Influence of Molecular Motions on NQR Echoes

N. A. Sergeev[1], A. M. Panich[2], and M. Olszewski[1]

[1] Institute of Physics, University of Szczecin, Szczecin, Poland
[2] Department of Physics, Ben-Gurion University of the Negev, Beer Sheva, Israel

Abstract. The influence of thermal molecular motions on spin echo decay in pure nuclear quadrupole resonance (NQR) is considered. Our calculations show that the Hahn echo decay is caused by dipole-dipole interaction of the nuclear spins and is strongly affected by molecular mobility that can lead to the shortening of the echo decay with increased temperature. Slow molecular motion yields an exponential τ^3 time dependence, while fast motion yields an exponential decay. The outlined theory allows us to explain an unusual shortening of the ^{35}Cl NQR echo decay on heating in thiourea-C_2Cl_6 inclusion compound.

1 Introduction

The line width of zero-field nuclear quadrupole resonance (NQR) in solids is usually determined by the distribution of electric field gradients (EFG) and by dipole-dipole interactions in a system. In pulse NQR, the inhomogeneous quadrupolar and homogeneous dipolar interactions lead to the formation of the NQR echo signals [1–11]. Up to now, a number of papers concerning the analysis of two-pulse NQR echoes due to inhomogeneous electric quadrupolar interactions of nuclei have been published [1–10]. In 1977, Pratt [11] studied the formation of the NQR spin echo due to the homogeneous dipolar interactions. He showed that the two-pulse 90_0°-τ-$90_{90^\circ}^\circ$-t sequence leads to the formation of the NQR echo signal (dipolar NQR echo), which is similar to the solid-echo signal in nuclear magnetic resonance (NMR) [12, 13].

In the NMR case, it was well established that echo signals in solids may be significantly distorted in the slow-motion region [14–17]. The nature of this distortion can be used to obtain the information about motional mechanism and motional parameters of molecular groups in solids. However, such effects in pure NQR have hardly been studied. The objective of the present paper is to study the influence of the thermal molecular motions on the NQR echo decay. Our calculations show that due to dipole-dipole interaction of nuclear spins (i) slow molecular motion yields exponential τ^3 dependence of the echo decay, while fast

motion yields usual exponential decay, and (ii) the thermal motions can lead to the shortening of the echo decay with increased temperature. The outlined theory allows us to explain an unusual shortening of the spin-spin relaxation time T_2 on heating in thiourea-C_2Cl_6 inclusion compound.

2 Theory

Let us consider a nucleus with spin $I = 3/2$. In the laboratory frame, its Hamiltonian is ($\hbar = 1$) [11]

$$\mathcal{H}_L = \frac{\omega_Q}{2}\left[I_z^2 - \frac{1}{3}I(I+1)\right] - \omega_1(I_X \sin\theta + I_Z \cos\theta)\cdot\cos(\omega t) + \mathcal{H}_d$$

$$\equiv \frac{\omega_Q}{2}\mathcal{H}_Q + \mathcal{H}_1(t) + \mathcal{H}_d. \tag{1}$$

Here ω_Q is the NQR frequency [18]. The first term of the Hamiltonian describes nuclear quadrupolar interaction; for simplicity, we assume that the asymmetry parameter of the EFG tensor is equal to zero. The second term describes the coupling of the nuclear spins with the applied radio-frequency (RF) field. Angle θ determines the orientation of the RF coil relative to the z-axis, which coincides with the orientation of the symmetry axis of the EFG tensor. The third term of the Hamiltonian describes dipole-dipole interaction among nuclei.

Let us assume that random molecular motions of a quadrupolar nucleus yield the time dependence of the quadrupolar and dipolar interaction Hamiltonians, and write the Hamiltonian Eq. (1) in the form

$$\mathcal{H}_L = \frac{\omega_Q}{2}\mathcal{H}_Q + \mathcal{H}_1(t) + \mathcal{H}_e(t). \tag{2}$$

In Eq. (2), quadrupolar Hamiltonian ($\omega_Q \mathcal{H}_Q/2$) is the Hamiltonian which describes the quadrupolar interaction of the nucleus in the case when the molecular motion is absent and

$$\mathcal{H}_e(t) = \mathcal{H}_Q(t) + \mathcal{H}_d(t), \tag{3}$$

where $\mathcal{H}_Q(t)$ is the time-dependent part of quadrupolar interaction Hamiltonian. In the absence of the molecular motion $\mathcal{H}_Q(t) \equiv 0$ and

$$\mathcal{H}_e \equiv \mathcal{H}_d. \tag{4}$$

We assume that $\|\omega_Q\mathcal{H}_Q/2\| \gg \|\mathcal{H}_1(t)\|$, $\|\mathcal{H}_e(t)\|$ and will examine the evolution of the spin system in an interaction representation in which any operator $A(t)$ has the form [18]

$$\tilde{A}(t) = \exp(i\frac{\omega}{2}\mathcal{H}_Q t) \cdot A(t) \cdot \exp(-i\frac{\omega}{2}\mathcal{H}_Q t).$$

Here ω is the frequency of the applied RF field.

