1

Perspective and Introductory Remarks

1.1 What Do Muons Bring to Chemistry?

Like their leptonic cousins, the electron and positron, muons come in two charge states, μ^+ and μ^-. They were first discovered in cosmic ray showers [1] and have been actively studied in accelerator-based experiments ever since. The discovery of parity violation in muon decay [2, 3] soon led to studies of the interactions of muons in matter and the development of various experimental techniques commonly referred to as 'μSR', for muon spin rotation/relaxation/resonance, and here collectively known as 'Muon Spin Spectroscopy'.

The fundamentals and applications of μSR to solid-state physics are well covered in a variety of texts [4-8]. In contrast, the current book focuses on the importance of muons in chemistry. There has been only one previous book dedicated to this subject, but this was published in 1983 [9] and there have been major developments in the field since then.

Particle physicists view the negative muon as a heavy electron, and indeed it plays this role in muonic atom chemistry. However most chemical studies of muons make use of the antiparticle, the positive muon. The muon rest mass is 105.66 MeV, which is 206.8 times heavier than the electron, and 0.1126 (roughly 1/9th) the mass of a proton. The single-electron atom with μ^+ as nucleus is known as muonium (Mu = μ^+e^-), and from a chemical point of view this can be viewed as the lightest isotope of hydrogen.

At the other end of the mass scale, the interaction of an energetic negative muon with helium can result in the muonic helium atom, i.e. a helium atom in which one electron has been replaced with a μ^-. Given the large mass of the muon (relative to the electron) the μ^- resides in a tight atomic orbital close to the nucleus, where it effectively screens half of the nuclear charge. Thus Heμ is a single-electron atom with an effective nuclear charge of +1, just like the H atom [10].

The properties of a single-electron atom of nuclear charge Ze are readily calculated by either the Bohr atomic model or standard quantum mechanics. The allowed electron energies are given by

$$E_n = -\frac{m_r Z^2 e^4}{2n^2 \hbar^2 (4\pi\varepsilon_0)^2} \tag{1.1}$$

and the Bohr radius (charge separation for the lowest energy state of the atom) is

$$a_0 = \frac{\hbar^2}{m_r Z e^2}(4\pi\varepsilon_0), \tag{1.2}$$

where e is the elementary charge, ε_0 is the electric constant (vacuum permittivity), $\hbar$ is the Planck constant divided by 2π, and m_r is the reduced mass for the two-body system:

$$m_r = \frac{m_e m_N}{m_e + m_N}, \tag{1.3}$$

where m_e and m_N are the electron mass and the mass of the nucleus, respectively. As long as m_N is large compared with m_e, the reduced mass is approximately equal to m_e. Thus the fundamental atomic properties given by Eqs. (1.1) and (1.2) depend only weakly on nuclear mass. This is why isotopes are considered to have the same chemistry – ionization energies and charge separation are the key *chemical* properties of atoms.

Isotopes are normally thought of as atoms with the same number of protons (same Z) but differing numbers of neutrons in their nuclei. However, application of Eqs. (1.1)–(1.3) shows that the series of single-electron atoms Mu, H, D, T, Heμ (Figure 1.1) should have the same chemistry. Their atomic properties are summarized in Table 1.1.

Thus muonium and Heμ can be expected to react in the same manner as the other atomic hydrogen isotopes, e.g.

Abstraction	$Mu + H_2 \rightarrow MuH + H$
Addition to unsaturated molecules	$Mu + CH_2{=}CH_2 \rightarrow MuCH_2{-}CH_2{}^{\bullet}$
Oxidation–reduction	$Mu + Ag^+ \rightarrow Mu^+ + Ag^0$
Acid–base	$Mu + OH^- \rightarrow MuOH + e^-$
Electron spin exchange	$Mu(\uparrow) + NO(\downarrow) \rightarrow Mu(\downarrow) + NO(\uparrow)$

Of course, the rate constants can vary with isotopic mass, and this is the basis of the kinetic isotope effect discussed in later chapters. At this stage it is sufficient to point out that muons greatly extend the range of isotope effect studies, providing a remarkable mass range of 36 from Mu to Heμ.

