NQR Study of AlBr$_3$ Complexes with Donor-Acceptor O–Al Bond *

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^{81}Br and ^{27}Al NQR were observed in AlBr$_3$ complexes with 4-XC$_6$H$_4$NO$_2$(X = H, Cl, Br, I, CH$_3$, and C$_2$H$_5$), C$_6$H$_5$COBr, (C$_6$H$_5$)$_2$CO, and (C$_2$H$_5$)$_2$O. In the 4-XC$_6$H$_4$NO$_2$ complexes, the ^{27}Al quadrupole coupling constants (QCC's) were well correlated with the Hammett σ_p's of the para-substituents, i.e., electron-withdrawing groups caused reduction of the charge density of O–Al bonds which resulted in large ^{27}Al QCC's and vice versa. The temperature dependences of the ^{81}Br NQR frequencies and quadrupolar spin-lattice relaxation times showed that the 4-C$_2$H$_5$C$_6$H$_4$NO$_2$ and C$_6$H$_5$COBr complexes undergo phase transitions at 154 K and around 200 K, respectively, and show hindered rotation of the AlBr$_3$ groups at higher temperatures, and that the (C$_2$H$_5$)$_2$O complex reorients above ca. 120 K.

Introduction

AlBr$_3$ forms donor-acceptor complexes with donor molecules containing N, O, or S; the nature of these complexes has been studied by Br NQR measurements [1–6]. The mean shift $\Delta\nu_m$ in the ^{81}Br NQR frequencies at 77 K on complex formation is defined as [1]

$$\Delta\nu_m = \nu_m(\mathrm{Al_2Br_6}) - \left(\sum_{i=1}^{n} \gamma_i \nu_i\right) \Big/ n, \tag{1}$$

where n is the multiplicity of the spectrum and γ_i the relative intensity. The mean frequency ν_m for Al$_2$Br$_6$ was calculated from the NQR frequencies $\nu(^{81}\mathrm{Br})$ = 95.055 and 96.426 MHz, of two NQR lines assigned to the terminal bromines. $\Delta\nu_m$ depends linearly on the heat of formation, ΔH, of the complexes RR′SO$_2$ · AlBr$_3$ and RR′SO$_2$ · 2 AlBr$_3$ [2]. There is no correlation between $\Delta\nu_m$ and the shift $\Delta\nu$(C=O) of the carbonyl stretching frequency on formation of the complexes (RC$_6$H$_4$)$_2$C=O · AlBr$_3$ [3], and there is neither a definite relation between $\Delta\nu_m$ and $\Delta\nu$(C=O) nor between $\Delta\nu_m$ and ΔH on formation of complexes RR′C=O · AlBr$_3$ [1, 4]. In these cases, the differences among the $\Delta\nu_m$'s, i.e., the differences in donor strengths of ligand molecules were considered to be overshadowed by the crystal field [1, 3]. ^{27}Al quadrupole coupling constants (QCC's) are a good measure for the degree of charge transfer [5, 6]. Therefore we have performed ^{27}Al NQR measurements to make sure whether the above explanation is true or not.

Experimental

The formation of 1:1 AlBr$_3$ complexes with para-substituted nitrobenzenes (4-XC$_6$H$_4$NO$_2$) and benzoyl bromide (C$_6$H$_5$COBr) was confirmed by infrared (IR) spectroscopy [7, 8]. The 1:1 complexes were prepared by mixing a CS$_2$ solution of AlBr$_3$ with the appropriate donor molecules in the same solvent and crystallized by evaporation of CS$_2$ under reduced pressure. AlBr$_3$ complexes are very sensitive to moisture like AlBr$_3$ itself and were handled under dry N$_2$ atmosphere. The 4-C$_2$H$_5$C$_6$H$_4$NO$_2$ complex was crystallized from hexane-CS$_2$ solution under reduced pressure or by keeping the CS$_2$ solution at −10°C in a

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refrigerator. The $4\text{-}IC_6H_4NO_2$ complex was prepared by refluxing the CS_2 solution and recrystallized from the hot solution. Although two modifications were reported for both $C_6H_5NO_2$ and $4\text{-}CH_3C_6H_4NO_2$ complexes [7], we obtained only one form of each. Br elementary analyses were performed by decomposing the molecular complexes with water. For the most of the molecular complexes a water-insoluble deposit was left. The Br contents were determined by the potentiometric titration; the results are listed in Table 1.

