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# Muon Depolarization and the Chemistry of Muonium in Liquids

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# Muon Depolarization and the Chemistry of Muonium in Liquids

Jesse Herman Brewer

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## ABSTRACT

Polarized positive muons are stopped in liquids containing dissolved reagents. Their polarization is measured by observing positrons from the asymmetric decay as the muon spins precess in a magnetic field. As the reagent concentration is varied, the apparent initial magnitude and direction (phase) of the polarization change markedly, due to the "muonium mechanism": muons form free muonium and are depolarized in a fraction of a nanosecond via the hyperfine interaction unless the muonium reacts chemically in even shorter times to place the muon in a diamagnetic compound. The observed dependence of the magnitude and phase of the polarization upon reagent concentration confirms the validity of this model and allows extraction of chemical rate constants for fast reactions of muonium (chemically a light isotope of atomic hydrogen). A more complicated situation is also observed, in which muonium reacts to place the muon in a radical compound, where further depolarization takes place via the hyperfine interaction with the unpaired electron. The theory is expanded to include such processes.

## I. INTRODUCTION

### A. Historical Background

Nature has generously provided physicists with parity violation in the weak interaction, which not only furnishes interesting phenomena to study, but also generates techniques with which to study them. A case in point is the  $\pi$ - $\mu$ - $e$  decay series:  $\pi^+ \rightarrow \mu^+ + \nu_\mu$  followed by  $\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$ . Thanks to the unique helicity of the neutrino, the  $\mu^+$  from  $\pi^+$  decay has 100% negative helicity, making it easy to obtain a highly polarized  $\mu^+$  beam by momentum separation of a decaying  $\pi^+$  beam. The muons are then gracious enough to emit the positrons from their decay preferentially along their spins, so that an ensemble of positive muons effectively broadcasts its polarization in a shower of positrons.<sup>1</sup>

These phenomena have been the subject of much investigation in their own right, but they have also made possible the study of processes outside the realm of weak interactions. For instance, a series of experiments utilizing the asymmetric decay of the muon has provided one of the most sensitive tests of quantum electrodynamics.<sup>2,3,4</sup> A critical measurement in this series is the ratio of the muon magnetic moment to that of the proton:  $\mu_\mu/\mu_p$ . This number was recently measured by Crowe et. al.<sup>4</sup> to an accuracy of 2.8 parts per million at the 184 in. Cyclotron in Berkeley, and out of that experiment grew the present study of the interactions of muons with matter. This work has continued with the original apparatus essentially unchanged, and has touched upon

a variety of phenomena, among them the chemical interactions of muonium in liquids, the subject of this dissertation.

## B. Experimental Approach

A relatively simple technique is used in this experiment: a polarized beam of positive muons is stopped in a target in a uniform magnetic field perpendicular to the polarization direction. A counter telescope is arranged (see Fig. 1) with its axis in the plane perpendicular to the field. As a muon precesses in that plane at its Larmor frequency, its spin sweeps past the counter telescope at every revolution; when the decay occurs, the probability of intercepting the positron is enhanced when the muon spin points toward the telescope. Thus if the time from the muon's entry into the target until the positron's exit through the telescope is measured repeatedly, a histogram of the measured times will reflect both the precession and the muon's exponential decay, as shown in Fig. 2. The distribution of times is given by

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

where  $N_0$  = a normalizing factor (in counts/bin)

$B$  = time-independent background (random events)

$\tau_\mu$  = the mean muon lifetime, 2.20  $\mu$ sec

$A$  = "asymmetry" (relative amplitude of the precession)

$T_2$  = transverse relaxation time (usually  $\sim \mu$ sec)

$\omega_\mu$  = muon Larmor frequency,  $0.85 \times 10^5$  rad/sec per gauss

$\phi$  = phase of the precession at  $t = 0$ .

All the parameters except  $\tau_\mu$  (which is known) are extracted from the experimental histogram by a  $\chi^2$  minimization fit, which also returns an estimate of the uncertainties in each parameter.

This process is repeated many times, using targets consisting of different amounts of reagent dissolved in a given solvent, and the resultant plots of A and  $\phi$  versus reagent concentration are compared with the predictions of the theory of the depolarizing mechanism.

Clearly, at a given field strength, the resolution with which the initial phase can be determined is limited by the time resolution of the apparatus, since an error in  $\omega_{\mu} t$  is equivalent to an error in  $\phi$ . With our system, the time resolution was on the order of 1 nsec; at 100 gauss, this corresponds to  $\omega_{\mu} \Delta t \sim \frac{1}{2}^{\circ}$ . Other systematic uncertainties boosted the error bars on the phase to the order of  $\pm 1-2^{\circ}$ , which was still sufficiently accurate to resolve effects characteristic to the theory. The importance of the phase measurement is stressed because it is unique to this experiment and because the phase behavior is an unambiguous test for the validity of the theory.

Figure 1 - TARGET AREA AND COUNTER ARRANGEMENT

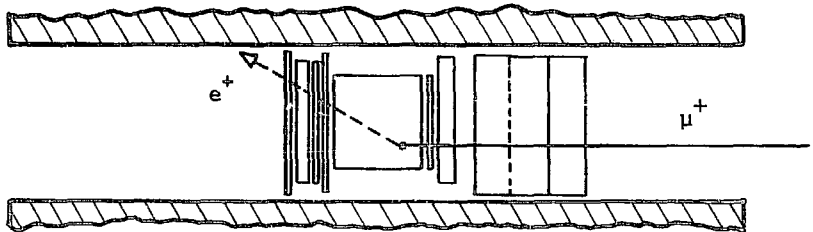
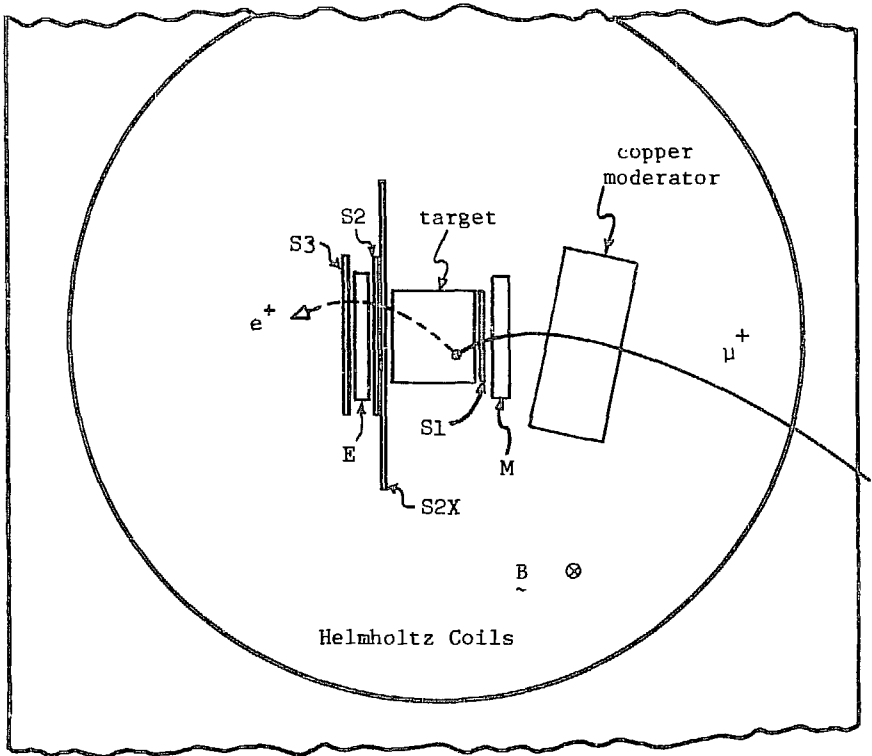
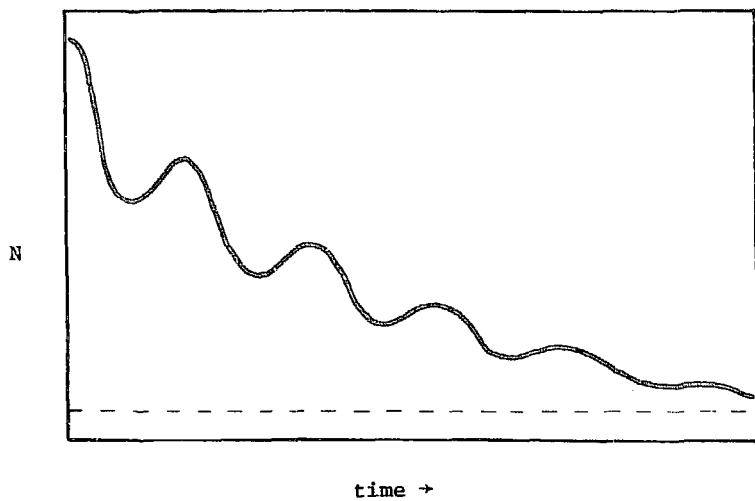




Figure 2 - EXPERIMENTAL HISTOGRAM OF TIME FROM  $\mu^+$  STOP  
UNTIL  $e^+$  DETECTION



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

$N_0$  = a normalizing factor (in counts/bin)

$B$  = time-independent background (random events)

$\tau_\mu$  = the mean muon lifetime, 2.20  $\mu\text{sec}$

$A$  = "asymmetry" (relative amplitude of the precession)

$T_2$  = transverse relaxation time ( $\sim$  microseconds)

$\omega_\mu$  = muon Larmor frequency,  $0.85 \times 10^5$  rad/sec per gauss

$\phi$  = phase of the precession at  $t = 0$

### C. Theoretical Primer

The experimental asymmetry  $A$  is the product of an empirical quantity  $A_0$  and a theoretical quantity  $P_{res}$ .  $A_0$  is the maximum possible asymmetry consistent with beam polarization, counter geometry, positron absorption in the target, and the details of the weak decay. It is difficult (though not impossible) to calculate  $A_0$  by Monte Carlo methods; fortunately,  $A_0$  can be obtained by fitting the concentration-dependence of the polarization, as will be seen later, and therefore  $A_0$  may be considered an empirical number.  $P_{res}$ , the "residual polarization", is a measure of the effect of the target medium upon the muon polarization within a few nanoseconds after the muon stops. Note that the transverse relaxation time  $T_2$  accounts for any continuing depolarization;  $P_{res}$  must be unity unless the muons are strongly depolarized for a very short time and then become immune to the depolarizing mechanism. Similarly, the initial phase  $\phi$  reflects only rapid motion of the spin at very early times, ceasing within a few nsec. In light of this, any dependence of  $P_{res}$  or  $\phi$  upon the chemical properties of the medium can only be attributed to a very short-lived interaction far stronger than the interaction of the muon's magnetic moment with the external field.

Such a dependence was noted as early as 1957 by a number of different groups;<sup>5</sup> since then, several theories have been offered to account for it, all involving the temporary formation of muonium, the hydrogen-like atom  $\mu^+e^-$ , herein designated Mu. The theory of the "proper muonium mechanism" was originally developed to explain the contrast between the complete depolarization of

muons in insulators and the lack of any depolarization in metals. Thus the summary given by Nosov and Iakovleva<sup>6</sup> describes various general situations in solids, but gives little attention to liquids. The same is true of an early paper by Ivanter and Smilga<sup>7</sup> in which the Laplace transform method is used to obtain explicit formulas for the depolarization. Firsov and Byakov<sup>8</sup> had meanwhile suggested that the theory could be applied to studies of the chemistry of muonium, and later Ivanter and Smilga published another paper<sup>9</sup> developing the formalism to apply to this case.

Despite some objections to the application of this model to solids<sup>10</sup>, most evidence supports its general validity, and it is certainly true for liquids, once it has been expanded to include radical formation. Its validity, which will be demonstrated herein, makes possible many studies of interactions of muons with matter, in particular the extraction of chemical rate constants for reactions of Mu atoms with various reagents in liquid media. Since muonium is chemically a light isotope of hydrogen, with  $m_{\text{Mu}}/m_{\text{H}} = 0.1126$ , these rate constants may be compared with those for analogous reactions of atomic hydrogen to study isotopic effects; or, in absence of measurements with hydrogen, we may predict its rate constants in the context of a simple kinetic theory in terms of the values observed for muonium.

Although the technique described here is only effective for measuring very fast reactions (rate constants  $\geq 10^9$  liters per mole-sec), these are among the most difficult to measure by other methods. Thus chemists are provided with a valuable tool complementing those they already possess. It is therefore of great

importance to prove the validity of the theory -- the central conclusion resulting from this work.

## II. THE THEORY OF $\mu^+$ DEPOLARIZATION

### A. The "Proper" Muonium Mechanism

#### 1. Spin Evolution in Muonium

Positive muons coming to rest in a typical liquid medium have a high probability of forming muonium atoms by stripping electrons from molecules of the medium.<sup>11</sup> The muonium quickly reaches its ground state (1S) by collision or radiation. Once formed, the muonium is thermalized within about  $10^{-11}$  sec.<sup>12</sup> Therefore, within approximately  $10^{-11}$  sec. from the time a muon comes to rest, it forms a spin system with an electron, in which the electron is statistically unpolarized and the muon is 100% polarized (Imperfect polarization of the muon beam is merely a multiplicative factor in all results, and can therefore be absorbed into the empirical quantity  $A_0$ .)

This spin system has 4 linearly independent states, and therefore its density matrix has 16 elements, 15 of which are independent. The density matrix can be expanded in orthogonal spin operators, in terms of the muon and electron polarizations  $\underline{P}^\mu$  and  $\underline{P}^e$  and their "cross-correlations"  $b_{ij}$ :

$$\rho = 1/4(1_4 + \underline{P}^\mu \cdot \underline{\sigma}^\mu + \underline{P}^e \cdot \underline{\sigma}^e + \sum_{ij} b_{ij} \sigma_i^\mu \sigma_j^e) \quad (2)$$

where  $1_4$  is the  $4 \times 4$  unit matrix, and  $\underline{\sigma}^\mu$  and  $\underline{\sigma}^e$  are the muon and electron Pauli spin operators ( $\underline{s}^\mu = \hbar/2 \underline{\sigma}^\mu$  and  $\underline{s}^e = \hbar/2 \underline{\sigma}^e$ ). The set of operators  $\{1_4, \sigma_i^\mu, \sigma_j^e, \text{ and } \sigma_m^\mu \sigma_n^e\}$  form an orthonormal basis.

In the absence of any external influences, the hamiltonian of this spin system is just the Fermi contact interaction, or hyperfine interaction:

$$H_o = \frac{1}{4} \hbar \omega_o (\underline{\sigma}^\mu \cdot \underline{\sigma}^e) \quad (3)$$

where  $\omega_o = 2.804 \times 10^{10}$  radians/second is the hyperfine frequency<sup>2</sup>, given by

$$\hbar \omega_o = \frac{32}{3} \pi \mu_\mu \mu_e |\Psi(0)|^2$$

where  $\mu_\mu = g_\mu e\hbar/4m_\mu c$  and  $\mu_e = g_e e\hbar/4m_e c$  are the magnetic moments of the muon and electron, and  $|\Psi(0)|^2 = 1/\pi a_o^3 = m^3 e^6/\pi \hbar^6$  is the electron probability density at the muon ( $m$  is the reduced mass). In terms of the masses alone,

$$\mu_\mu \approx \zeta \mu_e \quad \text{where} \quad \zeta \equiv \frac{m_e}{m_\mu} = \frac{1}{206.76}$$

When an external magnetic field  $\underline{B}$  is applied to the system, two more parts are added to the hamiltonian:

$$H_1 = -\frac{1}{2} \hbar \underline{\omega}^\mu \cdot \underline{\sigma}^\mu \quad \text{and} \quad H_2 = -\frac{1}{2} \hbar \underline{\omega}^e \cdot \underline{\sigma}^e \quad (4)$$

where  $\underline{\omega}^\mu = 2 \mu_\mu \underline{B}/\hbar$  and  $\underline{\omega}^e = -2 \mu_e \underline{B}/\hbar$  are the muon and electron Larmor frequencies. Note that  $\underline{\omega}^\mu \approx -\zeta \underline{\omega}^e$ .

Working in the Schrödinger picture, the equation of motion of the density matrix can be written  $\dot{\rho} = -\frac{i}{\hbar} [H, \rho]$ . The "proper" muonium mechanism also takes into account interactions of the muonium electron's spin with the medium, in the form of the Wangness-Bloch equation:<sup>13, 14</sup>

$$\dot{\rho} = -\frac{i}{\hbar} [\hat{H}, \rho] - \frac{\pi}{\hbar} \text{Tr}_b [\hat{V}, [\hat{V}, \rho \rho_b]] \quad (5)$$

where  $\hat{H} = H_0 + H_1 + H_2$ ,  $\text{Tr}_b$  is the trace over the part of the world density matrix which describes the medium "b",  $\rho_b$  is the equilibrium density matrix of the medium, and  $\hat{V}$  is the part of the operator  $\hat{V}$  which is diagonal in the energy;  $\hat{V}$  describes the interaction of the electron with the medium. It is assumed that  $\hat{V}$  is analogous to relaxation mechanisms in the context of ESR phenomena, producing a relaxation rate  $\nu$  imposed upon the electron spin.<sup>6</sup> Although  $\nu$  is included in the formalism for the sake of generality, all fits to experimental data in liquids are made with  $\nu = 0$ , since such relaxation phenomena are presumed to be insignificant in liquids. (This is borne out by our study of concentrated  $\text{Mn}^{++}$  solutions<sup>15</sup>, where no " $\nu$  effects" are observed, even in 10 M solutions.)

Writing out the commutators and equating coefficients of the orthogonal operators  $\{1, \sigma_i^\mu, \sigma_j^e, \sigma_m^\mu \sigma_n^e\}$  on the left and right sides of equation (5) gives the equations of motion of the parameters of the density matrix:

$$\dot{P}_k^\mu = \sum_{ij} \epsilon_{ijk} \left( -\frac{1}{2} \omega_0 b_{ij} + P_i^\mu \omega_j^\mu \right) \quad (6a)$$

$$\dot{P}_k^e = \sum_{ij} \epsilon_{ijk} \left( +\frac{1}{2} \omega_0 b_{ij} + P_i^e \omega_j^e \right) - 2 \nu P_k^e \quad (6b)$$

$$\begin{aligned} \dot{b}_{ij} = & \frac{1}{2} \omega_0 \sum_k \epsilon_{ijk} (P_k^\mu - P_k^e) + \sum_{mn} (\omega_n^e \epsilon_{mni} b_{mj} \\ & + \omega_n^\mu \epsilon_{mni} b_{mj}) - 2 \nu b_{ij} \end{aligned} \quad (6c)$$

where  $\epsilon_{ijk}$  is the Levi-Civita antisymmetric symbol.

Choosing the  $\hat{z}$ -direction along the field ( $\underline{B} = B \hat{z}$ ) allows separation of these equations into one subset describing polarizations parallel to the field and another subset describing polarizations perpendicular to the field. We are concerned here with the latter set, since  $\underline{P}^\mu$  is initially along  $\hat{x}$ .

The transverse-field case of equations (6) can be written compactly as

$$\hat{\underline{P}} = i A_m \hat{\underline{P}} \quad (7)$$

where  $\hat{\underline{P}}$  is the complex 4-component vector

$$\hat{\underline{P}} \equiv \begin{pmatrix} P_x^\mu + i P_y^\mu \\ P_x^e + i P_y^e \\ b_{xz} + i b_{yz} \\ b_{zx} + i b_{zy} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \text{at } t = 0 \quad (8)$$

(analogous to that defined by Ivanter and Smilga<sup>7</sup>) and  $A_m$  is the  $4 \times 4$  matrix

$$A_m \equiv \begin{pmatrix} -\zeta\omega_e & 0 & \frac{1}{2}\omega_o & -\frac{1}{2}\omega_o \\ 0 & 2iv_\perp + \omega_e & -\frac{1}{2}\omega_o & \frac{1}{2}\omega_o \\ \frac{1}{2}\omega_o & -\frac{1}{2}\omega_o & 2iv_\parallel - \zeta\omega_e & 0 \\ -\frac{1}{2}\omega_o & \frac{1}{2}\omega_o & 0 & 2iv_\perp + \omega_e \end{pmatrix} \quad (9)$$

where  $\omega_e \equiv |\underline{\omega}^e|$  and (following Ivanter's paper<sup>16</sup>)  $v$  is explicitly broken up into parts describing longitudinal relaxation ( $v_\parallel$ ) and transverse relaxation ( $v_\perp$ ). A dimensionless quantity often referred to is  $x \equiv \omega_e/\omega_o$ , in terms of which the critical field  $B_o = 1588$  gauss is defined as the field for which  $x = 1$ .



Usually this is turned around, since  $\omega_e$  is proportional to  $B$ , to define  $B = x B_0$  or  $x = B/B_0$ .  $B_0$  may be thought of semiclassically as the field at the electron due to the muon's magnetic moment.

## 2. Chemical Lifetime of Muonium

Having obtained the equations of motion of the muonium spin system, we return to the experimental question: how does muonium formation affect the observed precession of an ensemble of muon spins? If the muons remain in muonium indefinitely, no muon precession will be seen at all; in such cases we would watch for precession of the triplet state of muonium at a frequency  $\omega_{\text{Mu}} \approx \frac{1}{2} \omega_e \approx \frac{2}{\zeta} \omega_\mu = 103.38 \omega_\mu$ . We are therefore interested in a process in which free muonium forms for a short time and then relinquishes the muon to an environment in which the muon spin is acted upon only by the external field.

One such process is chemical reaction of the muonium with a reagent to place the muons in diamagnetic compounds, where all the electrons occur in pairs with opposite spins, so that the muon sees no net hyperfine interaction. Therefore muons in diamagnetic compounds precess essentially like free muons, except for small effects such as chemical shielding.

This process can be written



where  $\text{Mu}$  denotes muonium,  $\text{X}$  denotes the reagent, and  $\text{D}$  the diamagnetic product. The reaction will occur at some rate proportional to the concentration of the reagent  $\text{X}$ ; the constant of

proportionality is the chemical rate constant,  $k_{\text{mxd}}$ , so that the rate of the reaction is  $k_{\text{mxd}}[X]$  (square brackets denote concentration). The triple subscript may seem unnecessarily unwieldy at this point, but it will serve as a handy mnemonic later, when other reactions are included.

The free muonium thus "decays" exponentially into diamagnetic compounds, with a lifetime  $\tau_{\text{mxd}}$  given by

$$\tau_{\text{mxd}} = \frac{1}{k_{\text{mxd}}[X]} \quad (11)$$

Thus the probability that a muonium atom will remain uncombined until time  $t$  is  $\exp(-t/\tau_{\text{mxd}})$ , and the probability that the chemical reaction will take place within an interval  $dt$  of time  $t$  is  $\exp(-t/\tau_{\text{mxd}}) \frac{dt}{\tau_{\text{mxd}}}$ .

