

Relaxation Processes in NQR Multiple-Pulse Spin-Locking*

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A theory of the spin-lattice and spin-spin relaxation processes in quadrupole spin systems with $I > 1/2$ in the situation of the multiple-pulse NQR spin locking is proposed for the pulse sequence MW-4. The theory is based on the assumption that for $t \gtrsim T_2$ the change of the spin system is a quasi-equilibrium process. Rate equations for inverse generalized temperatures are obtained and the kinetic coefficients calculated for the case of exponential correlation functions. The above assumption was confirmed for some substances containing the ^{35}Cl and ^{123}Sb , and the time constant T_{1e} characterizing the spin echo signal decay was investigated and compared with the time constant T_{1q} in the case of continuous spin locking.

Introduction

1. A theory of multiple-pulse excitation of quadrupole spin systems was proposed sometime ago [1, 2] without taking into account any relaxation processes. In the present paper this theory is generalized by considering relaxation processes due to both spin-lattice and spin-spin interactions in the situation of multiple-pulse spin locking. The only spin-lattice relaxation mechanism considered is the thermal modulation of the electric field gradient. The theory is developed for the pulse sequence $\Phi_{\psi_0}^{(0)} - (\tau - \Phi_{\psi} - \tau)$ [3, 4] and for $I > 1/2$ (any other pulse sequence could be considered as well) on the supposition that during times later than $\sim T_2$ after the beginning of the pulse sequence the change of the spin system is slow enough to be considered as a quasi-equilibrium process $T_2 \sim \omega_{\text{loc}}^{-1} \equiv (\gamma H_{\text{loc}})^{-1}$.

The linear rate equations for the inverse generalized temperatures which enter the corresponding state operator were obtained by means of the usual technique. The kinetic coefficients of these equations were calculated for the exponential correlation functions.

2. To check the above supposition in a concrete case, the following experiment was performed: the nuclei ^{35}Cl ($I = 3/2$) and ^{123}Sb ($I = 7/2$) were investigated in polycrystalline samples of SbCl_3 , C_2Cl_6 , and CCl_3COOH at 77 K; the time constant T_2

was found experimentally; for the pulse sequence used and times $\gtrsim T_2$ the signal decay was observed with a time constant $T_{1e} \gg T_2$, which is considered to confirm the supposition in question. Using the same substances, some more experiments were done aimed at the study of the time constant T_{1e} and the initial value $M^{eq}(T_2)$ of the quasi-equilibrium magnetization in dependence on τ and the resonance offset $\Delta \equiv \omega_0 - \omega$, and at a comparison of T_{1e} and the time constant T_{1q} characterizing the continuous spin locking situation.

Theory

1. In the operator representation used in [1, 2, 5] the von Neumann equation of the quadrupole spin system is (with $\hbar = 1$)

$$i \frac{d\varrho}{dt} = [\mathcal{H}(t), \varrho(t)] \quad (1)$$

with the Hamiltonian

$$\mathcal{H}(t) = f(t)(\mathbf{a}\mathbf{S}) + \mathcal{H}_{\text{dd}}^{\text{sec}} + \mathcal{H}_{\text{SL}}(t). \quad (2)$$

Here $f(t)$ is the pulse function [1, 2], \mathbf{a} the unit vector of the effective field ω_e [1, 2], \mathbf{S} the effective spin operator [1, 2], $\mathcal{H}_{\text{dd}}^{\text{sec}} = \sum_m \mathcal{H}_{\text{dd}}^{(m)}$ with $m = 0, \pm 1, \pm 2$, the secular part of the dipole-dipole interaction operator [2], and $\mathcal{H}_{\text{SL}}(t) = \sum_q F_q(t) A_q$ the spin-lattice interaction operator (see [6]), the only spin-lattice interaction mechanism considered being the thermal modulation of the electric field gradient.

2. After the unitary transformation removing the rapid (with respect to T_2) part of $\varrho(t)$ (see [7–9]),

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the evolution of the slow part $\tilde{\rho}(t)$ of $\rho(t)$ is given by the von Neumann equation

$$i \frac{d\tilde{\rho}}{dt} = [\tilde{\mathcal{H}}(t), \tilde{\rho}(t)] \quad (3)$$

with the Hamiltonian

$$\begin{aligned} \mathcal{H}(t) = & -\omega_e(\mathbf{a}\mathbf{S}) + \mathcal{H}_{dd}^0 + \sum_{kr} (e^{ik\pi t/\tau} R_k^r \\ & + e^{-ik\pi t/\tau} R_k^r) + \tilde{\mathcal{H}}_{SL}(t). \end{aligned} \quad (4)$$

Here \mathcal{H}_{dd}^0 is the part of the operator $\mathcal{H}_{dd}^{\text{sec}}$ commuting with the operator $\mathbf{a} \cdot \mathbf{S}$, and the operators R_k^r characterize the interaction between the dipole-dipole system and the r.f. field, each R_k^r being effective on condition $k\pi/\tau = r\omega_e$, where 2τ is the interval between pulses.

