Hydrogen Bond Studies. 108. A Nuclear Magnetic Relaxation Study of Molecular Motion in Solid Trimethylammonium Iodide, Bromide, Chloride, and Hydrogen Oxalate*

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Spin–lattice relaxation times in the laboratory frame at 60.16 and 20.00 MHz are reported for trimethylammonium iodide, bromide, chloride, and hydrogen oxalate in the temperature range 150–400 K. A model that makes it possible to analyze the experimental data on the basis of different assumptions regarding the reorientational motions of the methyl groups, the cations as a whole, and the correlations between these two types of motion is developed. No conclusions are drawn about the correlation since the two models investigated result in almost equally good fits with the experimental relaxation times. However, time factors, activation energies, and scale factors for the intramethyl relaxation constants could be determined from the refinements since the results were close for the two models, and thus apparently insensitive to reasonable assumptions about the correlations.

INTRODUCTION

Trimethylammonium iodide, bromide, chloride, and hydrogen oxalate (denoted herein by TMAI, TMAB, TMAC, and TMAHOX, respectively) all crystallize in the space group $P2_1/m$ in such a way that each cation is divided by a mirror plane. Crystal structure determinations have shown that the intermolecular arrangement in the room temperature phase of TMAC (*1*) is different from that in TMAI (*2*), and that both differ from the situation in TMAHOX (*3*). X ray investigations (*2, 4, 5*) have shown that the crystal structures of TMAB and TMAI are similar.

The second moment versus temperature curves for TMAI (*5*), TMAB (*5*), TMAC (*6, 7*), and TMAHOX (*5*) show a narrowing that is consistent with the assumption that above 220, 220, 200, and 180 K, respectively, the methyl groups and the cation as a whole reorient around their pseudo-symmetry axes at a rate that is fast compared to the linewidth.

A differential thermal analysis (*8*) indicates a phase transition in TMAC at 308 K.

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Preliminary X ray diffraction data on the high temperature phase (α-TMAC) indicate a tetragonal structure with the fourfold axis along the c-axis of the phase, which is stable at room temperature (β-TMAC) (9). The fourfold axis is close to or coincident with the N–H$\cdots$Cl hydrogen bond. This is inconsistent with the molecular geometry unless the ion is disordered, statically or dynamically, among the 12 equivalent orientations about this direction. An NMR investigation of a similar situation in monomethylammonium chloride (10) has shown that the cation in this case reorients quite freely with a very low hindering barrier. Schlaak (11) has analyzed the shapes of Raman bands in TMAC and concluded that the rate of the reorientations of the cations is about 2.5 × 10^{12} Hz in the α-phase. Consequently, the relaxation caused by this motion is quite small.

The molecular motion in trimethylamine and related compounds has been investigated by several techniques. Further references and a table of activation energies for the methyl group reorientations may be found in (12), where the coupling between the methyl group librations is discussed also.

An estimate of the activation barrier in β-TMAC has been made from wide-line data using the conventional assumption that the motion is characterized by a single activation energy and a single correlation time (7). However, it is apparent from the experimental data presented in this paper that the Zeeman spin–lattice relaxation is actually caused by more than one kind of reorientational motion. The slopes of the log T_1 versus $1000/T$ curves at temperatures above the T_1 minima are quite different from those below. A more general model than that assumed in the conventional BPP theory is needed to account for the motion in this present case. Most derivations of theoretical expressions for T_1 consider only the intramethyl interactions (13–16). A somewhat qualitative intermethyl correction (17–18) to such an intramethyl relaxation model (16) has been introduced recently.

The theory developed below, though intended here for a trimethylammonium ion $(CH_3)_3NH^+$, constitutes a general method that can be applied to almost any molecule undergoing thermal reorientations (as an example, see (19)). The present treatment uses the fact that in most solids the proton–proton vectors can have only a limited number of equilibrium orientations. Further, it is a simple matter to include several reorientation rates that correspond to the final configurations attainable through single reorientations of various kinds. The effect of the dipolar interaction on $1/T_1$ is evaluated for three different kinds of proton pairs: (a) the protons are both in the same methyl group, (b) one proton belongs to a methyl group and the other does not, and (c) the protons belong to separate methyl groups. The theory is used to explain the observed T_1 data for TMAI, TMAB, TMAC, and TMAHOX. The activation energies and preexponential factors for different motions are determined by fitting the theoretical expressions to the experimental results.

PROTON ZEEMAN SPIN–LATTICE RELAXATION OF TRIMETHYLAMMONIUM IONS

Reorientation Rates

The protons in a trimethylammonium ion $(CH_3)_3NH^+$ are labeled as shown in Fig. 1. Protons 1, 4, and 7 are at pseudo-equivalent positions, as are 2, 5, and 8, and 3, 6, and 9, respectively. To define the reorientation rates, we consider the positions a proton pair

originally at the positions 1 and 4 (here denoted 14) can reach: (a) positions 15, 16, 24, and 34 by reorientations of the individual methyl groups at a rate $r/3$, and 14 at a rate $2r/3$; (b) rotationally equivalent positions 14, 47, 71 by rotations of the whole ion at a rate $R/3$; (c) positions 15, 16, 24, 34, 48, 49, 57, 67, 72, 73, 81, and 91 (one proton at a rotationally equivalent site and the other at a nonequivalent site) by reorientations of the whole ion and one methyl group at a rate $R'/12$; and (d) positions 25, 26, 35, 36, 58, 59, 68, 69, 82, 83, 92, and 93 (both protons at rotationally nonequivalent sites) by reorientations of the whole ion and both methyl groups at a rate $R''/12$.
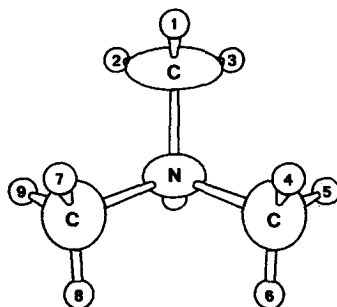

FIG. 1. The trimethylammonium ion showing the labeling used for the protons. The structural data for TMAHOX have been used, and the ellipsoids of the heavy atoms are scaled to include 50% probability.

