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Theoretical Calculation of Carbon-13 Spin Relaxation Parameters for Motional Processes Described by A Three-Correlation-Time Model

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The exact equations of the C-13 spin relaxation parameters for the Howarth's model are given. This model involves three independent random motions of the internuclear vectors between chemically bonded proton and ^{13}C nuclei, *i.e.* an isotropic random motion, a librational random motion within a cone and a diffusional random rotation about an axis with a fixed angle.

INTRODUCTION

The nuclear spin relaxation is caused in principle by any perturbation involving Fourier components that correspond to the differences between the energy levels within the spin system. However, it is widely found that the spin relaxation of nuclei such as ^{1}H and ^{13}C is predominantly archieved by the time-fluctuation of the dipole-dipole interaction between the spin-having nuclei. Particularly in natural abundance ^{13}C nmr the spin relaxation is predominantly carried out by the dipole-dipole interaction between chemically bonded ^{13}C and ^{1}H, because the interaction between ^{13}C themselves can be neglected due to the low concentration (1.1%) and the interaction abruptly diminishes with increasing internuclear distance. Since the chemical shifts of individual carbons of substances are well distingushable with each other in ^{13}C nmr, the investigation of the spin relaxation provides detailed information of the time-fluctuation of the internuclear vectors relating to individual carbons. Nevertheless, in order to obtain the worthy knowledge it is necessary to establish the formulae that correlate the relaxation phenomena to the time-fluctuation of the internuclear vectors. If the internuclear vectors undergo a spherical random motion, the relaxation phenomena can be described by a correlation time which characterizes the rate of the random motion. However, the internuclear vectors in real substances, particularly in polymers, do not undergo such a simple random motion as expected. Some models of the motion such as the ellipsoid model undergoing random rotations have been proposed and examined in relation to the relaxation phenomena on real substances such as proteins.

We have found that the ^{13}C relaxation phenomena of polymers such as terephthalic acid polyesters[1)] and polyethylene[2,3)] can be well understood by use of the 3-τ model which was proposed by Howarth.[4,5)] However, he connected his 2-τ librational model[4)] to Woessner's 2-τ rotational model[6,7)] and the equations were not derived mathematically.

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Therefore, in this paper we will derive the exact equations of the relaxation parameters for this 3-τ model.

THEORY

The ^{13}C spin relaxation parameters on substances including only ^{13}C and ^{1}H as spin-having nuclei are described in terms of the spectral densities as follows, if the relaxation is conducted only by the dipole-dipole interaction between the nuclei.

$$\frac{1}{NT_1}=\frac{\gamma_C^2\gamma_H^2\hbar^2}{16r^6}[J_0(\omega_H-\omega_C)+18J_1(\omega_C)+9J_2(\omega_H+\omega_C)] \tag{1}$$

$$\frac{1}{NT_2}=\frac{\gamma_C^2\gamma_H^2\hbar^2}{32r^6}[4J_0(0)+J_0(\omega_H-\omega_C)+18J_1(\omega_C)+36J_1(\omega_H)+9J_2(\omega_H+\omega_C)] \tag{2}$$

$$\mathrm{NOE}=1+\frac{9J_2(\omega_H+\omega_C)-J_0(\omega_H-\omega_C)}{J_0(\omega_H-\omega_C)+18J_1(\omega_C)+9J_2(\omega_H+\omega_C)}\cdot\frac{\gamma_H}{\gamma_C} \tag{3}$$

Here, T_1, T_2 and NOE are the spin-lattice and spin-spin relaxation times and nuclear Overhauser enhancement, respectively. γ_C, γ_H and ω_C, ω_H denote the magnetogyric ratios and Larmor frequencies of ^{13}C and ^{1}H, respectively. $\hbar$ is the Planck's constant $h/2\pi$. r is the internuclear distance between ^{13}C and ^{1}H. Here, the relaxation conducted by only the dipolar interaction between chemically bonded ^{13}C and ^{1}H is considered and r is treated to be constant. N denotes the number of ^{1}H bonded chemically to ^{13}C under consideration.

The spectral densities $J_m(\omega)$ are defined to be the Fourier transforms of the correlation functions of the orientation functions F_m which are functions of the C-H internuclear vector r(hereafter designated as C-H vector) as

$$J_m(\omega)=\int_{-\infty}^{\infty}\langle F_m^*(t+\tau)F_m(t)\rangle\exp(i\omega\tau)d\tau \tag{4}$$

with $m=0$, 1 and 2,
where the angular bracket designates the average of the spin ensemble. The orientation functions F_m are described in terms of the direction cosines x, y, z of the C-H vector in a rectangular coordinates in the laboratory reference frame where z axis is parallel to the static magnetic field H_0;

$$\begin{aligned}F_0&=1-3z^2\\F_1&=(x+iy)z\\F_2&=(x+iy)^2\end{aligned} \tag{5}$$

with $x^2+y^2+z^2=1$.
Since the direction cosines x, y and z are time-dependent, the orientation functions F_m become time-dependent. The ensemble averages of the correlation functions $\langle F_m^*(t+\tau)F_m(t)\rangle$ are considered to be independent of t and dependent only on the time difference τ, so far as concerned with the spin ensemble in a steady state. If the C-H vector undergoes a sperical random rotation, the correlation functions follow simple exponential decay and the spectral densities for all m's are described as

$$J_m(\omega)=\langle|F_m(t)|^2\rangle\frac{2\tau_I}{1+\omega^2\tau_I{}^2} \tag{6}$$

where τ_I is the correlation time that characterizes the spherical random rotation. Then, the relaxation parameters such as T_1, T_2 and NOE can be formulated by substitution of Eq. (6) in Eqs. (1), (2) and (3) in terms of τ_I as described in a standard text book of NMR.

In this paper, however, we will derive the formulae for the relaxation parameters in the case that the C-H vector undergoes an anisotropic random motion including plural independent random motions. It is assumed that the random motion of the C-H vector in the laboratory frame can be expressed by superposition of plural independent motions. Consider rectangular coordinates S_1, S_2, $\cdots$, S_k that are correlated by orthogonal transformations. It is assumed that S_1 is the frame to describe the most inner motion of r and S_k the laboratory frame and frame S_j is transformed to the S_{j-1} by Euler angles ϕ_j, θ_j and ψ_j which are rotations about the z-axis of the frame S_j, about the new y-axis, and about the final z-axis, respectively. Then, the direction cosines x, y, z of r in the laboratory frame can be correlated to the direction cosines x_1, y_1, and z_1 in the frame S_1 by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}=\boldsymbol{A}_k\,\boldsymbol{A}_{k-1}\ldots\boldsymbol{A}_2\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \tag{7}$$

where $\boldsymbol{A}_i$ is the inverse matrix of the orthogonal transformation matrix that transforms S_i to S_{i-1}. The matrix $\boldsymbol{A}_i$ are expressed as

$$\boldsymbol{A}_i=\begin{pmatrix} \cos\phi_i\cos\theta_i\cos\psi_i-\sin\phi_i\sin\psi_i & -\cos\phi_i\cos\theta_i\sin\psi_i-\sin\phi_i\cos\psi_i & \cos\phi_i\sin\theta_i \\ \sin\phi_i\cos\theta_i\cos\psi_i+\cos\phi_i\sin\psi_i & -\sin\phi_i\cos\theta_i\sin\psi_i+\cos\phi_i\cos\psi_i & \sin\phi_i\sin\theta_i \\ -\sin\theta_i\cos\psi_i & \sin\theta_i\sin\psi_i & \cos\theta_i \end{pmatrix} \tag{8}$$

Therefore, the time-dependence of the direction cosines, in the laboratory frame,

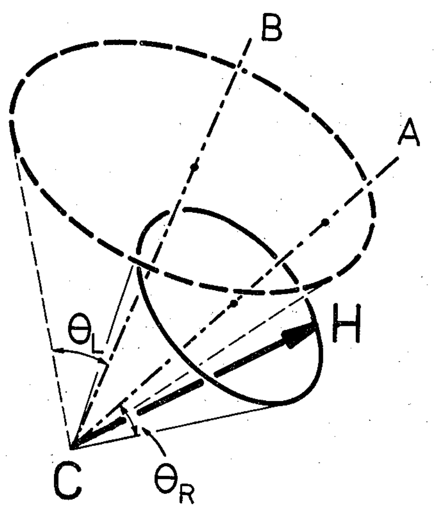

Fig. 1. Schematic diagram of 3-τ model for the motion of the internuclear C-H vector.

