

Cationic motions studied by  $^1\text{H}$  and  $^2\text{H}$  nuclear magnetic resonance, x-ray powder diffraction and thermal measurements in solid  $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{X}$ ,  $\text{CH}_3(\text{CH}_2)_2\text{ND}_3\text{X}$  and  $\text{CD}_3(\text{CH}_2)_2\text{NH}_3\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ )

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# Cationic motions studied by $^1\text{H}$ and $^2\text{H}$ nuclear magnetic resonance, x-ray powder diffraction and thermal measurements in solid $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{X}$ , $\text{CH}_3(\text{CH}_2)_2\text{ND}_3\text{X}$ and $\text{CD}_3(\text{CH}_2)_2\text{NH}_3\text{X}$ ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and $\text{I}$ )

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## Abstract

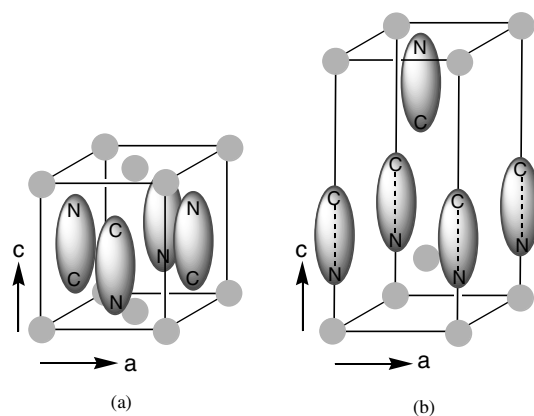
Dynamic behaviour of cations in propylammonium fluoride, chloride, bromide and iodide has been investigated by x-ray powder diffraction, thermal and  $^1\text{H}$  and  $^2\text{H}$  nuclear magnetic resonance measurements. The mobilities of the cations at room temperature were shown to be in the order iodide > bromide > chloride  $\gg$  fluoride corresponding to the order of anion size. It was found that propylammonium fluoride has no rotator phase. In the highest-temperature phase in chloride, a highly disordered cationic state was obtained and the fluctuation angle of the cationic axis was estimated to be about  $30^\circ$ .

## 1. Introduction

The highest-temperature solid phases in *n*-alkylammonium chloride, bromide and iodide with alkyl chains longer than  $\text{C}_3$  form a tetragonal crystal,  $P4/nmm$ , with a bilayer lamellar-type structure ( $\alpha'$ -form) [1] as shown in figure 1. In propylammonium halides, only chloride was reported to take this structure. The highest-temperature phase in propylammonium bromide and iodide and also the room temperature phase of the chloride were shown to have the structure ( $\alpha$ -form) [2, 3] shown in figure 1, which has the same space group as the  $\alpha'$ -form with about a halved *c*-length. In both crystals, the alkylammonium cations are expected to be dynamically disordered about their long axes: the so-called rotator phase.

Cationic motions in  $\alpha$ - and  $\alpha'$ -phases in propylammonium chloride and bromide have been studied by  $^1\text{H}$  nuclear magnetic resonance (NMR) and electrical conductivity [4] measurement, and the axial rotation and self-diffusion of the cations in the rotator phases have

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**Figure 1.** Schematic models of two tetragonal crystal structures in alkylammonium halides, (a) the  $\alpha$ -form and (b) the  $\alpha'$ -form. The two structures belong to the same space group,  $P4/nmm$ . Alkylammonium and halide ions occupy sites on fourfold axes.

been reported. There has, however, been no detailed discussion of the bromide because of the instability of the highest-temperature phase. For iodide and fluoride, no studies on the dynamics in crystals have been reported.

In this study, we investigated the detailed dynamics of propylammonium cations in these halides by means of differential thermal analysis (DTA), differential scanning calorimetry (DSC), x-ray powder diffraction and  $^1\text{H}$  and  $^2\text{H}$  NMR measurements, especially for the highest-temperature phases, and tried to clarify differences in dynamics of the crystals among these halides.

## 2. Experimental details

$\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ , abbreviated to  $\text{C}_3\text{X}$ ) and  $\text{CD}_3(\text{CH}_2)_2\text{NH}_3\text{X}$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ , abbreviated to  $\text{Cd}_3\text{X}$ ) were prepared by neutralizing propylamine and propylamine- $\text{d}_3$  (CDN, 99.4 at.%), respectively, with corresponding acid solutions of hydrogen halides. The specimens obtained, except for the fluoride, were recrystallized from ethanol. Prepared fluoride crystals were used for measurements without further purification.  $\text{CH}_3(\text{CH}_2)_2\text{ND}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ , abbreviated to  $\text{Nd}_3\text{X}$ ) were obtained by recrystallizing  $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{X}$  three times from heavy water (Isotec, 99.96 at.%).

