The Quasistationary States in Multipulse NQR *

D. Ya. Osokin, V. L. Ermakov, R. H. Kurbanov, and V. A. Shagalov

Nuclear Magnetism Laboratory, E. K. Zavoisky Kazan Physical Technical Institute,
Sibirski Trakt. Kazan, Russia

I. Introduction

Pulsed spin-locking in nitrogen-14 NQR [1] excited unremitting interest both of theorists and experimenters. A number of theoretical approaches have been worked out to explain this phenomenon [2–7]. Most of them used the concepts adopted in NMR disregarding the peculiarities of NQR. In this paper we would like to give an explanation of NQR spin-locking taking into account these peculiarities. But our main aim is to report new experimental results in order to facilitate the verification of theoretical models. On the other hand these experiments can stimulate further development of the theory and applications of multipulse regimes in NQR.

II. Theory

The Hamiltonian of quadrupole interactions

$$\mathcal{H} = \frac{e^2 q Q}{4}[3 J_z^2 - J^2 + \eta(J_x^2 - J_y^2)], \qquad (1)$$

using the fictitious spin $\frac{1}{2}$ operators, can be written for $J = 1$ as

$$\mathcal{H} = \omega_p S_z^p + \tfrac{1}{3}(\omega_q - \omega_r)(S_z^q - S_z^r), \qquad (2)$$

where $\dfrac{e^2 q Q}{4}$ is the nuclear quadrupole coupling constant, $\omega_p, \omega_q, \omega_r$ are transition frequencies, and S_z^p, S_z^q, S_z^r are the fictitious spin $\frac{1}{2}$ operators [8].

In such a representation there are three equivalent forms of this equation arising from cyclic permutation of indices. Each form consists of a polarization

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vector and an alignment tensor [9], all the operators of the vector space commuting with the alignment tensor operator. This fact enables one to utilize the vector model in a wide range of calculations and in particular to write down the effective Hamiltonians for r.f. pulses and frequency offset.

a) Phase Alternated Multipulse Sequence (PAMS)

Assuming the r.f. pulses to be directed along the X axis of the "p" subspace one obtains the following expressions for the direction cosines of the rotation axis:

$$c_x = 0,$$

$$c_y = \frac{\sin\left(\dfrac{\varphi}{2}\right)}{\sqrt{1 - \cos^2\left(\dfrac{\varphi}{2}\right)\sin^2(\varDelta\tau)}} = -\sin\alpha, \qquad (3)$$

$$c_z = \frac{\cos\left(\dfrac{\varphi}{2}\right)\cos(\varDelta\tau)}{\sqrt{1 - \cos^2\left(\dfrac{\varphi}{2}\right)\sin^2(\varDelta\tau)}} = \cos\alpha.$$

The rotation angle can be derived from

$$\sin\left(\frac{\delta}{4}\right) = \cos\left(\frac{\varphi}{2}\right)\sin(\varDelta\tau). \qquad (4)$$

Then the effective Hamiltonian can be written as

$$\mathcal{H}_{\mathrm{ef}} = \frac{\delta}{4\tau}(S_z^p \cos\alpha - S_y^p \sin\alpha).$$

Expanding $\sin\left(\dfrac{\delta}{4}\right)$ for small δ and $\varDelta\tau$ one obtains the expression for $\mathcal{H}_{\mathrm{ef}}$ in the form of the average Hamiltonian [3]

$$\mathcal{H}_{\mathrm{ef}}' = \mathcal{H}_{\mathrm{av}} = \varDelta\left(S_z^p \cos\left(\frac{\varphi}{2}\right) - S_z^p \sin\left(\frac{\varphi}{2}\right)\right)\cos\left(\frac{\varphi}{2}\right).$$

b) Pulsed Spin-locking (PSL)

