Muon Spin Rotation/Relaxation/Resonance (μSR)

Understanding the fundamental physical properties of matter at a microscopic level enables the extension of existing technologies and leads to the development of reliable new materials for tomorrow's applications. For these reasons, scientists are interested in studying microscopic structures and processes in a wide range of materials. Only through experimental verification can one establish physical laws describing their inner workings. Since we cannot see such small-scale phenomena directly with our eyes, we must rely on experimental methods that can probe deep inside materials for us. The μSR technique is one such method. It makes use of a short-lived subatomic particle called a *muon,* whose spin and charge are exquisitely sensitive local magnetic and electronic probes of matter. μSR's place amongst those experimental techniques that utilize a *probe magnetic moment* to investigate matter is distinguishable by its extreme sensitivity to magnetism and its unique time window for dynamical processes. Researchers generally use the μSR technique to tackle fundamental problems in condensed matter physics and chemistry that one cannot investigate by other means.

What Are Muons?

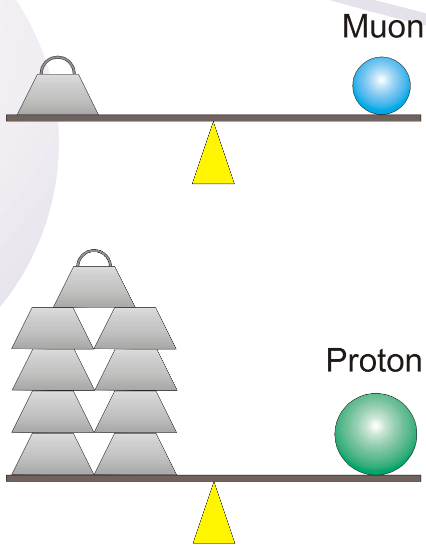
In 1937, the muon was discovered as secondary radiation from cosmic rays. With a mass about 200 times that of an electron (or 9 times less than that of a proton) the muon appeared to be simply a heavier version of the electron. The mere existence of the muon was so completely unexpected at the time that its discovery prompted the following remark:

***"Who ordered that?"* – I.I. Rabi –**

Unlike the electron, the muon is an unstable particle, living for only about two millionths of a second. Muons carry a positive (μ^+) or negative (μ^-) charge, and spontaneously decay into a positron (or an electron) and a neutrino-anti-neutrino pair as follows:

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$$

$$\mu^- \rightarrow e^- + \bar{\nu}_e + \nu_\mu$$



Solid-state physicists and chemists generally think of the muon as a light proton.

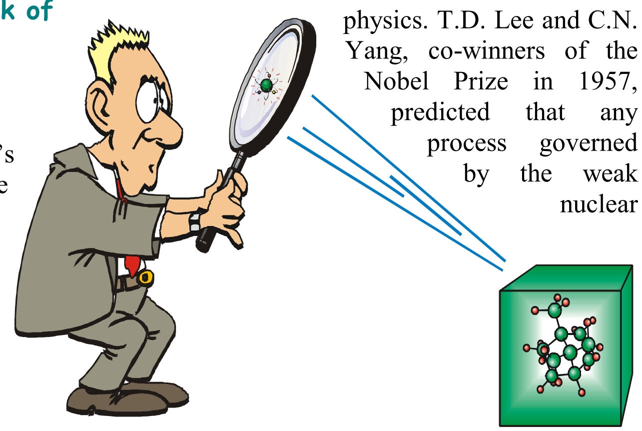
High up in the earth's atmosphere, muons are naturally created by the interaction of cosmic rays with gas molecules. Here on earth we can produce muons using a particle accelerator. Muons are charged spin-½ particles that can couple to their local environment via their spin. The muon's magnetic moment is 3.18 times larger than a proton. Thus when implanted in matter this feature makes them an extremely sensitive microscopic probe of magnetism.

The Birth of μSR

The acronym μSR was coined in 1974 to grace the cover of the first issue of the *μSR Newsletter*, in which the following definition and explanation were given:

μSR stands for Muon Spin Relaxation, Rotation, Resonance, Research or what have you. The intention of the mnemonic acronym is to draw attention to the analogy with NMR and ESR, the range of whose applications is well known. Any study of the interactions of the muon spin by virtue of the asymmetric decay is considered μSR, but this definition is not intended to exclude any peripherally related phenomena, especially if relevant to the use of the muon's magnetic moment as a delicate probe of matter.

The story of μSR began with an American revolution in theoretical physics. T.D. Lee and C.N. Yang, co-winners of the Nobel Prize in 1957, predicted that any process governed by the weak nuclear



μSR is a collection of methods that uses the muon spin to look at structural and dynamical processes in the bulk of a material on an atomic scale.

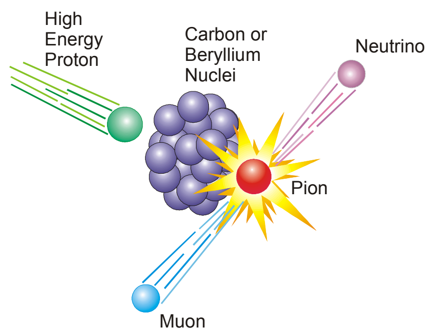
interaction might not have a corresponding "mirror image" process of equal probability. Prior to their suggestion it was firmly believed by the physics community that if a reaction were viewed in a mirror, the mirror image was *a priori* just as likely to occur as the original process — a principle known as *parity* symmetry.

Although parity "violation" was first observed in kaon decay, credit for its experimental discovery is usually given to C.S. Wu *et al.* who confirmed its existence in the β-decay of ^{60}Co. However, at almost the same time experiments were performed at the Nevis cyclotron of Columbia University by R.L. Garwin, L.M. Lederman and M. Weinrich, and at the Chicago cyclotron by J.I. Friedman and V.L. Telegdi, which showed a dramatic effect in the decay of pions to muons and the subsequent decay of muons to electrons, neutrinos and anti-neutrinos. The Nevis group suggested in their landmark paper that *non-conservation of parity* in muon decay might furnish a sensitive general-purpose probe of matter. The history of μSR began with that experiment. In the modern μSR method, the lifetime experience of the muon in matter is passed on to us by way of its decay into a positron (electron), which we can easily detect.

Making Muons

Although muons are produced in a variety of high-energy processes and elementary particle decays, μSR requires low energy muons that will stop in the samples being studied. Low-energy muons are available in the required intensities only from ordinary two-body *pion decay*. Thus, before making a source of muons, one must make pions. Pions are produced in sufficient numbers from collisions of *high-energy protons* (>500 MeV) with the nuclei of an intermediate target. A light element such as carbon or beryllium is used for the primary target in order to maximize pion production, while minimizing multiple scattering of the proton beam. The charged pions that are produced live for only about 26 billionths of a second and then decay into a muon and muon neutrino (anti-neutrino):

$$\pi^+ \rightarrow \mu^+ + \nu_u$$
$$\pi^- \rightarrow \mu^- + \bar{\nu}_\mu$$



Muon beams are made here on earth using high-energy protons to produce short-lived pions.

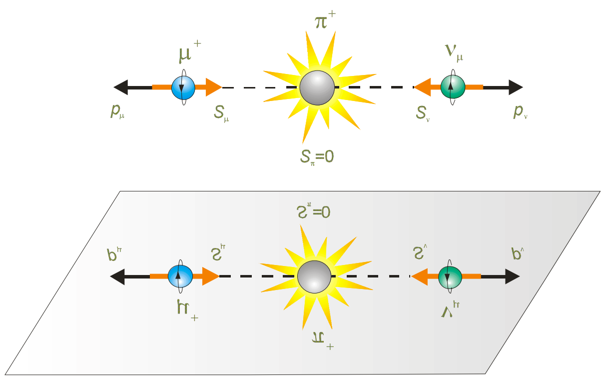
Most positive muon (μ^+) beams at a μSR facility are generated from pions decaying at rest in the surface layer of the primary production target — hence the common name, *surface muons*. The muon is emitted isotropically from the pion with momentum p_μ = 29.8 MeV/c and kinetic energy 4.119 MeV (in the rest frame of the π^+). Unfortunately, this mode is not available for negative muons (μ^-) because a negative pion stopping in the production target almost always undergoes nuclear capture from low-lying orbitals of pionic atoms before it has a chance to decay. This problem is overcome by allowing the pions to *decay in flight* within a long superconducting solenoid. The muons that are emitted opposite to the direction of the pion momentum are called *backward muons*, which can be selectively extracted by a bending magnet. While this method can also be used for μ^+SR, for μ^-SR there is no alternative. Compared to surface muon beams, *backward muon beams* have higher momentum (approximately 50-100 MeV/c), a larger momentum spread (and therefore lower stopping density) and much larger phase space (and therefore lower luminosity). While the two latter features are less desirable, backward muons are the only means of studying samples contained in a thick target vessel. Such vessels are used in studies of gases or liquids and studies of high-pressure effects.

Why Does μSR Work?

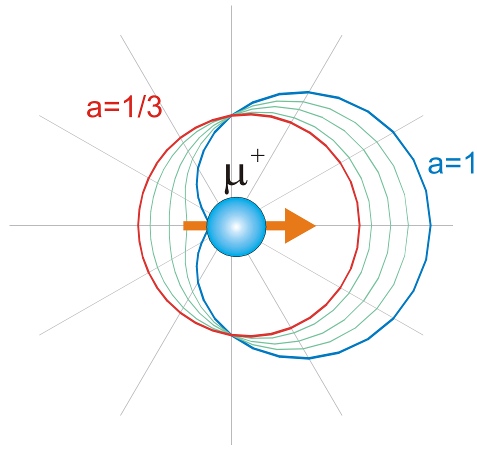
The μSR technique is made possible by the unique properties of the pion and muon decays:

First, thanks to maximal *parity violation* in the weak interaction decay of pions, surface muons are perfectly spin polarized opposite to their momenta, so when a muon is transported down the beam line to stop in the sample being studied, it arrives nearly *100% spin polarized*. This is a significant improvement on other magnetic resonance probes such as nuclear magnetic resonance (NMR) and electron spin resonance (ESR) methods that must rely upon thermal equilibrium spin polarization in a magnetic field— so that sufficient polarization is often achieved only at low temperatures and/or in strong magnetic fields.