In the interaction representation, the density operator $\tilde{\rho}(t)$ is described by [18]

$$i\frac{d\tilde{\rho}(t)}{dt} = [(\tilde{\mathcal{H}}_L - \frac{\omega}{2}\mathcal{H}_Q), \tilde{\rho}(t)].\qquad(5)$$

With Eq. (A15) and by assuming that $\omega_1 \gg \|\mathcal{H}_e(t)\|$, we obtain

$$\tilde{\mathcal{H}}_i \equiv \tilde{\mathcal{H}}_L - \frac{\omega}{2}\mathcal{H}_Q = \frac{\Delta\omega}{2}\mathcal{H}_Q - \frac{1}{2}\omega_1\sin\theta\cdot\tilde{\mathcal{H}}_{1s} - \frac{1}{2}\omega_1\tilde{\mathcal{H}}_{1ns}(t),\qquad(6)$$

where $\Delta\omega = \omega_Q - \omega$ and

$$\tilde{\mathcal{H}}_{1s} = A,\qquad(7)$$

$$\tilde{\mathcal{H}}_{1ns}(t) = 2[\cos\theta\cdot I_Z + \sin\theta\cdot(I_X - A)]\cdot\cos(\omega t)$$
$$+ \sin\theta\cdot A\cdot\cos(2\omega t) - \sin\theta\cdot B\cdot\sin(2\omega t).\qquad(8)$$

In Eqs. (7) and (8)

$$A = \frac{1}{4}I_X + I_Z I_X I_Z$$

and

$$B = \frac{1}{2}(I_Z I_Y + I_Y I_Z).$$

The Hamiltonian Eq. (6) contains a time-independent part, as well as time-dependent parts oscillating at ω and 2ω. By retaining in the Hamiltonian Eq. (6) the time-independent part only (secular approximation [18]), one can write

$$\tilde{\mathcal{H}}_i \approx \frac{\Delta\omega}{2}H_Q - \frac{1}{2}\omega_1\sin\theta\cdot A.\qquad(9)$$

The formal solution of Eq. (5) with Hamiltonian Eq. (9) is

$$\tilde{\rho}(t) = \exp(-i\tilde{\mathcal{H}}_i t)\rho(0)\exp(i\tilde{\mathcal{H}}_i t).\qquad(10)$$

Let us consider an ensemble of quadrupolar nuclei having spin $I = 3/2$. The thermal equilibrium density operator $\rho(0)$ of the ensemble before applying the RF field can be written as [18]

$$\rho(0) = \beta \frac{\omega_Q}{2} \mathcal{H}_Q,$$

where $\beta = 1/kT$; T is the temperature of lattice.

With Eq. (A17) and by assuming that $\omega_1 \gg \Delta\omega$, from Eq. (10) we obtain

$$\tilde{\rho}(t) = \beta \cdot \left[\cos(\omega_1' t) \cdot \frac{\omega_Q}{2} \mathcal{H}_Q + \frac{\omega_Q}{\sqrt{3}} \sin(\omega_1' t) \cdot B \right], \qquad (11)$$

where $\omega_1' = \dfrac{\sqrt{3}}{2} \omega_1 \sin\theta$.

If the first RF pulse is a $\pi/2$-pulse ($\omega_1' t_1 = \pi/2$, where t_1 is the pulse length), from Eq. (11) we have

$$\tilde{\rho}(t_1) = \beta \cdot \frac{\omega_Q}{\sqrt{3}} \cdot B.$$

After the RF pulse, the interaction Hamiltonian describing the free evolution of the density operator is

$$\tilde{\mathcal{H}}_f = \frac{\Delta\omega}{2} \mathcal{H}_Q + \tilde{\mathcal{H}}_e(t), \qquad (12)$$

where

$$\tilde{\mathcal{H}}_e(t) = \tilde{\mathcal{H}}_Q(t) + \tilde{\mathcal{H}}_d(t). \qquad (13)$$

By retaining again in the Hamiltonian Eq. (13) only the terms which commute with quadrupolar interaction Hamiltonian H_Q (secular approximation [18]), one can replace Eq. (13) by Hamiltonian

$$\tilde{\mathcal{H}}_e(t) \cong \mathcal{H}_e(t) = \mathcal{H}_{Qs}(t) + \mathcal{H}_{ds}(t). \qquad (14)$$

In Eq. (14) $\mathcal{H}_{Qs}(t)$ and $\mathcal{H}_{ds}(t)$ are the secular parts of the time-dependent quadrupolar Hamiltonian ($[\mathcal{H}_{Qs}, \mathcal{H}_Q] = 0$) and the dipolar Hamiltonian $\mathcal{H}_d$ ($[\mathcal{H}_{ds}, \mathcal{H}_Q] = 0$) [7, 11, 18, 19], respectively.

In the interaction representation we have the following expression for the density operator at time τ [18, 20]

$$\tilde{\rho}(\tau, t_1) \sim \beta \cdot \exp(-i\Delta\omega\mathcal{H}_Q\tau/2) \left[B - i\int_{t_1}^{\tau} L_e(t')B dt' \right.$$

$$\left. - \int_{t_1}^{\tau} dt'' \int_{t_1}^{t''} L_e(t'')L_e(t')dt'B + \dots \right] \exp(i\Delta\omega\mathcal{H}_Q\tau/2), \qquad (15)$$

where $L_e(t') = [\mathcal{H}_e(t'),...]$ is the Liouville superoperator in the interaction representation.

