Theory of Spin Pumping and Relaxation in Systems with a Low Concentration of Electron Spin Resonance Centers

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A model is developed to describe nuclear relaxation and spin pumping caused by sparsely distributed electronic spins. It is assumed that the nuclei which are outside the interaction sphere of the paramagnetic centers are influenced indirectly via a fast diffusion process. Nuclei close to the electron spins are assumed to combine with these to form spin pairs of finite lifetime τ. Spin pumping and relaxation in these pairs is described phenomenologically. The coupling with a radio-frequency power source is described in terms of a spectral distribution function with Lorentzian shape. Simultaneous spin flips, made possible by the static part of the spin-spin interaction, are included. The equations for two-spin relaxation are generalized to account for the fluid motion and electron spin relaxation as two independent sources of randomness. The results for relaxation and spin pumping are adapted to various special cases and compared with experiments. In particular, qualitative changes in the pumping process are shown to take place when the constant external magnetic field is changed from low to high values.

I. INTRODUCTION

SPIN pumping has, on occasion,[1-6] been used to investigate nonuniform systems in which the (electronic) pumping centers are far outnumbered by the nuclei, of which the polarization is measured. The process involved can be presented in reasonable approximation by a set of equations describing spin flips induced by pumping and by relaxation in neighboring electronic and nuclear spins and describing relaxation and diffusion of spin polarization for the remaining nuclei. These equations are coupled by the condition that the flux of spin polarization is continuous. Bloembergen[7] has used a similar model for calculating the nuclear relaxation in solids. In this paper, we use this approach to calculate wall effects on nuclear relaxation in fluids and to derive expressions for the nuclear polarization obtained by spin pumping as a function of the power level. A simplified treatment of this problem has been published elsewhere.[8] Our model, though quite general, is subject to the following assumptions:

(1) All nuclear spins which are under the direct influence of the pumping centers are equivalent.

(2) The diffusion, if it is an important factor at all, is fast, i.e., it spans the average distance between pumping centers in a time short compared with the relaxation time of the spins to be polarized. This assumption leads to a steady-state polarization which is practically uniform over the sample and independent of the geometrical arrangement of the pumping centers.

(3) The quanta exchanged with the power source and also those exchanged with the lattice in relaxation processes are equal to electronic and nuclear quanta in the external field $\hbar\gamma_e H_0$ and $\hbar\gamma_n H_0$, or linear combinations thereof, $\hbar(\gamma_e \pm \gamma_n)H_0$.

In Sec. II, we develop and solve the general equations, treating the various transition rates as arbitrary parameters. In Sec. III, we derive expressions for the transition rates which we expect to be applicable in the case that there are two simultaneous sources of randomness in the spin–spin interaction, one due to motion, the other due to independent mechanisms of relaxation for the electronic spins. In Sec. IV, explicit expressions are derived for several cases of interest that give qualitatively different results. In Sec. V, the physical content of these expressions is discussed and compared with experimental evidence.

II. BASIC EQUATIONS

The nuclear spins in the sample are divided into two groups: (1) those belonging to the pumping centers, and (2) those which can be polarized only indirectly by diffusion. The nuclei in group (1) are combined with the electron spins of the pumping centers to form spin pairs to which we apply equations describing the relaxation and the transitions induced by the radio-frequency source. For the nuclei in group (2), there is only a relaxation term. The coupling between the two groups

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[2] J. P. Borel and P. Cornaz, Compt. rend. **247**, 1988 (1958).
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[7] N. Bloembergen, Physica **15**, 386 (1949).
[8] H. C. Torrey, J. Korringa, D. O. Seevers, and J. Uebersfeld, Phys. Rev. Letters **3**, 418 (1959).

is expressed by a spin transfer term, with characteristic time, τ. In applications, τ will be interpreted as characterizing the exchange of molecules between the pumping centers and other parts of the system.

Recently Leifson and Jeffries[9] have treated the "solid-state" dynamic polarization by a simple model in which the effect of diffusion is assumed to be equivalent to all nuclei sharing the electrons which are the source of their polarizations. This model leads to rate equations resembling Eq. (1) but in which population ratios and average transition rates appear. In contrast, we treat a general two-spin system with definite transition rates to give the polarization of nuclei at the pumping sites. We then consider (in Sec. II2) the transport of such polarization to other regions under the assumptions stated in Sec. I.

1. Equations of Motion for the Pumping Centers

The spin pairs are described in the representation applicable when the spin–spin interaction is either unresolved or small compared with $\gamma_n H_0$. For simplicity we assume that both spins have magnitude $\frac{1}{2}$. For the purpose of definition, the four resulting states are given in Fig. 1 for the case that the magnetic dipole moments have opposite sign. Let n_i be the occupation probability of level i, and $n_i{}^0 = \epsilon_i / \sum \epsilon_i$, the occupation at thermal equilibrium, where $\epsilon_i = \exp(-E_i/kT)$. The time dependence of n_i under omission of diffusion is given by:

$$dn_i/dt = \sum_k W_{ik}(n_k/\epsilon_k - n_i/\epsilon_i) + \sum_k A_{ik}(n_k - n_i). \quad (1)$$

