Muon Depolarization and the Chemistry of Muonium in Liquids

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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 π-μ-e decay series: $\pi^+ \to \mu^+ + \nu_\mu$ followed by $\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu$. Thanks to the unique helicity of the neutrino, the μ^+ from π^+ decay has 100% negative helicity, making it easy to obtain a highly polarized μ^+ beam by momentum separation of a decaying π^+ 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.[1]

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 electro-dynamics. [2,3,4]   A critical measurement in this series is the ratio of the muon magnetic moment to that of the proton: μ_μ/μ_p. This number was recently measured by Crowe et. al. [4]   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

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

where N_o = a normalizing factor (in counts/bin)

B = time-independent background (random events)

τ_μ = the mean muon lifetime, 2.20 μsec

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

T_2 = transverse relaxation time (usually $\sim$ μsec)

ω_μ = muon Larmor frequency, 0.85×10^5 rad/sec per gauss

ϕ = phase of the precession at $t = 0$.

All the parameters except τ_μ (which is known) are extracted from the experimental histogram by a χ^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 ϕ 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 ϕ. With our system, the time resolution was on the order of 1 nsec; at 100 gauss, this corresponds to $\omega_\mu \Delta t \sim \frac{1°}{2}$. Other systematic uncertainties boosted the error bars on the phase to the order of $\pm$ 1-2°, 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
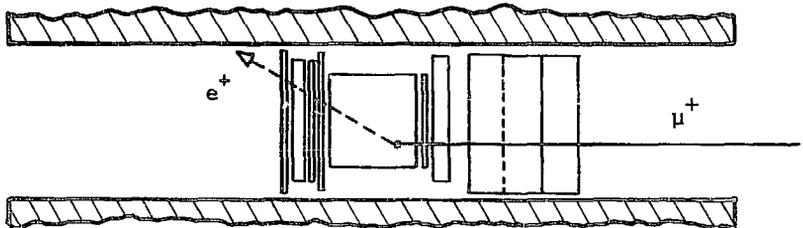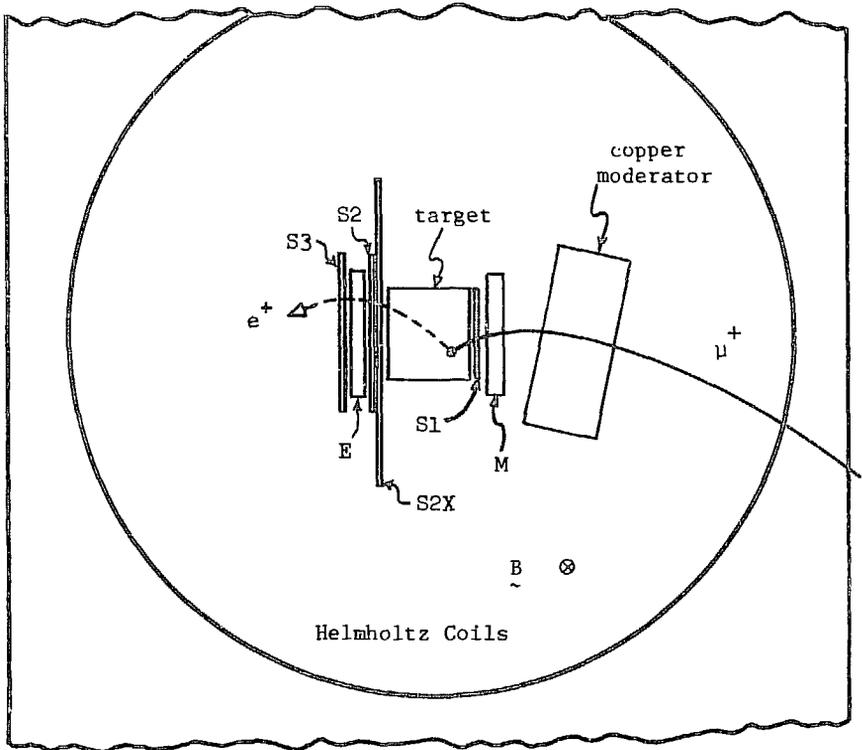
Figure 2 — EXPERIMENTAL HISTOGRAM OF TIME FROM μ^+ STOP

UNTIL e^+ DETECTION
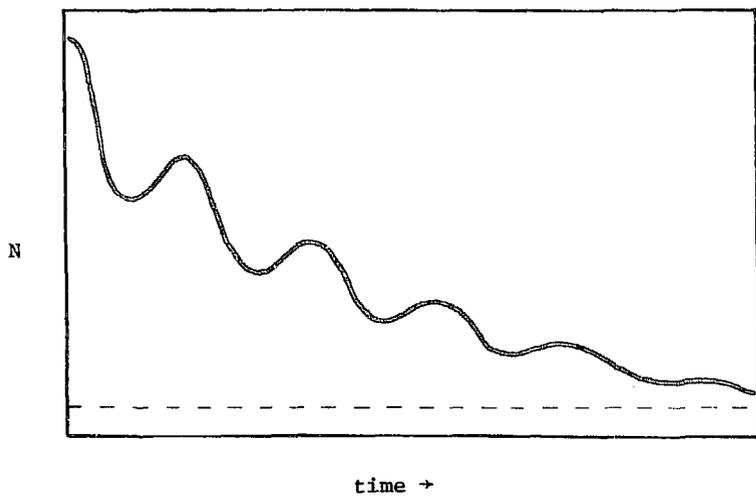
N

time →

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

N_o = a normalizing factor (in counts/bin)

B = time-independent background (random events)

τ_μ = the mean muon lifetime, 2.20 μsec

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

T_2 = transverse relaxation time (∿ microseconds)

ω_μ = muon Larmor frequency, 0.85×10^5 rad/sec per gauss

ϕ = phase of the precession at $t = 0$

<center>C.   Theoretical Primer</center>

The experimental asymmetry A is the product of an empirical quantity A_o and a theoretical quantity P_{res}. A_o 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_o by Monte Carlo methods; fortunately, A_o can be obtained by fitting the concentration-dependence of the polarization, as will be seen later, and therefore A_o 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 ϕ 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 ϕ 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;[5]   since then, several theories have been offered to account for it, all involving the temporary formation of muonium, the hydrogen-like atom μ^+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[6] describes various
general situations in solids, but gives little attention to liquids.
The same is true of an early paper by Ivanter and Smilga[7] in which
the Laplace transform method is used to obtain explicit formulas
for the depolarization. Firsov and Byakov[8] had meanwhile suggest-
ed that the theory could be applied to studies of the chemistry
of muonium, and later Ivanter and Smilga published another paper[9]
developing the formalism to apply to this case.

Despite some objections to the application of this model
to solids[10], 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 here-
in, makes possible many studies of interactions of muons with mat-
ter, 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
$m_{Mu}/m_H = 0.1126$, 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 pre-
dict 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 $\gtrsim 10^9$ 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 posess. It is therefore of great

importance to prove the validity of the theory -- the central con-

clusion resulting from this work.

II. THE THEORY OF μ^+ 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.[11] The muonium quickly reaches its ground state (1S) by collision or radiation. Once formed, the muonium is thermalized within about 10^{-11} sec.[12] 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_o.)

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 $\underset{\sim}{P}^\mu$ and $\underset{\sim}{P}^e$ and their "cross-correlations" b_{ij}:

$$\rho = 1/4(1_4 + \underset{\sim}{P}^\mu \cdot \underset{\sim}{\sigma}^\mu + \underset{\sim}{P}^e \cdot \underset{\sim}{\sigma}^e + \Sigma_{ij} \, b_{ij} \, \sigma_i^\mu \, \sigma_j^e) \tag{2}$$

where 1_4 is the 4×4 unit matrix, and $\underset{\sim}{\sigma}^\mu$ and $\underset{\sim}{\sigma}^e$ are the muon and electron Pauli spin operators ($\underset{\sim}{s}^\mu = \hbar/2 \, \underset{\sim}{\sigma}^\mu$ and $\underset{\sim}{s}^e = \hbar/2 \, \underset{\sim}{\sigma}^e$). 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:

$$H_o = \frac{1}{4} \hbar \, \omega_o \, (\underset{\sim}{\sigma}^\mu \cdot \underset{\sim}{\sigma}^e) \tag{3}$$

where $\omega_o = 2.804 \times 10^{10}$ radians/second is the hyperfine frequency[2], 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,

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

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

$$H_1 = -\frac{1}{2} \hbar \, \underset{\sim}{\omega}^\mu \cdot \underset{\sim}{\sigma}^\mu \quad \text{and} \quad H_2 = -\frac{1}{2} \hbar \, \underset{\sim}{\omega}^e \cdot \underset{\sim}{\sigma}^e \tag{4}$$

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

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 Wangsness-Bloch equation:[13,14]

$$\dot{\rho} = - \frac{i}{\hbar} [\hat{H}, \rho] - \frac{\pi}{\hbar} Tr_b [\hat{\bar{V}}, [\hat{\bar{V}}, \rho \rho_b]] \tag{5}$$

where $\hat{H} = H_o + H_1 + H_2$, Tr_b is the trace over the part of the world density matrix which describes the medium "b", ρ_b is the equilibrium density matrix of the medium, and $\hat{\bar{V}}$ 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 ν imposed upon the elec-tron spin.[6] Although ν 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 Mn^{++} solutions[15], where no "ν effects" are observed, even in 10 $\underline{M}$ solutions.)

Writing out the commutators and equating coefficients of the orthogonal operators $\{1_4, \sigma_i^\mu, \sigma_j^e, \sigma_m^\mu \sigma_n^e\}$ on the left and right sides of equation (5) gives the equations of motion of the param-eters of the density matrix:

$$\dot{P}_k^\mu = \Sigma_{ij} \, \varepsilon_{ijk} \, (- \frac{1}{2} \, \omega_o \, b_{ij} + P_i^\mu \, \omega_j^\mu) \tag{6a}$$

$$\dot{P}_k^e = \Sigma_{ij} \, \varepsilon_{ijk} \, (+ \frac{1}{2} \, \omega_o \, b_{ij} + P_i^e \, \omega_j^e) - 2 \, \nu \, P_k^e \tag{6b}$$

$$\dot{b}_{ij} = \frac{1}{2} \, \omega_o \, \Sigma_k \, \varepsilon_{ijk} (P_k^\mu - P_k^e) + \Sigma_{mn} (\, \omega_n^e \, \varepsilon_{mnj} \, b_{im}$$

$$+ \, \omega_n^\mu \, \varepsilon_{mni} \, b_{mj}) - 2 \, \nu \, b_{ij} \tag{6c}$$

where ε_{ijk} is the Levi-Civita antisymmetric symbol.

Choosing the $\hat{z}$-direction along the field ($\underset{\sim}{B} = B\,\hat{z}$) 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 $\underset{\sim}{P}^\mu$ is initially along $\hat{x}$.

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

$$\dot{\hat{P}} = i\,A_m\,\hat{P} \tag{7}$$

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

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

(analogous to that defined by Ivanter and Smilga[7]) and A_m is the 4×4 matrix

$$A_m \equiv \begin{pmatrix} -\zeta\omega_e & 0 & \frac{1}{2}\,\omega_o & -\frac{1}{2}\,\omega_o \\ 0 & 2i\nu_\perp + \omega_e & -\frac{1}{2}\,\omega_o & \frac{1}{2}\,\omega_o \\ \frac{1}{2}\,\omega_o & -\frac{1}{2}\,\omega_o & 2i\nu_\parallel - \zeta\omega_e & 0 \\ -\frac{1}{2}\,\omega_o & \frac{1}{2}\,\omega_o & 0 & 2i\nu_\perp + \omega_e \end{pmatrix} \tag{9}$$

where $\omega_e \equiv |\underset{\sim}{\omega}^e|$ and (following Ivanter's paper [16]) ν is explicitly broken up into parts describing longitudinal relaxation ($\nu_\parallel$) and transverse relaxation ($\nu_\perp$). 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 ω_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 $\omega_{Mu} \simeq \frac{1}{2} \omega_e \simeq \frac{2}{\zeta} \omega_\mu = 103.38 \omega_\mu$. 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

$$Mu + X \rightarrow D \tag{10}$$

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

proportionality is the chemical rate constant, k_{mxd} , so that the rate of the reaction is $k_{mxd}[X]$ (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 τ_{mxd} given by

$$\tau_{mxd} = \frac{1}{k_{mxd}[X]} \tag{11}$$

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

3. The Residual Polarization

We observe the amplitude and phase of the "free" muon precession at times long compared to τ_{mxd}; the residual polarization P_{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, $P(t) = P_x^\mu + i P_y^\mu$, we are therefore fitting the observed time dependence to the form $P'(t) = P_{res} \exp[i\omega_\mu t]$, treating P_{res} as a constant; to obtain P_{res} theoretically, then, we let $t \to \infty$, 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 Δt which is much less than the period of muon precession but much greater than the period of muonium precession:

$$P_{res} = \lim_{t \to \infty} \left\langle P(t) \exp[-i\omega_\mu t] \right\rangle \qquad (12)$$

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 $\exp[-t/\tau_{mxd}]$, and its time dependence is just $\hat{P}_1(t)$. (Recall the definition [8].) This contribution is thus

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

which, for finite τ_{mxd}, survives neither the limit nor the average in equation (12), and so contributes nothing to P_{res}. The whole contribution to P_{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:

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

The residual polarization is thus given by

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

Ivanter and Smilga[7] 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_{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_{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 acheives this, and call the resultant diagonal matrix D^m, whose diagonal elements are the eigenvalues λ_i^m :

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

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

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

$$\tag{17}$$

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

$\hat{P}_1(t)$ 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:

$$U^d_{ij}(t,t') = \delta_{ij} \delta_{i1} \exp[i\omega_\mu(t - t')] \tag{18}$$

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 $\exp[-t/\tau_{mxd}] \, dt_1/\tau_{mxd}$. In all cases the contribution to $P(t)$ from muons experiencing the fate "q" is

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

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

$$P(t) = \Sigma_i \, P(q_i,t) \tag{20}$$

The sum over q_i 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 sentance, 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 compet-
ing 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[11], 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[12]) they may participate in chemical
reactions which are energetically forbidden to thermal muonium,
due to large activation energies and/or highly endothermic react-
ions. 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[17], 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 $A_o h$. 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 un- paired 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· is a radical. However, results from hot tritium chemistry[17] indicate that this reaction is un- favorable 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 ex- clusively at t = 0 by epithermal reactions (r = 1), and later re- acts with the reagent X to form a diamagnetic compound D:

$$R + X \rightarrow D \tag{21}$$

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 ω_r for ω_o and relabel all the operators accord-
ingly. That is, $A_m(\omega_o) \rightarrow A_r(\omega_r)$ and in place of equations (16)
and (17) we have

$$R^{-1} A_r R = D^r \quad \text{where} \quad D^r_{ij} = \delta_{ij} \lambda^r_i \tag{22}$$

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

$$\tag{23}$$

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

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):

$$Mu + S \rightarrow R\cdot \qquad\qquad\qquad (24)$$

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

$$[S] \text{ (moles/liter)} = 1000 \, \rho_S/W_S$$

where ρ_S is its density (gm/cm^3) and W_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:

$$Mu + X \rightarrow R\cdot \qquad\qquad\qquad (25)$$

for which the reaction rate is $1/\tau_{mxr} = k_{mxr}[X]$. 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:

$$R\cdot + S \rightarrow D \hspace{4em} (26)$$

at a rate $1/\tau_{rsd} = k_{rsd}[S]$. (Note that this is formally equiv-
alent to the spontaneous decomposition of an unstable radical into
diamagnetic products containing muonium, since the rate is inde-
pendent of reagent concentration in both cases.) This reaction
has been ruled out in all our analysis, with the following ration-
ale: in the first place, no such reaction has seemed chemically
plausible in the cases studies; furthermore, if it occurs slowly,
it is quickly overpowered by the competing reaction described be-
low as more reagent is added, or else no muons escape depolariza-
tion; 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 mu-
onium mechanism. Therefore we assume $k_{rsd} < 10^7$ liters/mole-sec,
which is too slow to affect the residual polarization.

