Multiple echos in the effective field of multipulse trains in nuclear quadrupole resonance

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Multiple echos were obtained in the effective field of a multipulse nuclear quadrupole resonance train. The intensity of the echo signals decays according to a double-exponential law. The decay time in the "short" exponential function was measured and the dependence of the decay on the interval between the pulses and the number of cycles in a "supercycle" in the train were measured. It was found that in the "long" exponential function the echo signals merge into pairs.

In a previous paper we reported the observation of echos in the effective field of a multipulse train (echos on the envelope of the echo signals) which were formed as a result of phase conjugation of the rf filling of the pulses after a definite number of cycles in the train or after the application of an additional pulse between cycles.[1] The decay time of an echo formed in this manner is several times longer than the decay time of a standard echo in the same sample.

Under certain conditions the phase conjugation of the rf filling of the pulses in the train changes the sign of the effective Hamiltonian. This explains the formation of an echo on the envelope of the echo signals. On the basis of the formal analogy between the effective Hamiltonian of a multipulse train and the Hamiltonian of a stationary rf field and detuning, this method is similar to the one used to form the so-called rotational echo in NMR by inversion of the phase of a stationary rf field.[2] Proceeding from this reasoning, we performed experiments on repeated inversion of the phase of the rf field in a multipulse train and we obtained multiecho signals on the envelope of the echo signals in the train.

The experiment was performed on several single-crystal samples of sodium nitrate $NaNO_2$ (NQR ^{14}N) at a temperature of 77 K and a frequency of 4.93125 MHz ($\Delta f = 0$), corresponding to the transition $+ \leftrightarrow 0$. In this transition the spin-spin relaxation time is $T_2 \simeq 7$ ms, the spin-lattice relaxation time is $T_1 \simeq 1$ s, and the inverse line width is $T_2^* \simeq 1.5$ ms. A coherent multipulse spectrometer, manufactured domestically, was used. A description of the spectrometer is given in Ref. 3.

The experiments were performed with the aid of a modified multipulse train with alternating phases[1] (MPTAP)

$$\varphi_x - (\tau - \psi_y - 2\tau - \psi_{-y} - \tau)_N, \tag{1}$$

where φ_x is the rotation angle of the nuclear magnetization prepared by a pulse applied

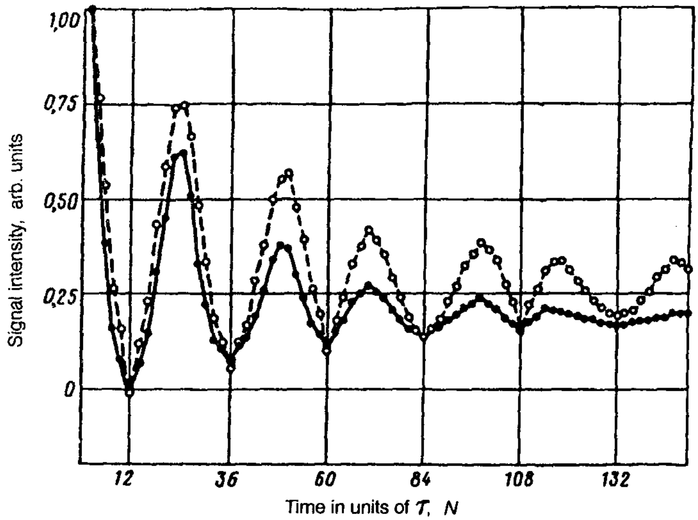

FIG. 1. Echo signals in the multipulse train (3) with $n=3$ for $\tau=0.3$ms (○—dashed curve) and 0.6 ms (●—solid line), $\psi=\pi/2$, $\psi=\pi$. The grid is drawn at the points where supercycles start (terminate). The samples were obtained in each window of the train (with a time interval of 2τ).

along the X axis, ψ_y is the rotation angle due to a pulse train applied along the Y axis (shifted in phase by 90° with respect to the preparatory pulse), $\tau(2\tau)$ is the interval between the pulses, and N is an integer (the number of cycles in a train). Sampling (extraction of information) was conducted at the center of each window, i.e., at a time τ following each pulse in the train. The signal obtained in this manner is reminiscent of the decay of free induction in a standard one-pulse experiment, but its duration is longer.[1] Phase conjugation in the nth cycle, i.e., the use of the train

$$\varphi_x-(\tau-\psi_y-2\tau-\psi_{-y}-\tau)_n-(\tau-\psi_{-y}-2\tau-\psi_y-\tau)_N, \tag{2}$$

leads to the formation of an echo signal on the envelope of echo signals with a maximum occurring every $2n$ cycles after the start of the train.[1]