W_{ik} is the relaxation matrix, $W_{ik}=W_{ki}$; the symmetric matrix A_{ik} describes the transitions induced by the power source. In view of our assumption (3), we have $W_{12}=W_{34}$, $W_{13}=W_{24}$. We will use an alternative notation, p, q, r, s, for the remaining four elements, as indicated in Fig. 1. For A_{ik}, we take, in line with our phenomenological approach, functions of the frequency ω of the form corresponding to a Lorentzian line shape

$$A_{13}=A_{24}\equiv A = \frac{1}{2}\frac{\gamma_e{}^2 H_1{}^2 \Gamma}{(\omega-\omega_e)^2+\Gamma^2},$$

$$A_{14}\equiv B_+ = \frac{1}{2}\frac{\alpha^2\gamma_e{}^2 H_1{}^2\Gamma_+}{(\omega-\omega_e-\omega_n)^2+\Gamma_+{}^2}, \quad (2)$$

$$A_{23}\equiv B_- = \frac{1}{2}\frac{\alpha^2\gamma_e{}^2 H_1{}^2\Gamma_-}{(\omega-\omega_e+\omega_n)^2+\Gamma_-{}^2}.$$

Here, H_1 is half the amplitude of the radio-frequency field; ω its frequency; $\omega_e=\gamma_e H_0$; $\omega_n=\gamma_n H_0$; Γ and $\Gamma_\pm$ are the half-widths of the transition, usually denoted as $1/T_2$. In using Eq. (2) in conjunction with Eq. (1) for all values of H_1, we disregard saturational effects other than those arising through the differences in the popula-

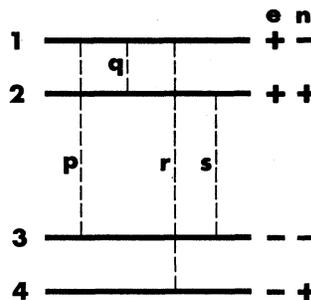[9] O. S. Leifson and C. D. Jeffries, Phys. Rev. **122**, 1781 (1961).

FIG. 1. Energy levels and transition rates for a dipolar-coupled spin pair each with spin magnitude of $\frac{1}{2}$ and dipole moments of opposite sign.

tion of the levels. If the line is inhomogeneously broadened, Γ is the half-width of any of its homogeneous components.

α^2 gives the probability of double spin absorption, which is known to produce the polarization effects first reported in references 1 and 10.[1,10] We will refer to this effect as the "double effect." α measures the mixing of states caused by the "static" part of the spin–spin interaction. It is calculated in Sec. III. We take $A_{12}=A_{34}=0$ because the frequency ω is supposed to be near the electron resonance frequency ω_e.

Defining

$$X_i = n_i/\epsilon_i - n_i{}^0/\epsilon_i,$$

applying the transformation

$$Y_1 = -X_1 + X_2 - X_3 + X_4,$$
$$Y_2 = X_1 + X_2 - X_3 - X_4,$$
$$Y_3 = X_1 - X_2 - X_3 + X_4,$$
$$Y_4 = X_1 + X_2 + X_3 + X_4,$$

and neglecting the Boltzmann factors in the resulting relaxation terms, Eq. (1) becomes

$$dY_1/dt = -\Gamma_1 Y_1 - \Gamma_3 Y_2 - V_1, \quad (3a)$$
$$dY_2/dt = -\Gamma_3 Y_1 - \Gamma_2 Y_2 - V_2, \quad (3b)$$
$$dY_3/dt = -2\Gamma_4 Y_3 - V_3, \quad (3c)$$

where

$$\Gamma_1 = 2q + r + s,$$
$$\Gamma_2 = 2p + r + s,$$
$$\Gamma_3 = s - r,$$
$$\Gamma_4 = p + q.$$

The terms V_i are linear expressions in A, $B_\pm$, containing Boltzmann factors. In the usual high-temperature approximation, we have

$$V_1 = B_1 Y_1 - B_2(Y_2 - S_0),$$
$$V_2 = B_2 Y_2 + (2A + B_1)(Y_2 - S_0), \quad (4)$$
$$V_3 = 2A Y_3.$$

Here $B_i = B_+ \pm B_-$ and $S_0 = \frac{1}{4}(-\epsilon_1 - \epsilon_2 + \epsilon_3 + \epsilon_4)$. S_0 is, therefore, in the approximation that the nuclear Boltzmann factors are put equal to unity, equal to the elec-

[10] A. Abragam and G. Proctor, Compt. rend. **246**, 2253 (1958).

tron spin polarization in thermal equilibrium. Our assumption about the relaxation matrix, i.e., $W_{12}=W_{34}$ and $W_{13}=W_{24}$, is thus a sufficient and necessary condition that in the high temperature approximation the variable Y_3 disappears from the equations for Y_1 and Y_2. Y_1 and Y_2 are, in the same approximation as above, the deviations of the nuclear and electronic spin polarizations from their equilibrium values. The term neglected in Eq. (4), though finite at extremely high power, are of no practical importance.

2. Transport of Spin Polarization

The coupling of Eqs. (3) with equations describing the relaxation of group (2) nuclei are discussed for a general model, from which cases of interest can be obtained by specialization. We assume that the paramagnetic centers are confined to a region, such as a surface layer on a solid–liquid interface, which contains many nuclei outside the pumping centers. We will refer to the remaining nuclei, outside this region, as those in "bulk." The migration within the "surface layer" is described by a transition time or correlation time τ_s, the transition from the surface layer to the bulk by a time τ. $T_s{}^0$ denotes the thermal relaxation time in the layer for nuclei outside pumping centers; $T_1{}^0$ is the bulk relaxation time. A distinction between $T_1{}^0$ and $T_s{}^0$ is necessary because τ_s will differ from τ_0, the bulk correlation time, thus changing the relaxation due to nuclear interaction, possibly by several orders of magnitude; also $T_s{}^0$ can have contributions from magnetic sites other than the pumping centers.