For an intramethyl pair, the rates can be expressed in terms of r, R, R', and R''. However, note that an intramethyl pair, through reorientations labeled by R', can reach an equivalent as well as nonequivalent site in other methyl groups. The total reorientation rate for the whole ion is $R + R' + R''$ and for the methyl group $r + R + R' + R''$. If only the motion of the methyl group relative to the cation is considered, the latter rate becomes $r + \frac{3}{4}R' + \frac{3}{2}R''$.

Rate Equations for an Intramethyl Proton Pair

Consider the motion of a proton pair originally at 12. Let p_{ij}, $ij = 12, 23, 31, 45, 56, 64, 78, 89, 97$ be the probability of finding this proton pair at ij at a later time t. Then, by symmetry,

$$p_{23} = p_{31}, \qquad p_{45} = p_{78}, \qquad p_{56} = p_{64} = p_{89} = p_{97}. \qquad [1]$$

The time variation of p_{12} is described by the differential equation

$$\dot{p}_{12} = -\left(\frac{2}{3}r + \frac{2}{3}R + \frac{5}{6}R' + R''\right)p_{12} + \left(\frac{r}{3} + \frac{R'}{12} + \frac{R''}{6}\right)(p_{23} + p_{31})$$

$$+ \left(\frac{R}{3} + \frac{R'}{6}\right)(p_{45} + p_{78}) + \left(\frac{R'}{12} + \frac{R''}{6}\right)(p_{56} + p_{64} + p_{89} + p_{97}). \qquad [2]$$

Similar equations can be written for $\dot{p}_{23}$, $\dot{p}_{45}$, and $\dot{p}_{56}$. When the symmetry relations [1] are taken into account, these equations lead to

$$\frac{d}{dt}\begin{pmatrix} p_{12} \\ p_{23} \\ p_{45} \\ p_{56} \end{pmatrix}$$

$$= \begin{pmatrix} d_{11} & \frac{2}{3}r+\frac{R'}{6}+\frac{R''}{3} & \frac{2}{3}R+\frac{R'}{3} & \frac{R'}{3}+\frac{2}{3}R'' \\ \frac{r}{3}+\frac{R'}{12}+\frac{R''}{6} & d_{22} & \frac{R'}{6}+\frac{R''}{3} & \frac{2}{3}R+\frac{R'}{2}+\frac{R''}{3} \\ \frac{R}{3}+\frac{R'}{6} & \frac{R'}{6}+\frac{R''}{3} & d_{33} & \frac{2}{3}r+\frac{R'}{3}+\frac{2}{3}R'' \\ \frac{R'}{12}+\frac{R''}{6} & \frac{R}{3}+\frac{R'}{4}+\frac{R''}{6} & \frac{r}{3}+\frac{R'}{6}+\frac{R''}{3} & d_{44} \end{pmatrix}\begin{pmatrix} p_{12} \\ p_{23} \\ p_{45} \\ p_{56} \end{pmatrix} \qquad [3]$$

where each diagonal element is equal to minus the sum of all other elements on the same horizontal line; for example, $d_{11} = -(\frac{2}{3}r + \frac{2}{3}R + \frac{5}{6}R' + R'')$. The solution of the coupled equations [3] is made easier by using linear combinations $p_{12} + 2p_{23}$, $p_{45} + 2p_{56}$, $p_{12} - p_{23}$, and $p_{45} - p_{56}$. These quantities are coupled to each other in pairs. For example,

$$\frac{d}{dt}\begin{pmatrix} p_{12}-p_{23} \\ p_{45}-p_{56} \end{pmatrix} = \begin{pmatrix} -\left(r+\frac{2}{3}R+\frac{11}{12}R'+\frac{7}{6}R''\right) & \frac{2}{3}R+\frac{R'}{6}-\frac{R''}{3} \\ \frac{R}{3}+\frac{R'}{12}-\frac{R''}{6} & -\left(r+\frac{R}{3}+\frac{5}{6}R'+\frac{4}{3}R''\right) \end{pmatrix}\begin{pmatrix} p_{12}-p_{23} \\ p_{45}-p_{56} \end{pmatrix}$$

[4]

Eqs. [4] and the corresponding ones for $p_{12} + 2p_{23}$ and $p_{45} + 2p_{56}$ are solved for the initial condition $p_{12}(0) = 1$, $p_{23}(0) = p_{45}(0) = p_{56}(0) = 0$. From these solutions we obtain

$$\begin{pmatrix} p_{12} \\ p_{23} \\ p_{45} \\ p_{56} \end{pmatrix} = \frac{1}{9}\begin{pmatrix} 2 & 4 & 2 & 1 \\ -1 & -2 & 2 & 1 \\ 2 & -2 & -1 & 1 \\ -1 & 1 & -1 & 1 \end{pmatrix}\begin{pmatrix} e^{-k_1 t} \\ e^{-k_2 t} \\ e^{-k_3 t} \\ 1 \end{pmatrix} \qquad [5]$$

where

$$k_1 = r + \tfrac{3}{4}R' + \tfrac{3}{2}R''$$
$$k_2 = r + R + R' + R'' \qquad [6]$$
$$k_3 = R + R' + R''.$$

The methyl proton-lone proton (the proton outside the methyl groups in the trimethylammonium ion) motion can be treated quite identically. The only change in Eqs. [3]–[5] is to replace p_{12}, p_{23}, p_{45}, and p_{56} by p_{1e}, p_{2e}, p_{4e}, and p_{5e}, respectively, where e refers to the lone proton.

