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

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Received June 10, 1983

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 13C 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 1H and 13C is predominantly achieved by the time-fluctuation of the dipole-dipole interaction between the spin-having nuclei. Particularly in natural abundance 13C nmr the spin relaxation is predominantly carried out by the dipole-dipole interaction between chemically bonded 13C and 1H, because the interaction between 13C 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 distinguishable with each other in 13C 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 13C relaxation phenomena of polymers such as terephthalic acid polyesters1) and polyethylene2,3) 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 model4) to Woessner's 2-τ rotational model6,7) 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 $^{13}\text{C}$ spin relaxation parameters on substances including only $^{13}\text{C}$ and $^1\text{H}$ 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.

\[
\frac{1}{N T_1} = \frac{\gamma_c^2 \gamma_H^2 h^2}{16 \pi^6} \left[ J_0(\omega_H - \omega_C) + 18 J_1(\omega_C) + 9 J_2(\omega_H + \omega_C) \right] 
\]

\[
\frac{1}{N T_2} = \frac{\gamma_c^2 \gamma_H^2 h^2}{32 \pi^6} \left[ 4 J_0(0) + J_0(\omega_H - \omega_C) + 18 J_1(\omega_C) + 36 J_1(\omega_H) + 9 J_2(\omega_H + \omega_C) \right] 
\]

\[
\text{NOE} = \frac{9 J_2(\omega_H + \omega_C) - J_0(\omega_H - \omega_C)}{J_0(\omega_H - \omega_C) + 18 J_1(\omega_C) + 9 J_2(\omega_H + \omega_C)} \cdot \frac{\gamma_H}{\gamma_C} 
\]

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

\[
J_m(\omega) = \int_{-\infty}^{\infty} \langle F_m(\tau) F_m(t) \rangle \exp(i\omega \tau) d\tau 
\]

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 $H_0$;

\[
F_0 = 1 - 3s^2 \\
F_1 = (x + iy)s \\
F_2 = (x + iy)^2
\]

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 $\langle F_m(\tau + \tau) F_m(\tau) \rangle$ are considered to be independent of $\tau$ and dependent only on the time difference $\tau$, so far as concerned with the spin ensemble in a steady state. If the C-H vector undergoes a spherical random rotation, the correlation functions follow simple exponential decay and the spectral densities for all $m$'s are described as
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\[ J_n(\omega) = \langle |F_n(t)|^2 \rangle \frac{2\tau_I}{1 + \omega^2 \tau_I^2} \]  

(6)

where \( \tau_I \) 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 \( \tau_I \) 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 \( S_1, S_2, \ldots, S_k \) 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 \( S_i \) is transformed to the \( S_{i-1} \) by Euler angles \( \phi_j, \theta_j \) and \( \psi_j \) 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 \( x_1, y_1, z_1 \) in the frame \( S_1 \) by

\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} = A_k A_{k-1} \ldots A_2 \begin{pmatrix}
  x_1 \\
  y_1 \\
  z_1
\end{pmatrix}
\]  

(7)

where \( A_i \) is the inverse matrix of the orthogonal transformation matrix that transforms \( S_i \) to \( S_{i-1} \). The matrix \( A_i \) are expressed as

\[
A_i = \begin{bmatrix}
\cos \phi_i & \sin \phi_i & 0 \\
\sin \phi_i \cos \theta_i & \cos \phi_i \cos \theta_i & \sin \phi_i \sin \psi_i \\
-\sin \psi_i & \cos \psi_i & 0
\end{bmatrix}
\]  

(8)

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

![Fig. 1. Schematic diagram of 3-\( \tau \) model for the motion of the internuclear C-H vector.](231)
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-\( \tau \) motion" of \( r \) which was proposed by Howarth \(^4\) by connecting his "2\( \tau \) librational motion" to "Woessner's 2\( \tau \) 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 \( \theta_R \), and the axis \( A \) further librates about another axis \( B \) within a solid cone of a vertical angle \( \theta_L \) (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

\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} = A_2 \cdot A_3 \begin{pmatrix}
  x_1 \\
  y_1 \\
  z_1
\end{pmatrix}
\]

with

\[
\begin{aligned}
x_1 &= \cos \phi_1 \sin \theta_1 \\
y_1 &= \sin \phi_1 \sin \theta_1 \\
z_1 &= \cos \theta_1 \\
\theta_1 &= \theta_R
\end{aligned}
\]

Let the axes \( A \) and \( B \) the z-axes in the frames \( S_1 \) and \( S_2 \), respectively, then the angles \( \phi_2 \) and \( \phi_3 \) 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

\[
A_i = \begin{pmatrix}
  \cos \phi_i \cos \theta_i & -\sin \phi_i & \cos \phi_i \sin \theta_i \\
  \sin \phi_i \cos \theta_i & \cos \phi_i & \sin \phi_i \sin \theta_i \\
  -\sin \theta_i & 0 & \cos \theta_i
\end{pmatrix}
\]

for \( i = 2 \) and 3.

