Drop in free polarization after steady-state saturation of a packet of biLorentzian lines

A. I. Burshteĭn, A. A. Zharikov, and V. S. Malinovskiĭ

Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR

(Submitted 13 December 1988)
Zh. Eksp. Teor. Fiz. **96**, 2061–2072 (December 1989)

The rate of free polarization decay has been calculated exactly as a function of the saturating field under conditions of uncorrelated frequency migration along the biLorentzian profile. The limits of applicability of results obtained by means of perturbation theory (valid in the limit of rapid frequency modulation) have been determined. It is shown that the exact theory can describe the experimental data of Ref. 9 if the modulation is assumed to be slow.

INTRODUCTION

Of late, a large number of theoretical publications have dealt with the effect of a strong field on the processes of relaxation of two-level systems (TLS).[1-8] The impetus for this research was an experiment carried out by DeVoe and Brewer,[9] who measured the rate of free polarization decay (FPD), after the saturating variable field was turned off, as a function of the amplitude of this field.

The sample used was a crystal of LaF_3 with Pr^{3+} impurity. The $^3H_4$–$^1D_2$ transition which they studied between the electronic states of trivalent praseodymium in lanthanum trifluoride exhibits a marked inhomogeneous broadening (2.5 GHz) (Ref. 4) due to dispersion of the crystal field. Magnetic interaction with fluorine nuclei also leads to inhomogeneous broadening of the spectral lines, but its width is considerably smaller, and therefore, the broad inhomogeneous profile is assumed to be broken up into a collection of packets. Reorientation of the nuclei, which leads to a change in the local fields around the ions, causes modulation of the transition frequency or spectral exchange within a packet. Rapid exchange transforms the latter into a homogeneous line with a width equal to the rate of phase relaxation. The FPD rate was assumed to be similar after saturation in rapid exchange. However, it was found experimentally that this rate is markedly suppressed as the field increases. This field dependence of the FPD rate sharply contradicted the calculated rate obtained from the Bloch equations. There were good reasons to doubt the inapplicability of these equations to the description of the interaction of a strong field with a TLS, even if the latter was inhomogeneously broadened.

As an alternative, perturbation theory (PT) for random frequency detuning $\varepsilon(t)$ has been used in the majority of studies to account for the effect. This theory holds exactly in the rapid modulation (homogeneous broadening) limit if there exists a finite second moment $\overline{\varepsilon^2} = d^2$ such that $q^2 = d^2\tau_0^2 \ll 1$ (τ_0 being the frequency correlation time). Perturbation theory makes it possible to describe the effect of suppression of homogeneous broadening by a field, but the authors obtained quantitative agreement with experiment by setting $q^2 = 0.6$–1.1, which places PT at the edge of applicability. On the other hand, it is not certain that the exchange is in fact rapid. According to Ref. 8, $q^2 = 11.5$. In view of this fact, it is necessary to determine whether the suppression effect takes place in slow exchange (in a quasistatic situation). This can only be done by turning to an exact theory free from the limitations of PT.

Such a theory is that of sudden modulation,[10,11] which makes it possible to find the average response of a TLS to a purely discontinuous Markovian noise, which $\varepsilon(t)$ will henceforth be assumed to be. Such a perturbation changes abruptly at successive instants of time obeying a Poisson distribution, while remaining constant in the intervals between them, the average duration of which is equal to τ_0. For simplicity the discussion will be confined to the special case of an uncorrelated process. This case is characterized by the fact that the values of ε before and after the discontinuity are independent and distributed in accordance with equilibrium distribution $\varphi(\varepsilon)$. These statistics are determined by the shape of the frequency packet, which is usually assumed to be Gaussian. Actually, the distribution is Gaussian if the spin environment of the ions is close-packed and can be transformed into a Lorentzian shape in a magnetically dilute system.[12]

In the present work, therefore, we shall model the situation by using a biLorentzian distribution, which makes it possible to obtain an analytic solution for the FPD signal. Like the Gaussian distribution, it has a finite second moment, which makes it possible to apply PT to it and then compare the result with the exact solution. On the other hand, the biLorentzian distribution contains as a special case the Lorentzian distribution, to which PT is not applicable at all, since its dispersion is infinite. In this case, the exchange can also be slow or rapid, but it is never weak in the sense of perturbation theory.[13,14] Knowing the exact solution, we can use this example to ascertain the legitimacy of another approximate calculation of FPD, which holds over a wider range.

The main conclusions of the present work consist in the following: (a) PT appreciably exaggerates the FPD rate in low fields even when $q^2 = 0.5$; (b) agreement between the exact calculation and the experimental data for LaF_3:Pr^{3+} is reached at values $q = 2$–4, i.e., in the region of slow exchange, where PT is not applicable at all.