Table 1. Br contents of $AlBr_3$ complexes.

Donor	Found (%)	Calc. (%)
$C_6H_5NO_2$	61.06[a]	61.50
$4\text{-}CH_3C_6H_4NO_2$	58.68[b]	59.36
$4\text{-}C_2H_5C_6H_4NO_2$	55.65[b]	57.37
$4\text{-}ClC_6H_4NO_2$	55.15[b]	56.51
$4\text{-}BrC_6H_4NO_2$	50.03[b]	51.15
$4\text{-}IC_6H_4NO_2$	44.88[b]	46.49
C_6H_5COBr	70.69[b, c]	70.76
$(C_6H_5)_2CO$	52.09[b]	53.33
$(C_2H_5)_2O$	69.41	70.35

[a] Insoluble oil was left.
[b] Insoluble solid deposit was left.
[c] Including carbonyl Br atom.

^{81}Br NQR was observed with a superregenerative-type spectrometer and ^{27}Al NQR by the $^{81}Br\text{-}^{27}Al$ spin echo double resonance (SEDOR) method [9, 10], using Matec pulsed NQR spectrometers. The spin-lattice relaxation time (T_1) was measured by observing the free induction decay (FID) following after a $90°\text{-}\tau\text{-}90°$ pulse sequence or the FID of the echo signals after a $180°\text{-}\tau\text{-}90°\text{-}\tau'\text{-}180°$ pulse sequence, where τ and τ' denote delay times. DTA measurements were carried out with a homemade apparatus.

Results and Discussion

The ^{81}Br NQR frequencies for $AlBr_3$ complexes at liquid N_2 temperature are listed in Table 2. Each line both in the $4\text{-}CH_3C_6H_4NO_2$ and $4\text{-}C_2H_5C_6H_4NO_2$ complexes could be assigned to two $AlBr_3$ groups labeled a and b, according to the results of the SEDOR experiment. The average ^{81}Br NQR frequency for each nitrobenzene derivative complex was within ± 0.7 MHz of the mean value for all complexes, 84.75 MHz. The average value of the $\Delta\nu_m$'s was 10.99 MHz and smaller than 13.05 MHz for $(RC_6H_4)_2C{=}O$ complexes [3] and 15.16 MHz for $RCH_3C{=}O$ complexes [1] and comparable to 10.56 MHz for R–O–R complexes [11]. The ^{27}Al NQR parameters are listed in Table 3. From IR measurement it was concluded that an O–Al bond between an O in a nitro group and $AlBr_3$ is formed in $AlBr_3$ complexes with $4\text{-}XC_6H_4NO_2$, and that the shifts of the symmetric stretching vibration of the nitro group by formation of the complexes depends on the nature of X [7]. In addition, we have found that there is a correlation between ^{27}Al QCC's and Hammett σ_p's [12]. The ^{27}Al QCC's are plotted against Hammett σ_p's of X in Fig. 1; the bars cover the calculated values on the assumption that η ranges from 0.0 to 0.3, according to the values for $4\text{-}ClC_6H_4NO_2$ and $C_6H_5NO_2$ complexes. We consider that the electron withdrawing capacity of X affects the electron density of the O–Al bond.

Table 2. ^{81}Br NQR frequencies ν of $AlBr_3$ complexes at liquid N_2 temperature.

