Pulsed spin locking in nuclear quadrupole resonance of ^{14}N

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The time and frequency characteristics of NQR signals in a multipulse sequence called pulsed spin locking are investigated experimentally. Experimental curves of the echo-signal envelope in the sequence are given for different values of frequency detuning. These curves show that detuning causes the equilibrium value of the transverse magnetization to differ from zero. Plots are also obtained for the quasistationary (settling within a time on the order of T_2) value of the transverse magnetization vs frequency, of the equilibrium transverse magnetization vs the frequency and the interval between the pulses, and of the effective fall-off time of the echo-signal envelope vs the interval between pulses. The results are discussed.

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1. INTRODUCTION

Observation of multiple echo signals in NQR of ^{14}N (Ref. 1) with the aid of a multipulse sequence $\varphi_0^{90°} - (\tau - \varphi - \tau)^n$, where $\varphi = \gamma H_1 t_w$, H_1 is the amplitude of the radiofrequency field, t_w is the pulse duration, and γ is the gyromagnetic ratio, uncovers a possibility of greatly increasing the sensitivity of pulsed NQR spectrometers, when searching for new lines, by increasing the number of accumulations per unit time; it increases also the accuracy of relaxation measurements. A detailed investigation of the temporal and spectral characteristics of NQR signals obtained in this sequence is therefore of interest both for further development of experimental methods and as a check on the applicability to NQR of various pulsed-spin-locking theories previously developed for NMR.

2. EXPERIMENTAL TECHNIQUE

The measurements were performed with the coherent pulsed NQR spectrometer briefly described earlier.[2] The sample was a single crystal of sodium nitrite $NaNO_2$ grown from the melt. Its perfection as a single crystal, i.e., the absence of scatter in the orientation of the principal axes of the electric-field-gradient tensors at the ^{14}N nuclei, was verified with the aid of the Zeeman effect and NQR. The gist of this verification is briefly the following. When a weak magnetic field is applied to a sample containing quadrupole nuclei, the NQR frequencies undergo a shift that depends on the mutual orientation of the external field and the principal axes of the electric-field-gradient tensor. In a polycrystal these orientations are arbitrary, so that the NQR lines are broadened. In a single crystal the frequency shift should occur without broadening of the line. In the sample investigated we observed a line shift exceeding its inhomogeneous width without a noticeable line broadening.

All the measurements were made at liquid-nitrogen temperature (77 K) at the upper-transition frequency $f_{+0} = 4.93125$ MHz.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the envelopes of the echo signals in the multipulse sequence $\varphi_0^{\mp 90°} - (\tau - \varphi - \tau)^n$ without detuning and for a frequency detuning $\Delta f = 0.5$ kHz at $\tau = 0.5$ msec and $t_{w0} = t_w = 50\ \mu$sec, corresponding to 90° rotation of the nuclear-magnetization vector. It is possible to distinguish on the curves three sections with different dynamic processes in the spin system. In the initial section a quasistationary state is rapidly established within a time on the order of the spin-spin relaxation time T_2; this corresponds to establishment of equilibrium in the dipole reservoir; the envelope of the echo signal takes in this case the form of undamped oscillations. This is followed by relaxation of the quasistationary state to a state of equilibrium with the lattice; in the general case this relaxation is described by a biexponential law. The third section corresponds to equilibrium with the lattice; it is characterized by a nonzero transverse magnetization having a sinusoidal dependence on the detuning (Fig. 2). At exact resonance the quasistationary levels relax to zero value. At a detuning $+0.5$ kHz, the quasistationary level in the sequence $\varphi_0^{+90°} - (\tau - \varphi - \tau)^n$ practically coincides with the equilibrium value. The transverse magnetization in the sequence $\varphi_0^{-90°} - (\tau - \varphi - \tau)^n$ relaxes to the same level, but with an initial value having the opposite sign.

The experimental dependences of the quasistationary levels (curves 1 and 3) and the level at equilibrium with the lattice (curve 2) on the detuning are shown in Fig. 3. They were obtained at a smooth variation of the carrier frequency of the sounding pulses and accumulation of the transient NQR signals in a single-channel storage. Curves 1 and 3 were obtained for the sequences $\varphi_0^{\mp 90°} - (\tau - \varphi - \tau)^n$ at $n = 16$ and $\tau = 0.5$ msec, i.e., for a pulse-train duration 16 msec $\approx 2T_2$. Curve 2 was obtained for a continuous train of pulses spaced 2τ apart (R. A. Marino and co-workers[3] called such a train a "strong off-resonance comb"). Curves 1 and 3 determine the initial level from which the relaxation begins, while curve 2 determines the level reached by the spin system as a result of relaxation. Curve 2 is antisymmetric to the exact-resonance frequency (4.93125 MHz) and attenuates oscillating at a period $1/\tau$ when the detuning is increased. Curve 1 can be approximated by the expression

$$[A \cos (2\pi\Delta f \cdot 2\tau) - B \sin (2\pi\Delta f\tau) + C] F(\Delta f),$$

where $F(\Delta f)$ is a slowly varying function while A, B, and C are constants.

