Local probe investigation of spin and charge dynamics in organic semiconductors

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- MuSR - spin relaxation

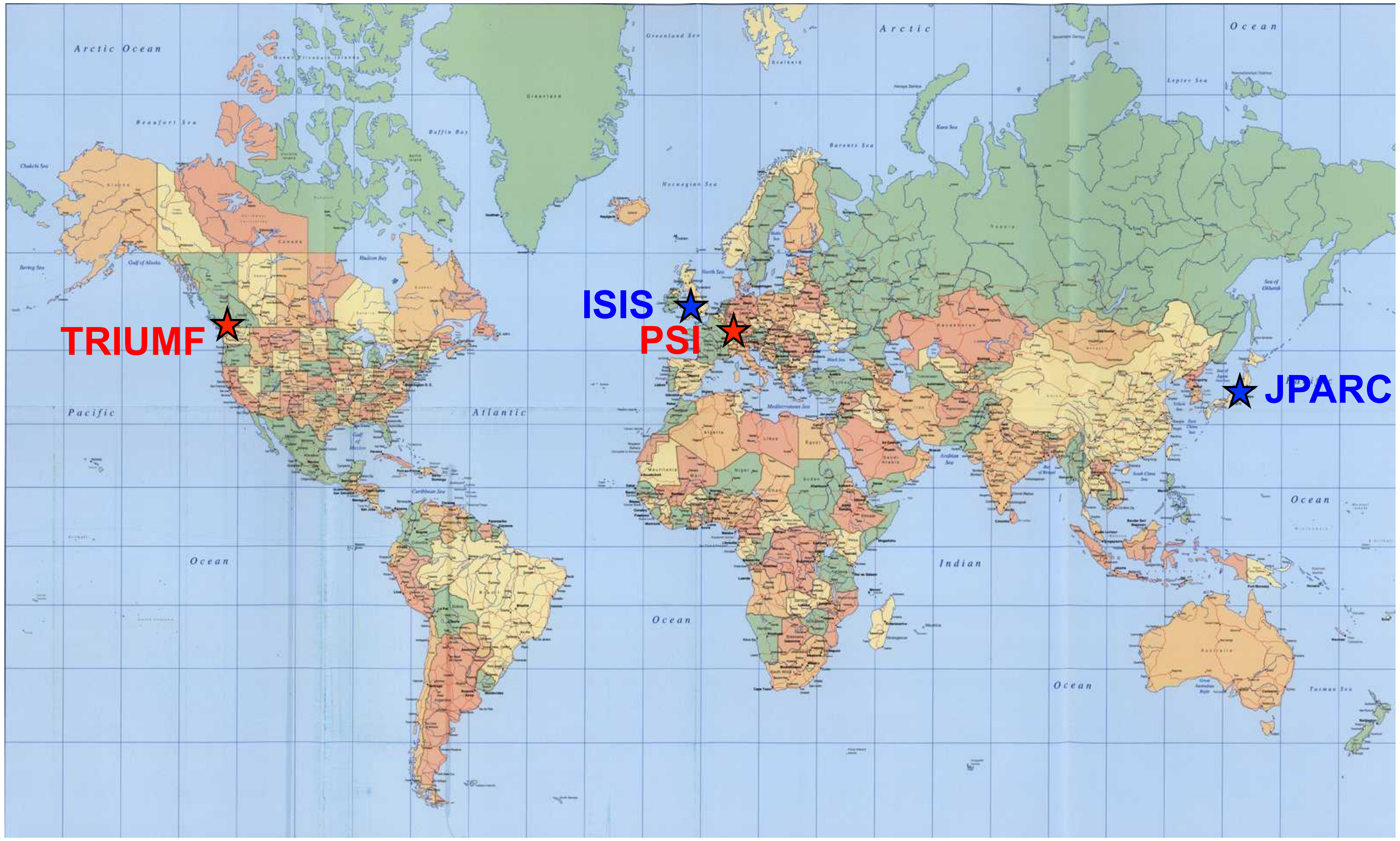
- Photomusr - the background

- Excitonic physics probed with temporal and spatial resolution

- Complexities and the future

Muon spin spectroscopy

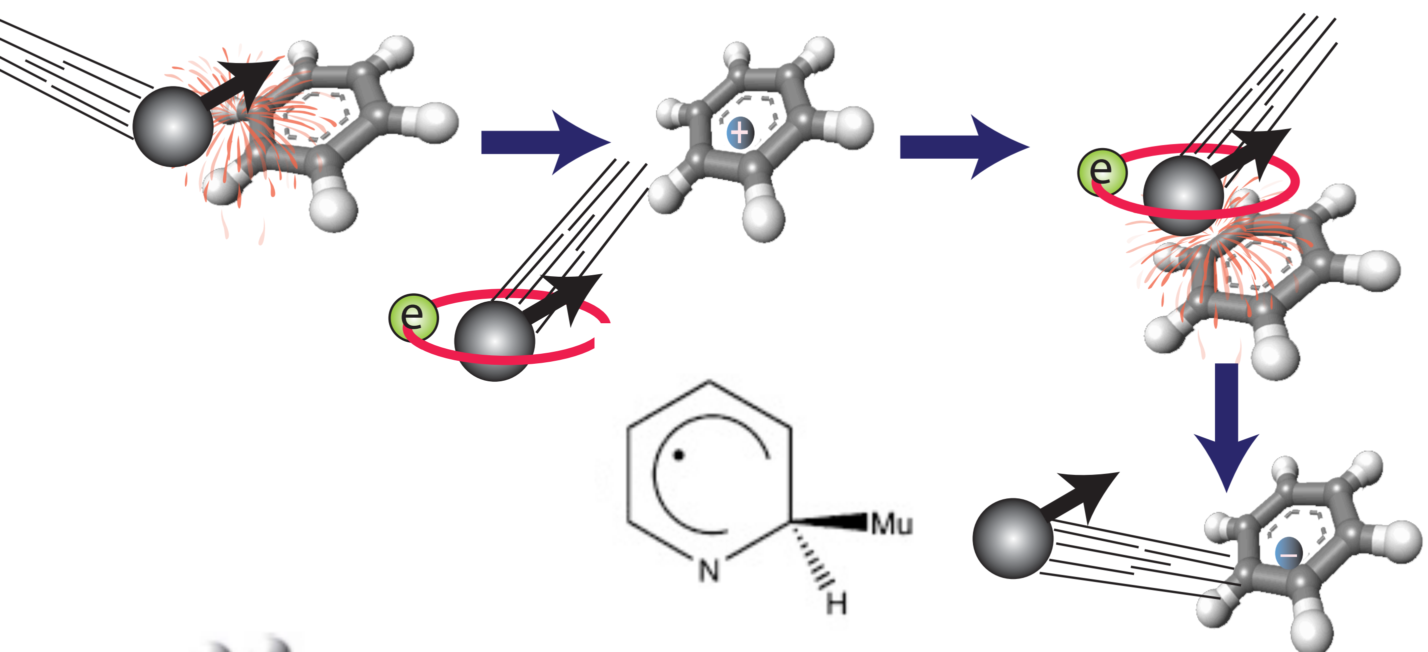
Primary International Facilities for μSR

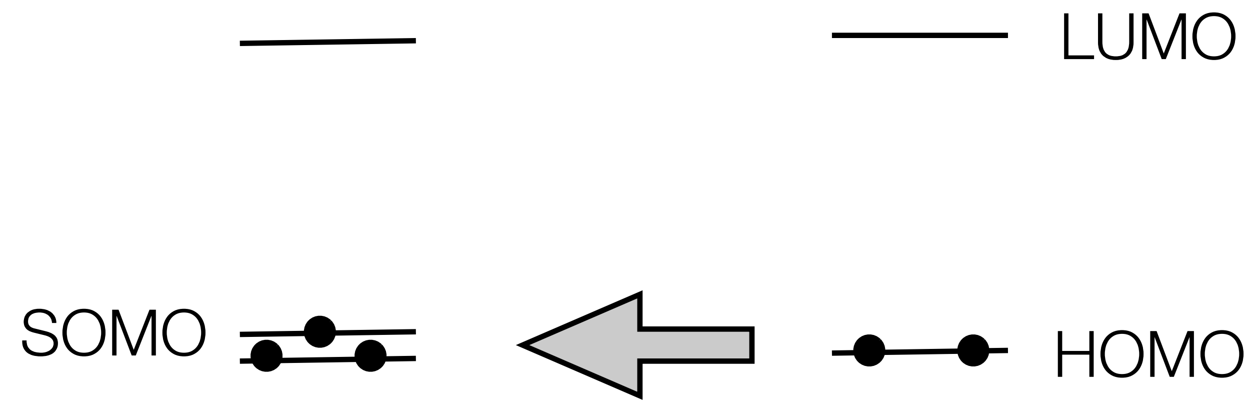


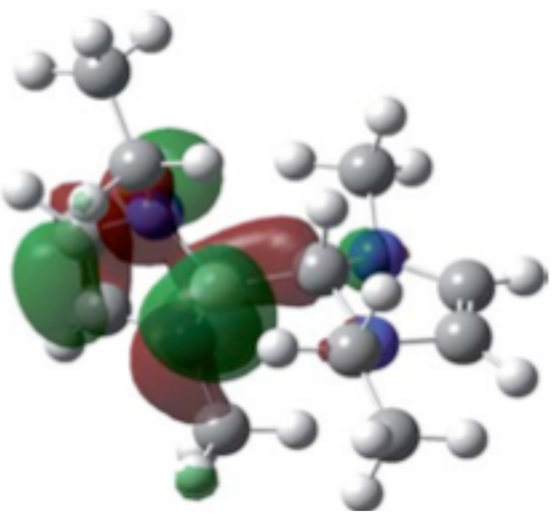
Continuous sources

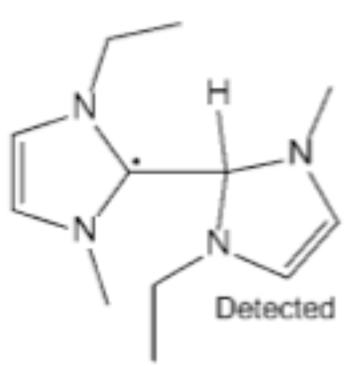
Pulsed sources

Muonium

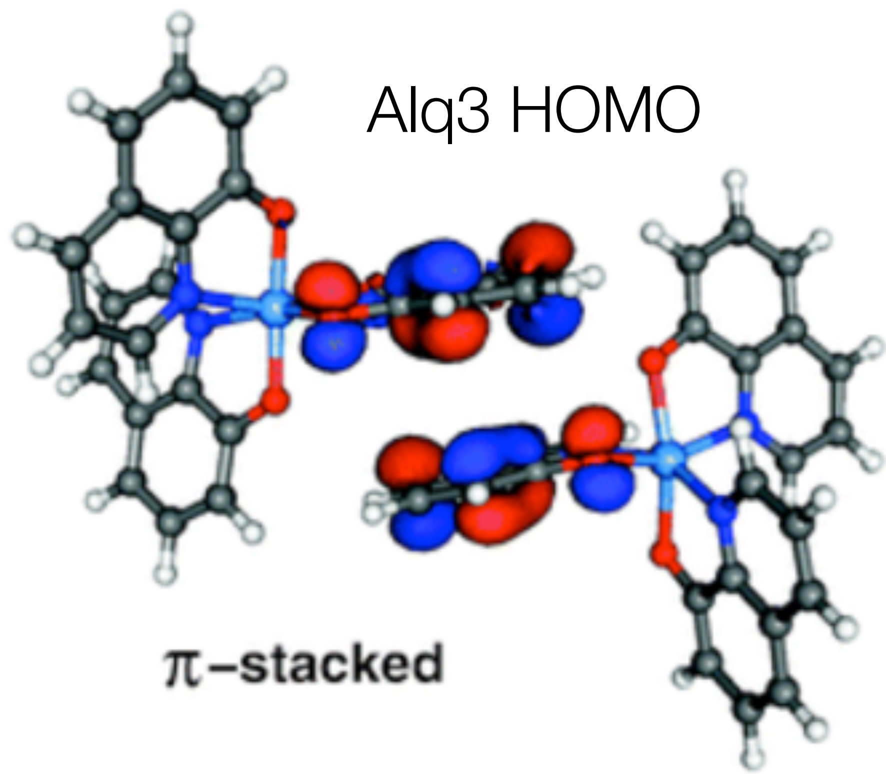




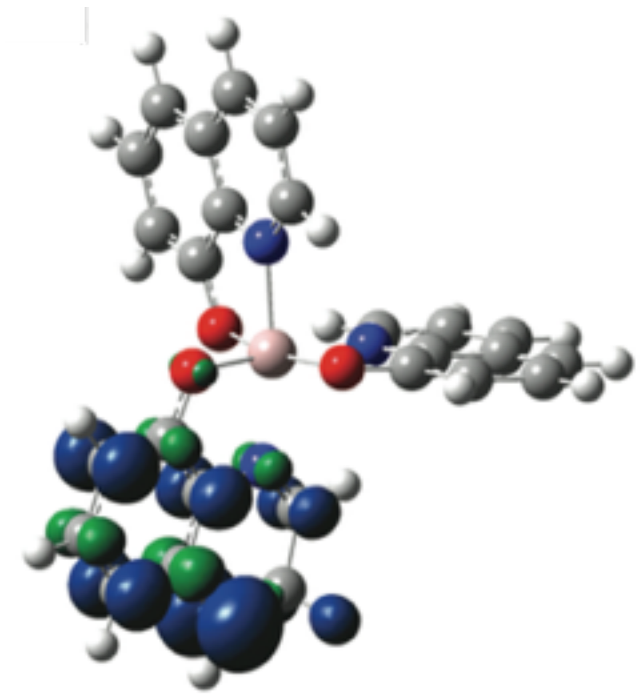




Sherren et al., Chem. Sci 2, 2173 (2011)



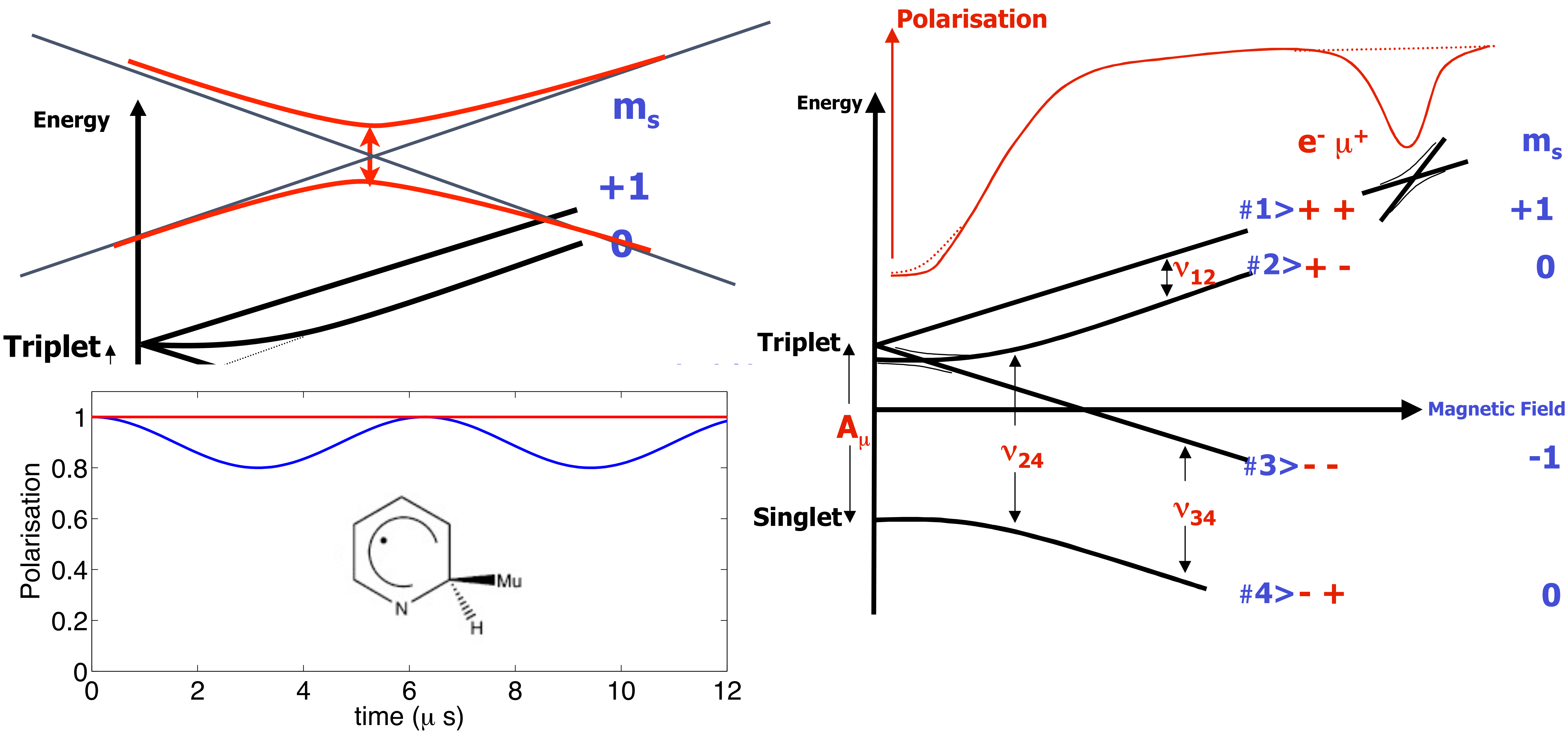
Alq3 SOMO



Baumeier et al., Phys. Chem. Chem. Phys.12, 11103-11113 (2010)

Muon - Electron system; *Breit - Rabi diagram*

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

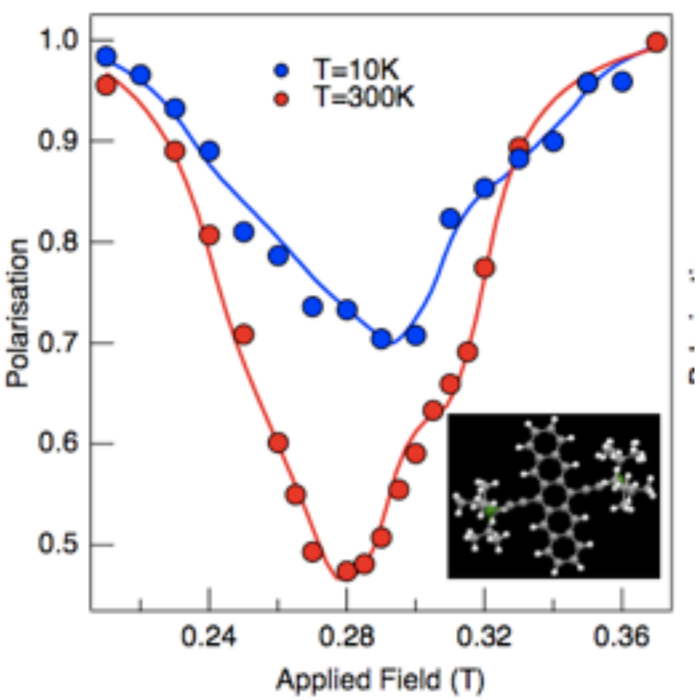


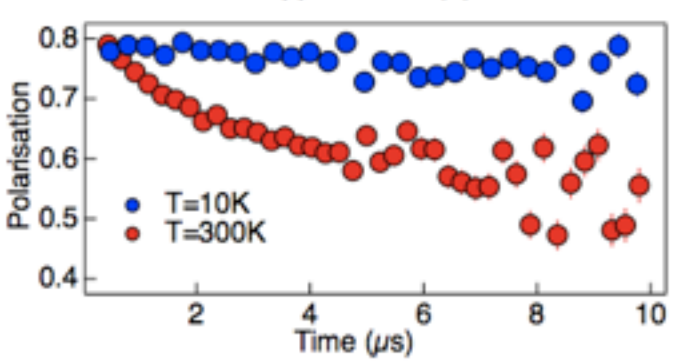
Brilliant.... localised spin probe, level crossings, change of polarisation....
But what can you do with it?