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

$$R\cdot + X \rightarrow D \hspace{4em} (27)$$

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

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 possibil-
ities 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 in 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] << [S]), these are the most restrictive assumptions in the theory.

The reaction lifetimes τ_{mxd}, τ_{msr} or τ_{mxr}, and τ_{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

$$\tau_{md} = \tau_{mxd} \tag{28a}$$

$$\tau_{rd} = \tau_{rxd} \tag{28b}$$

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

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

$$\frac{1}{\tau_m} = \frac{1}{\tau_{md}} + \frac{1}{\tau_{mr}} \tag{29}$$

τ_m is therefore the actual "chemical lifetime" of the muonium.

The generalized time evolution operator for this process is

$$U_q(t,0) = U^d(t,t_2) \; U^r(t_2,t_1) \; U^m(t_1,0) \tag{30}$$

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

$$p(q) = (1 - h - r) \; \exp[-(t_2 - t_1)/\tau_{rd}] \; \frac{dt_2}{\tau_{rd}}$$

$$\cdot \; \exp[-t_1/\tau_m] \; \frac{dt_1}{\tau_{mr}} \tag{31}$$

where $\exp[-t_1/\tau_m]$ is used rather than $\exp[-t_1/\tau_{mr}]$ in recognition of the fact that Mu + X → D is a process competing with Mu + (S or X) → R· which shortens the overall chemical lifetime of the muonium, τ_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.
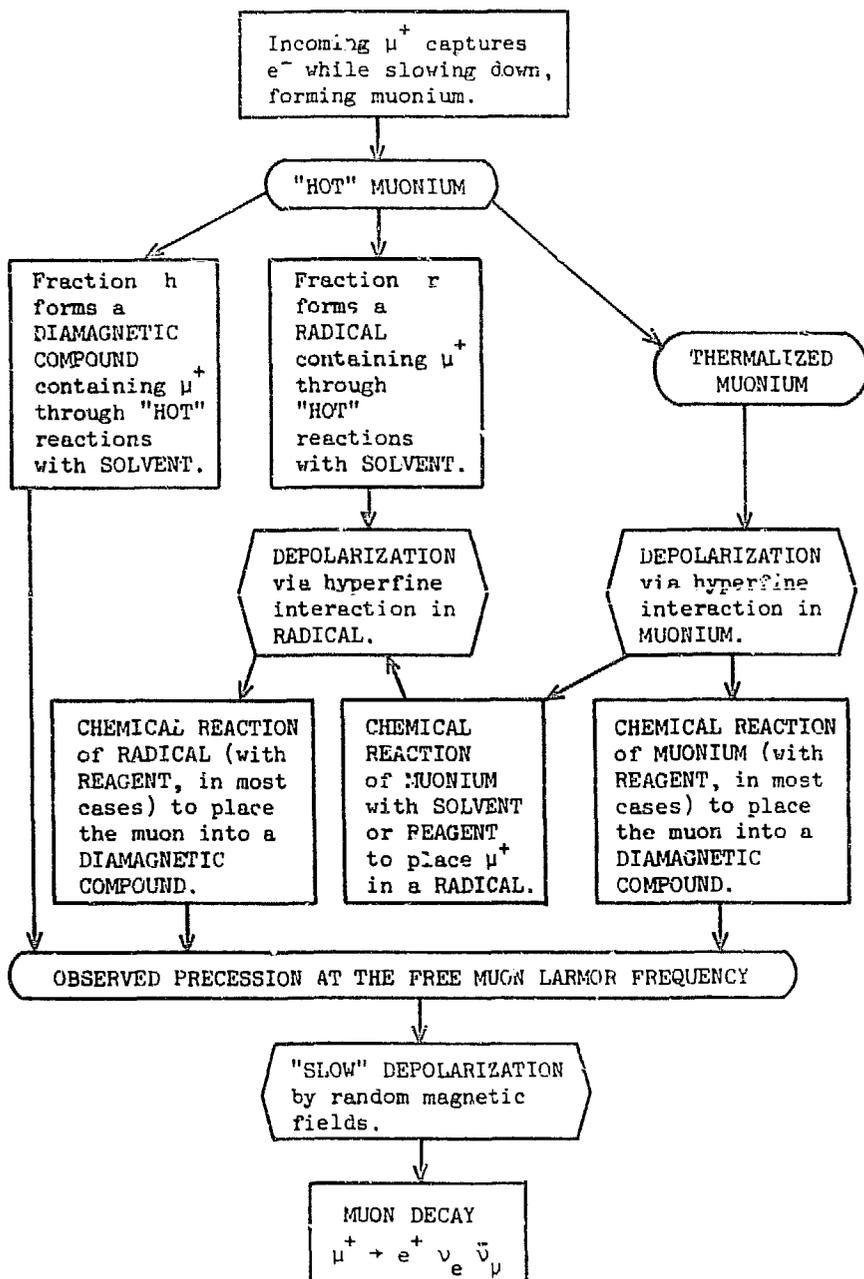
Figure 3 — FLOW CHART OF DEPOLARIZATION MECHANISM

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_{mxd} = chemical rate constant for the reaction Mu + X → D

k_{msd} = chemical rate constant for the reaction Mu + S → D

k_{mxr} = chemical rate constant for the reaction Mu + X → R

k_{msr} = chemical rate constant for the reaction Mu + S → R

k_{rxd} = chemical rate constant for the reaction R + X → D

k_{rsd} = chemical rate constant for the reaction R + S → D

        In each case, the rate (in $\sec^{-1}$) 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:

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

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

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

$\tau_m = [1/\tau_{md} + 1/\tau_{mr}]^{-1}$ = "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

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

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

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

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

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

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

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

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

Combining this with

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

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

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

where

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

(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_2" stands for evolution in a diamagnetic

compound (D) since combining epithermally at $t \simeq 0$.

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

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

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

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

3) MUONIUM → DIAMAGNETIC: "q_3" stands for evolution in free Mu

until time t_1, 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

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

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

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

Integration over all possible values of t_1 gives $P_3(t)$,

the overall contribution from the generic class "q_3":

$$P_3(t) \equiv \int_{t_1=0}^{t} P(q_3,t)$$

$$= \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{md}} \Sigma_k \frac{F_k}{\alpha_k} (\exp[\alpha_k t] - 1) \tag{36}$$

4) STILL-FREE HOT RADICAL: "q_4" stands for evolution in radical

(R) since combining epithermally at $t \simeq 0$.

This case is strictly analogous to case (1), except that

the radical takes the place of the muonium.

$$P(q_4,t) = \exp[i\omega_\mu t]\; r\; \Sigma_k\; G_k \exp[\beta_k t] \tag{37}$$

where

$$G_k \equiv R_{1k} \ [R^{-1}]_{k1} \tag{38}$$

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

5) HOT RADICAL → DIAMAGNETIC: "q_5" 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 evo-

lution 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_5" is

$$P_5(t) = \exp[i\omega_\mu t] \ \frac{r}{\tau_{rd}} \ \sum_k \frac{G_k}{\beta_k} \ (\exp[\beta_k t] - 1) \tag{40}$$

6) STILL-FREE CHEMICAL RADICAL: "q_6" stands for evolution in Mu

until time t_1, chemical combination at time t_1 to form R,

and subsequent evolution in R. Here

$$U_{q_6}(t,0) = U^r(t,t_1) \ U^m(t_1,0)$$

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

$$\{U_{q_6}(t,0) \ \hat{P}(0)\}_1 = \sum_{ijk} R_{1i} \ \exp[i\lambda_i^r(t-t_1)] \ [R^{-1}]_{ij}$$

$$\cdot M_{jk} \ \exp[i\lambda_k^m t_1] \ [M^{-1}]_{k1}$$

$$= \sum_{ik} W_{ik} \ \exp[i\lambda_i^r t] \ \exp[i(\lambda_k^m - \lambda_i^r)t_1]$$

where

$$W_{ik} \equiv \sum_j R_{1i} \ [R^{-1}]_{ij} \ M_{jk} \ [M^{-1}]_{k1}. \tag{41}$$

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

$$P(q_6, t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr}}$$

$$\cdot \Sigma_{ik} W_{ik} \exp[\beta_i t] \cdot \exp[(\alpha_k - \beta_i)t_1] \, dt_1$$

The overall contribution from the generic class "q_6" is

$$P_6(t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr}}$$

$$\cdot \Sigma_{ik} \frac{W_{ik}}{(\alpha_k - \beta_i)} (\exp[\alpha_k t] - \exp[\beta_i t]) \qquad (42)$$

7) MUONIUM → RADICAL → DIAMAGNETIC: "q_7" stands for evolution

until time t_1 in muonium, reaction at time t_1 to form R,

evolution in R until time t_2, reaction at time t_2 to form

D, and subsequent evolution in D.

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

$$\{U_{q_7}(t,0) \, \hat{P}(0)\}_i = \exp[i\omega_\mu(t-t_2)]$$

$$\cdot \Sigma_{ik} W_{ik} \exp[i\lambda_i^r t_2] \cdot \exp[i(\lambda_k^m - \lambda_i^r)t_1].$$

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

$$P(q_7, t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr} \, \tau_{rd}}$$

$$\cdot \Sigma_{ik} W_{ik} \exp[\beta_i t_2] \, dt_2 \cdot \exp[(\alpha_k - \beta_i)t_1] \, dt_1.$$

The overall contribution from muons experiencing fates of

the type "q_7" with all possible values of t_1 and t_2

is then

$$P_7(t) \equiv \int_{t_2=0}^{t} \int_{t_1=0}^{t_2} P(q_7, t)$$

$$= \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr} \tau_{rd}}$$

$$\cdot \sum_{ik} \frac{W_{ik}}{(\alpha_k - \beta_i)} \left[\frac{1}{\alpha_k} \{\exp[\alpha_k t] - 1\} \right.$$

$$\left. - \frac{1}{\beta_i} \{\exp[\beta_i t] - 1\} \right] \qquad (43)$$

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

$$P(t) = P(q_1, t) + P(q_2, t) + P_3(t) + P(q_4, t)$$
$$+ P_5(t) + P_6(t) + P_7(t). \qquad (44)$$

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_{res} from $P(t)$ by simply dropping off the Larmor precession term $\exp[i\omega_\mu t]$, letting $t \to \infty$, 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_{res}. Thus

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

Recalling the definitions of α_k and β_k, we may under most

Figure 23 — H_2O_2 at 100 gauss: Fit Assuming

Proper Muonium Mechanism

HYDROGEN PEROXIDE IN WATER AT 100 GAUSS
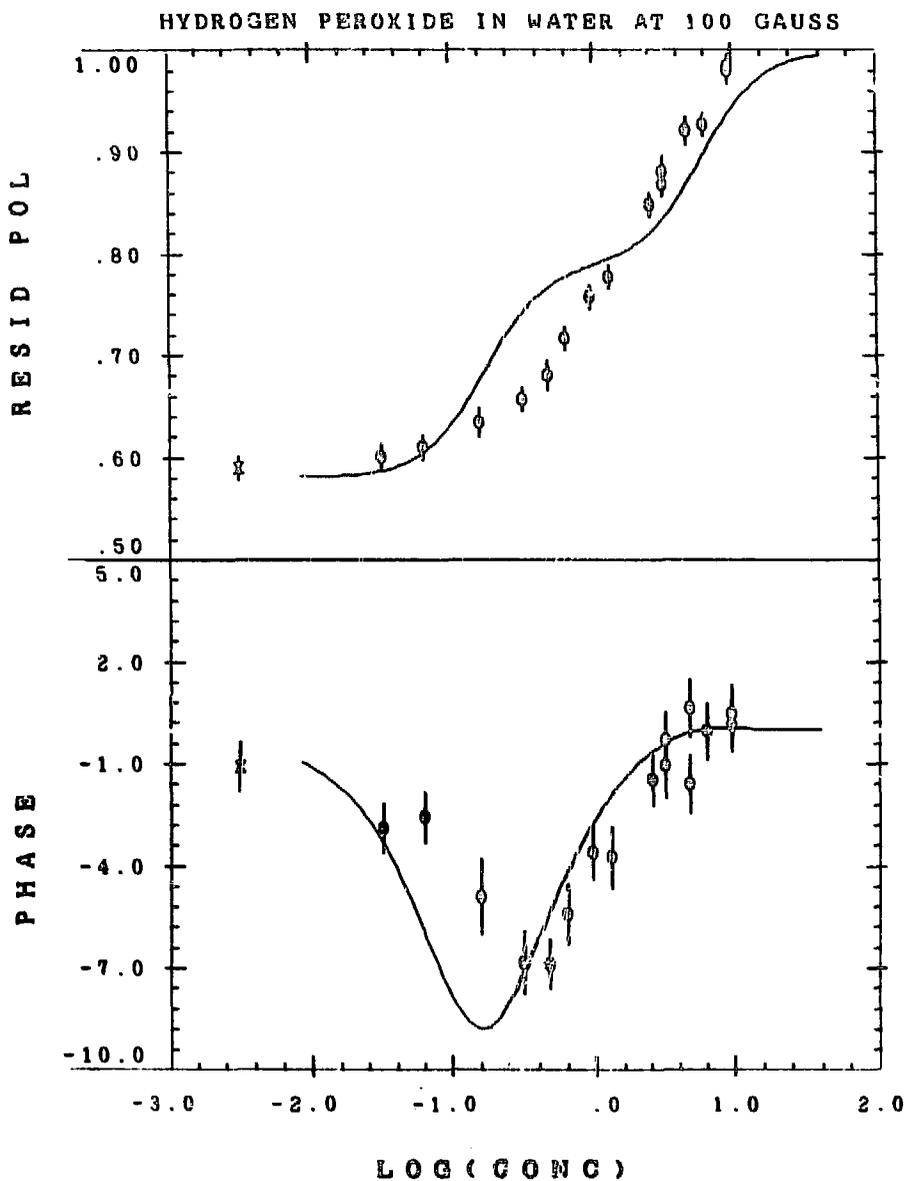
E. An Example

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 ω_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

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

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 τ to form a diamagnetic compound; once it has reacted, its polarization no longer changes on this time scale. Clearly, if τ is much shorter than τ_1 (shown on Fig. 4), nothing much has happened to the muon polarization by the time it reacts -- i.e., $P_{res} \simeq 1$, and there is no depolarization. If $\tau \approx \tau_1$, muons have "dropped out" of the evolving process at various times averaging to τ_1, and P_{res} will drop to something like 1/2. Now note what happens when τ is intermediate between τ_1 and τ_2: P_{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 τ, 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 τ_2 and τ_3 closer to τ_1 until, when B is on the order of the effective hyperfine field (1588 gauss), τ_1 and τ_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 τ_1, τ_2, and τ_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 $\tau = \tau_3$.

