Proton Spin Lattice Relaxation in the Dimethylammonium Group

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Introduction

Compounds containing dimethylammonium (DMA) are known to undergo structural phase transitions. These phase changes are normally associated with subtle changes in the dynamics of the DMA groups [1–5]. Proton spin lattice relaxation time \( T_1 \) measurements of this molecular group provide a convenient and powerful tool to study its dynamics. However, the data on these systems are not appropriately analyzed so far, due to the lack of relevant theoretical calculations in terms of all dynamical parameters associated with this group. The \( T_1 \) data have been analyzed by assigning the observed relaxation to the methyl group dynamics only, whereas, in principle, the DMA ion undergoes more complicated dynamics [1]. This paper aims at deriving an analytical expression for the relaxation rates, taking into account the dynamics of the DMA group in addition to the dynamics of the methyl group. The outcome of this calculation is used to analyze the published data [2] on tris-dimethylammonium nonabromo diantimonat, yielding for the first time dynamical information about the DMA ion as a whole.

Proton Spin Lattice Relaxation in DMA Groups

The four types of plausible motions of the DMA ion, relevant in the present experiments, are [1]: (i) three fold reorientations of the methyl groups around their three fold symmetric axes, (ii) two fold rotations of the DMA group around its diad axis, (iii) \( n \)-fold reorientations of the DMA group around its diad axis, and (iv) isotropic tumbling of the whole DMA group (see Figure 1). Out of these, (iii) and (iv) do not preserve the symmetry of the DMA group and hence are expected to be quite hindered, taking place only at very high temperatures. In this paper, an expression for the relaxation rate \( T_1^{-1} \) of the group is derived considering only the first two types of dynamics, modelling both intra- and inter-methyl proton-proton dipolar interactions as well as lone proton-methyl proton interactions. The general methodology of these calculations is similar to the treatment of Sjoblom and Punkkinen [6] for trimethylammonium group.

The magnetic dipolar interaction (which is the dominant relaxation mechanism for protons in the DMA ion), between two protons \( m \) and \( n \) is

\[
\mathcal{H}^m_n = \sum_{\mu = -2}^2 F^{(\mu)} S^{(\mu)}_{mn},
\]

where the \( S^{(\mu)}_{mn} \)'s are the components of the second rank irreducible tensor operators involving spin variables, and the \( F^{(\mu)}_{mn} \)'s are the corresponding spatial functions given by

\[
F^{(0)}_{mn} = \gamma^2 \frac{\hbar^2}{r^3_{mn}} (1 - 3 \cos^2 \theta_{mn}),
\]

\[
F^{(1)}_{mn} = F^{(-1)*}_{mn} = \gamma^2 \frac{\hbar^2}{r^3_{mn}} \sin \theta_{mn} \cos \theta_{mn} e^{-i\phi_{mn}},
\]

\[
F^{(2)}_{mn} = F^{(-2)*}_{mn} = \gamma^2 \frac{\hbar^2}{r^3_{mn}} \sin^2 \theta_{mn} e^{-2i\phi_{mn}}.
\]
Here \((r_{mn}, \theta_{mn}, \phi_{mn})\) is the vector joining the protons \(m\) and \(n\) expressed in spherical coordinates. These quantities become time dependent due to the molecular motions, and their fluctuations, \(X_{mn}(\omega)\), are

\[
X_{mn}(\omega) = F_{mn}(\omega) - F_{mn}^{(u)}. \tag{3}
\]

The spin lattice relaxation rate of the proton \(m\) due to its dipolar interaction with proton \(n\), in the Redfield limit, is given by [7]

\[
(T_1^{-1})_{mn} = \frac{3}{2} \frac{I(I+1)}{h^2} J_{mn}^{(1)}(\omega_0) + J_{mn}^{(2)}(2\omega_0), \tag{4}
\]

where

\[
J_{mn}(\omega_0) = \int_{-\infty}^{\infty} G_{mn}(\omega_0, \tau) e^{-i\omega_0 \tau} d\tau \tag{5}
\]

is the spectral density function, and the corresponding auto correlation functions are given by

\[
G_{mn}(\tau) = \langle X_{mn}(\omega) X_{mn}^{*}(t+\tau) \rangle. \tag{6}
\]

In calculating the value of \(T_1\) of any proton in the DMA group, the pair wise interactions between protons can be restricted to a good approximation to those within the DMA group.

