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Transient Interactions in Solution by
Intermolecular Spin Coupling

Final Report - 19 Jan 76 to 18 Jan 77

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28 Feb 77

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A. Introduction

This report describes research work at Georgetown University during the period 19 Jan 76 to 18 Jan 77 supported in part by grant number DAAG29-76-G-0132. These projects define and characterize, on the basis of molecular dynamics, the physical processes that govern the interactions between dissimilar molecules. The goals of the research program were:

- 1) to develop the physical and mathematical model that describes the saturation behavior of a solute nitroxide free radical when monitored through the polarization of solute nuclei, and to test this model experimentally;
- 2) to apply this theory of nitroxide radical interactions to studies of defects using spin-tagging with nitroxide radicals; and
- 3) to examine and to test experimentally the role of partitioning in ternary solutions.

B. Theoretical Introduction

The experimental basis for the research program is dynamic nuclear polarization (DNP), a double resonance technique in which the interaction of an unpaired electron spin on one molecule with a nuclear spin on another molecule is monitored by saturating the electron spin resonance (ESR) line and observing the effect on the chosen nuclear magnetic resonance (NMR) line (Ref.1). In the simplest case, the experiment can be examined by considering the interaction between the free radical unpaired electron and a proton on the solvent molecule. The four combined spin states are shown in the diagram with the relaxation transitions which couple them. The transitions p,q,r, and s correspond to relaxation transitions for the coupled electron and nuclear spins

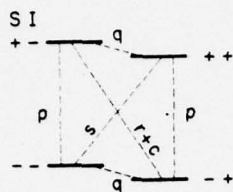


Figure 1

arising from a dipolar interaction, and are identical except for a constant and changes in the respective frequencies corresponding to the energy difference between the coupled states. The scalar interaction, shown as c in the figure, also couples the two spins. The scalar and dipolar contributions to the unpaired electron-nuclear spin coupling are directly related to the DNP ultimate enhancement

$$U_{\infty} = \frac{\gamma_S}{\gamma_I} \cdot \frac{r-s+c}{2q+r+s+c}$$

which can be determined from observed enhancements, $G(P)$, as a function of applied power, extrapolated to infinite applied power (saturation function $S_e(P)$ going to one) and infinite radical concentration (leakage factor f going to one).

$$G(P) = \frac{A(P) - A(O)}{A(O)} = U_{\infty} \cdot f \cdot S_e(P)$$

Simultaneous measurement of the overall nuclear relaxation rate as a function of paramagnetic species concentration gives the sum of the dipolar and scalar coupling strengths, $(2q+r+s+c)$, and thus, with the DNP results, allows detection of small changes in the absolute magnitude of the two mechanisms. DNP, in conjunction with low-field relaxation rates, is ideally suited to studying interactions that occur on the 10^{-8} to 10^{-11} sec time-scale. On a much shorter time-scale than possible for NMR or ESR studies on similar systems for unaveraged, identifiable effects to appear, DNP produces tangible evidence on the strength and duration of the interaction.

C. Accomplishments during the period of the grant

During the period of the grant, significant progress has been made on the important problems posed in the proposal. Four journal publications have appeared since the beginning of the grant period (Ref.2-5). In addition, three manuscripts have either recently been submitted or will be submitted shortly. (See list at the end of report.) These articles represent accomplishments on both this and the previous research grant. (DAHCO-4-75-G-0042) Contact with the personnel at the Electronics Technology and Devices Laboratory, USAECOM, Ft. Monmouth, N.J., has been maintained during the grant period through three visits to ET and D by the principal investigator. Both Dr. John Helbert and Dr. Edward Poindexter visited the principal investigator in Washington, D.C. during the grant year.

The major accomplishments of the research program are summarized below.

a) Experimental studies of the effect on fluorine nucleus-free radical interactions by chlorine atoms bound to the same carbon atom were analyzed to reveal an important case in which the promotion of transmission of spin information occurs from solute to solvent species. This work involving ^1H and ^{19}F polarizations in CFCl_3 and CFCl_2H has recently been published (Ref.5).

b) Significant variations in the observed ^{19}F interaction with free radical electrons have been observed with different added solvents using typical fluorocarbon-protonated solvent systems. These results are also seen with ^1H , ^2H , ^{31}P , and ^7Li . Such results are important for examining the role of partitioning in ternary solutions. Work is continuing on this important area of research, and some of the results have been published recently (Ref.2-5).

c) A new method for obtaining T_1 measurements at low magnetic field strengths for solvent nuclei in nitroxide solutions has been developed. This technique monitors the inversion rate following saturation, with the interval between the two inverting pulses varied by changing the observation frequency rather than the magnitude of the fixed component of the magnetic field.

d) Work initiated at ET and D Laboratory involving the use of nitroxide spin labels to tag silanol groups on the surface of various silicon oxide materials has been examined and discussed. The potential usefulness of spin-labeling in electronics was illustrated by labeling silanols in quartz surfaces (piezoelectric resonators), on oxidized silicon (MOS integrated circuits), and in evaluation of various surface passivation techniques. This work has recently been submitted for publication.