μ⁺ POLARIZATION ALONG INITIAL DIRECTION
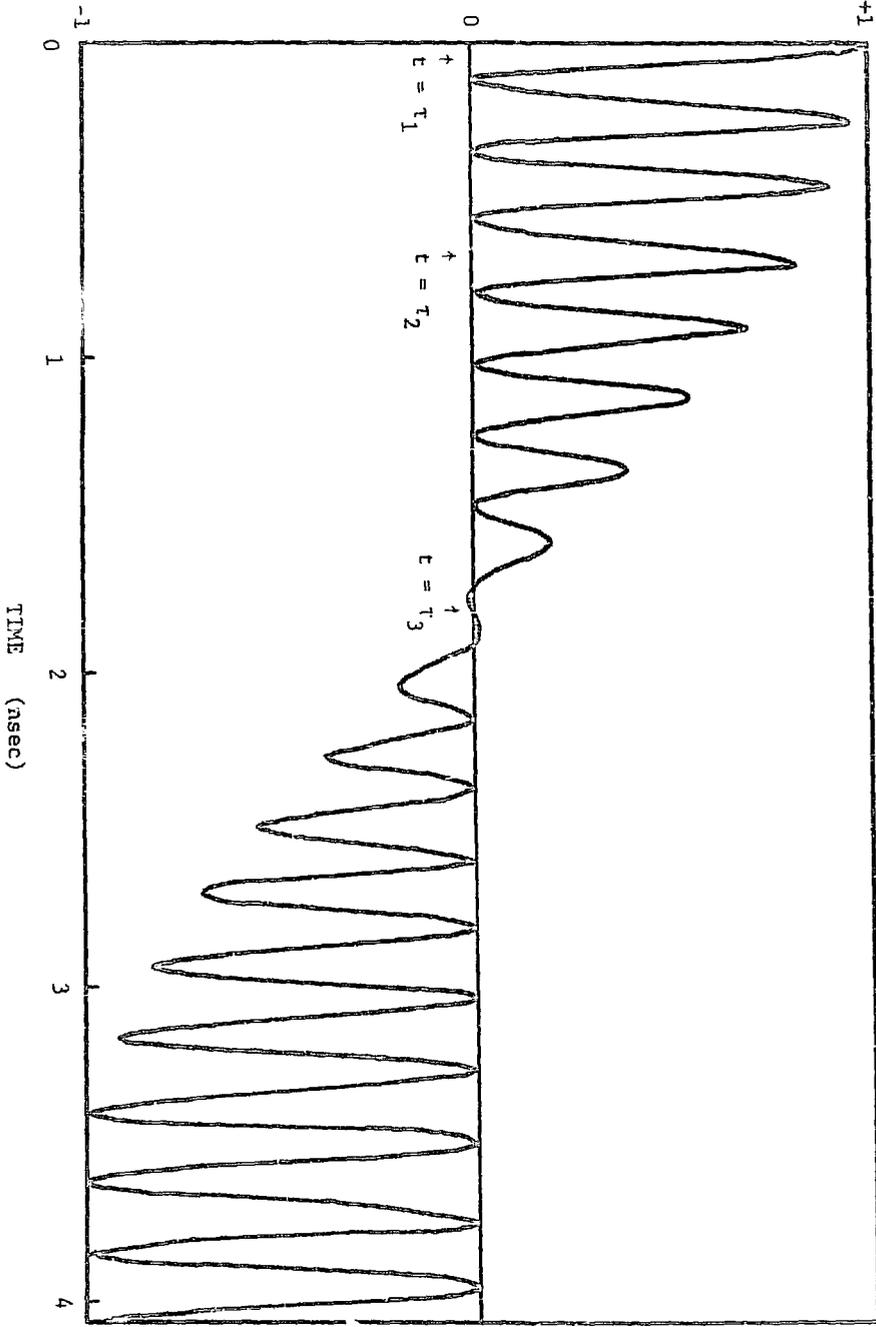
Figure 4 — EVOLUTION OF MUONIUM IN 100 GAUSS

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

CHEMICAL LIFETIME OF FREE MUONIUM (nsec)
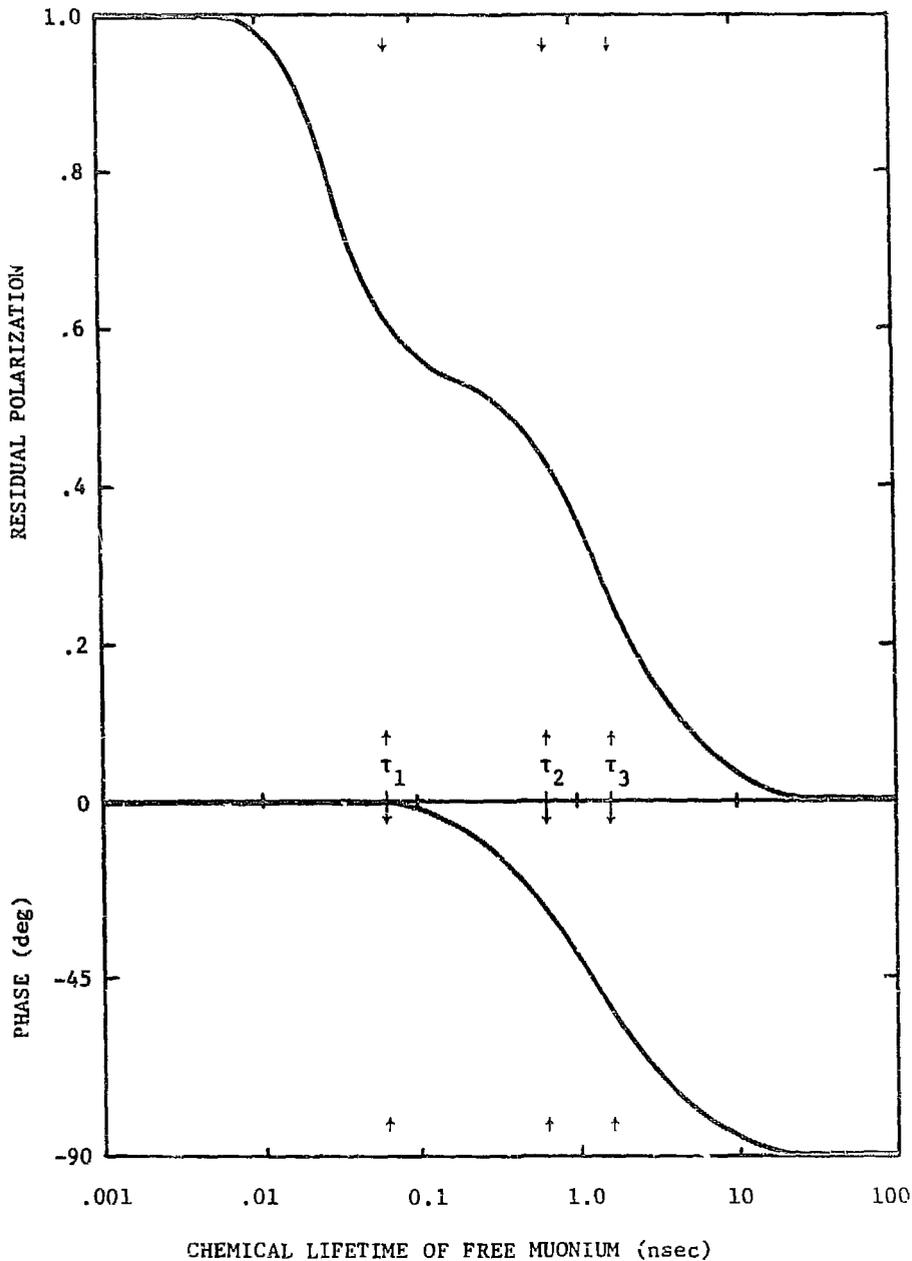
Figure 6 - EVOLUTION OF MUONIUM IN 100 GAUSS:

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

direction
perpendicular
to both $\underline{B}$
and $\underline{P}_\mu(0)$

rapid modulation
at frequency ω_o

$t = \tau_1$

$t = 0$

MAGNETIC FIELD $\odot$

$t = \tau_3$

$t = \tau_2$

mean value
precesses at
"muonium
frequency" ω_{Mu}

initial polarization
direction
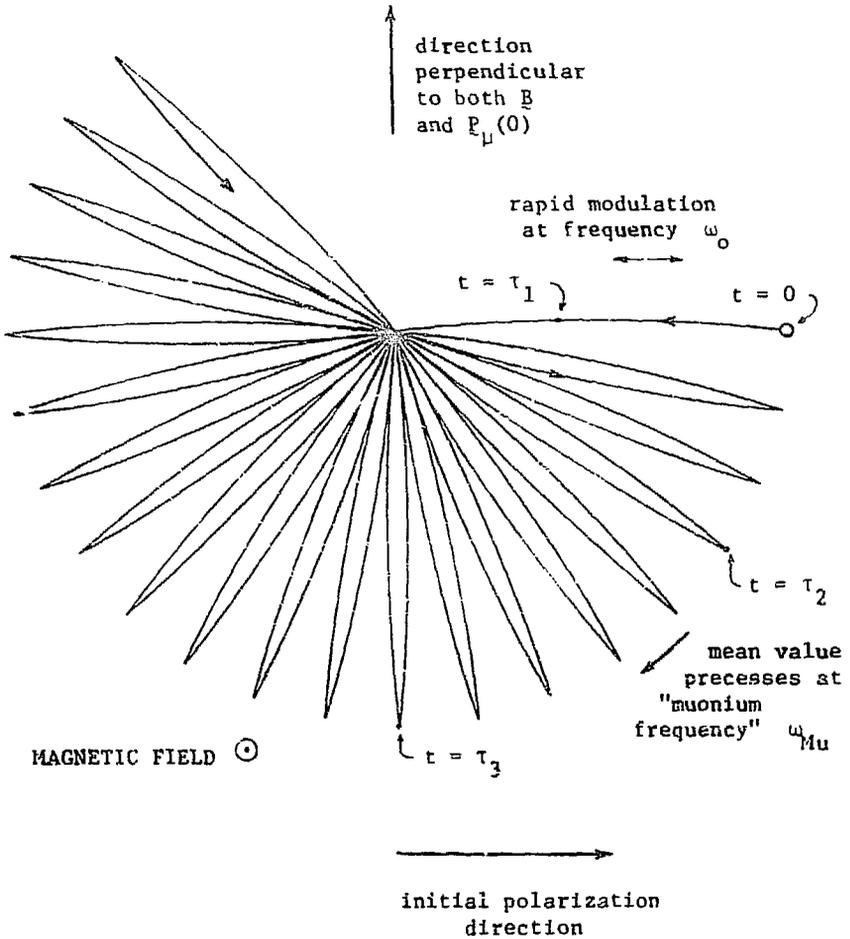
III. EXPERIMENTAL TECHNIQUE

With only a few changes, the apparatus used in this experiment was the same which was used by Crowe et. al.[4] 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 μ^+ beam is obtained by momentum separation of a π^+ 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° enter the first bending magnet ("Leander") about 60 in. from the production target, and are bent through about 78° 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°, with "backward" muons emerging at larger angles and "forward" muons emerging at about 73°. 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 con-
servation 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 stop-
ping 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 inter-
actions.

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 $\Delta B/B_o \sim 10^{-4}$

for $B_o = 4500$ gauss, $\Delta B/B_o \sim 10^{-3}$ for $B_o = 1000$ gauss,

$\Delta B/B_o \leq 10^{-2}$ for $B_o = 200$ gauss, and $\Delta B/B_o \sim 10^{-3}$ for $B_o = 100$

gauss.

740 MeV
proton beam

8 in. quad
doublet
"CIRCE"

copper
target

200 MeV/c pions

"LEANDER"
29 in. × 36 in.
"H" magnet

CONCRETE
SHIELDING

102°

12 in. quad
triplet
"ELECTRA I"
"HERO"
"ELECTRA II"

29 in. × 36 in.
"H" magnet
"TITAN"

230 MeV/c muons

107°
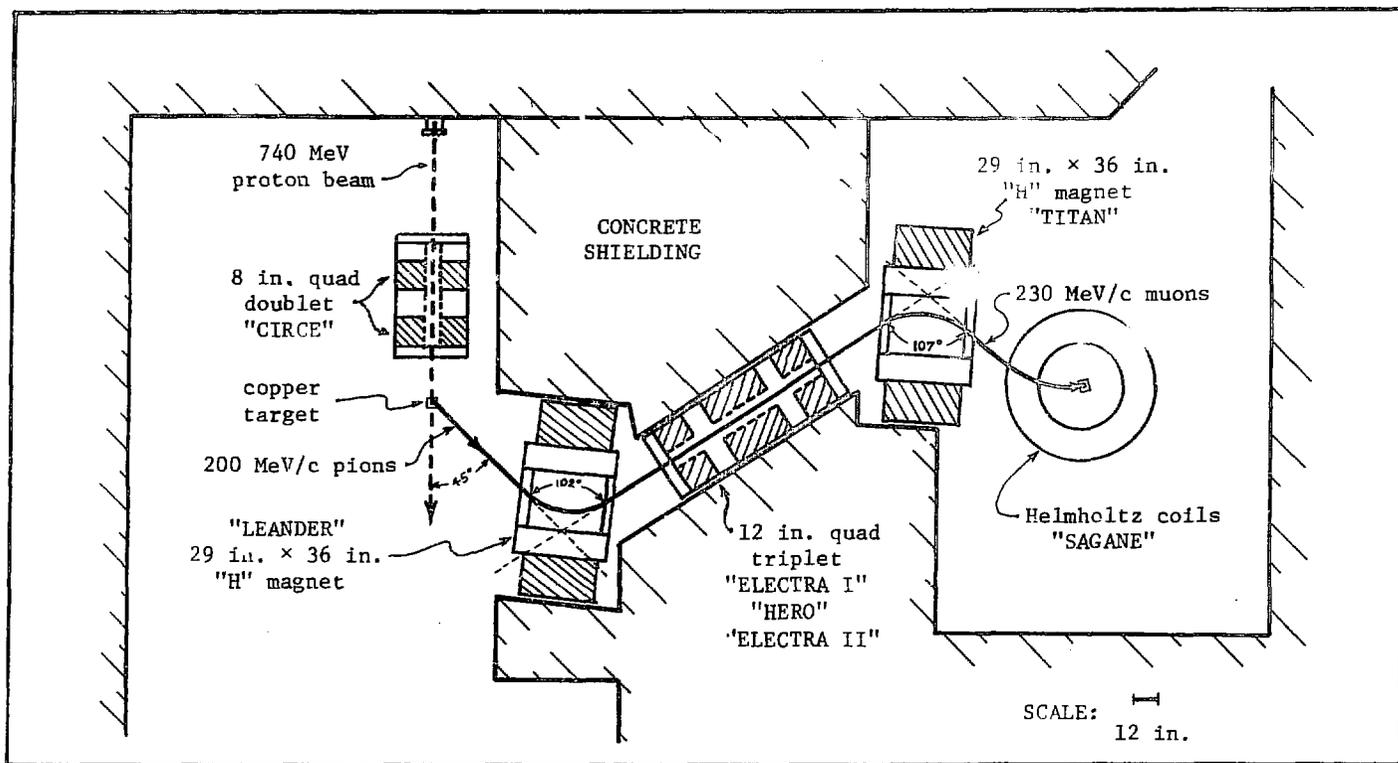
Helmholtz coils
"SAGANE"

SCALE:
12 in.

