PHENOMENOLOGICAL MODEL FOR THE NEW EFFECT IN DYNAMIC POLARIZATION*

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We propose a phenomenological model involving the cross-coupling of the allowed and forbidden epr transitions between electrons belonging to neighboring packets of an inhomogeneously broadened epr spectrum. This model yields all the observed qualitative features of the new effect in dynamic polarization previously reported.

In a previous communication[1] we reported the empirical evidence of a new effect in the dymanic polarization of protons in chemically doped plastics at liquid-helium temperatures.[2] We there attributed this new effect to some mechanism of spin-spin interaction, which described the qualitative behavior of our results. This Letter presents a phenomenological model for a specific form of spin-spin interaction.

We assume essentially the Portis[3] picture of the structure of inhomogeneously broadened epr due primarily to hfs. The epr line then consists of many narrow packets of electrons e^j ($j=1,2,3,\cdots$), with populations N^j, in proximity to each other. Each packet of electrons couples dipolarly with n^j protons. Consider three such packets whose resonant frequencies satisfy

$$\nu_e{}^i = (2\pi)^{-1}\gamma_e(H'+H_{\rm loc}{}^i),$$

$$\nu_e{}^{i\pm1} = (2\pi)^{-1}\gamma_e(H'+H_{\rm loc}{}^{i\pm1})$$

$$= \nu_e{}^i \mp \nu_n = (2\pi)^{-1}\gamma_e(H'+H_{\rm loc}{}^i)\mp\nu_n, \quad (1)$$

where ν_n is the nmr frequency of the protons at a given applied external magnetic field H', $H_{\rm loc}{}^j$ is the local magnetic field for the jth packet, and γ_e is the gyromagnetic ratio of the electron. Figure 1 shows the energy levels for representative electrons in weak dipolar coupling with a proton for each of these three packets together with the relevant stimulated transition rates $W_1{}^j$ through $W_3{}^j$ and the relaxation rates $w_1{}^j$ through $w_3{}^j$. The direct excitation of transitions $W_2{}^j$ and $W_3{}^j$ by an applied rf magnetic field gives rise to the "solid effect" discussed in great detail by many investigators.[4-6] For our phenomenological model, we propose here two additional transition rates $W_5{}^j$ and $W_6{}^j$ which represent the cross-coupling between $W_2{}^i$ and $W_1{}^{i-1}$, $W_1{}^i$ and $W_3{}^{i-1}$ ($W_5{}^i$); or between $W_3{}^i$ and $W_1{}^{i+1}$, $W_1{}^i$ and $W_2{}^{i+1}$ ($W_6{}^i$). An essentially identical form of interaction was first implied by Kessenikh, Manenkov,[7] and Pyatnitskii in their treatment of dynamic polarization of protons in irradiated polyethylene. However, their results are not valid for the very high electron polarizations germane to our case. Moreover, our treatment of the microwave power dependence is simpler, allowing us to approximate the power dependence in closed form.

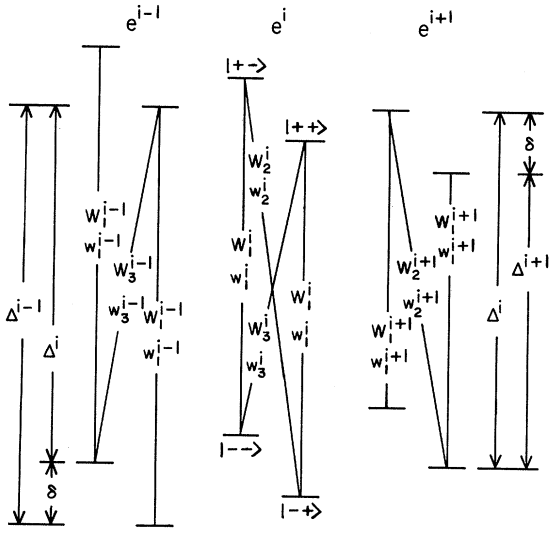

FIG. 1. The energy levels and pertinent connecting rates for the packets of Eq. (1). The Δ^i are total electron splittings; $W_5{}^i$ couples transitions $W_1{}^{i-1}$ to $W_2{}^i$ and $W_1{}^i$ to $W_3{}^{i-1}$, $W_6{}^i$ couples $W_1{}^{i+1}$ to $W_3{}^i$ and $W_1{}^i$ to $W_2{}^{i+1}$. The proton rates $W_4{}^i$ and $w_4{}^i$ are not shown.

