PHYSICAL REVIEW B VOLUME 23, NUMBER 3 1 FEBRUARY 1981

Pulse saturation behavior of inhomogeneously broadened lines. I. Slow spectral diffusion case

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(Received 8 July 1980)

A model involving several coupled thermodynamic reservoirs is used to describe the behavior of inhomogeneously broadened absorption and dispersion signals under resonant and nonresonant stationary weak-pulse saturation. This model allows a good reproduction of the hole-burning and dipolar-reservoir effects observed on absorption lines and predicts similar, as yet unobserved, effects for dispersion signals.

I. INTRODUCTION

Usual attempts to explain the saturation effects in magnetic resonance, whether for homogeneous[1–3] or for inhomogeneous[4–7] solid systems, involve thermodynamic models.[8] The spin system is divided into several thermodynamic reservoirs, each with a defined temperature, which are coupled to each other and to the oscillating fields and the lattice.[1–8] The number of these reservoirs depends upon the strength of the spin-spin interactions (and associated rates of spectral-diffusion processes) and also on the saturation level.[4–7] We have previously applied such models in the study of the continuous-saturation behavior of inhomogeneously broadened lines (IBL's) in the cases of rapid[7(a)] and slow[7(b)] spectral diffusion. Here, we apply the multiple-reservoir model[7(b)] to investigate the saturation behavior of IBL's under resonant and nonresonant stationary pulses. This helps us reproduce the hole-burning and dipolar-reservoir effects observed on absorption lines[9,10] and predict similar effects for dispersion signals, which have not yet been observed.

Our model and treatment are outlined in Sec. II. Section III exhibits the results obtained in a few typical cases and discusses the interest of the multiple-reservoir model for investigating the effects of resonant and nonresonant saturation on homogeneous and inhomogeneous lines.

II. MODEL AND TREATMENT

The saturation method is that described by Holcomb *et al.*[11] and Mefed and Rodak[10] for NMR and by Atsarkin[9] for EPR. A strong oscillating field B_{1s}, of fixed angular frequency ω_s, is used to saturate the signal measured with a weak oscillating field B_1, of variable angular frequency $\omega(B_1 \ll B_{1s})$. With a pulse repetition period τ much shorter than the spin-lattice relaxation time T_1 and a saturating field B_{1s} for the single pulse much smaller than the static local field $\langle \Delta B_i^z \rangle$ responsible for the inhomogeneous broadening (itself assumed to be much smaller than the applied magnetic field B_0^z), one can ensure the stationary saturation regime in the weak-saturation limit.[9] This allows the following treatment.

In Provotorov's theory[1] as extended to the multiple-reservoir model,[5,7(b)] the state of the spin system, after a lapse of time much longer than the spin-spin relaxation time T_2, is described by the reduced density operator

$$\rho(t) = \frac{\exp\left[-\sum_{i=1}^{n} \beta_i(t)\mathcal{H}_{z_i} - \beta_D(t)\mathcal{H}_D\right]}{\mathrm{Tr(numerator)}} . \quad (1)$$

The first term in the exponent is the sum of n Zeeman terms, each of which corresponds to a subset of N_i equivalent spins with Larmor frequency $\omega_i = \gamma(B_0^z + \Delta B_i^z)$ (spin-packet model[12,13]). Since Zeeman-energy transfer is more efficient when spin packets have a closer frequency, one can assign different temperatures, $1/k\beta_i$, to the Zeeman degrees of freedom associated with different spin packets.[5] The second term in the exponent is responsible for the homogeneous broadening of the line and includes all secular spin-spin terms commuting with each Zeeman term. Within this (dipolar) term, interpacket secular terms, $\mathcal{H}_{D_{ij}}$, can induce energy transfer between intrapacket secular terms, $\mathcal{H}_{D_i}$, without changing Zeeman energies. When $\langle \mathcal{H}_{D_i} \rangle \sim \langle \mathcal{H}_{D_{ij}} \rangle$, it thus becomes possible to define a single dipolar reservoir, with temperature $1/k\beta_D$. This has been experimentally confirmed by Atsarkin.[9]

