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Molecular Reorientation in $AlBr_3 \cdot NH_3$, as Studied by the ^{81}Br Nuclear Quadrupole Resonance

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The temperature dependence of the ^{81}Br nuclear quadrupole resonance (NQR) frequencies and spin-lattice relaxation times (T_{1Q}) of ^{81}Br NQR have been measured in aluminum tribromide–ammonia (1/1), $AlBr_3 \cdot NH_3$, crystals. The ^{81}Br NQR spectrum consists of 6 lines, which are ascribed to two $AlBr_3$ groups. This has been confirmed by the observation of ^{27}Al NQR using the $^{81}Br \leftrightarrow ^{27}Al$ spin echo double resonance method. A ^{81}Br T_{1Q} measurement revealed that the activation energies for the reorientation of the $AlBr_3$ groups or the molecular tumbling of $AlBr_3 \cdot NH_3$ are 61.1 and 81.6 kJ mol^{-1}. The difference in the activation energies was reflected in the temperatures of the fade-out of the ^{81}Br NQR lines at $T_f = 320$ and 350 K, respectively.

The existence of $AlBr_3 \cdot NH_3$ and $AlCl_3 \cdot NH_3$ in the vapor phase is known, and has an ideal D_{3h} symmetry.[1,2] The molecular structure of $AlCl_3 \cdot NH_3$ in the vapor phase is also maintained in the solid state.[3] By adding ammonia to $AlCl_3 \cdot NH_3$, ionic compounds, e.g., $AlCl_3 \cdot 2NH_3$ ($[AlCl_2(NH_3)_4]^+ \cdot [AlCl_4]^-$) and $AlCl_3 \cdot 3NH_3$ ($[AlCl_2(NH_3)_4]^+ \cdot [AlCl_4(NH_3)_2]^-$), are formed.[4,5]

We investigated the motion of the $AlBr_3$ group in neutral $AlBr_3 \cdot L$ (L=ligand) molecular complexes;[6] two of us have studied the motion of $AlBr_4^-$ anions in ionic compounds, $AlBr_3 \cdot 2CH_3CN$ and $AlBr_3 \cdot 1.5CH_3CN$, in which solid compounds have to be formulated as $\{[AlBr(CH_3CN)_5]^{2+} \cdot 2[AlBr_4]^- \cdot CH_3CN\}$ and $\{[Al(CH_3CN)_6]^{3+} \cdot 3[AlBr_4]^-\}$, respectively.[7] We have started to observe the NQR of ^{35}Cl and ^{81}Br in order to define the characteristics of the motions in aluminum trihalide–ammonia ($1/n$) crystals.

Experimental

The starting materials used to prepare $AlBr_3 \cdot NH_3$ are $AlBr_3$ and $AlBr_3 \cdot 6NH_3$. $AlBr_3 \cdot 6NH_3$ was prepared by streaming NH_3 gas over $AlBr_3$ at room temperature. $AlBr_3 \cdot NH_3$ was prepared by heating a mixture of a stoichiometric amount of $AlBr_3 \cdot 6NH_3$ and $AlBr_3$ in a sealed tube; the product was purified by using the Bridgeman method. $AlBr_3 \cdot NH_3$ melts at 398 K. Found: Br, 83.62%. Calcd: Br, 84.49%.

^{81}Br NQR was observed on an oscilloscope by using a superregenerative-type oscillator. The spin-lattice relaxation times ($T_{1Q}(^{81}Br)$) were measured using a Matec pulsed spectrometer (Model 5100+525 and a receiver Model 625). $T_{1Q}(^{81}Br)$ was determined by observing the free induction decay (FID) following a 90°-τ-90° pulse sequence, or the echo signals after a 180°-τ-90°-τ'-180° pulse sequence. The NQR frequencies were determined within an accuracy of ±10 kHz. The ^{27}Al NQR was observed by the $^{81}Br \leftrightarrow ^{27}Al$ spin echo double resonance (SEDOR) method.[8,9] The ^1H NMR spectra were observed at 60 MHz using a wide-line NMR spectrometer (JEOL-JNM-FW60).