We assume specifically that transition rates $W_5{}^j$ and $W_6{}^j$ are effectively much larger than the forbidden transition rates $W_2{}^j$ and $W_3{}^j$, because of the spin-spin interaction among the electrons. The enhanced transition rates could be visualized as caused by the increased virtual photon density over the real applied photon density on account of the saturation of the allowed transitions $W_1{}^j$. This assumption is the essence of our phenomenological model for the explanation of the new effect in dynamic polarization.

To show that this model gives the correct qualitative features, we see from Fig. 1 that W_2^i enhances the proton polarization in the negative sense, whereas W_3^i enhances it in the positive sense due to the pure "solid effect." These "forbidden" transitions are located symmetrically about the maximum of the "allowed" transition. When microwave power is applied at $H'=H_0$, i.e., at the center of the epr, the virtual photons produced in the saturation of the "allowed" transition are equally coupled to the two "forbidden" transitions, giving a net enhancement of unity. However, when power is applied at $H'>H_0$ ($<H_0$) i.e., above (below) the epr center, the situation is no longer symmetric and the "forbidden" transition above (below) the "allowed" is preferentially coupled, producing a net positive (negative) enhancement, as was observed. Since the cross-coupling involves both the "allowed" and the "forbidden" transitions, it is quite possible to have enhancement maxima somewhere between the maxima of the "allowed" and "forbidden" transitions, producing the reduced peak separations reported previously. Moreover, since the competing processes are always present it would be unlikely for the new effect to give a flat region of unity enhancement near $H'=H_0$.

The rate equations for the spin system will consist of two parts: terms corresponding to the conventional "solid effect" (SE) plus additional terms for the new "cross effect" (CE). In the notation of Ref. 4, and assuming $\bar{W}_5^i = RN^{i-1}$, $\bar{W}_6^i = RN^{i+1}$, where R is some constant rate related to T_{2e}^{-1}, the CE contribution to the rate equation for the protons in the jth packet is

$$(d\bar{n}_2^{\,j}/dt)_{CE} = R[(\bar{n}_1^{\,j}N_1^{\,j}N_2^{\,j-1} - \bar{n}_2^{\,j}N_2^{\,j}N_1^{\,j-1})N^{j-1} + (\bar{n}_1^{\,j}N_2^{\,j}N_1^{\,j+1} - \bar{n}_2^{\,j}N_1^{\,j}N_2^{\,j+1})N^{j+1}]. \tag{2}$$

Note that, considering Eqs. (1), these rates conserve a Boltzmann equilibrium as they stand. In terms of polarizations, Eq. (2) becomes

$$(d\bar{p}^j/dt)_{CE} = \tfrac{1}{2}R\{N^{j-1}[P^j - P^{j-1} - \bar{p}^j(1-P^jP^{j-1})] - N^{j+1}[P^j - P^{j+1} + \bar{p}^j(1-P^jP^{j+1})]\}. \tag{3}$$

The SE term may be written immediately,[4-6]

$$(d\bar{p}^j/dt)_{SE} = [2\bar{w}_4 + \bar{\sigma}w(1-P^jP_0^{\,j})](p_0 - \bar{p}^j) - \bar{W}_2^{\,j}(\bar{p}^j - P^j) - \bar{W}_3^{\,j}(\bar{p}^j + P^j), \tag{4}$$

where $2\bar{w}_4$ is the "extraneous" proton relaxation rate and $w = T_{1e}^{-1}$, the electron spin-lattice relaxation rate. For a given H', the $\bar{W}_{2,3}^{\,j}$ are large over only a small range of j, i.e., they affect only a small portion of the total spin populations. We shall therefore neglect the $\bar{W}_{2,3}^{\,j}$; however, in the final electron equation we will retain the term in W_1^j, since the cross-coupling within the allowed line can distribute the effect of $\bar{W}_1^{\,j}$ over a large fraction of the populations.

We now define a continuous field variable x and the normalized epr line shape, $g(x)$, such that $x=0$ marks the center of the epr, and define a constant r such that $\frac{1}{2}RN^j = rg(x^j)$. The combined analog of Eqs. (3) and (4) is then

$$\begin{aligned} d\bar{p}(x)/dt = {} & r\beta(x)[p_0 - \bar{p}(x)] + rg(x-\delta)\{P(x) - P(x-\delta) - \bar{p}(x)[1-P(x)P(x-\delta)]\} \\ & - rg(x+\delta)\{P(x) - P(x+\delta) + \bar{p}(x)[1-P(x)P(x+\delta)]\}, \end{aligned} \tag{5}$$

where

$$\beta(x) = r^{-1}\{2\bar{w}_4 + \bar{\sigma}w[1-P(x)P_0(x)]\}.$$

Taking the sample average of the steady-state solution of (5) while neglecting the small term in p_0 gives

$$\langle \bar{p}(x)\rangle_{av} = \int_{-\infty}^{\infty} \frac{\{g(x-\delta)[P(x)-P(x-\delta)] - g(x+\delta)[P(x)-P(x+\delta)]\}g(x)dx}{\beta(x) + g(x-\delta)[1-P(x)P(x-\delta)] + g(x+\delta)[1-P(x)P(x+\delta)]}. \tag{6}$$

