

An Effect of Deuteration on Ion Motions and Hydrogen Bondings in Guanidinium Tetrafluoroborate

J. Wąsicki, M. Grottel*, A. Kozak, and Z. Pająk

Institute of Physics, A. Mickiewicz University, Poznań, Poland

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The fluorine spin-lattice relaxation time as well as NMR second moment for perdeuterated guanidinium tetrafluoroborate were studied over a wide range of temperature.

An analytical solution of a set of coupled differential equations describing the time variation of nuclear magnetisations for four unlike spin systems was applied to analyse all cross-relaxation effects in the compound. Activation parameters $E_a^F = 19.3$ kJ/mole and $\tau_0^F = 9 \cdot 10^{-14}$ s for the isotropic anion reorientation were derived.

A coupling of rotational modes of cation and anion was found. Significant lowering of the melting point explained by a weakening of the hydrogen bonds involves diminishing of the ion activation energies due to the large positive isotope effect.

Introduction

A single-crystal X-ray analysis has shown [1] that the guanidinium tetrafluoroborate crystallizes in the trigonal space group R3m, with $a = 5.265(1)$ Å, $\alpha = 90.09(2)^\circ$ and $Z = 1$. The guanidinium cation and tetrafluoroborate anion, connected by the N–H...F hydrogen bonds, form layers perpendicular to [111].

To describe ion motions in $C(NH_2)_3BF_4$ the proton and fluorine NMR second moment as well as spin-lattice relaxation time T_1 were studied over a wide range of temperature [1]. To interpret the non-exponential 1H and ^{19}F magnetisation behaviour, cross-relaxation effects were considered and an analytical solution of a set of coupled differential equations describing the time variation of nuclear magnetisations for three unlike spins was derived. It enabled to extract precise values of activation parameters for ion reorientations, that is an isotropic anion reorientation and C_3 reorientation of the guanidinium cation. It was found that the two plots corresponding to the temperature dependences of the correlation times of the two ions converge (in the accuracy limit) at the melting point (450 K). This effect, revealed also in the other compounds [2, 3], seems to indicate the existence of a new kind of coupling of rotational modes of cations and anions at first-order phase transitions.

In [4] we succeeded in deriving the solution of a set of coupled differential equations describing the time variation of nuclear magnetisations for four unlike spins. Since perdeuterated guanidinium tetrafluoroborate seemed to be a good example of such a system an NMR study of this compound was undertaken. It enabled us to calculate more precisely than in $C(NH_2)_3BF_4$ all intra- as well as inter-ionic dipolar interactions and to find activation parameters for the anion reorientation. It seemed interesting to find also how the deuteration of the compound influences the ion motions, coupling of rotational modes and temperature of the phase transition.

Experimental

$C(ND_2)_3BF_4$ was prepared from purified $C(NH_2)_3BF_4$ obtained as described in [1] by multiple exchange with D_2O . The product was then ground to a fine powder, dried, degassed and sealed off.

Fluorine second moment investigations were made with a cw NMR spectrometer operating at the Larmor frequency of 26.3 MHz. Measurements of the spin-lattice relaxation time T_1 were performed using a laboratory-made pulse spectrometer operating at 60 MHz by a $\pi/2 - \tau - \pi/2$ pulse sequence or by a saturation method.

The temperature of the sample was controlled by means of a gas-flow cryostat and monitored with a Pt resistor to an accuracy of about 1 K.

The melting point was measured for the sample sealed into a glass ampoule in an argon atmosphere.

* Department of Physics, Academy of Agriculture, Poznań, Poland.

Reprint requests to Prof. Z. Pająk, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.

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Results

Experimental results of fluorine NMR second moments obtained for the deuterated guanidinium tetrafluoroborate are presented in Figure 1. The value of 15.4 G^2 registered at 130 K decreases to 0.6 G^2 reached above 250 K. It was not possible to register unsaturated NMR absorption lines below 130 K because of long spin-lattice relaxation times.

Results of the fluorine spin-lattice relaxation times are shown in Fig. 2 as a $\log T_1$ plot against inverse temperature. The solid lines in the figure are model-based fits to the experimental data. At temperatures higher than 200 K a non-exponential magnetisation decay is observed. The decay curves are decomposed into two exponentials with different T_1 yielding the results shown in Figure 2. For both plots one can see T_1 minima of 15 ms at 220 K and of 33 ms at 208 K for short and long components, respectively.

The melting point was found to be at 435 K.

Calculations and Discussion

Assuming the same crystal structure for $\text{C}(\text{ND}_2)_3\text{BF}_4$ as for $\text{C}(\text{NH}_2)_3\text{BF}_4$ one can expect the theoretical fluorine second moment for a rigid lattice to be 19.4 G^2 . This value is not achieved at the lowest temperatures studied. The decrease to a value of 0.6 G^2 is caused by the onset of isotropic reorientation of BF_4 anions. The second moment at high temperatures is by 0.7 G^2 lower than found for the undeuterated salt, since there is no more fluorine-proton interaction in the compound.

