Free induction and echo during nonresonant excitation of inhomogeneously broadened NMR line

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When an inhomogeneously broadened spin system is excited by rf pulses whose frequency deviates from the resonant frequency by an amount δ which is greater than the Rabi frequency ω_1, an interference arises between magnetization oscillations with a variable frequency $\tilde{\omega}_1 = \omega_1 t^*$ and oscillations at the detuning frequency. Here $\omega_1 = \gamma H_1$, where γ is the gyromagnetic ratio, and H_1 is the amplitude of the rf field. The quantity t^* is a dimensionless function of the time, the length of the pulses, and the time interval between them. Under these conditions, an isolated response is formed in the induction signal after the first pulse. After the second pulse, four isolated responses, differing in amplitude, form, and the echo signal has eight satellites in addition to a central peak. The satellites are positioned symmetrically with respect to this central peak. The temporal positions of the responses are determined by the lengths of the pulses and by the ratio ω_1/δ. The analytic expressions derived here agree well with proton-magnetic-resonance experiments. The possibility of using these signals to determine relaxation times is analyzed.

1. INTRODUCTION

When a single electromagnetic field pulse is applied to an inhomogeneously broadened spin system, a response reminiscent of an echo signal (the one-pulse echo[1]) is formed. If two pulses are applied, one may observe a series of echo signals which are clearly separated in time (multicomponent echo).[2–4] The one-pulse echo was observed more than 30 years ago in NMR;[5] it was subsequently observed in ferroelectrics[6] and in the optical range.[7] The multicomponent echo was observed about 10 years ago in a study of NMR in magnetically ordered systems. Nevertheless, opinion is still divided regarding the mechanism responsible for these effects. The one-pulse echo is interpreted variously as the result of a nonresonant excitation of a spin system,[8] part of an oscillating induction signal,[9] or a consequence of distortions of a pulse near its leading and trailing edges.[10] The latter mechanism is also invoked to explain the multicomponent echo.[10] The multicomponent echo has also been attributed to particular features of the internal structure of magnetically ordered systems which lead to an inhomogeneous distribution of the Rabi frequency.[3]

These models are not supported by a quantitative analysis, and they do not explain all the existing experimental data. For example, incorporating the distortions of pulses leads to an approximate explanation of the times at which the one-pulse and multicomponent echoes appear, but it fails to describe the shape and amplitude of the signals. An inhomogeneous distribution of the Rabi frequency makes it possible to describe[3] the transformation of the central part of the echo signal, but it does not reflect the overall multicomponent structure of this signal. With regard to an oscillating induction during resonant excitation, we note that it is reminiscent of the echo signal only if the area under the pulse is $\omega_1 t_1 \approx 2\pi$, where $\omega_1 = \gamma H_1$ is the Rabi frequency, γ is the gyromagnetic ratio, and H_1 and t_1 are respectively the amplitude and length of the rf pulse. Incorporating the difference between the frequency of the line center and that of the exciting pulse leads to an explanation of the time at which the one-pulse echo signal appears, and it predicts a cubic dependence of the amplitude of this signal on the amplitude of the rf pulse and the magnitude of the detuning.[1] Only recently, after numerous attempts, has it been found possible to reproduce the one-pulse echo through numerical analysis.[8] However, an experimental test[11] of the results of Ref. 8 revealed a discrepancy between the behavior of the signal amplitude as a function of the detuning predicted by the theory and the behavior observed experimentally. Also under doubt is the cubic dependence of the amplitude of the one-pulse echo on ω_1, since we know that the amplitude of a signal after one-pulse excitation is proportional to ω_1 if $\omega_1 \gg \sigma$, where σ is the inhomogeneous linewidth,[12] while it is proportional to ω_1^2 if $\omega_1 \ll \sigma$ (Ref. 9). Consequently, the nature of the signal called the "one-pulse echo" cannot be regarded as a settled question.

Because of difficulties in controlling the experimental conditions under which the one-pulse and multicomponent echoes are studied, it is not possible to unambiguously distinguish the contribution of each of the proposed mechanisms in the observed signals. There is a further uncertainty in this question because there are no analytic expressions for the responses of inhomogeneously broadened systems according to the various models. In contrast with the other mechanisms, a nonresonant excitation can be realized in any system. It is not associated with imperfections of the apparatus. A nonresonant excitation is accordingly the topic of primary interest for quantitative analysis.

In the present paper we offer an analytic description of the response of inhomogeneously broadened systems to a nonresonant excitation by one or two pulses. We also report an experimental test of the expressions derived. The test was carried out under controllable conditions with a familiar two-level spin system: protons in water.