Another facet of isotopes that finds great utility in chemistry is their application as tracers. Reaction mechanisms are often deduced or tested by following the fate
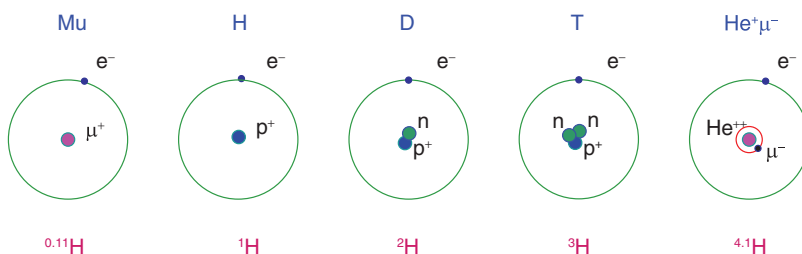

Figure 1.1 The series of single-electron atoms which behave as isotopes of hydrogen.

Table 1.1 Mass, reduced mass, ionization energy and atomic radius of hydrogen isotopes.

	Mu = μ^+e^-	H = p^+e^-	D = np^+e^-	T = nnp^+e^-	Heμ = $[^4$He$\mu^-]^+e^-$
Mass (u)	0.114	1.01	2.01	3.01	4.11
m_r/m_e	0.9952	0.9995	0.9997	0.9998	0.9999
I.E. = $-E_1$ (eV)	13.548	13.606	13.609	13.611	13.611
r_1 (Å)	0.5314	0.5292	0.5290	0.5290	0.5290

of 'labelled' molecules. The labelling may be radioactive (e.g. tritium) or spin (e.g. deuterium). Muonium qualifies in both categories: the positive muon spontaneously decays with a mean lifetime of 2.197 μs, irrespective of medium, and it has spin ½, just like a proton but with a larger magnetic moment (by a factor of 3.183). Both of these properties are utilized in muon spin spectroscopy. Furthermore, the relatively low intensity of muon beams means that each Mu atom is effectively isolated, so cross-reactions are avoided.

The addition of Mu to unsaturated bonds results in the formation of muonium-labelled molecules (formally referred to as 'muoniated' radicals [11]). Radicals are atoms or molecules that have one or more unpaired electrons, and are therefore typically highly reactive. They play an important role in chemistry, often as intermediates in reactions, but their transient nature makes them challenging to study with conventional spectroscopic techniques. Muoniated radicals are studied for similar reasons that Mu is studied in place of H, either to explore isotope effects, or to use Mu as a tracer. In the latter case, it could be to investigate radicals that would be difficult to produce or study with other spectroscopic techniques. Alternatively, the aim could be to label specific parts of a complex system to learn about the dynamics and local environment. Chapters 6–9 contain many examples of these varied uses.

Some Comments on Nomenclature
The common isotopes of hydrogen are named protium (H), deuterium (D) and tritium (T), and if a similar convention were followed for Mu it would be named muium. Indeed, according to the nomenclature of particle physics, the 'onium' ending implies the bound state of a particle with its antiparticle (e.g. positronium, Ps = e^+e^-). Nevertheless, the term muonium for μ^+e^- has been in use since 1957 [3] and is so well entrenched that it is endorsed by IUPAC [11].

Older literature used the term *muonated* radical instead of muoniated radical. This practice has been discontinued, as 'muonation' is now defined [11] to be the equivalent of protonation, i.e. the addition of Mu^+ rather than neutral Mu. Even older literature refers to *muonic* radicals. The adjective 'muonic' is now reserved for negative muon entities.