DSC and DTA measurements were carried out with a Seiko DSC 120 calorimeter and a home-built apparatus, respectively. X-ray powder diffraction patterns were taken by a Philips X'Pert PW3040/00 diffractometer with  $\text{Cu K}\alpha$  radiation.

Second moments  $M_2$  of the  $^1\text{H}$  NMR line were obtained with a Bruker SXP-100 spectrometer and a Bruker MSL-300 system by applying the solid-echo method [5].  $^2\text{H}$  NMR spectra were measured by the MSL-300 system. The  $^1\text{H}$  NMR  $T_1$  was determined with the Bruker SXP-100 spectrometer by applying the inversion–recovery method. The experimental error in  $T_1$  was estimated to be within 10%. The sample temperature was controlled by the  $\text{N}_2$  gas flow method with an accuracy of 1 K.

## 3. Results and discussion

### 3.1. Thermal measurements and x-ray diffraction

Phase transition temperatures  $T_{tr}$  and enthalpy and entropy changes ( $\Delta_{tr}H$ ,  $\Delta_{tr}S$ ) obtained from DTA and DSC measurements are listed in table 1. We call the solid phases obtained I, II

**Table 1.** Phase transition temperatures  $T_{tr}$ , enthalpies  $\Delta_{tr}H$  and entropies  $\Delta_{tr}S$  obtained by DTA and DSC measurements. Melting is shown in parentheses.

	$T_{tr}$ (K)		$\Delta_{tr}H$ (kJ mol <sup>-1</sup> )	$\Delta_{tr}S$ (J K <sup>-1</sup> mol <sup>-1</sup> )
	DTA	DSC		
C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> F	219.5 ± 0.5	—	(19.7 ± 1.2)	(48.8 ± 3.0)
	225.0 ± 0.5	—		
C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> Cl	186.7 ± 0.5	188 <sup>a</sup>	1.15 <sup>a</sup>	6.14 <sup>a</sup>
	405.7 ± 0.5	408 <sup>a</sup>	4.15 <sup>a</sup>	10.22 <sup>a</sup>
	(437.5 ± 0.5)	(439) <sup>a</sup>	(5.90)	(13.4) <sup>a</sup>
C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> Br	161.5 ± 1.0	163 ± 1.0	1.69 ± 0.02	10.4 ± 0.1
	(456.7 ± 0.2)	(458.3 ± 1.0)	(10.1 ± 0.1)	(22.1 ± 0.5)
C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> I	179.0 ± 5.0	188.3 ± 5.0	0.36 ± 0.05	1.9 ± 0.3
	244.5 ± 5.0	246.6 ± 2.0	6.17 ± 0.7	25.0 ± 3.0
		(461.0 ± 4.0)	(9.86 ± 1.3)	(21.0 ± 3.0)

and so on in the order of temperature decrease.  $T_{tr}$ -values obtained from DTA measurements on chloride and bromide agree with the DTA data reported by Fukada *et al* [4] within experimental errors. The fact that the  $\Delta_{tr}S$  values at transitions from phase II to III observed in chloride and from phase II to I in chloride, bromide and iodide were of the same order as their melting entropies imply that phase I in these three compounds and phase II in chloride are highly disordered. On the other hand, the transition entropies at the solid–solid phase transitions in fluoride were small and hardly observed in DSC.

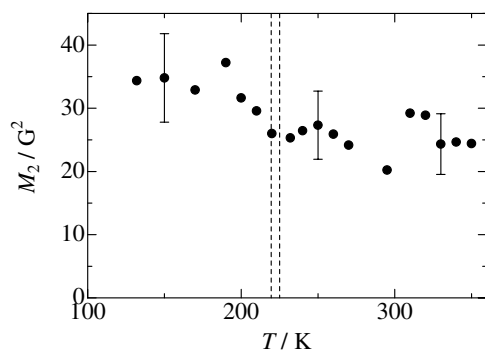
X-ray diffraction patterns obtained at room temperature for phase II of chloride and phase I of bromide and iodide could be reproduced by assuming the structure with space group  $P4/nmm$  reported for these phases [1]. The pattern obtained for phase I of fluoride at room temperature could not be explained by this space group, suggesting that this phase in fluoride has a symmetry lower than tetragonal.