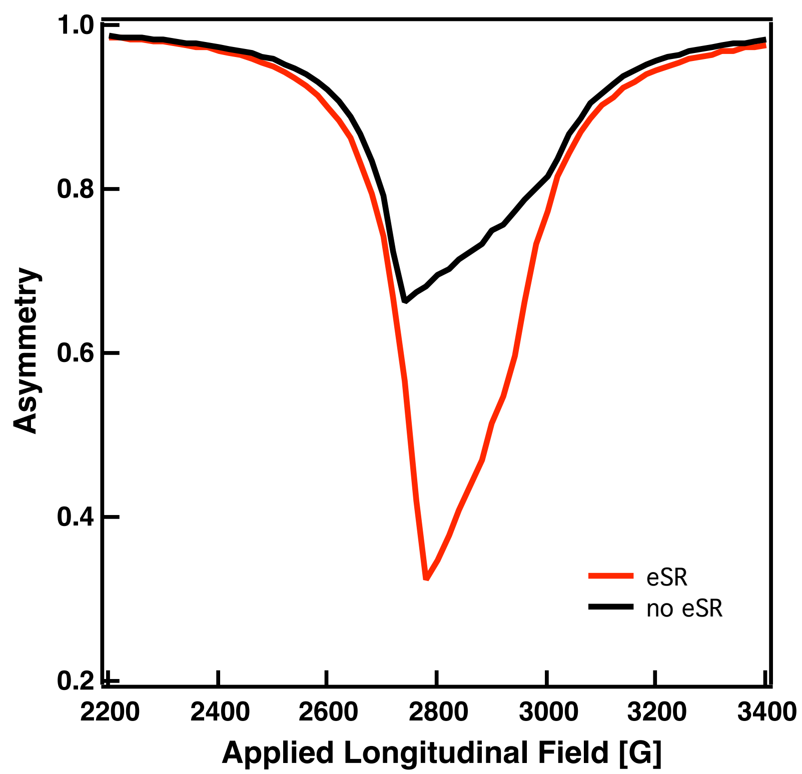
Example 1.... electron (hole?) spin relaxation

TIPS-Pentacene: crystalline

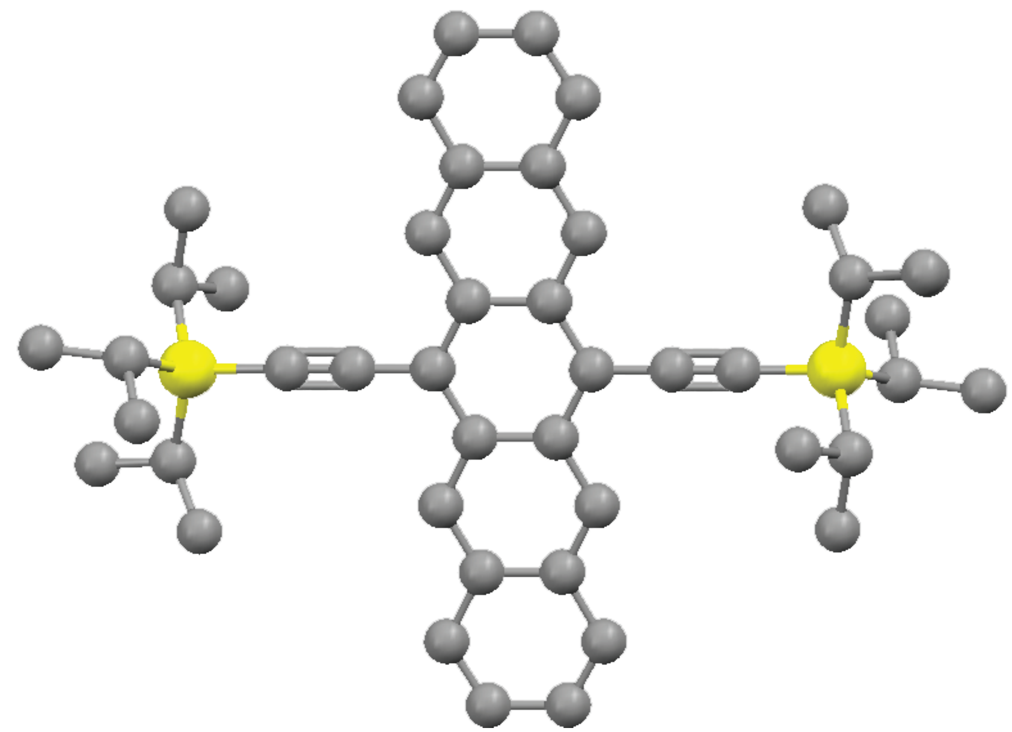
Amplitude roughly proportional to eSR







a)



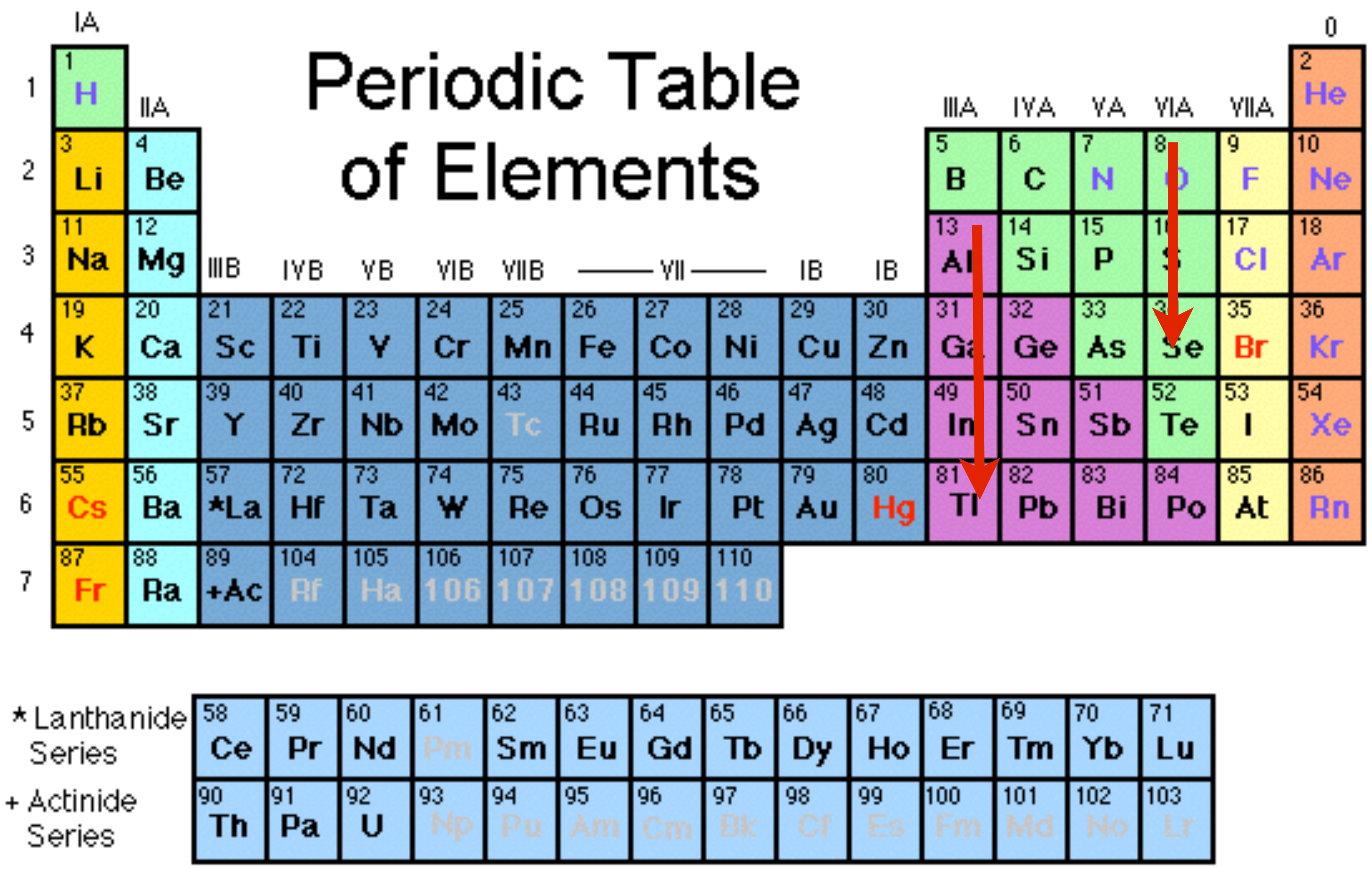
e^- spin-flips changes *amplitude* of resonance (in <1MHz limit)

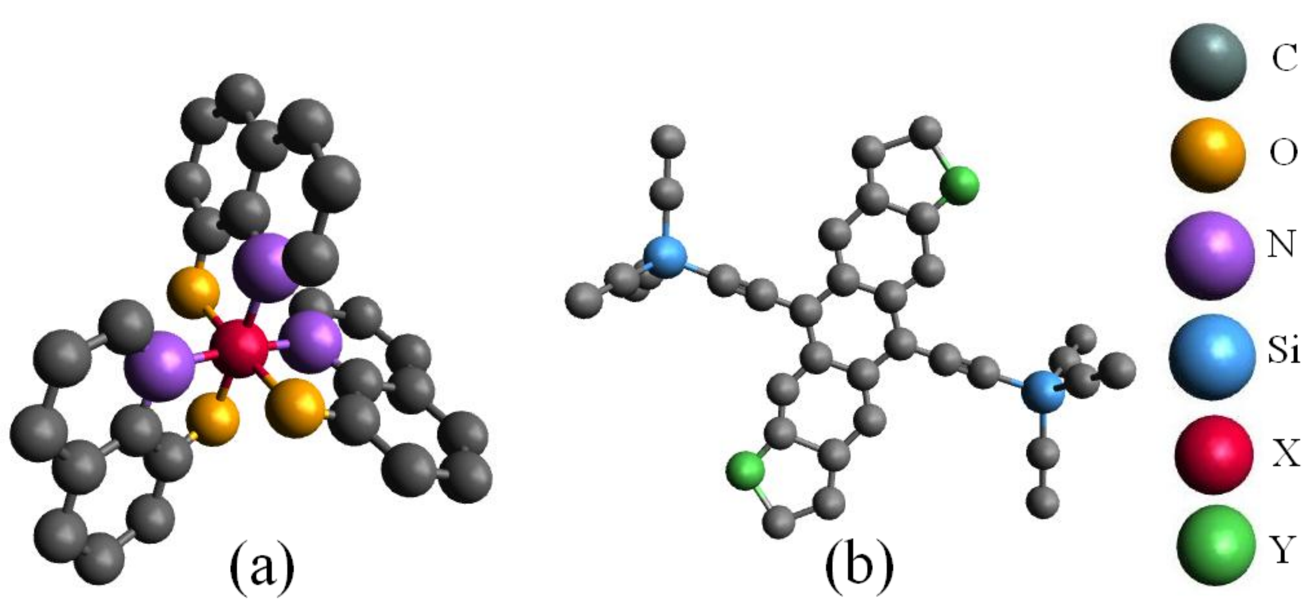
Heming et al., Hyp. Interactions 32 727 (1986)

Can extract *localised* e^- spin relaxation rate as function of T

L Schulz & A J Drew et al., *Phys. Rev. B* **84**, 085209 (2011); L Nuccio, L Schulz & A J Drew, *J. Phys D: Appl. Phys.* 47, 473001 (2014)

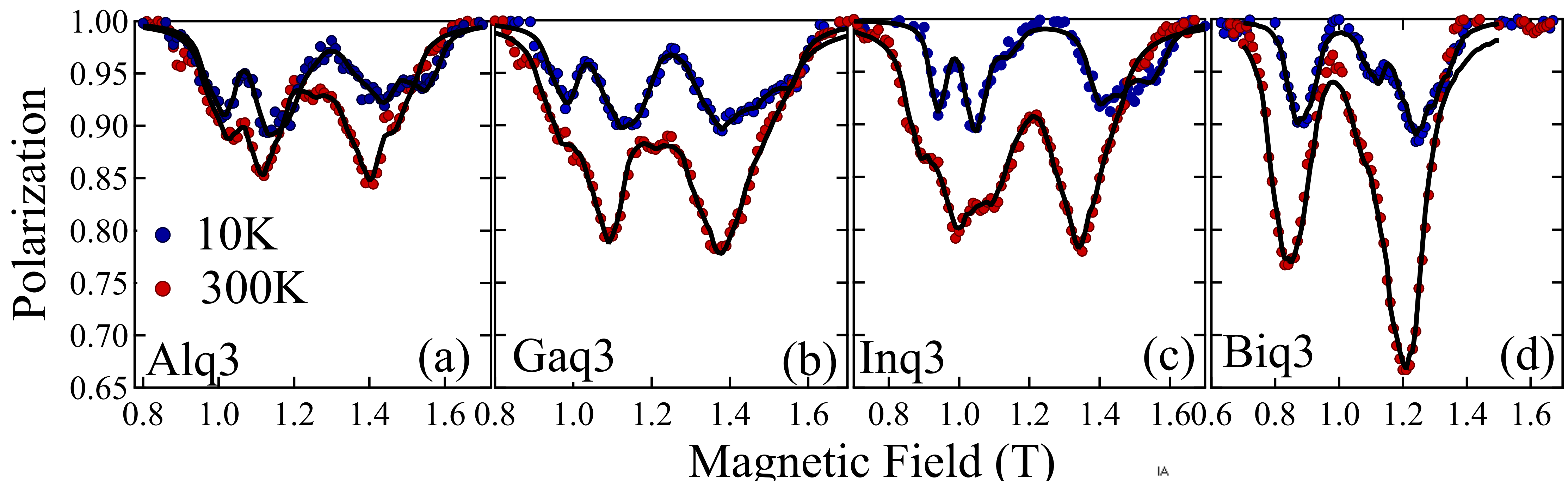
Periodic table



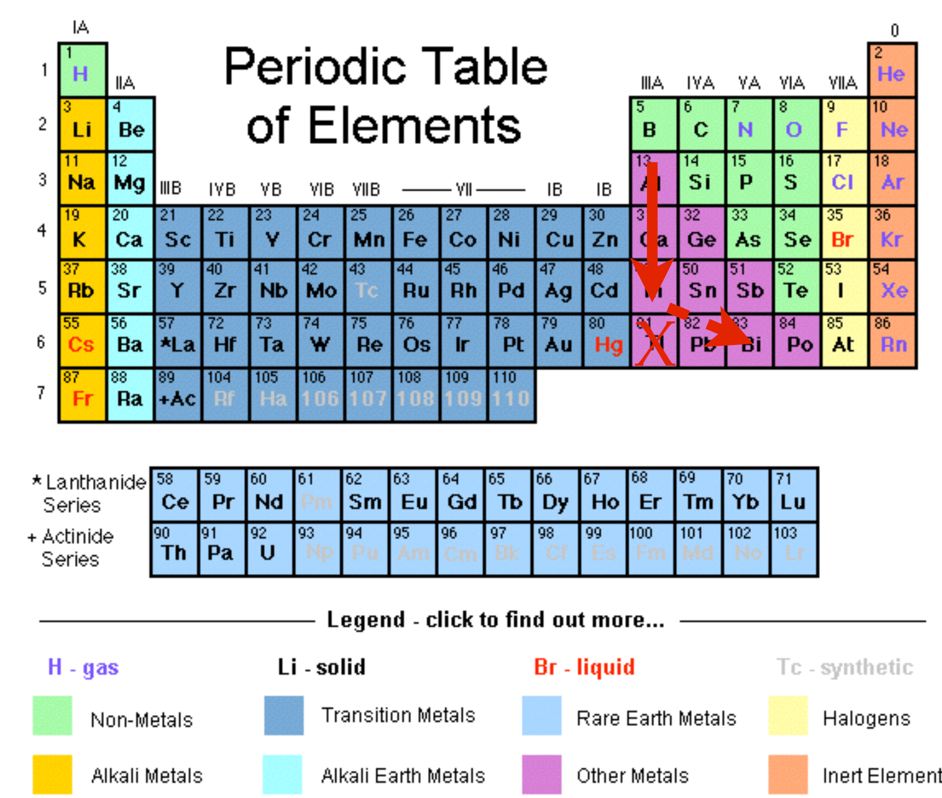


Can we differentiate between SO and HFC driven electron spin relaxation rate?