Let N_p, N_s, and N be the number of nuclei in the pumping centers, in other parts of the surface layer, and in the bulk, respectively, and let Y_s and Y be the deviation of the average nuclear polarization from the thermal equilibrium value in the surface and the bulk, respectively. When it is now assumed that the diffusion in the surface layer as well as in the bulk is fast in the sense of condition (2) of the introduction, and that $N_p \ll N_s \ll N$, one has

$$dY_s/dt = -(Y_s/T_s{}^0) + (N_p/N_s)$$
$$\times [(Y_1-Y_s)/\tau_s] - (Y_s-Y)/\tau, \quad (5a)$$

$$dY/dt = -(Y/T_1{}^0) + (N_s/N)[(Y_s-Y)/\tau]$$
$$+ (N_p/N)[(Y_1-Y)/\tau], \quad (5b)$$

while a term $-(Y_1-Y_s)/\tau_s - (Y_1-Y)/\tau$ is added to the right-hand member of Eq. (3a). With the notation

$$b_s = (1/T_s{}^0) + (N_p/N_s)/\tau_s + (1/\tau),$$
$$b = (1/T_1{}^0) + (N_s+N_p)/N\tau, \quad (6)$$
$$\Gamma_1' = \Gamma_1 + (1/\tau) + (1/\tau_s),$$

we therefore have

$$dY_1/dt = -(\Gamma_1'+B_1)Y_1 - (\Gamma_3-B_2)Y_2 + (Y_s/\tau_s)$$
$$+ (Y/\tau) - S_0 B_2, \quad (7a)$$

$$dY_2/dt = -(\Gamma_3-B_2)Y_1 - (2A+B_1+\Gamma_2)Y_2$$
$$+ S_0(2A+B_1), \quad (7b)$$

$$dY_s/dt = (N_p/N_s)(Y_1/\tau_s) - b_s Y_s + (Y/\tau), \quad (7c)$$

$$dY/dt = (N_p/N)(Y_1/\tau) - bY + (N_s/N)(Y_s/\tau). \quad (7d)$$

The Eqs. (7) can now be used to calculate the steady state values of Y_i for a given power level. These are obtained by equating dY_i/dt to zero. We are particularly interested in the bulk polarization Y which is most easily observed. One can also calculate the relaxation rates of the system; these are obtained by equating A, B_1, and B_2 to zero and taking $dY_i/dt = -rY_i$. This gives four roots $r_1 \cdots r_4$. When a single relaxation rate is observed, as is commonly the case, it may be identified with the lowest of the roots, $r_1 = 1/T_1$, which must then be much smaller than the other roots.

In order to obtain Y, we bring Eqs. (7c) and (7d) for the steady state into the form

$$Y_s = C_s Y, \quad Y_1 = CY,$$

where

$$C_s = [(N/N_s)(\tau/\tau_s)b + (1/\tau)]/[b_s + (1/\tau_s)], \quad (8)$$
$$C = (N/N_p)\tau b - (N_s/N_p)C_s.$$

Eliminating Y_1, Y_2, Y_3, one has

$$Y = \frac{S_0 F_1(\omega)}{C - \Gamma_2/(\Gamma_5{}^2\tau') + F_2(\omega)/(\Gamma_5{}^2\tau')}, \quad (9a)$$

where

$$F_1(\omega) = [\Gamma_2 B_2 + \Gamma_3(2A+B_1)]/D(\omega), \quad (9b)$$

$$F_2(\omega) = [(2A+B_1)\Gamma_3{}^2 + (2A+\Gamma_2)B_1\Gamma_2 + 2\Gamma_2\Gamma_3 B_2$$
$$+ (B_1{}^2-B_2{}^2)\Gamma_2]/D(\omega), \quad (9c)$$

$$D(\omega) = (2A+B_1+\Gamma_2)(\Gamma_1'+B_1) - (\Gamma_3-B_2)^2,$$
$$\Gamma_5{}^2 = \Gamma_1'\Gamma_2 - \Gamma_3{}^2, \quad (9d)$$
$$1/\tau' = (C_s/\tau_s) + (1/\tau).$$

Equations (9) apply to a homogeneously broadened electron resonance line. For an inhomogeneously broadened line, one should use the following averaging procedure: Let the resonance frequencies of the pumping centers have a distribution $g(\omega_e - \bar{\omega}_e)$ around the average value $\bar{\omega}_e$. Each center has its own Y_1 and Y_2, obeying equations of the form (7a) and (7b), but there is only one Y_s and one Y, and in Eqs. (7c) and (7d), Y_1 must be replaced by its average value $\bar{Y}_1$. This is obtained from the equations replacing (7a) and (7b) by eliminating Y_2, solving for Y_1 as a function of Y_s and Y, and averaging. The solution of Eqs. (7c) and (7d) is then of the form of Eq. (9a), but with F_1 and F_2 being replaced by their average value

$$\bar{F}_{1,2}(\omega) = \int g(\omega_e - \bar{\omega}_e) F_{1,2}(\omega-\omega_e) d\omega_e.$$