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 "μ", and is logically defined by

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

and the signature of a positron exiting from a μ^+ decay is "e":

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

A simplified diagram of the fast logic is shown in Fig. 8. The pulses "μ" 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
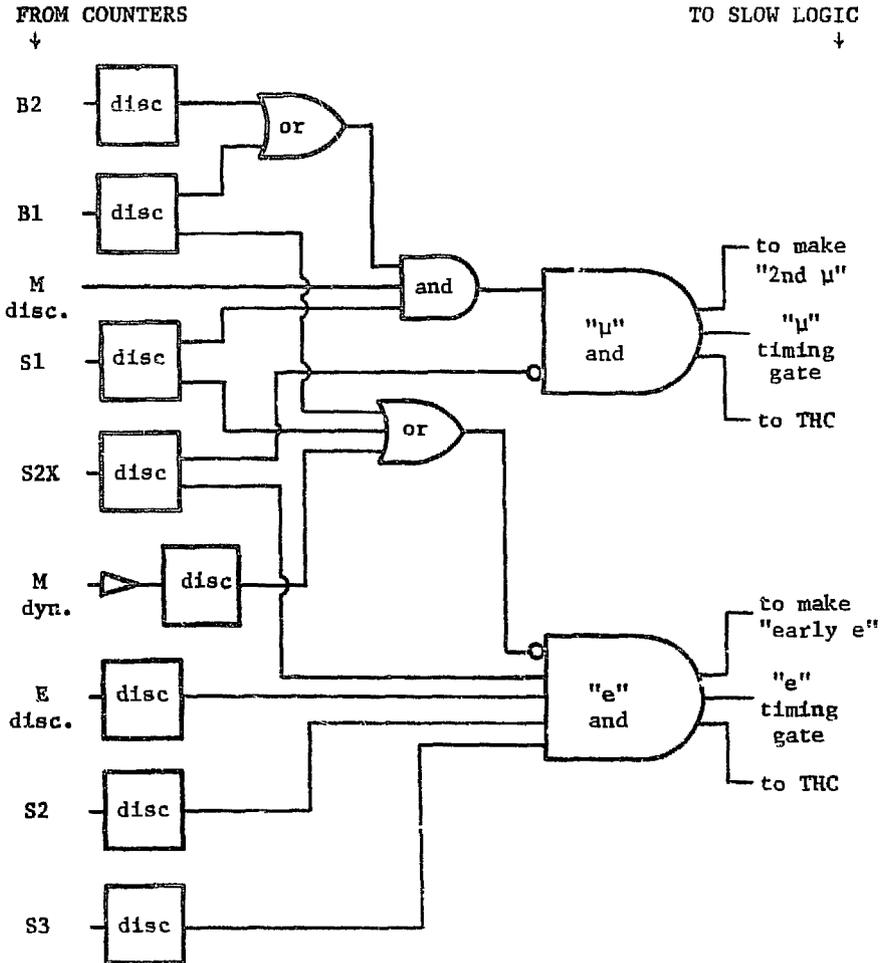
C. Slow Electronics and On-Line Computer

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 μsec, 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 μsec - $(t_e - t_\mu)$. A good deal of "slow" logic was required to accomplish this procedure.

The 20 μsec 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 μsec); 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 discriminato⁻, 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 "μ" 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 ∿ 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 μ" (a second muon stopped in the target before the first decayed), "2nd e" (two "e" pulses were generated after only one "μ" pulse; one must be spur-

ious), and "Early E" (fast timing counter E fired within 1 μsec
preceeding the "μ" 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 nor-
mal events. The relative frequency of various types of "bad"
events was typically

No 2nd μ, 2nd e, or Early E	∿ 90	%
2nd μ only	9.1	%
2nd e only	.6	%
Early E only	.4	%
Early E and 2nd μ	.06	%
Early E and 2nd e	.004	%
2nd μ and 2nd e	.3	%
2nd μ, 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 infor-
mation 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 com-
puter; 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 — <u>BLOCK DIAGRAM</u> <u>OF</u> <u>LOGIC</u> <u>NETWORK</u>
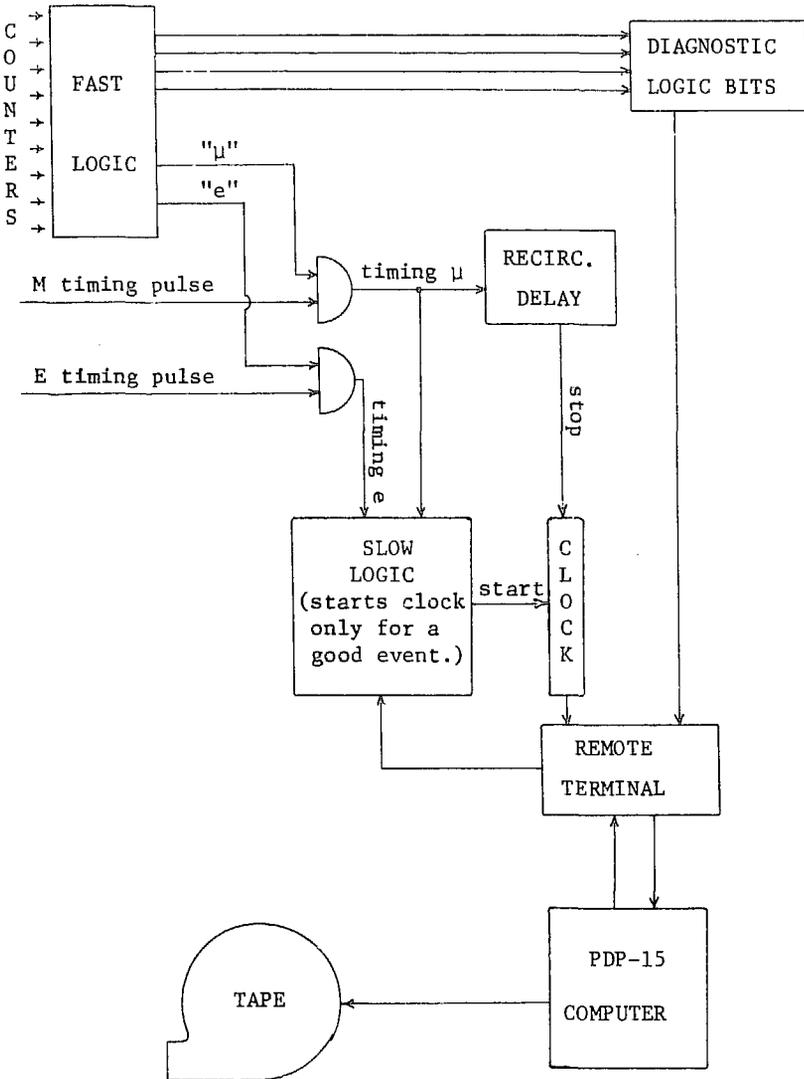
D. Data Reduction and Analysis Programs

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 χ^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 μsec for the muon lifetime τ_μ; the program returned χ^2 and the best estimates for the parameters N_o, B, A, T_2, ω_μ, and ϕ, specifying the error in the determination of each.

The results were checked for consistency, and then the parameters A and ϕ 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_o, ϕ_o, h, and k_{mxd}. Of these, the first two are phenomenological: A_o is the limiting value of the asymmetry due to beam

polarization, counter geometry, etc., and represents the high-concentration asymptote of $A([X])$; ϕ_o 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 ϕ as $[X] \to \infty$. Thus, in the figures showing best fits to the data, the quantities plotted against reagent concentration are "Polarization" = A/A_o and "Phase" = $\phi - \phi_o$.

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 ϕ_o; 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 ϕ 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[18]

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

where P is the steric factor, σ 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 μ_{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 $\mu_{AB} \simeq m_A$. 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"

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

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 and 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:[18]

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

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:

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

where $\bar{v}_{AS}$ is the mean relative thermal velocity between A and S, λ_{AS} is the mean free path of A in S, μ_{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 $\mu_{AS} \simeq m_A$, 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[a]

REAGENT	pH	RATE CONSTANT FOR HYDROGEN (liters/mole-sec)	EQUIVALENT RATE CONSTANT FOR MUONIUM	METHOD
Br_2		$\sim 10^{10}$	$\sim 3 \times 10^{10}$	pulse radiolysis (p. r.)
ClO_4^-	0	nil	nil	?
Fe^{+++}	0.1	8×10^7	2.4×10^8	O_2
"	0.1	1.6×10^6	4.8×10^6	Fe^{++}
"	0	$< 2 \times 10^6$	$< 6 \times 10^6$	O_2
"	0.4	1.2×10^6	3.6×10^6	O_2
"	1.6	2.2×10^7	6.6×10^7	O_2
"	2	9.0×10^7	2.7×10^8	p. r.
"	2.1	9.5×10^7	2.85×10^8	O_2
"	2.1	9.6×10^7	2.88×10^8	D_2
$Fe(OH)_2^+$	–	7.5×10^8	2.25×10^9	p. r.
$FeCl^{++}$	0.1	4.5×10^9	1.35×10^{10}	O_2
$FeCl_2^+$	0.1	9×10^9	2.7×10^{10}	O_2
H_2O_2	acid	5×10^7	1.5×10^8	O_2
"	.4-3	1.6×10^8	4.8×10^8	p. r.
"	2	9×10^7	2.7×10^8	p. r.
"	–	6.1×10^7	1.83×10^8	p. r.
I_2	0.4	4×10^{10}	1.2×10^{11}	O_2
NO_3^-	11-13	$\sim 7 \times 10^6$	$\sim 2.1 \times 10^7$	acetate
"	7	2.4×10^7	7.2×10^7	2-propanol
"	1.1	1.2×10^7	3.6×10^7	H
"	2.0	1.3×10^7	3.9×10^7	H

[a]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
NO_3^-	4.7	9.1×10^6	2.73×10^7	H
"	7	9.3×10^6	2.79×10^7	H
"	10-13	3.8×10^6	1.14×10^7	H
"	7	7×10^6	2.1×10^7	ethanol
"	acid	2.3×10^7	6.9×10^7	2-propanol
"	6	1.8×10^7	5.4×10^7	2-D-2-propanol
O_2	acid	1.2×10^{10}	3.6×10^{10}	p. r.
"	.4-3	2.6×10^{10}	7.8×10^{10}	p. r.
"	2	1.9×10^{10}	5.7×10^{10}	p. r.
OH^-	7.5-12.5	1.2×10^7	3.6×10^7	chloroacetate
"	11-13	2.3×10^7	6.9×10^7	formate, acetane
"		1.8×10^7	5.4×10^7	p. r.
"		2.6×10^7	7.8×10^7	ethanol
"		2.3×10^7	6.9×10^7	p. r.
CH_3OH	1	1.6×10^6	4.8×10^6	Fe^{+++}
"	7	1.7×10^6	5.1×10^6	$Fe(CN)_6^{-3}$
"	7	1.6×10^6	4.8×10^6	NO_2^-
"	7	1.65×10^6	4.95×10^6	D-formate
"	2	1.6×10^6	4.8×10^6	Ag^+, (p. r.)
"	-	4.6×10^6	1.38×10^7	OH^-
nitro-benzene	7	1.7×10^9	4.1×10^9	2-propanol

B. <u>Verification</u> <u>of</u> <u>the</u> <u>Proper</u> <u>Muonium</u> <u>Mechanism</u>

Figure 10 shows the observed dependence of P_{res} and ϕ 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 $\tau = k_{mxd}[X]$, 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 ϕ 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 rad-
icals, 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 invol-
ving 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[19]
of 4×10^{10} liters/mole-sec for the reaction $H + I_2 \rightarrow HI + I$,
when the latter is multiplied by the "kinetic ratio" of 3.

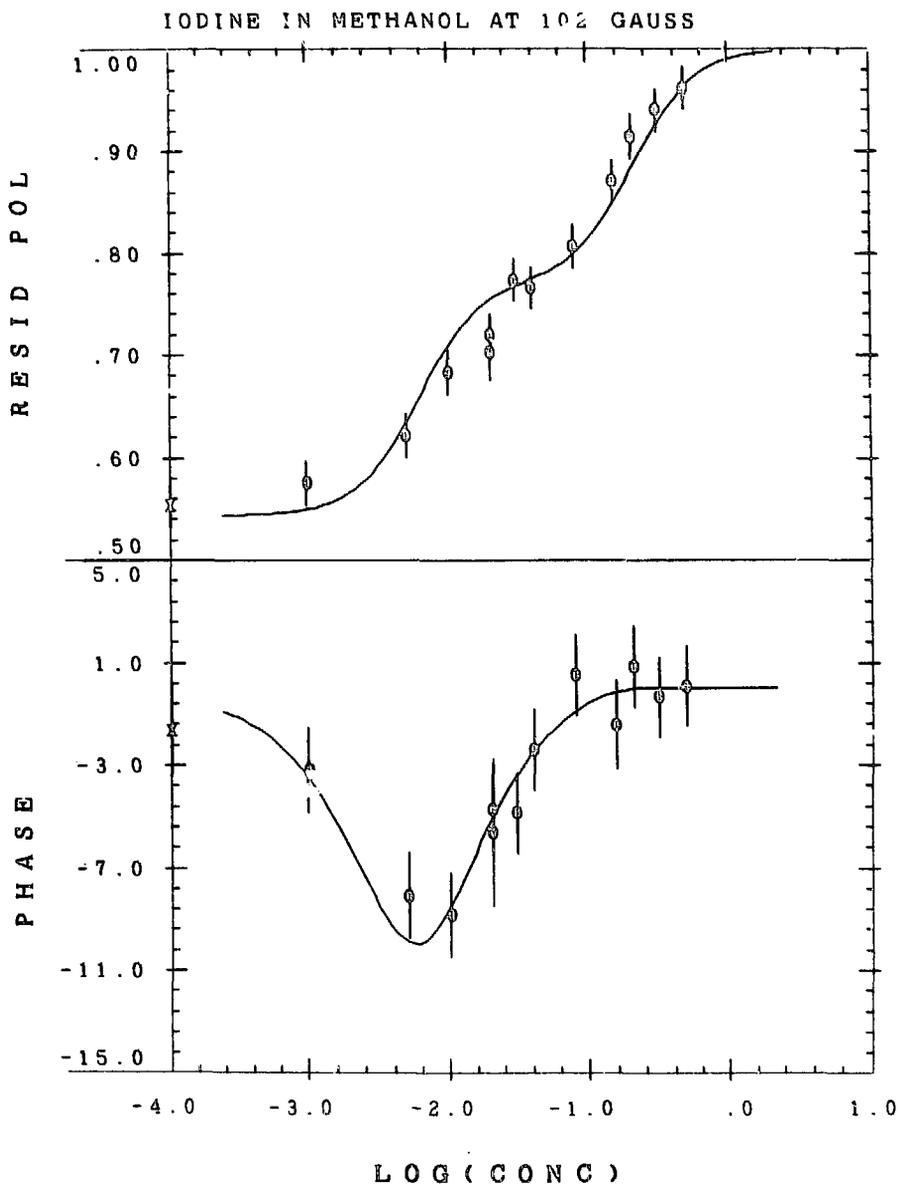Figure 10 - I$_2$ in CH$_3$OH at 102 gauss: Proper Muonium