Second, when the muon decays it emits a fast decay positron (electron) preferentially along the direction of its spin due to the parity violating decay. From a single decay positron we cannot be certain which direction the muon spin is pointing in the sample. However, by measuring the *anisotropic distribution* of the decay positrons from a bunch of muons deposited at the same conditions, one can determine the statistical average direction of the spin polarization of the muon ensemble. The time evolution of the muon spin polarization depends sensitively on the spatial distribution and dynamical fluctuations of the muons' magnetic environment.



Parity-violating collinear decay of a pion π^+ at rest into a muon μ^+ and a muonic neutrino ν_μ.



Angular distribution of the positrons from the muon decay: $W(E,\theta) = 1 + a(E)\cos(\theta)$. When all positron energies E are sampled with equal probability the asymmetry parameter has the value $a = 1/3$ (red curve).

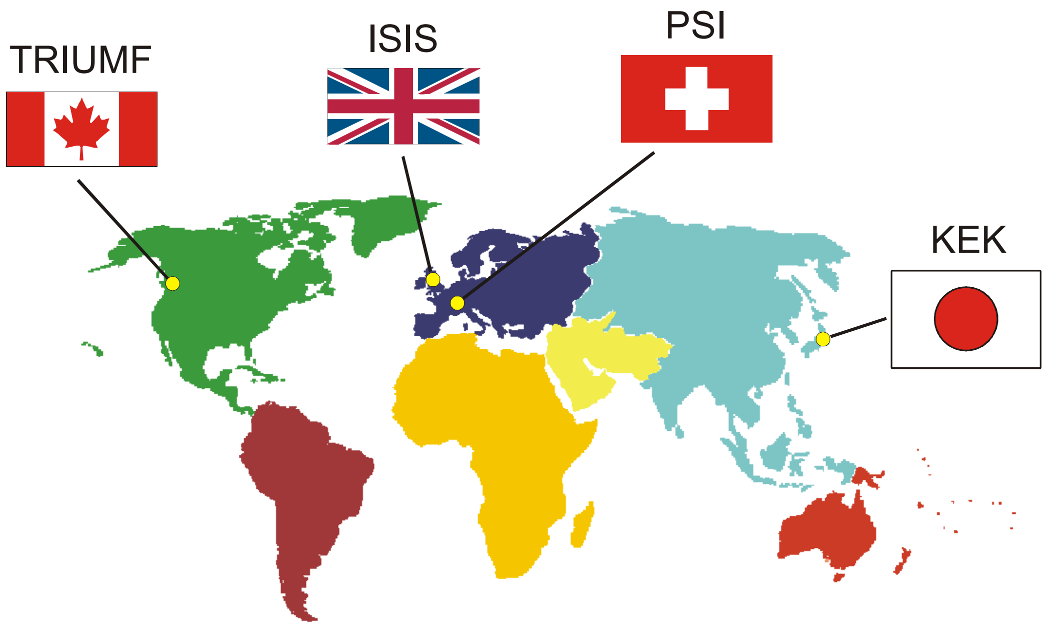
μSR Facilities

The muon beams currently available for μSR are distinguishable by their time structure:

Continuous Wave (CW) facilities deliver a *nearly continuous* source of protons that are used to produce muons that arrive at the experimental stations without any distinct time structure. The great advantage of this type of muon beam is that the time resolution of the μSR apparatus can be made quite small (~100 ps) with an appropriate choice of detectors and electronic detection scheme. Better time resolution allows detection of larger magnetic fields and fast relaxing signals. On the other hand, the muon-stopping rate is limited by the muon lifetime, because consecutive muon decay events must be rejected over a time interval of many muon lifetimes to avoid ambiguity in relating a decay positron (electron) to its parent muon — a situation called "pileup". In the CW μSR technique, each individual "unpiled-up" muon and its decay positron are individually counted. However, recent innovations in detector design that make more efficient use of the available muons are rapidly reducing the constraints imposed by the maximum muon-stopping rate at CW sources.

Pulsed beam facilities direct intense bunched proton pulses produced from a synchrotron or linac onto the muon production target. The pulse structure of the primary surface muon beam reflects the pulse structure of the proton beam, but with the pulses further smeared out by the pion lifetime. A general requirement of the μSR technique at a pulsed muon source is that the time width of the muon pulse must be considerably shorter than the muon lifetime, while the pulse repetition period must be longer than the muon lifetime. The width of the muon pulse limits the time resolution, because all the muons in a given pulse are counted together, and the muons do not all arrive simultaneously. Because the pulse widths are on the order of 10 ns, a pulsed beam cannot compete with a CW beam in providing information on fast μ^+ relaxation rates and cannot be used to measure large magnetic fields. The advantages of a pulsed muon beam are that in principle one can use the entire incoming muon intensity and there is almost no background in the μSR signal due to accidental coincidences between the incoming muons and decay positrons (electrons). The virtual absence of background related to contamination of the beam with particles other than muons allows detection of muon decay events beyond 10 muon lifetimes — providing greater sensitivity to the form of the muon relaxation function. A pulsed muon source is also ideally suited for resonance studies, since an RF field and/or light illumination can be synchronized with the muon pulses.

The Paul Scherrer Institute (PSI) located in Switzerland and the Tri-University Meson Facility (TRIUMF) in Canada, are both home to intense *continuous* muon beams. The PSI and TRIUMF facilities use a *cyclotron* to accelerate protons to approximately three quarters the speed of light. The Booster Muon (BOOM) facility at the high energy accelerator research organization (KEK) Meson Science Laboratory in Japan and ISIS at the Rutherford Appleton Laboratory (RAL) in the United Kingdom are sources of *pulsed* muon beams. In 1994, the Japanese Institute of Physical and Chemical Research (RIKEN) constructed a pulsed muon facility at ISIS. Today the RIKEN-RAL facility produces the world's most intense source of backward decay muons. In the near future pulsed muon beams will become available for μSR studies at the High Intensity Proton Accelerator Facility in Japan.

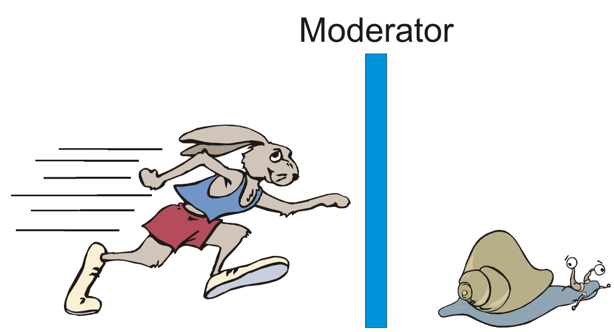


μSR facilities of the world.

Ultra-Low Energy Muons

While conventional surface muon beams can be used to investigate rather small samples, there is a desire for still lower energy muons that can be stopped near sample surfaces, in thin films and near multi-layer interfaces. A number of ingenious methods have been used in attempts to produce "ultra-slow" muon beams, however to date the most successful approach has been simple moderation in a thin degrader consisting of a condensed van der Waals gas (Ar or N_2). Fortunately, the "moderated muons" remain highly polarized. At the PSI muon facility moderated positive muon beams with tunable energies in the range of 0.5 to 30 keV are produced. This energy range corresponds to implantation depths in solids of *less than a nanometer* to several hundred nanometers. One drawback of the moderation method is that the intensity of the ultra-low energy muon beam emerging from the downstream side of the moderator is reduced several orders of magnitude below that of the incident surface muon beam. Nevertheless, ultra-low energy muons have the potential to revolutionize μSR, having recently demonstrated their applicability to investigations of surfaces and thin-film samples by addressing some longstanding issues in condensed matter physics. Their recent arrival means that researchers can use the μSR technique as a tool to directly compare information on magnetic phenomena observed near the surface to that observed in the bulk of the same sample.

Ultra-low energy muon beams can be used to investigate thin films, surfaces and multi-layered compounds. These structures are important for future technologies.

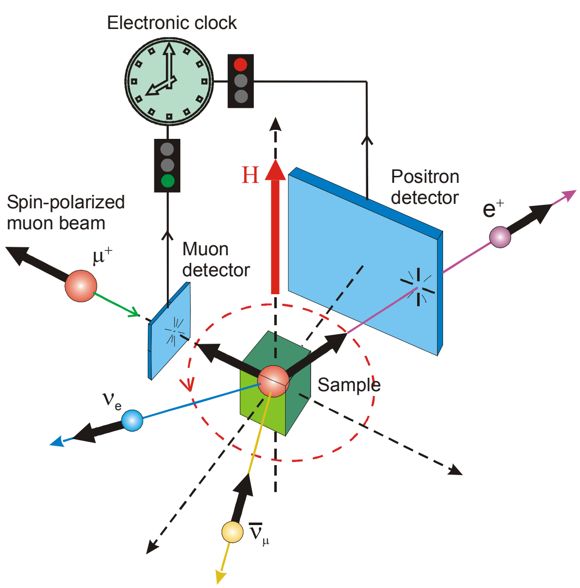


The Many Faces of μSR

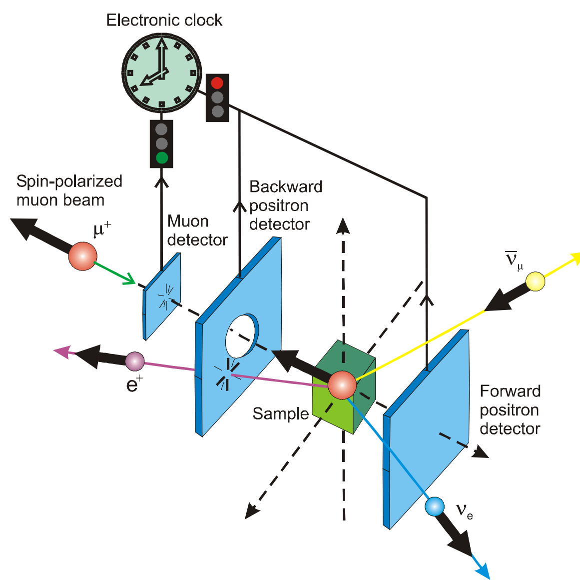
When using μSR spectroscopy to study matter, one has the flexibility of choosing from a number of different experimental configurations:

Transverse Field Muon Spin Rotation (TF-μSR) involves the application of an external magnetic field perpendicular (transverse) to the initial direction of the muon spin polarization. The muon spin precesses about the transverse field, with a frequency that is proportional to the size of the field at the muon site in the material. The TF-μSR configuration can be used to measure the magnetic field distribution of the vortex lattice in a type-II superconductor or the μ^+ Knight shift in metallic systems (The *Knight shift* is the fractional difference between the magnetic field at the muon site and the externally applied field).

