Muon chemistry experiments in the gas phase with pulsed surface muons at ISIS

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Introduction

Target cells have been developed for gas phase experiments at ISIS using implanted positive muons. Cells were designed for both radio frequency (RF) and level crossing (ALC) measurements in high magnetic fields, allowing working pressures of up to 50 bar using a surface muon beam. Initially cells were fabricated from the polymer PEEK, enabling the RF cavity to be mounted external to the cell for optimal positioning. However, engineering cells of sufficient strength proved difficult, with further problems arising due to the outgassing of impurities from the PEEK material. To overcome these difficulties, all-metal cells were developed. The design and performance of both cells and RF cavity were characterised during cell commissioning.

The target cells have been designed for use in the ISIS high field spectrometer (HiFi). Initial studies investigated both diamagnetic (μ^+) and muonium (Mu – a bound μ^+e^- system) states formed in inert gases. Subsequent work has focussed on developing aspects of muonium chemistry, investigating both the spectroscopy of muoniated radicals through ALC and the study of chemical reaction kinetics in the gas phase. Preliminary results obtained from both applications are reported.

Cell design

The design of a gas cell for ALC and RF µSR inevitably involves satisfying a number of conflicting criteria. Firstly, the cell body should be chemically inert, non-magnetic and strong enough to withstand the required working pressure. Ideally, the muon response in the material should be predictable as a significant fraction of the incident beam will inevitably be scattered into the body. Secondly, the beam window must be sufficiently thin to allow the passage of a (~4 MeV) surface muon beam without significant attenuation. Ideally both the cell body and window should be electrical insulators to permit the RF cavity to be located external to the cell for easy adjustment and to avoid interaction between the cavity and the gas sample. Finally, the length of the cell should be sufficient to stop the muons in the gas over a useful pressure range.

Window design parameters were investigated by Monte Carlo simulation of the muon stopping profile using the SRIM-2000 code [1]. The sample output for a cell using a Mylar window and containing nitrogen gas is shown in Figure 1(a). The simulations illustrate that the centre of the muon stopping distribution shifts substantially with gas pressure. For conventional µSR measurements the cell may be moved to ensure this distribution remains centred within the spectrometer. For RF techniques, however, it is the position of muon stops relative to the RF cavity that is important to the quality of the measurement; the RF coil generates an optimal field over a restricted volume and muons stopping outside this region will experience restricted RF amplitude together with gradients in the RF field. Commissioning measurements shown in Figure 1(b) confirmed a gross effect on the muon signal measured in argon gas using a fixed RF cavity, with the amplitude of the diamagnetic RF signal changing significantly as the gas pressure is increased.

While simulations provide a good method of optimising the window thickness for muon transport, experimental work is required to ensure the windows are sufficiently strong to withstand the required working pressure and are durable enough to reliably execute multiple pressure cycles. Significant time was spent testing burst pressures of candidate window materials. Intriguingly, these tests demonstrated that laminate windows could routinely support a higher pressure than those made from a single equivalent thickness of identical material. For example, a 0.125 mm single layer window could be rated for a working pressure of 25 bar while a five layer laminate of 0.025 mm sheets offered an increased working pressure of 35 bar. Unfortunately, the laminate windows were more susceptible to fatigue after multiple pressure cycles, with cracks developing around the seal made with the inner foil. Therefore, laminate windows are reserved for experiments requiring the highest working pressures, with single layered windows being preferred for other measurements.

Commissioning the gas cells

Work initially focused on the development of gas cells composed of the engineering polymer PEEK, as this material appeared ideal for solving many of the design criteria and had also been used in previous RF studies in gases [2]. Unfortunately, during both testing and commissioning, problems were encountered arising from the PEEK construction:

Polymers lacked sufficient strength to achieve the desired working pressure. Initially, cells were made with the body and window machined from a single 30mm diameter rod of PEEK. However, with a window of thickness 0.6mm, a working pressure no greater than 14 bar could be achieved. The desired pressure of 50 bar was obtained using a laminate Mylar window of total thickness 0.7 mm (~100 mg/cm^2) and diameter 20 mm clamped to a PEEK body. However, less than 20% of incident muons were implanted in the gas sample using this configuration.

The outgassing of unknown impurities from the PEEK leads to inconsistent results. Figure 2(a) shows a strong Mu signal measured in Neon – a gas known from previous work [3] to have a diamagnetic fraction of close to 100%. In this case it seems likely that a charge neutralization reaction occurs involving the Neμ^+ ion and an unknown impurity, forming Mu. Results were also found to be dependent on the duration of the experiment, and Figure 2(b) shows the relaxation rate of the muon molecular ions formed in nitrogen gas increases significantly over the 16 hour period of the experiment. Again, Mu formation due to impurities outgassing from the cell walls is a likely cause.

