Echo signals in two-pulse delayed nutation

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It was established that two-pulse delayed nutation in spin systems characterized by inhomogeneous broadening gives rise to four echo signals which appear at times that depend on the duration of a conditioning pulse t_1, on the delay τ between the pulses, and on the ratio of the Rabi frequency ω_1 to the line width. Nonresonant excitation (when the detuning from a resonance is $\delta \neq 0$) creates additional responses due to zeroth beats between oscillations of spin packets at a frequency $\Omega_i = \omega_1 (t' - \alpha_i)/[(t' - \alpha_i)^2 - \tau^2]^{1/2}$ ($\alpha_i = 0, \pm t_1$; t' is the time measured from the beginning of the second pulse) and at the generalized Rabi frequency $(\delta^2 + \omega_1^2)^{1/2}$. The formation of such signals is confirmed by experiments carried out on proton magnetic resonance. Determination of the relaxation times with the aid of the observed signals combines the advantages of the methods employing free evolution of the investigated system and of the echo in a rotating coordinate system.

1. INTRODUCTION

Transient oscillations or nutation[1] are among the simplest processes investigated by transient spectroscopy of quantum systems.[2] These effects appear after abrupt activation of an interaction between a quantum system and an alternating electromagnetic field, and they are of the same nature in different spectral ranges (NMR, ESR, optical resonance). The use of transient nutation in determination of the dipole moments of transitions has certain advantages over other methods.[2,3] On the other hand, although decay of nutation carries information on relaxation processes, it is not always convenient to determine the relaxation constants from such decay because its rate is governed not only by the relaxation processes in question but also by inhomogeneities of the interacting fields.[1,4] Recent experimental investigations of ESR in quartz[5] have shown that these factors may be insufficient to describe the nutation decay rate. Nevertheless, an analysis of the decay of nutation is valuable as the simplest variant for the investigation in real time of relaxation processes in the presence of an exciting electromagnetic field.

In this situation it would be desirable to find variants of the nutation effect which would make it possible to separate different decay mechanisms. In particular, it is suggested in Ref. 2 that the rate of energy relaxation can be determined with the aid of what is known as delayed nutation, when use is made of the fact that the peak value of the absorption during the first nutation half-period (initial peak) is proportional to the initial difference between the populations of the relevant levels. If a system is perturbed out of its thermal equilibrium and is then allowed to relax for a time τ and is subjected again to the interaction with radiation, the change in the initial peak considered as a function of τ can be used to determine the population difference at this moment in time and, consequently, the energy relaxation rate. In practice, this method can be realized by the application of a first (conditioning) pulse of finite duration t_1 and then, after an interval τ, of a second extended pulse during which two-pulse delayed nutation is recorded. This method has been used already to determine the rate of relaxation of levels in some molecular gases.[2,6,7]

A theoretical analysis of delayed nutation in Ref. 2 gives an expression for the absorption signal which is limited to terms proportional to the population difference at the moment $t_1 + \tau$. In fact, the authors of Ref. 2 allowed only for the initial condition governing the population difference which represents the action of a conditioning pulse and subsequent relaxation in a time interval τ and they ignored two other initial conditions governing the polarizability of the medium. We shall show theoretically that a full allowance for the initial conditions gives rise to echo signals in two-pulse delayed nutation and we shall consider the possibility of determination of the relaxation times with the aid of these signals. An experimental verification of the analytic expressions was made by us for the case of NMR, so that we shall use the magnetic resonance terminology.

2. THEORETICAL ANALYSIS

Let us assume that the spin system is subjected to the action of an rf field whose amplitude $H_1(t)$ varies in accordance with the law:

$$H_1(t) = \begin{cases} H_1, & 0<t<t_1, \\ 0, & t_1<t<t_1+\tau, \\ H_1, & t_1+\tau<t<\infty. \end{cases} \tag{1}$$

