

## Influence of Molecular Hindered Rotations on NQR Spin Echoes

By N. A. Sergeev\*

Institute of Physics, Szczecin University, 70-451 Szczecin, Poland

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### *Molecular Rotations / NQR / Spin Echoes*

The influence of the hindered reorientations of  $\text{CCl}_3$  groups on the decay of NQR spin echo signals has been investigated. In contrast to the well known literature approaches to the solution of this problem we do not use the perturbation theory of Bloembergen, Purcell and Pound. (PACS codes: 76.60.-k; 76.60.Gv; 76.60.Lz)

### 1. Introduction

At present it is well established by Nuclear Magnetic Resonance (NMR) and Nuclear Quadrupolar Resonance (NQR) methods, that there are hindered rotations of molecules in crystals. The hindered rotations of molecules lead to the distortions of NMR spin echo signals and the nature of these distortions may be used to obtain information about the rotational mechanisms and the motional parameters of the molecules in solids [1–4]. In the case of NQR the nuclear quadrupolar and dipolar interactions lead to the formation and to the decay of NQR echo signals [5–14]. Up to now, a number of papers concerning analysis of the influence of molecular reorientations and oscillations on the decay of NQR echo signals due to electric quadrupolar interactions of nuclei have been published [15–36]. It has been shown theoretically and experimentally, that in the low temperatures ( $\omega_Q \tau_c \gg 1$ , where  $\omega_Q$  is the NQR resonant frequency, and  $\tau_c$  is the correlation time of the stochastic molecular motions) the relation  $T_2 \ll T_1$  ( $T_2$  is the spin–spin and  $T_1$  is the spin–lattice relaxation times) is fulfilled and  $T_2 \sim \tau_c$ . In the higher temperatures region ( $\omega_Q \tau_c \ll 1$ ) the relation  $T_2 = T_1$  is fulfilled and  $T_2 \sim \tau_c^{-1}$ . In these works it was assumed that the NQR spin echo signal attenuates exponentially with the spin phase-memory time  $T_2$  and this time was calculated using the perturbation theory of Bloembergen, Purcell and Pound (BPP) [14].

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\* E-mail: sergeev@wmf.univ.szczecin.pl

However, it has been shown in [37] that the decay of the NQR echo signals caused by dipolar interactions in solids with hindered rotations is not exponential and so in this case the assumption about spin phase-memory time  $T_2$  is incorrect.

The main purpose of this paper is a study of the influence of the hindered reorientation of molecular  $\text{CCl}_3$  groups on the decay of NQR echo signal caused by the nuclear quadrupolar interactions without using the approximation of the perturbation theory of BPP. In our approach we use the theory of relaxation of quadrupolar echo signals, which has been proposed in [38].

## 2. Theory

### 2.1 Hamiltonian of quadrupolar nucleus

Hamiltonian of a quadrupolar nucleus of spin  $I$  can be written in the coordinate system  $x, y, z$  fixed in space as [14]

$$H_Q = \frac{1}{6} \sum_{n=-2}^{n=2} (-1)^n Q_{-n} V_n. \quad (1)$$

Here

$$Q_0 = \frac{\sqrt{6}P}{2} [3I_z^2 - I(I+1)], \quad (2a)$$

$$Q_1 = Q_{-1}^* = \frac{3P}{2} [I_z I_+ + I_+ I_z], \quad (2b)$$

$$Q_2 = Q_{-2}^* = \frac{3P}{2} I_+^2, \quad (2c)$$

$$P = \frac{eQ}{I(2I-1)}, \quad (2d)$$

$$V_0 = \frac{\sqrt{6}}{2} V_{ZZ}, \quad (2e)$$

$$V_{\pm 1} = \pm V_{XZ} - iV_{YZ}, \quad (2f)$$

$$V_{\pm 2} = \frac{1}{2}(V_{XX} - V_{YY}) \pm iV_{XY}. \quad (2g)$$

All denotations in Eqs. (1) and (2) are standard [14].

