

## $^1\text{H}$ and $^{19}\text{F}$ NMR Study of Ammonium Ion Motion in Ammonium Trifluorostannate (II)

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The temperature dependences of the second moment and spin-lattice relaxation time of  $^1\text{H}$  and  $^{19}\text{F}$  NMR were measured on ammonium trifluorostannate (II)  $\text{NH}_4\text{SnF}_3$ . It was found that the  $\text{NH}_4^+$  ions having a  $\text{C}_3$  symmetry in the crystal undergo overall reorientations with an activation energy of  $22 \text{ kJ mol}^{-1}$ .

Ammonium trifluorostannate (II)  $\text{NH}_4\text{SnF}_3$  forms trigonal crystals with the space group  $\text{R}\bar{3}$  at room temperature [1, 2]. Both the nitrogen and tin atoms in isolated  $\text{NH}_4^+$  and  $\text{SnF}_3^-$  ions, respectively, are on the  $\text{C}_3$  symmetry axis of the crystal. One of the N–H bonds in an  $\text{NH}_4^+$  ion is on the  $\text{C}_3$  axis and directs to the center of a  $\text{SnF}_3^-$  trigonal pyramid, making a trifurcated hydrogen bond. The N...F distances are 300 pm. The remaining three hydrogens of the  $\text{NH}_4^+$  ion are normally hydrogen-bonding with fluoride ions belonging to different  $\text{SnF}_3^-$  ions. The N...F distances are 275 pm. Thus, the  $\text{NH}_4^+$  ion in  $\text{NH}_4\text{SnF}_3$  forms two kinds of very different hydrogen bonds. In order to study the motion of the  $\text{NH}_4^+$  ions forming such unique hydrogen bonds, we measured the second moments  $M_2$  and spin-lattice relaxation times  $T_1$  of  $^1\text{H}$  and  $^{19}\text{F}$  NMR of this complex.

Ammonium trifluorostannate (II) was crystallized from an aqueous solution of  $\text{SnF}_2$  and a slight excess of  $\text{NH}_4\text{HF}_2$  [2, 3]. The colorless crystals were filtered off, washed with methanol and dried over NaOH in a desiccator.  $\text{NH}_4\text{SnF}_3$  thus obtained was identified by powder X-ray diffraction.

Continuous-wave  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL JNM-MW 40S spectrometer.  $^1\text{H}$  and  $^{19}\text{F}$  spin-lattice relaxation times  $T_1$  were measured at 20 and 18.814 MHz (the external magnetic field is ca. 0.47 T for both nuclei), respectively, by using pulsed NMR spectrometers already described [4, 5]. The usual  $180^\circ$ - $t$ - $90^\circ$  pulse sequence was used for the determination of  $T_1$ . Temperatures were determined by a copper-Constantan thermocouple within an accuracy of  $\pm 1 \text{ K}$  for the  $T_1$  measurements and of  $\pm 2 \text{ K}$  for the  $M_2$  measurements.

The second moments of  $^1\text{H}$  and  $^{19}\text{F}$  NMR absorptions ( $M_{2\text{H}}$  and  $M_{2\text{F}}$ , respectively) were measured from 77 K to room temperature. At 77 K,  $M_{2\text{H}}$  and  $M_{2\text{F}}$  were  $50 \times 10^{-8}$  and  $11 \times 10^{-8} \text{ T}^2$ , respectively. With increasing temperature, each  $M_2$  decreased in a temperature range 120–180 K, and reached a plateau value above 180 K. The plateau values of  $M_{2\text{H}}$  and  $M_{2\text{F}}$  were  $4 \times 10^{-8}$  and  $7 \times 10^{-8} \text{ T}^2$ , respectively.

The decrease of  $M_{2\text{H}}$  is very large compared with that of  $M_{2\text{F}}$ , suggesting the occurrence of isotropic reorientation of the  $\text{NH}_4^+$  ions. Therefore, the theoretical  $M_{2\text{H}}$  and  $M_{2\text{F}}$  were calculated for the models of rigid lattice and of isotropically

reorienting  $\text{NH}_4^+$  ions. Magnetic dipolar interactions between  $^1\text{H}$  and  $^1\text{H}$ ,  $^1\text{H}$  and  $^{19}\text{F}$ , and  $^{19}\text{F}$  and  $^{19}\text{F}$  nuclei were taken into account in the  $M_2$  calculations. All interproton distances in an  $\text{NH}_4^+$  ion were assumed to be 170 pm for the rigid lattice model, and for the reorienting  $\text{NH}_4^+$  ion model the interionic contribution to  $M_2$  was estimated by placing four  $\text{NH}_4^+$  ion protons at the nitrogen site. The results were  $M_{2\text{H}} = 53.1 \times 10^{-8}$  and  $M_{2\text{F}} = 12.5 \times 10^{-8} \text{ T}^2$  for the rigid lattice model and  $M_{2\text{H}} = 2.7 \times 10^{-8}$  and  $M_{2\text{F}} = 6.2 \times 10^{-8} \text{ T}^2$  for the reorienting  $\text{NH}_4^+$  ion model. These calculated  $M_2$  values are in good agreement with the corresponding values observed at low and high temperatures, indicating that the  $\text{NH}_4^+$  ions are rigidly fixed below 120 K and undergo isotropic reorientation above 180 K.