Rate Equations for Protons in Separate Methyl Groups

Let the intermethyl proton pair be initially at 14. By symmetry we know then that

$$p_{15} = p_{16} = p_{24} = p_{34}$$
$$p_{25} = p_{26} = p_{35} = p_{36}$$

$$p_{58} = p_{59} = p_{68} = p_{69} = p_{82} = p_{83} = p_{92} = p_{93} \tag{7}$$
$$p_{57} = p_{67} = p_{48} = p_{49} = p_{72} = p_{73} = p_{81} = p_{91}$$
$$p_{47} = p_{71}.$$

For the six remaining unknown probabilities, we obtain differential equations similar to [2]. When the symmetry conditions [7] are taken into account, these equations can be written:

$$\frac{d}{dt}\begin{pmatrix} p_{14} \\ p_{15} \\ p_{25} \\ p_{58} \\ p_{57} \\ p_{47} \end{pmatrix} = $$

$$\begin{pmatrix} \sigma_{11} & \frac{4}{3}r+\frac{R'}{3} & \frac{R''}{3} & \frac{2}{3}R'' & \frac{2}{3}R' & \frac{2}{3}R \\ \frac{r}{3}+\frac{R'}{12} & \sigma_{22} & \frac{2}{3}r+\frac{R'}{6}+\frac{R''}{6} & \frac{R'}{3}+\frac{R''}{3} & \frac{2}{3}R+\frac{R'}{6}+\frac{R''}{3} & \frac{R'}{6} \\ \frac{R''}{12} & \frac{2}{3}r+\frac{R'}{6}+\frac{R''}{6} & \sigma_{33} & \frac{2}{3}R+\frac{R'}{3}+\frac{R''}{6} & \frac{R'}{3}+\frac{R''}{3} & \frac{R''}{6} \\ \frac{R''}{12} & \frac{R'}{6}+\frac{R''}{6} & \frac{R}{3}+\frac{R'}{6}+\frac{R''}{12} & \sigma_{44} & \frac{2}{3}r+\frac{R'}{3}+\frac{R''}{3} & \frac{R''}{6} \\ \frac{R'}{12} & \frac{R}{3}+\frac{R'}{12}+\frac{R''}{6} & \frac{R'}{6}+\frac{R''}{6} & \frac{2}{3}r+\frac{R'}{3}+\frac{R''}{3} & \sigma_{55} & \frac{r}{3}+\frac{R'}{6} \\ \frac{R}{3} & \frac{R'}{3} & \frac{R''}{3} & \frac{2}{3}R'' & \frac{4}{3}r+\frac{2}{3}R' & \sigma_{66} \end{pmatrix}$$

$$\times \begin{pmatrix} p_{14} \\ p_{15} \\ p_{25} \\ p_{58} \\ p_{57} \\ p_{47} \end{pmatrix} \tag{8}$$

Here again, each diagonal element is equal to minus the sum of all other elements on the same horizontal line. The differential equations [8] can be reduced to three sets of pairs of simultaneous equations by using the linear combinations $p_{14} + 4p_{15} + 4p_{25}$, $p_{47} + 4p_{57} + 4p_{58}$, $p_{14} + p_{15} - 2p_{25}$, $p_{47} + p_{57} - 2p_{58}$, $p_{14} - 2p_{15} + p_{25}$, and $p_{47} - 2p_{57} + p_{58}$. These combinations are solved for the initial condition $p_{14}(0) = 1$, $p_{15}(0) = p_{25}(0) = p_{47}(0) = p_{57}(0) = p_{58}(0) = 0$, giving

$$
\begin{pmatrix} p_{14} \\ p_{15} \\ p_{25} \\ p_{58} \\ p_{57} \\ p_{47} \end{pmatrix} = \frac{1}{27} \begin{pmatrix} 4 & 8 & 2 & 4 & 8 & 1 \\ 1 & 2 & 2 & -2 & -4 & 1 \\ -2 & -4 & 2 & 1 & 2 & 1 \\ -2 & 2 & -1 & 1 & -1 & 1 \\ 1 & -1 & -1 & -2 & 2 & 1 \\ 4 & -4 & -1 & 4 & -4 & 1 \end{pmatrix} \begin{pmatrix} e^{-k_1 t} \\ e^{-k_2 t} \\ e^{-k_3 t} \\ e^{-k_4 t} \\ e^{-k_5 t} \\ 1 \end{pmatrix} \qquad [9]
$$

The quantities k_1, k_2, and k_3 are given by Eq. [6] and

$$
\begin{aligned}
k_4 &= 2r + \tfrac{3}{2}R' + \tfrac{3}{4}R'' \\
k_5 &= 2r + R + R' + R''.
\end{aligned} \qquad [10]
$$