Donor		ν/MHz		
$C_6H_5NO_2$		83.83 (2),	84.84 (1)	
$4\text{-}CH_3C_6H_4NO_2$	a	83.44 (2),	87.39 (1)	
	b	84.35 (1),	84.99 (1),	85.72 (1)
$4\text{-}C_2H_5C_6H_4NO_2$	a	84.43 (1),	85.26 (1),	86.65 (1)
	b	82.16 (1),	83.67 (1),	86.54 (1)
$4\text{-}ClC_6H_4NO_2$		83.62 (1),	84.67 (1),	86.22 (1)
$4\text{-}BrC_6H_4NO_2$		83.50 (1),	84.79 (1),	86.18 (1)
$4\text{-}IC_6H_4NO_2$		81.97 (1),	86.54 (1),	86.84 (1)
C_6H_5COBr		81.85 (1),	83.96 (1),	85.13 (1)
$(C_6H_5)_2CO$		79.13 (1),	81.47 (1),	82.48 (1)
$(C_2H_5)_2CO$		82.03 (1),	84.00 (1),	84.37 (1)

Intensity ratios in the parentheses.

Table 3. ^{27}Al NQR parameters of $AlBr_3$ complexes at liquid N_2 temperature.

Donor		ν_1/MHz	ν_2/MHz	η	e^2Qq/h/MHz
$C_6H_5NO_2$		1.072	1.912	0.312	6.491
$4\text{-}CH_3C_6H_4NO_2$	a	1.031	–	–	6.88*
	b	0.910	–	–	6.02*
$4\text{-}C_2H_5C_6H_4NO_2$	a	1.049	–	–	7.00*
	b	1.009	–	–	6.72*
$4\text{-}ClC_6H_4NO_2$		1.349	2.678	0.076	8.937
$4\text{-}BrC_6H_4NO_2$		1.355	–	–	9.03*
$4\text{-}IC_6H_4NO_2$		1.341	–	–	8.94*
C_6H_5COBr		1.061	–	–	7.07*
$(C_6H_5)_2CO$		1.131	–	–	7.54*
$(C_2H_5)_2O$		0.596	1.152	0.165	3.860

* Calculated value assuming $\eta = 0$.

According to the the Townes-Dailey method, on the assumption that the $AlBr_3$ group has C_{3v} symmetry, the ^{27}Al QCC depends on the difference between the

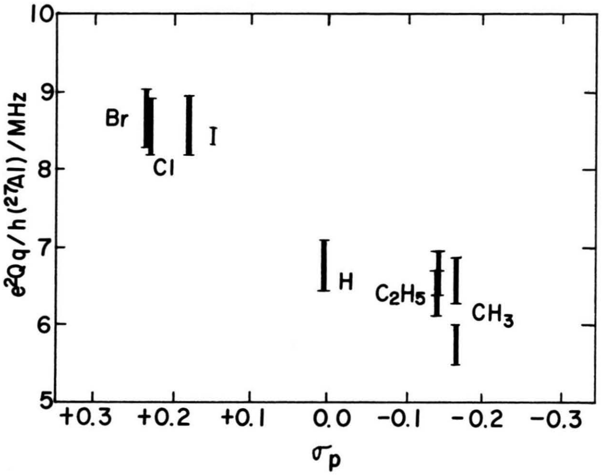

Fig. 1. Ranges of $e^2Qq/h(^{27}Al)$ against Hammett σ_p values. CH_3 and so on denote para-substituents X of $4\text{-}XC_6H_4NO_2 \cdot AlBr_3$

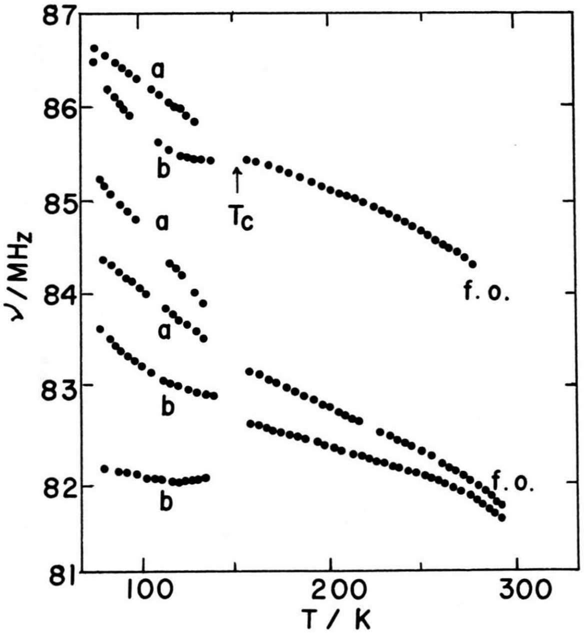

Fig. 2. Temperature dependence of ^{81}Br NQR frequencies for $4\text{-}C_2H_5C_6H_4NO_2 \cdot AlBr_3$.