### 3. The Residual Polarization

We observe the amplitude and phase of the "free" muon precession at times long compared to  $\tau_{\text{mxd}}$ ; the residual polarization  $P_{\text{res}}$  is what appears to have been the initial magnitude and direction of the muon polarization if the observed precession is extrapolated back to  $t = 0$ . In terms of the complex polarization of the muon,  $P(t) = p_x^{\text{ll}} + i p_y^{\text{ll}}$ , we are therefore fitting the observed time dependence to the form  $P'(t) = P_{\text{res}} \exp[i\omega_{\mu} t]$ , treating  $P_{\text{res}}$  as a constant; to obtain  $P_{\text{res}}$  theoretically, then, we let  $t \rightarrow \infty$ , divide the exact detailed time dependence  $P(t)$  by the Larmor precession factor  $\exp[i\omega_{\mu} t]$ , and average over a typical time interval  $\Delta t$  which is much less than the period of muon precession but much greater than the period of muonium precession:

$$P_{\text{res}} = \lim_{t \rightarrow \infty} \langle P(t) \exp[-i\omega_{\mu} t] \rangle \quad (12)$$

The exact time dependence  $P(t)$  has two contributions. The first part comes from muonium which is still free at time  $t$ ; the fraction of the muon ensemble experiencing this fate is  $\exp[-t/\tau_{\text{mxd}}]$ , and its time dependence is just  $\hat{P}_1(t)$ . (Recall the definition [8].) This contribution is thus

$$P_{\text{Mu}}(t) = \hat{P}_1(t) \exp[-t/\tau_{\text{mxd}}] \quad (13)$$

which, for finite  $\tau_{\text{mxd}}$ , survives neither the limit nor the average in equation (12), and so contributes nothing to  $P_{\text{res}}$ . The whole contribution to  $P_{\text{res}}$  comes from the other part, due to muonium which reacted at various times  $t_1 < t$ , subsequently evolving in diamagnetic compounds, where the muon precesses at the Larmor frequency. This contribution is in the form of an integral over  $t_1$  of the overall evolution of a muon which evolves until  $t_1$  in muonium and from  $t_1$  until  $t$  in a diamagnetic compound, multiplied by the probability of such a series of events:

$$P_{\text{Mu} \rightarrow \text{D}}(t) = \int_0^t \hat{P}_1(t_1) \exp[i\omega_{\mu}(t - t_1)] \cdot \exp[-t_1/\tau_{\text{mxd}}] \frac{dt_1}{\tau_{\text{mxd}}} \quad (14)$$

The residual polarization is thus given by

$$P_{\text{res}} = \int_0^{\infty} \hat{P}_1(t_1) \exp[-(i\omega_{\mu} + 1/\tau_{\text{mxd}})t_1] \frac{dt_1}{\tau_{\text{mxd}}} . \quad (15)$$

Ivanter and Smilga<sup>7</sup> took advantage of the form of equation (15) to obtain an explicit formula for the residual polarization

by the method of Laplace transforms. We must develop a more general approach, however, in anticipation of more complicated situations where the Laplace transform technique is inapplicable.

### B. Explicit Time Dependence

Without resort to Laplace transforms,  $P_{\text{res}}$  can only be expressed analytically in terms of known quantities if  $\hat{P}_1(t)$  is known. Given this information, however, it is just as easy to calculate  $P(t)$ , the explicit time dependence of the polarization of the entire ensemble of muons, from equations (13) and (14).  $P_{\text{res}}$  can then be obtained from equation (12).

To obtain  $\hat{P}_1(t)$  analytically we must diagonalize the matrix  $A_m$ . Let  $M$  be the orthogonal matrix which achieves this, and call the resultant diagonal matrix  $D^m$ , whose diagonal elements are the eigenvalues  $\lambda_i^m$  :

$$M^{-1} A_m M = D^m \quad \text{where} \quad D_{ij}^m = \delta_{ij} \lambda_i^m \quad (16)$$

The finite time evolution operator for the muon spin in muonium is defined by

$$U^m(t, t') = M \exp[iD^m(t - t')] M^{-1} \quad (17)$$

$$\text{so that} \quad \hat{P}(t) = U^m(t, t') \hat{P}(t')$$

$\hat{P}_1(t)$  is then just the first component of  $\hat{P}(t) = U^m(t, 0) \hat{P}(0)$ . This result may be substituted back into equations (13) and (14) to give  $P(t)$ ; but let us first prepare our theoretical apparatus for more complicated situations by generalizing the procedure used to obtain these equations.

Let "q" be a complete label for the fate of a given fraction of the muon ensemble; for instance, if certain muons evolve

in muonium until time  $t_1$ , thereupon reacting chemically and evolving subsequently in diamagnetic molecules, "q" is to specify both the sequence of events and the time  $t_1$ . The operator  $U_q(t,0)$  -- in general a time-ordered product of evolution operators -- will describe the detailed time-dependence of those muons, given by  $\hat{P}(q,t) = U_q(t,0) \hat{P}(0)$ . For the example mentioned,  $U_q$  takes the form  $U_q(t,0) = U^d(t,t_1) U^m(t_1,0)$ , where  $U^d$  is the time evolution operator for muons in diamagnetic molecules:

$$U_{ij}^d(t,t') = \delta_{ij} \delta_{i1} \exp[i\omega_{\mu}(t - t')] \quad (18)$$

The fraction of the ensemble experiencing fate "q" is designated  $p(q)$ . For the example in question, if the reaction occurs within  $dt_1$  of  $t_1$ ,  $p(q)$  is given by  $\exp[-t/\tau_{\text{mxd}}] dt_1/\tau_{\text{mxd}}$ . In all cases the contribution to  $P(t)$  from muons experiencing the fate "q" is

$$P(q,t) = p(q) \cdot [U_q(t,0) \hat{P}(0)]_1 \quad (19)$$

and so if all possible fates " $q_1$ " are taken into account, the time dependence of the entire ensemble can be calculated:

$$P(t) = \sum_1 P(q_1,t) \quad (20)$$

The sum over  $q_1$  may of course involve integrations (e.g., over the unspecified time  $t_1$ ).

This may seem an unnecessarily elaborate way of expressing that which was earlier explained in one sentence, but in the more complicated processes to be treated in the next section, this formalism facilitates bookkeeping. It is now time to place the proper muonium mechanism in perspective as only one of a variety of pro-

cesses which retard and enhance the depolarization of muons in liquids; all are interrelated, and all combine to produce a net time dependence  $P(t)$  and a dependence of the residual polarization on  $[X]$  which show much more variety than the pure proper muonium mechanism.

### C. Other Mechanisms

Figure 3 gives a conceptual picture of the various competing processes which will be discussed in this section; the book-keeping difficulty mentioned in the last section should now be evident. It should be emphasized that Fig. 3 is not intended to show all possible processes, but only those which appear to be the most dominant in the cases studied.

#### 1. Hot Chemistry

Muons are most apt to form muonium in slowing down when they reach "atomic" electron velocities<sup>11</sup>, i.e., around  $v \sim \alpha c$ ; electrons may be repeatedly lost and recaptured until the kinetic energy drops below the ionization energy, about 13.5 eV. From then until they reach thermal equilibrium with their surroundings (a time of about  $10^{-11}$  sec<sup>12</sup>) they may participate in chemical reactions which are energetically forbidden to thermal muonium, due to large activation energies and/or highly endothermic reactions. Typical examples are the postulated "hot" reactions  $Mu^* + H_2O \rightarrow H + MuOH$  (hydrogen replacement) and  $Mu^* + H_2O \rightarrow MuH + OH$  (hydrogen abstraction), where the asterisk denotes that the muonium is epithermal (hot). The reactions with water were chosen as examples because they have been extensively studied via hot tritium chemistry<sup>17</sup>, and because they are quite significant in our data. The fraction  $h$  of hot muonium atoms reacting in this way in water is approximately 0.55, so that about half the muons in aqueous solutions enter diamagnetic compounds essentially



at  $t = 0$ , giving an irreducible minimum muon asymmetry equal to  $A_0 h$ . Similar effects are seen in every solvent we have used.

Another possibility is the epithermal reaction of muonium to form a radical  $R$ , in which there is an unpaired electron which interacts with the muon spin via a hyperfine coupling of strength  $\hbar\omega_r$ , analogous to that in muonium but presumably weaker. The fraction of muonium reacting through this channel is designated  $r$ . If we assume that the interaction between the muon and the unpaired electron is a pure contact interaction, this spin system is perfectly analogous to muonium, and its depolarizing effect upon the muon spin is similar. An example would be the reaction  $Mu^* + H_2O \rightarrow H_2 + MuO\cdot$  where  $MuO\cdot$  is a radical. However, results from hot tritium chemistry<sup>17</sup> indicate that this reaction is unfavorable compared to the two reactions with water which lead to diamagnetic compounds.

## 2. Pure Radical Mechanism

To further develop the analogy between the radical and muonium, consider a situation in which the radical is formed exclusively at  $t = 0$  by epithermal reactions ( $r = 1$ ), and later reacts with the reagent  $X$  to form a diamagnetic compound  $D$ :



The chemical rate constant for this process is  $k_{rxd}$ , implying a "chemical lifetime" for the radical of  $\tau_{rxd} = ([X] k_{rxd})^{-1}$ , in perfect analogy with equation (11) for the chemical lifetime of muonium in the proper muonium mechanism. In fact, all the equa-

tions of that mechanism apply to this situation also, provided we substitute  $\omega_r$  for  $\omega_o$  and relabel all the operators accordingly. That is,  $A_o(\omega_o) \rightarrow A_r(\omega_r)$  and in place of equations (16) and (17) we have

$$R^{-1} A_r R = D^r \quad \text{where} \quad D_{ij}^r = \delta_{ij} \lambda_i^r \quad (22)$$

$$\text{and} \quad U^r(t, t') = R \exp[iD^r(t - t')] R^{-1} \quad (23)$$

so that  $\hat{P}(t) = U^r(t, t') \hat{P}(t')$

The most striking difference between these two mechanisms is that the critical field in the pure radical mechanism is given by  $B_r = (\omega_r/\omega_o) B_o$ , presumably less than  $B_o = 1588$  gauss. This means that the Paschen-Bach region is reached at lower field, which significantly affects the shape of the dependence of  $P_{res}$  on  $[X]$ .

### 3. "Muonium-Plus-Radical" Mechanism

The mechanisms discussed so far require no theoretical apparatus beyond the Laplace transform technique of Ivanter and Smilga; it is in this section that we encounter the mechanism for the description of which the time evolution operator formalism was introduced. Suppose the muon thermalizes and evolves for an unspecified time  $t_1$  in free muonium, whereupon it reacts chemically to form a radical, in which it evolves from  $t_1$  until  $t_2$ , when it reacts chemically again to form a diamagnetic molecule. If both times are short enough, some polarization will survive, and the dependence of  $P_{res}$  on reagent concentration may be exotic.

Four different rate constants could be involved here, depending upon the reaction partners of muonium and the radical. Consider the two possible ways a radical may form chemically: First, by reaction with the solvent itself (labelled S):



for which the reaction rate is  $1/\tau_{\text{msr}} = k_{\text{msr}}[\text{S}]$ . The concentration [S] of the solvent is given by

$$[\text{S}] \text{ (moles/liter)} = 1000 \rho_{\text{S}}/W_{\text{S}}$$

where  $\rho_{\text{S}}$  is its density ( $\text{gm/cm}^3$ ) and  $W_{\text{S}}$  is its gram formula weight. [S] is approximately independent of [X], as long as only moderate amounts of reagent are added. The second mode of radical formation is by reaction of muonium with the reagent:



for which the reaction rate is  $1/\tau_{\text{mxr}} = k_{\text{mxr}}[\text{X}]$ . Clearly, these two different reactions would produce different radicals; the same subscript "r" is used because it is assumed that in any given type of solution, only one of the processes is significant. This mild theoretical restriction is imposed only for practical reasons: should a situation exist in which two different types of radicals were formed, it is doubtful whether the data could provide enough information to make it possible to sort out all the rate constants.

Similarly, the reaction converting the radical into a diamagnetic compound may be either of two types. The radical may react with the solvent:



at a rate  $1/\tau_{\text{rsd}} = k_{\text{rsd}}[S]$ . (Note that this is formally equivalent to the spontaneous decomposition of an unstable radical into diamagnetic products containing muonium, since the rate is independent of reagent concentration in both cases.) This reaction has been ruled out in all our analysis, with the following rationale: in the first place, no such reaction has seemed chemically plausible in the cases studied; furthermore, if it occurs slowly, it is quickly overpowered by the competing reaction described below as more reagent is added, or else no muons escape depolarization; and if it occurs quickly, the amount of depolarization would depend only on the time muonium took to react to form the radical -- a situation which would be indistinguishable from the proper muonium mechanism. Therefore we assume  $k_{\text{rsd}} < 10^7$  liters/mole-sec, which is too slow to affect the residual polarization.

In the competing reaction, the radical reacts with the reagent:



at a rate  $1/\tau_{\text{rxd}} = k_{\text{rxd}}[X]$ .

The relevant rate constants are summarized in Table I, along with the hot chemistry parameters and the various chemical lifetimes. Naturally, the list is not exhaustive. Such possibilities as unstable diamagnetic molecules or three-stage reactions are omitted in order to maintain a minimal degree of clarity; they are relatively easy to merge with the procedure using the

evolution operator formalism.

It should be emphasized that in any given type of solution the muonium is presumed to form diamagnetic compounds only by reaction with the reagent, and radical compounds by reaction with either the solvent or the reagent, but not both; and that the radical is presumed to combine exclusively with the reagent. Along with the requirement of the "dilute limit" ( $[X] \ll [S]$ ), these are the most restrictive assumptions in the theory.

The reaction lifetimes  $\tau_{\text{mxd}}$ ,  $\tau_{\text{msr}}$  or  $\tau_{\text{mxr}}$ , and  $\tau_{\text{rxd}}$  are the relevant quantities to the theory, which predicts  $P(t)$  for a given reagent concentration. Clearly, it does not matter to the theory what the reaction partners are, but only how long they take to react; therefore the middle index is superfluous, and may be eliminated by defining

$$\tau_{\text{md}} = \tau_{\text{mxd}} \quad (28a)$$

$$\tau_{\text{rd}} = \tau_{\text{rxd}} \quad (28b)$$

$$\tau_{\text{mr}} = \tau_{\text{msr}} \quad \text{or} \quad \tau_{\text{mxr}} \quad (28c)$$

In terms of these, the overall rate at which muonium is removed from solution is given by

$$\frac{1}{\tau_{\text{m}}} = \frac{1}{\tau_{\text{md}}} + \frac{1}{\tau_{\text{mr}}} \quad (29)$$

$\tau_{\text{m}}$  is therefore the actual "chemical lifetime" of the muonium.

The generalized time evolution operator for this process is

$$U_q(t,0) = U^d(t,t_2) U^r(t_2,t_1) U^m(t_1,0) \quad (30)$$

where  $U^d$ ,  $U^r$ , and  $U^m$  were defined in (18), (13), and (17), respectively. The probability of such a series of events occurring with "internal times"  $t_1$  and  $t_2$  in the intervals  $dt_1$  and  $dt_2$  is

$$p(q) = (1 - h - r) \exp[-(t_2 - t_1)/\tau_{rd}] \frac{dt_2}{\tau_{rd}} \\ \cdot \exp[-t_1/\tau_m] \frac{dt_1}{\tau_{mr}} \quad (31)$$

where  $\exp[-t_1/\tau_m]$  is used rather than  $\exp[-t_1/\tau_{mr}]$  in recognition of the fact that  $Mu + X \rightarrow D$  is a process competing with  $Mu + (S \text{ or } X) \rightarrow R$  which shortens the overall chemical lifetime of the muonium,  $\tau_m$ .

We may now write out all the contributions to the ensemble muon polarization  $P(t)$ , and extract a general formula for the residual polarization.

Figure 3 - FLOW CHART OF DEPOLARIZATION MECHANISM

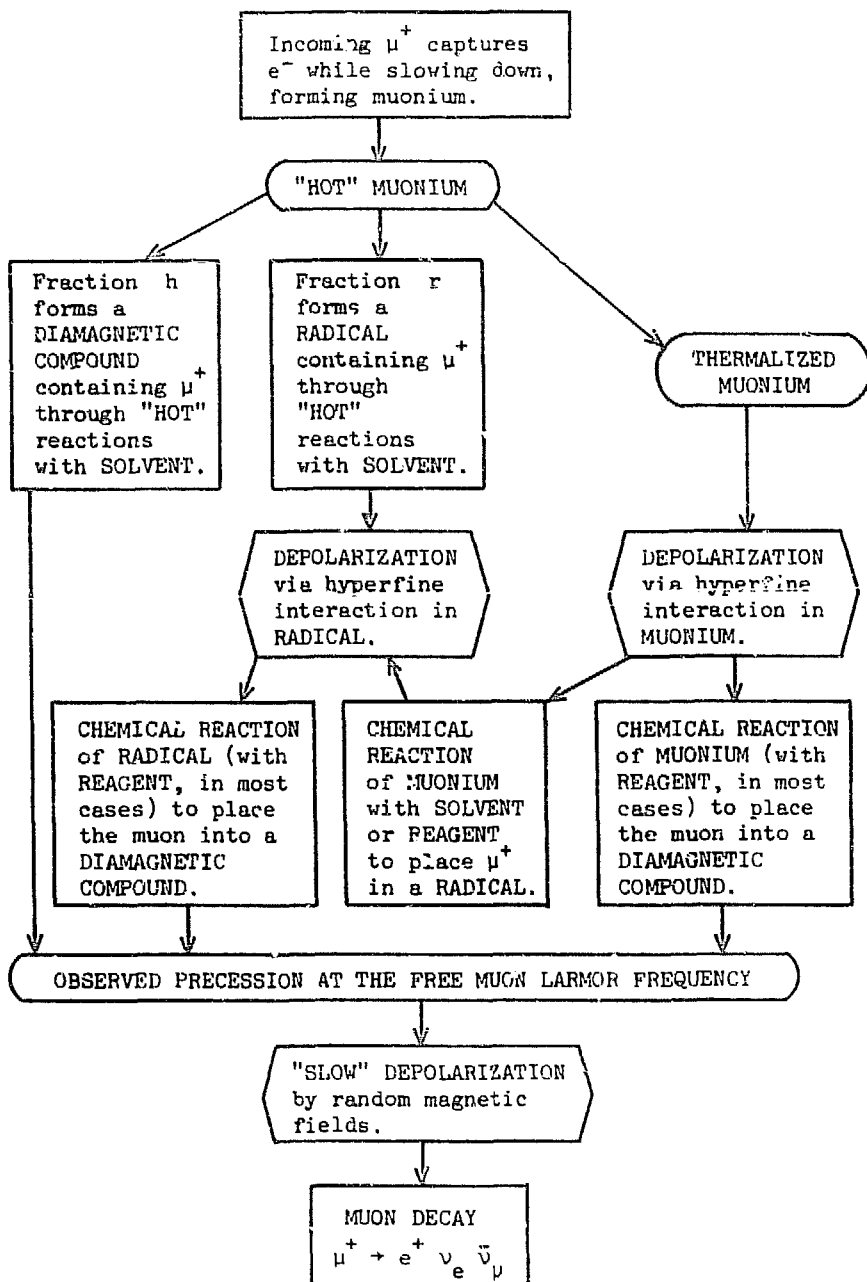


Table I - PARAMETERS OF THE THEORY

[X] = concentration of reagent "X"

[S] = concentration of pure solvent "S" (density/formula weight)

h = fraction of muonium reacting epithermally to form a Diamagnetic Compound (D)

r = fraction of muonium reacting epithermally to form a Radical (R)

$k_{\text{mxd}}$  = chemical rate constant for the reaction  $\text{Mu} + \text{X} \rightarrow \text{D}$

$k_{\text{msd}}$  = chemical rate constant for the reaction  $\text{Mu} + \text{S} \rightarrow \text{D}$

$k_{\text{mxr}}$  = chemical rate constant for the reaction  $\text{Mu} + \text{X} \rightarrow \text{R}$

$k_{\text{msr}}$  = chemical rate constant for the reaction  $\text{Mu} + \text{S} \rightarrow \text{R}$

$k_{\text{rxd}}$  = chemical rate constant for the reaction  $\text{R} + \text{X} \rightarrow \text{D}$

$k_{\text{rsd}}$  = chemical rate constant for the reaction  $\text{R} + \text{S} \rightarrow \text{D}$

In each case, the rate (in  $\text{sec}^{-1}$ ) at which reaction "i" occurs is given by  $\Lambda_i = k_i[Z]$ , where "Z" is either "X" or "S", whichever is the appropriate reactant.

The "lifetime" with respect to reaction "i" is given by  $\tau_i = 1/\Lambda_i$ . The following "lifetimes" are then defined:

$$\tau_{\text{md}} = [1/\tau_{\text{mxd}} + 1/\tau_{\text{msd}}]^{-1}$$

$$\tau_{\text{mr}} = [1/\tau_{\text{mxr}} + 1/\tau_{\text{msr}}]^{-1}$$

$$\tau_{\text{rd}} = [1/\tau_{\text{rxd}} + 1/\tau_{\text{rsd}}]^{-1} = \text{"chemical lifetime" of the radical}$$

$$\tau_{\text{m}} = [1/\tau_{\text{md}} + 1/\tau_{\text{mr}}]^{-1} = \text{"chemical lifetime" of muonium}$$



### D. The Polarization

#### 1. General Time-Dependence

We may now list all the contributions to  $P(t)$  from the processes shown in Fig. 4.

1) STILL-FREE MUONIUM: " $q_1$ " stands for evolution in free Mu from

$$t = 0 \text{ until the present time } t. \quad U_{q_1}(t,0) = U^m(t,0), \text{ so}$$

$$\{U_{q_1}(t,0) \hat{P}(0)\}_1 = \{U^m(t,0) \hat{P}(0)\}_1$$

$$= \{M \exp[iD^m t] M^{-1} \hat{P}(0)\}_1.$$

Since  $\hat{P}_j(0) = \delta_{j1}$ , the above is just

$$\sum_i \delta_{i1} \sum_{kj} M_{ik} \exp[i\lambda_k^m t] [M^{-1}]_{kj} \delta_{j1}$$

$$= \sum_k M_{1k} \exp[i\lambda_k^m t] [M^{-1}]_{k1}$$

$$= \sum_k F_k \exp[i\lambda_k^m t], \text{ where}$$

$$F_k \equiv M_{1k} [M^{-1}]_{k1} \quad (32)$$

Combining this with

$$p(q_1) = (1 - h - r) \exp[-t/\tau_m] \text{ gives}$$

$$P(q_1, t) = (1 - h - r) \sum_k F_k \exp[(i\lambda_k^m - 1/\tau_m)t]$$

$$= \exp[i\omega_\mu t] (1 - h - r) \sum_k F_k \exp[\alpha_k t] \quad (33)$$

where

$$\alpha_k \equiv -1/\tau_m + i(\lambda_k^m - \omega_\mu) \quad (34)$$

(The arrangement of terms to place the Larmor precession factor  $\exp[i\omega_\mu t]$  outside all the rest will be convenient later, when we extract the residual polarization.)

- 2) HOT DIAMAGNETIC: "q<sub>2</sub>" stands for evolution in a diamagnetic compound (D) since combining epithermally at t = 0.

$$U_{q_2}(t, 0) = U^d(t, 0), \text{ so}$$

$$\{U_{q_2}(t, 0) \hat{P}(0)\}_1 = \exp[i\omega_\mu t].$$

Therefore, since  $p(q_2) = h$ ,

$$P(q_2, t) = h \exp[i\omega_\mu t]. \quad (35)$$

- 3) MUONIUM → DIAMAGNETIC: "q<sub>3</sub>" stands for evolution in free Mu until time t<sub>1</sub>, when Mu combines chemically to form D, and subsequent evolution in D.

Here  $U_{q_3}(t, 0) = U^d(t, t_1) U^m(t_1, 0)$ , so

$$\{U_{q_3}(t, 0) \hat{P}(0)\}_1 = \exp[i\omega_\mu(t - t_1)] \sum_k F_k \exp[i\lambda_k^m t_1]$$

and  $p(q_3) = (1 - h - r) \frac{dt_1}{\tau_{md}} \exp[-t_1/\tau_m]$ . Thus

$$P(q_3, t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{md}} \sum_k F_k \exp[\alpha_k t_1] dt_1.$$

Integration over all possible values of t<sub>1</sub> gives P<sub>3</sub>(t), the overall contribution from the generic class "q<sub>3</sub>":

$$\begin{aligned} P_3(t) &\equiv \int_{t_1=0}^t P(q_3, t) \\ &= \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{md}} \sum_k \frac{F_k}{\alpha_k} (\exp[\alpha_k t] - 1) \end{aligned} \quad (36)$$

- 4) STILL-FREE HOT RADICAL: "q<sub>4</sub>" stands for evolution in radical (R) since combining epithermally at t = 0.

