CHEMISTRY OF MUONS

Sukhvinder Kaur,
Madhuri Pohakar *(S.Y. Chem. Engg.)*

Elementary particles can be divided into two classes on the basis of the spins:

**Bosons* are particles with integer spin in h-bar units.
**Fermions* are particles with odd number half-integer h-bar units of spin. (1/2, 3/2, 5/2...) Matter particles *quarks* and *leptons* are fermions with 1/2 unit of spin.

Antimatter is a material made from anti-particles. Any particle and its antiparticle have identical mass and spin but opposite charges. *Spin* is the angular momentum carried by a particle. For composite particles, the spin is made up from the combination of the spins of the constituents plus the angular momentum of their motion around one-another. For *fundamental particles*, spin is an intrinsic and inherently quantum property.In quantum theories all angular momenta due to motion of one object around another are given as integer multiples of Planck's constant divided by (2/p). This quantity is called *h*-bar and is 6.58 x 10^{-25} GeV seconds.

Matter can be classified as:

Matter

bosons	**fermions**	
	leptons	**quarks**
	1. electron	1. bottom
	2. neutrino	2. charm
	3. *muon*	3. down
	4. tau	4. up
	5. proton	5. strange
	6. neutron	6. top

Muons

What is an elementary particle, which is classified as *anti-* matter and constitutes the main component of our exposure to cosmic rays on earth good for in chemistry? Its microsecond lifetime makes it too elusive to allow the production of bottles of new compounds.Nevertheless, as will be shown here, the exotic particle forms the nucleus of an atom which is chemically well behaved. It can be substituted for protons in molecules where it acts as a spy, radiating off information of interest to the chemist.

A muon is a lepton – a fundamental particle that does not interact strongly with other particles and belongs, formally to the 'electron' category.As chemical species, however muons may behave as electrons or as protons, depending on their charge. Thus there are 2 types of muons:

1. The *negative muon*, acts like a heavy electron, i.e., its mass is 207 times of that of an electron and has the same spin as that of an electron. It has finite lifetime of 2.2 microseconds.It decays in reaction:

$$\mu \rightarrow e^- + \upsilon_e + \upsilon_\mu$$

2. The *positive muon*, on the other hand, is more of a light proton than a heavy positron. It is a particle with a mass of 1/9 th the proton mass, with spin half and an associated magnetic moment, which is 3.18 times the proton moment, and a lifetime of 2.2 microseconds. It decays in the reaction:

$$\mu^+ \rightarrow e^+ + \nu_e + \nu^-_\mu$$

The positive muon together with a negative electron forms an atom that is normally dubbed 'muonium' (μ^+e^-). Muonium (Mu) is equivalent to protium (pe) - the lightest isotope of hydrogen and shows the chemical properties of a protium atom, undergoing both H-atom abstraction and addition reactions. *Thus muonium atom can be regarded as an ultra-light isotope of hydrogen.*

Muon Production:

Although muons exist in cosmic radiation, very high fluxes are required for research purpose which are obtained by bombarding a target of suitable material (carbon or beryllium) with medium energy protons from a particle accelerator. Among the products of the ensuing nuclear reactions are pions, π^+, the binding components of nuclei ; these decay on a nanosecond timescale to muons , μ^+, which may be implanted into matter to study the magnetic properties of solid - state , liquid - phase and gas – phase systems .Highly specialised

factories are required to produce intense beams of muons. These are called meson factories. Some of them are the Paul Scherrer Institute in Switzlerland, the Rutherford Appleton Laboratory in the U.K, TRIUMF (Canada) , KEK (Japan) , LAMPF (US).

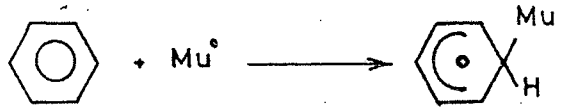
The decay of pions produces muon by the following reaction:

$$\pi^{+} \rightarrow \mu^{+} + \nu_{H}$$

The muon from pion decay is forced to have negative helicity i.e its spin always points in the direction opposite to its momentum. This is of great significance experimentally, for it ensures that a muon beam coming off in a given direction from pion decay at rest will be 100 % polarized opposite to its momentum.