For convenience here we direct the r.f. field along the Y axis. Then the direction cosines are

$$c_x = 0,$$

$$c_y = \frac{\sin\left(\dfrac{\varphi}{2}\right)}{\sqrt{1 - \cos^2\left(\dfrac{\varphi}{2}\right)\cos^2(\Delta\tau)}} = -\sin\alpha, \qquad (5)$$

$$c_z = \frac{\cos\left(\dfrac{\varphi}{2}\right)\sin(\Delta\tau)}{\sqrt{1 - \cos^2\left(\dfrac{\varphi}{2}\right)\cos^2(\Delta\tau)}} = \cos\alpha.$$

For the rotation angle one obtains

$$\cos\left(\frac{\delta}{2}\right) = \cos\left(\frac{\varphi}{2}\right)\sin(\Delta\tau). \qquad (6)$$

The expression for the effective Hamiltonian resembles that described above that for the PAMS in formal notation

$$\mathcal{H}_{\text{ef}} = \frac{\delta}{2\tau}\left(S_z^{\text{p}}\cos\alpha - S_y^{\text{p}}\sin\alpha\right).$$

Comparison of the expressions for the direction cosines and rotation angles for these two sequences shows that the former can be obtained from the latter by replacing $\sin(\Delta\tau)$ by $\cos(\Delta\tau)$, and vice versa. In other words effective Hamiltonians for PAMS and PSL are shifted in the frequency scale with respect to each other by a quarter of a period ($\Delta\tau/4$).

Now we can proceed to solve the quantum Liouville equation with these effective Hamiltonians and the density matrix after application of the preparatory pulse provided that $\omega_{\text{rf}} = \omega_{\text{p}}$,

$$\begin{aligned}
\varrho_i &= \tfrac{1}{3}[1] - \beta[\omega_{\text{p}}(S_z^{\text{p}}\cos\psi_1 - S_y^{\text{p}}\sin\psi_1) \\
&\quad + \tfrac{1}{3}(\omega_{\text{q}} - \omega_{\text{r}})(S_z^{\text{q}} - S_z^{\text{r}})] \\
&\sim \beta\omega(S_z^{\text{p}}\cos\psi_1 - S_y^{\text{p}}\sin\psi_1), \qquad (7)
\end{aligned}$$

where β is the inverse temperature, ω_{p} the transition frequency in the subspace "p", and $\psi_1 = t_{w_1}$, ω_1 is the rotation angle of the preparatory pulse. We omit the last term in (7) since the operator $(S_z^{\text{q}} - S_z^{\text{r}})$ commutes with all the operators of the subspace "p".

In the "p"-subspace the solution of the quantum Liouville equation is equivalent to a rotation in vector space which is given by the expression [10]

$$\begin{aligned}
J' &= e^{-i\psi\,n\,J}\,J\,e^{+i\psi\,n\,J} \\
&= n(n\times J) + (J - n(n\times J))\cos\psi - (n\times J)\sin\psi, \qquad (8)
\end{aligned}$$

where the first term is the projection of the vector J on the rotation axis and the other two ones determine the directions of the orthogonal components.

In the fictitious spin-$\frac{1}{2}$ operator representation the solution of the Liouville equation

$$\begin{aligned}
\varrho_1 &= \beta\omega_{\text{p}}\{\cos(\alpha - \psi_1)(S_z^{\text{p}}\cos\alpha - S_y^{\text{p}}\sin\alpha) \qquad (9) \\
&\quad + \sin(\alpha - \psi)[(S_z^{\text{p}}\cos\alpha + S_y^{\text{p}}\sin\alpha)\cos(n\delta) - S_x^{\text{p}}\sin(n\delta)]\}
\end{aligned}$$

consists of the time independent term which commutes with the effective Hamiltonian and the two oscillation terms. The first describes a quasistationary state. Substituting the expressions for $\cos\alpha$ and $\sin\alpha$ one obtains for PAMS