This case is strictly analogous to case (1), except that the radical takes the place of the muonium.

$$P(q_4, t) = \exp[i\omega_\mu t] r \sum_k G_k \exp[\beta_k t] \quad (37)$$

where

$$G_{lk} \equiv R_{lk} [R^{-1}]_{kl} \quad (38)$$

$$\text{and } \beta_k \equiv -1/\tau_{rd} + i(\lambda_k^r - \omega_\mu) \quad (39)$$

- 5) HOT RADICAL  $\rightarrow$  DIAMAGNETIC: "q<sub>5</sub>" stands for epithermal entry into R at  $t = 0$ , followed by evolution in R until time  $t_1$ , when R combines chemically to form D, and subsequent evolution in D. This case is strictly analogous to case (3), except that the radical plays the role of muonium in (3). The overall contribution from the generic class "q<sub>5</sub>" is

$$P_5(t) = \exp[i\omega_\mu t] \frac{\tau}{\tau_{rd}} \tau_k \frac{G_k}{\beta_k} (\exp[\beta_k t] - 1) \quad (40)$$

- 6) STILL-FREE CHEMICAL RADICAL: "q<sub>6</sub>" stands for evolution in Mu until time  $t_1$ , chemical combination at time  $t_1$  to form R, and subsequent evolution in R. Here

$$U_{q_6}(t, 0) = U^r(t, t_1) U^m(t_1, 0) \\ = R \exp[iD^r(t-t_1)] R^{-1} M \exp[iD^m t_1] M^{-1}, \text{ so}$$

$$\{U_{q_6}(t, 0) \hat{P}(0)\}_i = \sum_{ijk} R_{ij} \exp[i\lambda_i^r(t-t_1)] [R^{-1}]_{ij} \\ \cdot M_{jk} \exp[i\lambda_k^m t_1] [M^{-1}]_{kl} \\ = \sum_{ik} W_{ik} \exp[i\lambda_i^r t] \exp[i(\lambda_k^m - \lambda_i^r)t_1]$$

where

$$W_{ik} \equiv \sum_j R_{ij} [R^{-1}]_{ij} M_{jk} [M^{-1}]_{kl} \quad (41)$$

Combining this with

$$p(q_6) = (1 - h - r) \exp[-(t-t_1)/\tau_{rd}] \frac{dt_1}{\tau_{mr}} \exp[-t_1/\tau_m]$$

gives

$$P(q_6, t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr}} \cdot \sum_{ik} W_{ik} \exp[\beta_i t] \cdot \exp[(\alpha_k - \beta_i)t_1] dt_1$$

The overall contribution from the generic class "q<sub>6</sub>" is

$$P_6(t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr}} \cdot \sum_{ik} \frac{W_{ik}}{(\alpha_k - \beta_i)} (\exp[\alpha_k t] - \exp[\beta_i t]) \quad (42)$$

7) MUONIUM → RADICAL → DIAMAGNETIC: "q<sub>7</sub>" stands for evolution

until time t<sub>1</sub> in muonium, reaction at time t<sub>1</sub> to form R, evolution in R until time t<sub>2</sub>, reaction at time t<sub>2</sub> to form D, and subsequent evolution in D.

$$U_{q_7}(t, 0) = U^d(t, t_2) U^r(t_2, t_1) U^m(t_1, 0). \quad \text{Thus}$$

$$\{U_{q_7}(t, 0) \hat{P}(0)\}_i = \exp[i\omega_\mu(t-t_2)] \cdot \sum_{ik} W_{ik} \exp[i\lambda_i^r t_2] \cdot \exp[i(\lambda_k^m - \lambda_i^r)t_1].$$

Combining this with

$$p(q_7) = (1 - h - r) \frac{dt_2}{\tau_{rd}} \exp[-(t_2 - t_1)/\tau_{rd}] \cdot \frac{dt_1}{\tau_{mr}} \exp[-t_1/\tau_m]$$

gives

$$P(q_7, t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr} \tau_{rd}} \cdot \sum_{ik} W_{ik} \exp[\beta_i t_2] dt_2 \cdot \exp[(\alpha_k - \beta_i)t_1] dt_1.$$

The overall contribution from muons experiencing fates of the type "q<sub>7</sub>" with all possible values of t<sub>1</sub> and t<sub>2</sub> is then

$$\begin{aligned}
P_7(t) &\equiv \int_{t_2=0}^t \int_{t_1=0}^{t_2} P(q_7, t) \\
&= \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr} \tau_{rd}} \\
&\cdot \sum_{1k} \frac{W_{1k}}{(\alpha_k - \beta_1)} \left( \frac{1}{\alpha_k} \{ \exp[\alpha_k t] - 1 \} \right. \\
&\quad \left. - \frac{1}{\beta_1} \{ \exp[\beta_1 t] - 1 \} \right) \quad (43)
\end{aligned}$$

We now have the formula for the muon polarization at an arbitrary time  $t$ :

$$\begin{aligned}
P(t) = P(q_1, t) + P(q_2, t) + P_3(t) + P(q_4, t) \\
+ P_5(t) + P_6(t) + P_7(t). \quad (44)
\end{aligned}$$

Note that this is the exact time dependence of the muon polarization, involving no approximations beyond the assumption that Fig. 4 is a complete picture of the possible fates of a muon.

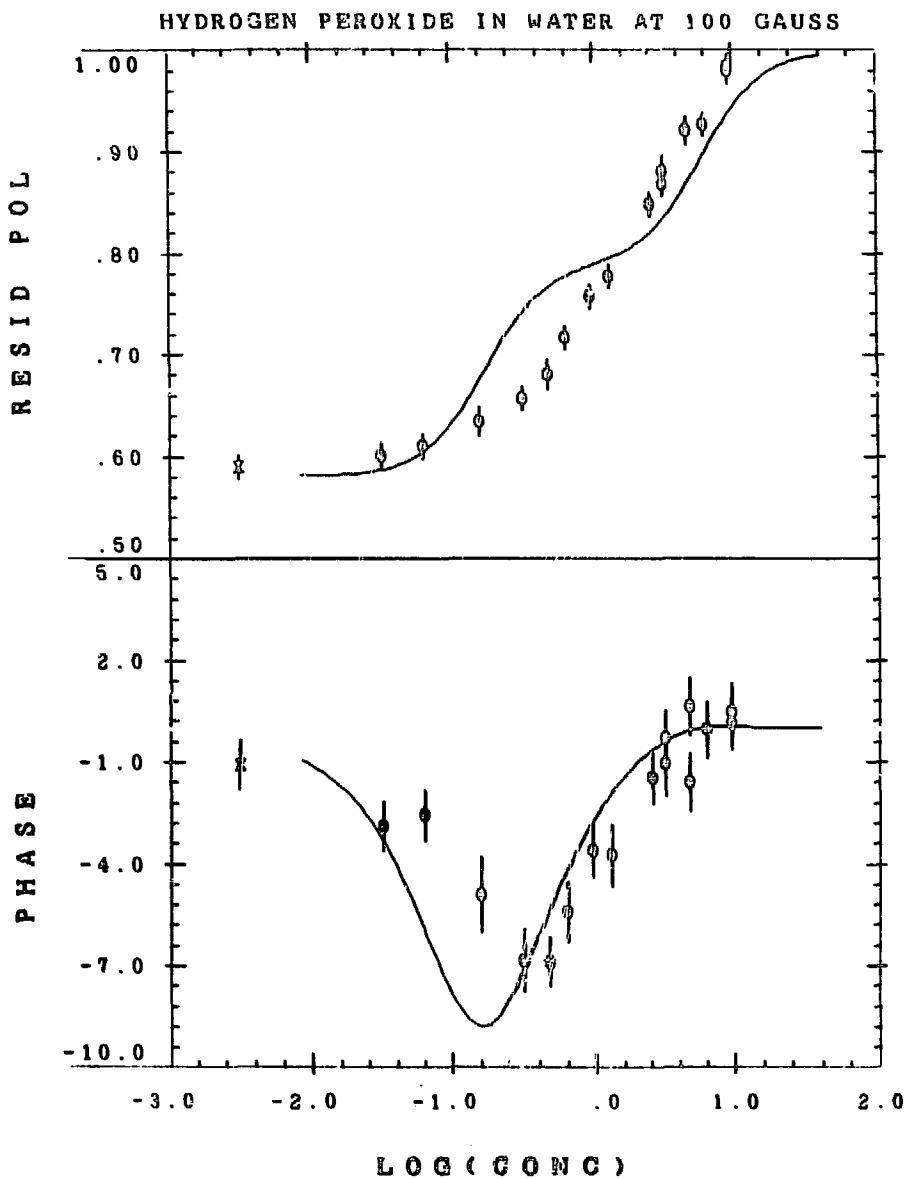
## 2. The Residual Polarization

We have conveniently ordered all terms in  $P(t)$  so that they are in the form  $\exp[i\omega_\mu t] P'$ , making it trivial to get  $P_{\text{res}}$  from  $P(t)$  by simply dropping off the Larmor precession term  $\exp[i\omega_\mu t]$ , letting  $t \rightarrow \infty$ , and keeping only those terms which do not go to zero or continue to oscillate at frequencies beyond practical resolution. Clearly only the terms  $P(q_2, t)$ ,  $P_3(t)$ ,  $P_5(t)$ , and  $P_7(t)$  contribute to  $P_{\text{res}}$ . Thus

$$P_{\text{res}} = \lim_{t \rightarrow \infty} \exp[-i\omega_\mu t] \{ P(q_2, t) + P_3(t) + P_5(t) + P_7(t) \}.$$

Recalling the definitions of  $\alpha_k$  and  $\beta_k$ , we may under most

Figure 23 -  $\text{H}_2\text{O}_2$  at 10G gauss: Fit Assuming  
Proper Muonium Mechanism



### E. An Example

In order to better understand the dependence of the residual polarization on reagent concentration in the simplest case, let us first consider the evolution of the muon polarization in muonium in a 100 gauss transverse field, in the absence of relaxation or chemical reactions. Figure 4 shows the evolution of the  $\hat{x}$  - component of the muon spin. The rapid oscillations reflect the mixed singlet-triplet state and have a characteristic frequency of  $\omega_0$ . An apparatus unable to resolve such rapid oscillations (i.e., any we might imagine) would record the slower oscillation of their average value at the "muonium frequency", given by

$$\omega_{\text{Mu}} \approx \frac{1}{2} \left( \frac{m_{\mu}}{m_e} \right) \omega_{\mu} = 103.38 \omega_{\mu}$$

The amplitude of those oscillations would be 1/2 the maximum allowed by geometry and beam polarization (i.e.,  $1/2 A_0$ ).

Now, suppose that (in accordance with the proper muonium mechanism) the muonium evolves as in Fig. 4, but reacts chemically in some mean time  $\tau$  to form a diamagnetic compound; once it has reacted, its polarization no longer changes on this time scale. Clearly, if  $\tau$  is much shorter than  $\tau_1$  (shown on Fig. 4), nothing much has happened to the muon polarization by the time it reacts -- i.e.,  $P_{\text{res}} \approx 1$ , and there is no depolarization. If  $\tau \approx \tau_1$ , muons have "dropped out" of the evolving process at various times averaging to  $\tau_1$ , and  $P_{\text{res}}$  will drop to something like 1/2. Now note what happens when  $\tau$  is intermediate between  $\tau_1$  and  $\tau_2$ :  $P_{\text{res}}$

is still  $\sim 1/2$ , since polarization values for all the reaction times are oscillating between 0 and 1. But when  $\tau \gg \tau_3$ , the mean itself begins to oscillate between  $+1/2$  and  $-1/2$ , and eventually muons have equal chances of dropping out of the oscillations at positive and negative polarization, and  $P_{res}$  goes to zero. In Fig. 5  $P_{res}$  is shown as a function of  $\tau$ , and the "shoulder" or "plateau" effect in the region  $\tau_1 < \tau < \tau_2$  is evident. In stronger magnetic fields, the muonium precession is faster, bringing  $\tau_2$  and  $\tau_3$  closer to  $\tau_1$  until, when  $B$  is on the order of the effective hyperfine field (1588 gauss),  $\tau_1$  and  $\tau_2$  are nearly equal and the "plateau effect" disappears. This effect is particularly characteristic of the proper muonium mechanism, making lower field values more attractive experimentally.

Radicals, with substantially smaller hyperfine frequencies than muonium, exhibit the plateau only at proportionally lower fields -- usually experimentally impractical. This serves to distinguish cases involving radical formation from cases of the proper muonium mechanism, as we shall see; however, an even more delicate test for the specific mechanism is the phase behavior.

Fig. 6 shows, for the same muonium as in Fig. 4, the locus traced out by the tip of the muon polarization vector in the plane perpendicular to the magnetic field. Polarization magnitude and direction at the characteristic times  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are indicated. In conjunction with Fig. 4, this should give a reasonable visual image of the two-dimensional evolution of the polarization vector. Note that the "hyperfine" oscillations" do not involve much rotation, but consist mainly of an amplitude



modulation. The muonium precession, on the other hand, does not appreciably change the amplitude, but merely rotates the mean polarization. Clearly, the largest change of apparent initial phase of the muon polarization vector is achieved when  $\tau \sim \tau_3$ , for then many of the muons will have "dropped out" out the process with their polarization rotated by large angles, predominantly on one side of the  $\hat{x}$ -axis. Unfortunately, this situation also corresponds to almost complete depolarization (see Fig. 5), and since in all real situations there is a constant, unrotated "hot chemistry component" in the polarization, the polarization emerging from chemical processes must not be too small (even though rotated considerably) or it will not appreciably shift the phase of the net polarization. As a result, real situations always show a peak in the phase deviation in the region of  $\tau = \tau_3$ .

$\mu^+$  POLARIZATION ALONG INITIAL DIRECTION

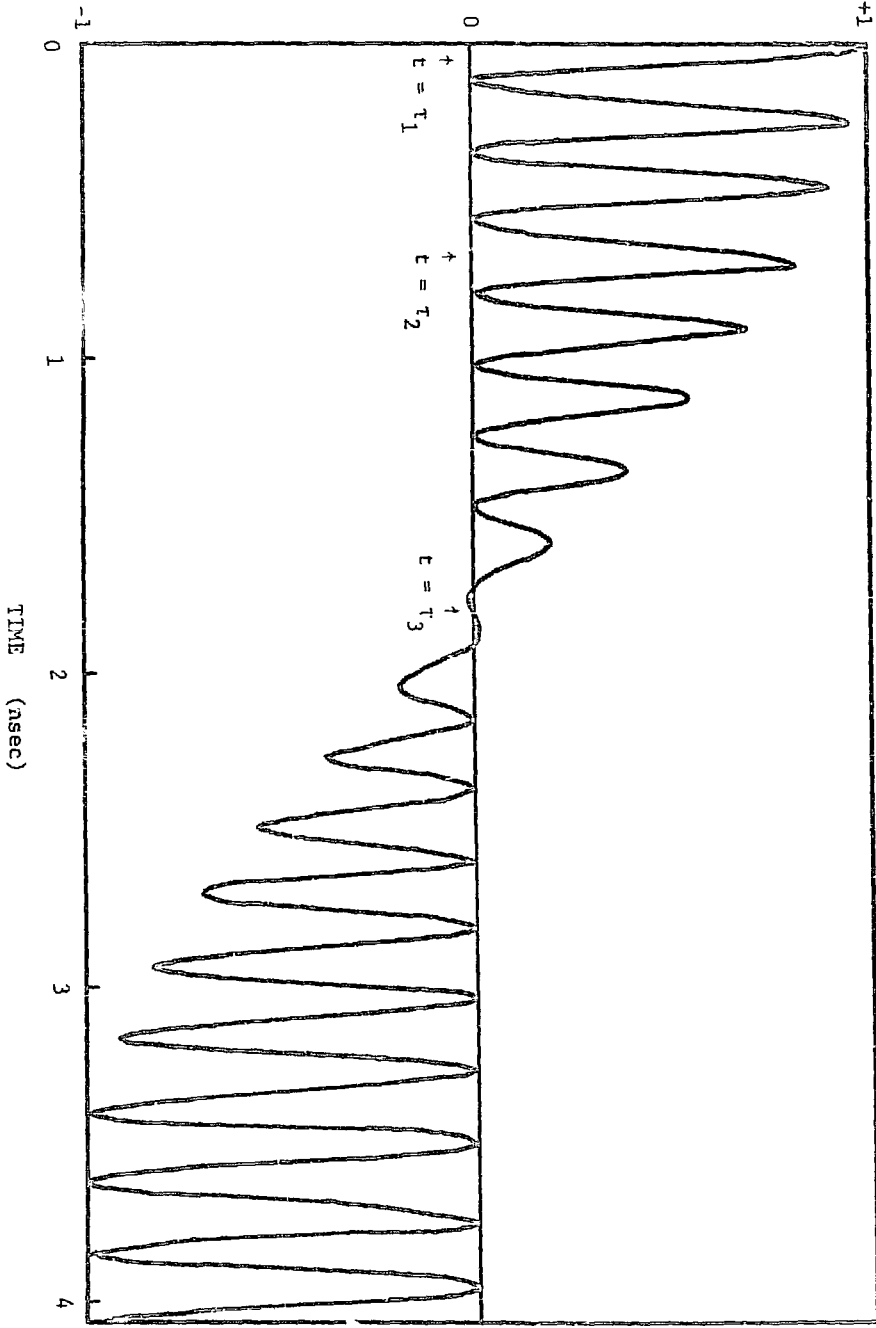


Figure 4 - EVOLUTION OF MUONUM IN 100 GAUSS

Figure 5 - RESIDUAL POLARIZATION AS A FUNCTION OF THE "CHEMICAL LIFETIME" OF FREE MUONIUM IN THE "PROPER" MUONIUM MECHANISM.

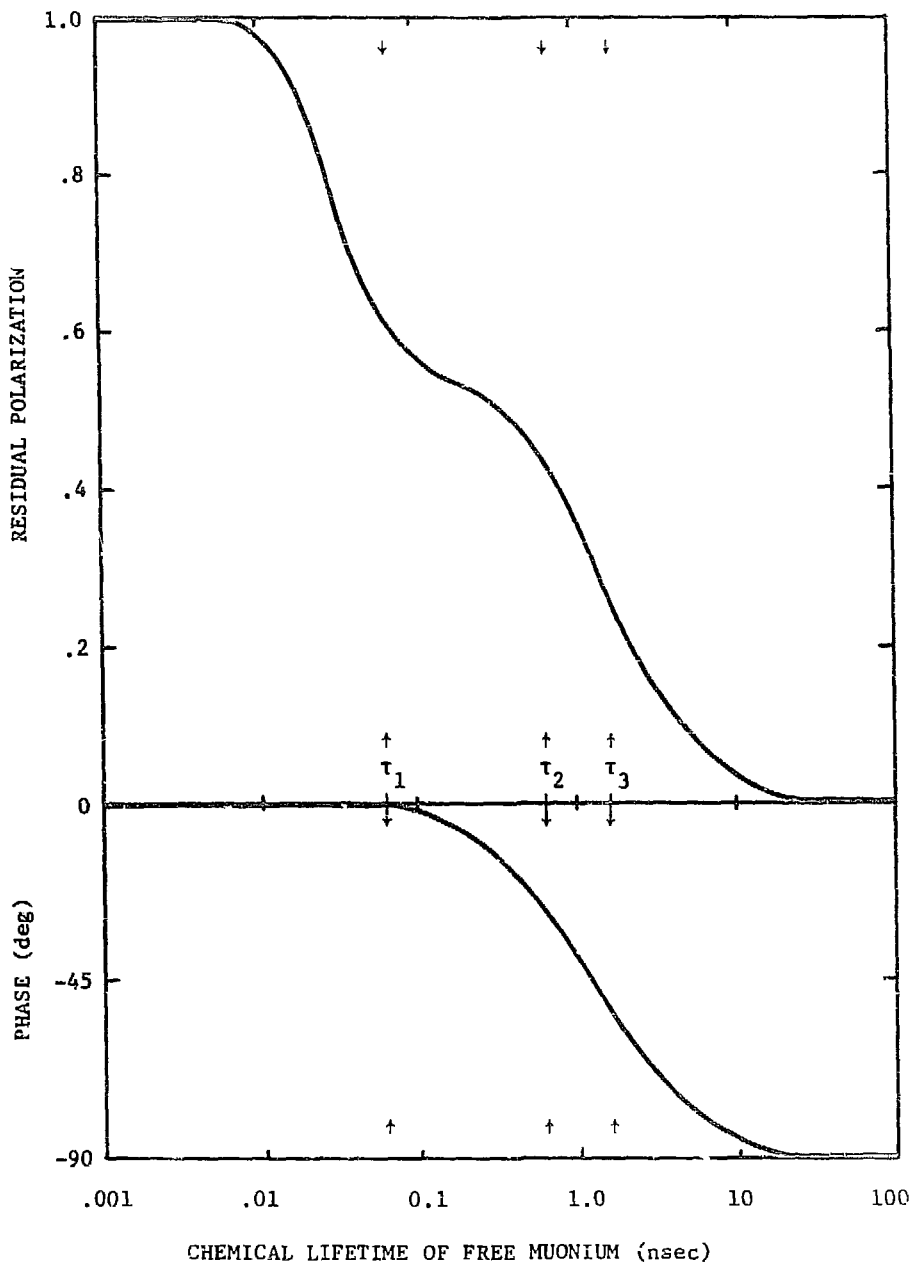
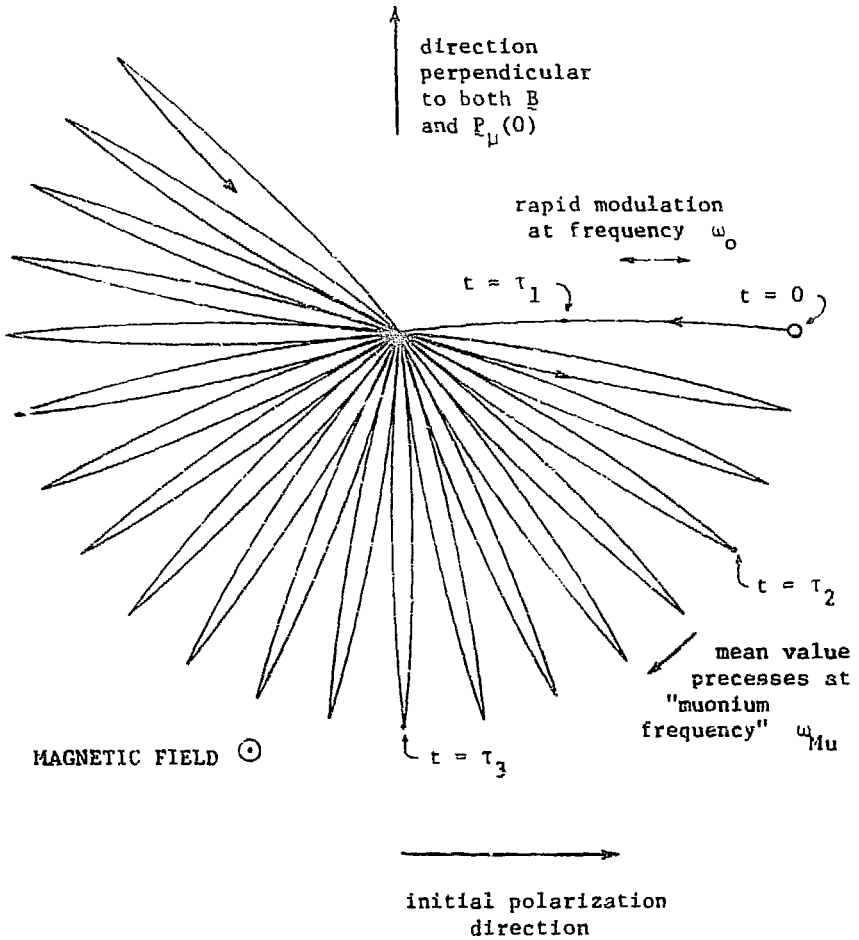


Figure 6 - EVOLUTION OF MUONIUM IN 100 GAUSS:

Locus Traced Out by the Tip of the  
Muon Polarization Vector in the Plane  
Perpendicular to the Magnetic Field.



