International Advanced School on Muon Spectroscopy

Stimulation Methods 2: Laser

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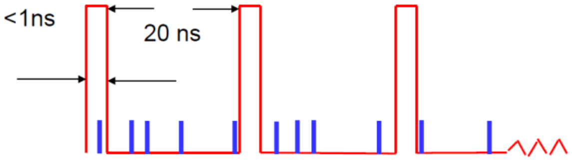
ISIS Neutron and Muon Source, STFC

22 Aug. 2019

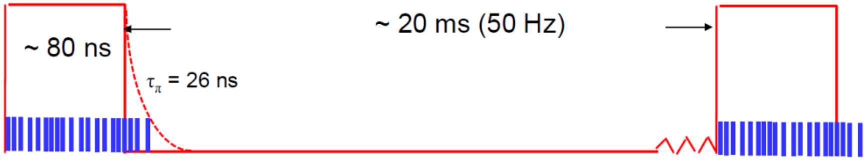
How to use pulsed stimuli?

Muon sources come in two ‘flavours’ …

- ‘continuous beam’ (PSI, TRIUMF), muons arrive randomly



- ‘pulsed beam’ (ISIS, J-PARC), all muons in short bunches



Pulsed stimulations in μSR…

Many possible, but these are typical …

- Radio-frequency (RF) resonance
- Currents
- Magnetic fields
- Electric fields
- Acoustic resonance
- Illumination (flash lamp and laser)
- …

→ Photoexcited μSR … “photo-μSR”

photo-μSR: What is it ?

- Light-pump muon-probe experiment
  - utilising standard μSR techniques
  - muon probes the photo-induced effect
  - track dynamics
- Has been done in various muon facilities
- Still in growing phase

Representative works:

KEK

- S. Chu, et al. Phys. Rev. Lett. 60, 101 (1988).
- K. Shimomura, et al. Hyperfine Interactions 120–121, 595 (1999).

TRIUMF

- I. Fan, et al. Phys. Rev. B 77, 035203 (2008).

PSI

- T. Prokscha, et al. Scientific Reports 3, (2013).

RIKEN-RAL

- R. Kadono, et al. Phys. Rev. Lett. 73, 2724 (1994).

ISIS

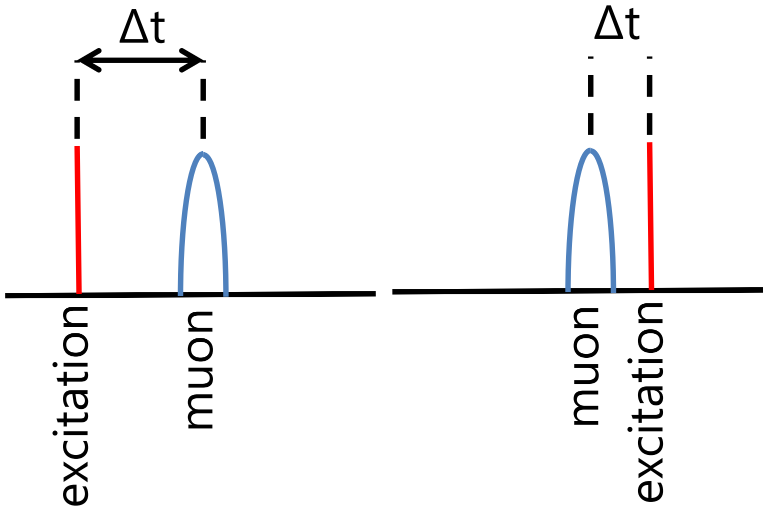
- K. Wang, Nat Mater 16, 467 (2017).
- K. Yokoyama, Phys. Rev. Lett. 119, 226601 (2017).

Outline of talk

- Techniques
  - How photo-μSR technique works
  - Light sources
  - Things to remember for designing experiments
- Case studies
  - Carrier kinetics measurements in semiconductor
  - Excited molecules 1: organic semiconductor
  - Excited molecules 2: reaction kinetics

Pulsed muon + pulsed light source

Advantages:



- Arbitrary pulse timing:
  wide range of dynamics
- Pulsed laser … lots of photons packed in a short pulse
- Smaller disturbance on the system
  - less local heating
  - Can provide large stimulation

Light source

Pulsed

Lasers

\+ Flashlamps

Continuous

Lamps

LED

\+ CW laser

Photoexcitation by pulsed laser light:

- High peak intensity
- Short pulse
- Wavelength conversion
  - optical parametric oscillator, dye laser, etc.
- Monochromatic
  - excite specific energy
  - polarisation control (e.g. circularly polarized light)
- Collimated beam
  - easy to calculate fluence

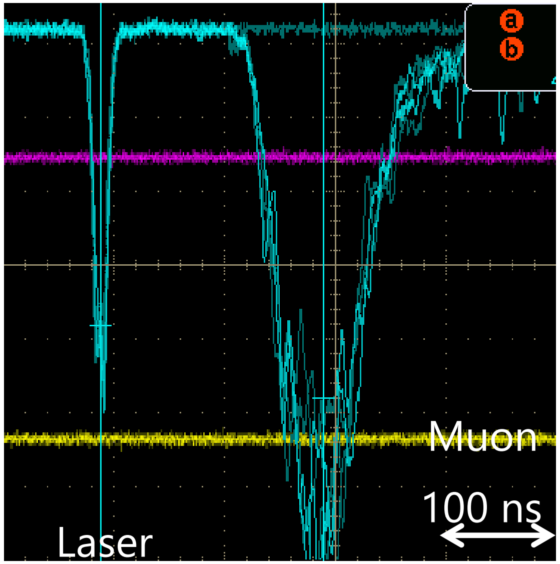
… enables more quantitative measurements

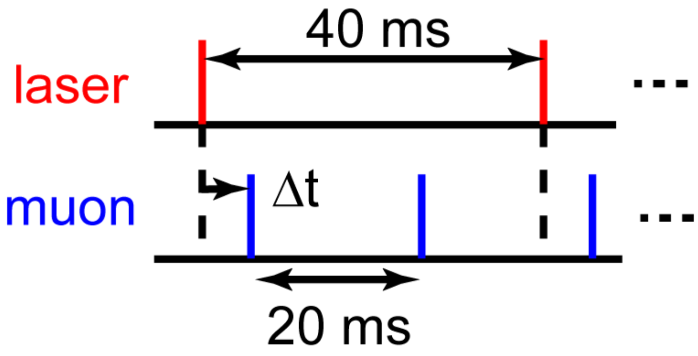
Disadvantage:

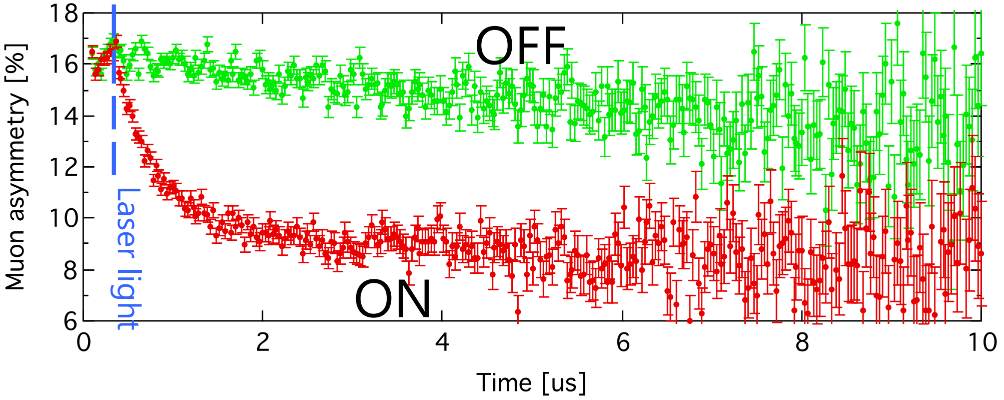
- Health & Safety
- Complicated optical setup
- Expensive

Nanosecond lasers match up nicely

- Time scales. Pulse FWHM:
  - muon 70 ns, laser 10 ns
  - and data bin <16 ns
- Repetition rate:
  - muon 50 Hz, laser 25 Hz



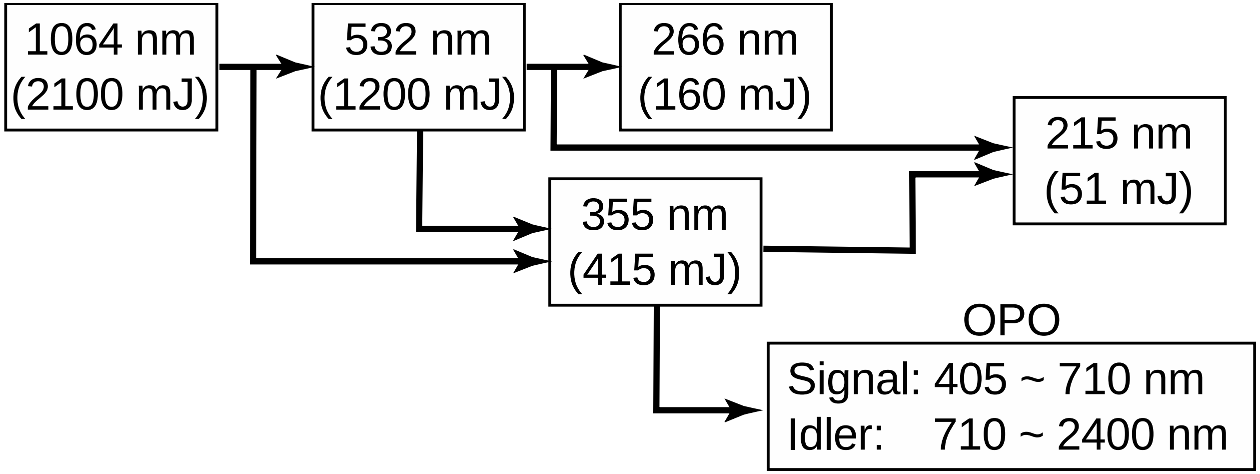




- Measure Light-ON/OFF spectrum alternately
- Can remove long-term drift

Our laser system

- ns Q-switched Nd:YAG & harmonic generation units
- Optical parametric oscillator (OPO)



1064 nm (2100 mJ)

532 nm (1200 mJ)

266 nm (160 mJ)

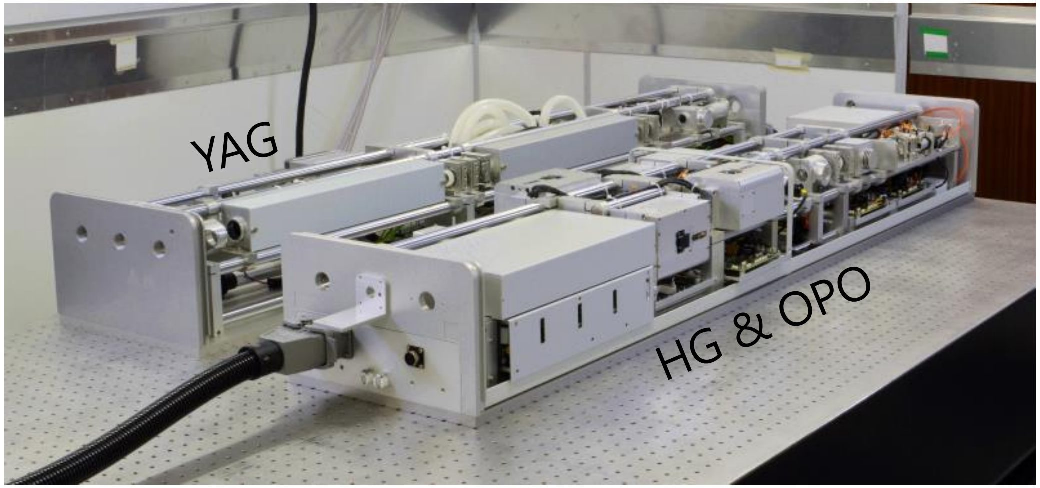
215 nm (51 mJ)