A strong radical signal originating from the cell body significantly complicates interpretation of ALC measurements of gas samples, potentially masking weak sample signals. Transverse field measurements demonstrated PEEK to have a small diamagnetic fraction (P_D ~ 0.1), a useful property if the diamagnetic fraction in the gas is to be investigated. However, repolarization data (Figure 3(a)) demonstrated that the full polarization could be recovered in a 4.5 kG field, with the form of the curve suggesting 90% of the muons form a radical state with a hyperfine coupling of approximately 250 G. Recent ALC measurements (Figure 3(b)) show a broad feature between 1.4 and 2.3 T, consistent with multiple overlapping Δ_1 and methylene proton Δ_0 resonances of cyclohexadienyl radicals under restricted rotational motion.

Unfortunately, these difficulties meant that the PEEK cells were unusable for μSR measurements and there was no option but to develop the all-metal cell shown in Figure 4(a). The cell comprised of a non-magnetic grade stainless steel body, with a clamped window (sealed against a copper gasket) optimally composed of a seven layer laminate of 0.025 mm titanium sheets, giving a working pressure of 50 bar. Crucially, the system has been demonstrated to remain clean over extended periods. The clear disadvantage of moving to the metal system was the need to position the RF cavity internal to the cell. This dictates the coil is mounted in a fixed position, thus restricting measurements to a comparatively narrow pressure range. Additionally, this cell configuration required a high pressure RF feedthrough (sourced from Ceramaseal, New York). The RF cavity is shown in Figure 4(b), and comprises a three turn saddle coil wound on a ceramic former of length 6 cm and outside diameter 3 cm. Surprisingly, no problems have been encountered running RF in the gas environment.

The performance of the RF cavity was investigated by measuring resonance signals for muons implanted in nitrogen gas. Figures 5(a) and (b) show field sweeps for muons thermalizing in their diamagnetic and paramagnetic states respectively, with a loss of asymmetry being measured at resonance due to the precession of the implanted muon about the RF field. For the diamagnetic species, the resonance is measured at a field of approximately 965 G, as anticipated for an RF frequency of 13 MHz. In Figure 5(b), the ν_{12} and ν_{23} transitions expected for Mu are clearly resolved at an RF frequency of 105 MHz. The on-resonance diamagnetic signal in nitrogen, shown in Figure 5(c), confirms an RF field strength, B_1, of approximately 10 G at a working frequency of 10 MHz. Considering the volume of the cavity, this represents a good performance. While a saddle coil configuration has been used for the present experiments, Birdcage or Litz coils may be preferred at higher frequencies.

Spectroscopy of Muoniated Radicals in the Gas Phase

Electron spin resonance spectroscopy (ESR) is the most commonly used spectroscopic technique for studying radicals in solids and liquids. However, the technique cannot easily be used to study gas phase radicals of more than a few atoms due to strong coupling between the spin, rotational, and orbital angular momenta. μSR does not suffer to nearly the same degree from this problem, since electron spin relaxation is indirectly transferred to the muon via the hyperfine interaction, potentially making it superior to ESR for gas phase measurements [4].

The measurement of organic radicals in the gas phase using conventional transverse field μSR can be challenging since detection depends on Mu addition being sufficiently rapid to avoid loss of spin polarisation in the Mu precursor state [5, 6]. However, slowly formed species can be readily studied if longitudinal field techniques are applied. ALC has already proved to be an important tool for characterizing gas phase radicals [7-9] despite the measurement being limited to the study of nuclear hyperfine couplings [4]. In contrast, RF methods should enable the direct measurement of both muon and nuclear hyperfine couplings even in systems that lack nuclear moments. When used in tandem, these techniques should enable the direct observation and characterisation of final state species, providing insight into reaction pathways important in their formation. Gas phase measurements are of particular importance where the environment modifies the hyperfine coupling [10, 11]; in this case a study in the gas phase permits measurement in dilution, that is essential if a proper comparison with theory [11] is to be made.

To demonstrate the potential for radical spectroscopy, preliminary measurements were carried out at 300K to observe both the ethyl [8] and tert-butyl [9] radicals formed when muons are implanted in gaseous ethene and isobutene respectively. Results are shown in Figure 6. The resonance positions are characteristic of the radicals and reflect the muon and proton hyperfine interactions. Distinct peaks in the relaxation, λ, and corresponding reduction of the integral asymmetry occur for each group of magnetically equivalent nuclei in the system, with resonances governed by the selection rule $\Delta(m_\mu+m_n) = 0$. The data has been compared to previous work [8, 12] and excellent agreement has been found for the proton hyperfine constants in both systems.