The hindered rotation of the molecule in crystal leads to the time dependencies of the components  $V_n$  of the electric field gradient (EFG) tensor. Introducing the coordinate system  $(\xi, \theta, \zeta)$  rigidly attached to the investigated

molecules we can write [18, 19]

$$V_n = \sum_{m=-2}^2 T_{mn}^{(2)}(\alpha, \beta, \gamma) V_m', \quad (3)$$

where  $T_{mn}^{(2)}(\alpha, \beta, \gamma)$  are the general spherical functions [14] and  $V_m'$  are the components of EFG tensor in the coordinate system  $(\xi, \theta, \zeta)$ .

We will consider further the molecular crystals in which there are the hindered rotations of  $\text{CCl}_3$  groups about their three fold symmetry axes. In  $\text{CCl}_3$  group the EFG tensor on the site of  $^{35}\text{Cl}$  nucleus has the axially symmetry and the major axis of EFG tensor coincides with C–Cl chemical bond [36]. Choosing the coordinate system  $(\xi, \theta, \zeta)$  so that  $\zeta$ -axis is coincided with C–Cl chemical bond and using Eq. (3) we obtain

$$V_0 = \frac{\sqrt{6}}{4} q (3 \cos^2 \beta - 1), \quad (4a)$$

$$V_{\pm 1} = i \frac{3}{4} q \sin(2\beta) \exp(\mp i\alpha), \quad (4b)$$

$$V_{\pm 2} = -\frac{3}{4} q \sin^2 \beta \exp(\mp i2\alpha), \quad (4c)$$

where  $q$  is the major component of EFG tensor and angle  $\beta$  is the angle between the  $z$ -axis and  $\zeta$ -axis.

Inserting Eqs. (4) into Eq. (1) we obtain the following Hamiltonian for quadrupole nucleus

$$\begin{aligned} H_Q = & \frac{1}{4} \omega_Q (3 \cos^2 \beta - 1) \left[ I_z^2 - \frac{1}{3} I(I+1) \right] \\ & + i \frac{3}{4} \omega_Q \sin(2\beta) [(I_z I_- + I_- I_z) \exp(-i\alpha) - (I_z I_+ + I_+ I_z) \exp(i\alpha)] \\ & - \frac{3}{4} \omega_Q \sin^2 \beta [I_+^2 \exp(-i2\alpha) + I_-^2 \exp(i2\alpha)], \end{aligned} \quad (5a)$$

where

$$\omega_Q = \frac{3eQq}{2I(2I-1)\hbar} \quad (5b)$$

is the resonance NQR frequency [14, 36].

If the  $\text{CCl}_3$  group rotates about  $z$ -axis the angle  $\alpha$  between  $x$  and  $\xi$  axes in Hamiltonian (5a) becomes the random function of the time. Hence in the case of hindered rotation of  $\text{CCl}_3$  group the Hamiltonian (5a) consists of two terms

$$H_Q(t) = H_{0Q} + H_{1Q}(t). \quad (6)$$

The first part  $H_{0Q}$  of the Hamiltonian (6) is obtained by averaging  $H_Q(t)$  over the time

$$H_{0Q} \equiv \overline{H_Q(t)} = \lim_{t \rightarrow \infty} \left[ \frac{1}{t} \int_0^t H_Q(t') dt' \right] \quad (7)$$

and the second part  $H_{1Q}(t)$  is the fluctuating part

$$H_{1Q}(t) = H_Q(t) - \overline{H_Q(t)}. \quad (8)$$

From Eq. (5a) we easily find

$$H_{0Q} = \frac{1}{4} \omega_Q (3 \cos^2 \beta - 1) \left[ I_z^2 - \frac{1}{3} I(I+1) \right], \quad (9)$$

and

$$\begin{aligned} H_{1Q} = & i \frac{3}{4} \omega_Q \sin(2\beta) [(I_z I_- + I_- I_z) \exp(-i\alpha) - (I_z I_+ + I_+ I_z) \exp(i\alpha)] \\ & - \frac{3}{4} \omega_Q \sin^2 \beta [I_+^2 \exp(-i2\alpha) + I_-^2 \exp(i2\alpha)]. \end{aligned} \quad (10)$$

## 2.2 Relaxation of quadrupolar two-pulse echo signals

Let us consider a response of a quadrupolar spin system to a two-pulse sequence  $R_1 - \tau - R_1 - t$ , where  $R_1$  and  $R_2$  describe the actions of the first and second rf pulses. We assume that during the action of rf pulse the fluctuating part  $H_{1Q}(t)$  of a Hamiltonian can be omitted. We choose also as our starting point the following well known perturbation equation for the reduced spin density matrix  $\rho^*(t)$  [14]

$$\rho^*(t) = \rho^*(0) - \int_0^t dt' \int_0^\infty [[\rho^*(0), H_{1Q}^*(t')], H_{1Q}^*(t' - t'')] dt'' \quad (11)$$

The approximations inherent in Eq. (11) are thoroughly discussed by Abragam [14].