METHODS OF CALCULATION OF THE FPD SIGNAL

We shall consider the interaction of a single impurity ion, represented by a TLS, with a monochromatic wave $\mathscr{E} = E_0 \exp(i\omega t)$. The latter causes transitions between the TLS levels, whose frequency

$$\frac{E_2(t)-E_1(t)}{\hbar} = \omega_0+\varepsilon(t) \tag{1}$$

is a stationary random variable; its mean value ω_0 and detun-

 0038-5646/89/121164-07$04.00 © 1990 American Institute of Physics

ing distribution $\varphi(\varepsilon)$ are conserved in time. In a coordinate system rotating together with the field, the TLS density matrix $\hat{\rho}$ satisfies a Liouville kinetic equation of the form

$$\dot{\mathbf{X}}=-(\hat{L}_0+i\xi(t)\hat{L}_1)\mathbf{X}+\hat{\Lambda}, \qquad (2)$$

where

$$\mathbf{X}=\begin{pmatrix}\sigma_{12}\\ \sigma_{21}\\ n\end{pmatrix},\quad \hat{L}_0=\begin{pmatrix}1/\tilde{T}_2-iz & 0 & -iw/2\\ 0 & 1/\tilde{T}_2+iz & iw/2\\ -iw & iw & 1/\tilde{T}_1\end{pmatrix}, \qquad (2a)$$

$$\hat{L}_1=\begin{pmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0\end{pmatrix},\quad \hat{\Lambda}=\begin{pmatrix}0\\ 0\\ n_0/\tilde{T}_1\end{pmatrix}, \qquad (2b)$$

the time being chosen in units of τ_0; $z=(\omega_0-\omega)\tau_0$ is the frequency detuning in units of τ_0^{-1}; $\xi(t)=\varepsilon(t)\tau_0$; $w=\chi\tau_0$; χ is the Rabi frequency; $n=\rho_{22}-\rho_{11}$ is the difference between the level populations $(E_2>E_1)$; $\sigma_{12}=\sigma_{21}^{*}=\rho_{12}\exp(-i\omega t)$; $\tilde{T}_1$, and $\tilde{T}_2$ are the longitudinal and transverse relaxation times in units of $\tau_0(\tilde{T}_{1,2}=T_{1,2}/\tau_0)$.

After the field is switched off ($w=0$), Eq. (2) is easily integrated, but its solution should be averaged over the realization of the random process $\xi(t)$;

$$\overline{\sigma_{12}}(t)=\left\langle \sigma_{12}^{s}\exp\left\{izt+i\int_0^t\xi(t')dt'-t/\tilde{T}_2\right\}\right\rangle. \qquad (3)$$

The angular brackets and bar in Eq. (3) denote this averaging; σ_{12}^{s} is the initial polarization, produced by the action of the saturating field. This polarization is determined by the stationary solution of Eq. (2) for $w\neq 0$. To determine the FPD signal, it is necessary to perform the averaging $\overline{\sigma_{12}}(t)$ over a wide nonuniform frequency distribution $\Phi(z)$. Considering that the dispersion of the distribution $\Phi(z)$ is much greater than the saturation region, we shall assume $\Phi(z)=\Phi_0=\text{const}$. Then the signal shape will be given by the expression[15,16]

$$R(t)=\Phi_0\,\mathrm{Im}\int\overline{\sigma_{12}}(t)\,dz. \qquad (4)$$

Usually, in the determination of $R(t)$, one neglects the correlation of the TLS frequency fluctuations before and after the field is switched off. This makes it possible to decorrelate, σ_{12}^{s} and the exponential in Eq. (3) and average them separately. Then the formula becomes much simpler:

$$\overline{\sigma_{12}}(t)=\overline{\sigma_{12}^{s}}K(t)\exp\{(iz-1/\tilde{T}_2)t\}, \qquad (5)$$

where

$$K(t)=\left\langle\exp\left\{i\int_0^t\xi(t')dt'\right\}\right\rangle$$

is the correlation function of the frequency modulation. Thus the problem reduces to calculating $K(t)$ and the average stationary value $\overline{\sigma_{12}^{s}}$.

Only perturbation theory for a fluctuating frequency has been used for this purpose thus far.[1-5] However, this is entirely optional; both $K(t)$ and $\overline{\sigma_{12}^{s}}$ can be calculated exactly. By using them in the decorrelated equation (5), one can hope to extend the scope of applicability of the approximate results. We shall return to this question below, but first consider a rigorous method of calculating the FPD.

UNCORRELATED MARKOVIAN FREQUENCY MODULATION

If the TLS frequency is modulated by a purely discontinuous, stationary Markov process, then according to the sudden modulation theory the averaging in Eq. (3) may be represented as follows:

$$\overline{\sigma_{12}}(t)=\int d\xi\,\exp\{izt-t/\tilde{T}_2\}K(\xi,t)\sigma_{12}^{s}(\xi), \qquad (6)$$

where $K(\xi,t)$ and $\sigma_{12}^{s}(\xi)$ are partial or conditional averages, whose argument for $t=0$ is identical with and equal to ξ. For the Laplace transform $\overline{\sigma_{12}}(p)$ we obtain from Eq. (6)

$$\overline{\sigma_{12}}(p)=\int_0^\infty\overline{\sigma_{12}}(t)\exp\{-pt\}dt=\int d\xi\,K(\xi,p)\sigma_{12}^{s}(\xi),$$
$$K(\xi,p)=\int_0^\infty\exp\{-(p+1/\tilde{T}_2-iz)t\}K(\xi,t)\,dt. \qquad (7)$$

According to Ref. 17, for the Laplace transform of a partial function of frequency modulation we have

$$K(\xi,p)=\frac{1}{p+t_2-i(z+\xi)}\left[1-\int\frac{\varphi(\xi)d\xi}{p+t_2-i(z+\xi)}\right]^{-1},$$

where $t_2=1+1/\tilde{T}_2$.