### III. EXPERIMENTAL TECHNIQUE

With only a few changes, the apparatus used in this experiment was the same which was used by Crowe et. al.<sup>4</sup> in their precision measurement of the muon magnetic moment. At the time of writing of this dissertation (Spring, 1972) a description of that experiment has been accepted for publication in the Physical Review; therefore, this discussion will concentrate only on those aspects of the hardware and software which differ from the earlier study or are of special significance conceptually.

#### A. Beam Line and Magnetic Field

A polarized  $\mu^+$  beam is obtained by momentum separation of a  $\pi^+$  beam decaying in flight (see Fig. 7). The external proton beam from the Berkeley 184 in. Cyclotron strikes a copper target just downstream of the first external focussing magnet ("Circe"); the target is positioned to intercept only the edge of the beam, so that the experiment can run parasitically with the main users downstream. Pions produced with momenta  $\sim 200$  MeV/c at angles  $\sim 45^\circ$  enter the first bending magnet ("Leander") about 60 in. from the production target, and are bent through about  $78^\circ$  to enter a triplet of quadrupoles ("Electra I", "Hero", and "Electra II") some 90 in. long. About half of the pions decay before entering the second bending magnet ("Titan") in which the remaining pions are bent through about  $84^\circ$ , with "backward" muons emerging at larger angles and "forward" muons emerging at about  $73^\circ$ . The stopping target is about 60 in. from the center of Titan, so that

the forward muons are separated from the pions by about 12 in. at the target. It is thus possible to remove the unwanted components from the beam by collimation, selective moderation in a degrader (1 in. of copper), and counter geometry, so that we stop mainly forward muons in the target.

As a result of the definite negative helicity of the neutrino, muons from the decay  $\pi^+ \rightarrow \mu^+ \nu_\mu$  are required by conservation of angular momentum to have negative helicity in the pion rest frame, so that forward muons are polarized opposite to their momentum in the laboratory. Thus the sample of muons stopping in the target have an initial polarization of about 80% pointing in the backward direction, toward Titan.

The entire beam line up to the downstream side of Titan is in a helium atmosphere, to reduce scattering and pion interactions.

Under typical running conditions, about 1500 muons per second enter the stopping target, a 3 in. cube of thin Mylar filled with a liquid (typically water). Approximately 70% of the muons stop in the target, with a "contamination" of less than 4% stopping in the target walls, counter wrappings, and the "S1" counter (see Fig. 1). The asymmetry data are perturbed by less than 2% due to muons stopping outside the target.

The target is in a vertical magnetic field created by two large Helmholtz coils ("Sagane" and the "Red Trim Coil"); field homogeneity is adjusted by means of two small coils ("E-W Trim" and "N-S Trim"). For fields greater than 1000 gauss, a fifth coil was placed in a circuit with an NMR feedback loop which

counteracted variations of the field with time. The homogeneity of the field in the target region was on the order of  $\Delta B/B_0 \sim 10^{-4}$  for  $B_0 = 4500$  gauss,  $\Delta B/B_0 \sim 10^{-3}$  for  $B_0 = 1000$  gauss,  $\Delta B/B_0 \leq 10^{-2}$  for  $B_0 = 200$  gauss, and  $\Delta B/B_0 \sim 10^{-3}$  for  $B_0 = 100$  gauss.

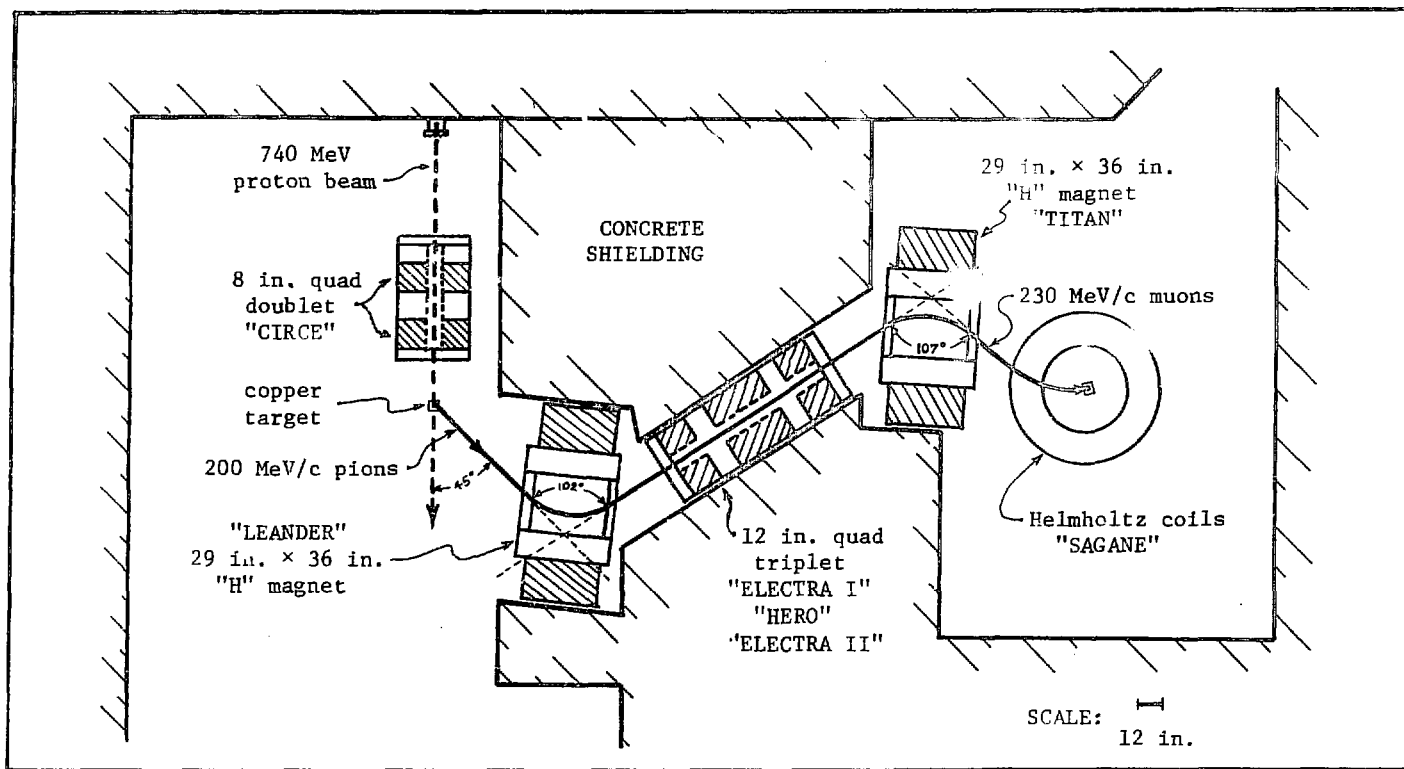


Figure 7 - BEAM LINE



### B. Counters and Fast Electronics

The counter arrangement is shown schematically in Fig. 1. Not shown in that diagram are the two "B" counters, just downstream of Titan, which were used to establish correlation with incoming muons. The signature of a stopping muon is called " $\mu$ ", and is logically defined by

$$\mu = B \cdot M \cdot S1 \cdot \overline{S2X} \quad \text{where } B = B1 + B2 \quad (48)$$

and the signature of a positron exiting from a  $\mu^+$  decay is "e":

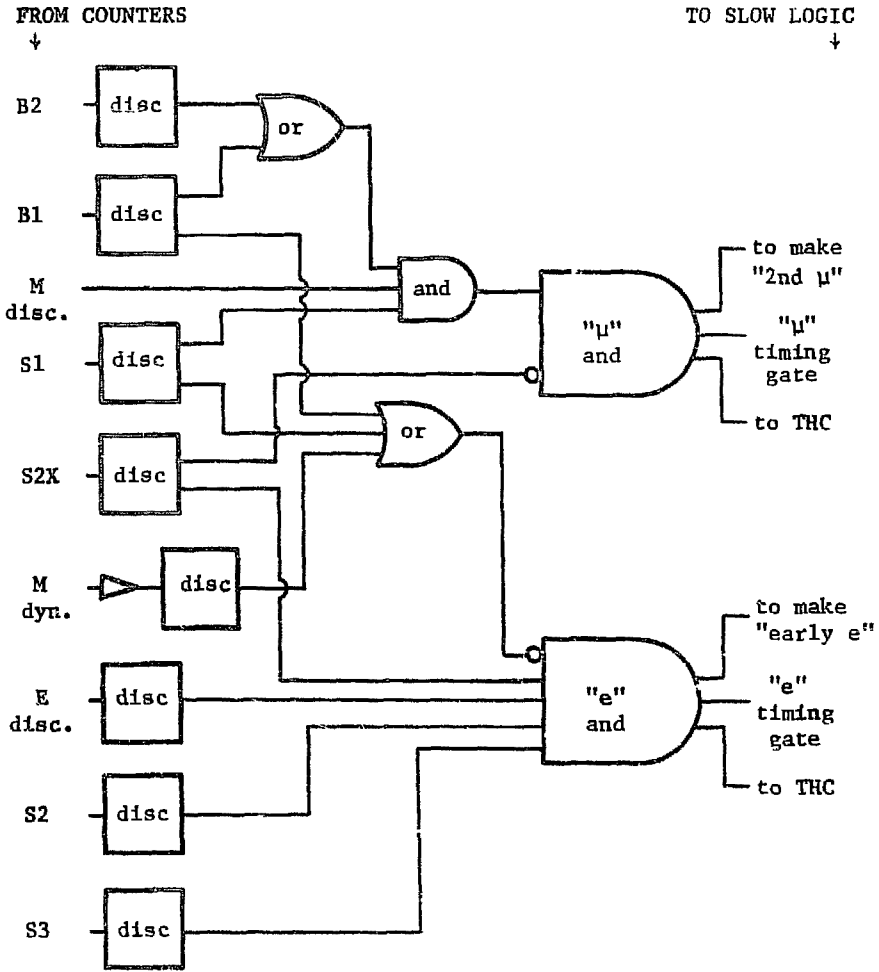
$$e = \overline{(B1 + S1 + M)} \cdot S2X \cdot E \cdot S2 \cdot S3 \quad (49)$$

A simplified diagram of the fast logic is shown in Fig. 8. The pulses " $\mu$ " and "e" were used as gates in coincidence with timing pulses from counters M and E to form the starting and stopping pulses for the clock (see next section).

The timing counters M and E were made from 1/2 in. of NE111 scintillator coupled via 2 in. diameter light pipes to Amperex XP-1021 phototubes (later changed to RCA 8575 tubes). To obtain the best possible time resolution, the two-discriminator method was used: a counter's output pulse was split and fed into two discriminators, after only about 10 ft. signal cables. The first discriminator was set at .4 V, and its output was fed into the "inhibit" of the second discriminator, which was set at 20 mV. This insured that the timing pulses corresponded to the leading edges of phototube pulses at least .4 V in magnitude.

Figure 8

FAST LOGIC



### C. Slow Electronics and On-Line Computer

The time between the stopping muon and the outgoing positron was measured directly by a Hewlett-Packard type 5360A Computing Counter, used in its interval-measuring mode, henceforth referred to as "the clock". Its time base is generated by an internal crystal-generated 10 MHz oscillator; the start and stop times are interpolated within the 100 nsec least count by an analog device, and the interpolation is converted to digital information using the same reference frequency. The clock digitizes time to a nominal resolution of 0.1 nsec. Its deadtime is rather long, and once a starting pulse is given, it can only be reset by a stopping pulse. Since we only detect decay positrons in our counter telescope for  $\sim 5\%$  of the stopping muons, it was necessary to "store" the muon pulse in a recirculating delay cable for 20  $\mu$ sec, starting the clock on the electron signal only if an  $e^+$  was detected within that time, and then stopping with the delayed muon pulse. Thus the time registered by the clock was  $20 \mu\text{sec} - (t_e - t_\mu)$ . A good deal of "slow" logic was required to accomplish this procedure.

The 20  $\mu$ sec recirculating delay worked as follows: an input pulse was fed into a discriminator, whose output was sent through a 200 nsec cable in a temperature-controlled environment; the returning pulse was split and sent back through the original discriminator and into the cable again (hence "recirculating"), and also into a decade scaler. The overflow of the decade scaler was sent to a second decade scaler, which overflowed in turn after

the signal had made 100 trips through the cable (20  $\mu$ sec); this overflow was used both to inhibit the discriminator (stopping the recirculation) and in coincidence with the last signal from the cable to create the timing pulse to be sent to the clock. The weakest link in this system was the discriminator, which had to "pass along" the pulse 100 times. Even so, the time jitter introduced by this technique was found to be less than that in the counter pulses.

Since the recirculating delay was subject to slow changes due to gentle temperature variations, one in every 142 events was started on the prompt muon pulse, rather than the electron pulse, thereby giving a direct measurement of the delay length. A running average was kept of this number in the histogramming, and the times recorded by the clock were subtracted from that average to obtain  $t_e - t_\mu$  for each event. Furthermore, in order to define  $t = 0$  precisely, the first few thousand events in each of the more recent runs were taken with the anticoincidences removed, so that a muon passing straight through all the counters would trigger both an "e" and a " $\mu$ " at the same physical time. These events were cryptically referred to as "straight-throughs". The width of the "straight-through" peak, moreover, defined the practical timing resolution, and was  $\sim 1$  nsec (FWHM).

Several logic bits were sent to the computer along with each event, to identify events with potentially undesirable features. The most important of these were "2nd  $\mu$ " (a second muon stopped in the target before the first decayed), "2nd e" (two "e" pulses were generated after only one " $\mu$ " pulse; one must be spur-

ious), and "Early E" (fast timing counter E fired within 1  $\mu$ sec preceeding the " $\mu$ " pulse, possibly affecting the time of the real E signal due to dead time). Any one of these logical bits caused the event to be rejected. There were also some further bits to insure consistency and distinguish "straight-throughs" from normal events. The relative frequency of various types of "bad" events was typically

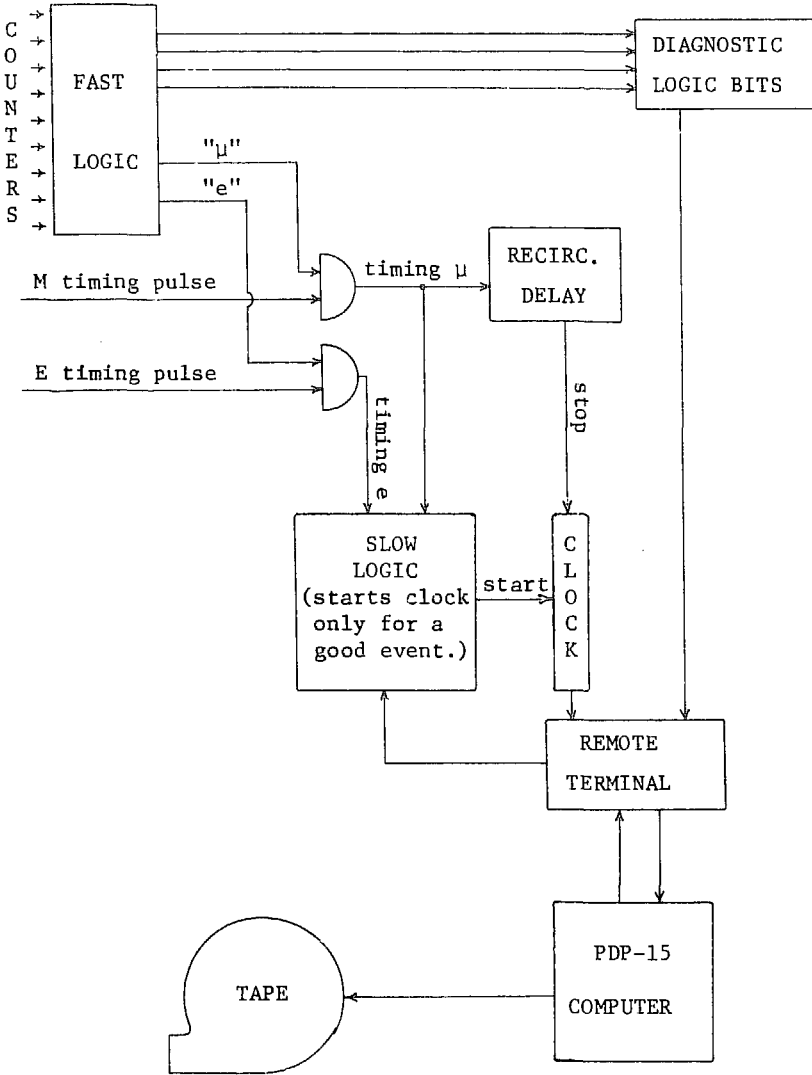
No 2nd $\mu$ , 2nd e, or Early E	$\sim$ 90	%
2nd $\mu$ only	9.1	%
2nd e only	.6	%
Early E only	.4	%
Early E and 2nd $\mu$	.06	%
Early E and 2nd e	.004	%
2nd $\mu$ and 2nd e	.3	%
2nd $\mu$ , 2nd e, and Early E	.002	%

For each event, the digitized time measured by the HP clock, the logic bits described above, and certain other information was transferred to the on-line computer, which was initially a Digital Equipment Corporation PDP-5, and later a DEC PDP-15. The computer made certain checks of the consistency of the data, monitored the "life functions" of the experiment, and stored the data in a buffer which held 142 events. When the buffer was full, the data were written out directly onto magnetic tape, and a new buffer started. The data was never modified by the on-line computer; its function was supervisory and diagnostic. Therefore, although the on-line checks were invaluable in a practical sense,

they are of little interest here.

Figure 9 shows a simplified block diagram outlining the flow of data from the counters through the logic to the computer and onto magnetic tape.

Figure 9 - BLOCK DIAGRAM OF LOGIC NETWORK



#### D. Data Reduction and Analysis Programs

Each run consisted of about a million events recorded on magnetic tape. This tape was converted by the Control Data Corporation 6600 computer into a histogram of the times measured on the HP clock, rejecting all "bad" events (those with "bad" logic bits on or with inconsistent information). The resultant histograms were typically 20,000 bins long, with each bin 0.5 nsec wide, and with typically  $\sim 200$  counts/bin in the early bins.

A histogram was fitted by a  $\chi^2$  minimization program centered around an efficient multi-parameter variable metric minimization routine called VARMIT, available from the disc library of the Berkeley CDC 6600 system. The experimental histogram was fitted to the theoretical distribution described in the Introduction and in Fig. 2, using a fixed value of 2.20  $\mu$ sec for the muon lifetime  $\tau_\mu$ ; the program returned  $\chi^2$  and the best estimates for the parameters  $N_0$ , B, A,  $T_2$ ,  $\omega_\mu$ , and  $\phi$ , specifying the error in the determination of each.

The results were checked for consistency, and then the parameters A and  $\phi$  for a series of runs at different reagent concentrations were sent to the theoretical program, which extracted rate constants, etc. This program also utilized VARMIT, and could fit up to 8 parameters at once; however, the user had the option to hold any parameter fixed. For example, when fitting an example of the proper muonium mechanism, the parameters fitted would be  $A_0$ ,  $\phi_0$ , h, and  $k_{\text{mxd}}$ . Of these, the first two are phenomenological:  $A_0$  is the limiting value of the asymmetry due to beam



polarization, counter geometry, etc., and represents the high-concentration asymptote of  $A([X])$ ;  $\phi_0$  is the angle between the polarization of muons in the stopping beam and the axis of symmetry of the positron counter telescope, and similarly should correspond to the limiting value of  $\phi$  as  $[X] \rightarrow \infty$ . Thus, in the figures showing best fits to the data, the quantities plotted against reagent concentration are "Polarization" =  $A/A_0$  and "Phase" =  $\phi - \phi_0$ .

As might be expected, a change in the geometry of the counters affects the observed asymmetry for a given polarization, and even more significantly shifts the phenomenological angle  $\phi_0$ ; while some such changes were made during the course of the experiment, care was taken to preserve the geometry for all runs in any "set" forming a series of points for  $A$  and  $\phi$  versus reagent concentration  $[X]$ .

## IV. RESULTS

A. Relevance to Hydrogen Atom Chemistry

The theory of chemical kinetics is not to be summarized in a short space; however, since the only chemically significant difference between muonium and atomic hydrogen is in their masses, a few simplified relations borrowed from the literature can help relate the chemical reaction rates of these two atoms.

In gases, the rate constant for the reaction  $A + B \rightarrow C$  (where C may represent multiple products in some cases) is given approximately by<sup>18</sup>

$$k = P \sigma \bar{v} \exp(-E/RT) = P \pi (r_A + r_B)^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \exp(-E/RT) \quad (50)$$

where P is the steric factor,  $\sigma$  the geometrical collision cross section,  $\bar{v}$  the mean thermal relative velocity between A and B, E the activation energy for the reaction,  $r_A + r_B$  the effective combined radius of the colliding molecules A and B, R the gas constant,  $k_B$  the Boltzmann constant, and  $\mu_{AB}$  the reduced mass, given by  $1/\mu_{AB} = 1/m_A + 1/m_B$ . In most cases, if A is muonium or hydrogen, B is much heavier than A and  $\mu_{AB} \approx m_A$ . The radii of muonium and hydrogen are virtually identical, so that unless the activation energy depends on the mass, the only difference in the reaction rates of Mu and H is due to the different thermal velocities, giving the "kinetic ratio"

$$\frac{k(\text{Mu} + B \rightarrow C)}{k(\text{H} + B \rightarrow C)} \approx \left( \frac{m_H}{m_{\text{Mu}}} \right)^{\frac{1}{2}} \approx 3 \quad (51)$$

In liquids, the situation is rather different. The above

treatment assumes that reagent molecules do not even collide with solvent molecules; in fact the "solvent" in gas phase kinetics is just vacuum, for this sort of treatment. Such an approach is ludicrous in liquids, where each reagent molecule is continually surrounded by solvent molecules which severely restrict its thermal motion. In liquids the reactants must diffuse through the solvent to find each other, and when they do approach they are apt to stay in each other's presence for some time. Whereas in gases the reactants collide in the familiar sense, in liquids it is more appropriate to call the period of proximity an "encounter". Since an encounter gives the partners a good chance to react, there is often an almost certain probability of reaction in any encounter -- in which case the reaction is only hindered by the rate at which they diffuse through the solvent. Such reactions are called "diffusion-limited" or "diffusion-controlled". In these cases the reaction rate is just equal to the rate at which an A molecule encounters B molecules, divided by the concentration of B:<sup>18</sup>

$$k \approx \frac{3 N (D_{AS} + D_{BS})}{[S] (r_A + r_B)^2} \quad (52)$$

where N is the average number of nearest neighbor molecules of the reactant which diffuses fastest,  $D_{AS}$  and  $D_{BS}$  are the diffusion constants of A and B through S, and [S] is the concentration of S. When A is hydrogen or muonium,  $D_{AS}$  will generally dominate  $D_{BS}$ , in which case N is the average number of nearest neighbors which A sees in its crowded environment. For a crude approximation to  $D_{AS}$  we can borrow a familiar result from elementary statistical

mechanics:

$$D_{AS} \approx \frac{1}{3} \bar{v}_{AS} \lambda_{AS} = \frac{1}{3} \left( \frac{8k_B T}{\pi \mu_{AS}} \right)^{\frac{1}{2}} \times \frac{1}{\sqrt{2} n_S \sigma_{AS}} \quad (53)$$

where  $\bar{v}_{AS}$  is the mean relative thermal velocity between A and S,  $\lambda_{AS}$  is the mean free path of A in S,  $\mu_{AS}$  is the reduced mass, given by  $1/\mu_{AS} = 1/m_A + 1/m_S$ ,  $n_S$  is the volume density of S molecules, and  $\sigma_{AS} = \pi(r_A + r_S)^2$  is the geometrical cross-section for A molecules impinging upon S molecules.

