Relaxation of $^{121}\text{Sb}$ NQR in Antimony Trichloride due to Raman Process

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Z. Naturforsch. 56a, 777–784 (2001); received August 21, 2001

The spin-lattice relaxation times of $^{121}\text{Sb}$ nuclear quadrupole resonance in SbCl$_3$ have been measured from 4.2 K to the m. p., 346 K. The result is analyzed with a theory of the Raman process based on covalency and discussed in comparison with the previous result for $^{35}\text{Cl}$ nuclei.

Key words: SbCl$_3$; $^{121}\text{Sb}$-NQR; Relaxation Times; Raman Process; Covalency.

1. Introduction

In the preceding papers [1–5] we have shown that the relaxation of NMR and NQR in several non-metallic compounds can be accounted for by a theory [6] of the Raman process based on covalency. In the case of SbCl$_3$ we reported that only on the chlorine NQR [2]. For this compound we also reported that a relaxation mechanism due to a certain kind of molecular motions works at high temperature. Now, two problems are left: The one is whether the relaxation of antimony nuclei can also be accounted for by the theory and whether the results are consistent with those for the chlorine nuclei. The other is whether the contribution of the molecular motions is also observed for the relaxation of antimony nuclei. However, there are several difficulties in applying the theory to antimony nuclei. In the next section the method of the measurement of the relaxation times of $^{121}\text{Sb}$ nuclei in SbCl$_3$ is described, and in the following section the results are presented. In Sect. 4, the expressions for the transition probabilities of the antimony nuclei are presented in a rather general form and the problems are discussed together with the difficulties. The conclusion is given in Section 5.

2. Experimental Procedure

As shown in Fig. 1, the energy diagram of $^{121}\text{Sb}$ nuclei (spin 5/2) consists of three levels $E_m(m = \pm 1/2, \pm 3/2, \pm 5/2)$, and three transitions $\nu_i(i=1, 2, 3)$ can be observed owing to a finite value of the asymmetry parameter $\eta$. Irrespective of the responsible interaction, the relaxation in a three-level system is governed by two relaxation times, $T_{1+}$ and $T_{1-}$, and they are expressed with the transition probabilities $W_\alpha(\alpha = a, b, c)$ defined in Fig. 1 as follows:

$$T_{1\pm}^{-1} = W_a + W_b + W_c 
\pm \frac{1}{\sqrt{2}} \sqrt{(W_b - W_c)^2 + (W_c - W_b)^2 + (W_a - W_b)^2},$$

(1)

where the upper and lower signs of the suffix of $T_{1\pm}$ correspond to those on the right hand side, respectively.

The recovery of the signal intensity $S_i(t)$ ($i = 1, 2, 3$) of the $\nu_i$-line following application of a pulse at time $t = 0$

![Fig. 1. Energy levels $E_m(m = \pm 1/2, \pm 3/2, \pm 5/2)$, resonance frequencies $\nu_i(i = 1, 2, 3)$, and upward transition probabilities $W_\alpha(\alpha = a, b, c)$ for a three-level system. The corresponding downward transition probabilities are written as $W_\alpha(1 + \Delta_\alpha)$ $(i = 1, 2, 3)$.
Energy levels are specified by the magnetic quantum number $m$ of the eigen states for $\eta = 0$.](image-url)
is represented as
\[
\frac{S_i(\infty) - S_i(t)}{S_i(\infty)} = a_{i+} \exp \left( -\frac{t}{T_{1+}} \right) + a_{i-} \exp \left( -\frac{t}{T_{1-}} \right).
\]