3. It is our aim to obtain the time dependence $A(t)$ of the amplitude of the quadrupole spin echo signal due to the spin-lattice and spin-spin interactions and to the action of the r.f. field. This will be done on the supposition that the change of the spin system state may be considered as a quasi-equilibrium process for $t \gtrsim T_2 \sim \omega_{\text{loc}}^{-1} \equiv (\gamma H_{\text{loc}})^{-1}$, where H_{loc} is the average characteristic of the inner magnetic field owing to the spin-spin interaction; if the Bloch equation is valid, T_2 has the order of magnitude of the transverse relaxation time entering this equation and characterizes the spin echo signal decay if the pulse sequence $\Phi_{\psi_0}^{(0)} - (\tau - \Phi_{\psi_0} - \tau)^N$ is used (that is the sequences from the introduction in the particular case $\psi = \psi_0$).

4. In the framework of the customary ‘‘spin temperature approach’’, the quasi-equilibrium process mentioned may be described, in the high temperature approximation, by the state operator

$$\begin{aligned} \tilde{\rho}^{\text{eq}}(t) = & Z^{-1} [1 - \beta_e^{\text{eq}}(t) \omega_e(\mathbf{a}\mathbf{S}) \\ & - \beta_d^{\text{eq}}(t) \mathcal{H}_{dd}^0 - \sum'_m P_m^{\text{eq}}(t) e_{mm}], \end{aligned} \quad (5)$$

where e_{mm} are the projection operators introduced in [10], and the indices in the last term on the right hand side number the points of the spectrum of the main part of the Hamiltonian (see [5]), the dash denoting the omission of those influenced by the r.f. field.

5. To calculate $A(t)$, we are in need of the inverse generalized temperatures $\beta_e^{\text{eq}}(t)$, $\beta_d^{\text{eq}}(t)$, $P_m^{\text{eq}}(t)$. The corresponding rate equations may be obtained by

the usual procedure (see [6]); they are (eq and t being omitted):

$$\begin{aligned} \frac{d\beta_e}{dt} = & -\sum_{kr} W_k^r \left(\beta_e - \frac{\omega_k^r}{\omega_e} \beta_d \right) - T_{1e}^{-1} (\beta_e - \beta_e^{\text{L}}) \\ & - \sum_{mn} W_{mn}^e (P_m - P_n), \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{d\beta_d}{dt} = & \sum_{kr} W_k^r \frac{(\omega_k^r)^2}{\omega_{\text{loc}}^2} \left(\frac{\omega_e}{\omega_k^r} \beta_e - \beta_d \right) \\ & - T_{1d}^{-1} (\beta_d - \beta_d^{\text{L}}), \end{aligned} \quad (7)$$

$$\frac{dP_m}{dt} = T_{1m}^{-1} (\beta_e - \beta_e^{\text{L}}) - \sum_m W_{mn} (P_m - P_n), \quad (8)$$

where $\omega_k^r \equiv \omega_e - k\pi/\tau r$ and β_{L} is the lattice inverse temperature. The expressions of the kinetic coefficients of (6)–(8) being very complicated, they are not given here. The dependence of the kinetic coefficients on the pulse sequence parameters and the lattice motion characteristics is given by the functions

$$\begin{aligned} f^{(q)}(\omega_{mn} - l\omega_e) \\ = \sum_k \mathcal{T}_q \left(\omega_{mn} - \frac{k\pi}{\tau} - l\omega_e \right) \frac{\sin^2(\frac{1}{2}l\Theta)}{(2k\pi + l\Theta)^2}, \end{aligned} \quad (9)$$

where $l = 0, \pm 1/2 \pm 1$, $\Theta \equiv 2\tau\omega_e$, $\mathcal{T}_q(\omega)$ are the spectral densities of the lattice motion (see [6]), and ω_{mn} the transition frequencies of the main part of the Hamiltonian.