The expression for the v component of the magnetization (absorption signal) of a two-level spin system obtained ignoring relaxation processes can be written in the form[2]

$$v(t) = v_0 \Big[-\frac{\Delta}{\beta} \sin\beta(t-t_1-\tau)\, u(t_1+\tau) + \cos\beta(t-t_1-\tau) \times v(t_1+\tau) + \frac{\omega_1}{\beta} \sin\beta(t-t_1-\tau)\, w(t_1+\tau) \Big], \tag{2}$$

where $t \geqslant t_1 + \tau$,

$$u(t_1+\tau) = \frac{\Delta}{\beta}(1-\cos\beta t_1)\cos\Delta\tau + \sin\beta t_1 \sin\Delta\tau, \tag{3a}$$

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$$v(t_1+\tau) = -\frac{\Delta}{\beta}(1-\cos\beta t_1)\sin\Delta\tau + \sin\beta t_1\cos\Delta\tau, \tag{3b}$$

$$w(t_1+\tau) = 1 - \frac{\omega_1^2}{\beta^2}(1-\cos\beta t_1), \tag{3c}$$

$\beta = [\Delta^2 + \omega_1^2]^{1/2}$, $\omega_1 = \gamma H_1$ is the Rabi frequency, v_0 is the equilibrium difference between the populations, Δ is the scatter of the frequencies of spin packets, and γ is the gyromagnetic ratio. The expressions in the system (3) are the initial conditions for the response and depend on the parameters of a conditioning pulse and of the dephasing in the interval τ.

In further analysis of Eq. (2) we have to average this equation over the profile of an inhomogeneously broadened line

$$\langle v(t)\rangle = \int_{-\infty}^{\infty} v(t) g(\Delta-\delta)\,d\Delta, \tag{4}$$

where $g(\Delta-\delta)$ is the form factor of the line, $\delta = \omega_0 - \omega$ is the detuning (offset) from a resonance, ω_0 is the central frequency of the resonance line, and ω is the carrier frequency of an rf pulse.

The integrals in Eq. (4) were calculated for $\delta = 0$ in the case of an infinite line width σ ($\sigma \gg \omega_1$) (Ref. 2). An analytic expression for these integrals can be obtained in the case of arbitrary relationships between σ, ω_1, and δ by regrouping the terms and writing down Eq. (4) as follows:

$$\langle v(t')\rangle = v_0\Big[I(t') + \sum_{i=1}^{3}(F_i^{(+)}(t') + F_i^{(-)}(t'))\Big], \tag{5}$$

where $t' = t - t_1 - \tau \geqslant 0$,

$$I(t') = \omega_1 \int_{-\infty}^{\infty}\Big\{\frac{1}{\beta}\sin\beta t' + \frac{\omega_1^2}{\beta^3}\Big[\frac{1}{2}\sin\beta(t'+t_1) - \sin\beta t' + \frac{1}{2}\sin\beta(t'-t_1)\Big]\Big\} g(\Delta-\delta)\,d\Delta, \tag{5a}$$

$$F_1^{(\pm)}(t') = \mp\frac{\omega_1}{2}\int_{-\infty}^{\infty}\frac{\Delta}{\beta^2}\Big[1\pm\frac{\Delta}{\beta}\Big]\sin(\beta t'\pm\Delta\tau) g(\Delta-\delta)\,d\Delta, \tag{5b}$$

$$F_2^{(\pm)}(t') = \frac{\omega_1}{4}\int_{-\infty}^{\infty}\frac{1}{\beta}\Big[1\pm\frac{\Delta}{\beta}\Big]^2 \sin(\beta(t'+t_1)\pm\Delta\tau) g(\Delta-\delta)\,d\Delta, \tag{5c}$$

$$F_3^{(\pm)}(t') = -\frac{\omega_1^3}{4}\int_{-\infty}^{\infty}\frac{1}{\beta^3}\sin(\beta(t'-t_1)\pm\Delta\tau) g(\Delta-\delta)\,d\Delta. \tag{5d}$$

In Eq. (5a) only the first term describing the usual nutation after the second pulse is independent of the previous history of the spin system. In the remaining terms the second describes also nutation from the moment $t' = 0$, whereas the first and third terms contribute to nutation in antiphase relative to one another. At $t' = 0$ these contributions compensate each other out, but when $t' > 0$ their sum is generally finite. This can be said also about Eqs. (5b)–(5d). For convenience, we shall call the nutation response observed directly after the second pulse [described by Eq. (5a)] the first-order nutation and the response at times of the order of $t' \approx \tau$ and $\tau \pm t_1$ [described by Eqs. (5b)–(5d)] the second-order nutation.