Example 2: is SOI or HFI responsible for eSR?



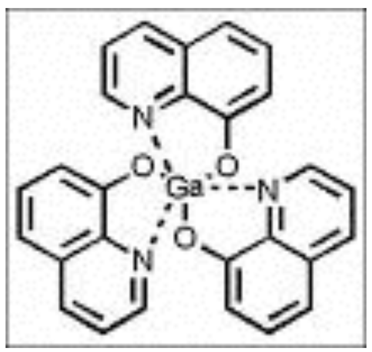
Amplitude roughly proportional to eSR

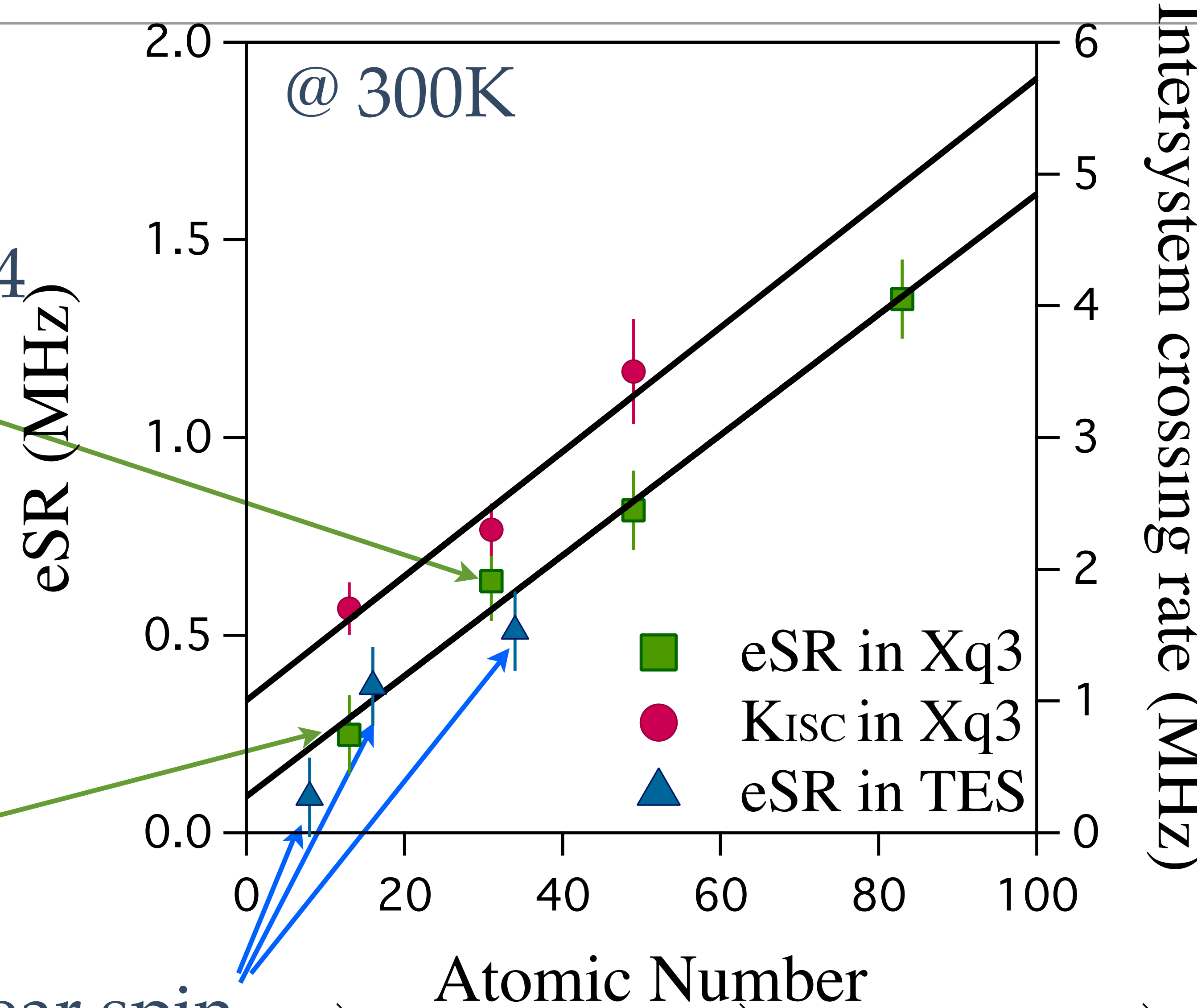


L Nuccio & A J Drew et al., *Phys. Rev. Lett.* **110**, 216602 (2013)

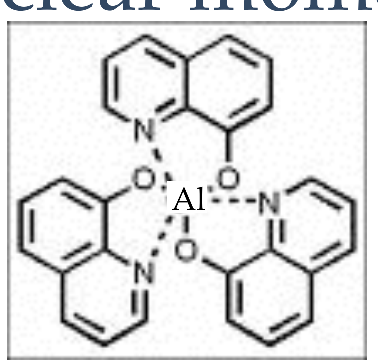
Example 2: is SOI or HFI responsible for eSR?

Ga:
Two spin 3/2 isotopes
nuclear moment: 2.02 & 2.54

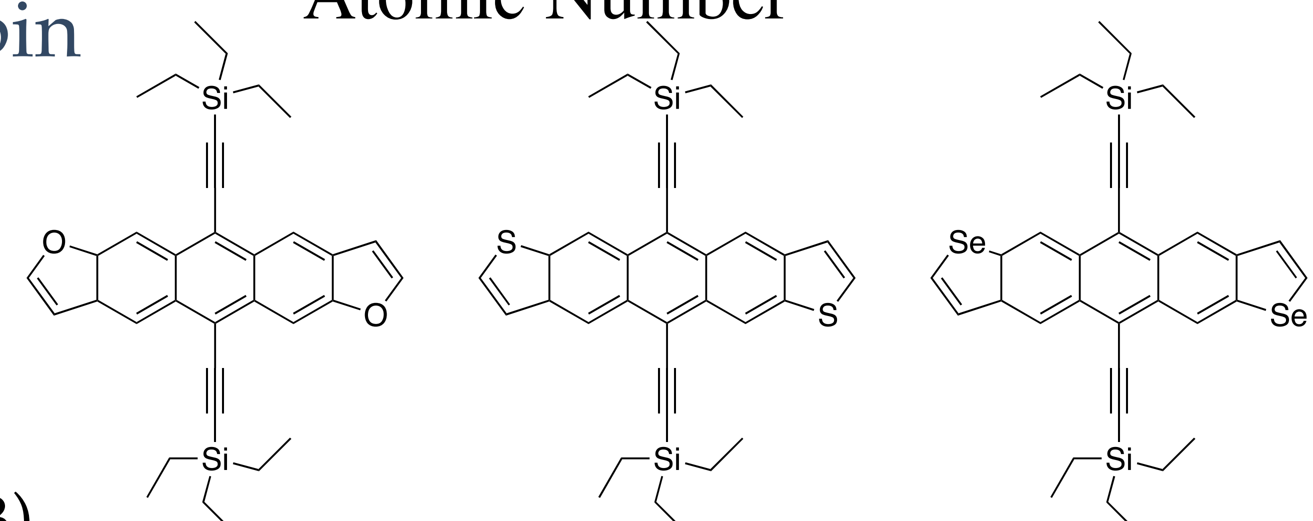




Al:
spin 5/2
nuclear moment: 3.64



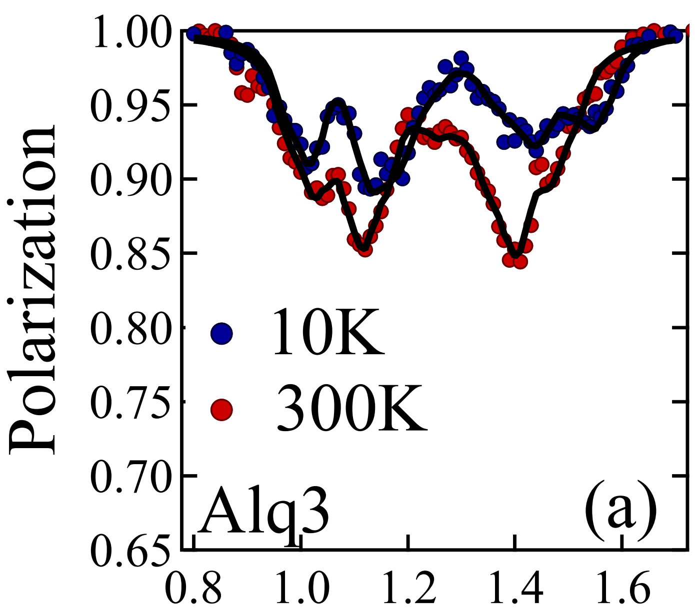
Zero nuclear spin

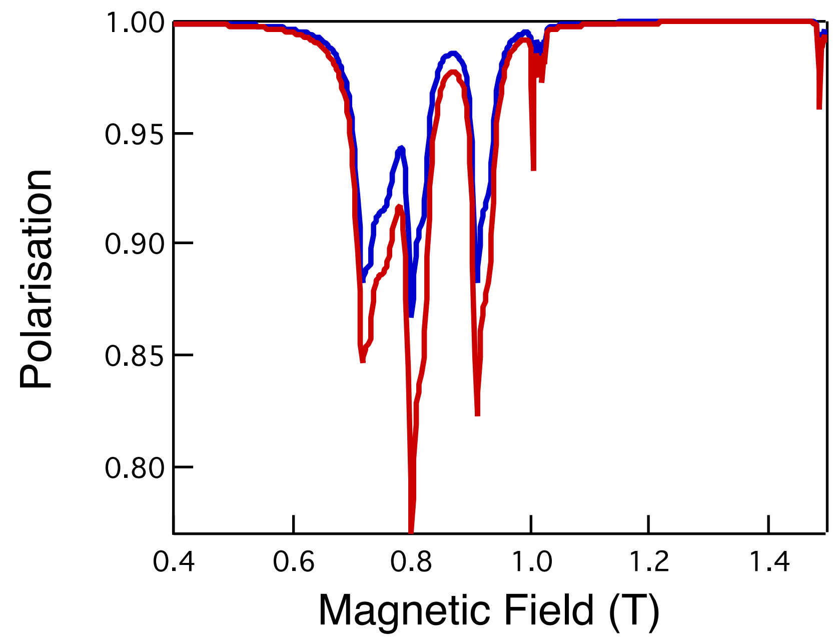


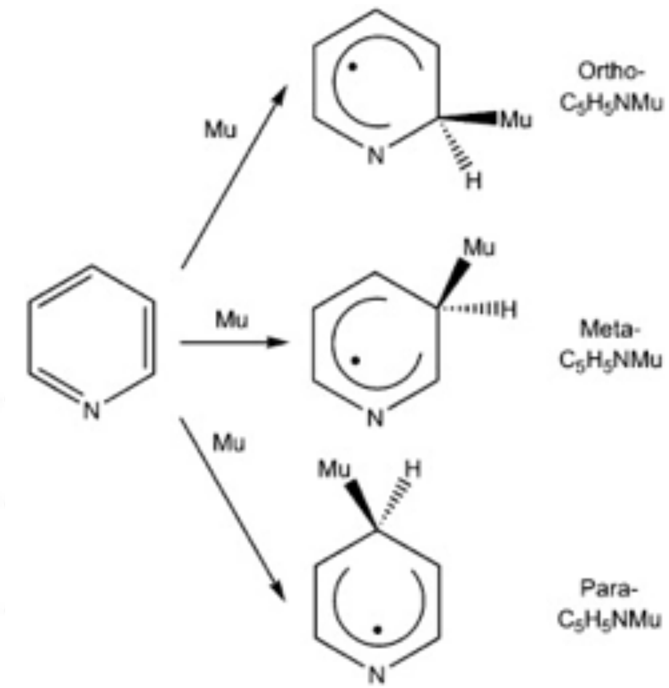
L Nuccio & A J Drew et al.,
Phys. Rev. Lett. **110**, 216602 (2013)

The future.... positional sensitivity?

The devil is in the detail.....



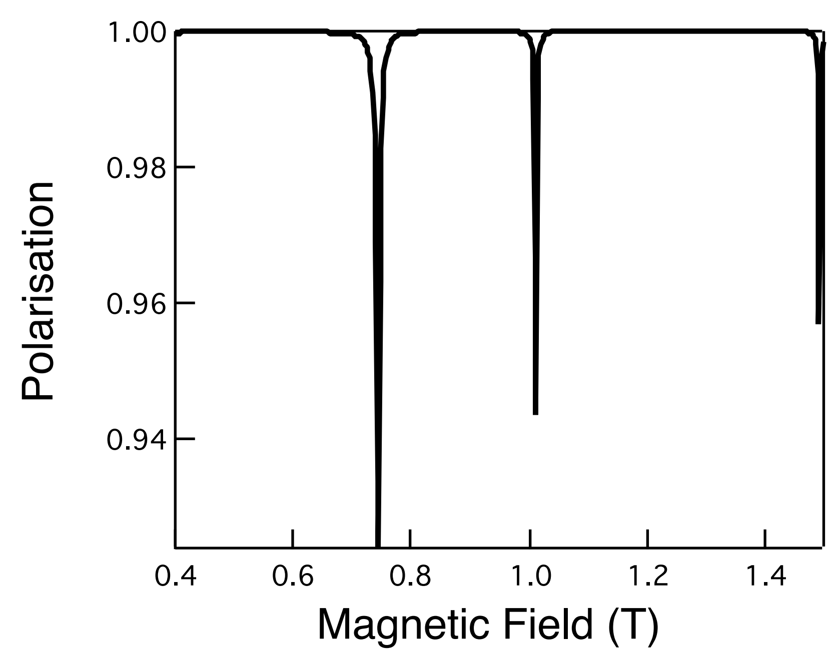


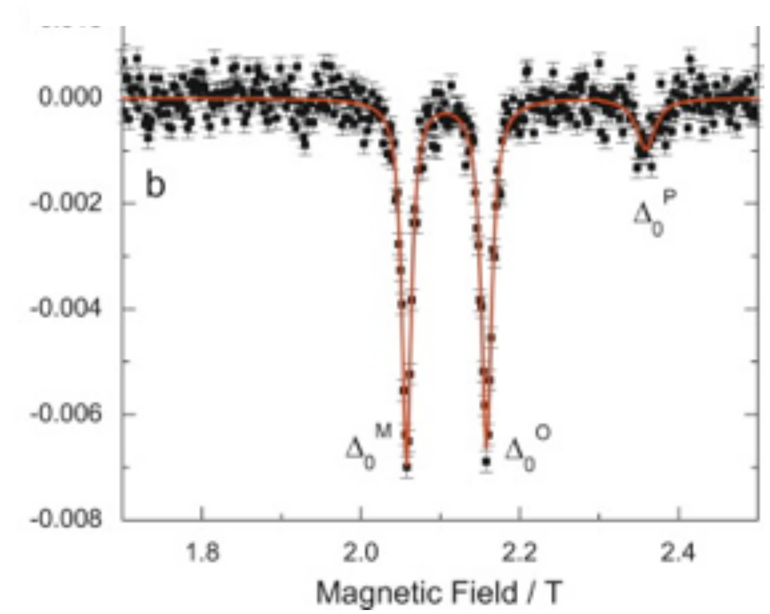


Superposition of signals

Turn on eSR

Turn off dipolar coupling





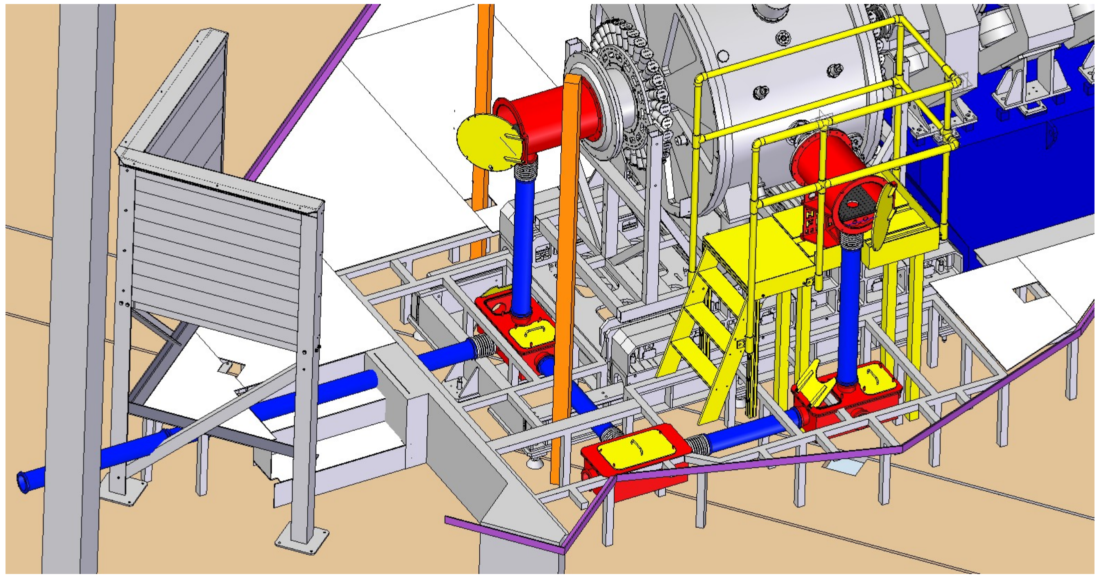
L Nuccio, L Schulz & A J Drew et al., *Phys. Rev. Lett.* **110**, 216602 (2013)

L Nuccio, L Schulz & A J Drew, *J. Phys D: Appl. Phys.* (2014), at press

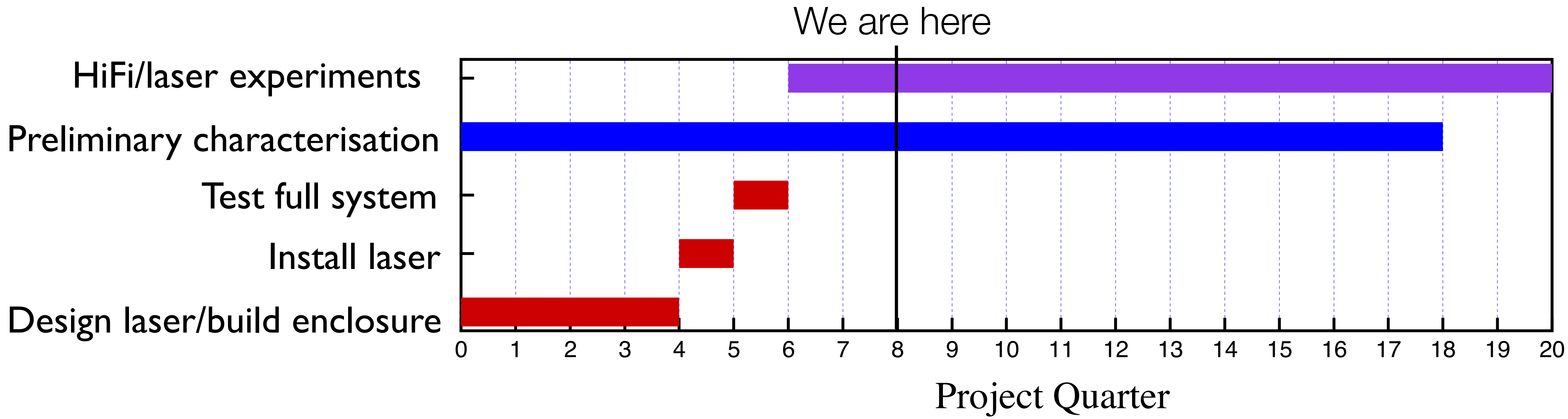
Spins in organic semiconductors: recent developments in the application of muons

Brilliant.... positional sensitivity if one moves to liquids....
But what can you do with it?