of the vector r involving plural independent motions can be formulated by the Euler angles in each transformation matrix with x_1, y_1 and z_1. We are dealing with "the 3-τ motion" of r which was proposed by Howarth[4] by connecting his "2-τ librational motion" to "Woessner's 2-τ rotational motion" with an intuitively derived formula, as shown schematically in Fig. 1. *It is assumed that the C-H vector r undergoes a random diffusional rotation about an axis(A) with a vertical angle θ_R, and the axis A further librates about another axis(B) within a solid cone of a vertical angle θ_L (in other words the axis A is assumed to move at random among infinite number of equilibrium positions in this cone), and finally the axis B undergoes a spherical random rotation in the laboratory frame.* In this case, Eq. (7) reduces to

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{A}_3 \cdot \boldsymbol{A}_2 \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \tag{9}$$

with

$$\begin{aligned} x_1 &= \cos\phi_1 \sin\theta_1 \\ y_1 &= \sin\phi_1 \sin\theta_1 \\ z_1 &= \cos\theta_1 \\ \theta_1 &= \theta_R \end{aligned} \tag{10}$$

Let the axes A and B the z-axes in the frames S_1 and S_2, respectively, then the angles ψ_2 and ψ_3 can be treated as zero, because it is sufficient for this mode of motion to define the z-axis of S_1 (axis A) in S_2 and the z-axis of S_2 (axis B) in S_3 (laboratory frame). Then, the matrix elements in Eq. (9) reduce to

$$\boldsymbol{A}_i = \begin{pmatrix} \cos\phi_i \cos\theta_i & -\sin\phi_i & \cos\phi_i \sin\theta_i \\ \sin\phi_i \cos\theta_i & \cos\phi_i & \sin\phi_i \sin\theta_i \\ -\sin\theta_i & 0 & \cos\theta_i \end{pmatrix} \tag{11}$$

for $i=2$ and 3.

Here, θ_i and ϕ_i are considered to fluctuate at random with time in the ranges of $\theta_2 = 0 \sim \theta_L$, $\phi_2 = 0 \sim 2\pi$, and $\theta_3 = 0 \sim \pi$, $\phi_3 = 0 \sim 2\pi$. By use of Eqs. (9), (10), and (11), the orientation functions defined in Eq. (5) can be expressed by the summation of products of f, g, and h functions as

$$F_m(t) = \sum_{j,k=1}^{5} f_{jk}^{(m)}(t)\, g_{jk}^{(m)}(t)\, h_{jk}^{(m)}(t) \tag{12}$$

Here $h_{jk}^{(m)}(t)$ are the functions of θ_1 and ϕ_1 arising from the stochastic rotational motion of r, and $g_{jk}^{(m)}(t)$ are the functions of θ_2 and ϕ_2 arising from the librational motion of the axis A, and $f_{jk}^{(m)}(t)$ are the functions of θ_3 and ϕ_3 arising from the spherical motion of the axis B. The functions $f_{jk}^{(m)}(t)$, $g_{jk}^{(m)}(t)$ and $h_{jk}^{(m)}(t)$ are listed in Table I for each m, the derivation of which is given in Appendix 1. Since the three elementary motions are assumed here to be independent with each other, the correlation functions of the orientation functions F_m can be expressed in the product summation of the respective correlation functions of f, g, h functions as

Table I. $f_{jk}^{(m)}$, $g_{jk}^{(m)}$, $h_{jk}^{(m)}$ Functions

(a) $m=0$

$f_{1k}=-(3/4)\sin^2\theta_1 e^{2i\phi_1}$ $f_{2k}=-(3/4)\sin^2\theta_1 e^{-2i\phi_1}$ $f_{3k}=-3\sin\theta_1\cos\theta_1 e^{i\phi_1}$ $f_{4k}=-3\sin\theta_1\cos\theta_1 e^{-i\phi_1}$ $f_{5k}=-(1/2)(3\cos^2\theta_1-1)$ for all k's	$g_{11}=(1/2)(\cos^2\theta_2+2\cos\theta_2+1)e^{2i\phi_2}$ $g_{12}=(1/2)(\cos^2\theta_2-2\cos\theta_2+1)e^{-2i\phi_2}$ $g_{13}=(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{i\phi_2}$ $g_{14}=(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{-i\phi_2}$ $g_{15}=-\sqrt{3/2}\sin^2\theta_2$
$h_{j1}=(1/2)\sin^2\theta_3$ $h_{j2}=(1/2)\sin^2\theta_3$ $h_{j3}=\sin\theta_3\cos\theta_3$ $h_{j4}=\sin\theta_3\cos\theta_3$ $h_{j5}=-\sqrt{1/6}(3\cos^2\theta_3-1)$ for all j's	$g_{21}=(1/2)(\cos^2\theta_2-2\cos\theta_2+1)e^{2i\phi_2}$ $g_{22}=(1/2)(\cos^2\theta_2+2\cos\theta_2+1)e^{-2i\phi_2}$ $g_{23}=(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{i\phi_2}$ $g_{24}=(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{-i\phi_2}$ $g_{25}=-\sqrt{3/2}\sin^2\theta_2$
	$g_{31}=(1/2)(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{2i\phi_2}$ $g_{32}=(1/2)(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{-2i\phi_2}$ $g_{33}=-(1/2)(2\cos^2\theta_2+\cos\theta_2-1)e^{i\phi_2}$ $g_{34}=-(1/2)(2\cos^2\theta_2-\cos\theta_2-1)e^{-i\phi_2}$ $g_{35}=\sqrt{3/2}\sin\theta_2\cos\theta_2$
	$g_{41}=(1/2)(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{2i\phi_2}$ $g_{42}=(1/2)(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{-2i\phi_2}$ $g_{43}=-(1/2)(2\cos^2\theta_2-\cos\theta_2-1)e^{i\phi_2}$ $g_{44}=-(1/2)(2\cos^2\theta_2+\cos\theta_2-1)e^{-i\phi_2}$ $g_{45}=\sqrt{3/2}\sin\theta_2\cos\theta_2$
	$g_{51}=-(3/2)\sin^2\theta_2 e^{2i\phi_2}$ $g_{52}=-(3/2)\sin^2\theta_2 e^{-2i\phi_2}$ $g_{53}=3\sin\theta_2\cos\theta_2 e^{i\phi_2}$ $g_{54}=3\sin\theta_2\cos\theta_2 e^{-i\phi_2}$ $g_{55}=\sqrt{3/2}(3\cos^2\theta_2-1)$

(b) $m=1$

$f_{1k}=(1/4)\sin^2\theta_1 e^{2i\phi_1}$ $f_{2k}=(1/4)\sin^2\theta_1 e^{-2i\phi_1}$ $f_{3k}=(1/2)\sin\theta_1\cos\theta_1 e^{i\phi_1}$ $f_{4k}=(1/2)\sin\theta_1\cos\theta_1 e^{-i\phi_1}$ $f_{5k}=-(1/2)(3\cos^2\theta_1-1)$ for all k's	$g_{11}=-\sqrt{3/8}(\cos^2\theta_2+2\cos\theta_2+1)e^{2i\phi_2}$ $g_{12}=-\sqrt{3/8}(\cos^2\theta_2-2\cos\theta_2+1)e^{-2i\phi_2}$ $g_{13}=\sqrt{3/2}(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{i\phi_2}$ $g_{14}=\sqrt{3/2}(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{-i\phi_2}$ $g_{15}=(3/2)\sin^2\theta_2$
$h_{j1}=\sqrt{1/6}(\sin\theta_3\cos\theta_3+\sin\theta_3)e^{i\phi_3}$ $h_{j2}=\sqrt{1/6}(\sin\theta_3\cos\theta_3-\sin\theta_3)e^{i\phi_3}$ $h_{j3}=-\sqrt{1/6}(2\cos^2\theta_3+\cos\theta_3-1)e^{i\phi_3}$ $h_{j4}=-\sqrt{1/6}(2\cos^2\theta_3-\cos\theta_3-1)e^{i\phi_3}$ $h_{j5}=\sin\theta_3\cos\theta_3 e^{i\phi_3}$ for all j's	$g_{21}=-\sqrt{3/8}(\cos^2\theta_2-2\cos\theta_2+1)e^{2i\phi_2}$ $g_{22}=-\sqrt{3/8}(\cos^2\theta_2+2\cos\theta_2+1)e^{-2i\phi_2}$ $g_{23}=\sqrt{3/2}(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{i\phi_2}$ $g_{24}=\sqrt{3/2}(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{-i\phi_2}$ $g_{25}=(3/2)\sin^2\theta_2$
	$g_{31}=-\sqrt{3/2}(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{2i\phi_2}$ $g_{32}=-\sqrt{3/2}(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{-2i\phi_2}$ $g_{33}=-\sqrt{3/2}(2\cos^2\theta_2+\cos\theta_2-1)e^{i\phi_2}$ $g_{34}=-\sqrt{3/2}(2\cos^2\theta_2-\cos\theta_2-1)e^{-i\phi_2}$ $g_{35}=-3\sin\theta_2\cos\theta_2$