Correlation Functions

The Zeeman spin–lattice relaxation is determined by the time-dependent lattice functions

$$
X_{mn}^{(\mu)} = F_{mn}^{(\mu)} - \overline{F_{mn}^{(\mu)}} \qquad [11]
$$

in the dipolar Hamiltonian

$$
\mathscr{H}_D = \sum_{\mu=-2}^{2} \sum_{m<n} F_{mn}^{(\mu)} S_{mn}^{(\mu)},
$$

where

$$
\begin{aligned}
F_{mn}^{(0)} &= \frac{\gamma^2 \hbar^2}{r_{mn}^3} (1 - 3\cos^2 \theta_{mn}) \\
F_{mn}^{(1)} &= F_{mn}^{(-1)*} = \frac{\gamma^2 \hbar^2}{r_{mn}^3} \sin \theta_{mn} \cos \theta_{mn} e^{-i\phi_{mn}} \\
F_{mn}^{(2)} &= F_{mn}^{(-2)*} = \frac{\gamma^2 \hbar^2}{r_{mn}^3} \sin^2 \theta_{mn} e^{-i2\phi_{mn}}
\end{aligned} \qquad [12]
$$

and $S_{mn}^{(\mu)}$'s are the corresponding spin operators. In [11], $\overline{F_{mn}^{(\mu)}}$ is $F_{mn}^{(\mu)}$ averaged over the motion of the protons. The average intramolecular proton pair correlation function associated with any of the functions $X^{(\mu)}$ can be written (dropping the index μ temporarily):

$$
G(t)_{\text{intra}} = \tfrac{1}{9}[\langle X_{12}^*(0) X_{12}(t) \rangle + \langle X_{23}^*(0) X_{23}(t) \rangle + \cdots + \langle X_{91}^*(0) X_{91}(t) \rangle] \qquad [13]
$$

(the brackets contain nine terms). $X_{mn}^*(0) X_{mn}(t)$ can be expressed in terms of the probabilities [5], for example:

$$
\begin{aligned}
\langle X_{12}^*(0) X_{12}(t) \rangle = X_{12}^*(0) \, [&p_{12} X_{12}(0) + p_{23}(X_{23}(0) + X_{31}(0)) + p_{45}(X_{45}(0) + X_{78}(0)) \\
&+ p_{56}(X_{56}(0) + X_{64}(0) + X_{89}(0) + X_{97}(0))].
\end{aligned} \qquad [14]
$$

Inserting $X_{mn}{}^*(0) X_{mn}(t)$'s as given by [14] into [13] we obtain ($X_{mn}{}^*(0)$ is written as $X_{mn}{}^*$):

$$G^{(\mu)}(t)_{\text{intra}} = p_{12} C_1{}^{(\mu)} + p_{23} C_2{}^{(\mu)} + p_{45} C_3{}^{(\mu)} + p_{56} C_4{}^{(\mu)} \qquad [15]$$

where

$$C_1{}^{(\mu)} = \tfrac{1}{9}[|X_{12}{}^{(\mu)}|^2 + |X_{23}{}^{(\mu)}|^2 + |X_{31}{}^{(\mu)}|^2 + |X_{45}{}^{(\mu)}|^2 + |X_{56}{}^{(\mu)}|^2$$
$$+ |X_{64}{}^{(\mu)}|^2 + |X_{78}{}^{(\mu)}|^2 + |X_{89}{}^{(\mu)}|^2 + |X_{91}{}^{(\mu)}|^2]$$

$$C_2{}^{(\mu)} = \tfrac{2}{9} \operatorname{Re}\,[(X_{23}{}^{(\mu)} + X_{31}{}^{(\mu)}) X_{12}{}^{(-\mu)} + (X_{56}{}^{(\mu)} + X_{64}{}^{(\mu)}) X_{45}{}^{(-\mu)}$$
$$+ (X_{89}{}^{(\mu)} + X_{97}{}^{(\mu)}) X_{78}{}^{(-\mu)} + X_{23}{}^{(\mu)} X_{31}{}^{(-\mu)} + X_{56}{}^{(\mu)} X_{64}{}^{(-\mu)} + X_{89}{}^{(\mu)} X_{97}{}^{(-\mu)}]$$

$$C_3{}^{(\mu)} = \tfrac{2}{9} \operatorname{Re}\,[(X_{45}{}^{(\mu)} + X_{78}{}^{(\mu)}) X_{12}{}^{(-\mu)} + (X_{64}{}^{(\mu)} + X_{97}{}^{(\mu)}) X_{31}{}^{(-\mu)}$$
$$+ (X_{56}{}^{(\mu)} + X_{89}{}^{(\mu)}) X_{23}{}^{(-\mu)} + X_{78}{}^{(\mu)} X_{45}{}^{(-\mu)} + X_{97}{}^{(\mu)} X_{64}{}^{(-\mu)} + X_{89}{}^{(\mu)} X_{56}{}^{(-\mu)}]$$

$$C_4{}^{(\mu)} = \tfrac{2}{9} \operatorname{Re}\,[(X_{56}{}^{(\mu)} + X_{64}{}^{(\mu)} + X_{89}{}^{(\mu)} + X_{97}{}^{(\mu)}) X_{12}{}^{(-\mu)}$$
$$+ (X_{45}{}^{(\mu)} + X_{56}{}^{(\mu)} + X_{78}{}^{(\mu)} + X_{89}{}^{(\mu)}) X_{31}{}^{(-\mu)}$$
$$+ (X_{45}{}^{(\mu)} + X_{64}{}^{(\mu)} + X_{78}{}^{(\mu)} + X_{97}{}^{(\mu)}) X_{23}{}^{(-\mu)} + (X_{89}{}^{(\mu)} + X_{97}{}^{(\mu)}) X_{45}{}^{(-\mu)}$$
$$+ (X_{78}{}^{(\mu)} + X_{89}{}^{(-\mu)}) X_{64}{}^{(-\mu)} + (X_{97}{}^{(\mu)} + X_{78}{}^{(\mu)}) X_{56}{}^{(-\mu)}]. \qquad [16]$$