In general Eq. (6) gives the net dynamic polarization if $g(x)$ and $P(x)$ are known. The line shape $g(x)$ is directly measured by epr techniques.

A useful average property of $P(x)$ under conditions of microwave saturation of the spins located at x' in the line may be derived by taking the sample average of the electron rate equation in steady state. For this purpose define a "saturating ensemble" shape function $\lambda(x,x')$ such that

$$P(x,x') \equiv P_0(x)[1-\epsilon\lambda(x,x')], \tag{7}$$

where $0 \leq \epsilon \leq 1$, $\lambda(x',x')=1$, and define

$$\Omega \equiv \int_{-\infty}^{\infty} \lambda(x,x')dx. \tag{8}$$

The parameters Ω and ϵ are, respectively, the "saturating ensemble" width and amplitude; in general, both may be functions of x' and microwave power. The electron rate equation is

$$dP(x)/dt = w[P_0(x)-P(x)]-2W_1(x)P(x) + \text{cross-coupling terms}, \tag{9}$$

where the dependence on x' is understood. By detailed balance, the sample average of the cross terms vanishes. Under the assumption that $P(x,x')$ and $g(x)$ are slowly varying with respect to $W_1(x,x')$, which has a width of the order of the inverse electron transverse relaxation time $\omega \approx \pi(\gamma_e T_{2e})^{-1}$, Eq. (9) then yields

$$\epsilon(x',t) \approx tg(x')[\langle\lambda(x,x')\rangle_{\text{av}} + tg(x')]^{-1}, \tag{10}$$

where $t = \pi\gamma_e H_1^2 T_{1e}$ is a saturation parameter, with H_1 being the usual amplitude of the applied rf.

Figure 2 shows the results of applying Eqs. (6)-(10) to the case of the samples reported in Ref. 1, under the assumptions that $g(x)$ is the same shape as that observed at $H_0 = 3$ kG, and that $\lambda(x-x')$ is a Gaussian with Ω independent of x' and t. To simplify fitting procedures, let $\beta(x) = [1-P(x)P_0(x)]\beta_0$. The fits were obtained by sampling computer output, selecting the best simultaneous fits to the curves of E vs H' and the observed power dependence of the data. The power dependence given by Eq. (10) for different values of x' is in qualitative agreement with the observations of Ref. 1. To strengthen the evidence of the three-parameter fits given here, the same model as applied to a series of experiments at $H_0 = 3$ kG will be presented elsewhere to show that the values of Ω, t, and $\beta(x)$ required by the model are consistent with those deduced by other more direct means. We will also present there a more detailed development of the theory outlined here.

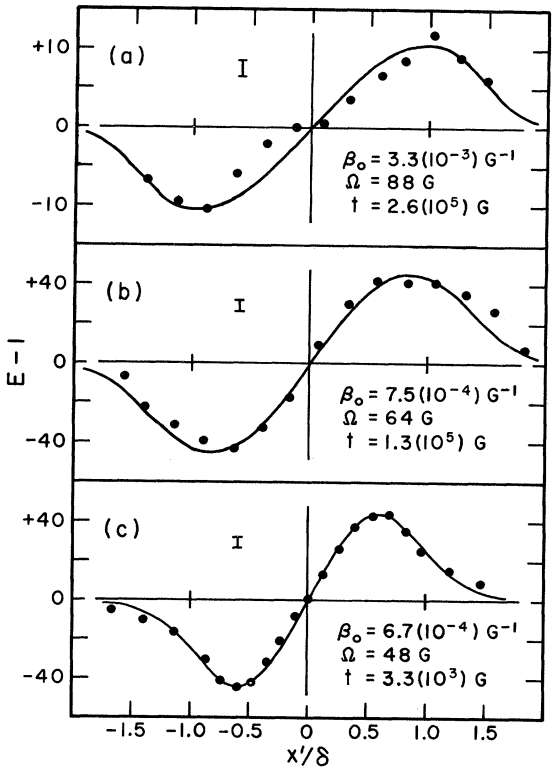

FIG. 2. The circles are the experimental free-proton dynamic enhancements at 4.2°K and 70 GHz of Ref. 1, for Ley's radical in polystyrene at percents by weight of (a) 0.25%, (b) 1.5%, and (c) 5.0%. The theoretical curves are obtained with the parameter values listed.