When the effect of applying a $\pi/2$ pulse on the $v_1$-line is regarded as only equalizing the populations of the corresponding two levels, the coefficients for the $v_1$-line following the saturation of the $v_1$-line are written as
\[
a_{i+} = \frac{-1/T_{1-} + (1/2 + v_2/v_1)(W_b - W_c)}{1/T_{1+} - 1/T_{1-}} \quad (3)
\]
with
\[
a_{i+} + a_{i-} = 1\quad (4)
\]
The derivation of (3) is given in Appendix A. The coefficients for the recovery of the $v_2$-line under the same condition are written as
\[
a_{2+} = \frac{v_1/2v_2 T_{1-} - (1 + v_1/2v_2)(2W_b + W_c)}{1/T_{1+} - 1/T_{1-}} \quad (5)
\]
with
\[
a_{2+} + a_{2-} = -\frac{v_1}{2v_2} \quad (6)
\]
Similarly, when the effect of applying a $\pi$ pulse on the $v_1$-line is regarded as reversing the population of the corresponding levels, the coefficients for the $v_1$-line following the reversal of the $v_1$-line is given by
\[
a_{i+} = \frac{-2/T_{1+} + 2W_a + (1 + v_1/v_2)W_b + (v_2/v_1)W_c}{1/T_{1+} - 1/T_{1-}} \quad (7)
\]
with
\[
a_{1+} + a_{1-} = 2 \quad (8)
\]
The coefficients for the recovery of the $v_2$-line under this condition are determined as
\[
a_{2+} = \frac{v_1/v_2 T_{1-} - (v_1/v_2)W_a - 2(1 + v_1/v_2)W_b - W_c}{1/T_{1+} - 1/T_{1-}} \quad (9)
\]
with
\[
a_{2+} + a_{2-} = -\frac{v_1}{v_2} \quad (10)
\]
The coefficients for the recovery curve of any line following the saturation or the reversal of any line are determined in such a way. The transition probabilities $W_a$ can be determined from the experiment of the saturation recovery on only one of the resonance lines, for example, through (1) and (3) from the values of $T_{1+}$, $T_{1-}$ and $a_{i+}$. However, to determine them uniquely, another experiment is required. Since it is not easy to deal with two frequencies at the same time, in the present study the recovery of the $v_1$-line following the $v_1$-line saturation was examined, and the extra solutions were removed by the examination of the recovery of the $v_1$-line following the reversal of the $v_1$-line.

The energy diagram for $^{121}$Sb nuclei (spin 7/2) consists of four levels, and the relaxation is governed by three time constants. Also, for a system with more than two relaxation times they can, in principle, be determined separately either by the usual method that the contribution appearing as the decay tail is subtracted from the whole recovery curve one after another on a log plot of $[S(\infty) - S(t)]/S(\infty)$, or by a least-squares-fitting with a computer. However, the requirements on the signal-to-noise ratio and the stability rapidly become hard as the number of the involved relaxation times increases. In the present study only $^{121}$Sb nuclei were treated.

The sample and the apparatus were the same as in [2]. A signal averaging was employed with repeating times longer than several times of $T_1$ at given temperatures. A least-squares-fitting of (2) to the recovery curve was performed to obtain $T_{1+}$, $T_{1-}$ and $a_{1+}$.

In observing the recovery at a given temperature, the rf pulses were applied with the exact resonance frequency. On the other hand, in analyzing the data using (1), (3), and (7) such an accuracy of the frequency is not required and the values reported in [7] were used for $v_2$.

### 3. Results

The temperature dependence of the frequency $v_1$ of the $^{121}$Sb NQR measured by us can be represented by the polynomial
\[
v_1(T) = c_0 + c_1T + c_2T^2 + c_3T^3 \quad (11)
\]
with the values of the coefficients given in Table 1. The result agrees with those reported over various temperature ranges by several groups [7].

Figure 2 shows the temperature dependence of two relaxation times $T_{1+}$ and $T_{1-}$. For the cases where the measurement was done more than one times at the same temperature, the averaged values are shown. Roughly
Table 1. Coefficients of ν(T) according to (11), determined by a least-squares-fitting for 57 data from 4.2 to 346 K, and standard deviation σ.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>c₀</td>
<td>59.8805 (MHz)</td>
</tr>
<tr>
<td>c₁</td>
<td>-2.79493 x 10⁴ (MHz/K)</td>
</tr>
<tr>
<td>c₂</td>
<td>-2.42091 x 10⁻⁵ (MHz/K²)</td>
</tr>
<tr>
<td>c₃</td>
<td>-1.81582 x 10⁻⁸ (MHz/K³)</td>
</tr>
<tr>
<td>σ</td>
<td>0.0064842 (MHz)</td>
</tr>
</tbody>
</table>

decreased from about 0.9 at low temperatures to about 0.5 at high temperatures.