If the second RF pulse of the length t_2 is applied after the time interval τ, the density operator becomes

$$\rho(t_2,\tau,t_1) = R_2(t_2) \cdot \tilde{\rho}(\tau,t_1) \cdot R_2^{-1}(t_2), \tag{16}$$

where $R_2(t_2)$ describes the action of the second RF pulse, and this operator has, according to Eq. (9), the form $(\omega_1 \gg \Delta\omega)$

$$R_2(t_2) = \exp\left(i\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right).$$

By inserting Eq. (15) into Eq. (16) we obtain

$$\tilde{\rho}(t_2,\tau,t_1) \sim \beta \cdot \exp(-i\Delta\omega\mathcal{H}_Q\tau/2)\left[\hat{B} - i\int_{t_1}^{\tau} \hat{L}_e(t')\hat{B}dt' \right.$$

$$\left. -\int_{t_1}^{\tau}dt''\int_{t_1}^{t''} \hat{L}_e(t'')\hat{L}_e(t')\hat{B}dt + ... \right]\exp(i\Delta\omega\mathcal{H}_Q\tau/2). \tag{17}$$

Here we have used the notation $\hat{D} = R_2^{-1}(t_2)DR_2(t_2)$ with any operator D.

If the second RF pulse is a π-pulse, with Eqs. (A17) and (A18) we have

$$\hat{\mathcal{H}}_Q = \exp\left(-\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right) \cdot \mathcal{H}_Q \cdot \exp\left(\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right) = -\mathcal{H}_Q, \tag{18}$$

$$\hat{B} = \exp\left(-\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right) \cdot B \cdot \exp\left(\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right) = -B, \tag{19}$$

$$\hat{L}_e = \exp\left(-\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right) \cdot L_e \cdot \exp\left(\frac{1}{2}\omega_1 \sin\theta \cdot At_2\right) = -L_e. \tag{20}$$

From Eqs. (18) and (19) it follows that the second π-pulse reverses the signs of the quadrupolar interaction Hamiltonian and the operator B.

With Eqs. (18)–(20) we can write Eq. (17) as

$$\tilde{\rho}(t_2,\tau,t_1) \sim \beta \cdot \exp(i\Delta\omega\mathcal{H}_Q\tau/2)\left[B + i\int_{t_1}^{\tau} L_e(t')Bdt' \right.$$

$$\left. +\int_{t_1}^{\tau}dt''\int_{t_1}^{t''} L_e(t'')L_e(t')Bdt' + ... \right]\exp(-i\Delta\omega\mathcal{H}_Q\tau/2).$$

After the second RF pulse, the free evolution of the density operator is again described by Hamiltonian Eq. (12), and at time t (measured from the beginning of the first pulse) the density operator has the form

$$\tilde{\rho}(t,t_2,\tau,t_1) \sim \beta \cdot \exp(-i\Delta\omega\mathcal{H}_Q(t-2\tau)/2)\left[B + i\int_{t_1}^{\tau} L_e(t')Bdt' - i\int_{\tau+t_2}^{t} L_e(t')Bdt' \right.$$

$$- \int_{t_1}^{\tau}dt''\int_{t_1}^{t''}L_e(t'')L_e(t')Bdt' + \int_{\tau+t_2}^{t}dt''\int_{t_1}^{\tau}L_e(t'')L_e(t')Bdt'$$

$$\left. - \int_{\tau+t_2}^{t}dt''\int_{\tau+t_2}^{t''}L_e(t'')L_e(t')Bdt' + ... \right]\exp(i\Delta\omega\mathcal{H}_Q(t-2\tau)/2).$$

The observed transient response of the ensemble of spins after two pulses is proportional to time-dependent terms of $\tilde{I}_X$ and $\tilde{I}_Z$ resolved along the axis of the coil [18]

$$V(t,t_2,\tau,t_1) \sim \mathrm{Tr}[\overline{\tilde{\rho}(t,t_2,\tau,t_1)} \cdot (\tilde{I}_X \sin\theta + \tilde{I}_Z \cos\theta)],$$

where the upper bar denotes the average of the density operator on the random interaction Hamiltonian $\tilde{H}_e(t)$.

With Eq. (A15) we obtain the following expression for the signal amplitude after two pulses:

$$V(t,t_2,\tau,t_1) \sim \beta \cdot \mathrm{Tr}\left\{ B \cdot \exp(-i\Delta\omega\mathcal{H}_Q(t-2\tau)/2)\left[B + i\int_{t_1}^{\tau} L_e(t')Bdt' - i\int_{\tau+t_2}^{t} L_e(t')Bdt' \right.\right.$$

$$- \int_{t_1}^{\tau}dt''\int_{t_1}^{t''}L_e(t'')L_e(t')Bdt' + \int_{\tau+t_2}^{t}dt''\int_{t_1}^{\tau}L_e(t'')L_e(t')Bdt'$$

$$\left.\left. - \int_{\tau+t_2}^{t}dt''\int_{\tau+t_2}^{t''}L_e(t'')L_e(t')Bdt' + ... \right]\exp(i\Delta\omega\mathcal{H}_Q(t-2\tau)/2)\right\}. \qquad (21)$$

From Eq. (21) it follows that the echo amplitude after two pulses at the time $t = 2\tau$ does not depend on the $\Delta\omega$. This fact indicates that at $t = 2\tau$ inhomogeneous quadrupolar interactions lead to the formation of the NQR echo signal. The decay of this echo signal is determined, according to Eq. (21), by

$$V(t = 2\tau,t_2,\tau,t_1) \sim \beta \cdot \left[1 - \int_0^{\tau}dt''\int_0^{t''}h(t'',t')dt' \right.$$

$$\left. + \int_{\tau}^{t=2\tau}dt''\int_0^{\tau}h(t'',t')dt' - \int_{\tau}^{t=2\tau}dt''\int_{\tau}^{t''}h(t'',t')dt' + ... \right]. \qquad (22)$$