Let the rate of the three fold reorientation (\(C_3\) rotation) of the methyl groups be \(r\) and the rate of the two fold reorientation of the DMA group around its diad axis (diad rotations) be \(R\). Now, to take the statistical inter-dependence of these motions into account, let the rate of coupled \(C_3\) rotation of one methyl group and diad rotation be \(R'\), and that of the coupled \(C_3\) rotations of two methyl groups and the diad rotation be \(R''\). Referring to Fig. 1, consider the motions of a proton pair initially at positions 1 and 2 (denoted by 12). A \(C_3\) rotation of the methyl group can transfer this pair to position 23 or 31 at a rate of \(r/3\) and to position 12 at a rate of \(2r/3\). Similarly, different coupled motions
can transfer the initial pair 12 to 23, 31, 56, and 64 at a rate $R'/4$, to 12, 45 at a rate $R''/4$, and to 23, 31, 56, and 64 at a rate $R''/8$. Let $p_{ij}(t)$ be the probability of finding this pair at a position $ij$ after a time $t$. Due to symmetry, $p_{23}(t) = p_{31}(t)$ and $p_{56}(t) = p_{64}(t)$, and hence only four probabilities ($p_{ij}$, $ij = 12, 23, 45, 56$) are independent. The above arguments can be elegantly summarized in the form of a detailed balance equation for the rate of change of a pair probability function, say $p_{12}(t)$, as

$$
\dot{p}_{12}(t) = -\left(\frac{2}{3}r + \frac{R}{2} + R' + \frac{3}{4}R''\right)p_{12}(t) + \left(\frac{r}{3} + \frac{R'}{4} + \frac{R''}{8}\right)(p_{23}(t) + p_{31}(t))
$$

Taking suitable linear combinations of these probabilities, these equations can be decoupled to give

$$
\begin{pmatrix}
\dot{p}_{12}(t) \\
\dot{p}_{23}(t) \\
\dot{p}_{45}(t) \\
\dot{p}_{56}(t)
\end{pmatrix} =
\begin{pmatrix}
\left(\frac{2}{3}r + \frac{R}{2} + R' + \frac{3}{4}R''\right) & \left(\frac{2r}{3} + \frac{R'}{2} + \frac{R''}{4}\right) & \left(\frac{R}{2} + \frac{R'}{4}\right) & \left(\frac{R}{2} + \frac{R''}{4}\right) \\
\left(\frac{r}{3} + \frac{R'}{4} + \frac{R''}{8}\right) & \left(-\frac{r}{3} + \frac{R'}{2} + \frac{3}{4}R' + \frac{5}{8}R''\right) & \left(-\frac{r}{3} + \frac{R'}{2} + \frac{R'}{4}\right) & \left(-\frac{r}{3} + \frac{R'}{2} + \frac{3}{4}R''\right) \\
\left(R' + \frac{R''}{4}\right) & \left(-\frac{R'}{2} + \frac{R''}{4}\right) & \left(-\frac{2}{3}r + \frac{R'}{2} + \frac{3}{4}R''\right) & \left(-\frac{r}{3} + \frac{R'}{2} + \frac{3}{4}R''\right) \\
\left(R' + \frac{R''}{8}\right) & \left(-\frac{R'}{2} + \frac{R''}{4}\right) & \left(-\frac{r}{3} + \frac{R'}{2} + \frac{3}{4}R''\right) & \left(-\frac{r}{3} + \frac{R'}{2} + \frac{3}{4}R''\right)
\end{pmatrix}
\begin{pmatrix}
p_{12}(t) \\
p_{23}(t) \\
p_{45}(t) \\
p_{56}(t)
\end{pmatrix}
$$