Substituting $K(\xi,p)$ into Eq. (7), we find

$$\overline{\sigma_{12}}(p)=\int\frac{\sigma_{12}^{s}(\xi)d\xi}{p+t_2-i(z+\xi)}\left[1-\int\frac{\varphi(\xi)d\xi}{p+t_2-i(z+\xi)}\right]^{-1}. \qquad (8)$$

To determine the stationary value of $\sigma_{12}^{s}(\xi)$, we use the kinetic equation for the density matrix, obtained in the theory of uncorrelated sudden modulation,[10] which can be written in the form

$$\dot{\mathbf{X}}(\xi,t)=-(\hat{L}+i\xi\hat{L}_1)\mathbf{X}(\xi,t)+\varphi(\xi)(\overline{\mathbf{X}}+\hat{\Lambda}), \qquad (9)$$

where $\hat{L}=\hat{L}_0+\hat{1}$. Setting $\dot{\mathbf{X}}(\xi,t)=0$, we find

$$\mathbf{X}_s=\varphi(\xi)\hat{\mathscr{L}}(\xi)[\mathbf{X}_s+\hat{\Lambda}], \qquad (10)$$

where $\hat{\mathscr{L}}(\xi)=[\hat{L}+i\xi\hat{L}_1]^{-1}$. Hence for the average stationary elements of the density matrix we obtain

$$\overline{\mathbf{X}}_s=\langle\hat{\mathscr{L}}\rangle(\hat{1}-\langle\hat{\mathscr{L}}\rangle)^{-1}\hat{\Lambda}, \qquad (11)$$

where $\langle\hat{\mathscr{L}}\rangle=\int\varphi(\xi)\hat{\mathscr{L}}(\xi)d\xi$. Using Eqs. (10) and (11), one can find the following relationship between the stationary "partials" and averages:

$$\mathbf{X}_s=\varphi(\xi)\hat{\mathscr{L}}(\xi)\langle\hat{\mathscr{L}}\rangle^{-1}\overline{\mathbf{X}}_s. \qquad (12)$$

Eliminating $\overline{X}_s$ from Eqs. (11) and (12), we recover the result found in Ref. 6.

Using the explicit form $\hat{\mathscr{L}}(\xi)$, we obtain

$$\sigma_{12}^{s}(\xi)=\frac{\varphi(\xi)}{D_0D}\Big\{[\varkappa^2I_0+I_1(z+\xi)]\overline{\sigma_{12}^{s}}+it_2[I_0(z+\xi)-I_1]\Big(\bar{u}_s+i\frac{\varkappa^2}{t_2^2}\bar{v}_s\Big)\Big/2\Big\}, \qquad (13)$$

where the following notation was used:

$$\varkappa^2=t_2^2[1+w^2/t_1t_2],\quad t_1=1+1/T_1,$$

$$D=\varkappa^2+(z+\xi)^2,\qquad \sigma_{12}=\frac{u+iv}{2},$$

$$I_0=\int d\xi\,\varphi(\xi)/D,$$

$$I_1=\int d\xi\,(z+\xi)\varphi(\xi)/D,\qquad D_0=\varkappa^2I_0^2+I_1^2.$$

For the average stationary values $\overline{\sigma_{12}^s}$ we obtain from Eq. (11)

$$\overline{\sigma_{12}^s}=\frac{n_0w}{2}\,\frac{-I_1+i(t_2I_0-D_0)}{1+(I_0t_2-D_0)(w^2T_1/t_1-1)-I_0\varkappa^2t_2}. \tag{14}$$

Equations (8), (13), and (14) were obtained for an arbitrary form of the equilibrium distribution $\varphi(\xi)$. They determine the general solution of the FPD signal, valid for any field strength and any frequency modulation rate. To obtain the explicit form of the FPD signal, it is now necessary to turn to specific equilibrium distributions $\varphi(\xi)$.

BILORENTZIAN EQUILIBRIUM DISTRIBUTION

If, as was done in Ref. 6, a Gaussian profile is chosen for $\varphi(\xi)$, difficulties arise in inverting the Laplace transform $\overline{\sigma_{12}}(p)$ and in further integration with respect to z, needed in Eq. (4). To obtain an explicit analytic solution, we propose to use the so-called biLorentzian distribution:

$$\varphi(\xi)=\frac{ab(a+b)}{\pi}\,\frac{1}{(\xi^2+a^2)(\xi^2+b^2)}. \tag{15}$$

The second moment of this distribution is

$$\overline{\xi^2}=\int \xi^2\varphi(\xi)\,d\xi=ab,$$

and its tails fall as ξ^{-1}. By applying the calculation method discussed above, we shall be able to compare the results obtained with those of PT and determine the limits of applicability of PT. In addition, such a distribution makes it possible to pass in the limit $b\to\infty$ to the Lorentzian distribution

$$\varphi(\xi)=\frac{1}{\pi}\,\frac{a}{\xi^2+a^2}. \tag{16}$$

Since the latter has no second moment ($\overline{\xi^2}=\infty$), PT is not applicable to it, i.e., the frequency perturbation should not be considered small anywhere.