Here we assumed that $t_1,t_2 \ll \tau,t$ and denoted

$$h(t'',t') = \frac{\text{Tr}\{B\overline{L_e(t'')L_e(t')B}\}}{\text{Tr}(B^2)}.$$

In order to calculate the correlation function $h(t'',t')$ we consider the simple model of the molecular motion in solids. We assume that the time dependence of the interaction Hamiltonian $\mathcal{H}_e$ is caused by rotation or diffusion jumps of molecular groups (containing both resonant and nonresonant nuclei) between discrete lattice sites Ω_k ($k = 1,2,...,n$) [20]. We assume that the random process describing the molecular motions in solids is a stationary Markovian process [20–22]. For the stationary Markovian process the correlation function $h(t'',t')$ depends only on $|t'' - t'|$, and for $h(t) > 0$ ($t > 0$) it can be written as [20–22]

$$h(t) = \frac{1}{\text{Tr}(B^2)} \cdot \text{Tr}\{B\sum_i\sum_{l,m}P(\Omega_l)P(\Omega_l,0 \mid \Omega_m,t)[\mathcal{H}_e^i(\Omega_l),[\mathcal{H}_e^i(\Omega_m),B]]\}. \quad (23)$$

Here $P(\Omega_l)$ is the probability that the random Hamiltonian $\mathcal{H}_e^i(t)$ is equal to $\mathcal{H}_e^i(\Omega_l)$ at time $t = 0$, while $P(\Omega_l,0|\Omega_m,t)$ is the conditional probability that if at time $t = 0$ the random Hamiltonian $\mathcal{H}_e^i(t)$ was equal to $\mathcal{H}_e^i(\Omega_l)$, then at time t this random Hamiltonian will be equal to $\mathcal{H}_e^i(\Omega_m)$.

For the random Markovian process the conditional probability $P(\Omega_l,0|\Omega_m,t)$ satisfies the Smoluchowski equation [21, 22]

$$\frac{\partial}{\partial t}P(\Omega_l,0 \mid \Omega_m,t) = \sum_{k=1}^{n}P(\Omega_l,0 \mid \Omega_k,t)W_{km}, \quad (24)$$

with the conditions

$$P(\Omega_l,0 \mid \Omega_m,0) = \delta_{lm},$$

$$\sum_{m=1}^{n}P(\Omega_l,0 \mid \Omega_m,t) = 1,$$

$$\sum_{m=1}^{n}W_{lm} = 0. \quad (25)$$

In Eq. (25) W_{km} ($k \neq m$) are the rate constants, which describe the probability that the random variable $\Omega(t)$ changes from Ω_k to Ω_m by one jump.

Assuming that ($l \neq m$)

$$W_{lm} = \frac{1}{n\tau_c},$$

where τ_c is the correlation time of the motional process, it is easy to obtain from Eq. (24) that

$$P(\Omega_l, 0 \mid \Omega_m, t) = \frac{1}{n}[1 - \exp(-t/\tau_c)] + \exp(-t/\tau_c)\delta_{lm}. \tag{26}$$

By inserting Eq. (26) into Eq. (23) and assuming that $P(\Omega_l) = 1/n$ we have

$$h(\mid t \mid) = \overline{N_2} + \Delta N_2 \exp\left(-\frac{\mid t \mid}{\tau_c}\right). \tag{27}$$

Here

$$\overline{N_2} = \frac{\mathrm{Tr}\{B[\overline{\mathscr{H}_e},[\overline{\mathscr{H}_e},B]]\}}{\mathrm{Tr}(B^2)},$$

$$\overline{\mathscr{H}_e} = \sum_i \left[\frac{1}{n}\sum_{k=1}^{n}\mathscr{H}_e^i(\Omega_k)\right].$$

In Eq. (27) $\Delta N_2 = N_2 - \overline{N_2}$, where

$$N_2 = \frac{\mathrm{Tr}\{B[\mathscr{H}_e,[\mathscr{H}_e,B]]\}}{\mathrm{Tr}(B^2)}. \tag{28}$$

Here $\mathscr{H}_e$ is the interaction Hamiltonian Eq. (3) of the quadrupolar nucleus for the case of no molecular motions in solid. In this case according to Eq. (4) $\mathscr{H}_e \equiv \mathscr{H}_d$ and from Eq. (28) it follows that

$$N_2 \equiv M_{2d} = \frac{\mathrm{Tr}\{B_1[\mathscr{H}_d,[\mathscr{H}_d,B_1]]\}}{\mathrm{Tr}(B_1^2)}.$$

It is easy to see that N_2 is the dipolar interaction contribution to the second moment of NQR spectra in a rigid lattice [18].

