Muon Spin Spectroscopy

Exploiting a novel resonance technique

Muons provide a very sensitive probe of the atomic-level properties of materials. Muon techniques are available at the European facilities, enabling unique phenomena to be investigated.

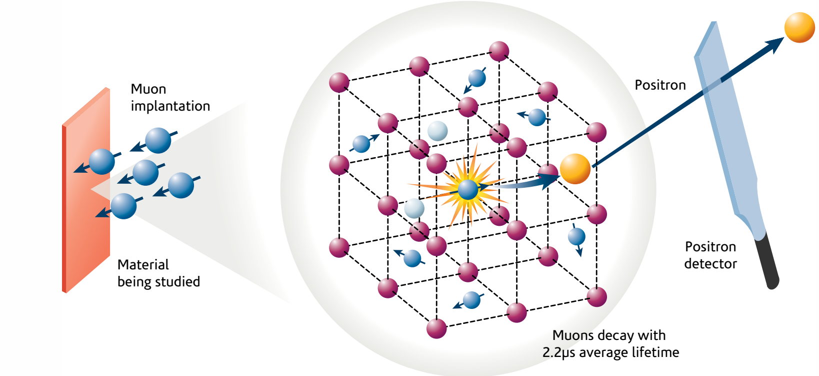
Examples of how muon spectroscopy can be used for novel measurements include:

- Probing superconductivity; vortex states, length scales and small spontaneous fields.
- Studying both static and dynamic behaviour in magnetic systems: from bulk ordered states to more novel topics such as spin liquids and low dimensional magnetism.
- Investigating magnetic behaviour at interfaces and surfaces.
- Characterising hydrogen behaviour in semiconductors, minerals and hydrogen storage materials.
- Measuring ionic diffusion coefficients in battery materials.
- Investigating molecular dynamics and electron spin relaxation at a molecular level.
- Studying reaction kinetics and unusual bonding.

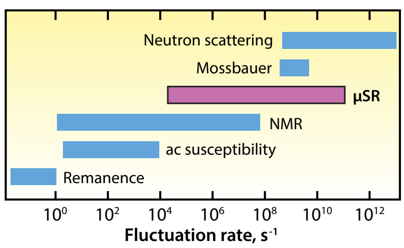
This leaflet provides examples of the unique information that can be gained from the muon technique.

A quick introduction to the muon technique

Muon spin spectroscopy is less well known than other spin spectroscopic techniques such as NMR and EPR, but it provides researchers with an important tool that can be used to study a wide range of problems in physics and chemistry.



The muon technique involves implanting spin-polarised $S=½$ positive muons into a material where they act as a local probe. Muons are short-lived particles, decaying after an average lifetime of 2.2 μs to produce positrons. The decay positrons which emerge from a sample after muon implantation are detected revealing information about the muons' behaviour inside the material – particularly about how the muon polarisation changed within the sample. This, in turn, enables us to deduce information about the properties of the material on an atomic scale, and to probe the system on a unique timescale.



Muons are very sensitive probes of magnetic systems, often able to detect effects that are too weak to be seen by other methods; as well as allowing both static and dynamic magnetic behaviour to be investigated. The penetration depth of low energy muons can be varied by tuning their momentum, allowing behaviour at surfaces and interfaces to be probed. Muons also have a wide variety of other applications – for example, in studies of superconductors (where the vortex lattice can be probed and characteristic length scales determined), molecular systems and chemical reactions, novel battery materials and a variety of organic systems. In some studies, the positive muon can be thought of as being like a light proton (muons have a mass of one ninth of the proton mass); implanted muons can sometimes pick up an electron to form a light isotope of hydrogen called muonium (Mu). By following muon behaviour inside a material we can learn about proton and hydrogen behaviour. This is important in semiconducting materials, proton conductors, hydrogen storage materials and insulating materials.

