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"FAST" DEPOLARIZATION OF POSITIVE MUONS IN SOLUTION--THE CHEMISTRY OF ATOMIC MUONIUM*

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The initial magnitude and direction of the residual asymmetry in the decays of polarized positive muons stopped in solutions in transverse magnetic fields are observed to depend strongly upon the concentration of dissolved compounds. Such effects were seen in methanol solutions of I_2 and in aqueous solutions of $FeCl_3$ and $Fe(ClO_4)_3$. The underlying fast depolarization mechanism can be qualitatively and quantitatively understood by assuming muonium formation with subsequent chemical reaction of the atomic muonium with dissolved compounds.

Positive muons stopping in pure noble gases almost always form the neutral hydrogen-like muonium atom (μ^+e^-),[1] hereafter designated Mu. The existence of Mu has been inferred from observation in gases of hyperfine structure transitions[2] and rapid precession in a transverse field.[3-5] Presumably muons stopped in liquids and solids also form Mu; in these cases, chemical activity significantly shortens the lifetime of the free Mu, so that Mu has been observed only in a few relatively inert solids. In muon precession experiments, the apparatus is designed to detect precession only at the muon Larmor frequency (1/103 that of Mu in weak fields), and in a practical sense muons which form Mu appear

depolarized. The observation of strong variation of the muon decay asymmetry with chemical composition in the target implies the existence of Mu that remains chemically uncombined for $\lesssim 10^{-8}$ sec. Depolarizing processes with time scales longer than a few nsec are observed directly, since the typical apparatus has a resolution $\approx$ 1 nsec. Such an effect has been observed in sulfur.[6] In all cases treated here, however, "fast" depolarization takes place before observation begins.

"Slow" depolarization may also take place on a time scale of μsec,[7,8] but the "residual" asymmetry discussed here is the value extrapolated to zero time, and reflects only "fast" effects.

The hyperfine structure of the Mu ground state and its relation to the muon decay asymmetry have been discussed by many authors.[9] It should be pointed out, however, the Mu formation alone does not cause relaxation of the muon spin in a thermodynamic sense. To account for this, additional irreversible processes are necessary. The removal of muons from the free Mu state at random times by chemical reaction into diamagnetic compounds constitutes such a process.

If the Mu electron's spin is coupled to the medium, causing "spin flips" at a frequency ν, the hyperfine coupling may be partly or completely broken. The remaining coupling produces a transfer of longitudinal muon polarization to the lattice or medium--an additional irreversible process. In transverse magnetic fields the depolarization decreases with increasing ν.

The superposition of muons emerging from free Mu at different times causes an overall depolarization by "dephasing," and may also produce a rotation of the initial polarization direction. The observation of such changes in initial phase is therefore evidence for the initial existence of muons in Mu atoms.

The foregoing mechanisms have been described analytically by

Ivanter and Smilga,[10] using the Wangsness-Bloch equations for the time dependence of the density matrix.

After the incoming muons capture electrons, the resultant Mu atoms are thermalized in $\approx 10^{-12}$ sec.[11] Prior to this time these "hot" atoms have sufficient kinetic energy to experience reactions that are energetically suppressed for thermalized atoms. Thus a substantial fraction (h) may enter diamagnetic compounds through the "hot chemistry channel" before they are influenced by the muonium depolarization mechanism; these muons are not depolarized, regardless of field or concentration. This fraction is responsible for the residual polarization observed in relatively inert gases, liquids, and solids, in which Mu formation is likely, when ν is small and the mean chemical lifetime of Mu is long. The Mu hot atom channel can be related to hot tritium chemistry.[11]

The theoretical expression for the residual polarization, including the contribution from the hot atom channel, has been given by Ivanter and Smilga:[12]

$$\vec{P} = h\,\vec{P}_0 + (1 - h)\,\vec{P}(\tau, \nu, B), \qquad (1)$$

where $\vec{P}_0$ is the polarization of muons emerging from hot atom reactions into diamagnetic compounds and is along $\hat{x}$, the beam polarization direction. Imperfect beam polarization is absorbed into the experimental parameter A_0, as seen later. $\vec{P}(\tau, \nu, B)$ is the polarization of muons emerging from Mu into diamagnetic compounds via ordinary chemical reactions (where τ is the mean chemical lifetime of free Mu), and may differ from $\vec{P}_0$ in both magnitude and direction. With the field B held constant, the observed polarization is a function of ν and τ that may depend upon the concentration of dissolved reagents.[13] In dilute solutions, the reaction rate of Mu is described by

