Abstract. Longitudinal field muon spin relaxation (LF-µSR) has been used to measure the magnetic field dependence of the longitudinal field muon spin relaxation rates \( \lambda_{\mu} = 1/T_{\mu}^{\mu} \) of two muoniated radicals, 2-muoxyp-2-yl radical (formed by Mu addition to acetone) and the muoniated 1,2-dicarboxyvinyl radical dianion (formed by Mu addition to the 1,2-dicarboxyacetylene dianion), in aqueous solution. The rotational correlations time of the radicals in solution at 298 K were determined from the magnetic field dependence of \( \lambda_{\mu} \) and were found to be 32 ± 2 ps for the 2-muoxyp-2-yl radical and 55 ± 3 ps for the muoniated 1,2-dicarboxyvinyl radical dianion.

1. Introduction
The measurement of nuclear and electron spin relaxation rates as a function of magnetic field and temperature can give useful information about molecular dynamics of free radicals in the liquid-phase and the interaction between the radical and the solvent [1, 2, 3]. Electron paramagnetic resonance is the main technique used to study free radicals; however, measurements are often difficult in solution due to the high reactivity of the radical species. In such cases, there can be important advantages in using muon spectroscopic techniques to study muoniated isotopomers of the radicals. These methods and their role in free radical chemistry have been extensively reviewed [4, 5], so only a basic description is given here. A beam of spin-polarized positive muons is injected into a sample and the positron produced by the decay of each muon detected. Muons can pick up a radiolytic electron and form Mu, which is considered to be a light isotope of hydrogen. This species can then react with unsaturated molecules to produce a muoniated radical, where the muon is a ∼100% polarized spin label. The parity-violating decay of the muon provides a convenient way to monitor the evolution of the muon spin polarization, and its lifetime (2.2 μs) is comparable to many molecular processes.

In this paper we report measurements of the magnetic field dependence of the longitudinal field muon spin relaxation rates \( \lambda_{\mu} = 1/T_{\mu}^{\mu} \) of two muoniated radicals, 2-muoxyp-2-yl radical (formed by Mu addition to acetone [6]) and the muoniated 1,2-dicarboxyvinyl radical dianion (formed by Mu addition to the 1,2-dicarboxyacetylene dianion [7]), in aqueous solution. The structures of the muoniated radicals are shown in Fig. 1. The electron spin-lattice relaxation
times ($T_1^*$) of the non-muoniated isotopomers of the radicals have been previously measured using EPR spectroscopy [2, 3] but only at one field, which provides insufficient data to determine the rotational correlation time. The rotational correlation time of a muoniated radical can be determined by measuring the magnetic field dependence of $\lambda_{\mu}$ [8]. The goal of these experiments was to determine whether the reorientational dynamics of an open shell species in solution are significantly different from the closed shell analogues.

2. Experimental

Two samples were used in these experiments; a 1.0 M aqueous solution of acetone and a 0.5 M aqueous solution of sodium acetylenedicarboxylate ($\text{Na}_2\text{C}_4\text{O}_4$). Acetone was purchased from Sigma-Aldrich and dissolved in Millipore water. Acetylenedicarboxylic acid was purchased from Fluka. The 0.5 M aqueous solution of $\text{Na}_2\text{C}_4\text{O}_4$ was prepared by dissolving acetylenedicarboxylic acid in Millipore water and titrating with NaOH. Molecular oxygen was removed from the solutions by repeated cycles of freezing, pumping and thawing; a necessary step to avoid Heisenberg spin-exchange between the $\text{O}_2$ and the Mu or radical species contributing to the spin relaxation rate.

The samples were sealed in a titanium cell with a 100 $\mu$m titanium window, through which surface muons (28 MeV c$^{-1}$) can penetrate. The sample cells were mounted in a Closed Cycle Cryocooler to control the temperature at 298 K. Measurements were made using the EMU spectrometer at the ISIS Pulsed Muon Facility, STFC Rutherford Appleton Laboratory [9, 10].