2. ONE-PULSE FREE INDUCTION

Let us assume that a two-level spin system is excited by a single rf pulse, whose carrier frequency ω is shifted by an

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amount δ from the central frequency of the transition, ω_0. We ignore relaxation processes. We can then write the following expression[13] for the v component of the magnetization (the absorption signal) of this system after the excitation:

$$v(t)=v_0\omega_1\left\{\left[\frac{\sin\beta t_1}{\beta}\cos(\Delta+\delta)(t-t_1)+\frac{\Delta+\delta}{\beta^2}\cos\beta t_1\sin(\Delta+\delta)(t-t_1)\right]-\frac{\Delta+\delta}{\beta^2}\sin(\Delta+\delta)(t-t_1)\right\}=J_1(t)+J_2(t),\quad t>t_1, \tag{1}$$

where

$$\beta=[(\Delta+\delta)^2+\omega_1^2]^{1/2},\quad \delta=\omega_0-\omega,\quad \omega_1=\gamma H_1,$$

Δ is the frequency spread of the spin packets, and v_0 is the initial difference between populations.

To pursue the analysis, we must average Eq. (1) over the inhomogeneously broadened lineshape, whose form factor we denote by $g(\Delta)$;

$$\langle v(t)\rangle=\int_{-\infty}^{\infty}d\Delta g(\Delta)v(t)=I_1(t)+I_2(t). \tag{2}$$

The integrals in (2) were recently evaluated[9] for $\delta=0$ for an infinite linewidth, $\sigma\gg\omega_1$. We have undertaken an effort to derive analytic expression (2) for arbitrary relations among δ, σ, and ω_1.

Let us analyze (2) for the time interval $t_1\leqslant t\leqslant 2t_1$. It turns out that the behavior of the integral I_1 in this time interval can be approximated quite well by the leading term [which is proportional to $(\omega_1 t_1)^{-1/2}$] in the asymptotic expansion of this integral at $\omega_1 t_1\gg 1$. Using the known methods for asymptotic estimates of integrals,[14] we can then write

$$I_1(t)\approx v_0(2\pi\omega_1)^{1/2}\frac{(2t_1-t)^{3/4}}{t_1 t^{1/4}}\{g(\omega_1 t^*-\delta)+g(\omega_1 t^*+\delta)\}\times\sin(\omega_1[t(2t_1-t)]^{1/2}+\pi/4)+O(1/\omega_1 t_1), \tag{3}$$

where

$$t^*=(t-t_1)/[t(2t_1-t)]^{1/2},\quad t_1\leqslant t\leqslant 2t_1.$$

In the particular case of an infinitely wide inhomogeneous line [$g(x)=\text{const}$] and with $\delta=0$, Eq. (3) becomes the corresponding asymptotic expression which was derived in Ref. 9 for the induction. The remaining integral in (2) can be evaluated exactly for an arbitrary symmetric lineshape function by means of the theory of residues. For example, for the Lorentzian function $g(\Delta)=\sigma/\pi(\Delta^2+\sigma^2)$ it is

$$I_2(t)=-\frac{v_0\omega_1}{\alpha_+^2-4\omega_1^2\sigma^2}\{\sigma\alpha_-\exp[-\omega_1(t-t_1)]+[\sigma\alpha_+\sin\delta(t-t_1)-\sigma\alpha_-\cos\delta(t-t_1)]\exp[-\sigma(t-t_1)]\}, \tag{4}$$

where

$$\alpha_\pm=\delta^2+\sigma^2\pm\omega_1^2,\quad t>t_1.$$

On the interval $t>2t_1$, the first integral in (2) for a Lorentzian function can also be evaluated by the theory of residues. The resulting expression has a structure similar to that of expression (4); it is lengthy, and we will not reproduce it here.

According to the results which have been derived, the one-pulse free-induction signal (Fig. 1) can be represented on the interval $t_1\leqslant t\leqslant 2t_1$ as the sum of two components, which are oscillating at frequencies δ and

$$\tilde{\omega}_1=\omega_1(t-t_1)/[t(2t_1-t)]^{1/2}=\omega_1 t^*.$$

The decay of the one-pulse free induction is by a power law [see (3)] and by an exponential law [see (4)] with rates σ and ω_1. While the oscillations with the variable Rabi frequency $\tilde{\omega}_1$ disappear at $t=2t_1$ (in accordance with the conclusions of Ref. 9), a modulation of the one-pulse free induction at the frequency δ also occurs at $t>t_1$. Expressions (3) and (4) hold for arbitrary relations among ω_1, σ, and δ, provided that the condition $\omega_1 t_1>1$ holds. It can be seen from (3) and (4) that the one-pulse free induction does not depend on the sign of δ. If $\delta\neq 0$, the expression in braces (curly brackets) in (3) has a maximum. For a Lorentzian function, this maximum corresponds to the time

$$t_m=t_1\left\{1+\left[1+\frac{\omega_1^2}{\delta^2+[(\delta^2+\sigma^2)^{1/2}-\delta]^2}\right]\right\}^{-1/2}. \tag{5}$$