When the expressions for p_{mn} from [5] are inserted in [15], we finally obtain

$$G^{(\mu)}(t)_{\text{intra}} = \tfrac{1}{9} \sum_{i=1}^{3} K_i{}^{(\mu)} e^{-k_i t}. \qquad [17]$$

The quantities $K_i{}^{(\mu)}$, $\mu = 0, 1, 2$, are defined by

$$K_1{}^{(\mu)} = 2C_1{}^{(\mu)} - C_2{}^{(\mu)} + 2C_3{}^{(\mu)} - C_4{}^{(\mu)}$$
$$K_2{}^{(\mu)} = 4C_1{}^{(\mu)} - 2C_2{}^{(\mu)} - 2C_3{}^{(\mu)} + C_4{}^{(\mu)} \qquad [18]$$
$$K_3{}^{(\mu)} = 2C_1{}^{(\mu)} + 2C_2{}^{(\mu)} - C_3{}^{(\mu)} - C_4{}^{(\mu)}.$$

Note that no constant term appears in [17].

The correlation functions for a lone proton-methyl proton pair can be derived in exactly the same way, giving an expression very similar to [18] in which $M_i{}^{(\mu)}$ appears instead of $K_i{}^{(\mu)}$.

A similar calculation for intermethyl proton pairs yields

$$G^{(\mu)}(t)_{\text{inter}} = \tfrac{1}{27} \sum_{i=1}^{5} L_i{}^{(\mu)} e^{-k_i t} \qquad [19]$$

where

$$\begin{pmatrix} L_1{}^{(\mu)} \\ L_2{}^{(\mu)} \\ L_3{}^{(\mu)} \\ L_4{}^{(\mu)} \\ L_5{}^{(\mu)} \end{pmatrix} = \begin{pmatrix} 4 & 1 & -2 & -2 & 1 & 4 \\ 8 & 2 & -4 & 2 & -1 & -4 \\ 2 & 2 & 2 & -1 & -1 & -1 \\ 4 & -2 & 1 & 1 & -2 & 4 \\ 8 & -4 & 2 & -1 & 2 & -4 \end{pmatrix} \begin{pmatrix} D_1{}^{(\mu)} \\ D_2{}^{(\mu)} \\ D_3{}^{(\mu)} \\ D_4{}^{(\mu)} \\ D_5{}^{(\mu)} \\ D_6{}^{(\mu)} \end{pmatrix} \qquad [20]$$

The quantities $D_i{}^{(\mu)}$, $\mu = 0, \pm 1, \pm 2$, are in turn:

$$D_1{}^{(\mu)} = \tfrac{1}{27} \operatorname{Re} \text{ (the sum of the 27 terms of the type } X_{14}{}^{(\mu)} X_{14}{}^{(-\mu)})$$
$$D_2{}^{(\mu)} = \tfrac{1}{27} \operatorname{Re} \text{ (the sum of the 108 terms of the type } X_{14}{}^{(\mu)} X_{15}{}^{(-\mu)})$$
$$D_3{}^{(\mu)} = \tfrac{1}{27} \operatorname{Re} \text{ (the sum of the 108 terms of the type } X_{14}{}^{(\mu)} X_{25}{}^{(-\mu)})$$

$$D_4^{(\mu)} = \tfrac{1}{27}\,\mathrm{Re}\ \text{(the sum of the 216 terms of the type } X_{14}^{(\mu)}\,X_{58}^{(-\mu)})$$

$$D_5^{(\mu)} = \tfrac{1}{27}\,\mathrm{Re}\ \text{(the sum of the 216 terms of the type } X_{14}^{(\mu)}\,X_{57}^{(-\mu)})$$

$$D_6^{(\mu)} = \tfrac{1}{27}\,\mathrm{Re}\ \text{(the sum of the 54 terms of the type } X_{14}^{(\mu)}\,X_{47}^{(-\mu)}).$$

Although $C_i^{(\mu)}$ and $D_i^{(\mu)}$ are expressed in terms of the time-dependent functions $X_{mn}^{(\mu)}$, eqs. [17] and [19] are valid also for $C_i^{(\mu)}$ and $D_i^{(\mu)}$ calculated in terms of the functions $F_{mn}^{(\mu)}$ (cf. Eqs. [11] and [12]). This can easily be proven by writing $F_{mn}^{(\mu)} - \overline{F_{mn}^{(\mu)}}$ instead of $X_{mn}^{(\mu)}$, and by realizing that all terms containing $\overline{F_{mn}^{(\mu)}}$'s cancel out in the coefficients of $e^{-k_i t}$. In the numerical calculations the total lattice functions $F_{mn}^{(\mu)}$ are used instead of the time-dependent parts $X_{mn}^{(\mu)}$.