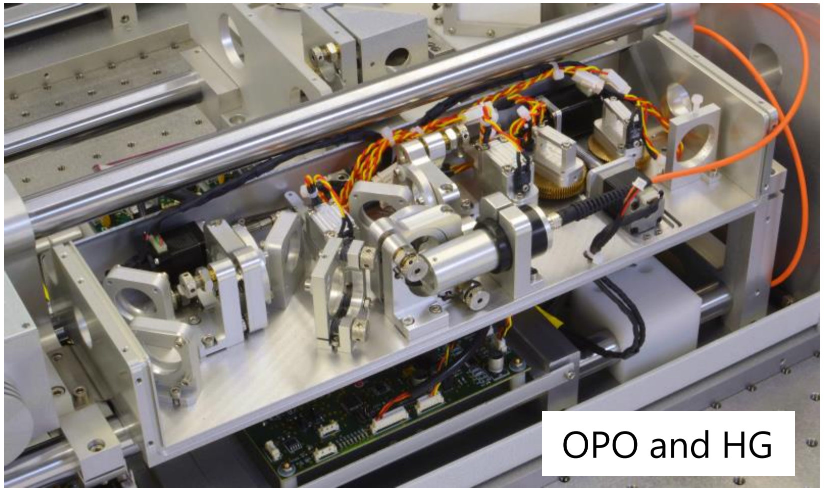
355 nm (415 mJ)

OPO

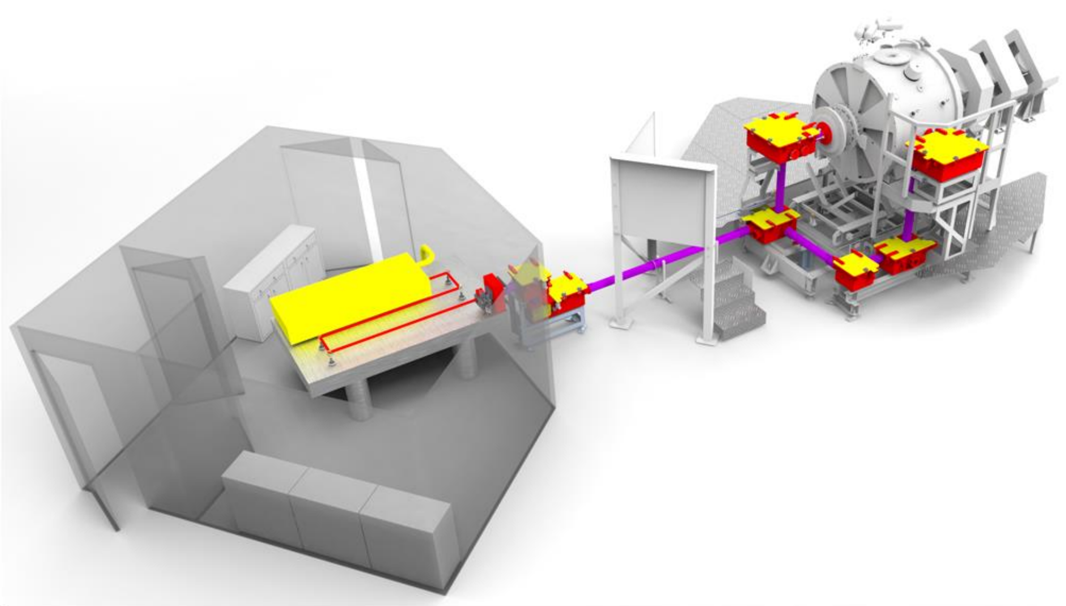
Signal: 405 ~ 710 nm

Idler: 710 ~ 2400 nm

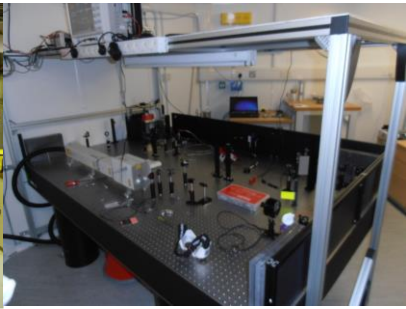


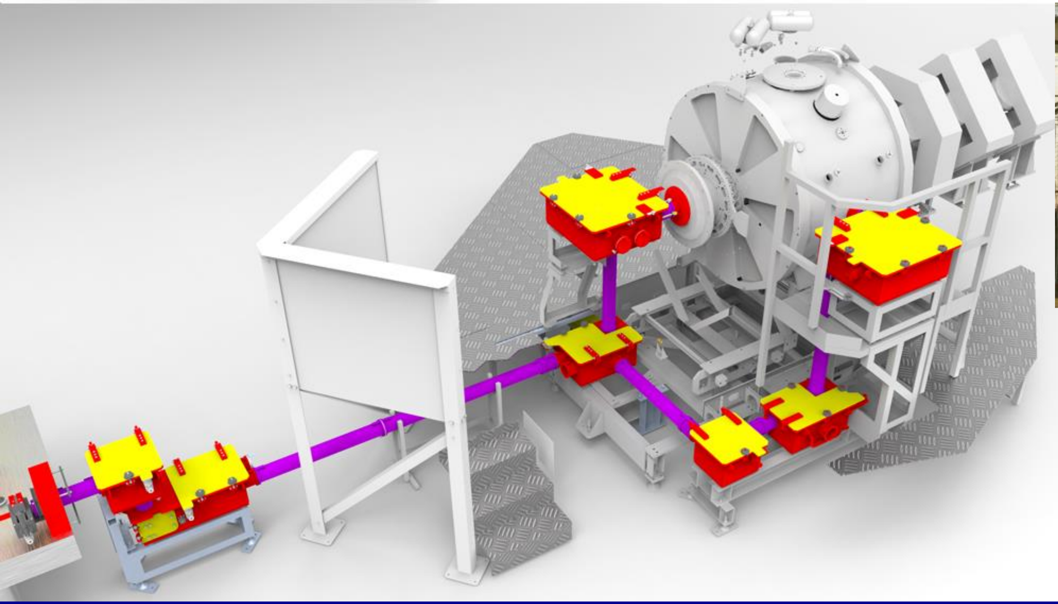


HiFi Laser System



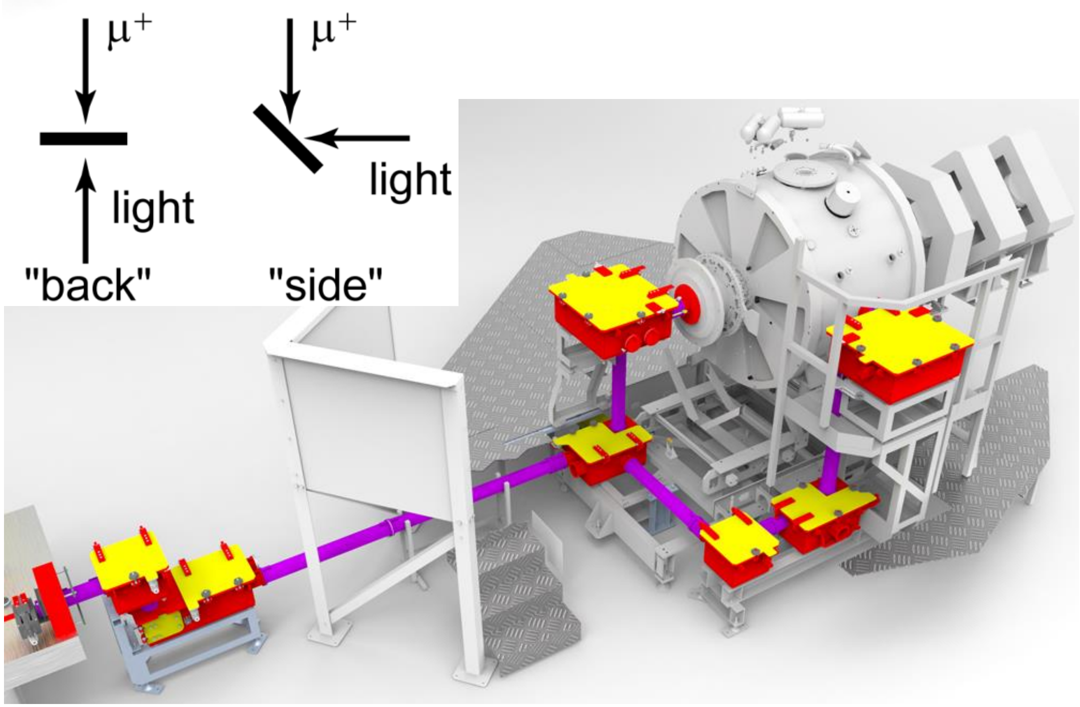
- Two optical setups in ISIS
  - ARGUS … good for low field measurements
  - HIFI … high-field, easier optics handling



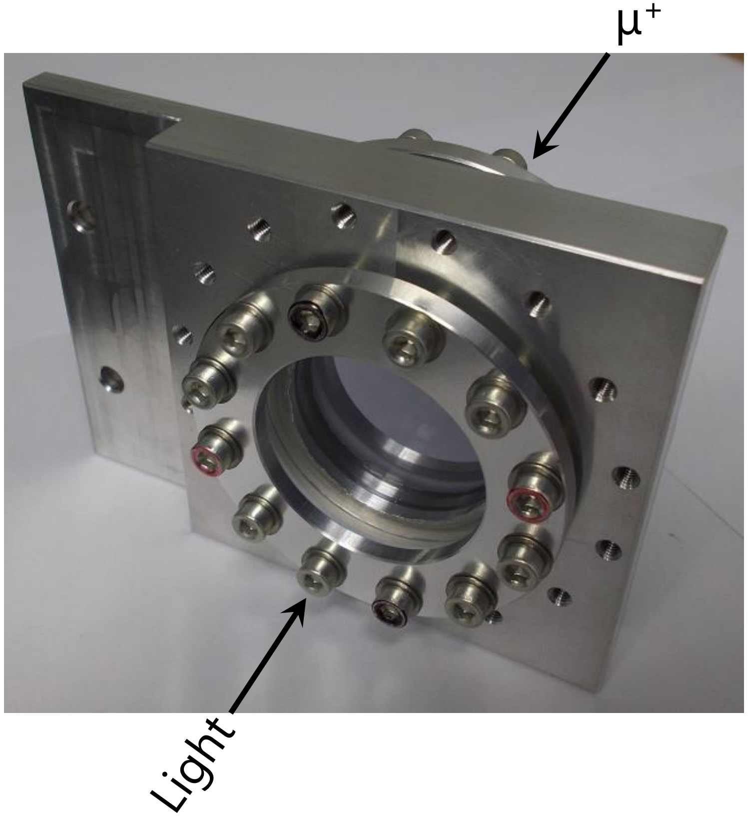


- Laser cabin in the down stream of HiFi
- Laser beam transported through tubes
- Beam Entry Chamber attached for photo-μSR experiments

Geometry



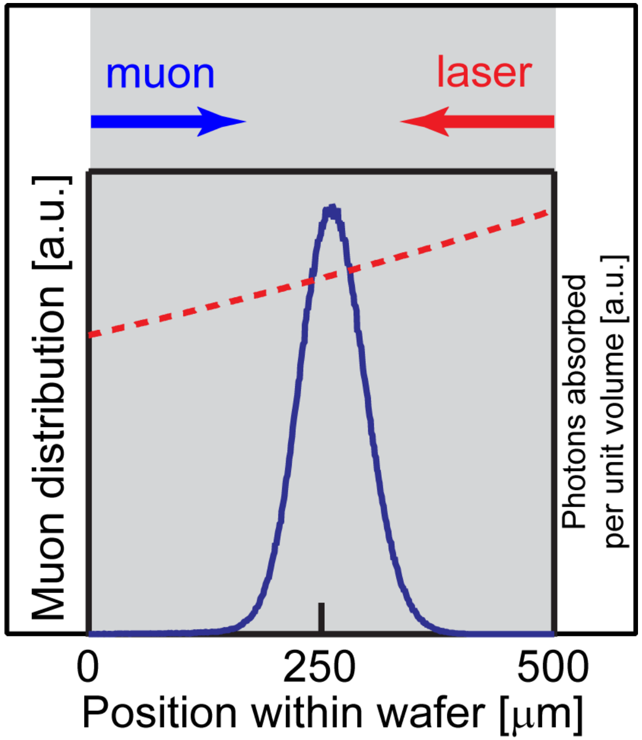
- Two possible beam geometries
- We normally use the “back-pump” geometry



- Sample cell with optical window
- Mounted on CCR

Spatial overlap

Muon & photons: need spatial overlap in sample



- Muon: Gaussian-like distribution
  - can be calculated with *e.g.* musrSim
- Photons: (if optically uniform) exponential decay ($e^{-\alpha z}$) with absorption coefficient α [cm^{-1}]
  - need α for getting fluence at muon position
  - α depends on wavelength
- Lateral size:
  - muon beam size: ~10 mm
  - laser: variable (better expanded for entire coverage)

Before designing a photo-μSR experiment…

- Optically uniform sample, if possible
- How likely a muon can encounter the photo-induced effect?
  - *e.g.* injected excess carriers in semiconductors are v. mobile (e^- in Si can diffuse 1 mm in 1 ms)
- Absorption length? And how much laser power do you need?