For the distribution (15) we obtain

$$I_0=\frac{1}{\varkappa}\,\frac{z^2\varkappa+(\varkappa+a)(\varkappa+b)(\varkappa+a+b)}{[z^2+(\varkappa+a)^2][z^2+(\varkappa+b)^2]},$$

$$I_1=\frac{z[z^2+(\varkappa+a+b)^2-ab]}{[z^2+(\varkappa+a)^2][z^2+(\varkappa+b)^2]},$$

$$D_0=\frac{z^2+(\varkappa+a+b)^2}{[z^2+(\varkappa+a)^2][z^2+(\varkappa+b)^2]}.$$

For the Laplace transform $\overline{\sigma_{12}}(p)$, determined in Eq. (8), we obtain

$$\overline{\sigma_{12}}(p)=K(p)\overline{\sigma_{12}^s}-K'(p)\overline{\beta^s}-K'(p)\frac{1}{p+t_2+\varkappa}\overline{\alpha^s}, \tag{17a}$$

where

$$K(p)=\frac{p-iz-(p_1+p_2-1/T_2)}{(p-iz-p_1+1/T_2)(p-iz-p_2+1/T_2)},$$

$$K'(p)=\frac{-p_1p_2}{(p-iz-p_1+1/T_2)(p-iz-p_2+1/T_2)},$$

$$p_{1,2}=-\frac{1}{2}\{1+a+b\pm[(1+a+b)^2-4ab]^{1/2}\},$$

$$\overline{\sigma_{12}^s}=\frac{n_0w}{2}\times\frac{[z^2+(\varkappa+a+b)^2](i/T_2-z)+ab[z+it_2(\varkappa+a+b)/\varkappa]}{z^4+B_1z^2+C_1}, \tag{17b}$$

$$\overline{\beta^s}=\frac{n_0w}{2}\times\frac{iz^2+z[1/T_2+t_2(\varkappa+a+b)/\varkappa]-i\varkappa[(\varkappa+a+b)/T_2+abt_2/\varkappa]/t_2}{z^4+B_1z^2+C_1}, \tag{17c}$$

$$\overline{\alpha^s}=\frac{n_0w}{2}(a+b)\left(1-\frac{t_2}{\varkappa}\right)\times\frac{iz^2-z[\varkappa+a+b+\varkappa/t_2T_2]-i\varkappa[(\varkappa+a+b)/T_2+abt_2/\varkappa]/t_2}{z^4+B_1z^2+C_1} \tag{17d}$$

$$B_1=(\varkappa+a+b)^2+1/T_2^2+w^2T_1/T_2-2ab,$$

$$C_1=[(\varkappa+a+b)/T_2+abt_2/\varkappa]\times[(\varkappa+a+b)/T_2+ab\varkappa/t_2+w^2T_1(\varkappa+a+b)].$$

Performing an inverse Laplace transformation, we find from Eq. (17a)

$$\overline{\sigma_{12}}(t)=\exp\{-(1/T_2-iz)t\}[K(t)\overline{\sigma_{12}^s}-\acute{K}(t)\overline{\beta^s}]-\int_0^t L(z,\tau)\exp\{-(t_2+\varkappa)(t-\tau)\}d\tau, \tag{18a}$$

$$L(z,\tau)=\exp\{-(1/T_2-iz)\tau\}\acute{K}(\tau)\overline{\alpha^s}, \tag{18b}$$

$$K(t)=\frac{1}{p_1-p_2}[p_1\exp(p_2t)-p_2\exp(p_1t)], \tag{18c}$$

$$\acute{K}(t)=\frac{p_1p_2}{p_1-p_2}[\exp(p_2t)-\exp(p_1t)]. \tag{18d}$$

Only the first term in Eq. (18a) reproduces the decorrelated equation (5) exactly. The remaining terms allow for the correlation of the frequency fluctuations before and after the saturating field is switched off.

Free from the limitation of PT, we can use Eqs. (18) directly in Eq. (4). Thus for the FPD signal we obtain the final expression

$$R(t)=\frac{n_0 w\pi\Phi_0}{2C_1^{1/2}(2C_1^{1/2}+B_1)^{1/2}}$$

$$\times\Big\{\exp(-t/\tilde{T}_2)\,[K(t)\,[R_1K_1(t)+R_2K_2(t)]$$

$$+\dot{K}(t)\,[R_3K_1(t)+R_4K_2(t)]]$$

$$+\int_0^t L(\tau)\exp[-(t_2+\varkappa)(t-\tau)]\,d\tau\Big\}, \qquad (19)$$

where

$$L(\tau)=\exp(-\tau/\tilde{T}_2)\dot{K}(\tau)\,[R_5K_1(\tau)-R_6\tilde{K}_2(\tau)], \qquad (20)$$

$$R_1=(\varkappa+a+b)\,[(\varkappa+a+b)/\tilde{T}_2+abt_2/\varkappa]$$
$$+C_1^{1/2}[1/\tilde{T}_2-(2C_1^{1/2}+B_1)^{1/2}], \qquad (21a)$$

$$R_2=(\varkappa+a+b)^2-ab+C_1^{1/2}+(2C_1^{1/2}+B_1)^{1/2}[1/\tilde{T}_2-(2C_1^{1/2}+B_1)^{1/2}], \qquad (21b)$$

$$R_3=\varkappa/t_2[(\varkappa+a+b)/\tilde{T}_2+abt_2/\varkappa]-C_1^{1/2}, \qquad (21c)$$

$$R_4=1/\tilde{T}_2+\frac{t_2}{\varkappa}(\varkappa+a+b)-(2C_1^{1/2}+B_1)^{1/2}, \qquad (21d)$$

$$R_5=(a+b)\left(1-\frac{t_2}{\varkappa}\right)\left[ab+\frac{\varkappa}{t_2}(\varkappa+a+b)/\tilde{T}_2-C_1^{1/2}\right], \qquad (21e)$$

$$R_6=(a+b)\left(1-\frac{t_2}{\varkappa}\right)\left[\varkappa+a+b+\varkappa/t_2\tilde{T}_2+(2C_1^{1/2}+B_1)^{1/2}\right], \qquad (21f)$$

