Experimental investigation of relaxation processes in multipulse NMR experiments

L. N. Erofeev and B. A. Shumm

Institute of Chemical Physics, USSR Academy of Sciences
(Submitted 9 December 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 3, 161–164 (5 February 1978)

The behavior of the temporal decrease of the nuclear magnetization M_x as a function of ϕ_x and of τ under the influence of a sequence of pulses of the type $90^0_y-\tau-(\phi_x-2\tau)^n$ was investigated. Discrepancies are revealed between the observed experimental fact and the average-Hamiltonian theory presently used in multipulse NMR experiments.

PACS numbers: 76.60.Es, 75.10.Dg

In multipulse experiments on line narrowing in NMR spectra of solid compounds, extensive use in being made of the average-Hamiltonian theory.[1-4] In a recently published paper,[5] however, it is noted that some singularities of the relaxation of the nuclear magnetization in the multipulse experiment cannot be reconciled with the average-Hamiltonian theory.

For a detailed study of this discrepancy we have considered the decrease of the magnetization (M_x) of single-crystal CaF_2 in the [111] orientation parallel to H_0 under the influence of a cyclic sequence of pulses of the type $90^0_y-\tau-(\phi_x-2\tau)^n$, where ϕ_x is the RF pulse that rotates the magnetization around the x axis through an angle ϕ in the rotating coordinate frame.

The investigations were performed with a multipulse NMR spectrometer developed at our institute,[6] with a resonant frequency 57.8 MHz for ^{19}F nuclei.

The characteristic picture of the prolonged decrease of the magnetization, obtained under the influence of the indicated sequence of pulses, is shown in Fig. 1. One can separate in the observed decrease two regimes: I—a short transient of duration up to several times T_2 (T_2 is the transverse-relaxation time), characterized by a decrease of the magnetization from a value M_0 to the value M_x. II—steady-state regime, where the magnetization M_x decreases slowly to zero with a time constant T_{2e}, which can reach hundreds of milliseconds.

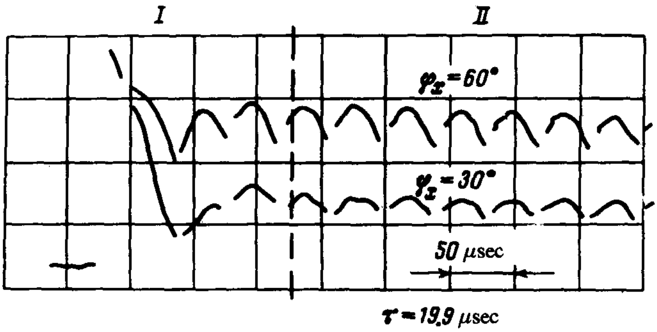

FIG. 1. Oscillograms of the initial sections of the decreases of the nuclear magnetization M_x: I—transient regime, II—steady-state regime.

We have investigated the variation of the magnetization M_x as a function of ϕ_x and τ. It was established that the decrease of the magnetization in the intervals between the pulses ϕ_x is bell-shaped. Figure 1 shows the initial sections of the long decrease at two values of the angles ϕ. The bell-shaped changes of the amplitude of the magnetization M_x characterize the physical mechanism of the long decrease and increase with increasing ϕ and τ. The repetition period of the bells is always equal to 2τ. The singularities observed by us of the behavior of the magnetization cannot be explained by the average-Hamiltonian theory,[1-4]

We have next investigated in detail the dependence of the time constant of the

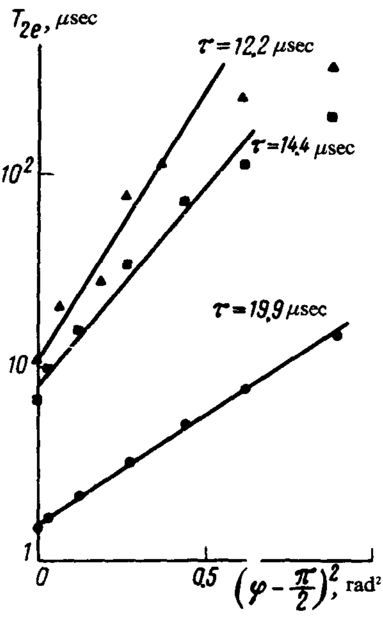

FIG. 2. Dependence of T_{2e} on $(\phi-\pi/2)^2$, where $\phi<\pi/2$. The slope of the solid lines corresponds to $B=9.9\times10^{-10}$ (sec/rad)² in formula (1).