Longitudinal Field Muon Spin Relaxation (LF-μSR) involves the application of an external magnetic field parallel to the initial direction of the muon spin polarization. Here one measures the time evolution of the muon polarization along its original direction. Alternatively, such measurements may be performed in the absence of an external field, a configuration called *Zero Field Muon Spin Relaxation* (ZF-μSR). ZF-μSR is a very sensitive method of detecting weak internal magnetism, that arises due to ordered magnetic moments, or random fields that are static or fluctuating with time. The capability of studying materials in zero external field is a tremendous advantage over other magnetic resonance techniques.



Schematic of a transverse field (TF) μSR setup.

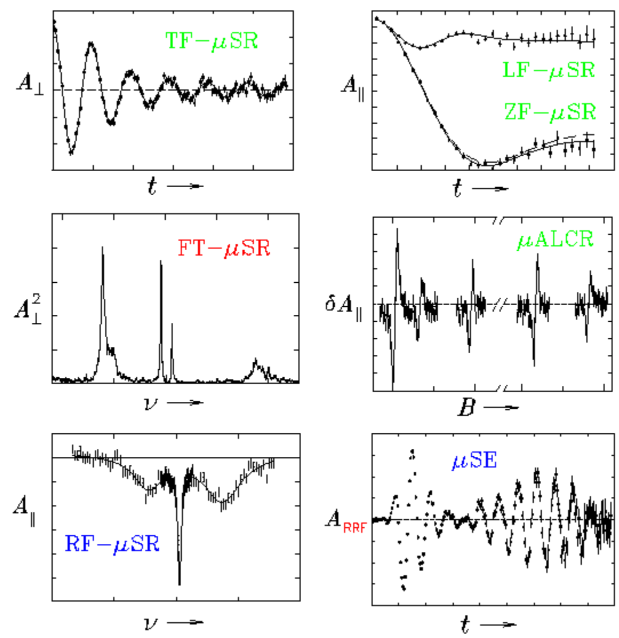


Schematic of a zero field (ZF) μSR setup.

A typical experimental setup consisting of three orthogonal pairs of Helmholtz coils, a cryostat and numerous detectors, which can be used to perform TF-, LF- and ZF-μSR measurements.

Muon Spin Resonance is a variation of more traditional magnetic resonance techniques like NMR and ESR. A static magnetic field is applied parallel to the initial muon spin polarization and a RF field is used to reorient the muon spin. *Resonance* occurs when the RF frequency matches an energy level splitting of one of the muon states present in the system under investigation. This condition is detected as a loss of muon polarization.

There are still other types of μSR experiments one can perform: (Avoided) Level Crossing Resonance (μLCR or μACLR) describes the situation where the muon Zeeman splitting is tuned with a magnetic (or electric) field to match the combined Zeeman and quadrupolar splitting of a neighboring spin system. The muon ensemble loses polarization in a sort of "flip-flop" mutual transition with its neighbors. Muon Spin Echo (μSE) is similar to conventional NMR spin echo, although the muon spin echo can also be observed in zero external magnetic field. It is used only in specialized cases to separate dynamic and static contributions to the local magnetic field. Within each class of experimental configurations described here there is a large sub-class of possible experimental setups that can be used to cater to a particular application.



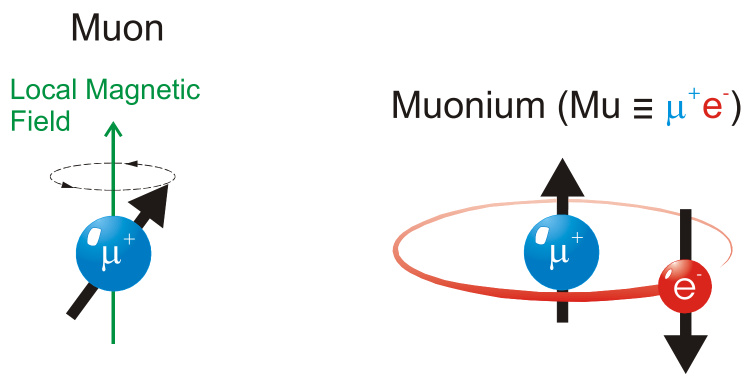
Examples of μSR spectra for different experimental configurations.

Positive vs. Negative

Although either *positive* or *negative* muons can be used to perform μSR, their very different behavior in matter makes μ^+ the preferred "muon of choice" for most condensed matter physics or chemistry applications. While μ^+ avoids the positively charged nuclei in the host material, μ^- behaves as a *heavy electron* and is easily captured into the atomic orbitals. Because it is "heavy", the μ^- quickly cascades to the atomic 1s ground state in close proximity to host nuclei. On its way down the muon loses a significant amount of spin polarization and radiation is produced that introduces undesirable signal noise. Once there, the significant overlap between muon and nuclear wave functions can result in *nuclear capture*. While the lifetimes of a free μ^+ and a μ^- are the same (2.197 μs), the measured mean lifetime in matter is considerably shorter for the μ^- because of the capture by nuclei. The reduction is greater for heavier nuclei with larger atomic number Z. Together the complications of increased noise, reduced polarization, and shorter lifetimes mean that μ^-SR is used only in certain selected cases.

μ^+ in Matter

The positive muon is a prototypical atomic probe, best thought of as a "hydrogen-like center", that can often extract a characterization of the microscopic magnetic or electronic environment that is very difficult (or indeed impossible) to obtain by other means. In a crystalline solid the μ^+ is *repelled* by the charge of the host nuclei, but in a molecular gas or liquid it is *attracted* to the electron cloud around the host molecules. In a solid μ^+ generally comes to rest at an interstitial site of high symmetry between the lattice ions, where it exists in a diamagnetic state as a "quasi-free" probe. However, in oxides the μ^+ may localize near an oxygen atom, forming a μ-O bond similar to an OH "hydrogen" bond. In certain materials (*e.g.* semiconductors) a μ^+ can pick up an electron to form *muonium* (Mu ≡ μ^+e^-) which has almost the same Bohr radius and ionization potential, but a mass 9 times smaller than hydrogen (H ≡ p^+e^-). In such instances, the electron is the extremely sensitive probe that passes on what it senses to the μ^+ by way of its *hyperfine coupling*.



Positive muons in matter probe their local environment either directly or through a captured electron.

Scientific Applications

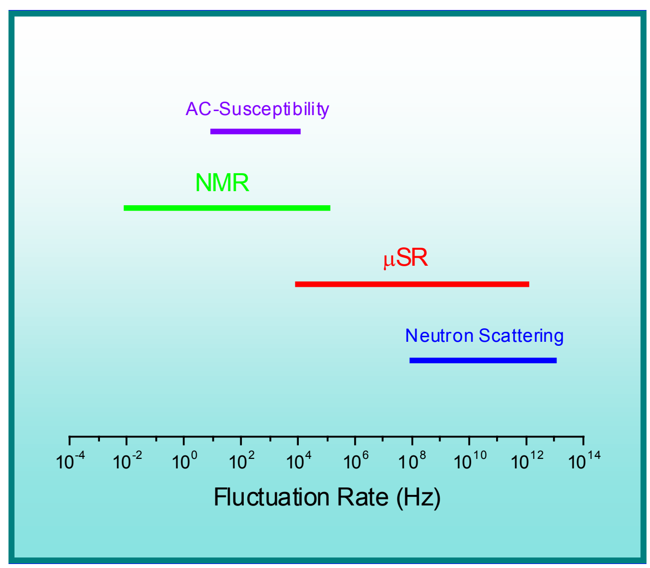
The μSR techniques are primarily used for basic studies in condensed matter physics and chemistry. In condensed matter physics research, the muon is a sensitive probe of internal magnetic fields and electronic configurations of materials. The utility of μSR in chemistry (and even in semiconductor physics) rests on the isotopic substitution of the muon for a proton. In general, μSR gives information that is complementary to that provided by other well-recognized techniques such as neutron scattering, ESR and NMR. There are of course significant differences between these techniques, resulting in clear advantages of using more than one. Some of the unique capabilities of μSR are as follows:

- The μSR technique is unmatched in its *extreme* sensitivity to small internal magnetic fields (~0.1 G) — able to detect fields of nuclear and electronic origin. In systems with very small and/or dilute and/or random ordered moments, μSR is often the only method available for clear detection of such phenomena.

- The μSR technique can measure magnetic fluctuation rates in the range 10^4 to 10^{12} Hz, depending on the size of the magnetic field at the muon site. This unique time window bridges the gap between fluctuation rates sensed with the NMR and neutron scattering techniques.