### 3.2. Second-moment $M_2$ for the <sup>1</sup>H NMR line in C<sub>3</sub>F and C<sub>3</sub>I

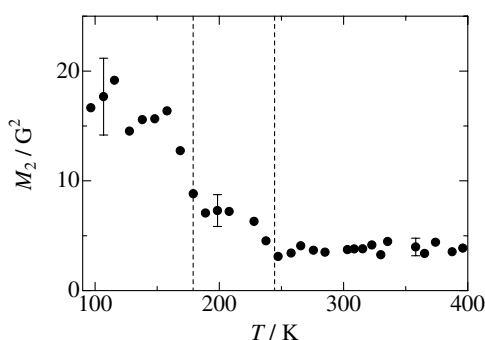
Motional states of propylammonium ions in C<sub>3</sub>Cl and C<sub>3</sub>Br had been studied by means of  $M_2$ -measurements [4]. To determine the motional states in C<sub>3</sub>F and C<sub>3</sub>I, we conducted <sup>1</sup>H NMR  $M_2$ -measurements. The temperature dependences of  $M_2$  measured for fluoride and iodide are shown in figures 2 and 3, respectively.  $M_2$  for fluoride decreased gradually from about 35 G<sup>2</sup> for phase III to about 25 G<sup>2</sup> for phase I. In iodide, steep decreases of  $M_2$  from 16 G<sup>2</sup> for phase III to 7 G<sup>2</sup> for phase II and to 4 G<sup>2</sup> for phase I were observed.

To explain these data, we calculate  $M_2$ -values for various motional states of the cation by Van Vleck's method [6] and show the results in table 2. Inter-cationic contributions to  $M_2$  were roughly estimated to be about 20% of the intra-cationic contribution [4] although they depend on the crystal structure.  $M_2$ -values for fluoride should be larger than these estimates because of contributions from <sup>19</sup>F nuclei with a large magnetic moment.

We can see from table 2 that no cationic motion other than the methyl rotation is activated in fluoride even at 350 K, indicating that fluoride has no rotator phase. In iodide, on the other hand, methyl and ammonium rotations are activated even at 100 K and the axial rotation of the cation as a whole was observed in phase I. Intermediate  $M_2$ -values observed in phase II can be understood on the basis of reorientation of the cation around its long axis in an asymmetric potential made by a lower symmetry of crystal field than C<sub>4</sub> where the averaging by this



**Figure 2.** The temperature dependence of the second moment ( $M_2$ ) of  $^1\text{H}$  NMR lines observed for propylammonium fluoride. The vertical lines show transition temperatures obtained by DTA.



**Figure 3.** The temperature dependence of the second moment ( $M_2$ ) of  $^1\text{H}$  NMR lines observed for propylammonium iodide. Vertical lines show transition temperatures obtained by DTA.

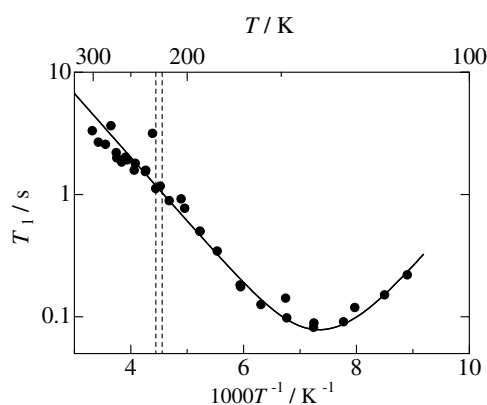
**Table 2.**  $M_2$ -values calculated for possible motional states in a propylammonium cation. The values contain a rough estimate of inter-cationic contributions of 20% of the intra-cationic contributions (shown in the parentheses) assuming the all-trans-conformation.

Motional mode	Rigid	$\text{CH}_3$ rotation	$(\text{CH}_3 + \text{NH}_3)$ rotation	$(\text{CH}_3 + \text{NH}_3)$ rotation + chain rotation
$M_2/\text{G}^2$	30.7	24.8	16.8	5.0
	(25.6)	(20.7)	(14.0)	(4.2)

motion is imperfect. It can be concluded that phase I in iodide is isomorphous with the room temperature phases in chloride and bromide is a rotator phase and phase II in iodide is also expected to be a rotator phase.  $M_2$ -values in the room temperature  $\alpha$ -phase in chloride (phase II), bromide (phase I) [4] and iodide (phase I), isomorphous with each other, were of the order of chloride ( $5.1 \text{ G}^2$ ) < bromide ( $4.8 \text{ G}^2$ ) < iodide ( $3.8 \text{ G}^2$ ). This implies that the fluctuation amplitude of the cationic motion becomes large with the increase of the anion size.