The LF-$\mu$SR technique involves measuring the asymmetry of the muon decay, $a(t)$, as a function of time. The asymmetry is proportional to the muon polarization along the $z$-axis (i.e. the beam axis). The asymmetry is obtained by counting the number of positrons detected in the forward ($N_F$) and backward ($N_B$) counters (with respect to the muon beam momentum) as a function of time after the implantation of the muons.

$$a(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) - \alpha N_B(t)}$$

where $\alpha$ is a measure of the relative efficiencies of the forward and backward detectors, and was determined by measuring the spin rotation spectrum in a small transverse field (20 G). Decay events from each detector are accumulated over many muon pulses and formed into separate histograms each of total length 32 $\mu$s with a timing resolution of 16 ns. The maximum asymmetry of the EMU spectrometer, $a_{\text{max}}$, was determined by carrying out a similar spin rotation measurement for muons stopped in a silver plate - where all the muons are in a diamagnetic environment.

Spin relaxation in a multilevel system, as for the radicals studied here, is properly described by the sum of several exponential terms [11]. Properties of the system, such as a distribution of...
correlation times, local environments or, perhaps, hindered molecular dynamics may, however, complicate this analysis, and a form of the stretch exponential (Eq. 2) can frequently be expected. The time dependence of the asymmetry was modelled with the following equation,

$$a(t) = a_D + a_R e^{-(\lambda_\mu t)^\beta}$$

(2)

where $a_D$ is the asymmetry due to muons in diamagnetic environments and is equal to the precession amplitude in a 20 G transverse field, $a_R$ is the asymmetry due to muons in a paramagnetic species, $\lambda_\mu$ is the muon spin lattice relaxation rate ($= 1/T_1^\mu$) and $\beta$ is the stretch exponent. In our case, data for the (CH$_3$)$_2$COMu radical could be adequately modelled with $\beta$ fixed at 1; in contrast, however, the vinyl radical dianion displays a root exponential time dependence at fields above 10 G. The initial polarization of the paramagnetic species is given by:

$$P_R = \frac{a(0) - a_D}{a_{\text{max}} - a_D}$$

(3)

3. Results and Discussion

We obtained LF-$\mu$SR spectra of all samples as a function of longitudinal magnetic field and examples for both (CH$_3$)$_2$COMu and C$_4$O$_4$Mu$^2-$ are shown in Figure 2.

The identity of the paramagnetic species was confirmed by measuring the initial polarization as a function of the applied magnetic field. This is typically called a repolarization curve and the inflection point is related to $A_\mu$ as described by the following equation:

$$P_z = \frac{\frac{1}{2} + x^2}{1 + x^2}$$

(4)

where $x = \gamma_e B/A_\mu$ and $\gamma_e$ is the electron gyromagnetic ratio.

The outcome is unambiguous for muons stopped in water (shown as the blue line in Fig. 3), where the repolarization of the prompt Mu state yields a curve with a single well defined inflection point that gives a fitted value for $A_\mu = 4836 \pm 156$ MHz. This value can be contrasted with an accurate measurement made using spin rotation methods that gives $A_\mu = 4432.4 \pm 1$ MHz [12], suggesting that large errors might be expected for coupling constants determined by repolarization.
In comparison to the repolarization curve measured for Mu in aqueous solution, the curves measured for the transient radicals (also shown in Fig. 3) clearly exhibit a more complex polarization recovery with field, with both curves apparently containing two components. Multiple components to a repolarization curve can indicate either the formation and coexistence of multiple paramagnetic species or that the lifetime of the Mu precursor is long with respect to $1/A_{\mu} \sim 0.2$ ns. The latter case is expected for the present system since the molecular species being studied are in dilute solution. The rate of Mu addition to acetone in a concentrated aqueous solution was determined to be $(8.5 \pm 2.1) \times 10^7$ $M^{-1}s^{-1}$ [13] so we expect the lifetime of Mu in the 1.0 M acetone solution to be $\sim 12$ ns.