To interpret the relaxation data obtained in the deuterated guanidinium tetrafluoroborate we have considered cross-relaxation effects in the ^{19}F , ^{11}B , ^{10}B , ^2D , and ^{14}N spin system. Since the fluorine-nitrogen interaction is negligibly small we could reduce the system to four unlike spins and then solve the set of coupled differential equations describing the time variation of nuclear magnetisations [4]:

$$[\mathbf{R}] = \begin{bmatrix} -R_{\text{FF}} & -R_{\text{F}^{11}\text{B}} & -R_{\text{F}^{10}\text{B}} & -R_{\text{FD}} \\ -R_{^{11}\text{B}\text{F}} & -R_{^{11}\text{B}^{11}\text{B}} & -R_{^{11}\text{B}^{10}\text{B}} & -R_{^{11}\text{B}\text{D}} \\ -R_{^{10}\text{B}\text{F}} & -R_{^{10}\text{B}^{11}\text{B}} & -R_{^{10}\text{B}^{10}\text{B}} & -R_{^{10}\text{B}\text{D}} \\ -R_{\text{DF}} & -R_{\text{D}^{11}\text{B}} & -R_{\text{D}^{10}\text{B}} & -R_{\text{DD}} \end{bmatrix},$$

where $[\mathbf{R}]$ is a total relaxation matrix.

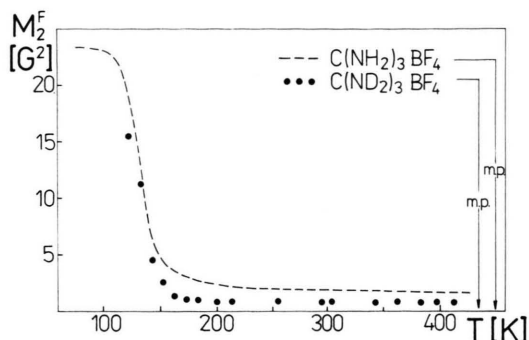


Fig. 1. Temperature dependence of the fluorine second moment (the dashed line presents the plot obtained in [1] for $\text{C}(\text{NH}_2)_3\text{BF}_4$).

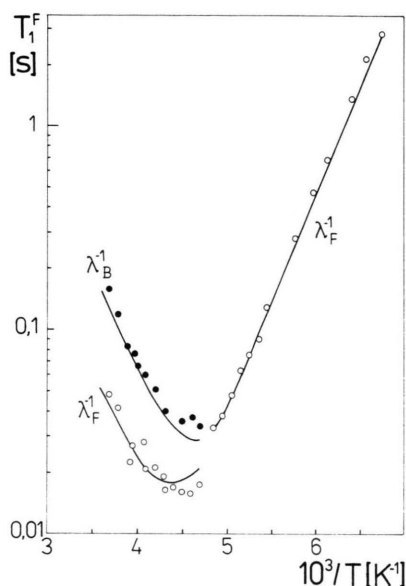


Fig. 2. Temperature dependence of the fluorine spin-lattice relaxation time T_1 .

Assuming the same interatomic distances in $\text{C}(\text{ND}_2)_3\text{BF}_4$ as in the undeuterated salt we could apply the values of reduced second moments: $\Delta M_2(\text{F}-\text{F}) = 7.85 \text{ G}^2$, $\Delta M_2(\text{F}-^{11}\text{B}) = 9.79 \text{ G}^2$, $\Delta M_2(\text{F}-^{10}\text{B}) = 0.82 \text{ G}^2$ (found in [1], Table 6) and additionally $\Delta M_2(\text{F}-^2\text{D}) = 0.2 \text{ G}^2$ to calculate the relaxation matrix elements according to the formula

$$R_{\text{II}} = \frac{2}{3} \gamma_{\text{I}}^2 \Delta M_2(I-I) \cdot g_1(\omega_{\text{I}}, \tau) + \frac{1}{2} \sum_s \gamma_{\text{I}}^2 \Delta M_2(I-S) \cdot g_2(\omega_{\text{I}}, \omega_{\text{S}}, \tau),$$

$$R_{\text{IS}} = \frac{1}{2} \gamma_{\text{S}}^2 \Delta M_2(S-I) \cdot g_3(\omega_{\text{I}}, \omega_{\text{S}}, \tau),$$

where

$$\begin{aligned} g_1(\omega_1, \tau) &= \tau / (1 + \omega_1^2 \tau^2) + 4\tau / (1 + 4\omega_1^2 \tau^2), \\ g_2(\omega_1, \omega_S, \tau) &= \tau / [1 + (\omega_1 - \omega_S)^2 \tau^2] \\ &\quad + 3\tau / (1 + \omega_1^2 \tau^2) + 6\tau / [1 + (\omega_1 + \omega_S)^2 \tau^2], \\ g_3(\omega_1, \omega_S, \tau) &= -\tau / [1 + (\omega_1 - \omega_S)^2 \tau^2] \\ &\quad + 6\tau / [1 + (\omega_1 + \omega_S)^2 \tau^2]. \end{aligned}$$

The Arrhenius correlation time τ is ascribed here to the BF_4 reorientation.

