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INTRODUCTION

Although a muon exists for only two millionths of a second, this is time enough for it to participate in many of the fundamental chemical processes available to stable charged particles. One can produce either positive or negative muons, and since they have a mass intermediate between that of the proton and the electron, it is not surprising that the positive muon tends to behave as if it were a light proton, while the negative muon behaves as if it were a heavy electron.

1.1 Muons

Muons (μ) are elementary particles of the lepton family which occur, transiently, as part of the natural decay scheme of pions (π), as indicated by the overall sequence in Eq. [1.1].



Their origin and occurrence, therefore, require a source of pions. These are the lightest and commonest of the mesons, but they appear in nature extremely rarely, only when cosmic particles interact with the atmosphere. However, pions are readily created in one of three charge states (π^+ , π^- or π^0) during high-energy nuclear collisions. This is because nuclear glue can be thought of as the exchange of ‘virtual’ pions between nucleons, so that the production of pions outside the nucleus can occur when a nuclear collision exceeds the rest mass of a pion (0.15 amu, or 140 MeV). Consequently, copious fluxes of pions are manufactured at targets in the beams of the world’s several accelerators capable of producing protons at energies much greater than 140 MeV. When the short-lived positive or negative pion decays it creates an energetic muon of the same charge. The muon lives for 2.2 μs , on average, before decaying to an energetic electron of the same charge. Table 1.1 gives some idea of the interrelation of these particles, and Figure 1.1 gives an indication of their production in a beamline of a high-energy proton accelerator.

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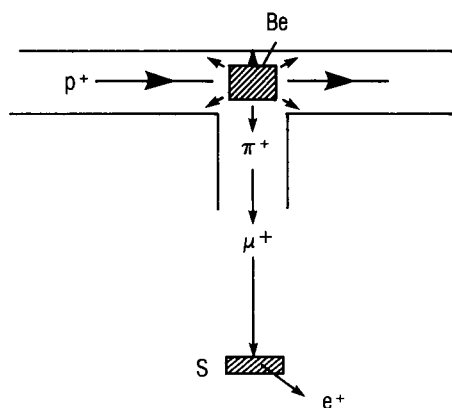
During their 2.2- μs lifetime the muons can lose their kinetic energy by collisions with the molecules of a medium and thereby come to rest, and react chemically. In fact, this thermalization and initial chemical association takes a very short period of time ($<10^{-9}$ s in all media other than low pressure gases), so there is a relatively long period of time – from about 10^{-9} s to 2×10^{-6} s – during which the muon may be incorporated in a chemical entity which is capable of ordinary chemical behaviour, including diffusion and reaction. Once the muon decays, this chemical species disintegrates; but because of the muon's

Table 1.1. *Properties of the particles e, μ , π and p*

Symbol	Particle	Family	Mass (m_e) ^(a)	Spin	Antiparticle	Mean lifetime	Decay mode
e^-	Electron	Lepton	1	1/2	Positron (e^+)	∞	(e^+ annihilates)
μ^-	Muon	Lepton	207	1/2	Positive muon (μ^+)	2.2 μs	$\mu^- \rightarrow e^- + \bar{\nu}_e + \nu_\mu$
π^+	Pion	Meson	273	0	Negative pion (π^-)	26 ns	$\pi^+ \rightarrow \mu^+ + \nu_\mu$
p^+	Proton	Baryon	1836	1/2	Antiproton (p^-)	∞	(p^- annihilates)

(a) The mass of the electron, m_e , equals 0.000549 amu or 9.11×10^{-31} kg.

Figure 1.1. Schematic diagram showing the production of a μ^+ beam from a high-energy proton beam bombarding a Be target. Some of the π^+ produced are collected in the magnetic fields of a secondary beam-line, decay to μ^+ , which then stop in the sample (S) and eventually decay to e^+ .



unique physical properties it is possible to follow its existence prior to decay and to make certain deductions about the chemistry that occurred.