	$g_{41}=-\sqrt{3/2}\,(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{2i\phi_2}$ $g_{42}=-\sqrt{3/2}\,(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{-2i\phi_2}$ $g_{43}=-\sqrt{3/2}\,(2\cos^2\theta_2-\cos\theta_2-1)e^{i\phi_2}$ $g_{44}=-\sqrt{3/2}\,(2\cos^2\theta_2+\cos\theta_2-1)e^{-i\phi_2}$ $g_{45}=-3\sin\theta_2\cos\theta_2$
	$g_{51}=\sqrt{3/8}\,\sin^2\theta_2 e^{2i\phi_2}$ $g_{52}=\sqrt{3/8}\,\sin^2\theta_2 e^{-2i\phi_2}$ $g_{53}=\sqrt{3/2}\,\sin\theta_2\cos\theta_2 e^{i\phi_2}$ $g_{54}=\sqrt{3/2}\,\sin\theta_2\cos\theta_2 e^{-i\phi_2}$ $g_{55}=-(1/2)(3\cos^2\theta_2-1)$

(c) $m=2$

$f_{1k}=(1/4)\sin^2\theta_1 e^{2i\phi_1}$ $f_{2k}=(1/4)\sin^2\theta_1 e^{-2i\phi_1}$ $f_{3k}=\sin\theta_1\cos\theta_1 e^{i\phi_1}$ $f_{4k}=\sin\theta_1\cos\theta_1 e^{-i\phi_1}$ $f_{5k}=(1/2)(3\cos\theta_1-1)$ for all k's	$g_{11}=\sqrt{3/2}\,(\cos^2\theta_2+2\cos\theta_2+1)e^{2i\phi_2}$ $g_{12}=\sqrt{3/2}\,(\cos^2\theta_2-2\cos\theta_2+1)e^{-2i\phi_2}$ $g_{13}=-\sqrt{6}\,(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{i\phi_2}$ $g_{14}=-\sqrt{6}\,(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{-i\phi_2}$ $g_{15}=3\sin^2\theta_2$
$h_{j1}=\sqrt{1/24}\,(\cos^2\theta_3+2\cos\theta_3+1)e^{2i\phi_3}$ $h_{j2}=\sqrt{1/24}\,(\cos^2\theta_3-2\cos\theta_3+1)e^{2i\phi_3}$ $h_{j3}=\sqrt{1/6}\,(\sin\theta_3\cos\theta_3+\sin\theta_3)e^{2i\phi_3}$ $h_{j4}=\sqrt{1/6}\,(\sin\theta_3\cos\theta_3-\sin\theta_3)e^{2i\phi_3}$ $h_{j5}=(1/2)\sin^2\theta_3 e^{2i\phi_3}$ for all j's	$g_{21}=\sqrt{3/2}\,(\cos^2\theta_2-2\cos\theta_2+1)e^{2i\phi_2}$ $g_{22}=\sqrt{3/2}\,(\cos^2\theta_2+2\cos\theta_2+1)e^{-2i\phi_2}$ $g_{23}=-\sqrt{6}\,(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{i\phi_2}$ $g_{24}=-\sqrt{6}\,(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{-i\phi_2}$ $g_{25}=3\sin^2\theta_2$
	$g_{31}=\sqrt{3/2}\,(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{2i\phi_2}$ $g_{32}=\sqrt{3/2}\,(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{-2i\phi_2}$ $g_{33}=\sqrt{3/2}\,(2\cos^2\theta_2+\cos\theta_2-1)e^{i\phi_2}$ $g_{34}=\sqrt{3/2}\,(2\cos^2\theta_2-\cos\theta_2-1)e^{-i\phi_2}$ $g_{35}=-3\sin\theta_2\cos\theta_2$
	$g_{41}=\sqrt{3/2}\,(\sin\theta_2\cos\theta_2-\sin\theta_2)e^{2i\phi_2}$ $g_{42}=\sqrt{3/2}\,(\sin\theta_2\cos\theta_2+\sin\theta_2)e^{-2i\phi_2}$ $g_{43}=\sqrt{3/2}\,(2\cos^2\theta_2-\cos\theta_2-1)e^{i\phi_2}$ $g_{44}=\sqrt{3/2}\,(2\cos^2\theta_2+\cos\theta_2-1)e^{-i\phi_2}$ $g_{45}=-3\sin\theta_2\cos\theta_2$
	$g_{51}=\sqrt{3/2}\,\sin^2\theta_2 e^{2i\phi_2}$ $g_{52}=\sqrt{3/2}\,\sin^2\theta_2 e^{-2i\phi_2}$ $g_{53}=\sqrt{6}\,\sin\theta_2\cos\theta_2 e^{i\phi_2}$ $g_{54}=\sqrt{6}\,\sin\theta_2\cos\theta_2 e^{-i\phi_2}$ $g_{55}=(3\cos^2\theta_2-1)$

$$\begin{aligned}&\langle F_m{}^*(t+\tau)F_m(t)\rangle\\ &\doteq\langle[\sum_{j,k} f_{jk}^{(m)}(t+\tau)g_{jk}^{(m)}(t+\tau)h_{ij}^{(m)}(t+\tau)]^*[\sum_{l,n} f_{ln}^{(m)}(t)g_{ln}^{(m)}(t)h_{ln}^{(m)}(t)]\rangle\\ &=\sum_{\substack{j,k,\\ l,n}}\langle f_{jk}^{*(m)}(t+\tau)f_{ln}^{(m)}(t)\rangle\langle g_{jk}^{*(m)}(t+\tau)g_{ln}^{(m)}(t)\rangle\langle h_{jk}^{*(m)}(t+\tau)h_{ln}^{(m)}(t)\rangle\end{aligned}\tag{13}$$

Consider first the correlation functions of the f functions relating to the stochastic rotational motion. In this motion of the C-H vector r with a constant $\theta_1=\theta_R$ in the frame S_1, the probability $p(\phi_{10}+\Delta\phi_1, \tau)$ that ϕ_1 takes a value of $\phi_{10}+\Delta\phi_1$ at time $t+\tau$ when ϕ_1 was ϕ_{10} at an arbitrary time t will be given by a Gaussian distribution as[6]

$$p(\phi_{10}+\Delta\phi_1, \tau)=\frac{1}{2}(\pi\tau\tau_R^{-1})^{-1/2}e^{-\tau_R\Delta\phi_1^2/4\tau} \tag{14}$$

Then, an actual calculation with use of Table I yields,

$$\begin{aligned}\langle f_{jk}^{*(m)}(t+\tau)f_{ln}^{(m)}(t)\rangle&=\left\langle\left[\int_{-\infty}^{\infty}f_{jk}^{*(m)}(\phi_{10}+\Delta\phi_1)p(\phi_{10}+\Delta\phi_1, \tau)d\Delta\phi_1\right]f_{ln}^{(m)}(\phi_{10})\right\rangle\\&=K\langle f_{jk}^{*(m)}(\phi_{10})f_{ln}^{(m)}(\phi_{10})\rangle\end{aligned} \tag{15}$$

with

$$\begin{aligned}K&=e^{-4|\tau|/\tau_R} && \text{for } j=l=1 \text{ or } 2\\&=e^{-|\tau|/\tau_R} && \text{for } j=l=3 \text{ or } 4\\&=1 && \text{for } j=l=5\\&=0 && \text{for } j\neq l\end{aligned} \tag{16}$$

for all m's (also independent of k and n as revealed in Table I).