If $\delta\gg\sigma$, expression (5) becomes the expression derived in Ref. 1:

$$t_m=t_1[1+|\delta|/(\delta^2+\omega_1^2)^{1/2}].$$

What are the optimum conditions for the appearance of a maximum in expression (3)? Under the conditions $\sigma>\omega_1$ and ω_1, $\sigma>\delta$ (or $\omega_1<\delta<\sigma$), we have

$$I_1(t_m)\sim v_0\omega_1^2/\sigma^{1/2}\delta t_1^{1/2},$$

while under the conditions $\delta>\omega_1$, σ, for arbitrary ω_1/σ, we have

$$I_1(t_m)\sim v_0\omega_1^2/\sigma\delta^{1/2}t_1^{1/2}.$$

The expression in braces in (3) reaches a maximum at $t=t_m$ under the condition $\delta\gg\sigma$; this maximum value is $1/(\pi\sigma)$. The condition that the maximum must occur near $2t_1$ thus requires $\delta>\omega_1$. The amplitude of the maximum increases with increasing ω_1. Consequently, the optimum conditions for the appearance of a maximum are $\omega_1\geqslant\sigma$ and $\delta>\sigma$, ω_1. It follows from these estimates that $I_1(t_m)\propto\omega_1^2$. In other words, the minimum nonlinearity for this signal is quadratic, while we have $I_2(t_m)\propto\omega_1$. This quantity corresponds to the ordinary first-order induction signal.[12]

Physically, the presence of a maximum on the one-pulse free-induction signal during nonresonant excitation of an inhomogeneous line corresponds to an equality of the instantaneous Rabi frequency and the detuning. The instantaneous Rabi frequency in (3), $\tilde{\omega}_1=\omega t^*$, is equal to δ at the time

$$t=t_1[1+|\delta|/(\delta^2+\omega_1^2)^{1/2}],$$

which corresponds to the maximum of the expression in braces in (3). We thus see the reason for the condition $\delta>\omega_1$, which is imposed on the observation of the one-pulse echo. The second condition, $\omega_1\geqslant\sigma$, is associated with the sharpness of the resonance, since the effective width $g(\omega_1 t^*-\delta)$ is σ/ω_1.