The most useful attributes of the muon stem from its spin polarization, and from the violation of the parity invariance principle both as μ is formed and when it decays. This will be discussed in detail in chapter 3; but, for the moment, suffice it to say that there is a technique known as muon spin rotation (μ SR) which enables one to observe the precession of the muon's spin in a transverse magnetic field, by observing the decay-electrons in a given direction as a function of time (Garwin, Lederman & Weinrich, 1957). The actual precession frequency depends upon the magnetic properties of the particular type of chemical association with which the muon is involved. In μ SR one observes a spin-precession signal superposed on a lifetime histogram. This provides three pieces of useful information: from the frequency of precession one characterizes various chemical states of the muon; from the decay of the signal one evaluates a rate of reaction; and from the initial amplitude of the signal one calculates a yield – the probability that a muon will initially form that particular chemical state.

1.2 Muonium: a light isotope of hydrogen

In the days when only three elementary particles were known (the electron, proton and neutron) it was clear that hydrogen – specifically protium, ^1H – was the simplest possible atom. It also happens to be the most abundant atom in our universe, in the biosphere, in the human body, and in the living cell. But with the discovery of other charged particles, most of which are intrinsically unstable, it became possible to envisage, and to produce, other neutral 'atoms' which are probably more 'elementary' – at least in terms of quark theory. One such atom is muonium, used here with the chemical symbol Mu. It consists of the positive muon associated with an orbital electron. Muonium differs from protium only by virtue of having the light, short-lived positive muon as its nucleus rather than a proton. Its chemistry occupies nearly half of this monograph.

Although the mass of the muon is only one ninth that of the proton, it is still so much more massive than the electron that the reduced-mass of Mu is virtually the same as that of H. Thus the Born–Oppenheimer approximation can be used and one sees that the electron orbitals in H and Mu are equivalent in shape, size and energy. Therefore, muonium has essentially the same electronic structure, ionization energy, electron affinity, and Bohr radius as protium, deuterium and tritium. Their chemistries should differ from each other only by virtue of their different masses. In this sense Mu is unequivocally an *isotope* of H. (If it were argued that, by definition, isotopes must differ from each other

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only by the number of neutrons in the nucleus, then one should counter with the following argument. Within the framework of meson exchange theory, neutrons and protons are merely different charge states of the same nucleon: so that to 'extract' a neutron from a proton results in a pion (π^+) - which rapidly decays to a muon (μ^+)! Quark theory also, doubtless, allows one to circumvent the old definition of isotope in the case of muonium.)

With Mu as an isotope of ^1H , ^2H and ^3H , one has available the unique sensitivity provided by mass ratios of 9, 18 and 27. It is to be expected, therefore, that one of the most important roles for Mu in chemistry will be as a highly sensitive measure of mass-dependent effects, particularly, of kinetic isotope effects.

Some of the atomic properties of tritium, protium, muonium and positronium are given for comparison purposes in Table 1.2.

Muonium, like tritium, is radioactive. Hence it can be observed through its decay particle with great sensitivity, one at a time, using the powerful tools of nuclear physics. As already noted, for the specific case of the muon, it can also be studied through its spin polarization by μSR in addition to simple radiochemical techniques. One of the identifiable chemical states accessible to μSR is that of the free muonium atom (Hughes, McColm, Ziock & Prepost, 1960). Others include muonium incorporated in various free radicals. Furthermore, the yields and rates of reaction from these states are observed on the 10^{-9} to 10^{-5} s timescale - the very period over which many fundamental physicochemical interactions occur.

So that, in addition to its use in the study of isotope effects, muonium can act as a handle on hydrogen atom processes which are not observable by conventional methods. This use of muonium in monitoring H is its second major importance in chemistry. A third interest lies in studying muonium for its own sake - as an exotic artificial atom with some unique properties. The fourth interest lies in using Mu as a probe of the magnetic structure of materials.

Table 1.2. Comparison of some of the properties of Mu with ^1H , ^3H and Ps (positronium, e^+e^-)

Atom	Mass (/ m_e)	Reduced-mass (/ m_e)	Bohr radius (nm)	Ionization energy (eV)
^3H	5498	0.9998	0.05290	13.603
^1H	1837	0.9995	0.05292	13.599
Mu	208	0.9952	0.05315	13.541
Ps	2	0.5000	0.106	6.8

1.3 Other artificial atoms

Before delving into the chemistry of muons and muonium, it is appropriate to list other artificial ‘atoms’ derived from the combination of elementary particles, in case any of them is potentially superior to muonium as a light hydrogen isotope.