Taking suitable linear combinations of these probabilities, these equations can be decoupled to give

$$
\begin{pmatrix}
\dot{p}_{12} - \dot{p}_{23} \\
\dot{p}_{45} - \dot{p}_{56}
\end{pmatrix} =
\begin{pmatrix}
\left(r + \frac{R}{2} + \frac{5R'}{4} + \frac{7R''}{8}\right) & \left(R - \frac{R'}{2} + \frac{R''}{8}\right) \\
\left(R - \frac{R'}{2} + \frac{R''}{8}\right) & \left(r + \frac{R}{2} + \frac{5R'}{4} + \frac{7R''}{8}\right)
\end{pmatrix}
\begin{pmatrix}
\left(p_{12} - p_{23}\right) \\
\left(p_{45} - p_{56}\right)
\end{pmatrix}
$$

and

$$
\begin{pmatrix}
\dot{p}_{12} + 2\dot{p}_{23} \\
\dot{p}_{45} + 2\dot{p}_{56}
\end{pmatrix} = \frac{1}{2}(R + R' + R'')(\begin{pmatrix}-1 & +1 \\
+1 & -1
\end{pmatrix})
\begin{pmatrix}
p_{12} + 2p_{23} \\
p_{45} + 2p_{56}
\end{pmatrix}
$$

The solutions, with the initial condition $p_{12}(0) = 1$, $p_{ij}(0) = 0$ for $ij = 23, 45, 56$, are written as

$$
\begin{pmatrix}
p_{12}(t) \\
p_{23}(t) \\
p_{45}(t) \\
p_{56}(t)
\end{pmatrix} = \frac{1}{6}
\begin{pmatrix}
2 & 2 & 1 & 1 \\
-1 & -1 & 1 & 1 \\
2 & -2 & -1 & 1 \\
-1 & 1 & -1 & 1
\end{pmatrix}
\begin{pmatrix}
e^{-k_{1}t} \\
e^{-k_{2}t} \\
e^{-k_{3}t} \\
e^{-k_{4}t}
\end{pmatrix},
$$

where

$$
k_{1} = r + \frac{3R'}{2} + \frac{3R''}{4},
$$

$$
k_{2} = r + R' + R' + R''
$$

and

$$
k_{3} = R + R' + R''.
$$
Similar results are obtained for the probabilities involving lone proton–methyl proton (lp–mp) pair, like $i_{ij} = 71$ (Figure 1).

Time modulations of the dipolar interactions among inter-methyl pairs can similarly be taken into account. Considering a proton pair like 14 (Fig. 1) at $t = 0$, various jump probabilities to other pair locations connected by the above proposed dynamics can be calculated. After taking symmetry considerations into account (i.e. $p_{15} = p_{16} = p_{24} = p_{34}$ and $p_{25} = p_{26} = p_{35} = p_{36}$) the detailed balance equation for the independent probabilities ($p_{14}$, $p_{15}$, and $p_{25}$) assumes the form

$$
\begin{pmatrix}
    p_{14}(t) \\
    p_{15}(t) \\
    p_{25}(t)
\end{pmatrix} =
\begin{pmatrix}
    -\left(\frac{4r}{3} + R + R'\right) \\
    \left(\frac{r + R'}{4}\right) - \left(\frac{r + 3R'}{4} + \frac{R''}{2}\right) \\
    \left(\frac{R''}{2}\right) - \left(\frac{2r + R'}{2} + \frac{R''}{2}\right)
\end{pmatrix} 
\begin{pmatrix}
    p_{14} \\
    p_{15} \\
    p_{25}
\end{pmatrix}.
$$

(15)

Solutions with the initial condition $p_{14}(0) = 1$ and $p_{15}(0) = p_{25}(0) = 0$ are obtained as

$$
\begin{pmatrix}
p_{14} \\
p_{15} \\
p_{25}
\end{pmatrix} = \frac{1}{9} \begin{pmatrix} 4 & 4 & 1 \\ -2 & 1 & 1 \\ 1 & -2 & 1 \end{pmatrix} \begin{pmatrix} e^{-kt} \\ e^{-kt} \end{pmatrix},
$$