The "observable" relaxation rates $r_1 \cdots r_4$ are easily obtained in the limiting case that $T_1{}^0$ is very long compared with all other times, and that $\Gamma_1'\Gamma_2 \gg \Gamma_3{}^2$. The latter inequality would hold, e.g., when the electronic relaxation is fast, or the time τ short. One of the rates is then

$$r_4 = 1/T_{1e} = \Gamma_2,$$

i.e., T_{1e} is the electronic thermal relaxation time. The three other rates can in this approximation be attributed to the three groups of protons. They will be denoted $r_1 = 1/T_1$, $r_s = 1/T_s$, and $r_p = 1/T_p$, respectively. They are the modifications due to spin transport of the corresponding quantities $1/T_1{}^0$, $1/T_s{}^0$, and $1/T_p{}^0 \equiv \Gamma_1$. We still differentiate between two cases: (a) $\tau_s \gg \tau$ and (b) $\tau_s \ll \tau$, and find for T_1:

(a) $1/T_1 = (1/T_1{}^0) + (N_s/N)/(T_s{}^0 + \tau)$
$$+ (N_p/N)/(T_p{}^0 + \tau), \quad (10a)$$

(b) $1/T_1 = (1/T_1{}^0) + [(N_s + N_p)N]/(T_{s+p} + \tau), \quad (10b)$

where
$$1/T_{s+p} = (1/T_s{}^0) + (N_p/N_s)/(T_p{}^0 + \tau_s).$$

Due to the assumption, $N_p \ll N_s$, we find for the other rates in both cases:

$$1/T_s = b_s \equiv (1/T_s{}^0) + (N_p/N_s)/\tau_s + (1/\tau),$$
$$1/T_p = \Gamma_1' \equiv (1/T_p{}^0) + (1/\tau_s) + (1/\tau). \quad (10c)$$

Equations (9) can be simplified somewhat in these two cases.

In the following, we will give special results only for case (a). The solutions given in Eqs. (9) and (10) can also be used to describe the properties of an adsorbed layer without any bulk fluid present. This case is obtained by first taking $\tau_s = \infty$, $N_s = 0$, and then replacing τ by τ_s, N by N_s, $T_1{}^0$ by $T_s{}^0$. The case that the entire system is made up of pumping centers is described by Eqs. (9) with the replacement $C = 1$, $\tau' = \infty$.

III. EVALUATION OF TRANSITION RATES AND MIXING PARAMETER

The transition rates p, q, r, and s and the mixing parameter α, introduced in Sec. II, can be evaluated from the spin–spin intreaction, if the random perturbations are described in terms of correlation times. Solomon[11] calculated the relaxation matrix for a two-spin system under conditions typical for a liquid, in the case that the spin–spin interaction, modulated by random relative motion, is the only source of relaxation for both spins. Abragam[12] has dealt with the effect typical for a solid, in which the only source of randomness is the electron spin relaxation. He[10] has also shown that this leads to the double effect. In the case, which is of interest to us, both relative motion and electron spin relaxation are present, e.g., when the nuclei belong to fluid layers

on a solid surface which contains paramagnetic centers, these results must be combined. We will not attempt to derive complete expressions in this paper. We will limit the discussion to the case that the two spins have only a dipole interaction, and make some further simplifications.

Recently, Bloembergen and Morgan[13] have given a generalization as indicated above for the case of nuclear relaxation in paramagnetic ion solutions. These authors obtained the Hamiltonian for the nuclear spin system by inserting, for the electron spin operators appearing in the interaction, random variables with a correlation time equal to the electron spin relaxation time T_e, assuming $T_e = T_{2e}$.[14] These appear thus multiplied with the random coefficients involving the motional correlation time τ_c. Assuming statistical independence, this gives an over-all variation with a correlation time $(1/\tau_c + 1/T_e)^{-1}$. This correlation time then replaces τ_c in the usual expressions for the nuclear relaxation times. However, one does not obtain q, r, and s separately, but only $2q + r + s$. Dohnanyi[15] investigated the general case that the nuclear motion is anisotropic, and $T_{1e} \neq T_{2e}$ which is more appropriate for the present problem. He used the theory of Kubo and Tomita[16] with dipole–dipole interaction only, and obtained the first terms of an expansion of the relaxation rates valid when the effects of electron spin relaxation are small corrections to the effects of liquid motion. The result for the total nuclear relaxation is in agreement with reference 13, but in addition separate contributions from q, r, and s to $2q + r + s$ can be identified. Expressions in closed form cannot easily be inferred from his result, however. As a reasonable compromise, pending a more complete theoretical evaluation, we will use the following expressions:

$$q = \frac{3}{20} K \frac{1}{\tau_c} \frac{\tau_1{}^2}{1 + \omega_n{}^2 \tau_1{}^2} \quad (11)$$

with

$$r = r' + r'', \quad s = s' + s'', \quad (12a)$$

$$r' = \frac{s'}{6} = \frac{1}{10} K \frac{\tau_2}{1 + \omega_e{}^2 \tau_2{}^2}, \quad (12b)$$

where

$$r'' = s'' = \frac{3}{20} K \frac{1}{T_{1e}} \frac{\tau_1{}^2}{1 + \omega_n{}^2 \tau_1{}^2}, \quad (12c)$$

where

$$\tau_1{}^{-1} = \tau_c{}^{-1} + T_{1e}{}^{-1},$$
$$\tau_2{}^{-1} = \tau_c{}^{-1} + T_{2e}{}^{-1}, \quad (13)$$
$$K = \hbar^2 \gamma_e{}^2 \gamma_n{}^2 / \langle r \rangle^6.$$

[13] N. Bloembergen and L. O. Morgan, J. Chem. Phys. 34, 842 (1961).
[14] Throughout this paper, T_{1e} and T_{2e} are the electronic relaxation times neglecting the contribution from the electron–nuclear interaction.
[15] J. S. Dohnanyi, Phys. Rev. 125, 1824 (1962).
[16] R. Kubo and K. Tomita, J. Phys. Soc. (Japan) 9, 888 (1954).

