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Mechanism for μ^+ Depolarization in Liquids -- Muonium Chemistry with Radical Formation*†

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ABSTRACT

The phenomenon of environment-dependent "fast" depolarization of stopped positive muons is described in terms of a theoretical model. The formalism is similar to that developed by Ivanter and Smilga to describe the "proper muonium mechanism," but has been adapted and expanded to include situations involving more than one strongly depolarizing influence (i. e., muonium and a molecular radical). For a plausible situation in dilute solutions with transverse applied magnetic field, the exact time dependence of the muon polarization is derived formally, with the "residual polarization" emerging as a limit. The result can be applied to the study of muonium chemistry.

INTRODUCTION

Thanks to the maximal nonconservation of parity in the weak interaction, it is possible to study the depolarization of stopped positive muons in matter. Polarized muons are produced from the decay of pions,[1] and can be collected in a beam and stopped in a target. They subsequently decay with a mean lifetime of 2.2 μsec, emitting a positron preferentially in the direction of their polarization.[1] By detecting the positrons, one can measure the magnitude and direction of the muon polarization as a function of the time of the decay. A typical experimental technique is to place the target in an external magnetic field perpendicular to the muon polarization, causing the muon spins to precess at their Larmor frequency. A positron detector is placed in the plane of precession. The probability per unit time of detecting a decay positron varies sinusoidally as the muon polarization sweeps past the detector. Repeatedly measuring the time from a muon's entry into the target until detection of its decay positron (if intercepted) is statistically equivalent to monitoring the time dependence of the polarization of an ensemble of initially polarized muons.

Since the earliest applications of this technique[2] it has been noted that the apparent initial magnitude of the muon polarization is strongly dependent upon the characteristics of the medium in which the muons are stopped. Recent results[3] indicate that the apparent initial direction of the polarization (and thus the initial phase of the precession) also varies with the medium. Since the muon beam enters the target with a well-defined polarization, these phenomena must be due to a "fast" depolarization mechanism which affects the muons briefly just after they stop, and then desists completely. Any continuing depolarization

would be reflected in the time dependence of the decay positron distribution, and could thus be observed directly. The practical limit of time resolution is typically on the order of 1 nsec, and most experiments cannot detect decay positrons until a few nsec after the muon stops. This sets the time scale for "fast" depolarization at a few nsec or less.

These phenomena were explained qualitatively by Nosov and Iakovleva[4] in terms of the "proper muonium mechanism": a positive muon captures an electron to form a hydrogen-like muonium (Mu) atom. The hyperfine interaction in muonium causes a rapid motion of the muon spin, which leads to depolarization of the muon. This process stops when the muonium reacts chemically to leave the muon in a diamagnetic compound. Thereafter, the muon will precess in the applied magnetic field at approximately the free-muon Larmor frequency, ω_μ,[5] allowing measurement of the residual polarization P_{res} by methods such as that described above.

The theory of the proper muonium mechanism was developed by Ivanter and Smilga[6-9] into an elegant formalism which predicts P_{res} in terms of the chemical and electrical properties of the medium.[10] Early experimental data on μ^+ depolarization in liquids[3] were in agreement with this mechanism.

However, more recent experimental results[13] are inconsistent with the proper muonium mechanism, and indicate that the complete mechanism is usually more complicated, at least in liquids. Before the predictions of the theory can be made to agree with the data, the following process must be incorporated into the formalism: muonium may react chemically to place the muon in a free radical (a paramagnetic

molecule), in which the hyperfine interaction between the muon and the unpaired electron causes further muon depolarization until the radical in turn reacts to leave the muon in a diamagnetic compound. The development given herein shows how the theory of the depolarizing mechanism can be reformulated to include this possibility. Although any muon environment can be treated similarly, specific emphasis is placed upon the mechanism in liquids, due to the experimental convenience of liquids and the immediate application to the study of the chemistry of muonium in liquids. An expression for P_{res} is derived which should adequately describe muon depolarization in dilute solutions.

DEPOLARIZING MECHANISM IN LIQUIDS

We consider a beam of polarized positive muons stopping in a target in a uniform magnetic field perpendicular to their polarization. To facilitate treatment of muonium chemistry, we assume that the target consists of a reagent "X" dissolved in a liquid solvent "S," in the "dilute limit" where the concentration [S] of solvent molecules is approximately independent of the concentration [X] of reagent.

Positive muons coming to rest have a high probability of forming Mu atoms while still energetic by stripping electrons from molecules of the medium.[14] These atoms thermalize within about 10^{-11} sec of their formation[15] unless "hot" chemical reactions take place during their epithermal collisions with molecules of the medium.[14] If a muon ends up in a diamagnetic molecule [D] through a hot reaction, its polarization is preserved. However, if it ends up in thermalized Mu or in a radical "R," its spin will oscillate and rotate rapidly under the combined influence of the hyperfine interaction and the external field until an

ordinary (thermal) chemical reaction places the muon in a diamagnetic environment. Since each muon "emerges" from Mu or R at a different time, the ensemble of muons is depolarized by "dephasing." In addition, since rotations due to precession of triplet muonium are all in one sense, the direction of P_{res} will be rotated slightly with respect to the beam polarization direction.

Figure 1 shows a representative selection of competing processes for muons in liquids. An expression for P_{res} will be derived using Fig. 1 as a model.

FORMULATION OF THE PROBLEM

The residual polarization P_{res} is what appears to have been the initial muon polarization if the observed precession of "free" muons is extrapolated back to zero time. Any muons still in muonium or radicals at observation times are considered in a practical sense to be completely depolarized, since they do not exhibit precession at the muon Larmor frequency. The fact that the muons eventually decay is ignored in this analysis, since the only muons of experimental interest are those that survive until observation times, long after "fast" depolarization has ceased.

The residual polarization has a direction as well as a magnitude; this is included formally by letting P_{res} be a complex quantity, the real part of which is the component of residual polarization along the original beam polarization direction $\hat{x}$, and the imaginary part of which is the component along the direction $\hat{y}$ perpendicular to both $\hat{x}$ and the magnetic field $\underset{\sim}{B} = B\,\hat{z}$. Variations of the phase of P_{res} with target medium are often more informative than the behavior of the magnitude.

Mathematically, the residual polarization is obtained from the exact time dependence P(t) of the whole muon ensemble by dividing out the Larmor precession factor $\exp[i\omega_\mu t]$ and letting the time go to infinity. When there is only one depolarizing influence, one can take advantage of this by using the Laplace transform technique to circumvent the solution of the equations of motion.[6] However, this method depends upon the assumption that the muon spin evolves in only one environment until it gets into a diamagnetic compound, and so cannot be used in the two-stage evolution involved here (Mu→R→D). It is necessary in general to obtain explicit expressions for all contributions to the muon polarization. The sum of these gives, in the limit described above, the residual polarization.