Repeated inversion of the phase maintained by the sequence

$$\varphi_x-(\tau-\psi_y-2\tau-\psi_{-y}-\tau)_n-[(\tau-\psi_{-y}-2\tau-\psi_y-\tau)_{2n}$$
$$-(\tau-\psi_y-2\tau-\psi_{-y}-\tau)_{2n}]_N \tag{3}$$

produces a decaying series of echo signals (Fig. 1). The decay time is several times longer than the standard decay time T_2 (7 ms) of echo signals in this sample. Figure 1 shows the intensity of the signals in the windows of the sequence as a function of time in units of τ for two values of τ: $\tau=0.3$ and 0.6 ms. The effective decay time T_{2e} is virtually identical for these two values: 48τ and 40τ, respectively; i.e., the real decay time increases as the interpulse interval increases. The decay of the envelope of the echo signals in this train is approximated well by an exponential function. The decay time determined for this function is plotted as a function of τ in Fig. 2.

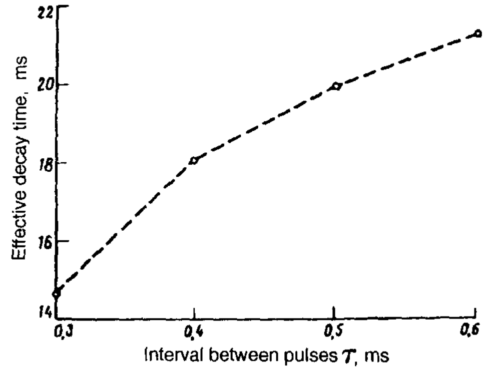

FIG. 2. Effective decay time of echo signals as a function of the time interval 2τ between the pulses in the train (3) for a short exponential with $n=3$.

Figure 3 is a plot of the decay time as a function of the number n of cycles in a supercycle. This time increases almost linearly from T_2 for $n=1$ to $\simeq 25$ ms. In each case the maximum decay time is approximately the same and equal to the lifetime measured by a method similar to Hahn's method, i.e., one that uses the train (2) and in which n is varied.

A more detailed investigation (over longer time intervals) makes it possible to observe the existence of a second, slowly decaying exponential function and "pairing" of the echo signals, i.e., doubling of their formation period (Fig. 4). The Fourier transform of this dependence exhibits a sharp peak corresponding to a subharmonic of the repetition frequency of the supercycle (Fig. 5).

The effective Hamiltonian for MPTAP can be written in the following form using one-transition operators[4] : [5]

$$H_e=\frac{1}{2\tau}\cos^{-1}\left(1-2\cos^2\frac{\psi}{2}\sin^2\Delta\tau\right)(c_zS_z^p-c_xS_x^p),$$

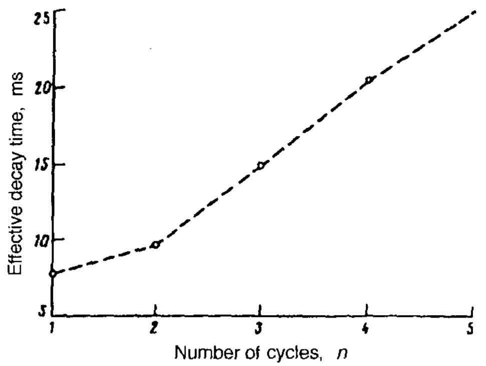

FIG. 3. Effective decay time as a function of the number $2n$ of cycles in a supercycle with $\tau=0.3$ ms.

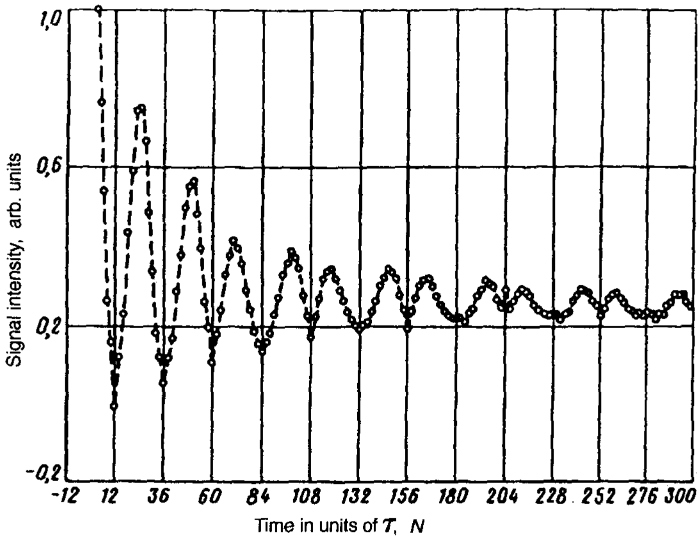

FIG. 4. Same as Fig. 1 but with $\tau = 0.3$ ms on long time intervals.