For the case of isotropic molecular reorientation $\overline{N_2} = 0$ and the correlation function can be written as

$$h(\mid t \mid) = M_{2d}\exp\left(-\frac{\mid t \mid}{\tau_c}\right). \tag{29}$$

With the correlation function Eq. (29) and calculating the integrals in Eq. (22) we obtain the following expressions for the NQR echo signal ($t = 2\tau$, i.e., equal to the doubled delay between RF pulses):

$$V(t = 2\tau, \tau_c) = \beta \cdot \left\{1 - M_{2d}\tau_c^2\left[-3 + \frac{2\tau}{\tau_c} - \exp\left(-\frac{2\tau}{\tau_c}\right) + 4\exp\left(-\frac{\tau}{\tau_c}\right)\right]\right\}$$

$$\approx \beta \cdot \exp\left(-\frac{2\tau}{T_{2d}}\right), \tag{30}$$

where

$$T_{2d}^{-1} = M_{2d} \frac{\tau_c^2}{\tau} \left[-\frac{3}{2} + \frac{\tau}{\tau_c} - \frac{1}{2} \exp\left(-\frac{2\tau}{\tau_c} \right) + 2\exp\left(-\frac{\tau}{\tau_c} \right) \right]. \tag{31}$$

From Eq. (30) it follows that the Hahn echo decay after the π-τ-$\pi/2$ pulse sequence in pure NQR is determined by the nuclear dipole-dipole interactions. The thermal fluctuations of quadrupolar interaction caused by molecular motion do not influence the echo decay.

It is interesting to note that the obtained expression Eq. (30) coincides with the expression describing the relaxation of the solid-echo signal in NMR [15]. We note that this expression is also well known in EPR spectroscopy [23].

If $\tau/\tau_c \gg 1$ (fast-motion region), one can obtain from Eqs. (30) and (31) [15, 23] that

$$V(t = 2\tau, \tau_c) \approx \beta \cdot \exp(-2M_{2d} \cdot \tau\tau_c). \tag{32}$$

If $\tau < \tau_c$ (slow-motion region), Eqs. (30) and (31) yield the spin-echo envelope decay [15, 23]

$$V(t = 2\tau, \tau_c) \approx \beta \cdot \exp\left(-\frac{2M_{2d}}{3\tau_c} \cdot \tau^3 \right). \tag{33}$$

According to the above theory, the time-cubed exponent of Eq. (33) contributes to the spin-spin relaxation at the initial part of the echo decay, when delays between pulses τ are short in comparison to τ_c, and then gradually turns to the ordinary exponent (Eq. (32)) which determines the tail part of the decay. Usually, the spin-spin relaxation time is determined as a time of the echo amplitude decay by a factor of e. Thus, if the $\tau_c > \tau$ region is present in the experiment, the "effective" value of the spin-spin relaxation time T_2 obtained from the echo decay is shorter than that resulting from the usual exponential behavior.

We note that the time-cubed dependence of the echo signals decays is known in NMR and NQR [18, 24, 25]. In NMR, such dependence is usually observed in the case of molecular diffusion through a gradient of the external magnetic field [18]. In NQR and quadrupolar-perturbed NMR measurements, the time-cubed dependence of the spin-echo decay has been observed in structurally incommensurate systems and was attributed to the slow motion of the modulation wave [24, 25]. As shown above, such time-cubed decay of the echo signals may also be observed in the case of slow thermal motions (molecular rotation or diffusion) in solids when $\tau < \tau_c$.

3 Results and Discussion

We apply the obtained theoretical results for the analysis of temperature dependences of the NQR spin-echo decays in thiourea-C_2Cl_6 inclusion compound,