$$\begin{aligned}
\varrho_1 &= \frac{\beta\omega_{\text{p}}}{\cos\left(\dfrac{\delta}{4}\right)}\left\{\left[\cos\left(\frac{\varphi}{2} - \psi_1\right) - (1 - \cos(\Delta\tau))\cos\left(\frac{\varphi}{2}\right)\cos\psi_1\right](S_z^{\text{p}}\cos\alpha - S_y^{\text{p}}\sin\alpha) \right. \qquad (10) \\
&\quad \left. + \left[\sin\left(\frac{\varphi}{2} - \psi_1\right) + (1 - \cos(\Delta\tau))\cos\left(\frac{\varphi}{2}\right)\sin\psi_1\right][(S_z^{\text{p}}\sin\alpha + S_y^{\text{p}}\cos\alpha)\cos(\delta n) - S_x^{\text{p}}\sin(\delta n)]\right\}
\end{aligned}$$

and for PSL

$$\begin{aligned}
\varrho_1 &= \frac{\beta\omega_{\text{p}}}{\sin\left(\dfrac{\delta}{2}\right)}\left\{\left[\cos\left(\frac{\varphi}{2} - \psi_1\right) - (1 - \sin(\Delta\tau))\cos\left(\frac{\varphi}{2}\right)\cos\psi_1\right](S_z^{\text{p}}\cos\alpha - S_y^{\text{p}}\sin\alpha) \right. \qquad (11) \\
&\quad \left. + \left[\sin\left(\frac{\varphi}{2} - \psi_1\right) + (1 - \sin(\Delta\tau))\cos\left(\frac{\varphi}{2}\right)\sin\psi_1\right][(S_z^{\text{p}}\sin\alpha + S_y^{\text{p}}\cos\alpha)\cos(\delta n) - S_x^{\text{p}}\sin(\delta n)]\right\}.
\end{aligned}$$

Spin-locking is often supposed to occur when $\cos(\delta n) = 1$. As it may be seen from (4) and (6), δ depends on Δ and φ. In NMR, where the inhomogeneous broadening is very small, Δ represents the artificially introduced resonance offset and can be varied at will. In NQR Δ includes inhomogeneous broadening in addition, its value being of the order of $1/\tau$. So it is impossible to put $\cos(\delta n) = 1$ in NQR, but fortunately it is not necessary. The time independent term in (10) and (11), which represents the projection of initial density matrix on the effective Hamiltonian describes the spin-locking phenomena. The term of the density matrix commuting with the Hamiltonian (or directly along the Hamiltonian) is known to describe longitudinal magnetization in this Hamiltonian representation. The transverse magnetization, described by orthogonal terms, decays due to the distribution of Δ and φ. The decay of transverse magnetization manifests the establishment of a quasistationary state of the spin system. This state can be described by the spin temperature

$$\beta_{qs} = \frac{\beta \omega_p 4\tau}{\delta} \cos(\alpha - \psi_1). \tag{12}$$

Now we need to take into account the Hamiltonian of homonuclear dipole-dipole interactions. In interaction representation it can be written as

$$\mathcal{H}_D = 2 \sum_{m=p}^{r} \Omega_m (S_x^m S_x^m + S_y^m S_y^m) \tag{13}$$

and consists of three commuting terms (at least in the two particle approximation). That enables one to suppose the existence of three integrals of motion for dipole-dipole interaction reservoir [7]. But zero-trace of the tensor of dipole-dipole interactions retains two independent integrals of motion only. The first term of dipole Hamiltonian describes the flip-flop processes in the subspace of the irradiated pair of levels "p". The second term describes the processes through the third level (in "q" and "r" subspaces) [7, 11]. The operator formalism introduced in [12] provides a convenient way for deviding the dipole reservoir in two baths. In this way one can also divide the two particle density matrix into two parts, one of them commuting with the Hamiltonian of dipole-dipole interactions. This part gives rise to the quasistationary state. Mixing of the thermodynamic baths leads to a new spin temperature for the observable integral of motion:

Further evolution of the spin system will be governed by spin lattice relaxation processes. We omit the detailed discussion of these processes [13] and pay our attention to the final magnetization only. This magnetization is established when the system consisting of spins and r.f. field achieves equilibrium with the lattice. Its value can be obtained by solving the Liouville equation for the effective Hamiltonian with Boltzmann density matrix as the initial value:

$$\varrho_{eq} = \beta \omega_p (S_z^p \cos\alpha - S_y^p \sin\alpha) \cos\alpha. \tag{15}$$

For PAMS

$$\varrho_{eq} = \frac{\beta \omega_p \cos(\Delta\tau) \cos\left(\dfrac{\varphi}{2}\right)}{1 - \sin^2(\Delta\tau) \cos^2\left(\dfrac{\varphi}{2}\right)}$$
$$\cdot \left(S_z^p \cos(\Delta\tau) \cos\left(\frac{\varphi}{2}\right) - S_y^p \sin\left(\frac{\varphi}{2}\right) \right) \tag{16}$$

and for PSL

$$\varrho_{eq} = \frac{\beta \omega_p \sin(\Delta\tau) \cos\left(\dfrac{\varphi}{2}\right)}{1 - \cos^2(\Delta\tau) \cos^2\left(\dfrac{\varphi}{2}\right)}$$
$$\cdot \left(S_z^p \sin(\Delta\tau) \cos\left(\frac{\varphi}{2}\right) - S_y^p \sin\left(\frac{\varphi}{2}\right) \right) \tag{17}$$

These expressions seem to be most appropriate for experimental verification.

III. Experiment and Discussion

All the experimental results have been obtained with the home made pulsed NQR spectrometer briefly discussed in [3].

The equilibrium density matrix (16), (17) is equal to zero when $\varphi = \pi$ both for PAMS and PSL.

For $\varphi = \frac{\pi}{2}$

$$\langle S_y^p \rangle_{PAMS} = \mathrm{Sp}(\varrho_{eq} S_y^p) = \frac{\beta \omega_p \cos(\Delta\tau)}{1 + \cos^2(\Delta\tau)}, \tag{18}$$

$$\langle S_y^p \rangle_{PSL} = \frac{\beta \omega_p \sin(\Delta\tau)}{1 + \sin^2(\Delta\tau)}. \tag{19}$$

$$\beta_{qs}' = \frac{\beta \omega_p 4\tau}{3\delta} \left[1 + \frac{32 \omega_{ef}^2 \cos^2\alpha}{(\Omega_D^p)^2 (1 + 3\cos\alpha)^2 \sin^2\alpha + 16 \omega_{ef}^2 \cos^2\alpha} \right] \cos(\alpha - \psi_1). \tag{14}$$
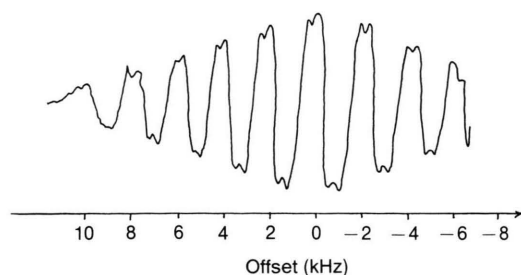
Fig. 1. Frequency dependence of the amplitude of echo signals in stationary state obtained with the continuous phase alternated multi pulse sequence. Pulse rotation angle equals 90°, pulse duration is 25 μs, $\tau = 0.5$ ms, rate of frequency scanning is 2 kHz per minute.