Figure 1 shows the temperature dependences of  $^1\text{H}$  and  $^{19}\text{F}$   $T_1$  ( $T_{1\text{H}}$  and  $T_{1\text{F}}$ , respectively). A  $T_{1\text{H}}$  minimum of 4 ms and a  $T_{1\text{F}}$  minimum of 28 ms were located at 210 and 195 K, respectively. Below ca. 190 K, nonexponential decays of the magnetization recovery for the  $T_1$  measurements were observed for both nuclei. This nonexponentiality is assignable to the heteronuclear dipolar cross coupling between  $^1\text{H}$  and  $^{19}\text{F}$  nuclei [6–8]. In this case, the magnetization recovery curve was assumed to be the superimposition of two exponential decays, and a short ( $T_{1s}$ ) and a long ( $T_{1l}$ ) component were manually determined as shown in Figure 1. Experimentally equal values of each component were obtained for both

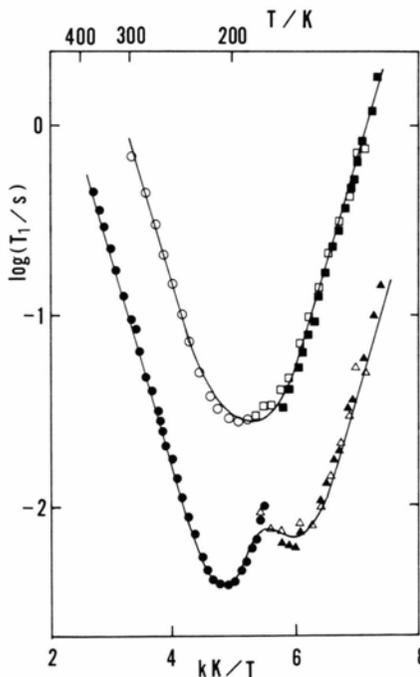


Fig. 1. Temperature dependences of spin-lattice relaxation times  $T_1$  of  $^1\text{H}$  (●, ■, and ▲) and  $^{19}\text{F}$  (○, □, and △) NMR measured at 20 and 18.814 MHz, respectively, for  $\text{NH}_4\text{SnF}_3$ . Below ca. 190 K, nonexponential recovery of magnetization in the  $T_1$  measurements was observed for both nuclei, yielding a long (■ and □) and a short (▲ and △)  $T_1$  component.

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nuclei. A  $T_{1s}$  minimum of ca. 7 ms was observed near 165 K.

By referring the results of  $M_2$ , the observed  $T_1$  was analyzed by the model of the  $\text{NH}_4^+$  ion reorientation. The relaxation rates ( $T_1^{-1}$ ) of interacting  $^1\text{H}$  and  $^{19}\text{F}$  nuclei in  $\text{NH}_4\text{SnF}_3$  are the eigen values of the relaxation rate matrix [6–8]

$$\begin{pmatrix} R_{\text{HH}} & R_{\text{HF}} \\ R_{\text{FH}} & R_{\text{FF}} \end{pmatrix}. \quad (1)$$

The components of the relaxation matrix are given as

$$R_{\text{HH}} = (2/3)\gamma_{\text{H}}^2 \Delta M_2(\text{H}-\text{H}) f(\omega_{\text{H}}, \tau) + (1/2)\gamma_{\text{H}}^2 \Delta M_2(\text{H}-\text{F}) g(\omega_{\text{H}}, \omega_{\text{F}}, \tau), \quad (2a)$$

$$R_{\text{HF}} = (1/2)\gamma_{\text{H}}^2 \Delta M_2(\text{H}-\text{F}) g'(\omega_{\text{H}}, \omega_{\text{F}}, \tau), \quad (2b)$$

$$R_{\text{FF}} = (1/2)\gamma_{\text{F}}^2 \Delta M_2(\text{F}-\text{H}) g(\omega_{\text{F}}, \omega_{\text{H}}, \tau) \approx (4/3)(1/2)\gamma_{\text{H}}^2 \Delta M_2(\text{H}-\text{F}) g(\omega_{\text{H}}, \omega_{\text{F}}, \tau), \quad (2c)$$

$$R_{\text{FH}} = (1/2)\gamma_{\text{F}}^2 \Delta M_2(\text{F}-\text{H}) g'(\omega_{\text{F}}, \omega_{\text{H}}, \tau) \approx (4/3)R_{\text{HF}}. \quad (2d)$$