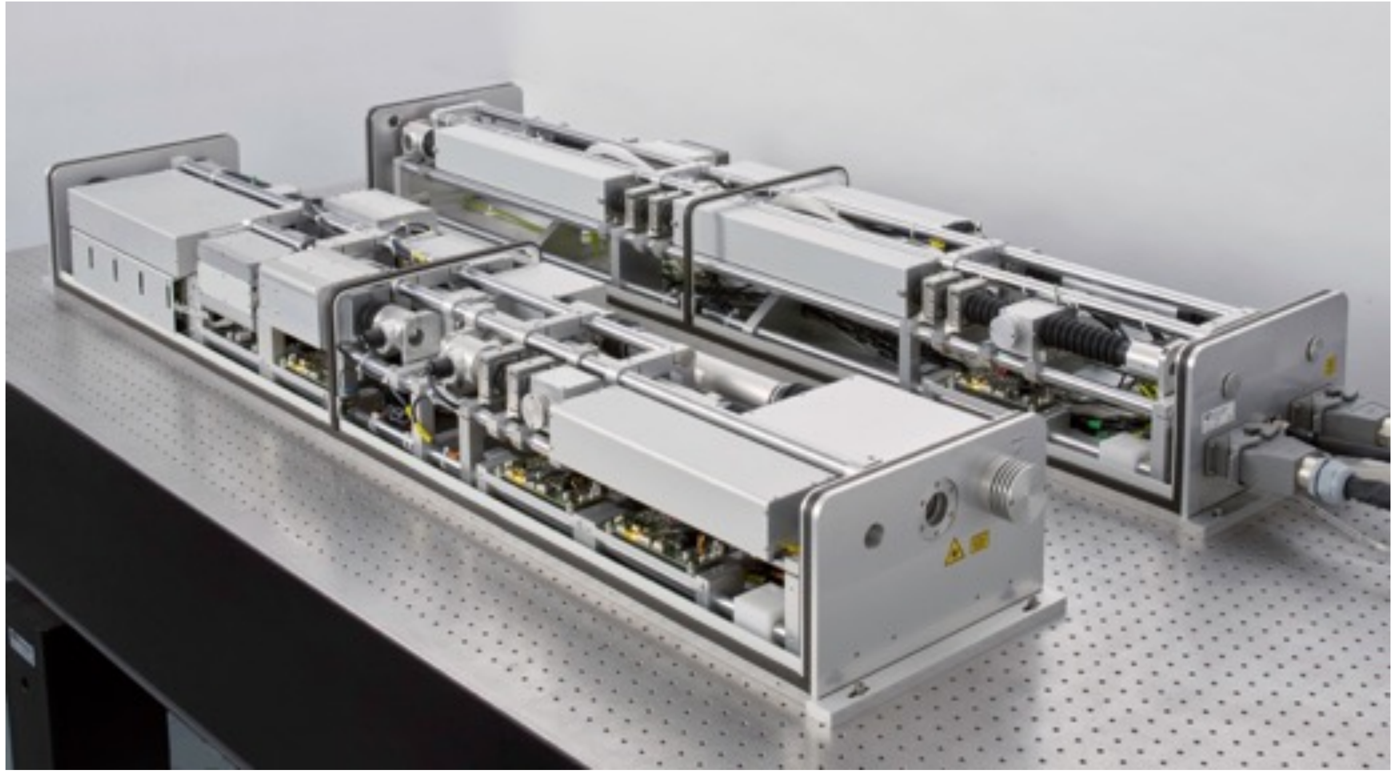
Excited states at high fields....

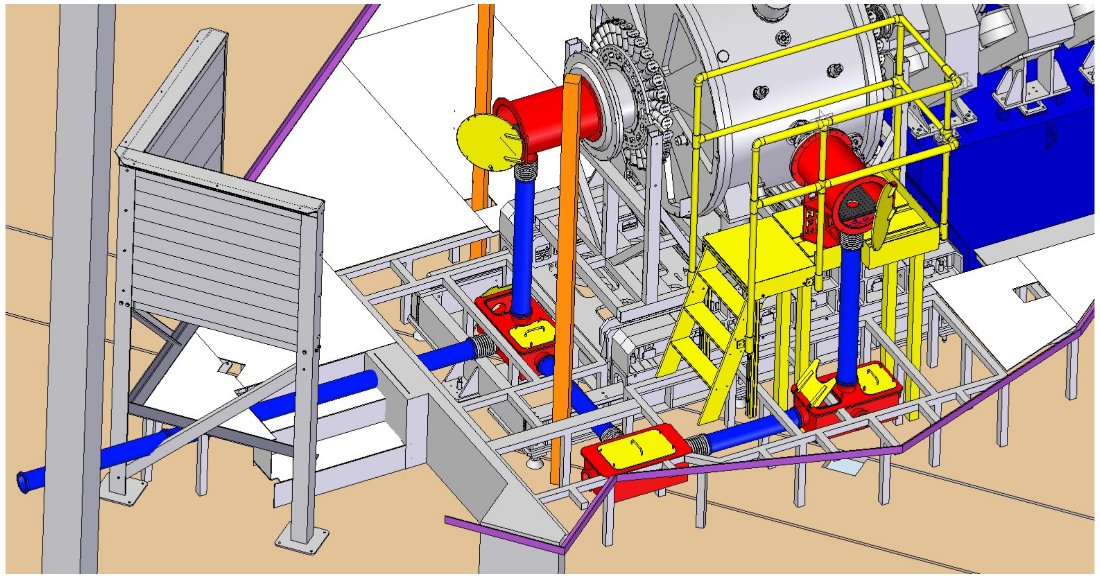


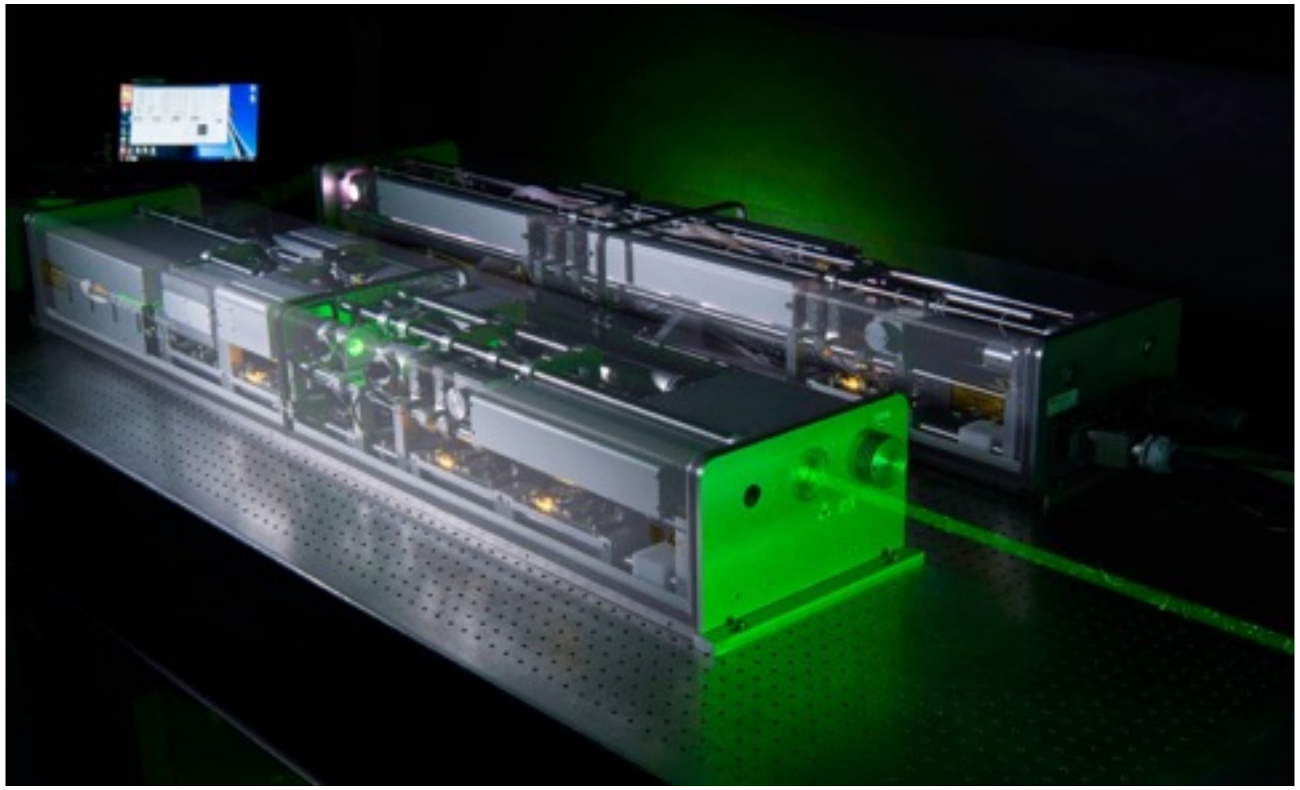
- Nd- YAG pumped OPO
- Switchable between modes of operation:
  - Nd-YAG
    - 2.5 J per 5 ns pulse at 1064 nm
    - Fixed-wavelength harmonics available: 1064nm, 532nm, 355nm, 266nm and 213nm
  - OPO
    - Tuneable between 200nm and 2000nm,
    - No less than 50mJ / pulse over full wavelength range
- Delay lines on triggers to allow time resolved measurements:
  - Delay lines to ~20ms (ISIS pulse separation)
  - Time resolution: ISIS pulse width



Light excitations at high fields....

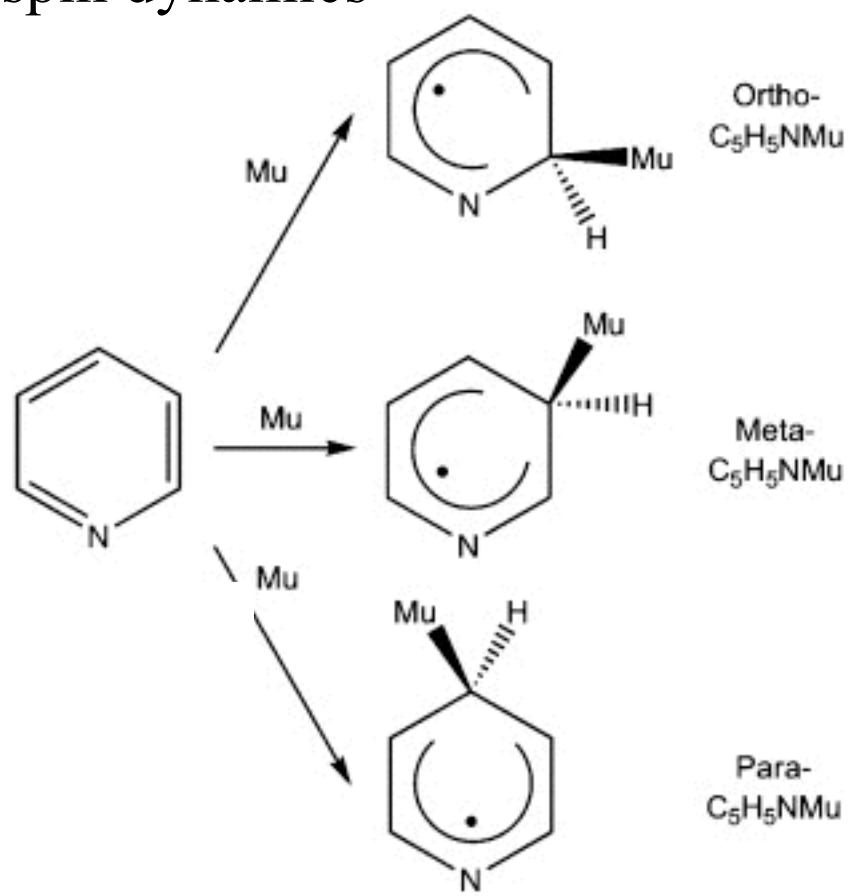


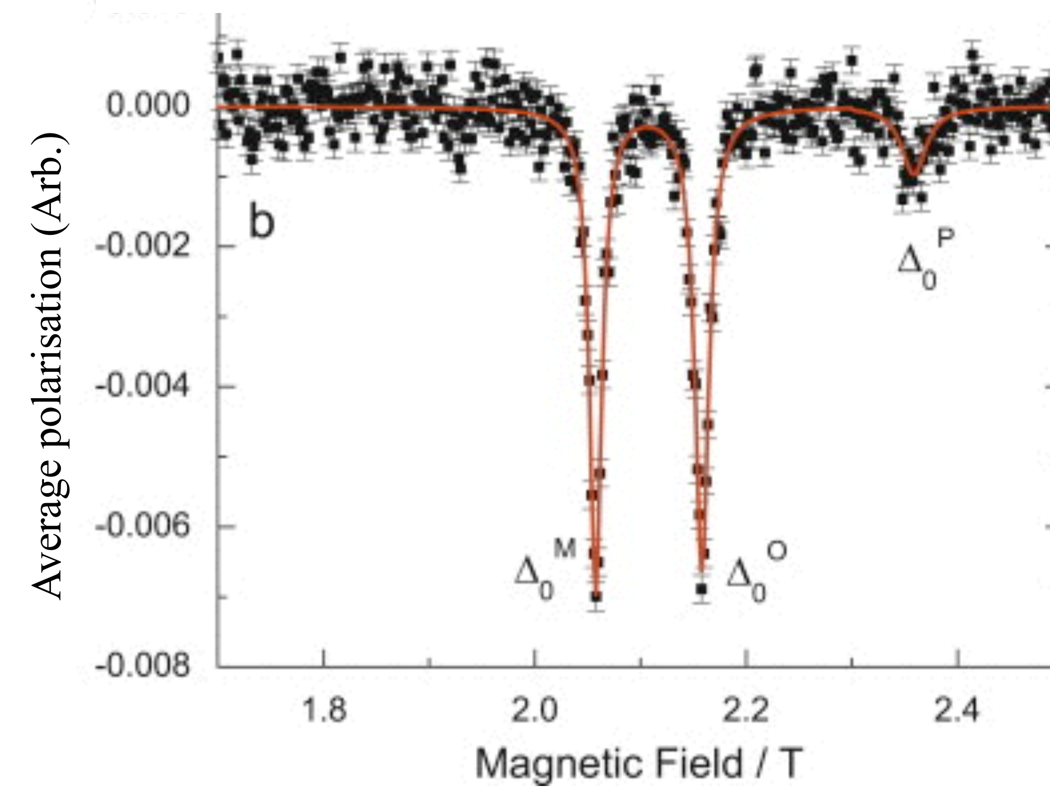


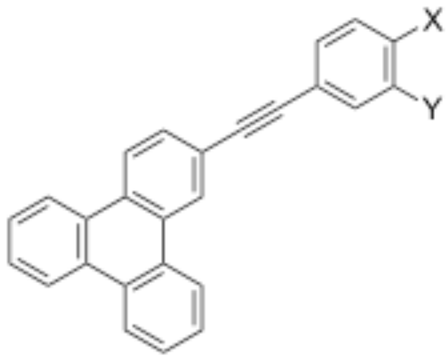


What can you do?