2.1. First-order nutation

After the substitution $\Delta/\beta = \sin y$, Eq. (5a) becomes

$$I(t') = \omega_1 \int_{-\pi/2}^{\pi/2}\Big\{\cos^{-1} y \sin\Big(\frac{\omega_1 t'}{\cos y}\Big) + \frac{1}{2}\Big[-\sin\Big(\frac{\omega_1 t'}{\cos y}+y\Big) - \sin\Big(\frac{\omega_1 t'}{\cos y}-y\Big) + \frac{1}{2}\sin\Big(\frac{\omega_1(t'+t_1)}{\cos y}+y\Big) + \frac{1}{2}\sin\Big(\frac{\omega_1(t'+t_1)}{\cos y}-y\Big) + \frac{1}{2}\sin\Big(\frac{\omega_1(t'-t_1)}{\cos y}+y\Big) + \frac{1}{2}\sin\Big(\frac{\omega_1(t'-t_1)}{\cos y}-y\Big)\Big]\Big\} g(\omega_1 \operatorname{tg} y-\delta)\,dy. \tag{6}$$

We shall introduce the large parameter of the problem in the form of the quantity $\omega_1(t'-\alpha_i) > 1$, where $i = 1, 2, 3$; $\alpha_1 = 0$, $\alpha_2 = -t_1$, $\alpha_3 = t_1$. Then the behavior of the integrals in Eq. (6) can be approximated quite satisfactorily by the principal term in the asymptotic expansion at a stationary phase point,[8] which is found from the equation

$$\sin y_{0i} = -\frac{1}{2}[[\omega_1^2(t-\alpha_i)^2+4]^{1/2} - \omega_1(t-\alpha_i)]. \tag{7}$$

After calculations, we find that Eq. (6) is given by

$$I(t) \approx \omega_1(2\pi)^{1/2}\Big[(\pi/2)^{1/2} J_0((-\omega_1 t'/\sin y_{01})^{1/2}) G(\varkappa_1-\delta) \times (1+\sin^2 y_{01})^{-1/2} + \sum_{i=1}^{2}(-2)^i \Phi(y_{0i}) \mp \Phi(y_{03})/4\Big], \tag{8}$$

where

$$\Phi(y_{0i}) = [-\omega_1(t'-\alpha_i)\sin^3 y_{0i}]^{1/4} \sin\Big[\Big(-\frac{\omega_1(t'-\alpha_i)}{\sin y_{0i}}\Big)^{1/2} + y_{0i} + \frac{\pi}{4}\Big] G(\varkappa_i-\delta)/(1+\sin^2 y_{0i})^{1/2},$$

$G(\varkappa_i - \delta) = g(\varkappa_i - \delta) + g(\varkappa_i + \delta)$, $\varkappa_i = \omega_1(-\sin y_{0i}/[\omega_1(t-\alpha_i)])^{1/2}$, and $J_0(x)$ is a Bessel function of zeroth order. If $t' > \alpha_3$, then in the last term of Eq. (8) we take the sign (+) whereas for $t' < \alpha_3$ we take the sign (−) and instead of $(t' - \alpha_3)$ we substitute $(\alpha_3 - t')$.

It is clear from Eq. (8) that the decay of the nutation signal obeys a complex power law modulated by oscillations of variable frequencies $\Omega_i = [\omega_1/[-(t-\alpha_i)\sin y_{0i}]]^{1/2}$, which become equal to ω_1 after a long time.

We shall consider first the case when $\delta = 0$. An analysis of the terms in Eq. (8) shows that the envelopes of the last three terms have extrema at moments $t'_{0i} - \alpha_i = (1-R^2)/(\omega_1 R)$, where

$$R = \pm[(2+A^2-(A^4+6A^2+1)^{1/2})/(3-2A^2)]^{1/2}, \quad A = \omega_1/\sigma.$$

If $\omega_1 t_1 > (1-R^2)/R$, then at $t' > 0$ there is a minimum at a moment $t'_{03} = t_1 - (1-R^2)/\omega_1 R$, maxima at moments $t'_{01} = (1-R^2)/(\omega_1 R)$ and $t'_{03} = t_1 + (1-R^2)/(\omega_1 R)$, and a maximum corresponding to an initial nutation peak [first term in Eq. (8)]. It follows from the above that against the background of the nutation process we can observe two signals, one of which corresponds to the initial nutation peak directly after the second pulse and the second is delayed relative to the latter by $\sim t_1$ (Fig. 1). If $\omega_1 t_1 < (1-R^2)/(\omega_1 R)$, the second response begins to approach the initial peak and finally merges with it. This is precisely the situation observed in the experiments reported in Ref. 2.