Here, \( \theta_i \) and \( \phi_i \) are considered to fluctuate at random with time in the ranges of \( \theta_2 = 0 \sim \theta_{i2}, \phi_2 = 0 \sim 2\pi \), 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

\[
F_m(t) = \sum_{j,k=1}^{5} F^{(m)}_{jk}(t) g^{(m)}(t) h^{(m)}_{jk}(t)
\]

Here \( F^{(m)}_{jk}(t) \) are the functions of \( \theta_i \) and \( \phi_i \) arising from the stochastic rotational motion of \( r \), and \( g^{(m)}(t) \) are the functions of \( \theta_3 \) and \( \phi_3 \) arising from the librational motion of the axis \( A \), and \( h^{(m)}_{jk}(t) \) are the functions of \( \theta_3 \) and \( \phi_3 \) arising from the spherical motion of the axis \( B \). The functions \( F^{(m)}_{jk}(t), g^{(m)}(t) \) and \( h^{(m)}_{jk}(t) \) 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) \( m = 0 \)

<table>
<thead>
<tr>
<th>( f_{jk} )</th>
<th>( g_{jk} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{1k} = -3(3/4) \sin^2 \theta_1 e^{i2 \theta_1} )</td>
<td>( g_{11} = (1/2)(\cos^2 \theta_2 + 2 \cos \theta_2 + 1)e^{i4 \theta_2} )</td>
</tr>
<tr>
<td>( f_{2k} = -3(3/4) \sin^2 \theta_1 e^{-i2 \theta_1} )</td>
<td>( g_{12} = (1/2)(\cos^2 \theta_2 - 2 \cos \theta_2 + 1)e^{-i4 \theta_2} )</td>
</tr>
<tr>
<td>( f_{3k} = -3 \sin \theta_1 \cos \theta_1 e^{i \theta_1} )</td>
<td>( g_{13} = (\sin \theta_1 \cos \theta_2 + \sin \theta_2)e^{i \theta_1} )</td>
</tr>
<tr>
<td>( f_{4k} = -3 \sin \theta_1 \cos \theta_1 e^{-i \theta_1} )</td>
<td>( g_{14} = (\sin \theta_1 \cos \theta_2 - \sin \theta_2)e^{-i \theta_1} )</td>
</tr>
<tr>
<td>( f_{5k} = -(1/2)(3 \cos^2 \theta_1 - 1) )</td>
<td>( g_{15} = -\sqrt{3}/2 \sin^2 \theta_2 )</td>
</tr>
<tr>
<td>( \text{for all } k's )</td>
<td>( \text{for all } k's )</td>
</tr>
<tr>
<td>( h_{1j} = (1/2) \sin^2 \theta_2 )</td>
<td>( g_{21} = (1/2)(\cos^2 \theta_2 - 2 \cos \theta_2 + 1)e^{i \theta_2} )</td>
</tr>
<tr>
<td>( h_{2j} = \sin \theta_2 \cos \theta_2 )</td>
<td>( g_{22} = (1/2)(\cos^2 \theta_2 - 2 \cos \theta_2 + 1)e^{-i \theta_2} )</td>
</tr>
<tr>
<td>( h_{3j} = \sin \theta_2 \cos \theta_2 )</td>
<td>( g_{23} = (\sin \theta_1 \cos \theta_2 + \sin \theta_2)e^{i \theta_2} )</td>
</tr>
<tr>
<td>( h_{4j} = -\sqrt{1/6} (3 \cos^2 \theta_3 - 1) )</td>
<td>( g_{24} = (\sin \theta_1 \cos \theta_2 - \sin \theta_2)e^{-i \theta_2} )</td>
</tr>
<tr>
<td>( \text{for all } j's )</td>
<td>( \text{for all } j's )</td>
</tr>
</tbody>
</table>

(b) \( m = 1 \)

