^{1}H and ^{19}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}H and ^{19}F NMR were measured on ammonium trifluorostannate (II) NH_4SnF_3. It was found that the NH_4^+ ions having a C_3 symmetry in the crystal undergo overall reorientations with an activation energy of 22 kJ mol^{-1}.

Ammonium trifluorostannate (II) NH_4SnF_3 forms trigonal crystals with the space group $R\bar{3}$ at room temperature [1, 2]. Both the nitrogen and tin atoms in isolated NH_4^+ and SnF_3^- ions, respectively, are on the C_3 symmetry axis of the crystal. One of the N–H bonds in an NH_4^+ ion is on the C_3 axis and directs to the center of a SnF_3^- trigonal pyramid, making a trifurcated hydrogen bond. The N ... F distances are 300 pm. The remaining three hydrogens of the NH_4^+ ion are normally hydrogen-bonding with fluoride ions belonging to different SnF_3^- ions. The N ... F distances are 275 pm. Thus, the NH_4^+ ion in NH_4SnF_3 forms two kinds of very different hydrogen bonds. In order to study the motion of the NH_4^+ ions forming such unique hydrogen bonds, we measured the second moments M_2 and spin-lattice relaxation times T_1 of ^{1}H and ^{19}F NMR of this complex.

Ammonium trifluorostannate (II) was crystallyzed from an aqueous solution of SnF_2 and a slight excess of NH_4HF_2 [2, 3]. The colorless crystals were filtered off, washed with methanol and dried over NaOH in a desiccator. NH_4SnF_3 thus obtained was identified by powder X-ray diffraction.

Continuous-wave ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNM-MW 40S spectrometer. ^{1}H and ^{19}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°-t-90° pulse sequence was used for the determination of T_1. Temperatures were determined by a copper-Constantan thermocouple within an accuracy of ± 1 K for the T_1 measurements and of ± 2 K for the M_2 measurements.

The second moments of ^{1}H and ^{19}F NMR absorptions (M_{2H} and M_{2F}, respectively) were measured from 77 K to room temperature. At 77 K, M_{2H} and M_{2F} were 50×10^{-8} and 11×10^{-8} 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_{2H} and M_{2F} were 4×10^{-8} and 7×10^{-8} T^2, respectively.

The decrease of M_{2H} is very large compared with that of M_{2F}, suggesting the occurrence of isotropic reorientation of the NH_4^+ ions. Therefore, the theoretical M_{2H} and M_{2F} were calculated for the models of rigid lattice and of isotropically reorienting NH_4^+ ions. Magnetic dipolar interactions between ^{1}H and ^{1}H, ^{1}H and ^{19}F, and ^{19}F and ^{19}F nuclei were taken into account in the M_2 calculations. All interproton distances in an NH_4^+ ion were assumed to be 170 pm for the rigid lattice model, and for the reorienting NH_4^+ ion model the interionic contribution to M_2 was estimated by placing four NH_4^+ ion protons at the nitrogen site. The results were $M_{2H} = 53.1 \times 10^{-8}$ and $M_{2F} = 12.5 \times 10^{-8}$ T^2 for the rigid lattice model and $M_{2H} = 2.7 \times 10^{-8}$ and $M_{2F} = 6.2 \times 10^{-8}$ T^2 for the reorienting 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 NH_4^+ ions are rigidly fixed below 120 K and undergo isotropic reorientation above 180 K.

Figure 1 shows the temperature dependences of ^{1}H and ^{19}F T_1 (T_{1H} and T_{1F}, respectively). A T_{1H} minimum of 4 ms and a T_{1F} 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}H and ^{19}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

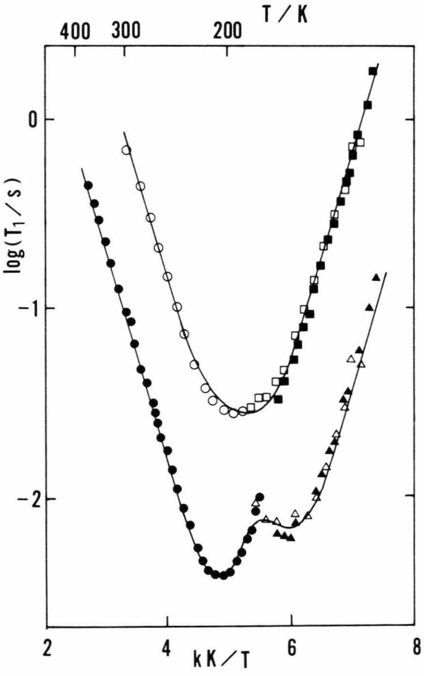

Fig. 1. Temperature dependences of spin-lattice relaxation times T_1 of ^{1}H (●, ■, and ▲) and ^{19}F (○, □, and △) NMR measured at 20 and 18.814 MHz, respectively, for NH_4SnF_3. Below ca. 190 K, nonexponential recovery of magnetization in the T_1 measurements was observed for both nuclei, yielding 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 NH_4^+ ion reorientation. The relaxation rates (T_1^{-1}) of interacting ^1H and ^{19}F nuclei in NH_4SnF_3 are the eigen values of the relaxation rate matrix [6–8]