[11] I. Solomon, Phys. Rev. 99, 559 (1955).
[12] A. Abragam, Phys. Rev. 98, 1729 (1955).

This gives for the relaxation time of the nucleus:

$$\Gamma_1 = 2q + r + s = \frac{1}{10} K \left(\frac{3\tau_1}{1 + \omega_n^2 \tau_1^2} + \frac{7\tau_2}{1 + \omega_e^2 \tau_2^2} \right), \quad (14)$$

which is an obvious generalization of the expression in reference 13.

The varous terms appearing in q, r, and s can be made plausible in the following way: The expression for q describes a process where only the proton flips, exchanging its energy with the liquid motion (as indicated by the factor $1/\tau_c$) but under influence of a frequency spectrum characterized by τ_1. Other terms in q, which are the result of a double flip, "followed" by an electron flip in opposite direction, and contain ω_e in the denominator, are indicated by Dohnanyi's work, but could not be obtained unambiguously. In r' and s' the frequency spectrum is modified, and the energy is transferred in part to the liquid motion, in part to the solid lattice via the electrons. The terms r'' and s'', which vanish when $T_{1e} \to \infty$, describe transitions in which the energy is entirely transferred to the electron system. These terms are the cause of ambiguity in the decomposition of Dohnanyi's results. They represent a modification of the double effect under influence of the random motion, and can be derived independently in the following manner:

In the limit $\tau_c \to \infty$ the states are mixed due to the static interaction between the spins. If α_0 is the coefficient of the static mixing (due to dipole interaction in our model), an electron spin flip is, with a probability $|\alpha_0|^2$, accompanied by a nuclear flip. This gives equal contributions to r and to s of the amount $|\alpha_0|^2/2T_{1e}$, as was first observed by Abragam. Under the influence of the two kinds of random motion, the spins are decoupled. This gives

$$|\alpha|^2 = |\alpha_0|^2 [\omega_n^2 \tau_1^2 / (1 + \omega_n^2 \tau_1^2)]. \quad (15)$$

$|\alpha_0|$ has a value of the order of magnitude unity in weak fields; in "strong" fields one finds, using perturbation theory and averaging over-all directions:

$$|\alpha_0|^2 = \tfrac{3}{10} K \omega_n^{-2}. \quad (16)$$

Inserting this in the equation

$$r'' = s'' = |\alpha|/2T_{1e}, \quad (17)$$

one obtains Eq. (12c). For the discussion in the following section it is important that the denominator in r'' and s'' contains ω_n, and not ω_e, as in r' and s'.

The value of $|\alpha|^2$ of Eq. (15) should also be used in Eq. (2).

Finally, in the equation for p, as given by

$$p = \frac{1}{2T_{1e}} + \frac{3}{20} K \frac{\tau_c}{1 + \omega_e^2 \tau_c^2}, \quad (18)$$

the second term will be modified, but the first term dominates strongly and remains unaltered.

IV. APPLICATION TO SPECIAL CASES

1. The Liquid Effect

When $\Gamma_3 \neq 0$ ($r \neq s$) and when its value is of the same order of magnitude as the other relaxation rates, the term $2\Gamma_3 A$ in the numerator of F_1 in Eq. (9b) dominates, and all terms in B can be neglected. This situation arises when $r'' = s'' \ll (r', s')$. Under this condition the polarization produced in the pumping centers is due to the Overhauser effect. As mentioned above, we only consider the dipole–dipole case. In order to see under what conditions this inequality is satisfied, we note that from Eqs. (13) and (14) and the above discussion of the value of $|\alpha_0|$, it follows that r''/r' is a monotonically increasing function of the external field strength H_0, beginning with the value zero for $H_0 \approx 0$. In the high-field limit we have from Eq. (15)

$$r''/r' = (\tau_c/T_{1e})(\gamma_e/\gamma_n)^2. \quad (19)$$

Therefore, if $\tau_c/T_{1e} \ll (\gamma_n/\gamma_e)^2$ we have $r'' \ll r'$ for all values of H_0. If, on the other hand, $\tau_c/T_{1e} \gg (\gamma_n/\gamma_e)^2$, there will be a field strength H_c, such that $r'' \ll r'$ for $H_0 \ll H_c$ but $r'' \gg r'$ for $H_0 \gg H_c$.

When the inequality $r'' \ll r'$ is obeyed, we have

$$F_1(\omega) = F_2(\omega)/\Gamma_3 = \frac{2A\Gamma_3}{\Gamma_5^2 + 2A\Gamma_1'}. \quad (20)$$