The values of T₁⁺, T₁⁻ and a₁⁺ were converted into Wₐ, Wₐ, and Wₖ by the use of (1) and (3). The extra solution could be removed definitely by observing the inversion recovery at 77 K. The observation at one temperature is sufficient for this purpose, because if the exchange of the solutions happened at any temperature, the temperatures dependence of Wₐ would exhibit a discontinuity in spite of the continuity of the T₁⁺'s. Figure 3 shows the temperature dependence of a thus determined set of Wₐ's, where only the data points up to 280 K are plotted because above it the scattering rapidly becomes large owing to the lowering of the signal intensity.

The values of T₂ and Tₙ are 860 and 19.5 μs, respectively, at 77 K.

4. Analysis and Discussion

4.1. Relaxation Mechanism

In the case of chlorine nuclei, the magnetic and the quadrupolar relaxation mechanisms could be discrimi-
nated simply by comparing the isotopic ratio of the observed $T_1$ with the squared ratios of the magnetic dipole moments and the quadrupole moments. This method cannot be applied in the case of antimony nuclei, because the expressions for $T_1$ differ between $^{121}$Sb and $^{123}$Sb nuclei, and moreover it is difficult to separately determine three $T_1$'s for $^{123}$Sb nuclei with sufficient accuracy.

As seen in Fig. 2, the temperature dependence of $T_1$ approaches a $T^{-3}$ dependence at high temperatures except above 250 K. This suggests that the Raman process is dominant, as in the case of $^{35}$Cl nuclei. In the following the relaxation is analyzed by assuming the Raman process alone.

4.2. Raman Process

We have shown that a theory of the Raman process based on covalency [6] can account for the relaxation in several compounds [1-5]. The theory assumes some conditions. Parts of them have been released by our extension. First, the condition of inversion symmetry of the molecule was made ineffective by including cross-terms in the calculation of $L\nu(ka)$, as shown later. Second, the condition of equivalence of the ions was loosened to the condition of equi-distance by using different $N_\mu$ and $D\nu$ values for different bond pairs as shown below. For the quadrupolar relaxation, the transition probabilities from the level $m$ to level $m + \mu$ ($\mu = 1, 2$), $P(m, m + \mu)$, are written as [8]

\[
P(m, m + 1) = \frac{(2m + 1)^2(I - m)(I + m + 1)}{2I(2I - 1)^2} W_1,
\]

\[
P(m, m + 2) = \frac{(I - m - 1)(I + m + 2)(I - m)(I + m + 1)}{2I(2I - 1)^2} W_2.
\]

(12)

If in an AB$_2$ type molecule the condition of axial symmetry for the EFG about the bond A-B is satisfied, $W_\mu(\mu = 1, 2)$ for nuclei A is expressed as

\[
W_1 = \frac{10 A^2 c^3}{\pi^3 a^2 d^2/3} T^{*2}
\]

\[
\times \sum_{(n, n')} \sum_{\nu = 1}^3 N_1 \nu(\phi_{nn'}) D\nu(T^*, \phi_{nn'})
\]

\[
W_2 = \frac{40 A^2 c^3}{\pi^3 a d^2/3} T^{*2}
\]

\[
\times \sum_{(n, n')} \sum_{\nu = 1}^3 N_2 \nu(\phi_{nn'}) D\nu(T^*, \phi_{nn'})
\]

(13)

where

\[
A' = \frac{3}{100} e^2 Q \left\langle \frac{1}{r^3} \right\rangle_A
\]

for spin $I = 5/2$. $\langle r^{-3} \rangle_A$ means the expectation value with respect to the valence $p$ electron of an A atom. In (13) the first summation is made over the combination of bonds $n$ and $n'$ between A and B atoms. To avoid the unduly increase of the suffix $\nu$ with increase of the number of bonds, $N_\mu$ and $D\nu$ are regarded as functions of the angle $\phi_{nn'}$ between bonds $n$ and $n'$. $N_\mu$ is also a function of $\Lambda$, as shown in Appendix B, where $\Lambda$ is a measure of covalency of the bond [6]. $a$ denotes the bond length, $d$ the density, $T^*$ the temperature reduced by the Debye temperature $\theta_D$. $c$ is defined as $c = k_R a$ with the maximum wave number $k_D = (6 \pi^2 N/\nu)^{1/3}$, $N$ being the number of atoms in the unit cell of volume $V$. $\nu = v k_R / (v k_D)$ is the sound velocity. $D\nu$ is defined as

\[
D\nu(T^*, \phi_{nn'}) =\frac{T^*}{\pi} \int_0^\infty \frac{x^2 e^{-x}}{(x^2 - 1)^3} L\nu(c T^* x, \phi_{nn'}) dx
\]

