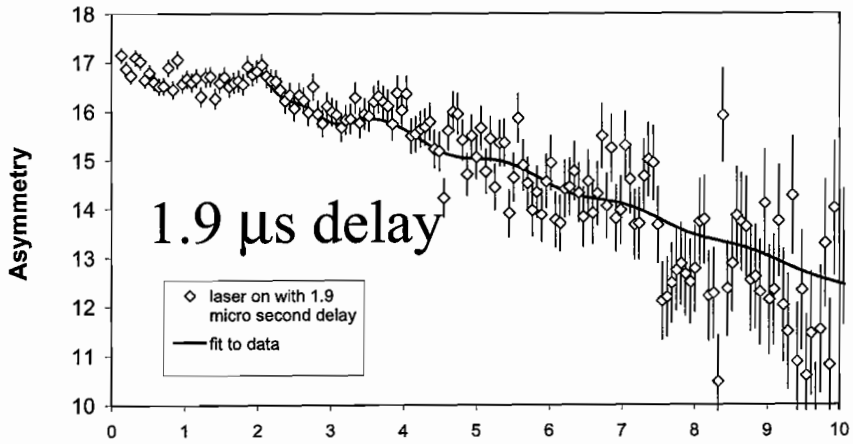


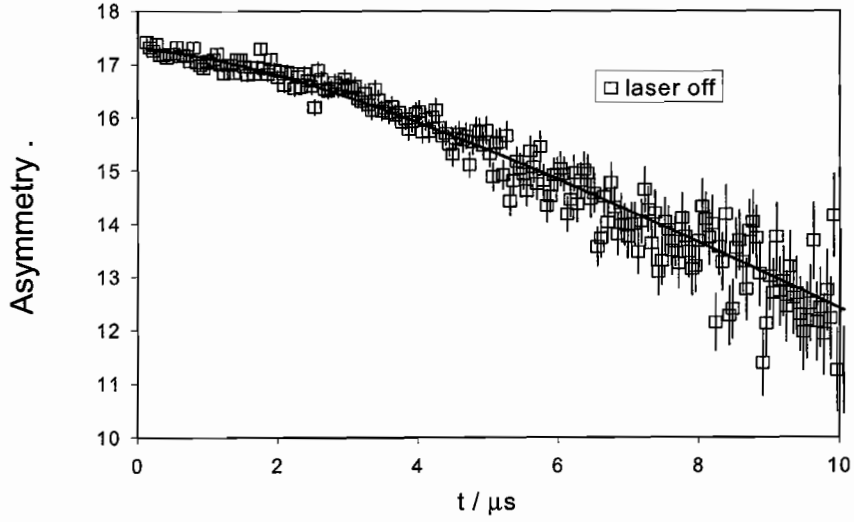


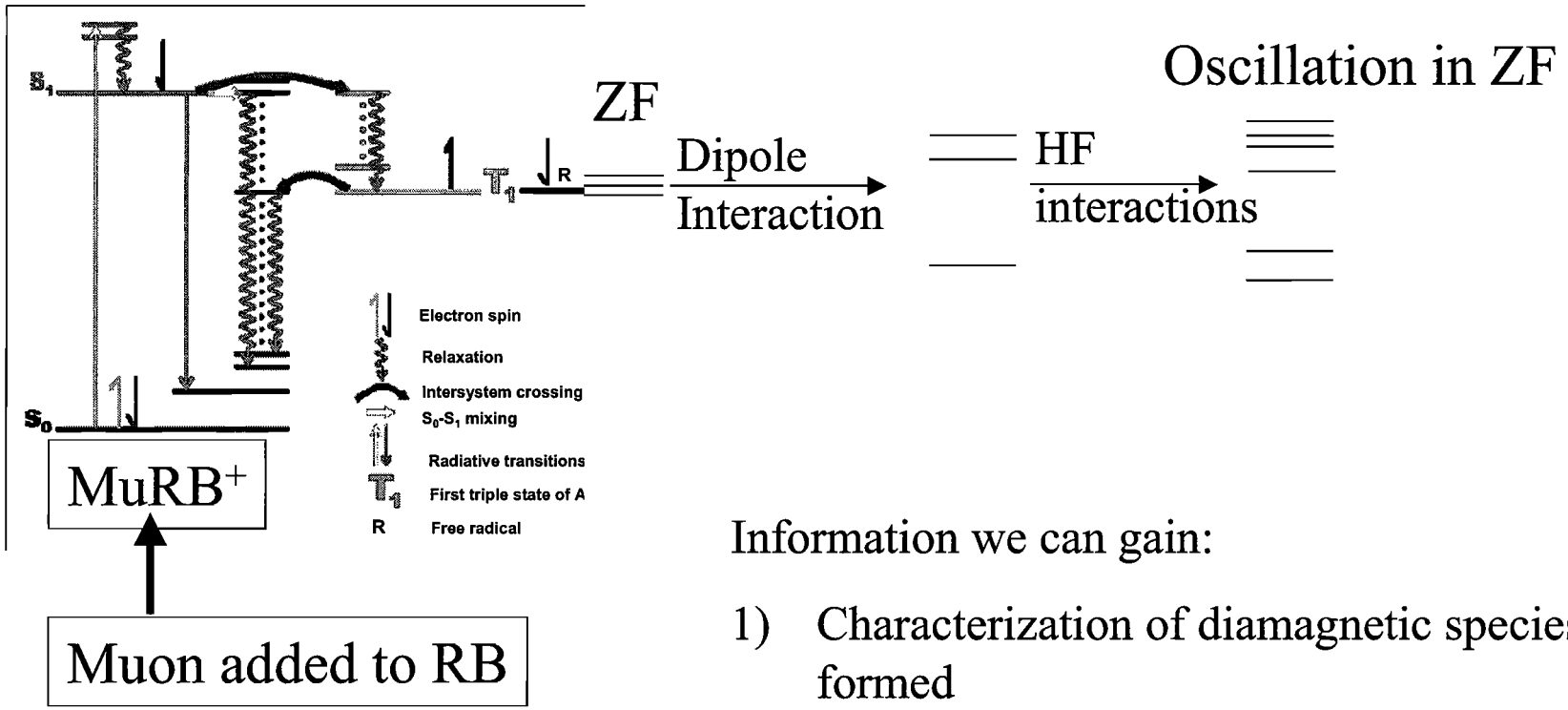
ZF experiments on powder