population numbers of the Br–Al bonding orbital b_{Al} and the O–Al bonding orbital a_{Al}, and on the bond angle $<$Br–Al–Br, θ. This is expressed by [13]

$$e^2Qq_{zz}/h(^{27}Al) = (a_{Al} - b_{Al})\{-3\cos\theta/(1-\cos\theta)\} \cdot (1+\varepsilon_{Al}\varrho_{Al})\, e^2Qq_{at}/h(^{27}Al), \quad (2)$$

where ε_{Al} is the correction for the ionization ($\varepsilon_{Al} = 0.27$ [14]), ϱ_{Al} the positive charge on the Al atom expressed by $\varrho_{Al} = 3 - (3b_{Al} + a_{Al})$, and $e^2Qq_{at}/h(^{27}Al)$ the atomic QCC (equal to -37.52 MHz). On the other hand, the ^{81}Br QCC is given by

$$e^2Qq_{zz}/h(^{81}Br) = \{(1-s)(b_{Br}-2)/(1+\varepsilon_{Br}\varrho_{Br})\}\, e^2Qq_{at}/h(^{81}Br), \quad (3)$$

where s is the s-character of the Al–Br bonding orbital ($s = 0.15$), b_{Br} the population of this orbital, ϱ_{Br} the negative charge on the Br atom expressed by $\varrho_{Br} = b_{Br} - 1$, $\varepsilon_{Br} = 0.13$, and $e^2Qq_{at}/h(^{81}Br) = -643.032$ MHz. The value of a_{Al} can be obtained, provided that $b_{Al} + b_{Br} = 2$, $e^2Qq_{zz}/h(^{81}Br) > 0$ and $e^2Qq_{zz}/h(^{27}Al) > 0$, and that $\theta = 106°-113°$ according to the results of the Zeeman effects on NQR lines [5, 6], although the molecular structure is not available at present.

Assuming $\eta = 0$ for ^{81}Br nuclei over all complexes, the value of a_{Al} for the largest observed value of ^{27}Al QCC was 0.09 for $\theta = 106°$ or 0.15 for $\theta = 113°$, and the value of a_{Al} for the smallest observed one was 0.17 for $\theta = 106°$ or 0.21 for $\theta = 113°$. It is apparent that, if X is electron withdrawing group, the amount of charge transfer to Al, i.e., a_{Al} is reduced, and that the difference between b_{Al} and a_{Al} increases to result in an increase of the ^{27}Al QCC. This finding shows that the ^{27}Al QCC is a good measure of the charge transfer, even if the differences among the $\Delta\nu_m$ values are small over all complexes. But this result is valid as long as the same kind of donors is concerned. The $\Delta\nu_m$ values of ^{81}Br NQR frequencies and the ^{27}Al QCC's show no correlation among the complexes with donors of different types, for instance, in the case of the $(C_2H_5)_2O$, $(C_6H_5)_2C{=}O$, and C_6H_5COBr complexes and especially in the case of different atoms as the donor center, for instance the CH_3CN complex ($\Delta\nu_m = 14.7$ MHz and $e^2Qq/h(^{27}Al) = 5.054$ MHz) [6].