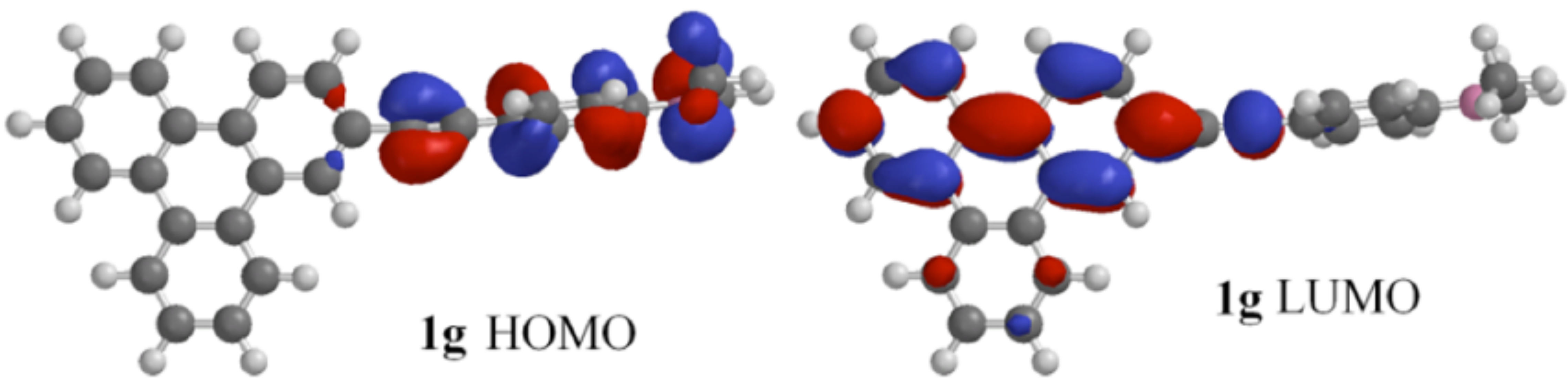
Sensitive to electronic spin dynamics
(temporal and spatial)





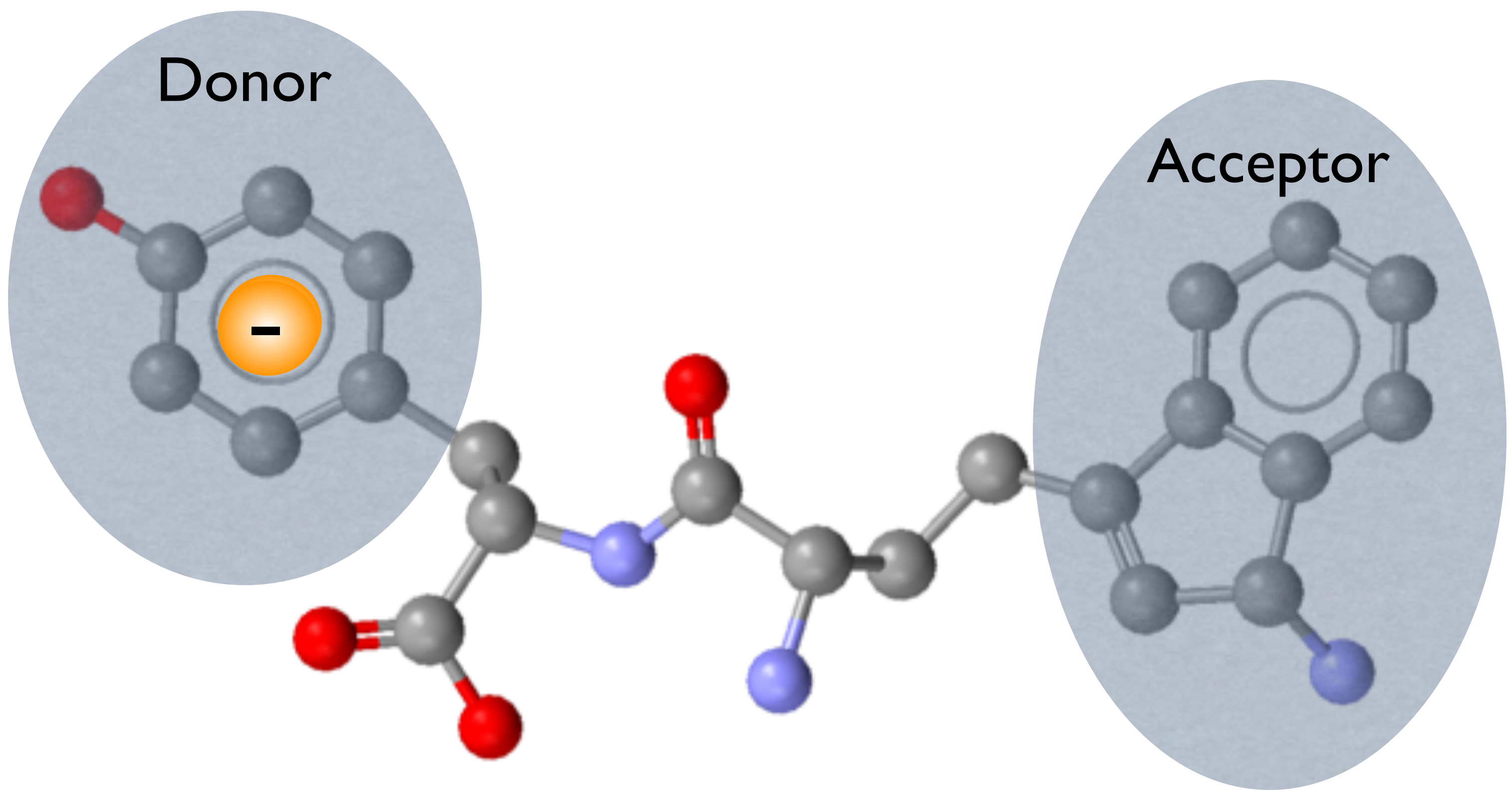


1a X = Y =H; **1b** X = H, Y = CF_3; **1c** X = CN, Y = H;
1d X = COMe, Y = H; **1e** X = COPh, Y = H;
1f X = Y = $OC_{10}H_{21}$; **1g** X = NMe_2, Y = H

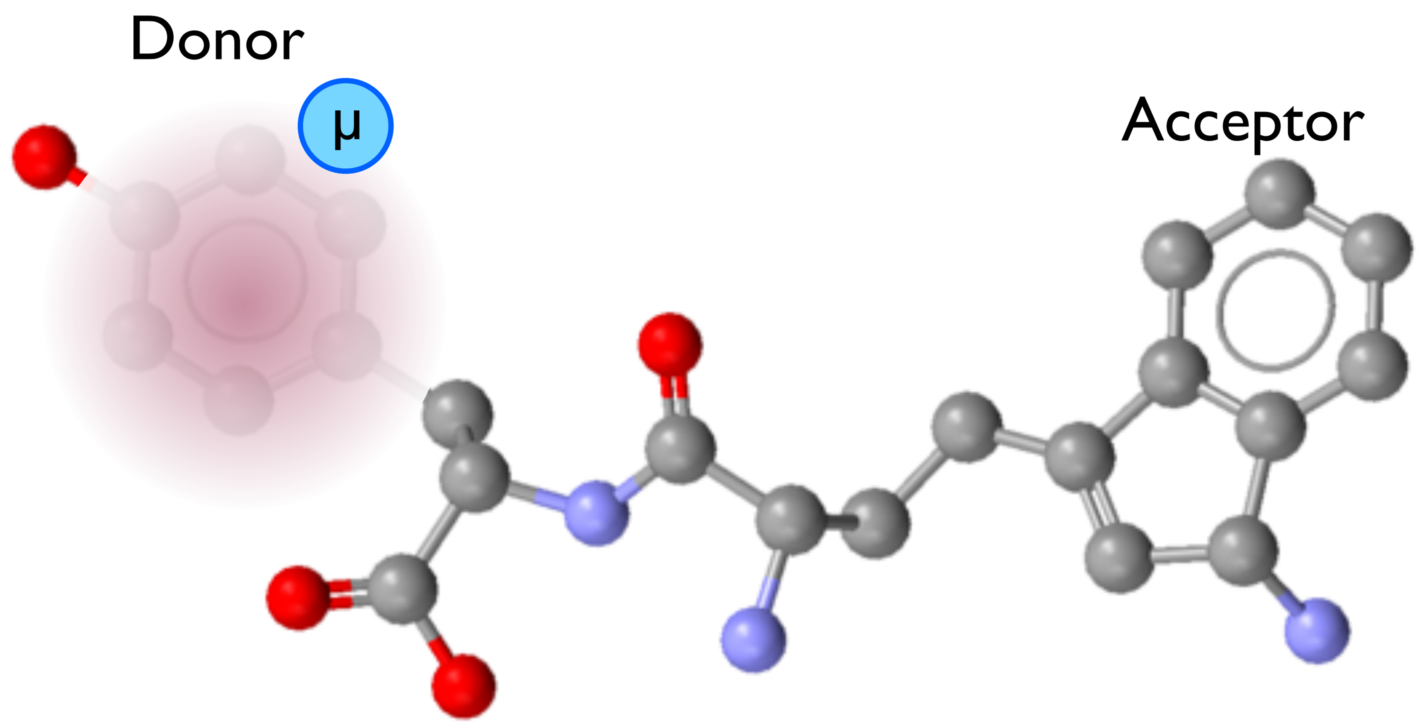


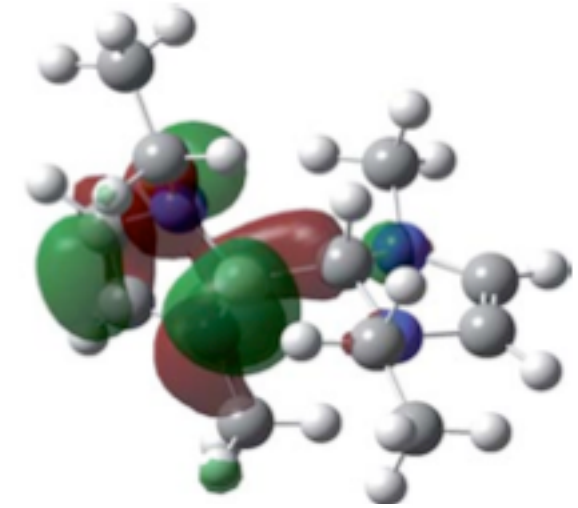
Nandy et al., Beilstein J. Org. Chem. **2010,** *6,* 992–1001.

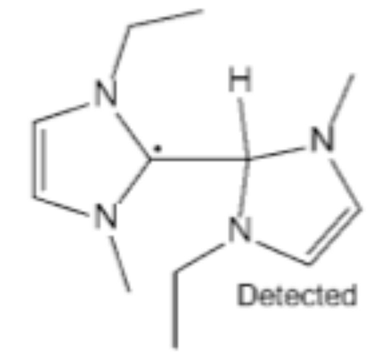
Electron transfer



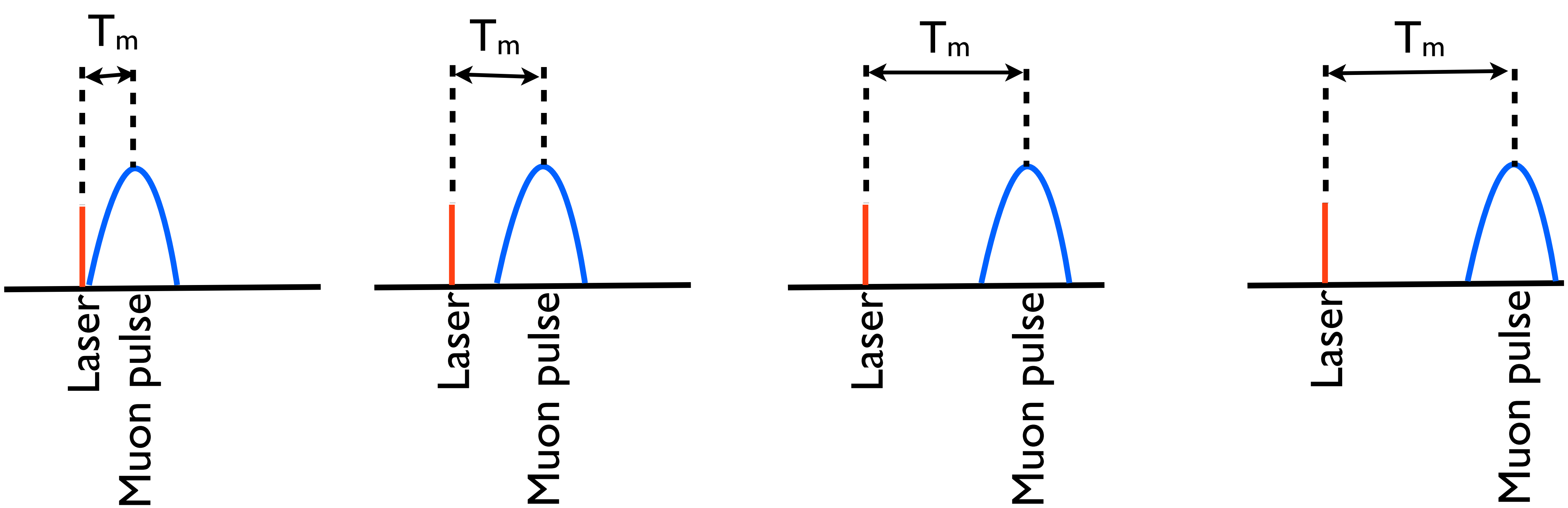
Electron transfer



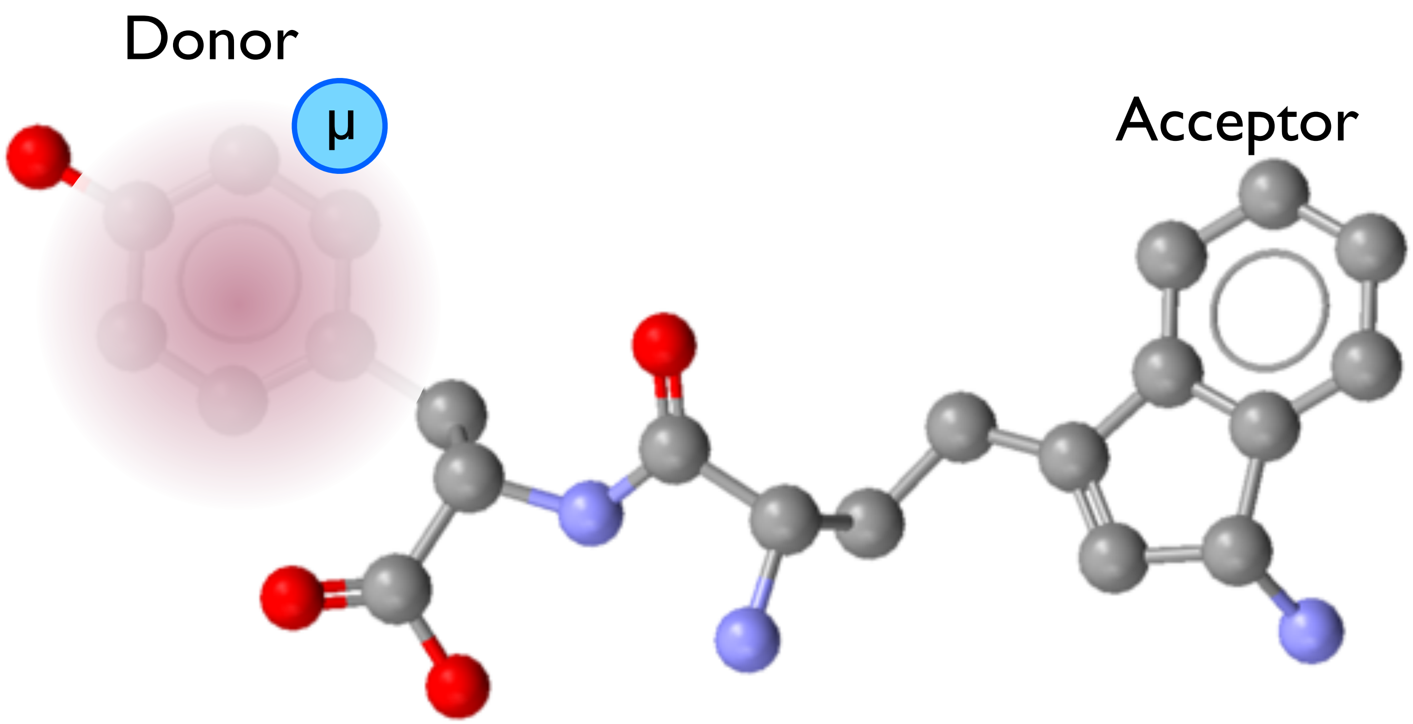


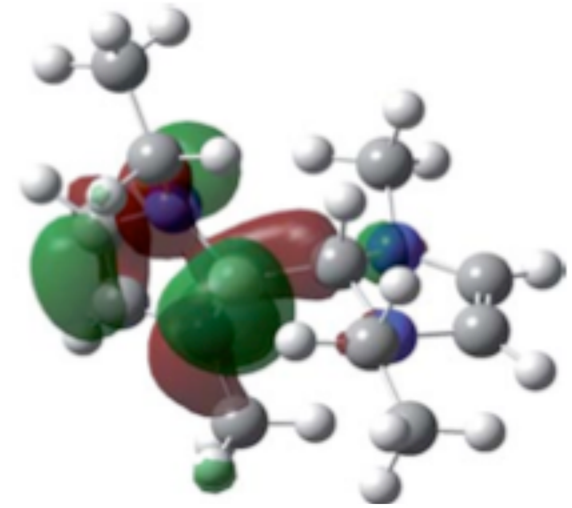


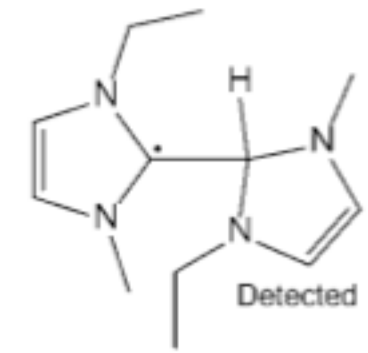
Sherren et al., Chem. Sci 2, 2173 (2011)