<table>
<thead>
<tr>
<th>( f_{jk} )</th>
<th>( g_{jk} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{1k} = (1/4) \sin^2 \theta_1 e^{i2 \theta_1} )</td>
<td>( g_{11} = -\sqrt{3}/8 (\cos^2 \theta_2 + 2 \cos \theta_2 + 1)e^{i4 \theta_2} )</td>
</tr>
<tr>
<td>( f_{2k} = (1/4) \sin^2 \theta_1 e^{-i2 \theta_1} )</td>
<td>( g_{12} = -\sqrt{3}/8 (\cos^2 \theta_2 - 2 \cos \theta_2 + 1)e^{-i4 \theta_2} )</td>
</tr>
<tr>
<td>( f_{3k} = (1/2) \sin \theta_1 \cos \theta_1 e^{i \theta_1} )</td>
<td>( g_{13} = \sqrt{3}/2 (\sin \theta_1 \cos \theta_2 + \sin \theta_2)e^{i \theta_1} )</td>
</tr>
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<td>( f_{4k} = (1/2) \sin \theta_1 \cos \theta_1 e^{-i \theta_1} )</td>
<td>( g_{14} = \sqrt{3}/2 (\sin \theta_1 \cos \theta_2 - \sin \theta_2)e^{-i \theta_1} )</td>
</tr>
<tr>
<td>( f_{5k} = -(1/2)(3 \cos^2 \theta_1 - 1) )</td>
<td>( g_{15} = (3/2) \sin^2 \theta_2 )</td>
</tr>
<tr>
<td>( \text{for all } k's )</td>
<td>( \text{for all } k's )</td>
</tr>
<tr>
<td>( h_{1j} = \sqrt{1/6} (\sin \theta_2 \cos \theta_3 + \sin \theta_2)e^{i \theta_2} )</td>
<td>( g_{21} = -\sqrt{3}/8 (\cos^2 \theta_2 - 2 \cos \theta_2 + 1)e^{i \theta_2} )</td>
</tr>
<tr>
<td>( h_{2j} = \sqrt{1/6} (\sin \theta_2 \cos \theta_3 - \sin \theta_2)e^{i \theta_2} )</td>
<td>( g_{22} = -\sqrt{3}/8 (\cos^2 \theta_2 + 2 \cos \theta_2 + 1)e^{-i \theta_2} )</td>
</tr>
<tr>
<td>( h_{3j} = -\sqrt{1/6} (2 \cos^2 \theta_3 + \cos \theta_3 - 1)e^{i \theta_2} )</td>
<td>( g_{23} = \sqrt{3}/2 (\sin \theta_2 \cos \theta_2 + \sin \theta_2)e^{i \theta_2} )</td>
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<td>( g_{24} = \sqrt{3}/2 (\sin \theta_2 \cos \theta_2 - \sin \theta_2)e^{-i \theta_2} )</td>
</tr>
<tr>
<td>( h_{5j} = \sin \theta_2 \cos \theta_2 e^{i \theta_2} )</td>
<td>( g_{25} = (3/2) \sin^2 \theta_2 )</td>
</tr>
<tr>
<td>( \text{for all } j's )</td>
<td>( \text{for all } j's )</td>
</tr>
</tbody>
</table>
\[
\langle F_m^* (t) F_m(t) \rangle 
\]
\[
= \langle \left\{ \sum_{i,j,k} f_{j,k}^m (t) g_{j,k}^m (t) \delta_{ij} (t) \right\}^* \left\{ \sum_{i,n} f_{i,n}^m (t) g_{i,n}^m (t) \delta_{in} (t) \right\} \rangle 
\]
\[
= \sum_{i,j,k} \langle f_{j,k}^m (t) \rangle \langle f_{j,k}^m (t) \rangle \langle g_{j,k}^m (t) \rangle \langle g_{j,k}^m (t) \rangle \langle \delta_{ij} (t) \rangle \langle \delta_{in} (t) \rangle 
\]
\[
= \sum_{i,j,k} \langle f_{j,k}^m (t) \rangle \langle g_{j,k}^m (t) \rangle \langle \delta_{ij} (t) \rangle \langle \delta_{in} (t) \rangle 
\]
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 \( p(\phi_1 + \Delta \phi_1, \tau) \) that \( \phi_1 \) takes a value of \( \phi_1 + \Delta \phi_1 \) at time \( t+\tau \) when \( \phi_1 \) was \( \phi_1 \) at an arbitrary time \( t \) will be given by a Gaussian distribution as\(^6\)

\[
p(\phi_1 + \Delta \phi_1, \tau) = \frac{1}{\sqrt{2\pi\tau R}} e^{-\frac{(\phi_1 + \Delta \phi_1 - \phi_1)^2}{2\tau R}}
\]

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

\[
\langle f^{* m}(t+\tau)f^{m}_{in}(t) \rangle = \int f^{* m}(\phi_1 + \Delta \phi_1) p(\phi_1 + \Delta \phi_1, \tau) d\Delta \phi_1
\]

\[
= K \langle f^{* m}(\phi_1 + \Delta \phi_1) f^{m}_{in}(\phi_1) \rangle
\]

with

\[
K = e^{-\frac{4j\Omega}{R}} \quad \text{for} \quad j = 1 \text{ or } 2
\]

\[
e^{-\frac{4j\Omega}{R}} \quad \text{for} \quad j = 3 \text{ or } 4
\]

\[
e^{-\frac{1}{2}\Omega} \quad \text{for} \quad j = 5
\]

\[
e^{-\frac{1}{2}\Omega} \quad \text{for} \quad j \neq I
\]

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 \( \phi_1 \) so far as concerned with a steady state, it is evident from Table I that \( \langle f^{* m}(t+\tau)f^{m}_{in}(t) \rangle \) becomes zero unless \( j = I \). On the other hand, when \( j = I \), Eq. (15) reduces to

\[
\langle f^{* m}(t+\tau)f^{m}_{in}(t) \rangle = K \langle f^{* m}(\phi_1 + \Delta \phi_1) f^{m}_{in}(\phi_1) \rangle
\]

\[
= K \langle f^{* m}(\phi_1 + \Delta \phi_1) f^{m}_{in}(\phi_1) \rangle
\]

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

\[
\langle f^{* (0)}(t+\tau)f^{(0)}_{in}(t) \rangle = \frac{3}{4} C R e^{-\frac{4j\Omega}{R}} \quad \text{for} \quad j = 1, 2
\]

\[
= 3B R e^{-\frac{1}{2}\Omega} \quad \text{for} \quad j = 3, 4
\]

\[
= A_R \quad \text{for} \quad j = 5
\]

\[
\langle f^{* (1)}(t+\tau)f^{(1)}_{in}(t) \rangle = \frac{1}{12} C R e^{-\frac{4j\Omega}{R}} \quad \text{for} \quad j = 1, 2
\]

\[
= \frac{1}{12} B R e^{-\frac{1}{2}\Omega} \quad \text{for} \quad j = 3, 4
\]

\[
= A_R \quad \text{for} \quad j = 5
\]

\[
\langle f^{* (2)}(t+\tau)f^{(2)}_{in}(t) \rangle = \frac{1}{12} C R e^{-\frac{4j\Omega}{R}} \quad \text{for} \quad j = 1, 2
\]

\[
= \frac{1}{3} B R e^{-\frac{1}{2}\Omega} \quad \text{for} \quad j = 3, 4
\]

\[
= A_R \quad \text{for} \quad j = 5
\]