e) Experimental work has shown that the behavior of low concentration nitroxide samples is general, with all such species to have been investigated behaving similarly. The most extensive work has been done with di-tert-butyl nitroxide (DTBN) and 4-hydroxy-2,2,6,6-tetramethyl piperid-1-yloxy (HPNO).

f) The mathematical model describing the intermolecular coupling of the solvent and solute spin systems was extended to very low nitroxide spin label concentrations. This calculation predicted that, though the inverse of the solvent nuclear polarization can be approximated as increasing linearly with the inverse of the radical concentration in the region of moderate radical concentration, the behavior at very low radical concentrations will deviate from linearity. This calculation was then tested experimentally by examining the polarization of the protons of benzene by HPNO free radical in the range of radical concentrations from $0.00053M$ to $0.005M$. These new experimental data confirmed the prediction of the mathematical model described in 1) above. A mechanism is now available by which the very complex data obtained in nitroxide spin-label studies can be analyzed. Details of this work

are presented in the rest of this report and will be submitted for publication shortly.

D. Saturation Behavior of Nitroxide Spin Labels at Low Fields

The complexities introduced by the three-line ESR spectrum of the nitroxide radical have introduced additional considerations and uncertainties that preclude full utilization of the low field DNP technique. Three general experimental observations inconsistent with previous descriptions must be accounted for by any model that is developed. First, the unequal observed enhancements at the three peaks in the nitroxide spectrum must be accounted for. Second, the observed enhancements for protons must approach the full dipolar limit of $-\frac{1}{2} \gamma_S/\gamma_I$, rather than $1/3$ that value as predicted classically (Ref.6). But most importantly, the model must predict the way in which DNP ultimate enhancements can be obtained by extrapolating observed enhancements as a function of power and radical concentration.

Model for DNP Results with Low Concentration Nitroxide Radicals

The model requires a diagram representing the spin states of the interacting radical and solvent nucleus that is more complex than the four level diagram traditionally used for DNP and shown in Figure 1. In Figure 2, three adjacent diagrams of the type shown in Figure 1 are shown, each one of which corresponds to one of the three spin states in the ^{14}N atom on the nitroxide radicals. Thus approximately one-third of all the interactions of the solvent nuclei will be with radicals in the spin states indicated in each of the three sets.

Within each of these sets, the levels are connected by the relaxation transitions labeled p,q,r,s, and c as before, but the pumping radiofrequency power is only resonant with one set of levels and is shown as F in the figure. In the absence of any mechanism that links sets I, II, and III, one can consider that one-third of the solvent-radical interactions belong to each of the three sets and saturation of the ESR line of one of the three sets would lead to only $1/3$ of the solvent nuclei being polarized, as predicted previously (Ref.6).

