

NQR MULTIPLE-PULSE SPIN-LOCKING AS A METHOD OF STUDY OF MOLECULAR MOTIONS IN SOLIDS

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ABSTRACT

The theoretical treatment presented here takes into account the slow molecular motions of the lattice; the pulse angular duration of the MW-4 sequence is also found, ensuring the maximum value of the amplitude of spin-locking echo signals. The results of a number of experimental measurements aimed at obtaining data on the temperature dependence of the multiple-pulse spin-locking relaxation time T_{1e} are given.

INTRODUCTION

In the papers [1-3] on multiple-pulse NQR spin-locking the effective Hamiltonian and the rate equations for the inverse generalized temperatures were obtained and the kinetic coefficients of these equations were calculated for the exponential correlation functions. In refs. 1-4 the supposition was accepted for the time $t \geq T_2 \sim \omega_{10c}^{-1} \equiv (\gamma H_{10c})^{-1}$ after the beginning of the pulse sequence the processes in the spin system are slow enough to be considered as quasi-equilibrium ones; this supposition was demonstrated experimentally.

In this paper these quasi-equilibrium processes are studied in more detail and the initial value $M_{eq}(T_2, \phi)$ of the quasi-equilibrium magnetization in dependence on the pulse angular duration ϕ in the case of multiple-pulse spin-locking is calculated. Moreover, the processes of nuclear quadrupole spin-lattice relaxation due to the slow reorientation and torsional oscillation (librational) mechanisms [5,6] are studied.

THEORY

(1) The spin system of the quadrupole nuclei involved in the reorientation motion can be described by the state operators ρ^{ν} and $\rho^{\nu'} = \mathbf{D}^+(\nu, \nu') \rho^{\nu} \mathbf{D}(\nu, \nu')$ which obey the equation [7,8]

$$\frac{d\rho^\nu}{dt} = -i[\mathcal{H}^\nu(t), \rho^\nu(t)] + \sum_{\nu'} \{w^{\nu\nu'} \rho^{\nu'}(t) - w^{\nu'\nu} \rho^\nu(t)\} \quad (1)$$

here ρ^ν and $\rho^{\nu'}$ are the state operators of the spin system in the positions ν and ν' , respectively; $\mathbf{D}(\nu, \nu')$ is the Wigner matrix [9], which can be put down as a series with respect to the projection operators e_{mn}^j corresponding to the j nucleus in the ν' position

$$\mathbf{D}(\nu, \nu') = \sum_j \sum_{mn} \mathbf{D}_{mn}^j(\nu, \nu') e_{mn}^{j\nu} \quad (2)$$

$$\mathcal{H}^\nu(t) = \mathcal{H}_Q^\nu + \mathcal{H}_d^\nu + \mathcal{H}_1^\nu(t) + \mathcal{H}_{\text{SL}}^\nu(t) \quad (3)$$

$$\mathcal{H}_Q^\nu(t) = (2I+1)^{-1} \sum_j \sum_{mn} \omega_{mn}^{j\nu} e_{mn}^{j\nu} \quad (4)$$

where \mathcal{H}_Q^ν represents the interaction of the molecular spin system (spin I) with the electric field gradient (EFG); $\omega_{mn}^{j\nu} = \lambda_m^{j\nu} - \lambda_n^{j\nu}$, $\lambda_m^{j\nu}$ are the eigenvalues of the operator \mathcal{H}_Q^ν ; $\mathcal{H}_1^\nu(t)$ characterizes the action of the r.f. field on the spin system [1-3]. By the $\mathcal{H}_{\text{SL}}^\nu(t)$ only spin-lattice interaction to the modulation and torsional oscillation spin-lattice relaxation mechanisms are taken into account, according to [10]

$$\mathcal{H}_{\text{SL}}^\nu(t) = \sum_j \sum_q \mathbf{F}_q^j(t) A_{-q}^j \quad (5)$$

The second term of the right hand side of eqn. (1) describes the reorientation motion between ν and ν' positions.

(2) Let us perform the unitary transformation

$$\tilde{\rho}^\nu(t) = V^{\nu+}(t) \rho^\nu(t) V^\nu(t) \quad (6)$$

with the operator

$$V^\nu(t) = U^\nu(t) P^\nu(t) [1 + C^\nu(t)] \quad (7)$$

where $U^\nu(t)$, $P^\nu(t)$, and $C^\nu(t)$ obey the following equations of motion and initial conditions

$$i \frac{dU^\nu(t)}{dt} = \mathcal{H}_Q^\nu U^\nu(t)$$

$$U^\nu(0) = 1$$

$$i \frac{dP^\nu(t)}{dt} = U^{+\nu}(t) \mathcal{H}_1^\nu(t) U^\nu(t) P^\nu(t) - P^\nu(t) H_0^\nu \quad (8)$$