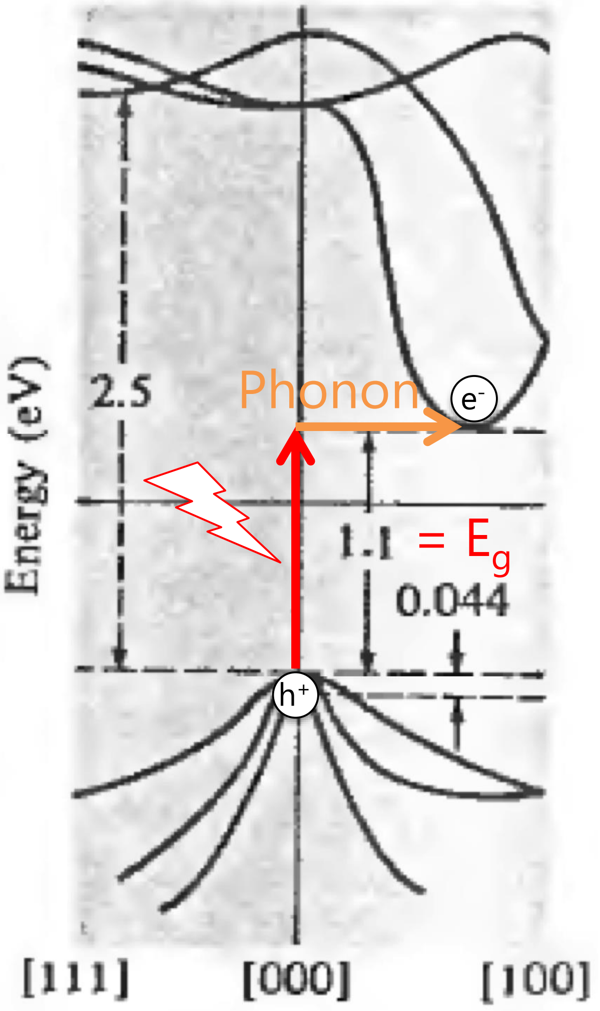
Case study #1

Measuring excess carrier kinetics in semiconductors (Si & Ge)

- K. Yokoyama, J. S. Lord, J. Miao, P. Murahari, and A. J. Drew, Phys. Rev. Lett. 119, 226601 (2017).
- K. Yokoyama, J. S. Lord, P. W. Mengyan, M. R. Goeks, and R. L. Lichti, ArXiv:1906.07464 [Cond-Mat] (2019).

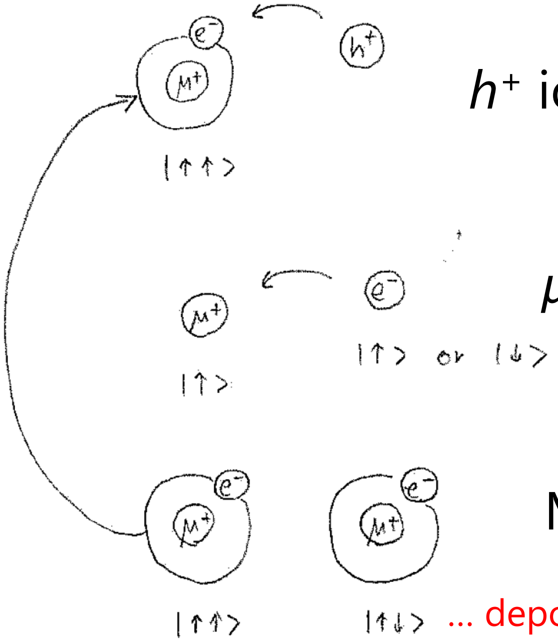
Excess carriers depolarises μ^+ spin

Silicon



- Photon creates *e*-*h* pair (excess carriers)
- Indirect transition (requires phonon)

Charge exchange interaction



h^+ ionizes a bound e^-

μ^+ captures another e^-

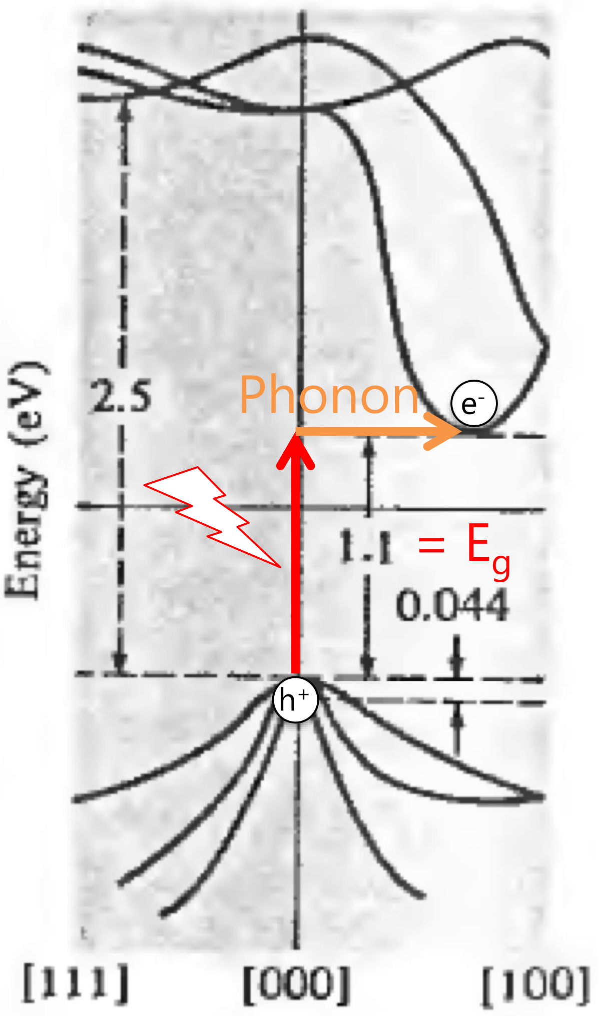
Mu forms again

... depolarizes due to HF interaction

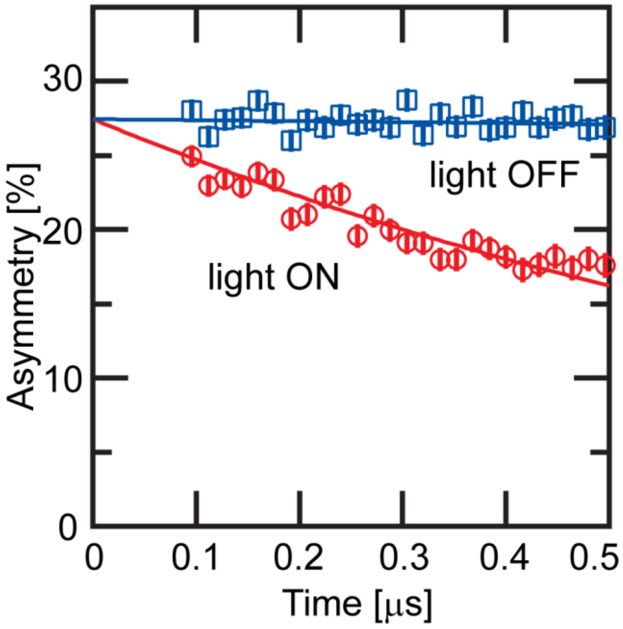
- <u>Carrier injection causes the muon spin depolarisation</u>

Figure on the left was adapted from Ashcroft, N. and Mermin, N. (1976) Solid State Physics. Harcourt Brace College Publishers, New York.

Excess carriers depolarises μ^+ spin



- Indirect transition (requires phonon)
- Photon creates *e*-*h* pair (excess carriers)

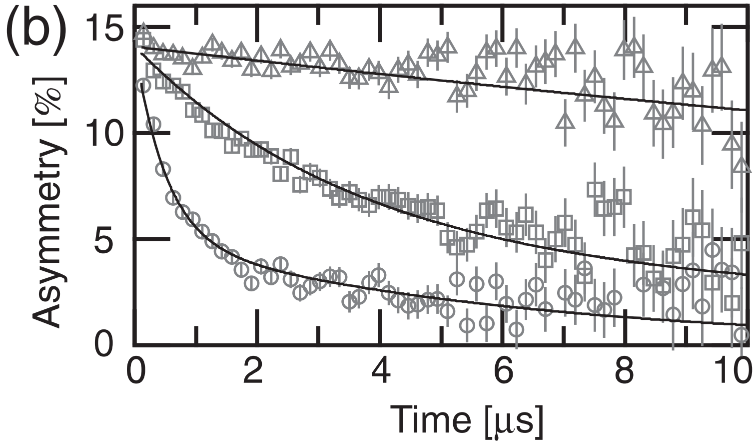


light pulse arrives just before muon

- <u>Carrier injection causes the muon spin depolarisation</u>

Figure on the left was adapted from Ashcroft, N. and Mermin, N. (1976) Solid State Physics. Harcourt Brace College Publishers, New York.

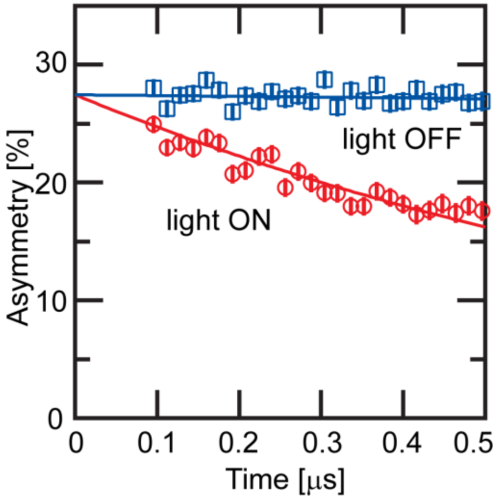
Characterise Δn with relaxation rate



- More carrier injection gives faster relaxation

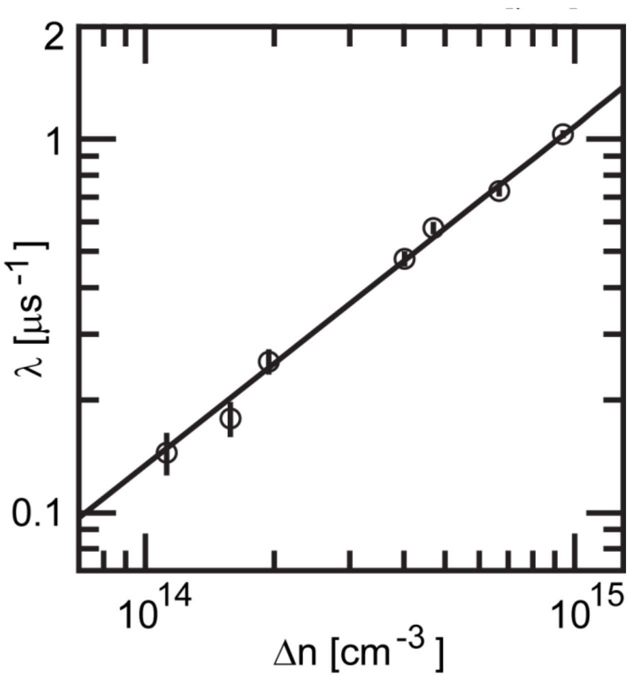
  … can we use this to measure excess carrier density *Δn* [cm^{-3}]?