(15)

with

\[
L_1(ka, \phi_{nn'}) = \left[ \frac{1}{2} f(ka\sqrt{2(1 - \cos\phi_{nn'})}) \right]^2,
\]

\[
L_2(ka, \phi_{nn'}) = \left[ \frac{1}{2} f(2ka\sqrt{2(1 + \cos\phi_{nn'})}) \right]^2,
\]

\[
L_3(ka, \phi_{nn'}) = 2 \left[ \frac{1}{2} f(ka\sqrt{2(1 - \cos\phi_{nn'})}) \right]^2
\]

\[
\times \left[ 1 - 2 f(ka) + \frac{1}{2} f(2ka\sqrt{2(1 - \cos\phi_{nn'})}) \right],
\]

(16)

where

4.3. Transition Probabilities

When $\eta$ is small and consequently the mixing among the states can be neglected, $W_\mu$ is given by summing up $P(1/2 \rightarrow 3/2)$, $P(-1/2 \rightarrow -3/2)$, and $P(-1/2 \rightarrow 3/2)$, and
Table 2. Crystal [9] and $^{121}$Sb NQR [10] data of SbCl$_3$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$V$ ($\text{Å}^3$)</th>
<th>$a$ (Å)</th>
<th>$\phi$ (°)</th>
<th>$d$ (g/cm$^3$)</th>
<th>$\epsilon^2 Q_{\text{dipol}}$ (MHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>482.3</td>
<td>2.340</td>
<td>95.70</td>
<td>3.141</td>
<td>383.762$^a$</td>
<td>0.187035$^a$</td>
</tr>
<tr>
<td></td>
<td>(Sb-Cl$_1$)</td>
<td>(Cl$_1$-Sb-Cl$_3$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.368</td>
<td>90.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Sb-Cl$_{1,3}$)</td>
<td>(Cl$_3$-Sb-Cl$_1$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ at 78.6 K.

$P(1/2 \rightarrow -3/2)$, while $W_b$ is given as a sum of $P(3/2 \rightarrow 5/2)$ and $P(-3/2 \rightarrow -5/2)$, and $W_c$ is given as a sum of $P(1/2 \rightarrow 5/2)$ and $P(-1/2 \rightarrow -5/2)$. The use of (12) for these $P(m, m')$'s yields

$$W_a = \frac{4}{5} W_1 + \frac{9}{5} W_2, \quad W_b = 2 W_1, \quad W_c = W_2.$$ (17)

Then, we get the following forms convenient for fitting:

$$W_a T^{-2} = (\tau_a \theta_a^2)^{-1} \left[ \sum_{\nu=1}^{3} \epsilon_{a}(\phi_1) D_{\nu}(T^*, \phi_1) + \epsilon_{a}(\phi_2) \right] + \sum_{\nu=1}^{3} D_{\nu}(T^*, \phi_2).$$ (18)

where

$$\frac{1}{\tau_a} = \frac{9}{1250} \pi a^2 d^2 v^3 N_{11}(\phi_1),$$

$$\frac{1}{\tau_b} = \frac{9}{500} \pi a^2 d^2 v^3 N_{11}(\phi_1),$$

$$\frac{1}{\tau_c} = \frac{9}{250} \pi a^2 d^2 v^3 N_{21}(\phi_1).$$ (19)

and

$$\epsilon_{a}(\phi_{nn'}) = \frac{N_{11}(\phi_{nn'}) + 9 N_{21}(\phi_{nn'})}{N_{11}(\phi_1)},$$

$$\epsilon_{b}(\phi_{nn'}) = \frac{N_{11}(\phi_{nn'})}{N_{11}(\phi_1)},$$

$$\epsilon_{c}(\phi_{nn'}) = \frac{N_{21}(\phi_{nn'})}{N_{21}(\phi_1)}.$$ (20)

Though $\eta$ for the Sb nuclei of SbCl$_3$ is not so small as shown in Table 2, in the following it is assumed to vanish for brevity. Consequently, agreement between the experiment and the theory is not pursued with high accuracy.