1.2 Muon Facilities and Background to Experimental Muon Techniques

There are currently four nuclear accelerators in the world that produce intense beams of spin-polarized muons: the TRIUMF cyclotron in Vancouver, Canada; the ISIS Facility at the Rutherford Appleton Laboratory in the UK; the Paul Scherrer Institute (PSI) in Switzerland; and the Japan Proton Accelerator Research Complex (JPARC) at Tokai in Japan. These accelerators have different features, but all generate muons from the decay of charged pions, $\pi^{\pm}$, which are themselves produced from the nuclear reactions of energetic protons. Pion production targets typically feed several muon beamlines, and at some accelerators there are two targets per proton beam. Nevertheless, the total number of muon beamlines suitable for muon spin spectroscopy is less than twenty worldwide.

TRIUMF and PSI produce quasi-continuous (CW) beams, while ISIS and J-PARC are pulsed sources. The CW facilities produce muons one at a time, with an even but stochastic time distribution. Such beams permit the use of single-particle counting techniques and the high time resolution necessary for studying fast processes and high precession frequencies. Pulsed machines produce bursts of muons at a relatively low repetition rate. The width of the muon burst ($\sim$100 ns) precludes high time resolution. On the other hand, the long interval between pulses (20 ms at ISIS; 40 ms at J-PARC) provides a very clean background for studying slow processes. Furthermore, pulsed machines are inherently suitable for experiments that require intermittent stimulation, such as pulsed RF or laser excitation.

Of particular importance to muon spin spectroscopy is that muons produced from pion decay are 100% spin-polarized (in the rest frame of the pion), with their spins aligned anti-parallel to their momentum (for μ^+; parallel for μ^-). In general, this polarization is retained in μ^+ which stop in matter, although negative muons can lose as much as 80% polarization in their capture and thermalization process. This is a key factor in the sensitivity of muon spin spectroscopy, compared to conventional magnetic resonance that relies on thermal population of spin states.

Another important feature of muon spin spectroscopy stems from parity violation in muon decay. This is a three-body process:

$$\mu^+ \rightarrow e^+ + \nu_e + \overline{\nu}_{\mu}$$
$$\mu^- \rightarrow e^- + \overline{\nu}_e + \nu_{\mu} \tag{1.4}$$

which produces a positron (or electron from μ^-) and two neutrinos ($\overline{\nu}$ is an anti-neutrino). Of these only the positron (or electron) is detected, but most importantly there is angular correlation between the positron momentum and the muon spin direction at the moment of its decay. The maximum of the probability distribution is aligned with the muon spin, so that a commonly stated description is that the positron is emitted preferentially in the direction of the muon spin. Further details of muon production and decay are given in Chapter 2. Suffice it to say here that muon spin polarization can be monitored by counting decay positrons in specific directions. There is no need for a stimulating field (radio-frequency in NMR or microwave in ESR) to interrogate the spin system.

1.3   The Development of Muonium Chemistry

The advent of muonium chemistry can be traced right back to the first demonstration of parity violation in muon decay in 1957, when it was remarked that the muon asymmetry depends on material [2], and that this might be due to the possibility of muonium formation [3]. A systematic survey of simple materials was published in the following year [12], although muonium itself was not detected directly until 1960, in a target of argon gas at ~50 bar pressure [13]. By 1966 understanding had developed to the extent that Hughes could write in a review article that 'Muonium can be regarded as a light isotope of hydrogen' [14].

The earliest experiments were conducted in the United States, at the cyclotron laboratories located at the University of Chicago and Columbia University. Within a few years, however, investigations of muonium chemistry were undertaken at the JINR synchrocyclotron at Dubna, Russia. Various attempts were made to deduce the rate constants for reactions of muonium from muon asymmetry values, and it was even suggested that the muonium data could be used to calculate rate constants for atomic hydrogen [15]. Remarkably, both kinetic isotope effects and the formation of muoniated radicals were discussed as early as 1963 [16]. Another advance from Russia was the first detection of Mu precession in solids – in quartz, in solid carbon dioxide and in ice [17]. This was followed by studies of two-frequency Mu precession [18], from which the muonium hyperfine frequency can be calculated (see Section 2.6.1).