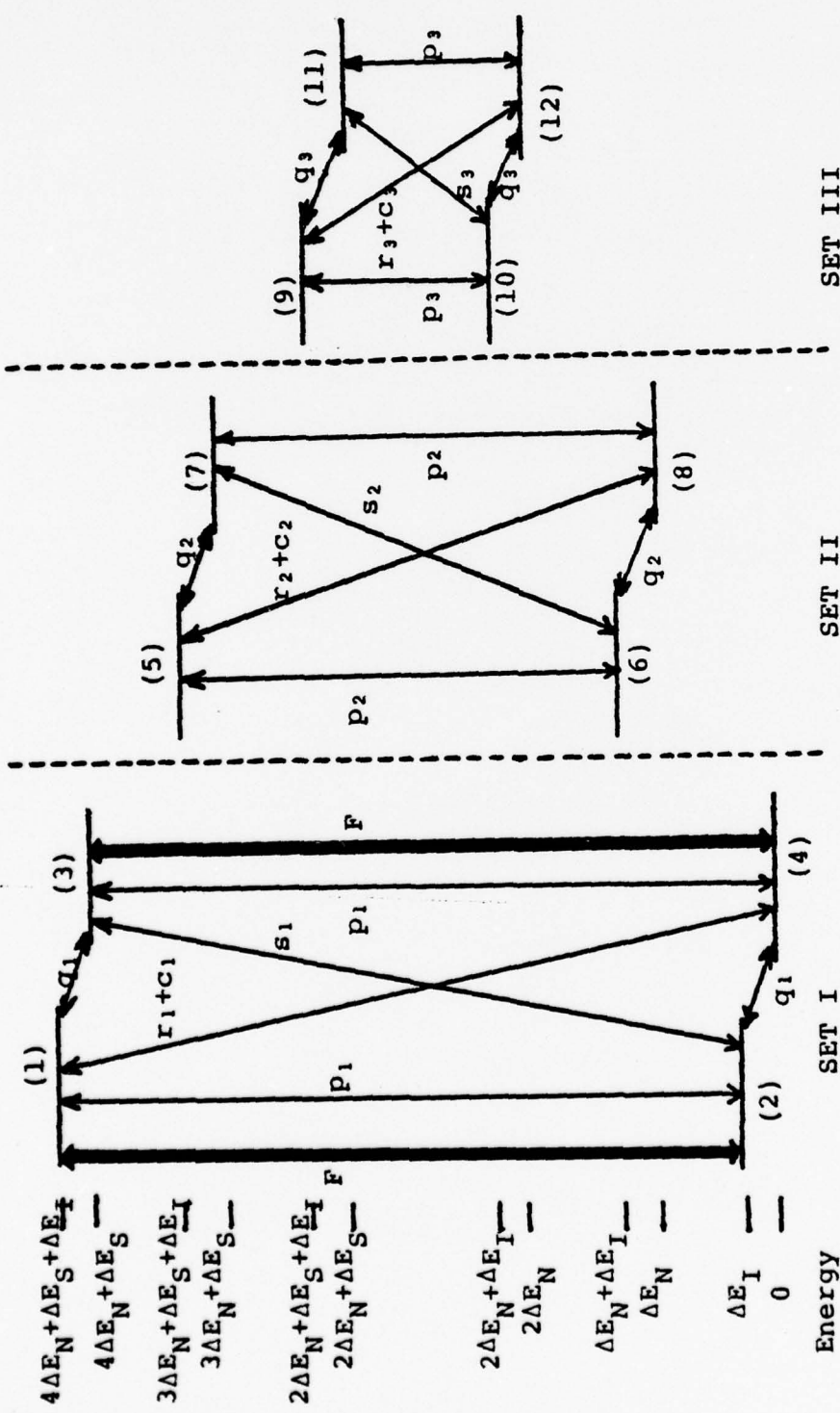


Figure 2: Energy Level Diagram for a Spin 1/2 Solvent Interacting with a Spin 1/2 Nitroxide Radical Electron the States of Which Are Split by a Spin 1 ^{14}N Atom

Though other mechanisms by which the three sets become linked may be proposed, one based on exchange is an attractive and effective model. Many exchange based transitions may be included, but only a limited number are effective in transferring polarization from the pumped set to the others. In these transitions the solvent nuclear spin states are assumed to stay constant, and the ^{14}N spin states on the two interacting radicals are conserved, as are the total electron spins. The transitions included in this model are:



One can write down the rate equations that describe the populations of each of the twelve states. Representative equations, one for a state involved in the pumping and one for a state not directly involved, are given below.

$$\begin{aligned}
 \frac{dN_1}{dt} = & (p_1 + F + r_1 + c_1 + q_1)N_1 + (p_1^* + F)N_2 + q_1^*N_3 + (r_1^* + c_1^*)N_4 - \\
 & k_1N_1N_6 + k_2N_2N_5 - k_5N_1N_{10} + k_6N_2N_9
 \end{aligned}$$

$$\begin{aligned}
 \frac{dN_5}{dt} = & -(p_2 + q_2 + r_2 + c_2)N_5 + p_2^*N_6 + q_2^*N_7 + (r_2^* + c_2^*)N_8 + \\
 & k_1N_1N_6 - k_2N_2N_5 - k_9N_5N_{10} + k_{10}N_9N_6
 \end{aligned}$$

Symbols of the type s_i and s_i^* are pairs of forward and reverse rate processes related by the principle of microscopic reversibility:

$$s_1^* = s_1 \exp(-\Delta E_{32}/kT) \approx s_1.$$

For the small energy differences between states, these can be taken as equal. Further, the energy differences are assumed to be small enough that all processes of the same letter are equal, i.e., that $s_1=s_2=s_3$, $q_1=q_2=q_3$, etc.

The first simplification in the equations comes by writing the total population of a given state to be the sum of the unpumped equilibrium population and the shift in population induced by pumping on the system.

$$N_1 = N_1^e + n_1 \quad \text{and} \quad \frac{dN_1}{dt} = \frac{dn_1}{dt}.$$

The total populations in each of the three sets will be conserved, thus there are three constraint equations of the type given below.

$$n_1 + n_2 + n_3 + n_4 = 0.$$

Realizing that $p_1 N_1^e = p_1^* N_2^e$, $k_1 N_1^e N_6^e = k_2 N_2^e N_5^e$ and keeping only first order terms in the expansion, twelve equations of the types given below are obtained:

$$\frac{dn_1}{dt} = -(p+r+c+q+F+2\kappa)n_1 + (p+F+2\kappa)n_2 + qn_3 + (r+c)n_4 + \kappa n_5 -$$

$$\kappa n_6 + \kappa n_9 - \kappa n_{10} + F\Pi = 0$$

$$\frac{dn_5}{dt} = -(p+q+r+c+2\kappa)n_5 + (p+2\kappa)n_6 + qn_7 + (r+c)n_8 + \kappa n_1 - \kappa n_2 +$$

$$\kappa n_9 - \kappa n_{10} = 0,$$

$$\text{where } \kappa = k_1 N_6^e = (k_1) N_1^e$$

$$\Pi = (N_2^e - N_1^e) = (N_4^e - N_3^e) \approx \frac{1}{12} \left(4 \frac{\Delta E_N}{kT} + \frac{\Delta E_S}{kT} \right)$$

These equations have been set equal to zero for the case where the constant application of applied radiofrequency power as one attempts to saturate the transition causes a shift to a new steady state that is time independent.