- Muons can be implanted into any material (gas, liquid or solid) and the μSR method applied to samples in a large variety of environments (*e.g.* any temperature, magnetic fields up to 8 T, electric fields, high pressure, irradiated with light, applied RF pulses *etc*.). Because the muon is an implanted guest in the host material, the μSR technique is not limited to specific target nuclei, as is the case for NMR, Mössbauer spectroscopy and perturbed γ-γ angular correlation (PAC). Furthermore it has a special advantage in the study of materials containing elements that strongly adsorb neutrons.

- Difficulties associated with the preparation of large uniform samples make the μSR technique an invaluable tool for characterizing new and exciting materials. The emergence of new "low-background" detection schemes that can operate in cryogenic environments, and the availability of ultra-low energy muons, means that today there is little restriction on sample size — a great advantage over neutron scattering which is limited by the requirement of large samples. μSR can now be used routinely to investigate samples with surface areas as small as 10^{-1} cm^2. The μSR method can be applied to single crystals, polycrystalline samples and thin films.



The μSR technique has a unique time window for the study of magnetic fluctuations in materials that is complementary to other experimental techniques.

• μSR studies provide information integrated over k-space. However, there are some advantages to the loss of momentum information. For example, magnetic phase transitions are more easily discovered with μSR than by neutron scattering. This feature also facilitates the study of magnetic phenomena having short-range and/or random spatial correlations.

• Magnetic and non-magnetic regions co-existing in the same specimen result in distinct μSR signals whose amplitudes are proportional to the volume of the sample occupied by the particular phase. Thus the μSR technique recognizes and provides quantitative information on coexisting and competing phases in a material.

Limitations: All experimental techniques have their limitations, which is why researchers rely on information from many different probes of matter. *Sometimes* the interpretation of a μSR experiment can benefit from knowing the precise stopping site of the muon in the material. While knowledge of the muon site(s) is easily determined in some systems, in other cases the location of the muon is not known. One must also be conscious of the fact that the muon is an impurity in the host material and in *some cases* may strongly perturb its local environment. A μSR scientist interested in the properties of the material being studied (and not the properties of the muon) learns to recognize this situation and applies the technique to those systems that are more "accommodating" for the muon.

Magnetic Systems

The study of magnetism is the most common area of application of μSR, due to the sensitivity of the muon to small fields and its capability to probe both static and dynamic local field distributions. Muons have been used to probe an enormous variety of magnetic and quasi-magnetic materials in order to map out microscopic field distributions and compare the results with theoretical calculations. A few examples of the various magnetic systems studied with μSR are given below.

Magnetically Ordered & Spin-Glass Systems

Magnetic order in a material is easily identifiable in a μSR experiment as discrete oscillation frequencies in zero applied magnetic field. The magnitude of the oscillating signal can provide information on the directions of local fields. In some materials, μSR has been the only technique applicable for observing magnetic order.

The μSR technique has provided definitive new information on dynamic spin fluctuations and static spin polarization of spin-glass systems, in a time window nicely complementary to neutron and other probes. The sensitivity of μSR to slow spin fluctuations allows detailed studies of critical slowing-down behavior. The ability to perform μSR measurements in zero field has been especially useful for spin-glass systems, which are quite sensitive to the application of external magnetic fields. μSR provides a full signal even when the internal field is random in magnitude. This feature often allows μSR studies in spin-glass systems where the NMR signal is wiped out due to randomness and/or fast relaxation phenomena.

Selected Recent Works:

van Lierop, J. and Ryan, D.H. Spin dynamics in a frustrated magnet. *Physical Review Letters* **86**, 4390-4393 (2001).

Shengelaya, A. *et al.* Giant oxygen isotope effect on the spin glass transition in $La_{2-x}Sr_xCu_{1-z}Mn_zO_4$ as revealed by muon spin rotation. *Physical Review Letters* **83**, 5142-5145 (1999).

Keren, A., Mendels, P., Campbell, I.A. and Lord, J. Probing the spin-spin dynamical autocorrelation function in a spin glass above T_g via muon spin relaxation. *Physical Review Letters* **77**, 1386-1389 (1996).

Lappas, A. *et al.* Spontaneous magnetic ordering in the fullerene charge-transfer salt (TDAE)C_{60}. *Science* **267**, 1799-1801 (1995).

Frustrated Spin Systems

There is currently much active research on random and/or geometrically frustrated spin systems, where the magnetic ions occupy the vertices of edge or corner sharing triangular units. In these cases the natural magnetic coupling between ions is geometrically frustrated, while the translational symmetry of the lattice is preserved. Such systems pose formidable theoretical and experimental barriers to effective understanding.

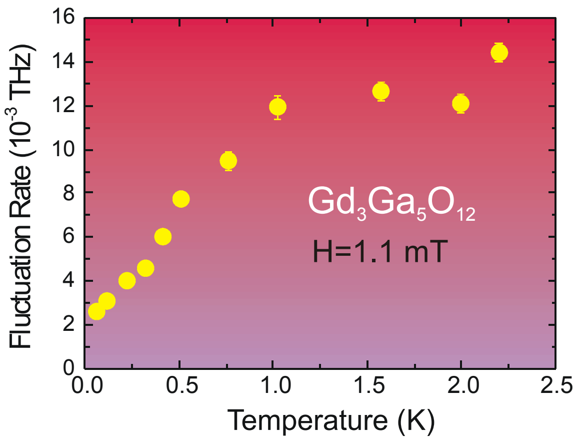
The μSR technique has been particularly effective at elucidating spin dynamics occurring over a broad range of frequencies (between 10^4 - 10^{11} Hz), extending the range accessible with neutron scattering, NMR or magnetic susceptibility. μSR studies have shown that (in contrast to canonical spin systems) dynamic spin fluctuations persist at zero temperature in many geometrically frustrated systems — suggesting that quantum spin fluctuations play an important role.

Selected Recent Works:

Hodges, J. *et al.* First-order transition in the spin dynamics of geometrically frustrated $Yb_2Ti_2O_7$. *Physical Review Letters* **88**, 077204 (2002).

Keren, A. *et al.* Magnetic dilution in the geometrically frustrated $SrCr_{9p}Ga_{12-9p}O_{19}$ and the role of local dynamics: A muon spin relaxation study. *Physical Review Letters* **84**, 3450-3453 (2000).

Gardner, J.S. *et al.* Cooperative paramagnetism in the geometrically frustrated pyrochlore antiferromagnet $Tb_2Ti_2O_7$. *Physical Review Letters* **82**, 1012-1015 (1999).



In contrast to other experimental methods, LF-μSR measurements of the geometrically frustrated antiferromagnet $Gd_3Ga_5O_{12}$ clearly show that the Gd spins fluctuate near zero temperature [Dunsiger *et al.*, Physical Review Letters **85**, 3504 (2000)].

Colossal Magnetoresistance

"Colossal" magnetoresistance (CMR), whereby the electrical resistance of a material changes by orders of magnitude in the presence of an external magnetic field, occurs in certain manganese-oxide compounds. This property makes these materials appealing for future use in a wide range of electronic devices, such as read heads for hard disks, magnetic storage and sensing devices. Furthermore, CMR materials have drawn a great deal of attention over the last several years as archetypal examples of materials in which the spin, charge and lattice degrees of freedom are tightly coupled.

The μSR technique has provided important, new information on the spin dynamics in these systems, that can be combined with the structural and transport information obtained by other experimental methods — completing in part the spin-charge-lattice measurement triad. Among the most interesting findings is the existence of spatial inhomogeneity in the spin dynamics. Because these systems are very sensitive to applied magnetic fields (hence the origin of the "CMR" appellation), the ability to carry out μSR experiments in zero applied field, unlike in the case of NMR, for example, is a distinct advantage.

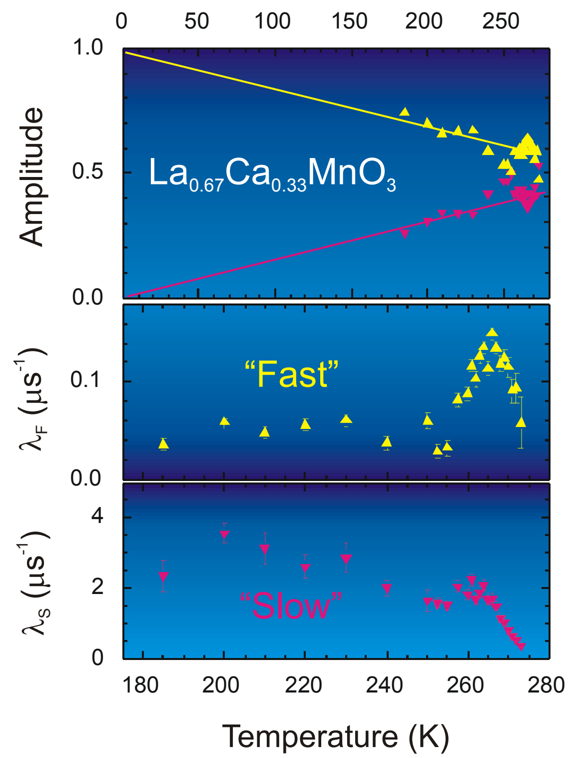
Selected Recent Works:

Allodi, G. *et al.* Ultraslow polaron dynamics in low-doped manganites from ^{139}La NMR-NQR and muon spin rotation. *Physical Review Letters* **87**, 127206 (2001).

Heffner, R.H. *et al.* Observation of two time scales in the ferromagnetic manganite $La_{1-x}Ca_xMnO_3$, $x \approx 0.3$. *Physical Review Letters* **85**, 3285-3288 (2000).

Bewley, R.I. *et al.* Muon-spin-relaxation studies of magnetic order and dynamics of the $n = 2$ Ruddlesden-Popper phases $Sr_2RMn_2O_7$ (R = Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho). *Physical Review B* 60, 12286-12293 (1999).

Heffner, R.H. *et al.* Effects of reduced dimensionality on spin dynamics in the layered perovskite $La_{1.4}Sr_{1.6}Mn_2O_7$. *Physical Review Letters* **81**, 1706-1709 (1998).