where

(235)
Next consider the correlation functions of the $g$ functions. The A-axis in the frame $S_2$ can be defined by $\theta_2$ that is the angle to z-axis (B-axis) and $\phi_2$ 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 $\theta_2$ about itself and rotation of $\phi_2$ about y-axis of $S_1$. Let the position at $\theta_2, \phi_2$ be represented by a solid angle $\Omega(\theta_2, \phi_2)\seteq 2\sin \theta_2 d\theta_2 d\phi_2$, $0\leq \theta_2 \leq \pi, 0\leq \phi_2 \leq 2\pi$. In the librational motion assumed here, if the A-axis was at $\Omega_0$ at time $t$, the probability that the A-axis still remains at $\Omega_0$ can be considered to be $e^{-t/r_L}$ and the probability finding the A-axis at another position $\Omega_1$ at time $t+\tau$ be $1-e^{-t/r_L}$. Accordingly, the correlation functions of the $g$ functions can be written as

$$
<g_{jk}(t+\tau)g_{in}(t)> = \left< \left[ \int_{\Omega_1} \sigma_{jk}(\Omega_1)(1-e^{-t/r_L})d\Omega_1 + \sigma_{jk}(\Omega_0)e^{-t/r_L} \right] \sigma_{in}(\Omega) \right>_{\Omega} = (1-e^{-t/r_L})\left< \sigma_{jk}(\Omega_1)\sigma_{in}(\Omega) \right>_{\Omega} + e^{-t/r_L}\left< \sigma_{jk}(\Omega_0)\sigma_{in}(\Omega) \right>_{\Omega} = (1-e^{-t/r_L})\left< \sigma_{jk}(\Omega_1)\sigma_{in}(\Omega_0) + e^{-t/r_L}\sigma_{jk}(\Omega_0)\sigma_{in}(\Omega) \right>_{\Omega}
$$

Here, the average of the spin ensemble at an arbitrary time is assumed to be equivalent to the average over available values of $\Omega_0$ and $\Omega_1$.

It is found by examining the $g$ functions in Table I that $<g_{jk}(\Omega_1)\sigma_{in}(\Omega_0)> = 0$ unless $k=5, n=5$ and that $<g_{jk}(\Omega_0)\sigma_{in}(\Omega_0)> = 0$ unless $k=n$.

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

$$
<F_{m}(t+\tau)F_{m}(t)> = \left< \sum_{j,k} f_{jk}^{*}(t+\tau)f_{jk}^{*}(t)g_{jk}^{*}(t+\tau)g_{jk}(t)h_{jk}^{*}(t+\tau)h_{jk}(t) \right> (21)
$$

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

$$
<|h_{jk}^{*}(t+\tau)|^2> = <|h_{jk}(t)|^2> e^{-t/r_L} (22)
$$

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

$$
<|h_{jk}(t)|^2> = \int_{\theta_3=0}^{\pi} \int_{\phi_3=0}^{2\pi} h_{jk}^{*}(\theta_3, \phi_3)^2 \sin \theta_3 d\theta_3 d\phi_3 / \int_{\theta_3=0}^{\pi} \int_{\phi_3=0}^{2\pi} \sin \theta_3 d\theta_3 d\phi_3
$$

By use of Table I, we have

$$
<|h_{jk}^{*}(t)|^2> = 2/15 (23)
$$

for all $m$'s.

Therefore, Eq. (21) can be rewritten as
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\[ \langle F_m^{(n)}(t+\tau)F_m(t) \rangle = \frac{2}{15} e^{-\tau/\tau_1} \sum_j \left[ \langle f_j^{(n)}(t+\tau) f_j^{(n)}(t) \rangle \sum_k \langle g_j^{(m)(n)}(t+\tau) g_j^{(m)(n)}(t) \rangle \right] \]  \tag{24} \]

where \( \langle f_j^{(n)}(t+\tau) f_j^{(n)}(t) \rangle \) 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

\[ \sum_k \langle g_j^{(m)(n)}(t+\tau) g_j^{(m)(n)}(t) \rangle \]

\[ = (1-e^{-\tau/\tau_L}) \langle g_j^{(m)}(O) \rangle \Delta + e^{-\tau/\tau_L} \sum_k \langle g_j^{(m)}(O) g_j^{(m)}(O) \rangle \Delta \]

\[ = (1-e^{-\tau/\tau_L}) \langle g_j^{(m)}(O) \rangle \Delta^2 + e^{-\tau/\tau_L} \sum_k \langle | g_j^{(m)}(O) |^2 \rangle \Delta \]  \tag{25} \]

Here, the average of \( g_j^{(m)}(O) \) and \( | g_j^{(m)}(O) |^2 \) over \( O \) can be carried out by the relation,

\[ \langle \Phi(O) \rangle_\Delta = \frac{\int_\Delta \Phi(\Omega) d\Omega}{\int_\Delta d\Omega} \]

\[ = \int_0^{\pi/2} \int_0^{\pi/2} \Phi(\theta, \phi_0) \sin \theta d\theta d\phi_0 / \int_0^{\pi/2} \int_0^{\pi/2} \sin \theta d\theta d\phi_0 \]

where \( \Phi(O) = g_j^{(m)}(O) \) or \( | g_j^{(m)}(O) |^2 \).