the reaction formula

$$\frac{dp}{dt} = -\,k[N],\ p, \qquad (2)$$

where p is the probability that Mu is still uncombined, [N] is the concentration of dissolved reagent, and k is the chemical rate constant for the reaction that removes Mu from solution. The chemical lifetime of free Mu is

$$\tau = \frac{1}{k[N]}. \qquad (3)$$

Thus we have analytic expressions for the magnitude $P = |\vec{P}|$ and the phase $\phi = \arccos\left(\frac{\vec{P}\cdot\hat{x}}{P}\right)$ of the residual polarization. For the explicit expression of Eq. (1), see Ref. 12.

The aim of this experiment was to verify Eq. (1) and use it to study the chemical behaviour of Mu, analogous to atomic hydrogen.[15] For each substance studied, a series of runs differing only in the concentration of dissolved material provided data of residual asymmetry as a function of concentration; by using (1) and (3), and this information, a value for the chemical rate constant k was calculated. In the case of I_2 in methanol, it was also possible to measure the initial phase as a function of concentration, where only Mu formation could produce any variation. I_2 and Fe^{+++} were chosen because they are known as good scavengers; reactions of Mu with these compounds can be expected to be more or less diffusion-limited:

$$Fe^{+++} + (\mu^+ e^-) \rightarrow Fe^{++} + \mu^+,$$

$$Mu + I_2 \rightarrow MuI + I.$$

Fe^{+++} solutions were prepared in 0.02 N acids of the appropriate anions.

The residual asymmetry was measured in transverse magnetic fields of 1000 and 4500 Oe as a function of concentration. A

description of the apparatus and detection method can be found in Ref. 11. The experimental histogram of the counting rate (0.5-nsec bins) as a function of time was in each case fitted to the distribution

$$N(t) = N_0\{\exp(-t/\tau_\mu)[1 + A\exp(-t/T_2)\cos(\omega t + \phi)] + B\},$$

in which τ_μ = 2.198 μsec = mean muon lifetime,

ω = muon Larmor frequency (0.85×10^5 Hz/Oe),

$A = A_0|\vec{P}|$ = experimental asymmetry,

A_0 = maximum possible asymmetry for the given beam polarization and target and counter geometry (i.e., the asymmetry corresponding to no depolarization),

B = time-independent background,

ϕ = initial phase of the precession, and

T_2 = "slow" (μsec scale) transverse relaxation time seen in paramagnetic solutions.[8, 14]

A variable-metric χ^2 fit to the data produced values and errors for all these parameters. The fraction h of hot-chemistry reactions was determined by comparing the asymmetry observed in the pure solvent (assumed virtually inert with respect to "cold" reactions) with the completely "repolarized" asymmetry observed at high concentrations; the latter is assumed to correspond to P = 1, and thus gives the parameter A_0. In both methanol and water, h was close to 1/2.

As can be seen from Figs. 1 and 2 (upper) this model fits the asymmetry data fairly well, allowing one to determine chemical rate constants with some precision. The final results are given in Table I.

The only chemical distinction between Mu and atomic hydrogen is the difference in their masses. In any collision or diffusion picture, the rate constant is proportional to the mean velocity, $(8kT/\pi\mu)^{1/2}$, where μ is the reduced mass; thus to a good

approximation

$$\frac{k\,(Mu)}{k\,(H)} = \left[\frac{m\,(H)}{m(Mu)}\right]^{1/2} = 3.0. \qquad (4)$$

Thus a measurement by Sweet and Thomas[17] of the absolute rate constant $k = 9.0\times10^7$ liters/mole-sec for the reaction $H + Fe^{+++} \rightarrow H^+ + Fe^{++}$ in H_2SO_4(pH 2.1) corresponds to a rate constant of 0.27×10^9 liters/mole-sec for the analogous reaction with Mu. This is 1.7×10^{-2} of our result, a rather large difference to attribute to the different anions.

For values of $h \approx 0.5$, the initial phase of the polarization is visible only in fields of 1000 Oe and less, so that we have only one set of data including phase measurements, the I_2 in methanol at 1000 Oe (Fig. 2, lower). It is evident that there is some variation of the phase in the sensitive region, which amounts to conclusive evidence for muonium formation, since in the nonmagnetic I_2 solutions there is no interaction besides the hyperfine coupling that could rotate the muon spin through a significant angle in the times ($\approx 10^{-9}$ sec) in which this process must occur. Therefore we can confidently apply the theory of the muonium mechanism in this and future studies to extract chemical rate constants for such processes as these, and perhaps for more complex and interesting cases.