A phenomenological model that describes the latter situation was first proposed by Cox, for deep and shallow-donor states in semiconductors [14] and, more recently, developed by Fleming et al. during a study of Mu adducts of bromine [15]. The model suggests a modified function for the repolarization curve, of the form:

$$P_R = f_O + f_S \times \frac{1}{2} + \frac{x_{Mu}^2}{1 + x_{Mu}^2} \times \frac{1}{2} + \frac{x_R^2}{1 + x_R^2}$$

(5)

where $x_{Mu} = \gamma_e B/A_{\mu}^{Mu}$ models the precursor Mu state and $x_R = \gamma_e B/A_{\mu}^{R}$ the final radical state. Nuclear couplings are accommodated to a limited extent by an ‘offset’ parameter, $f_O$, with errors due to changes in $\alpha$ with magnetic field accounted for by a ‘scaling factor’, $f_S$.

Using this equation to fit the curves obtained for the transient radicals, with the muon hfcc of Mu fixed at 4432.4 MHz [12], provides an estimate for the muon hfcc of the final state for each radical species. Values obtained are shown in Table 1 together with muon hfccs determined using spin rotation methods for identical systems in high concentration. Considering that repolarization curves are a notoriously poor method of determining muon hfccs and the given limitations of the fitting model, large errors in determining the hfccs are likely - certainly much larger than the statistical errors determined from the fit and quoted in the table. The results obtained from the repolarization measurements are therefore of limited quantitative value, but importantly provide a good indication that final state radical species are formed as anticipated in this system.

Table 1. Comparison of muon hyperfine coupling constants determined by TF-$\mu$SR and repolarization curves.

| Sample      | Radical     | $A_{\mu}^{TF-\mu SR}$ / MHz | $B_0$ / G | $A_{\mu}^{repol}$ / MHz |
|-------------|-------------|------------------------------|-----------|-------------------------|
| 1.0 M acetone | (H$_3$C)$_2$COMu | $\sim 22$ | $19 \pm 2$ | $53 \pm 6$ |
| 0.5 Na$_2$C$_4$O$_4$ | C$_4$O$_4$Mu$^{2-}$ | $493.8 \pm 0.2$ | $132 \pm 23$ | $370 \pm 64$ |

$^a$ Ref. [6], $^b$ Ref. [7]

Fitted values for the relaxation rate, $\lambda_{\mu}$, in both (H$_3$C)$_2$COMu and C$_4$O$_4$Mu$^{2-}$ are shown in Fig. 4, and were found to depend on the applied magnetic field in a similar manner. Fleming et al. thoroughly investigated the magnetic field dependence of $\lambda_{\mu}$ of the muoniated ethyl radical in the gas phase [8]. There are several relaxation processes, which dominate at different values of the applied magnetic field. A muon spin flip can be induced directly or indirectly by flipping the electron spin, which is coupled to the muon via the hyperfine interaction, or by coupled muon-electron “flip-flop” or “flip-flip” processes. The field dependence of $\lambda_{\mu}$ for both (H$_3$C)$_2$COMu and C$_4$O$_4$Mu$^{2-}$ could best be fit using the expression given by Fleming et al. for
Figure 3. Repolarization curves for Mu formed in water, 0.5 M Na$_2$C$_4$O$_4$ in water and 1.0 M acetone in water. The solid lines for (H$_3$C)$_2$COMu and C$_4$O$_4$Mu$^{2-}$ are fits using equation 5.

coupled processes with the addition of a field-independent relaxation term, $\lambda_0$:

$$\lambda_\mu = \lambda_0 + \frac{2\Delta_{ME}^2\tau_c}{1 + (\gamma_e\tau_c)^2} \cdot B^2$$

(6)

where $\Delta_{ME}$ is the matrix element and $\tau_c$ is the motional correlation time. From the magnetic field dependence of the relaxation data we have determined that $\tau_c$ of (H$_3$C)$_2$COMu is 32 $\pm$ 2 ps and $\tau_c$ of C$_4$O$_4$Mu$^{2-}$ is 55 $\pm$ 3 ps.