An actual calculation yields,

\[ \langle g_j^{(0)} \rangle^2 = 4C_L \quad \text{for } j=1, 2 \]

\[ = B_L \quad \text{for } j=3, 4 \]

\[ = 6A_L \quad \text{for } j=5 \]

\[ \langle g_j^{(1)} \rangle^2 = 6C_L \quad \text{for } j=1, 2 \]

\[ = 6B_L \quad \text{for } j=3, 4 \]

\[ = A_L \quad \text{for } j=5 \]

\[ \langle g_j^{(2)} \rangle^2 = 24C_L \quad \text{for } j=1, 2 \]

\[ = 6B_L \quad \text{for } j=3, 4 \]

\[ = 4A_L \quad \text{for } j=5 \]  \tag{26} \]

where

\[ A_L = \cos^2 \theta_L (1+\cos \theta_L)^2 / 4 \]

\[ B_L = \sin^2 \theta_L (1+\cos \theta_L)^2 / 6 \]

\[ C_L = (\cos \theta_L + 2)^2 (\cos \theta_L - 1)^2 / 24 \]  \tag{27} \]

and, for example,

\[ \sum_k | g_j^{(0)} |^2 = 4 \quad \text{for } j=1, 2 \]

\[ = 1 \quad \text{for } j=3, 4 \]

\[ = 6 \quad \text{for } j=5 \]  \tag{28} \]
Substitution of Eqs. (26) and (28) in Eq. (25) yields
\[ \sum_k \langle g^{(0)}_{jk}(t+\tau) g^{(0)}_{jk}(t) \rangle = 4[C_L + (1-C_L)e^{-i\tau/T_L}] \text{ for } j=1, 2 \]
\[ = B_L + (1-B_L)e^{-i\tau/T_L} \text{ for } j=3, 4 \]
\[ = 6(A_L + (1-A_L)e^{-i\tau/T_L}) \text{ for } j=5 \]
\[ \sum_k \langle g^{(1)}_{jk}(t+\tau) g^{(1)}_{jk}(t) \rangle = 6[C_L + (1-C_L)e^{-i\tau/T_L}] \text{ for } j=1, 2 \]
\[ = B_L + (1-B_L)e^{-i\tau/T_L} \text{ for } j=3, 4 \]
\[ = A_L + (1-A_L)e^{-i\tau/T_L} \text{ for } j=5 \]
\[ \sum_k \langle g^{(2)}_{jk}(t+\tau) g^{(2)}_{jk}(t) \rangle = 24[C_L + (1-C_L)e^{-i\tau/T_L}] \text{ for } j=1, 2 \]
\[ = 6(B_L + (1-B_L)e^{-i\tau/T_L}) \text{ for } j=3, 4 \]
\[ = 4(A_L + (1-A_L)e^{-i\tau/T_L}) \text{ for } j=5 \]

Substitution of Eq. (29) in Eq. (24) with Eq. (18) yields the correlation functions of the orientation functions of the C-H vector,
\[ \langle F_m^*(t+\tau) F_m(t) \rangle = K_m[A_R A_L e^{-i\tau/T_L} + A_R (1-A_L)e^{-i\tau/T_1} + B_R B_L e^{-i\tau/T_2} + B_R (1-B_L)e^{-i\tau/T_3} + C_R C_L e^{-i\tau/T_4} + C_R (1-C_L)e^{-i\tau/T_5}] \]

with
\[ K_0 = 4/5 \]
\[ K_1 = 2/15 \]
\[ K_2 = 8/15 \]

and
\[ \tau_1^{-1} = \tau_L^{-1} + \tau_L^{-1} \]
\[ \tau_2^{-1} = \tau_R^{-1} + \tau_L^{-1} \]
\[ \tau_3^{-1} = \tau_R^{-1} + \tau_L^{-1} + \tau_L^{-1} \]
\[ \tau_4^{-1} = 4\tau_R^{-1} + \tau_L^{-1} \]
\[ \tau_5^{-1} = 4\tau_R^{-1} + \tau_L^{-1} + \tau_L^{-1} \]

Fourier transformation of \( \langle F_m^*(t+\tau) F_m(t) \rangle \) yields the spectral densities as
\[ J_m(\omega) = K_m A_R A_L \frac{2\tau_1}{1+\omega^2\tau_1^2} + A_R (1-A_L) \frac{2\tau_1}{1+\omega^2\tau_1^2} + B_R B_L \frac{2\tau_2}{1+\omega^2\tau_2^2} + B_R (1-B_L) \frac{2\tau_2}{1+\omega^2\tau_2^2} + C_R C_L \frac{2\tau_4}{1+\omega^2\tau_4^2} + C_R (1-C_L) \frac{2\tau_5}{1+\omega^2\tau_5^2} \]

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 \( \tau_I, \tau_L, \tau_R \)
that describe the respective independent motions involving in the "3-t 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,\textsuperscript{4) connecting intuitively the formula of Weossner's 2$t \tau$ rotational motion to that of his 2$t \tau$ 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 $\theta_L$. Therefore, the Howarth's equation is not valid in general. Nevertheless, when $\tau_1$ and $\tau_L$ are much larger than $\tau_{R}(\tau_1, \tau_L \gg \tau_{R})$, $\tau_2$, $\tau_3 \approx \tau_8$ and $\tau_4, \tau_5 \approx \tau_8 / 4$ and the terms including $B_8B_L$, $C_8C_L$ in Eq. (33) can be neglected in comparison with the terms including only $B_8$ and $C_8$, respectively. Accordingly, in such a case Eq. (33) becomes equivalent to the Howarth's equation. Hence, our previous analysis\textsuperscript{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-$\tau$ model. In Fig. 3 the value of $NT_1$ is plotted against $\tau_L$ for different $\theta_L$'s while other parameters are fixed as $\tau_1/\tau_L=10^3$, $\tau_R=10^{-13}s$, $\theta_R=30^\circ$. The parameters fixed here roughly correspond to those determined for real polyethylene samples\textsuperscript{6,7,8)} as the most probable values. The $NT_1$ shows single minimum at about $5 \times 10^{-11}$ s of $\tau_L$ when $\theta_L<10^\circ$ but an additional minimum appears at about $5 \times 10^{-9}$ s with increasing $\theta_L$. The latter minimum at $5 \times 10^{-9}$ s remains while the former minimum disappears with further increasing $\theta_L$ above $80^\circ$. It is noted here that $\tau_L$ of $5 \times 10^{-11}$ s for the former minimum corresponds to $5 \times 10^{-9}$ s of $\tau_I$ which is equivalent to the value of $\tau_L$ for the latter minimum and the value of $5 \times 10^{-9}$ s is roughly equivalent to $1/\omega_C(\approx 6 \times 10^{-9}$ s).
Hence it is concluded that the minimum of $NT_1$ appears when the value of $\tau_I$ or $\tau_L$ reaches the reciprocal of the Larmor frequency of $^{13}$C.