Chemical Reaction kinetics studied through RF resonance methods

Hydrogen abstraction reactions ($H + RH \rightarrow H_2 + R\cdot$) are key steps in free radical mechanisms that dominate the combustion and atmospheric chemistry of the alkane hydrocarbons (RH) [13] and, as such, merit study for their relevance to current environmental concerns. The lower mass alkanes also provide important test cases for H-atom reaction rate theory for polyatomic systems [14-17]. Due to the remarkably light mass of the muon (approximately 1/9th m_H), studies of Mu reactivity provide unique tests of quantum mass effects in rate theory, including in the alkanes [16, 17].

Since H-atom abstraction rates with propane are faster than for methane or ethane, due to lower activation barriers , these provide ideal cases for the measurement of *slow* reaction rates, near room temperature, by *RF resonance*, on a timescale of approximately 10 µs – i.e. far too slow to be investigated by the TF-µSR technique. The measurement of reaction rates is also important in itself for making comparisons with absolute reaction rates predicted by theory.

Detailed measurements of the non-delayed RF signal for six propane partial pressures provide good evidence for a slow reaction in forming a diamagnetic product. The data was analysed using the model proposed by Morozumi *et al* [18] to obtain the time, τ, for the Mu + C_3H_8 reaction. A plot of the reaction rate ($1/\tau$) vs. propane partial pressure is shown in Figure 7, and a fit to the expected straight line dependence yields an average rate constant, k_{Mu}, of $(7.8 \pm 0.5)\times10^{-16}$ cm^3s^{-1}. Surprisingly, this value is only about a factor of three slower than that of H + C_3H_8 [15], suggesting a large contribution from quantum tunnelling. To our knowledge, this is the first measurement of such a slow Mu reaction rate in gases by any technique, and firmly establishes the utility of pulsed beams and RF techniques for the study of such systems.

Conclusion

All-metal gas cells have been developed and commissioned for the HiFi spectrometer at ISIS, that work well for both ALC and RF chemical kinetics measurements with a pulsed surface muon beam. PEEK cells were investigated, but were deemed unsuitable for use both due to the outgassing of impurities and the formation of a muoniated radical state in the polymer.

Acknowledgements

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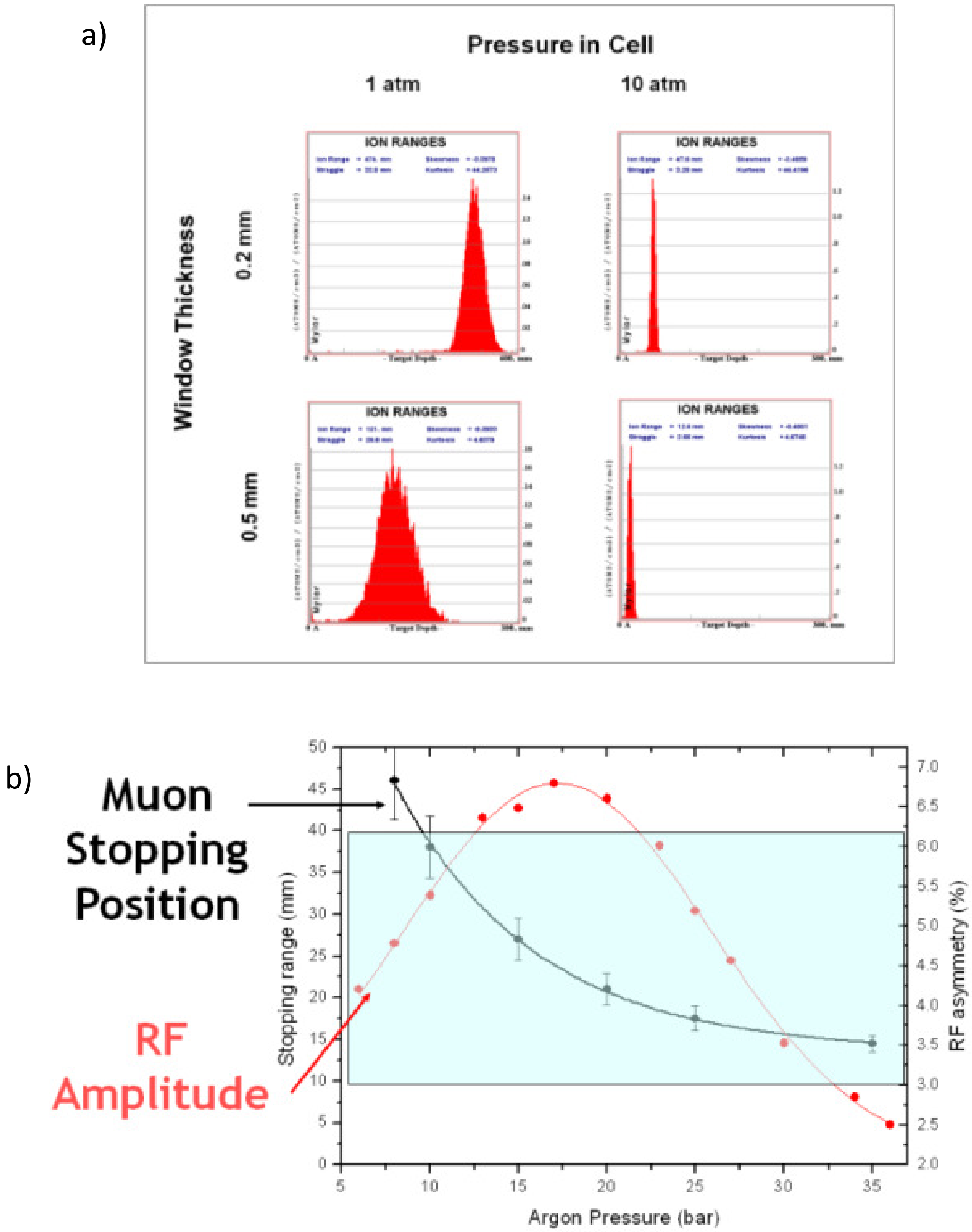