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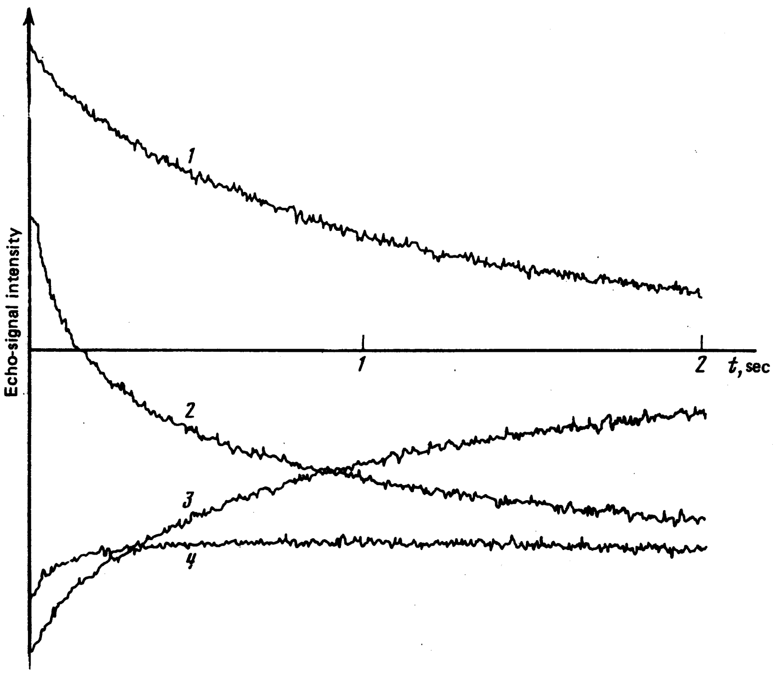

FIG. 1. Envelopes of echo signals for the sequences $\varphi_0^{-90^\circ} - (\tau - \varphi - \tau)^n$ (curves 1 and 2) and $\varphi_0^{+90^\circ} - (\tau - \varphi - \tau)^n$ (curves 3 and 4) at frequencies 4.93125 MHz (zero detuning; curves 1, 3) and 4.93175 MHz ($\Delta f = 0.5$ MHz; curves 2, 4) at $\tau = 0.5$ msec.

The presence of an observable transverse magnetization after the end of the transient process indicates that the spin temperature steadies in a coordinate frame rotated through a certain angle relative to the principal axes of the electric-field-gradient tensor, i.e. the quantization axes no longer coincide with the principal ones. The minima of curves 1 and 3 show that the position of the quantization axes in the new (rotated) coordinate frame depends on the frequency detuning.

The equilibrium transverse magnetization varies sinusoidally with the detuning. It can therefore be assumed that the quasistationary transverse magnetization shown in Fig. 3 (curves 1 and 3) is a superposition of a final state $B\sin(2\pi\Delta f\tau)$ produced by the pulses of the train, and an initial state $A\cos(2\pi\Delta f{\cdot}2\tau) + C$ produced by the preparatory pulse. The factor $F(\Delta f)$ is the envelope of the complex spectrum of the pulses of the sequence t_{w1}, distorted by the spectrum of the preparatory pulse t_{w0}, as follows from the dependence of $F(\Delta f)$ on the phase of the RF carrier of this pulse (curves 1 and 3).

The dependence of the equilibrium value of the transverse magnetization on the interval 2τ between the pulses

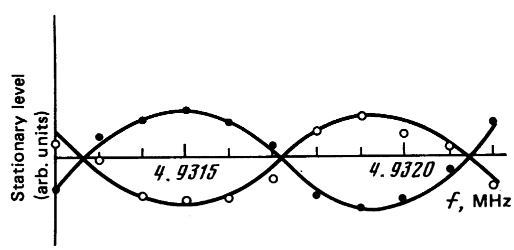

FIG. 2. Stationary level of transverse magnetization vs the sounding-pulse carrier frequency at $\tau = 1.2$ msec; light circles—pulse phase in the sequence $\psi = 0^\circ$, dark—$\psi = 180^\circ$.

takes the form of damped oscillations (Fig. 4) with a period $1/\Delta f$. The envelope of the oscillations is well approximated by a Gaussian law and is apparently the Fourier transform of the line due to the dipole-dipole interactions.

The dependence of the average damping time T_2 of echo-signal envelope (when it is approximated by a single exponential law) on the interval between the pulses is shown in a logarithmic scale in Fig. 5 (curve 1). It has two sections with a weak dependence on τ (0.3 msec $< \tau <$ 0.6 msec and 0.8 msec $< \tau <$ 1.4 msec) and two sections with an abrupt decrease of T_{2e}, which can be approximated by the power-law relation $T_{2e} \propto \tau^{-k}$, with $k \approx 1.9$ and $k \approx 4.3$ in the intervals 0.6 msec $< \tau <$ 0.8 msec and 1.4 msec $< \tau <$ 2.5 msec, respectively. Resolution of the envelope fall-off into two exponentials yields two time constants, T_{2e}^s and T_{2e}^l, which vary with equal slopes as functions of τ (Fig. 5, curves 2 and 3). The contribution of the rapidly damped exponential, however, increases with increasing τ. The sections with the steep decrease on curves 2 and 3 yield $k = 2$ and 4. The larger value of k on curve 1 (4.3) is due to the increase of the contribution of the smaller T_{2e} component with increasing τ.