Information we can gain:

1) Characterization of diamagnetic species formed

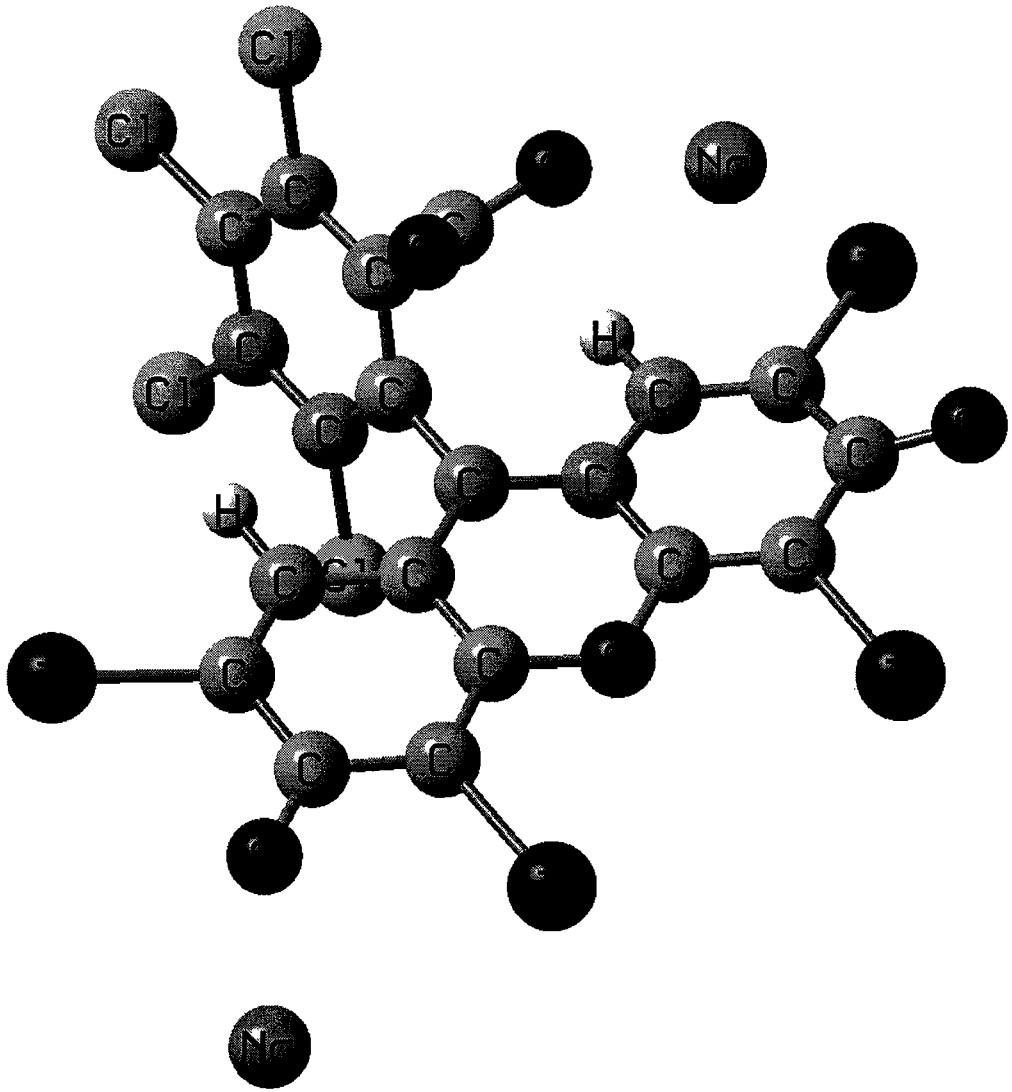
2) Electron distribution in the ionic triplet states of molecules