4.4. Debye Temperature

In the crystal, one Cl atom of SbCl$_3$ occupies site I (Cl(1)) and two occupy site II (Cl(2) and Cl(3)). $N_{\mu\nu}$ is calculated for the principal axis system of the EFG at Sb nuclei, as shown in Figure 4. The direction cosines of the Sb–Cl(1) bond is denoted by $(\alpha, \beta, \gamma)$, and those of Sb–Cl(2) and Sb–Cl(3) bonds by $(\alpha', \beta', \gamma')$ and $(\alpha', -\beta', \gamma')$, respectively. The following relation is assumed for the measure of covalency $\lambda$ as in [1–5]:

$$\lambda \propto \exp \left( -\frac{r}{\varrho} \right),$$ (21)

where $\varrho$ is the repulsive range parameter and $r$ the atomic distance. Using a value $a = 2.359$ Å as the weighted average of bond lengths together with a value $\varrho = 0.345$ Å [6] we can express $N_{\mu\nu}$ as a function of $\gamma$ and $\gamma'$ only, as shown in Appendix B. Then we obtain the values listed in Table 3 for $N_{\mu\nu}$. The values of $\epsilon(\phi_{nn'})$...
are obtained from the values of \( N_{\mu\nu}(\phi_{\mu\nu}) \) through (20). \( D_e(\phi_{\mu\nu}) \) was calculated numerically for various \( T^* \). Then (18) can be fitted to each \( W_\alpha T^{-2} \) in Fig. 3 by scaling \( W_\alpha \) and \( T \) respectively with \( \tau_\alpha \) and \( \theta_\alpha \) as fitting parameters. The results are shown in Table 4. In the fitting of \( W_\alpha \) and \( W_c \), \( \theta_\alpha \) was fixed at the value obtained for \( W_p \), 98.2 K, because the scattering is large and reasonable values were not obtained for them. Data up to 250 K were employed because above this temperature contributions from molecular motions seems to be significant. The value of \( \theta_\alpha \) obtained from the \( ^3\text{Cl} \) relaxation was 141.2 K. On the other hand, from the X-ray analysis values from 106.1 to 121.2 K are obtained for Sb atoms [2].

### Table 4. The results of the fitting of \( W_\alpha T^{-2} \) (\( \alpha = a, b, c \)).

<table>
<thead>
<tr>
<th>( \theta_\alpha (\text{K}) )</th>
<th>( W_a )</th>
<th>( W_b )</th>
<th>( W_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(98.2)</td>
<td>98.2</td>
<td>(98.2)</td>
<td>0.2457</td>
</tr>
<tr>
<td>0.0858</td>
<td>0.0199</td>
<td>0.0621</td>
<td></td>
</tr>
</tbody>
</table>

4.5. Covalency

In the case of halogen nuclei the coupling constants for the free atoms are reported, so that the values of \( \lambda \) could be determined from the values of \( \tau \) and could be compared with the ratio of the coupling constant of the molecule to that of the free atom, \( f = e^2 Q_{\text{mol}} e^2 Q_{\text{at}} \) [1-3]. In the case of antimony nuclei the coupling constant for the free atom is not reported. Moreover, \( \lambda \) should not be compared directly with \( f \). However, since \( r^{-3}\text{Sb} = (5/4) q_{\text{at}} \) for a p electron, \( e^2 Q(r^{-3})_{\text{Sb}} \) can be replaced by \( (5/4)e^2 Q_{\text{mol}}/f \). Then we can use the value in Table 2 for \( e^2 Q_{\text{mol}} \) and get the following expression for \( \tau_\alpha \) from (19):

\[
\tau_\alpha = \frac{\tau_\alpha^0 (f/\lambda)^2}{\lambda/\lambda},
\]