Because the key of this model lies in the nature of the epr line and because most of the organic free radicals exhibit similar characteristics of inhomogeneously broadened epr lines when present in dilute form in most host materials, we believe that the model developed here would be generally applicable to such materials.

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SPONTANEOUS APPEARANCE OF PICOSECOND PULSES IN RUBY AND Nd:GLASS LASERS

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Picosecond light pulses have been observed to appear spontaneously in ruby and Nd:glass lasers Q-switched by means of a rotating mirror. This striking phenomenon is explained on the basis of coherence effects. The implication is that lasers with broad linewidths will quite generally tend to oscillate as pulse-regenerative oscillators.

We have observed the spontaneous appearance of picosecond (10^{-12} sec) duration light pulses from a ruby laser and a neodymium:glass laser Q-switched at room temperature by means of a rotating mirror. Two-photon fluorescence pulse collision and speed-up techniques[1,2] have been used to display these pulses directly. Figure 1(a) is a photograph of the blue fluorescence produced in a 1.8-cm-long cell of dibenzanthracene in benzene when a beam of picosecond pulses at 0.53 μ, entering the cell from the left, is reflected upon itself by a mirror located at the right end of the trace. The green light pulses at 0.53 μ are derived from the 1.06-μ output of the Nd:glass laser by phase-matched second harmonic generation in KH_2PO_4. The individual pulses each have a duration of less than 1.0 psec; they emerge from the laser in the form of trains of 5-10 pulses 67 psec apart, giving rise to the uniformly spaced spots in Fig. 1, as in the experiment of Giordmaine, Rentzepis, Shapiro and Wecht.[1] Brighter fluorescence spots occur where the picosecond pulses reflected from the mirror overlap the oncoming ones. The spot width is a direct measurement of the pulse duration. The 67-psec spacing of the pulses corresponds to twice the width of an interferometer flat used as the output reflector of the laser. The flat had a 80% reflective dielectric coating on the side facing the laser rod. Note that for our laser the round-trip transit time $2L/c$ was 3.3 nsec, where L is the effective length of the cavity and c the speed of light.

Similar but longer fluorescence spots were also produced in a benzene solution of 9,10-diphenylanthracene by the output beam of a Q-switched ruby laser constructed in exactly the same manner as the Nd:glass laser described above. The ruby laser pulses were found to have an average duration of approximately 10 psec.

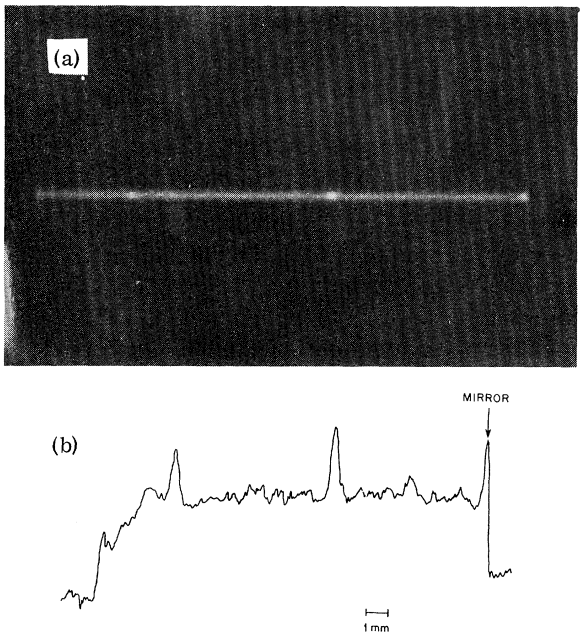

FIG. 1. (a) Fluorescence trace produced by a train of picosecond pulses spaced 67 psec, entering the cell from the left, and reflected upon itself by a mirror (not visible) located at the right end of the track. The pulses are derived from a Nd:glass laser, Q-switched by a rotating mirror. (b) Photodensitometer tracing of the fluorescence tracks. Numerical data on the fluorescent intensities observed will be found in Ref. 1.

The output power waveforms as observed with a fast (0.3-nsec risetime) photodiode and Tektronix 519 oscilloscope (overall system risetime 0.5 nsec) were found to have the usual "hill" shape,[3] about 20 nsec at half-height with a generally small ripple at the cavity round-