Need for Research

Despite its discovery 60 years ago as a component of cosmic radiation, most chemists would probably not recognise the muon as a constituent of atoms and molecules. However muons are subject to Coulomb force that governs chemistry, and so may be considered quite legitimately as part of an atom, just like protons and electrons. The negative muon finds little application in chemistry, but are used in nuclear structure research and to promote nuclear fusion. Also muonium can be used to study kinetics and regioselectivities of hydrogen atom reactions It reacts with unsaturated bonds by addition, as in:



MUONATED CYCLOHEXADIENYL RADICAL

$$R_2C{=}S + M\dot{u} \longrightarrow R_2C(M\dot{u})-\dot{S}$$

MUONATED THIYL RADICAL.

leaving thereby the muon as a polarized spin label chemical bound in a free radical. In this way it has proven particularly useful for the investigation of structure, reaction kinetics, and reorientational dynamics of organic radicals.

The availability of positive muon in the form of energetic beams with a spin polarization close to 100% at the ports of suitable accelerators led to its successful application as a magnetic probe in matter. The experimental technique has been termed as **μSR**, which stands for **Muon Spin Rotation**.

The two main applications of muons can be explained as follows:

1.Muon Catalysed Fusion:

To ensure enough energy for the future while preserving the environment our civilization must invest in long term basic research. A conventional method to obtain fusion is to merge atomic nuclei at enormous temperatures (some hundred million degrees) and / or pressures, in the so called plasma. In contrast, muon catalysed fusion (μCF) may proceed at terrestrial temperatures and pressures, and therefore the apparent difficulties with plasma heating and confinement are avoided. In this method, fusion reactions are spontaneously catalysed by negative muons in a cold (less than 1200 K) mixture of deuterium and tritium, via formation of muonic molecules such as dtμ. These molecules are held together by chemical bonding induced by muons instead of electrons.

The most important feature of muonic species is their compact size caused by the large mass of the muon. Since the molecular dimensions are inversely proportional to the reduced mass of the binding particle, the muonic molecules are ~ *200 times smaller than* the ordinary (electronic) ones, and have very high vibrational energy. The closely vibrating nuclei can overcome the repulsive Coulombic barrier and enter the strong force interaction range, with fusion as a result. After the fusion event, the muon becomes free and can continue to catalyse new fusions, each releasing an energy of 17.6 MeV. Because the muon can be 'reused', it can trigger the release of energy which greatly exceeds its own rest mass .One gram of muons can yield an energy equivalent to conventional chemical burning of 1000 tons of matter!

The number of fusions of muon can create during its short lifetime depends on the molecular formation rate, or, since this is not a one step process, on a series of microscopic reaction rates which jointly determine the time between consecutive fusions.

1.1. The μCF Chain

(The course of events)

1.1.1 Formation of Muonic Atom: When a short – lived muon enters the deuterium – tritium mixture, the race against time begins .In less than a nanosecond muonic atoms dm or tm are formed.

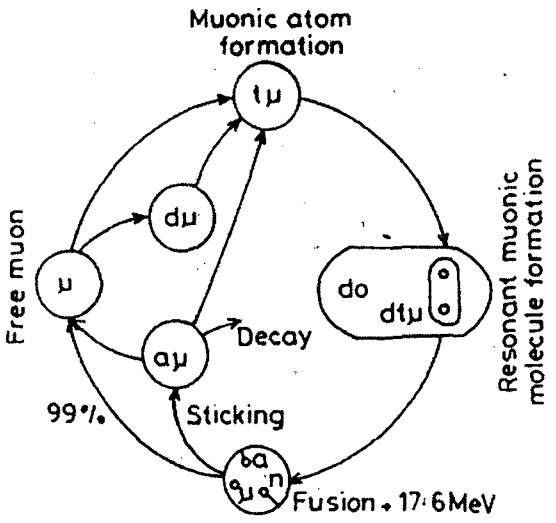


Fig.1. (The mCF Chain)

The muonic atom formation occurs in three steps:

1.1.1.a. *Muon stopping* : In order to be captured the muon must first slow down from its initial velocity characteristic pion decay (E = 4.3 MeV) or a beam injection device to a velocity comparable to that of hydrogenic electrons.