In Eq. (11)

$$\rho^*(t) = \exp(iH_{0Q}t) \rho(t) \exp(-iH_{0Q}t) \quad (12)$$

and

$$H_{1Q}^*(t) = \exp(iH_{0Q}t) H_{1Q}(t) \exp(-iH_{0Q}t) \quad (13)$$

are the density matrix and the random Hamiltonian in an interaction representation.

The general expression for the signal  $V(\tau, t)$  following a  $R_1 - \tau - R_1 - t$  pulse sequence is given by [14]

$$V(\tau, t) \sim \text{Tr}\{\overline{\rho(\tau, t)}I_+\}, \quad (14)$$

where  $\overline{\rho(\tau, t)}$  is the average spin density matrix over the random fluctuations of the Hamiltonian  $H_{1Q}(t)$  and  $I_+ = I_x + iI_y$  [14].

Using Eq. (11) it is easily to obtain the averaged spin density matrix  $\overline{\rho(\tau, t)}$ . Indeed, if after the first  $R_1$  rf pulse ( $t = 0$ ) the density matrix has the form [14]

$$\rho^*(0) = \rho(0) = R_1 H_{0Q} R_1^{-1}, \quad (15)$$

then according to Eq. (11) the reduced density matrix at the time  $\tau$  becomes

$$\rho^*(\tau) = \rho^*(0) - \int_0^\tau dt' \int_0^\infty [[\rho^*(0), H_{1Q}^*(t')], H_{1Q}^*(t' - t'')] dt''. \quad (16)$$

Substituting Eq. (16) into Eq. (12) yields

$$\rho(\tau) = \exp(-iH_{0Q}\tau)\rho^*(\tau)\exp(iH_{0Q}\tau). \quad (17)$$

If at the time  $\tau$  after the first rf pulse, the second pulse  $R_2$  is applied, the spin density matrix becomes

$$\rho(\tau^+) = R_2 \rho(\tau) R_2^{-1}. \quad (18)$$

After the second rf pulse the evolution of the reduced spin density matrix is again described by Eq. (11) with the initial condition

$$\begin{aligned} \rho^*(0) &\equiv \rho(\tau^+) = R_2 \exp(-iH_{0Q}\tau)\rho^*(\tau)\exp(iH_{0Q}\tau)R_2^{-1} \\ &= R_2 \exp(-iH_{0Q}\tau)\rho(0)\exp(iH_{0Q}\tau)R_2^{-1} \\ &\quad - R_2 \exp(-iH_{0Q}\tau) \left\{ \int_0^\tau dt' \int_0^\infty [[\rho(0), H_{1Q}^*(t'')], H_{1Q}^*(t' - t'')] dt'' \right\} \\ &\quad \times \exp(iH_{0Q}\tau)R_2^{-1}. \end{aligned} \quad (19)$$

Inserting Eq. (19) in Eq. (11) and retaining only the terms proportional to  $||H_{1Q}^*||^2$  we obtain for the average spin density matrix  $\overline{\rho(\tau, t)}$  the following expression

$$\overline{\rho(\tau, t)} = A_0(\tau, t) - A_1(\tau, t) - A_2(\tau, t), \quad (20)$$

where

$$A_0(\tau, t) = \exp[-iH_{0Q}(t - \tau)]R_2 \exp(-iH_{0Q}\tau)\rho(0) \exp(iH_{0Q}\tau)R_2^{-1} \\ \times \exp[iH_{0Q}(t - \tau)]. \quad (21)$$