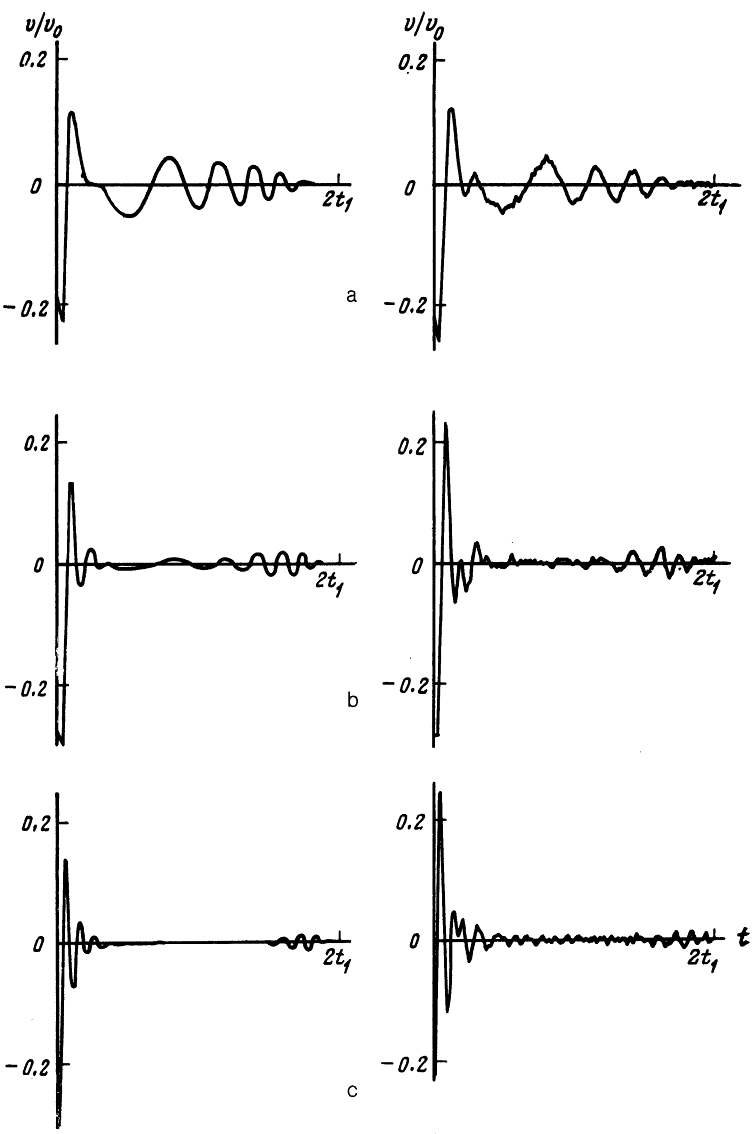

FIG. 1. Observed (at the right) and calculated (at the left) one-pulse induction signals for $\omega_1 t_1 = 20\pi$, $t_1 = 3.8$ ms, and $\sigma = \omega_1$. a—$\omega_1/\delta = 1$; b—0.67; c—0.5.

To find a qualitative explanation of the results, we write $I_1(t)$ in (2) in the following form for the case $\delta = 0$:

$$I_1(t)=\frac{v_0\omega_1}{2}\left\{\sum_i\left[\beta_i^{-1}\left(\frac{\Delta_i}{\beta_i}+1\right)\sin\varphi_{1i}+\beta_i^{-1}\left(-\frac{\Delta_i}{\beta_i}+1\right)\sin\varphi_{2i}\right]g(\Delta_i)\right\},\qquad(6)$$

where $\varphi_{1,2i} = \beta_i t_1 \pm \Delta_i(t - t_1)$. It is not difficult to see that the harmonic oscillations for which the condition $\partial\varphi_{1,2i}/\partial\Delta_i = 0$ (this is the condition under which the phases have stationary points[14]) holds makes the maximum contribution in (6). For the first (second) term in (6), the stationary point is $\Delta_{1,2} = \mp\omega_1 t$*. We sees that the stationary points are identical for all spin packets of an inhomogeneously broadened line, and as time elapses they move off in different directions from the central frequency of the transition (Fig. 2, a). At the stationary points which are coordinated in this manner, the amplitude A and the phase φ of the oscillations in both terms in (6) are given by the following expressions for the case of a symmetric form function of the inhomogeneously broadened line:

$$\varphi_1(t)=\varphi_2(t)=\omega_1[t(2t_1-t)]^{1/2},\qquad(7a)$$

$$A_1(t)=A_2(t)=\frac{v_0 t^{1/2}(2t_1-t)^{3/2}}{t_1^2}\,g\left(\frac{\omega_1(t-t_1)}{[t(2t_1-t)]^{1/2}}\right).\qquad(7b)$$

In this case, the one-pulse free induction is a superposition of coherent emissions from spin packets which are positioned symmetrically with respect to ω_0 and whose oscillation phases and amplitudes are equal at each time. The amplitude of the resultant oscillation is seen from (7b) to reach a maximum at the time $t = t_1$ and to then decrease, vanishing at $t = 2t_1$.

In the case $\delta \neq 0$, the coordinated stationary points become equal to $\Delta_{1,2} - \delta$, i.e., they move away from the frequency of the exciting pulse, ω (Fig. 2,b), rather than from

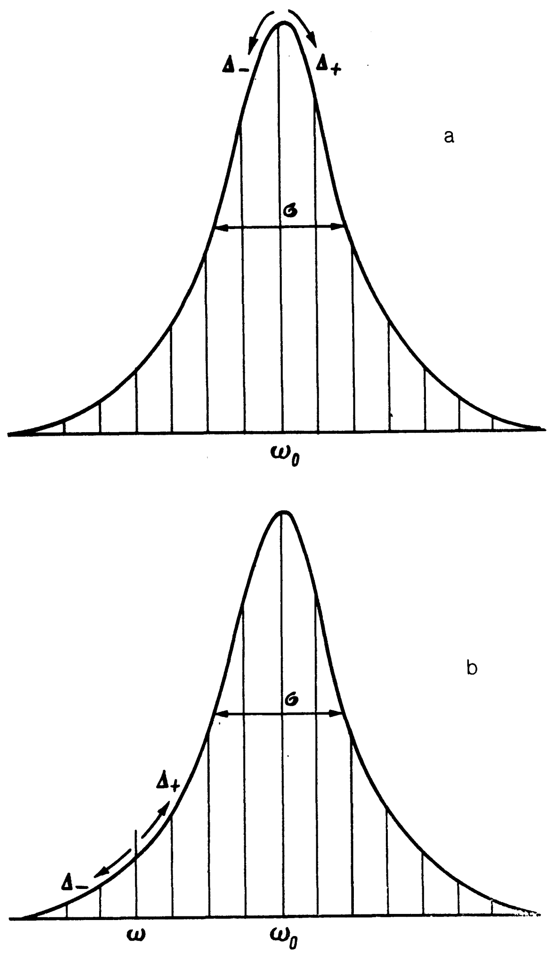

FIG. 2. Behavior of stationary points during (a) resonant and (b) nonresonant excitation of an inhomogeneous line.