ZF-μSR measurements of the CMR material $La_{0.67}Ca_{0.33}MnO_3$ reveal two spatially separated regions that possess very different Mn-ion spin dynamics [Heffner *et al.*, Physical Review Letters **85**, 3285 (2000)].

Low-Dimensional Systems

The combination of μSR and inelastic neutron scattering makes it possible to determine the ground state spin configuration and spin dynamics of low-dimensional materials such as spin-ladder, spin-Peierls and Haldane gap systems. These systems are composed of magnetic atoms that, in contradiction to the expectations of classical physics, may not display spin freezing at zero temperature. This may be due to either quantum fluctuations, as in true one-dimensional or frustrated spin systems, or the formation of a quantum mechanical singlet ground state. ZF-μSR is *unparalleled* in its ability to determine the presence or absence of small static magnetic fields. Thus, if μSR detects no static magnetic fields within the sample at low temperatures, then the spins have not frozen, and the system must be either fluctuating or in a singlet state. Inelastic neutron scattering measurements can determine the presence or absence of an energy gap in the ground state. The combination of these two techniques is an extremely powerful way to probe possible singlet ground state systems.

Selected Recent Works:

Carretta, P. *et al.* Very-low-frequency excitations in frustrated two-dimensional S=1/2 Heisenberg antiferromagnets. *Physical Review Letters* **88**, 047601 (2002).

Larkin, M.I. *et al.* Crossover from dilute to majority spin freezing in two leg ladder system Sr(Cu, Zn)$_2$O$_3$. *Physical Review Letters* **85**, 1982-1985 (2000).

Kojima, K.M. *et al.* Antiferromagnetic order with spatially inhomogeneous ordered moment size of Zn- and Si-doped CuGeO$_3$. *Physical Review Letters* **79**, 503-506 (1997).

Heavy Fermion Systems

Heavy fermion compounds containing rare earth elements such as Ce or Yb, or actinide elements such as U, have charge carriers with effective masses several hundred times the mass of a bare electron. These systems are characterized by a wealth of different ground states, arising from the Kondo interaction between localized *f*-electronic moments and itinerant conduction electrons. At low temperatures, some of the materials exhibit complex magnetic behavior, while others display superconductivity. Theoretical interpretations of these systems push the limits of Fermi-liquid theory. Due to its extreme sensitivity to small internal magnetic fields and its ability to provide information on spatially inhomogeneous magnetism, the μSR technique has greatly improved our understanding of heavy-fermion systems. The μSR method has been used to identify magnetic order in these systems, detect extremely small magnetic moments beyond the sensitivity of other techniques and provide detailed information on the hybridization between localized and conduction electrons via μ^+-Knight shift measurements.

Selected Recent Works:

Krishnamurthy, V.V. *et al.* Non-Fermi liquid spin dynamics in CeCoGe$_{3-x}$Si$_x$ for x = 1.2 and 1.5. *Physical Review Letters* **88**, 046402 (2002).

MacLaughlin, D.E. *et al.* Glassy spin dynamics in non-Fermi liquid UCu$_{5-x}$Pd$_x$, x = 1.0 and 1.5. *Physical Review Letters* **87**, 066402 (2001).

Kalvius, G.M., Noakes, D.R. and Hartmann, O. μSR studies of rare earth and actinide magnetic materials, in G.H. Lander, K.A. Gschneider and L.Eyring (eds.), Handbook on the Physics and Chemistry of Rare Earths (Elsevier, 2001), Vol. 32, p.55.

Yaouanc, A. *et al.* Evidence for a two component magnetic response in UPt$_3$. *Physical Review Letters* **84**, 2702-2705 (2000).

Amato, A. Heavy-fermion systems studied by the μSR technique. *Reviews of Modern Physics* **69**, 1119-1179 (1997).

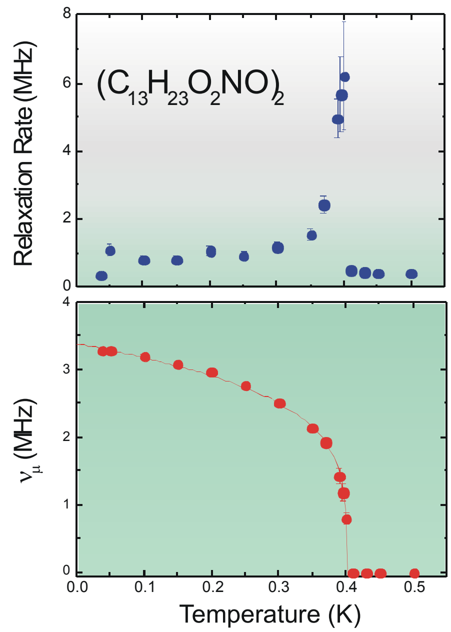
Quasicrystals

Quasicrystals are solid materials that display long-range orientational order without translational periodicity, generating neutron diffraction patterns with five- and ten-fold (or other) point symmetries not allowed by any crystalline space groups. Their very existence expands the conventional definition of a crystal lattice. Together μSR and neutron scattering have been used to provide a detailed picture of the magnetic correlations in these systems.

Selected Recent Works:

Noakes, D.R., Kalvius, G.M. and Hartmann, O. Random anisotropy causes wide distribution of relaxation rates in Tb-Mg-Zn quasicrystals and amorphous DyAg. *Physical Review B* **11**, 132413 (2002).

Noakes, D.R. *et al.* Spin dynamics and freezing in magnetic rare-earth quasicrystals. *Physics Letters A* **238**, 197-202 (1998).



Zero-field μSR measurements in the organic metamagnet TANOL suberate ($C_{13}H_{23}O_2NO_2$) show that the ordered magnetic state is characteristic of a two-dimensional magnet. [Blundell *et al.*, Physica B **289-290**, 116 (2000)].

Molecular Magnets & Clusters

Molecular-based magnets are a relatively new class of synthetic materials, made up of nanometer-size molecules containing a handful of interacting magnetic ions. A versatile feature of these systems is that chemists can modify the magnetic interactions within and between neighboring molecules in a controlled manner. Inorganic materials composed of well-defined clusters of magnetically active atoms are also of great current interest. There are numerous anticipated technological and biomedical applications of molecular magnets, such as components of quantum computing, photonic switches, catalysts, magnetic filtering of blood and the enhancement of magnetic resonance imaging signals. A high priority in this new field is the determination of the local magnetic properties. As a unique local probe of magnetism, μSR is being used more and more to provide microscopic information on the static and dynamical magnetic properties of these systems. Future studies of molecular magnets with the μSR technique will contribute significantly to the development and optimization of their magnetic properties.

Selected Recent Works:

Le, L.P. *et al.*, Dynamic spin fluctuations in the molecular ferromagnet (DmeFc)(TCNE). *Physical Review B* **65**, 024432 (2001).

Gatteschi, D., Carretta, P. and Lascialfari, A. Molecular magnets and magnetic nanoparticles: new opportunities for μSR investigations. *Phyisca B* **289-290**, 94-105 (2000).

Jestädt, Th. *et al.* Layered transition metal molecular magnets studied with implanted muons. *Synthetic Metals* **103**, 2325 (1999).

Lascialfari, A., *et al*. Thermal fluctuations in the magnetic ground state of the molecular cluster $Mn_{12}O_{12}$ acetate from μSR and Proton NMR. *Physical Review Letters* **81**, 3773-3776 (1998)

Superconductors

The discovery of high-temperature (high-T_c) cuprate superconductors in 1986 fueled a flurry of worldwide research activity, due to the potential widespread applications of these materials and the "new physics" that they may hold. At the forefront of this research have been experimental investigations with the μSR technique, studying a wide range of phenomena in many different classes of superconductors.

Magnetic Phases & Phase Separation

Shortly after the discovery of high-T_c superconductors, ZF-μSR provided the first evidence for static magnetic order in the undoped parent compound La_2CuO_4. Since then μSR has played a major role in determining magnetic phase diagrams, particularly in high-T_c and heavy-fermion systems.

The interplay of superconductivity and magnetism on a microscopic scale is a central theoretical and experimental issue in condensed matter physics. Because of its high sensitivity to small internal magnetic fields and its ability to determine the volume fraction of magnetic phases, μSR is ideally suited to addressing this fundamental issue. For example, a μSR investigation of the ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ showed that the ferromagnetic phase in this material is homogeneous on a microscopic scale and is unaltered by the formation of superconductivity. On the other hand, a μSR study showed that magnetic order and superconductivity compete rather than coexist at a microscopic level in the heavy-fermion material $CeCu_{2.2}Si_2$.

Selected Recent Works:

Kanigel, A. *et al.* Common energy scale for magnetism and superconductivity in underdoped cuprates: a muon spin resonance investigation of $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$. *Physical Review Letters* **88**, 137003 (2002).

Klauss, H.H. *et al.* From antiferromagnetic order to static magnetic stripes: the phase diagram of $(La,Eu)_{2-x}Sr_xCuO_4$. *Physical Review Letters* **85**, 4590-4593 (2000).

de Visser, A. *et al.* Magnetic quantum critical point and superconductivity in UPt_3 doped with Pd. *Physical Review Letters* **85**, 3005-3008 (2000).

Niedermayer, Ch., *et al.* Common phase diagram for antiferromagnetism in $La_{2-x}Sr_xCuO_4$ and $Y_{1-x}Ca_xBa_2Cu_3O_6$ as seen by muon spin rotation. *Physical Review Letters* **80**, 3843-3846 (1998).

Bernhard, C. *et al.* Coexistence of ferromagnetism and superconductivity in the hybrid ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ studied by muon spin rotation and dc magnetization. *Physical Review B* **59**, 14099-14107 (1999).