(16)

where

$$k_4 = 2r + \frac{3R'}{2} + \frac{3R''}{4}
$$

and

$$k_5 = r + \frac{3R'}{2} + \frac{3R''}{2}.
$$

**Correlation Functions**

Equation (4) expresses the relaxation rate of $m$-th proton due to its dipolar interaction with $n$-th proton modulated in time due to the relocation of this pair in different configurations arising from the permissible molecular motions with different probabilities. To be able to find the total relaxation rate of, say, this $m$-th proton, this equation has to be summed over all protons with which it interacts. Further, the overall relaxation rate of the DMA molecular group is computed by averaging the relaxation rates of individual protons in this group, under the common Zeeman spin temperature approximation [7]. Thus the average proton pair correlation functions are the relevant objects to be computed to proceed further with the objective. Now the average intra-methyl group proton pair correlation function can be expanded, suppressing the index $\mu$, as

$$G(t)_{\text{intra}} = \frac{1}{6} [\langle X_{12}^* (0) X_{12} (t) \rangle + \langle X_{23}^* (0) X_{23} (t) \rangle + \ldots + \langle X_{64}^* (0) X_{64} (t) \rangle].$$

(19)

These pair correlation functions in the above equation are then to be evaluated making use of jump probabilities in (11). The result for one of the pair functions, say $\langle X_{12}^* (0) X_{12} (t) \rangle$, is

$$\langle X_{12}^* (0) X_{12} (t) \rangle = \sum_{i,j} p_{ij} \langle X_{ij}^* (0) X_{ij} (t) \rangle,$$

(20)

Similar expressions can be written for the other pair correlation functions in (19). Substituting all these expressions in (19) one obtains

$$G_{\text{intra}}^{(\mu)} (t) = p_{12} C_{1}^{(\mu)} + p_{23} C_{2}^{(\mu)} + p_{45} C_{3}^{(\mu)} + p_{56} C_{4}^{(\mu)},$$

(21)

for $G_{\text{intra}}^{(\mu)} (t)$ in (21) the average correlation function can be written as

$$G_{\text{intra}}^{(\mu)} (t) = \sum_{i=1}^{3} k_{i}^{(\mu)} e^{-k_{i} t},$$

(23)
where
\[ K^{(a)}_1 = \frac{1}{6} [2C_1^{(a)} - C_2^{(a)} + 2C_3^{(a)} - C_4^{(a)}], \]  
(24a)
\[ K^{(a)}_2 = \frac{1}{6} [2C_1^{(a)} - C_2^{(a)} - 2C_3^{(a)} + C_4^{(a)}], \]  
(24b)
and
\[ K^{(a)}_3 = \frac{1}{6} [C_1^{(a)} + C_2^{(a)} - C_3^{(a)} - C_4^{(a)}]. \]  
(24c)

Since the expression for jump probabilities of an \( lp-mp \) pair are the same as those of intra-methyl proton pairs, one gets similar expressions for the corresponding correlation functions, i.e.

\[ G^{(a)}_{lp-mp}(t) = \sum_{i=1}^{3} M_i^{(a)} e^{-k_it}, \]  
(25)

The quantities pertaining to \( lp-mp \) interactions, viz., \( M_i^{(a)} \)'s and \( D_i^{(a)} \)'s, correspond to the quantities \( K_i^{(a)} \) and \( C_i^{(a)} \), respectively, introduced earlier for intra-methyl interactions, and they satisfy similar relationships as in the earlier case (see (23) and (24)).