The large number of theoretical[4–6] and experimental[4,5,7] studies of multipulse NMR permits a comparative analysis of the results. In the general case the quasistationary levels relax to a nonzero state of equilibrium with the lattice. These states can be attributed to the appearance of a nonzero component of the effective field along the quantization axis,[8,9] a component having a harmonic dependence on the detuning.

The dependence of the effective damping time T_{2e} of the transverse magnetization on the interval between the pulses in NQR is similar to a certain degree to the corresponding dependence in NMR. They differ in the presence of sections with a weak dependence on τ (see Fig. 5). The order of magnitude of T_{2e} decreases on the initial section in a time equal to

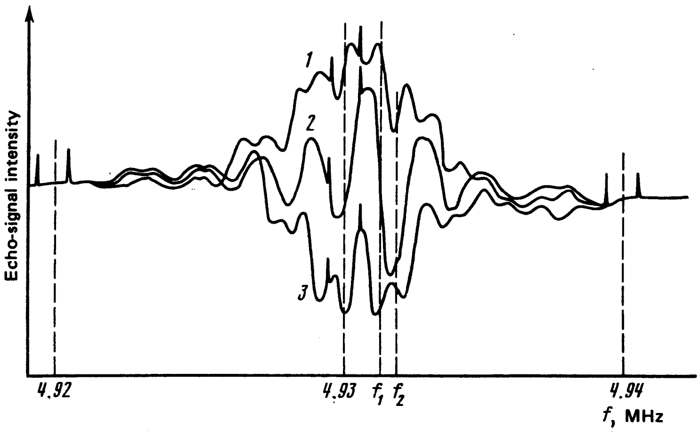

FIG. 3. Frequency dependence of transverse magnetization in the sequence $\varphi_0^{\mp 90°} - (\tau - \varphi - \tau)^{16}$ (curves 2 and 3) and in a continuous sequence of pulses $\varphi - 2\tau - \varphi - 2\tau - ...$ (curve 2); $\tau = 0.5$ msec. $f_1 = 4.93125$ MHz and $f_2 = 4.93175$ MHz are the frequencies at which the echo-signal envelopes shown in Fig. 1 were measured.

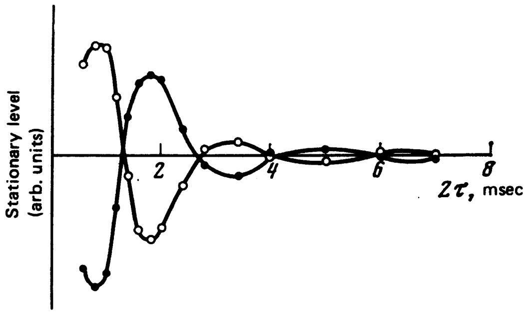

FIG. 4. Stationary level of transverse magnetization vs the interval 2τ at the frequency 4.9320 MHz ($\Delta f = 0.75$ kHz); light circles—$\psi = 0°$, dark—$\psi = 180°$.

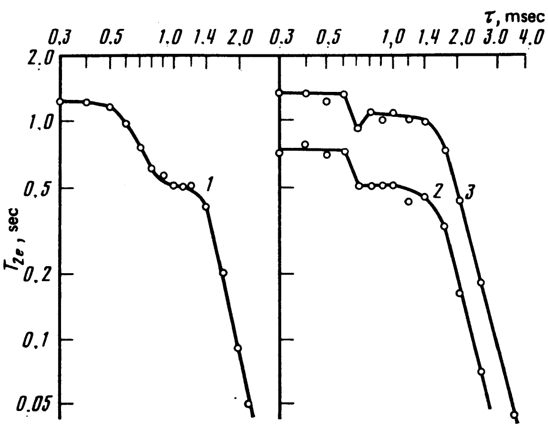

FIG. 5. Damping time (T_{2e}) of the echo-signal envelope in the sequence $\varphi_0^{90°} - (\tau - \varphi - \tau)^n$ vs τ when approximated by a single exponential (curve 1) and by two exponentials (curves 2 and 3).

the spin-relaxation time measured for the same sample by other methods. Consequently T_{2e} is determined here by the spin-lattice relaxation processes. The first abrupt decrease is apparently attributable to the three-level spectrum of the spin $I = 1$ in the effective field and to the possibility of realizing transitions with $\Delta m = 2$. It is still difficult to explain the second flat section. Finally, the abrupt decrease at the end of the plot agrees well with the four-spin absorption of external field photons at the pulse-repetition frequency.

A more detailed explanation of the results calls for a detailed extension of the existing theories to include quadrupole spin systems.

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