  … Relaxation rate *λ* for light ON spectrum is a measure of *Δn*



- Need: relationship between *λ vs. Δn*
- *Δn(Δt=0)* is measurable
  - Size of beam spot
  - Pulse energy
  - Absorption coefficient
- Can get *λ vs. Δn* by changing pulse energy
- Assumption: *Δn* stays const. within the time window (0.5 μs)

Making a calibration curve

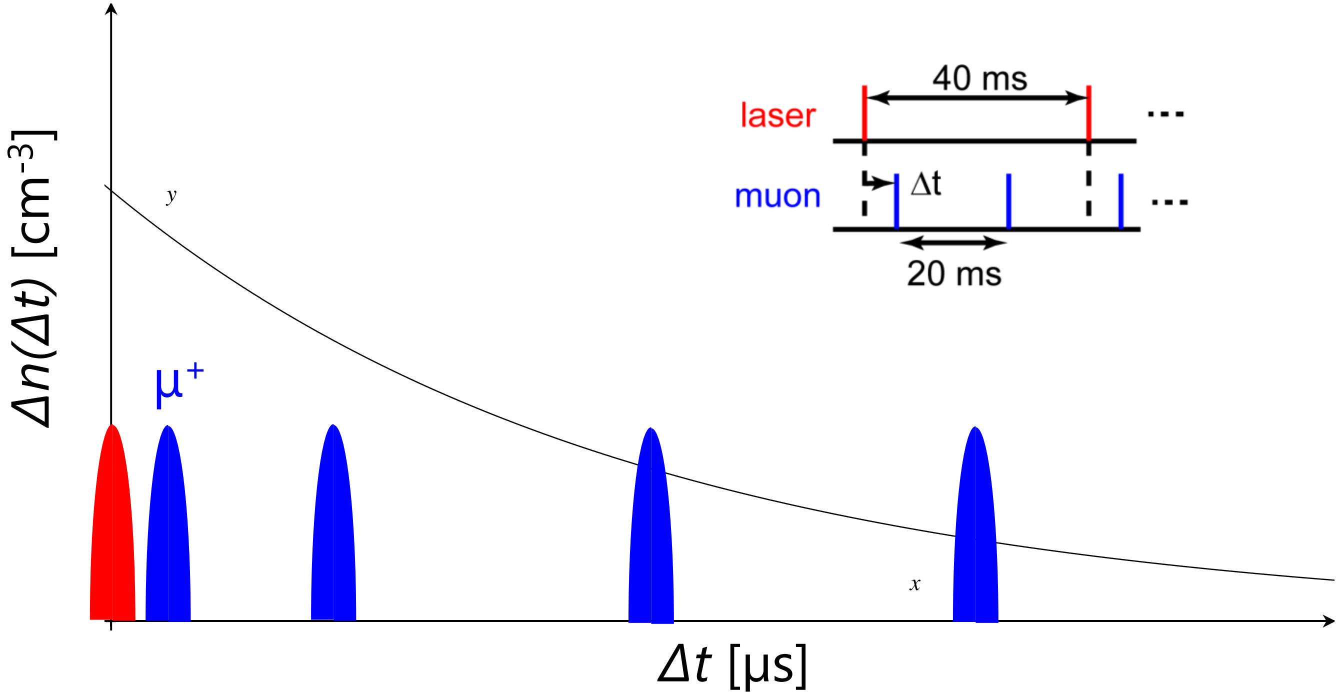


- *λ vs. Δn*: data points can be fit with a power law:

$$\lambda = \beta \left(\frac{\Delta n}{\Delta n_0} \right)^{\alpha}$$

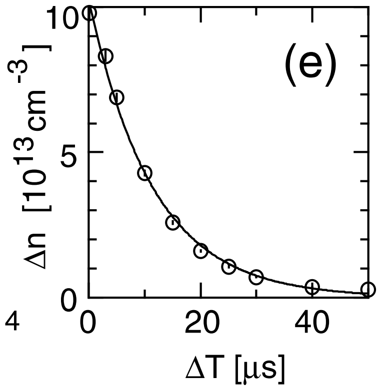
- The curve allows us to calculate *Δn* from a measured *λ*

Carrier lifetime spectrum



Now fix $\Delta n(\Delta t=0)$ and change the delay time Δt, measure λ, and get Δn

… gives a carrier lifetime spectrum

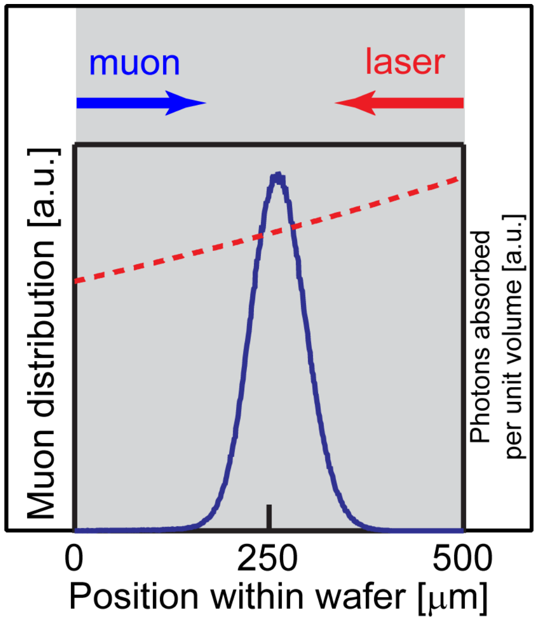


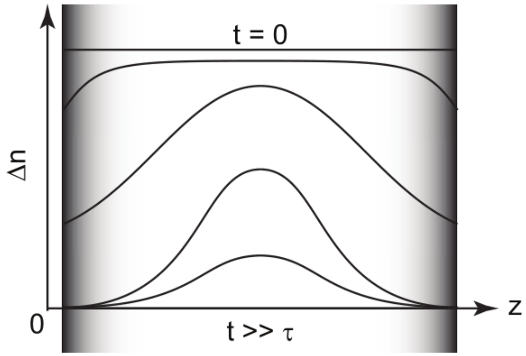
Carrier lifetime spectrum

Yet another technique for lifetime spectroscopy
e.g. photoconductance, microwave reflection etc.

- Mu: common in semiconductors
  … applicable to other systems?
- Something new in photo-μSR ?

Muons are localised





- Spatially localized probe
- Lifetime spectrum measured at the centre
- Can get transport properties?

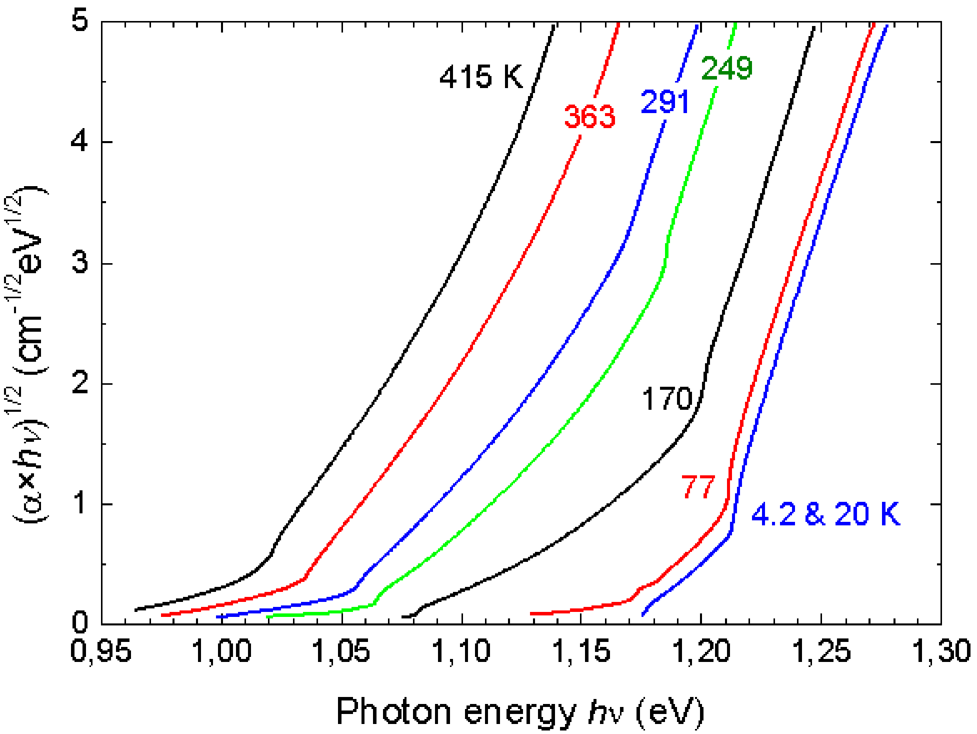
… to test this,

- Wafer with fast surface recombination
- With a long carrier lifetime (>100 μs)

… See the diffusion-driven surface recombination?

Uniform carrier injection

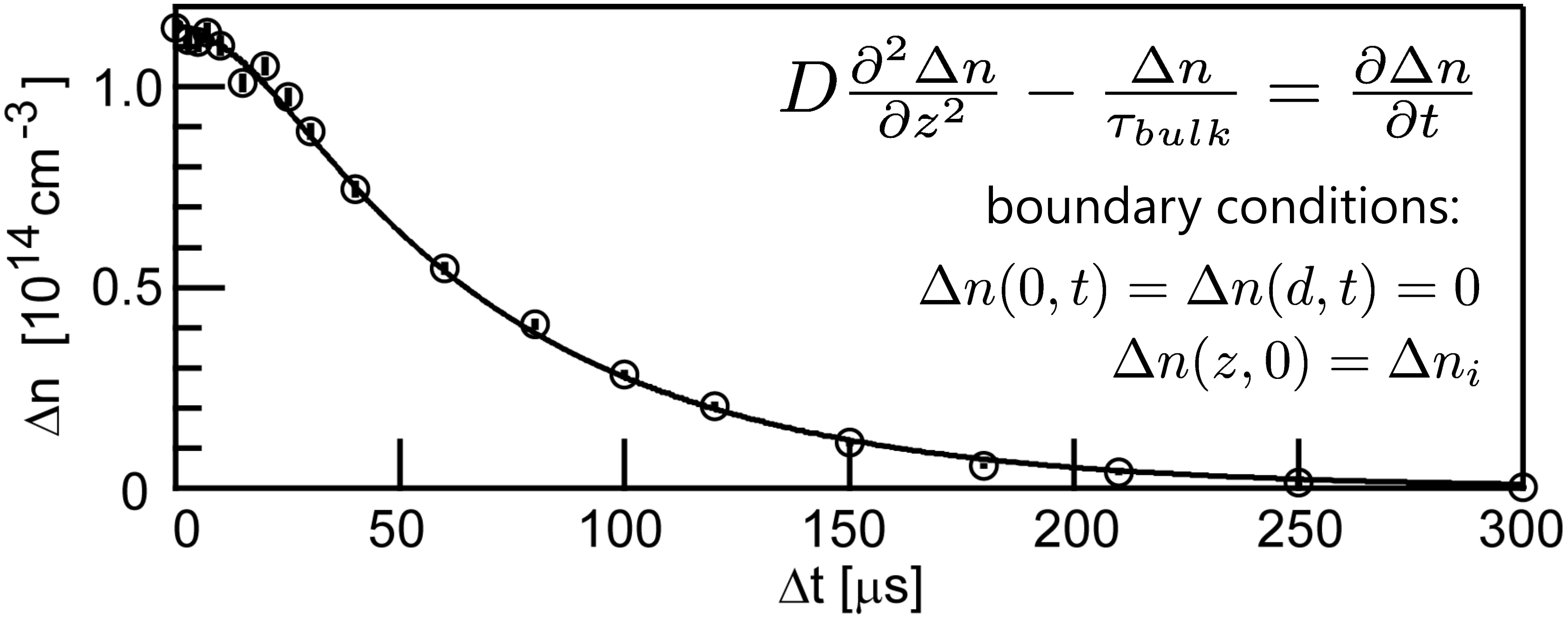
To make the analysis simpler, let's choose a low *α* for (nearly) uniform carrier injection *e.g.* α = 10 cm^{-1} gives 1 mm for absorption length



There are tail states, which allows a low *α*

Figure was adapted from G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 111, 1245 (1958).

