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Jun 1982SPIN DEPOLARIZATION IN MUONIUM BY
HYDRATED ELECTRONSPaul W. PERCIVAL, Jean-Claude BRODOVITCH and
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Simon Fraser University, Burnaby, B.C., Canada V5A 1S6Abstract

The missing fraction of muon polarization in water is shown to originate from encounters between muonium and hydrated electrons. This takes place at about 1 ns after the primary events in which muonium and hydrated electrons are born.

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If spin polarized positive muons are stopped in pure water two different species can be identified on the basis of their muon precession signals [1]. One signal is attributed to muonium [2], the hydrogen-like atom made up of a positive muon and an electron ($\mu \equiv \mu^+e^-$). Its amplitude corresponds to a fraction $P_M = 0.196 \pm 0.003$ of the initial polarization of the muon beam [3]. The second signal arises from muons in a diamagnetic environment, most likely in the form of muonium substituted water, μODH . The diamagnetic fraction corresponds to $P_D = 0.622 \pm 0.006$ [3]. Part of the initial polarization, $P_L = 0.182$, is left unaccounted for and is termed "the missing fraction".

Analysis of the magnetic field dependence of P_D for aqueous solutions of sodium nitrate indicated a larger muonium fraction than for pure water, and it was concluded that the missing fraction arises from partial depolarization of the muonium fraction at some time prior to direct observation of the muonium precession signal [3]. This view was supported by a further study using solutions of potassium chromate [4]. Furthermore, longitudinal field experiments suggested that the depolarization stems from spin relaxation rather than chemical reaction of muonium [4]. These results are all consistent with the hypothesis [3] that the missing fraction is caused by spin exchange encounters between muonium and one or other of the transient paramagnetic species (X) formed in the radiolysis of water along the muon track. A similar suggestion has been made to account for the fast relaxation exhibited by half of the muonium signal in liquid argon and for the missing fractions in liquid xenon and krypton [5]. The fast signal decay in argon occurs with a relaxation time of about 50 ns. Faster decays are

unlikely to be resolved using currently available μ SR technology.

The timescale for the missing fraction depolarization in water was estimated to be 2-100 ns [4] on the basis of the results for nitrate and chromate solutions. However, these ions react at high rates (table 1) with both muonium and e_{aq}^- , the principal contender for X, so it is not possible to tell if inhibition of the missing fraction process is due to scavenging of e_{aq}^- or Mu. Indeed, if scavenging of Mu is instrumental then the spin exchange hypothesis represented in scheme (1)

in which S is the scavenger under study may be replaced with a simpler scheme (2) but for which the nature of the depolarization process is unknown.

The experiments described in this paper were devised to distinguish between the above two schemes, to test the identity of X, and to narrow the time range over which the missing fraction can be deduced to operate. Our strategy entailed the use of strongly acidic solutions in which e_{aq}^- would be very quickly transformed to H atoms. Now, previous work has already shown that the missing fraction is unaffected even in 5M HCl [3]. The new departure was use of nitrate as scavenger in the acidic medium. Under these conditions the scavenger reacts over two orders of magnitude faster with Mu than with X (now H).

Experiments were performed at TRIUMF using a "backward" muon beam

and standard transverse field μ SR techniques [1]. The samples consisted of solutions of 0.1 M and 0.5 M sodium nitrate in 1.8 M sulphuric acid, and a "blank" of sulphuric acid alone. Each sample was investigated at six different magnetic fields from 50 G to 1600 G. μ SR histograms were simultaneously accumulated for three different positron telescopes. Measurements of muon asymmetry A_D were converted to muon polarization P_D by calibration against the corresponding measurements of A_D for the sulphuric acid sample, for which $P_D = 0.622$ was assumed. Values of P_D determined from the three histograms were then averaged to give the results plotted in fig. 1. The uncertainty in the points is ± 0.012 .

The dependence of P_D on magnetic field (B) was analysed separately for each nitrate concentration by computer fit to the expression

$$P_D = h_D + (1 - h_D - h_L) P_{\text{res}}(B, \lambda) \quad (3)$$

$P_{\text{res}}(B, \lambda)$ is a function which describes how the fraction of muon polarization conserved in the reaction of muonium to diamagnetic product varies with reaction rate $\lambda = k[\text{NO}_3^-]$ and field [3]. h_D is the field independent initial diamagnetic fraction, and h_L represents muonium which has been depolarized prior to reaction with nitrate, i.e. the missing fraction.