the central frequency of the transition. One of the stationary points then moves into the wing of the line, while the other moves toward its center. The phases of the corresponding oscillations in (7a) are again equal, but the amplitudes are now different, because of the relation $g(\Delta_{1,2}-\delta)\neq g(\Delta_{1,2}+\delta)$. The amplitude of the oscillations which have a stationary point $\Delta_2^{(l)}-\delta$ thus increases as time elapses, while that for the stationary point $\Delta_2^{(l)}-\delta$ decreases. In the case $\Delta_1^{(l)}=\delta$ we observe a maximum: a one-pulse echo.

We turn now to an analysis of the first-order free induction in (4). In the case $\delta=0$, it is

$$I_2(t)=-\frac{v_0\omega_1\sigma}{\sigma^2-\omega_1^2}\{\exp[-\omega_1(t-t_1)]-\exp[-\sigma(t-t_1)]\},\quad (8)$$

in agreement with the result of Ref. 9. At the time

$$t=t_1+\ln(\omega_1/\sigma)(\omega_1-\sigma)^{-1}$$

relation (8) has an extremum for arbitrary ω_1 and σ, except in the case $\omega=1=\sigma$, in which we have $I_2(t)=0$ over the entire time interval. In the case $\omega_1>\sigma$, the function $I_2(t)$ in (8) goes through a maximum, while in the case $\omega_1<\sigma$ it goes through a minimum. In the case $\delta\neq 0$, this extremum is modulated at the frequency δ; in the case $\sigma=\omega_1$, we have $I_2(t)=0$ only at $t=t_1$. At $t>2t_1$, the response oscillates at the frequency δ, falling off gradually with decay constants σ and ω_1. This signal is characterized by a linear ω_1 dependence (at small ω_1).

The relaxation in the case of a nonresonant excitation can be dealt with in a simple manner in the case $T_1=T_2$, where T_1 and T_2 are respectively the longitudinal and transverse relaxation times. In this approximation, expression (3) must be multiplied by $\exp[-(t_1+t_m)/T_2]$. We see from (3) that

$$I_1(t_1,t_m)\sim t_1^{-1/2}\exp[-(t_1+t_m)/T_2],$$

in other words, the one-pulse free induction depends on t_1 not only through a relaxation coefficient. This circumstance must be taken into account in determining relaxation times by means of the one-pulse echo. In the case $T_1\neq T_2$, the expressions for the one-pulse free induction are quite complicated and are inconvenient for determining the relaxation times.

3. TWO-PULSE FREE INDUCTION

Let us use the method of the preceding section of this paper to calculate the two-pulse free-induction signal generated after the excitation of a two-level system by two pulses with identical deviations from resonance, δ, with areas $\omega_1 t_1$, $\omega_2 t_2>1$, which are separated by a time interval $\tau<T_1$, T_2. We work from the expression for the v component of the two-pulse free-induction magnetization, which is given in Ref. 13, among other places:

$$v(t)=\frac{v_0\omega_1}{\beta^4}\{[(\Delta+\delta)^2+\omega_1^2\cos\beta t_1]\times[\beta\sin\beta t_2\cos(\Delta+\delta)(t-t_1-t_2-\tau)-(\Delta+\delta)(1-\cos\beta t_2)\sin(\Delta+\delta)(t-t_1-t_2-\tau)]\},\quad (9)$$

where $t\geqslant t_1+t_2+\tau$.

Taking an average of (9) over the inhomogeneously broadened lineshape, we find

$$\langle v(t)\rangle\approx v_0\left(\frac{\pi\omega_1}{8}\right)^{1/2}\left\{\sum_{i=1}^{4}\Phi_i\sin\left[\omega_1(t_i^2-x^2)^{1/2}+\frac{\pi}{4}\right]\times\left[g\left(\frac{x\omega_1}{(t_i^2-x^2)^{1/2}}-\delta\right)+g\left(\frac{x\omega_1}{(t_i^2-x^2)^{1/2}}+\delta\right)\right]\right\}-v_0\omega_1\int_{-\infty}^{\infty}\frac{y^3}{(y^2+\omega_1^2)^2}\sin(yx)g(y-\delta)\,dy,\quad (10)$$

where

$$\Phi_1=x(t_1^2-x^2)^{3/4}/t_1^3,$$
$$\Phi_2=x^2(t_2-x)^{3/4}(t_2+x)^{-1/4}/t_2^3,$$
$$\Phi_3=-\mathrm{sign}(t_3)(t_3+x)(t_3^2-x^2)^{3/4}/2t_3^3,$$
$$\Phi_4=(t_4-x)(t_4^2-x^2)^{3/4}/2t_4^3,$$
$$x=t-(t_1+t_2+\tau),\quad t_3=t_1-t_2,\quad t_4=t_1+t_2.$$