The shaded blue area represents the region occupied by the coil within the metal cell.

Figure 1: Sample SRIM calculations (a) for a cell using a Mylar window and containing nitrogen gas, and (b) the diamagnetic RF signal relative to the muon stopping distribution within the gas cell and RF coil

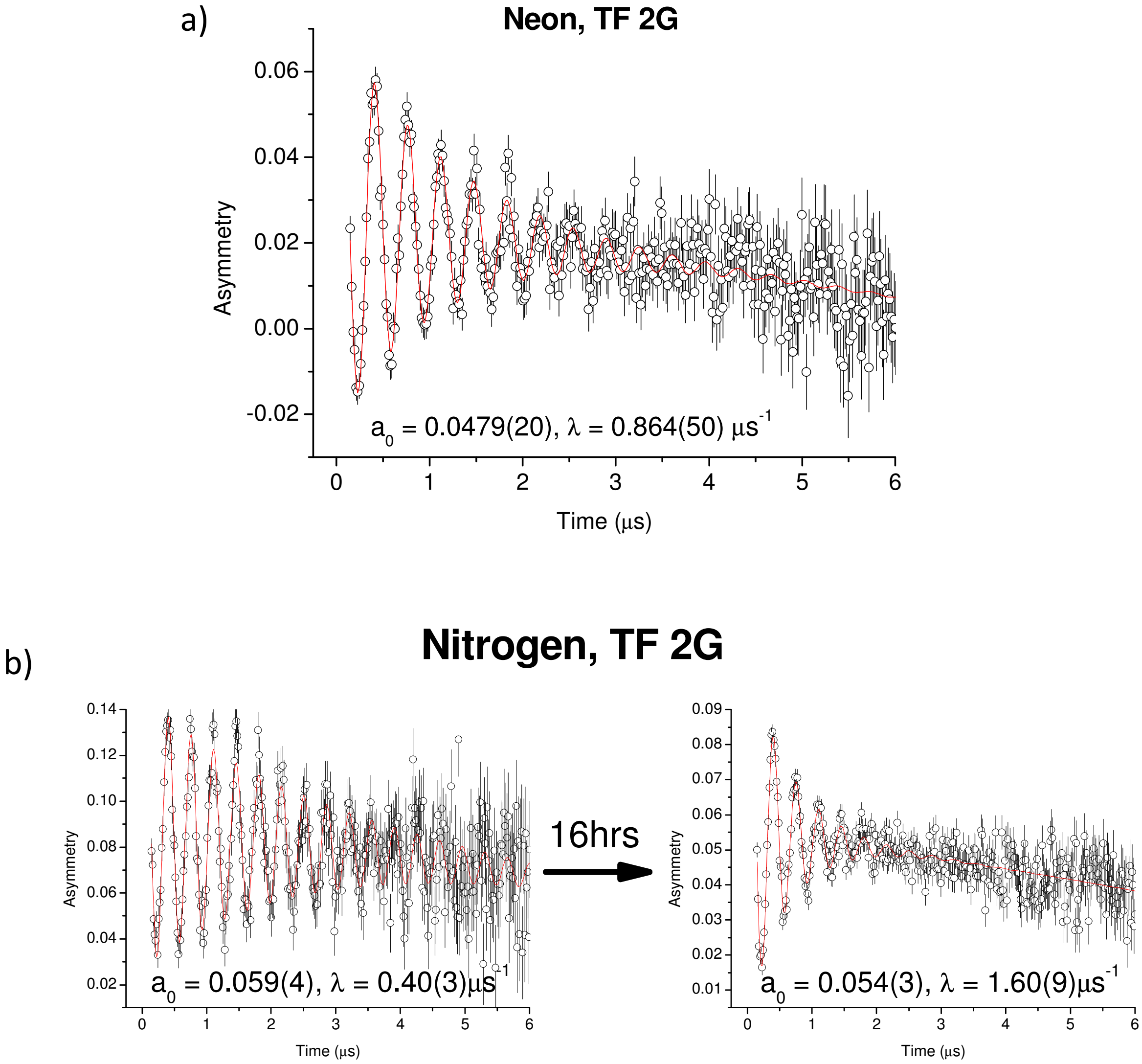


Figure 2: Outgassing of impurities from the PEEK polymer leads to (a) an unexpected Mu signal measured in neon and (b) a background relaxation (for nitrogen) that develops with time.