Finally, the average correlation function involving inter-methyl proton pairs can similarly be expressed as

\[ G^{(a)}_{inter}(t) = \sum_{i=4}^{9} L_i^{(a)} e^{-k_it}, \]  
(26)

where
\[ L_4^{(a)} = \frac{1}{9} (4E_1^{(a)} - 2E_2^{(a)} + E_3^{(a)}), \]  
(27a)
and
\[ L_5^{(a)} = \frac{1}{9} (4E_1^{(a)} + E_2^{(a)} - 2E_3^{(a)}). \]  
(27b)

Here, the \( E_i^{(a)} \)'s are suitable expansions in terms of the relevant \( X_{ij}^{(a)} \)'s, given by

\[ E_1^{(a)} = \frac{1}{9} [ |X_{12}^{(a)}(0)|^2 + |X_{13}^{(a)}(0)|^2 + |X_{14}^{(a)}(0)|^2], \]  
(28a)

\[ E_2^{(a)} = \frac{2}{9} \text{Re} [ |X_{12}^{(a)}(0)|^2 + |X_{13}^{(a)}(0)|^2 + |X_{14}^{(a)}(0)|^2 + |X_{35}^{(a)}(0)|^2 + |X_{36}^{(a)}(0)|^2 + |X_{45}^{(a)}(0)|^2 + |X_{46}^{(a)}(0)|^2 + |X_{56}^{(a)}(0)|^2], \]  
(28b)

\[ E_3^{(a)} = \frac{2}{9} \text{Re} [ |X_{12}^{(a)}(0)|^2 + |X_{13}^{(a)}(0)|^2 + |X_{14}^{(a)}(0)|^2 + |X_{35}^{(a)}(0)|^2 + |X_{36}^{(a)}(0)|^2 + |X_{45}^{(a)}(0)|^2 + |X_{46}^{(a)}(0)|^2 + |X_{56}^{(a)}(0)|^2]. \]  
(28c)

Numerical Calculations

In order to obtain the values of the relaxation constants in (30) \( K_i^{(a)}, M_i^{(a)}, \) and \( L_i^{(a)} \) for a given physical situation, the bond lengths and angles for the DMA ion given by Andrew and Canepa [1] are used. To make the results applicable to polycrystalline samples (which is typically the case), these relaxation constants are powder averaged. This is accomplished by first considering one of the sides of the cube centering the DMA group (Fig. 1) to be parallel with the magnetic field (say, \( z \)-axis), and finding the coordinates of all protons for the given dimensions of the DMA group.
Table 1. The relaxation constants ($\times 10^8$ sec$^{-2}$) in (30) for the dimethylammonium molecular group.

<table>
<thead>
<tr>
<th>$\mu$</th>
<th>$i$</th>
<th>$K_i^{(\mu)}$</th>
<th>$M_i^{(\mu)}$</th>
<th>$L_i^{(\mu)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>30.59</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>25.43</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11.88</td>
<td>4.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>122.34</td>
<td>12.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>101.74</td>
<td>7.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>47.5</td>
<td>17.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>5.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>6.17</td>
<td></td>
</tr>
</tbody>
</table>

Then, for this orientation $K_i^{(\mu)}$, $M_i^{(\mu)}$, and $L_i^{(\mu)}$ can be calculated using (24) and (27). Now different orientations of the DMA group are obtained by changing the polar coordinates ($\theta$ and $\phi$) of the side that is parallel to the magnetic field, in small steps ($0-\pi$ for $\theta$, and $0-2\pi$ for $\phi$). For each orientation the coordinates of all protons are calculated using appropriate Wigner rotation matrices, and corresponding relaxation constants are calculated. Finally, the relaxation coefficients thus obtained for all these chosen orientations are averaged. Table 1 gives the values of these parameters, obtained after averaging over 256 isotropically distributed orientations of the DMA molecule. It has been observed that averaging over only 64 orientations leads to a negligible error (less than 1%) in the relaxation coefficients.