References on the muon technique include:

- ***Muon spin rotation, relaxation and resonance: Applications to condensed matter***, *A. Yaouanc, P. Dalmas de Réotier, Oxford University Press, ISBN 0199596476 (2010).*
- ***Spin polarised muons in condensed matter physics***, *S.J. Blundell, Contemporary Physics* ***40***, *175 (1999).*
- ***The positive muon and μSR spectroscopy: powerful tools for investigating the structure and dynamics of free radicals and spin probes in complex systems***, *I. McKenzie, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* ***109***, *65-112 (2013).*

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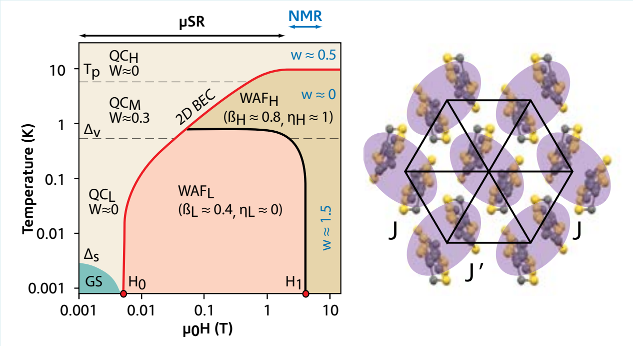
Example Applications of the Muon as a Magnetic Probe

Quantum Magnetism

μSR is able to map out phase diagrams of low moment systems at very low temperatures and applied fields.

The extended field and temperature regimes offered by the latest muon spectrometers enable complex phase diagrams and unusual phases to be investigated. A quantum spin liquid is one such intriguing state where a system of strongly interacting magnetic spins avoids a magnetically ordered ground state, even at the lowest temperatures. Measurements of spin liquid systems such as the Mott insulator χ-(BEDTTTF)$_2$ $Cu_2(CN)_3$, have demonstrated no obvious signature for conventional magnetic ordering to 20 mK.



The rich phase diagram (left) of χ-(BEDTTTF)$_2$ $Cu_2(CN)_3$ is readily explored using muon techniques. Compared to conventional resonance techniques, muon spectroscopy enables measurements over a greatly extended field range, reaching to lower fields.

F. L. Pratt et al., Nature ***471****, 612 (2011).*

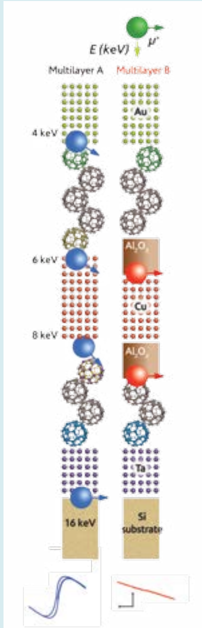
Surfaces & Interfaces

Low energy muons can be implanted at different depths allowing surfaces and interfaces to be probed.

The energy of muon beams can be tuned allowing them to be implanted at different depths within materials. Using low energy muons (LEM) enables us to probe magnetic behaviour at surfaces and interfaces as well as within the bulk of materials.

Recently this technique has been used to study how the Stoner Criterion can be overcome to induce room temperature ferromagnetism in normally para- or diamagnetic materials. This can be achieved via the interface between a metallic thin film (e.g. diamagnetic Cu) and an electron withdrawing C_{60} molecular layer.

LEM μSR measurements on Cu/C_{60} multilayers show that spin-ordered states are found at and close to the metal-molecule interface, which simulations indicate are based on a magnetic hardening of the metal atoms due to electron transfer.



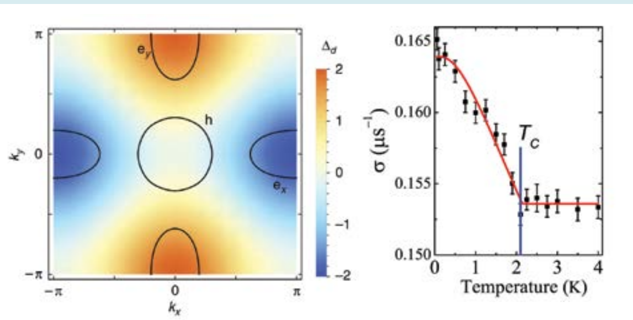
A schematic diagram illustrating how the LEM measurement in Cu/C_{60} multilayers was performed.

F. Al Ma'Mari et al., Nature ***524****, 69 (2015).*

Superconductivity

Muons are a sensitive probe of length scales, symmetry and spontaneous fields in superconductors.

Understanding the symmetry of the superconducting state is critical and muons can determine the nature of the superconducting gap. The optimally doped iron pnictide superconductor $Ba_{0.65}Rb_{0.35}Fe_2As_2$ was investigated under pressure showing the promotion of a nodal gap, most likely d-wave in origin. Also, the onset of spontaneous fields at T_c is a key indicator of time reversal symmetry breaking, as seen in $LaNiGa_2$, implying triplet pairing.