Realizing that all n 's in a given set will be of roughly the same order of magnitude and that $p=p_B+p_{IS}$, F , and κ are in general much greater than r, s, c , or q ($=q_B+q_{IS}$), those terms that are very small can be eliminated from the set of 12 equations.

$$-(p+r+c+q+F+2\kappa)n_1 + (p+F+2\kappa)n_2 + \kappa n_5 - \kappa n_6 + \kappa n_9 - \kappa n_{10} = -F\Pi$$

$$-(p+r+q+c+2\kappa)n_5 + (p+2\kappa)n_6 + \kappa n_1 - \kappa n_2 + \kappa n_9 - \kappa n_{10} = 0.$$

The equations that are derived from the pumped set show the magnitude of the pumping F in two places on the left side of the equation and a non-zero constant proportional to F on the right side. The other states yield equations that are equal to zero and have no terms including F .

After a great deal of algebra, one obtains the following expressions for these equations:

$$n_1 = \left(\frac{q+s}{2q+r+s+c}\right) \frac{(p+\kappa) F\Pi}{[(p+\kappa)(p+F)+2\kappa p]} = -n_4$$

$$n_2 = -\left(\frac{r+c+q}{2q+r+s+c}\right) \frac{(p+\kappa) F\Pi}{[(p+\kappa)(p+F)+2\kappa p]} = -n_3$$

$$n_5 = n_9 = -n_8 = -n_{12} = \left(\frac{q+s}{2q+r+s+c}\right) \frac{\kappa F\Pi}{[(p+\kappa)(p+F)+2\kappa p]}$$

$$n_6 = n_{10} = -n_7 = -n_{11} = -\left(\frac{r+c+q}{2q+r+s+c}\right) \frac{\kappa F\Pi}{[(p+\kappa)(p+F)+2\kappa p]}$$

Following the general method used effectively by Solomon (Ref.7), and used successfully to treat nuclei with spins other than 1/2 (Ref.8,9), the nuclear polarizations of each set can be examined independently, though one must realize that the experiment does not actually do this. The theoretical description of the real experimental situation will be considered shortly.

To a very good first approximation the unpumped nuclear magnetizations in each of the three sets are the same.

$$I_z^0(I) = (N_1^e - N_3^e + N_2^e - N_4^e) = - \frac{\Delta E_I}{6kT} = I_z^0(II) = I_z^0(III)$$

The pumped nuclear magnetization of the first set (the set actually pumped) is different than that on the second and third sets.

$$\Delta I_z(I) = (n_1 - n_3 + n_2 - n_4) = - \left(\frac{2(r-s+c)}{(2q+r+s+c)} \right) \frac{(p+\kappa) F \Pi}{[(p+\kappa)(p+F)+2\kappa p]}$$

$$\Delta I_z(II) = \Delta I_z(III) = - \left(\frac{2(r-s+c)}{(2q+r+s+c)} \right) \frac{\kappa F \Pi}{[(p+\kappa)(p+F)+2\kappa p]}$$

The electron magnetization in the pumped set also differs from that in the unpumped sets.

$$\Delta S_z(I) = (n_1 - n_2 + n_3 - n_4) = \frac{2(p+\kappa) F \Pi}{[(p+\kappa)(p+F)+2\kappa p]}$$

$$\Delta S_z(II) = \Delta S_z(III) = \frac{2\kappa F \Pi}{[(p+\kappa)(p+F)+2\kappa p]}$$

Recalling the way that Π was defined:

$$\Pi = (N_2^e - N_1^e) = \frac{1}{12} \left(4 \frac{\Delta E_N}{kT} + \frac{\Delta E_N}{kT} \right), \quad \text{substituting for } \Pi,$$

the observed enhancements for each set can be calculated.

$$G_I(P) = \frac{I_Z(I) - I_Z^O(I)}{I_Z^O(I)} = \frac{\Delta I_Z(I)}{I_Z^O(I)} =$$

$$\left(\frac{(r-s+c)}{(2q+r+s+c)} \right) \left(\frac{4\Delta E_N + \Delta E_S}{\Delta E_I} \right) \left(\frac{(p+\kappa)F}{[(p+\kappa)(p+F)+2\kappa p]} \right)$$

$$G_{II}(P) = G_{III}(P) = \left(\frac{(r-s+c)}{(2q+r+s+c)} \right) \left(\frac{4\Delta E_N + \Delta E_S}{\Delta E_I} \right) \left(\frac{\kappa F}{[(p+\kappa)(p+F)+2\kappa p]} \right)$$

Each of these three expressions for the observed enhancements consists of three terms. The first term really should be written as:

$$\frac{r-s+c}{2q+r+s+c} = \frac{r-s+c}{2q_{IS}+r+s+c+2q_B} = \frac{\Gamma_N[R\cdot]}{\Gamma_N[R\cdot]+2q_B} = f.$$

The numerator contains only terms directly proportional to the radical concentration. The denominator includes a term directly proportional to the radical concentration and a term independent of radical concentration. When inverted, this becomes

$$\frac{\Gamma_N}{\Gamma_N} + \frac{2q_B}{\Gamma_N} \left[\frac{1}{R\cdot} \right] = \frac{1}{f}.$$

Unlike the previously investigated cases for DNP, the third term in each of the expressions for $G(P)$ in this case includes radical concentration dependent terms, namely the κ 's.