3) Structural parameters (RF-Laser-μSR)

4) Chemical dynamics of triplet states

The strategy to characterize muoniated diamagnetic molecules

1) The laser wavelength will be tuned through the corresponding transition band
2) μSR methods can be used as detection method for laser absorption to unravel the wavelength that causes the maximum effect
3) If laser excitation would have caused the formation of new free radicals through photochemical reactions, the formed free radicals could be studied in a time-resolved manner by delaying laser pulse relative to the muon pulse
4) In this way, we will be able to characterize both ground states by following the effect of laser as a function of wavelength and excited states or photochemical products through their hyperfine interactions.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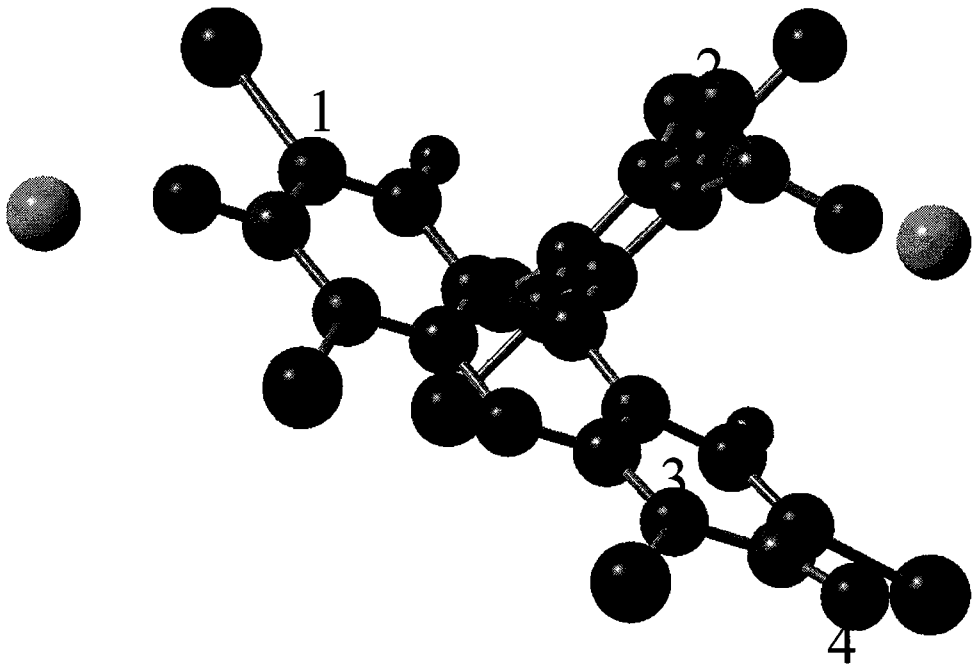