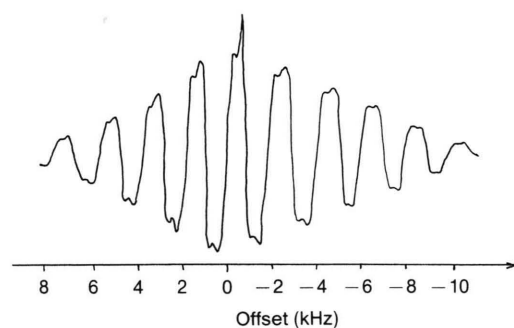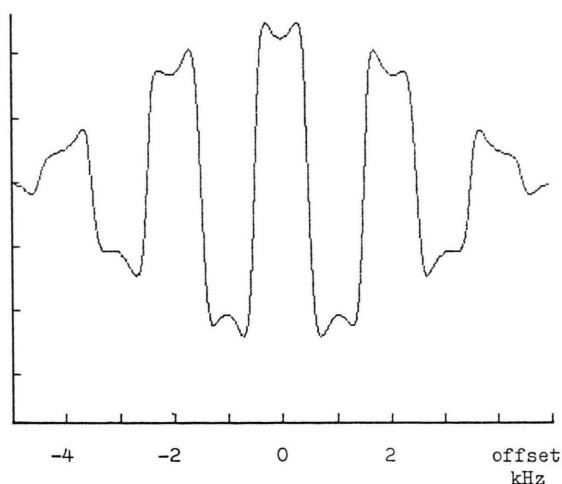Fig. 2. The same as in Fig. 1 for continuous pulsed spin-locking.

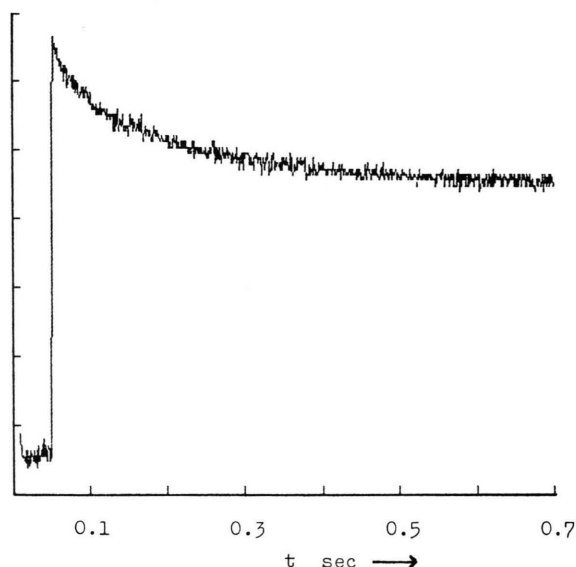Fig. 3. Frequency dependence calculated using (18) and values of Figure 1.

Fig. 4. Spin lattice relaxation caused by a frequency shift from 4.9308 mHz to 4.9303 mHz in continuous PAMS; $\tau = 0.75$ ms.

Continuous multipulse sequences of phase alternated (for PAMS) and in phase (for PSL) pulses were used to satisfy the condition required in [3]. The frequency dependence of the amplitudes of spin echo signals obtained with this sequence are shown in Figs. 1 and 2. For the purpose of comparison with the theory we present Fig. 3, depicting the frequency dependence computed using (18). It is very difficult to distinguish Fig. 1 from Figure 3.

At first sight the continuous multipulse sequences seem to be effective in searching for new NQR lines. However, the experiment shows that increasing of the velocity of frequency scanning decreases the magnitude of lines. It is found that the rate of the amplitude changing can not exceed the rate of spin-lattice relaxation. This suggestion can be confirmed by an experiment, the results of which are shown in Figure 4. The PAMS is applied until the establishment of the equilibrium state with observable magnetization depending on the resonance offset (Δf) and rotation angle (φ). Then the resonance offset changes suddenly, the change chosen not exceeding $1/\tau$ and inhomogeneous