$$A_1(\tau, t) = \exp(-iH_{0Q}t)R_2 \exp(-iH_{0Q}\tau) \\ \times \left\{ \int_0^\tau dt' \int_0^\infty \overline{[[\rho(0), H_{1Q}^*(t')], H_{1Q}^*(t' - t'')]} dt'' \right\} \\ \times \exp(iH_{0Q}\tau)R_2^{-1} \exp(iH_{0Q}t). \quad (22)$$

$$A_2(\tau, t) = \exp(-iH_{0Q}t) \\ \times \left\{ \int_\tau^t dt' \int_0^\infty \overline{[[R_2 \exp(-iH_{0Q}\tau)\rho(0) \exp(iH_{0Q}\tau)R_2^{-1}, H_{1Q}^*(t')], H_{1Q}^*(t' - t'')]} dt'' \right\} \\ \times \exp(iH_{0Q}t). \quad (23)$$

The first term  $A_0(\tau, t)$  in Eq. (20) does not consist the random variables and exclusively this term in the average spin density matrix determines the conditions at which the echo signal may be formed. Substituting only the term  $A_0(\tau, t)$  into Eq. (14) yields

$$\text{Tr}\{A_0(\tau, t)I_+\} = \sum_{a,b,c,d} \langle a|R_2|b\rangle \langle b|\rho(0)|c\rangle \langle c|R_2^{-1}|d\rangle \langle d|I_+|a\rangle \\ \times \exp\{i[(E_d - E_a)t - (E_b - E_c)\tau]\}, \quad (24)$$

where  $E_n$  and  $|n\rangle$  ( $n = a, b, c, d$ ) are the eigenvalues and eigenfunctions of the Hamiltonian  $H_{0Q}$

$$H_{0Q}|n\rangle = E_n|n\rangle. \quad (25)$$

Eq. (24) indicates, that an echo signal will be observed at the time  $t = t_e$ , if  $t_e$  is

$$t_e = \tau \frac{E_b - E_c}{E_d - E_a}. \quad (26)$$

Let us consider now the terms  $A_1(\tau, t)$  and  $A_2(\tau, t)$ . Using Eq. (25), the matrix element  $\langle a|A_1(\tau, t)|d\rangle$  can be written as

$$\langle a|A_1(\tau, t)|d\rangle = \sum_{b,c} \exp\{i[(E_d - E_a)t - (E_b - E_c)\tau]\} \\ \times \langle a|R_2|b\rangle \langle b|\overline{K(\tau)}|c\rangle \langle c|R_2^{-1}|d\rangle, \quad (27)$$

where

$$\begin{aligned}
\langle b | \overline{K(\tau)} | c \rangle = & \sum_{e,f} \left\{ \langle b | \rho(0) | e \rangle \int_0^\tau dt' \exp [i(E_e - E_c)t'] \int_0^\infty dt'' G_{efc}(t', t'') \right. \\
& \times \exp [i(E_c - E_f)t''] \\
& - \langle e | \rho(0) | f \rangle \int_0^\tau dt' \exp [i(E_b + E_f - E_e - E_c)t'] \\
& \times \int_0^\infty dt'' G_{befc}(t', t'') \exp [i(E_c - E_f)t''] \\
& - \langle e | \rho(0) | f \rangle \int_0^\tau dt' \exp [i(E_b + E_f - E_e - E_c)t'] \\
& \times \int_0^\infty dt'' G_{fcb}(t', t'') \exp [i(E_c - E_b)t''] \\
& + \langle f | \rho(0) | c \rangle \int_0^\tau dt' \exp [i(E_b - E_f)t'] \\
& \left. \times \int_0^\infty dt'' G_{efbc}(t', t'') \exp [i(E_e - E_b)t''] \right\} \quad (28)
\end{aligned}$$

and

$$G_{abcd}(t', t'') = \overline{\langle a | H_{1Q}(t') | b \rangle \langle c | H_{1Q}(t' - t'') | d \rangle} \quad (29)$$

are the correlation functions of the random Hamiltonian  $H_{1Q}(t)$  [14].

If the random process leading to the fluctuations of  $H_{1Q}(t)$  is stationary the correlation functions  $G_{abcd}(t', t'')$  depend only on  $|t'' - t'|$  and do not depend on  $t'$  [14].