In case of repeated fusion event the initial motion of muon stems from dtμ decay

$$dt\mu \rightarrow \alpha + n + \mu$$

whereby muon typically gains a velocity of ~ 2a.u. (atomic units of time) corresponding to an energy of E ~ 10Kev.The inelastic scattering does not contribute appreciably to muon stopping .The energy loss is caused mainly by excitation and ionisation of the hydrogenic target.

1.1.1.b. *Muon capture*: Muons can replace electrons in ordinary atoms, forming muonic atoms. The orbital radius(r), the energy (E), the orbital velocity (v) of a muon moving in a circular orbit characterised by the principal quantum number n are:

$$r = \frac{n^2 h^2}{m_{x\mu} Ze^2}$$

$$E_n = \frac{-Ze^2}{2r_n} = \frac{-m_{x\mu} Z^2 e^4}{2n^2 h^2}$$

$$v_n = \frac{Ze^2}{nh}$$

where,
$m_x\mu$ is the reduced mass of muon and the nucleus (x = p , d , t for hydrogen isotopes i.e protium,deuterium,tritium).A muon moves $m_x m$ times closer to the nucleus than an electron does, with the same linear speed but with $m_x\mu$ times higher orbiting frequency. Capture of muons by hydrogen isotope atoms occurs primarily by the process:

$$\mu + D_{1s} = (d\mu)_{nl} + e$$

If the muon first forms a dμ atom, it will be likely transferred to the heavier triton, since the binding energy of tμ (2711 eV) exceeds that of the dμ atom (2663eV).

$$d\mu + t = t\mu + d$$

The cross section for the muon capture decreases rapidly at collision energies exceeding the ionisation potential of the target atom where the ionisation process takes over. The muon can be captured in any orbital such that the energy is conserved .The muon is captured most favorably at velocities roughly an order of magnitude less than those of electrons in the ground state.

1.1.1.c. *De-excitation process*: One needs to know the energy distribution of the muonic atoms in the ground and excited states in the form of a distribution function F_n (E, t), where E is the collisional energy, t is time, and n the principal quantum number of the muonic atom. This information is crucial for understanding of the next stage in the μCF chain, which is the muonic molecule formation. This motivates the study of de-excitation processes. The muon captured into a highly excited state of a muonic atom is quickly de-excited by a variety of radiative and collisional processes which are important at high mixture densities, whereas at low densities the de-excitation occurs predominantly via radiative processes. Hence the de-excitation time will generally depend on the density of the medium, which dictates the relative importance of the radiative and collisional de-excitations occurring at different rates. The collisional de-excitation is due to interactions with hydrogen molecules, of which the most important ones are chemical dissociation, Stark mixing and coulombic de-excitation. The relative importance of these processes depends on the excitation stage of the muonic atom.

(i) The *chemical de- excitation* process is important for high initial excitations with

$$(d\mu)_{ni} + D_2 = (D^+_3 \mu) = (d\mu)_{nf} + D + D$$

The muonic atom looses the energy needed for dissociation of the D molecule (4.7 eV or more) and is expected to emerge with a kinetic energy of around

1 eV. The rates of the chemical de-excitation might be slightly dependent on the molecular isotope.

(ii) The *Coulomb de- excitation, i.e.* the process

$$(d\mu)_n + d \rightarrow (d\mu)_{n-k} + d$$

is also important, at least for high excitation levels n>10, where the rates are comparable to those for chemical dissociation . An important feature of Coulomb de-excitation is that it remains operative for highly excited states, growing with n.