Figure 4 indicates the dependence of $NT_1$ on $\tau_L$ for different ratios $\tau_I/\tau_L$ when other parameters are fixed as $\theta_L=60^\circ$, $\theta_R=30^\circ$, $\tau_R=10^{-12}$ s. Each curve seems to comprise two components involving the minimum value at either $\tau_L$ or $\tau_I=1/\omega_C$. When $\tau_I/\tau_L < 10$, because of the closeness of the minimum positions of the two components there
appears only one minimum. As the ratio $\tau_i/\tau_L$ increases, the minimum relating to $\tau_i$ becomes distinguishable from that relating to $\tau_L$. Furthermore, it is seen that, when $\tau_i/\tau_L>10^3$ the $N\tau_1$ vs. $\tau_L$ curves become nearly identical in the range of $\tau_L>2 \times 10^{-7} s$ ($\tau_i>2 \times 10^{-7} s$). This implies that the spherical random motion with a correlation time longer than $2 \times 10^{-7} s$ has no effect on the value of $N\tau_1$ according to Eq. (33).

Figure 5 shows the relationship between $N\tau_1$ and $\tau_L$ for different $\theta_R$'s. It is evident that the value of $\theta_R$ determines primarily the value of $N\tau_1$ at the minimum.

![Graph showing $N\tau_1$ vs. $\tau_L$](image)

Fig. 5. $N\tau_1$ vs. $\tau_L$ for different values of $\theta_R$, when $\tau_i/\tau_L=10^2$, $\theta_L=60^\circ$, $\tau_R=10^{-12} s$.

![Graph showing NOE vs. $\tau_L$](image)

Fig. 6. NOE vs. $\tau_L$ for different values of $\theta_L$, when $\tau_i/\tau_L=10^2$, $\theta_R=10^{-12} s$, $\theta_R=30^\circ$. (241)
In Fig. 6 the value of NOE is plotted against $\tau_L$ for different $\theta_L$'s. As the value of $\tau_L$ increases from $10^{-12}$ s, the NOE's show minima as a result that $\tau_i$ 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 $\tau_L$ 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. $\tau_L$ for different ratios $\tau_i/\tau_L$. 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 $\tau_i$ for different ratios $\tau_i/\tau_L$. It is seen that the value of $NT_2$ is determined by primarily $\tau_i$, rather insensible to shorter correlation times $\tau_L$ and $\tau_R$. 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

![Figure 7: NOE vs. $\tau_L$ for different values of $\tau_i/\tau_L$, when $\theta_L=60^\circ$, $\tau_R=10^{-12}$ s, $\theta_R=30^\circ$.](image7)

![Figure 8: $NT_2$ vs. $\tau_i$ different values of $\tau_i/\tau_L$, when $\theta_L=60^\circ$, $\tau_R=10^{-12}$ s, $\theta_R=30^\circ$.](image8)
rather longer $\tau_l$ contributes to this term while other random motions with shorter $\tau_L$ or $\tau_k$ do not contribute to any spectral density.

**APPENDIX 1**

"Description of the Correlation Functions in the Form $F_m = \sum_{j,k=1}^{3} f_j^{(m)}(\theta_1, \phi_1) g_j^{(m)}(\theta_2, \phi_2) h_j^{(m)}(\theta_3, \phi_3)$ as Listed in Table I."

If we define $C$ to be the product $A_3$ and $A_2$, the direction cosines $x$, $y$ and $z$ are described as

$$x = c_{11}x_1 + c_{12}y_1 + c_{13}z_1$$
$$y = c_{21}x_1 + c_{22}y_1 + c_{23}z_1$$
$$z = c_{31}x_1 + c_{32}y_1 + c_{33}z_1$$

Here, $c_{ij}$ is the $ij$ element of $C$ defined as $c_{ij} = \sum_{k=1}^{3}(a_{ik})^2(a_{kj})^2$. Therefore, the correlation function for $m=0$ given by Eq. (5) is expressed as

$$F_0(t) = 1 - 3(c_{31}x_1 + c_{32}y_1 + c_{33}z_1)^2$$
$$= -(3/4)a_{+1} \sin^2 \theta_1 \cos^2 \phi_1 - (3/4)a_{-1} \sin^2 \theta_1 \cos^2 \phi_1$$
$$- 3a_{+2} \sin \theta_1 \cos \theta_1 \sin \phi_1 - 3a_{-2} \sin \theta_1 \cos \theta_1 \sin \phi_1$$
$$- (3/2)a_{2} \sin^2 \theta_1 - a_{4}$$

where

$$a_{+1} = (c_{31}^2 + c_{32}^2 + c_{33}^2)^2$$
$$a_{+2} = (c_{31}^2 + c_{32}^2) c_{33}$$
$$a_{2} = c_{31}^2 + c_{32}^2 - 2c_{33}^2$$
$$a_{4} = 3c_{33}^2 - 1$$