Since the average of the spin ensemble that is indicated by the angular bracket is considered to be equivalent to the average in relation to ϕ_{10} so far as concerned with a steady state, it is evident from Table I that $\langle f_{jk}^{*(m)}(\phi_{10})f_{ln}^{(m)}(\phi_{10})\rangle$ becomes zero unless $j=l$. On the other hand, when $j=l$, Eq. (15) reduces to

$$\begin{aligned}\langle f_{jk}^{*(m)}(t+\tau)f_{jn}(t)\rangle&=K\langle f_{jk}^{*(m)}(\phi_{10})f_{jk}^{(m)}(\phi_{10})\rangle\\&=K\langle|f_{jk}^{(m)}(\phi_{10})|^2\rangle\end{aligned} \tag{17}$$

Therefore, Eq. (17) with Eq. (16) and Table I yield actual forms of the correlation functions as

$$\begin{aligned}\langle f_{jk}^{*(0)}(t+\tau)f_{jn}^{(0)}(t)\rangle&=\frac{3}{4}C_Re^{-4|\tau|/\tau_R} && \text{for } j=1, 2\\&=3B_Re^{-|\tau|/\tau_R} && \text{for } j=3, 4\\&=A_R && \text{for } j=5\\\langle f_{jk}^{*(1)}(t+\tau)f_{jn}^{(1)}(t)\rangle&=\frac{1}{12}C_Re^{-4|\tau|/\tau_R} && \text{for } j=1, 2\\&=\frac{1}{12}B_Re^{-|\tau|/\tau_R} && \text{for } j=3, 4\\&=A_R && \text{for } j=5\\\langle f_{jk}^{*(2)}(t+\tau)f_{jn}^{(2)}(t)\rangle&=\frac{1}{12}C_Re^{-4|\tau|/\tau_R} && \text{for } j=1, 2\\&=\frac{1}{3}B_Re^{-|\tau|/\tau_R} && \text{for } j=3, 4\\&=A_R && \text{for } j=5\end{aligned} \tag{18}$$

where

$$A_R=(1/4)(3\cos^2\theta_R-1)^2$$
$$B_R=3\sin^2\theta_R\cos^2\theta_R \tag{19}$$
$$C_R=(3/4)\sin^4\theta_R$$

Next consider the correlation functions of the g functions. The A-axis in the frame S_2 can be defined by θ_2 that is the angle to z-axis (B-axis) and ϕ_2 that is the angle of the projection of the A-axis on x–y plane to x-axis in S_2 since z-axis (B axis) of S_2 is transformed to z-axis (A-axis) of S_1 by rotation of ϕ_2 about itself and rotation of θ_2 about y-axis of S_1. Let the position at θ_2, ϕ_2 be represented by a solid angle $\Omega(\theta_2, \phi_2)$; $d\Omega=\sin\theta_2 d\theta_2 d\phi_2$, $0\leqq\theta_2\leqq\theta_L$, $0\leqq\phi_2\leqq 2\pi$. In the librational motion assumed here, if the A-axis was at Ω_0 at time t, the probability that the A-axis still remains at Ω_0 can be considered to be $e^{-\tau/\tau_L}$ and the probability finding the A-axis at another position Ω_1 at time $t+\tau$ be $1-e^{-\tau/\tau_L}$. Accordingly, the correlation functions of the g functions can be written as

$$\begin{aligned}
&\langle g_{jk}^{*(m)}(t+\tau)g_{ln}^{(m)}(t)\rangle\\
&=\left\langle\left\{\left[\int_{\Omega_1} g_{jk}^{*(m)}(\Omega_1)(1-e^{-\tau/\tau_L})d\Omega_1\Big/\int_{\Omega_1} d\Omega_1\right]+g_{jk}^{*(m)}(\Omega_0)e^{-\tau/\tau_L}\right\}g_{ln}^{(m)}(\Omega_0)\right\rangle_{\Omega_0}\\
&=(1-e^{-\tau/\tau_L})\langle\langle g_{jk}^{*(m)}(\Omega_1)\rangle_{\Omega_1} g_{ln}^{(m)}(\Omega_0)\rangle_{\Omega_0}+e^{-\tau/\tau_L}\langle g_{jk}^{*(m)}(\Omega_0)g_{ln}^{(m)}(\Omega_0)\rangle_{\Omega_0}\\
&=(1-e^{-\tau/\tau_L})\langle g_{jk}^{*(m)}(\Omega_1)\rangle_{\Omega_1}\langle g_{ln}^{(m)}(\Omega_0)\rangle_{\Omega_0}+e^{-\tau/\tau_L}\langle g_{jk}^{*(m)}(\Omega_0)g_{ln}^{(m)}(\Omega_0)\rangle_{\Omega_0}
\end{aligned} \tag{20}$$

Here, the average of the spin ensemble at an arbitrary time is assumed to be equivalent to the average over available values of Ω_0 and Ω_1.

It is found by examining the g functions in Table I that $\langle g_{jk}^{*(m)}(\Omega_1)\rangle_{\Omega_1}$, $\langle g_{ln}^{(m)}(\Omega_0)\rangle_{\Omega_0}=0$ unless $k=5$, $n=5$ and that $\langle g_{jk}^{*(m)}(\Omega_0)g_{ln}^{(m)}(\Omega_0)\rangle=0$ unless $k=n$.

Accordingly, with the results of Eq. (16) the cross terms in Eq. (13) disappear and Eq. (13) reduce to

$$\langle F_m^*(t+\tau)F_m(t)\rangle=\sum_{j,k}\langle f_{jk}^{*(m)}(t+\tau)f_{jk}^{(m)}(t)\rangle\langle g_{jk}^{*(m)}(t+\tau)g_{jk}^{(m)}(t)\rangle\langle h_{jk}^{*(m)}(t+\tau)h_{jk}^{(m)}(t)\rangle \tag{21}$$

Since the axis B is assumed to undergo a spherical random rotation in the laboratory frame, all self-correlation functions of $h_{jk}^{(m)}$ may follow exponential decays as

$$\langle h_{jk}^{*(m)}(t+\tau)h_{jk}^{(m)}(t)\rangle=\langle|h_{jk}^{(m)}(t)|^2\rangle e^{-|\tau|/\tau_I} \tag{22}$$

The average of the square of $|h_{jk}^{(m)}|$ at an arbitrary time over the spin ensemble can be calculated assuming that

$$\langle|h_{jk}^{(m)}(t)|^2\rangle=\int_{\theta_3=0}^{\pi}\int_{\phi_3=0}^{2\pi}h_{jk}^{(m)}(\theta_3, \phi_3)^2\sin\theta_3 d\theta_3 d\phi_3\Big/\int_{\theta_3=0}^{\pi}\int_{\phi_3=0}^{2\pi}\sin\theta_3\, d\theta_3 d\phi_3$$

By use of Table I, we have

$$\langle|h_{jk}^{(m)}(t)|^2\rangle=2/15 \tag{23}$$

for all m's.

Therefore, Eq. (21) can be rewritten as

$$\langle F_m^*(t+\tau)F_m(t)\rangle$$
$$=\frac{2}{15}e^{-|\tau|/\tau_I}\sum_j[\langle f_{jk'}^{*(m)}(t+\tau)f_{jk'}^{(m)}(t)\rangle\sum_k\langle g_{jk}^{*(m)}(t+\tau)g_{jk}^{(m)}(t)\rangle] \tag{24}$$

where $\langle f_{jk'}^{*(m)}(t+\tau)f_{jk'}^{(m)}(t)\rangle$ is taken out of the summation in relation to k because it is equivalent for all k's.