Inserting this in Eq. (9a) we find, for a homogeneously broadened line:

$$Y_h = S_0 f(\Gamma_3/\Gamma_1) A/(A + \lambda). \quad (21)$$

The factor f is at most equal to one, and is given by

$$f = (N_p/N)[(T_{1a}\Gamma_1)/(1 + \Gamma_1\tau)], \quad (22)$$

where T_{1a} is obtained from Eq. (10a) and is therefore equal to the observable nuclear relaxation time in the case that $\tau_s \gg \tau$. Furthermore, we have

$$\lambda = \tfrac{1}{2}(\Gamma_2 - h\Gamma_3^2/\Gamma_1) \quad (23)$$

with

$$h = (f + \tau\Gamma_1)/(1 + \tau\Gamma_1) \leq 1. \quad (24)$$

In most cases of interest, Eq. (23) can be approximated by

$$\lambda = \tfrac{1}{2}\Gamma_2 = 1/2T_{1e}.$$

When we assume furthermore that $\tau_s \gg \tau$ we find, with use of Eqs. (10a)–(10d)

$$Y_h = -S_0 a \frac{P}{1 + P + (\omega - \omega_e)^2/\Gamma^2}, \quad (25)$$

where P is the power in dimensionless units

$$P = \gamma_e^2 H_1^2 / \Gamma_2 \Gamma, \qquad (26)$$

and where

$$a = f\Gamma_3/\Gamma_1 = (N_p/N)(T_p/\tau)T_1\Gamma_3. \qquad (27)$$

Thus, we find that the polarization is proportional to N_p/N, i.e., the concentration of pumping centers, as was to be expected. The proportionality to $T_1\Gamma_3$, i.e., to the ratio of the rate of production by pumping to the rate of relaxation in the bulk, and to T_p/τ, i.e., to the ratio of the rate of transfer between pumping sites and bulk to the rate of relaxation in the pumping sites, is also plausible. A relation equivalent to (25) with this approximate value for a was obtained previously from a simplified treatment of the model.[8]

When the line is inhomogeneously broadened, the average values $\bar{F}_1$ and $\bar{F}_2$ should be inserted in (9a). However, $\bar{F}_2$ in (9a) is negligible with respect to the first term in the denominator for all values of H_1. This follows from the relation $F_2 = \Gamma_3 F_1$ and from the fact that, without the first term, which accounts for the reduction due to diffusion and relaxation, the formula gives a result even larger than the unreduced effect. Therefore, the result Y_{in} for an inhomogeneously broadened line can be obtained directly from (25) by averaging:

$$Y_{\text{in}} = \bar{Y}_h = -S_0 a \int g(\omega_e - \bar{\omega}_e) \frac{A(\omega - \omega_e)}{A(\omega - \omega_e) + \Gamma_2/2} d\omega_e. \qquad (28)$$

We assume a Gaussian distribution

$$g(\omega_e - \bar{\omega}_e) = (k/\sqrt{\pi}) \exp[-k^2(\omega_e - \bar{\omega}_e)^2],$$

and define as usual

$$\pi g(0) = k\sqrt{\pi} = T_2^* = (\gamma_e \Delta H)^{-1}.$$

With the frequency at resonance $\omega = \bar{\omega}_e$, one finds

$$Y_{\text{in}} = -S_0 a \left(\frac{H_1}{\Delta H}\right)^2 \frac{\Gamma}{\Gamma_2} \frac{e^{\delta^2}}{\delta\sqrt{\pi}} [1 - \text{erf}(\delta)], \qquad (29)$$

where

$$\delta^2 = (\Gamma^2/\pi)(1+P)/(\gamma_e \Delta H)^2.$$

For "low" power, one has $\delta \ll 1$, and Eq. (29) gives

$$Y_{\text{in}} = -S_0 a(\Gamma/\gamma_e \Delta H)[P/(1+P)^{1/2}], \quad (\delta \ll 1). \qquad (30)$$

For high power, if one completely saturates the inhomogeneous line so that $\delta \gg 1$, Eq. (29) becomes

$$Y_{\text{in}} = -S_0 a, \quad (\delta \gg 1). \qquad (31)$$

2. The Double Effect

We now consider the case that $p \gg (r,s) \gg (s-r, q)$. This case is realized when, e.g., $T_{1e} \ll \tau_c$, i.e., when the electron relaxation is the dominant source of randomness. Then the inequality $\tau_c/T_{1e} \gg (\gamma_n/\gamma_e)^2$ is a fortiori satisfied, and we have $r'' \gg r'$ for not too weak fields. The situation in the pumping centers is now the same as specified by Abragam[12] and gives rise to a polarization effect as reported by Uebersfeld[1] on benzene in a char and by Abragam[10] in nuclear spin pairs in LiF. Under these conditions we neglect Γ_3 in (9), and also $B_1^2 - B_2^2$, which is always small. Furthermore, Γ_1' is neglected with respect to Γ_2 where permissible. We assume that the width of all three lines is equal, i.e., $\Gamma = \Gamma_+ = \Gamma_-$. Finally, from Sec. III3 we have, with the above inequality $|\alpha|^2 = \Gamma_1/\Gamma_2$.

Besides distinguishing between a homogeneous and an inhomogeneous line, we must now also specify whether a homogeneous component is resolved or not, i.e., whether

$$(\alpha): \omega_n \gg \Gamma \quad \text{or} \quad (\beta): \omega_n \ll \Gamma.$$

We find from Eq. (9) for a homogeneous line

$$Y_{h,\alpha}(\omega = \omega_e \pm \omega_n) = \pm \tfrac{1}{2} S_0 f \frac{P}{1 + (P/2)[(\Gamma_1/\Gamma_2) + h + (\Gamma^2/2\omega_n^2)] + (P^2 h \Gamma^2/8\omega_n^2)}, \qquad (32\alpha)$$

and

$$Y_{h,\beta} = S_0 f \frac{2P\omega_n(\omega - \omega_e)/\Gamma^2}{\{1 + P + [(\omega - \omega_e)^2/\Gamma^2]\}\{1 + hP + [(\omega - \omega_e)^2/\Gamma^2]\}}. \qquad (32\beta)$$