Since by use of Eq. (11) $c_{31}$, $c_{32}$ and $c_{33}$ are described as functions of $\theta_2$, $\phi_2$ and $\theta_3$, Eq. (A-3) reduces to

$$a_{+1} = -(\sin \theta_2 \cos \theta_2 \cos \phi_2 - \cos \theta_2 \sin \theta_2 \sin \theta_3 \sin \phi_3)^2$$
$$= (1/4) \sin^2 \theta_2 (\cos^2 \theta_2 + 2 \cos \theta_2 + 1) e^{2i\phi_2}$$
$$+ (1/4) \sin^2 \theta_2 (\cos^2 \theta_2 - 2 \cos \theta_2 + 1) e^{-2i\phi_2}$$
$$+ \sin \theta_2 \cos \theta_2 \sin \theta_2 \sin \theta_2 \sin \theta_3 \cos \phi_2 e^{i\phi_2}$$
$$+ \sin \theta_2 \cos \theta_2 \sin \theta_2 \sin \theta_2 \cos \phi_2 e^{-i\phi_2}$$
$$+ (1/2)(3 \cos^2 \theta_2 - 1) \sin^2 \theta_2$$

$$a_{+2} = -(\sin \theta_2 \cos \theta_2 \cos \phi_2 - \cos \theta_2 \sin \theta_2 \sin \theta_3 \sin \phi_3)$$
$$\times (\sin \theta_2 \sin \theta_2 \cos \phi_2 + \cos \theta_2 \cos \theta_2)$$
$$= (1/4) \sin^2 \theta_2 \sin \theta_2 \cos \theta_2 \sin \theta_2 \sin \theta_3 \cos \phi_2$$
$$+ (1/4) \sin^2 \theta_2 \sin \theta_2 \cos \theta_2 \sin \theta_2 \cos \phi_2$$
$$- (1/2) \sin \theta_2 \cos \theta_2 (2 \cos^2 \theta_2 + 2 \cos \theta_2 - 1) e^{i\phi_2}$$
$$- (1/2) \sin \theta_2 \cos \theta_2 (2 \cos^2 \theta_2 + 2 \cos \theta_2 - 1) e^{-i\phi_2}$$
$$- (1/2)(3 \cos^2 \theta_2 - 1) \sin \theta_2 \cos \theta_2$$

(243)
\[ a_3 = \frac{3}{4} \sin^2 \theta_3 \sin^2 \theta_2 e^{2i\phi_2} - \frac{3}{4} \sin^2 \theta_3 \sin^2 \theta_2 e^{-2i\phi_2} + 3 \sin \theta_3 \cos \theta_3 \sin \theta_2 \cos \theta_2 e^{i\phi_2} + 3 \sin \theta_3 \cos \theta_3 \sin \theta_2 \cos \theta_2 e^{-i\phi_2} - \frac{1}{2} (3 \cos^2 \theta_2 - 1) (3 \cos^2 \theta_2 - 1) \] (A-6)

and

\[ a_4 = -a_3 \] (A-7)

Therefore, substitution of Eqs. (A-4), (A-5), (A-6), and (A-7) for \( a_{\pm 1}, a_{\pm 2}, a_3 \) and \( a_4 \) 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

\[
\begin{align*}
\mathcal{F}_1(t) &= \frac{1}{2} \beta_{\pm 1} \sin^2 \theta_1 e^{2i\phi_1} + \frac{1}{4} \beta_{-1} \sin^2 \theta_1 e^{-2i\phi_1} \\
&+ \frac{1}{2} \beta_{-2} \sin \theta_1 \cos \theta_1 e^{i\phi_1} + \frac{1}{2} \beta_{-2} \sin \theta_1 \cos \theta_1 e^{-i\phi_1} \\
&+ \frac{1}{2} \beta_{-3} \sin^2 \theta_1 + \beta_4
\end{align*}
\] (A-8)

with

\[
\begin{align*}
\beta_{\pm 1} &= e^{i\phi_1} \left[ -\frac{1}{4} (\sin \theta_3 \cos \theta_3 + \sin \theta_3)(\cos^2 \theta_2 + 2 \cos \theta_2 + 1) e^{2i\phi_2} \\
&- \frac{1}{4} (\sin \theta_3 \cos \theta_3 - \sin \theta_3)(\cos^2 \theta_2 + 2 \cos \theta_2 + 1) e^{-2i\phi_2} \\
&- \frac{1}{2} (2 \cos^2 \theta_3 + \cos \theta_3 - 1)(\sin \theta_2 \cos \theta_2 + \sin \theta_2) e^{i\phi_2} \\
&- \frac{1}{2} (2 \cos^2 \theta_3 - \cos \theta_3 - 1)(\sin \theta_2 \cos \theta_2 + \sin \theta_2) e^{-i\phi_2} \\
&+ \frac{3}{2} \sin \theta_2 \cos \theta_2 \sin^2 \theta_2 \right]\end{align*}
\] (A-9)