Introducing the frequencies  $\omega_{ab}$

$$\omega_{ab} = E_a - E_b \quad (30)$$

and defining the spectral density functions as [14]

$$J_{abcd}(\omega) = \int_0^\infty dt'' G_{abcd}(t'', t'') \exp(i\omega t''), \quad (31)$$

we obtain

$$\begin{aligned}
\langle b | \overline{K(\tau)} | c \rangle = & \sum_{e,f} \left\{ \langle b | \rho(0) | e \rangle J_{effc}(\omega_{cf}) \int_0^\tau dt' \exp(i\omega_{ec}t') \right. \\
& - \langle e | \rho(0) | f \rangle J_{befc}(\omega_{cf}) \int_0^\tau dt' \exp[i(\omega_{be} - \omega_{cf})t'] \\
& - \langle e | \rho(0) | f \rangle J_{fbec}(\omega_{eb}) \int_0^\tau dt' \exp[i(\omega_{be} - \omega_{cf})t'] \\
& \left. + \langle f | \rho(0) | c \rangle J_{efbc}(\omega_{eb}) \int_0^\tau dt' \exp(i\omega_{bf}t') \right\}. \quad (32)
\end{aligned}$$

In Eq. (32) the terms  $\int_0^\tau dt' \exp(i\omega t')$  with  $\omega \neq 0$  are unimportant, because these terms oscillate with high frequencies and in the time scale  $(0, \tau)$  give zero [14, 38]. Retaining in Eq. (32) only the terms for which  $\omega = 0$  gives

$$\begin{aligned}
\langle b | \overline{K(\tau)} | c \rangle = & \tau \left\{ \langle b | \rho(0) | c \rangle \left[ -J_{bbcc}(0) - J_{cbbb}(0) \right. \right. \\
& \left. \left. + \sum_f [J_{effc}(\omega_{cf}) + J_{fbbf}(\omega_{fb})] \right] \right. \\
& \left. - \delta_{bc} \sum_f \langle f | \rho(0) | f \rangle [J_{cfcf}(\omega_{cf}) + J_{fbbf}(\omega_{fb})] \right\}. \quad (33)
\end{aligned}$$

Inserting Eq. (33) in Eq. (27), we have

$$\begin{aligned}
\langle a | A_1(\tau, t) | d \rangle = & \tau \left\{ \sum_{b,c} \langle a | R_2 | b \rangle \langle b | \rho(0) | c \rangle \langle c | R_2^{-1} | d \rangle \right. \\
& \times \exp\{i[(E_d - E_a)t - (E_b - E_c)\tau]\} \\
& \times \left[ -J_{bbcc}(0) - J_{cbbb}(0) + \sum_f [J_{effc}(\omega_{cf}) + J_{fbbf}(\omega_{fb})] \right] \\
& - \exp[i(E_d - E_a)t] \sum_{b,c} \langle a | R_2 | b \rangle \langle c | \rho(0) | c \rangle \langle b | R_2^{-1} | d \rangle \\
& \left. \times [J_{bccb}(\omega_{bc}) + J_{cbbc}(\omega_{cb})] \right\}. \quad (34)
\end{aligned}$$

Eq. (34) contains the two types of the high-frequency oscillating terms:  $\exp[i(\omega_{da}t - \omega_{bc}\tau)]$  and  $\exp(i\omega_{da}t)$ . For the time  $t = t_e$  the first exponential

according to Eq. (26) equals unity for all times  $\tau$ . The second exponential term depends only on  $t$  and may be neglected at the echo signal consideration [14, 38]. Omitting these oscillating terms in Eq. (34) we may write

$$\begin{aligned} \langle a | A_1(\tau, t) | d \rangle = \tau & \left\{ \sum_{b,c} \langle a | R_2 | b \rangle \langle b | \rho(0) | c \rangle \langle c | R_2^{-1} | d \rangle \right. \\ & \left. \times \left[ -J_{bbcc}(0) - J_{ccbb}(0) + \sum_f [J_{effc}(\omega_{cf}) + J_{fbbf}(\omega_{fb})] \right] \right\}. \end{aligned} \quad (35)$$