$$P^\nu(0) = 1$$

$$i \frac{dC^\nu(t)}{dt} = [H_0^\nu, C^\nu(t)] - H_1^\nu + P^{+\nu}(t) \mathcal{H}_d^\nu P^\nu(t)$$

$$C^\nu(0) = 0$$

where $\mathcal{H}_d^\nu = \sum_m \mathcal{H}_d^{\nu m}$ with $m=0, \pm 1, \pm 2$ is the secular part of the dipole-dipole interaction operator [2]. After the transformation (6) the evolution of the slow part $\tilde{\rho}^\nu(t)$ of $\rho^\nu(t)$ to the second order approximation with respect to the parameter $\epsilon = t_c H_{10c} \ll 1$ is given by the equation

$$\frac{d\tilde{\rho}^\nu(t)}{dt} = -i[H_{\text{eff}}^\nu - C^\nu(t)H_1^\nu + \mathcal{H}_d^\nu(t)C^\nu(t) + \tilde{\mathcal{H}}_{\text{SL}}(t)\tilde{\rho}^\nu(t)] + \sum_{\nu'} \{w^{\nu\nu'}\tilde{\rho}^{\nu'}(t) - w^{\nu'\nu}\tilde{\rho}^\nu(t)\} \quad (9)$$

where $H_{\text{eff}}^\nu = H_0^\nu + H_1^\nu$ is the effective time-independent Hamiltonian,

$$H_0^\nu = \omega_e S_1^\nu \quad (10)$$

$$H_1^\nu = \mathcal{H}_d^{0\nu} + \frac{t_c}{\phi_1} \sum_{m \neq 0} \frac{m\phi}{2} \text{ctg} \frac{m\phi}{2} \mathcal{H}_d^{m\nu} \quad (11)$$

$\omega_e = \phi_1/t_c$, $\phi_1 = \phi$ for $\omega_e \lesssim \omega_{10c}$ and $\phi_1 = \pi - \phi$ for $\omega_e > \omega_{10c}$ and t_c is the interval between pulses.

(3) The norms $\|H_0^\nu\|$ and $\|H_1^\nu\|$ are equal to 1 and ϵ , respectively. According to eqns. (9)–(11) it is probable that the role of H_{eff}^ν is greater than the role of all terms remaining in the right hand side of (9) for the time $\lesssim T_2$. It may be considered as an argument for the supposition that for $t \gtrsim T_2$ the processes in the spin system are quasi-equilibrium and may be described, in the high temperature approximation, by the state operator [3,13]

$$\rho_{\text{qe}}^\nu = 1 - \alpha H_0^\nu - \beta H_1^\nu - \sum_n P_n e^{\nu n} \quad (12)$$

where $\alpha(t)$, $\beta(t)$, and $P_n(t)$ are the inverse generalized temperatures. For $\omega_e \sim \omega_{10c}$ one may accept that $\alpha \simeq \beta$. On the basis of what was said above, one can consider H_{eff}^ν as a quasi-constant for $t \lesssim T_2$, which gives the expression of the $M_{\text{eq}}(\phi)$

$$M_{\text{eq}} = M_0 \left\{ 1 + 2 \left[\sum_{m \neq 0} \left(\frac{m\phi}{2} \cot \frac{m\phi}{2} \right)^2 \frac{Sp(\mathcal{H}_d^m \mathcal{H}_d^{-m})}{Sp(H_0)^2} + \frac{N}{\phi_1^2} \frac{Sp(\mathcal{H}_d^0)^2}{Sp(H_0)^2} \right] \right\}^{-1} \quad (13)$$

where M_0 is the initial magnetization immediately after the first pulse, $N=0$ for $\omega_e \geq \omega_{10c}$ and $N=1$ for $\omega_e < \omega_{10c}$ [11,12].

(4) Further evolution of the spin system is the slow change of the inverse generalized temperatures $\alpha(t)$, $\beta(t)$, and $P_n(t)$. By the usual procedure (see ref. 10), the rate equations for determining $\alpha(t)$, $\beta(t)$, $P_n(t)$ can be obtained. For the modulation and torsional oscillation mechanisms of the relaxation they are

$$\begin{aligned}\frac{d\alpha}{dt} &= - \sum_{kr} W_k^r \left(\alpha - \frac{\omega_k^r}{\omega_e} \beta \right) - T_{1e}^{-1} (\beta_e - \beta_L) - \sum_{mn} W_{mn}^e (P_m - P_n) \\ \frac{d\beta}{dt} &= \sum_{kr} W_k^r \frac{(\omega_k^r)^2}{\omega_{1oc}^2} \left(\frac{\omega_e}{\omega_k^r} \alpha - \beta \right) - T_{1d}^{-1} (\beta - \beta_L) \\ \frac{dP}{dt} &= T_{1m}^{-1} (\alpha - \beta_L) - \sum_{mn} W_{mn} (P_m - P_n)\end{aligned}\quad (14)$$

where $\omega_k^r = \omega_e - 2 \frac{k\pi}{rt_c}$ and $\beta_L = (kT)^{-1}$ is the lattice inverse temperature. To calculate the kinetic coefficients one needs the correlation functions of the lattice motion. They are