The initial values $\beta_e^{\text{eq}}(T_2)$, $\beta_d^{\text{eq}}(T_2)$, $P_m^{\text{eq}}(T_2)$, which are necessary to get the concrete solution of the rate equations (6)–(8), are to be obtained using the condition of the quasi-conservation of the corresponding quantities during the interval $\sim T_2$, namely: $\text{Sp } \tilde{\rho}_+(0) Q = \text{Sp } \tilde{\rho}^{\text{eq}} Q$ with $Q \equiv \omega_e \mathbf{a}\mathbf{S}$, \mathcal{H}_{dd}^0 , $\sum'_m \lambda_m^{(0)} e_{mm}$, where $\tilde{\rho}_+(0) = \rho_+(0)$ is the state

operator immediately after the first pulse, and $\lambda_m^{(0)}$ are the eigenvalues of the Hamiltonian’s main part.

6. To calculate the kinetic coefficients using (9), one has to know the correlators $g_{qq'}$ of the lattice motion (see [6]). In the case of exponential correlators [11]

$$\begin{aligned} g_{qq'}(\tau) = & \langle F^{(q)}(t) F^{(-q')} (t - \tau) \rangle \\ = & \delta_{qq'} \langle F_q^2(0) \rangle \exp\{-|\tau|/\tau_q\} \end{aligned} \quad (10)$$

the functions $f^{(q)}$ are

$$f^{(q)}(\omega_{mn} - l\omega_c) = \langle F_q^{-2}(0) \rangle \tau_q \cdot \left(\frac{1}{1 + \tau_q^2 \omega_{mn}^2} + \frac{\omega_{mn} \tau_q \sin(l\theta)}{\tau(1 + \tau_q^2 \omega_{mn}^2)^2} - \frac{\tau_q}{2\tau} [1 - \cos(l\theta)] \right) \frac{(1 - \omega_{mn}^2 \tau_q^2) \operatorname{sh}\left(\frac{2\tau}{\tau_q}\right) + 2\omega_{mn} \tau_q \sin(2\tau\omega_{mn} - l\theta)}{(1 + \omega_{mn}^2 \tau_q^2)^2 \left[\operatorname{ch}\left(\frac{2\tau}{\tau_q}\right) - \cos(2\tau\omega_{mn} - l\theta) \right]} \quad (11)$$

These expressions give the dependence of the kinetic coefficients on the correlation times τ_q and the pulse sequence parameters τ and θ .

7. In the particular case of the equidistant spectrum of the main part of the Hamiltonian, the expressions (11) coincide with those obtained in [12–14].

Experimental

1. Formerly experimental investigations in the domain of the NQR multiple-pulse spectroscopy were performed only on substances containing ^{14}N nuclei ($I=1$) [15, 16]. In this paper the results of experiments made on the substances indicated in the Introduction are presented.

2. Some experiments were made to verify the supposition of the quasi-equilibrium character of the spin locking decay of the spin echo signal amplitude for $t \gtrsim T_2$. In Fig. 1 the echo signals for the ^{123}Sb nuclei in SbCl_3 are shown vs t for the pulse sequences

$$(\pi/2)_0 - (\tau - \pi_{\pi/2} - \tau)^N \quad \text{and}$$

$$(\pi/2)_0 - (\tau - \pi_0 - \tau)^N$$

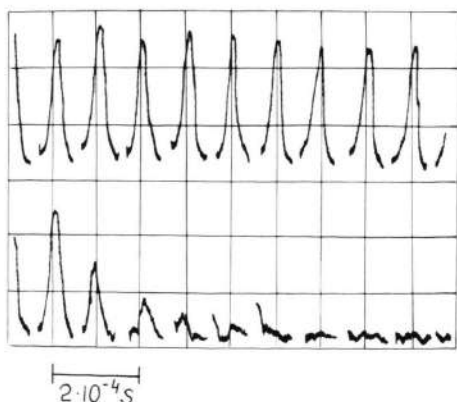


Fig. 1. The oscillograms of the echo signals of ^{123}Sb in polycrystalline SbCl_3 as functions of the pulse sequences $(\pi/2)_0 - (\tau - \pi_{\pi/2} - \tau)^N$ and $(\pi/2)_0 - (\tau - \pi_0 - \tau)^N$ (upper and lower parts of the figure, respectively), frequency is 39.118 MHz.

(upper and lower parts of the figure, respectively). Figure 2 shows the envelope of the signals represented in the upper part of Figure 1. The same envelope for the ^{35}Cl nuclei in CCl_3COOH is shown in Figure 3. These results may be considered as confirming the supposition in question in the case of the substances investigated.