The kinetics of the β_i's and β_D are described by Provotorov's equations,[1] which are written, in the multiple-reservoir model,[7(b)]

$$\dot{\beta}_i(t) = -P_i(\Delta_{is})\beta_{iD}(t) - \sum_{j(\neq i)}^{n} W_{ij}(\Delta_{ij})\beta_{ijD}(t) - (1/T_1)[\beta_i(t) - \beta_L] \quad (i = 1, \ldots, n) , \tag{2a}$$

$$\dot{\beta}_D(t) = \left[\frac{1}{\Delta\omega_D^2}\right]\left[\sum_{i=1}^{n} p_i\omega_i\Delta_{is}P_i(\Delta_{is})\beta_{iD}(t) + \sum_{i<j}^{n} p_i\omega_i\Delta_{ij}W_{ij}(\Delta_{ij})\beta_{ijD}(t)\right] - \left[\frac{1}{T_1'}\right][\beta_D(t) - \beta_L] , \tag{2b}$$

with

$$\beta_{iD}(t) = \beta_i(t) - (\Delta_{is}/\omega_i)\beta_D(t) ,$$

$$\beta_{ijD}(t) = \beta_i(t) - [\omega_j\beta_j(t) + \Delta_{ij}\beta_D(t)]/\omega_i ,$$

where

$$\Delta_{is} = \omega_i - \omega_s, \quad \Delta_{ij} = \omega_i - \omega_j ,$$

$$\Delta\omega_D^2 = \mathrm{Tr}(\mathcal{H}_D^2)/\hbar^2\,\mathrm{Tr}(S^{z2}), \quad p_i = N_i/N .$$

The term $(k\beta_L)^{-1}$ is the lattice temperature at thermal equilibrium, and $1/T_1$ and $1/T_1'$ are the Zeeman and dipolar spin-lattice relaxation rates, respectively. $P_i(\Delta_{is})$ is the transition probability function for spin packet i, due to the saturating field B_{1s}; and $W_{ij}(\Delta_{ij})$ is the cross-relaxation function from spin packet i to spin packet j, due to that part of nonsecular dipolar interactions which conserves the total spin projection. For a concentration of spins $f \equiv N/N_0 << 1$ (N_0 being the total number of lattice sites), one can represent these two functions by cut-Lorentzian line shapes and express their widths using the method of moments.[7(b)] For a random distribution of spins, it can be shown that the magnitude of W_{ij} depends linearly on $f_j \equiv N_j/N_0 = p_j f$ and can thus be related to ω_j via the spin-packet envelope $p_j(\omega_j)$.

In the stationary weak-pulse saturation case, considered here, the dispersion and absorption signals are functions of the steady-state solutions β_{ist} $(i = 1, \ldots, n)$ and β_{Dst} of Eqs. (2a) and (2b)

$$\chi'(\omega)B_1 = \frac{\chi_0 B_1}{2\beta_L}\left[\beta_{Dst} + \sum_{i=1}^{n}\omega_i\left[\beta_{ist} - \frac{\Delta_i}{\omega_i}\beta_{Dst}\right]p_i(\omega_i)\pi g'(\Delta_i)\right] , \tag{3}$$

$$\chi''(\omega)B_1 = \frac{\chi_0 B_1}{2\beta_L}\sum_{i=1}^{n}\omega_i\left[\beta_{ist} - \frac{\Delta_i}{\omega_i}\beta_{Dst}\right]p_i(\omega_i)\pi g(\Delta_i) . \tag{4}$$

Here χ_0 is the static susceptibility of the sample, $\Delta_i = \omega_i - \omega$, and $g(\Delta_i)$ and $g'(\Delta_i)$ are the unsaturated spin-packet absorption and dispersion line shapes, respectively. It is convenient to introduce the following parameters:

$$A = \Delta\omega_D/\Delta\omega_G \equiv 1/\Delta\omega_G T_2 ,$$

$$R_{(s)} = (\omega_{(s)} - \omega_0)T_2, \quad S = \gamma B_{1s}(T_1T_2)^{1/2} ,$$

$$K^2 = \left[\frac{\Delta\omega_G^2}{\Delta\omega_D^2}\right]\left[\frac{T_1'}{T_1}\right] = \frac{A^{-2}T_1'}{T_1}, \quad Y^2 = \overline{M}_2^{\,\mathrm{CR}}/\Delta\omega_G^2 , \tag{5}$$

where $\Delta\omega_D^2$ has been defined with Eq. (2b) and represents the width of the spin-packet line shape $g(\Delta_i)$,

$$\Delta\omega_G^2 = \mathrm{Tr}\left[\left[\gamma\hbar\sum_{i=1}^{n}\Delta B_i^z S_i^z\right]^2\right]\Big/\hbar^2\,\mathrm{Tr}(S^{z2}) = \sum_{i=1}^{n} p_i\Delta\omega_i^2$$

defines the width of the spin-packet envelope $p_i(\omega_i)$, the cross-relaxation second-moment scaling factor $\overline{M}_2^{\,\mathrm{CR}} = \gamma^4\hbar^2/r_0^6$ with r_0 being the distance of closest possible approach between two spins,[7(c)] and $\omega_0 = \gamma B_0^z$. These parameters can be used as input data in a computer program which determines the steady-state solutions of Eqs. (2a) and (2b) and the functions given by Eqs. (3) and (4). Currently there are no analytical solutions of Eqs. (2a) and (2b), those given by Atsarkin and Demidov[14] being appropriate only for a special combination of the Zeeman and dipolar temperatures. Results obtained with our program for absorption and dispersion signals are displayed in Figs. 1 and 2, respectively, with different ratios of homogeneous to inhomogeneous broadening ($A = 0.2$ and 2.0) and under resonant and nonresonant conditions of saturation ($R_s = 0$ and 2) with increasing intensity ($S = 0, 1, 3, 10$). These results are discussed below.