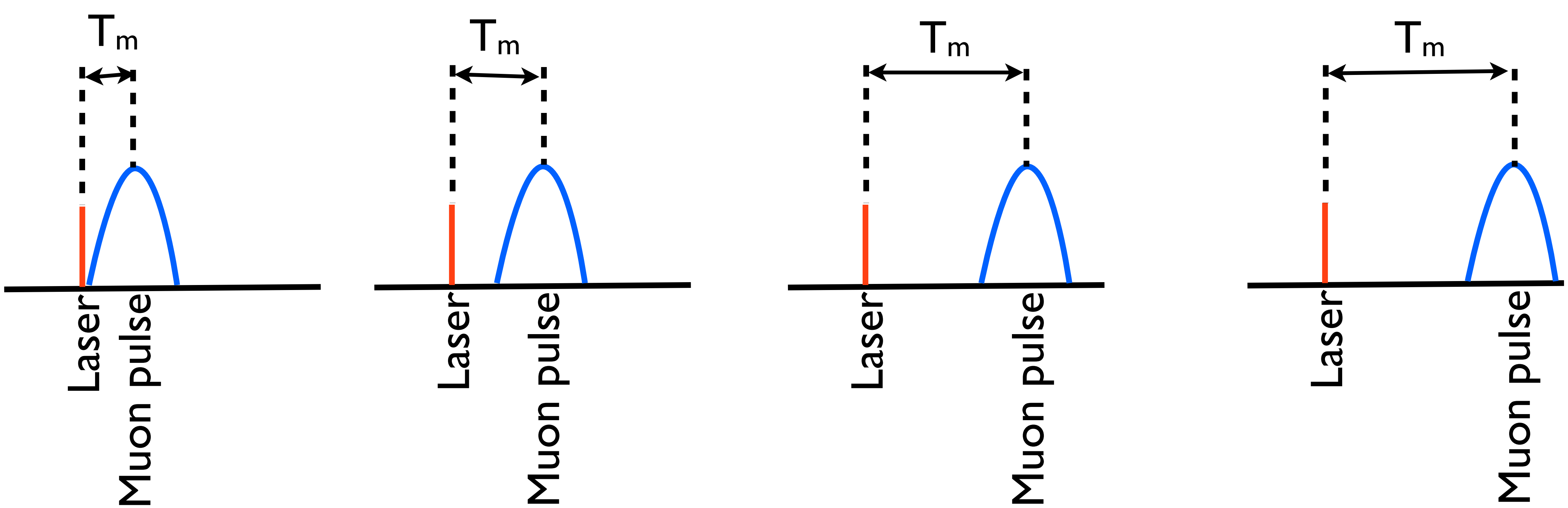
Electron transfer



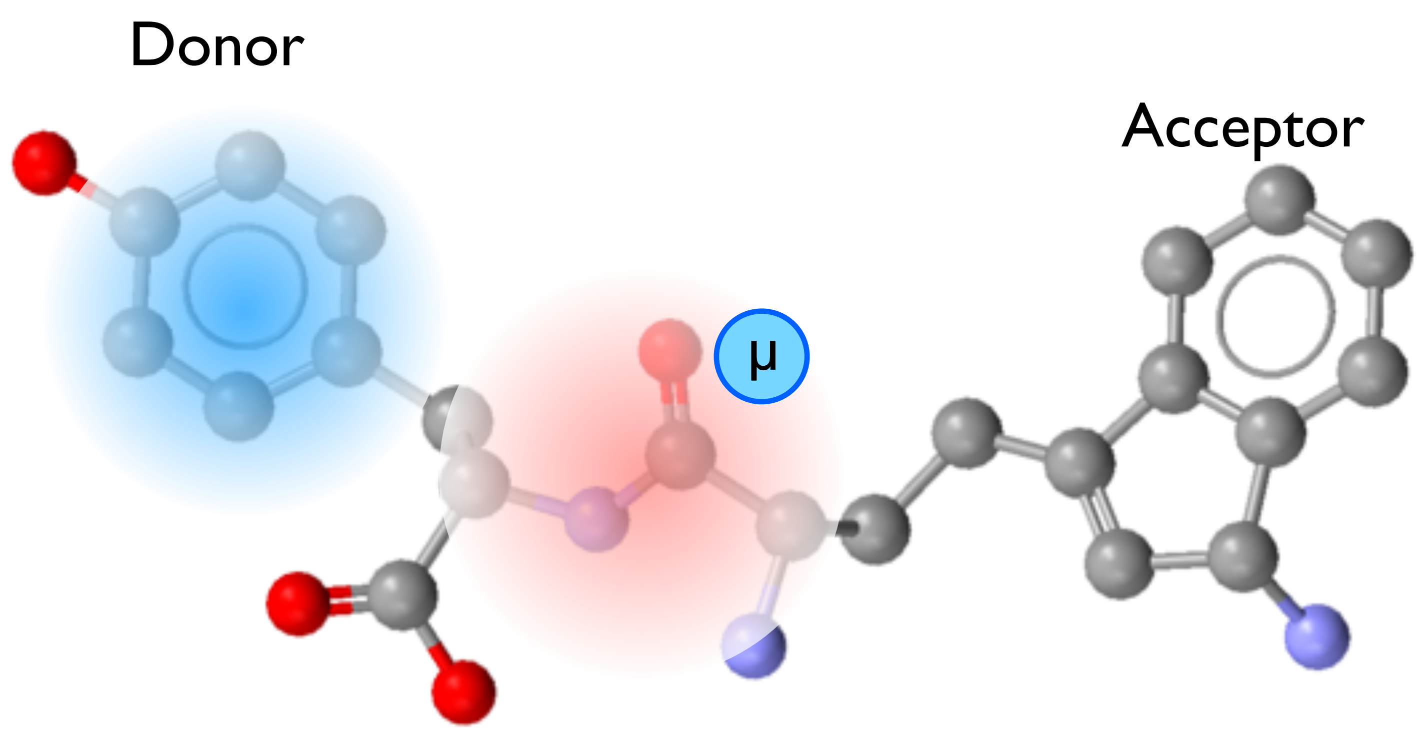


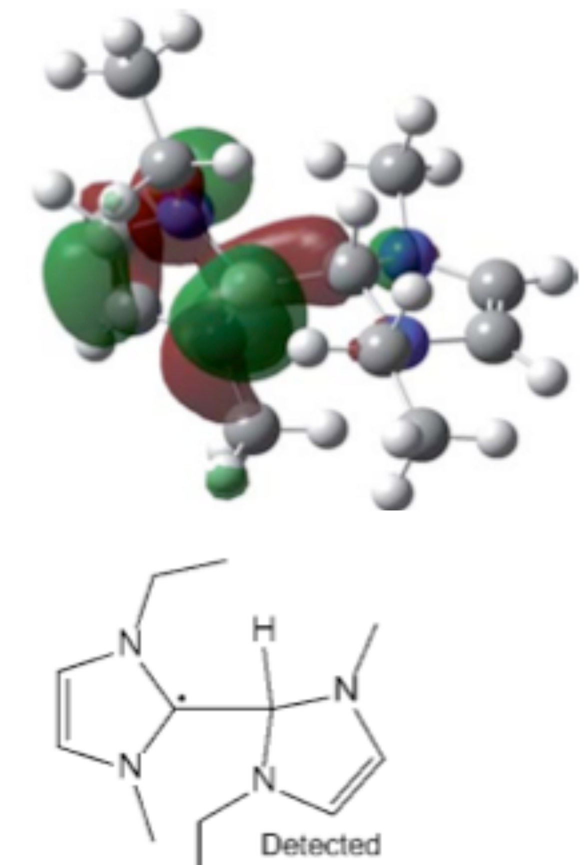


Sherren et al., Chem. Sci 2, 2173 (2011)

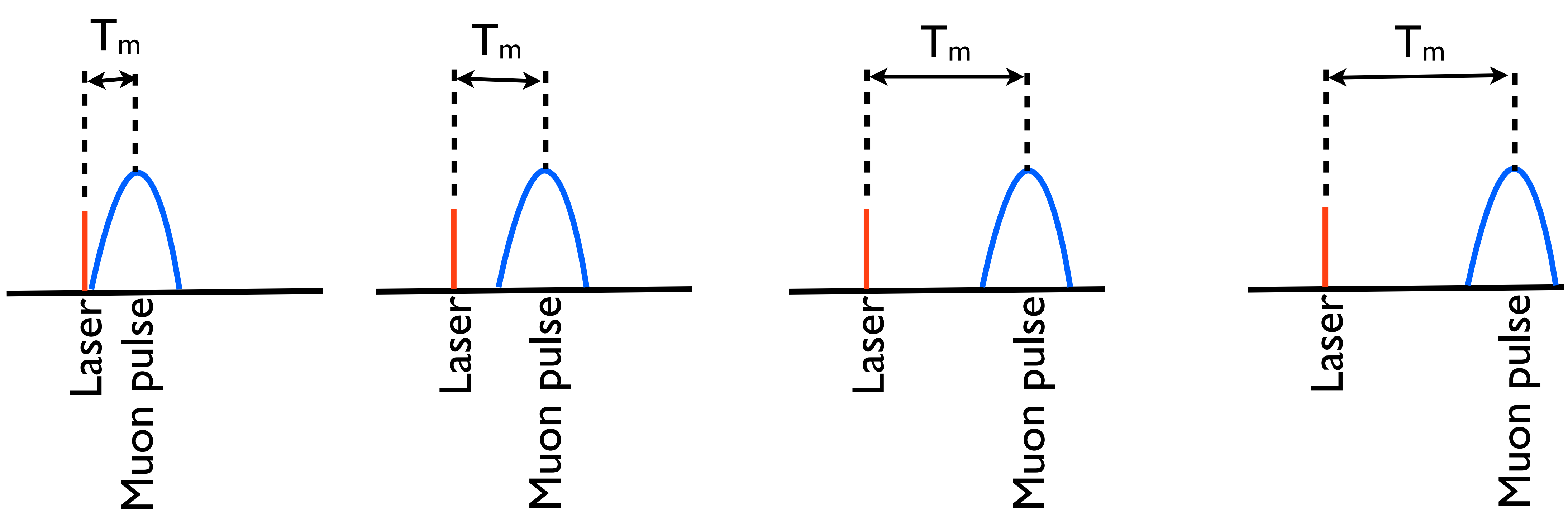


Electron transfer





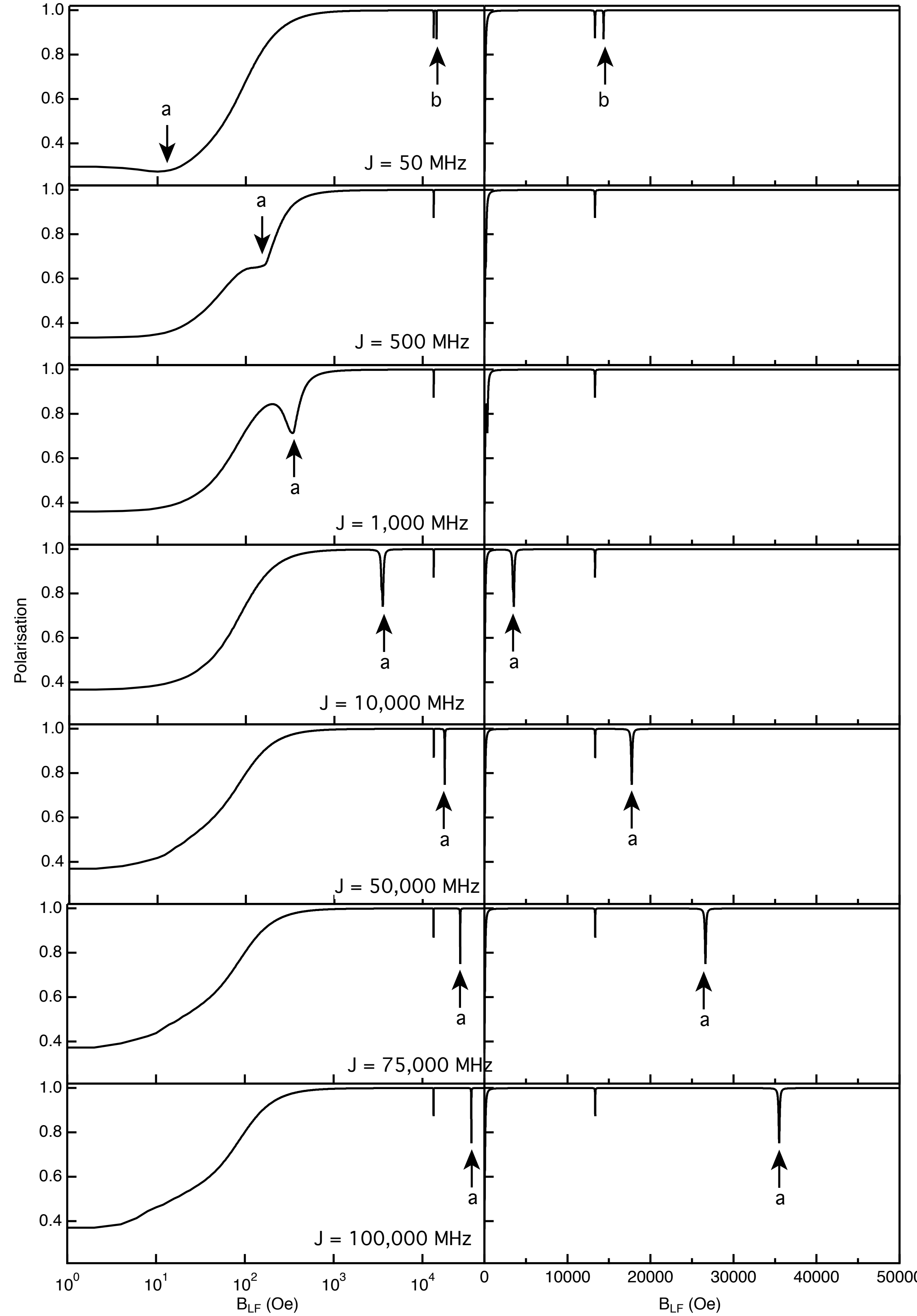
Sherren et al., Chem. Sci 2, 2173 (2011)



What would you see?

It's complicated...

- Additional ALC lines
- Shifting of existing ALCs
- Different muonium chemistry
- .....

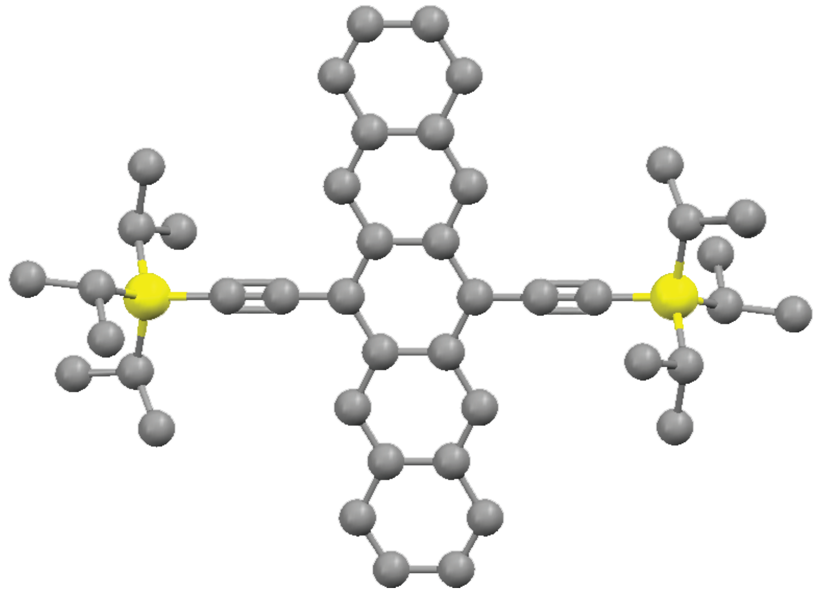


K Yokoyama, & A J Drew et al., *Phys. Scr.* 88, 068511 (2013)

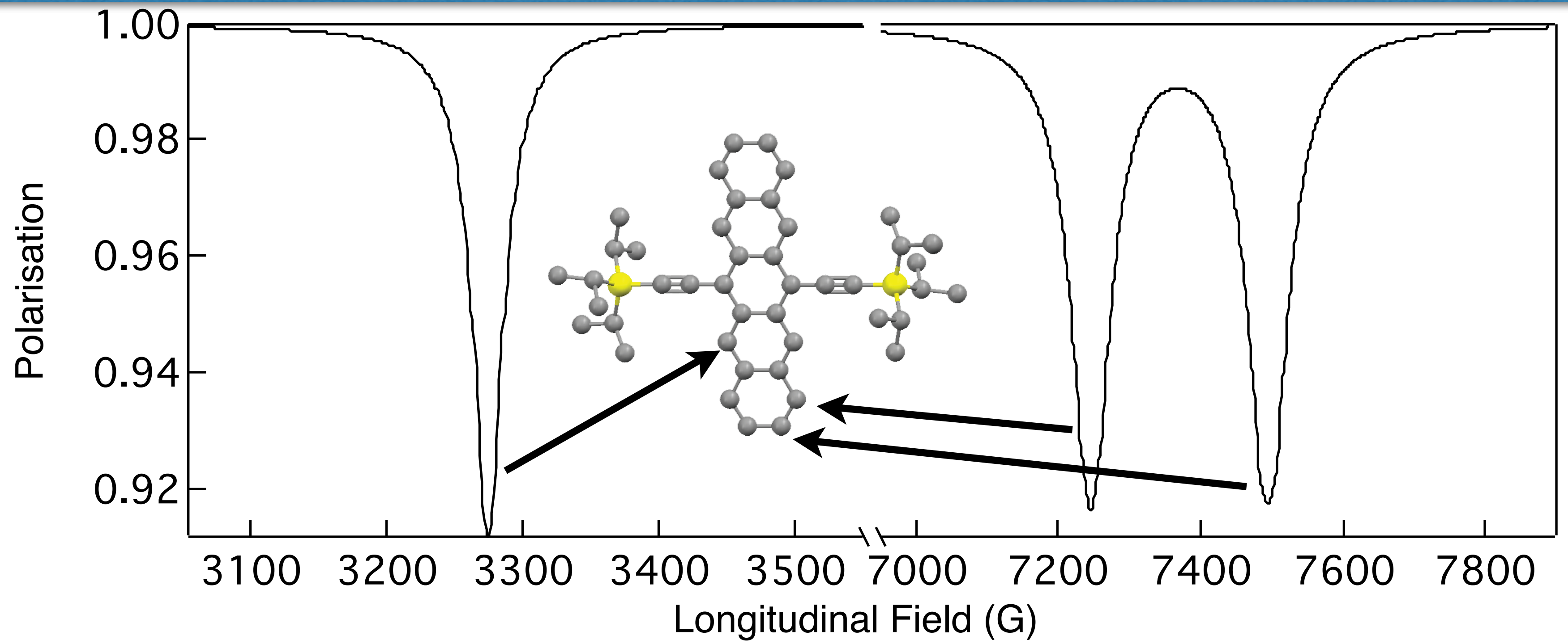
KISS (Keep It Simple Stupid): TIPS-pentacene

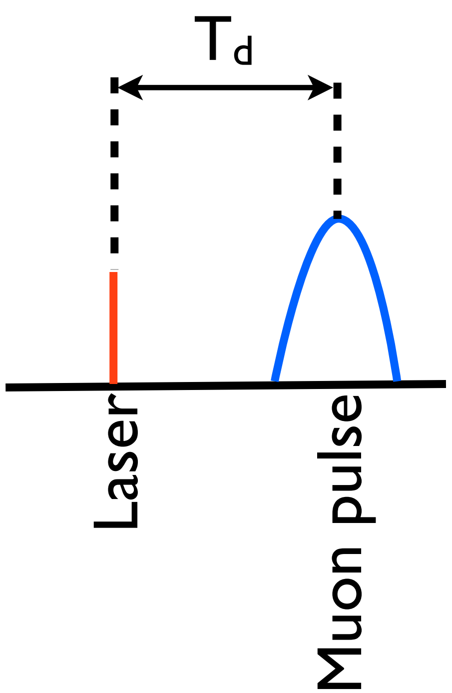
Why TIPS?