The second term is that which in the normal case reduces to γ_S/γ_I . In this case, the relation that holds is

$$\frac{4\Delta E_N + E_S}{\Delta E_I} = \frac{\omega_{ESR}}{\omega_{NMR}},$$

the ratio of the frequency used to saturate the ESR line to the NMR observation frequency. Two important observations should be made, however. First, if the observation frequency for protons is now 306 kHz as is most favorable for nitroxide radical solutions, this will result in a dipolar limit of $(-210.6 \text{ MHz}/2.306 \text{ kHz})$ which equals -344 rather than -329.5 as previously encountered in all low-field DNP experiments with a proton observation frequency of 319.7 kHz. Likewise, if the low field peak and high field peak were saturated, limits of -428 and -279 respectively would be obtained. That the observed enhancement depends on $\omega_{\text{ESR}}/\omega_{\text{NMR}}$ now accounts for the unequal observed enhancements at the three peaks in the nitroxide spectrum, thus answering the first of the three problems raised at the beginning of this section.

Moreover, note that, in all three sets, $G_I(P)$, $G_{II}(P)$, and $G_{III}(P)$ depend on the same ratio $\omega_{\text{ESR}}/\omega_{\text{NMR}}$. Thus the magnitude of the polarization in all three sets depends solely on the frequencies in the pumped transition. If, instead, one were to pump the middle line, one would obtain $(2\Delta E_N + \Delta E_S)/\Delta E_I$, while if the upfield line were pumped, one would obtain $\Delta E_S/\Delta E_I$.

The last term in the equations for $G_I(P)$, $G_{II}(P)$, and $G_{III}(P)$ must now be examined. One observes that this term for the two unpumped transitions is the same, but is different for the pumped transition. This difference becomes crucial when the equation describing the actual observed DNP signal is examined.

$$I_z^0 = (N_1^e - N_3^e + N_2^e - N_4^e + N_5^e - N_7^e + N_6^e - N_8^e + N_9^e - N_{11}^e + N_{10}^e - N_{12}^e) =$$

$$-\frac{\Delta E_I}{2kT}$$

$$\Delta I_z = -2 \left[\frac{r-s+c}{2q_{IS}+r+s+c+2q_B} \right] \left[\frac{4\Delta E_N + \Delta E_S}{12kT} \right] \left[\frac{(p+3\kappa)F}{[(p+\kappa)(p+F)+2\kappa p]} \right]$$

$$G(P) = \frac{\Delta I_z}{I_z^0} = \left[\frac{r-s+c}{2q_{IS}+r+s+c+2q_B} \right] \left[\frac{4\Delta E_N + \Delta E_S}{\Delta E_I} \right] \left[\frac{(p+3\kappa)F}{3[(p+\kappa)(p+F)+2\kappa p]} \right].$$

The first two terms are as before for the individual transitions. The product of the first two terms will, for simplicity in subsequent operations, be labeled U_F . For the next several steps, it will be convenient to consider the behavior of $1/G(P)$.

$$\frac{1}{G(P)} = \frac{3}{U_F} \left[\frac{(p+\kappa)(p+F)+2\kappa p}{(p+3\kappa)F} \right] = \frac{3}{U_F} \left[\frac{p+\kappa}{p+3\kappa} + \frac{p}{F} \right].$$

In the limit where the saturation power is very high, $F \gg p$.

$$\lim_{F \rightarrow \infty} \frac{1}{G(P)} = \frac{3}{U_F} \left[\frac{p+\kappa}{p+3\kappa} \right] = \frac{1}{G_\infty}.$$

If there is no exchange mechanism coupling the two sets of states, then $\kappa \approx 0$.

$$\lim_{\kappa \rightarrow 0} \frac{1}{G_\infty} = \frac{3}{U_F} \left[\frac{p}{p} \right] = \frac{3}{U_F} = \frac{1}{U_\infty}.$$

Thus U_∞ for the case of no exchange and complete saturation is $U_F/3$. Thus in that limit the ultimate enhancements obtained will be $1/3$ those that would be observed if one could simultaneously saturate all the ESR linewidth, and if the frequencies $\omega_I = 319.7$ kHz and $\omega_S = 210.6$ MHz are used with the leakage factor of one, the dipolar limit using this model turns out to be -110 , as the classical calculation predicted (Ref.6).