broadening. And one observes that the magnetization equals the projection of the initial density matrix on the new effecive Hamiltonian that relaxes to a new equilibrium value. The same picture can be observed when changing the time interval τ. This phenomenon can be treated as the spin-lattice relaxation on quasienergy levels. The concept of quasienergy was firstly proposed by Zeldovich in [14]; the description of this concept is given in a recent paper by Casati and Moli-
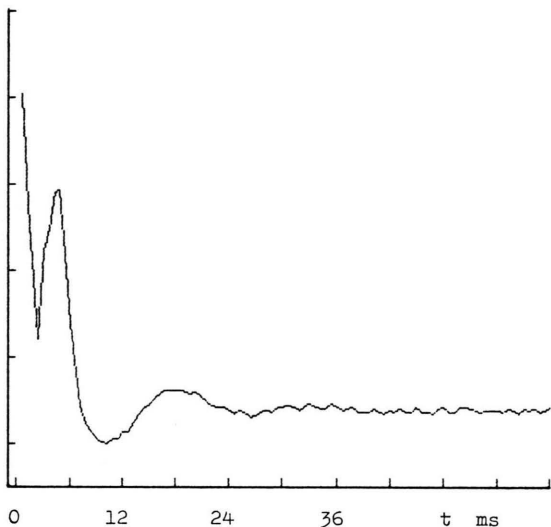
Fig. 5. Echo signal of spin echo envelope in modified PAMS formed by reversing the r.f. field. $\tau = 0.3$ ms, $\Delta = 0$, $\psi = 180°$.
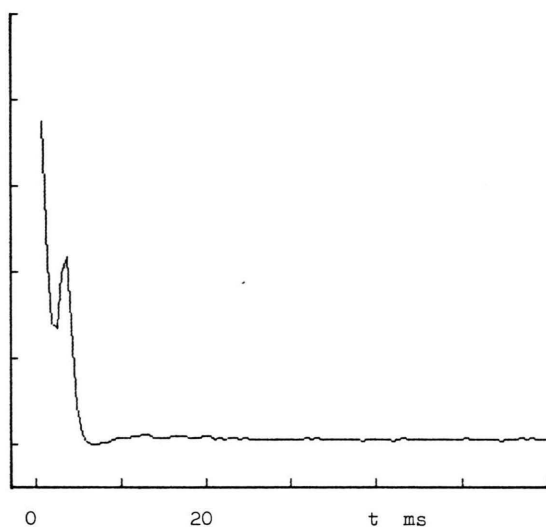

Fig. 6. Echo signal of spin echo envelope in modified PAMS formed by an additional 180° pulse.

nary [15]. From this point of view the Figs. 1 and 2 demonstrate the quasienergy spectra for PAMS and PSL. Starting from this concept, one can suppose free induction and echo signals in the effective Hamiltonian representation to be observable. As it follows from (9), the application of the multipulse sequence originates an oscillating transverse magnetization

$$M_\perp = \sin\left(\frac{\varphi}{2} - \psi_1\right)$$

$$\cdot [(S_z^p \sin \alpha + S_y^p \cos \alpha) \cos(\delta n) - S_x^p \sin(\delta n)]$$

$$= \sin\left(\frac{\varphi}{2} - \psi_1\right)[S_y \cos(\delta n) - S_x \sin(\delta n)], \quad (20)$$

which is orthogonal to the quasistationary state

$$\varrho_{qs} = \cos(\alpha - \psi_1)(S_z^p \cos \alpha - S_y^p \sin \alpha)$$

$$= \cos(\alpha - \psi_1) S_z. \quad (21)$$

Figure 5 shows the result of the application of modified PAMS that confirms the above suggestion. To remove the background of the quasistationary state we observed the X component of magnetization shifting the phase of the reference voltage in a phase sensitive detector by 90°, and to enlarge the initial value of magnetization the preparatory pulse was directed along the Y axis. At the beginning of the plot (Fig. 5) one can see the decay of magnetization due to distribution of rotation angle (δ) values. After n cycles the phases of r.f. pulses had been changed by 180°, that

reverses the direction of the effective Hamiltonian. This gives rise to formation of the echo signal in the time interval $2nt_c$. This experiment proves that the resonances (when $\cos \delta = 0$) contribute nothing to the creating of quasistationary states in NQR.