(iii)The effect caused by the strong electric field (of the order of 1 a.u.) experienced by the muonic atom during close collisions with the nuclei of other atoms is called the *Stark effect.* The electric field splits the energy levels and induces oscillations among the resulting n^2 sublevels. This effect influences the overall de-excitation time of the d atoms because:

a. The distribution of the angular momentum of dμ , being non-statistical after the capture process, is rearranged in time shorter than a collision time into a statistical distribution.

b. Those radiative transitions that are primarily forbidden may become allowed (notably the ground state can be reached from the 2s state after the Stark transition to the 2p state).

c. Upon very close collisions the neighboring energy levels shift and broaden to the extent that they overlap: such process leads to Stark transition with change of the quantum number n accompanied by the acceleration of the collisional partners. Thus even Stark de-excitation may produce 'hot' atoms with an energy of few eVs.

1.1.2.Formation of Muonic Molecule: During collisions with D_2, T_2 or DT molecules, the tm atom behaves as a heavy neutron, because it is neutral, very tightly bound and very small compared to electronic molecules. Hence, it can penetrate the 'host' molecule without breaking its electronic shell, and a close collision with the deuteron nucleus can take place. During such a collision a muonic molecule may be formed, provided the right kinematical conditions are met. In this respect two basic formation mechanisms are distinguished. In the *direct process,* the energy of newly formed molecules is released through the ejection of one of the electrons of D_2 molecule,

$$t\mu + D_2 \rightarrow <(dt\mu)\, de> + e$$

where the <...> brackets denote the electronic muonic hybrid molecule .

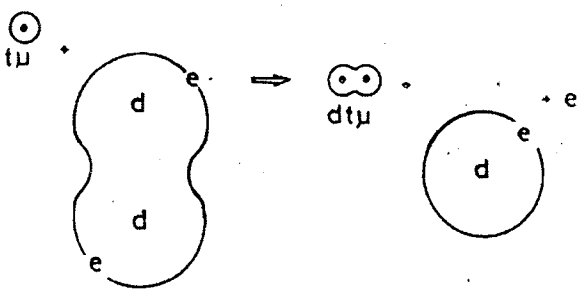


Fig 2. (Direct formation of dtμ in D - tμ collision. The released binding energy is carried away by an electron)

This process is not efficient, and that led to the rejection of muon catalysed fusion as the possible energy source during the early stage of its history. The discovery of the so called resonant mechanism stirred renewed interest in the fusion. In the resonant process the binding energy of dtm is released via excitation of rotational and vibrational levels of the hosting electronics molecule. This host molecule stays intact, while the intrinsic dtm molecule acts as one of the nuclei

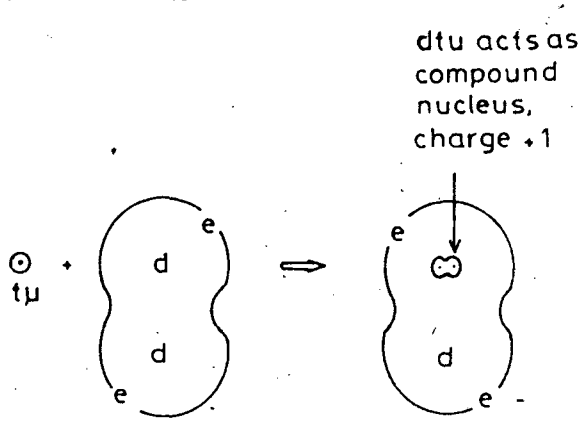


Fig.3. (Resonant formation of dtμ in D_2 – tμ collision .The dtμ binding energy is transferred to the rovibrational motion of the hybrid hosting molecule).