[2.95(NH$_2$)$_2$CS]·C$_2$Cl$_6$. In this compound, the guest molecules are entrapped within the unidirectional, nonintersecting tunnels of a hydrogen-bonded thiourea network and pack within van der Waals contact of each other [26, 27]. ^{35}Cl NQR measurements of powder thiourea-C$_2$Cl$_6$ in the temperature range from 20 to 90 K have been made on a Tecmag pulse spectrometer at 40.4–40.7 MHz. NQR spectra of powder samples of thiourea-C$_2$Cl$_6$ cover a range of several hundred kilohertz, which is too broad to be excited by the RF $\pi/2$ pulse. Therefore, the spectra were obtained with computer-controlled point-by-point frequency sweep and acquisition of the Hahn echo amplitude at each specified frequency. These measurements have been done at a reduced RF power with rather long, "soft" pulses ($\pi/2$ pulse was 26 μs) in order to excite only a small portion of NQR line. The echo amplitude obtained represents the intensity of the actual NQR line at the specified frequency. The maxima of the Fourier transform of echoes have shown the same line shape. ^{35}Cl NQR spectra of the compound under study [28, 29] comprise two lines in the temperature range from 73 to 90 K and three lines at 20 to 73 K (Fig. 1). The spin-lattice relaxation time T_1 has been measured with the π-τ-$\pi/2$ inversion recovery sequence. Spin-spin relaxation has been measured with the $\pi/2$-τ-π spin-echo sequence. The spin-spin relaxation time T_2 was taken as the time of the decay of the echo amplitude by a factor of e. Experimental T_1 values at temperatures of 70–90 K are given in Fig. 2. Temperature depen-
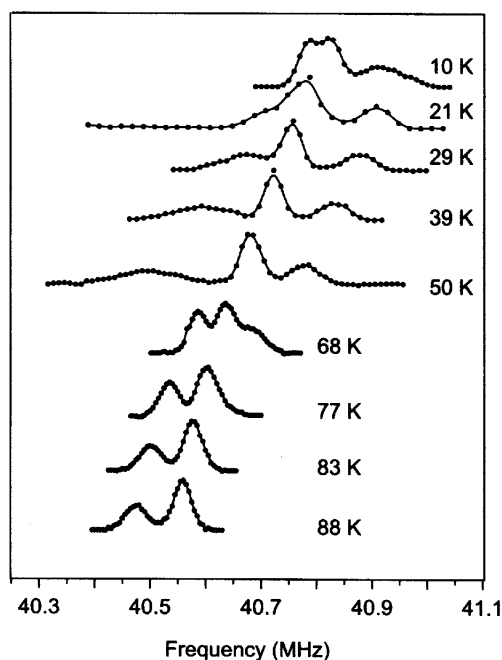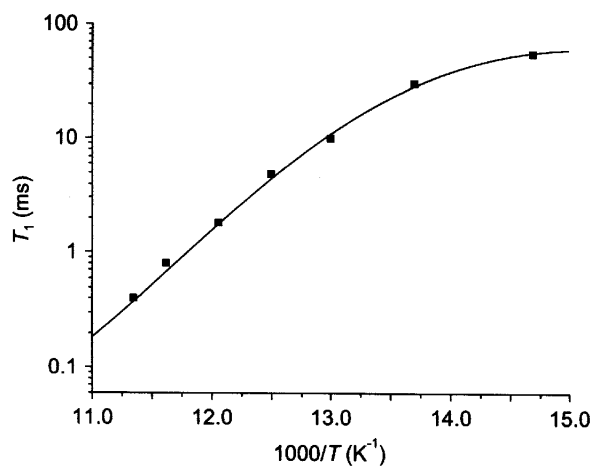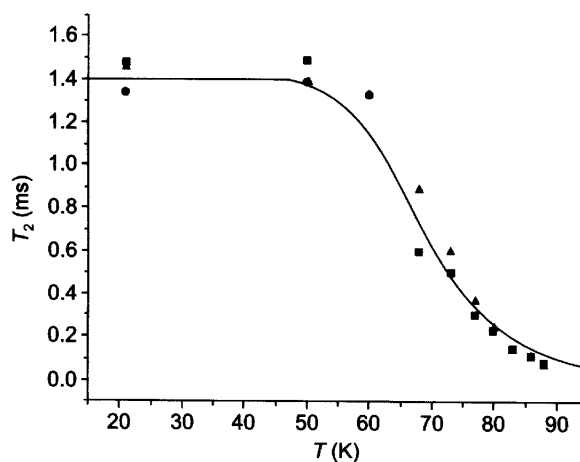

Fig. 1. ^{35}Cl NQR spectra of thiourea-C$_2$Cl$_6$ inclusion compound at different temperatures.

Fig. 2. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_1 in thiourea-C_2Cl_6 inclusion compound measured at the high-frequency peak. The solid line is the theoretical curve described by Eq. (34).

dence of the experimental T_2 values for different resonance peaks is shown in Fig. 3.

The experimental temperature dependence of the spin-lattice relaxation time T_1 in the temperature range from 60 to 90 K (Fig. 2) is typical for the spin-lattice relaxation due to the reorientation of C-Cl_3 groups [28], and the experimental data are well described by the equation derived in ref. 9

Fig. 3. Temperature dependence of the ^{35}Cl NQR spin-spin relaxation time T_2 in thiourea-C_2Cl_6 inclusion compound. The solid line is the theoretical curve described by Eq. (37). Squares, triangles and circles refer to the low-, medium-, and high-frequency resonances, respectively.

$$T_1^{-1}(\text{ms}^{-1}) = 1.15 \cdot 10^{-5} T^{1.72} + (4/3) \cdot \tau_c^{-1}, \tag{34}$$

where the correlation time of the molecular reorientation τ_c is

$$\tau_c = (10^{-14} \text{ s}) \cdot \exp(18.3 \, \text{kJ} \cdot \text{mol}^{-1} / RT). \tag{35}$$

(The values of $\Delta E = 18.3 \, \text{kJ} \cdot \text{mol}^{-1}$ and $\tau_0 = 10^{-14}$ s were obtained from the fit of the $T_1(1/T)$ curve in the temperature range of 70–90 K). The calculation of τ_c from Eq. (35) yields the values of τ_c from 0.3 ms at $T = 90$ K to 0.38 s at $T = 70$ K. Measurements of the Hahn echo show that T_2 is almost constant at 20–55 K. Higher temperature yields a significant shortening of the echo decay with heating (Fig. 3). Usually, it is assumed that spin-spin relaxation in NQR is governed mostly by flip-flop processes of the dipolar interaction of nuclear spins. Therefore, one can suggest that any thermally induced fluctuations of these interactions should yield an elongation of T_2; an opposite behavior, from the first sight, is hardly explainable. However, such explanation may be found from the theory outlined above. When measuring T_2 in our experiments, the delay τ between $\pi/2$ and π pulses was varied from 10 μs to 0.3–1 ms (depending on temperature). From the calculated values of τ_c shown above, it follows that in the temperature range under study we mostly deal with $\tau < \tau_c$, or, in other words, with the slow motion.

Let us analyze the experimental data on the spin-spin relaxation time T_2 by Eq. (31). The expression Eq. (31) is true at different values of τ. However, since we deal with $\tau < \tau_c$, we can analyze the experimental data on the spin-spin relaxation time T_2 by Eq. (33) with

$$T_{2d}^{-1} = \frac{\langle M_{2d} \rangle}{3\tau_c} \cdot \tau^2. \tag{36}$$

Here $\langle M_{2d} \rangle$ is the dipolar interaction contribution to the second moment of NQR spectra of a polycrystalline sample.