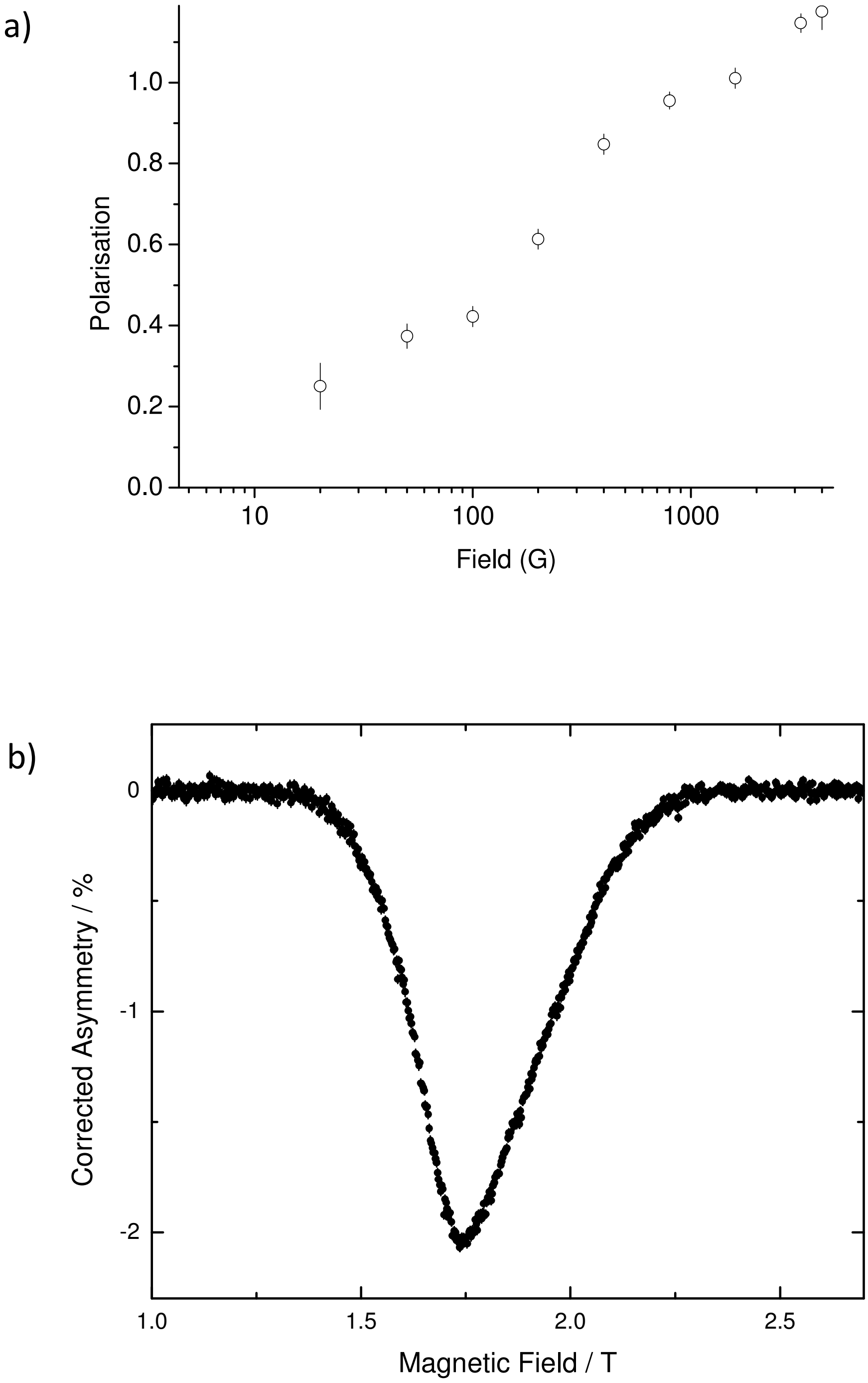


Figure 3: Characterisation of the paramagnetic fraction formed in PEEK. Repolarisation data (a) and ALC measurements (b) suggest 90% of implanted muons form a radical state with a coupling of ~250G