### 3.3. $^1\text{H}$ NMR $T_1$ in $\text{C}_3\text{F}$ and $\text{C}_3\text{I}$

We measured the  $^1\text{H}$   $T_1$  to reveal cationic motions in detail. In the case where the relaxation is caused by the fluctuation of magnetic dipole–dipole interactions from molecular motions, the relaxation rate  $T_1^{-1}$  can be assumed to be given by the superposition of respective contributions



**Figure 4.** The temperature dependence of the  $^1\text{H}$  NMR spin-lattice relaxation time ( $T_1$ ) observed at 33.8 MHz in propylammonium fluoride. Vertical lines show transition temperatures obtained by DTA and the solid curve is the best-fitted curve calculated by applying equations (2) and (3) in the text.

**Table 3.** Motional constants  $C$  and activation energies  $E_a$  derived by curve fitting of the temperature dependences of  $T_1$  observed in  $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{F}$  and  $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{I}$ .

	$C$ ( $10^9 \text{ s}^{-2}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	Motional mode
$\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{F}$	1.9	$10 \pm 1$	$\text{CH}_3$ rotation
$\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{I}$			
Phases II and III	2.3	$10 \pm 1$	$\text{CH}_3$ rotation
	1.6	$10.5 \pm 1$	$\text{NH}_3$ rotation
	1.2	$23 \pm 2$	Anisotropic chain rotation
Phase I	—	$10 \pm 1$	Chain rotation

expressed as

$$T_{1\text{total}}^{-1} = \sum T_1^{-1} \quad (1)$$

where each  $T_1$  is given by a BPP-type function [7]:

$$T_1^{-1} = C \left\{ \frac{\tau}{1 + \omega^2 \tau^2} + \frac{4\tau}{1 + 4\omega^2 \tau^2} \right\} \quad (2)$$

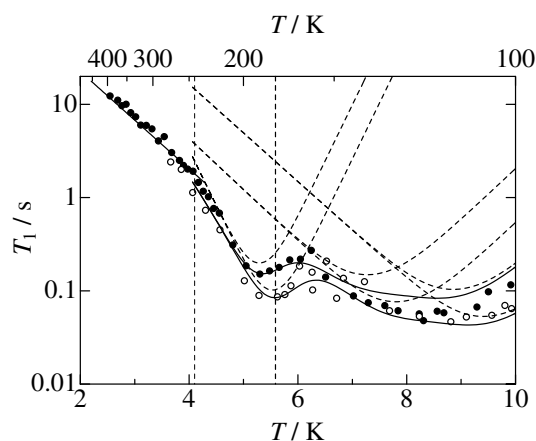
where  $C$  is the motional constant,  $\omega$  is the  $^1\text{H}$  Larmor frequency and  $\tau$  is the correlation time of the motion obeying the Arrhenius equation:

$$\tau = \tau_0 \exp(E_a/RT). \quad (3)$$

Here  $\tau_0$  and  $E_a$  denote the correlation time at infinite temperature and the activation energy of the motion, respectively.

Temperature dependences of  $^1\text{H}$  NMR  $T_1$  for fluoride and iodide are shown in figures 4 and 5, respectively. A single  $T_1$ -minimum was observed in fluoride around 140 K.  $T_1$  in fluoride could be fitted by a single BPP function (figure 3). A possible motion for this relaxation is the terminal methyl rotation relating to the analysis of  $M_2$  given above. The best-fitted motional parameters are listed in table 3. A small deviation of the fitted curve from the experimental data in phase I is attributable to the influence of phase transitions.

In iodide, since marked influences of the phase transition from III to II on the  $^1\text{H}$  relaxation could not be observed, the experimental data were fitted by the superposition of three BPP



**Figure 5.** Temperature dependences of the  $^1\text{H}$  NMR  $T_1$  observed at 54.0 (●) and 27.7 MHz (○) in propylammonium iodide. Vertical lines show transition temperatures obtained by DTA. Solid curves are the best-fitted curves calculated by the superposition of the broken curves derived from equations (1)–(3) in the text.

curves. Three motional modes corresponding to these relaxations are attributed to methyl and ammonium rotations, and the anisotropic axial reorientation as a whole, as discussed in the  $M_2$ -analysis. The  $T_1$ -slope changed obviously at the transition point (II to I) and above that temperature the  $T_1$ -value can be considered to be governed mainly by the cationic axial rotation.