For $\tau_c \to \infty$ (the case of a rigid lattice), Eq. (33) yields $V(t = 2\tau, \tau_c) \to 1$ and thus $T_{2d} \to \infty$. However, the decay of the echo signal is observed also in the case of the rigid lattice. As shown in refs. 12 and 13, the decay of the NMR echo signal in the rigid lattice is due to the high-order terms of the dipole-dipole interaction. These terms are proportional to the fourth moment M_4 of the NQR spectrum (caused by the dipole-dipole interaction) and were not included in our consideration. We will denote the spin-spin relaxation rate caused by these additional terms as T_{2X}^{-1} and assume that it does not depend on temperature [18]. Since T_{2d} was taken as the time of the decay of the echo amplitude by a factor of e and is in the order of the average doubled delay between pulses used in the experiment ($T_{2d} \sim 2\tau$), from Eq. (36), we have

$$\frac{1}{T_{2d}} = \frac{1}{2\tau} = \frac{M_{2d}}{3\tau_c} \cdot \tau^2.$$

From this equation we obtain

$$\tau = \left(\frac{3\tau_c}{2M_{2d}}\right)^{1/3}.$$

By inserting this equation into Eq. (36), we have

$$T_{2d}^{-1} = \frac{M_{2d}}{3\tau_c}\tau^2 = \left(\frac{M_{2d}}{12\tau_c}\right)^{1/3}.$$

By taking into account the relaxation rate T_{2X}^{-1} we can write the following expression for the effective rate of the echo decay T_2^{-1}

$$T_2^{-1} = T_{2X}^{-1} + \left(\frac{M_{2d}}{12\tau_c}\right)^{1/3}. \tag{37}$$

where T_{2X}^{-1} is the rate of the echo decay due to the additional temperature-independent mechanism of the spin-spin relaxation. Here M_{2d} is the dipolar contribution to the second moment of ^{35}Cl NQR spectra in the rigid lattice.

The solid line in Fig. 3 shows the theoretical curve for the decay of the echo amplitude, as calculated from Eq. (37) with τ_c from Eq. (35). The best fit between theory and experiment we obtain at $T_{2X} = 1.4$ ms and $(M_{2d})^{1/2} = 8$ kHz. Thus, thermal motions of nuclei lead to the shortening of the NQR echo decay with increasing temperature. As seen from Fig. 3, satisfactory agreement between theoretical and experimental curves was obtained. We note that, unfortunately, the value of M_2 caused by the ^{35}Cl-^1H dipole-dipole interaction cannot be determined from the experiment, since the line width of the ^{35}Cl NQR spectra is mostly due to the distribution of EFGs and does not reflect the dipolar coupling of nuclei. The estimation of the ^{35}Cl-^1H dipole-dipole contribution to the second moment of ^{35}Cl nuclei for the rigid lattice leads to the value M_2 of about 1 kHz^2.

4 Conclusion

We have shown that, due to the dipole-dipole interaction of nuclear spins, the slow thermal motions of nuclei can lead to the shortening of the NQR echo decay with increasing temperature. The obtained result explains the observed temperature dependences of the NQR spin echoes of ^{35}Cl nuclei in thiourea-hexachloro-ethane inclusion compound.

Appendix

We wish to calculate $|\tilde{A}(t)\rangle$, where

$$|\tilde{A}(t)\rangle = \exp(i\mathscr{H}t) \cdot A \cdot \exp(-i\mathscr{H}t) \equiv \exp(i\hat{L}t) \cdot |A\rangle$$

and the Liouville superoperator $\hat{L}$ is related with interaction Hamiltonian $\mathscr{H}$ by

$$\hat{L} = [\mathscr{H}, \ldots].$$

The formal solution of this problem may be obtained with the formalism of Mori [30–32]. In the Liouville space the ket-vector $|\tilde{A}(t)\rangle$ may be expressed as the superposition [30–32]

$$|\tilde{A}(t)\rangle = \sum_{n=0}^{\infty} G_n(t) \, |n\rangle \qquad (A1)$$

of the ket-vectors $|n\rangle$ which form an orthogonal set

$$\frac{\langle n|m\rangle}{\langle n|n\rangle} = \delta_{nm} \qquad (A2)$$

with the inner product defined as

$$\langle n|m\rangle = \mathrm{Tr}(n^+ m). \qquad (A3)$$

These vectors satisfy the recurrence relation [30–32]

$$0\rangle = A, \qquad (A4a)$$

$$|n\rangle = \hat{L} \, |n-1\rangle - v_{n-2}^2 \, |n-2\rangle, \qquad (A4b)$$

where

$$v_n^2 = \frac{\langle n+1|n+1\rangle}{\langle n|n\rangle} \qquad (A5)$$

and

$$v_{-1}^2 = v_{-2}^2 = 0. \qquad (A6)$$

The functions $G_n(t)$ in Eq. (A1) satisfy the system of equations [30–32]

$$-\mathrm{i}\frac{\mathrm{d}G_0}{\mathrm{d}t} = v_0^2 G_1,$$

$$\ldots$$

$$-\mathrm{i}\frac{\mathrm{d}G_n}{\mathrm{d}t} = G_{n-1} + v_n^2 G_{n+1}. \qquad (A7)$$