Mechanism

IODINE IN METHANOL AT 102 GAUSS

Figure 11 — I_2 in CH_3OH at 1000 gauss: Proper Muonium Mechanism

IODINE IN METHANOL AT 1000 GAUSS
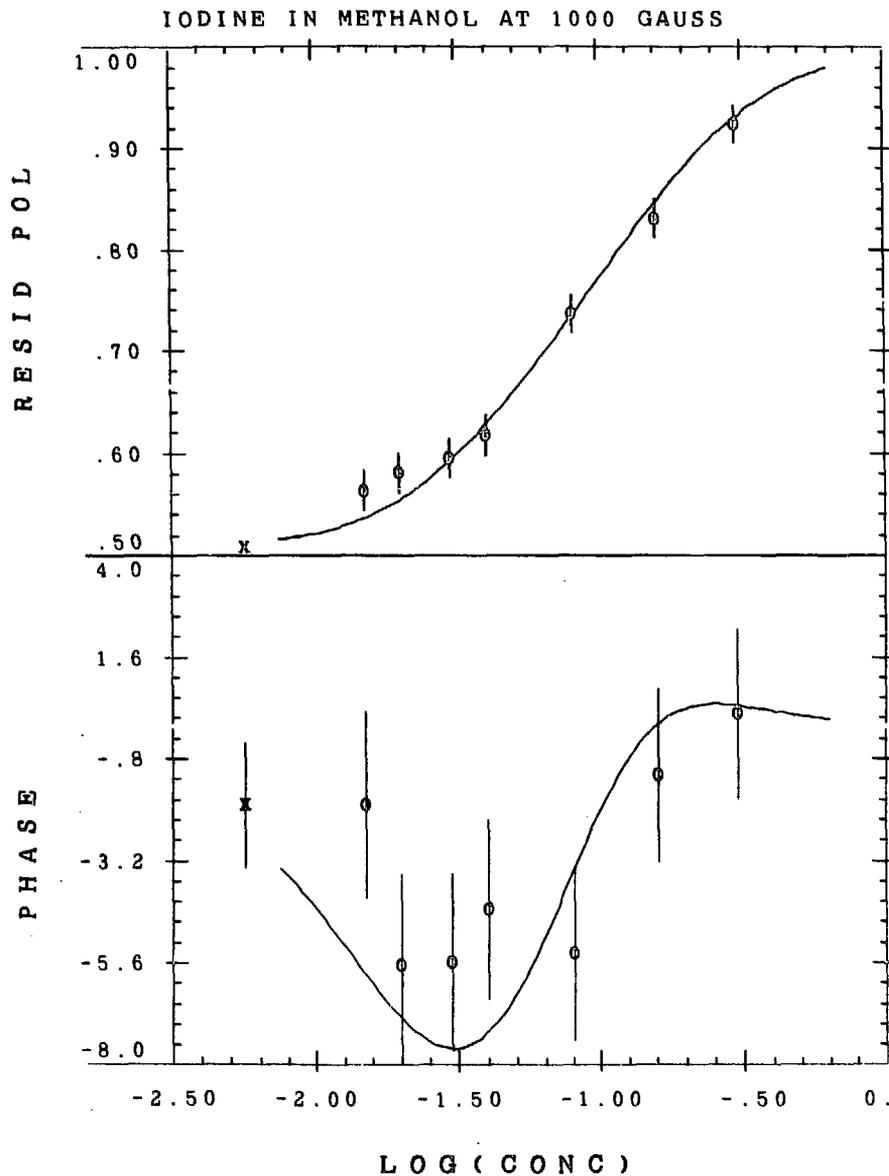
Figure 12 — I$_2$ in CH$_3$OH at 4500 gauss: Proper Muonium

Mechanism

IODINE IN METHANOL AT 4500 GAUSS
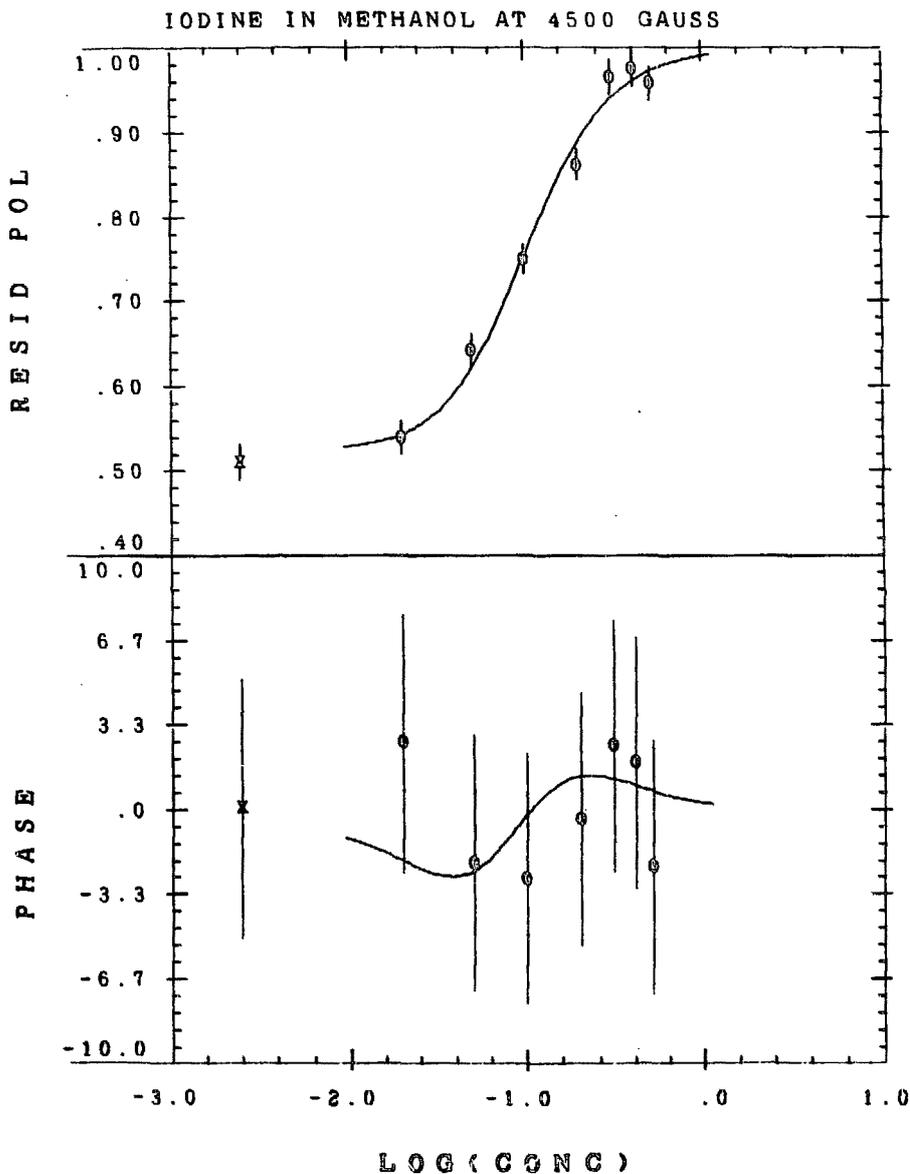
Table III - BEST FITS TO "PROPER" MUONIUM MECHANISM

| REAGENT	SOLVENT	FIELD (gauss)	A_o	ϕ_o (degrees)	h	$k_{mxd} \times 10^{-10}$ (liters/mole-sec)	$\dfrac{\chi^2}{\text{deg. fr.}}$	MECHANISM CORRECT?
I_2	CH_3OH	103	$.24 \pm .01$	15.5 ± 1.0	$.54 \pm .02$	16.7 ± 2.0	~ 2	yes
"	"	1000	$.27 \pm .02$	105 ± 2[a]	$.52 \pm .02$	11.4 ± 2.0	~ 3.5	yes
"	"	4500	$.27 \pm .02$	$\sim$	$.54 \pm .02$	13.4 ± 2.0		yes
$FeCl_3$	H_2O	4500	$.31 \pm .02$	$\sim$	$.51 \pm .02$	2.1 ± 0.2	~ 1	?
$Fe(ClO_4)_3$	H_2O	4500	$.30 \pm .02$	$\sim$	$.55 \pm .02$	1.7 ± 0.2	~ 6	no
"	"	100	$.275$[b]	15.5[b]	$.55$[b]	0.24	~ 100	no
$HClO_4$	H_2O	4400	$.275$[b]	$\sim$	$.54 \pm .01$	0.12	~ 2	?
HNO_3	H_2O	4500	$.30 \pm .01$	$\sim$	$.54 \pm .01$	0.64	~ 1.5	no
"	"	100	$.275$[b]	16.2 ± 4.0	$.55$[b]	0.62	~ 11	no
H_2O_2	H_2O	100	$.26 \pm .02$	11.4 ± 1.2	$.58 \pm .02$	0.45	~ 3	no

[a] $t = 0$ not defined; ϕ_o therefore arbitrary.   [b] Parameter held constant; not fitted.

Errors quoted are approximate. χ^2/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[21] strictly in terms of the proper muonium mechanism, postulating that the only important reaction was

$$Mu + Fe^{+++} \rightarrow \mu^+ + Fe^{++} \tag{54}$$
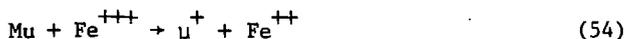
where either the free muon or the product of its subsequent reaction with anions in solution consitutes a diamagnetic environment for the muon.

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[22]), 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_{mxd} in $FeCl_3$ 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, Fe^{+++} is known to form hydroxides readily, and the higher rate for reactions of H atoms with $Fe(OH)^+_2$ suggests that this process may be dominant in $FeCl_3$ solutions; reaction with the species $FeCl^{++}$ and $FeCl^+_2$, if present, are even higher. Thus, the situation with $FeCl_3$ 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 - FeCl$_3$ (solid curve with triangles) and

Fe(ClO$_4$)$_3$ (dashed curve with dots) at 4500 gauss:

Fit Assuming Proper Mucnium Mechanism
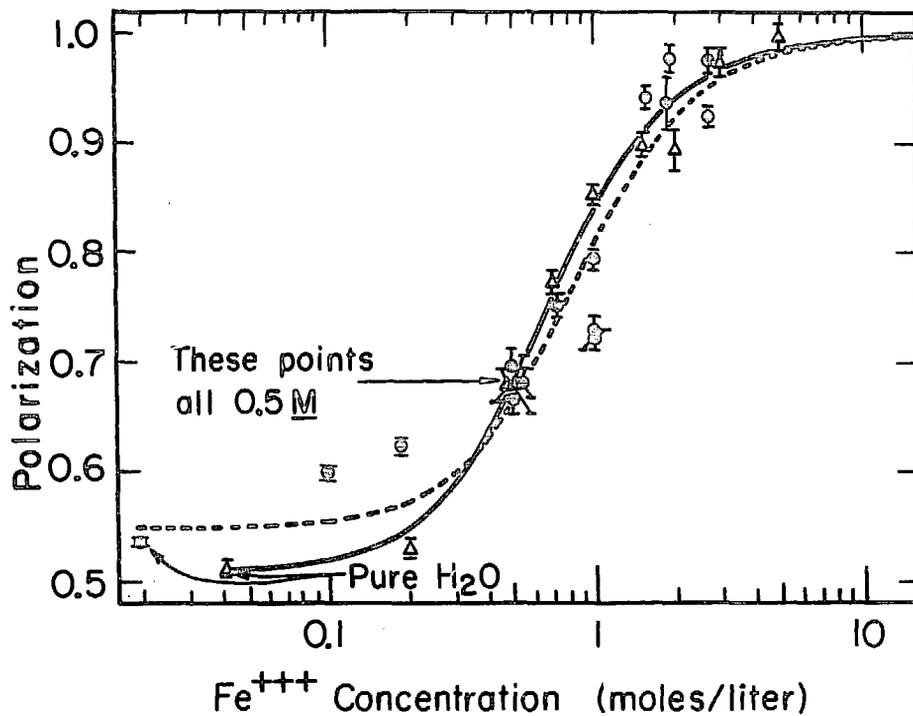

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## D. Evidence for Radical Formation

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[22], 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 [23, 24], 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

$$Mu + Br_2 \xrightarrow{(k_{mxd})} MuBr + Br \qquad (55)$$
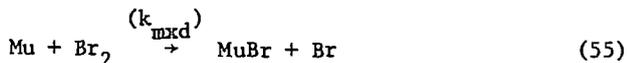
and also (competitively) with the benzene to form the muonium analog
of the radical cyclohexadienyl ($C_6H_7\cdot$), according to

$$Mu + C_6H_6 \xrightarrow{(k_{msr})} C_6H_6Mu\cdot \qquad (56)$$
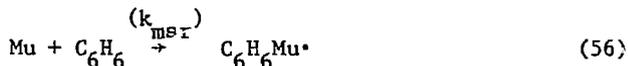
Second, the radical is presumed to react subsequently with the
bromine to place the muonium into a diamagnetic compound, according
to

$$C_6H_6Mu\cdot + Br_2 \xrightarrow{(k_{rxd})} D \text{ (unidentified).} \qquad (57)$$
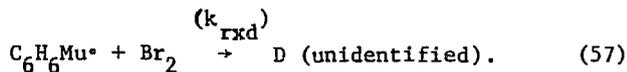
In this and all other examples of radical formation we
treat, it is assumed that the "radical hot fraction" r is zero.
In the other examples, the radical is formed by reaction with the
reagent, rather than with the solvent, in which case r is
required to be zero by the assumption of the "dilute limit"
(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, epthermal 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 $\underline{M}$, which was insufficient to give full "repolarization". Nevertheless, when the parameters for I_2 in C_6H_6 are allowed to vary freely (given as starting values the best fit for Br_2 in C_6H_6), a best fit is obtained for values consistent with the Br_2 results. The results for Br_2 and I_2 in C_6H_6 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 [23], whose effective hyperfine field at the site of the extra proton is known[25] to be 47.71 gauss (isotropic average),

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

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

Melville and Robb[24] measured a rate constant of 5.88×10^8 liters/mole-sec for the reaction $H + C_6H_6 \rightarrow C_6H_7$, 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_2 in C_6H_6, where the best determination is made.

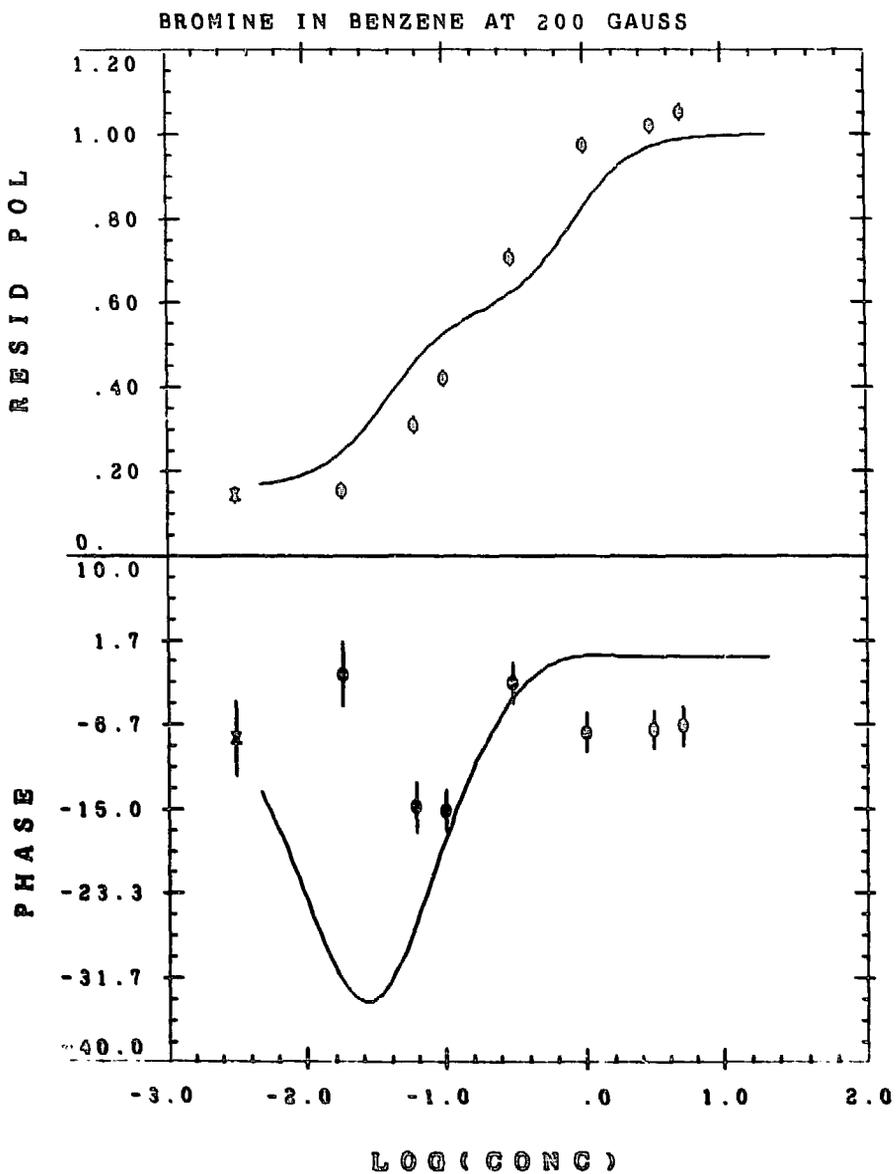Figure 14 — Br$_2$ in C$_6$H$_6$ at 200 gauss:

Fit Assuming Proper Muonium Mechanism

BROMINE IN BENZENE AT 200 GAUSS

Figure 15 - Br_2 in C_6H_6 at 200 gauss:

Fit Including Radical Formation

BROMINE IN BENZENE AT 200 GAUSS
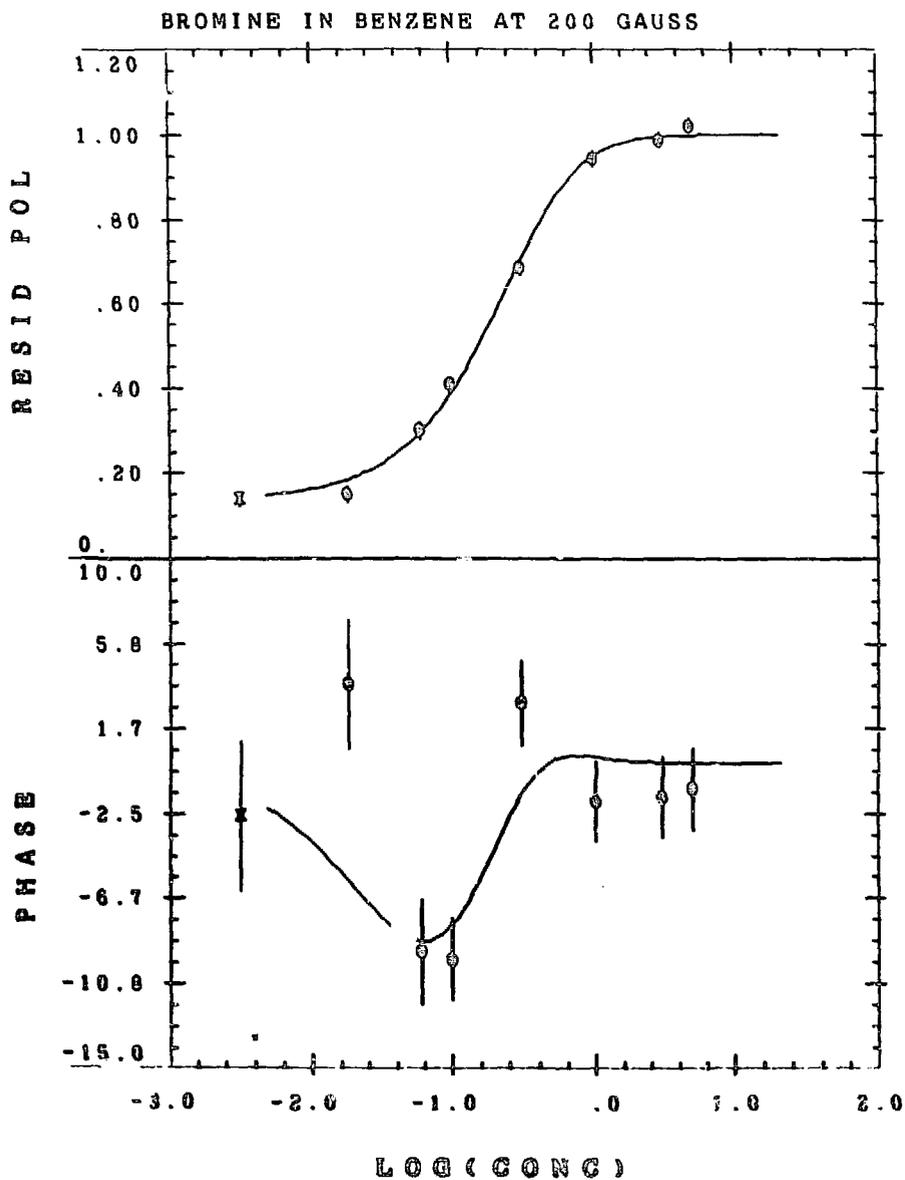
Figure 16 - I_2 in C_6H_6 at 200 gauss:

Fit Including Radical Formation

IODINE IN BENZENE AT 200 GAUSS
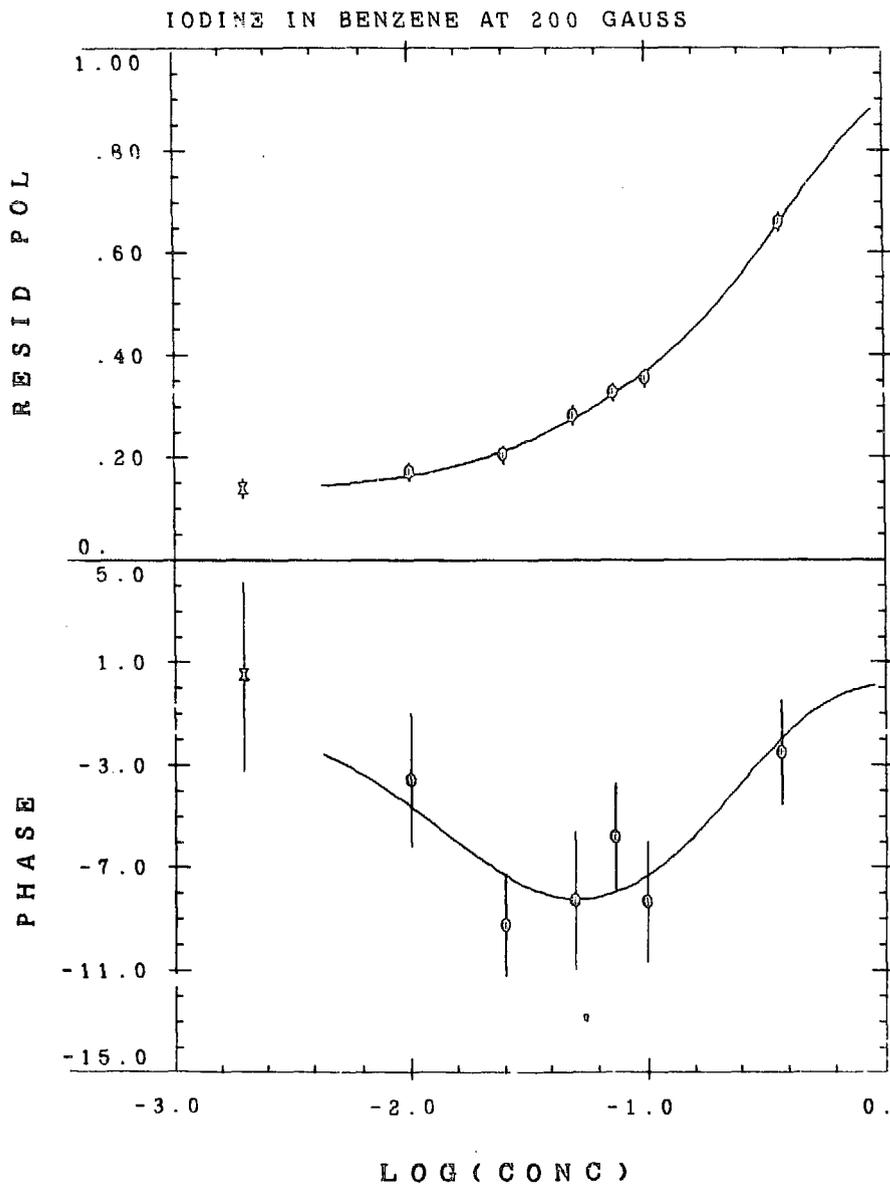
2. Acids

As mentioned earlier, our studies of HCl in aqueous solution confirmed the findings of Swanson[22], which showed that HCl does not appreciably change P_{res} from the value observed in pure water. Therefore, no combination of reactions between Mu, H^+, and Cl^- leads to a diamagnetic compound containing Mu in times shorter than about 10 nsec, even in 10 $\underline{M}$ solutions. However, addition of nitric acid to water causes marked "repolarization", with a maximal asymmetry reached at about 10 $\underline{M}$. 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 HNO_3 to form a radical, which subsequently reacts with HNO_3 to place the muonium in a diamagnetic compound, the generalized mechanism gives quite plausible results for the case of 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 ω_r/ω_o was chosen by minimizing χ^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 NO_3^- , (see Table II) none of which predicts a value of more

than 7.2×10^7 liters/mole-sec for the analogous reaction of muonium. Such a low rate is totally incapble of explaining the observed fast reactions of muonium in 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 $HClO_4$ in water at 4400 gauss. However, we have not yet undertaken a study of $HClO_4$ 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 $Fe(ClO_4)_3$ 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 $Fe(ClO_4)_3$ to form a radical, which subsequently reacts with $Fe(ClO_4)_3$ to place Mu in a diamagnetic compound (see Fig. 22). This suggests that we might expect to see evidence for radical formation in $HClO_4$ if we lower the field to 100 gauss.
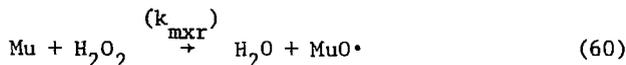
3. Hydrogen Peroxide

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
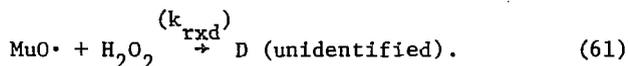
containing muonium, presumably according to

$$Mu + H_2O_2 \xrightarrow{(k_{mxd})} MuHO + HO\cdot \qquad (59)$$
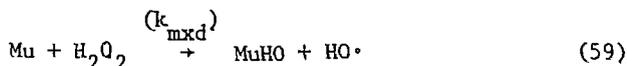
and (competitively) to form a radical containing muonium, presumably according to

$$Mu + H_2O_2 \xrightarrow{(k_{mxr})} H_2O + MuO\cdot \qquad (60)$$

and that the radical MuO· subsequently reacts with the H_2O_2 to form a diamagnetic compound containing muonium:

$$MuO\cdot + H_2O_2 \xrightarrow{(k_{rxd})} D \text{ (unidentified)}. \qquad (61)$$

Now, processes in hydrogen peroxide solution are notoriously complex, and these are undoubtedly not the only reactions taking place (for instance, the radical 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 HO· is known[26] to be 41.3 gauss (isotropic average), predicting $\omega_r/\omega_o = .0825$ (recall equation (58)). When ω_r/ω_o was given various different values, the best fits were in the region $.05 < \dfrac{\omega_r}{\omega_o} < .25$, with the best fit for $\omega_r/\omega_o = .175$; thus the best fit is consistent with the theoretical value.

It is annoying that again, as in the case of HNO_3 and $HClO_4$, 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 — HNO$_3$ at 4500 gauss: Fit Assuming

Proper Muonium Mechanism

NITRIC ACID IN WATER AT 4500 GAUSS
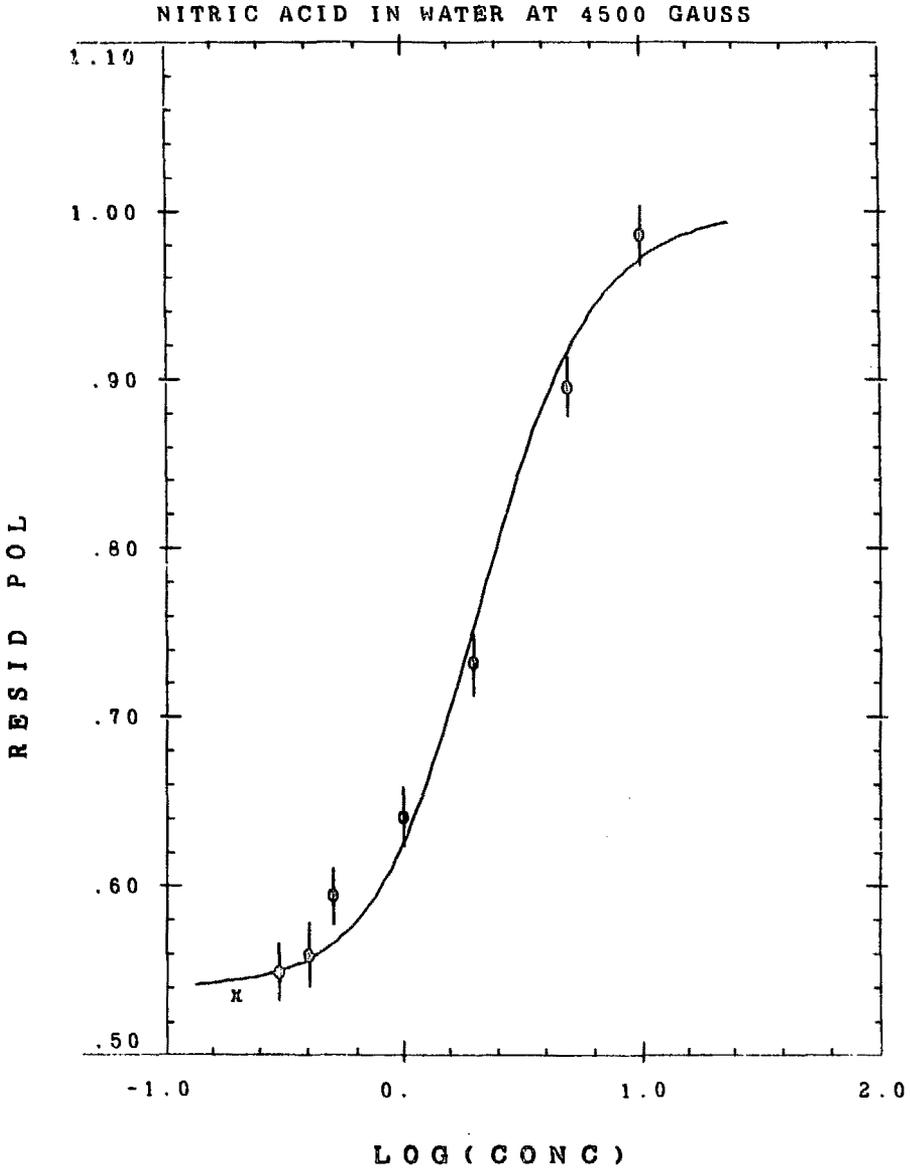
Figure 18 — HNO$_3$ at 100 gauss: Fit Assuming