The first term in (10) can be thought of as the sum as the one-pulse free induction which is generated after the system is excited by four pulses with respective lengths $|t_1 - t_2|$, t_1, t_2 and $t_1 + t_1$. Consequently, as was shown in Sec. 2, there exists, for each one-pulse free-induction signal, a time at which zero beats appear between the oscillations with frequencies $\tilde{\omega}_1$ and δ. These times are found from the condition

$$\omega_1 x (t_i^2 - x^2)^{-1/2} = |\delta|$$

to be

$$t_{m1} = t_2 + \tau + t_1(1+\alpha),$$
$$t_{m2} = t_1 + \tau + t_2(1+\alpha),$$
$$t_{m3} = \tau + |t_1 - t_2|(1+\alpha),$$
$$t_{m4} = \tau + (t_1 + t_2)(1+\alpha),$$

where $\alpha = |\delta|(\delta^2 + \omega_1^2)^{1/2}$. Four signals, differing in amplitude and separated in time, thus arise in the two-pulse free induction. Figure 3 shows examples of these signals for the case $t_1 = 2t_2$.

As in the case of the one-pulse free induction, the maximum nonlinearity for these responses is quadratic. The integral in (10) can easily be calculated by residues, but we will not present that calculation here because the resulting expression is quite complicated. It, like the one-pulse free-induction signal, oscillates at the frequency δ and decays exponentially at rates σ and ω_1. At small values of ω_1 it depends linearly on ω_1 and makes the maximum contribution to the two-pulse free induction just after the end of the second pulse.

Of particular interest for the case of the two-pulse free induction is the possibility of determining the relaxation times T_1 in a study of multicomponent signals, since incorporating the relaxation in the interval between pulses leads to a multiplication of (10) by $\exp(-\tau/T_1)$. This circumstance may prove useful for determining the time T_1 for entities in which a stimulated echo is not observed because T_2 and T_1 are small.

4. SPIN ECHO

We turn now to the magnetization of a spin system, which is responsible for a spin-echo signal under conditions similar to those for the two-pulse free induction. After making some asymptotic estimate, we find the following expression for the spin echo:

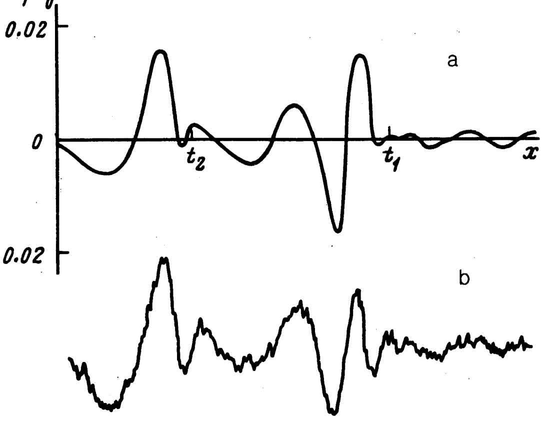

FIG. 3. Two-pulse free induction $\sigma/\omega_1 = 0.5$, $\omega_1/\delta = 0.5$, $\omega_1 t_1 = 2\omega_1 t_2 = 8\pi$. a—Theoretical; b—experimental.

$$\langle v(t)\rangle \approx -v_0(\pi\omega_1)^{1/2}\Big\{\sum_{i=1}^{4} F_i \sin\Big[\omega_1(t_i^2 - z^2)^{1/2} + \frac{\pi}{4}\Big] \times \Big[g\Big(\frac{\omega_1 z}{(t_i^2 - z^2)^{1/2}} - \delta\Big) + g\Big(\frac{\omega_1 z}{(t_i^2 - z^2)^{1/2}} + \delta\Big)\Big] + \frac{\omega_1^3}{2}\int_{-\infty}^{\infty} \frac{y \sin yz}{(y^2 + \omega_1^2)^2}\, g(y - \delta)\, dy\Big\}, \tag{11}$$

where

$$F_1 = (t_1 + z)(t_1^2 - z^2)^{3/4}/2t_1^3,$$
$$F_2 = z(t_2^2 - z^2)^{3/4}/2t_2^3,$$
$$F_3 = -\mathrm{sign}(t_3)(t_3 + z)(t_3^2 - z^2)^{3/4}/4t_3^3,$$
$$F_4 = -(t_4 + z)(t_4^2 - z^2)^{3/4}/4t_4^3, \quad z = t - t_1 - t_2 - 2\tau.$$