Results and Discussion

Six ^{81}Br NQR lines were observed for $AlBr_3 \cdot NH_3$ at room temperature and at 77 K. This NQR result agrees with the crystal structure determined at room temperature by Jacobs and co-workers.[10] The compound crystallizes at room temperature in the orthorhombic space group Pbca and with $Z=16$ formula units per unit cell. Consequently, there are two molecules of $AlBr_3 \cdot NH_3$ as the asymmetric unit (6 independent Br atoms, 2 independent Al atoms, and 2 independent N atoms). This is also supported by the observation of SEDOR (shown below). The temperature dependence of the ^{81}Br NQR frequencies ($77 \leqq T/K \leqq 350$) in $AlBr_3 \cdot NH_3$ is shown in Fig. 1. It is common practice to describe the temperature dependence of the NQR frequencies by the following power series:

$$\nu_i = \sum a_j \cdot T^j, \quad -1 \leqq j \leqq 2. \tag{1}$$

The ^{81}Br NQR frequencies at 77 and 297 K are listed in Table 1, and the coefficients of the polynomial are given in Table 2. The ν_2, ν_3, and ν_6 lines show abnormal temperature dependences of the NQR frequencies ($\nu(T)$). They have a concave curvature at around 150 K in contrast to the results of classical Bayer theory for $\nu(T)$,[11]

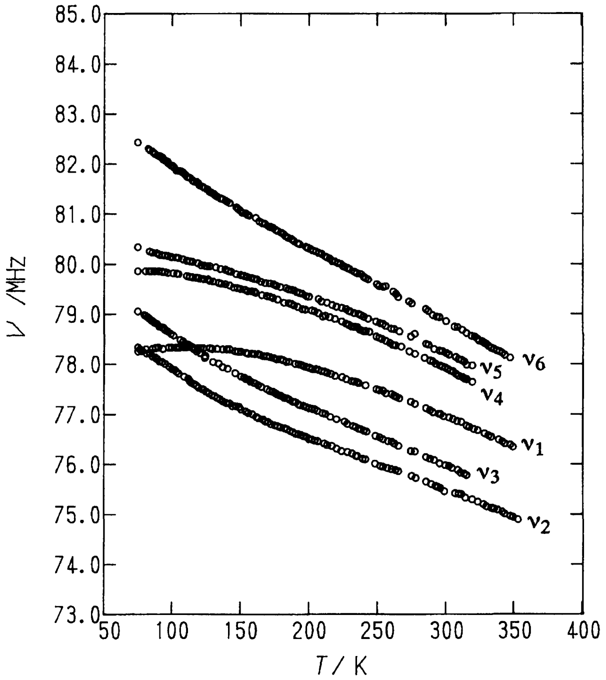

Fig. 1. Temperature dependence of the ^{81}Br NQR sextet. The running numbers ν_{1-6} increase with increasing frequencies measured at 77 K.

Table 1. ^{81}Br NQR Frequencies of $AlBr_3 \cdot NH_3$ at 77 and 297 K

ν_i [a]	ν/MHz T/K=77	ν/MHz T/K=297
ν_1	78.250	76.030
ν_2	78.332	75.539
ν_3	79.052	76.012
ν_4	79.909	77.974
ν_5	80.299	78.291
ν_6	82.437	78.939

a) The numbering i of the frequencies is increasing with increasing frequency at 77 K.

Table 2. Coefficients a_j of the Power Series $\nu_i = f(T) = \sum a_j \cdot T^j$

ν_i	Z [a]	σ [b]	a_0	a_{-1}	$a_1 \cdot 10^3$	$a_2 \cdot 10^6$
		kHz	MHz	MHz K	MHz K^{-1}	MHz K^{-2}
ν_1	94	11.52	79.752	−86.850	−3.993	−14.263
ν_2	105	24.16	77.536	110.767	−7.075	−3.197
ν_3	91	18.52	78.634	94.992	−9.690	−0.511
ν_4	90	16.34	80.097	−0.208	−0.472	−22.500
ν_5	84	14.94	80.594	0.047	−2.634	−17.267
ν_6	124	18.40	82.082	93.358	−9.469	−7.493

a) Z is the number of the experimental points. b) σ is the standard deviation.