The same consideration for the term  $A_2(\tau, t)$  gives the following expression for the matrix element  $\langle a | A_2(\tau, t) | d \rangle$ :

$$\begin{aligned} \langle a | A_2(\tau, t) | d \rangle = t_e & \left\{ \sum_{b,c} \langle a | R_2 | b \rangle \langle b | \rho(0) | c \rangle \langle c | R_2^{-1} | d \rangle \right. \\ & \left. \times \left[ -J_{aadd}(0) - J_{daaa}(0) + \sum_f [J_{dffd}(\omega_{df}) + J_{faaf}(\omega_{af})] \right] \right\}. \end{aligned} \quad (36)$$

Inserting Eqs. (21), (35) and (36) into Eq. (14) we obtain the following general expression for the two-pulse echo signal

$$V(\tau, t_e) = \sum_{a,b,c,d} A_{abcd} R_{abcd}(\tau, t_e). \quad (37)$$

The matrix elements  $A_{abcd}$  in Eq. (37) are independent of the time fluctuations of the interaction Hamiltonian  $H_{1Q}(t)$  and have the form

$$A_{abcd} = \langle a | R_2 | b \rangle \langle b | R_1 H_{0Q} R_1^{-1} | c \rangle \langle c | R_2^{-1} | d \rangle \langle d | I_+ | a \rangle. \quad (38)$$

The matrix elements  $R_{abcd}(\tau, t_e)$  which describe the relaxation of the two-pulse echo signals are

$$R_{abcd}(\tau, t_e) = 1 - \tau T_{2bc}^{-1} - t_e T_{2ad}^{-1} \approx \exp(-\tau T_{2bc}^{-1} - t_e T_{2ad}^{-1}), \quad (39)$$

where

$$T_{2bc}^{-1} = -2J_{bbcc}(0) + \sum_f [J_{bffb}(\omega_{ba}) + J_{effc}(\omega_{cf})] \quad (40)$$

and

$$T_{2ad}^{-1} = -2J_{aadd}(0) + \sum_f [J_{affa}(\omega_{fa}) + J_{dffd}(\omega_{df})]. \quad (41)$$

### 3. Influence of hindered rotations of $\text{CCl}_3$ group on NQR echoes

Let us apply the obtained general expression (37) and consider the influence of the hindered rotations of  $\text{CCl}_3$  groups on NQR echo signal of  $^{53}\text{Cl}$  nuclei. The Hamiltonians  $H_{0Q}$  and  $H_{1Q}(t)$  have in this case the forms (9) and (10).

To contrast with NMR, in NQR the rf pulses are selective pulses [39, 40] and for example for a nucleus with spin  $I = 3/2$  the rf pulses connect only the states  $|\pm 3/2\rangle$  and  $|\pm 1/2\rangle$ . The states  $|+1/2\rangle$  and  $|-1/2\rangle$  (states  $|+3/2\rangle$  and  $|-3/2\rangle$ ) are not connected by rf pulses. This fundamental difference from NMR and NQR allows to consider only two eigenstates of Hamiltonian  $H_{0Q}$ :  $|+3/2\rangle$  and  $|+1/2\rangle$  (or  $|-3/2\rangle$  and  $|-1/2\rangle$ ) and write for two-pulse signal  $V(\tau, t_e)$  at  $t_e = \tau$  the following expression

$$V(\tau, t_e = \tau) = V(0) \exp\left(-\frac{2\tau}{T_2}\right), \quad (42)$$

where

$$V(0) \sim \left\langle \frac{1}{2} \left| R_2 \left| \frac{3}{2} \right\rangle \left\langle \frac{3}{2} \right| \rho(0) \left| \frac{1}{2} \right\rangle \left\langle \frac{1}{2} \right| R_2^{-1} \left| \frac{3}{2} \right\rangle \left\langle \frac{3}{2} \right| I_+ \left| \frac{1}{2} \right\rangle \right. \quad (43)$$

is the amplitude of the echo signal when  $\tau \rightarrow 0$  and

$$\begin{aligned} T_2^{-1} = & -2J_{3/2,3/2,1/2,1/2}(0) + J_{3/2,3/2,3/2,3/2}(0) + J_{1/2,1/2,1/2,1/2}(0) \\ & + J_{3/2,1/2,1/2,3/2}(-\omega) + J_{1/2,3/2,3/2,1/2}(-\omega) + J_{3/2,-1/2,-1/2,3/2}(-\omega) \\ & + J_{1/2,-3/2,-3/2,1/2}(-\omega). \end{aligned} \quad (44)$$