On the other hand, for the case where exchange is important and $\kappa \gg p$, then

$$\lim_{\kappa \rightarrow \infty} \frac{1}{G_\infty} = \frac{3}{U_F} \frac{\kappa}{3\kappa} = \frac{1}{U_F} = \frac{1}{U_\infty}$$

and U_∞ goes to the full dipolar limit of U_F .

In actual fact the experiments performed fall into the middle of these two extremes, and the details of this behavior become important. Recalling that

$$\kappa = k_i N_j^e = \kappa'(R\cdot)$$

one realizes that κ depends to first order on the radical concentration.

$$\frac{1}{G_\infty} = \frac{3}{U_F} \frac{p + \kappa'(R\cdot)}{p + 3\kappa'(R\cdot)}$$

If, for the moment, we neglect the fact that the U_F term also includes radical concentration dependence in the form of f , Figure 3 shows the plot that is obtained when U_F/G_∞ is plotted as a function of $(R\cdot)$. As can be seen, the curve that is obtained is not linear, but goes to 3 at very low radical concentrations and to 1 at high radical concentrations.

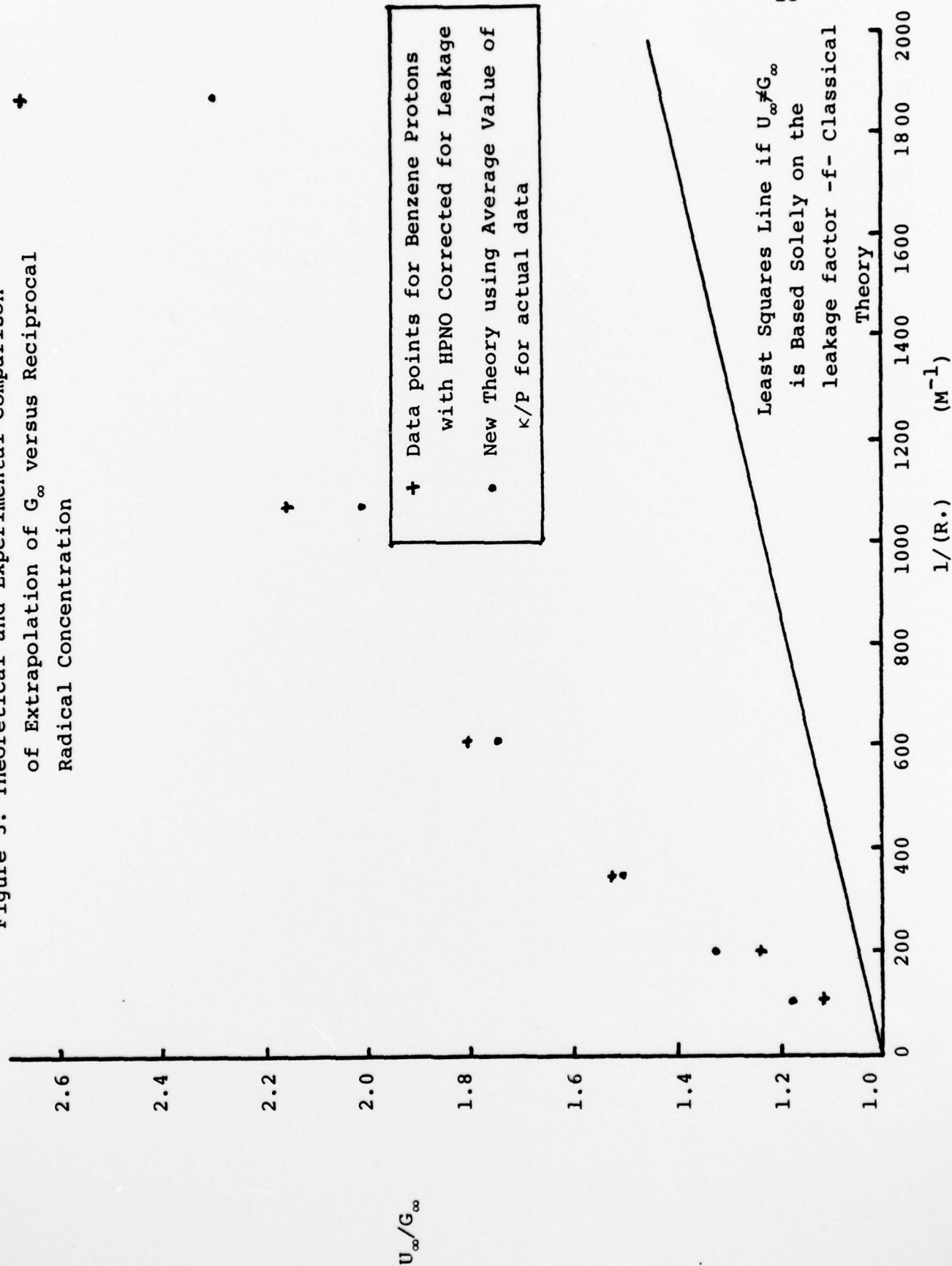
The details of results that can be obtained experimentally must now be examined.