which predicts a continuous decrease (and increasing slope) of the NQR frequencies along with increasing temperature in molecular crystals. One possible reason for this abnormal temperature dependence is the effect of a reorientation of the NH_3 groups and/or the $AlBr_3$ groups on the electric field gradients (EFG's) at the Br atoms, as seen for some ammonium compounds.[12—14] In this case, however, the N···Br distances are in the 355—393 pm range and are slightly longer than the normal N–H···Br hydrogen bond distance (337 pm).[15] Another possible reason for the complex temperature dependence is the anisotropic expansion of the unit cell upon heating, as given by the explanation of the abnormal temperature dependences of the NQR frequencies in $(CH_3NH_3)_2CdBr_4$.[16,17]

Three of the ^{81}Br NQR lines disappeared at around 320 K; the other three lines disappeared at around 350 K. This disappearance is considered to be due to a reorientation of the $AlBr_3$ groups or the molecular tumbling of the $AlBr_3 \cdot NH_3$ molecules (discussed below). Two fade-out temperatures also indicate that two crystallographically independent $AlBr_3$ groups exist in the crystal. From $\nu_i = f(T)$ (see Fig. 1) we are able to assign ν_3, ν_4, and ν_5 to one of the $AlBr_3$ groups, then ν_1, ν_2, and ν_6 to the other. We could also confirm the existence of two $AlBr_3$ groups by $^{81}\mathrm{Br} \leftrightarrow {}^{27}\mathrm{Al}$ SEDOR experiments. The results are listed in Table 3; they show that Br atoms assigned to ν_1, ν_2, and ν_6 belong to the Al(a) atom, and that the Br atoms assigned to ν_3, ν_4, and ν_5 are bonded to Al(b). The quadrupole coupling constants, $e^2Qq(^{27}\mathrm{Al})/h$, and the asymmetry parameters, $\eta(^{27}\mathrm{Al})$, deduced from frequency measurements, are also listed in Table 3. The $e^2Qq(^{27}\mathrm{Al})/h$ value of Al(a) is slightly larger than that of Al(b). These values are, however, considerably smaller than those found for $AlBr_3$ complexes containing O–Al bonds.[6] The $\eta(^{27}\mathrm{Al})$ of Al(a) is considerably larger than that of Al(b), indicating that the tetrahedron of $(H_3N)Al(a)Br_3$ is more

Table 3. a) ^{27}Al NQR Frequencies of $AlBr_3 \cdot NH_3$ at 77 K Measured by SEDOR
b) Averaged ^{27}Al NQR Frequencies, Nuclear Quadrupole Coupling Constant $e^2Qq(^{27}\mathrm{Al})/h$ and Asymmetry Parameter $\eta(^{27}\mathrm{Al})$

a)

$\nu_i(^{81}\mathrm{Br})$	$\nu_{1/2}$/kHz [a]	$\nu_{3/2}$/kHz [a]	Assignment
ν_1	256.1	419.6	Al(a)
ν_2	256.1	419.7	Al(a)
ν_6	—	—	Al(a)
ν_3	177.0	345.0	Al(b)
ν_4	175.8	354.0	Al(b)
ν_5	177.7	352.9	Al(b)

b)

Nucleus	$\nu_{1/2}$/kHz	$\nu_{3/2}$/kHz	$e^2Qq(^{27}\mathrm{Al})/h$/MHz	$\eta(^{27}\mathrm{Al})$
Al(a)	256.1	419.6	1.447	0.425
Al(b)	176.8	350.8	1.176	0.036

a) $\nu_{1/2}$ and $\nu_{3/2}$ are the transitions $m=1/2 \leftrightarrow m=3/2$ and $m=3/2 \leftrightarrow m=5/2$, respectively. The SEDOR $\nu_6(^{81}\mathrm{Br}) \leftrightarrow {}^{27}\mathrm{Al}$ was not followed up.