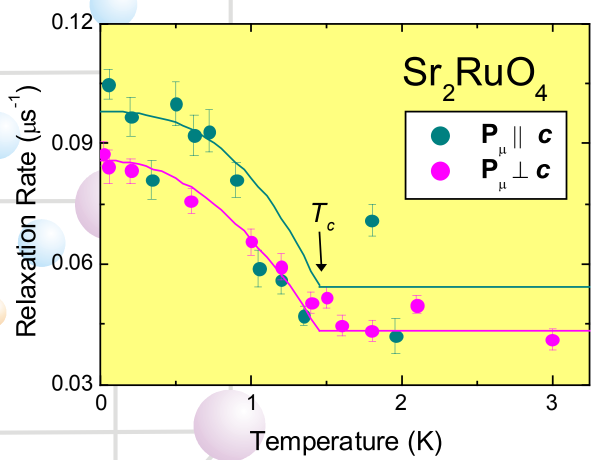
Nachumi, B. *et al.* Muon spin relaxation studies of Zn-substitution effects in high- T_c cuprate Superconductors. *Physical Review Letters* **77**, 5421-5424 (1996).

Luke, G.M. *et al.* Competition between magnetic order and superconductivity in $CeCu_{2.2}Si_2$. *Physical Review Letters* **73**, 1853–1856 (1994).

Weak Magnetism

An important application of the μSR technique in the study of unconventional superconductors is the detection of weak magnetism that is beyond the sensitivity of other experimental probes. The breaking of time-reversal symmetry (TRS) in certain unconventional superconductors results in the formation of static internal magnetic fields in the superconducting phase. Since the spontaneous fields are extremely small (of the order of 0.1 to 1.0 G), the muon is the only probe that has enough sensitivity to detect them. Evidence for TRS breaking has been found using ZF-μSR in several different types of superconductors.

Recently, ZF-μSR measurements of the high-T_c superconductor $YBa_2Cu_3O_{6+x}$ have revealed the presence of extremely weak magnetism at high doping concentrations. While the origin of the weak magnetism is most likely related to charge segregation, this study emphasizes the extreme sensitivity of the muon and its value as a local probe.



Zero-field (ZF) relaxation rate in Sr_2RuO_4 with the initial muon spin polarization perpendicular and parallel to the c-axis of the crystal. [Luke *et al.*, Nature **394**, 558 (1998)].

Selected Recent Works:

Sonier, J.E. *et al.* Anomalous weak magnetism in superconducting $YBa_2Cu_3O_{6+x}$. *Science* **292**, 1692-1695 (2001).

Luke, G.M. *et al.* Time-reversal symmetry-breaking superconductivity in Sr_2RuO_4. *Nature* **394**, 558-561 (1998).

Vortex Phases

In a sizeable applied magnetic field a type II superconductor is characterized by a large internal field inhomogeneity due to the penetration of quantized flux lines, called *vortices*. In general, this field distribution is a function of both space and time. Today there is much interest in the study of this unique phase of matter in unconventional systems, such as the high-T_c, borocarbide, organic and heavy-fermion superconductors. μSR and small-angle neutron scattering (SANS) have been two very important techniques used in the investigation of the structure of vortices within the bulk of superconductors. In addition to studies of the ideal periodic array of vortices in clean samples, these techniques can be used to investigate vortex fluctuations, pinning, melting, and decomposition of the flux lines into two-dimensional "pancake" vortices. With μSR one can also probe vortices at the surface of a superconductor using ultra-low energy muons. An experiment of this nature has provided the first experimental evidence that the size of a vortex increases near the surface of a superconductor.

Selected Recent Works:

Miller, R.I. *et al.* Evidence for static magnetism in the vortex cores of ortho-II $YBa_2Cu_3O_{6.50}$. *Physical Review Letters* **88**, 137002 (2002).

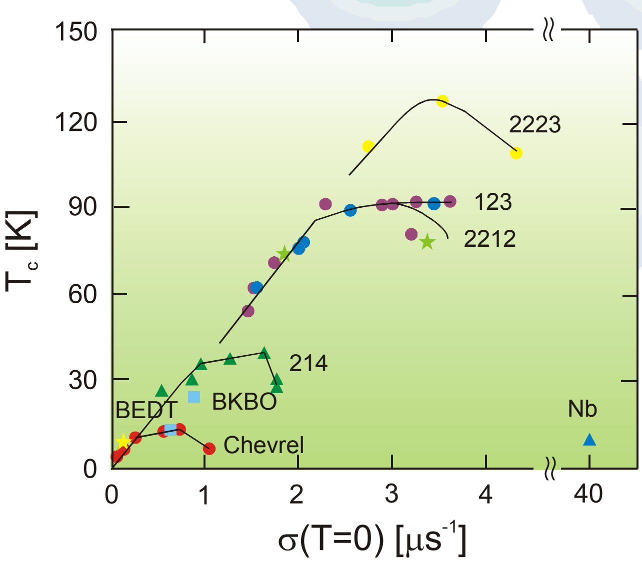
Sonier, J.E., Brewer, J.H. and Kiefl, R.F. μSR studies of the vortex state in type-II superconductors. *Reviews of Modern Physics* **72**, 769-811 (2000).

Blasius, T. *et al.* Evidence for a two-stage melting transition of the vortex matter in $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ single crystals obtained by muon spin rotation. *Physical Review Letters* **82**, 4926-4929 (1999).

Niedermayer, Ch. *et al.* Direct observation of a flux line lattice field distribution across an $YBa_2Cu_3O_{7-\delta}$ surface by low energy muons. *Physical Review Letters* **83**, 3932-3935 (1999).

Kossler, W.J. *et al.* Transparency of the *ab* planes of $Bi_2Sr_2CaCu_2O_{8+\delta}$ to magnetic fields. *Physical Review Letters* **80**, 592-595 (1998).

Lee, S.L. *et al.* Investigation of vortex behavior in the organic superconductor *kappa -(BEDT-TTF)$_2$Cu(SCN)$_2$* using muon spin rotation. *Physical Review Letters* **79**, 1563-1566 (1997).

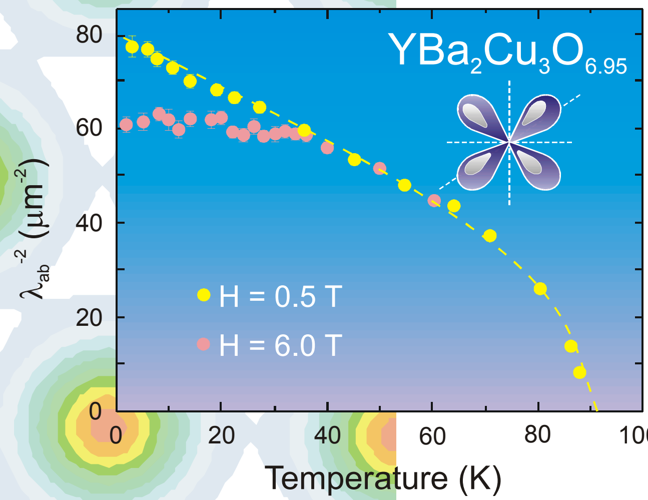


The universal behavior found for the variation of T_c with the TF-μSR depolarization rate σ (the so-called "Uemura plot") was a significant contribution to the field of superconductivity [Uemura *et al.*, Physical Review Letters **66**, 2665 (1991)].

Characteristic Length Scales

The magnetic penetration depth λ is a fundamental length scale that is related to the density and pairing symmetry of the superconducting carriers. Most experimental methods determine the behavior of λ near the sample surface in the so-called *Meissner phase*. However, only a few of these techniques can measure the *absolute* value of λ and most cannot measure values of λ in excess of 1000 nm, as found in several heavy fermion superconductors. Ultra-low energy muons can be used to provide an absolute value of λ determined near the surface of a sample in either the Meissner phase (with no limit on the magnitude of λ) or in the vortex phase. Recently, ultra-low energy muons have been used to provide the first direct experimental proof that magnetic field decays exponentially as a function of distance from the surface of a superconductor, as was first predicted in 1935.

Surface muon beams can also be used to measure λ in the vortex state, but in the *bulk* rather than near the sample's surface. Unlike SANS, the μSR technique can be used to study small uniform crystals. From measurements of this kind, one also obtains information related to the behavior of *individual vortices*. The ability to probe vortices at milli-Kelvin temperatures in the bulk is a great advantage of μSR.



TF-μSR measurements of the magnetic penetration depth λ_{ab} provided early evidence for unconventional *d*-wave pairing of charge carriers in the vortex state of high-T_c superconductors [Sonier *et al.*, Physical Review Letters **72**, 744 (1994) & **83**, 4156 (1999)].

Selected Recent Works:

Bernhard, C.J. *et al.* Anomalous peak in the superconducting condensate density of cuprate high-T_c superconductors at a unique doping state. *Physical Review Letters* **86**, 1614-1617 (2001).

Miller, R.I. *et al.* Low temperature limit of the vortex core radius and the Kramer-Pesch effect in $NbSe_2$. *Physical Review Letters* **85**, 1540-1543 (2000).

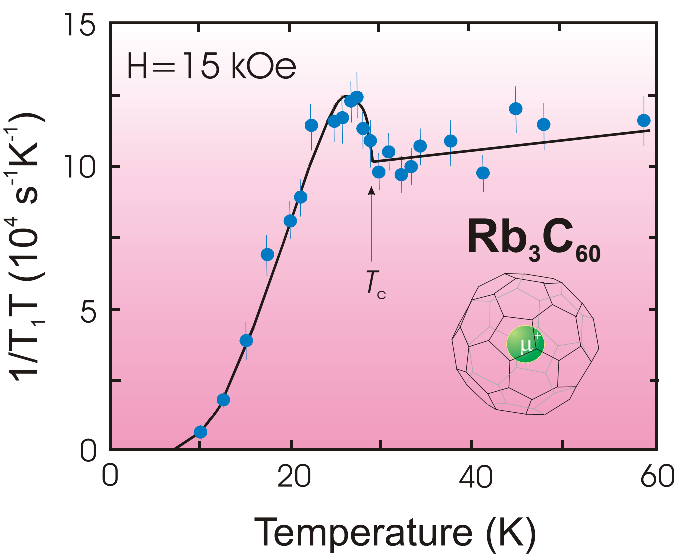
Jackson, T.J. *et al.* Depth-resolved profile of the magnetic field beneath the surface of a superconductor with a few nm resolution. *Physical Review Letters* **84**, 4958-4961 (2000).