Table 1.3 lists the most plausible two-component neutral atoms under four categories: those with orbital electrons; their antiparticle equivalents; the particle-antiparticle pairs; and mesic atoms – with orbital muons or pions. Atoms containing kaons may be conspicuous by their absence from this list, in a few years time.

Although it has not yet been detected, π^+e^- (‘pium’) is probably formed when pions are stopped in many media. But, having zero spin (Table 1.1) there is no possibility of a pion spin rotation technique to match μ SR. Its intrinsic lifetime will be given by that of the pion (26 nanoseconds), which is one hundred-fold shorter than Mu. Its chemical lifetime should be comparable to that of Mu in the same medium, except by virtue of its mass being 32% larger. From these considerations, π^+e^- seems to have no advantages over μ^+e^- as a hydrogen isotope, and has some distinct disadvantages.

None of the antimatter atoms has been produced in sufficient quantities for chemical study as they require an encounter between two rare particles (or an antimatter conversion). Likewise, for $\mu^+\mu^-$, $\pi^+\pi^-$ and p^+p^- , though the bound

Table 1.3. *Some of the simplest artificial atoms*

Atoms with electrons	Anti-atoms	Particle-antiparticle pairs	Mesic or muonic atoms
μ^+e^- (muonium) ^(a)	μ^-e^+	e^+e^- (positronium)	$p^+\mu^-$ (muonic hydrogen)
π^+e^- (‘pium’)	π^-e^+	$\mu^+\mu^-$ (‘mumuonium’) ^(b)	$p^+\pi^-$ (pionic hydrogen)
p^+e^- (protium) ^(c)	p^-e^+	$\pi^+\pi^-$ (‘pionium’)	
		p^+p^- (protonium)	
		$c\bar{c}$ (charmonium)	

(a) In retrospect one can see that the suffix ‘onium’ should really have been reserved for the particle-antiparticle pairs. However, the Mu atom which is the central theme of this book was named just after positronium. Following protium, deuterium and tritium, it should have been called muium; but since the positive muon is the antiparticle (because muons are leptons) it should be antimuium though muantium sounds better. It is probably too late to change now.

(b) This species should have been called muonium but will now have to be given an artificial name such as mumuonium. Hopefully pium and pionium will be used as in the Table.

(c) Protium is the only stable atom in the Table and, of course, occurs naturally as well as artificially.

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states of each of these is important in particle physics. In addition, the bound states of charmonium (and other quarkoniums which are sufficiently heavy to be non-relativistic, such as bottomonium and toponium) have provided real advances in quantum chromodynamics with regard to colour force (Bloom & Feldman, 1982). The chemistry of the latter species could be of interest because of their very small size – but they are much more difficult to produce than the small mesic atoms. All of these species are rather short-lived for chemical studies. In fact positronium (Ps) is the only atom in columns 2 or 3 of Table 1.3 with any chemical significance at the present time. Ps readily occurs in most materials at the end of β^+ tracks, simply by the positron capturing an electron as it approaches thermal energy. Its chemistry has been widely studied, as referred to below.

Finally, the mesic atoms are of increasing importance in chemistry. There is, presumably, a whole Periodic Table of possible atoms in which an electron is replaced by μ^- or π^- . Muonic and pionic hydrogen merely represent the simplest such atoms. Due to the much larger reduced-masses of these atoms compared with protium, the μ^- or π^- orbitals are very much closer to the nucleus so these two atoms are extremely small. Transitions between orbitals involve high-energy X-rays, rather than visible or UV photons as in electron atoms. The existence of bound states of muonic atoms is proved by their characteristic X-rays. Lifetimes are typically of the order of microseconds and these atoms have an increasingly important role to play in certain branches of chemistry, including analytical chemistry (see chapter 10). Due to the strong interaction of mesons with nuclei, the analogous pionic atoms are much shorter-lived and the orbital transitions (X-ray production) are often severely curtailed by nucleon capture. Nevertheless, the chemistry of pionic hydrogen is under active study and of some general interest (Horvath, 1981).