A1 Evaluation of $I_{X,Y}(t) = exp(iL_Q t) \cdot I_{X,Y}$

In this case the interaction Hamiltonian $\mathcal{H}$ is the quadrupolar interaction Hamiltonian

$$\mathcal{H} = \frac{\omega}{2}\left[I_z^2 - \frac{1}{3}I(I+1) \right] \equiv \frac{\omega}{2}\mathcal{H}_Q. \tag{A8}$$

With Eq. (A4) and the interaction Hamiltonian (A8), we obtain for $I = 3/2$

$$|0_X\rangle = I_X, \qquad\qquad |0_Y\rangle = I_Y,$$

$$|1_X\rangle = i\omega \cdot B, \qquad\qquad |1_Y\rangle = -i\omega \cdot D,$$

$$|2_X\rangle = \omega^2 \cdot \left(A - \frac{3}{5}I_X \right), \qquad |2_Y\rangle = \omega^2 \cdot \left(C - \frac{3}{5}I_Y \right), \tag{A9}$$

$$|n_X\rangle = 0, n \geq 3, \qquad\qquad |n_X\rangle = 0, n \geq 3,$$

where

$$A = \frac{1}{4}I_X + I_Z I_X I_Z, \tag{A10a}$$

$$B = \frac{1}{2}(I_Y I_Z + I_Z I_Y), \tag{A10b}$$

$$C = \frac{1}{4}I_Y + I_Z I_Y I_Z, \tag{A10c}$$

$$D = \frac{1}{2}(I_X I_Z + I_Z I_X). \tag{A10d}$$

It is easy to show that

$$[H_Q, A] = 2iB, \qquad [B, H_Q] = 2iA, \qquad [A, B] = 2iH_Q, \tag{A11a}$$

$$[H_Q, D] = 2iC, \qquad [C, H_Q] = 2iD, \qquad [D, C] = 2iH_Q. \tag{A11b}$$

With Eq. (A13) and ket-vectors (A9) we have $(\alpha = X, Y)$

$$v_{\alpha,0}^2 = \frac{3}{5}\omega^2, \tag{A12a}$$

$$v_{\alpha,1}^2 = \frac{2}{5}\omega^2, \tag{A12b}$$

$$v_{\alpha,n}^2 = 0, n \geq 2. \tag{A12c}$$

For the interaction Hamiltonian (A8) and $I = 3/2$ it follows that $(\alpha = X, Y)$

$$G_0^{(\alpha)}(t) = \frac{\mathrm{Tr}[I_\alpha \exp(\mathrm{i}L_Q t)I_\alpha]}{\mathrm{Tr}(I_\alpha^2)} = \frac{2}{5} + \frac{3}{5}\cos(\omega t). \tag{A13}$$

With Eq. (A13) and Eqs. (A7), (A12) we obtain

$$G_1^{(\alpha)}(t) = \frac{\mathrm{i}}{v_{\alpha,0}^2} \cdot \frac{\mathrm{d}G_0^{(\alpha)}(t)}{\mathrm{d}t} = -\mathrm{i}\frac{1}{\omega}\sin(\omega t), \tag{A14a}$$

$$G_2^{(\alpha)}(t) = \frac{1}{v_{\alpha,1}^2}\left[\mathrm{i}\frac{\mathrm{d}G_1^{(\alpha)}(t)}{\mathrm{d}t} - G_0^{(\alpha)}(t)\right] = \frac{1}{\omega^2}[\cos(\omega t) - 1] \tag{A14b}$$

and from Eqs. (A1), (A9)–(A14) we have

$$\tilde{I}_X(t) \equiv \exp(\mathrm{i}L_Q t) \cdot I_X = (I_X - A_1) + A_1 \cdot \cos(\omega t) - B_1 \cdot \sin(\omega t), \tag{A15a}$$

$$\tilde{I}_Y(t) \equiv \exp(\mathrm{i}L_Q t) \cdot I_Y = (I_Y - C_1) + C_1 \cdot \cos(\omega t) + D_1 \cdot \sin(\omega t). \tag{A15b}$$

A2 Evaluation of $\tilde{X}(t) = \exp(\mathrm{i}Lt) \cdot X$

In this case the interaction Hamiltonian has the form

$$\mathscr{H} = -\frac{1}{2}\omega_1 \sin\theta \cdot A. \tag{A16}$$

With Eqs. (A1)–(A7) and interaction Hamiltonian (A16), we obtain for $I = 3/2$ the following expressions

$$\exp\left(-\frac{1}{2}\omega_1 \sin\theta \cdot A \cdot t\right) \cdot H_Q \cdot \exp\left(\frac{1}{2}\omega_1 \sin\theta \cdot A \cdot t\right)$$

$$= H_Q \cdot \cos(\omega_1' t) + \frac{2}{\sqrt{3}}B \cdot \sin(\omega_1' t), \tag{A17}$$

$$\exp\left(-\frac{1}{2}\omega_1 \sin\theta \cdot A \cdot t\right) \cdot B \cdot \exp\left(\frac{1}{2}\omega_1 \sin\theta \cdot A \cdot t\right)$$

$$= B \cdot \cos(\omega_1' t) - \frac{2}{\sqrt{3}}H_Q \cdot \sin(\omega_1' t), \tag{A18}$$

where

$$\omega_1' = \frac{\sqrt{3}}{2}\omega_1 \cdot \sin\theta.$$

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Authors' address: Nikolai A. Sergeev, Institute of Physics, University of Szczecin, 70-451 Szczecin, Poland
E-mail: sergeev@wmf.univ.szczecin.pl