Proper Muonium Mechanism

NITRIC ACID IN WATER AT 100 GAUSS
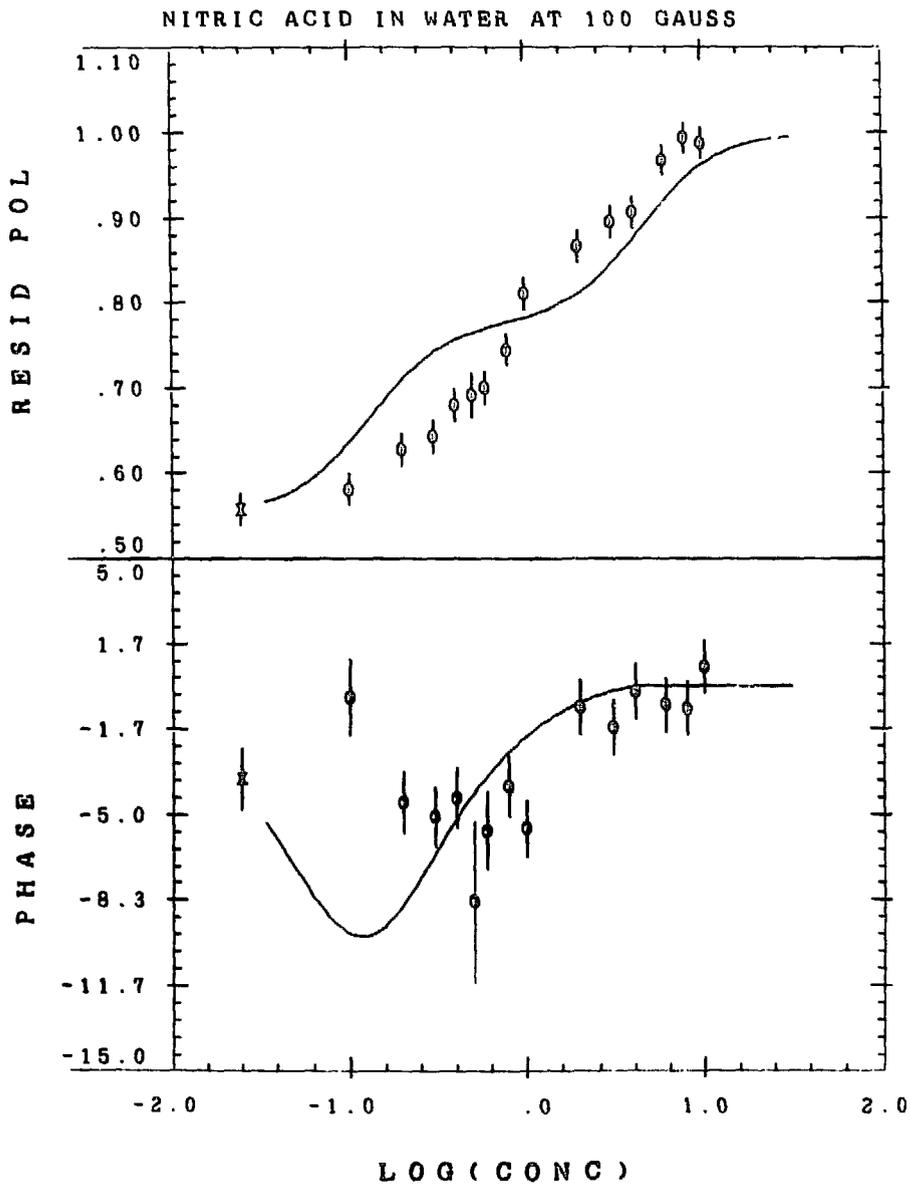
Figure 19 – HNO$_3$ at 100 gauss: Fit Including

Radical Formation

NITRIC ACID IN WATER AT 100 GAUSS
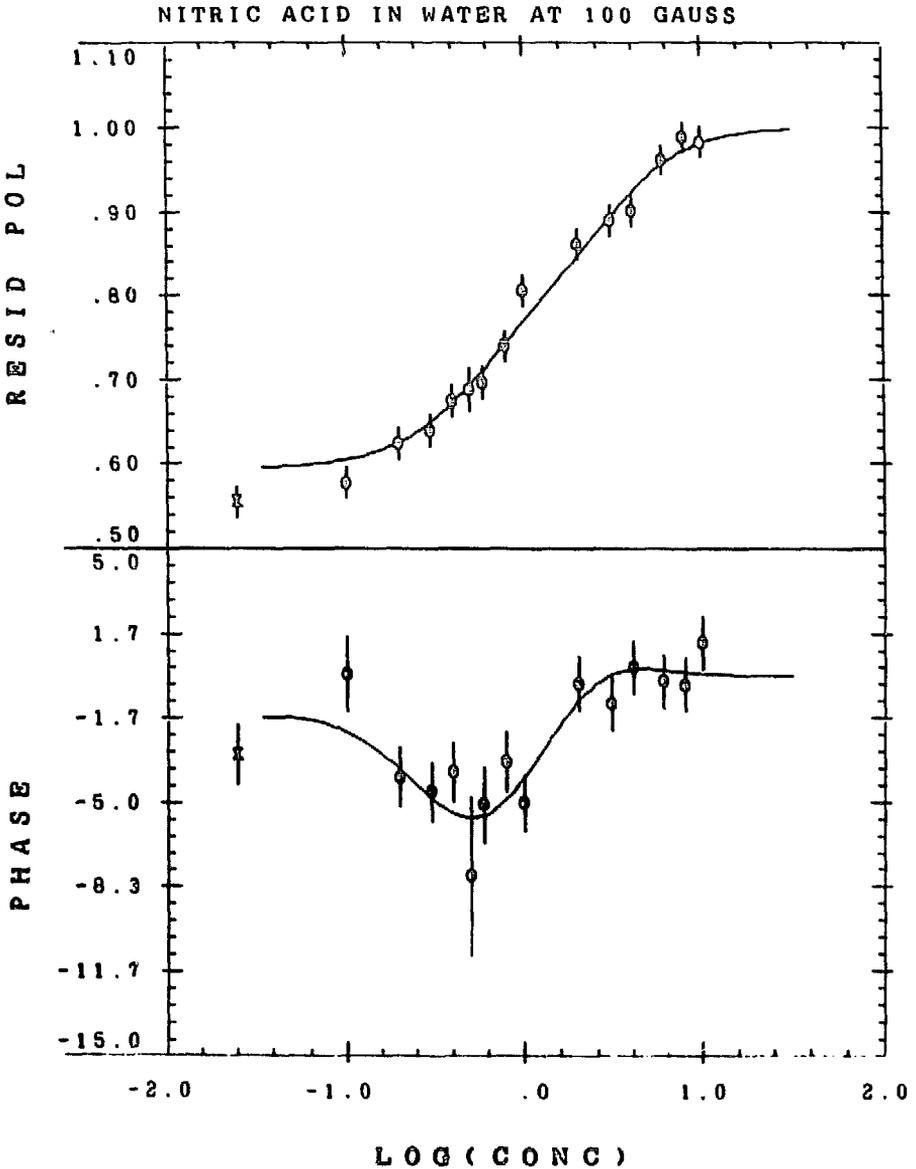
Figure 20 - HClO$_4$ at 4400 gauss: Fit Assuming

Proper Muonium Mechanism

PERCHLORIC ACID IN WATER AT 4400 GAUSS
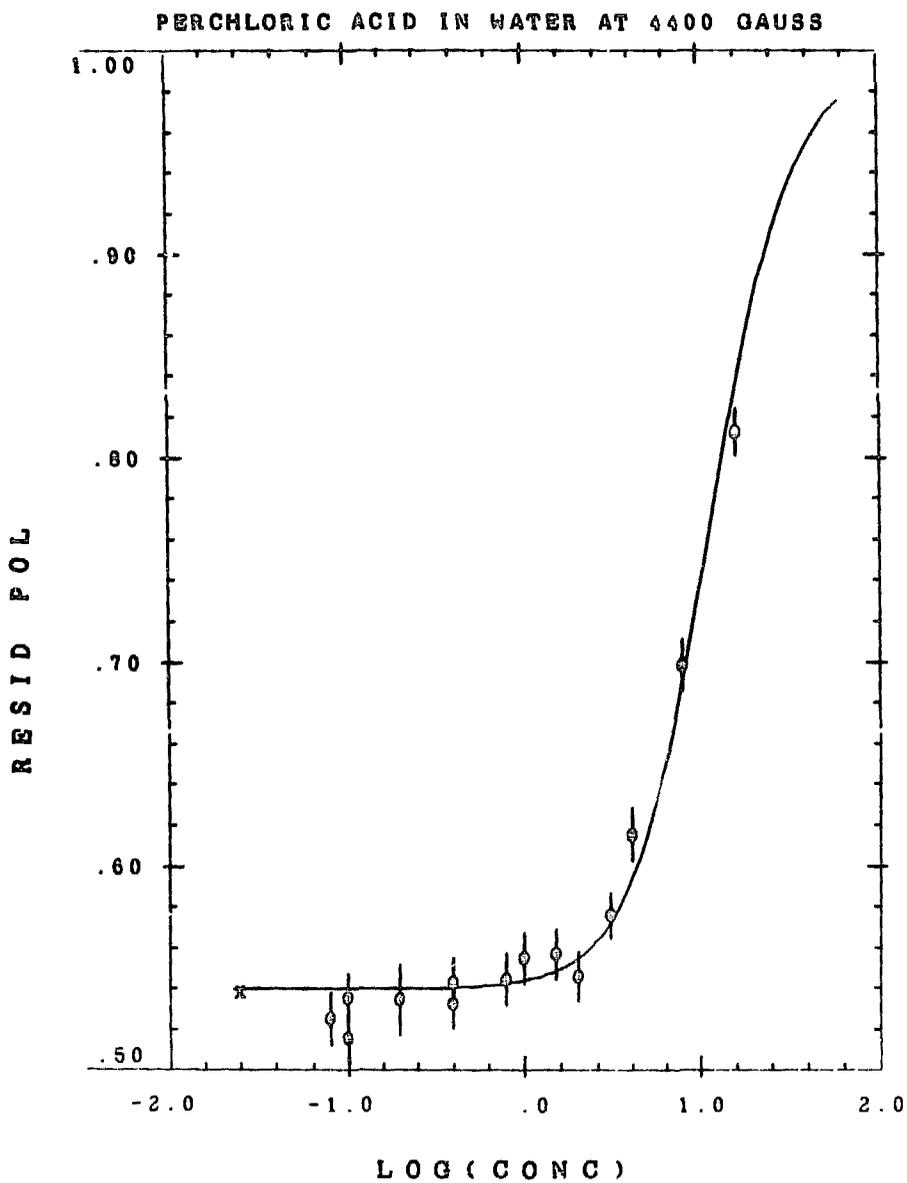
Figure 21 - Fe(ClO$_4$)$_3$ at 100 gauss: Fit Assuming

Proper Muonium Mechanism

FERRIC PERCHLORATE IN WATER AT 100 GAUSS
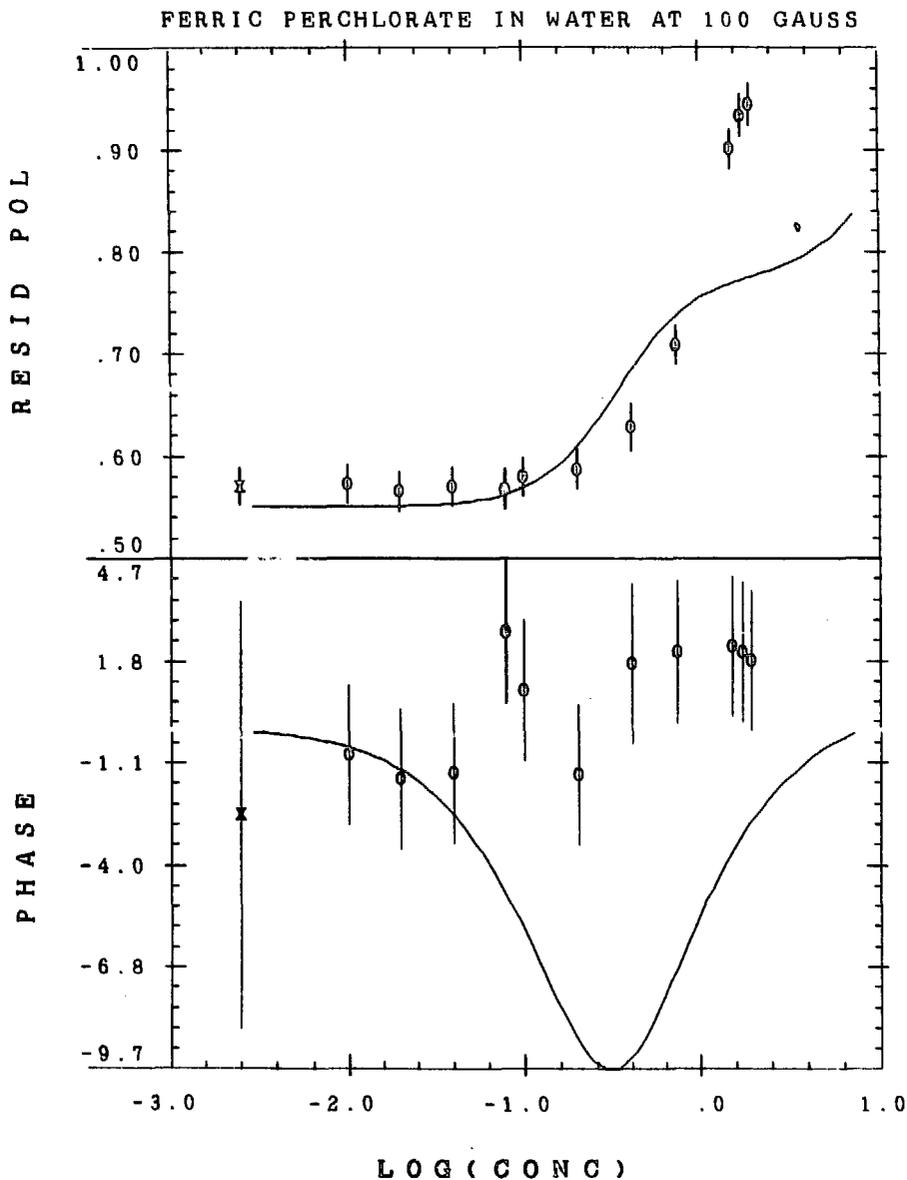
Figure 22 – Fe(ClO$_4$)$_3$ at 100 gauss: Fit Including