THE EQUATIONS OF MOTION

In either muonium or a simple radical, the spin system consists initially of an unpolarized electron and a polarized muon, interacting with each other via the hyperfine coupling and individually with the external field.

The density matrix of this spin system 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}:

$$\rho = \frac{1}{4}\left(1 + \underset{\sim}{P}^\mu \cdot \underset{\sim}{\sigma}^\mu + \underset{\sim}{P}^e \cdot \underset{\sim}{\sigma}^e + \sum_{ij} b_{ij}\sigma_i^\mu \sigma_j^e\right), \qquad (1)$$

where $\underset{\sim}{\sigma}^\mu$ and $\underset{\sim}{\sigma}^e$ are the spin operators for the muon and electron. The basic Hamiltonian for the isolated spin system is

$$H = \frac{1}{4}\hbar\omega_h(\underset{\sim}{\sigma}^\mu \cdot \underset{\sim}{\sigma}^e) + \frac{1}{2}\hbar\underset{\sim}{\omega}^\mu \cdot \underset{\sim}{\sigma}^\mu + \frac{1}{2}\hbar\,\underset{\sim}{\omega}^e \cdot \underset{\sim}{\sigma}^e, \qquad (2)$$

where ω_h is the hyperfine frequency (for muonium, $\omega_h = \omega_0 = 2.8\times 10^{10}$ rad/sec) and $\underset{\sim}{\omega}^{\mu}$ and $\underset{\sim}{\omega}^{e}$ are the muon and electron Larmor frequencies, given by $\underset{\sim}{\omega}^{e} = g_e e\underset{\sim}{B}/2m_e c$ and $\underset{\sim}{\omega}^{\mu} = -\zeta\,\underset{\sim}{\omega}^{e}$, where $\zeta = m_e/m_\mu = 1/206.77$ if the difference between g_e and g_μ is neglected.

An additional interaction V is included which describes the interaction of the electron spin with the outside world; V is analogous to relaxation mechanisms in ESR phenomena, producing a relaxation rate ν of the electron spin. Formally, the resultant equation of motion for the density matrix (in the Schrödinger picture) is the Wangsness-Bloch equation:[16]

$$\dot{\rho} = -\frac{i}{\hbar}[H,\rho] - \frac{\pi}{\hbar}\,\mathrm{Tr}_b[\overline{V},[\overline{V},\rho\rho_b]]\,, \tag{3}$$

where 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 $\overline{V}$ is the part of the operator V which is diagonal in the energy.

Writing out commutators and equating coefficients of the orthogonal operators $\{1, \sigma_i^{\mu}, \sigma_j^{e}, \sigma_m^{\mu}\sigma_n^{e}\}$ on the left and right sides of equation (3) gives the equations of motion of the parameters of the density matrix:

$$\dot{P}_k^{\mu} = \Sigma_{ij}\,\epsilon_{ijk}\,\left(-\frac{1}{2}\omega_h b_{ij} - P_i^{\mu}\omega_j^{\mu}\right), \tag{4a}$$

$$\dot{P}_k^{e} = \Sigma_{ij}\,\epsilon_{ijk}\left(+\frac{1}{2}\omega_h b_{ij} - P_i^{e}\omega_j^{e}\right) - 2\nu P_k^{e}, \tag{4b}$$

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

$$+\,\omega_n^{\mu}\,\epsilon_{mni}\,b_{mj}) - 2\nu\, b_{ij}\,. \tag{4c}$$

These equations separate 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 subset. The $\hat{z}$ direction is taken to be along the field, and the $\hat{x}$ direction is the initial muon polarization direction.

The transverse-field case of equations (4) can be written compactly as

$$\dot{\underset{\sim}{\Pi}} = i A \underset{\sim}{\Pi} , \tag{5}$$

where $\underset{\sim}{\Pi}$ is the complex 4-component vector (analogous to that defined by Ivanter and Smilga[6])

$$\underset{\sim}{\Pi} \equiv \begin{pmatrix} P_x^\mu + i P_y^\mu \\ P_x^e + i P_y^e \\ b_{xz} + i b_{yz} \\ b_{zx} + i b_{zy} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \text{at } t = 0 \tag{6}$$

and A is the 4×4 matrix

$$A = \frac{\omega_h}{2} \begin{pmatrix} -2\zeta x & 0 & 1 & -1 \\ 0 & i\gamma + 2x & -1 & 1 \\ 1 & -1 & i\gamma - 2\zeta x & 0 \\ -1 & 1 & 0 & i\gamma + 2x \end{pmatrix}, \tag{7}$$

where $\gamma = 4\nu/\omega_h$ and $x = |\underset{\sim}{\omega}^e| / \omega_h = B/B_h$; B_h is the effective hyperfine field, and may be thought of as the effective field at the electron due to the muon's magnetic dipole. For muonium, $B_h = B_0 = 1588$ G; for radicals, with weaker hyperfine couplings, $B_h = B_r$ will be much smaller.

The equations of motion (5) apply to both the muonium and radical environments. For muonium, $A = A_m$, where A_m is given by (7) with $\omega_h = \omega_0$, $B_h = B_0$, and $\nu = \nu_m$, the relaxation rate of the electron in

muonium through interactions with the medium. Similarly, in the radical $A = A_r$, given by (7) with $\omega_h = \omega_r$, $B_h = B_r$, and $\nu = \nu_r$.

In all the subsequent discussion, it is assumed that ν_m and ν_r are negligibly small compared with ω_0 and ω_r, respectively, and also small compared to the precession frequency ω_{Mu} of triplet muonium. Thus electron relaxation in liquids is presumed to be too slow to noticeably affect the residual polarization. ESR data on hydrogen atoms in solution support this assumption.[17] However, ν is retained in the formalism to maintain generality. Although some simplification would result from the complete omission of ν, this model may later find applications in situations where it is not negligible. Some radicals, for instance, may be expected to have a depolarizing effect on the unpaired electron; and the mechanism for muon depolarization in solids is dramatically affected by electron relaxation.[4]

FORM OF THE ENSEMBLE POLARIZATION

The matrix A can be diagonalized to form the matrix D with eigenvalues λ_i. This is facilitated when $\nu = 0$, since A is then a real symmetric matrix. Let M and R be the orthogonal matrices which diagonalize A_m and A_r, respectively:

$$M^{-1} A_m M = D^m \qquad \text{and} \qquad R^{-1} A_r R = D^r \tag{8}$$

so that

$$D^m_{ij} = \delta_{ij} \lambda^m_i \quad \text{and} \quad D^r_{ij} = \delta_{ij} \lambda^r_i \ . \tag{9}$$