If $\delta \neq 0$, a similar analysis is difficult to carry out, but if δ is sufficiently large, the moments of appearance of extrema can be estimated from the value of $G(\varkappa_i)$, which is maximal when $\varkappa_i = \delta$. Then, the moments of appearance of signals are given by $t'_{0i} - \alpha_i = \omega_1/[\delta[\delta^2+\omega_1^2]^{1/2}] = \xi$. At these moments the instantaneous frequencies are $\Omega_i = [\delta^2+\omega_1^2]^{1/2}$, i.e., zeroth beats are observed between oscillations of spin packets at the variable frequency Ω_1 and at the generalized Rabi frequency $[\delta^2+\omega_1^2]^{1/2}$.

We shall now consider the optimal conditions for the observation of signals. If $\delta = 0$, the amplitudes of the maxima are proportional to ω_1/σ, whereas for $\delta \neq 0$ the ω_1 dependence is governed by the relationship between ω_1 and δ. If $\omega_1 > \delta$, then

$$\Phi(y_{0i}) \propto (\omega_1/\sigma)(\delta/\omega_1)^{1/2},$$

for $\omega_1 < \delta$, we have

$$\Phi(y_{0i}) \propto (\delta/\sigma)(\omega_1/\delta)^{3/2},$$

whereas the amplitude of the first term in Eq. (8) is proportional to $(\omega_1/\delta)(\delta/\sigma)$ in the first and second cases. The condition for separation of the initial nutation peak and of the signal delayed by t_1 ($\omega_1 t_1 > \xi$) is satisfied when $\delta > \omega_1$. Hence, it follows that the conditions most favorable for the experimental observation of the delayed signal are $\delta > \omega_1$ and $\delta > \sigma$. Using the condition of the "sharpness" of resonances $\omega_1 > \sigma$, we finally obtain $\sigma < \omega_1 < \delta$.

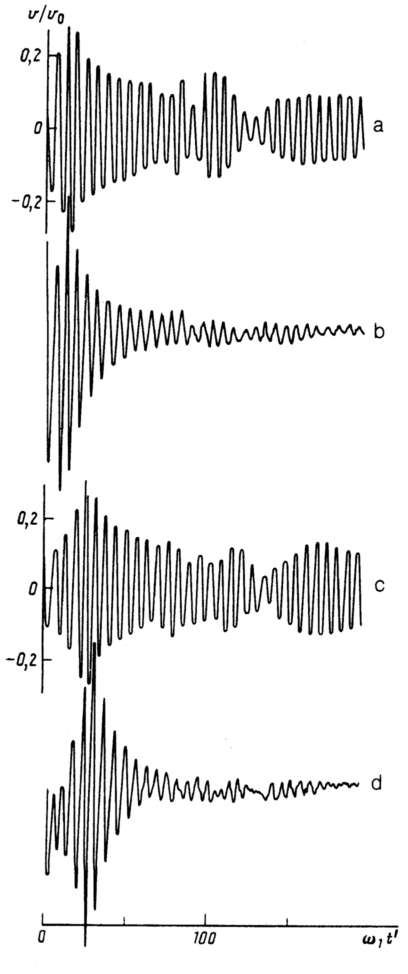

FIG. 1. Delayed two-pulse nutation in the resonant excitation case: a), c) theory; b), d) experiments; $\omega_1/\sigma = 1$, $\omega_1\tau = 16\pi$, $\omega_1 t_1 = 4\pi$ (a and b), 8π (c, d).