### 3.4. $^2\text{H}$ NMR spectra in $\text{Nd}_3\text{X}$ ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and $\text{Cd}_3\text{X}$ ( $X = \text{Cl}, \text{Br}$ )

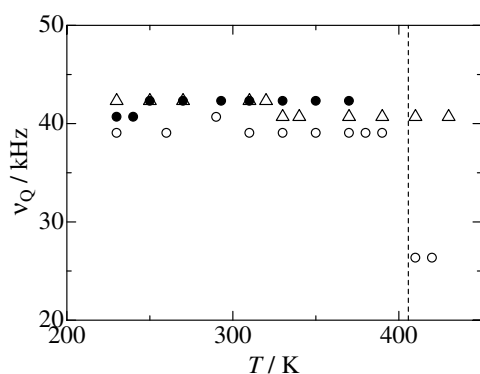
The  $^2\text{H}$  NMR linewidth is expected to be a sensitive probe for detecting slight changes in molecular motions. When a rotational motion takes place, the  $^2\text{H}$  quadrupole coupling constant  $\overline{\nu_Q}$  is reduced to [8]

$$\overline{\nu_Q} = \left| \frac{3 \cos^2 \theta - 1}{2} \right| \nu_Q \quad (4)$$

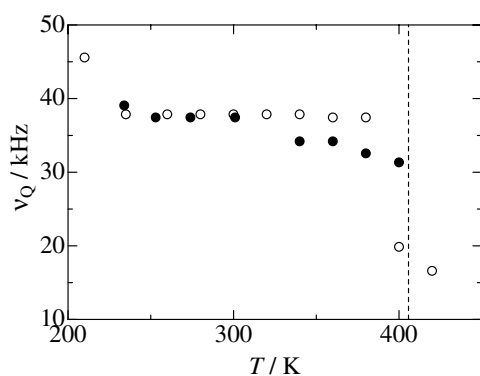
where  $\theta$  is the angle between the principal axis of the electric field gradient tensor and the rotation axis.

All  $^2\text{H}$  NMR spectra observed for  $\text{ND}_3^+$  and  $\text{CD}_3$  groups showed typical Pake patterns. Figures 6 and 7 show the temperature dependences of  $\nu_Q$  estimated from spectra observed for the rotator phase for  $\text{Nd}_3\text{Cl}$ ,  $\text{Nd}_3\text{Br}$ ,  $\text{Nd}_3\text{I}$  and  $\text{Cd}_3\text{Cl}$ ,  $\text{Cd}_3\text{Br}$ , respectively, by assuming the asymmetry parameter  $\eta = 0$ . The three  $\text{Nd}_3\text{X}$  gave almost the same  $\nu_Q$ -values of  $41 \pm 2$  kHz, almost independent of temperature in the  $\alpha$ -phase. At 410 K ( $\alpha'$ -phase)  $\text{Nd}_3\text{Cl}$  showed a much small  $\nu_Q$  of about 13 kHz. In  $\text{Cd}_3\text{X}$ , chloride gave a constant  $\nu_Q$  of 38 kHz in the  $\alpha$ -phase, while, for bromide, it decreased gradually from 39 to 31 kHz with the temperature increase. The value for chloride decreased drastically at the transition to the  $\alpha'$ -phase to less than 10 kHz.

These  $\nu_Q$ -values observed for the  $\alpha$ -phase in these compounds were much smaller than 58 and 55 kHz calculated for  $-\text{ND}_3^+$  and  $-\text{CD}_3$  rotations, respectively, by using reported values 173 kHz for  $\text{C}_2\text{H}_5\text{ND}_3\text{Cl}$  [9] and 165 kHz for  $(\text{CD}_3)_2\text{NH}_2\text{Cl}$  [10], respectively, for rigid cations, where we used equation (4) with the tetrahedral angle  $\theta = 70.5^\circ$  for calculation. This further reduction in  $\nu_Q$ -values implies that some motions in chain skeletons have been activated in this phase. The experimental values of  $41 \pm 2$  kHz observed for the  $\alpha$ -phase of



**Figure 6.** Temperature dependences of quadrupole coupling constants ( $\nu_Q$ ) determined from  $^2\text{H}$  NMR spectra observed for  $\text{CH}_3(\text{CH}_2)_2\text{ND}_3\text{X}$ , X = Cl (○), Br (●) and I (△). The vertical line shows the phase transition temperature obtained for  $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{Cl}$  by DTA.