Sonier, J.E. *et al.* Field induced reduction of the low-temperature superfluid density in $YBa_2Cu_3O_{6.95}$. *Physical Review Letters* **83**, 4156-4159 (1999).

Pairing Properties

In certain systems there are yet other ways the μSR technique can be used to provide information on the nature of the superconducting state. The sizeable μ^+-Knight shift observed in heavy-fermion superconductors can be used to study the change in the local static spin susceptibility below T_c due to the formation of Cooper pairs. TF-μSR measurements of this nature have provided new information on the symmetry of the Cooper pair wave function in several of these systems.

In fulleride superconductors a fraction of the implanted μ^+ form muonium inside the C_{60} cage (*i.e. endohedral* Mu). The electron bound to the μ^+ undergoes frequent spin flips due to coupling with the *quasiparticles*. The enormous enhancement of the spin-lattice relaxation rate ($1/T_1$) of the Mu over that typical of the nuclei probed with NMR, provided the first clear evidence for a *Hebel-Slichter peak* — characteristic of a classic BCS superconductor.



Muon spin relaxation in Rb_3C_{60} resulting from the interaction of muonium with quasiparticles revealed a "Hebel-Slichter peak" below T_c. This feature which had not been observed with NMR indicates that fullerenes are conventional BCS superconductors. [Kiefl *et al.*, Physical Review Letters **70**, 3987 (1993)].

Selected Recent Works:

Sonier, J.E. *et al.* μ^+ Knight shift measurements in $U_{0.965}Th_{0.035}Be_{13}$ single crystals. *Physical Review Letters* **85**, 2581-2824 (2000).

Kiefl, R.F. *et al.* Coherence peak and superconducting energy gap in Rb_3C_{60} observed by muon spin relaxation. *Physical Review Letters* **70**, 3987-3990 (1993).

Transport

The transport of neutral or charged particles in matter is an important mechanism for various physical, chemical and biological phenomena:

Quantum Diffusion

With a mass intermediate between an electron and a proton, the positive muon (μ^+) and muonium (Mu) atom are ideal particles for investigating the phenomenon of *quantum diffusion* at low temperatures. The development of modern theories of quantum tunneling of light interstitials has had as its root cause the motivational information provided by μSR experiments that are extremely sensitive to the μ^+ and Mu mobilities. Studies in solids have revealed band-like motion of particles at low temperatures and the dependence on interactions with crystalline imperfections and lattice excitations in materials.

Selected Recent Works:

Kadono, R., Higemoto, W., Nagamine, K. and Pratt, F.L. An atom in the Bloch state. *Physical Review Letters* **83**, 987-990 (1999).

Storchak, V.G. *et al.* Destruction of bandlike propagation in orientationally ordered crystals. *Physical Review Letters* **82**, 2729-2732 (1999).

Kadono, R. *et al.* Quantum diffusion of the positive muon in superconducting tantalum. *Physical Review Letters* **79**, 107-110 (1997).

Electron Transport in Non-Metals

Many nonconducting materials become ionized in high electric fields, resulting in an excess of "free" electrons. The material then becomes conducting. This phenomenon, known as *electrical breakdown* is a serious problem for high-voltage equipment, such as power transformers, because the high voltage cannot be maintained as charge flows through the insulating material. The μSR technique has provided detailed knowledge about the transport mechanisms of radiolysis electrons in insulators by way of quantitative measurements of the mobility of charge carriers liberated in the muon's ionization track. An electric field (EF) μSR technique has been applied to various rare gas (Ne, Ar and Xe) solids ("cryocrystals") to study the effects of electric field on the formation of muonium arising from radiolysis electrons that have enough mobility to reach the stopped μ^+. These studies have direct consequences for the design of rare-gas charged particle detectors. The EF-μSR method has also been extended to the investigation of muonium formation via transport of radiolysis electrons in more conventional insulators and semiconductors, such as sapphire, quartz, Si and GaAs.

Selected Recent Works:

Storchak, V.G. *et al.* Electron localization in a disordered insulating host. *Physical Review Letters* **85**, 166-169 (2000).

Storchak, V.G. *et al.* Muonium formation via electron transport in solid nitrogen. *Physical Review B* **59**, 10559-10572 (1999).

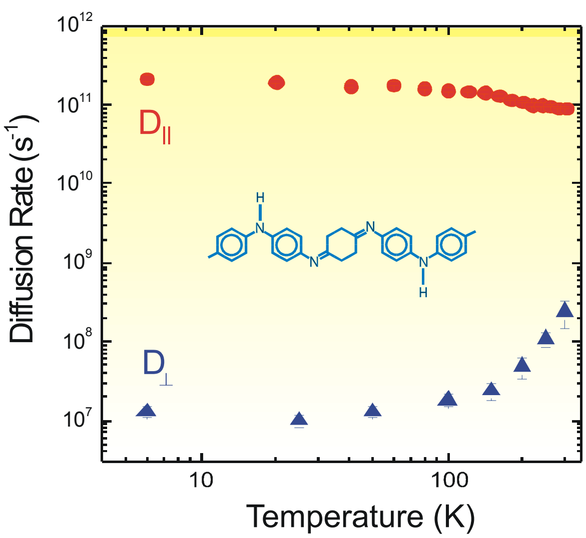
Conducting Polymers

The μSR technique is well suited to probe local charge transport processes in conducting polymers. The pliability and unique electronic and optoelectronic properties of these polymers make them candidates for such uses as in plastic solar cells, solid-state lasers and flexible light-emitting diodes The increasing technological importance of these materials is driving a large effort in industry to improve their stability, lifetime, and efficiency. In the undoped state of a conducting polymer such as polyphenylenevinylene (PPV), muon implantation leads to the formation of a highly mobile negative polaron through the reaction of muonium with the polymer chains. Measurements of the intra-chain and inter-chain polaron diffusion rates are of fundamental importance in the development of these synthetic conductors, contributing significantly to our understanding of the charge transport mechanisms.

Selected Recent Works:

Blundell, S.J. *et al*. Muon-spin relaxation study of charge carrier dynamics in the conducting polymer PPV. *Synthetic Metals* **119**, 2005 (2001).

Pratt, F.L. *et al.* Anisotropic polaron motion in polyaniline studied by muon spin relaxation. *Physical Review Letters* **79**, 2855-2858 (1997).



The anisotropic diffusion rate of the muon-generated negative polaron in polyaniline both along and between polymer chains. The on-chain diffusion rate is limited by scattering from the phenylene ring librational modes above 150K, and by defect scattering at low temperatures [Pratt *et al.*, Synthetic Metals **101**, 323 (1999)].

Ion Mobility

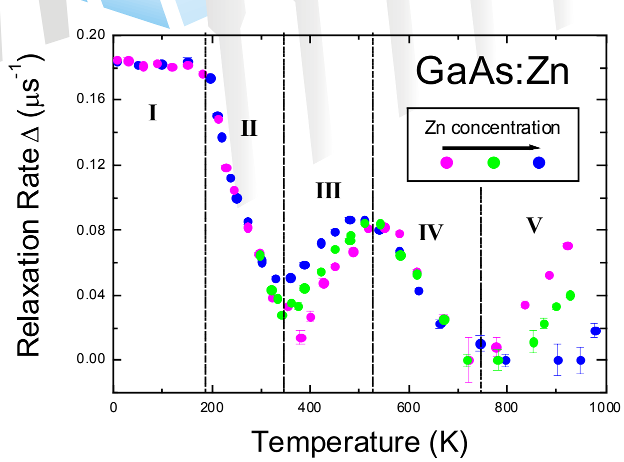
The μSR technique may be used to study ion mobility in materials by monitoring changes in the relaxation of the muon spin by the nuclear magnetic moment of the ion. μSR has been used to determine the mobility of Li^+ ions in $Li_x[Mn_{1.96}Li_{0.04}]O_4$. Such Li-based compounds are promising for use as cathodes materials in rechargeable batteries. The μSR measurements indicate that the onset temperature of Li^+ diffusion can be varied with changes in Li concentration and thus provide information relevant to optimizing battery performance.

Selected Recent Works:

Kaiser, C.T. *et al*. Li mobility in the battery cathode material $Li_x[Mn_{1.96}Li_{0.04}]O_4$ studied by muon-spin relaxation. *Physical Review B (Rapid Communication)* **62**, R9236 (2000).

Semiconductors

As a trace impurity atomic hydrogen (H) can have a profound effect on the electronic properties of semiconductors. It can "passivate" the electrical activity of donors and acceptors in crystalline semiconductors, "hydrogenate" dangling bonds in amorphous semiconductors and can even display its own electrical activity — all of which are important in the process of semiconductor fabrication. For low hydrogen concentrations microscopic details of how these processes occur are not accessible by standard magnetic resonance techniques. Isolated atomic hydrogen is nearly impossible to detect because of its high diffusivity and reactivity with other defects. Most of the experimental information on isolated hydrogen in technologically important semiconductors comes from μSR studies of muonium ($Mu \equiv \mu^+e^-$) which can exist in three charge states (Mu^0, Mu^+ and Mu^-) corresponding to the three distinct charge states of isolated hydrogen (H^0, H^+ and H^-) in semiconductors. As an experimental model for isolated hydrogen, μSR studies of semiconductors are the primary source of detailed information on the site migrations and dynamics of the charge states and how muonium diffuses and interacts with charge carriers.



"Trapping peaks" are observed in the ZF-μSR relaxation rate for the heavily doped p-type semiconductor GaAs:Zn, where positively charged muonium (Mu^+) diffuses fast enough to find the Zn acceptor atoms [Chow *et al.*, Physical Review Letters **87**, 216403 (2001)].