- Already know the muonium states & lots of experience with it
- Relatively small molecule
- Want to see whether we can measure excitons...No funny charge transfer states
- Undergoes singlet fission (with 200% quantum yield: Walker et al., Nat. Chem. 5, 1019 (2013))
- Triplet lifetime = 6.5 microseconds :-)
- Soluble (single molecule, can match muon penetration profile with optical absorption)
- Extensive DFT calculations done

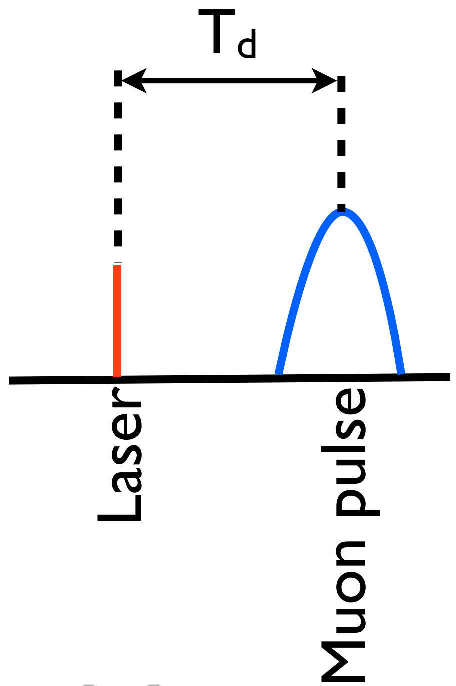


KISS (Keep It Simple Stupid): TIPS-pentacene

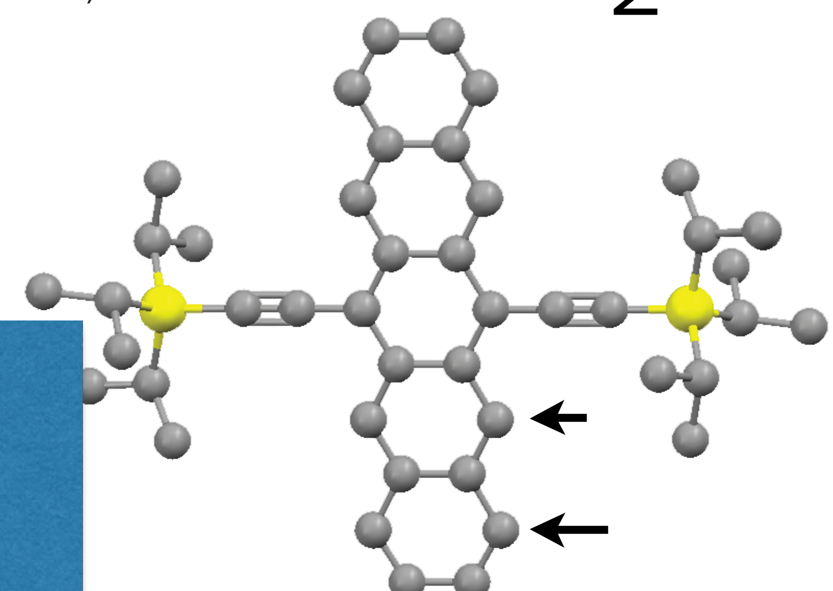




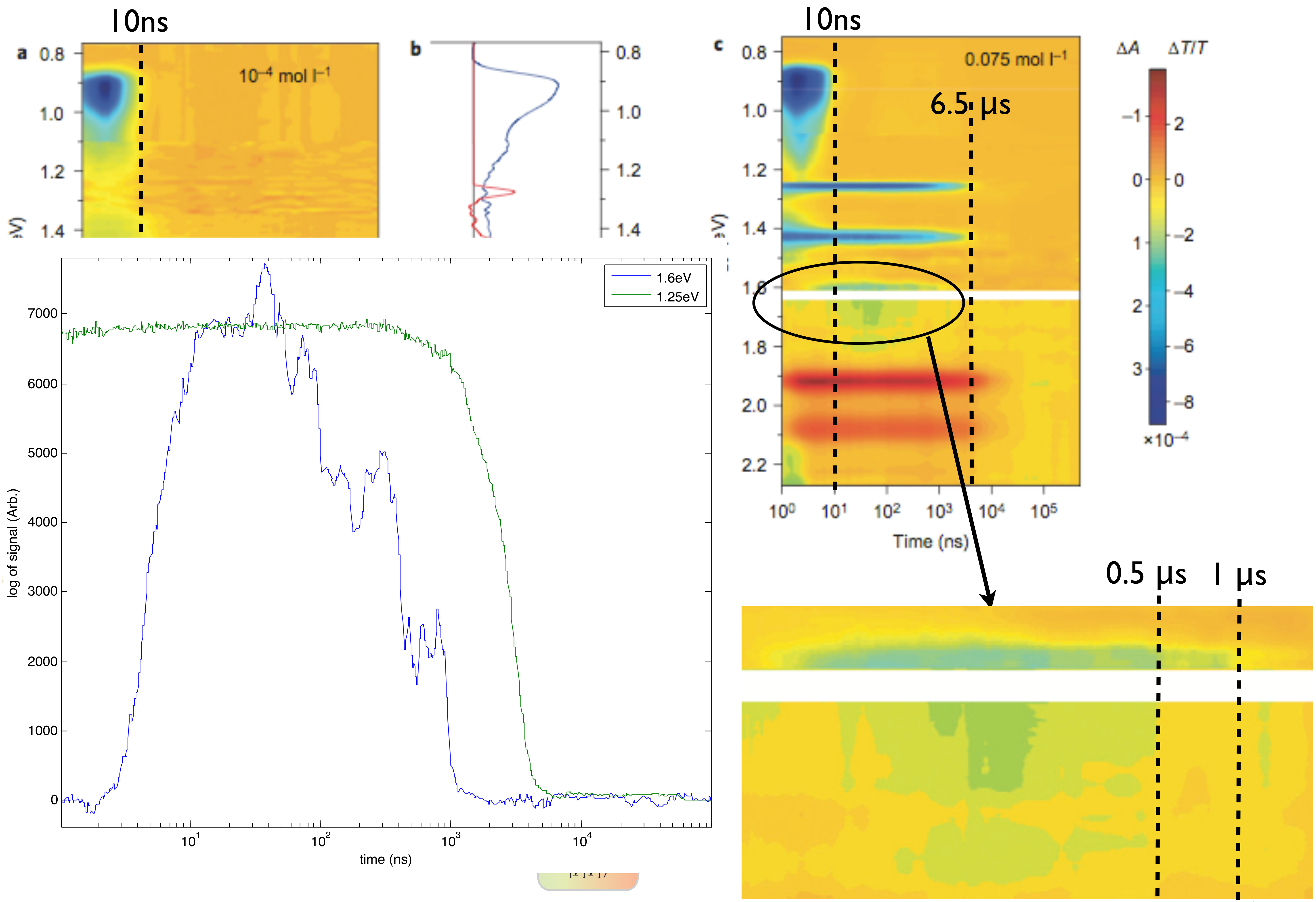
KISS (Keep It Simple Stupid): TIPS-pentacene



a)

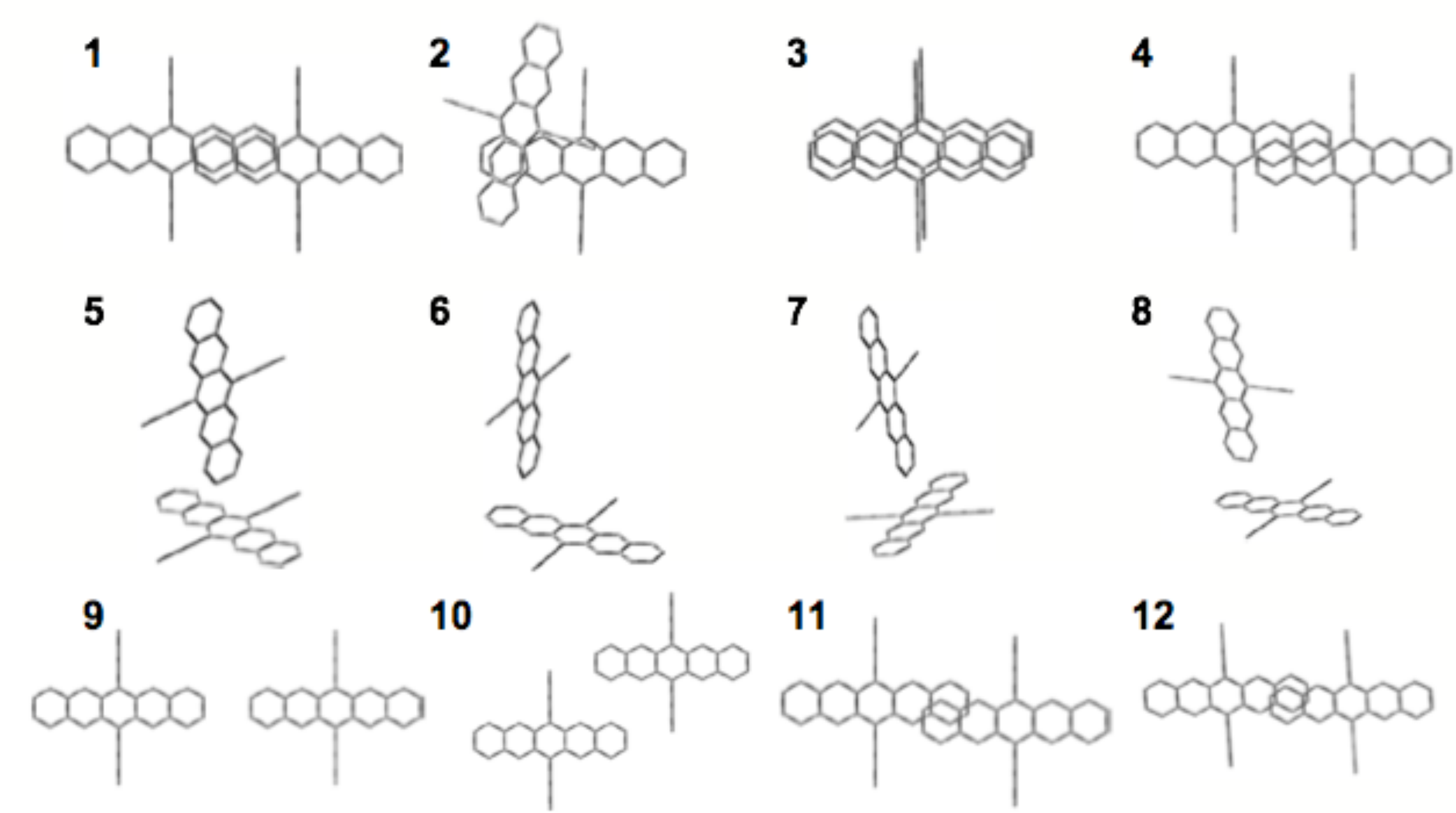


IWIKISS (I Wish I Kept It Simple Stupid)



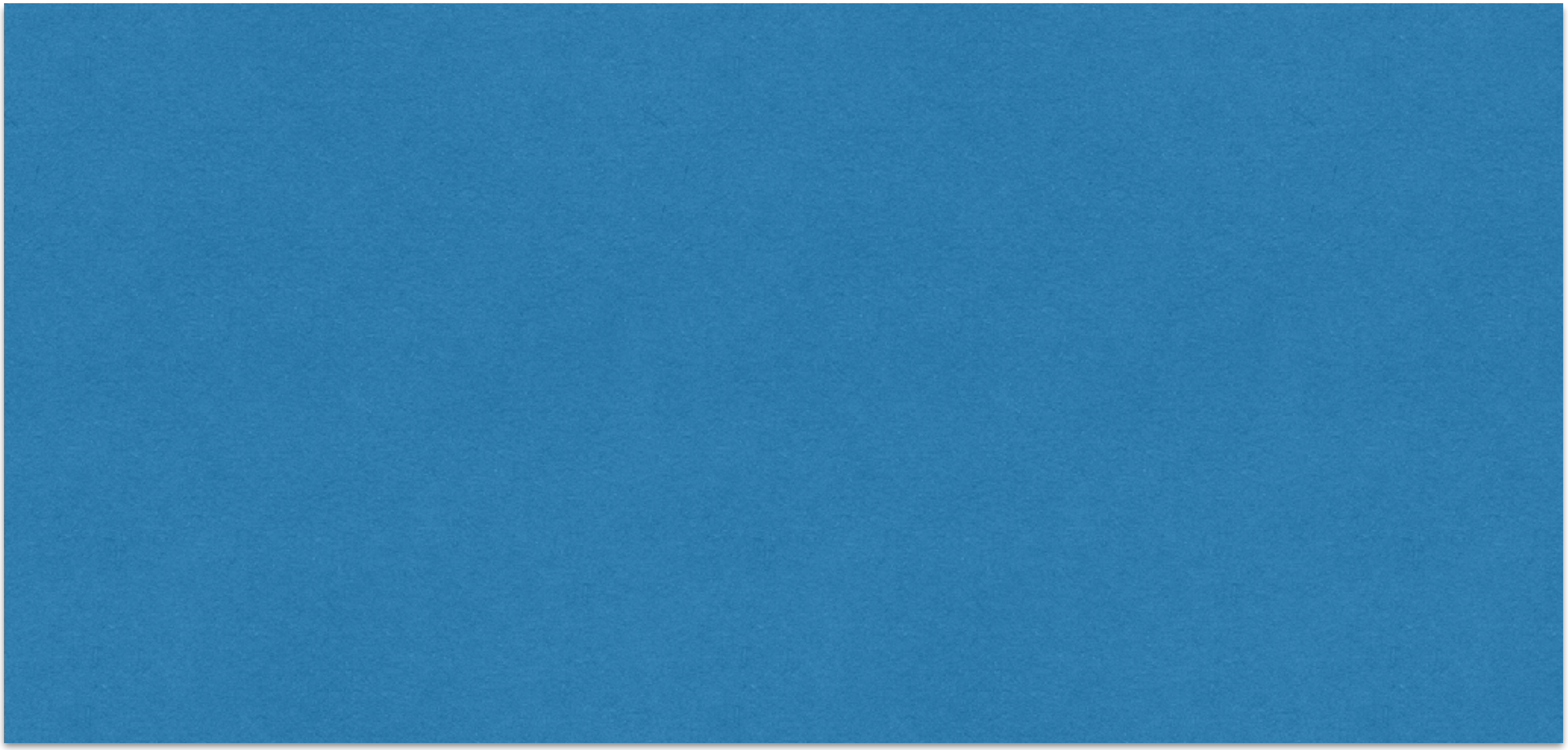
Walker et al., *Nat. Chem.* **5**, 1019 (2013)

IWIKISS (I Wish I Kept It Simple Stupid)



Walker et al., *Nat. Chem.* **5**, 1019 (2013)

IWIKISS (I Wish I Kept It Simple Stupid)

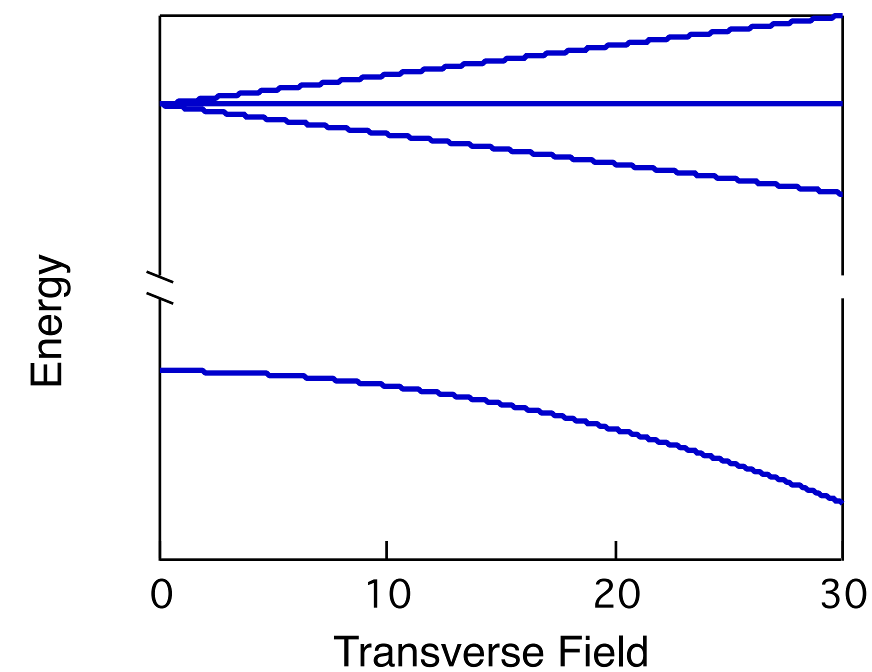


So what is going on here?