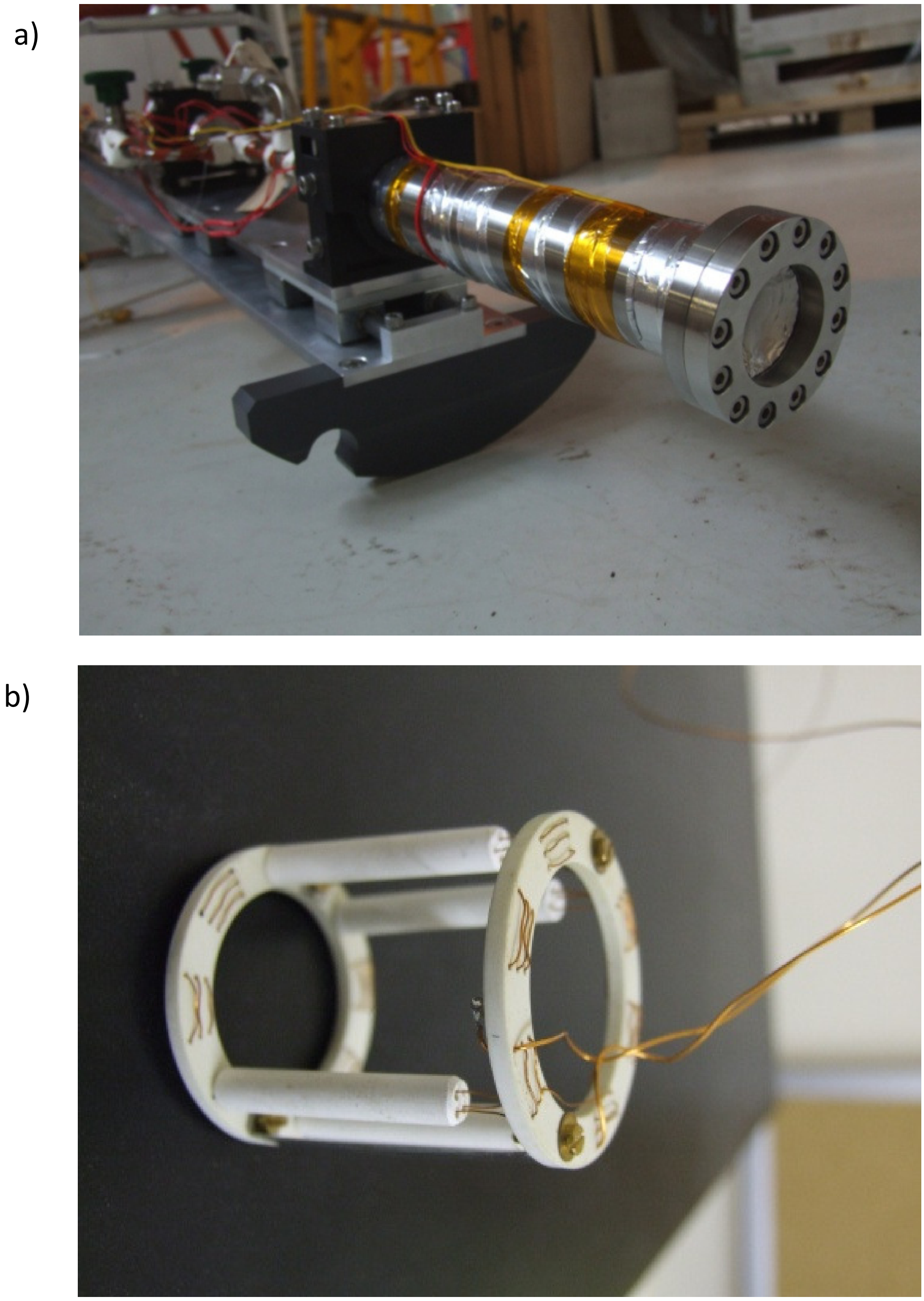
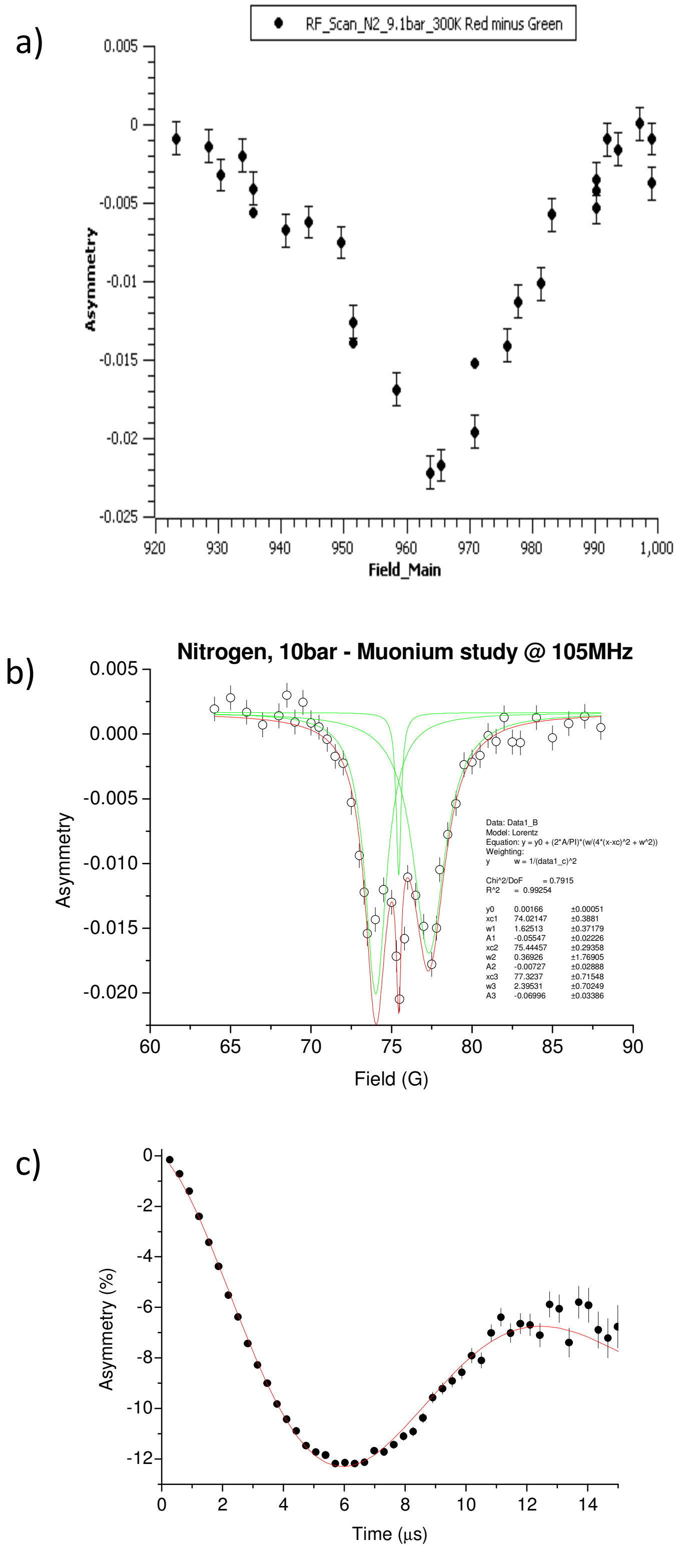


Figure 4: Metal gas cell (a) designed for the ISIS High Field spectrometer and (b) the internal RF coil.



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Data: Data1_B
Model: Lorentz
Equation: y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))
Weighting:
y          w = 1/(data1_c)^2

Chi^2/DoF        = 0.7915
R^2      =  0.99254

y0         0.00166          ±0.00051
xc1        74.02147         ±0.3881
w1         1.62513          ±0.37179
A1         -0.05547         ±0.02226
xc2        75.44457         ±0.29358
w2         0.36926          ±1.76905
A2         -0.00727         ±0.02888
xc3        77.3237          ±0.71548
w3         2.39531          ±0.70249
A3         -0.06996         ±0.03386
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Figure 5: Resonance field scans for diamagnetic muons (a) and Mu (b) for muons implanted in nitrogen gas. The precession of the diamagnetic fraction about the RF field at resonance is shown in (c).