\[
\begin{align*}
\beta_{\pm 2} &= e^{i\phi_2} \left[ -\frac{1}{2} (\sin \theta_3 \cos \theta_3 + \sin \theta_3)(\sin \theta_2 \cos \theta_2 + \sin \theta_2) e^{2i\phi_2} \\
&- \frac{1}{2} (\sin \theta_3 \cos \theta_3 - \sin \theta_3)(\sin \theta_2 \cos \theta_2 + \sin \theta_2) e^{-2i\phi_2} \\
&+ \frac{1}{2} (2 \cos^2 \theta_3 + \cos \theta_3 - 1)(2 \cos^2 \theta_2 + \cos \theta_2 - 1) e^{i\phi_2} \\
&+ \frac{1}{2} (2 \cos^2 \theta_3 - \cos \theta_3 - 1)(2 \cos^2 \theta_2 + \cos \theta_2 - 1) e^{-i\phi_2} \\
&- 3 \sin \theta_3 \cos \theta_3 \sin \theta_2 \cos \theta_2 \right]\end{align*}
\] (A-10)

\[
\begin{align*}
\beta_3 &= e^{i\phi_3} \left[ \frac{3}{4} (\sin \theta_3 \cos \theta_3 + \sin \theta_3) \sin^2 \theta_2 e^{2i\phi_2} \\
&+ \frac{3}{4} (\sin \theta_3 \cos \theta_3 - \sin \theta_3) \sin^2 \theta_2 e^{-2i\phi_2} \\
&- \frac{3}{2} (2 \cos^2 \theta_3 + \cos \theta_3 - 1) \sin \theta_3 \cos \theta_2 e^{i\phi_2} \\
&- \frac{3}{2} (2 \cos^2 \theta_3 - \cos \theta_3 - 1) \sin \theta_3 \cos \theta_2 e^{-i\phi_2} \right]
\end{align*}
\] (244)
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\[
-\frac{3}{2} \sin \theta_2 \cos \theta_2(3 \cos^2 \theta_2-1) \tag{A-11}
\]

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

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

\[
F_m(t) = \frac{1}{4} \gamma_{+1} \sin^2 \theta_1 e^{2i\phi_1} + \frac{1}{4} \gamma_{-1} \sin^2 \theta_1 e^{-2i\phi_1} + \gamma_{+2} \sin \theta_1 \cos \theta_1 e^{i\phi_2} + \gamma_{-2} \sin \theta_1 \cos \theta_1 e^{-i\phi_2} + \frac{1}{2} \gamma_3 \sin^2 \theta_1 + \gamma_4 \tag{A-13}
\]

with

\[
\gamma_{+1} = e^{2i\phi_1} \left[ \frac{1}{4} \left( \cos^2 \theta_3 + 2 \cos \theta_3 + 1 \right) \left( \cos^2 \theta_3 + 2 \cos \theta_3 + 1 \right) e^{2i\phi_2} + \frac{1}{4} \left( \cos^2 \theta_3 - 2 \cos \theta_3 + 1 \right) \left( \cos^2 \theta_3 + 2 \cos \theta_3 + 1 \right) e^{-2i\phi_2} - \left( \sin \theta_3 \cos \theta_3 + \sin \theta_3 \right) \left( \sin \theta_3 \cos \theta_3 + \sin \theta_3 \right) e^{i\phi_2} - \left( \sin \theta_3 \cos \theta_3 - \sin \theta_3 \right) \left( \sin \theta_3 \cos \theta_3 - \sin \theta_3 \right) e^{-i\phi_2} + \frac{3}{2} \sin^2 \theta_3 \sin \theta_2 \right] \tag{A-14}
\]

\[
\gamma_{+2} = e^{2i\phi_2} \left[ \frac{1}{4} \left( \cos^2 \theta_3 + 2 \cos \theta_3 + 1 \right) \left( \sin \theta_3 \cos \theta_3 + \sin \theta_3 \right) e^{2i\phi_2} + \frac{1}{4} \left( \cos^2 \theta_3 - 2 \cos \theta_3 + 1 \right) \left( \sin \theta_3 \cos \theta_3 + \sin \theta_3 \right) e^{-2i\phi_2} + \frac{1}{2} \sin \theta_3 \cos \theta_3 \left( 2 \cos^2 \theta_2 + \cos \theta_2 - 1 \right) e^{i\phi_2} + \frac{1}{2} \sin \theta_3 \cos \theta_3 \left( 2 \cos^2 \theta_2 + \cos \theta_2 - 1 \right) e^{-i\phi_2} - \frac{3}{2} \sin^2 \theta_3 \sin \theta_3 \cos \theta_3 \right] \tag{A-15}
\]

\[
\gamma_3 = e^{2i\phi_1} \left[ -\frac{3}{4} \left( \cos^2 \theta_3 + 2 \cos \theta_3 + 1 \right) \sin^2 \theta_3 e^{2i\phi_2} - \frac{3}{4} \left( \cos^2 \theta_3 - 2 \cos \theta_3 + 1 \right) \sin^2 \theta_3 e^{-2i\phi_2} - 3 (\sin \theta_3 \cos \theta_3 + \sin \theta_3) \sin \theta_3 \cos \theta_3 e^{i\phi_2} - 3 (\sin \theta_3 \cos \theta_3 - \sin \theta_3) \sin \theta_3 \cos \theta_3 e^{-i\phi_2} - \frac{3}{2} \sin^2 \theta_3 (3 \cos^2 \theta_2 - 1) \right] \tag{A-16}
\]

\[
\gamma_4 = -\frac{1}{3} \gamma_3 \tag{A-17}
\]
REFERENCES