In terms of these, the finite time evolution operators in the two important environments are

$$U^m(t, t') = M \exp[\, iD^m(t - t')] \ M^{-1} \tag{10}$$

and

$$U^r(t,t') = R \exp[iD^r(t-t')] R^{-1}, \tag{11}$$

so that $\underset{\sim}{\Pi}(t) = U^m(t,t')\underset{\sim}{\Pi}(t')$ in the muonium environment and $\underset{\sim}{\Pi}(t) = U^r(t,t')\underset{\sim}{\Pi}(t')$ in the radical environment. The evolution operator for muons in a diamagnetic environment is given by

$$U^d_{ij}(t,t') = \delta_{ij}\,\delta_{i1} \exp[i\omega_\mu(t-t')]. \tag{12}$$

The polarization at any time t is the sum of contributions from all possible sequences of events. If "q" is a complete label for the fate of a given fraction p(q) of the muon ensemble (including "internal" times of transition from one environment to the next) and $U_q(t,0)$ is the time evolution operator for that fraction, the contribution $P(q,t)$ to the ensemble muon polarization $P(t)$ from muons experiencing the fate "q" is just p(q) times the first component of the evolved vector $\underset{\sim}{\Pi}(t)$:

$$P(q,t) = p(q) \cdot [U_q(t,0)\underset{\sim}{\Pi}(0)]_1. \tag{13}$$

If all possible fates "q_i" are taken into account, the time dependence of the entire ensemble is

$$P(t) = \Sigma_i P(q_i,t). \tag{14}$$

This is a formal sum, and may include integrals over unobservable internal times.

In general $U_q(t,0)$ is a time-ordered product of evolution operators for the successive environments of the muons experiencing the fate "q." For example, consider the case "q_7": muonium thermalizes and reacts at time t_1 to form a radical, which subsequently reacts at time t_2 to form a diamagnetic compound. The overall time evolution operator for this process is $U_{q_7}(t,0) = U^d(t,t_2)\,U^r(t_2,t_1)\,U^m(t_1,0)$. Note the

assumption that muon and electron polarizations do not change discontinuously in the transition from the free muonium environment to the radical environment. The muonium electron is presumed to simply become less localized, taking up the role of the unpaired electron in the radical.

The form of p(q), the probability of a given sequence of events "$\underset{\sim}{q}$," is also most easily shown by example: consider the case "q_1," in which the muonium thermalizes and has still not reacted at the observation time t. The probability that muonium thermalizes without reacting epithermally is (1 - h - r), and if $\Lambda_m = 1/\tau_m$ is the rate at which muonium atoms react chemically, the probability that muonium is still free at time t is just $\exp[-t/\tau_m]$. Thus $p(q_1) = (1 - h - r)\exp[-t/\tau_m]$. The time τ_m is referred to as the "chemical lifetime" of a free muonium atom. The rate Λ_m is the sum of the rates at which different chemical reactions remove muonium from solution. For instance, if the only such reaction is $Mu + X \rightarrow D$ (rate Λ_{mxd}), then $\Lambda_m = \Lambda_{mxd}$. The rate Λ_{mxd} is proportional to the concentration [X] of the reagent; the constant of proportionality k_{mxd} is called the chemical rate constant.[18] Similar rate constants apply for all the reactions in question, as listed in Table I. Using this formalism one can easily write down $p(q_i)$ for all the q_i to be considered.

RESULTS IN LIQUIDS

Time Dependence of the Muon Polarization

Now $P(t)$ and P_{res} can be derived for the situation described in Fig. 1. The various contributions to $P(t)$ are as follows:

1) STILL-FREE MUONIUM: "q_1" stands for evolution in free Mu from $t = 0$ until the present time t. Since $U_{q_1}(t,0) = U^m(t,0)$,

$$\{U_{q_1}(t,0)\underset{\sim}{\Pi}(0)\}_1 = \{U^m(t,0)\,\underset{\sim}{\Pi}(0)\}_1$$

$$= \{M \exp[iD^m t]\, M^{-1}\,\underset{\sim}{\Pi}(0)\}_1 .$$

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

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

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

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

$$F_k \equiv M_{1k}\,[M^{-1}]_{k1} . \tag{15}$$

Combining this with

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

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

$$= \exp[i\omega_\mu t]\ (1 - h - r)\,\Sigma_k\, F_k \exp[\alpha_k t], \tag{16}$$

where

$$\alpha_k \equiv -1/\tau_m + i(\lambda_k^m - \omega_\mu). \tag{17}$$

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

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

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

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

$$P(q_2,t) = h \exp[i\omega_\mu t]. \tag{18}$$

3) MUONIUM → DIAMAGNETIC: "q_3" stands for evolution in free Mu until time t_1 ($\pm\, dt_1/2$), 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

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

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

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

Summation over all possible values of t_1 gives $P_3(t)$, the overall contribution from the generic class "q_3":

$$P_3(t) \equiv \sum_{t_1=0}^{t} P(q_3,t) \equiv \exp[i\omega_\mu t]\ \frac{(1-h-r)}{\tau_{md}}\, \Sigma_k F_k \int_{t_1=0}^{t} \times \exp[\alpha_k t_1]\, dt_1$$

$$= \exp[i\omega_\mu t]\ \frac{(1-h-r)}{\tau_{md}}\, \Sigma_k \frac{F_k}{\alpha_k} (\exp[\alpha_k t] - 1). \tag{19}$$

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.

$$P(q_4, t) = \exp[i\omega_\mu t]\ r\ \Sigma_k G_k \exp[\beta_k t]\,, \tag{20}$$

where

$$G_k \equiv R_{1k}[R^{-1}]_{k1} \tag{21}$$

and

$$\beta_k \equiv -1/\tau_{rd} + i(\lambda_k^r - \omega_\mu). \tag{22}$$

5) HOT RADICAL → DIAMAGNETIC: "q_5" stands for epithermal entry into R at $t \simeq 0$, followed by evolution in R until time $t_1(\pm dt_1/2)$ when R combines chemically to form D, and subsequent evolution in D This case is strictly analogous to case (3), except that the radical plays the role of muonium in (3). The overall contribution from the generic class "q_5" is

$$P_5(t) = \exp[i\omega_\mu t]\ \frac{r}{\tau_{rd}}\ \Sigma_k\ \frac{G_k}{\beta_k}\ (\exp[\beta_k t] - 1). \tag{23}$$