$$K_1(t)=\mathrm{Re}\left\{\frac{1}{z_1-z_2}[z_1\exp(iz_2t)-z_2\exp(iz_1t)]\right\}, \qquad (22a)$$

$$K_2(t)=\mathrm{Im}\left\{\frac{z_1z_2}{z_1-z_2}[\exp(iz_1t)-\exp(iz_2t)]\right\}, \qquad (22b)$$

$$z_1=\begin{cases}\dfrac{i}{2^{1/2}}[B_1+(B_1^2-4C_1)^{1/2}]^{1/2}, & B_1^2\geqslant 4C_1,\\ {}^1/_2[-(2C_1^{1/2}-B_1)^{1/2}+i(2C_1^{1/2}+B_1)^{1/2}], & B_1^2\leqslant 4C_1,\end{cases} \qquad (23)$$

$$z_2=\begin{cases}\dfrac{i}{2^{1/2}}[B_1-(B_1^2-4C_1)^{1/2}]^{1/2}, & B_1^2\geqslant 4C_1,\\ {}^1/_2[(2C_1^{1/2}-B_1)^{1/2}+i(2C_1^{1/2}+B_1)^{1/2}], & B_1^2\leqslant 4C_1.\end{cases} \qquad (24)$$

Considering that $q^2 = ab$, we can write the result of the perturbation theory[1] as follows:

$$R(t)=\frac{n_0w}{2}\pi\Phi_0\exp\{-(q^2+1/\tilde{T}_2)t\}[A_1\tilde{K}_1(t)+A_2\tilde{K}_2(t)], \qquad (25)$$

where

$$A_1=[C^{1/2}(1/\tilde{T}_2-2z_3)+\varkappa^2/\tilde{T}_2+q^2t_2]/(2z_3C^{1/2}),$$
$$A_2=[\varkappa^2-q^2-C^{1/2}+2z_3/\tilde{T}_2-B]/(2z_3C^{1/2}),$$

$$\tilde{K}_1(t)=\begin{cases}\dfrac{1}{z_1-z_2}[z_1\exp(-z_1t)-z_2\exp(-z_2t)], & B^2\geqslant 4C,\\ \exp(-z_3t)\left[\cos(z_4t)+\dfrac{z_3}{z_4}\sin(z_4t)\right], & B^2\leqslant 4C,\end{cases}$$

$$\tilde{K}_2(t)=\begin{cases}\dfrac{C^{1/2}}{z_1-z_2}[\exp(-z_1t)-\exp(-z_2t)], & B^2\geqslant 4C,\\ -\dfrac{C^{1/2}}{2^{1/2}z_4}\exp(-z_3t)\sin(z_4t), & B^2\leqslant 4C,\end{cases}$$

$$z_{1,2}=2^{-1/2}[B\pm(B^2-4C)^{1/2}]^{1/2},\quad z_{3,4}={}^1/_2(2C^{1/2}\pm B)^{1/2},$$
$$B=\varkappa^2+w^2T_1/\tilde{T}_2+1/\tilde{T}_2^2-2q^2,$$
$$C=(\varkappa/\tilde{T}_2+q^2t_2/\varkappa)(\varkappa/\tilde{T}_2+q^2\varkappa/t_2+w^2T_1\varkappa).$$

Expression (25) is obtained from the decorrelated equation (5), when for $\overline{\sigma_{12}^s}$ and $K(t)$, their approximate estimates from perturbation theory[1] are used. However, if the exact expressions for $K(t)$ and $\overline{\sigma_{12}^s}$, determined in Eqs. (18c) and (17a), are substituted into Eq. (5), we obtain for the FPD signal

$$R(t)=\frac{n_0w\pi\Phi_0}{2C_1^{1/2}(2C_1^{1/2}+B_1)^{1/2}}$$
$$\times\exp(-t/\tilde{T}_2)K(t)\,[R_1K_1(t)+R_2K_2(t)] \qquad (26)$$

(the time is given in units of τ_0 throughout). It will be shown below that the range of applicability of this result is wider than that of the result of PT.

LORENTZIAN EQUILIBRIUM DISTRIBUTION

As noted above, a Lorentzian distribution is of interest because in this case the PT ($q^2 = \infty$) cannot be constructed. At the same time, the exact solution of the problem exists, and it can be obtained by carrying out the passage to the limit $b\to\infty$ in the general expressions (19)–(24). For the signal shape we find

$$R(t)=R_0\exp\{-(1/\tilde{T}_2+a+F)t\}$$
$$\times\left[1+\frac{\Pi(1-\exp\{-(1+\varkappa-a-F)t\})}{1+\varkappa-a-F}\right], \qquad (27)$$

where

$$R_0=\frac{n_0w}{2}\pi\Phi_0\frac{1/\tilde{T}_2+at_2/\varkappa-F}{F},$$
$$F^2=(1/\tilde{T}_2+at_2/\varkappa)(1/\tilde{T}_2+a\varkappa/t_2+w^2\tilde{T}_1),$$
$$\Pi=\frac{a(F+a+\varkappa/\tilde{T}_2t_2)(F+1/\tilde{T}_2+at_2/\varkappa)}{(1/\tilde{T}_2+at_2/\varkappa)(1+\varkappa/t_2)(\varkappa t_1\tilde{T}_1+a)}.$$

The correction term in Eq. (27) allows for the correlation in the motion of the system before and after the field is switched off. If such a correlation did not exist, the initial condition created by the stationary preparation of the system would reproduce the detuning equilibrium distribution, and the method (5) would become valid. In this case, letting the parameter b in Eq. (26) approach infinity, we obtain

$$R(t)=R_0\exp\{-(1/\tilde{T}_2+a+F)t\}. \qquad (28)$$

Actually, as is evident from the solution (27), the FPD signal is described, in general, by not one, but two exponentials with different weight factors.