The resonance condition involves the proper energetic balance between the kinetic energy of E the colliding tm and D_2 the excitation energy of the molecular complex <(dtμ) dee>, and the binding energy E_b of the intrinsic dtμ:

$$E_T = E_{exc} - E_b$$

where the excitation energy is measured with respect to the ground state of the D_2 molecule. However the

resonant process can occur only at the well-defined thermal energy E_T which determines the optimal temperature for the fusion process, according to the Maxwell-Boltzmann law:

$$E_T = 3/2\ kT,$$

where k = 0.86 x 10^{-4} deg^{-1} eV is the Boltzmann constant. The optimal temperature has been estimated to be T~1800-2500K. Recent developments indicate that dtμ molecules may also be formed by *three-body collisions* of type

$$t\mu + d + X \rightarrow dt\mu + X$$

where the third body X can be an electron, a nucleon, or a neutral atom.

1.1.3.Fusion Process: Once the muonic molecule is formed (in its rovibrational excited state) it can quickly (within 10^{-10} secs) deexcite to the ground state, from where fusion is most efficient. The muon binds the nuclei in a very small volume (average internuclear distance R_0~ 7x10^{11} cm) and with a very high vibronic energy (ground state vibrational energy E_{vib} is ~ 400 eV.). Muonic binding produces collisional conditions characteristic for dense plasma, but at a local, microscopic scale. The corresponding plasma conditions would require a density r = $(1/R_0)^3$ ~ 10^9 LHD and a temperature T > E_{vib}/k ~ 10^6 K, like in the interior of stars! Under such conditions, penetration of the Coulombic barrier between the nuclei by tunnelling is very likely. In less than a picosecond, the nuclei are brought into the strong force interaction range, fuse via the nuclear reaction, and release the energy in the subsequent decay of the compound nucleus.

$$(dt\mu) \rightarrow (^5He)\mu \rightarrow \alpha + \mu + n + 17.6\ MeV$$

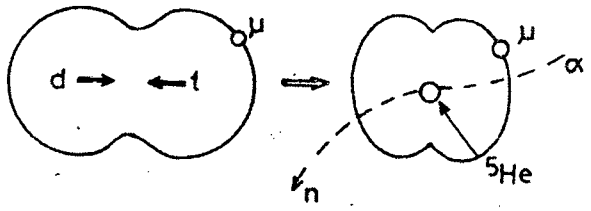


Fig.4. (Fusion by chemical confinement within the dtμ molecule. At the instant of nuclear reaction, the molecular orbital of dtμ resembles the atomic orbital of ^{5}Heμ.)

Chemical Confinement: In a muonic molecule, the d and t nuclei are enclosed in a small volume and repeatedly scatter off one another while being kept together by the muonic bond. This is generally referred to as chemical confinement.

1.1.4.Muon Sticking and Reactivation: After a fusion event, the muon is generally available for the next catalytic process, except when it binds to the a particle and thus becomes removed from the fusion reaction.

$$dt\mu \rightarrow (^5He)\mu \rightarrow \alpha\mu + n + 17.6\ MeV$$

The probability w^o_s that the muon will be bound to the a particle is given by the branching ratio between the two- and three-body fragmentation of the fusing $(^5He)\mu$ system

$$w^o_s = \frac{P(\alpha\mu + n)}{P(\alpha + n + \mu) + P(\alpha\mu + n)}$$

and is referred to as the initial sticking fraction.

A part of the muons bound to the a particle returns to the fusion chain by means of collisional detachment (via muon ionization $a\mu + d \rightarrow \alpha + d + \mu$, muon transfer $d + \alpha\mu = d\mu + \alpha$) when the am slows down in the fuel mixture .These stripping reactions counteract the sticking and so an effective can be introduced as

$$w^{eff}_s = w^o_s\ (1 - R)$$

where R is the *reactivation coefficient*, being a probability of collisional detachment of the muon. The sticking probability of muon is less than 1%.

1.2.Interphase of μCF to other fields

1. *Exotic chemistry*: The chain μCF illustrates a number of atomic, molecular and nuclear phenomena which occur when exotic particles penetrate matter. With the rapid development of accelerators, the exotic particles become easily accesible. The experimental studies of exotic atoms and molecules become as readily available as the studies of electronic species.