^{81}Br NQR frequencies of $4\text{-}C_2H_5C_6H_4NO_2 \cdot AlBr_3$ at temperatures between 77 and ca. 300 K are plotted in Figure 2. When the temperature increased from 77 K, we observed that all six lines disappeared at about 142 K on using the superregenerative spectrometer. This temperature was different from the one, 151 K, determined by the pulsed method, because it was probably due to line broadening. When increasing the temperature further, three NQR lines appeared with equal intensity at ca. 155 K, and these three lines disappeared at ca. 300 K. The DTA experiment showed

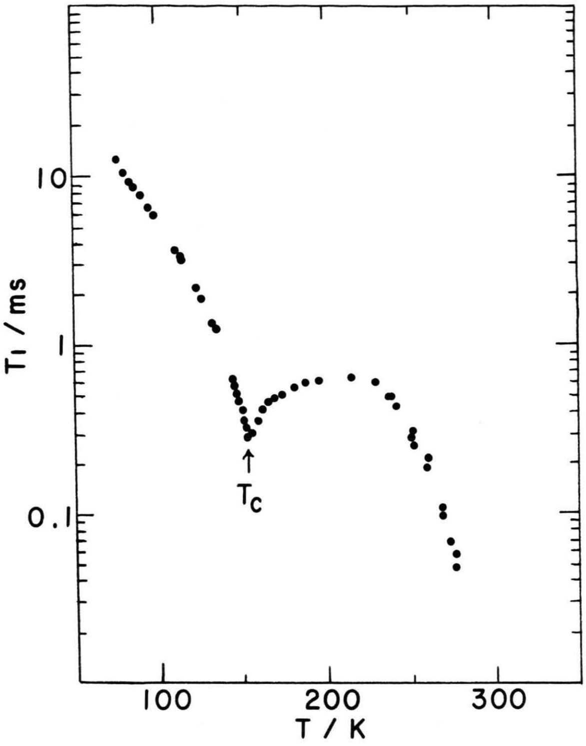

Fig. 3. Temperature dependence of the ^{81}Br quadrupolar spin-lattice relaxation time T_1 for $4\text{-}C_2H_5C_6H_4NO_2 \cdot AlBr_3$.

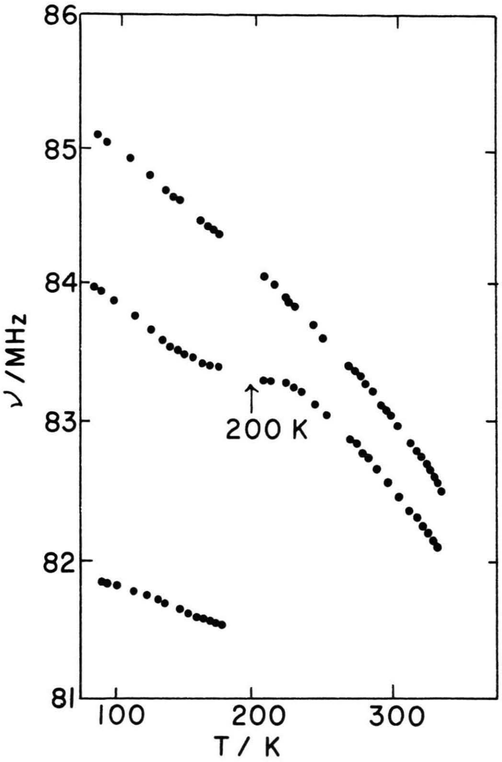

Fig. 4. Temperature dependence of the ^{81}Br NQR frequencies for $C_6H_5COBr \cdot AlBr_3$.

no heat anomaly in the range 140–160 K. The temperature dependence of T_1 for the ^{81}Br NQR line of the second lowest frequency is shown in Figure 3. It shows a sharp dip at 154 K, where there was no discontinuity of T_1, and a steep decrease of T_1 above ca. 250 K. We consider that a structural phase transition of second order takes place at 154 K, and that the hindered rotation of the $AlBr_3$ group about its three-fold axis becomes excited above 250 K, which causes the fade-out of the ^{81}Br NQR lines around 300 K.