Table I. Best fits to phenomenological parameters.

Field (Oe)	Solvent	Reagent	A_0	h	k (liters mole-sec)
4500	H_2O	$FeCl_3$	0.31 ± 0.02	0.51 ± 0.02	$(2.1 \pm 0.2) \times 10^{10}$
4500	H_2O	$Fe(ClO_4)_3$	0.30 ± 0.02	0.55 ± 0.02	$(1.66 \pm 0.2) \times 10^{10}$
4500	CH_3OH	I_2	0.27 ± 0.02	0.54 ± 0.02	$(1.34 \pm 0.2) \times 10^{11}$
1000	CH_3OH	I_2	0.27 ± 0.02	0.52 ± 0.02	$(1.14 \pm 0.2) \times 10^{11}$

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*Work done under auspices of the U. S. Atomic Energy Commission.

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[13] $\vec{P}(\tau, \nu, B)$ is negligibly affected by $\nu \lesssim 10^{10}$ sec^{-1}; values of $\nu \approx 10^{12}$ sec^{-1} would be required to produce the complete "repolarization" observed at high concentrations. Such an effect is impossible in diamagnetic solutions. To determine whether it could occur in paramagnetic solutions, we have measured the dependence of residual asymmetry upon Mn^{++} ion concentration in $MnCl_2$ solutions, and observed no significant "repolarization" in up to 5 M solutions; "ν effects" are therefore neglected in this treatment. In light of this, the analysis given in our earlier paper (Ref. 14) on muon depolarization in $Fe(NO_3)_3$ solutions is subject to reevaluation.

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[15]The idea of using Mu to study the reactions of atomic hydrogen was first proposed by Firsov and Byakov [Sov. Phys. JETP 20, 719 (1965); V. G. Firsov, Sov. Phys. JETP 21, 786 (1965)]. Their approach, however, seems to have been oversimplified (Ref. 12); related results in a later publication [A. I. Babaev, M. Ya. Balats, G. G. Miyasischeva, Yu. V. Obukhov, V. S. Roganov, and V. G. Firsov, Sov. Phys. JETP 23, 583 (1966)] must therefore be regarded as inconclusive. Reactions of atomic Mu in the gas phase have been studied by Mobley et. al.[16]

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Figure Captions

Fig. 1. Residual muon polarization for Fe^{+++} in H_2O at 4.5 kOe.

●---● $Fe(ClO_4)_3$; △—△ $FeCl_3$.

Fig. 2. (Upper). Residual muon polarization for I_2 in CH_3OH (lower) initial phase for I_2 in CH_3OH. ●---● 4.5 kOe, △—△ 1.0 kOe.