For an inhomogeneous line, $\bar{F}_2$ is again negligible. $\bar{F}_1$ is an odd function of $(\omega - \bar{\omega}_e)$. For large inhomogeneous broadening one can use the approximation

$$\bar{F}_1(\omega - \bar{\omega}_e) = \frac{\delta}{\delta\omega} g(\omega - \bar{\omega}_e) \int_{-\infty}^{+\infty} (\omega - \omega_e) F_1(\omega - \omega_e) d\omega_e$$

as long as one does not saturate the entire inhomogeneous line. One obtains for case (α), for low and intermediate power, defined by $P \ll (\Gamma_1'/\Gamma_1)(\omega_n^2/\Gamma^2)$:

$$Y_{\text{in},\alpha} = S_0 f \frac{\pi\omega_n \Gamma(\Gamma_1/\Gamma_1')P}{[1 + 1/2(\Gamma_1/\Gamma_1')P]^{1/2}} \frac{\delta}{\delta\omega} g(\omega - \bar{\omega}_e), \qquad (33\alpha)$$

and for higher power, $P \gg (\Gamma_1'/\Gamma_1)(\omega_n^2/\Gamma^2)$:

$$Y_{\text{in},\alpha} = S_0 f \frac{2\pi\omega_n \Gamma(\Gamma_1/\Gamma_1')P^{1/2}}{[1 + (\Gamma_1/\Gamma_1')^{1/2}]} \frac{\delta}{\delta\omega} g(\omega - \bar{\omega}_e). \qquad (34\alpha)$$

For case (β) one has, for any reasonable power level:

$$Y_{\text{in},\beta} = S_0 f \frac{2\pi\omega_n \Gamma(\Gamma_1/\Gamma_1')P}{(1+P)^{1/2} + [1 + (\Gamma_1/\Gamma_1')P]^{1/2}}$$

$$\times \frac{\delta}{\delta\omega} g(\omega - \omega_e). \qquad (34\beta)$$

For the intermediate case that $r''\gg r'$ but still $\tau_c<T_{1e}$ similar expressions could be developed without much difficulty, From Eqs. (25)–(33) the effects without diffusion are obtained by taking $f=1$, $h=1$, and $\tau=\infty$.

V. DISCUSSION

Some systems to which the above analysis could be applied are: (a) fluids contained in the pores of powders, gels or fiber mats; (b) stable colloidal suspensions. We will now examine some of the predictions of the theory and compare them with some of the experimental results for such systems.

1. Nuclear Thermal Relaxation Rates

In Sec. II, we derive some formulas for the observed nuclear thermal relaxation rate $1/T_1$ for a fluid as influenced by "wall effects." Equation (10a), which is applicable for the case where there is negligible mixing n the surface la yer, i.e., $\tau_s\gg\tau$, can be written as

$$(1/T_1)-(1/T_1{}^0)=(N_a/N)$$
$$\times[f_s/(T_s{}^0+\tau)+f_p/(T_p{}^0+\tau)], \quad (35)$$

where

$$N_a=N_s+N_p, \quad f_s=N_s/N_a, \quad f_p=N_p/N_a.$$

From Eq. (14), we have

$$\frac{1}{T_p{}^0}=\frac{1}{10}K\left[\frac{3\tau_1}{1+\omega_n{}^2\tau_1{}^2}+\frac{7\tau_2}{1+\omega_e{}^2\tau_2{}^2}\right].$$

If we assume for the sake of discussion the simple "local field" model of relaxation for the nuclei, N_s in the surface layer, then

$$\frac{1}{T_s{}^0}=G\frac{\tau_c}{1+\omega_n{}^2\tau_c{}^2}, \quad (36)$$

where $G=\gamma_n{}^2H_{loc}{}^2$. $H_{loc}{}^2$ is the mean square of the local field.

Let us now consider formula (35) in terms of three experimental variables: (1) concentration, N_a/N, (2) magnetic field strength, H_0, and (3) temperature, T.

Concentration Dependence

$$(1/T_1)-(1/T_1{}^0)\propto N_a/N. \quad (37)$$

This relationship is shown to be valid by the experiments of Winkler[17] on water in the pores of Al_2O_3 powder and by Poindexter[4] for a colloidal suspension of asphaltene in xylene. In these experiments the observed rate, $1/T_1$, decreased linearly with increasing amount of liquid over a wide range.

Magnetic Field Dependence

$$(1/T_1)-(1/T_1{}^0)\propto f_s/[T_s{}^0(H_0)+\tau]$$
$$+f_p/[T_p{}^0(H_0)+\tau]. \quad (38)$$

The local surface relaxation times $T_s{}^0(H_0)$ and $T_p{}^0(H_0)$ are functions of the applied magnetic field H_0. This is seen in Eqs. (14) and (36) by the dependence on ω_n and ω_e. As can be easily seen, a detailed study of field dependence of the rate $(1/T_1)-(1/T_1{}^0)$ results in information which can be interpreted in terms of the correlation times, τ_c, τ_1, and τ_2, and the relative numbers of nuclei f_s and f_p in the two kinds of surface sites. An example of the former is an analysis of the field-dependence data as reported by Brown[18] for a system of quartz powder and water. At a temperature of 100°C, and magnetic fields of 0.6, 36, 75, and 1500 G, $(1/T_1)-(1/T_1{}^0)=0.66, 0.29, 0.24$, and 0.24 sec^{-1}, respectively. If one assumes proton–proton interaction for the contribution that vanishes at high field, and that $\tau<T_s{}^0$ for, $H_0\leq0.6$ G, (the validity of assuming this inequality will be discussed in the next section), then $\omega_n{}^2\tau_c{}^2\approx1$ for $H_0\approx15$ G and $\tau_c\approx3\times10^{-6}$ sec. This would indicate an almost icelike structure for the interfacial water. One can test the validity of the assumption of the proton–proton interaction by diluting the water with D_2O.