As before, if A is hydrogen or muonium, usually  $\mu_{AS} \approx m_A$ , and we find that, as in the case of gases, the only explicit dependence of the rate constant on the mass of the lightest reactant is in the form  $k \sim 1/\sqrt{m_A}$ , so that the "kinetic ratio" of 3 between rate constants for muonium and those for hydrogen holds in liquids as well as gases, to a crude approximation. The most important difference is that in liquids the rate constants will depend strongly on the solvent used, and care must be taken to compare liquid-phase rate constants only when measured in the same solvent. For easy reference, Table II lists some hydrogen atom reaction rates and the equivalent rates for muonium predicted by the "kinetic ratio".

The predictions of such a simple treatment should not be expected to agree perfectly with experiment; in fact it is really the deviations from the "kinetic ratio" for  $k_{Mu}/k_H$  which are most interesting theoretically, since they may help in determining the dynamics of the reactions.

Table II - SELECTED H ATOM REACTION RATES<sup>a</sup>

REAGENT	pH	RATE CONSTANT FOR HYDROGEN (liters/mole-sec)	EQUIVALENT RATE CONSTANT FOR MUONIUM	METHOD
Br <sub>2</sub>		~ 10 <sup>10</sup>	~ 3 × 10 <sup>10</sup>	pulse radiolysis (p. r.)
ClO <sub>4</sub> <sup>-</sup>	0	nil	nil	?
Fe <sup>+++</sup>	0.1	8 × 10 <sup>7</sup>	2.4 × 10 <sup>8</sup>	O <sub>2</sub>
"	0.1	1.6 × 10 <sup>6</sup>	4.8 × 10 <sup>6</sup>	Fe <sup>++</sup>
"	0	< 2 × 10 <sup>6</sup>	< 6 × 10 <sup>6</sup>	O <sub>2</sub>
"	0.4	1.2 × 10 <sup>6</sup>	3.6 × 10 <sup>6</sup>	O <sub>2</sub>
"	1.6	2.2 × 10 <sup>7</sup>	6.6 × 10 <sup>7</sup>	O <sub>2</sub>
"	2	9.0 × 10 <sup>7</sup>	2.7 × 10 <sup>8</sup>	p. r.
"	2.1	9.5 × 10 <sup>7</sup>	2.85 × 10 <sup>8</sup>	O <sub>2</sub>
"	2.1	9.6 × 10 <sup>7</sup>	2.88 × 10 <sup>8</sup>	D <sub>2</sub>
Fe(OH) <sub>2</sub> <sup>+</sup>	-	7.5 × 10 <sup>8</sup>	2.25 × 10 <sup>9</sup>	p. r.
FeCl <sup>++</sup>	0.1	4.5 × 10 <sup>9</sup>	1.35 × 10 <sup>10</sup>	O <sub>2</sub>
FeCl <sub>2</sub> <sup>+</sup>	0.1	9 × 10 <sup>9</sup>	2.7 × 10 <sup>10</sup>	O <sub>2</sub>
H <sub>2</sub> O <sub>2</sub>	acid	5 × 10 <sup>7</sup>	1.5 × 10 <sup>8</sup>	O <sub>2</sub>
"	.4-3	1.6 × 10 <sup>8</sup>	4.8 × 10 <sup>8</sup>	p. r.
"	2	9 × 10 <sup>7</sup>	2.7 × 10 <sup>8</sup>	p. r.
"	-	6.1 × 10 <sup>7</sup>	1.83 × 10 <sup>8</sup>	p. r.
I <sub>2</sub>	0.4	4 × 10 <sup>10</sup>	1.2 × 10 <sup>11</sup>	O <sub>2</sub>
NO <sub>3</sub> <sup>-</sup>	11-13	~ 7 × 10 <sup>6</sup>	~ 2.1 × 10 <sup>7</sup>	acetate
"	7	2.4 × 10 <sup>7</sup>	7.2 × 10 <sup>7</sup>	2-propanol
"	1.1	1.2 × 10 <sup>7</sup>	3.6 × 10 <sup>7</sup>	H
"	2.0	1.3 × 10 <sup>7</sup>	3.9 × 10 <sup>7</sup>	H

<sup>a</sup>taken from M. Anbar and P. Neta, Int. J. Appl. Rad. and Isotopes 18, 493 (1967).

(cont'd)

Table II - SELECTED H ATOM REACTION RATES

REAGENT	pH	RATE CONSTANT FOR HYDROGEN (liters/mole-sec)	EQUIVALENT RATE CONSTANT FOR MUONIUM	METHOD
$\text{NO}_3^-$	4.7	$9.1 \times 10^6$	$2.73 \times 10^7$	H
"	7	$9.3 \times 10^6$	$2.79 \times 10^7$	H
"	10-13	$3.8 \times 10^6$	$1.14 \times 10^7$	H
"	7	$7 \times 10^6$	$2.1 \times 10^7$	ethanol
"	acid	$2.3 \times 10^7$	$6.9 \times 10^7$	2-propanol
"	6	$1.8 \times 10^7$	$5.4 \times 10^7$	2-D-2-propanol
$\text{O}_2$	acid	$1.2 \times 10^{10}$	$3.6 \times 10^{10}$	p. r.
"	.4-3	$2.6 \times 10^{10}$	$7.8 \times 10^{10}$	p. r.
"	2	$1.9 \times 10^{10}$	$5.7 \times 10^{10}$	p. r.
$\text{OH}^-$	7.5-12.5	$1.2 \times 10^7$	$3.6 \times 10^7$	chloroacetate
"	11-13	$2.3 \times 10^7$	$6.9 \times 10^7$	formate, acetane
"		$1.8 \times 10^7$	$5.4 \times 10^7$	p. r.
"		$2.6 \times 10^7$	$7.8 \times 10^7$	ethanol
"		$2.3 \times 10^7$	$6.9 \times 10^7$	p. r.
$\text{CH}_3\text{OH}$	1	$1.6 \times 10^6$	$4.8 \times 10^6$	$\text{Fe}^{+++}$
"	7	$1.7 \times 10^6$	$5.1 \times 10^6$	$\text{Fe}(\text{CN})_6^{-3}$
"	7	$1.6 \times 10^6$	$4.8 \times 10^6$	$\text{NO}_2^-$
"	7	$1.65 \times 10^6$	$4.95 \times 10^6$	D-formate
"	2	$1.6 \times 10^6$	$4.8 \times 10^6$	$\text{Ag}^+$ , (p. r.)
"	-	$4.6 \times 10^6$	$1.38 \times 10^7$	$\text{OH}^-$
nitro- benzene	7	$1.7 \times 10^9$	$4.1 \times 10^9$	2-propanol

### B. Verification of the Proper Muonium Mechanism

Figure 10 shows the observed dependence of  $P_{res}$  and  $\phi$  on the concentration  $[X]$  of iodine in methanol solution, in an external magnetic field of 102 gauss. The leftmost point in this and all such graphs corresponds to the data taken in the pure solvent. The point is actually infinitely far off-scale to the left, since the horizontal axis is  $\log_{10}$  of the concentration (in moles/liter). The curve through the points is the best fit to the theory, assuming that the muons are depolarized by the proper muonium mechanism; i.e., that no radical formation is involved. This corresponds to Fig. 5, taking  $\tau = k_{\text{mxd}}[X]$ , except that here the hot chemistry component  $h$  is nonzero (approximately 1/2, in fact), accounting for the nonzero value of  $P_{res}$  at zero concentration and the return of  $\phi$  to zero with vanishing concentration. The "plateau" in  $P_{res}([X])$  is noticeable, and the variation in phase is striking.

In Figure 11 are shown the results for iodine in methanol at 1000 gauss. The phase dip is still evident, though of smaller amplitude than at 102 gauss, but the "plateau" in the polarization is no longer evident. At 4500 gauss (shown in Fig. 12) the plateau is completely missing and the phase does not vary more than one or two degrees. Mainly for this reason, no useful phase information was extracted from the data at 4500 gauss. Table III shows the best values for the rate constants and other parameters for this and other fits to the proper muonium mechanism.

The case of  $I_2$  in  $CH_3OH$  is the best example found so far of the pure proper muonium mechanism. Not surprisingly, since

muonium itself is a radical many of its reaction products are radicals, and situations complicated by radical formation are at least as common as examples of the pure muonium mechanism. Due to the complicated and often ambiguous results of processes involving radicals, it is fortunate that there is at least one example of the simplest case, to demonstrate the validity of the model.

The rate constant of  $1.4 \pm .3 \times 10^{11}$  liters/mole-sec obtained for this reaction compares favorably with the value<sup>19</sup> of  $4 \times 10^{10}$  liters/mole-sec for the reaction  $H + I_2 \rightarrow HI + I$ , when the latter is multiplied by the "kinetic ratio" of 3.



Figure 10 -  $I_2$  in  $CH_3OH$  at 102 gauss: Proper Muonium

Mechanism

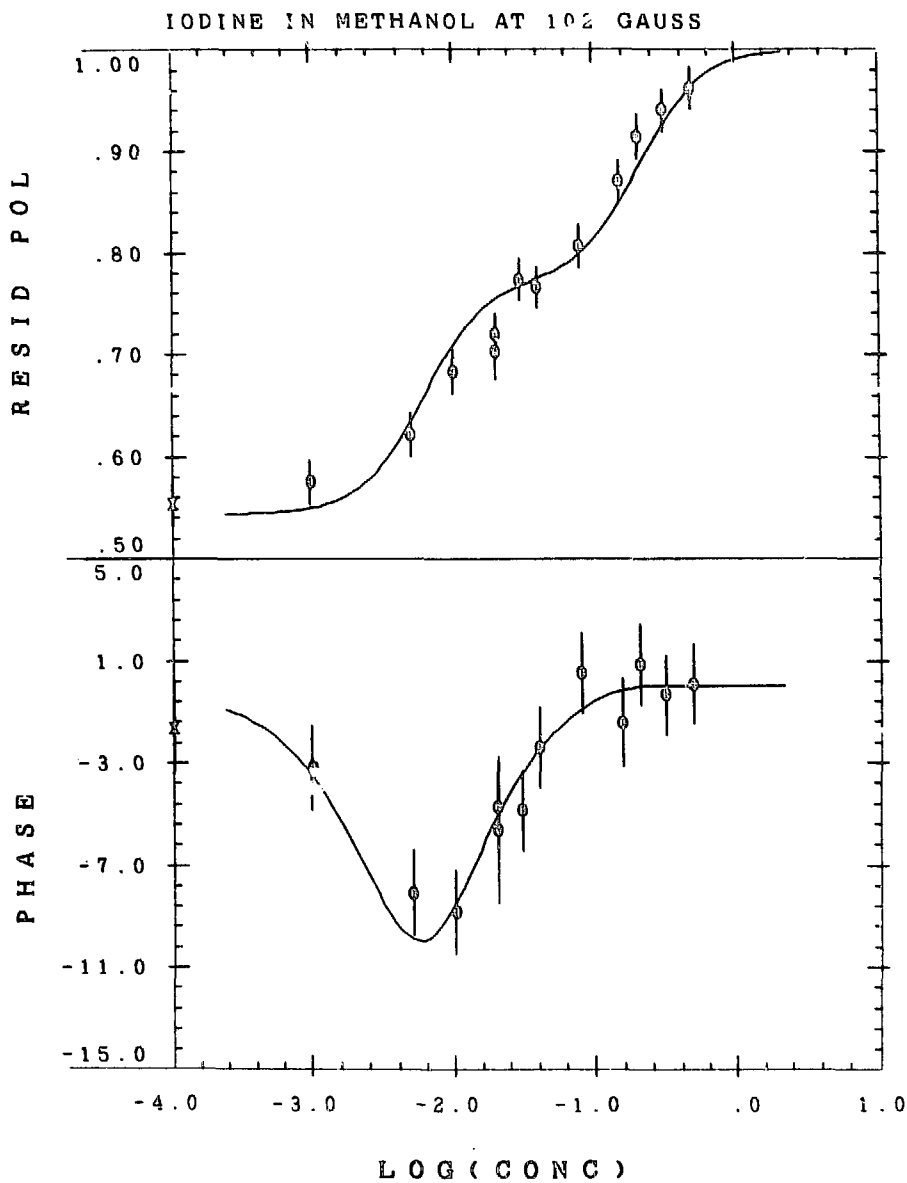


Figure 11 -  $I_2$  in  $CH_3OH$  at 1000 gauss: Proper Muonium

Mechanism

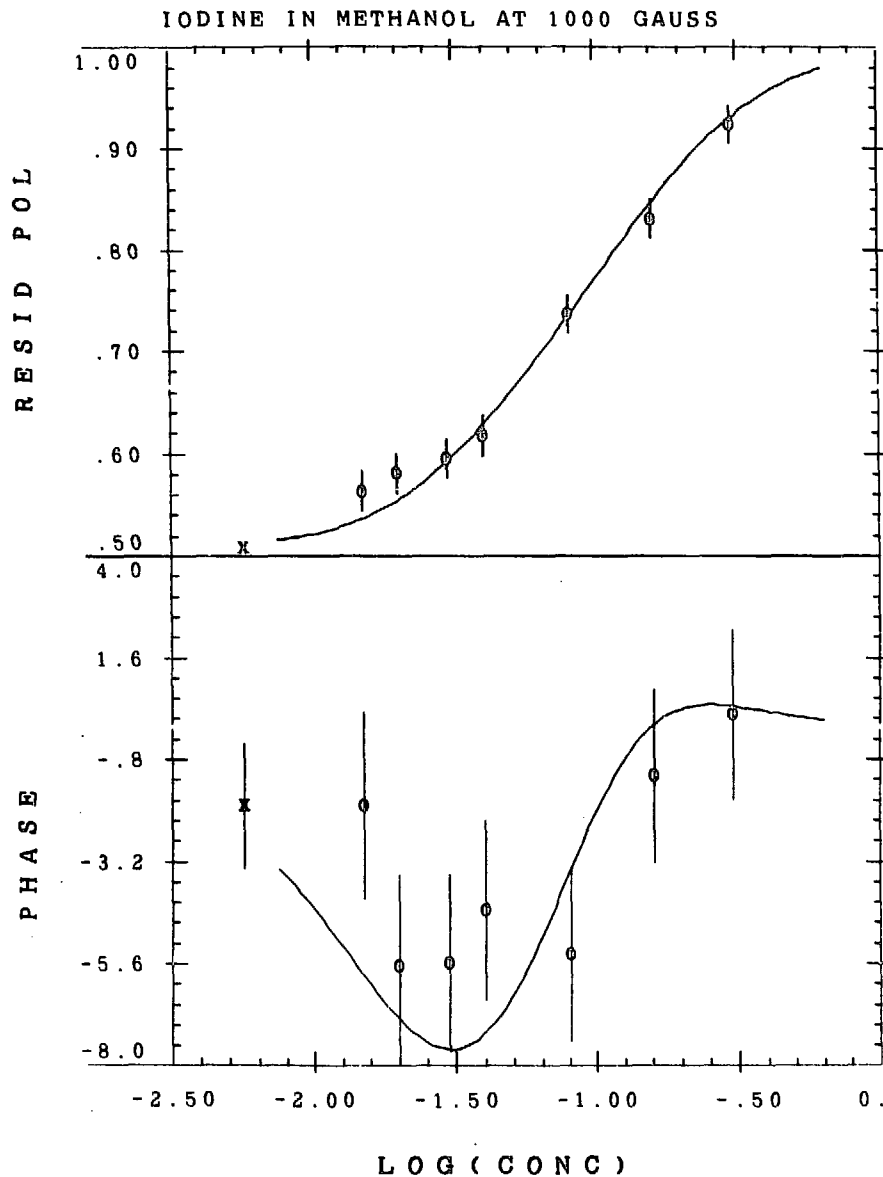


Figure 12 -  $I_2$  in  $CH_3OH$  at 4500 gauss: Proper Muonium  
Mechanism

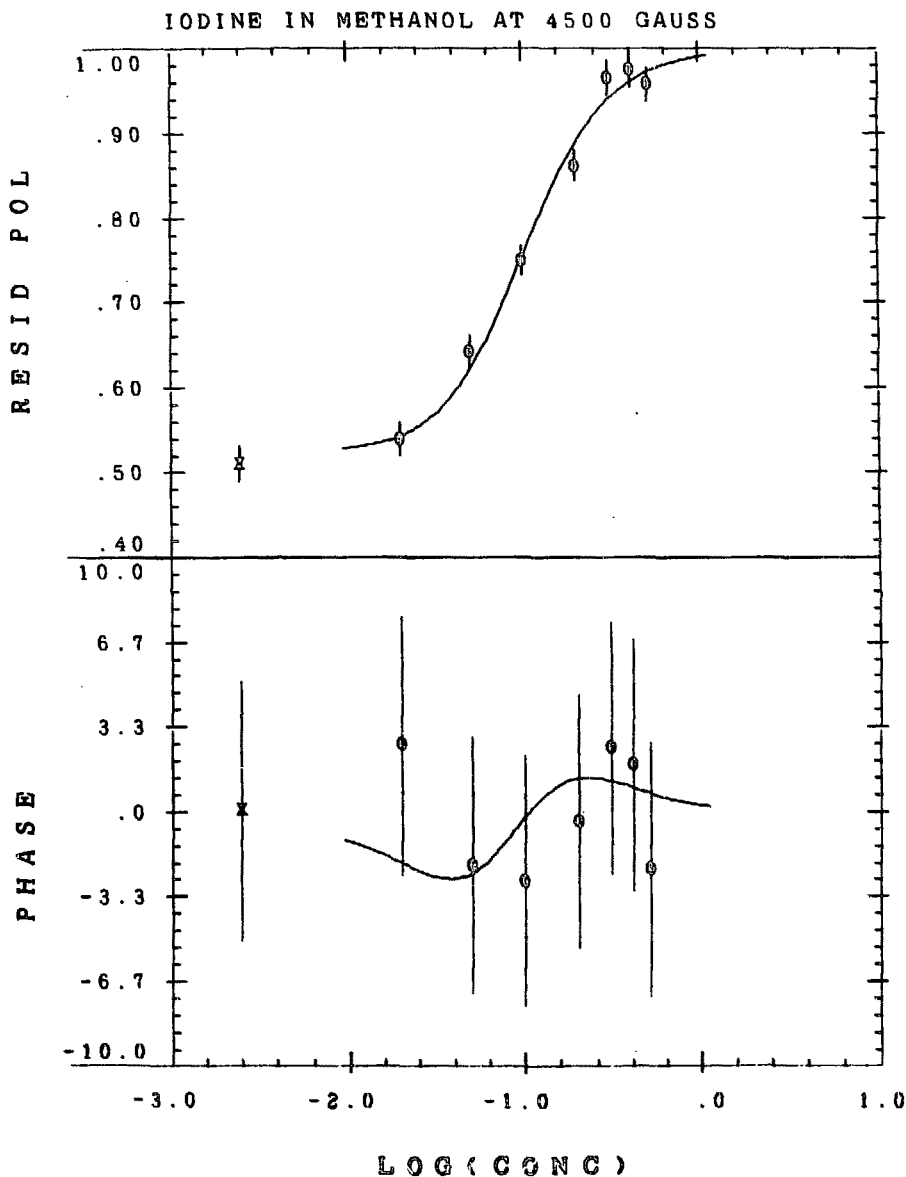


Table III - BEST FITS TO "PROPER" MUGNIUM MECHANISM

REAGENT	SOLVENT	FIELD (gauss)	$A_o$	$\phi_o$ (degrees)	$h$	$k_{\text{mxd}} \times 10^{-10}$ (liters/mole-sec)	$\frac{\chi^2}{\text{deg. fr.}}$	MECHANISM CORRECT?
I <sub>2</sub>	CH <sub>3</sub> OH	103	.24 ± .01	15.5 ± 1.0	.54 ± .02	16.7 ± 2.0	~2	yes
"	"	1000	.27 ± .02	105 ± 2 <sup>a</sup>	.52 ± .02	11.4 ± 2.0	~3.5	yes
"	"	4500	.27 ± .02	-	.54 ± .02	13.4 ± 2.0		yes
FeCl <sub>3</sub>	H <sub>2</sub> O	4500	.31 ± .02	-	.51 ± .02	2.1 ± 0.2	~1	?
Fe(ClO <sub>4</sub> ) <sub>3</sub>	H <sub>2</sub> O	4500	.30 ± .02	-	.55 ± .02	1.7 ± 0.2	~6	no
"	"	100	.275 <sup>b</sup>	15.5 <sup>b</sup>	.55 <sup>b</sup>	0.24	~100	no
HClO <sub>4</sub>	H <sub>2</sub> O	4400	.275 <sup>b</sup>	-	.54 ± .01	0.12	~2	?
HNO <sub>3</sub>	H <sub>2</sub> O	4500	.30 ± .01	-	.54 ± .01	0.64	~1.5	no
"	"	100	.275 <sup>b</sup>	16.2 ± 4.0	.55 <sup>b</sup>	0.62	~11	no
H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	100	.26 ± .02	11.4 ± 1.2	.58 ± .02	0.45	~3	no

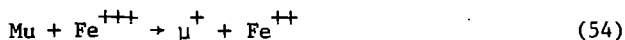
<sup>a</sup> $t = 0$  not defined;  $\phi_o$  therefore arbitrary.

<sup>b</sup>Parameter held constant; not fitted.

Errors quoted are approximate.  $\chi^2/\text{degree of freedom}$  is apt to have been overestimated, due to probable undetected systematic uncertainties.

### C. Candidates for the Proper Muonium Mechanism

Ferric chloride in water may be another example of the pure muonium mechanism, although we have not yet made the measurements which will test this hypothesis. Aqueous solutions of ferric chloride, ferric nitrate, and ferric perchlorate give similar curves of  $P_{res}(|X|)$ , much like that obtained for  $I_2$  in methanol, at fields of 4500 gauss and higher. Figure 13 shows  $FeCl_3$  (solid curve with triangles) and  $Fe(ClO_4)_3$  (dashed curve with solid dots) at 4500 gauss; the results for  $Fe(NO_3)_3$  at 11 gauss were presented (but wrongly interpreted) in Ref. 20. The results shown in Fig. 13 were first interpreted<sup>21</sup> strictly in terms of the proper muonium mechanism, postulating that the only important reaction was



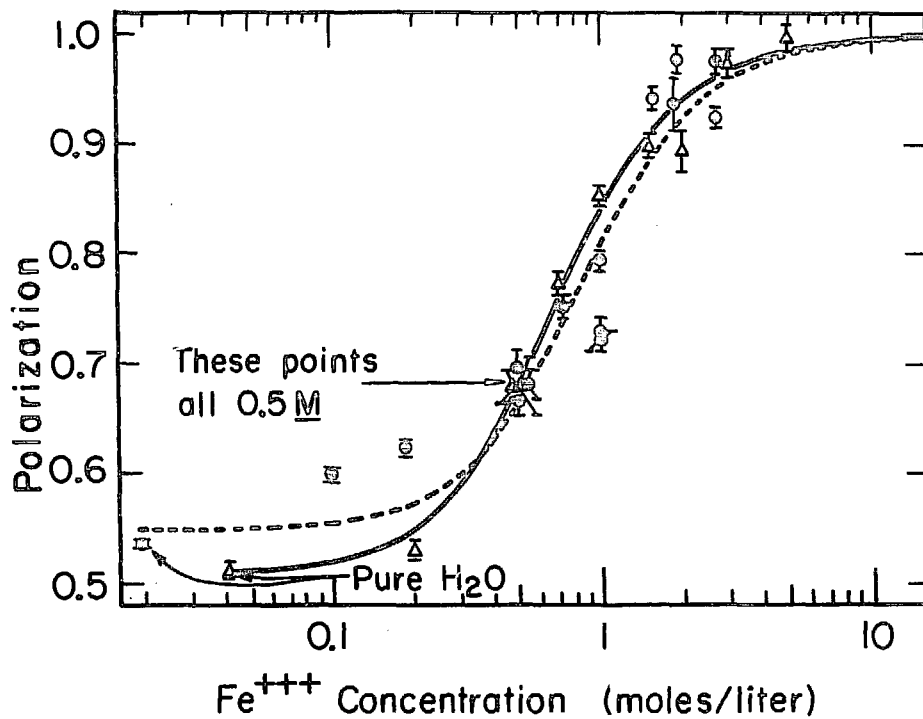
where either the free muon or the product of its subsequent reaction with anions in solution constitutes a diamagnetic environment for the muon.