Expression for the Proton Zeeman Spin–Lattice Relaxation Time

A general expression for $1/T_1$ of protons in the approximation assuming a common Zeeman spin temperature (20) (neglecting effects of the intramethyl dipolar coupling that may cause nonexponential relaxation (21)) is:

$$\frac{1}{T_1} = \frac{9}{8\hbar^2}(J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)), \qquad [21]$$

where

$$J^{(\mu)}(\mu\omega) = \int_{-\infty}^{\infty} G^{(\mu)}(t)\,e^{i\mu\omega t}\,dt.$$

Inserting the correlation functions [17] and [19] into [21] and carrying out the integration, we obtain for the protons in a trimethylammonium ion:

$$\frac{1}{T_1} = \frac{9}{20\hbar^2}\sum_{\mu=1}^{2}\left[\underbrace{\sum_{i=1}^{3} K_i^{(\mu)}\frac{k_i}{k_i^2 + (\mu\omega_0)^2}}_{\text{(intra)}} + \underbrace{\sum_{j=1}^{5} L_j^{(\mu)}\frac{k_j}{k_j^2 + (\mu\omega_0)^2}}_{\text{(inter)}} + \underbrace{\sum_{n=1}^{3} M_n^{(\mu)}\frac{k_n}{k_n^2 + (\mu\omega_0)^2}}_{\text{(lone proton)}}\right].$$

$$[22]$$

Eq. [22] uses the fact that a proton in a methyl group of a trimethylammonium ion is relaxed by two other protons in the same methyl group, six protons in the other two methyl groups, and one proton outside the methyl groups (lone proton). Further, the lone proton is relaxed by nine protons in the three methyl groups. The contributions of the protons outside the trimethylammonium ion and of the nitrogen nucleus are not taken into account.

When only the methyl group reorientations are considered, $k_1 = k_2 = r$ and the intramethyl contribution to $1/T_1$ is given by:

$$\frac{1}{T_1} = \frac{9}{20\hbar^2}\sum_{\mu=1}^{2}(6C_1^{(\mu)} - 3C_2^{(\mu)})\frac{r}{r^2 + (\mu\omega_0)^2}$$

in agreement with earlier derivations (13, 14, 22). A comparison with existing derivations for the two-motions case (16, 17) shows that the present method provides a more detailed description of the motion. Moreover, expressions not previously available were derived for the lone proton and intermethyl contributions.

Numerical Calculations

Numerical calculations were carried out for TMAHOX. The proton coordinates used were those of Thomas and Renne (*3*), except that a unique intramethyl proton–proton distance of 1.78 Å was used (the directions of the proton–proton vectors were those of Thomas and Renne). To obtain powder averages, the relevant quantities were evaluated for 64 orientations evenly distributed over one-half of a sphere. The factors appearing in Eq. [22] are given in Table 1 (eq. [22] must be multiplied by $\frac{10}{11}$ for the case

TABLE 1

THE RELAXATION CONSTANTS $K_i^{(\mu)}$, $M_i^{(\mu)}$, AND $L_i^{(\mu)}$ ($\times 10^8$ sec^{-2}) FOR A TRIMETHYLAMMONIUM ION[a]

μ	i	$K_i^{(\mu)}$ (intramethyl)	$M_i^{(\mu)}$ (lone proton)	$L_i^{(\mu)}$ (intermethyl)
1	1	24.22	1.74	0.63
	2	48.45	7.28	4.30
	3	19.99	11.68	6.86
	4			1.16
	5			2.39
2	1	94.84	6.83	2.56
	2	193.08	29.49	17.29
	3	81.22	46.65	28.16
	4			4.58
	5			9.78

[a] $\mu = 1, 2$; $i = 1, 2, 3, 4, 5$; these variables appear in the expression for the inverse Zeeman relaxation time, Eq. [22].

of TMAHOX to account for an extra proton outside the trimethylammonium ion Thus, we see that the lone-proton and intermethyl interactions speed up the relaxation considerably, the largest contribution occurring in terms containing k_3. Actually, these are just the terms for which Albert *et al.* (*17*) introduced a somewhat qualitative intermethyl correction. We now realize that in the case of the trimethylammonium ion, the efficiency of the lone proton exceeds that of the intermethyl interaction in relaxing the protons. As for the contribution from the intermethyl interaction, this is relatively insignificant (cf. Table 1).

The quantities k_i, $i = 1, 2, \ldots, 5$, depend on four different reorientation rates r, R, R', and R''. Writing the Arrhenius equations in the form

$$r = r_0 \exp(-A_r/kT),$$ [23]

where k is the Boltzmann constant, T is the absolute temperature, and r_0 and A_r are the pre-exponential factor and the activation energy for the methyl group reorientations, respectively, this leads to eight adjustable parameters. These parameters can be derived by fitting the theoretical expression to experimental results. To reduce the number of parameters we study two cases: (a) $R' = R'' = 0$, and (b) $R/3 = R'/12 = R''/12$. The k_i values for these special cases are given in Table 2. The assumption $R' = R'' = 0$ corresponds to a situation in which the reorientations of the methyl groups are completely

TABLE 2

The Rates k_i for the Assumptions $R' = R'' = 0$ and
$R/3 = R'/12 = R''/12$ ($\rho = 9R$)

	General result	$R' = R'' = 0$	$R/3 = R'/12 = R''/12$
k_1	$r + \frac{3}{4}R' + \frac{1}{2}R''$	r	$r + \rho$
k_2	$r + R + R' + R''$	$r + R$	$r + \rho$
k_3	$R + R' + R''$	R	ρ
k_4	$2r + \frac{1}{2}R' + \frac{3}{4}R''$	$2r$	$2r + \rho$
k_5	$2r + R + R' + R''$	$2r + R$	$2r + \rho$

uncorrelated to reorientations of the entire ions, i.e., the methyl groups retain their relative arrangement during a reorientation of the ion and vice versa. The assumption $R/3 = R'/12 = R''/12$ means that the individual methyl groups reorient freely during a reorientation of the whole ion.

EXPERIMENTAL

TMAI, TMAB, and TMAHOX were synthesized from commercial TMAC and the corresponding acids. The salts were recrystallized twice in either water or ethanol. The composition of TMAHOX was checked by permanganate titration. About 1 cm^3 of each substance was dried for a few weeks over silica gel, evacuated, and pumped for several hours, and finally sealed into glass vials.