Excess carrier dynamics



$$D\frac{\partial^2 \Delta n}{\partial z^2} - \frac{\Delta n}{\tau_{bulk}} = \frac{\partial \Delta n}{\partial t}$$

boundary conditions:

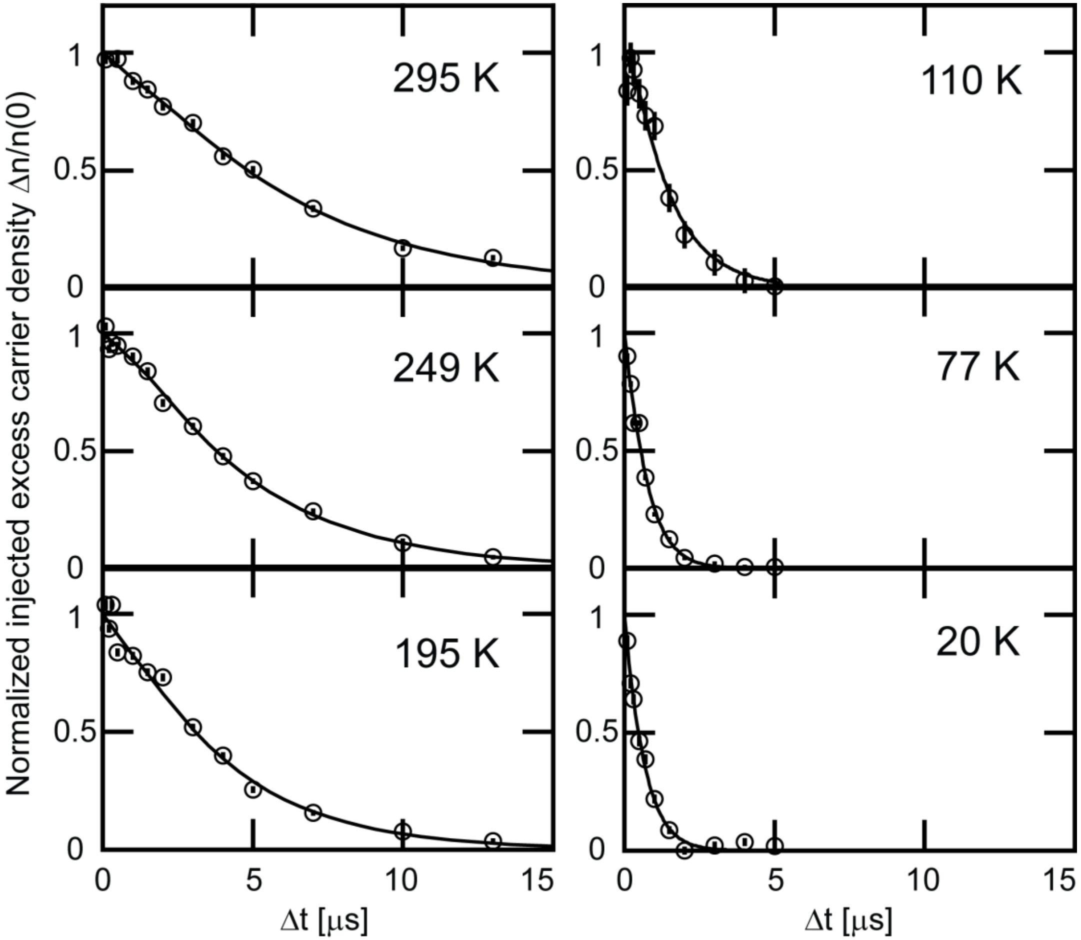
$$\Delta n(0,t) = \Delta n(d,t) = 0$$

$$\Delta n(z,0) = \Delta n_i$$

- A shoulder where the surface effect comes in
- Fit with a 1-D diffusion equation for *Δn(z=d/2, t)* with diffusion constant *D* & bulk carrier lifetime τ_{bulk} as fit parameters and boundary conditions
- *D* is the "effective" diffusivity including both *e* and *h* *i.e.* ambipolar diffusion

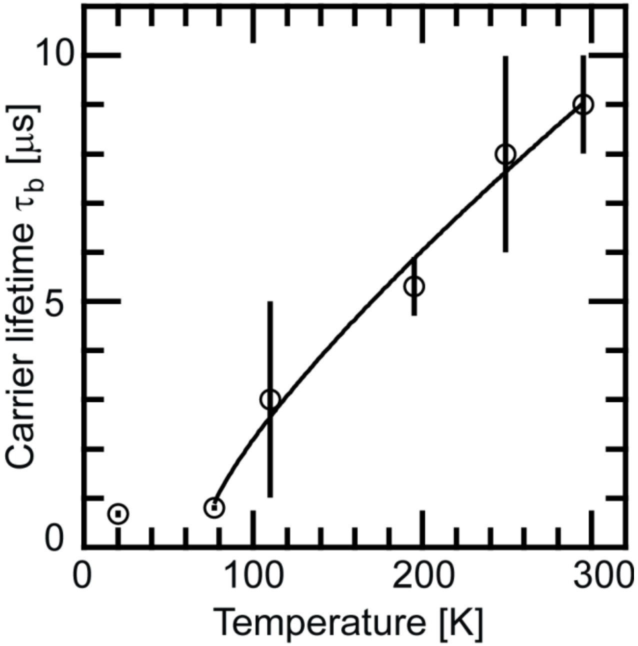
Temperature dependent measurements

- The method works in Ge in the same way
- Sample was cooled down
- Temperature dependent measurements to get $\tau_{bulk}(T)$ & mobility $\mu(T)$



Temperature dependent measurements

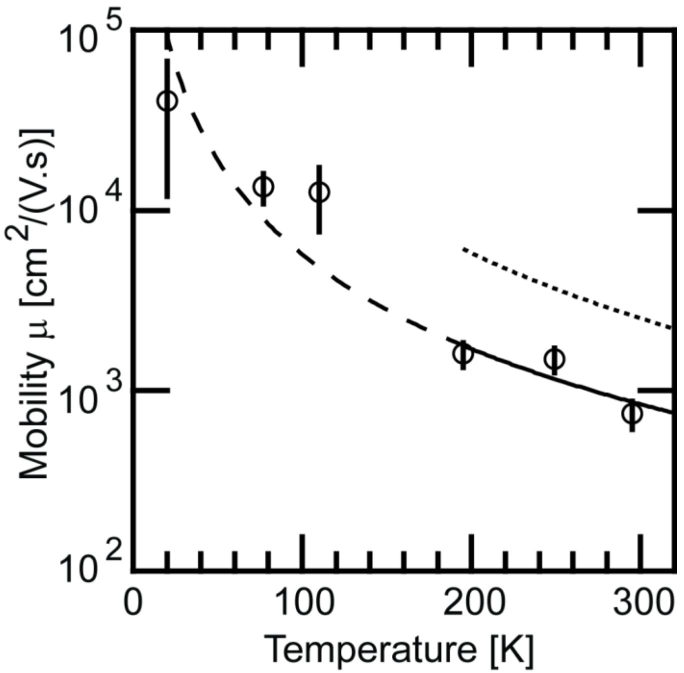
Bulk carrier lifetime τ_{bulk}



- $\tau_{bulk}(T)$ may show recombination mechanisms (& type of defect centres)
- Monotonic decrease with cooling, then stays constant
  - ➢ "excitonic Auger recombination"
- A carrier in a free exciton is captured & recombines in an impurity site
- Free exciton formation becomes the rate-limiting step
- All *e*-*h* forms free excitons <76 K

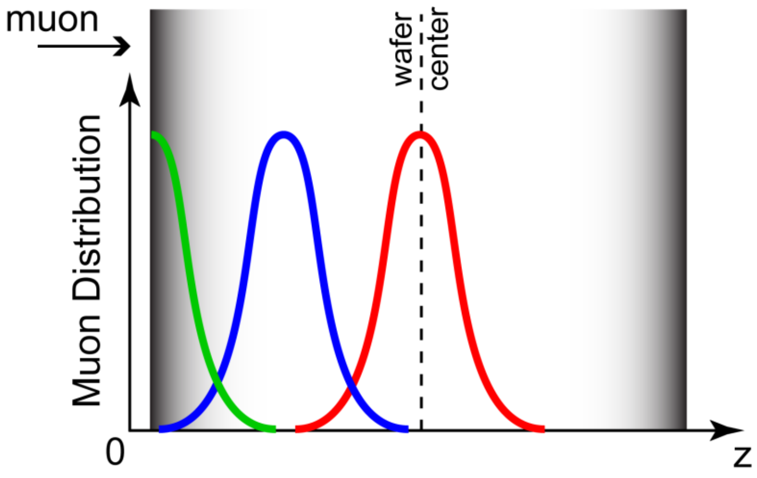
Temperature dependent measurements

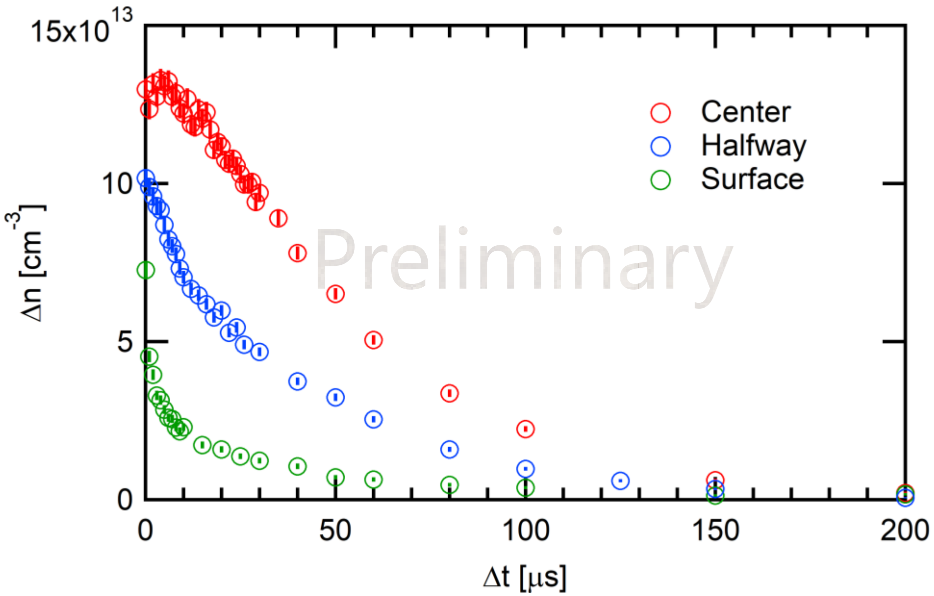
Carrier mobility μ



- Monotonic increase with cooling … less lattice scattering
- In high T, electrons (μ_e) and holes (μ_h) diffuse together
- In low T, exciton diffusion & impurity scattering are dominant
- In 20 K, D_{ex} = 69 cm^2/s … comparable with D_{ex} = 63 cm^2/s from a literature

Space-resolved measurement

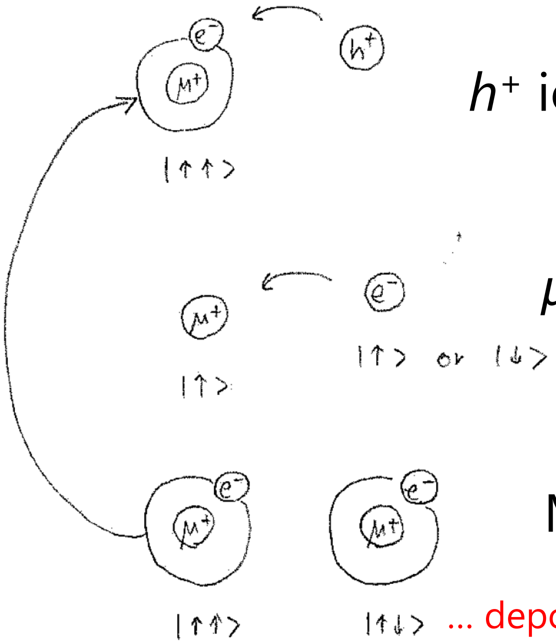




- Silicon, no surface passivation
- Degraders can change the implantation depth
  … can predict the position
- Faster recombination seen closer to the surface
- Spatial resolution is not so great; 130 μm FWHM
- Should help determining the fit parameters more accurately

Complex Mu dynamics

Charge exchange interaction



h^+ ionizes a bound e^-

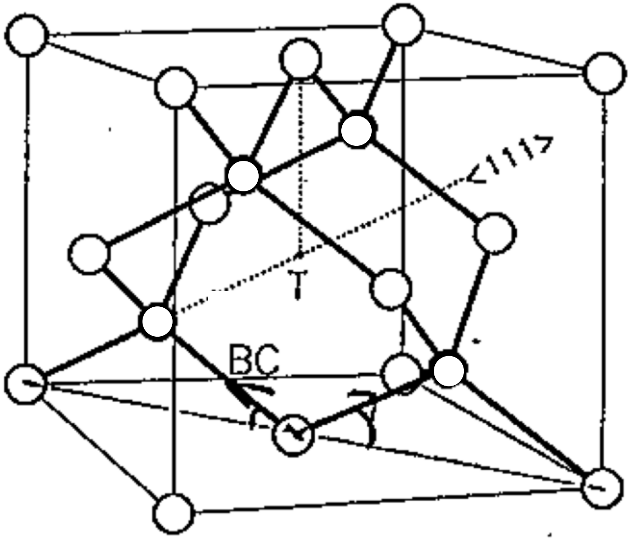
μ^+ captures another e^-

Mu forms again

... depolarizes due to HF interaction

- This is a oversimplified model
- In the real world it's more complicated ...