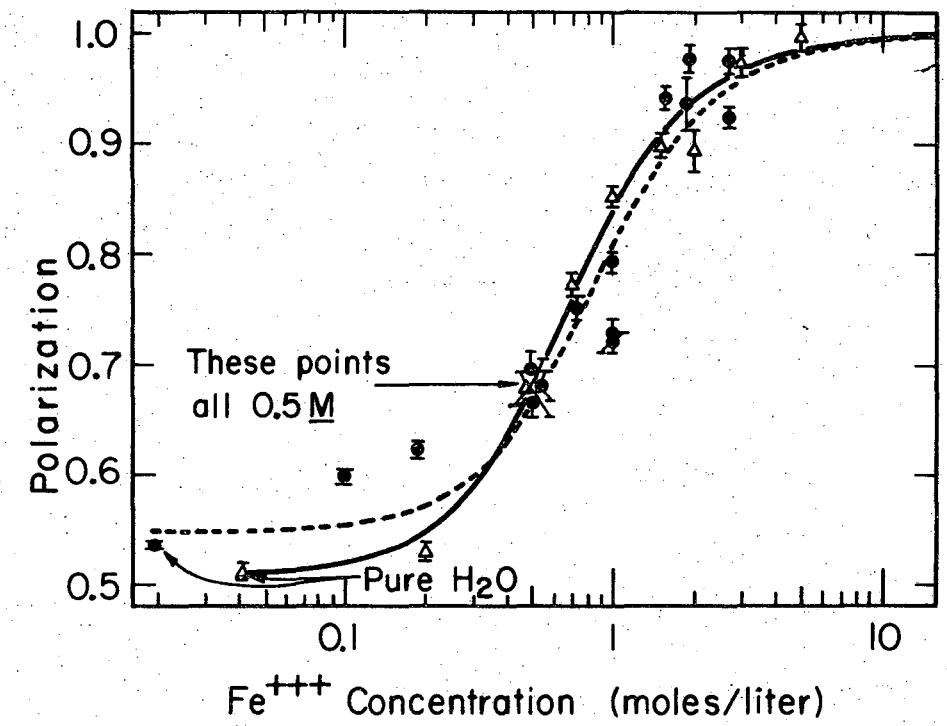

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Fig. 1

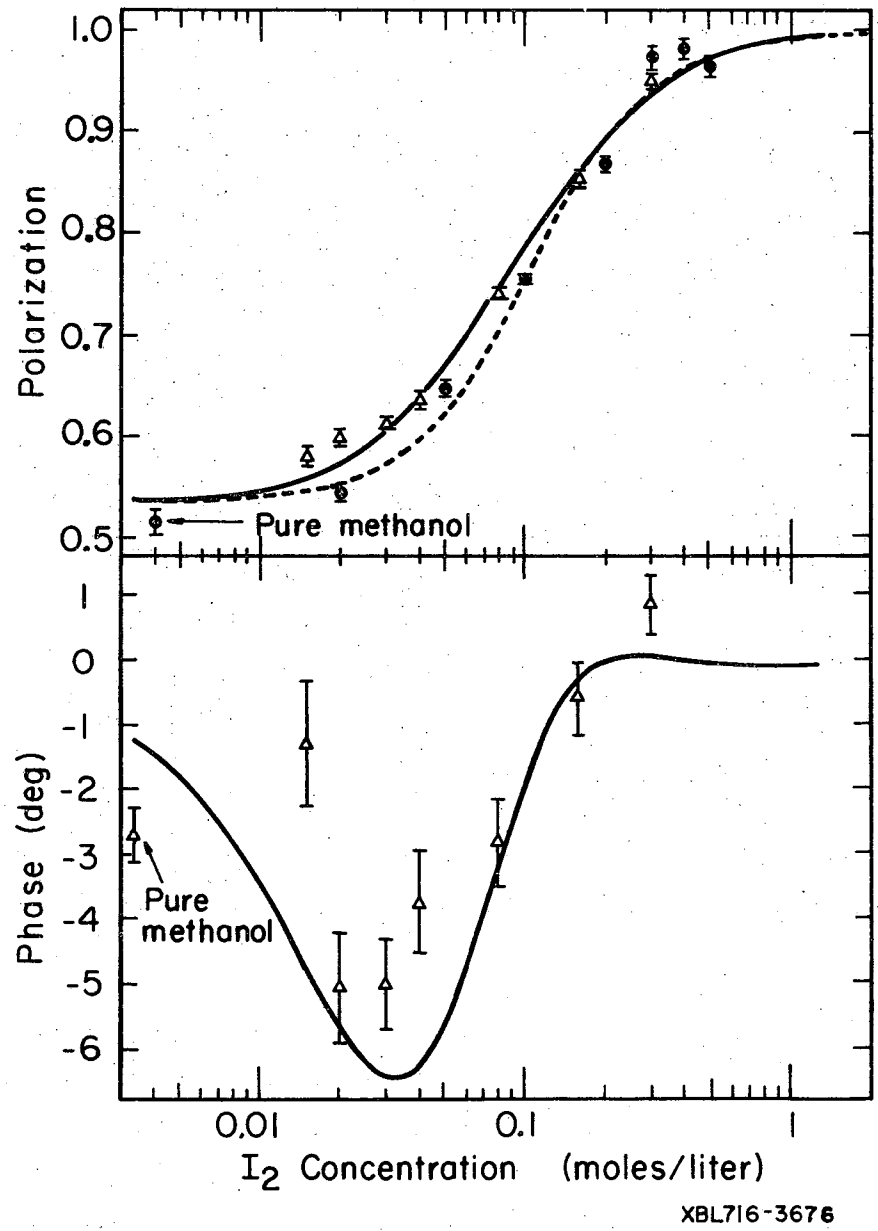
1.0
0.9
0.8
0.7
0.6
0.5
Polarization
Pure methanol
1
0
-1
-2
-3
-4
-5
-6
Phase (deg)
Pure methanol
0.01
0.1
1
I_2 Concentration (moles/liter)
XBL716-3676

Fig. 2

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