2. *Atomic and nuclear physics*: The most fascinating aspect of the theoretical work on μCF is that it contributes to the development of the 'grey area' between the nuclear and atomic physics, where both the Coulombic and the strong forces have to be taken into account .The interplay of atomic and nuclear physics is more pronounced in muonic system than in electronic ones, and μCF is very illustrative example of that.

3. *Astrophysics*: Studies of μCF provide very valuable information about the low energy fusion cross - sections of interest in astrophysics. The dynamical models of stars are very sensitive to the microsopic cross - sections for fusion reactions generating the stellar energyFrom the point of view of nuclear physics the thermonuclear fusion process in stars occur at very low energy E = *k* T~keV. The fusion cross - sections at such energies are very small and are therefore very difficult to measure in laboratories. The methods developed for calculations of mCF fusion rates are therefore useful for studies of the astronomical S factors in the E=0 limit.

4. *Ultra slow negative muon production:* So far it had been difficult to construct an intense beams of slow muons because the thermalized muons tend to form muonic atoms and cannot be liberated from the stopping material. Recently a new method for ultra slow muon production by means of repetitive μCF has been proposed. Slow negative muons might be used for studies of surfaces, with the possibility of analysing the uppermost atomic layers. Another interesting application is production of μ+μ- atoms for tests of quantum electrodynamics.

2. Muon spin rotation:

The muon has an intrinsic spin (I=1/2), as is the case for protons and electrons, and so magnetic resonance experiments are feasible. The most common technique is muon spin rotation (μSR), in which an external magnetic field (B) is applied in a direction transverse (at 90º) to the muon beam. The muon spins precess around the field axis at a rate proportional to the strength of the field (Larmor frequency) amounting to a classical rotation of the spins.

Larmor frequency = $\omega\mu = 2 p \gamma\mu B$
where, $\gamma\mu$ = 0.0136 MHz/G

Muon spins undergo precesssion on a microsecond timescale and by counting the positrons as a function of time the muon precession frequencies are revealed.The method is acutely sensitive to the formation of species containing unpaired electrons,i.e. muonium or free radicals . This is because an unpaired electron affects the muon magnetically so that two rotational frequencies are measured, corresponding to the electron spin states +1/2 and -1/2, which have opposing magnetic influences. The separation of these frequencies gives the ' hyperfine coupling ' that characterises the radical.

As in other forms of spectroscopy, the line widths of μSR spectra are sensitive to the lifetimes of particular states of the radical; this fact may be employed when determining the kinetics of radical reactions. Because the muon decays on a microsecond timescale, this is the timescale over which scientists may measure reaction rates; the muon provides ideal pseudo-first order conditions because just a single molecule (radical) is being measured at a time.

For the reaction R• + S Õ products, the rate constant (k) is obtained from the line-widths (λ) measured as a function of substrate concentrations [S]

$$(\lambda - \lambda_0) = k[S]$$

where λ_0 represents other conributions to the line-width ;for a unimolecular process , $(\lambda - \lambda_0)$ is the direct rate constant .

The lifetime of a particular radical state may also be limited by the molecular motion. Which is useful in determining details of molecular reorientation and diffusion of radicals in a variety of media ,including the surfaces of solid catalysts . Such information is important in important in understanding fundamental details of catalytic process such as cracking and oxidising hydrocarbons.which are partly mediated by free radicals.

When the reorientation motion is fast, as in a liquid, sharp lines are observed, but these broaden as the motion is slowed, for example by adsorption on a surface. By detailed analysis of the line widths λ, as a function of temperature, activation parameters for surface motion are obtained.

$$\lambda \alpha \tau ; \tau = \tau_\infty \exp (E/RT) .$$

Here t is the motional correlation time, τ_∞ is effectively the pre-exponential factor, in principle, reveals the details of the type of motion occurring.