6) STILL-FREE CHEMICAL RADICAL: "q_6" stands for evolution in Mu until time $t_1(\pm dt_1/2)$, chemical reaction at time t_1 to form R, and subsequent evolution in R. Here

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

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

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

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

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

where

$$W_{ik} \equiv \Sigma_j R_{1i} [R^{-1}]_{ij} M_{jk} [M^{-1}]_{k1} . \tag{24}$$

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

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

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

The overall contribution from the generic class "q_6" is

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

$$\times \Sigma_{ik} \frac{W_{ik}}{(\alpha_k - \beta_i)} (\exp[\alpha_k t] - \exp[\beta_i t]) . \tag{25}$$

7) MUONIUM → RADICAL → DIAMAGNETIC: "q_7" stands for evolution until time $t_1(\pm dt_1/2)$ in muonium, reaction at time t_1 to form R, evolution in R until time $t_2(\pm dt_2/2)$, reaction at time t_2 to form D, and subsequent evolution in D.

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

$$\{U_{q_7}(t, 0) \Pi(0)\}_1 = \exp[i\omega_\mu(t-t_2)]$$

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

Combining this with

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

$$\times \frac{dt_1}{\tau_{mr}} \exp[-t_1/\tau_m]$$

gives

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

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

The overall contribution from muons experiencing fates of the type "q_7" with all possible values of t_1 and t_2 is then

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

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

$$\times \Sigma_{ik} \frac{W_{ik}}{(\alpha_k - \beta_i)} \left(\frac{1}{\alpha_k} \{\exp[\alpha_k t] - 1\} - \frac{1}{\beta_i} \{\exp[\beta_i t] - 1\} \right) . \qquad (26)$$

The sum of all the preceding contributions is the polarization of the entire muon ensemble at an arbitrary time t:

$$P(t) = P(q_1, t) + P(q_2, t) + P_3(t) + P(q_4, t) + P_5(t) + P_6(t) + P_7(t) . \qquad (27)$$

This is the exact time dependence of the muon polarization, involving no approximations other than the assumption that Fig. 1 is a complete picture of the possible fates of a muon.

The Residual Polarization

All the terms in P(t) are conveniently arranged in the form $\exp[i\omega_\mu t]\ P'(t)$, facilitating the extraction of 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. Thus only the terms $P(q_2, t)$, $P_3(t)$, $P_5(t)$, and $P_7(t)$ contribute to P_{res}. The result is

$$P_{res} = \lim_{t \to \infty} \exp[-i\omega_\mu t]\,\{P(q_2, t) + P_3(t) + P_5(t) + P_7(t)\}\,. \tag{28}$$

In most circumstances equation (28) reduces to a rather simple explicit form. If the rate ν of relaxation of the electron is not too rapid (as is the case in liquids[17]),

$$\mathrm{Im}\,\lambda_k^m > -1/\tau_m \quad \text{and} \quad \mathrm{Im}\,\lambda_k^r > -1/\tau_{rd}, \tag{29}$$

in which case the following limits hold:

$$\lim_{t \to \infty} \exp[\alpha_k t] = \lim_{t \to \infty} \exp[\beta_k t] = 0\,. \tag{30}$$

Thus if the criteria (29) are met, the residual polarization from (27) can be written compactly as

$$P_{res} = h - \frac{(1 - h - r)}{\tau_{md}}\,\Sigma_k\,\frac{F_k}{\alpha_k} - \frac{r}{\tau_{rd}}\,\Sigma_k\,\frac{G_k}{\beta_k} + \frac{(1 - h - r)}{\tau_{mr}\,\tau_{rd}}\,\Sigma_{ik}\,\frac{W_{ik}}{\alpha_k\,\beta_i}\,. \tag{31}$$

APPLICATION

Equation (31) can be used to predict the magnitude and phase of P_{res} in terms of the following parameters: the applied field strength B, the electron relaxation rates for muonium (ν_m) and the radical (ν_r), the ratio ω_r/ω_0 of the hyperfine frequency in the radical to that in muonium, the epithermal reaction efficiencies h and r, the various chemical rate constants listed in Table I, and the concentrations of reagent and solvent, [X] and [S].

In liquids, it is usually convenient to vary [X] alone, obtaining curves of $P_{res}([X])$ which can be fitted to the theory (31) to obtain the most probable values for the other parameters. Such surveys have been performed on a variety of solutions.[13] Only in very few cases do the data agree with the "proper" muonium mechanism (without radical formation); more often, good fits can only be obtained by assuming that radicals play a significant role in the depolarizing process. A discussion of experimental results will be presented separately.

EXAMPLES

In order to understand the qualitative differences between some of the different curves of $P_{res}([X])$ predicted by equation (31), it is helpful to have a conceptual picture of the depolarizing mechanism. To this end, consider first the evolution of the muon polarization in free muonium in a 100-G transverse field, in the absence of relaxation or chemical reactions.

Figure 2 shows the time evolution of the projection of the muon polarization onto the initial polarization direction. The rapid oscillations have a characteristic frequency ω_0, which can be easily visualized if we imagine the situation in zero field: Mu is formed from initially

polarized muons and initially unpolarized electrons. If the axis of quantization is along the initial muon polarization direction, 50% of the initial muonium ensemble is in the state $|\uparrow\uparrow\rangle$, and 50% is in the state $|\uparrow\downarrow\rangle$ where the first arrow denotes the direction of the muon spin and the second the direction of the electron spin. The first state ($|\uparrow\uparrow\rangle = |1,+1\rangle$ in the basis $|F,M\rangle$) is an eigenstate and therefore stationary, but the state $|\uparrow\downarrow\rangle = (|1,0\rangle + |0,0\rangle)/\sqrt{2}$ is a superposition of two zero-field eigenstates separated in energy by $\hbar\omega_0$. Consequently the relative phase between $|1,0\rangle$ and $|0,0\rangle$ rotates at angular frequency ω_0, and the second half of the ensemble oscillates between $|\uparrow\downarrow\rangle$ and $(|1,0\rangle - |0,0\rangle)/\sqrt{2} = |\downarrow\uparrow\rangle$, in which the muon spin is reversed. Thus the muon polarization in the second half of the ensemble oscillates between +1 and -1. Combined with the constant polarization +1 for the first half of the ensemble, this produces a net ensemble muon polarization which oscillates between +1 and 0 at frequency ω_0.