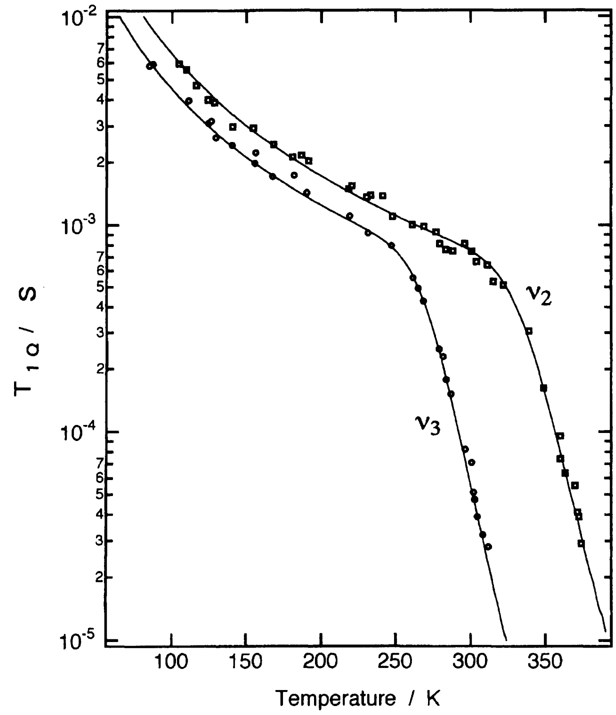

Fig. 2. Spin lattice relaxation time $T_{1Q}(^{81}Br)$ for ν_2 and ν_3 vs. temperature.

distorted than the tetrahedron $(H_3N)Al(b)Br_3$.

Figure 2 shows the temperature dependence of $T_{1Q}(^{81}Br)$ for ν_2 and ν_3. ν_1 and ν_6 show almost the same temperature dependence of T_{1Q} as ν_2, and ν_5 shows the same behavior as ν_3. We used the data for the ν_2 and ν_3 lines to analyze T_{1Q}. The ν_2 and ν_3 lines show a sharp decrease in T_{1Q} above 320 and 260 K, respectively. The T_{1Q} values for ν_2 and ν_3 can be reproduced by

$$\begin{aligned} &1/T_{1Q} = aT^m + b\exp(-E_a/RT), \\ &104 \leqq T/\text{K} \leqq 373 \text{ for } \nu_2(^{81}\text{Br}), \\ &84 \leqq T/\text{K} \leqq 315 \text{ for } \nu_3(^{81}\text{Br}). \end{aligned} \tag{2}$$

Fitting Eq. 2 to the experimental T_{1Q} values for ν_2 and ν_3 gives the a, m, b, and E_a parameters listed in Table 4. The T_{1Q} values, calculated from the obtained parameters, are indicated in Fig. 2 by solid lines. The value of m is 2 for a nuclear spin of 3/2 when the quadrupolar spin-lattice relaxation is governed by librational motions which cause an oscillation of the principal EFG axes of the resonant nucleus,[18,19] compared with the experimental values, 1.85 and 1.95, respectively. The difference between the two activation energies, 61.1 and 81.6 kJ mol^{-1}, is reflected in the difference between the temperatures (T_f's) for the fade-out of the NQR lines due to two $AlBr_3$ groups. The correlation between the T_f's and the activation energies of the reorientation of the $AlBr_3$ groups is seen from the data given in Table 5; however, the activation energies for the reorientation of the $AlBr_3$ groups in $AlBr_3{\cdot}NH_3$ are considerably larger than that observed for the other compounds listed; they are comparable to 69.5 and 70.7 kJ mol^{-1} for the isotropic reorientation of $AlBr_4^-$ ions in $AlBr_3{\cdot}2CH_3CN$.[7]

Table 4. Parameters Obtained by Best-Fit of Eq. 2 to the Experimental $T_{1Q}(^{81}Br)$ Values

Lines	$a/(s^{-1}\,K^m)$	m	b/s^{-1}	$E_a/(kJ\,mol^{-1})$
ν_2	0.191×10^{-1}	1.95	0.746×10^{16}	81.6
ν_3	0.447×10^{-1}	1.85	0.714×10^{15}	61.1