where \( \tau_\alpha^0 = 4.39 \times 10^{-4} \text{ s}, \tau_p^0 = 1.75 \times 10^{-4} \text{ s}, \) and \( \tau_\alpha^0 = 4.57 \times 10^{-4} \text{ s}. \) Equating these \( \tau_\alpha \) with the values in Table 4 we get for \( \lambda/\lambda \) the values of 0.0423, 0.0937, and 0.0858 from \( \tau_a, \tau_p, \) and \( \tau_c, \) respectively. To determine the value of \( \lambda \) another relation between \( f \) and \( \lambda \) is required. If, for the brevity, \( C_3 \) symmetry is assumed for the molecule and the Townes-Dailey's theory is applied, \( f \) is represented as [11]

\[
f = 2(1 - \cos^2 \theta) + \frac{3 \cos^2 \theta - 1}{\sin^2 \theta} \lambda
\]

\[
= \frac{3 \cos \phi}{1 - \cos \phi} \left( \frac{\lambda}{\lambda - 2} \right),
\]

where \( \theta \) denotes the angle each Sb-Cl makes with the \( C_3 \) axis and \( \phi \) is the angle between Sb-Cl bonds. The expression of the first line is derived by considering the sp³ hybridized orbitals, one of which accommodates two electrons of the lone pair and the remainder each accommodates \( \lambda \) electrons corresponding to the Sb-Cl bond. In going to the second line, the relation between \( \theta \) and \( \phi \) for this symmetry, \( \sin^2 \theta = 2(1 - \cos \phi)/3, \) is used. When a value of 94.13° is used for \( \phi \) as the weighted average, values of 0.017, 0.037, and 0.034 are obtained for \( \lambda, \) corresponding to the above obtained values for \( \lambda f \). These are by one order of magnitude smaller than the values of 0.284 and 0.260 for \( \lambda \) obtained from the \( ^3\text{Cl} \) relaxation [2]. Though the value of \( \lambda \) depends on \( \phi \), the situation is not improved even by taking into account the ambiguity of \( \phi \). Though the value of \( \lambda \) depends on \( \theta^2/2, \lambda \) is still much smaller even if the value of 141.2 K obtained from the \( ^3\text{Cl} \) relaxation is used.

The discrepancy is not restricted in the absolute magnitude. The relative magnitudes of \( \tau_\alpha \) expected from (19) are \( \tau_1^1: \tau_2^1: \tau_3^1 = N_{11}(\phi_{11})/5: N_{11}(\phi_{11})/2: N_{21}(\phi_{11}), \) which, according to Table 3, are 327:817:314, whereas the determined ones are 4.07:50.3:16.1 as calculated from Table 4. The third discrepancy lies in the ratio of \( T_{1+} \) and \( T_{1-} \). Substitution of (17) into (1) yields

\[
\begin{align*}
T_{1+}^{-1} &= \frac{14 (1 + w) + \sqrt{76 - 88 w + 61 w^2}}{14 (1 + w) + \sqrt{76 - 88 w + 61 w^2}}, \\
T_{1-}^{-1} &= \frac{14 (1 + w) + \sqrt{76 - 88 w + 61 w^2}}{14 (1 + w) + \sqrt{76 - 88 w + 61 w^2}},
\end{align*}
\]

where

\[
\begin{align*}
w &= \frac{W_2}{W_1} = \frac{4 \sum_{\{n, n'\}} \Sigma v N_{2v}(\phi_{nn'}) D_v(T^*, \phi_{nn'})}{\sum_{\{n, n'\}} \Sigma v N_{2v}(\phi_{nn'}) D_v(T^*, \phi_{nn'})}.
\end{align*}
\]

As \( w \) increases from 0, the ratio \( T_{1+}^{-1}/T_{1-}^{-1} \) decreases from 4.30 and takes a minimum 1.66 at \( w = 1.1 \) and approaches 3.52 at \( w = \infty \). The numerical calculation for SbCl₃ shows that, except \( T^* < 0.1, w \) takes a nearly constant value 0.76, corresponding to \( T_{1+}^{-1}/T_{1-}^{-1} = 1.74, \) whereas the observed values are close to 3.4. The fourth discrepancy appears in \( a_{1+} \), given by (3), which is written as

\[
a_{1+} = \frac{-9 - 16.5 w + \sqrt{76 - 88 w + 66 w^2}}{2 \sqrt{76 - 88 w + 66 w^2}}.
\]