With the application of a weak external magnetic field $B << B_0$ (the effective hyperfine field of 1588 G), the polarized triplet state $|\uparrow\uparrow\rangle$ precesses (in a sense opposite to that of the free muon) at the muonium Larmor frequency,

$$\omega_{Mu} = \frac{1}{2}\left(\frac{\mu_e - \mu_\mu}{\mu_\mu}\right)\omega_\mu = 102.88\,\omega_\mu .$$

Thus the motion depicted in Fig. 2 consists approximately of a rapid "hyperfine oscillation" with a period of 0.2441 nsec, superimposed upon a comparatively slow "muonium precession" whose period depends upon the field, i.e., 7.4 nsec at 100 G. In low field, the hyperfine oscillations do not involve rotation, but only a modulation of the polarization. The

muonium precession, on the other hand, is a pure rotation in the plane perpendicular to the field, changing the phase of the polarization. This simple conceptual model breaks down in stronger fields, of course, and is not strictly valid in any nonzero field, since $|1,0\rangle$ and $|0,0\rangle$ are eigenstates only in zero field.

Now suppose that muonium forms at t = 0 and evolves as in Fig. 2 until reacting chemically to form a diamagnetic compound. Once it has reacted, its polarization no longer changes (on this time scale). This is the situation in the proper muonium mechanism without hot chemistry. If the mean time τ for which muonium evolves before reacting is much shorter than τ_1 (shown in Fig. 2), the muon polarization is essentially unchanged and there is no depolarization ($P_{res} \approx 1$). If $\tau \approx \tau_1$, muons will "drop out" of the muonium environment at various times averaging to τ_1, and the average polarization P_{res} of the resultant ensemble drops to approximately 1/2. This situation persists for $\tau_1 \lesssim \tau \lesssim \tau_2$. When $\tau > \tau_3$, however, muonium precession causes the average projected polarization to oscillate between +1/2 and -1/2, so that muons have equal chances of dropping out of muonium with positive and negative polarizations, and P_{res} drops from 1/2 to 0. It is also in the region $\tau \approx \tau_2$ that P_{res} begins to be rotated due to muonium precession. This is manifested in the variation of the phase of P_{res} with τ.

Figure 3 shows the dependence of the magnitude and direction (phase) of P_{res} upon the mean chemical lifetime τ of muonium. The dashed curves represent the situation described above, with the times τ_1, τ_2, and τ_3 indicated. Note the "plateau" in the region $\tau_1 \lesssim \tau \lesssim \tau_2$,

where $|P_{res}| \approx 1/2$. The rotation of P_{res} in the region $\tau \gtrsim \tau_2$ is also apparent from the dependence of the phase upon τ.

In general, we must also include the effects of hot chemistry. If a fraction h of the muons are removed from muonium at essentially t = 0, we must multiply our previous value for P_{res} by (1 - h) and add it to a constant unrotated vector of length h. The solid curves in Fig. 3 show $P_{res}(\tau)$ for h = 0.5 (a typical value). Here the phase returns to zero at large τ, because the length of the rotated contribution to P_{res} shrinks to zero.

Recalling that $\tau = (k_{mxd}[X])^{-1}$ in the proper muonium mechanism, and assuming that no other parameters vary with [X], we can plot P_{res} as a function of [X] for a specified k_{mxd}. Figure 4 shows the magnitude and phase of P_{res} as a function of [X] for $k_{mxd} = 10^{10}$ liters/mole-sec and h = 0.5. The solid curves are for 100-G external field, and correspond to the solid curves in Fig. 3. The dotted curves are for 10-G external field, and show that slowing down the muonium precession broadens the plateau, as expected. The dashed curves are for $B = B_0 = 1588$ G, where the munoium precession frequency becomes comparable to the hyperfine frequency and the plateau disappears. Here the amplitude of the phase dip is also decreased, and there is a slight positive deviation for very short reaction times. For even higher fields, this phenomenon becomes more pronounced, until for $B \gtrsim 5000$ G the phase curve is almost flat.

Radicals, with substantially smaller hyperfine frequencies than muonium, produce the plateau effect at proportionally lower fields, which are usually experimentally impractical. Thus a field which is "low" for

muonium (say 100 G) may be "high" for the radical, facilitating an experimental test for the presence of radicals. Figure 5 shows several examples of physical interest. All are for B = 100 G, h = 0.5, and $r = \nu_m = \nu_r = 0$. The solid curves show the proper muonium mechanism (no radicals) with $k_{mxd} = 10^{10}$ liters/mole-sec and all other rate constants zero. These are the same as the solid curves in Fig. 4. The other sets of curves show situations involving a radical with $\omega_r = 0.1\ \omega_0$. For the dashed curves, the radical is formed from reaction of Mu with X, and the only nonzero rate constants are $k_{mxd} = 10^{10}$ liters/mole-sec, $k_{mxr} = 10^{11}$ liters/mole-sec, and $k_{rxd} = 10^{10}$ liters/mole-sec. For the dotted curves, the radical is formed from reaction of Mu with the solvent, and the nonzero rate constants are $k_{mxd} = 10^{10}$ liters/mole-sec, $[S]\,k_{msr} = 10^{11}\ \mathrm{sec}^{-1}$, and $k_{rxd} = 10^{10}$ liters/mole-sec. The loss of the plateau effect with the addition of radicals is apparent in both cases.

It should be noted that while other phenomena could cause a curve of $|P_{res}|$ with no plateau in low field, they would also destroy the phase deviation, which persists in the situations depicted in Fig. 5. For instance, a large value for ν_m would disrupt the coherent precession of the muonium system, thereby destroying the plateau, but necessarily eliminating the phase deviation at the same time. Similarly, a mechanism consisting only of a dependence of the hot fraction h upon [X] could cause a plateau-free "repolarization" but could not result in any phase deviation. Thus the observation of phase deviations without concomitant plateaus in $|P_{res}|$ should serve as a specific experimental test for the presence of radicals in the depolarization mechanism.

FOOTNOTES AND REFERENCES

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

†Excerpted from J. H. Brewer (Ph. D. thesis), Lawrence Berkeley Laboratory Report LBL-950 (1972).

‡Research fellow from SIN, Villigen, Switzerland.

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$[Mu] \leq 1$, $[X]$ is constant, and the problem reduces to the first-order equation $-d[Mu]/dt = \Lambda_{mxd}[Mu]$, where $\Lambda_{mxd} = k_{mxd}[X]$.

Table I. Parameters of the theory

$[X]$ = concentration of reagent "X"

$[S]$ = concentration of pure solvent "S" (density/molecular 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 $Mu + X \rightarrow D$

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

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

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

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

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

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

FIGURE CAPTIONS

Fig. 1. Flow chart model of depolarization mechanism in liquids.