The nodal d-wave state favoured by the application of pressure to the superconducting phase of $Ba_{0.65}Rb_{0.35}Fe_2As_2$ and the onset of spontaneous fields at T_c in $LaNiGa_2$.

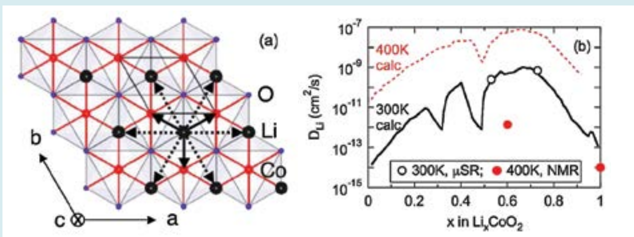
Z. Guguchia et al., Nature Communications ***6****, 8863 (2015).*
A. D. Hillier et al., Phys. Rev. Lett. ***109****, 097001 (2012).*

Ionic Conductors

μSR is able to probe intrinsic ion diffusion coefficients even in the presence of magnetic ions.

The diffusion of certain ions (e.g. Li^+, Na^+) past an implanted muon alters the local magnetic field at the muon site. This can allow the intrinsic ionic diffusion rate to be measured microscopically, even in the presence of magnetic ions.

The lithium diffusion rate in the battery material Li_xCoO_2 was measured from μSR experiments by studying the fluctuations in the local field at the muon site as the Li^+ ions diffuse past. The diffusion rate was found to be in excellent agreement with ab initio calculations despite the presence of magnetic Co ions, which affects the reliability of measurements made by other techniques such as NMR.



Li hopping pathways and hopping rates in Li_xCoO_2.

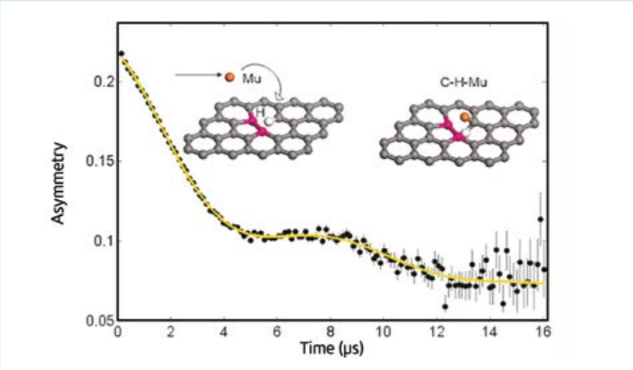
J. Sugiyama et al., Phys. Rev. Lett. ***103****, 147601 (2009).*

Example Applications of the Muon as a Proton Analogue

Hydrogen Storage

The high sensitivity of μSR allows the hydrogen storage properties of low density materials to be probed.

Graphene is a potential low-density hydrogen storage material. The high sensitivity of μSR measurements allowed the hydrogen storage behaviour of the low-density material, hydrogenated graphene to be investigated. The presence of a muon oscillation signal was observed, usually the fingerprint of magnetic order. In this case, however, it was found to arise from muon-hydrogen nuclear dipolar interactions, providing an insight into the mechanism of hydrogen storage in graphene.



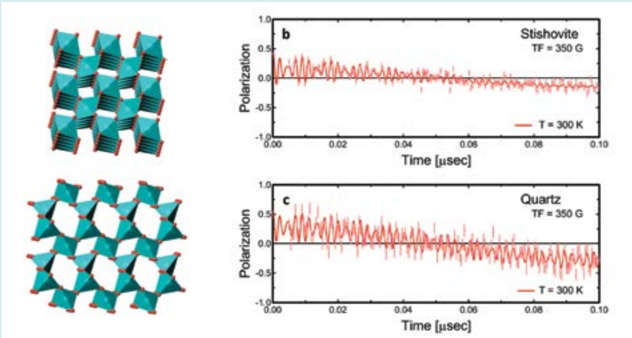
The oscillation in the muon decay asymmetry and the mechanism of muon addition to hydrogenated graphene.