Later investigation showed that while addition of as much as 10 moles/liter of HCl to water had no effect on  $P_{res}$  (as noted earlier by Swanson<sup>22</sup>), both  $HNO_3$  and  $HClO_4$  had a marked "repolarizing" effect on the muon precession. Therefore, while  $FeCl_3$  survives as a prime candidate for the proper muonium mechanism, reaction (54) is not adequate to characterize the processes in  $Fe(NO_3)_3$  and  $Fe(ClO_4)_4$ . Furthermore, the  $HNO_3$  results show strong evidence for radical formation, as will be seen later.

The extracted value of  $2.1 \pm 0.2 \times 10^{10}$  liters/mole-sec for the rate constant  $k_{\text{mxd}}$  in  $\text{FeCl}_3$  solutions is more than an order of magnitude above the highest value predicted by measurements in hydrogen (see Table II), if we believe reaction (54) to be the dominant mechanism. However,  $\text{Fe}^{+++}$  is known to form hydroxides readily, and the higher rate for reactions of H atoms with  $\text{Fe}(\text{OH})_2^+$  suggests that this process may be dominant in  $\text{FeCl}_3$  solutions; reaction with the species  $\text{FeCl}^{++}$  and  $\text{FeCl}_2^+$ , if present, are even higher. Thus, the situation with  $\text{FeCl}_3$  is probably more complicated than reaction (54) indicates, and at best we can hope that no radicals are formed containing muonium, in which case the situation will still be described by the proper muonium mechanism.

Other cases of the proper muonium mechanism undoubtedly exist, but it appears that they are the exception rather than the rule; they should be sought out, however, since the simplest cases allow the most precise determination of rate constants. If a reaction of atomic hydrogen is known to produce only diamagnetic compounds, and has a rate constant of more than  $10^9$  liters/mole-sec, this technique can be used to extract the rate constant for the analogous reaction of muonium to any accuracy of at least 20%.

Figure 13 -  $\text{FeCl}_3$  (solid curve with triangles) and  
 $\text{Fe}(\text{ClO}_4)_3$  (dashed curve with dots) at 4500 gauss:  
Fit Assuming Proper Mucnium Mechanism



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## D. Evidence for Radical Formation

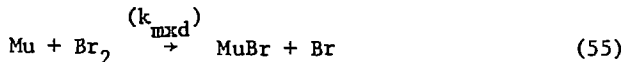
### 1. Benzene

The general theory including radical formation grew out of a study intended to exemplify the proper muonium mechanism: the case of bromine in benzene. Benzene was chosen as a solvent because of its known small asymmetry<sup>22</sup>, implying a hot fraction  $h \sim \frac{1}{8}$ , as compared to  $h \sim \frac{1}{2}$  in both water and methanol. The advantage of a low value of  $h$  is that the range through which  $P_{res}$  can be varied by chemical means is  $(1 - h)$ , which means that the statistical significance of the asymmetry data (given fixed errors) is only half as great for  $h = 1/2$  as for  $h = 0$ . Furthermore, since the contribution to  $P_{res}$  from  $h$  is always unrotated, phase variations are dramatically reduced by large values of  $h$ . For a reagent we chose bromine, both because of the analogy to iodine and because of its virtually unlimited solubility. Data were taken in a 200 gauss magnetic field so that the "plateau" would be visible.

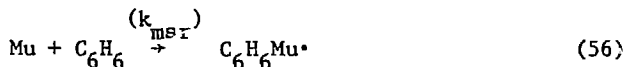
However, as can be seen in Fig. 14, the results were in strong disagreement with the predictions of the proper muonium mechanism. There is definitely no "plateau", and the phase variation is less sharp than predicted by the simple theory. The results in fact resemble the predictions of the proper muonium mechanism in a stronger magnetic field, and since the criterion for a "strong" field is that it be comparable with the effective hyperfine field, this observation led to a consideration of environments similar to muonium but with lower values of the effective hyperfine field (e.g., radicals).



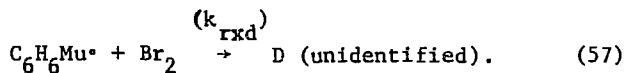
On the basis of other chemical studies <sup>23, 24</sup>, we made the following assumption about the chemical processes involved: first, that muonium reacts directly with the bromine to form a diamagnetic compound, according to



and also (competitively) with the benzene to form the muonium analog of the radical cyclohexadienyl ( $\text{C}_6\text{H}_7^\bullet$ ), according to



Second, the radical is presumed to react subsequently with the bromine to place the muonium into a diamagnetic compound, according to



In this and all other examples of radical formation we treat, it is assumed that the "radical hot fraction"  $r$  is zero. In the other examples, the radical is formed by reaction with the reagent, rather than with the solvent, in which case  $r$  is required to be zero by the assumption of the "dilute limit" (virtually no epithermal collisions with the reagent). In the case of benzene, the fits are rather insensitive to the distinction between a rapid "cold" reaction into the radical and a nonzero value for  $r$ . However, epithermal muonium seems rather unlikely to "stick" to benzene rings, so the assumption of  $r = 0$  in the case of benzene also seems justifiable.

Iodine was also used as a reagent in benzene, but the lower solubility limited concentrations to about 0.37 M, which was insufficient to give full "repolarization". Nevertheless, when the parameters for I<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> are allowed to vary freely (given as starting values the best fit for Br<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>), a best fit is obtained for values consistent with the Br<sub>2</sub> results. The results for Br<sub>2</sub> and I<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> are shown in Figs. 15 and 16, respectively; the best values for the fitted parameters are listed in Table IV.

Since the radical involved is presumed to be the muonium analog of cyclohexadienyl<sup>23</sup>, whose effective hyperfine field at the site of the extra proton is known<sup>25</sup> to be 47.71 gauss (isotropic average),

$$\frac{\omega_r}{\omega_o} = \frac{(47.71 \times \mu_\mu/\mu_p)}{1588} = 0.095 \quad (58)$$

In fact, when  $\frac{\omega_r}{\omega_o}$  was given various other values and best fits were obtained for each case, a minimum  $\chi^2$  was obtained for  $\frac{\omega_r}{\omega_o} \approx .03$ , with nearly as good results for  $\frac{\omega_r}{\omega_o}$  in the region from .01 to .07; the theoretical value is thus consistent with the best fit, within statistics.

Melville and Robb<sup>24</sup> measured a rate constant of  $5.88 \times 10^8$  liters/mole-sec for the reaction  $H + C_6H_6 \rightarrow C_6H_7^\cdot$ , corresponding to a rate constant of  $k_{msr} = 1.77 \times 10^9$  for reaction (56); this is consistent with our best value for  $k_{msr}$  in the case of Br<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>, where the best determination is made.

Figure 14 -  $\text{Br}_2$  in  $\text{C}_6\text{H}_6$  at 200 gauss:

Fit Assuming Proper Muonium Mechanism

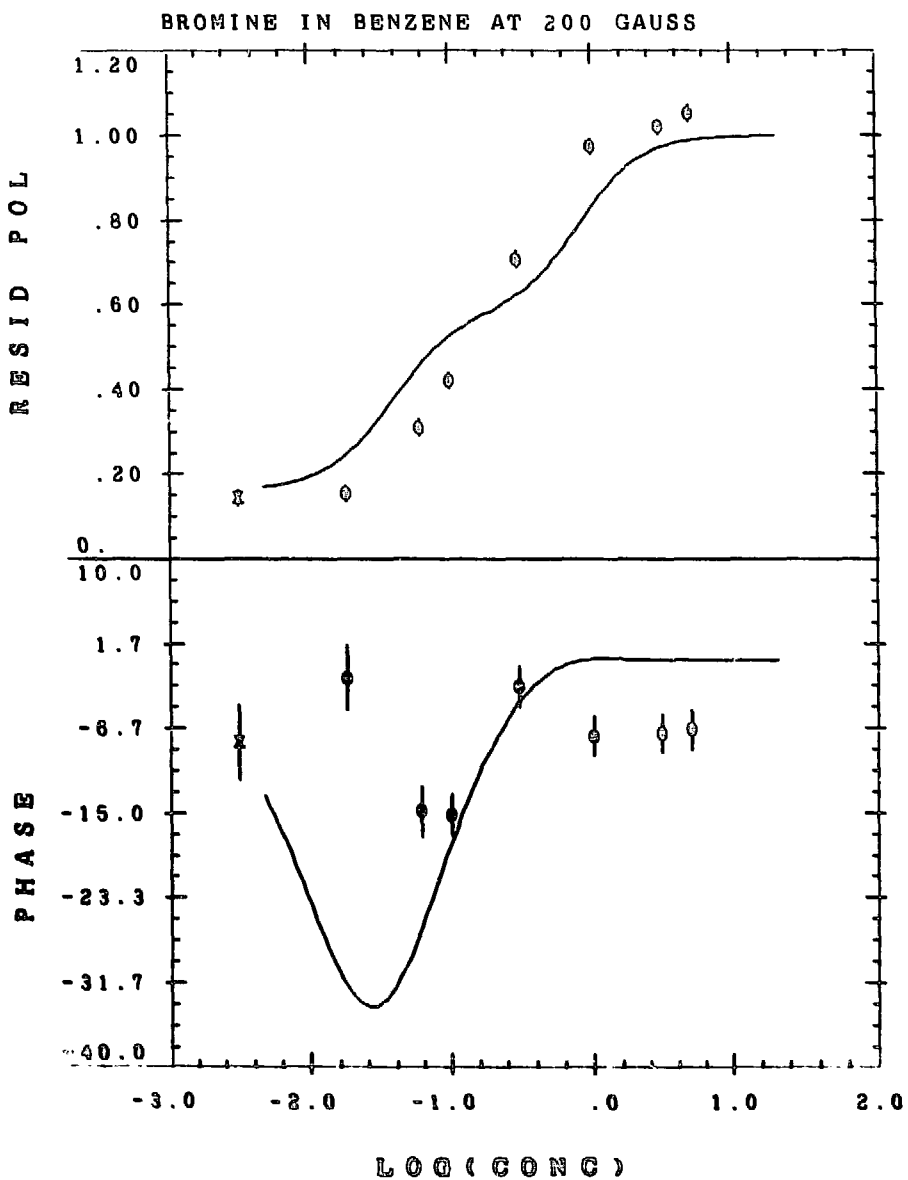


Figure 15 -  $\text{Br}_2$  in  $\text{C}_6\text{H}_6$  at 200 gauss:

Fit Including Radical Formation

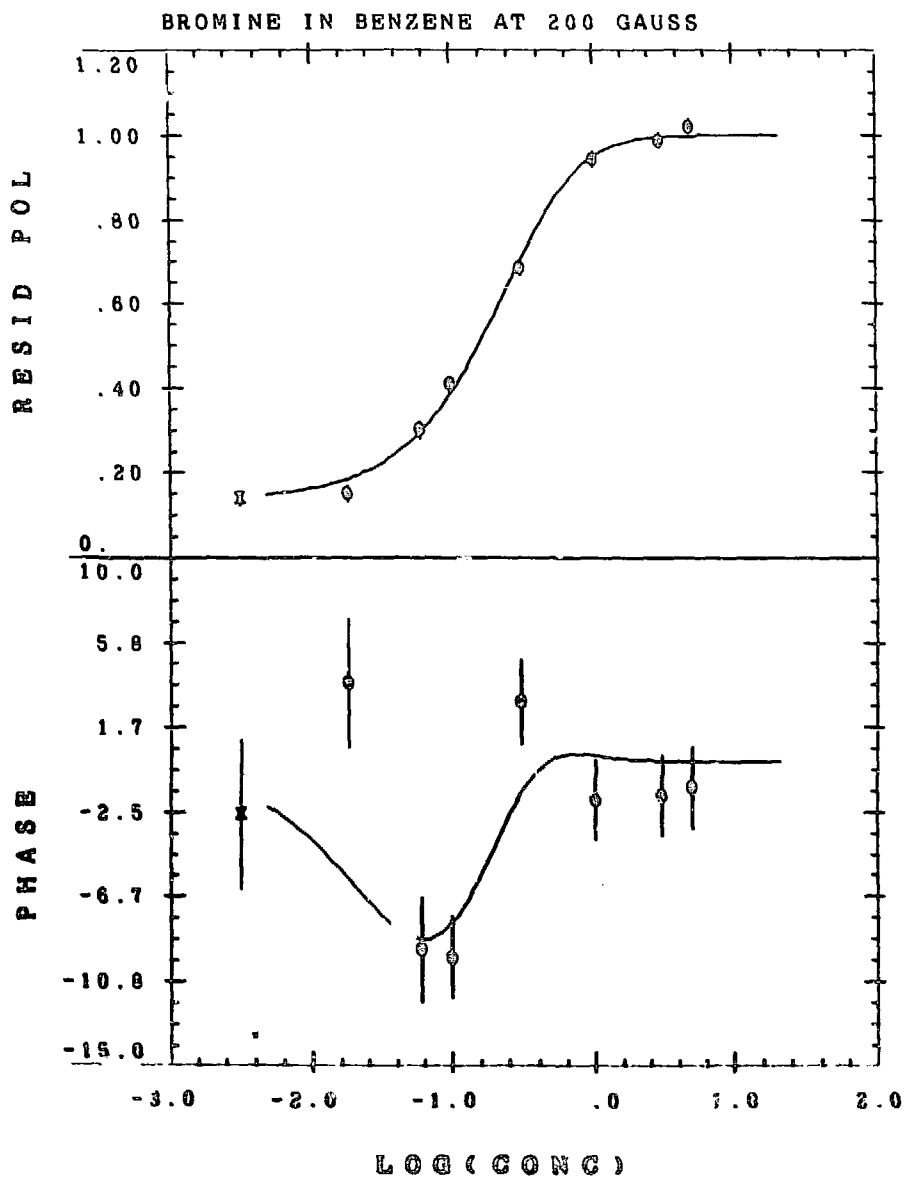
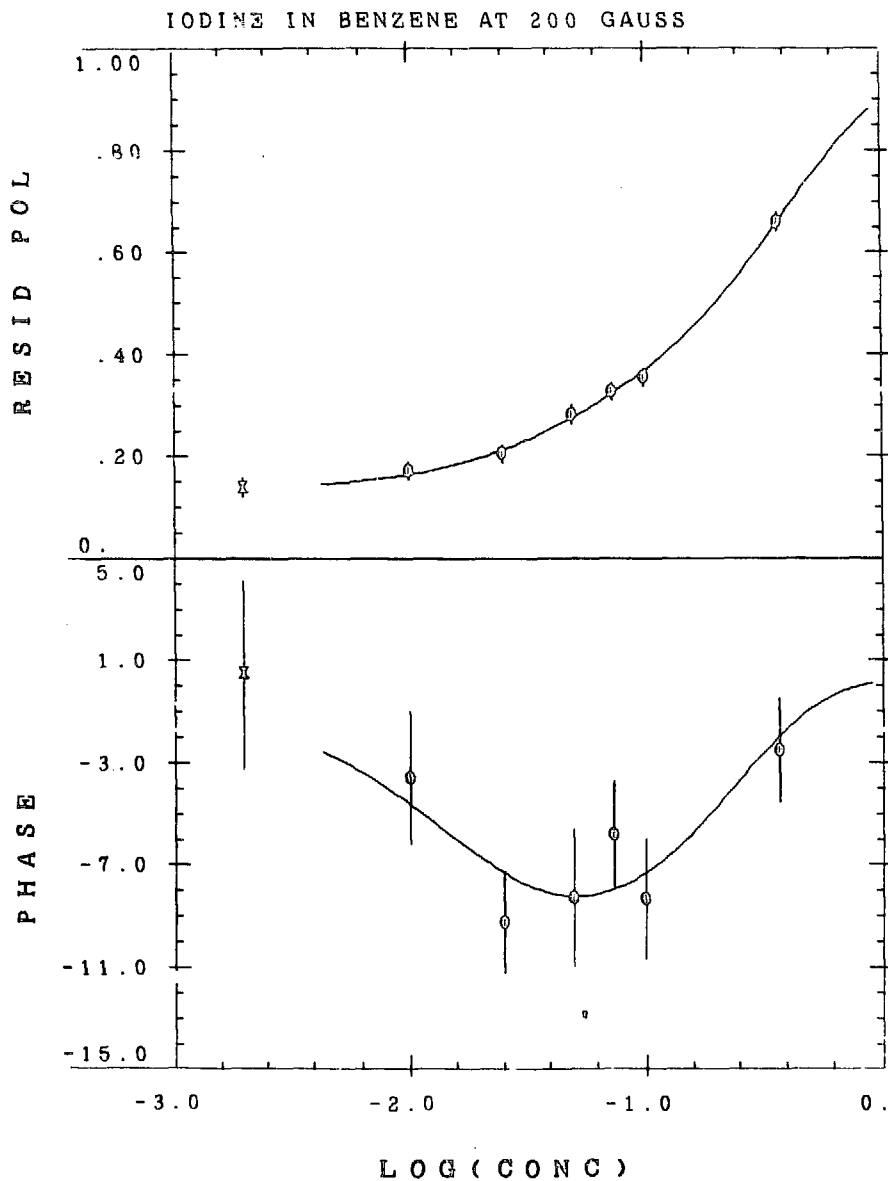


Figure 16 -  $I_2$  in  $C_6H_6$  at 200 gauss:

Fit Including Radical Formation



## 2. Acids

As mentioned earlier, our studies of HCl in aqueous solution confirmed the findings of Swanson<sup>22</sup>, which showed that HCl does not appreciably change  $P_{res}$  from the value observed in pure water. Therefore, no combination of reactions between  $\text{Mu}$ ,  $\text{H}^+$ , and  $\text{Cl}^-$  leads to a diamagnetic compound containing Mu in times shorter than about 10 nsec, even in 10 M solutions. However, addition of nitric acid to water causes marked "repolarization", with a maximal asymmetry reached at about 10 M. The data at 4500 gauss are shown in Fig. 17, along with the best fit using the proper muonium mechanism. The fit looks quite reasonable at 4500 gauss, but at 100 gauss the simple theory fails to fit the data, as can be seen from Fig. 18. The results of these fits are listed in Table III.

When it is assumed that Mu reacts with  $\text{HNO}_3$  to form a radical, which subsequently reacts with  $\text{HNO}_3$  to place the muonium in a diamagnetic compound, the generalized mechanism gives quite plausible results for the case of  $\text{HNO}_3$  in water at 100 gauss, as can be seen in Fig. 19. The results of the best fit are listed in Table IV. Note that we have not tried to identify either the radical or the reaction products, since a logical choice was not obvious to us; the value for  $\omega_r/\omega_o$  was chosen by minimizing  $\chi^2$ . These results have yet to be fully interpreted, but it is clear that, without specifying the species involved, we have a good idea of the types of processes taking place. This is rather confusing in light of the published rates for reaction of hydrogen atoms with  $\text{NO}_3^-$ , (see Table II) none of which predicts a value of more

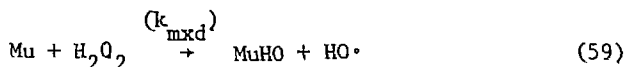
than  $7.2 \times 10^7$  liters/mole-sec for the analogous reaction of muonium. Such a low rate is totally incapable of explaining the observed fast reactions of muonium in  $\text{HNO}_3$  solution. The discrepancy is rather exciting, since it implies the existence of hitherto unexpected processes.

Similar results are seen in Fig. 20 for  $\text{HClO}_4$  in water at 4400 gauss. However, we have not yet undertaken a study of  $\text{HClO}_4$  at low field, and (as has been shown) the high-field data is insensitive to radical formation. Thus the existing results are interpreted only in terms of the proper muonium mechanism; the resultant fit is listed in Table III. However, preliminary data on solutions of  $\text{Fe}(\text{ClO}_4)_3$  in water at 100 gauss show total disagreement with the predictions of the proper muonium mechanism (see Fig. 21 and Table III), but moderately good agreement with the assumption that Mu reacts with  $\text{Fe}(\text{ClO}_4)_3$  to form a radical, which subsequently reacts with  $\text{Fe}(\text{ClO}_4)_3$  to place Mu in a diamagnetic compound (see Fig. 22). This suggests that we might expect to see evidence for radical formation in  $\text{HClO}_4$  if we lower the field to 100 gauss.

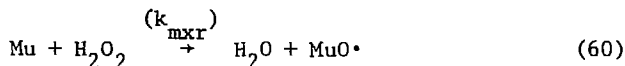
### 3. Hydrogen Peroxide

Perhaps the best example we have found of the general mechanism is the case of hydrogen peroxide in water at 100 gauss. Again, the fit assuming no radical formation is poor (see Fig. 23 and Table III); but, as can be seen from Fig. 24 and Table IV, we obtain an excellent fit to the data if we assume that muonium reacts with hydrogen peroxide to form a diamagnetic compound

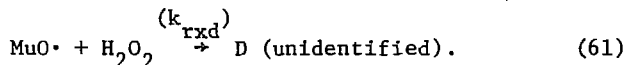
containing muonium, presumably according to



and (competitively) to form a radical containing muonium, presumably according to



and that the radical  $\text{MuO}\cdot$  subsequently reacts with the  $\text{H}_2\text{O}_2$  to form a diamagnetic compound containing muonium:



Now, processes in hydrogen peroxide solution are notoriously complex, and these are undoubtedly not the only reactions taking place (for instance, the radical  $\text{MuO}_2$  may form occasionally), but it seems reasonable that these processes should dominate, and the mechanism is not sensitive to trace reactions.

The effective hyperfine field at the proton in the hydroxyl radical  $\text{HO}\cdot$  is known<sup>26</sup> to be 41.3 gauss (isotropic average), predicting  $\omega_{\text{r}}/\omega_{\text{o}} = .0825$  (recall equation (58)). When  $\omega_{\text{r}}/\omega_{\text{o}}$  was given various different values, the best fits were in the region  $.05 < \frac{\omega_{\text{r}}}{\omega_{\text{o}}} < .25$ , with the best fit for  $\omega_{\text{r}}/\omega_{\text{o}} = .175$ ; thus the best fit is consistent with the theoretical value.

It is annoying that again, as in the case of  $\text{HNO}_3$  and  $\text{HClO}_4$ , all the extracted rate constants are much larger than predicted by the measured values for the analogous reactions of atomic hydrogen, as listed in Table II. In this case we have presumed to know the reactions involved, which places our results at odds with



the hydrogen data. This conflict has yet to be resolved.