Fig. 2. Evolution of muon polarization in free muonium in 100-G transverse field. P_x^{μ} = projection of μ^+ polarization along original polarization direction.

Fig. 3. Proper muonium mechanism in 100-G transverse field. Dependence of magnitude and phase of residual polarization upon chemical lifetime τ of free muonium. Positive phase is defined as being in the direction of μ^+ precession. Dashed curves -- no hot chemistry. Solid curves -- hot fraction h = 0.5.

Fig. 4. Proper muonium mechanism in several transverse fields. Dependence of P_{res} upon reagent concentration [X] when $\tau^{-1} = k[X]$ with $k = 10^{10}$ liters/mole-sec. Hot fraction h = 0.5. Solid curves -- B = 100 G. Dotted curves -- B = 10 G. Dashed curves -- $B = B_0 = 1588$ G.

Fig. 5. Various mechanisms in 100-G transverse field. Effect of radicals on $P_{res}([X])$. Hot fraction h = 0.5, $\omega_r = 0.1\,\omega_0$, $r = \nu_m = \nu_r = 0$, and $k_{mxd} = k_{rxd} = 10^{10}$ liters/mole-sec in each case. Solid curves -- proper muonium mechanism (no radical formation). Dotted curves -- $[S]\,k_{msr} = 10^{11}$ sec^{-1}. Dashed curves -- $k_{mxr} = 10^{11}$ liters/mole-sec.