Here,

$$f(\omega_I, \tau) = \tau / (1 + \omega_I^2 \tau^2) + 4\tau / (1 + 4\omega_I^2 \tau^2), \quad (3a)$$

$$g(\omega_I, \omega_J, \tau) = \tau / \{1 + (\omega_I - \omega_J)^2 \tau^2\} + 3\tau / (1 + \omega_I^2 \tau^2) + 6\tau / \{1 + (\omega_I + \omega_J)^2 \tau^2\}, \quad (3b)$$

$$g'(\omega_I, \omega_J, \tau) = -\tau / \{1 + (\omega_I - \omega_J)^2 \tau^2\} + 6\tau / \{1 + (\omega_I + \omega_J)^2 \tau^2\}. \quad (3c)$$

$\Delta M_2(I-J)$  represents a reduction of the second moment of  $I$  spins caused by averaging out the dipolar interactions between  $I$  and  $J$  spins through the  $\text{NH}_4^+$  ion reorientations.  $\gamma_I$  and  $\omega_I$  are the gyromagnetic ratio and Larmor frequency of  $I$  spins, respectively.  $\tau$  stands for the correlation time of the

$\text{NH}_4^+$  ion motion and the Arrhenius relation is usually assumed for  $\tau$ :

$$\tau = \tau_0 \exp(E_a/RT). \quad (4)$$

By adjusting  $\Delta M_2(\text{H}-\text{H})$ ,  $\Delta M_2(\text{H}-\text{F})$ ,  $\tau_0$  and  $E_a$  to fit the calculated  $T_1$  to the observed one, the motional parameters of the  $\text{NH}_4^+$  ions were determined:  $\Delta M_2(\text{H}-\text{H}) = 46 \times 10^{-8} \text{T}^2$ ,  $\Delta M_2(\text{H}-\text{F}) = 2.4 \times 10^{-8} \text{T}^2$ ,  $E_a = 22 \text{kJmol}^{-1}$ , and  $\tau_0 = 2.0 \times 10^{-14} \text{s}$ . The calculated  $T_1$  curves are shown in Figure 1. The  $\Delta M_2(\text{H}-\text{H})$  and  $\Delta M_2(\text{H}-\text{F})$  values from the  $T_1$  analysis are in agreement with  $46 \times 10^{-8}$  and  $4.2 \times 10^{-8} \text{T}^2$ , respectively, obtained from the  $M_2$  calculations. Therefore, the relaxation process of both the  $^1\text{H}$  and  $^{19}\text{F}$  nuclei in  $\text{NH}_4\text{SnF}_3$  is assignable to the isotropic reorientation of the cations. The deep  $T_{1\text{H}}$  minimum is mainly due to the contribution of the homonuclear  $^1\text{H}-^1\text{H}$  dipolar interaction, and the  $T_{1\text{F}}$  minimum at 165 K originates from the heteronuclear  $^1\text{H}-^{19}\text{F}$  dipolar coupling through the  $\tau / \{1 + (\omega_I - \omega_J)^2 \tau^2\}$  term.

From the standpoint of the site symmetry at the  $\text{NH}_4^+$  ion site alone it would be expected for the  $\text{NH}_4^+$  ions to undergo a reorientation about the  $C_3$  axis in preference to the overall reorientation. However, its possibility is experimentally excluded. This fact indicates that the three hydrogen bonds of the  $\text{NH}_4^+$  ion out of the  $C_3$  axis hinder the cation reorientation. In fact, Knop et al. showed from their infrared spectroscopic study that the hydrogen bond on the  $C_3$  axis is much weaker than the remaining three hydrogen bonds [9]. The  $E_a$  value of  $22 \text{kJmol}^{-1}$  is much smaller than  $39 \text{kJmol}^{-1}$  for  $\text{NH}_4\text{F}$ , in which the  $\text{NH}_4^+$  ion forms tetrahedrally four normal hydrogen bonds with an N...F distance of 271 pm [10], and is much larger than  $8.6 \text{kJmol}^{-1}$  for cubic  $(\text{NH}_4)_2\text{SiF}_6$ , in which the  $\text{NH}_4^+$  ion forms four trifurcated hydrogen bonds with an N...F distance of 300 pm [7]. In  $\text{NH}_4\text{SnF}_3$ , the  $\text{NH}_4^+$  ion forms three normal and a trifurcated hydrogen bond, and its  $E_a$  value is between the two limiting values mentioned above.

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