$$c_x = \frac{\sin\dfrac{\psi}{2}}{\sqrt{1-\cos^2\dfrac{\psi}{2}\cdot\sin^2\Delta\tau}}, \quad c_z = \frac{\cos\Delta\tau\cdot\cos\dfrac{\psi}{2}}{\sqrt{1-\cos^2\dfrac{\psi}{2}\cdot\sin^2\Delta\tau}}, \tag{4}$$

if the rf field is applied along the Y axis in the "p" subspace (in this case corresponding to the transition $+\leftrightarrow 0$). Here Δ is the inhomogeneous broadening or the frequency

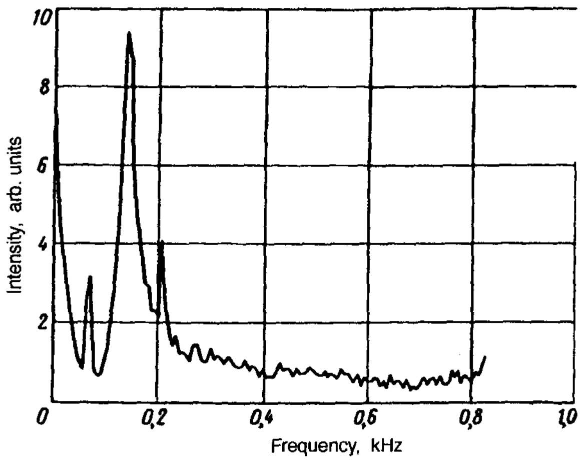

FIG. 5. Fourier transform of the time dependence shown in Fig. 4. The sharp peak lies at the frequency 70 Hz.

detuning, and S_x^p and S_z^p are one-transition spin operators[4] which are similar to the Pauli matrices for each subspace. If the preparatory pulse is also applied along the Y axis, i.e., it produces an initial magnetization along the X axis, then the projection of the density matrix prepared in this manner onto the effective Hamiltonian is different from zero, and since it commutes with the Hamiltonian, it locks in the transverse magnetization.

If the initial magnetization is oriented along the Y axis, as in the train (2), then its projection onto the effective Hamiltonian is equal to zero and it produces a rotation of the magnetization with the frequency

$$\omega_e=\frac{1}{2\tau}\cos^{-1}\left(1-2\cos^2\frac{\psi}{2}\sin^2\Delta\tau\right)$$

and decay of the magnetization as a result of the scatter in the frequencies. The solution of the Liouville equation for the initial density matrix $\rho_0 \sim S_y^p$ and the effective Hamiltonian (4) and then for the Hamiltonian obtained from (4) by changing the sign of c_x contains the coefficient $c_x^2 \cos \omega_e(t_1-t_2)$ in front of the operator of the observable S_y^p that describes the convergence of the isochromatic curves and has at $t_1=t_2=n\tau$ a maximum proportional to c_x^2. This solution can be repeated and an echo signal can be obtained again.

Another approach to the description of the echo train is to calculate the effective Hamiltonian for the supercycle in Eq. (3)

$$H_{e1}=\omega_{e1}(n_xS_x^p+n_zS_z^p), \quad \omega_{e1}=\frac{1}{8\tau}\cos^{-1}[1-2c_z^2\sin^2(4\omega_e\tau)],$$

$$n_x=\frac{2c_xc_z\sin^2(2\omega_e\tau)}{\sqrt{1-c_z^2\sin^2(4\omega_e\tau)}}, \quad n_z=\frac{1-c_z^2\sin^2(2\omega_e\tau)}{\sqrt{1-c_z^2\sin^2(4\omega_e\tau)}}. \tag{5}$$

For a train with 180° pulses it describes the rotation around the Z axis; the effective frequency is equal to zero and can be different from zero only because of the nonuniformity of the rf field. An experimental check shows that its influence is too weak, and that it has no effect on the actually observed decay times of the echo signals. Hence it follows that the decays are determined by the partially averaged dipole-dipole interaction Hamiltonian. This question, together with the questions associated with the appearance of a slowly decaying exponential and the "pairing" of echo signals, as well as the possibility of interpreting them by invoking nonlinear oscillations[6,7] will be examined in a separate paper.

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