Near the transition point T_c, T_1 obeys [15, 16]

$$(1/T_1) \propto \varepsilon^{\gamma} \quad \text{where} \quad \varepsilon = |T - T_c|/T_c, \tag{4}$$

with $\gamma = -0.50 \pm 0.04$ in the range $146\ \text{K} < T < 151\ \text{K}$ of the low temperature phase according to a least-squares procedure. Although there were few experimental points near T_c in the high temperature phase, we obtained $\gamma = -0.19 \pm 0.01$ in the range $155\ \text{K} < T < 174\ \text{K}$. It seems that the temperature variation of T_1 is not symmetric with respect to T_c. As already mentioned, activation of the reorientational motion above 250 K is probable. The T_1 curve was fitted to the equation $(1/T_1) = b \exp(-V/RT)$ to estimate the reorientational motion parameters using only the exponential part of the usual equation [16, 17]. The result is

$$b = 10^{10.6 \pm 0.5}\ \text{s}^{-1}, \quad V = 34.1 \pm 2.8\ \text{kJ mol}^{-1}$$
$$\text{for } T > 250\ \text{K}. \tag{5}$$

The obtained activation energy V is comparable with 30.2 kJ mol^{-1} for the hindered rotation of the $AlBr_3$ group in $NaAl_2Br_7$ which caused the fade-out of the ^{81}Br NQR lines at 250 K [18].

The ^{81}Br NQR frequencies of $C_6H_5COBr \cdot AlBr_3$ at temperatures between 77 and 330 K are plotted in Figure 4. When the sample was heated from 77 K, the three NQR lines disappeared around 175 K, which was observed on using a superregenerative spectrometer, although this temperature was different from the 194 K determined by the pulse method. On heating further, two weak NQR lines with an intensity ratio of ca. 2:1 in order of decreasing frequency appeared around 207 K and then became stronger while their intensity ratio gradually approached unity and was reversed at 222 K. The DTA experiment showed a

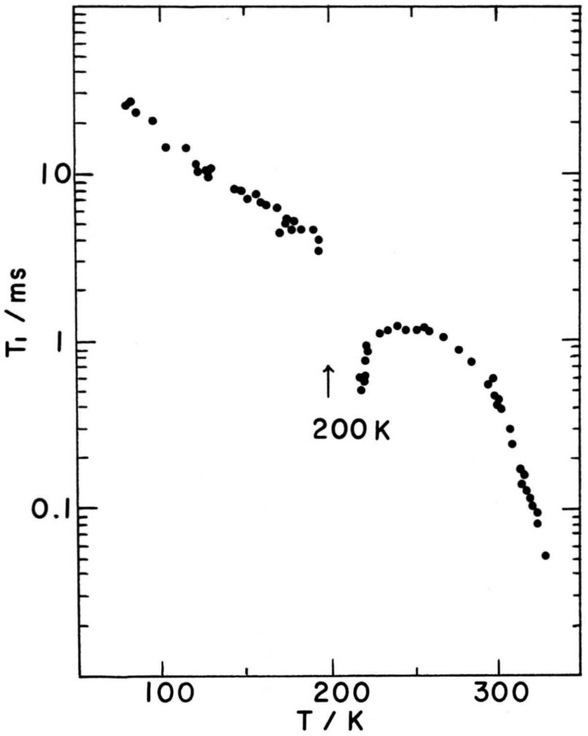

Fig. 5. Temperature dependence of the ^{81}Br quadrupolar spin-lattice relaxation tim T_1 for $C_6H_5COBr \cdot AlBr_3$.