Experiments to Test Details of Saturation Behavior of Nitroxide Radical Samples

In order to test the model given in the previous section, data must be very carefully obtained for a series of samples with varying radical concentration. Samples were prepared by successive dilution of a sample of a known amount of the free radical (HPNO) dissolved in benzene. Enhancements as a function of applied radiofrequency power at 210.6 MHz were observed for a proton frequency of 306 kHz. $1/G(P)$ was plotted as a function of $1/P$ to obtain as the y intercept the value $1/G_\infty$.

As mentioned in the previous section, the expression for $1/G_\infty$ includes radical dependence in U_F and in κ . To eliminate the radical concentration dependence in the terms in f , one can measure the nuclear relaxation time in order to correct

Figure 3: Theoretical and Experimental Comparison
of Extrapolation of G_{∞} versus Reciprocal
Radical Concentration



for leakage. Because of the unusual nature of the nitroxide radical solutions at such low concentrations, a modified procedure for obtaining low-field proton relaxation times in these solutions was required. In this case, the ESR line was saturated continuously for a time exceeding $5 \times$ the relaxation time, then the saturating field was turned off at exactly the same point in the field-varied sweep. The time between turning off the saturating field and sampling the nuclear spin state populations by a rapid passage technique was varied by slightly modifying the proton observation frequency while keeping the fixed magnetic field constant. Thus the proton was observed at a slightly different position in the total sweep on successive samplings. This method was especially effective for obtaining satisfactory results when, even in relatively narrow sweeps of the magnetic field, the ESR line shape changes drastically, thus precluding any effective means of varying the fixed field to obtain data.

The results of this experiment are shown in Figure 4 as $1/T_{\text{relax}}$ versus radical concentration. The quality of the straight line obtained is extremely good when compared with typical low-field relaxation data. These results now permit the leakage correction to be made in the values of G_{∞} obtained in the extrapolation of $1/G(P)$ versus $1/P$. If the leakage includes all the radical concentration dependence, a straight line of zero slope should be obtained when $1/G'_{\infty}$ is shown as a function of $(R \cdot)$. Figure 5 shows this plot such that both the corrected and uncorrected data are shown. The shape of the curve is of paramount importance. Though the uncorrected observed data appear relatively linear in the radical concentration, when corrected for leakage it is far from linear. The radical concentration dependence of the saturation function for the ESR line is thus shown experimentally to be very important.

Figure 4: Relaxation Rates ($1/T_{\text{obs}}$) for Benzene Protons as a Function of HPNO Radical Concentration

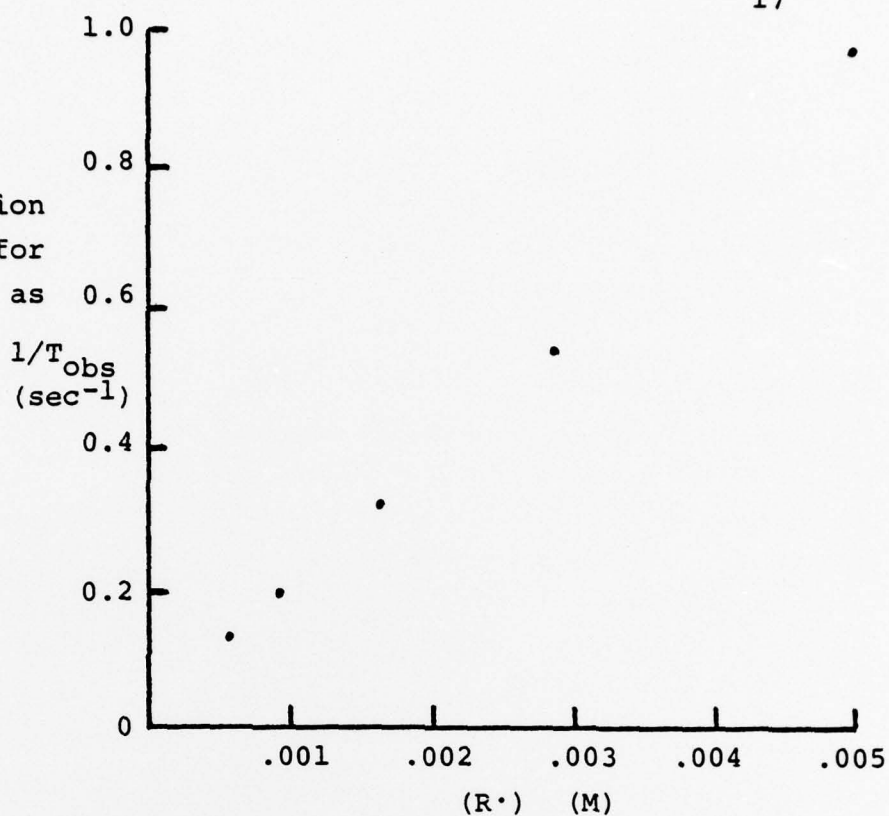
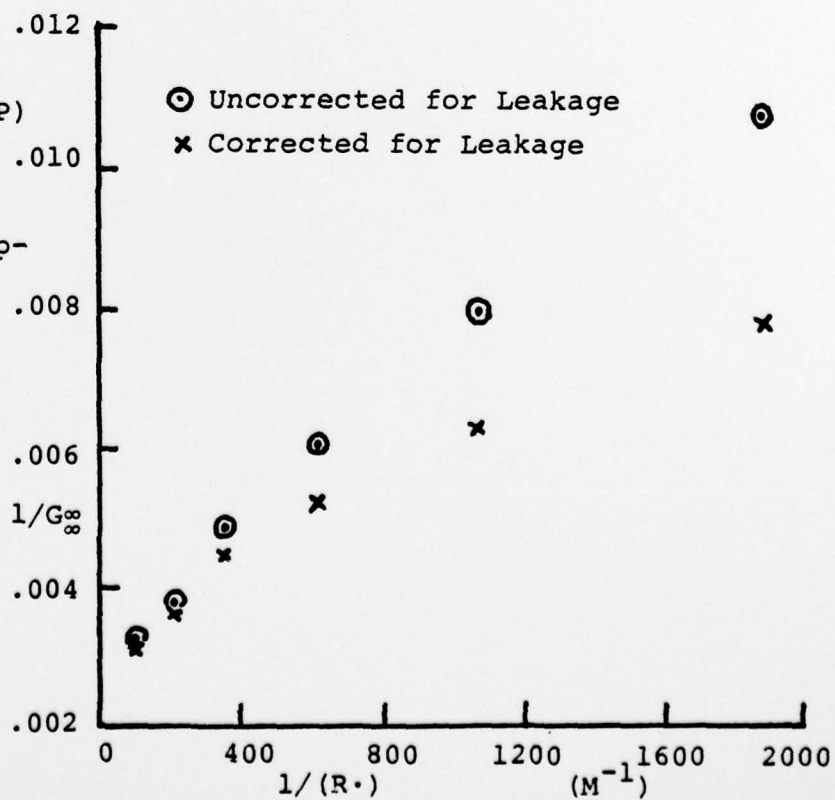