Figure 17 -  $\text{HNO}_3$  at 4500 gauss: Fit Assuming  
Proper Muonium Mechanism

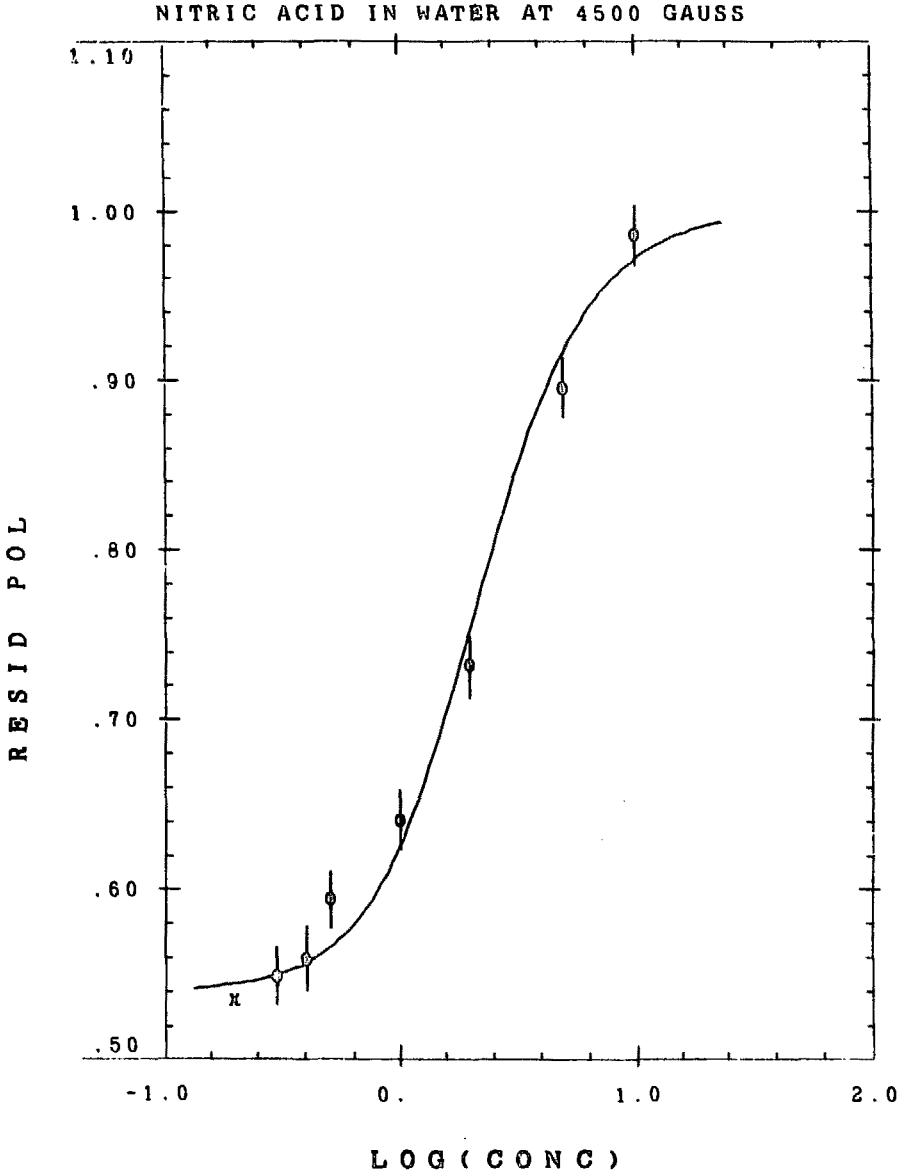


Figure 18 -  $\text{HNO}_3$  at 100 gauss: Fit Assuming  
Proper Muonium Mechanism

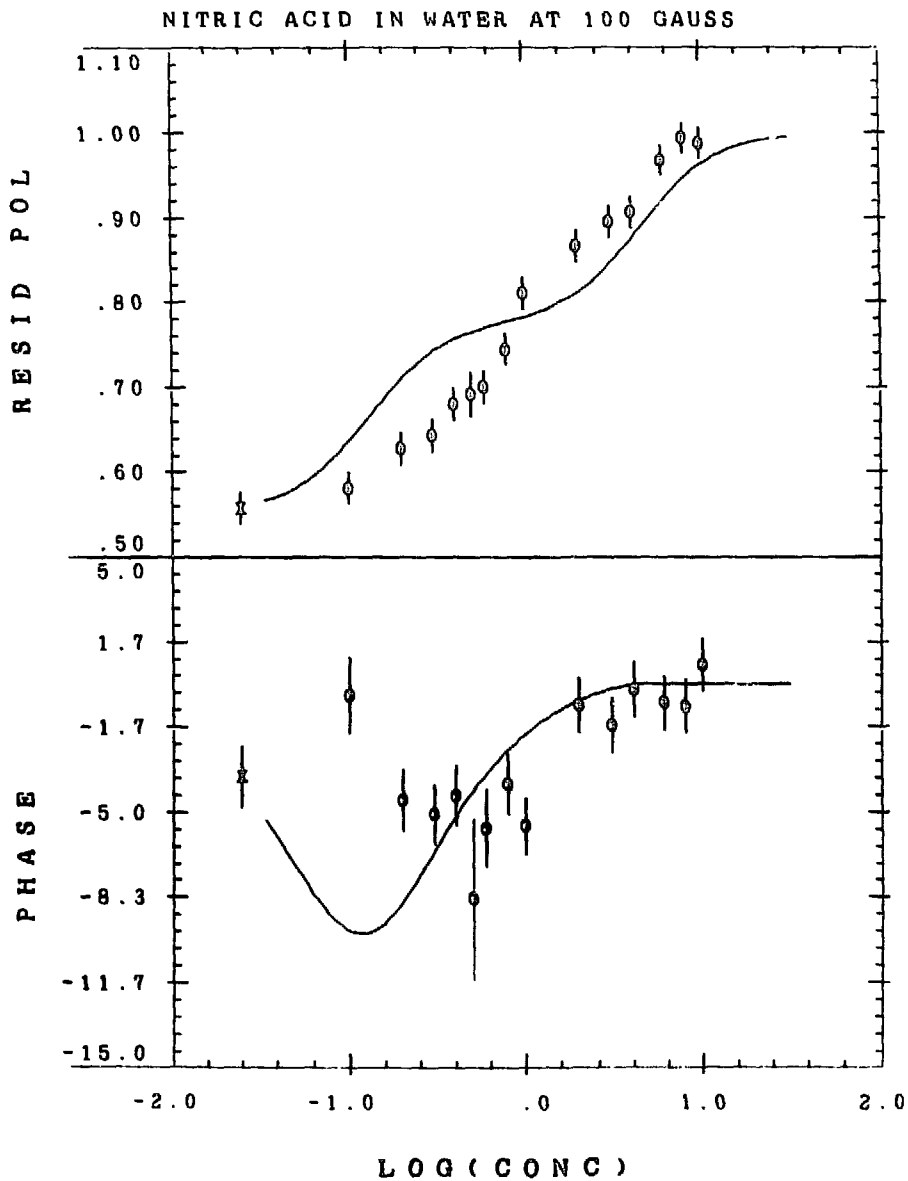


Figure 19 -  $\text{HNO}_3$  at 100 gauss: Fit Including  
Radical Formation

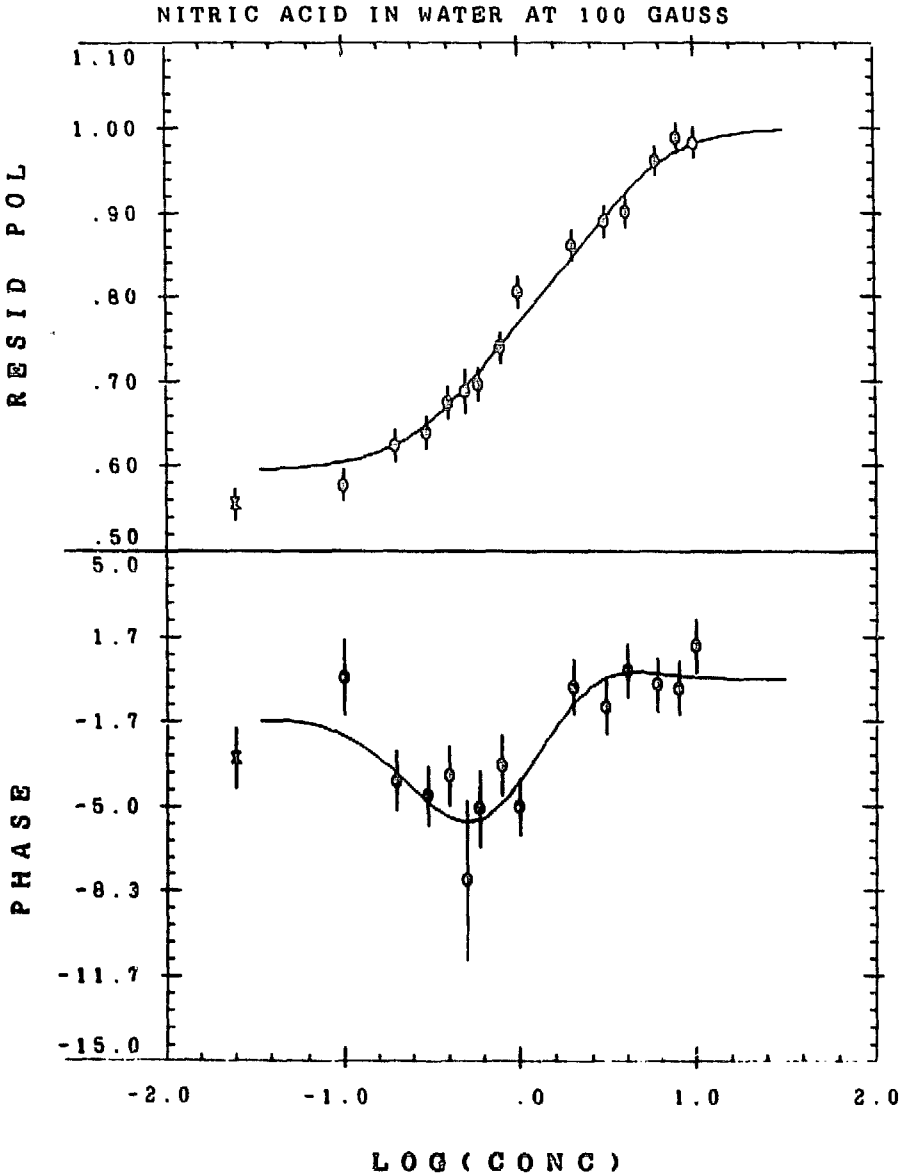


Figure 20 -  $\text{HClO}_4$  at 4400 gauss: Fit Assuming  
Proper Muonium Mechanism

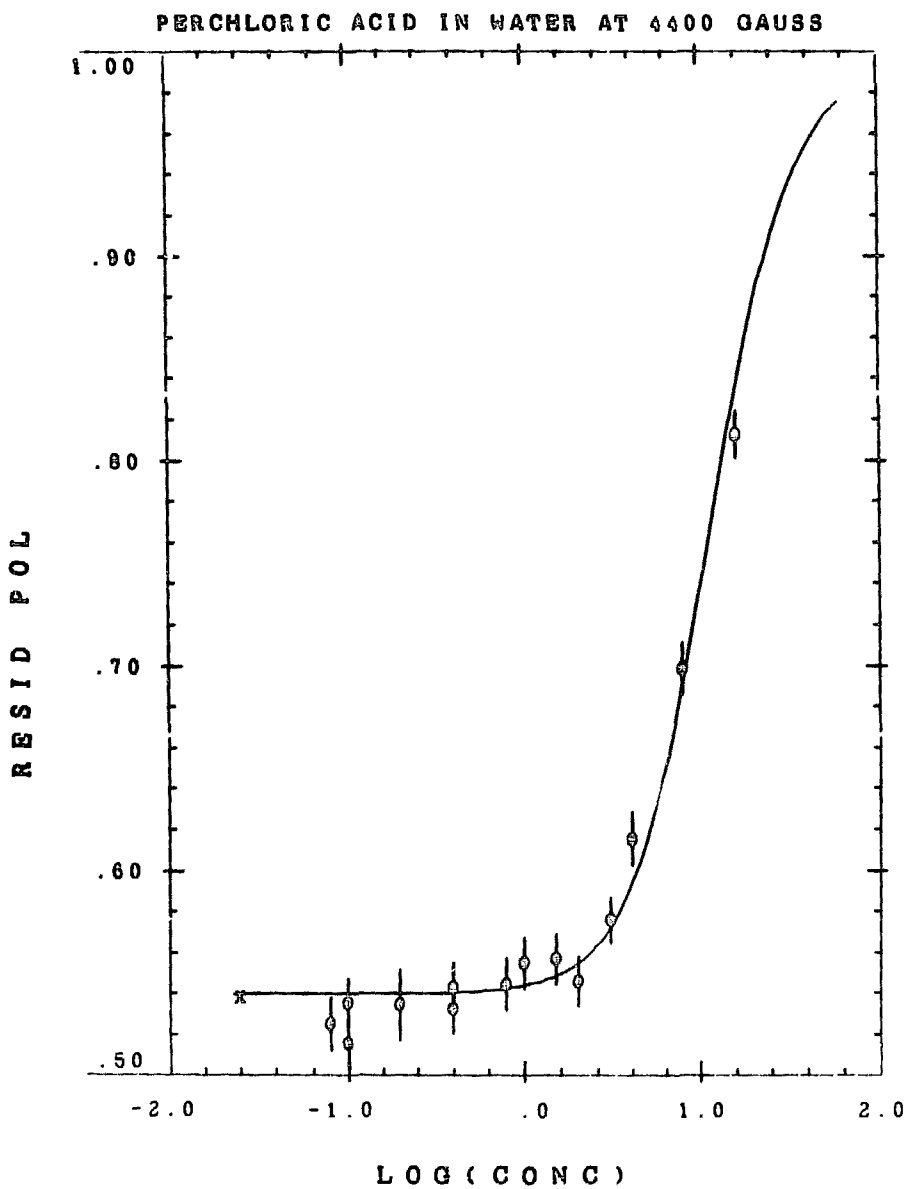


Figure 21 -  $\text{Fe}(\text{ClO}_4)_3$  at 100 gauss: Fit Assuming  
Proper Muonium Mechanism

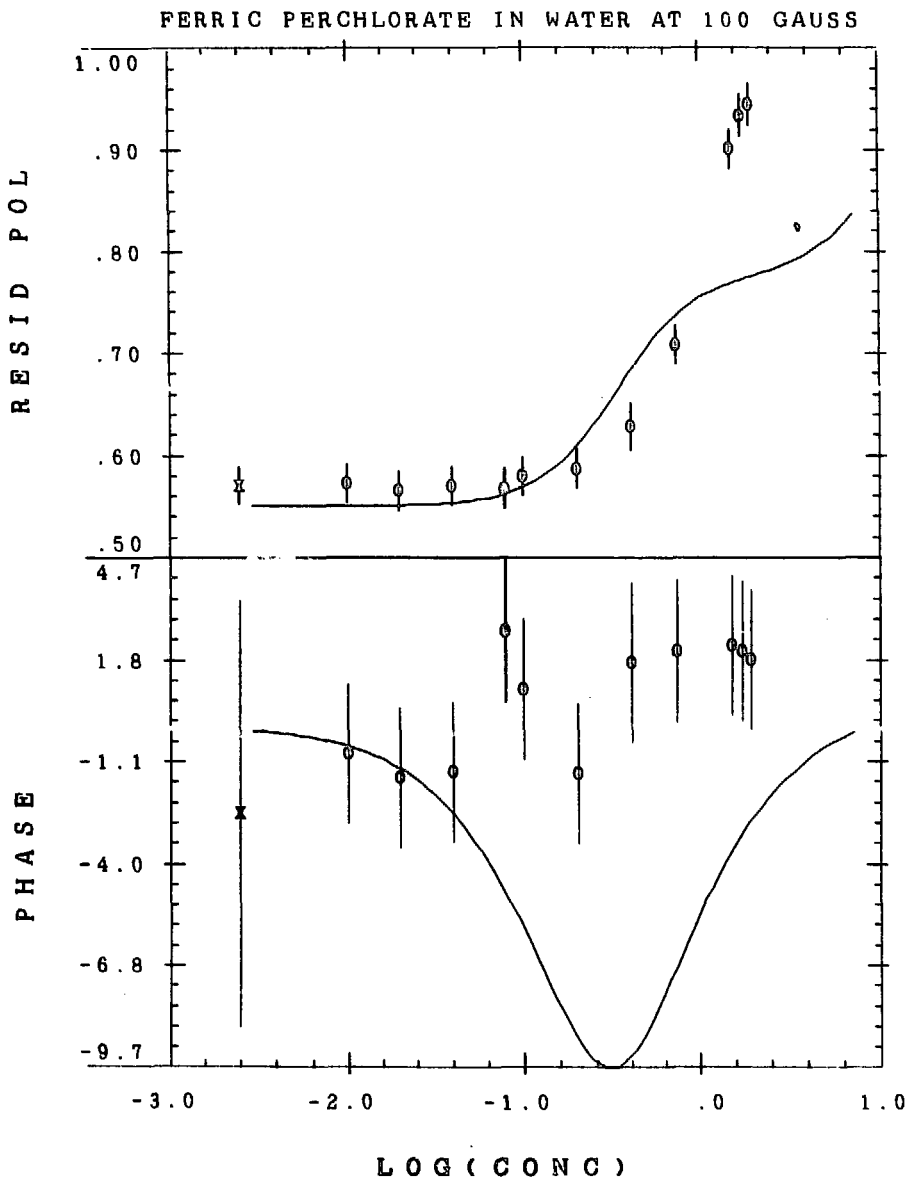


Figure 22 -  $\text{Fe}(\text{ClO}_4)_3$  at 100 gauss: Fit Including  
Radical Formation

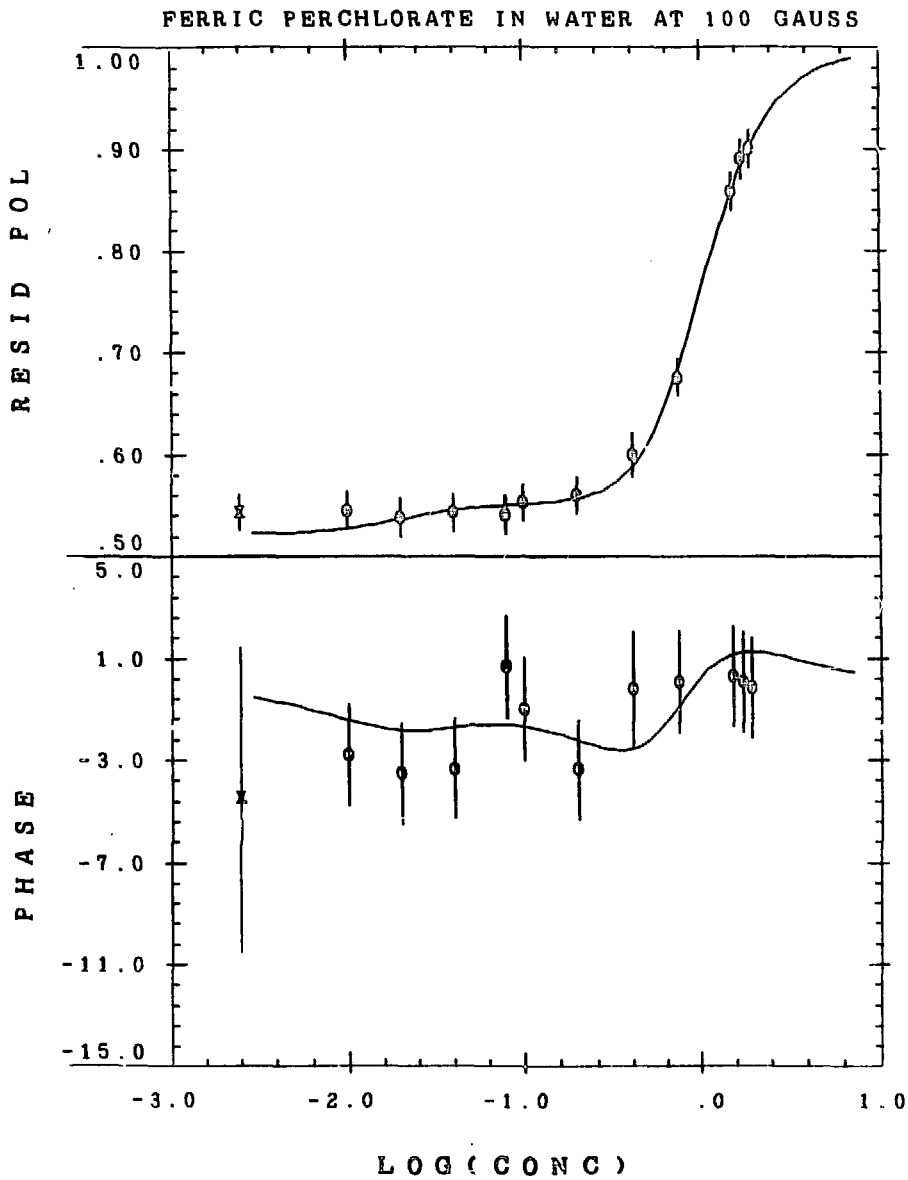


Figure 23 -  $\text{H}_2\text{O}_2$  at 10G gauss: Fit Assuming  
Proper Muonium Mechanism

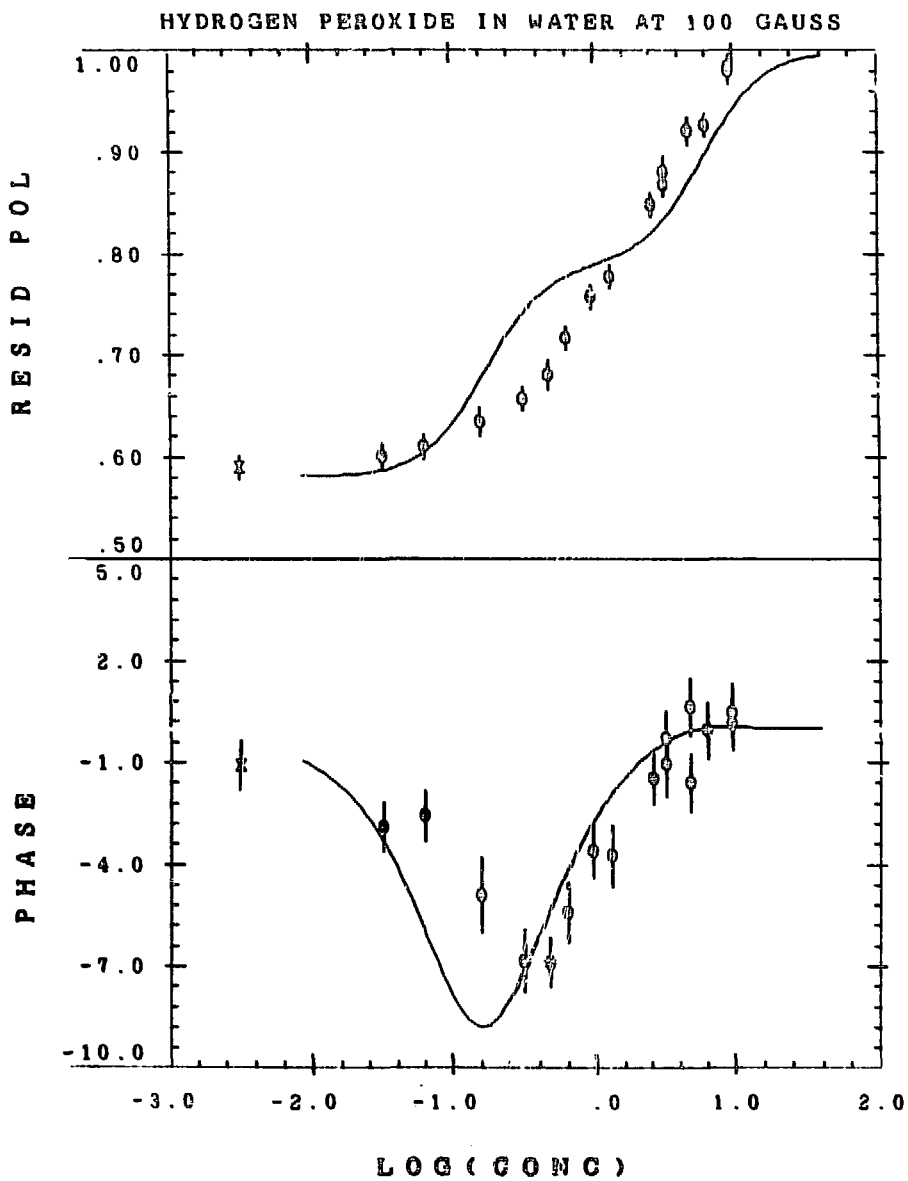




Figure 24 -  $\text{H}_2\text{O}_2$  at 100 gauss: Fit Including  
Radical Formation