At Columbia University there were early attempts to study gas-phase muonium reactivity by monitoring the muon polarization in longitudinal magnetic fields [19]. However, the first convincing measurements of muonium reaction rates were not until 1976, when Fleming et al. studied the decay of the characteristic transverse-field precession signal of muonium at the Lawrence Berkeley Laboratory [20]. Their ability to stop muons in gases at low pressures was due to a major advance in muon beam technology: the development of the surface muon beam (Section 2.1).

Despite many attempts in those early days, Mu precession had never been detected in liquid samples. Instead, the Berkeley researchers determined rate constants by fitting the concentration dependence of the magnitude and phase of the 'residual polarization' – transverse polarization in the diamagnetic products of muonium reactions [21] (see Section 5.4). They were also able to deduce the involvement of muoniated free radicals, again without direct detection [22]. A review article from that period gives a comprehensive account of the 'state of the art' of muonium chemistry in 1974 [23]. It also suggested the acronym μSR for 'muon (or muonium) spin relaxation, rotation, resonance, etc.', to suggest the analogy with NMR and ESR.

The next major advance came with the emergence of the 'meson factories' SIN (1968), TRIUMF (1968) and LAMPF (1972), accelerators designed to produce beams of protons in the energy range of 400 to 1000 MeV and capable of generating muon beams 100–1000 times more intense than hitherto.

It was at SIN (Swiss Institute for Nuclear Research, now part of the Paul Scherrer Institute) that muonium precession signals were first detected in liquids, originally in water [24] and then in other common solvents [25, 26]. A major

factor in this advance was the removal of dissolved oxygen from the samples. Being paramagnetic, oxygen can both react chemically with Mu and engage in non-reactive spin-exchange encounters (Section 7.4). Both of these interactions lead to loss of coherent Mu precession.

Another reason that Mu signals were so elusive in liquids is that they have small amplitudes, corresponding to about 20% of the original muon spin polarization. Since typically 60% of the muon spin polarization precesses at the diamagnetic frequency in liquids, this left 20% unaccounted – the so-called 'missing fraction' (Section 3.2). In contrast to liquid water, ice has a larger Mu fraction, smaller diamagnetic signal, and no missing fraction. There are also much larger Mu fractions in gases, and the work of Fleming et al. at TRIUMF showed that these depend largely on the muon thermalization process, in particular on charge-exchange cross sections [27]. Small deviations from expectations based on proton thermalization data were ascribed to competing hot-atom reactions of the Mu atom. The need to explain this puzzling phase dependence of the Mu fractions prompted the proposal of radiolysis effects, including the 'spur model' of muonium formation [28]. Until this time it was thought that positive muons would thermalize as muonium sufficiently far from the last charge exchange that it would escape any effects of radiation damage [23]. The partition of muons between muonium and diamagnetic compounds in the last 30 eV or so of thermalization was thought to arise from hot-atom reactions [29], modelled after the then current understanding of tritium chemistry. The spur model met considerable opposition for many years, and radiolysis effects were not generally accepted until the electric field studies of Storchak et al. [30]. Further details can be found in Chapter 3.

Whatever the mechanism of Mu formation in condensed matter, being able to detect its signal on a microsecond timescale made it possible to determine rate constants by measuring Mu decay rates in reactant solutions of known concentration [31]. Comparison of Mu rate constants with those of H soon revealed a wide range of kinetic isotope effects. Gas-phase reactivity is discussed in Chapter 4 and solution kinetics in Chapter 5.