The technique of formation of the echo described is known in theory [16] but seldom used in practice. It is more convenient to reverse the transverse magnetization instead of reversing the field of quantization. The formation of such a type of echo signals is depicted in Fig. 6, which is obtained by applying the additional 180° pulse between two successive cycles of the sequence. The analogous signals can be excited using PSL (Figure 7).

In conclusion, we would like to discuss new ^{14}N NQR multipulse experiments in a spin system with a small asymmetry parameter.

Previously, while studying the spin-lattice relaxation in methylamines [17], one of the authors found out the absence of echo-signals in trimethylamine, where the electric field gradient tensor on ^{14}N-nuclei sites has axial symmetry.

This fact stimulated the extending of our multipulse experiments on three level spin systems with doubly degenerated or close to degeneration levels. PAMS, PSL and WHH-4 were used to measure the decay time constants of spin echo envelopes and gave the approximately equal values shown in Figure 8. As it can be seen, the experiment demonstrates a nonlinear growth of the decay time constants with increasing of
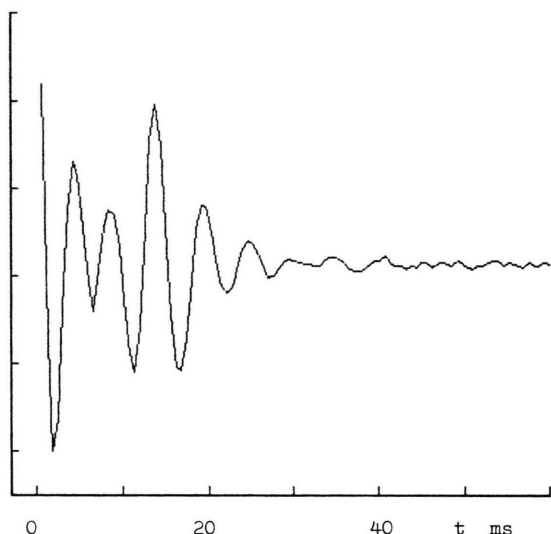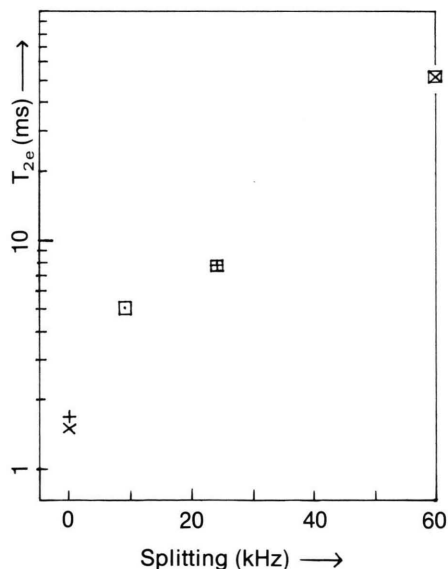
Fig. 7. The same as in Fig. 5 for modified PSL.

Fig. 8. Decay time constants T_{2e} vs. splitting of levels. PAMS was used to measure T_{2e} (+: $(CH_3)_3N$, ×: $C_6H_{12}N_4$, □: CH_3CN, ⊞: m-$NO_2C_6H_4N(CH_3)_2$, ⊠: p-$NO_2C_6H_4N(CH_3)_2$).

the asymmetry parameter η (or the value of level splitting). Echo signals in trimethylamine and hexamethylentetramine ($\eta = 0$) were not observed.