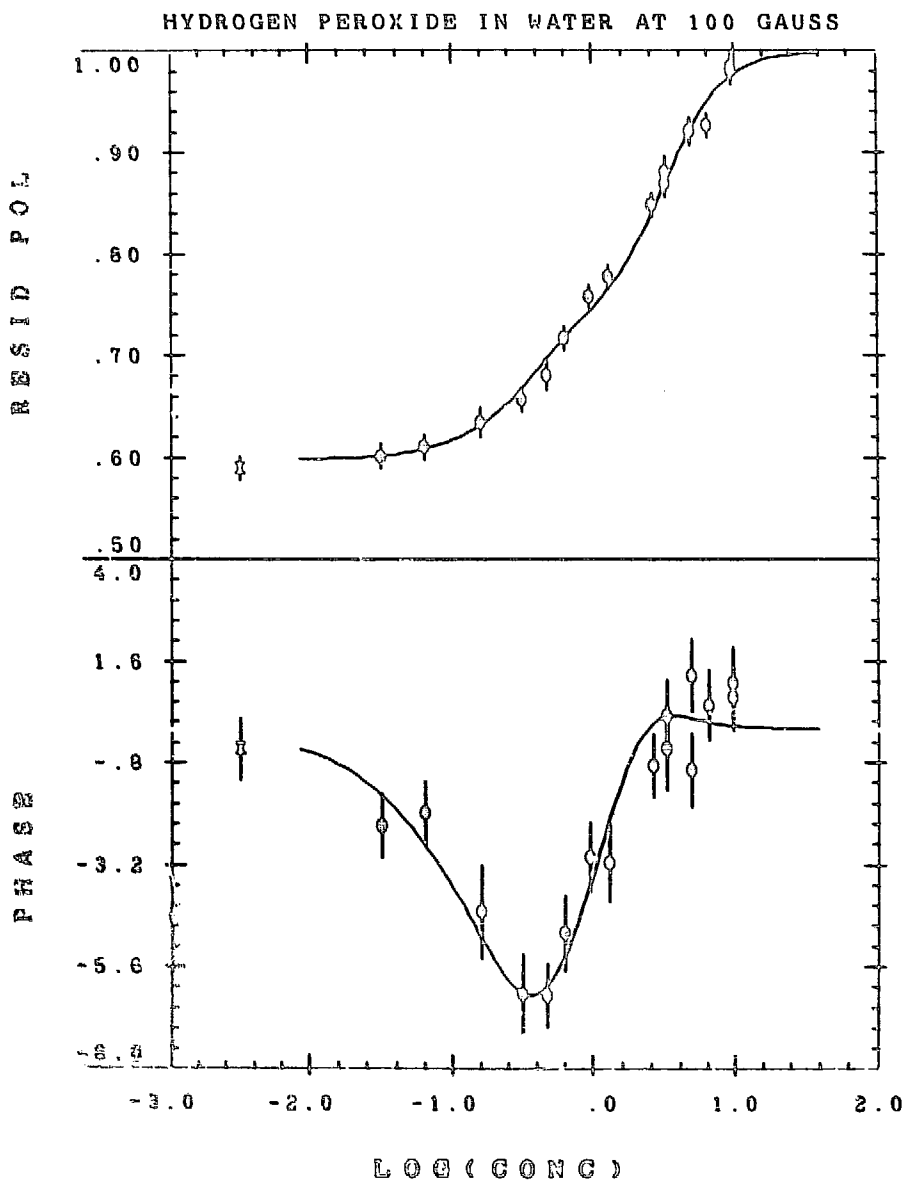


Table IV - BEST FITS TO GENERAL MECHANISM (WITH RADICALS)

REAGENT	SOLVENT	FIELD (gauss)	$\frac{\omega_r}{\omega_o}$ <sup>a</sup>	$\Lambda_o$	$\phi_o$ (deg)	h	RATE CONSTANTS $\times 10^{-10}$				$\frac{\chi^2}{\text{deg. fr.}}$
							$k_{mxd}$	$k_{rxd}$	(Z)	$k_{mzr}$	
H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	100	.083 <sup>b</sup>	.26 ±.01	10.82 ±.5	.59 ±.01	.24 ±.1	.14 ±.05	(X)	.83 ±.2	~ 1
HNO <sub>3</sub>	H <sub>2</sub> O	100	.125 <sup>c</sup>	.277 ±.05	15.76 ±.75	.546 ±.02	3.25 ±2.0	.111 ±.05	(X)	13.0 ±7.0	~ 1.5
Br <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	200	.095 <sup>d</sup>	.271 ±.005	38 ±1	.134 ±.01	9.5 ± 2	.36 ± .1	(S)	.125 ± .05	~ 2
I <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	200	.095 <sup>d</sup>	.272 ±.02	35 ±2	.128 ±.06	5.8 ± 2	.2 ± .1	(S)	.054 ± .03	~ 1

Rate constants in liters/mole-sec.

Errors are approximate. Differences in  $\phi_o$  are due to changes in counter geometry between series of runs.

<sup>a</sup>Values for  $\omega_r$  of specified radicals obtained by multiplying  $\mu_\mu/\mu_p = 3.18$  into measured value of hyperfine frequency for hydrogen version of radical (from Landolt & Bornstein ).

<sup>b</sup>Radical involved presumed to be MuO•

<sup>c</sup>Radical species not identified.

<sup>d</sup>Radical involved presumed to be C<sub>6</sub>H<sub>6</sub>Mu•

### E. Survey of Solvents; Hot Chemistry

Table V shows the asymmetries (and phases, for measurements at low fields) observed in some solvents; some measurements by other groups are shown for comparison in Table VI. These values should not be expected to be consistent within better than  $\sim 20\%$ , due to the geometrical and beam-related factors determining the parameter  $A_0$ , which vary between experiments (and indeed within our own data, due to minor changes in counter geometry, etc.). However, certain gross trends can be examined.

First, it should be clear that one can never tell from a single measurement whether the asymmetry observed in a given solvent is strictly due to hot chemistry ( $A = h A_0$ ) or partially due to thermal reaction of muonium with the solvent to form a diamagnetic compound (rate =  $k_{msd}[S]$ ). Thus many of the values quoted for  $h$  in Table V are open to question; this dilemma can be solved, however, by varying the magnetic field<sup>27</sup>; an asymmetry due to  $k_{msd}$  will always decrease markedly with increasing field (depolarization by muonium precession speeds up), whereas the asymmetry due only to  $h$  will stay constant, or even increase, since the curvature of low-energy decay positrons raises the bottom of the observed spectrum of  $e^+$  energies, and the asymmetry is an increasing function of positron energy. (This is about a 10-15% effect when we go from 100 gauss to 4500 gauss).

Since complete analyses have been made for solutions in water and methanol at several fields, with consistent results, we may be

sure that the asymmetries in these two solvents are due almost exclusively to hot reactions. Independent studies of this type<sup>27</sup> verify that the asymmetries observed in methanol, hexane, and neptane are due only to hot chemistry.

Asymmetries in hydrocarbons tend to increase with the number of hydrogen atoms per molecule, except when the compound is unsaturated, in which case the H atoms are presumably more tightly bound. Note the marked difference between hexene and cyclohexane, which differ only in bond structure, and the exceptionally low asymmetry in benzene, where the H atoms are particularly tightly bound by the "resonance" effect<sup>28</sup>. The high asymmetry observed in glycerol and in halide-substituted forms of methane may be due to thermal reactions.

The results obtained for muonium hot chemistry may be compared and combined with analogous results from hot tritium (T) chemistry<sup>12, 17</sup>, in which it is more difficult to tell "hot" from "cold" reaction products, but where it is possible to distinguish between different diamagnetic products (e.g., TH vs. THO in hot reactions with water).

We have not yet seriously attempted to develop the potentialities of this technique for studying hot atom chemistry; however, it seems clear that the field should benefit broadly from this technique<sup>29</sup>.

Table v - SURVEY OF SOLVENTS

SOLVENT NAME	FORMULA	A	$\phi$ (deg)	h	COMMENT
WATER	H <sub>2</sub> O	.15 ± .01	15 ± 4	.55 ± .01	no "cold" reaction
METHANOL	CH <sub>3</sub> OH	.13 ± .01	13 ± 3	.53 ± .01	"
BENZENE <sup>a</sup>	C <sub>6</sub> H <sub>6</sub>	.036±.005	33 ± 3	.13 ± .01	"cold" reaction to radical only
CARBON TETRACHLORIDE	CCl <sub>4</sub>	.272±.010	14 ± 3	~ 1.0 <sup>b</sup>	density may be a factor
GLYCEROL	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	.179±.010	13.5±3	~.65 <sup>b</sup>	"
HEXYNE	C <sub>6</sub> H <sub>10</sub>	.103±.010	6.5 ± 4	~.4 <sup>b</sup>	very unsaturated
HEXENE	C <sub>6</sub> H <sub>12</sub>	.119±.010	9 ± 3	~.45 <sup>b</sup>	unsaturated
HEXANE	C <sub>6</sub> H <sub>14</sub>	.145±.010	10 ± 3	~.55 <sup>b</sup>	saturated
CYCLOHEXANE	C <sub>6</sub> H <sub>12</sub>	.160±.010	8 ± 3	~.6 <sup>b</sup>	"

Errors are approximate.

Magnetic field is 100 gauss unless otherwise specified.

<sup>a</sup>Magnetic field = 200 gauss.

<sup>b</sup> assuming no "cold" reaction.

Table VI - SURVEY OF SOLVENTS: DATA FROM OTHER GROUPS

REF.	SOLVENT NAME	FORMULA	A	h	COMMENT
a	METHANOL	CH <sub>3</sub> OH		.61 ± .03	pure "hot"
a	HEXANE	C <sub>6</sub> H <sub>14</sub>		.61 ± .03	pure "hot"
a	HEPTANE	C <sub>7</sub> H <sub>16</sub>		.57 ± .05	pure "hot"
a	OCTANE	C <sub>8</sub> H <sub>18</sub>		.52 ± .05 <sup>k</sup>	saturated
b	CHLOROFORM	CHCl <sub>3</sub>	.190 ± .009	.76 ± .04 <sup>km</sup>	
b	BROMOFORM	CHBr <sub>3</sub>	.22 ± .01	.88 ± .04 <sup>km</sup>	field-indep.
b	BENZENE	C <sub>6</sub> H <sub>6</sub>	.035 ± .007	.14 ± .03 <sup>m</sup>	field-indep.
b	HEXYNE	C <sub>6</sub> H <sub>10</sub>	.115 ± .01	.46 ± .04 <sup>km</sup>	field-indep.
b	CYCLOHEXANE	C <sub>6</sub> H <sub>12</sub>	.160 ± .009	.64 ± .04 <sup>km</sup>	saturated
b	OCTANE	C <sub>8</sub> H <sub>18</sub>	.147 ± .008	.59 ± .03 <sup>km</sup>	saturated
b	POLYSTYRENE	(CH)	.04 ± .01	.16 ± .04 <sup>km</sup>	field-indep.
c	WATER	H <sub>2</sub> O	.141 ± .011	.62 ± .05 <sup>n</sup>	
c	CHLOROFORM	CHCl <sub>3</sub>	.184 ± .015	.80 ± .07 <sup>kn</sup>	
c	BENZENE	C <sub>6</sub> H <sub>6</sub>	.046 ± .012	.21 ± .05 <sup>n</sup>	
c	PROPANE	C <sub>3</sub> H <sub>8</sub>	.17 ± .02	.74 ± .09 <sup>kn</sup>	saturated
c	PHENYL- CYCLOHEXANE	C <sub>12</sub> H <sub>16</sub>	.084 ± .011	.37 ± .05 <sup>kn</sup>	
c	POLYSTYRENE	(CH)	.07 ± .01	.31 ± .04 <sup>kn</sup>	
c	POLYETHYLENE	(CH <sub>2</sub> )	.146 ± .012	.64 ± .05 <sup>kn</sup>	saturated

<sup>k</sup> Assuming no "cold" reaction of Mu into a diamagnetic compound.

<sup>m</sup> Using for A<sub>0</sub> a value .25 (a typical but arbitrary choice).

<sup>n</sup> Using for A<sub>0</sub> the value A<sub>C</sub> = .229 observed in graphite.

<sup>a</sup> From a study distinguishing "hot" from "cold" chemical effects via field dependence of the asymmetry: I.I. Gurevich *et. al.*, Sov. Phys. JETP Lett. 14, 297 (1971).

<sup>b</sup> From a survey of organic solvents: A.I. Babaev *et. al.*, Sov. Phys. JETP 23, 583 (1966).

<sup>c</sup> From an early survey: R.A. Swanson, Phys. Rev. 112, 580 (1958).

## SUMMARY

### A. Muons in Liquids

The central achievements of the work described herein are twofold: first, we have found at least one chemical system (iodine in methanol) for which the simple and elegant "proper muonium mechanism" accurately describes the behavior of the muon polarization. This verification was made possible by development of the technique of observing changes in the apparent initial phase of the muon precession. This provides a firm theoretical footing from which to step forward into less simple chemical realms. The second high point of this study was the discovery of those realms, and the expansion of the theory to include them. This development depends even more upon the phase measurements, which are more sensitive to the details of the mechanism than are the polarization data.

It is clear that this process is not yet finished; we have only demonstrated some possibilities. In order to extract reliable information about the specific processes involving radicals, for instance, it will be necessary to achieve higher precision and no doubt a more complete theoretical treatment. The precision will soon be readily available in the form of better statistics from high-intensity meson factories, and also from improved systematics. It seems evident, however, that a new experimental tool is now available to physical chemists who would study the reactions of a light isotope of atomic hydrogen.

Furthermore, muonium chemistry is but one aspect of the behavior of muons in liquid media which can be studied by the

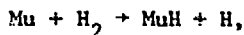
technique of muon depolarization measurements. "Hot" chemistry is particularly amenable to study by these methods, as we have seen; in fact, any study of thermal chemistry must take into account hot reactions, and vice versa. Relaxation phenomena, on the other hand, can provide information about short-range order in liquids which is difficult to obtain by other means -- as in the case of very concentrated  $\text{MnCl}_2$  solutions<sup>15</sup>. Further applications of this type may be expected to appear as the technique is developed further.



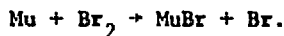
### B. Muons in Gases

Muonium has been formed in gases by many researchers, usually for the purpose of studying the hyperfine splitting.<sup>2,30</sup> However, the chemical interactions of muonium in the gas phase are also of great interest, since comparison with H atom chemistry is much less ambiguous when formula (50) can be used rather than formula (52) for the rate constants. Mobley et. al.<sup>31,32</sup> have demonstrated the possibility of studying both chemical and magnetic (e.g., spin-exchange) interactions of muonium atoms in gases.

A study of great interest would be the measurement of the chemical reaction rate of muonium with hydrogen,



which can be calculated, and has been measured for all the other available isotopes of hydrogen. The large isotopic effect would provide a more demanding test of theory. Similar studies might also profitably be made of reactions of muonium with halides, for instance



### C. Muons in Solids

Perhaps the most promising applications of muon depolarization studies are in the field of solids. Not only can one measure rapid relaxation of the muon's spin by incoherent local fields (analogous to the effects seen in paramagnetic solutions), but coherent effects can also be observed directly. For instance, the dipole field of protons at adjacent sites in the water of hydration of gypsum causes a coherent perturbing field on the muon, which has different values when the muon occupies different proton sites in the lattice. This causes a "beating" of the muon precession signal, which has been observed directly<sup>33</sup> and depends on the orientation of the crystal in the external magnetic field.

More recently, Gurevich et. al.<sup>34, 35</sup> studied muonium precession in inert crystals, and observed (in accordance with theory) a "beating" due to the splitting of the muonium precession into two frequencies, determined by the relative strength of the effective hyperfine field and the external field. The splitting can be analyzed to extract the hyperfine frequency. While the hyperfine frequency thus obtained for muonium in quartz was the same as in vacuum (within errors), muonium in germanium exhibited a different splitting, corresponding to a weaker hyperfine coupling. This has been interpreted<sup>35</sup> in terms of the local dielectric effect of the electron bands in germanium. We are now conducting an analogous study of silicon, with similar results.

#### D. Closing Remarks

The last three sections constitute an attempt to place the topic of this dissertation in perspective as a part of the expanding field of positive muon depolarization studies and their use in probing the interactions of "ordinary" matter. While knowledge of the depolarizing effects of the environment upon muons is as old as the discovery of parity violation in  $\mu$  decay<sup>5</sup>, it is only recently that the mechanisms involved have come to be well understood; and with understanding, as always, has come a series of more subtle questions and a list of possible applications.

The intent of this study of muons in liquids has been to improve the level of understanding of the depolarizing mechanism in liquids and to demonstrate the possibility of real applications of that understanding to the study of chemical reactions of muonium atoms; it is the author's opinion that both goals have been at least partially fulfilled. However, the theory is still in its infant stages, and many details (e.g., hot chemistry) have been glossed over for the sake of simplicity. The requirement of the "dilute limit" in solutions, for instance, is too restrictive; the formalism should be developed to allow correct treatment of mixtures in all proportions. The rewards in improved insights into the interactions of atoms and molecules may be enormous.

In a time when many cry out against the "waste" of vast sums of money and effort upon study of "exotic" physics, it is heartening to watch a field recently considered exotic bloom into a host of new opportunities for advancement of many branches of

science; the ultimate result of which will be, we hope, the improvement of man's capacity to care for himself and his environment. While the inevitable nature of the scientist is to seek understanding for its own sake, and not just for the sake of its practical applications, we can no longer avoid considering the consequences of those applications; and when they promise to be beneficial we would be fools not to rejoice.

## ACKNOWLEDGEMENTS

Now that I've finished the bulk of the task,  
 the poet can pull off the physicist's mask.  
 Dry prose is for physics, objective and terse;  
 I'd rather say thanks to my friends in verse.

The first honored victim of this rusty rhyme  
 is Don Miller, who came first in order of time;  
 as my first advisor, he gave me assistance  
 in spite of my habit of physics-resistance.

Next those who managed somehow to survive  
 Experiment number Ninety-Five:  
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 the others who stacked up and down the lead wall.

And especially Budnitz, who made the beast run  
 and taught me how several things should be done;  
 like how to cure the electronics' disease  
 with bubble gum, baling wire, and BNC's.

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I thank nonetheless, and also the many  
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## REFERENCES

1. J. D. Bjorken and S. D. Drell, Relativistic Quantum Mechanics, (McGraw-Hill, New York, 1964), pp. 261-268.
2. D. Favart, P. M. McIntyre, D. Y. Stowell, V. L. Telegdi, R. DeVoe, and R. A. Swanson, Phys. Rev. Lett. 27, 1336 (1971).
3. J. Bailey, W. Bartl, G. Von Bochmann, R. C. A. Brown, F. J. M. Farley, H. Jöstlein, E. Picasso, and R. W. Williams, Phys. Lett. 28B, 287 (1968).
4. J. F. Hague, J. E. Rothberg, A. Schenck, D. L. Williams, R. W. Williams, K. K. Young, and K. M. Crowe, Phys. Rev. Lett. 25, 628 (1970).
5. R. L. Garwin, L. M. Lederman, and M. Weinrich, Phys. Rev. 104, 1415 (1957); J. I. Friedman and V. L. Telegdi, Phys. Rev. 106, 1290 (1957); J. C. Sens, R. A. Swanson, V. L. Telegdi, and D. D. Yovanovitch, Phys. Rev. 107, 1465 (1957).
6. V. G. Nosov and I. V. Iakovleva, Soviet Phys. JETP 16, 1236 (1963).
7. I. G. Ivanter and V. P. Smilga, Soviet Phys. JETP 27, 301 (1968).
8. V. G. Firsov and V. M. Byakov, Soviet Phys. JETP 20, 719 (1965).
9. I. G. Ivanter and V. P. Smilga, Soviet Phys. JETP 28, 796 (1969).
10. B. Flacnstein, R. Prepost, and A. M. Sachs, Phys. Rev. 142,

217 (1966).

11. V. W. Hughes, *Ann. Revs. Nucl. Science* 16, 445 (1966).
12. S. K. Allison and M. Garcia-Munoz, Atomic and Molecular Processes, D. R. Bates, Ed., (Academic Press, New York, 1962), Ch. 19; R. Wolfgang, *Prog. Reaction Kinetics* 3, 99 (1965); F. S. Rowland, *J. Am. Chem. Soc.* 90, 4767 (1968).
13. R. K. Wangsness and F. Bloch, *Phys. Rev.* 89, 728 (1953).
14. U. Fano, *Revs. Mod. Phys.* 29, 74 (1957).
15. A. Schenck, D. L. Williams, J. H. Brewer, K. M. Crowe, and R. F. Johnson, *Chem. Phys. Lett.* 12, 544 (1972).
16. I. G. Ivanter, *Soviet Phys. JETP* 29, 761 (1969).
17. T. Kambara, R. M. White, and F. S. Rowland, *J. Inorg. Nucl. Chem.* 21, 210 (1961).
18. S. W. Benson, The Foundations of Chemical Kinetics, (McGraw-Hill, New York, 1960).
19. M. Anbar and P. Neta, *Int. J. Appl. Rad. and Isotopes* 18, 493 (1967).
20. A. Schenck, *Phys. Lett.* 32A, 19 (1970).
21. J. H. Brewer, K. M. Crowe, R. F. Johnson, A. Schenck, and R. W. Williams, *Phys. Rev. Lett.* 27, 297 (1971).
22. R. A. Swanson, *Phys. Rev.* 112, 580 (1958).
23. G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.* 63, 1713 (1941).
24. H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* A202, 181 (1950).
25. R. W. Fessenden and R. H. Schuler, *J. Chem. Phys. N. Y.* 38,



773 (1963).

26. J. A. McMillan, M. S. Matheson, and B. Smaller, *J. Chem. Phys. N. Y.* 33, 609 (1960).
27. I. I. Gurevich, E. A. Meleshko, I. A. Muratova, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, and B. V. Sokolov, *Soviet Phys. JETP Lett.* 14, 297 (1972).
28. See for example R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, (Addison-Wesley, New York, 1965), Vol. III, Section 10-4.
29. A. G. Maddock, "Current Developments in Nuclear and Radiochemistry in Relation to the Zürich 500 MeV Isochronous Cyclotron", a talk presented at the Conference on Future Applications of the 500 MeV Isochronous Cyclotron and its Injector, Zürich, March 1967 (unpublished).
30. W. E. Cleland, J. M. Bailey, M. Eckhause, V. W. Hughes, R. M. Mobley, R. Prepost, and J. E. Rothberg, *Phys. Rev. Lett.* 13, 202 (1964).
31. R. M. Mobley, J. J. Amato, V. W. Hughes, J. E. Rothberg, and P. A. Thompson, *J. Chem. Phys.* 47, 3074 (1967).
32. R. M. Mobley, "Interactions of Muonium with Atoms and Molecules", Ph. D. thesis, Yale University, 1967.
33. A. Schenck and K. M. Crowe, *Phys. Rev. Lett.* 26, 57 (1971).
34. I. I. Gurevich, I. G. Ivanter, L. A. Makariyna, E. A. Meleshko, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, V. P. Smilga, B. V. Sokolov, V. D. Shestakov, and I. V. Iakovleva, *Phys. Lett.* 29B, 387 (1969).
35. I. I. Gurevich, I. G. Ivanter, E. A. Meleshko, B. A.

Nikol'skii, V. S. Roganov, V. I. Selivanov, V. P. Smilga,  
B. V. Sokolov, and V. D. Shestakov, Soviet Phys. JETP  
33, 253 (1971).