2.2. Second-order nutation

Using the Fourier transformation we can readily show that the integrals of Eqs. (5b), (5c), and (5d) vanish in the intervals $(t-\alpha_i, \tau)$. The stationary phase method[8] can be used again to calculate the integrals in the intervals $t-\alpha_i > \tau$ if the large parameter of the problem is assumed to be $\omega_1\tau > 1$. We then have

$$\sum_{i=1}^{3}(F_i^{(+)}(t')+F_i^{(-)}(t')) \approx \omega_1(2\pi)^{1/2}\sum_{i=1}^{3}(\omega_1\tau)^{-1/2}\psi_i(\Delta_{0i}) \times \sin(\omega_1[(t'-\alpha_i)^2-\tau^2]^{1/2}+\pi/4)[g(\omega_1\Delta_{0i}-\delta)+g(\omega_1\Delta_{0i}+\delta)], \tag{9}$$

where

$$\Delta_{0i} = \tau/[(t'-\alpha_i)^2-\tau^2]^{1/2};$$

$$\psi_1(\Delta_{01}) = [\Delta_{01}^{3/2}/(1+\Delta_{01}^2)^{1/2}][1-\Delta_{01}/(1+\Delta_{01}^2)^{1/2}];$$

$$\psi_2(\Delta_{02}) = \Delta_{02}^{1/2}(1-\Delta_{02}/(1+\Delta_{02}^2)^{1/2})^2/2;$$

$$\psi_3(\Delta_{03}) = -\Delta_{02}^{1/2}/[2(1+\Delta_{03}^2)].$$

It should be pointed out that the authors of Ref. 2 calculated two-pulse nutation parameters ignoring the contributions described by Eqs. (5b)–(5d) to the nutation process and assuming incorrectly that these integrals vanish throughout the relevant time interval. We can see from Eq. (9) that the amplitude of nutation oscillations begins to increase at times $\sim\tau$ from the second pulse and it passes through maxima. If $\delta = 0$, it is possible to obtain an estimate of the maxima for the general case for the last term in Eq. (9), whereas in the case of other terms this is possible only in special cases. For example, the moment of formation of a maximum of the last term in Eq. (9) is

$$t'_{03} = t_1 + \tau[3+5A^2+(9A^4+46A^2+9)^{1/2}]^{1/2}/2^{1/2}A,$$

whereas for $A = 1$, we have

$$t'_{01} \approx 2\tau,\ t'_{02} \approx 2\tau(1+3^{1/2})-t_1.$$

However, if $A \gg 1$, then

$$t'_{01} \approx 1{,}53\tau,\ t'_{02} \approx 2\tau(1+2^{1/2})-t_1,\ t'_{03} = 2\tau+t_1,$$

i.e., when the field amplitude is increased the signals shift toward shorter times. The amplitude of these signals is governed by the quantity A, whereas the moment of their appearance depends also on the ratio τ/t_1 (Fig. 1). If $\tau \geqslant t_1$, the signals become separate, whereas for $\tau \gg t_1$ they merge into one asymmetric signal with a steep leading edge and a gently sloping trailing edge. In addition to these signals, two additional responses appear up to the moment 2τ. A numerical investigation shows that they are due to beats of the oscillations described by Eq. (9). Unfortunately, the beat condition cannot be derived in the analytic form because in the general case of interference of oscillations occurs not only the phases but also the amplitudes vary.

If $\delta \neq 0$, the expression in square brackets in Eq. (9) has a maximum every time that $\omega_1 \Delta_{0i} = \delta$, so that the maxima appear at moments

$$t_{0i}' - \alpha_i = [\delta^2 + \omega_1^2]^{1/2}\tau/\delta.$$

The zeroth beats then occur between oscillations at the variable frequencies

$$\Omega_i = \omega_1 (t' - \alpha_i)/[(t' - \alpha_i)^2 - \tau^2]^{1/2}$$

and at the frequency $(\delta^2 + \omega_1^2)^{1/2}$. It should be pointed out that in the nonresonant excitation case the moments of formation of the echo signals generated by free evolution of the spin system[9] correspond to the zeroth beats between the instantaneous frequencies of spin packets and the frequency δ.

If the detuning from a resonance is relatively small ($\delta < \omega_1$), the nonresonant signals are difficult to distinguish against the background response corresponding to the case when $\delta = 0$. An increase in δ/ω_1 results in their increasingly clear manifestation, whereas the response corresponding to $\delta = 0$ becomes weaker (Fig. 2).