Muonium states in intrinsic silicon



Two Mu sites:

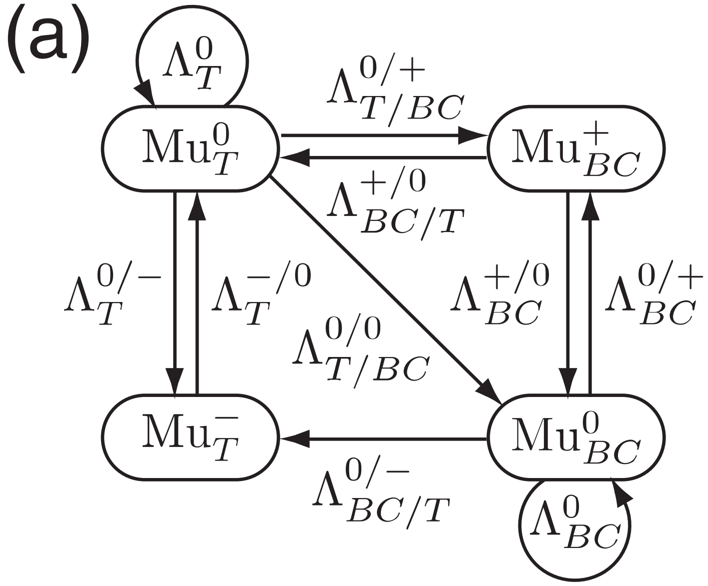
- Tetrahedral interstitial site (T-site)
- Bond-centered site (BC-site)

BC-site: Mu_{BC}^{0} & Mu_{BC}^{+}
T-site: Mu_{T}^{0} & Mu_{T}^{-}

They may exchange states dynamically

Figure was reproduced from K. H. Chow, B. Hitti, and R. F. Kiefl, in Semiconductors and Semimetals, edited by M. Stavola (Elsevier, 1998), pp. 137–207.

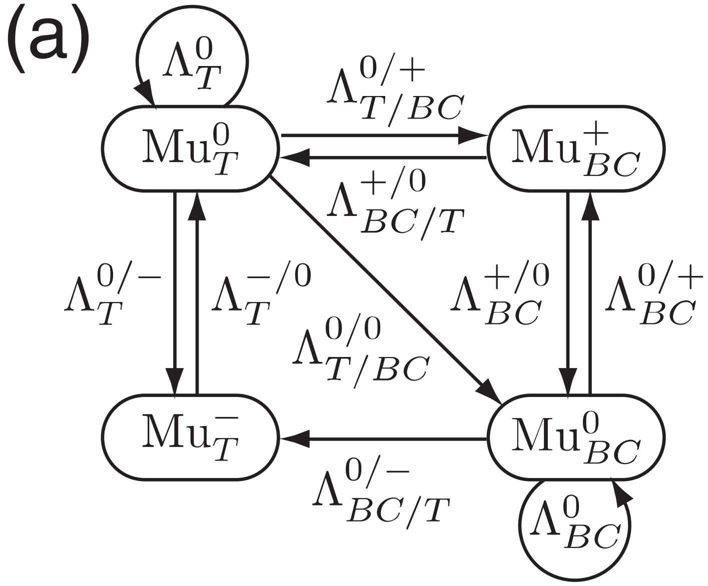
Carriers activate the network



Complex system…

- Site-change process
- Carrier exchange process
- Spin exchange process

Carriers activate the network



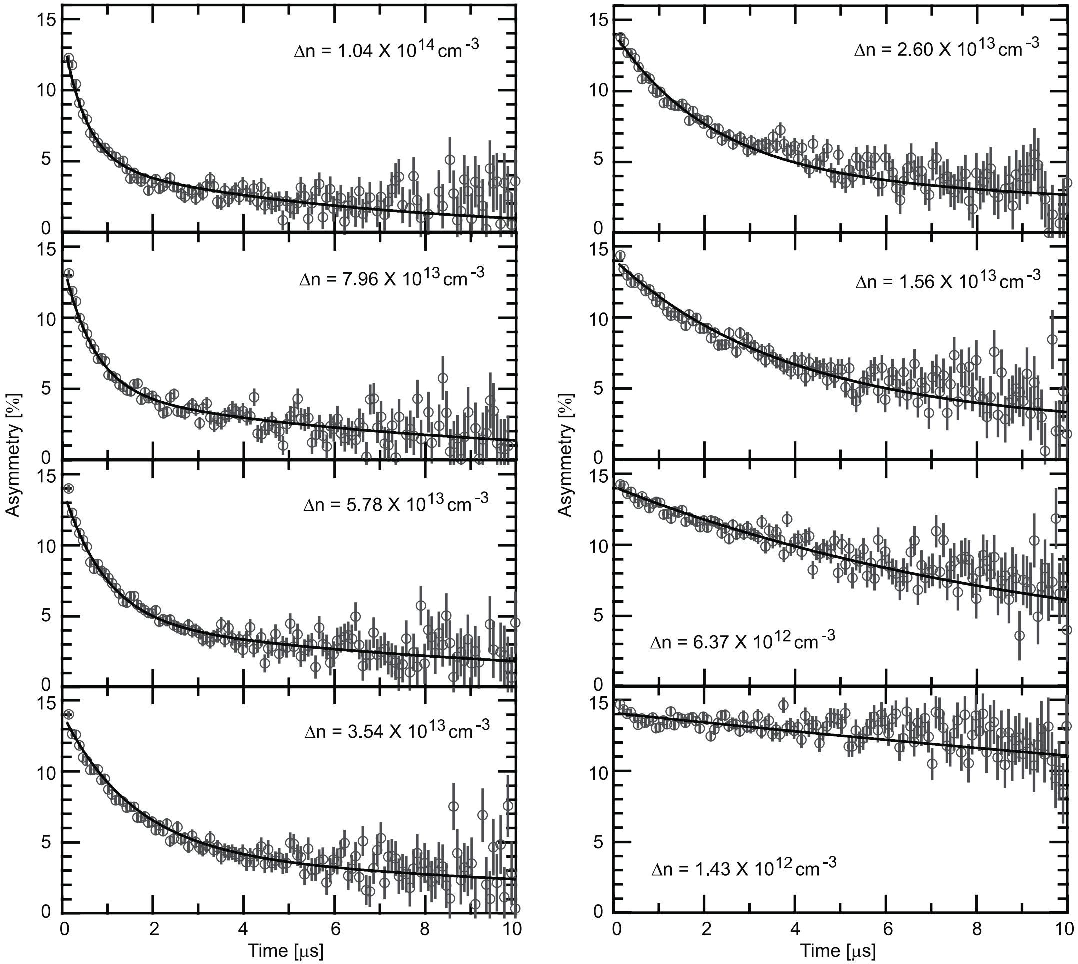
Mu^0_{BC} relaxation	$\Lambda^0_{BC} = n v_n \sigma^0_{BC}$
	$\Lambda^{0/+}_{BC} = \alpha^{0/+}_{BC} \exp[-E^{0/+}_{BC}/k_B T] + p v_p \sigma^{0/+}_{BC}$
	$\Lambda^{0/-}_{BC/T} = n v_n \sigma^{0/-}_{BC/T} \exp[-E^{0/-}_{BC/T}/k_B T]$
Mu^+_{BC} relaxation	$\Lambda^{+/0}_{BC} = n v_n \sigma^{+/0}_{BC}$
	$\Lambda^{+/0}_{BC/T} = n v_n \sigma^{+/0}_{BC/T} \exp[-E^{+/0}_{BC/T}/k_B T]$
Mu^0_T relaxation	$\Lambda^0_T = n v_n \sigma^0_T$
	$\Lambda^{0/0}_{T/BC} = \alpha^{0/0}_{T/BC} \exp[-E^{0/0}_{T/BC}/k_B T]$
	$\Lambda^{0/+}_{T/BC} = p v_p \sigma^{0/+}_{T/BC} \exp[-E^{0/+}_{T/BC}/k_B T]$
	$\Lambda^{0/-}_T = n v_n \sigma^{0/-}_T$
Mu^-_T relaxation	$\Lambda^{-/0}_T = \alpha^{-/0}_T \exp[-E^{-/0}_T/k_B T] + p v_p \sigma^{-/0}_T$

Transitions are characterised by

- Carrier density
- Absorption cross section
- Activation energy
- etc.

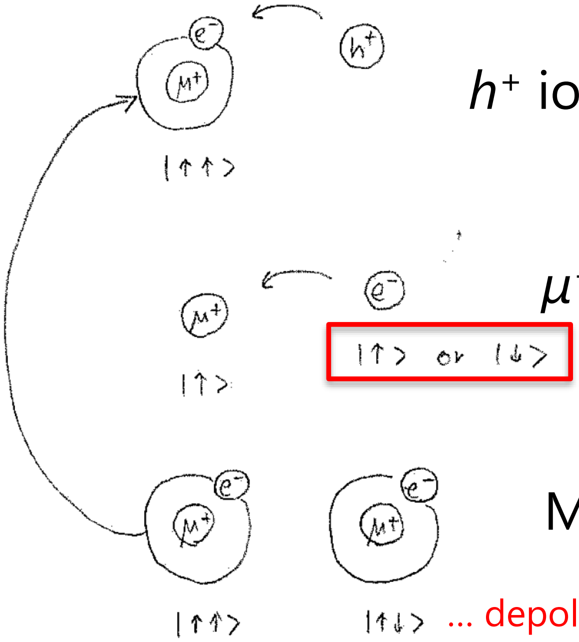
QUANTUM can solve the mechanism

Simultaneous fit for different carrier densities



What if there's more spin-up (or down) e^- ?

Charge exchange interaction



h^+ ionizes a bound e^-

μ^+ captures another e^-

Mu forms again

... depolarizes due to HF interaction

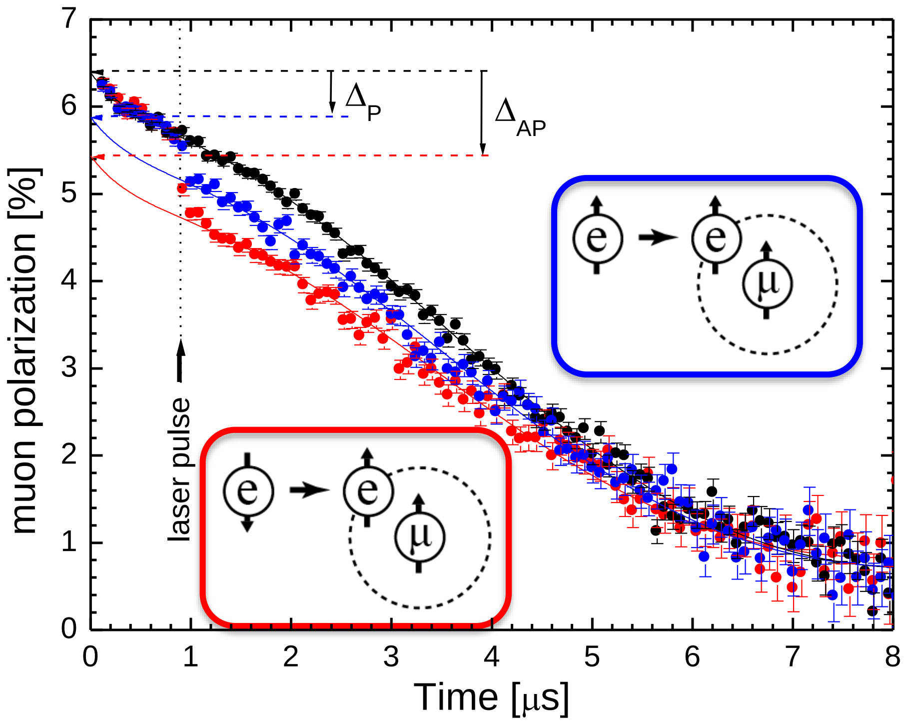
"Optical spin orientation" can choose which spin to excite

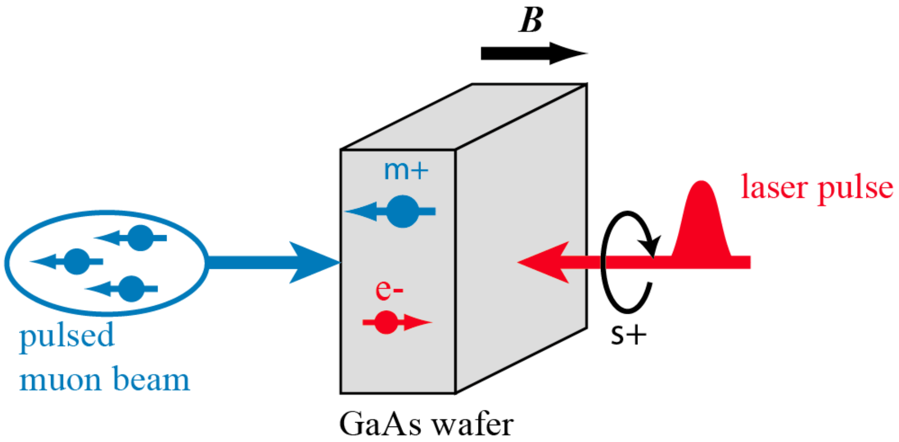
... circularly polarized light

... spin angular momentum of light transferred to electronic spin via spin-orbit interaction

Spin polarisation effect seen in GaAs

Optical spin orientation & ZF-μSR



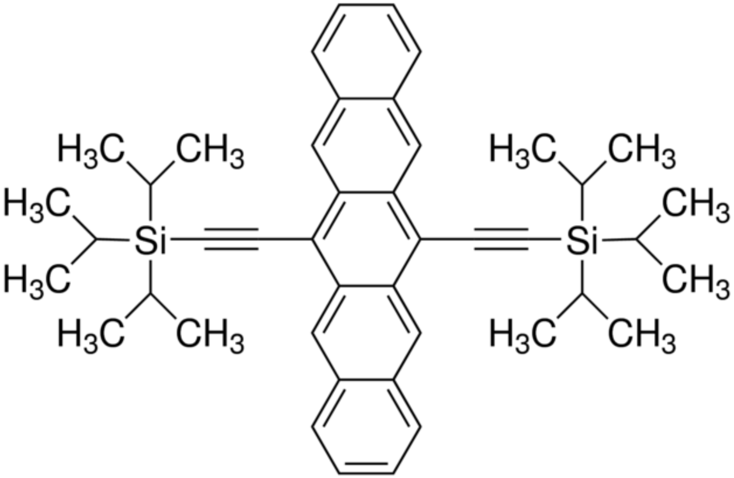


Parallel: less depolarisation

Anti-parallel: more

Case study #2

Photoexcitation of TIPS-Pentacene



- Organic semiconductor
- good optoelectronic properties
- Photovoltaic applications?