This model is tested by analyzing the relaxation data of Idziak and Jakubas [2], collected on a polycrystalline sample of (DMA)$_3$Sb$_2$Br$_9$. In this process it is assumed that these molecular motions are thermally activated and hence have the Arrhenius type of temperature (T) dependence, i.e., $r = \tau_c^{-1} = \tau_0^{-1} \cdot \exp \{ -E_a/k_B T \}$, where $\tau_c$ is the correlation time. In order to calculate $T_1$ minima with the present model (at a given Larmor frequency) arising due to DMA and CH$_3$ dynamics separately, substantially different dynamical parameters for the methyl group reorientation and the diad axis reorientation have been assumed to minimize the contribution of one dynamics at the $T_1$ minimum of the other. As a result, well separated $T_1$ minima on the temperature axis have been obtained (cross couplings are neglected for simplicity, i.e., $R'$ and $R'' = 0$). The $T_1$ minima are calculated from (30) with the relaxation constants given in Table 1 and are found to be 63.9 msec for CH$_3$ dynamics and 243 msec for DMA dynamics (at 90 MHz), respectively. The consistency of this model is checked by ensuring that the value of the $T_1$ minimum corresponding to the CH$_3$ dynamics, calculated by taking the appropriate limiting case ($R = R' = R'' = 0$) of the above model, agrees very well with the expected results [6]. The $T_1$ data of Idziak and Jakubas at 90 MHz, however, show a broad minimum of about 100 msec, and this value does not match with either of the computed minima, suggesting the presence of dynamically inequivalent molecular groups. In fact, the X-ray studies on this and other related compounds show the presence of inequivalent DMA ions in 2:1 ratio [8]. The earlier explanation of these data is indeed based on such an inequivalence [2], but only the methyl group dynamics, presumably in the absence of a relevant model, has been taken into consideration. However, due to the limitation of the model used in the earlier analysis (i.e., the absence of the dynamics of the DMA ion), the relaxation coefficients corresponding to both types of methyl groups were found to be considerably different, and both are smaller than theoretically expected ($8.05 \times 10^9$ sec$^{-2}$ for a proton–proton distance of 1.78 Å) [9]. The inequivalence in the dynamics of these groups is not expected to result in different relaxation coefficients because the origin of
these coefficients lies more with the details of the physical dimensions of the molecular groups than with the surrounding dynamic environment.

Now, in order to account for the observed broad minimum at some intermediate value of 100 msec, it is assumed here that inequivalent DMA groups as well as inequivalent CH$_3$ groups exist in 2:1 ratio in this compound. The observed broad minimum then is attributed to the dynamics of 1/3 of the DMA groups and 2/3 of the methyl groups (this is the combination which results in the observed value of the minimum). A minimum due to the remaining 2/3 DMA groups is expected to occur at temperatures above the range covered in the experiment (the data at high temperatures show this tendency), and the remaining 1/3 methyl groups perhaps lead to a minimum at very low temperatures not covered in this experiment. With this assignment of inequivalence the data are analysed using a nonlinear least squares method with the relaxation parameters given in Table 1, and the agreement between the experimental and theoretical values is reasonably good, as shown in Figure 2. The activation energy and preexponential factor, obtained are 2.2 ± 0.3 kcal/mole and 1.1 × 10$^{-12}$ sec, respectively, for the 2/3 DMA groups, while those of the 1/3 CH$_3$ groups are 1.8 ± 0.3 kcal/mole and 1.5 × 10$^{-12}$ sec, respectively. Obviously the assignment of minima can be done more definitively if the minima are better resolved. Experiments at lower Larmor frequencies normally provide better resolution, and perhaps such experiments are called for to confirm the proposed model for this compound. Such a multifrequency investigation of $T_1$ data in other compounds involving DMA groups is in progress.

**Conclusions**

An expression for the average spin lattice relaxation rate of protons in the DMA group, undergoing 3 fold reorientation of the CH$_3$ groups and 2 fold flips of the whole ion around the diad axis is derived within the Redfield limit, assuming common spin temperature. The results have been suitably averaged to make the model readily applicable to polycrystalline samples. Existing experimental data on (DMA)$_3$Sb$_2$Br$_9$ have been reanalysed using this model and bringing out a qualitatively different picture of the dynamical processes of the DMA ion in this system. There are several interesting solids where this model can be applied to study DMA dynamics through an analysis of proton $T_1$ data.