International Advanced School on Muon Spectroscopy

Stimulation Methods 2: Laser

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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
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**

**TRIUMF**

**PSI**

**RIKEN-RAL**

**ISIS**
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)

Signal: 405 ~ 710 nm
Idler: 710 ~ 2400 nm

Output relative to 440 nm [%]
Output relative to 941 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 $\alpha$ [cm$^{-1}$]
  - need $\alpha$ for getting fluence at muon position
  - $\alpha$ depends on wavelength

- Lateral size:
  - muon beam size: ~10 mm
  - laser: variable (better expanded for entire coverage)
Before designing a photo-\(\mu\)SR experiment...

- Optically uniform sample, if possible
- How likely a muon can encounter the photo-induced effect?
  - \textit{e.g.} injected excess carriers in semiconductors are very 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)

Excess carriers depolarises $\mu^+$ spin

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

**Charge exchange interaction**

$h^+$ ionizes a bound $e^-$

$\mu^+$ captures another $e^-$

Mu forms again

$\ldots$ depolarizes due to HF interaction

**Carrier injection causes the muon spin depolarisation**

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 $\mu^+$ spin

- Indirect transition (requires phonon)
- Photon creates $e-h$ pair (excess carriers)
- Carrier injection causes the muon spin depolarisation

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Characterise $\Delta n$ with relaxation rate

- More carrier injection gives faster relaxation
  
  ... can we use this to measure excess carrier density $\Delta n$ [cm$^{-3}$]?

  ... Relaxation rate $\lambda$ for light ON spectrum is a measure of $\Delta n$

- Need: relationship between $\lambda$ vs. $\Delta n$

- $\Delta n(\Delta t=0)$ is measurable
  
  - Size of beam spot
  - Pulse energy
  - Absorption coefficient

- Can get $\lambda$ vs. $\Delta n$ by changing pulse energy

- Assumption: $\Delta n$ stays const. within the time window (0.5 $\mu$s)
Making a calibration curve

- $\lambda$ vs. $\Delta n$: 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 $\Delta n$ from a measured $\lambda$
Now fix $\Delta n(\Delta t=0)$ and change the delay time $\Delta t$, measure $\lambda$, and get $\Delta n$.

... gives a 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 $\alpha$ for (nearly) uniform carrier injection e.g. $\alpha = 10 \text{ cm}^{-1}$ gives 1 mm for absorption length.

There are tail states, which allows a low $\alpha$.

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

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

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

boundary conditions:
\[
\Delta n(0, t) = \Delta n(d, t) = 0
\]
\[
\Delta n(z, 0) = \Delta n_i
\]
Temperature dependent measurements

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

Bulk carrier lifetime $\tau_{\text{bulk}}$

- $\tau_{\text{bulk}}(T)$ may show recombination mechanisms (and type of defect centres)
- Monotonic decrease with cooling, then stays constant
  - "excitonic Auger recombination"
- A carrier in a free exciton is captured and 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 $\mu$

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

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

Charge exchange interaction

- $h^+$ ionizes a bound $e^-$
- $\mu^+$ captures another $e^-$
- Mu forms again
- ... depolarizes due to HF interaction
Muonium states in intrinsic silicon

Two Mu sites:
- Tetrahedral interstitial site (T-site)
- Bond-centered site (BC-site)

BC-site: $\text{Mu}_{BC}^0 \& \text{Mu}_{BC}^+$
T-site: $\text{Mu}_T^0 \& \text{Mu}_T^-$

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

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 $e^-$
- $\mu^+$ captures another $e^-$
- Mu forms again

"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?


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?

What does muon see?

- 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

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 + H₂

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 $\text{H}_2(\nu=0) \rightarrow \text{H}_2(\nu=1)$ is $\sim 2.4 \mu$m ... 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 $\text{H}_2(\nu=1)$ state

Summary of the experiment

- Mu precession under TF 2G
- Light arriving at $\Delta t = 0$
- 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
  $$\text{Mu} + \text{H}_2\{1\} \xrightarrow{\lambda_1} \text{MuH} + \text{H}$$

- Test bench for the first-principle calculation

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