For molecules in H$_2$O at room temperature ($\eta = 1$ cP) $\tau_c$ can be approximated as

$$\tau_c(\text{ps}) \simeq 0.4 \times M_w$$

(7)

where $M_w$ is the molecular weight of the radical [3]. Thus the expected $\tau_c$ of (H$_3$C)$_2$COMu is $\sim$23 ps and the expected $\tau_c$ of C$_4$O$_4$Mu$^{2-}$ is $\sim$45 ps. The experimentally determined $\tau_c$ are therefore in good agreement with the predictions. The value of $\tau_c$ of C$_4$O$_4$Mu$^{2-}$ at 302 K reported in a previous publication from measurements of $\lambda_\mu$ in zero magnetic field (1.1 $\pm$ 0.1 ns [7]) appears to be off by a factor of $\sim$25 from the current measurement. In part this discrepancy may be due to the need to develop Eq. 6 to properly account for the root exponential behaviour of the data; however, a review of recent NMR literature [16] suggests this is likely to have minimal impact on the results obtained. Another source of error may be the value of the hyperfine anisotropy, derived from DFT calculations, that was used to determine $\tau_c$ in the zero field measurements. Further work is required to properly understand the origin of this discrepancy.

4. Conclusions
We have demonstrated that the rotational correlation times of transient radicals in solution can be determined using longitudinal field muon spin relaxation measurements. The measured
Figure 4. Magnetic field dependence of the longitudinal field muon spin relaxation rate for \((\text{H}_3\text{C})_2\text{COMu}\) and \(\text{C}_4\text{O}_4\text{Mu}^{2-}\). The solid lines for \((\text{H}_3\text{C})_2\text{COMu}\) and \(\text{C}_4\text{O}_4\text{Mu}^{2-}\) are fits using Eq. 6.

rotational correlation times are in good agreement with predictions based on approximations made for closed shell molecules. The rotational correlation time of \(\text{C}_4\text{O}_4\text{Mu}^{2-}\) determined from the magnetic field dependence of \(\lambda_\mu\) differs by \(\sim 25\) from the value determined from the temperature dependence of \(\lambda_\mu\) in zero field.

References

[1] Paul H 1975 Chem. Phys. Lett. 32 472
[2] Fessenden R W, Hornak J P and Venkataraman B 1981 J. Chem. Phys. 74 3694
[3] Bartels D M, Lawler R G and Trifunac A D 1985 J. Chem. Phys. 83 2686
[4] McKenzie I and Roduner E 2009 Naturwissenschaften 96 873
[5] McKenzie I 2013 Annu. Rep. Prog. Chem. C 109 65
[6] Hill A, Symons M C R, Cox S F J, De Renzi R, Scott C A, Bucci C and Vecli A 1985 J. Chem. Soc. Faraday Trans. 1 81 433
[7] McKenzie I 2011 Phys. Chem. Chem. Phys. 13 1168
[8] Fleming D G, Pan J J, Senba M, Arseneau D J, Kiefl R F, Shelley M Y, Cox S F J, Percival P W and Brodovitch J-C 1996 J. Chem. Phys. 105 7517
[9] Eaton G H, Clarke-Gayther M A, Scott C A, Uden C N and Williams W G 1994 Nucl. Instr. Meth. Phys. Res. A 342 319
[10] Giblin S R, Cottrell S P, King P J C, Tomlinson S, Jago S J S, Randall L J, Roberts M J, Norris J, Howarth S, Mutamba Q B, Rhodes N J and Akeroyd F A 2014 Nucl. Instr. Meth. Phys. Res. A 751 70
[11] Cox S F J 1998 Solid State Nucl. Magn. Reson. 11 103
[12] McKenzie I, Dilger H, Roduner E, Scheuermann R and Zimmermann U 2008 J. Phys. Chem. B 112 3070
[13] Venkateswaran K, Kiefl R F, Barnabas M V, Stadlbauer J M, Ng B W and Walker D C 1988 Chem. Phys. Lett. 145 289
[14] Cox S F J 2009 Rep. Prog. Phys. 72 116501
[15] Fleming D G, Cottrell S P, McKenzie I and Macrae R M 2012 Phys. Chem. Chem. Phys. 14 10953
[16] Kuhn A, Kunze M, Sreeraj P, Wiemhöfer H-D, Thangadurai V, Wilkening M and Heitjans P 2012 Solid State Nucl. Magn. Reson. 42 2