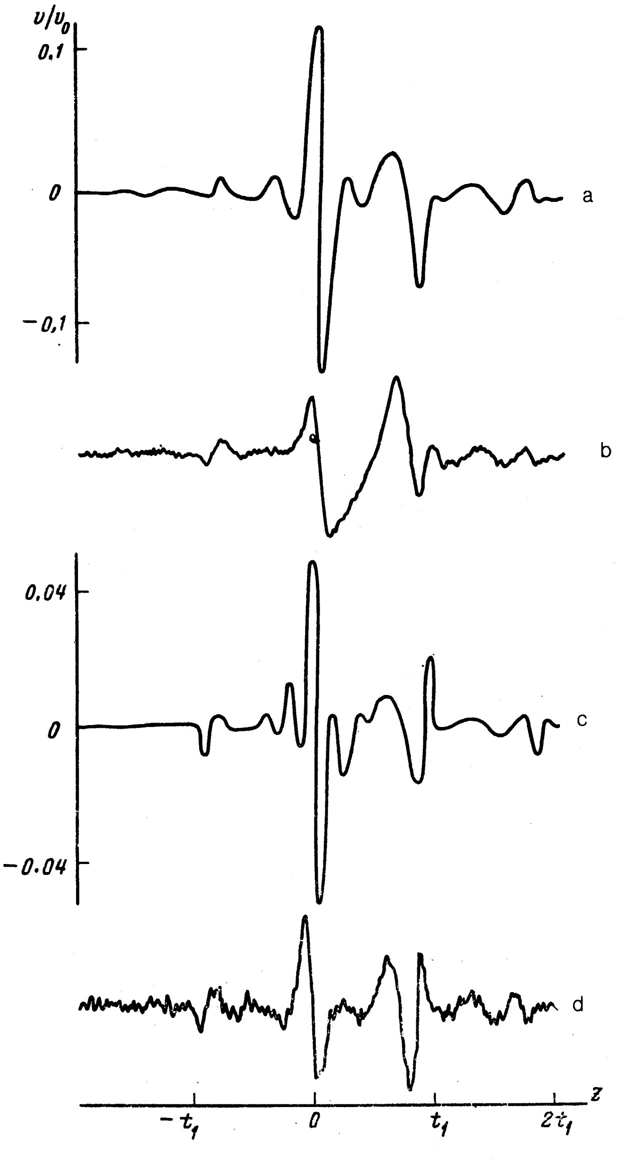

FIG. 4. Two-pulse echo for the case of equal pulse lengths $\omega_1 t_1 = \omega_1 t_2 = 4\pi$, $\tau = 5$ ms, $t_1 = 1$ ms, $\sigma/\omega_1 = 0.5$). $\delta/\omega_1 = 1.5$, a,c—Theoretical; b,d—experimental. a,b) $\delta/\omega_1 = 1.5$; c,d) 2.5. The gain for oscilloscope trace d is twice that for case b.

The spin echo is seen to consist of eight satellites, which are positioned symmetrically with respect to the central peak ($x=0$). This central peak is described by the integral in (11), which can easily be evaluated explicitly. the amplitude of the central peak is proportional to ω_1^3, while the dependence is quadratic for the satellites. The satellite formation times are $z_{i\pm} = \pm \alpha t_i$. The amplitudes of the satellites decrease with distance from the central peak because the terms in the sum in (11) "turn off" in succession. All the arguments in the discussion of the one-pulse and two-pulse free induction above remain valid for the spin echo.

If the exciting pulses are of equal length, the echo signal consists of five components (Fig. 4).

5. EXPERIMENTAL RESULTS

Experiments were carried out on a well-studied two-level system—protons in water—on a 14-MHz NMR spectrometer. A modulator produced rf pulses with an attenuation of at least 70 dB in the "off" state. The pulses were then fed to a power amplifier with a high-Q circuit, which corrected the spectral composition of the pulse with a rise time of about 7 μs. The pulses from the output of this amplifier were fed through a calibrated attenuator to an rf bridge. The difference signal from this bridge, a consequence of the interaction of the rf pulse with the spin system, was fed through an amplifier with a bandwidth of about 400 kHz to a phase-sensitive detector with a time constant of about 3 μs. We used a coherent digital summation of the detected signals. The inhomogeneous broadening of the NMR line was created by a controllable gradient of a polarizing magnetic field. The area under the applied pulses was determined from the Rabi oscillations observed during the pulses. All the pertinent parameters were monitored so that it would be possible to make a valid comparison of the data with the theoretical results.