K. Wang, A.J. Drew, et al. Nat Mater **16**, 467 (2017).

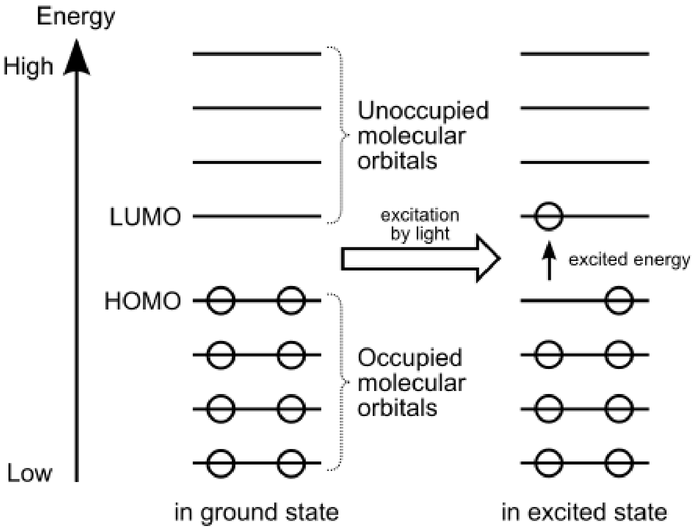
Figure was reproduced from K. Wang, et al. Nat Mater 16, 467 (2017).

Photoexcite an organic molecule

Bandgap in organic molecule:

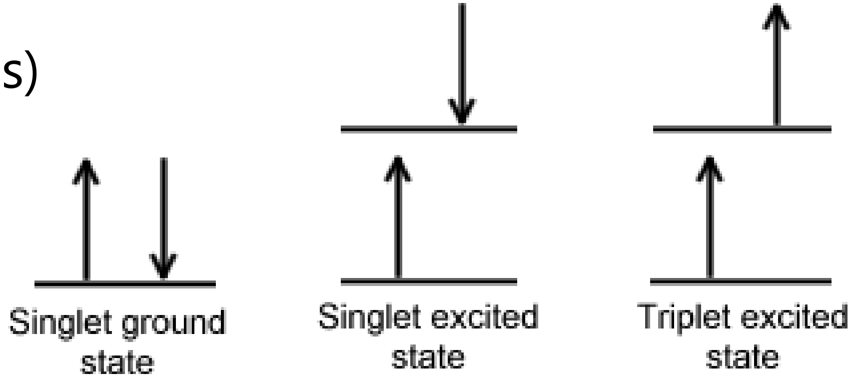
HOMO-LUMO gap

- Highest Occupied Molecular Orbit
- Lowest Unoccupied Molecular Orbit



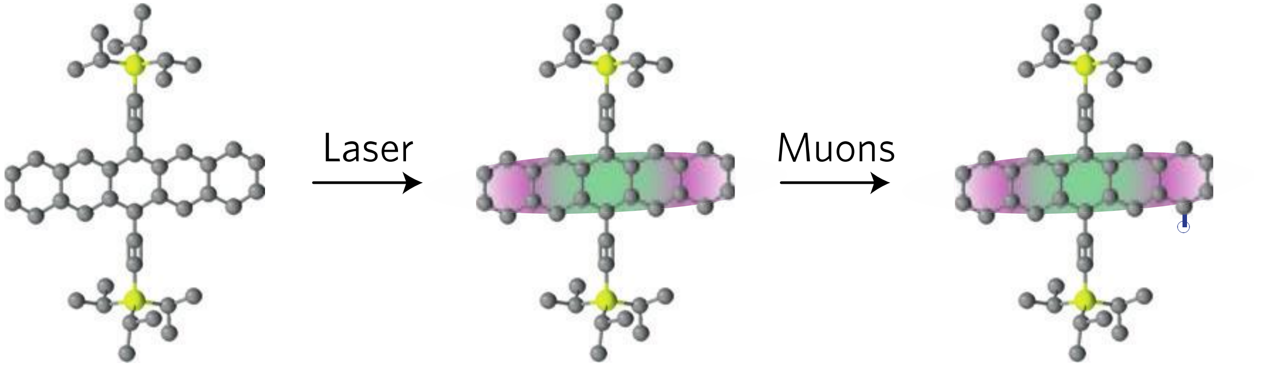
Singlet excited state (short lived, ~ns)
transferred to
triplet excited state (longer lifetime, ~μs)
via intersystem crossing

... can we measure the kinetics using muons?



Figures were reproduced from https://en.wikipedia.org/wiki/HOMO_and_LUMO and https://en.wikipedia.org/wiki/Singlet_state

What does muon see ?



Ground state
(before light and muons)

Excited state
(after light pulse)

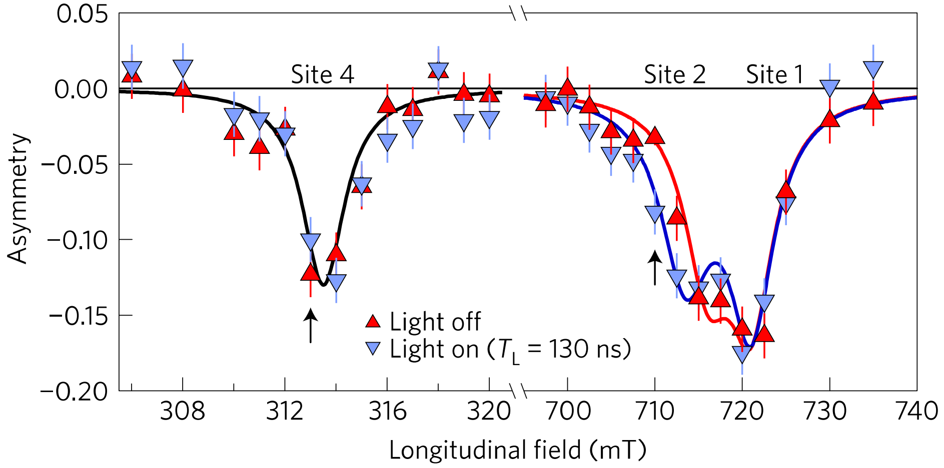
Muoniated state
(after muon pulse)

- Excited molecule has different electron wave function
- Should change the ALC signal

Figure was reproduced from K. Wang, et al. Nat Mater 16, 467 (2017).

Change in ALC spectrum

- Site assignment was done using DFT calculation
- Photoinduced change was in Site 2



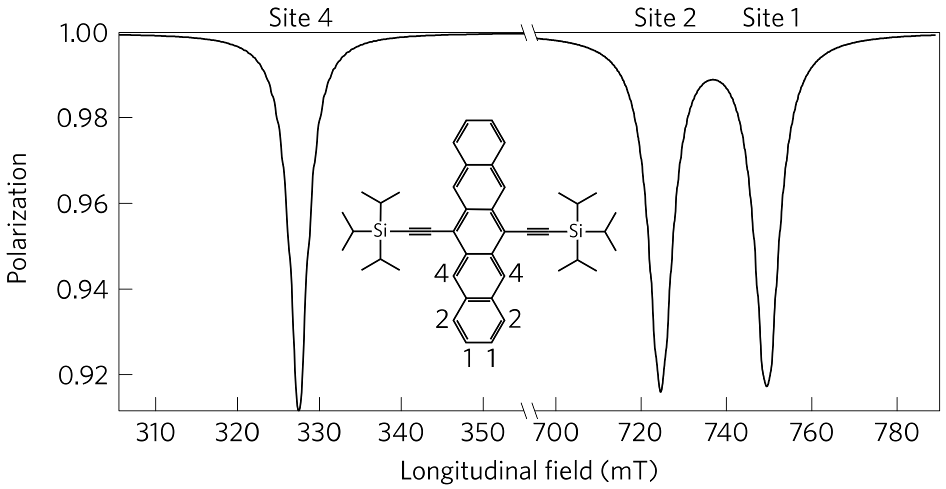
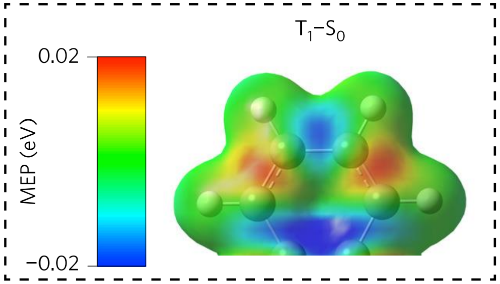


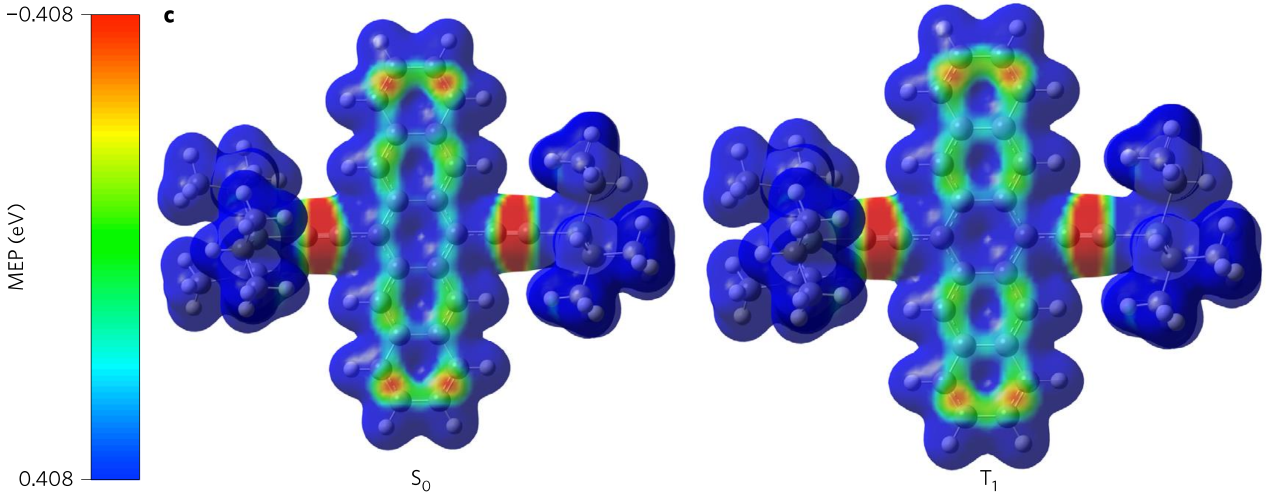
Figure was reproduced from K. Wang, et al. Nat Mater 16, 467 (2017).