Selected Recent Works:

Chow, K.H. *et al.* Muonium analog of hydrogen passivation: observation of the Mu^+-Zn^- reaction in GaAs. *Physical Review Letters* **87**, 216403 (2001).

Cox, S.F.J. *et al.* Experimental confirmation of the predicted shallow donor hydrogen state in zinc oxide. *Physical Review Letters* **86**, 2601-2604 (2001).

Chow, K.H. *et al.* Novel behavior of bond-centered muonium in heavily doped *n*-type silicon: Curie-like spin susceptibility and charge screening. *Physical Review Letters* **84**, 2251-2253 (2000).

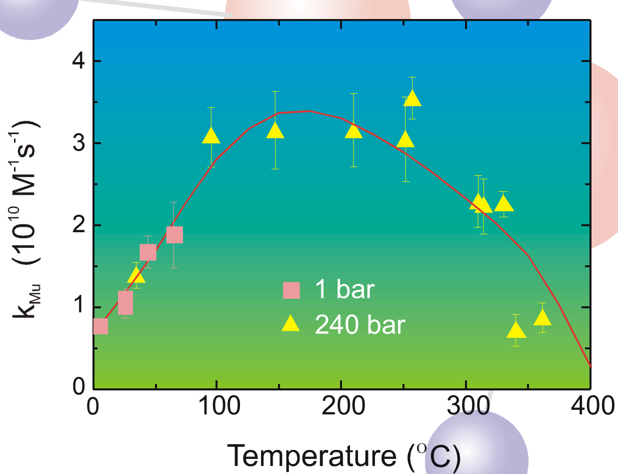
Gil, J.M. *et al.* Novel muonium state in CdS. *Physical Review Letters* **83**, 5294-5297 (1999).

Chemistry

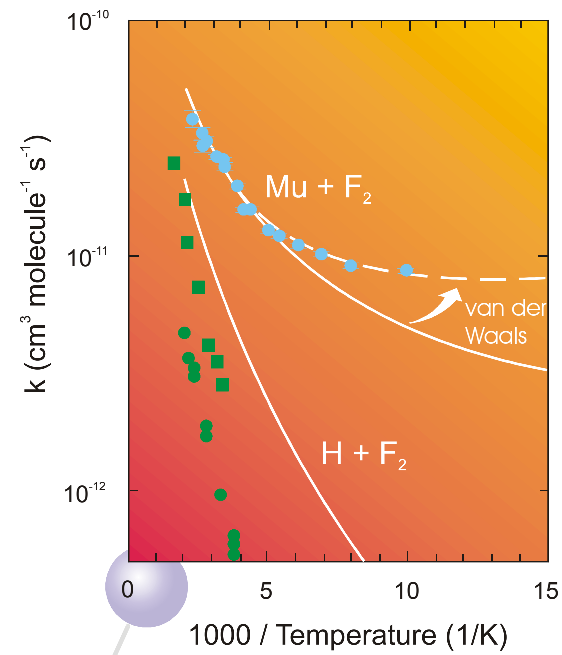
The hydrogen atom (H) is the lightest of all atoms and arguably one of the most important building blocks in chemistry. The study of the ultra-light H isotope muonium (Mu) has therefore had a major impact on those fields of physical chemistry that are concerned with understanding the roles of hydrogen and its reactions.

Chemical Reaction Kinetics and H Isotopes

The study of Mu reactivity provides unique tests of reaction theory, both in terms of zero-point energy shifts at the transition state and quantum tunneling. For example, the rate of the reaction Mu + H_2 → MuH + H is a fundamental benchmark for theoretical studies of chemical reaction dynamics. Depending on the nature of the reaction, the rate constant for a Mu reaction may be several orders of magnitude larger or smaller than the equivalent reaction of H. There is much current interest within the realm of combustion kinetics and in atmospheric and theoretical chemistry in the study of H(Mu)-atom reactions with O_2, NO, CO, N_2O, NO_2, *etc.*



Rate constants for the reaction of Mu with hydroquinone in water. The solid curve represents a model which takes into account diffusion, activation, and a reaction efficiency which depends on the number of collisions during the encounter lifetime of the reactants. [Ghandi *et al.*, Physical Chemistry Chemical Physics 4, 586-595 (2002)].



Arrhenius plot of the thermal rate constants for the H+F_2 and Mu+F_2 reactions. Comparison of theoretical calculations (solid and dashed curves) to the experimental rate constants for the Mu+F_2 reaction demonstrated that the van der Waals interaction plays an important role in the low-temperature behaviour of rate constants [Takayanagi & Kurosaki, Journal of Physical Chemistry A **101**, 7098-7104 (1997)].

Muonium studies in sub- and supercritical water provide unique information on a simple hydrophobic solute (H atom) in water over a wide range of temperature and pressure. The knowledge gained from studies of muonium reaction kinetics under such extreme conditions is required for the development of supercritical water reactors for the destruction of toxic waste, and is relevant to the radiation chemistry which occurs in the cooling cycle of pressurized water nuclear reactors.

Selected Recent Works:

Lossack, A.M., Roduner, E. and Bartels, D.M. Solvation and kinetic isotope effects in H and D abstraction reactions from formate ions by D, H and Mu atoms in aqueous solution. *Physical Chemistry Chemical Physics* **3**, 2031-2037 (2001).

Himmer, U. and Roduner, E. The addition reaction of X to O_2 (X = Mn, H, D): isotope effects in intra- and intermolecular energy transfer. *Physical Chemistry Chemical Physics* **2**, 339-347 (2000).

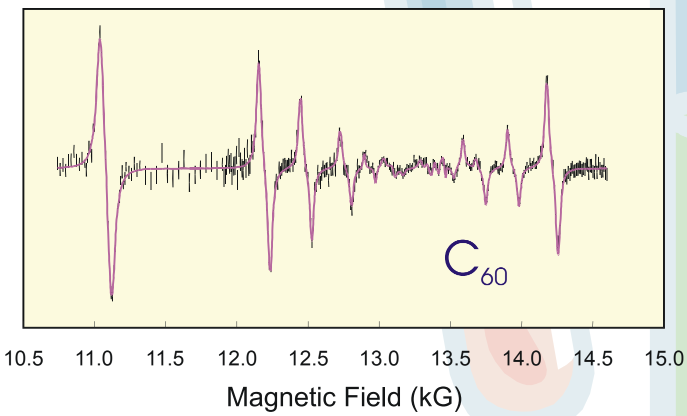
Percival, P.W. *et al.* Muonium in sub- and supercritical water. *Physical Chemistry Chemical Physics* **1**, 4999-5004 (1999).

Dilger, H. *et al.* Kinetics of the gas-phase addition of the ethyl radical and the tert-butyl radical to NO. *Journal of Physical Chemistry A* **102**, 6772 (1998).

Roduner, E. *et al.* Effect of mass on particle diffusion in liquids studied by electron spin exchange and chemical reaction of muonium with oxygen in aqueous solution. *J. Chem. Soc., Faraday Trans.* **91**, 1935 (1995).

Free Radical Systems

Muonium adds readily to double bonds in unsaturated organic molecules. The resultant *free radicals* have easily detected µSR signatures and can be investigated in great detail, whereas their hydrogenated analogues may not even be detectable. Several such radical species have been studied by the µSR technique. Hyperfine constants determined by the µALCR technique provide complementary information to that obtained by ESR. Studies of complex radicals in the gas phase are essentially impossible with conventional ESR, so µSR studies of the corresponding muoniated radical have proved invaluable. Such work has provided information on free radicals in an environment *free* from any "solvent" interactions — an important contribution to the magnetic resonance literature of such systems.



Analysis of the avoided level crossing resonances (µALCR) provides information on the unpaired spin distribution in the free radical formed when Mu (or H) adds to C_{60} [Percival *et al.*, Chemical Physics Letters **245**, 90 (1995)].

Selected Recent Works

Rhodes, C.J. *et al.* Hydrogen radioisotopic labelling studies using muonium: properties of thiyl radicals potentially relevant to cellular membrane damage. *Magnetic Resonance in Chemistry* **38**, S49-S57 (2000).

Rhodes, C.J., Dintinger, T.C. and Scott, C.A. Rates of motion for free radicals in zeolites as directly measured by longitudinal field muon spin relaxation. *Magnetic Resonance in Chemistry* **38**, 62-65 (2000).

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Biological Applications

The extreme sensitivity of the µSR technique to dynamics and weak magnetism makes it a potential tool for obtaining *microscopic* information in biological systems. One application is the study of structural and functional properties of *macro-molecules*. For example the µSR method has been demonstrated to be sensitive to the electron transfer process in the important protein *cytochrome c*. Although used only sparingly thus far for studies of this nature, future exploitation of the µSR technique will likely include increased biological applications.

Selected Recent Works

Cammarere, D. *et al.* First-principles determination of muon and muonium trapping sites in horse heart cytochrome c and investigation of magnetic hyperfine properties. *Physica B* **289-290**, 636-639 (2000).

Nagamine K. *et al.* Intra- and inter-molecular electron transfer in cytochrome c and myoglobin observed by the muon spin relaxation method. *Physica B* **289-290**, 631-635 (2000).

If you would like more details on any of the µSR facilities described in this brochure please visit the following Web sites:

The TRIUMF µSR User Facility ***http://musr.triumf.ca/***
Paul Scherrer Institut (PSI) Laboratory for Muon Spin Spectroscopy ***http://lmu.web.psi.ch/***
The ISIS Pulsed Muon Facility ***http://www.isis.rl.ac.uk/muons/***
KEK Meson Science Laboratory ***http://msl-www.kek.jp/***
The RIKEN-RAL Muon Facility ***http://nectar.nd.rl.ac.uk/~rikenral/***
High Intensity Proton Accelerator Facility ***http://jkj.tokai.jaeri.go.jp/***

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