Figure 5: Plots of y intercepts of $1/G(P)$ versus $1/P$ for Benzene Protons as a Function of Reciprocal Radical Concentration



For comparison with the theoretically derived curve, the experimental data is now also shown in Figure 3, as U_F/G_∞ versus $1/(R \cdot)$. In order to make this plot, an arbitrary choice of the κ/p ratio was selected for comparison purposes. As can be seen from the data, the experimental results agree much more successfully with the theoretical curve produced by this model than with that based solely on the leakage factor, data for which are shown as a straight line at the bottom of Figure 3.

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LIST OF PUBLICATIONS DURING GRANT PERIOD:

Publications that appeared during grant period:

Dynamic ^{19}F Polarization in Fluorinated Strained Cyclic Alkanes and Alkenes, R.D. Bates, Jr., B.E. Wagner, and E.H. Poindexter, J.Phys.Chem., 80, 320 (1976).

Dynamic Nuclear Polarization Studies of Labile Complex Formation between Lithium Ion and Nitronyl Nitroxide or Imidazoline-1-oxyl Radical Ligands, B.E. Wagner, J.W. Linowski, J.A. Potenza, R.D. Bates, Jr., J.N. Helbert, and E.H. Poindexter, J.Amer.Chem.Soc., 98, 4405 (1976).

Transient Intermolecular Spin Coupling of CHCl_3 with Di-*t*-butyl Nitroxide Free Radical, R.D. Bates, Jr., B.E. Wagner, and E.H. Poindexter, J.Phys.Chem., 81, 276 (1977).

Dynamic Polarization of ^1H and ^{19}F in CFCl_3 and CHCl_2H , R.D. Bates, Jr., J.Chem.Phys., 66, 1759 (1977).

Manuscripts to be submitted shortly:

Characterization of Silica Surfaces by Free Radical Spin Labels, B.E. Wagner, J.N. Helbert, E.H. Poindexter, and R.D. Bates, Jr.

Polarization of Solvent Nuclei by Nitroxide Radicals, R.D. Bates, Jr., B.E. Wagner, J.N. Helbert, and E.H. Poindexter.

Use of Nitroxide Spin Labels in Studies of Solvent-Solute Interactions, R.D. Bates, Jr. and W.S. Drozdowski.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experimental work on the promotion of spin information transmission from solute to solvent species by chlorine atoms was continued. The role of partitioning in ternary solutions has been investigated by observing ^2H , ^1H , ^{31}P , and ^7Li low-field NMR. The use of nitroxide spin labels to tag silanol groups on the surface of various silicon oxide materials has been examined. Experimental and theoretical work describing the intermolecular coupling of the solute and solvent spin systems was extended to very low spin label concentrations.		