A special or degenerate case is that of equal rates, i.e.,

$$a+F=1+\varkappa. \tag{29}$$

In this case it is easy to obtain from Eq. (27)

$$R(t)=R_0\exp\{-(1/\tilde{T}_2+a+F)t\}[1+\Pi t].$$

A simple analysis shows that for the characteristic decay times $(1/\tilde{T}_2+a+F)^{-1}$ the correction in this expression remains <1 for any parameter values, i.e., expression (28) is correct.

From the condition (29) one can readily obtain the following expression for the curve separating the regions of monoexponential and biexponential solutions:

$$a=\frac{(1+\varkappa)^2-w^2\tilde{T}_1/\tilde{T}_2}{2(1+\varkappa)+w^2\tilde{T}_1/\varkappa+2/\varkappa\tilde{T}_2}. \tag{30}$$

The approximation $1/\tilde{T}_2\ll 1$ was used here. For $a+F\ll 1+\varkappa$, the correction term in Eq. (27) damps out faster than the main term, and in addition, its amplitude $\Pi/(1+\varkappa-a-F)$ is small. Neglecting the correction term, we find that the decay proceeds exponentially, in accordance with expression (28).

For large a, when $a+F\gg 1+\varkappa$, the time scale is divided into two regions by the point $t=t_b$. In each of these regions, the solution can be considered to be approximately monoexponential (see Fig. 1):

$$R(t)=\begin{cases} R_0\exp\{-(1/\tilde{T}_2+a+F)t\}, & t\ll t_b, \quad (31a)\\ \dfrac{R_0\Pi}{F+a-1-\varkappa}\exp\{-(1/\tilde{T}_2+1+\varkappa)t\}, & t\gg t_b. \quad (31b)\end{cases}$$

The quantity t_b is determined from the condition

$$t_b=\frac{1}{F+a-1-\varkappa}\times\ln\left\{1+\frac{(F+a-1-\varkappa)(a+\varkappa\tilde{T}_1)(\varkappa+1)(1/\tilde{T}_2+a/\varkappa)}{a(a+F+\varkappa/\tilde{T}_2)(a/\varkappa+F+1/\tilde{T}_2)}\right\}$$

under which the correction term in Eq. (27) is equated to unity. For $t_b^{-1}\ll a+F$, the correction term can be neglected, and the solution is in the form of Eq. (31a), which is the same as Eq. (28). In the opposite case, in the range $t<t_b$, no appreciable relaxation takes place, and practically all of it develops in accordance with the law (31b). The boundary between these situations is determined by the curve

$$t_b^{-1}=a+F.$$

Taking this condition and the value for t_b into account, we obtain the following relationship for determining the boundary between the regions:

$$a/\tilde{T}_1=\varkappa\left[\frac{(e-1)^2w^2}{(\varkappa+1)^2}+\frac{2(e-1)}{\varkappa+1}-1\right]^{-1}\approx\varkappa. \tag{32}$$

Thus in the case of a Lorentzian distribution of the random frequency of a TLS, the calculation method based on uncoupling is valid if the relation $a/\tilde{T}_1<\varkappa$ holds. If $a/\tilde{T}_1>\varkappa$, it is necessary to take into account the correlation of the frequency change before and after the field is switched off.

INTEGRATED RATE OF FPD

It is evident from the above discussion that in general, the relaxation of free polarization is nonexponential. In this connection, a difficulty arises in the determination of the decay rate, which is equivalent to the damping rate of monoexponential kinetics. This difficulty can be circumvented by introducing the integrated rate, defined as follows:

$$\gamma=R(t=0)\Big/\left(\tau_0\int_0^\infty R(t)\,dt\right)$$
$$=\left[\pi\lim_{z\to\infty}z\,\mathrm{Re}\,\overline{\sigma_{12}{}'}+\int dz\,\mathrm{Im}\,\overline{\sigma_{12}{}'}\right]\Big/\left(\tau_0\,\mathrm{Im}\int dz\overline{\sigma_{12}}(p=0)\right). \tag{33}$$

Returning to the biLorentzian profile, for which expressions (17) and (19) are valid, we obtain

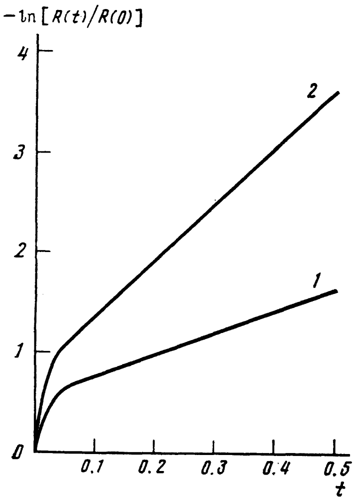

FIG. 1. Time dependence of FPD signal for an ensemble of Lorentz packets for different values of the saturating field: 1—$w=0.45$, 2—$w=4.5$; a—30, $\tilde{T}_1=22.55$.