(a) in the case of the modulation mechanism [5]

$$\langle F^{(q)}(t) F^{(q')}(t-\tau) \rangle = \delta_{qq'} \langle F_q^2(0) \rangle \exp\{-|\tau|/\tau_q\} \quad (15)$$

(b) in the case of the torsional oscillation mechanism

$$\begin{aligned}\langle F^{(0)}(t) F^{(0)}(t-\tau) \rangle &= \frac{q^2}{2} (3-\eta)^2 K_2(\tau) \\ \langle F^{(\pm 1)}(t) F^{(\pm 1)}(t-\tau) \rangle &= \frac{q^2}{24} (3-\eta)^2 K_1(\tau) \\ \langle F^{(\pm 2)}(t) F^{(\pm 2)}(t-\tau) \rangle &= \frac{q^2}{96} (3-\eta)^2 K_2(\tau)\end{aligned}\quad (16)$$

where q and η are the quadrupole constant and parameter asymmetry EFG, respectively and [5,14]

$$\begin{aligned}K_1(\tau) &= \frac{1}{2} \cos(\omega_t \tau) \frac{\hbar}{I_t \omega_t} \left[(1 - e^{-x}) e^{-\frac{|\tau|}{\tau_a}} + \frac{(3 - e^{-x})}{(e^x - 1)} e^{-\frac{|\tau|}{\tau_a}} \right] \\ K_2(\tau) &= \frac{4\hbar^2}{I_t^2 \omega_t^2} (e^{-x} - 1)^{-2} \left[(1 - e^{-x}) e^{-\frac{|\tau|}{\tau_a}} + (2chx - 1) e^{-\frac{|\tau|}{\tau_a}} \right]\end{aligned}\quad (17)$$

Here ω_t is the torsional frequency, I_t is the moment of inertia for molecular oscillation, $x = \frac{\hbar\omega}{kT}$, and τ_a are the torsional-level lifetimes [5,14].

The expressions of the kinetic coefficients entering eqn. (14) are dependent in a very complicated manner on the pulse sequence parameters and the lattice motion characteristics, so they are not given here.

(5) As a simple example, let us consider the reorientation mechanism of the nuclear spin 3/2, reorientation motion taking place about the 3-fold symmetry axis between the corresponding energy equivalent positions ν and ν' . Neglect-

ing the dipole–dipole interaction and all other mechanisms of the spin–lattice relaxation, for the inverse temperature α one obtains the equation (see eqn. (14))

$$\frac{d\alpha}{dt} = -T_{1e}^{-1}(\alpha - \beta_L) \quad (18)$$

where

$$T_{1e} = \tau_c \left[1 - \frac{1}{4} \cos\theta(1 + 3\cos^2\theta) \right]^{-1} \quad (19)$$

$\tau_c = \sum_{\nu'} w^{\nu\nu'}$, $w^{\nu\nu'} = w^{\nu'\nu}$ [6], θ is the angle of reorientation between Z_ν and $Z_{\nu'}$, principal axes of the EFG.

EXPERIMENTAL

(1) All measurements reported here were performed using a home-made multiple-pulse spectrometer. The temperature of the samples was controlled by a nitrogen gas-flow system in the range 77–300 K with an accuracy of ± 1 K. The MW-4 multiple-pulse sequence $90_x^0 - (t_c/2 - \phi_y^0 - t_c/2)^N$ was used for the measurement of the relaxation time T_{1e} .

(2) The initial quasi-equilibrium magnetization M_{eq} was studied as a function of pulse angle duration ϕ for mono- and polycrystalline SbCl_3 (Fig. 1). The experimental results for the monocrystalline sample are in good agreement with the expression (13). The dependence of $M_{eq}(\phi)$ for the polycrystalline sample is similar to those of monocrystalline one in the range of ϕ 0– $3\pi/2$, which makes it possible to use the concept of pulse angular duration for

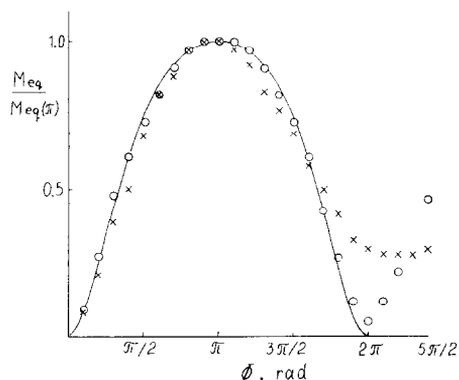


Fig. 1. Quasi-equilibrium magnetization M_{eq} vs. ϕ for ^{123}Sb in monocrystalline (\circ) and polycrystalline (\times) samples of SbCl_3 . Temperature is 77 K, frequency is 39.118 MHz.

both mono- and poly-crystalline samples. The quantity M_{eq} has a maximum for $\phi = \pi$; therefore π pulses should be used to have maximum signal-to-noise ratio in the NQR spin-locking.