But muonic or pionic hydrogen are of no importance as pseudo-isotopes of protium, because their Bohr radii and ionization energies are totally different from H. Also, their masses are virtually the same as H.

1.4 Positronium

When a positron associates with an electron in a bound quantum state it may appear either as a singlet ground state (*para*-Ps, with antiparallel spins) or as the triplet ground state (*ortho*-Ps, with parallel spins). These have virtually the same energy, but quite different lifetimes. The positron and electron of *p*-Ps annihilate by 2γ emission with a mean lifetime of 0.125 ns. This is too short for *p*-Ps to be of much use in chemical studies, at least until the response time of γ -detectors and associated electronics improves considerably. On the other hand, *o*-Ps is restricted by symmetry rules to 3γ annihilation and this is some

10^3 -fold slower. Thus the intrinsic lifetime of *o*-Ps is some 140 ns; but this can be realized only *in vacuo*. In most condensed media, due to the density of electrons, the lifetime of *o*-Ps is reduced to 1 or 2 ns because of positron pick-off reactions and subsequent annihilation by 2γ emission.

However, *o*-Ps lives just long enough in many systems of basic chemical interest for some of its fast chemical reactions to be studied through their effect on the *o*-Ps lifetime. It is also used as a probe of structure, particularly in solid state chemistry and physics. Despite real differences in the timescales and in the experimental methods involved, the development of muonium studies has been patterned to some extent on that of *o*-Ps. This will become evident from the references made to positronium in subsequent chapters.

But positronium should *not* be regarded as an isotope of hydrogen (or of muonium). In Ps there is no nucleus, because the two particles of which it is composed are of equal mass. As a result, they both orbit about the centre of mass and the effective size of Ps is about twice that of H. Thus the ionization energy is about half that of H, with the result that their basic chemical properties are quite different. As shown in Table 1.2, Ps and H are not a pair of atoms which differ merely in mass.

1.5 Isotope effects

Mass-dependent effects in chemistry mainly appear in three basic forms – kinetic effects, equilibrium (thermodynamic) effects, and spectroscopic or structural effects. It is the short lifetime of μ which militates against the use of μ SR for equilibrium studies, and for most spectroscopy – except by the muonium-radical studies and by future possibilities for single photon spectroscopic techniques. On the other hand, it is this short lifetime which makes μ SR feasible in the first place, and which allows one to probe the most interesting timescale of primary kinetic effects.

Kinetic isotope effects most often refer to the relative rate at which a reaction occurs when a reagent attacks a $^1\text{H-X}$ compared to a $^2\text{H-X}$ bond, for instance. Then the higher zero-point energy of the ^1H compound confers on it the faster rate, and one has a rate constant ratio favouring the lighter isotope. However, with regard to muonium studies, one is comparing the rate with which a free Mu atom reacts with a substrate relative to reaction by H atoms. Here, there are no differences in the zero point energies of the reactants, only of the activated complexes (transition states) and of the reaction products. Therefore, it is the heavier isotope which is favoured on energetic grounds.

It is unusual, but particularly useful, to have the isotope coming in the form of a free atom ready to react in a variety of ways (see section 1.6 below). By freeing the isotope from differences in vibrational and rotational energy in

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the reactants, one can focus attention exclusively on matters such as: quantum mechanical tunnelling; zero point energy effects in the activated complex; steric and orientation factors in the encounter; and the translational diffusion of the atom in solution – specifically its dependence on mass or volume.