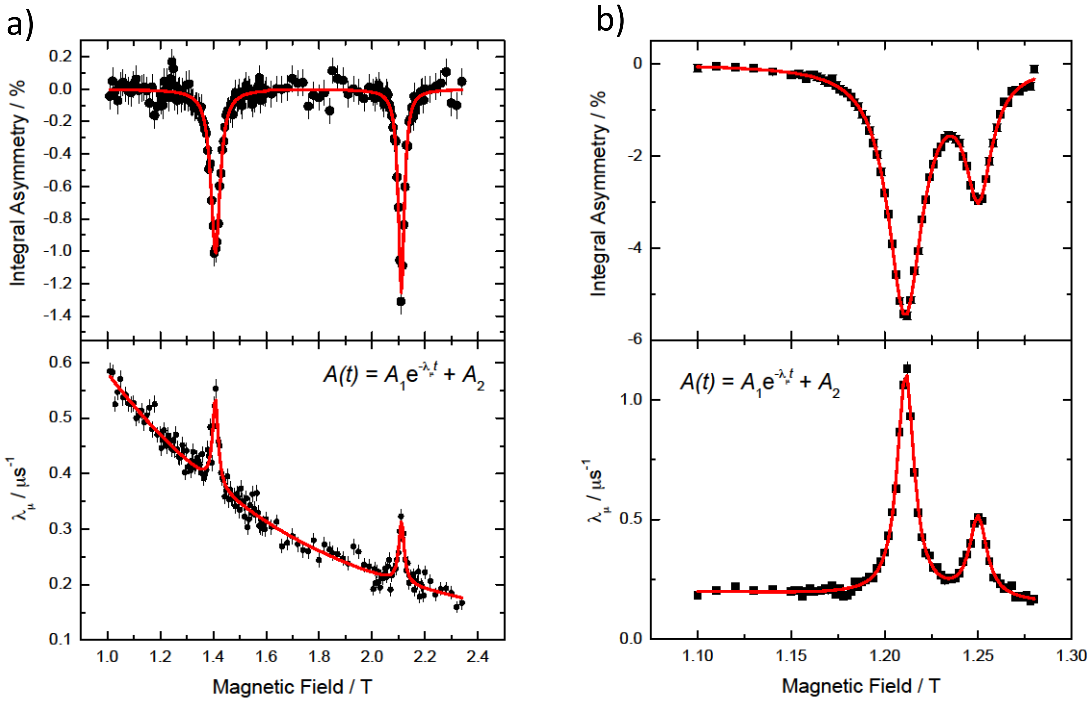

Figure 6: ALC data for the ethyl (a) and tert-butyl muoniated radicals (b) formed by implanting muons into gaseous ethene and isobutene respectively.

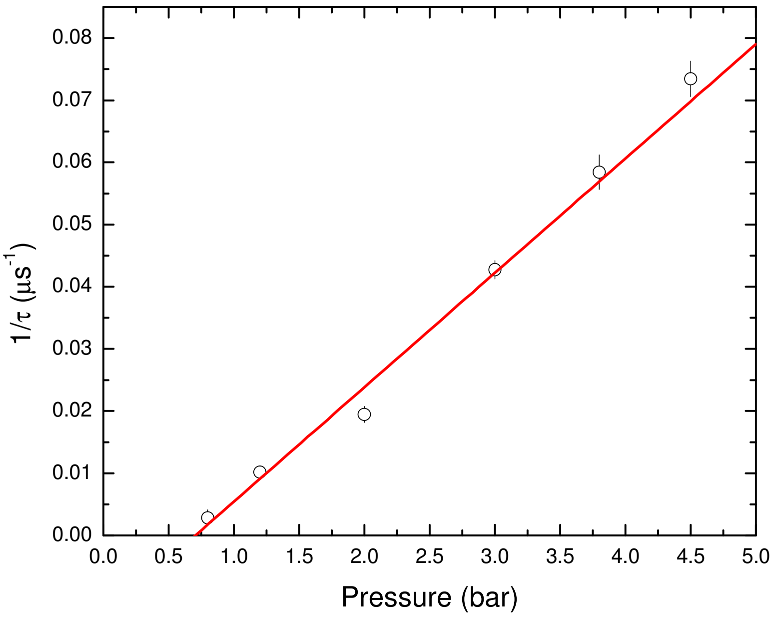

Figure 7: Plot of the fitted results for 1/τ as a function of propane partial pressure. A fit to this data yields a rate constant, k_{Mu}, of $(7.8 \pm 0.5)\times10^{-16}$ cm^3s^{-1}.