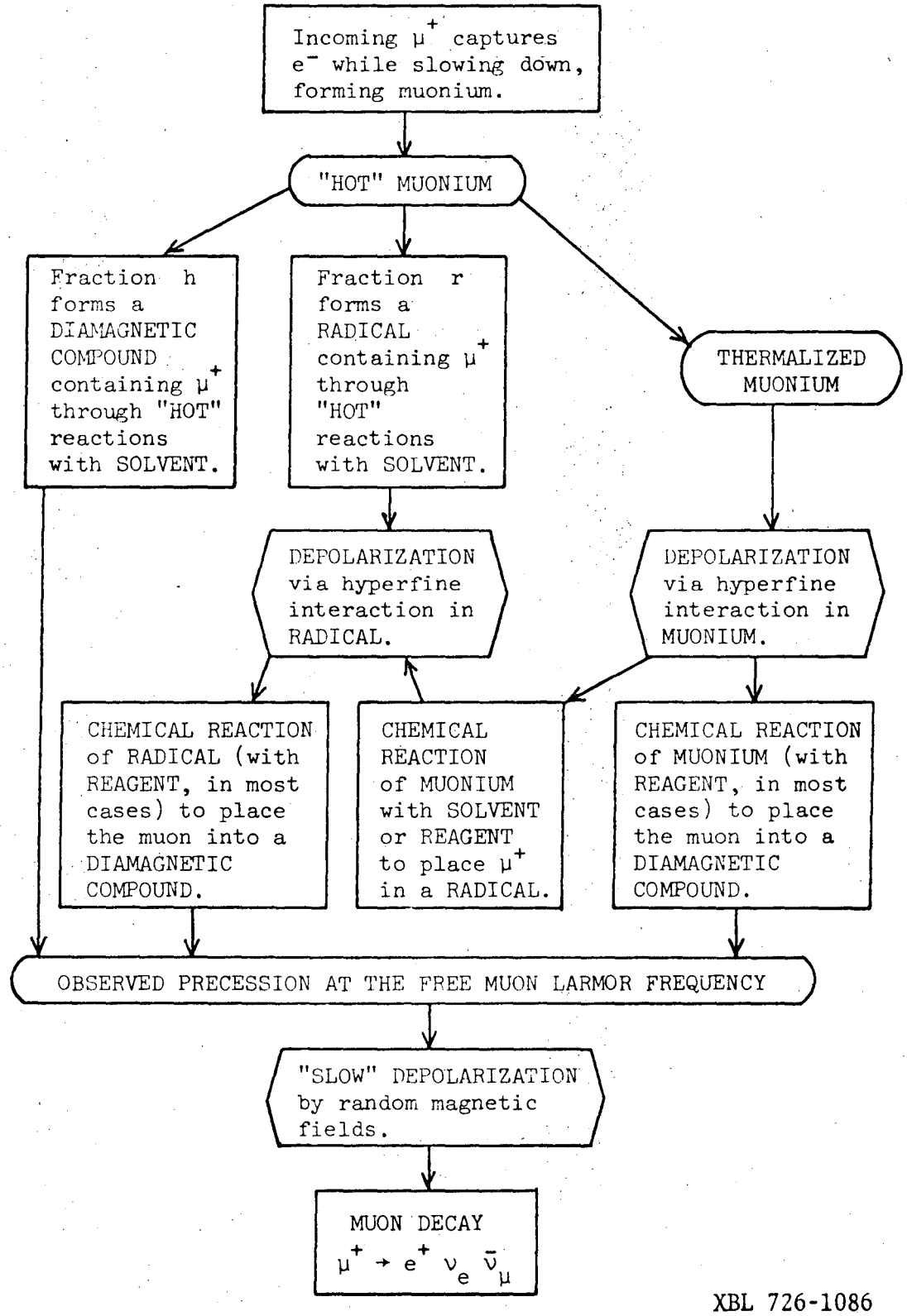

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Fig. 1

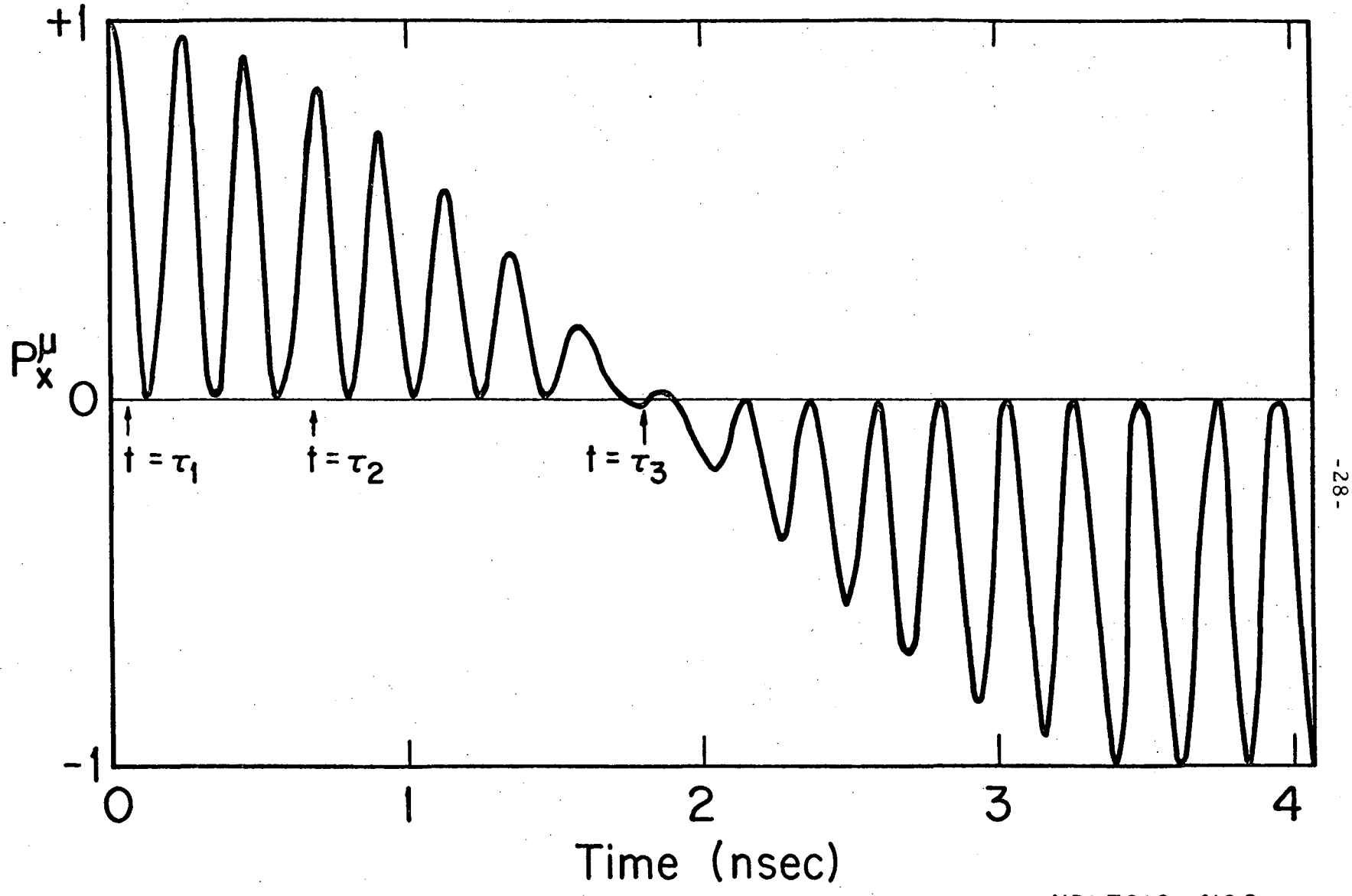

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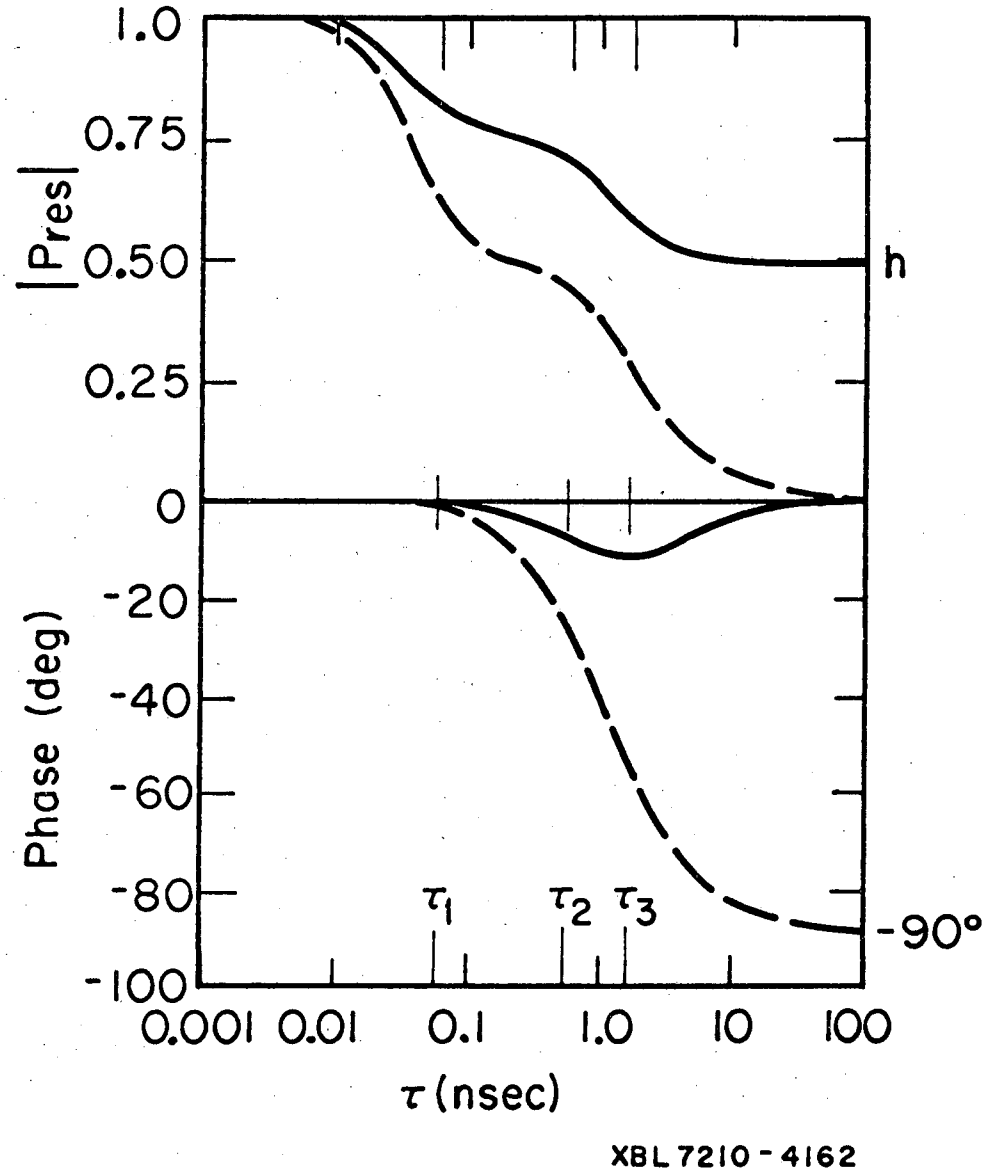
Fig. 2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0.50
0.25
0
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Phase (deg)
h
-90°
τ1
τ2
τ3
0.001
0.01
0.1
1.0
10
100
τ (nsec)
XBL 7210-4162