The activation energies obtained here are also explained by the molecular tumbling of the $AlBr_3{\cdot}NH_3$ molecules for the following reason. The ^{1}H NMR spectra were observed at temperatures between 105 K and the melting point. The second moment ($M_2(^1H)$) of the ^{1}H NMR spectra was nearly constant (5×10^{-8} T^2) in the $105 \leqq T/K \leqq 310$ range, and the ^{1}H NMR spectra were characteristic for a rapidly rotating NH_3 group. At temperatures above 310 K the second moment decreased down to 2.5×10^{-8} T^2 at 380 K and 0.7×10^{-8} T^2 at 5 degree below the melting point. Based on electron diffraction[1] the N–H distance in $AlBr_3{\cdot}NH_3$ is 1.057 Å, and the H–N–H angle is 114.5°. We can evaluate only the intramolecular contribution to $M_2(^1H)$ of the ^{1}H NMR spectra. It is 23.5×10^{-8} T^2 for the rigid NH_3 group and 5.8×10^{-8} T^2 for its C_3-rotation. It is apparent that the NH_3 group executes a rotation about its C_3-axis, even at 105 K. At temperatures above 310 K, a narrow ^{1}H NMR line of 0.3×10^{-4} T appeared, and then gradually increased in intensity up to the melting point. A preliminary measurement of $T_1(^1H)$ at 60 MHz showed that $T_1(^1H)$ increases from 3 s at 77 K to 11.8 s at 220 K, almost linearly with increasing temperature; it then decreases down to 10.2 s at 300 K. This temperature behavior of $T_1(^1H)$ can be explained as follows: C_3-rotation of the NH_3 group is executed and the $T_1(^1H)$ minimum due to this rotation might appear below 77 K. According to the $T_{1Q}(^{81}Br)$ data, some additional motion starts at around 260 K. If it is supposed that this motion is molecular tumbling of the $AlBr_3{\cdot}NH_3$ molecules, $T_1(^1H)$ should show a decrease due to an averaging of the dipolar interaction between

Table 5. Activation Energies, E_a for C_3-Reorientation of $AlBr_3$ Groups in Several $AlBr_3$ Complexes

Compounds	$E_a/(kJ\,mol^{-1})$	T_f/K[a]	Ref.
$AlBr_3{\cdot}(C_2H_5)_2O$	11.8	150	6)
$NaAl_2Br_7$	30.2	250	20)
$AlBr_3{\cdot}$ $[4\text{-}(C_2H_5)C_6H_4(NO_2)]$	34.1	300	6)
$NaAl_2Br_7$	43.5	320	20)
$AlBr_3{\cdot}C_6H_5COBr$	56.6	>330	6)
$AlBr_3{\cdot}NH_3$	61.1	320	This work
	81.6	350	This work

a) T_f is the observed fade-out temperature.

H atoms. This motion also would cause a decrease in the ^{1}H NMR line width above this temperature.

Conclusion

From the executed experiments (^{81}Br NQR, ^{27}Al NQR by ^{81}Br$\leftrightarrow$^{27}Al SEDOR, and ^{1}H NMR) we found that the two crystallographically inequivalent units of AlBr$_3$·NH$_3$ give different dynamical behaviors. We can also assign three of the ^{81}Br NQR lines (ν_1, ν_2, and ν_6) to one of the Al atoms, and the other three (ν_3, ν_4, and ν_5) to the second one, respectively. However, we cannot allocate each ^{81}Br NQR line to two crystallographic groups, Br$^{(1)}$Br$^{(2)}$Br$^{(3)}$Al$^{(1)}$ or Br$^{(4)}$Br$^{(5)}$Br$^{(6)}$Al$^{(2)}$.[10] This is also not possible on the basis of the distance-frequency relation, $\nu = a/d^3$, because of small differences in d(Al–Br). A solution of the problem would be a single-crystal Zeeman NQR of ^{81}Br in AlBr$_3$·NH$_3$.

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