How can we understand it

- DFT calculation predicts more electron density near Site 2
- Site 2 becomes more reactive



Difference



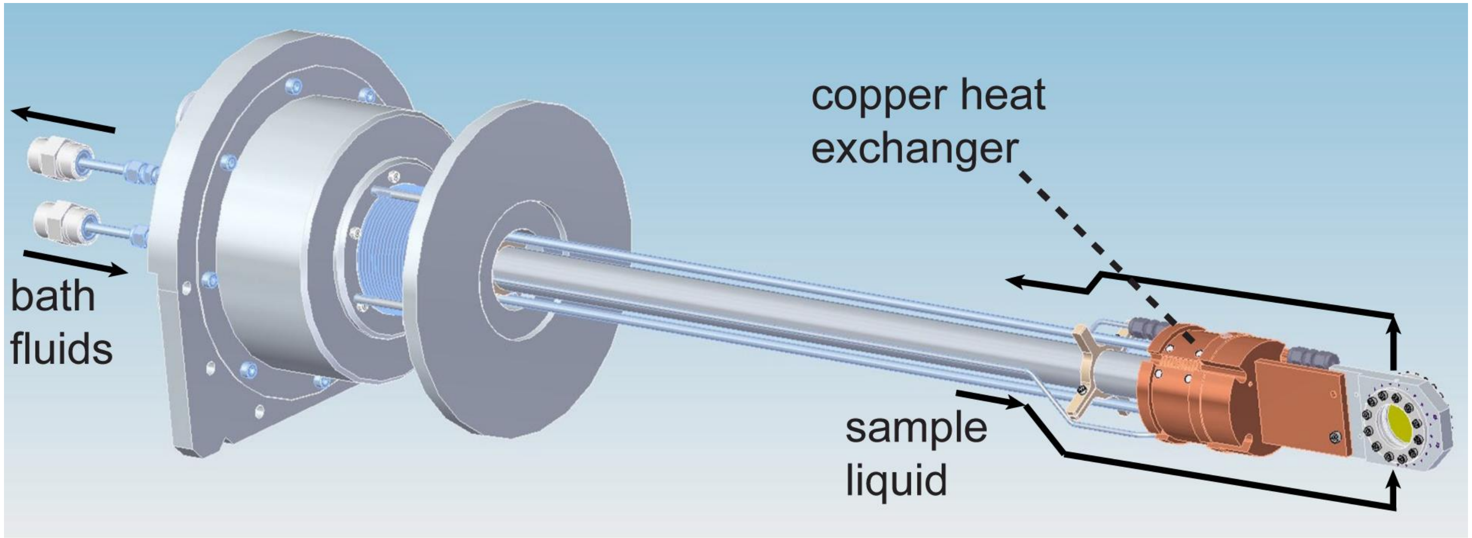
Ground state

Excited triplet state

Figure was reproduced from K. Wang, et al. Nat Mater 16, 467 (2017).

Difficulties in exciting liquid samples

- Poor heat dissipation … possible local heating
- Lower diffusivities … can Mu find excited molecules ?
- More concentration, shorter optical absorption length, less muon/photon overlap

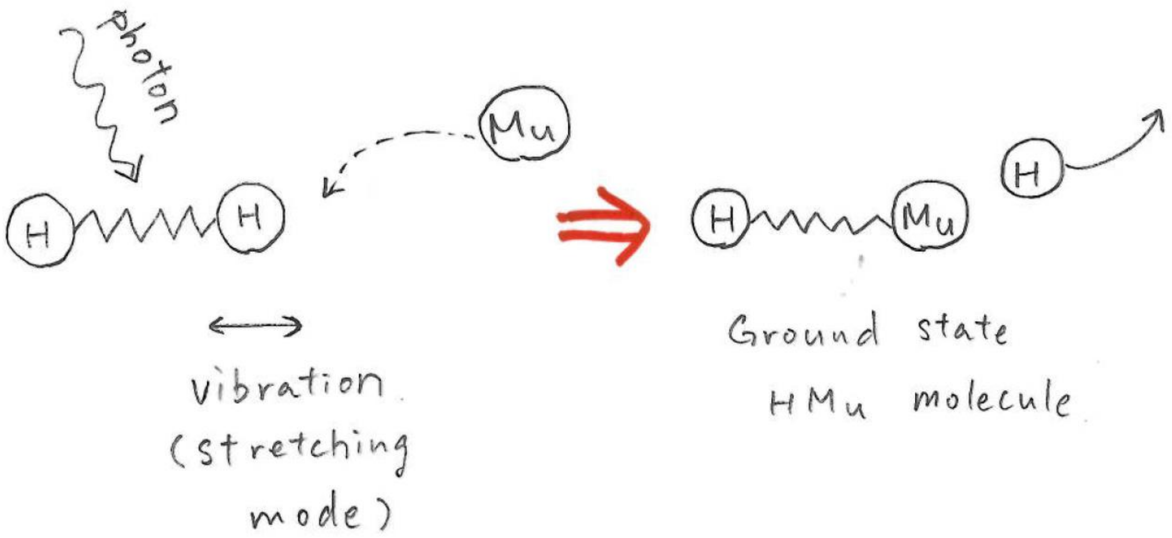


Case study #3

Reaction kinetics of Mu + H_2

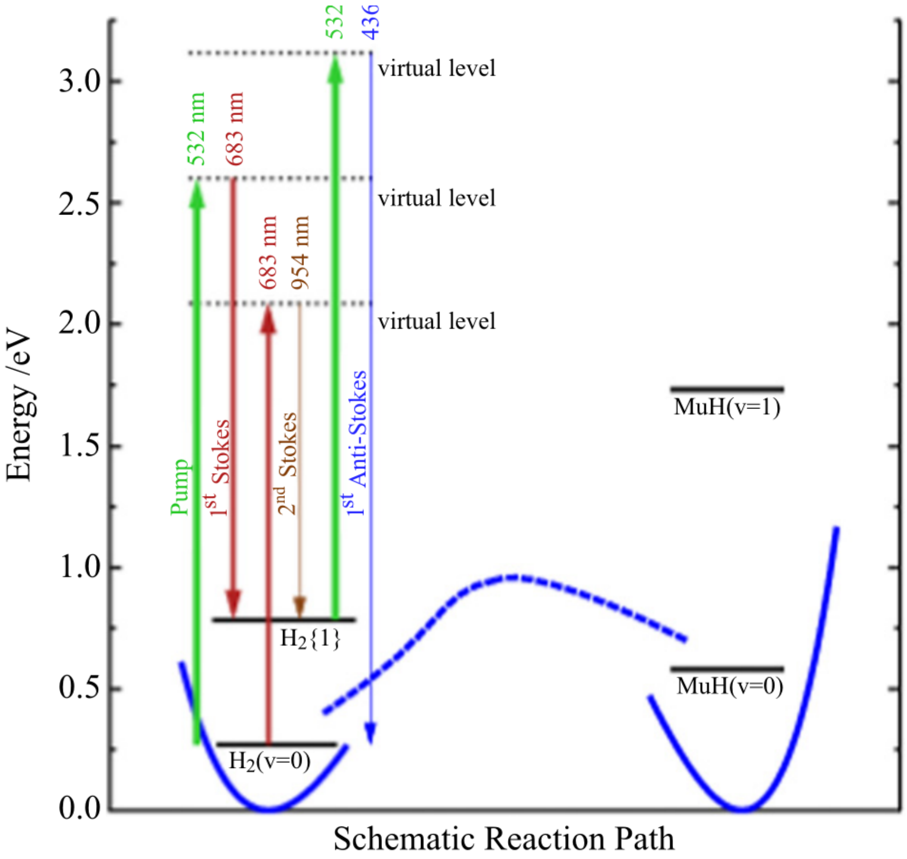
- P. Bakule, D. G. Fleming, et al. J. Phys. Chem. Lett. 3, 2755 (2012).
- P. Bakule, D. Fleming, et al. J. Phys. B: At. Mol. Opt. Phys. 48, 045204 (2015).

Summary of the experiment



- Photons excite H_2 molecules to the first vibrational excited state
- Reacts with Mu, forming H-Mu molecules
- Observed in Mu precession signal as reduction of Mu fraction (b/c Mu in H-Mu is diamagnetic)
- Need pressurized gas

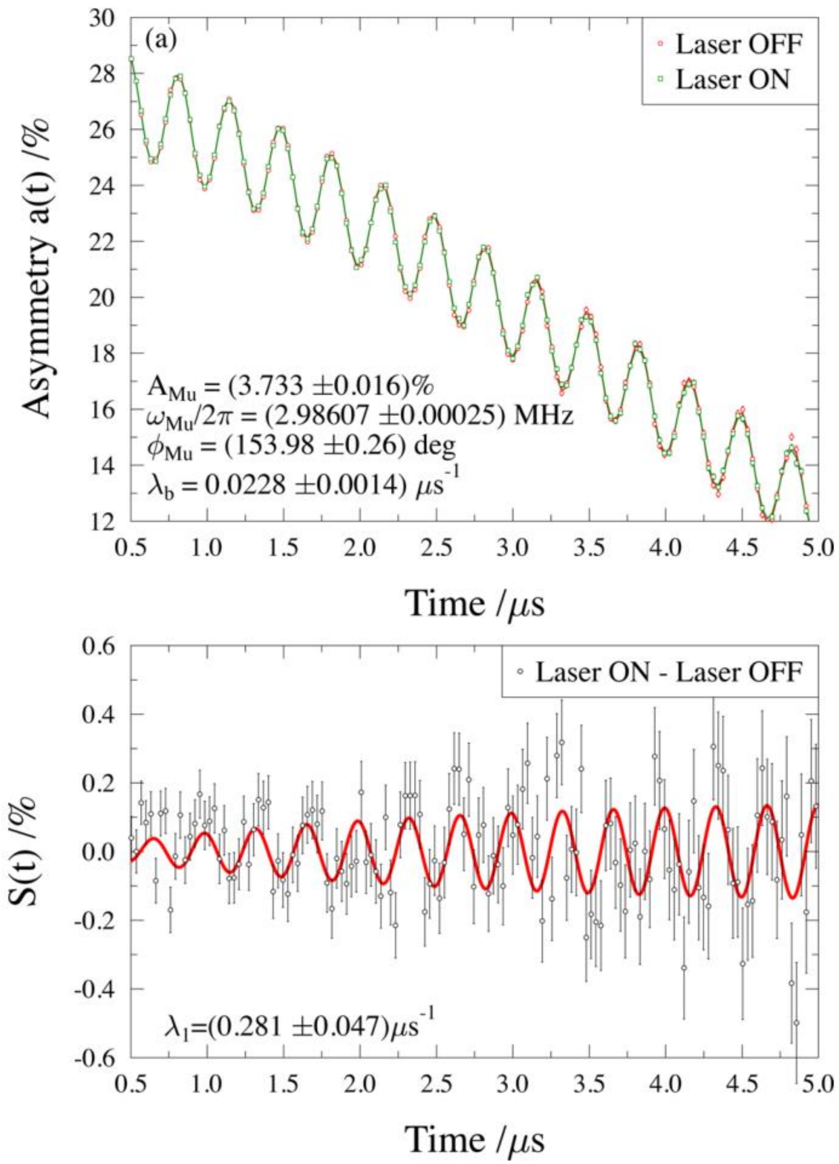
How to excite gaseous molecules?



- Wavelength for $H_2(\nu=0) \rightarrow H_2(\nu=1)$ is ~2.4 μm … difficult to get a high-power light source
- Simulated Raman Scattering
  … generates wavelength different from the pump
  … the energy difference is associated with vibrational/rotational/electronic states in material
  … used to be a method of wavelength conversion
- Can populate the $H_2(\nu=1)$ state

Figure was reproduced from P. Bakule, et al. J. Phys. B: At. Mol. Opt. Phys. 48, 045204 (2015).

Summary of the experiment



- Mu precession under TF 2G
- Light arriving at Δt = 0
- Laser OFF/ON … there’s a difference
- Laser (ON) – (OFF) makes it more clear
- The difference becomes larger b/c H-Mu population grows
- Can obtain the reaction rate for

$$\mathrm{Mu} + \mathrm{H_2}\{1\} \xrightarrow{\lambda_1} \mathrm{MuH} + \mathrm{H}$$

- Test bench for the first-principle calculation

Figure was reproduced from P. Bakule, et al. J. Phys. Chem. Lett. 3, 2755 (2012).

Planning an experiment

But you have to carefully plan your experiment:

- Muon/Photon spatial overlap
- How do photon/muon interact?
  - Sometimes you have to fight diluted nature of muon
  - e.g. photocarriers in Si diffuse and “find” Mu
- Ideal to know either optical character or muon signal
- More heating in lower T (heat capacity proportional to T^3)

Photons are everywhere … idea ??