(3) The temperature dependences of the spin-lattice relaxation times T_1 and T_{1e} for the polycrystalline SbCl_3 sample are shown in Fig. 2. The relaxation rate T_1^{-1} is described satisfactorily by the expression $T_1^{-1} = 1.68 \times 10^{-4} T^{2.7}$. This proves that molecular libration motion is the only mechanism of quadrupole relaxation in the sample. It was found that the magnetization decay in the case of the multiple-pulse spin-locking is not exponential; it is satisfactorily described as a sum of two exponents with the decay times T' and T'' , the greatest of which is chosen as T_{1e} . At high temperatures ($T \gtrsim 180$ K) the curves $T_1(T)$ and $T_{1e}(T)$ coincide, whereas at low temperatures $T_{1e} < T_1$. It was found also that at low temperatures T_{1e} was a function of the pulse sequence parameters t_c and ϕ .

(4) The influence of both the librations and the reorientations on the quadrupole spin-lattice relaxation in the case of the multiple-pulse spin-locking was studied experimentally in polycrystalline CCl_3PCl_4 for the ^{35}Cl nuclei of CCl_3 groups. Relaxation decay in this case was not exponential either. The molecular dynamics in this compound have been studied in detail [15] using the NQR method. It has been shown that reorientation of the CCl_3PCl_4 molecule as a whole around the long axis of the bipyramid results in exponential shortening of the relaxation time T_1 at temperatures above 220 K. We have investigated the temperature dependence of the relaxation time T_{1e} (Fig. 3). The low temperature part of $T_{1e}(T)$ due to the molecular librations is similar to those of SbCl_3 . Exponential shortening of T_{1e} at temperatures above 270 K

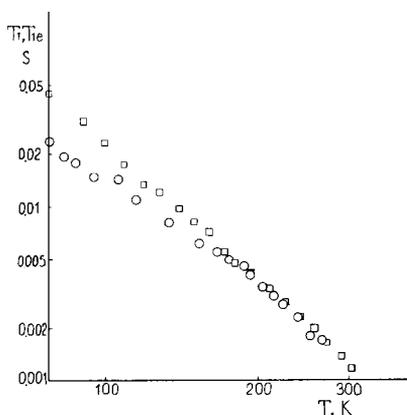


Fig. 2. Temperature dependence of relaxation times (\square) T_1 and (\circ) T_{1e} for ^{123}Sb in polycrystalline SbCl_3 .

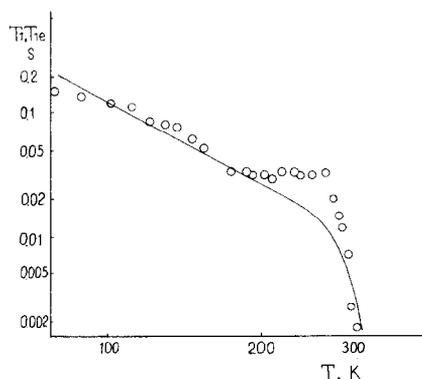


Fig. 3. Temperature dependence of relaxation time T_{1e} for ^{35}Cl in polycrystalline CCl_3PCl_4 . The full line is the dependence of T_1 relaxation time according to ref. 15.

confirms the existence of molecular reorientations. The unexpected temperature independence of T_{1e} was discovered in the range of ultra-slow molecular reorientations in the temperature range 200–270 K. For the sample investigated from the fact that $\cos\theta = -1/3$ and expression (19) it follows that $T_{1e} > T_1$ in the case of slow reorientations which is confirmed by Fig. 3. The independence of T_{1e} of the pulse sequence parameters in the case of the reorientations predicted by expressions (19) was observed experimentally.

CONCLUSION

NQR multiple-pulse spin-locking proved to be an effective method of study of molecular motions in solids for modulation, molecular librations, and reorientations as the mechanisms of quadrupole relaxation. Together with the traditional NQR methods, it allows us to obtain more information. For the case of librations and reorientations the theory proposed was confirmed by experimental results. However, an unexpected temperature independence of T_{1e} in the range of ultra-slow molecular reorientations was observed. We plan to examine this result theoretically. Experimental research on modulation relaxation mechanism is also planned.

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