Figure 1 shows oscilloscope traces of the v component of the magnetization detected after nonresonant one-pulse excitation. The observed signals correspond well to the theoretical responses calculated for a Gaussian lineshape. There is some discrepancy between the signals just after the end of the pulse, because the inhomogeneous line which is formed is not Gaussian. The observed behavior of the amplitude of the one-pulse echo signal as a function of the amplitude of the exciting pulse (Fig. 5) and as a function of the detuning from resonance (Fig. 1) also agrees with the theoretical predictions.

Figures 3 and 4 show signals observed during the nonresonant application of two pulses. The multicomponent structure of the two-pulse free induction and the echo discussed above can be identified well. The discrepancy between the theoretical and experimental behavior is, again in these cases, a consequence of a difference between the theoretical and actual lineshapes. Our studies of the amplitude and position of these responses as a function of the relations among ω_1, δ, and σ revealed a correspondence with the theoretical conclusions: (1) With increasing δ/ω_1, the distance between the components of the spin echo increases, while at $\delta/\omega_1 \ll 1$ the multicomponent structure degenerates into an oscillatory response if $\omega_1 t_i > 2\pi$. (2) With decreasing σ/ω_1, the signals become narrower and more intense. (3) With increasing $\omega_1 t_i$, each satellite acquires a modulated shape and decreases in amplitude.

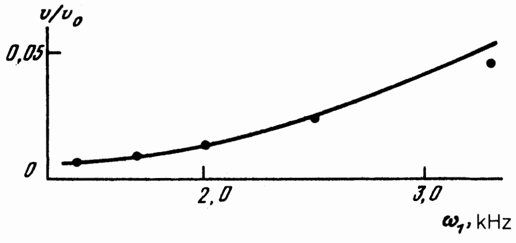

FIG. 5. Amplitude of the one-pulse echo versus the frequency of the rf field, ω_1, for $\omega_1 t_1 = 20\pi$, $\sigma = 2.6$ kHz, and $\delta = 3.0$ kHz.

6. DISCUSSION

It has been shown theoretically and experimentally in this study that an isolated signal is formed during nonresonant one-pulse excitation of an inhomogeneously broadened line of a spin system. The time at which it forms depends on the length of the pulse and the detuning from resonance. In the case of two-pulse excitation under these conditions, the free-induction and echo signals have a multicomponent structure, and the time interval between the components also depends on the lengths of the pulses and the detuning of the carrier frequency of the pulses from the central frequency of the line. This structure of the responses of the spin system is a consequence of zero beats between oscillations at the variable Rabi frequency and at the frequency of the detuning from resonance. An important aspect of the additional responses is their quadratic ω_1 dependence. Because of this characteristic, they should be classified as free-induction signals,[9] not an echo, which would have a cubic ω_1 dependence.[12] Note in this connection that the phrase "one-pulse echo" is unfortunate usage here. It derives from the excitation method, rather than the physics of the formation of the response.

As we have already stressed, the nonresonant nature of the excitation is not a consequence of particular features of the properties of spin systems. It may be manifested in a study of transient coherent effects in any other system, including optical resonances. Since this question has not been studied, one can apparently not rule out the possibility that a nonresonant nature of the excitation will be seen in observations of spin echoes in magnetically ordered systems. The resonant nature of the excitation in Refs. 2 and 3, for example, was monitored on the basis of the maximum of the two-pulse stimulated-echo signal (the first component of the induction signal after the second pulse) as the frequency of the exciting pulse was varied. Actually, relation (10) shows that if only the detuning from resonance is varied then the maximum of the first component of the two-pulse free-induction signal is reached under the condition

$$\omega_1 x (t_i^2 - x^2)^{-1/2} = \delta,$$

i.e., in the case of specifically nonresonant excitation. It is therefore not by chance that all the other results reported for equal pulse lengths in Refs. 2 and 3 can be explained by the expressions derived in the present paper. There is thus no need to invoke structural features of magnetic ordered systems in this case.

In the case of unequal pulse lengths, nine spin-echo responses and four two-pulse free-induction responses should form, according to (10) and (11). Ten responses were observed in Ref. 4 in magnetically concentrated substances in this case. The reasons for the discrepancy was the short time interval between pulses and the resulting superposition of responses on each other. The model of distortions of pulses near their fronts which was used in Ref. 10 to explain the results of Ref. 4 also leads to an approximate prediction of the times at which the nine spin-echo responses and only a single two-pulse free-induction response form. Unfortunately, the data reported in Ref. 4 are not a sufficient basis for identifying the mechanism for the appearance of the signals observed in this case. Information about the exciting pulses is necessary for determining whether there are amplitude, phase, or frequency distortions and for determining whether the carrier frequency of the exciting pulses was the same as the resonant frequency of the magnetic system.

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