Secondary proton echo in periodic double-pulse excitation

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Secondary proton echoes from aqueous solutions of a number of compounds were observed following periodic application of series of double RF pulses on the sample. The effect is theoretically interpreted.

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The phenomenological[1] and quantum[2] theories of spin echo predict the production of only one echo when a series of two radio-frequency pulses ($\xi_1-\tau-\xi_2$) is applied to a spin system. In a number of studies, however,[3-9] multiple echo responses were observed after the action of two pulses. Such effects were investigated in detail for nuclei in magnetically-ordered structures[3-6] and for nuclei with quadrupole interaction in solids.[7-9] We have observed secondary echoes following periodic repetition of series of double pulses in such simple systems as protons in aqueous solutions of paramagnetic ions and aluminates; a typical echo-signal oscillogram is shown in Fig. 1.

It is impossible to attribute the appearance of the multiple echoes in these experiments to the known mechanisms.[9] It is indicated in[10] that additional echoes can appear if the action of the pulses is preceded by a disequilibrium in the spin system. This mechanism seems unlikely in our situation, but the data of[10] are insufficient for a comparison with the experimental results.

We have examined in greater detail the formation of echo signals in the case of periodic repetition of a series of pulses $\xi_1-\tau-\xi_2$. The spin system was assumed to consist of a set of isochromatic Bloch groups that do not interact with one another. The relaxation processes in an isogroup during the time of action of pulses ξ_1 and ξ_2 were neglected. The initial values of the isogroup magnetization components were determined from the condition of "matching" the solutions of the equations of motion of the magnetization on the boundary between neighboring cycles. During the final stage, the echo response of the spin system was determined as the result of the interference of the transverse components of the magnetizations of all the isogroups. If the magnetizations of the isogroups in thermodynamic equilibrium are assumed to have a Gaussian frequency distribution function, i.e.,

$$g(\Delta\omega)=\frac{T_3}{\sqrt{2\pi}}\exp\left[-\frac{(\Delta\omega T_3)^2}{2}\right],$$

then we obtain for the amplitude of the principal echo

$$V(2\tau)\approx M_0\left\{1-\exp\left(-\frac{T-\tau}{T_1}\right)+\left[\exp\left(-\frac{T-\tau}{T_1}\right)-\exp\left(-\frac{T}{T_1}\right)\right]\cos\xi_2\right\}\sin\xi_1$$

$$\times\sin^2\frac{\xi_2}{2}\exp\left(-\frac{2\tau}{T_2}\right)+\frac{1}{2}M_0\left[1-\exp\left(-\frac{\tau}{T_1}\right)\right]$$

$$\times\exp\left(-\frac{\tau}{T_1}-\frac{T}{T_2}-\frac{T^2}{2T_3^2}\right)\sin\xi_1\sin^2\xi_2. \tag{1}$$

The amplitude of the second echo is then given by

$$V(3\tau)\approx M_0\left[1-\exp\left(-\frac{\tau}{T_1}\right)\right]\exp\left(-\frac{T+2\tau}{T_2}-\frac{T^2}{2T_3^2}\right)\cos^2\frac{\xi_1}{2}\sin^2\frac{\xi_2}{2}\sin\xi_2. \tag{2}$$

Here T_1 and T_2 are the times of the spin-lattice and spin-spin relaxation in the isogroup, T is the pulse repetition period, and M_0 is the equilibrium magnetization of the entire spin system. We do not present the cumbersome expressions for the amplitudes of the succeeding echoes.

If the repetition period of the series is large ($T\gg T_1$, T_2; usually $T_3<T_2$), i.e., the isogroup disequilibrium preceding the action of the pulse is small, then the secondary echoes are eliminated, and the amplitude of the principal echo is given by the well-known expression

$$V(2\tau,\ T\to\infty)\approx M_0\sin\xi_1\sin^2\frac{\xi_2}{2}\exp\left(-\frac{2\tau}{T_2}\right).$$

According to (1) and (2), the amplitudes of the principal and second echoes have different dependences on the echo excitation conditions (ξ_1, ξ_2, τ, T). Thus, at $\xi_2=180°$, the principal echo is maximal (assuming smallness of the second term in (1)), and the second

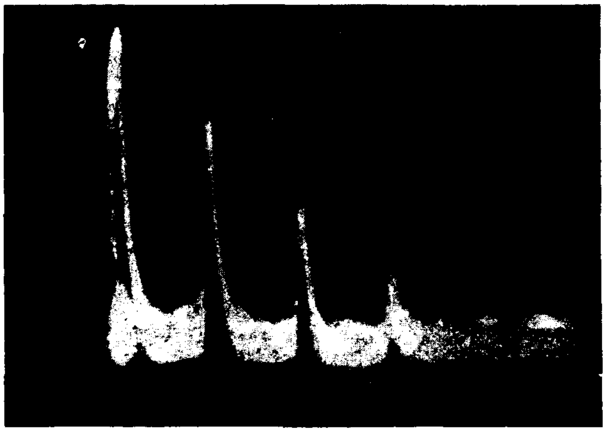

FIG. 1. Proton echo from aqueous solution of aluminate following a periodic repetition of a series of double RF pulses; $\tau=440$ μsec; $T=0.05$ sec. The peaks from left to right represent the response of the receiver to the second pulse and the principal, second, and third echoes.

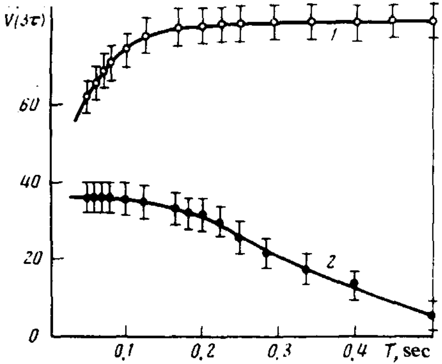

FIG. 2. Dependences of the amplitudes (arbitrary units) of the principal echo (1) and of the second echo (2) on the duration T of the period. The sample was an aqueous solution of aluminate; frequency 12 MHz; $\tau = 200$ μsec.

echo vanishes. With increasing τ, the intensity of the principal echo decreases, and that of the second echo reaches a maximum at $\tau_0 - -T_1 \ln[2T_1/(2T_1+T_2)]$. These regularities have been confirmed experimentally. Figure 2 shows the dependences of the amplitudes of the principal and second echoes on the duration of the period T, which agree well with the values predicted by (1) and (2).

The properties of the principal and secondary echoes obtained from a periodic sequence of pulse trains offer new possibilities of experimentally determining the characteristic times T_1, T_2, and T_3.

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