Axial symmetry of EFG tensor removes the dipole-dipole interaction quenching [18] that increases the dipole-dipole contribution to the line width and is usually regarded as being the reason of spin echo absence. We have computed this contribution in trimethylamine and have found it to be of the order of

20 Hz, that can be neglected as compared with the experimental value.

To calculate the contributions of inhomogeneous broadening and heteronuclear dipole-dipole interactions one should take into account the features of the spin system in question. For small η the three fold symmetry of the quadrupole Hamiltonian is destroyed and the alignment tensor becomes the principle term of the Hamiltonian whereas the polarization vector can be regarded as a perturbation. We have not found in the available literature a technique of calculating effective Hamiltonians for tensor operators. So we can calculate the average Hamiltonians only and have found that they commute with the initial density matrix.

To avoid some restrictions of the average Hamiltonian theory we have obtained expressions for two pulse echo signals which show a decrease of the echo value due to mixing of coherence but which can not explain its absence.

The influence of heteronuclear dipole-dipole interactions on the spin echo signal decay has been checked experimentally. Deuteration of acetonitril increases the decay time constant from 5.6 ms to 70 ms.

Therefore nitrogen-proton interactions play the leading role in transverse magnetization fading, although the above calculations contradict this result. To overcome these difficulties, other mechanisms of interaction should be proposed.

Dumping the cross-relaxation between the quadrupole and proton reservoir by means of the application of a weak constant magnetic field that shifts the proton spectrum beyond the limits of the distribution of the splitting frequencies due to small η does not lead to a sharp growth of the decay time constants. So the cross-relaxation can not be treated as the origin of the quenching of spin-locking in such a system neither.

All the circumstances force one to suggest a new model of irreversible processes. For $J = 1$ the quantization axes coincide with the Cartesian coordinate axes. When $\eta = 0$, the directions of the X and Y axes become uncertain. Any small vibrations of molecules and surrounding charges, local magnetic field fluctuations etc. should lead to small deviations of the asymmetry parameter from zero but to large changes of the X and Y principal axes positions. If this is the case, the coherencies excited by the first pulse representing the precession about these axes can accumulate a random geometrical phase that should lead to the irreversible signal decay.

[1] R. A. Marino and S. A. Klainer, J. Chem. Phys. **67,** 3388 (1977).
[2] R. S. Cantor and J. S. Waugh, J. Chem. Phys. **73,** 1054 (1980).
[3] D. Ya. Osokin, Phys. Stat. Sol. (b) **102,** 681 (1980).
[4] O. S. Zueva and A. R. Kessel, Fiz. Tver. Tela, Leningrad **21,** 3218 (1979).
[5] B. N. Provotorov and A. K. Hitrin, Pis'ma Zh. Eksp. Teor. Fiz. **34,** 165 (1981) [JETP Lett. **34,** 157 (1981)].
[6] N. E. Ainbinder and G. B. Furman, Zh. Eksp. Teor. Fiz. **85,** 988 (1983).
[7] M. Matti Maricq, Phys. Rev. **33,** 4501 (1986).
[8] S. Vega and A. Pines, J. Chem. Phys. **66,** 5624 (1977).
[9] K. Blum, Density Matrix. Theory and Application, Plenum Press, New York 1981.
[10] L. C. Bidenharn and J. D. Louck, Angular Momentum in Quantum Physics, Acklison-Wesley Publishing Company Reading, Massachusetts 1981.
[11] D. Ya. Osokin, Phys. Stat. Sol. (b) **109,** K 7 (1982).
[12] V. L. Ermakov and D. Ya. Osokin, Mol. Phys. **53,** 1335 (1984).
[13] D. Ya. Osokin, J. Molec. Struct. **83,** 243 (1983).
[14] Ya. B. Zeldovich, Sov. Phys. JETP **24,** 1006 (1967).
[15] J. Casati and L. Molinary, Progr. of Theor. Phys. Sp. No. 98 (1989).
[16] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.
[17] D. Ya. Osokin and I. A. Safin, Fiz. Tver. Tela, Leningrad **11,** 3608 (1969).
[18] G. W. Leppelmaier and E. L. Hahn, Phys. Rev. **141,** 724 (1966).
[19] M. V. Berry, Proc. Roy. Soc. Lond. A **392,** 45 (1984).