Radical Formation

FERRIC PERCHLORATE IN WATER AT 100 GAUSS

Figure 23 — H_2O_2 at 100 gauss: Fit Assuming

Proper Muonium Mechanism

HYDROGEN PEROXIDE IN WATER AT 100 GAUSS
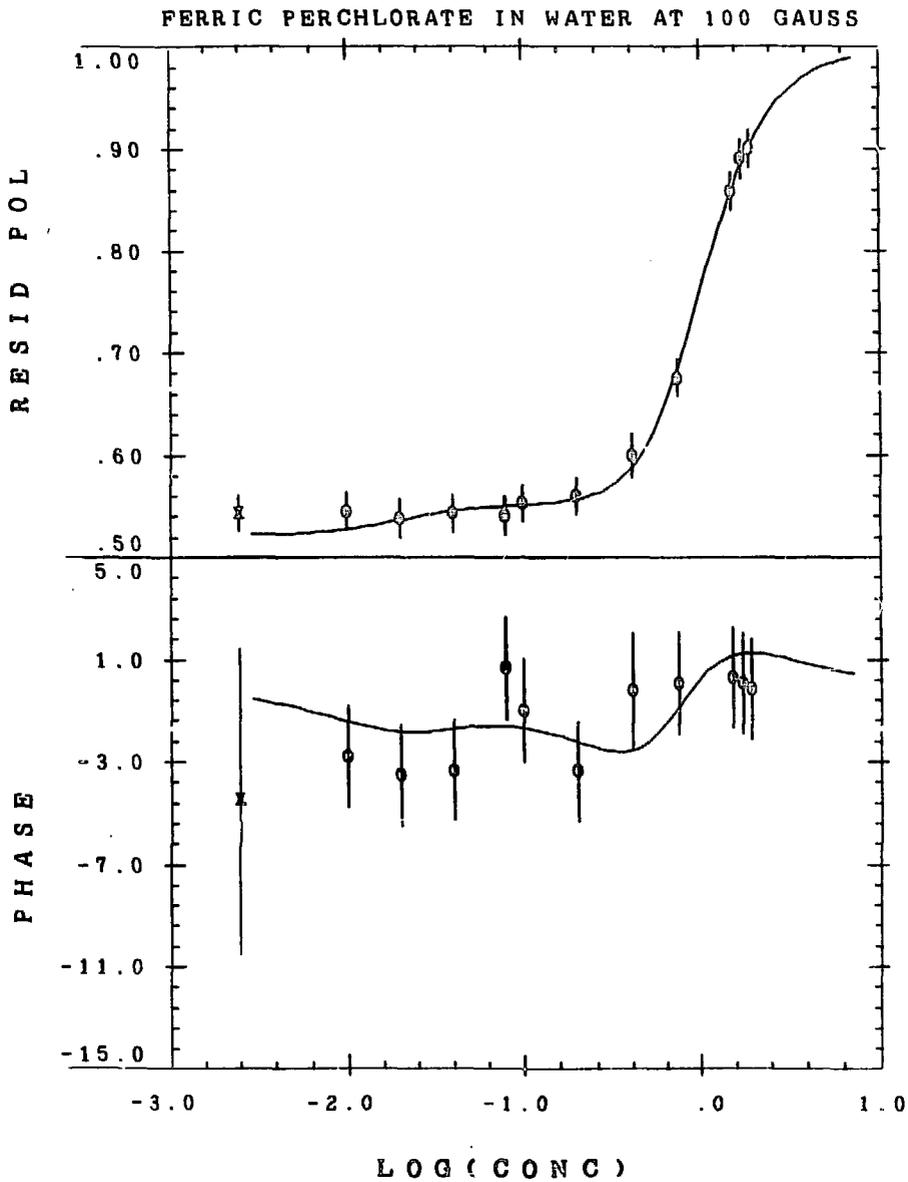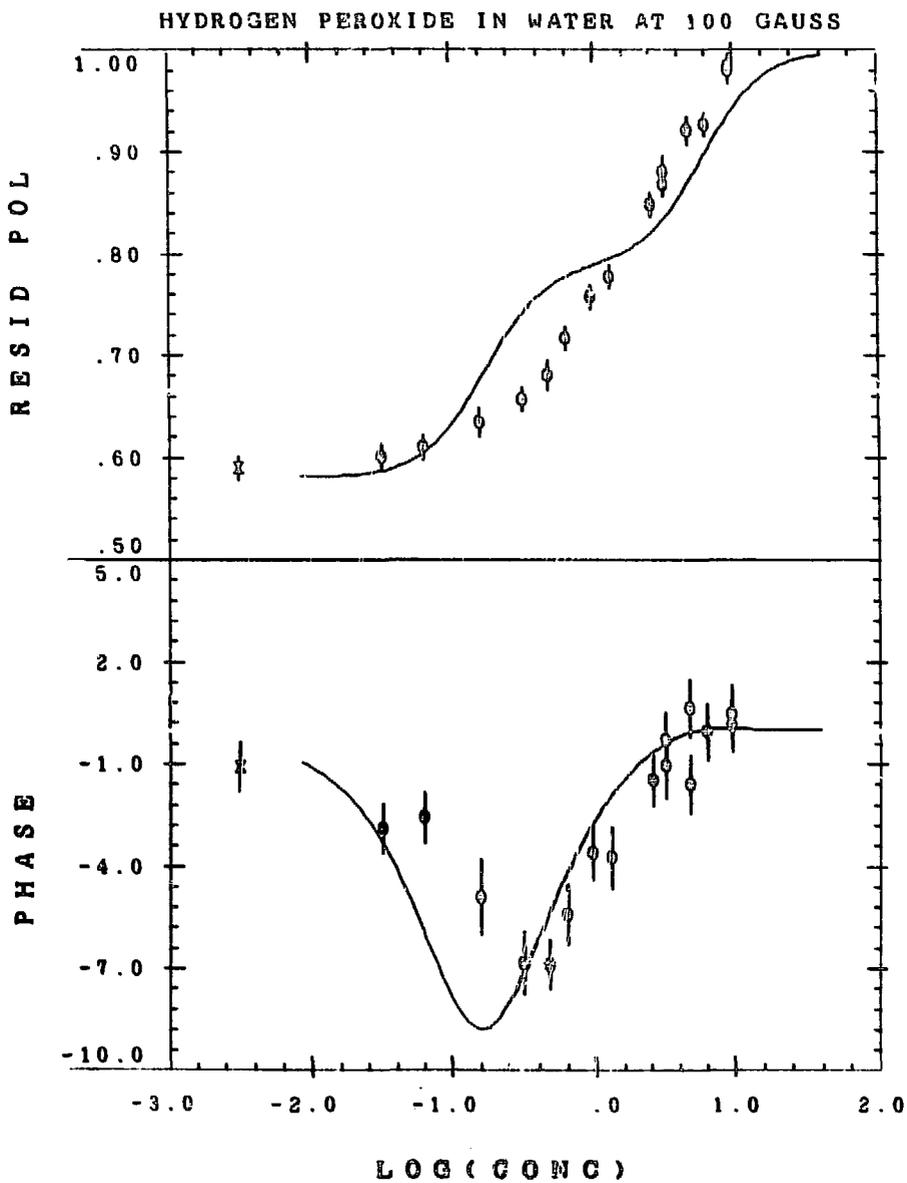
Figure 24   - H_2O_2 at 100 gauss: Fit Including

Radical Formation

HYDROGEN PEROXIDE IN WATER AT 100 GAUSS
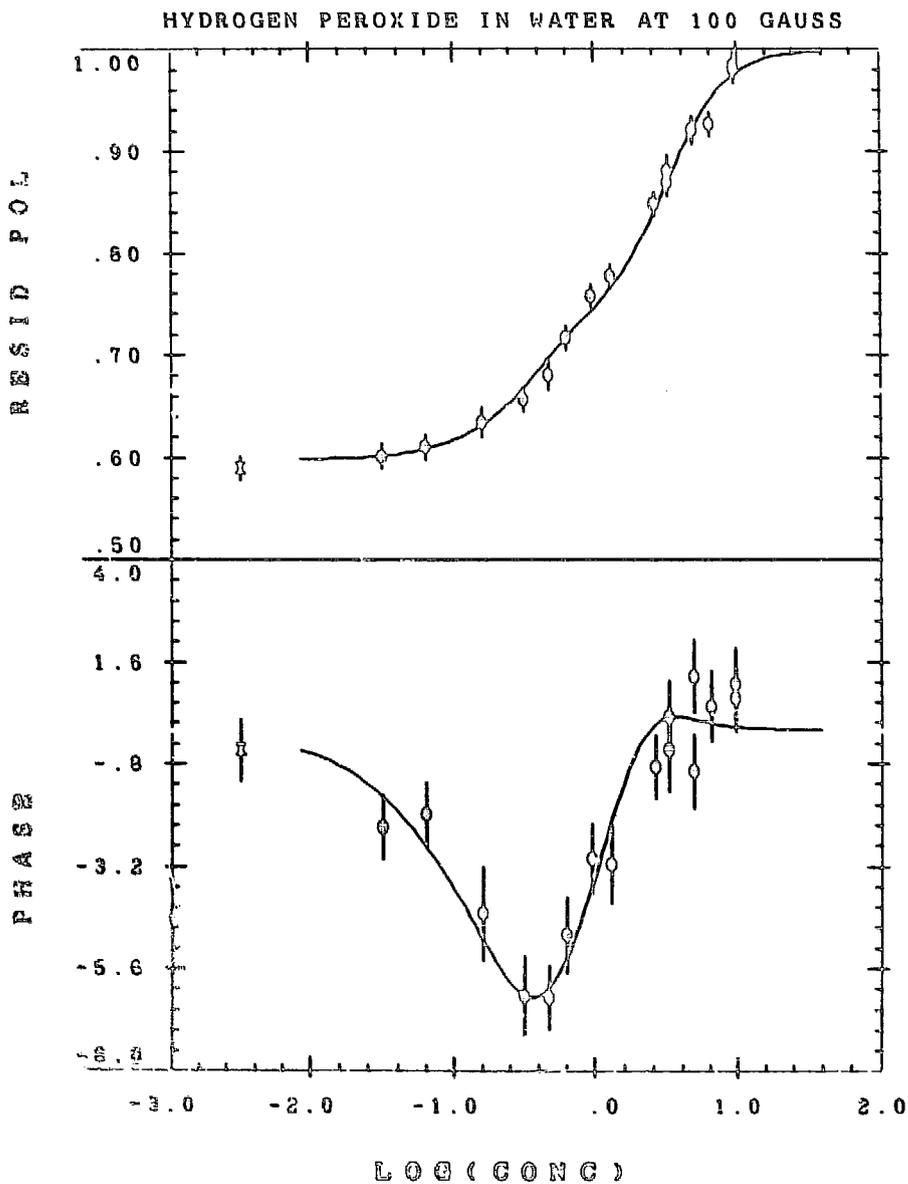
Table IV — BEST FITS TO GENERAL MECHANISM (WITH RADICALS)

REAGENT	SOLVENT	FIELD (gauss)	$\frac{\omega_r}{\omega_o}$ [a]	Λ_o	ϕ_o (deg)	h	RATE CONSTANTS $\times 10^{-10}$				$\frac{\chi^2}{deg.\ fr.}$
							k_{mxd}	k_{rxd}	(Z)	k_{mzr}	
H_2O_2	H_2O	100	$.083^b$	.26	10.82	.59	.24	.14	(X)	.83	~ 1
				±.01	±.5	±.01	±.1	±.05		±.2	
HNO_3	H_2O	100	$.125^c$	.277	15.76	.546	3.25	.111	(X)	13.0	~ 1.5
			±.05	±.01	±.75	±.02	±2.0	±.05		±7.0	
Br_2	C_6H_6	200	$.095^d$	.271	38	.134	9.5	.36	(S)	.125	~ 2
				±.005	±1	±.01	± 2	± .1		± .05	
I_2	C_6H_6	200	$.095^d$	.272	35	.128	5.8	.2	(S)	.054	~ 1
				±.02	±2	±.06	± 2	± .1		± .03	

Rate constants in liters/mole-sec.

Errors are approximate. Differences in ϕ_o are due to changes in counter geometry between series of runs.

[a]Values for ω_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   ).

[b]Radical involved presumed to be MuO·   [c]Radical species not identified.

[d]Radical involved presumed to be $C_6H_6Mu·$

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_o, 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 ($A = h\ A_o$) 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[27]; 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[27]
verify that the asymmetries observed in methanol, hexane, and
heptane 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[28]. The
high asymmetry observed in glycerol and in halide-substitued 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[12,17], 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[29].

Table V —   SURVEY OF SOLVENTS

SOLVENT NAME	FORMULA	A	ϕ (deg)	h	COMMENT
WATER	H_2O	.15 ± .01	15 ± 4	.55 ± .01	no "cold" reaction
METHANOL	CH_3OH	.13 ± .01	13 ± 3	.53 ± .01	"
BENZENE[a]	C_6H_6	.036±.005	33 ± 3	.13 ± .01	"cold" reaction to radical only
CARBON TETRACHLORIDE	CCl_4	.272±.010	14 ± 3	$\sim 1.0^b$	density may be a factor
GLYCEROL	$C_3H_8O_3$	.179±.010	13.5±3	$\sim.65^b$	"
HEXYNE	C_6H_{10}	.103±.010	6.5 ±4	$\sim.4^b$	very unsaturated
HEXENE	C_6H_{12}	.119±.010	9 ± 3	$\sim.45^b$	unsaturated
HEXANE	C_6H_{14}	.145±.010	10 ± 3	$\sim.55^b$	saturated
CYCLOHEXANE	C_6H_{12}	.160±.010	8 ± 3	$\sim.6^b$	"

Errors are approximate.

Magnetic field is 100 gauss unless otherwise specified.

[a] Magnetic field = 200 gauss.

[b] assuming no "cold" reaction.

Table VI —   SURVEY OF SOLVENTS: DATA FROM OTHER GROUPS

REF.	SOLVENT NAME	FORMULA	A	h	COMMENT
a	METHANOL	CH_3OH		$.61 \pm .03$	pure "hot"
a	HEXANE	C_6H_{14}		$.61 \pm .03$	pure "hot"
a	HEPTANE	C_7H_{16}		$.57 \pm .05$	pure "hot"
a	OCTANE	C_8H_{18}		$.52 \pm .05^{k}$	saturated
b	CHLOROFORM	$CHCl_3$	$.190\pm.009$	$.76 \pm .04^{km}$	
b	BROMOFORM	$CHBr_3$	$.22 \pm .01$	$.88 \pm .04^{km}$	field-indep.
b	BENZENE	C_6H_6	$.035\pm.007$	$.14 \pm .03^{m}$	field-indep.
b	HEXYNE	C_6H_{10}	$.115\pm.01$	$.46 \pm .04^{km}$	field-indep.
b	CYCLOHEXANE	C_6H_{12}	$.160\pm.009$	$.64 \pm .04^{km}$	saturated
b	OCTANE	C_8H_{18}	$.147\pm.008$	$.59 \pm .03^{km}$	saturated
b	POLYSTYRENE	(CH)	$.04 \pm .01$	$.16 \pm .04^{km}$	field-indep.
c	WATER	H_2O	$.141\pm.011$	$.62 \pm .05^{n}$	
c	CHLOROFORM	$CHCl_3$	$.184\pm.015$	$.80 \pm .07^{kn}$	
c	BENZENE	C_6H_6	$.046\pm.012$	$.21 \pm .05^{n}$	
c	PROPANE	C_3H_8	$.17 \pm .02$	$.74 \pm .09^{kn}$	saturated
c	PHENYL-CYCLOHEXANE	$C_{12}H_{16}$	$.084\pm.011$	$.37 \pm .05^{kn}$	
c	POLYSTYRENE	(CH)	$.07 \pm .01$	$.31 \pm .04^{kn}$	
c	POLYETHYLENE	(CH_2)	$.146\pm.012$	$.64 \pm .05^{kn}$	saturated

[k] Assuming no "cold" reaction of Mu into a diamagnetic compound.

[m] Using for A_o a value .25 (a typical but arbitrary choice).

[n] Using for A_o the value $A_C = .229$ observed in graphite.

[a] 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).

[b] From a survey of organic solvents: A.I. Babaev et. al.,
    Sov. Phys. JETP 23, 583 (1966).

[c] 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 $MnCl_2$ solutions[15]. 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.[2,30] 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.[31,32] 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,

$$Mu + H_2 \rightarrow MuH + H,$$

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

$$Mu + Br_2 \rightarrow MuBr + Br.$$
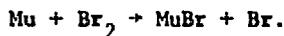
C. Muons in Solids

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[33] and depends on the orientation of the crystal in the external magnetic field.

More recently, Gurevich et. al.[34,35] 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[35] 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 μ decay[5], 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:

Bill Ross, Bob McCarthy, Bob Graven, and all

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.

The same goes for Vic Elisher and Bob Graven,

whose comments on gadjets are always worth saving,

and Ken Crowe, of course, who taught me much more

than just what the various gadjets were for.

Ken kicked my ass when it needed a kick,

and praise, when appropriate, came just as quick;

he guided my thinking, but not to excess,

away from the futile and towards the best.

To all of my colleagues in this current work:

without each the other we'd all go berserk.

Dick Johnson, Fred Gygax, Don Fleming, A. Schenck,

Jim E. and Don Austin, our new VISTA link.

To Pat Craig, whose debt we all have been in

each Owl Shift, from midnight until 8 AM.

And the highest of accolades must go to

our friends, Jimmy Vale and the Cyclotron crew.

The patience and help of my thesis committee,

who may not think this is particularly witty,

I thank nonetheless, and also the many

who taught me what physics I know (if any).

But most of all, I must thank my wife,

Suzanne, my colleague in the task of life;

for all that this thesis is symbolic of

wouldn't be worth much without her love.

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