Fig. 3

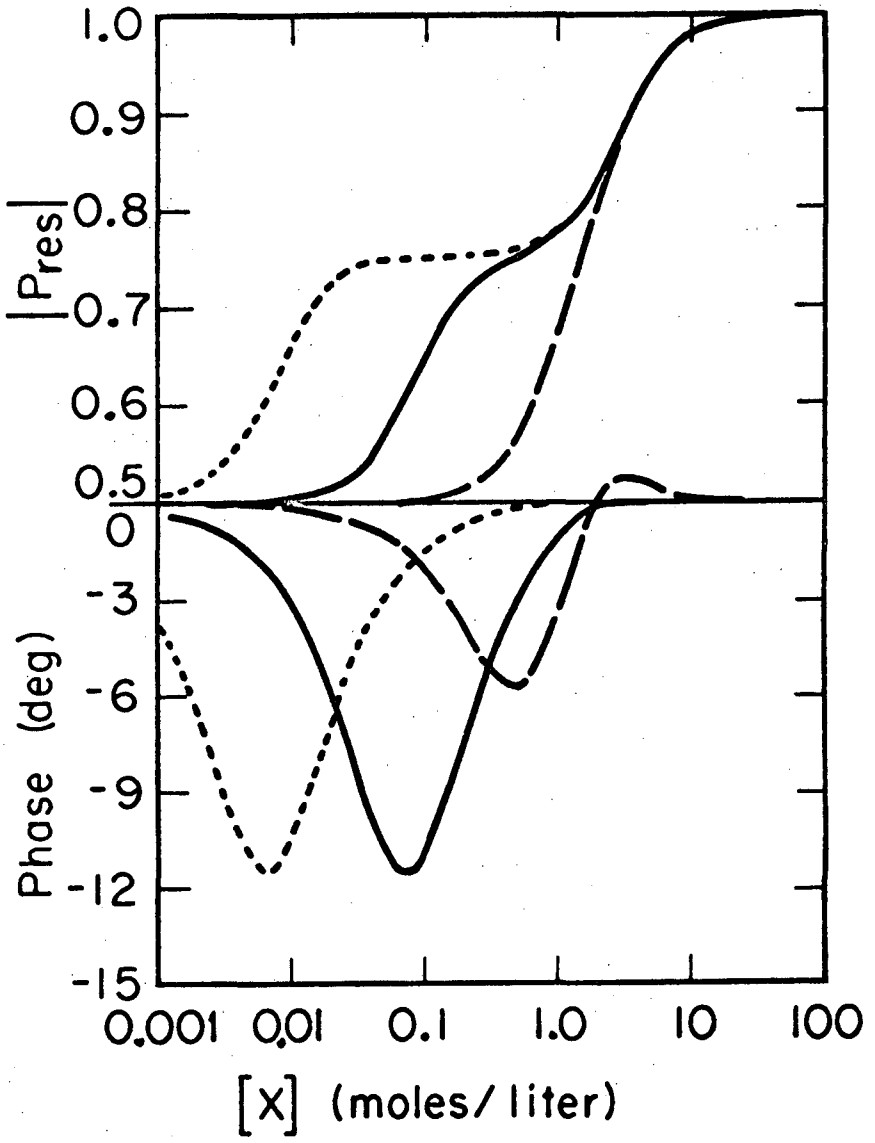

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Fig. 4

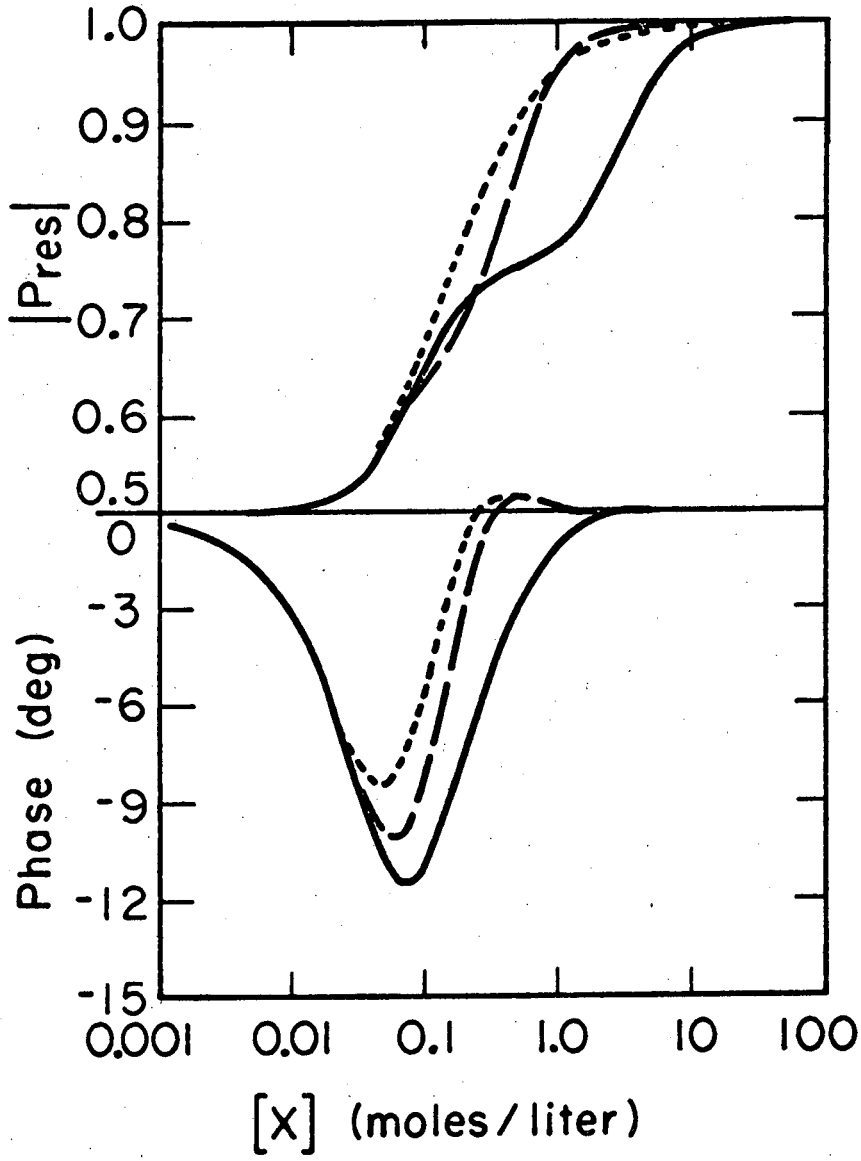

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Fig. 5

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