$$\begin{pmatrix} R_{HH} & R_{HF} \\ R_{FH} & R_{FF} \end{pmatrix}. \tag{1}$$

The components of the relaxation matrix are given as

$$\begin{aligned} R_{HH} &= (2/3)\gamma_H^2 \Delta M_2(H-H) f(\omega_H, \tau) \\ &\quad + (1/2)\gamma_H^2 \Delta M_2(H-F) g(\omega_H, \omega_F, \tau), && (2a) \\ R_{HF} &= (1/2)\gamma_H^2 \Delta M_2(H-F) g'(\omega_H, \omega_F, \tau), && (2b) \\ R_{FF} &= (1/2)\gamma_F^2 \Delta M_2(F-H) g(\omega_F, \omega_H, \tau), \\ &\approx (4/3)(1/2)\gamma_H^2 \Delta M_2(H-F) g(\omega_H, \omega_F, \tau), && (2c) \\ R_{FH} &= (1/2)\gamma_F^2 \Delta M_2(F-H) g'(\omega_F, \omega_H, \tau) \\ &\approx (4/3) R_{HF}. && (2d) \end{aligned}$$

Here,

$$\begin{aligned} f(\omega_I, \tau) &= \tau/(1+\omega_I^2\tau^2) + 4\tau/(1+4\omega_I^2\tau^2), && (3a) \\ g(\omega_I, \omega_J, \tau) &= \tau/\{1+(\omega_I-\omega_J)^2\tau^2\} + 3\tau/(1+\omega_I^2\tau^2) \\ &\quad + 6\tau/\{1+(\omega_I+\omega_J)^2\tau^2\}, && (3b) \\ g'(\omega_I, \omega_J, \tau) &= -\tau/\{1+(\omega_I-\omega_J)^2\tau^2\} \\ &\quad + 6\tau/\{1+(\omega_I+\omega_J)^2\tau^2\}. && (3c) \end{aligned}$$

$\Delta M_2(I-J)$ represents a reduction of the second moment of I spins caused by averaging out the dipolar interactions between I and J spins through the NH_4^+ ion reorientations. γ_I and ω_I are the gyromagnetic ratio and Larmor frequency of I spins, respectively. τ stands for the correlation time of the NH_4^+ ion motion and the Arrhenius relation is usually assumed for τ:

$$\tau = \tau_0 \exp(E_a/RT). \tag{4}$$

By adjusting $\Delta M_2(H-H)$, $\Delta M_2(H-F)$, τ_0 and E_a to fit the calculated T_1 to the observed one, the motional parameters of the NH_4^+ ions were determined: ΔM_2 (H – H) $= 46 \times 10^{-8}\,T^2$, ΔM_2 (H – F) $= 2.4 \times 10^{-8}\,T^2$, $E_a = 22$ kJmol^{-1}, and $\tau_0 = 2.0 \times 10^{-14}$ s. The calculated T_1 curves are shown in Figure 1. The ΔM_2 (H – H) and ΔM_2 (H – F) values from the T_1 analysis are in agreement with 46×10^{-8} and $4.2 \times 10^{-8}\,T^2$, respectively, obtained from the M_2 calculations. Therefore, the relaxation process of both the ^1H and ^{19}F nuclei in NH_4SnF_3 is assignable to the isotropic reorientation of the cations. The deep T_{1H} minimum is mainly due to the contribution of the homonuclear ^1H – ^1H dipolar interaction, and the T_{1s} minimum at 165 K originates from the heteronuclear ^1H – ^{19}F dipolar coupling through the $\tau/\{1+(\omega_I-\omega_J)^2\tau^2\}$ term.

From the standpoint of the site symmetry at the NH_4^+ ion site alone it would be expected for the 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 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 kJmol^{-1} is much smaller than 39 kJmol^{-1} for NH_4F, in which the 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 kJmol^{-1} for cubic $(NH_4)_2SiF_6$, in which the NH_4^+ ion forms four trifurcated hydrogen bonds with an N ... F distance of 300 pm [7]. In NH_4SnF_3, the 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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