*M. Riccò et al., Nano Lett., **11**(11), 4919-4922 (2011), M. Gaboardi et al., J. Mater. Chem. A **2**, 1039 (2014).*

Geophysics

μSR is able to probe hydrogen existing irregularly in matter such as in minerals.

μSR can be used to understand how water and hydrogen are stored, even irregularly, within minerals as the muon models the behaviour of a hydrogen ion. Understanding processes in minerals within the Earth is important as these control the dynamics and evolution of our planet. Muonium forms when muons are implanted in the high-pressure silicate mineral stishovite. The very large relaxation rate of the muonium spin polarisation and hyperfine-coupling suggest that the muonium (or hydrogen) does not bind to O or Si but is squeezed into small, anisotropic, interstitial voids, inferring the existence of neutral, atomic hydrogen in the deep mantle.



The structures of stishovite and quartz and a comparison of their transverse field spectra.

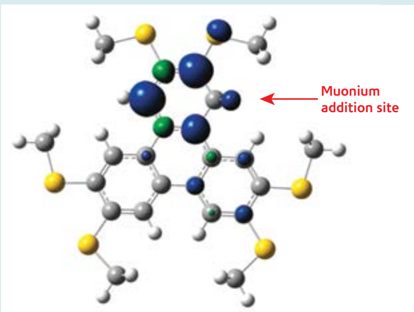
*N. Funamori et al., Scientific Reports **5**, 8437 (2015).*

Molecular Dynamics

μSR allows the study of intrinsic molecular dynamics and electron spin relaxation at a molecular level.

Muonium can add to unsaturated chemical bonds to form muoniated radical species. These species provide a unique probe for molecular dynamics and electron spin relaxation at a molecular level.

The discotic liquid crystal, HHTT, was studied using μSR, to investigate its potential application in future spin-based technologies. The muonium species adds to an unsaturated carbon atom in the ring, creating a muoniated radical. The broad avoided level crossing (ALC) resonances observed are caused by rapid electron spin relaxation, which increases with temperature. This is likely to be caused by the liquid-like motions of the molecules within the columns.



The optimized structure and distribution of unpaired electron spin density (green & blue) in the muoniated 1-HHTT radical. The muonium addition site on the ring is indicated.

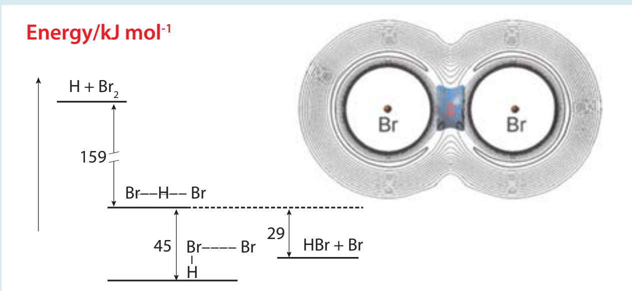
*I. McKenzie et al., Phys. Rev. E **87**, 012504 (2013).*

Kinetics & Bonding

Muonium acts as a light hydrogen isotope and can be used to investigate unusual bonding states.

The analogous behaviour of muons to light protons makes them an ideal probe of chemical processes including reaction kinetics and bonding interactions.

To investigate the possibility of the formation of Heavy-Light-Heavy vibrationally bound states, the Br-(H/Mu)-Br system was studied. The formation of a Br-Mu-Br vibrationally bonded species is predicted by the energetics of the system. Evidence for a radical species with an unusually large hyperfine coupling constant was found; however, DFT calculations of final state species suggest this is likely the result of the formation of the Mu···Br_2 van der Waals state.