III. RESULTS AND DISCUSSION

For resonant saturation, the smaller value of A induces the well-known hole-burning effect displayed in Fig. 1(a), whereas the larger value of A leads to the homogeneous saturation behavior shown in Fig. 1(b). In these conditions it can be shown, using Eqs. (2a) and (2b), that β_{Dst} remains equal to β_L whatever the values of T_1'/T_1 and B_{1s} and, consequently, that its contribution to $\chi''(\omega)B_1$ is negligible. So that widely different values of K^2 will give identical line shapes when saturating the line center. For non-

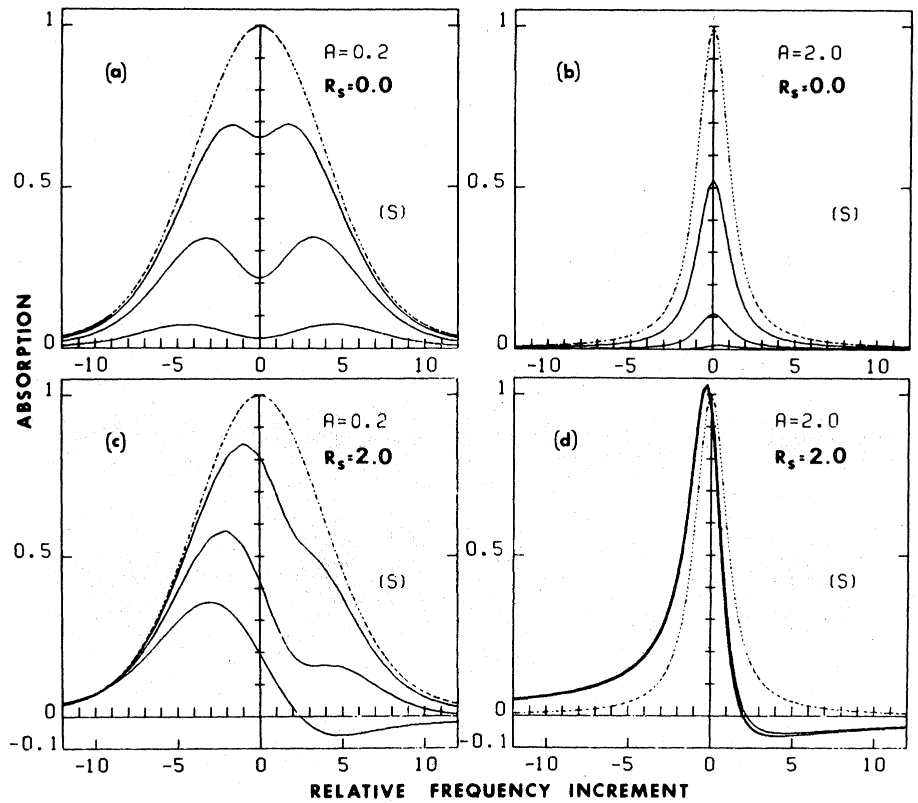

FIG. 1. (a)–(d) Standard absorption intensity vs R for different values of A and R_s, and $K^2=3$, $Y^2=1$. Dotted lines correspond to unsaturated shapes ($S=0$) and solid lines to increasingly saturated ones ($S=1,3,10$).

resonant saturation, on the contrary, the value taken by β_{Dst} will strongly depend upon the relative values of T_1'/T_1 and B_{1s} and may, therefore, contribute drastically to the saturation behavior of absorption lines through the second term of Eq. (4). The calculated curves given in Figs. 1(c) (for a small-A value) and 1(d) (for a large-A value) exhibit a shift of the maximum away from the point of application of the saturating field and increasing with S. Moreover, for sufficiently large values of S, one observes an induced emission on the saturated wing while the absorption on the other wing tends to be enhanced with respect to the unsaturated line. These latter asymmetry features are characteristic of dipolar-reservoir effects, whereas for smaller values of A and S the line shape is chiefly determined by the inhomogeneous distribution of β_{ist}'s produced by the spectral diffusion of saturation. Figures 1(c) and 1(d) are in close agreement with the experimental shapes measured for inhomogeneous EPR lines[9] and quasihomogeneous NMR lines,[10] respectively. When $K^2 << A^{-2}$, the equilibrium of the dipolar reservoir with the lattice is not perturbed by saturation and the above-described effects do not appear. We have also shown that the parameter Y has a negligible influence on line shapes for a large-A value [Figs. 1(b) and 1(d)] whereas for a small-A value [Figs. 1(a) and 1(c)] it affects the shape of the burned hole in a way similar to that in which the parameter A affects the shape of the line itself.