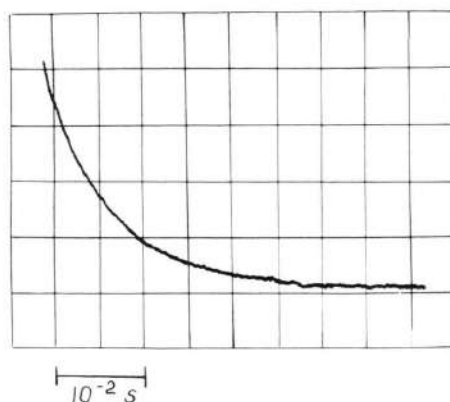


Fig. 2. The oscillogram of the envelope of the signals represented in the upper part of Figure 1.

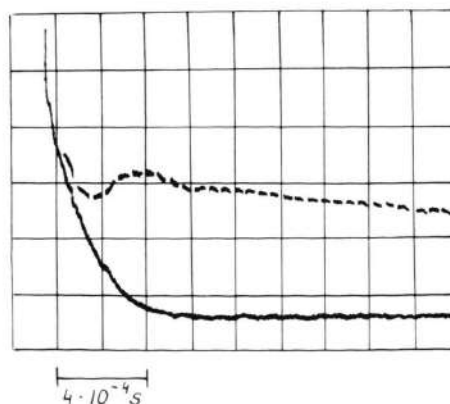


Fig. 3. The oscillograms of the same envelope as in Fig. 2 but for ^{35}Cl in polycrystalline CCl_3COOH and free induction decay in the same sample (upper and lower curves respectively), frequency is 39.969 MHz.

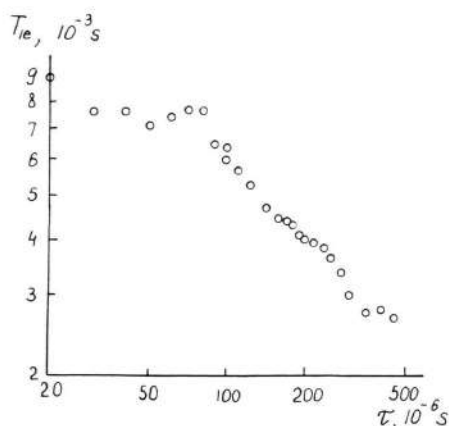


Fig. 4. T_{1e} vs. τ for ^{35}Cl in polycrystalline CCl_3COOH .

3. Some more experiments were performed aimed at a study of the τ -dependence of T_{1e} (see Fig. 4) and the quasi-equilibrium magnetization $M^{\text{eq}}(t)$, at the resonance offset Δ (it was found that for $\Delta \neq 0$ and arbitrary τ the time dependence of M^{eq} was essentially non-exponential), and at a comparison between T_{1e} and the time constant $T_{1\phi}$ [17] characterizing the continuous spin locking situation (it was noticed that near the resonance, T_{1e} increased when noticed that near the resonance, T_{1e} increased when τ decreased but always T_{1e} remained smaller than $T_{1\phi}$).

Conclusions

1. The theoretical approach to problems of the quadrupole spin system dynamics developed in this

paper is more general than the former approaches because in the framework of this approach the spectrum of the main part of the quadrupole Hamiltonian, the electric field gradient symmetry, and the applied r.f. field pulse sequence may be arbitrary. Due to this general character, our approach makes it possible to perform investigations important for the solid state physics (for example, to study the slow motions of molecules and molecular fragments in molecular crystals) in a greater number of interesting case than before.

2. On the other hand, the approach developed shares with the earlier ones a considerable limitation: it is fit only for cases of quasi-equilibrium processes in the spin systems considered. From the more general point of view, limitations of this kind are the inherent features of almost all the practically used theories of the non-equilibrium processes (for example, the so called "spin temperature theories", see [18]). This fact is closely connected with the almost generally held but nevertheless erroneous view that the quantities and methods of thermodynamics are suited only for the study of the equilibrium states and quasi-equilibrium processes. This conception prevents, without any reasonable motivation, the use of thermodynamics in the investigations of the non-equilibrium processes which are not slow enough to be considered as sequences of equilibrium states. General theories free from these limitations, and their applications to different kinetic problems exist, see e.g. [19, 20]. It is planned to use the ideas and methods of such theories in the NQR resonance and relaxation investigations.

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