The relaxation times were measured at 60.16 and 20.00 MHz on a Bruker B-KR 322s variable frequency pulsed NMR spectrometer. Saturation sequence $-90°$ pulses were used for relaxation times longer than about 7 sec, and 180–90° pulses for shorter times. The temperature was controlled by a gas-flow cryostat and was measured with a copper-constantan thermocouple to an accuracy of ± 2 K. After each small change of temperature, at least 5 min were allowed for the sample to reach thermal equilibrium. At each temperature, data were collected for about 10 different spacings between the pulses. Relaxation times were then obtained from iterative nonlinear least-squares refinement of the data to a precision of about 3 %. All decays of the magnetization were exponential. The calculations were carried out on ICL 1906A and IBM 1800 computers.

RESULTS AND DISCUSSION

The experimental relaxation times at different temperatures are shown for TMAI, TMAB, TMAC, and TMAHOX in Figs. 2a, 2b, 2c, and 2d, respectively. It is clear that a single BPP (23, 24) curve cannot be fitted to the experimental points successfully since the slopes are different on either side of the minima. Such fits were actually attempted, but the root-mean-square differences between the observed and calculated relaxation times were large (12.5, 14.1, 18.4, and 12.4% for TMAI, TMAB, β-TMAC, and TMAHOX, respectively).

An iterative nonlinear least-squares computer program was written so that time factors (τ_0) and activation energies for the reorientations of the methyl groups and the ions as a whole could be refined from the experimental data. This was done using
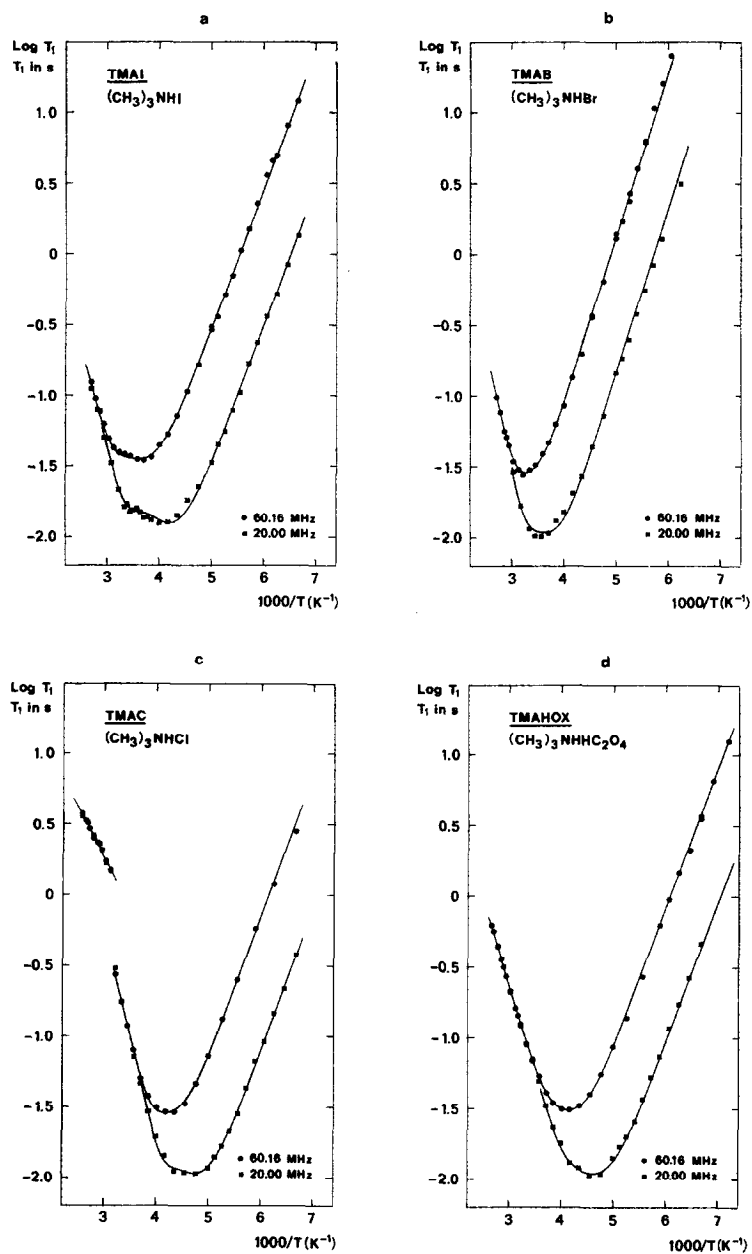
FIG. 2. The experimental data for (a) TMAI, (b) TMAB, (c) TMAC, and (d) TMAHOX together with the theoretical curves calculated from parameters given in Table 3 for the model that assumes no correlation between the motions of the methyl groups and the cations as a whole. The curve for α-TMAC is based on the parameters from a refinement based on the BPP-theory.