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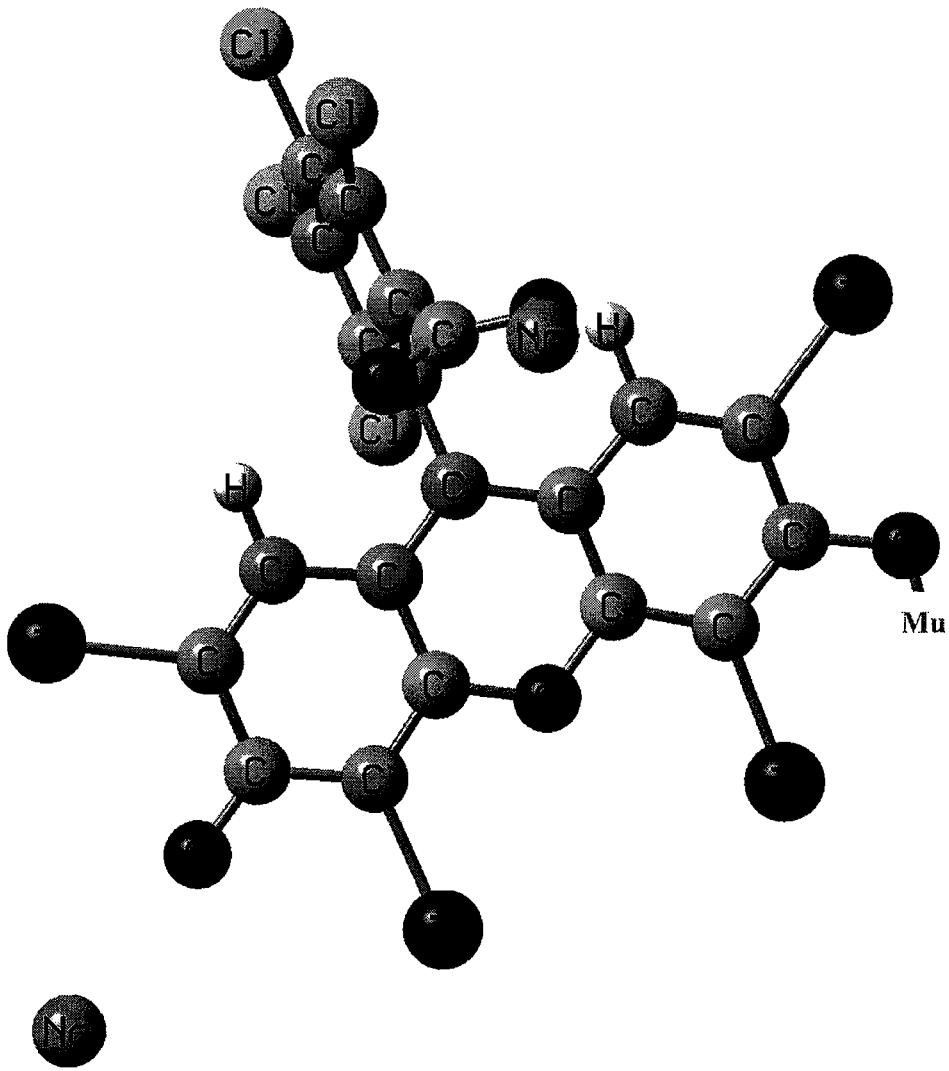
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Future

- Radical dynamics in the excited state
- Radical kinetics in the excited states
- Study chemistry of free radical and other transients involved in PDT

THANKS

- Organizers of the workshop
- Dr. P. King, Professor S. Cox
- Dr. J. Lord, Dr. I. Clark, Dr. S. Cottrell, Dr. C. Johnson, Dr. F. Pratt
- Professor D. Fleming

$ Centre for Molecular Structure and Dynamics $

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- Sample safety support, Matthew Dickson
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