Temperature Dependence

Let us consider again only one of the possible kinds of surface relaxing steps, i.e., one not associated with pumping centers. With H_0 adjusted so that $\omega_n{}^2\tau_c{}^2\ll1$, then Eq. (36) becomes

$$1/T_s{}^0=G\tau_c,$$

and by use of Eq. (35)

$$(1/T_1)-(1/T_1{}^0)\propto G\tau_c/(1+G\tau_c\tau). \quad (39a)$$

We assume that both τ_c and τ vary with temperature according to an Arrhenius law of the form $\exp(E/kT)$. Then for "low" temperatures:

$$G\tau_c\tau\ll1,$$

and

$$(1/T_1)-(1/T_1{}^0)\propto 1/\tau. \quad (39b)$$

For "high" temperatures:

$$G\tau_c\tau\ll1,$$

and

$$(1/T_1)-(1/T_1{}^0)\propto \tau_c. \quad (39c)$$

An example of data to which we can apply this analysis is again that reported by Brown[18] for quartz powder and water. For $H_0=0.6$ G, $(1/T_1)-(1/T_1{}^0)=0.47, 0.60, 0.66$, and 0.66 sec^{-1} at temperatures of 1.5, 20, 51, and 100°C, respectively. At low temperatures the rate is interpreted as being controlled by the resi-

[17] H. Winkler, Kolloid-Z. 161, 127 (1958).

[18] R. J. S. Brown, Bull. Am. Phys. Soc. 3, 23 (1958).

dence time, i.e., $\tau > T_s{}^0$, and at about 80°C, $\tau \approx T_s{}^0$. For temperatures greater than 80°C, $\tau < T_s{}^0$.

One of us[19] is making a detailed study of a colloidal suspension of monohydrated alumina in water to test quantitatively this relaxation theory.

2. Enhancement of Nuclear Spin Polarization

In Sec. IV, we derive some formulas for the enhancement of nuclear polarization Y by the spin pumping of electrons which are coupled to the nuclei through dipole–dipole forces. Let us consider these formulas in terms of four experimental variables: (1) concentration, N_p/N, (2) pumping power, P, (3) magnetic field strength, H_0, and (4) temperature, T.

Concentration Dependence

For all of the cases considered of the general equation (9) we see that
$$Y \propto f, \qquad (40)$$
where
$$f = (N_p/N)/(T_p{}^0+\tau)[(1/T_1{}^0)+(N_p/N)/(T_p{}^0+\tau)$$
$$+(N_s/N)/(T_s{}^0+\tau)]^{-1}.$$

Thus, the enhancement decreases with an increase of the fluid phase. This is in agreement with the observation of Poindexter[4] for a colloidal asphalt system, showing that the enhanced polarization is for the solvent protons and not the protons in the colloid.

Pumping Power

For both the liquid effect and the double effect we see that the functional form of the power dependence of the enhancement of nuclear polarization depends on whether the electron resonance is homogeneously or inhomogeneously broadened. For the case of the liquid effect, we see from Eqs. (25) and (30) that for $\omega=\omega_e$

$$Y_h \propto P/(1+P), \qquad (41a)$$
and
$$Y_{in} \propto P/(1+P)^{1/2}. \qquad (41b)$$

For a power dependence study it is important to prevent the sample from heating with increased power input because of the sensitivity of the enhancement to temperature which will be discussed below. In Poindexter's[4]

experiment the temperature was not controlled,[20] so we cannot compare the theory directly with the data. This work has been repeated,[21] and the enhancement observed can be described by Eq. (41b) showing that the asphalt resonance is inhomogeneously broadened.

Magnetic Field Strength

In Sec. IV, we show that for a system in which the relation $(\tau_c/T_{1e})(\gamma_e/\gamma_n)^2 \gg 1$ is satisfied there should be some critical magnetic field strength H_c such that $r'' \ll r'$ for $H_0 \ll H_c$ and $r'' \gg r'$ for $H_0 \gg H_c$. These inequalities describe the conditions necessary for the liquid effect and the double effect, respectively. One sees that the same system could exhibit the liquid effect at low magnetic fields and the double effect at high fields. Such a system has been reported. A natural crude oil which contains paramagnetic colloids of asphaltene was studied by Poindexter[3] at 18 G and the liquid effect was observed. Anderson[5] studied a crude oil at 3000 G and observed a double effect. Poindexter and Uebersfeld[22] have repeated the experiment, each using the same asphalt solution, and have also found the liquid effect at low field and double effect at high fields in agreement with the prediction.

Temperature Dependence

We have seen above that molecular correlation times are very important in determining the critical field H_c for the transiton from the liquid effect to the double effect and also the magnitude of the ultimate enhancement as governed by the factor f [Eq. (22)]. Since in general molecular correlation times are sensitive functions of temperature, we can expect strong temperature dependence. Poindexter (as mentioned above) has reported an increase in the enhancement with increasing temperature for the liquid effect and Anderson[5] reported "strong dependence" for the double effect.

[19] D. O. Seevers (to be published).

[20] E. Poindexter (private communication).
[21] E. Poindexter, J. Chem. Phys. (to be published).
[22] E. Poindexter and J. Uebersfeld, J. Chem. Phys. 36, 2706 (1962).