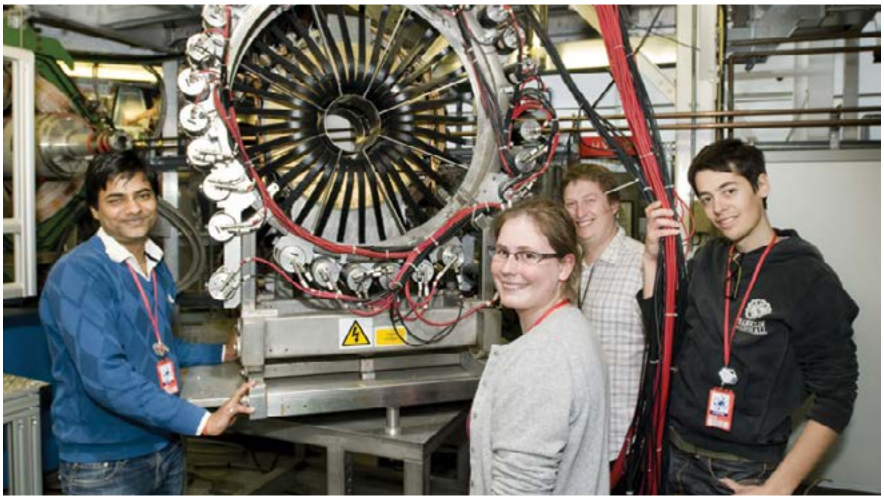


The relative energies of species in the Br-H-Br system and a representation of the Br-Mu-Br bond.

*D.G. Fleming et al., Phys. Chem. Chem. Phys. **14**, 10953 (2012). A. Nordrum, Scientific American **312**, (2015).*

Facilities for Muon Spectroscopy

Europe is fortunate in having two muon sources that are complementary. The beam structure of the SμS, located at the PSI in Switzerland, makes it ideally suited for applications where high timing resolution is essential, such as following fast muon precession in samples with high internal fields, or rapid spin depolarisation. In contrast, the pulsed muon beam operated by the STFC in the UK, allows low background time differential data to be captured at high data rates allowing slow relaxation times to be measured. It also enables the effect of beam synchronous stimuli (such as Radio Frequency or laser radiation) to be investigated. Together, these facilities provide beams of muons for a wide variety of atomic-level studies in condensed matter, molecular, chemical, biological, geological and engineering materials. Further details of the various instruments and sample environment equipment can be found on the facility web sites.



The MuSR spectrometer at ISIS. The MuSR detectors can be rotated by 90° allowing measurements to be made in both longitudinal and transverse applied fields. Experiments can be performed from 30 mK to 1000 K.

At both facilities a number of spectrometers are available with specialist sample environment equipment to enable a broad range of condensed matter and molecular studies on solid, liquid and gaseous samples. Measurements are typically carried out on samples with masses ranging from several grams down to a few 10's of milligrams, depending on the experimental setup.

Temperature studies can extend from millikelvin temperatures to 1300 K and solid-sample pressures up to 2.5 GPa can be applied. Experiments can be performed in zero applied field and at fields up to 5 T (ISIS) and 9.5 T (PSI).

Using the Facilities

Both facilities welcome experiment proposals from scientists of all disciplines. Calls for proposals occur twice a year: deadlines at ISIS are 16th April and 16th October, while at PSI deadlines are in June and December. Proposals can be made using the online systems available through the respective web pages – typically a two-page science case is required.

Members of both groups are always happy to help and are available to give advice on all aspects of muon science and running muon experiments. They can be contacted to discuss ideas for experiments, for technical and practical information on the muon instruments and to offer advice on proposals.

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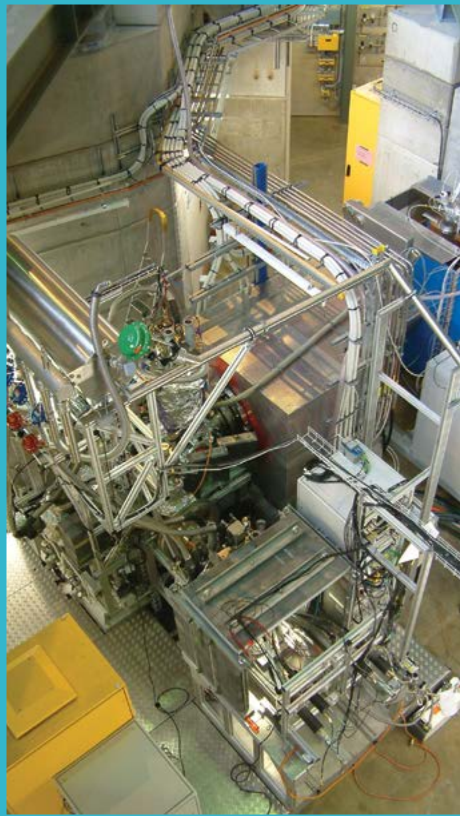

The LEM facility at PSI. The mean implantation energy of the muons can be tuned from 1 keV to 3 keV corresponding to tunable implantation depths of a few nanometers to 100's of nanometers.

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