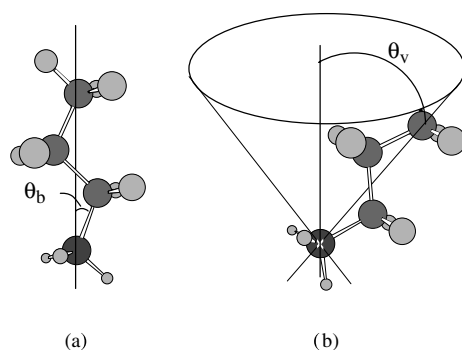


**Figure 7.** Temperature dependences of quadrupole coupling constants ( $\nu_Q$ ) determined from  $^2\text{H}$  NMR spectra observed in  $\text{CD}_3(\text{CH}_2)_2\text{NH}_3\text{X}$ , X = Cl (○) and Br (●). The vertical line shows the phase transition temperature obtained for  $\text{CH}_3(\text{CH}_2)_2\text{NH}_3\text{Cl}$  by DTA.

$\text{Nd}_3\text{X}$  (X = Cl, Br and I) and  $38 \pm 1$  kHz for the same phase of  $\text{Cd}_3\text{X}$  (X = Cl and Br) are roughly explainable on the basis of the calculated values 47 and 44 kHz, respectively, if one assumes axial rotation of the cation as a whole around the axis through the terminal C and N atoms, assuming the angle  $\theta_b = 21^\circ$  (figure 8(a)). The slight  $\nu_Q$ -reduction observed in the  $\alpha$ -phase of  $\text{Cd}_3\text{Br}$  implies that the N end is fixed by surrounding anions while the C end is expected to move more freely than in chloride.

In the  $\alpha'$ -phase of chloride, the large reduction in  $\nu_Q$  is attributable to the fluctuation of the rotational axis (figure 8(b)). Under an assumption of a random fluctuation of the axis within a cone in which the N atom is at the apex, the vertical angle  $\theta_V$  of the cone was estimated to be  $33 \pm 1^\circ$  from the  $\nu_Q$  of 26 kHz observed for  $\text{Nd}_3\text{Cl}$  at 410 K. This large  $\theta_V$  is attributable to the packing in the  $\alpha'$ -form being looser than that in the  $\alpha$ -form. On the other hand, the  $\nu_Q$  of 12 kHz obtained at 420 K for the  $\alpha'$ -phase of  $\text{Cd}_3\text{Cl}$  is much smaller than the 24 kHz calculated by using the above  $\theta_V$ . This implies a large fluctuation of the C end enabled by the non-rigidity of a propylammonium ion.





**Figure 8.** Schematic models of (a) axial rotation of the propylammonium cation as a whole and (b) random fluctuation of the cationic axis in a cone.

#### 4. Conclusions

The axial rotation of the cation as a whole was newly observed by  $^1\text{H}$  and  $^2\text{H}$  NMR methods in phases I ( $\alpha$ -phase) and II of propylammonium iodide. It can be concluded from these results that the  $\alpha$ -phase in propylammonium iodide, as well as those in chloride and bromide, and the low-temperature phase II with a symmetry lower than tetragonal are rotator phases. It was shown that the amplitude of the fluctuation at the C end of a cation in the  $\alpha$ -phase is increased in the order chloride < bromide < iodide while those at the N end are almost the same for these three compounds. This is because the N end is tightly bound to surrounding anions by hydrogen bonds while the C end feels only weak van der Waals force.

It was found that the  $\alpha'$ -phase (phase I) in chloride is a highly disordered state. The highest-temperature solid phase in *n*-alkylammonium halides with chains longer than  $\text{C}_3$  takes the  $\alpha'$ -phase, but only chloride forms this phase in propylammonium halides. This result can be explained by considering that weak van der Waals forces among short chain alkyl groups in propylammonium ions cannot maintain the crystal with the loose structure of the  $\alpha'$ -phase. Only in chloride can the electrostatic force between cations and anions be expected to be strong enough to maintain the  $\alpha'$ -phase. On the other hand, in propylammonium fluoride, the inter-ionic force is implied to be too strong for formation of a rotator phase.

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