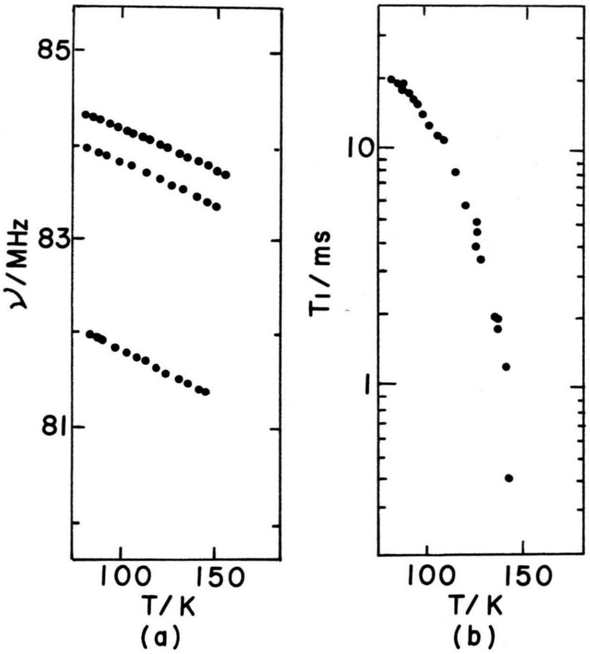

Fig. 6. (a) Temperature dependence of ^{81}Br NQR frequencies for $(C_2H_5)_2O \cdot AlBr_3$. (b) Temperature dependence of the ^{81}Br quadrupolar spin-lattice relaxation time T_1 for $(C_2H_5)_2O \cdot AlBr_3$

small shift of the base line at 214 K both on cooling from room temperature and on heating from 77 K; this temperature of 214 K was in agreement with the one where T_1 showed a minimum near 200 K.

In addition, a small heat anomaly sometimes appeared around 160 K on heating, this temperature differing considerably in the runs.

Figure 5 shows the temperature variation of T_1 for the middle line in the low temperature phase (LTP) and for the high-frequency line in the high temperature phase (HTP). In the LTP the amplitude of the echo signal decreased on approaching about 200 K. Some more experiments are necessary to clarify this phase transition. The change of the number of NQR lines with temperature was also observed in $C_6H_5COCl \cdot AlCl_3$ [3]. We consider that the $C_6H_5COBr \cdot AlBr_3$ molecule has C_S symmetry like $C_6H_5COCl \cdot AlCl_3$ at room temperature [19], and that a slight deviation from this symmetry occurs with decreasing temperature, as is the case with the $AlCl_3$ group in $C_6H_5COCl \cdot AlCl_3$ [3].

When the quadrupolar spin-lattice relaxation is governed by the libration involving oscillation of the principal EFG axes of resonant nuclei, T_1 for the nuclei having nuclear spin 3/2 is proportional to T^2 [20, 21]. We obtained the following relation, using the least-squares method:

$$1/T_1 = a\,T^m = 10^{-2.6\pm0.1}\,T^{2.18\pm0.07}$$

$$(81\ \mathrm{K} < T < 194\ \mathrm{K}) \qquad (6)$$

where T_1^{-1} is in s^{-1}, a in $s^{-1}\ K^{-m}$ and T in K. This shows T_1 is mainly determined by vibrational fluctuations of the Br EFG in this temperature range. Figure 5 also suggests that the reorientational motion of the $AlBr_3$ group takes place above ca. 300 K, although weak ^{81}Br NQR lines were observed even at 330 K. We obtained the following relation:

$$1/T_1 = 10^{13.2\pm0.4}\exp\left[-(56.6\pm2.4)/RT\right]$$

$$(297\ \mathrm{K} < T < 323\ \mathrm{K}) \qquad (7)$$

with units s^{-1} for T_1^{-1} and kJ mol^{-1} for RT.

The obtained activation energy is similar to the 43.5 kJ mol^{-1} obtained for the $AlBr_3$ group in $NaAl_2Br_7$, which caused the fade-out of the ^{81}Br NQR lines at 320 K [18].

Three ^{81}Br NQR lines were observed at 77 K in $(C_2H_5)_2O \cdot AlBr_3$. When the temperature was increased, the lines disappeared at ca. 156 K, as shown in Figure 6a. The temperature dependence of T_1 is shown in Fig. 6b for the highest-frequency ^{81}Br NQR line. Figure 6b shows the sharp decrease of T_1 with increasing temperature. In the same units as above we obtained the relation

$$1/T_1 = 10^{7.4 \pm 0.9} \exp[-(11.80 \pm 1.9)/RT] \quad (114\ \mathrm{K} < T < 141\ \mathrm{K}). \tag{8}$$

These findings indicate that the rotational freedom of the molecule, i.e., the rotation of the $AlBr_3$ group and/or the overall molecular rotation, become excited above ca. 120 K.

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