Muonium rate data can be compared with ^1H data, where available, and with tritium and positronium. The detection techniques are totally different for these four atoms. ^1H data have largely been obtained by observing the ESR absorption as a function of time following pulse radiolysis in solutions in which H-atoms are produced – highly acidic water, for instance. The limitation here is on the speed of response of the ESR method and on materials sufficiently soluble and inert in the medium (Fessenden & Schuler, 1970). In typical tritium studies, one measures the stable products formed when recoil tritium is produced by a nuclear reaction in the presence of the substrate. One deduces the thermal reaction rates from competition studies, and one corrects for hot reactions through the effect of scavengers (Wolfgang, 1965). In positronium studies, one measures the reduction in the lifetime of *o*-Ps caused by the presence of a high concentration of substrate (Ache, 1979). One can also make inferences from angular correlation and Doppler broadening effects. So μSR studies, on the whole, are the most versatile, because one directly obtains many parameters: the yields, decay rates and magnetic properties of the different muon states; conversion between these states; the hyperfine coupling constants for muonium radicals; and electron spin-exchange cross-sections where appropriate (see chapter 8). It is also interesting to note that these four techniques make measurements on quite different timescales – Ps at 10^{-9}s , Mu at 10^{-9} – 10^{-5}s , ^1H at 10^{-7} – 1s and ^3H at $>10^2\text{s}$. Inferences, deductions or interpolations therefore have to be made into overlapping timescales in order to draw comparisons.

1.6 H-atom reactions

Hydrogen was doomed to be one of the most important atoms by being the simplest and commonest. But it is also one of the most versatile in its reactions. It is most frequently thought of as a ‘reducing agent’, as in Eq. [1.2]:



but it may also act as a ‘Bronsted acid’ by transferring a proton, as in [1.3]



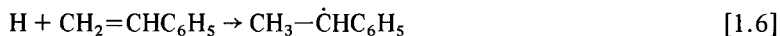
or it can ‘abstract’, as in [1.4]



or ‘substitute’, as in [1.5]



or 'add' to a multiple bond, as in [1.6]



or 'combine' with a paramagnetic molecule, as in [1.7]



or undergo 'electron spin exchange', such as [1.8].



In addition to these, there are many other reactions accessible to H atoms when they are electronically excited or have excess kinetic energy ('hot'). Because of this amazing versatility, the kinetic isotope effects pertaining to free H atoms are of particular importance in chemistry. As chapters 7, 8 and 9 will show, kinetic isotope effects varying by four orders of magnitude have been found for Mu compared to H.

Summary

Muonium would seem to be ideal as a light isotope of hydrogen for kinetic studies and as a monitor of H-atom reactions. Luckily there is the valuable technique of μSR , originally developed for particle and nuclear physics but now used mainly for solid state physics and muonium chemistry. Unfortunately, one is limited to doing this work only at high energy accelerators producing intense fluxes of pions, which means there is merely a handful of centres* around the world where muon and muonium chemistry can be studied.

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*These include: SIN near Zurich, Switzerland, LAMPF in Los Alamos, USA, KEK in Tsukuba, Japan, JINR in Dubna, USSR, CERN in Geneva, Switzerland, and TRIUMF in Vancouver, Canada.

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HISTORICAL PERSPECTIVES

The long-held belief that all the laws of physics would remain unchanged under space-inversion (parity), time-reversal, or charge-conjugation, was scuttled by events starting in 1956/57. The first to go was the principle of parity invariance, for processes governed by the weak interaction. It was found that neutrinos (ν) are always formed with negative helicity (spin and momentum vectors opposed), positive helicity for antineutrinos ($\bar{\nu}$). This means that the mirror image of any process involving either of these particles cannot occur, since mirror reflection (which is space-inversion, or parity) changes the sign of the helicity. For β^- particles formed in beta decay it means they all have the same helicity. For muons it means they are produced spin-polarized in reaction [2.1],



then decay asymmetrically (e^+ tends to be emitted along the muon's spin direction) in reaction [2.2].



The muon spin rotation technique (μ SR) utilizes both of these parity-violating interactions of the muon.

In the three-day period 15–17 January 1957, the editorial office of *The Physical Review* received three manuscripts: each one describing a separate novel experiment confirming the violation of parity in a weak interaction, as suggested by Lee & Yang (1956). The first of these papers described the experiments on polarized β^- decay that won for the principal author the Nobel Prize (Wu *et al.*, 1957). The second paper (Garwin, Lederman & Weinrich, 1957) verified parity-violation, by inventing the muon spin rotation technique and thereby proving the asymmetry inherent in reactions [2.1] and [2.2]. The third paper (Friedman & Telegdi, 1957) introduced the notion of a muonium atom, noting its spin-depolarizing effects due to the internal hyperfine interaction and the rapid precession of its total magnetic moment in the external magnetic field. These