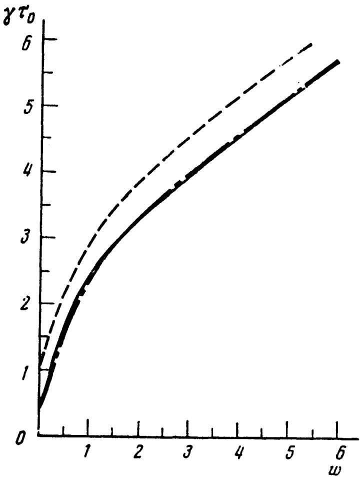

FIG. 2. Field dependence of integrated rates of FPD for $q^2=0.5$, $\tilde{T}_1=\tilde{T}_2/2=45.1$; dashed curve—perturbation theory; dot-dash curve—according to the decorrelated method based on uncoupling; continuous curve—exact calculation ($a=b$).

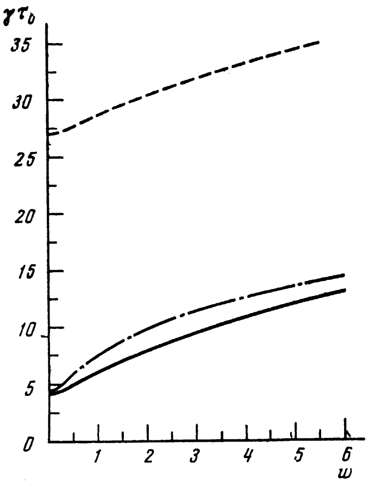

FIG. 3. Same as in Fig. 2, for $q^2 = 25$, $\tilde{T}_1 = \tilde{T}_2/2 = 22.55$.

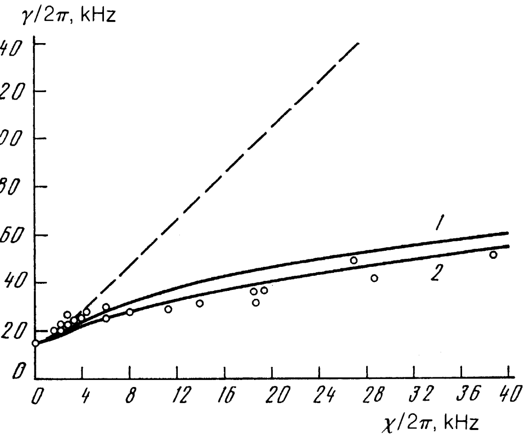

FIG. 5. Comparison of the field dependence of FPD rate with experiment: dashed curve—Bloch theory, continuous curve—exact calculation ($a = b$): 1—$q = 2$, $\tau_0 = 20\,\mu$sec; 2—$q = 3$, $\tau_0 = 29\,\mu$sec. O—experimental data of Ref. 9, $T_1 = 0.5\,\mu$sec.

$$\gamma = \frac{1}{\tau_0} R_1 \{ C_1^{1/2} [R_1 + (p_1 + p_2 - 1/\tilde{T}_2) R_2 + p_1 p_2 R_4 - p_1 p_2 R_6/(t_2 + \varkappa)] F_1 + C_1^{1/2} R_2 F_2 + [R_1 (p_1 + p_2 - 1/\tilde{T}_2) + p_1 p_2 R_3 + p_1 p_2 R_5/(t_2 + \varkappa)] F_3 \}^{-1}, \tag{34}$$

where

$$F_1 = (2C_1^{1/2} + B_1)^{1/2} \beta) F_0, \quad F_2 = (\alpha - C_1^{1/2})/F_0,$$
$$F_3 = -(\alpha + \beta (2C_1^{1/2} + B_1)^{1/2} + B_1 + C_1^{1/2})/F_0,$$
$$\alpha = (t_2 + a + b)/\tilde{T}_2 + ab, \ \beta = 1/\tilde{T}_2 + t_2 + a + b,$$
$$F_0 = \alpha(\alpha + B_1) + \beta (2C_1^{1/2} + B_1)^{1/2} (\alpha + C_1^{1/2}) + C_1^{1/2} (\beta^2 + C_1^{1/2}).$$

If Eq. (26) is used to calculate the FPD signal, the integrated rate is

$$\gamma^{(1)} = \frac{1}{\tau_0} R_1 \{ c_1^{1/2} [R_1 + (p_1 + p_2 - 1/\tilde{T}_2) R_2] F_1 + C_1^{''} R_2 F_2 + (p_1 + p_2 - 1/\tilde{T}_2) R_1 F_3 \}^{-1}. \tag{35}$$

From the calculation according to the perturbation theory (25) we obtain according to Eq. (33)

$$\gamma^{(2)} = \frac{1}{\tau_0} \frac{A_1 [(q^2 + 1/\tilde{T}_2)^2 + 2z_3 (q^2 + 1/\tilde{T}_2) + C^{1/2}]}{A_1 [q^2 + 1/\tilde{T}_2 + 2z_3] - A_2 C^{1/2}} \tag{36}$$

Figures 2 and 3 compare the field dependence of the integrated rates, calculated by the three methods indicated above. It is evident that in general, calculation of FPD signal from perturbation theory is already inapplicable when $q^2 = 0.5$, since the integrated rate $\gamma^{(2)}$ is equal to almost twice the exact value of γ in low fields (Fig. 2). As the field increases, the differences between $\gamma^{(2)}$ and γ decrease, since in strong fields, PT becomes valid again.[18]

On the other hand, the method of calculation of the integrated rate and signal of FPD using the decorrelated formula is valid both in the PT region and beyond its confines at moderate values of q (see Fig. 3).