The summation in relation to k in Eq. (21) can be carried out by use of Eq. (17) and the note cited to the equation. Thus, we have

$$\sum_k\langle g_{jk}^{*(m)}(t+\tau)g_{jk}^{(m)}(t)\rangle$$
$$=(1-e^{-\tau/\tau_L})\langle g_{j5}^{*(m)}(\Omega_1)\rangle_{\Omega_1}\langle g_{j5}^{(m)}(\Omega_0)\rangle_{\Omega_0}+e^{-\tau/\tau_L}\sum_k\langle g_{jk}^{*(m)}(\Omega_0)g_{jk}^{(m)}(\Omega_0)\rangle_{\Omega_0}$$
$$=(1-e^{-\tau/\tau_L})\langle g_{j5}^{(m)}(\Omega)\rangle_\Omega^{\ 2}+e^{-\tau/\tau_L}\sum_k\langle|g_{jk}^{(m)}(\Omega)|^2\rangle_\Omega \tag{25}$$

Here, the average of $g_{j5}^{(m)}(\Omega)$ and $|g_{jk}^{(m)}(\Omega)|^2$ over Ω can be carried out by the relation,

$$\langle\Phi(\Omega)\rangle_\Omega=\int_\Omega\Phi(\Omega)d\Omega\Big/\int_\Omega d\Omega$$
$$=\int_0^{\theta_L}\int_0^{2\pi}\Phi(\theta_2,\phi_2)\sin\theta_2 d\theta_2 d\phi_2\Big/\int_0^{\theta_L}\int_0^{2\pi}\sin\theta_2 d\theta_2 d\phi_2$$

where $\Phi(\Omega)=g_{j5}^{(m)}(\Omega)$ or $|g_{jk}^{(m)}(\Omega)|^2$.
An actual calculation yields,

$$\begin{aligned}
\langle g_{j5}^{(0)}\rangle^2&=4C_L && \text{for } j=1,2\\
&=B_L && \text{for } j=3,4\\
&=6A_L && \text{for } j=5\\
\langle g_{j5}^{(1)}\rangle^2&=6C_L && \text{for } j=1,2\\
&=6B_L && \text{for } j=3,4\\
&=A_L && \text{for } j=5\\
\langle g_{j5}^{(2)}\rangle^2&=24C_L && \text{for } j=1,2\\
&=6B_L && \text{for } j=3,4\\
&=4A_L && \text{for } j=5
\end{aligned} \tag{26}$$

where

$$\begin{aligned}
A_L&=\cos^2\theta_L(1+\cos\theta_L)^2/4\\
B_L&=\sin^2\theta_L(1+\cos\theta_L)^2/6\\
C_L&=(\cos\theta_L+2)^2(\cos\theta_L-1)^2/24
\end{aligned} \tag{27}$$

and, for example,

$$\begin{aligned}
\sum_k|g_{jk}^{(0)}|^2&=4 && \text{for } j=1,2\\
&=1 && \text{for } j=3,4\\
&=6 && \text{for } j=5
\end{aligned} \tag{28}$$

Substitution of Eqs. (26) and (28) in Eq. (25) yields

$$
\begin{aligned}
\sum_k \langle g_{jk}^{*(0)}(t+\tau)g_{jk}^{(0)}(t)\rangle &= 4[C_L+(1-C_L)e^{-|\tau|/\tau_L}] && \text{for } j=1, 2\\
&= B_L+(1-B_L)e^{-|\tau|/\tau_L} && \text{for } j=3, 4\\
&= 6[A_L+(1-A_L)e^{-|\tau|/\tau_L}] && \text{for } j=5\\
\sum_k \langle g_{jk}^{*(1)}(t+\tau)g_{jk}^{(1)}(t)\rangle &= 6[C_L+(1-C_L)e^{-|\tau|/\tau_L}] && \text{for } j=1, 2\\
&= 6[B_L+(1-B_L)e^{-|\tau|/\tau_L}] && \text{for } j=3, 4\\
&= A_L+(1-A_L)e^{-|\tau|/\tau_L} && \text{for } j=5\\
\sum_k \langle g_{jk}^{*(2)}(t+\tau)g_{jk}^{(2)}(t)\rangle &= 24[C_L+(1-C_L)e^{-|\tau|/\tau_L}] && \text{for } j=1, 2\\
&= 6[B_L+(1-B_L)e^{-|\tau|/\tau_L}] && \text{for } j=3, 4\\
&= 4[A_L+(1-A_L)e^{-|\tau|/\tau_L}] && \text{for } j=5
\end{aligned}
\tag{29}
$$

Substitution of Eq. (29) in Eq. (24) with Eq. (18) yields the correlation functions of the orientation functions of the C-H vector,

$$
\begin{aligned}
\langle F_m^*(t+\tau)F_m(t)\rangle = K_m[&A_RA_Le^{-|\tau|/\tau_I}+A_R(1-A_L)e^{-|\tau|/\tau_1}\\
&+B_RB_Le^{-|\tau|/\tau_2}+B_R(1-B_L)e^{-|\tau|/\tau_3}\\
&+C_RC_Le^{-|\tau|/\tau_4}+C_R(1-C_L)e^{-\tau/\tau_5}]
\end{aligned}
\tag{30}
$$

with

$$
\begin{aligned}
K_0&=4/5\\
K_1&=2/15\\
K_2&=8/15
\end{aligned}
\tag{31}
$$

and

$$
\begin{aligned}
\tau_1^{-1}&=\tau_L^{-1}+\tau_I^{-1}\\
\tau_2^{-1}&=\tau_R^{-1}+\tau_I^{-1}\\
\tau_3^{-1}&=\tau_R^{-1}+\tau_L^{-1}+\tau_I^{-1}\\
\tau_4^{-1}&=4\tau_R^{-1}+\tau_I^{-1}\\
\tau_5^{-1}&=4\tau_R^{-1}+\tau_L^{-1}+\tau_I^{-1}
\end{aligned}
\tag{32}
$$

Fourier transformation of $\langle F_m^*(t+\tau)F_m(t)\rangle$ yields the spectral densities as

$$
\begin{aligned}
J_m(\omega)=K_m\Big[&A_RA_L\frac{2\tau_I}{1+\omega^2\tau_I^2}+A_R(1-A_L)\frac{2\tau_1}{1+\omega^2\tau_1^2}\\
&+B_RB_L\frac{2\tau_2}{1+\omega^2\tau_2^2}+B_R(1-B_L)\frac{2\tau_3}{1+\omega^2\tau_3^2}\\
&+C_RC_L\frac{2\tau_4}{1+\omega^2\tau_4^2}+C_R(1-C_L)\frac{2\tau_5}{1+\omega^2\tau_5^2}\Big]
\end{aligned}
\tag{33}
$$

where A_R, B_R, C_R and A_L, B_L, C_L are given by Eqs. (19) and (27), respectively. Substitution of Eq. (33) for the $J_m(\omega)$'s in Eqs. (1), (2), and (3) yields the formulae of the spin relaxation parameters T_1, T_2 and NOE in terms of the correlation times τ_I, τ_L, τ_R

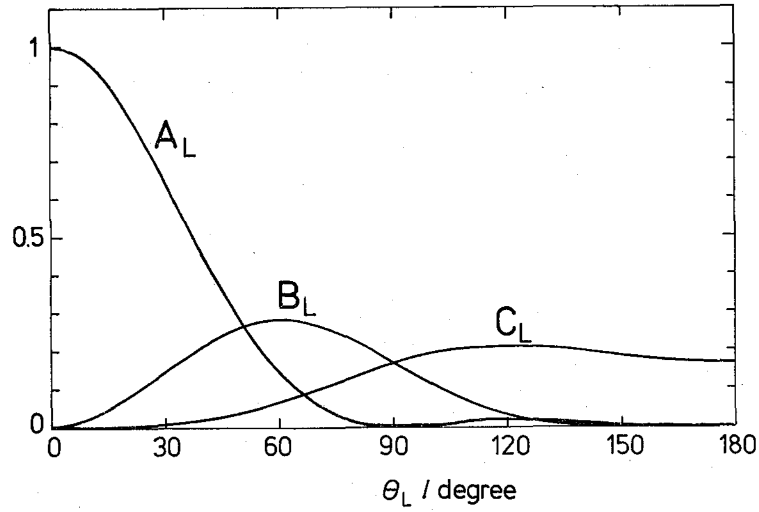

Fig. 2. Dependence of the parameters A_L, B_L and C_L defined by Eq. (27) on θ_L.

that describe the respective independent motions involving in the "the 3-τ motion" of the C-H vector.