Comparison of Figs. 1 and 2 reveals a saturation behavior of dispersion lines following closely that described for absorption lines in the corresponding case. This is due to the similarity between Eqs. (3) and (4) with the exception of the additional contribution of the dipolar-reservoir parameter β_{Dst} in $\chi'(\omega)B_1$. For resonant saturation, the smaller value of A induces a central line-splitting effect [Fig. 2(a)] resulting from the variations of the Zeeman-reservoir parameters β_{ist} in Eq. (3), whereas the larger value of A leads to a homogeneous saturation behavior [Fig. 2(b)] comparable in every way to that of the corresponding absorption. Here also widely differing values of K^2 give identical line shapes. For nonresonant saturation, one observes, for both A small [Fig. 2(c)] and A large [Fig. 2(d)], asymmetry features consistent with those described for the corresponding absorption shapes, characteristic of dipolar-

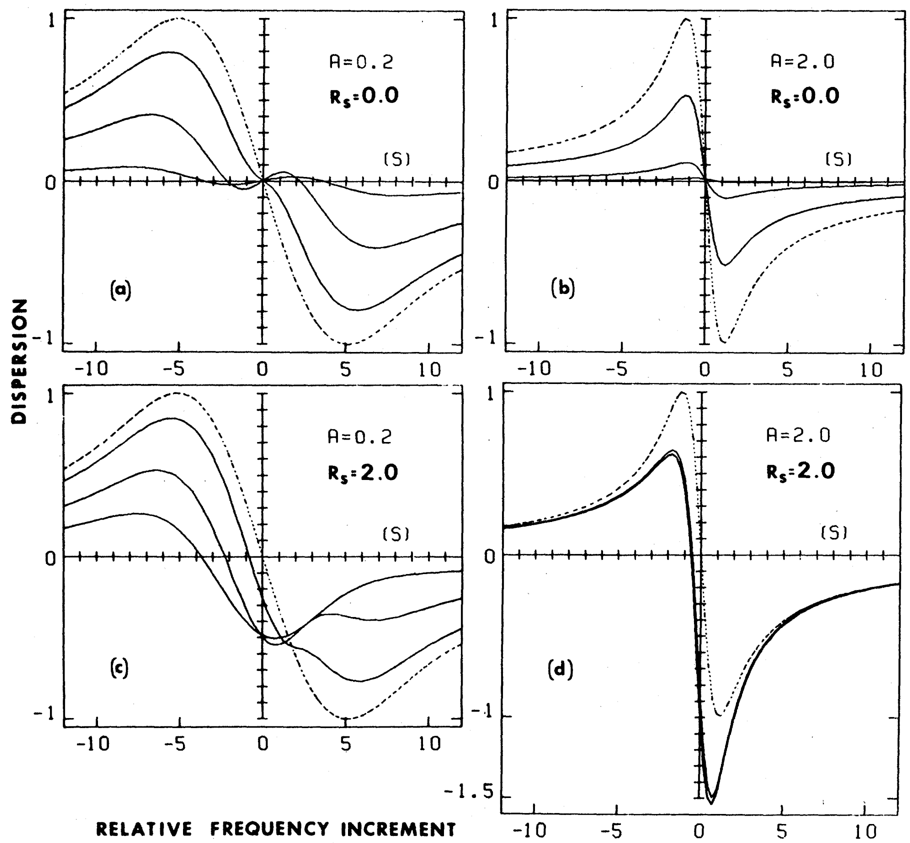

FIG. 2. (a)–(d) Standard dispersion intensity vs R for different values of A and R_s, and $K^2=3$, $Y^2=1$. Dotted lines correspond to unsaturated shapes ($S=0$) and solid lines to increasingly saturated ones ($S=1, 3, 10$).

reservoir effects, and also a displacement of the zero away from the point of application of the saturating field. When $K^2 << A^{-2}$, the line splitting resulting for a small-A value persists even for a very large-S value, whereas the saturation for a large-A value looks more symmetric than in Fig. 2(d) and less effective than in Fig. 2(b). Experimental studies of the saturation behavior of dispersion lines could then define a complementary approach, which might sometimes be more convenient, for investigating the inhomogeneous-broadening and dipolar-reservoir effects in solid spin systems.

It can be concluded that the multiple-reservoir model allows a good reproduction of all observed characteristic features of inhomogeneously broadened lines[9] under stationary weak-pulse saturation, whereas the two-reservoir model set up for homogeneous lines[10] and applied to inhomogeneous lines[9] allows only reproduction of those asymmetry features related to dipolar-reservoir effects.

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