It's complicated...

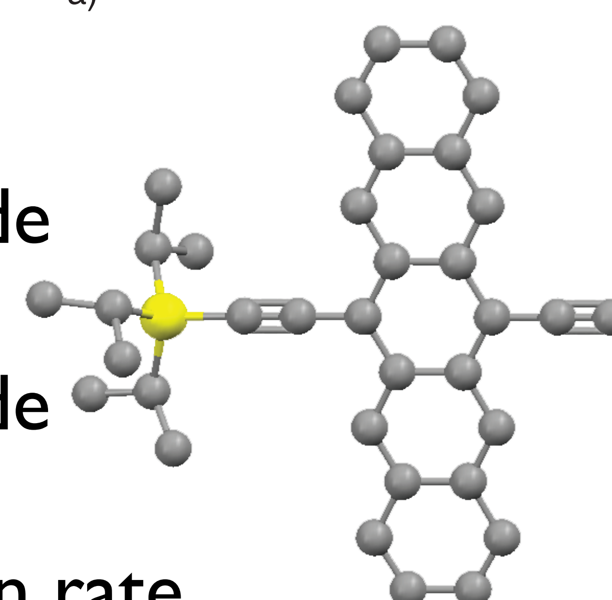
- Additional ALC lines	X	No change in LF repolarisation, Ochams Razor.
- Shifting of existing ALCs	??	Possible, but this might be for the 6.5us signal
- Different muonium chemistry	😍	See next few slides.....
- .....😍		

ITKISS (Impossible To Keep It Simple Stupid)



Three types of muon:
Vacuum muonium (fast triplet precession)
Bare muons (slow precession)
Reacted muonium (ALCs)

a)



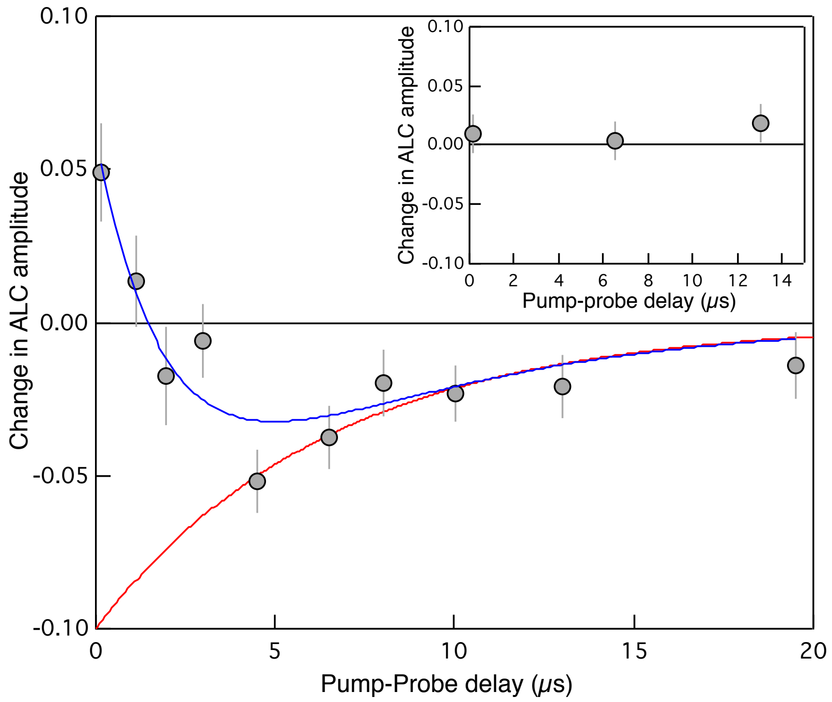
Reduction in T2 amplitude
+
Increase in ALC amplitude
=
Increase in muonium reaction rate

Summary

AKISS: Always Keep It Simple Stupid

- MuSR is not simple, but it is powerful
- Photo-MuSR is even more complex, but even more ***power***ful
- In principle, photo-MuSR can measure:
    - The presence of excitons
    - Photochemical reaction rates
    - Exiplexes, charge transfer....
    - Photomagnetism

    All of this with ***temporal and spatial resolution.***
- Spatial resolution: about 1 benzene ring;   Temporal resolution: 10 ns - 20 ms (<1ns with £30M)



IWIKISS: I Wish I Kept It Simple Stupid

- Two timescales of transient photoexcited species measured
- Time dependent tomography of photochemistry
- In principle, photo-MuSR can measure:
    - The presence of excitons
    - Photochemical reaction rates
    - Exciplexes, charge transfer, dissassociation....

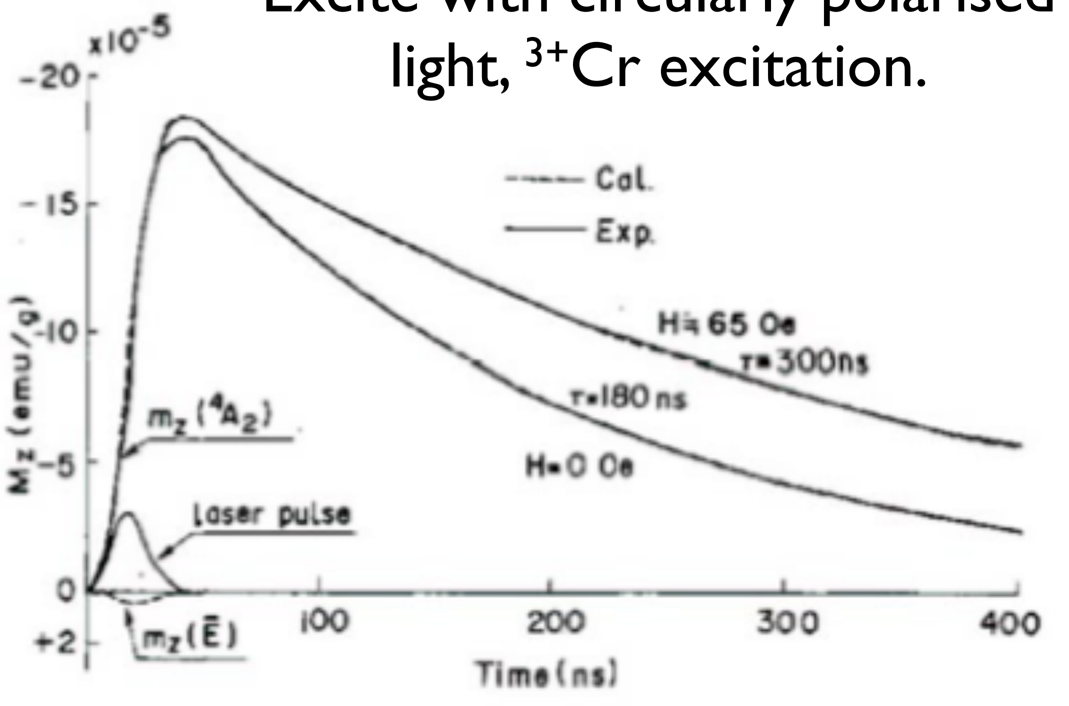
    All of this with ***temporal and spatial resolution.***
- Significant work to still be done on the fundamentals:
    - experiments on pyrene, anthracene and naphthalene planned
- Can definitely say that the ~1us signal is due to increased reaction rate
- 6.5us signal is still not identified, could be shifting of ALC to elsewhere

The plan (for world domination)

Excitonic physics in simple molecules

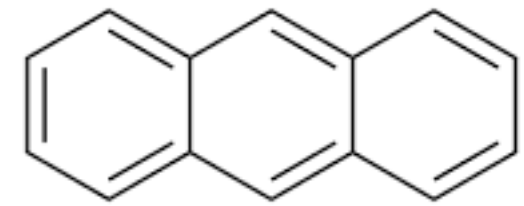
Photomagnetism in ruby

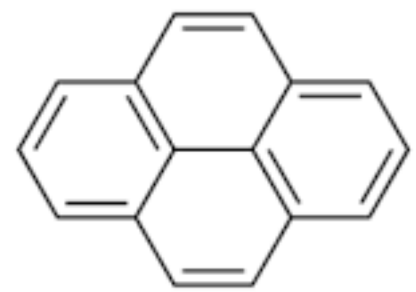
Excite with circularly polarised light, $^{3+}$Cr excitation.



T Tamaki et al., J. Phys. Soc. Japan. 45, 122 (1978)

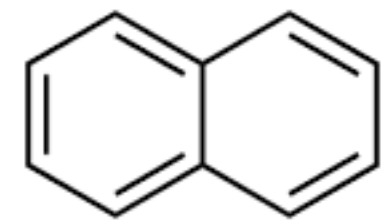
Triplet lifetime >1ms
Singlet fission possible





Singlet lifetime 400ms

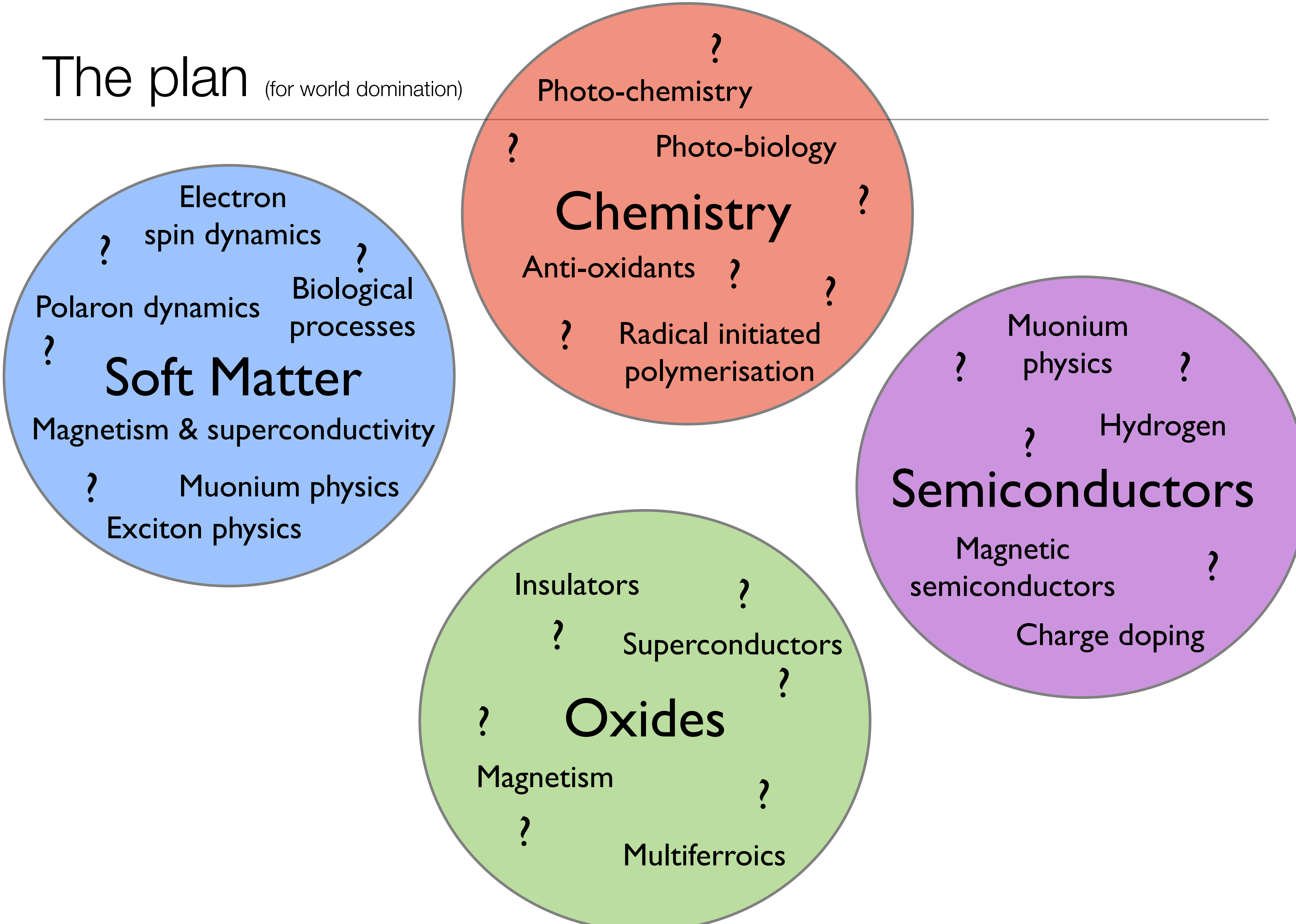
Triplet lifetime >1ms
Singlet fission possible



Plus experiments on Si, polypeptides, organic semiconductors, GaAs....

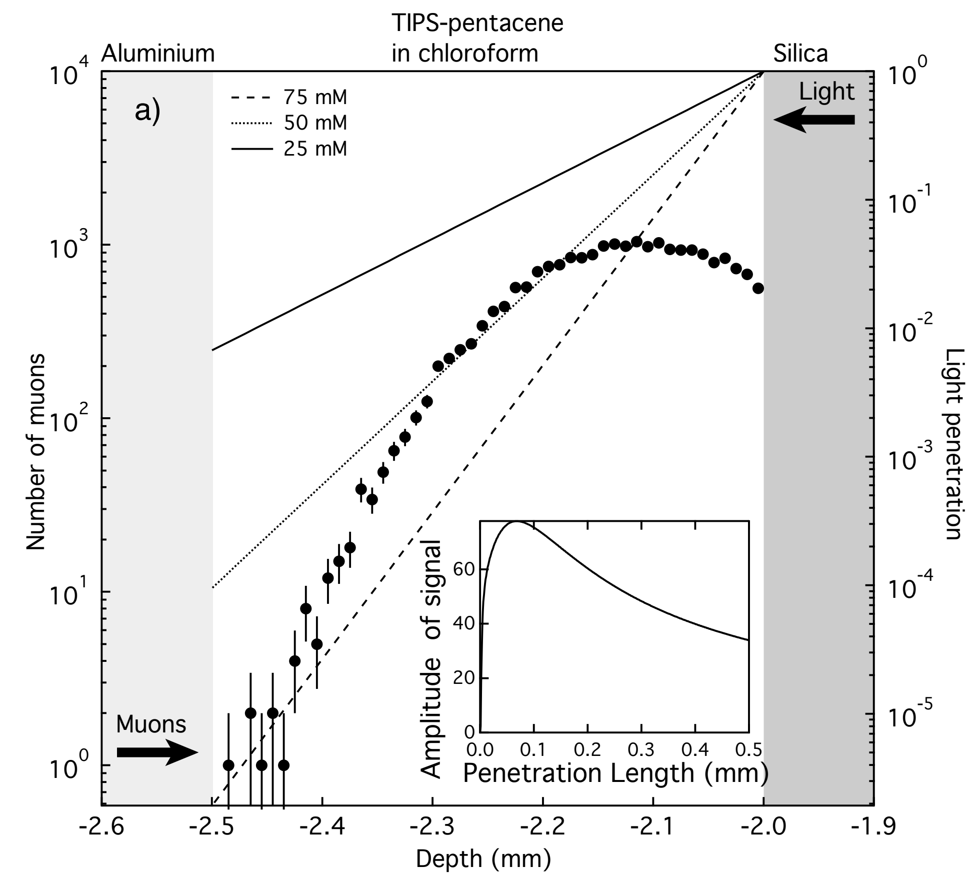
Into the future.... Japanese, American and European collaborators

The plan (for world domination)



What do we need from a future muon source?

Problem: How do we match muon stopping profile with light absorption length?



Currently: Complex sample environment.

JPARC LEM:

Pros:

- ~1ns resolution
- Pulsed technique,
- Possible high data rate?

Cons:

- New (relatively untested) spectrometer
- Would need to buy a <1ns tuneable laser + make modifications (£££).
- Polarisation loss?

Possibility with joint JSPS/EPSRC spintronics project: call in July 2015?

PSI LEM:

- Still ~100% polarised
- Existing spectrometer
- Light already available
- ~5ns tuneable laser (££)

- ~5ns resolution
- Not pulsed
  - Difficult pump-probe measurements
  - Difficult to trigger

Problem: How do we improve time resolution to access interesting physics (biology/chemistry) <10ns?

Currently: We don't. Limited to >100ns

JPARC LEM:

Pros:
- ~1ns resolution
- Pulsed technique,
- Possible high data rate?

Cons:
- New (relatively untested) spetrometer
- Would need to buy a <1ns tuneable laser + modifications (£££).
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Holy Grail?

- Tuneable energy (keV) muon beam
- Tuneable timing structure…
  Pulsed, but with pulse length and separation user tuneable
- High intensity beam (>100M useable events/hr)
- High LF field (>3T)

Conclusion: A shrubbery would be a lot easier.