The right hand side is negative for all values of \( w \), in contrast with the observed values \( a_{1+} = 0.5 - 0.9 \). These discrepancies may be attributed to the fact that this compound does not satisfy the conditions...
which are assumed in the theory of the Raman process based on covalency [6]. First, the theory assumes axial symmetry of the EFG around the bond, whereas in SbCl₃, even if covalency is supposed in only one Sb-Cl bond together with pure ionicity in other bonds, the lone pair electrons destroy the axial symmetry about that bond. In fact, when Sb⁺³ ion forms covalent bonding with one Cl atom with \( \lambda \) electrons in the orbital directed toward the Cl atom together with the lone pair, and the \( z \) axis is taken along the Sb-Cl bond, \( \eta \) is expressed as

\[
\eta = \frac{3(1 - \alpha^2) \sin^2 \theta}{(1 - \alpha^2)(2 - 3 \sin^2 \theta) + \lambda (1 - \beta^2)}, \tag{27}
\]

where \( \alpha \) and \( \beta \) denote the amounts of s-character of the lone pair orbital and the Sb-Cl bond orbital, respectively, and they are related with \( \phi \) by \( \alpha^2 = 2 \cot^2 \phi \) and \( \beta^2 = (3 \sin^2 \theta - 2)/3 \sin^2 \theta \). When any value obtained for \( \lambda \) is used together with the value \( \phi = 94.13^\circ \), \( |\eta| \) becomes larger than unity, far from the axial symmetry. Second, the finite \( T \) causes the mixing of the states, and then \( W_a (\alpha = a, b, c) \) is not related with \( W_i (i = 1, 2) \) by (17), and moreover \( W_0 \) is also required. The discrepancy about \( a_{1+} \) originates only from the neglect of the mixing. To meet the actual situation, the theory must be modified from the first stage and it is considerably laborious. In addition, the contribution from d electrons may have to be taken into consideration [10].

The expressions derived for \( W_1 \) and \( W_2 \), (13), may be applied to NMR in SbCl₅, for example, because the condition of axial symmetry is satisfied and in NMR the mixing is also negligible owing to the large Zeeman interaction. However, too small values of \( \lambda \) were also obtained for the bridging halogen nuclei in metal halides, [1, 3] and \(^{27}\)Al nuclei in AlBr₃, [4]. The present theory seems to give too large relaxation rates for multi-bond systems.

5. Conclusion

The spin lattice relaxation times of \(^{121}\)Sb NQR in SbCl₃ have been measured between 4.2 K and the melting point. They were converted into transition probabilities, and up to this point the results are correct. When they are compared with the theory of the Raman process based on covalency, significant discrepancies were found in several respects. All these discrepancies are attributed mainly to the neglect of the destruction of axial symmetry of the EFG about the bond by the lone pair. In addition, they originate partly from the neglect of mixing of the states among the levels and partly from the neglect of the contribution of d electrons. At high temperatures near the melting point a contribution of some molecular motions was observed as in the \(^{35}\)Cl relaxation.

Appendix A Derivation of the Recovery Curve

In the following the high temperature approximation is used. When the population of the level \( E_m (m = \pm 1/2, \pm 3/2, \pm 5/2) \) is denoted by \( N_i (i = |m| + 1/2) \), the rate equations are written as

\[
\frac{dN_1}{dt} = -N_1 [W_b(1 + \Delta_2) + W_c(1 + \Delta_3)]
\]

\[
+ N_2 W_b + N_1 W_c,
\]

\[
\frac{dN_2}{dt} = N_3 W_b(1 + \Delta_2) - N_2 [W_a(1 + \Delta_1) + W_b]
\]

\[
+ N_1 W_d,
\]

\[
\frac{dN_3}{dt} = N_3 W_c(1 + \Delta_3) + N_2 W_d(1 + \Delta_1)
\]

\[
- N_1 (W_c + W_d).
\]