In neutral solutions h_L was found to be zero for concentrations of nitrate 0.1 M and above [3]. The presence of acid makes a big difference, as attested by the results given in table 2. A pronounced missing fraction is evident, indicating that these concentrations of NO_3^- are insufficient to scavenge the agent responsible for the missing fraction prior to muonium reaction. Since the same concentrations of NO_3^- completely inhibit the missing fraction in neutral solution it

follows that scavenging of X is the crucial factor, i.e. scheme 1 is valid. Furthermore, X is identified as eaq^- (in neutral solution) since this is the only primary radiolysis product whose nature is so drastically altered in the presence of acid.

Confirmation of the reaction scheme now makes it possible to pin down the timescale of the missing fraction by consideration of the competition between muonium depolarization and the scavenging of Mu and/or $\text{X}(\text{eaq}^- \text{ or } \text{H})$. The effect of this competition is evident in table 3, which combines the new results with old data [3,4] and similar material from other work in progress (to be reported elsewhere). A reduced missing fraction is defined as the ratio of depolarized muonium (h_L) to the initial muonium yield ($1-h_D$). In table 3 the reduced missing fraction is correlated with the lifetimes (τ) of Mu and X. For sufficiently long lifetimes the reduced missing fraction takes its maximum value of 0.5, but if either $\tau(\text{Mu})$ or $\tau(\text{X})$ falls to 1 ns or so, the missing fraction is reduced, reaching zero for lifetimes as short as 0.5 ns. Thus extremes of 0.5 and 5 ns may be set on the timescale of the missing fraction.

Although the missing fraction develops in about 1 ns it would be misleading to interpret this as an approximate rate of muonium depolarization of $1 \times 10^9 \text{ s}^{-1}$. The kinetics are certainly non-homogeneous, and the actual spin exchange resulting in depolarization is instantaneous compared with the time for diffusion of Mu and eaq^- to the required encounter. Since Mu and eaq^- are estimated to diffuse only $\sim 2 \text{ nm}$ each in 1 ns, an encounter at this time implies that these species

are born close to one another, thus lending credence to the spur model of muonium formation [3,8].

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Table 1

Rate constants for some reactions in aqueous solution

Reactants	Rate constant ^a (M ⁻¹ s ⁻¹)	Reference
e _{aq} ⁻ + H _{aq} ⁺	1.2 × 10 ¹⁰	[6]
e _{aq} ⁻ + NO ₃ ⁻	2.0 × 10 ¹⁰	[6]
e _{aq} ⁻ + CrO ₄ ²⁻	5 × 10 ¹⁰	[7]
Mu + NO ₃ ⁻	2 × 10 ⁹	[3]
Mu + CrO ₄ ²⁻	2.5 × 10 ¹⁰	[8]
H + NO ₃ ⁻	7 × 10 ⁶	[9]

^aAppropriate high concentration values selected

Table 3

Reduced missing fractions in aqueous solutions

Solution	τ(Mu)/ns ^a	τ(X)/ns ^a	$\frac{h_L}{1-h_D}$
0.04M CrO ₄ ²⁻	1	0.5	0
0.1 M NO ₃ ⁻	5	0.5	0
1.0 M NO ₃ ⁻ + 1M H _{aq} ⁺	0.5	∞ ^b	0
10 M OH ⁻	0.6	∞	0.3
0.5 M NO ₃ ⁻ + 1.8M H _{aq} ⁺	1	∞	0.4
0.1 M NO ₃ ⁻ + 1.8 M H _{aq} ⁺	5	∞	0.5
pure water	∞	∞	0.5

^aLifetimes calculated from data of table 1^b∞ ≡ 10³ ns or longer

Table 2

Analysis of muon polarization in acidic nitrate solutions (1.8 M H_{aq}⁺)

[NO ₃ ⁻]/M	h _D	h _L	k/M ⁻¹ s ⁻¹
0.1	0.645 ± 0.004	0.177 ± 0.028	(3.6 ± 0.5) × 10 ⁹
0.5	0.680 ± 0.007	0.136 ± 0.021	(2.6 ± 0.7) × 10 ⁹

Figure Caption

Fig. 1. Muon polarization in acidic solutions of sodium nitrate. The smooth curves represent the best fits of eq. (3) to the data.