Of course, the direct study of muonium decay kinetics requires that the liquid solvent (or buffer gas) be non-reactive. By analogy with H it was expected that reaction of Mu with an unsaturated molecule should result in a free radical. However direct detection of muoniated radicals did not occur until 1978, when Emil Roduner, then a graduate student, proposed searching for the precession signals at high magnetic field [32]. These first experiments utilized pure organic liquids as targets, and even though hundreds of muoniated radicals have now been studied in liquids, including in solutions, the requirement for fast transfer of muon polarization from Mu to radical limits detection of radical precession signals to highly concentrated samples (Section 2.7.3). Nevertheless, muoniated radicals have also been studied in the gas phase, initially at high pressure [33], but later at pressures as low as 1 atm [34, 35].

As will be explained in Chapter 6, the isotropic muon hyperfine coupling constant can be readily determined from the precession frequencies of a muoniated radical. However, this is often not enough to identify the radical, and full characterization should include determination of the hyperfine constants of other spin-active nuclei,

typically protons in organic radicals. Abragam [36] suggested the means of doing this – avoided level-crossing resonance (ALCR) – and teams at TRIUMF [37] and SIN [38] raced to demonstrate the feasibility of the method. At SIN the experiment was limited by the available magnet, so the $(CH_3)_2\dot{C}OMu$ radical was chosen because its six equivalent protons give rise to a single resonance at only 1.5 kG. The TRI-UMF group had the advantage of a superconducting magnet, and were able to scan a wide field range and detect all four resonances due to the distinct fluorines in muoniated hexafluorocyclohexadienyl, C_6F_6Mu. Interestingly, this radical was also chosen to limit the scan range (3–12 kG), it having a muon hyperfine constant less than half that of C_6H_6Mu, whose avoided level-crossing resonances extend to almost 30 kG [39].

The ability to determine hyperfine constants (hfcs) for other nuclei in addition to the muon permits a more thorough investigation of intramolecular dynamics. Thus Ramos et al. [40] interpreted the temperature dependence of the muon hfc in the muoniated ethyl radical in terms of CH_2Mu rotation, but it was only with the advent of ALCR that the corresponding effect on the proton hfc could be followed, and even contrasted with the unsubstituted CH_3 groups in muoniated tert-butyl, $(CH_3)_2CH_2Mu$ [41]. These data eventually led to a deeper understanding of the origins of hyperfine isotope effects, i.e. why it is that muon hfcs are typically 10–30% larger than the equivalent proton hfcs scaled by the ratio of magnetic moments. This topic is discussed in Section 6.2.

Once the basic techniques of muon spin spectroscopy had been developed it became possible to extend muon studies to chemical problems difficult to solve by conventional means. An early example is the mapping of unpaired spin density in the $C_{60}H$ radical [42]. At that time theoretical and computational papers expressed divergent opinions ranging from localization of unpaired spin on a single carbon atom to complete delocalization over the C_{60} 'globe'. The first μSR paper on fullerenes [43] is interesting for two reasons. First, it predates ESR detection of $C_{60}H$ [44] – in fact the search for narrow ESR lines was guided by reports of the muon hfc in $C_{60}Mu$. Secondly, the μSR spectrum exhibited signals from encapsulated muonium, $Mu@C_{60}$, as well as from the exohedral muonium adduct $C_{60}Mu$. This was the first time that muonium and a muoniated radical had been detected simultaneously in the same sample.

The development of muonium chemistry was initially driven by advances in technology, resulting in both more intense beams and in new experimental techniques. These in turn enabled the study of more difficult problems. For example, extremely high data statistics were necessary to study the decay kinetics of the weak precession signals of muonic helium [45]. Similarly, an intense muon beam and novel experimental setup enabled the first observation of light emitted from a muonium-containing molecule, namely the chemiluminescence resulting from excimer transitions in the Rydberg molecule NeMu* [46]. However, development of the field in recent decades has largely involved applications in ever more complex systems and extreme environments: muonium and muoniated radicals on surfaces, in porous materials, in supercritical fluids and soft matter. Examples of all these will be given in subsequent chapters.

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