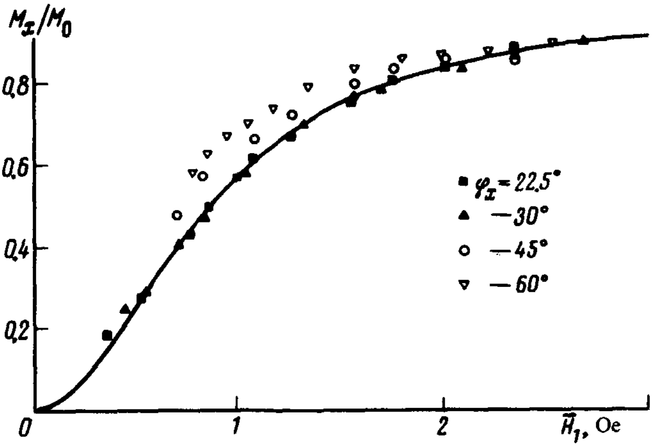

FIG. 3. Dependence of M_x/M_0 on $\bar{H}_1$, where $\bar{H}_1 = \gamma/2\gamma\tau$. The solid line corresponds to formula (5) at $H_{loc} = 0.85$ Oe.

long decrease (T_{2e}) on ϕ when τ was varied from 12 to 20 μsec. The experimental points shown in Fig. 2 fit well straight lines satisfying the formula (1) proposed by us for the variation of T_{2e}

$$\frac{1}{T_{2e}} = A(\tau)\exp\left[-\frac{B\left(\phi-\frac{\pi}{2}\right)^2}{\tau^2}\right], \tag{1}$$

where B is equal to 9.9×10^{-10} for all values of τ. The presented dependence contains an essential singularity in τ at $\phi\neq 90°$. This means that the function (1) cannot be expanded in powers of τ. This circumstance leads us to the conclusion that the theory of the average Hamiltonian, based on the assumption that $1/T_{2e}$ can be expanded in powers of τ, cannot be employed in principle for angles $\phi\neq 90°$.

Measurements of the dependence of T_{2e} on τ, carried out in the range of ϕ from 22.5 to 90°, have shown that at ϕ close to 90° we have

$$A(\tau) = a\tau^4. \tag{2}$$

For small angles ϕ (22.5°), the dependence has a different character and is described by the formula

$$\frac{1}{T_{2e}} = \phi^3\tau^8. \tag{3}$$

These results agree with the data obtained in[5] on the power-law dependence of τ (we are the first to obtain the ϕ dependence) and demonstrate that the average-Hamiltonian theory cannot be used to describe long decreases at $\phi\neq 90°$, in as much as in accordance with this theory the formula for $1/T_{2e}$ is of the form

$$\frac{1}{T_{2e}} \sim \left(\frac{\tau}{\phi}\right)^k, \tag{4}$$

where k is an integer. Measurements of the ratio of M_x to the initial magnetization M_0 as a function of the average high-frequency rotating magnetic field $\overline{H}_1$ at different ϕ are in good agreement with the formula

$$\frac{M_x}{M_0} = \frac{\overline{H}_1^2}{\overline{H}_1^2 + H_{\mathrm{loc}}^2} \tag{5}$$

proposed in[5] but only for small angles ϕ (22.5°). At larger ϕ (45 or 60°) the experimental curves shown in Fig. 3 deviate noticeably from formula (5). These differences indicate that the analogy noted in[5] between continuous spin-locking[7] and multipulse spin-locking holds true only for small ϕ.

This, in our opinion, necessitates a more detailed theoretical examination of the observed steady-state regimes, whose theory cannot be represented within the framework of the average-Hamiltonian method at $\phi \neq 90°$.

In conclusion, the authors thank B.N. Provotorov, G.B. Manelis, and É.B. Fel'dman for a useful discussion of the results and for help with the work.

[1]S.S. Waugh, L.M. Huber, and U. Haeberlin, Phys. Rev. Lett. **20**, 180 (1968).
[2]U. Haeberlin and J.S. Waugh, Phys. Rev. **175**, 453 (1968).
[3]W.A. Evans, Ann. Phys. (N.Y.) **48**, 72 (1986).
[4]P. Mansfield and D. Ware, Phys. Rev. **168**, 318 (1968).
[5]W.K. Rhim, D.P. Burum, and D.D. Elleman, Phys. Rev. Lett. **37**, 1764 (1976).
[6]L.N. Erofeev, O.D. Vetrov, B.A. Shumm, M. Sh. Isaev, and G.B. Manelis, Prib. Tekh. Eksp. No. 2, 145 (1977).
[7]S.R. Hartmann and E.L. Hahn, Phys. Rev. **128**, 2042 (1962).