Note here that if $C_L=B_L=A_L=\cos^2\theta_L\ (\cos\theta_L+1)^2/4$ Eq. (27) is equivalent to the formula for the spectral densities which was derived by Howarth,[4] connecting intuitively the formula of Weossner's 2τ rotational motion to that of his 2τ librational motion. The parameters A_L, B_L and C_L in Eq. (33) are, of course, different with each other as shown in Fig. 2. where A_L, B_L and C_L are plotted against θ_L. Therefore, the Howarth's equation is not valid in general. Nevertheless, when τ_I and τ_L are much larger than $\tau_R(\tau_I,\ \tau_L\gg\tau_R)$, τ_2, $\tau_3\approx\tau_R$ and τ_4, $\tau_5\approx\tau_R/4$ and the terms including B_RB_L, C_RC_L in Eq. (33) can be neglected in comparison with the terms including only B_R and C_R, respectively. Accordingly, in such a case Eq. (33) becomes equivalent to the Howarth's equation. Hence, our previous analysis[1–3] using Howarth's equation is not necessary to be revised.

RESULTS AND DISCUSSION

In this section we examine the dependence of the relaxation parameters T_1, T_2 and NOE on the correlation times according to Eq. (33) that has been derived on the basis of the 3-τ model. In Fig. 3 the value of NT_1 is plotted against τ_L for different θ_L's while other parameters are fixed as $\tau_I/\tau_L=10^2$, $\tau_R=10^{-12}$s, $\theta_R=30°$. The parameters fixed here roughly correspond to those determined for real polyethylene samples[2,3] as the most probable values. The NT_1 shows single minimum at about 5×10^{-11} s of τ_L when $\theta_L<10°$ but an additional minimum appears at about 5×10^{-9} s with increasing θ_L. The latter minimum at 5×10^{-9} s remains while the former minimum disappears with further increasing θ_L above 80°. It is noted here that τ_L of 5×10^{-11} s for the former minimum corresponds to 5×10^{-9} s of τ_I which is equivalent to the value of τ_L for the latter minimum and the value of 5×10^{-9} s is roughly equivalent to $1/\omega_C(\approx6\times10^{-9}$ s).

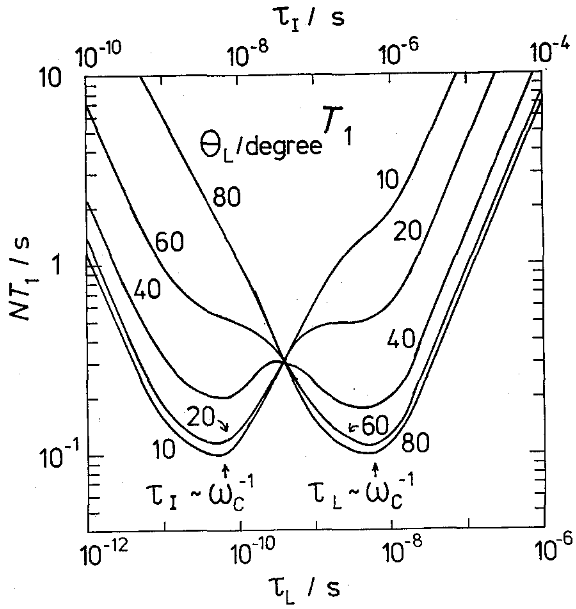

Fig. 3. NT_1. *vs* τ_L for different θ_L's indicated for each curve, when $\tau_I/\tau_L=10^2$, $\tau_R=10^{-12}$ s, $\theta_R=30°$.

Hence it is concluded that the minimum of NT_1 appears when the value of τ_I or τ_L reaches the reciprocal of the Larmor frequency of ^{13}C.

Figure 4 indicates the dependence of NT_1 on τ_L for different ratios τ_I/τ_L when other parameters are fixed as $\theta_L=60°$, $\theta_R=30°$, $\tau_R=10^{-12}$ s. Each curve seems to comprise two components involving the minimum value at either τ_L or $\tau_I \approx 1/\omega_C$. When τ_I/τ_L <10, because of the closeness of the minimum positions of the two components there

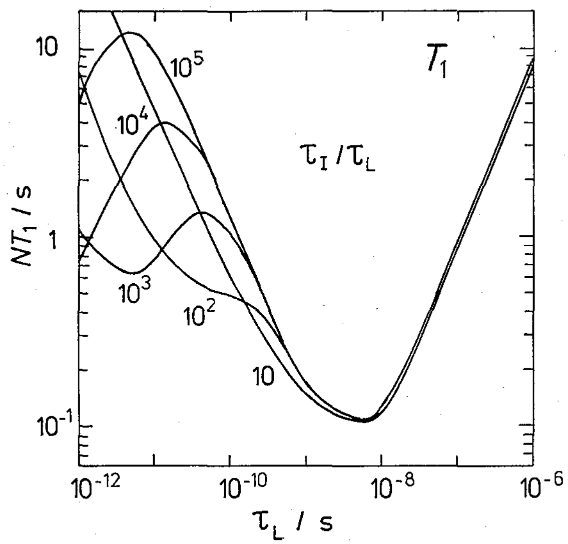

Fig. 4. NT_1 *vs.* τ_L for different values of τ_I/τ_L, when $\theta_L=60°$, $\tau_R=10^{-12}$ s, $\theta_R=30°$.

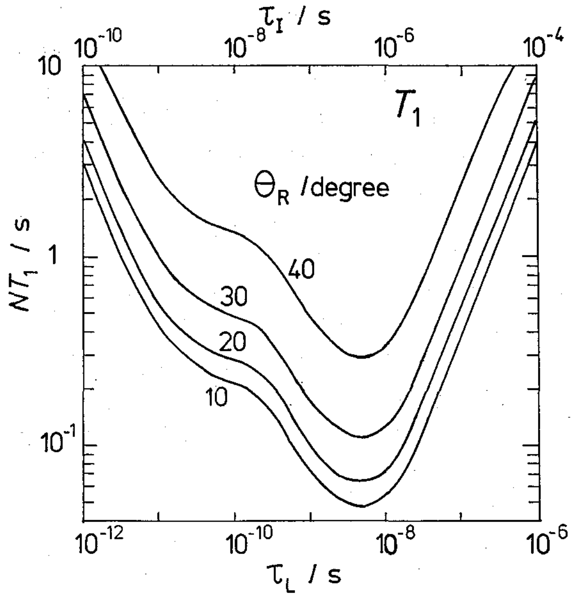

Fig. 5. NT_1 *vs.* τ_L for different values of θ_R, when $\tau_I/\tau_L=10^2$, $\theta_L=60°$, $\tau_R=10^{-12}$ s.

appears only one minimum. As the ratio τ_I/τ_L increases, the minimum relating to τ_I becomes distinguishable from that relating to τ_L. Furthermore, it is seen that, when $\tau_I/\tau_L>10^3$ the NT_1 vs. τ_L curves become nearly identical in the range of $\tau_L>2\times 10^{-10}$ s ($\tau_I>2\times10^{-7}$ s). This implies that the spherical random motion with a correlation time longer than 2×10^{-7} s has no effect on the value of NT_1 according to Eq. (33).

Figure 5 shows the relationship between NT_1 and τ_L for different θ_R's. It is evident that the value of θ_R determines primarily the value of NT_1 at the minimum.

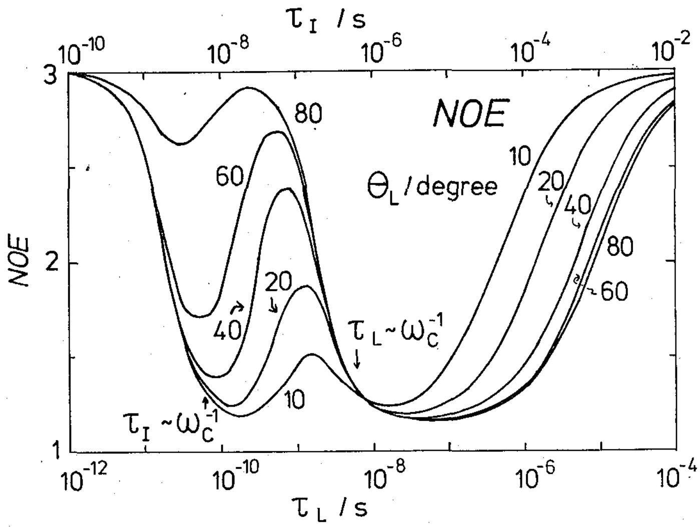

Fig. 6. NOE *vs.* τ_L for different values of θ_L, when $\tau_I/\tau_L=10^2$, $\tau_R=10^{-12}$ s, $\theta_R=30°$.