We shall now consider the ω_1 dependence of these signals. If $\delta = 0$, the responses are linear in ω_1. If $\delta \neq 0$ then for $\omega_1 > \delta$ the maximum of the moment t_{02} is proportional to $(\delta/\omega_1)(\delta/\sigma)(\delta\tau)^{-1/2}$, whereas at the moments t_{01} and t_{03} it is proportional to $(\delta/\sigma)(\delta\tau)^{-1/2}$. However, $\omega_1 < \delta$, the amplitude of the maximum at the moment t_{02} is proportional to $(\omega_1/\delta)^4(\delta/\sigma)(\delta\tau)^{-1/2}$, whereas at the moments t_{01} and t_{03} it is proportional to $(\omega_1/\delta)^2(\delta/\sigma)(\delta\tau)^{-1/2}$. The condition for finding the signals near τ requires that δ should be greater than ω_1. It is clear from Eq. (9) that the signal "width" is governed by the value of σ/ω_1, so that the response is sharp and narrow when $\omega_1 > \sigma$. Consequently, the optimal conditions for the observation of these maxima are specified by $\sigma < \omega_1 < \delta$. The strongest signals are those at the moments t_{01} and t_{03}, because they are proportional to ω_1^2/δ^2. Therefore, the weakest nonlinearity for these nutation signals is quadratic, whereas the response at the moment t_{02} the nonlinearity is of the fourth order.

3. EXPERIMENTAL RESULTS

We checked the analytic expressions obtained above in NMR ($\omega/2\pi = 14.4$ MHz) experiments using protons in water with admixtures of paramagnetic ions in order to reduce the relaxation times. The nutation signal was formed by altering the rf field amplitude and using a phase-sensitive detector. Recording of the signals during the action of rf pulses was possible when the matching of the rf channel was sufficiently good (60–80 dB). A controlled inhomogeneous broadening of the NMR line was created by a controlled gradient of a polarizing magnetic field. The nutation signal during a conditioning pulse was used to determine its area. The signal/noise ratio was increased by coherent digital summation of the signals.

Figure 1 shows the absorption signals recorded during the second rf pulse after conditioning pulses of different durations. The oscillograms obtained reveal characteristic properties of delayed nutation in the resonant ($\delta = 0$) excitation case. An example of delayed nutation in the nonresonant excitation case is shown in Fig. 2. In both cases the observed signals demonstrate the main features of the calculated responses. The discrepancies between the theoretical and experimental oscillograms can be attributed, on the one hand, to the difference between the real and Gaussian line profiles (the latter was used in the theory) and, on the other, due to the influence of relaxation processes (relaxation was ignored in the calculations).

It is clear from Fig. 1 that in the case of resonant excitation it is easy to identify the first-order nutation echo signals ($t \approx t_1$) as well as the second-order signals observed at moments $t_{01}' \approx 2\tau$ and $t_{03}' \approx 4\tau/2^{1/2} + t_1$. The response predicted for $t_{02}' \approx 2\tau(1 + 3^{1/2}) - t_1$ was not detected because of its lower amplitude and because of relaxation. The responses due to the nonresonant excitation were observed only when the detuning was comparable with the line width. A further increase in the detuning from a resonance reduced the amplitude of these responses in accordance with the theoretical predictions, and also because of relaxation, so that they became difficult to detect.

4. DISCUSSION

It was shown above that in the case of two-pulse delayed nutation in spin systems characterized by inhomogeneous broadening one can expect four separate signals whose appearance times depend on the duration of a conditioning pulse, on the delay between the pulses, and on the ratio of the Rabi frequency to the line width. In the nonresonant excitation case there are additional responses due to zeroth beats between oscillations of spin packets at the variable frequency Ω_i and at the generalized Rabi frequency.