Then we calculated the eigenvalues λ_r of the relaxation matrix $[\mathbf{R}]$ and their respective magnetisation amplitudes $A(r)$ as a function of temperature (see [4] formula (3) and (4)).

At temperatures higher than 200 K a theoretical analysis of the fluorine magnetisation behaviour satisfactorily explains an evident non-exponential magnetisation recovery due to the cross-relaxation between fluorine and boron nuclei. At the highest temperatures it was found that 84% of the magnetisation comes from the fluorine-fluorine interaction and 16% from the $^{19}\text{F}-^{11}\text{B}$ interaction ($^{19}\text{F}-^{10}\text{B}$ and $^{19}\text{F}-^2\text{D}$ interactions appeared negligibly small). Two such contributions to the fluorine magnetisation have also been observed in the experiment. A quadrupolar ^{11}B interaction was neglected in our calculations as was done in [1].

The deuteration of the compound, removing the fluorine-proton interaction, reveals the fluorine-boron interaction by a non-exponential fluorine magnetisation behaviour. In the protonated compound it was obscured by the comparable competitive proton and boron contributions to the fluorine magnetisation producing apparently a one-exponential magnetisation decay above the T_1^{F} minimum.

An advantage of the deuteration is especially seen on the low temperature side of the T_1^{F} minimum where the fluorine magnetisation decay becomes one-exponential revealing a pure fluorine-fluorine interaction.

The best fitting of theoretical eigenvalues λ_{F}^{-1} to the experimental T_1^{F} values as a function of temperature yielded the following Arrhenius activation parameters for the BF_4 reorientation: $E_{\text{a}}^{\text{F}} = 19.3$ kJ/mole and $\tau_0^{\text{F}} = 9 \cdot 10^{-14}$ s. The activation energy is by about 7% smaller (preexponential factor 3 times higher) than found for the protonated salt. Quantitatively the same changes in the activation parameters for the BF_4 anion reorientation were found in pyridinium tetrafluoroborate after deuteration of the compound [3, 5].

The knowledge of the activation parameters enabled us to compare the temperature dependences of the rotational correlation time for the BF_4 anion and for the guanidinium cation. Since the activation energy for BF_4 reorientation was found to be lower in $\text{C}(\text{ND}_2)_3\text{BF}_4$ than in $\text{C}(\text{NH}_2)_3\text{BF}_4$, obviously there must be a decrease in the cation-anion interactions and hence a lower energy barrier should be expected also for the deuterated guanidinium cation. So, it seemed reasonable to assume the same reduction of the activation parameters for the deuterated cation as for the anion reorientation. For the reduced values ($E_{\text{a}}^{\text{D}} = 35$ kJ/mole, $\tau_0^{\text{D}} = 3.8 \cdot 10^{-15}$ s) the temperature dependence of the cation correlation time was compared with the plot obtained for the anion. Both plots converge at temperature lower than for the undeuterated salt (see Figure 3). The convergence reveals also in this compound the existence of a coupling of rotational modes of two ionic sublattices. In the other salts [2] we have discovered that such a convergence took place at the phase transitions. Thus one could expect the same effect in $\text{C}(\text{ND}_2)_3\text{BF}_4$. Indeed, we found that the deuteration of the compound caused a significant lowering of the melting point, from 450 K to 435 K. This is evidence of a large isotope effect, which depends among others on the nature of the hydrogen bond in the system, on its symmetry and length [6–10]. Singh and Wood [7] have calculated the effect of isotopic substitution of hydrogen by deuterium on the $R(\text{A} \cdots \text{B})$ distance of an $\text{A}-\text{H} \cdots \text{B}$ hydrogen bond. They found that the $R(\text{A} \cdots \text{B})$ distance increases (positive isotope effect) on deuteration if the potential energy function contains a symmetric or asymmetric

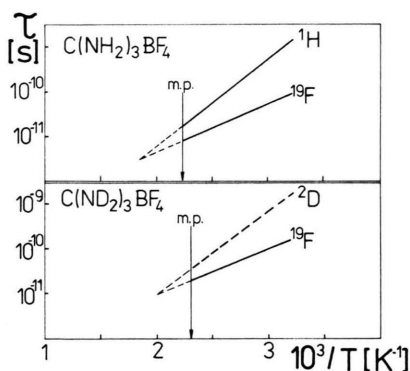


Fig. 3. Temperature dependences of correlation times for cations and anions in $\text{C}(\text{ND}_2)_3\text{BF}_4$ and $\text{C}(\text{NH}_2)_3\text{BF}_4$ (τ^{D} estimated from τ^{H}).

double minimum. Similar conclusions have been reached by Savelev and Sokolov [8]. On the other hand the $R(A \cdots B)$ distance decreases (negative isotope effect) on deuteration if the potential curve has a single symmetric minimum.

In the compound studied the lowering of the melting point can be explained by a diminishing strength of the hydrogen bonds $N-H \cdots F$, the potential energy having two minima. It is known that the weaker

these bonds are the lower is the thermal energy necessary to induce the phase transition.

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