In Eq. (44)

$$\omega = \frac{1}{2}\omega_Q(3\cos^2\beta - 1). \quad (45)$$

The Hamiltonian  $H_{1Q}(t)$  (10) has the following matrix elements

$$\begin{aligned} \langle m | H_{1Q}(t) | m \rangle &= 0, \\ \langle 3/2 | H_{1Q}(t) | 1/2 \rangle &= \langle 1/2 | H_{1Q} | 3/2 \rangle^* = -i \frac{3\sqrt{3}}{2} \omega_Q \sin(2\beta) \exp[i\alpha(t)], \\ \langle 3/2 | H_{1Q}(t) | -1/2 \rangle &= \langle -1/2 | H_{1Q}(t) | 3/2 \rangle^* \\ &= -\frac{3\sqrt{3}}{2} \omega_Q \sin^2\beta \exp[-i2\alpha(t)]. \end{aligned} \quad (46)$$

Using Eq. (46) we obtain from Eq. (44)

$$T_2^{-1} = \frac{27}{2} \omega_Q^2 \left\{ \sin^2(2\beta) \int_0^\infty [\overline{\cos \alpha(0) \cos \alpha(t')} + \overline{\sin \alpha(0) \sin \alpha(t')}] \times \exp(-i\omega t') dt' \right. \\ \left. + \sin^4 \beta \int_0^\infty [\overline{\cos 2\alpha(0) \cos 2\alpha(t')} + \overline{\sin 2\alpha(0) \sin 2\alpha(t')}] \times \exp(-i\omega t') dt' \right\}. \quad (47)$$

The correlation functions in Eq. (47) ( $\alpha(0) = 0$ ) are equal [41]

$$\overline{\cos \alpha(0) \cos \alpha(t')} = \overline{\sin \alpha(0) \sin \alpha(t')} = \overline{\cos 2\alpha(0) \cos 2\alpha(t')} \\ = \overline{\sin 2\alpha(0) \sin 2\alpha(t')} = \frac{1}{2} \exp\left(-\frac{|t'|}{\tau_c}\right), \quad (48)$$

where  $\tau_c$  is the correlation time.

Inserting Eq. (48) into Eq. (47) we obtain

$$T_2^{-1} = \frac{27}{2} \omega_Q^2 (\sin^2 2\beta + \sin^4 \beta) \frac{\tau_c}{1 + \frac{1}{4} \omega_Q^2 (3 \cos^2 \beta - 1)^2 \tau_c^2}. \quad (49)$$

For  $\text{CCl}_3$  group  $\cos \beta = 1/3$  [36] and from Eq. (49) we have

$$T_2^{-1} = \frac{16\omega_Q^2 \tau_c}{1 + \frac{1}{9} \omega_Q^2 \tau_c^2}. \quad (50)$$

Generally for the hindered rotating  $\text{CCl}_3$  groups in molecular crystal [4, 5] it is  $\omega_Q \tau_c \gg 1$  and hence, from Eq. (50) we have the well known results ( $T_2 \sim \tau_c$  [36])

$$T_2 = \frac{1}{144} \tau_c. \quad (51)$$

The hindered rotations of  $\text{CCl}_3$  groups give also the contribution to the spin-lattice relaxation time  $T_1$  [14, 36]

$$T_1 = \frac{3}{4} \tau_c. \quad (52)$$

Using Eq. (52) it easily obtain the well known relation ( $T_2 \ll T_1$ ) between  $T_2$  and  $T_1$  for the reorienting  $\text{CCl}_3$  group

$$T_2 = \frac{1}{108} T_1 \approx 10^{-2} T_1. \quad (53)$$

In the case of high temperature when  $\omega_Q \tau_c \ll 1$ , from Eq. (50) we have also the well known result ( $T_2 \sim \tau_c^{-1}$  [14, 36])

$$T_2^{-1} \cong 16\omega_Q^2 \tau_c. \quad (54)$$

In conclusion, it should be note that obtained in this paper results are well known in NQR spectroscopy [14, 21, 36]. But in contrast to the well known approaches to the solution of this problem [11, 15–19], we do not use the perturbation theory of BPP and in this respect our approach is more correct.

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