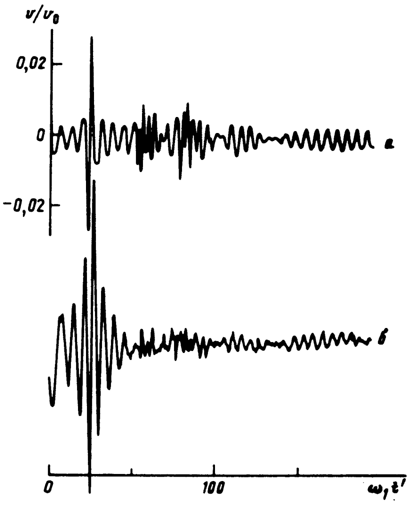

FIG. 2. Delayed two-pulse nutation in the nonresonant excitation case: (a is the theory and b are the experimental results); $\omega_1/\sigma = 1$, $\omega_1\tau = 16\pi$, $\omega_1 t_1 = 8\pi$, $\delta/\omega_1 = 2.5$.

The nutational (rotational) echo signals known earlier and generated during the action of an exciting electromagnetic field appear at a moment $2t_0$ as a result of a brief change at t_0 of the phase,[10-13] amplitude,[14,15] or frequency,[7,16] of an electromagnetic field, or the frequency of the investigated transition because of the Stark or Zeeman effects.[17-19] In some situations[1] [a) $\Delta = 0$; b) $T_1 = T_2$; c) $\omega_1 \gg T_1^{-1}$, T_2^{-1}] these signals can be used to determine the relaxation times in the optical[16] and rf[13,20] ranges. The nutational echo has been used also to study the influence of a high-power laser field on the relaxation of optical Cr^+ centers in ruby[21] and to determine the dipole moments of impurities in glasses.[13] However, in general, analytic expressions for the nutational echo are so complex that in most cases they are quite useless for the determination of relaxation parameters.

Our nutational echo signals make it possible to achieve considerable simplification when allowing for the relaxation processes. This is due to the existence in the course of formation of the nutational echo of an interval of free evolution of the system, which does not occur in earlier methods of transient spectroscopy in a rotating coordinate system and which makes it possible to carry out relaxation measurements using simple relationships without any limitations on the values of Δ, ω_1, T_1, or T_2. If $\tau \gg t_1$, then the relaxation must be allowed for only during the free evolution interval, which is a trivial matter when the Bloch equations are used: the expression for the first-order nutation of Eq. (8), which includes the initial value of the difference between the populations described by Eq. (3c), is multiplied by $\exp(-\tau/T_1)$ and the expression for the second-order nutation of Eq. (9), which includes the initial values given by Eqs. (3a) and (3b), is multiplied by $\exp(-\tau/T_2)$.

Such a simple dependence on the relaxation parameters makes it possible to use the observed echo signals to determine T_1 and T_2 without any limitations on the values of Δ, ω_1, T_1, or T_2, which is a clear advantage of this approach over other echo methods in the presence of an exciting field (nutational echo). On the other hand, in contrast to the induction signals and the primary and stimulated echo signals, usually employed to determine T_1 and T_2 and based on the existence of free evolution of the system, the signals under investigation here can be regarded as a variety of an echo in a rotating coordinate system and they are independent of the inhomogeneity of the exciting field.[22]

Moreover, the observed echo signals allow us to avoid the usual difficulties encountered in relaxation measurements in two-pulse delayed nutation.[2] The observation of an isolated echo signal at a moment t_1 not only eliminates the influence of inhomogeneities of the exciting electromagnetic field, but makes it possible to dispense with the requirement for apparatus with an extremely high time resolution necessary for undistorted recording of the initial nutation peak.[2] The use of such a signal also avoids superposition of the free induction signal when delayed nutation is due to the Stark (in optics) or Zeeman (in a magnetic resonance) switching of an excited packet within an inhomogeneously broadened line.

Variation of τ can be used to determine also T_2 by investigating the second-order nutation echo signals. However, the amplitude of these signals is proportional to $1/\tau^{1/2}$ [see Eq. (9)], i.e., it depends on τ not only via the relaxation factor $\exp[-(t' + t_1 + \tau)/T_2]$, so that in this case it is preferable to determine T_2 by varying t_1.

Our general description of two-pulse delay nutation in systems with inhomogeneously broadened lines thus reveals nutation echo signals which then combine the advantages of the methods based on free evolution of the system and of the echo in a rotating coordinate system when measurements are made of the relaxation times.

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