In Fig. 6 the value of NOE is plotted against τ_L for different θ_L's. As the value of τ_L increases from 10^{-12} s, the NOE's show minima as a result that τ_I reaches the order of $1/\omega_C$ and after passing maxima they again decrease until $\tau_L \approx 1/\omega_C$. With further increase of τ_L they increase again due to the random rotation with a fixed value of $\tau_R = 10^{-12}$ s. Figure 7 shows plots of NOE vs. τ_L for different ratios τ_I/τ_L. It is seen that the NOE's once approach 3 at $\tau_L \approx 10^{-10}$ s when $\tau_I/\tau_L = 10^3 \sim 10^5$.

In Fig. 8, the value of NT_2 is plotted against τ_I for different ratios τ_I/τ_L. It is seen that the value of NT_2 is determined by primarily τ_I, rather insensible to shorter correlation times τ_L and τ_R. This corresponds to the fact that NT_2 involves the term of zero-frequency spectral density according to Eq. (2) and the spherical random rotation with

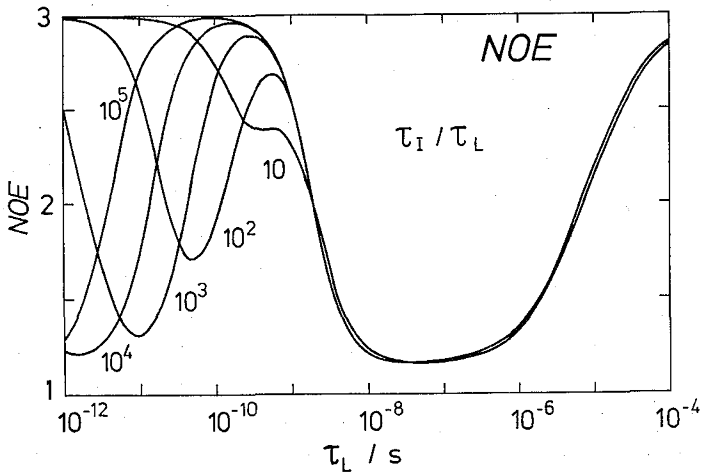

Fig. 7. NOE *vs.* τ_L for different values of τ_I/τ_L, when $\theta_L = 60°$, $\tau_R = 10^{-12}$ s, $\theta_R = 30°$.

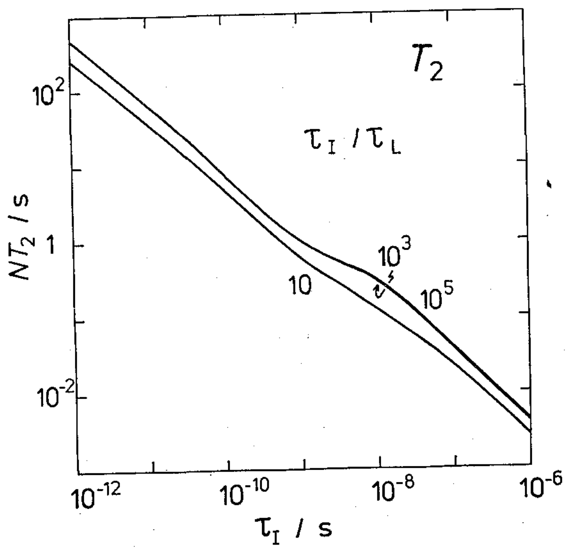

Fig. 8. NT_2 *vs.* τ_I different values of τ_I/τ_L, when $\theta_L = 60°$, $\tau_R = 10^{-12}$ s, $\theta_R = 30°$.

rather longer τ_I contributes to this term while other random motions with shorter τ_L or τ_R do not contribute to any spectral density.

APPENDIX 1

"Description of the Correlation Functions in the Form $F_m=\sum_{j,k=1}^{5} f_{jk}^{(m)}(\theta_1, \phi_1) g_{jk}^{(m)}(\theta_2, \phi_2) h_{jk}^{(m)}(\theta_3, \phi_3)$ as Listed in Table I."

If we define $\boldsymbol{C}$ to be the product $\boldsymbol{A}_3$ and $\boldsymbol{A}_2$, the direction cosines x, y and z are described as

$$\begin{aligned} x&=c_{11}x_1+c_{12}y_1+c_{13}z_1 \\ y&=c_{21}x_1+c_{22}y_1+c_{23}z_1 \\ z&=c_{31}x_1+c_{32}y_1+c_{33}z_1 \end{aligned} \tag{A–1}$$

Here, c_{ij} is the ij element of $\boldsymbol{C}$ defined as $c_{ij}=\sum_{k=1}^{3}(a_{ik})_3(a_{kj})_3$. Therefore, the correlation function for $m=0$ given by Eq. (5) is expressed as

$$\begin{aligned} F_0(t)&=1-3(c_{31}x_1+c_{32}y_1+c_{33}z_1)^2 \\ &=-(3/4)\alpha_{+1}\sin^2\theta_1 e^{2i\phi_1}-(3/4)\alpha_{-1}\sin^2\theta_1 e^{-2i\phi_1} \\ &\quad -3\alpha_{+2}\sin\theta_1\cos\theta_1 e^{i\phi_1}-3\alpha_{-2}\sin\theta_1\cos\theta_1 e^{-i\phi_1} \\ &\quad -(3/2)\alpha_3\sin^2\theta_1-\alpha_4 \end{aligned} \tag{A–2}$$

where

$$\begin{aligned} \alpha_{\pm1}&=(c_{31}\mp ic_{32})^2 \\ \alpha_{\pm2}&=(c_{31}\mp ic_{32})c_{33} \\ \alpha_3&=c_{31}{}^2+c_{32}{}^2-2c_{33}{}^2 \\ \alpha_4&=3c_{33}{}^2-1 \end{aligned} \tag{A–3}$$

Since by use of Eq. (11) c_{31}, c_{32} and c_{33} are described as functions of θ_2, ϕ_2 and θ_3, Eq. (A–3) reduces to

$$\begin{aligned} \alpha_{\pm1}&=(-\sin\theta_3\cos\theta_2\cos\phi_2-\cos\theta_3\sin\theta_2\mp i\sin\theta_3\sin\phi_2)^2 \\ &=(1/4)\sin^2\theta_3(\cos^2\theta_2\pm2\cos\theta_2+1)e^{2i\phi_2} \\ &\quad+(1/4)\sin^2\theta_3(\cos^2\theta_2\mp2\cos\theta_2+1)e^{-2i\phi_2} \\ &\quad+\sin\theta_3\cos\theta_3(\cos\theta_2\sin\theta_2\pm\sin\theta_2)e^{i\phi_2} \\ &\quad+\sin\theta_3\cos\theta_3(\cos\theta_2\sin\theta_2\mp\sin\theta_2)e^{-i\phi_2} \\ &\quad+(1/2)(3\cos^2\theta_3-1)\sin^2\theta_2 \end{aligned} \tag{A–4}$$

$$\begin{aligned} \alpha_{\pm2}&=(-\sin\theta_3\cos\theta_2\cos\phi_2-\cos\theta_3\sin\theta_2\mp i\sin\theta_3\sin\phi_2) \\ &\quad\times(-\sin\theta_3\sin\theta_2\cos\phi_2+\cos\theta_3\cos\theta_2) \\ &=(1/4)\sin^2\theta_3(\sin\theta_2\cos\theta_2\pm\sin\theta_2)e^{2i\phi_2} \\ &\quad+(1/4)\sin^2\theta_3(\sin\theta_2\cos\theta_2\mp\sin\theta_2)e^{-2i\phi_2} \\ &\quad-(1/2)\sin\theta_3\cos\theta_3(2\cos^2\theta_2\pm\cos\theta_2-1)e^{i\phi_2} \\ &\quad-(1/2)\sin\theta_3\cos\theta_3(2\cos^2\theta_2\mp\cos\theta_2-1)e^{-i\phi_2} \\ &\quad-(1/2)(3\cos^2\theta_3-1)\sin\theta_2\cos\theta_2 \end{aligned} \tag{A–5}$$

$$\alpha_3 = -(3/4)\sin^2\theta_3 \sin^2\theta_2 e^{2i\phi_2} - (3/4)\sin^2\theta_3 \sin^2\theta_2 e^{-2i\phi_2}$$
$$+3\sin\theta_3\cos\theta_3\sin\theta_2\cos\theta_2 e^{i\phi_2} + 3\sin\theta_3\cos\theta_3\sin\theta_2\cos\theta_2 e^{-i\phi_2}$$
$$-(1/2)(3\cos^2\theta_3 - 1)(3\cos^2\theta_2 - 1) \quad \text{(A-6)}$$

and

$$\alpha_4 = -\alpha_3 \quad \text{(A-7)}$$

Therefore, substitution of Eqs. (A-4), (A-5), (A-6), and (A-7) for $\alpha_{\pm1}$, $\alpha_{\pm2}$, α_3 and α_4 in Eq. (A-2) yields F_0 in the form $\sum_{j,k} f_{jk}\, g_{jk}\, h_{jk}$ as listed in Table I.