Applications of Muon Spin Rotation:

μSR finds its applications in the various fields as follows:

1. ***Thiyl Radicals:*** Thiyl radicals are formed in living cells during the repair of free radical damage to biomolecules by protein bound thiols or glutathione for example.Simple thiyl radicals are undetectable by Electron Spin Resonance (ESR) spectroscopy because of their Px ,Py orbital degeneracy ,which leads to extreme line-broadening . However, kinetic measurements can be made using pulse-radiolysis, but this

requires aqueous media. Thus it limits the understanding of processes in cell membranes, which are non-aqueous .

The μSR method does not require a medium of any particular kind because the muons are implanted into the sample where they both generate and label the radicals . The potential role of thiyl radicals in biological membranes,particularly in lipid peroxidation - a process that can destroy the structural integrity of the cells and is thought to be the central in the central to the ageing process can be studied .

2. ***Radicals in Zeolites***: Although chemists know that free radicals are involved in many zeolite-catalysed reactions , they are extremely difficult to study in zeolites ,certainly to conditions pertinent to catalysis.But because μSR is so sensitive it sees one molecular radical at a time - these termination processes are effectively suppressed ,and it is possible to use μSR to study radicals in solid catalysts.

3. ***Atmospheric Chemistry***: Because radicals play a key intermediary role both in atmospheric chemistry as a result of pollution and in combustion processes , studying them is crucial. Time differential longitudinal field μSR is extremely valuable in studying radicals in the gas phase and the kinetics of their reactions with atmospheric constituents such as O_2 and NO .

Comparison of Muon Spin Rotation with other spectroscopic techniques:

1. ***Advantages of μSR***: Most spectroscopic work on radicals involves ESR spectroscopy, but it does have limitations mainly in sensitivity and because it cannot see rapidly relaxing radicals for e.g.RO and RS .Sensitivity is not such a problem for mSR because spectra are obtained by accumulating single-particle events.And given that the underlying condition is measuring nuclear rather than electronic transition,it is subject to relaxation effects on a different timescale.So , for example ,RS radicals are readily detected despite their elusiveness to ESR ; this is also true for radicals in the gas phase.

   Together with the short lifetime of the muon it has the consequence that the muon technique can work with extremely low concentrations of the order of 20 or even single species in the entire sample at any given time.Even the lowest concentration of a solute is thus not depleted by chemical reactions during an experiment , and kinetics of biomolecular reactions are always of ideal pseudo -first order .Also,self- termination which imposes the principal limitation on radical concentrations for ESR experiments are absent.

   The limitation on the time resolution in ESR and NMR comes from the necessity to first create spin coherence .But in μSR muons are already convent when injected into the sample. The muon both forms and labels the radicals in whatever medium it is implanted, so long as an appropriate unsaturated substrate is present. Thus we can study media of different polarity and physical state to determine any influence on the structure, kinetics and motion of the radical.

2. *Limitations of μSR:* On the other hand, however, there some disadvantages of μSR also. The muon lifetime of 2.2microseconds poses a limitation on the time scale of the processes to be studied by μSR .It is responsible for the low frequency resolution which does not allow resolving chemical shifts and thus discriminating between diamagnetic muonated species. Only fast processes can be monitored, but it is only these which cannot be monitored by conventional methods.

Conclusion :

The current trends indicate growing interest in following areas: molecular dynamics of radicals in zeolites and other catalytic surfaces, the dynamics and reaction kinetics of radicals on atmospheric particulate matter; gas phase radical kinetic; semiconductors; and quantum chemistry. In addition the method shows great potential for studying radical reactions and electron transfer processes pertinent to membranes using models, such as micelles, as well as for investigating hydrogen atom reactions relevant to radiation biology.

References

1. Froelich.P., *Advances in Physics*,(1992). vol. 41, No.5, 405-508.
2. Rhodes.C.J.,*Chemistry In Britain*, Feb.1999, 20-22.
3. Roduner.E., *Chemical Society Review*, 1993, 337.
4. *Hans J. Ache, Positronium And Muonium Chem; The American Chemical Society 1979*.Chemical Society.