Eq. [22] together with the relaxation constants listed in Table 1 and the expressions for the correlation times given in Table 2. The first attempts at refinement showed that the theoretical relaxation times were systematically smaller than the experimental values. This was hardly surprising in view of the approximations involved in the calculations of the relaxation constants. These are very sensitive to the value used for the distance between the protons within the methyl groups (1.78 Å). Furthermore, the vibrational motion is a negligible source of relaxation (20) but effects the relaxation indirectly since the functions $F_{mn}{}^{(u)}$ in Eq. [12] must be averaged over this motion. The effect of these errors should be that the theoretical relaxation is too efficient. To account for this effect, a fifth parameter was introduced to serve as a scale-factor on the intramethyl group contributions. The results of the refinements for the two models described above are given in Table 3. If the values of the scaling parameters (for the $R' = R'' = 0$ model) are converted to apparent intramethyl group hydrogen–hydrogen distances, the values

TABLE 3

THE FINAL PARAMETERS FROM THE LEAST-SQUARES REFINEMENTS USING THE EXPERIMENTAL DATA ILLUSTRATED IN FIG. 2

Compound	Model[a]	RMS observed − calculated (%)	Scaling of intra-CH_3	τ_0 (10^{-14} sec)	E_A (kJ/mole)
TMAI	a	5.0	0.699 ± 0.013	38 ± 3	18.72 ± 0.11
				0.53 ± 0.27	33.4 ± 1.1
	b	4.9	0.705 ± 0.013	41 ± 3	18.64 ± 0.11
				0.69 ± 0.32	32.8 ± 1.1
TMAB	a	9.0	0.75 ± 0.03	23 ± 4	22.1 ± 0.2
				0.027 ± 0.049	42 ± 3
	b	9.3	0.75 ± 0.03	26 ± 5	22.0 ± 0.3
				0.078 ± 0.119	39 ± 3
β-TMAC	a	5.3	0.830 ± 0.018	7.4 ± 1.1	19.3 ± 0.2
				0.0028 ± 0.0016	37.8 ± 1.0
	b	4.5	0.825 ± 0.015	9.5 ± 1.3	18.93 ± 0.18
				0.013 ± 0.004	34.6 ± 0.7
TMAHOX	a	4.3	0.804 ± 0.013	13.2 ± 1.3	18.60 ± 0.13
				0.71 ± 0.12	26.9 ± 0.4
	b	4.3	0.800 ± 0.013	17 ± 2	18.33 ± 0.15
				1.26 ± 0.17	25.7 ± 0.3

[a] In Model a ($R' = R'' = 0$) the motions of the methyl groups and the ions as a whole are assumed to be completely uncorrelated, and in Model b it is assumed that the methyl groups reorient freely during a reorientation of the whole ion. The standard deviations given are based on the least-squares refinement only.

1.89, 1.87, 1.84, and 1.85 Å are obtained for TMAI, TMAB, β-TMAC, and TMAHOX, respectively. These values may be compared with the value of 1.76 Å, which has been obtained in a neutron diffraction study of the closely related compound dimethylammonium hydrogen oxalate (25). On the other hand, this latter value is expected to be

slightly shorter than the arithmetic mean because of the model used to describe the thermal motion (26).

Figure 2 illustrates the experimental points together with the independent model curves calculated from the parameters in Table 3. The root-mean-square values of the differences (as a percentage) between the observed and calculated relaxation times are about 5 % for TMAI, β-TMAC, and TMAHOX, and about 9 % for TMAB. In the latter case there is a slight systematic discrepancy between the observed and calculated values. Thus, the errors in the parameters for TMAB are probably somewhat larger than those given in Table 3 (which are a result of the least-squares fitting only).

As can be seen from Table 3, the agreement between the experimental and calculated relaxation times is about the same for the two models. Therefore, no conclusion can be drawn about the correlation between the two types of motion. The curves illustrated in Fig. 2 are therefore based on the parameters from the simplest model ($R' = R'' = 0$). Furthermore, the parameters from the two models agree to within about three times their combined standard deviations. Since the models used account for the extreme cases of a total absence of correlation and complete correlation, the parameters may be expected to be approximately the same for any intermediate assumption about the correlation between the two motions.

In view of this insensitivity to the detail of the frequency spectrum, and the small numerical values of the relaxation constants for the relaxation rates for $i = 4$ and $i = 5$ in Table 1, a further simpler model was tested in which r and $r + R$ were used instead of $2r$ and $2r + R$ (together with $R' = R'' = 0$). The parameters from this refinement agreed with the corresponding ones in Table 3 to well within one standard deviation.

The cations in α-TMAC reorient quite freely (cf. Introduction) and give rise to a relaxation that is negligible compared to the experimental values. Thus, only the reorientations of the methyl groups contribute to the relaxation, so that a BPP-model can be used in the refinement of the activation energy for the process. The value obtained is 13.4 ± 0.3 kJ/mole. The root-mean-square value for the difference (as a percentage) between the observed and calculated relaxation times becomes 2.7 %. The experimental data and calculated curve are shown in Fig. 2b.

The activation energies for the reorientations of the methyl groups (as listed in Table 3) fall within the range 15–22 kJ/mole obtained for the similar molecule trimethylamine (12). (A value obtained by wide-line NMR has been omitted for reasons given in the Introduction.) If we assume that there is no intermolecular contribution to the barrier for α-TMAC and that the intramolecular barriers are the same for the two phases, an estimate of 6 kJ/mole is obtained for the intermolecular contribution to the barrier for methyl group reorientation in β-TMAC. The corresponding value for trimethylamine is 3 kJ/mole (12).

The activation energies for reorientations of the entire cations depend only on the intermolecular interactions, and thus, they vary somewhat more than the barriers to methyl group reorientation. Such variations may be expected since the packings and sizes of the anions are different in the various compounds. The lowest value for the barrier was obtained for TMAHOX (27 kJ/mole). This may well be related to the result from the X ray study (3) that the methyl carbon lying in the mirror plane has a large amplitude of thermal vibration perpendicular to the plane (see Fig. 1). The possibility of disorder across this plane is also suggested in (3).

ACKNOWLEDGMENTS

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