Similarly, the correlation function for $m=1$ (Eq. (5)) is given as

$$F_1(t) = \frac{1}{4}\beta_{+1}\sin^2\theta_1 e^{2i\phi_1} + \frac{1}{4}\beta_{-1}\sin^2\theta_1 e^{-2i\phi_1}$$
$$+\frac{1}{2}\beta_{+2}\sin\theta_1\cos\theta_1 e^{i\phi_1} + \frac{1}{2}\beta_{-2}\sin\theta_1\cos\theta_1\, e^{-i\phi_1}$$
$$+\frac{1}{2}\beta_3\sin^2\theta_1 + \beta_4 \quad \text{(A-8)}$$

with

$$\beta_{\pm1} = e^{i\phi_3}\Big[-\frac{1}{4}(\sin\theta_3\cos\theta_3 + \sin\theta_3)(\cos^2\theta_2 \pm 2\cos\theta_2 + 1)e^{2i\phi_2}$$
$$-\frac{1}{4}(\sin\theta_3\cos\theta_3 - \sin\theta_3)(\cos^2\theta_2 \mp 2\cos\theta_2 + 1)e^{-2i\phi_2}$$
$$-\frac{1}{2}(2\cos^2\theta_3 + \cos\theta_3 - 1)(\sin\theta_2\cos\theta_2 \pm \sin\theta_2)e^{i\phi_2}$$
$$-\frac{1}{2}(2\cos^2\theta_3 - \cos\theta_3 - 1)(\sin\theta_2\cos\theta_2 \mp \sin\theta_2)e^{-i\phi_2}$$
$$+\frac{3}{2}\sin\theta_3\cos\theta_3\sin^2\theta_2\Big] \quad \text{(A-9)}$$

$$\beta_{\pm2} = e^{i\phi_3}\Big[-\frac{1}{2}(\sin\theta_3\cos\theta_3 + \sin\theta_3)(\sin\theta_2\cos\theta_2 \pm \sin\theta_2)e^{2i\phi_2}$$
$$-\frac{1}{2}(\sin\theta_3\cos\theta_3 - \sin\theta_3)(\sin\theta_2\cos\theta_2 \mp \sin\theta_2)e^{-2i\phi_2}$$
$$+\frac{1}{2}(2\cos^2\theta_3 + \cos\theta_3 - 1)(2\cos^2\theta_2 \pm \cos\theta_2 - 1)e^{i\phi_2}$$
$$+\frac{1}{2}(2\cos^2\theta_3 - \cos\theta_3 - 1)(2\cos^2\theta_2 \mp \cos\theta_2 - 1)e^{-i\phi_2}$$
$$-3\sin\theta_3\cos\theta_3\sin\theta_2\cos\theta_2\Big] \quad \text{(A-10)}$$

$$\beta_3 = e^{i\phi_3}\Big[\frac{3}{4}(\sin\theta_3\cos\theta_3 + \sin\theta_3)\sin^2\theta_2 e^{2i\phi_2}$$
$$+\frac{3}{4}(\sin\theta_3\cos\theta_3 - \sin\theta_3)\sin^2\theta_2 e^{-2i\phi_2}$$
$$-\frac{3}{2}(2\cos^2\theta_3 + \cos\theta_3 - 1)\sin\theta_2\cos\theta_2 e^{i\phi_2}$$
$$-\frac{3}{2}(2\cos^2\theta_3 - \cos\theta_2 - 1)\sin\theta_2\cos\theta_2 e^{-i\phi_2}$$

$$-\frac{3}{2}\sin\theta_3\cos\theta_3(3\cos^2\theta_2-1)\Big] \tag{A-11}$$

$$\beta_4=-\frac{1}{3}\beta_3 \tag{A-12}$$

Furthermore, the correlation function for $m=2$ (Eq. (5)) is

$$\begin{aligned}F_2(t)=&\frac{1}{4}\gamma_{+1}\sin^2\theta_1 e^{2i\phi_1}+\frac{1}{4}\gamma_{-1}\sin^2\theta_1 e^{-2i\phi_1}\\&+\gamma_{+2}\sin\theta_1\cos\theta_1 e^{i\phi_1}+\gamma_{-2}\sin\theta_1\cos\theta_1 e^{-i\phi_1}\\&+\frac{1}{2}\gamma_3\sin^2\theta_1+\gamma_4\end{aligned} \tag{A-13}$$

with

$$\begin{aligned}\gamma_{\pm1}=e^{2i\phi_3}\Big[&\frac{1}{4}(\cos^2\theta_3+2\cos\theta_2+1)(\cos^2\theta_2\pm2\cos\theta_2+1)e^{2i\phi_2}\\&+\frac{1}{4}(\cos^2\theta_3-2\cos\theta_2+1)(\cos^2\theta_2\mp2\cos\theta_2+1)e^{-2i\phi_2}\\&-(\sin\theta_3\cos\theta_3+\sin\theta_3)(\sin\theta_2\cos\theta_2\pm\sin\theta_2)e^{i\phi_2}\\&-(\sin\theta_3\cos\theta_3-\sin\theta_3)(\sin\theta_2\cos\theta_2\mp\sin\theta_2)e^{-i\phi_2}\\&+\frac{3}{2}\sin^2\theta_3\sin{}^2\theta_2\Big]\end{aligned} \tag{A-14}$$

$$\begin{aligned}\gamma_{\pm2}=e^{2i\phi_3}\Big[&\frac{1}{4}(\cos^2\theta_3+2\cos\theta_3+1)(\sin\theta_2\cos\theta_2\pm\sin\theta_2)e^{2i\phi_2}\\&+\frac{1}{4}(\cos^2\theta_3-2\cos\theta_3+1)(\sin\theta_2\cos\theta_2\mp\sin\theta_2)e^{-2i\phi_2}\\&+\frac{1}{2}(\sin\theta_3\cos\theta_3+\sin\theta_3)(2\cos^2\theta_2\pm\cos\theta_2-1)e^{i\phi_2}\\&+\frac{1}{2}(\sin\theta_3\cos\theta_3-\sin\theta_3)(2\cos^2\theta_2\mp\cos\theta_2-1)e^{-i\phi_2}\\&-\frac{3}{2}\sin^2\theta_3\sin\theta_2\cos\theta_2\Big]\end{aligned} \tag{A-15}$$

$$\begin{aligned}\gamma_3=e^{2i\phi_3}\Big[&-\frac{3}{4}(\cos^2\theta_3+2\cos\theta_3+1)\sin^2\theta_2 e^{2i\phi_2}\\&-\frac{3}{4}(\cos^2\theta_3-2\cos\theta_3+1)\sin^2\theta_2 e^{-2i\phi_2}\\&-3(\sin\theta_3\cos\theta_3+\sin\theta_3)\sin\theta_2\cos\theta_2 e^{i\phi_2}\\&-3(\sin\theta_3\cos\theta_3-\sin\theta_3)\sin\theta_2\cos\theta_2 e^{-i\phi_2}\\&-\frac{3}{2}\sin^2\theta_3(3\cos^2\theta_2-1)\Big]\end{aligned} \tag{A-16}$$

$$\gamma_4=-\frac{1}{3}\gamma_3 \tag{A-17}$$

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