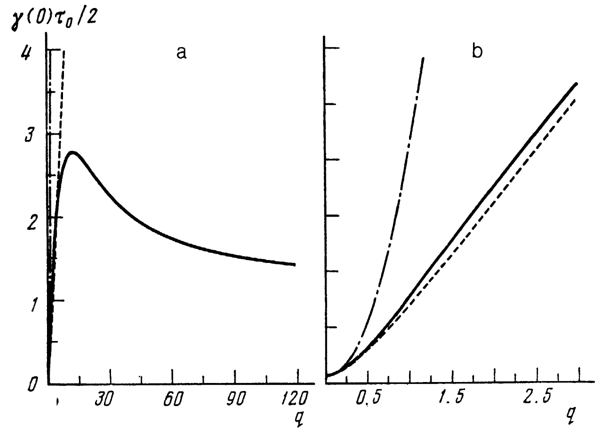

FIG. 4. Rate of FPD is zero fields ($\chi = 0$) as a function of narrowing parameter q: $\tilde{T}_1 = 17.32$; dot-dash curve—perturbation theory, dashed curve—according to the decorrelated method, continuous curve—exact result ($a = b$). The value of q varies in the range from 0 to 120 (a) and from 0 to 3 (b).

COMPARISON WITH EXPERIMENT

In the literature, the results of the experiments of Ref. 9 were interpreted mainly in the framework of perturbation theory. It was thus found that satisfactory agreement of theory and experiment is obtained at values of the parameter q^2 that are too high for perturbation theory: In Ref. 2, this quantity ranged from 0.7 to 1.1, and in Ref. 1, it was assumed to be 0.6. As follows from the above analysis, the agreement between theory and experiment thus obtained is insufficiently reliable. To explain the experimental results, it is necessary to use the exact theory, or, at moderate q, its decorrelated variant (see Fig. 4).

In the adjustment, it is convenient to use the value of $\gamma(\chi = 0)$ obtained by extrapolation of experimental points. In this case, for specific values of q, the magnitude of γ_0 is uniquely determined from the relation $\gamma(0)\tau_0$ (see Fig. 4). Figure 5 shows theoretical curves obtained for different values of q and τ_0. Good agreement with experiment was obtained for $q = 2$–3. The value of $\gamma(0)/2\pi$ was taken to be 16 kHz. From the relation $\gamma(0)\tau_0/2 = 0.9$ for $q = 2$ and $\gamma(0)\tau_0/2 = 1.3$ for $q = 3$ [see Fig. 4b], the values $\tau_0 = 20$ μsec and $\tau_0 = 29$ μsec, respectively, were determined. Note that a numerical calculation of the field dependence of FPD rate when the frequency migration has a diffusional character gives similar parameter values.[19] If such agreement is assumed satisfactory, it is necessary to recognize that the frequency modulation is slow, and that one cannot avoid turning to a theory which is an alternative to perturbation theory.

[1] P. A. Apanasevich, S. L. Kilin, A. P. Nizovtsev, and N. S. Onischenko, Opt. Commun. **52**, 279 (1984).
[2] M. Yamanoi and J. H. Eberly, J. Opt. Soc. Amer. B **1**, 751 (1984).
[3] K. Wodkiewicz and J. H. Eberly, Phys. Rev. A **32**, 992 (1985).
[4] A. Schenzle, M. Mitsunaga, R. G.DeVoe, and R. G. Brewer, Phys. Rev. A **30**, 325 (1984).
[5] E. Hanamura, J. Phys. Soc. Jpn. **52**, 3678 (1983).
[6] P. R. Berman and R.G. Brewer, Phys. Rev. A **32**, 2784 (1985).
[7] E. G. Pestov, Tr. Fiz. Inst. Akad. Nauk **187**, 60 (1988).
[8] A. R. Kessel', R. N. Shakhmuratov, and L. D. Eskin, Zh. Eksp. Teor. Fiz. **94**, No. 10, 202 (1988) [Sov. Phys. JETP **67**, 2071 (1988)].
[9] R. G. DeVoe and R. G. Brewer, Phys. Rev. Lett. **50**, 1268 (1983).
[10] A. I. Burshteĭn, *Quantum Kinetics*, NGU, Novosibirsk (1968).
[11] A. I. Burshteĭn, A. A. Zharikov, and S. I. Temkin, J. Phys. B **21**, 1907 (1988).
[12] A. Abraham, *Nuclear Magnetism*, Clarendon, Oxford (1961) [Russ. transl., IIL, Moscow (1963)].
[13] A. I. Burshtein, Chem. Phys. Lett. **83**, 335 (1981).
[14] A. I. Burshtein, S. G. Fedorenko, and A. Yu, Chem. Phys. Lett. **100**, 155 (1983).
[15] R. Shoemaker in *Laser and Coherence Spectroscopy*, J. Steinfeld (ed.), Plenum, New York (1978) [Russ. transl., Mir (1982)].
[16] R. G. Brewer, *Nonlinear Spectroscopy*, N. Blombergen (ed.), Elsevier-North Holland, New York (1977) [Russ. transl., Mir, Moscow (1979)].
[17] A. B. Doktorov and A. I. Burshteĭn, Zh. Eksp.Teor. Fiz. **63**, 784 (1972) [Sov. Phys. JETP **36**, 411 (1973)].
[18] A. I. Burshteĭn and V. S. Malinovsky, J. Opt. Soc. Amer. B (in press).
[19] J. Javanainen, Opt. Commun. **50**, 26 (1984).

Translated by Adam Peiperl