The solutions are given by

\[
N_i (t) = N_i (\infty) \left[ 1 - a_{i+} \exp \left( -\frac{t}{T_{i+}} \right) - a_{i-} \exp \left( -\frac{t}{T_{i-}} \right) \right],
\]

where \( N_i (\infty) \) are the values at thermal equilibrium and are written as

\[
N_3 (\infty) = \frac{N}{3} \left( 1 - \frac{1}{3} \Delta_1 - \frac{2}{3} \Delta_2 \right),
\]

\[
N_2 (\infty) = \frac{N}{3} \left( 1 - \frac{1}{3} \Delta_1 + \frac{1}{3} \Delta_2 \right),
\]

\[
N_1 (\infty) = \frac{N}{3} \left( 1 + \frac{2}{3} \Delta_1 + \frac{1}{3} \Delta_2 \right),
\]

where \( N \) denotes the total population and \( \Delta_i = \hbar \nu_i/k_B T \) \((i = 1, 2, 3)\). When a \( \pi/2 \) pulse is applied to the \( \nu_i \)-transition at time \( t = 0 \), the initial condition is given by

\[
N_3 (0) = N_3 (\infty),
\]

\[
N_1 (0) = N_2 (0) = \frac{1}{2} (N_1 (\infty) + N_2 (\infty))
\]

\[
= \frac{N}{3} \left( 1 + \frac{1}{6} \Delta_1 + \frac{1}{3} \Delta_2 \right).
\]
These use of these conditions yields
\[ a_{3+} + a_{3-} = 0, \]
\[ \frac{a_{3+}}{T_{1+}} + \frac{a_{3-}}{T_{1-}} = \left( \frac{1}{2} \Delta_1 + \Delta_2 \right) (W_b + W_c), \]
\[ a_{2+} + a_{2-} = -\frac{1}{2} \Delta_1, \]
\[ \frac{a_{2+}}{T_{1+}} + \frac{a_{2-}}{T_{1-}} = -\left( \frac{1}{2} \Delta_1 + \Delta_2 \right) W_b, \]
\[ a_{1+} + a_{1-} = \frac{1}{2} \Delta_1, \]
\[ \frac{a_{1+}}{T_{1+}} + \frac{a_{1-}}{T_{1-}} = -\left( \frac{1}{2} \Delta_1 + \Delta_2 \right) W_c. \]

These determine \( a_{3\pm} \) and \( a_{1\pm} \). Since the signal intensity is proportional to the population difference between the corresponding levels, the coefficients \( a_{3\pm} \) and \( a_{1\pm} \) are determined as in (3) and (5) in the text. In the case of application of a \( \pi \)-pulse the initial conditions are replaced by
\[ N_3(0) = N_3(\infty), \]
\[ N_2(0) = N_2(\infty), \]
\[ N_1(0) = N_1(\infty). \]

Appendix B Calculation of \( N_{\mu\nu} \)

\( N_{\mu\nu} \) is given as a sum of the term \( \Sigma_{pp'} w_{1n}^* w_{1'n} \) in (4.35) of [6] for the possible combinations of bonds \( n \) and \( n' \). If, in calculating the sums for various \( \phi_{nn'} \), the relations
\[ \alpha^2 + \gamma^2 = 1, \]
\[ \alpha'^2 + \beta'^2 + \gamma'^2 = 1, \]
\[ \alpha\gamma' + \gamma\alpha' = \cos \phi_{12} = \cos \phi_{13}, \]
\[ \alpha'^2 - \beta'^2 + \gamma'^2 = \cos \phi_{23} \]
are used to eliminate \( \alpha, \alpha', \) and \( \beta' \), we obtain \( N_{\mu\nu}(\phi_{nn'}) \) as a function of \( \lambda \) and \( \gamma' \) and variables \( u \) and \( v \) defined as
\[ u = \frac{1}{2} \lambda' - \lambda, \]
\[ v = 4\lambda - \frac{5}{2} a\lambda' + \frac{1}{2} a^2 \lambda'', \]
where \( \lambda' \) and \( \lambda'' \) are the first and second derivatives with respect to \( r \).

[4] N. Okubo, M. Igarashi, and R. Yoshizaki, Z. Naturforsch. 51a, 277 (1996), where the term \( (1/15) (3\cos^2 \phi - 1) v^2 \) in the brackets of (7) should be multiplied by \( \cos^2 \phi \), and '94 (1994)' in [14] should read '91'.