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Cation complex motion and hydrogen bonds in guanidinium nitrate

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Abstract. Proton NMR linewidths and second moments, and spin–lattice relaxation times in the laboratory (12 and 60 MHz) and in rotating frames ($H_1 = 9 \times 10^{-4}$ T) were studied for polycrystalline guanidinium nitrate over a temperature range covering three solid phases. An analysis of the experimental results enabled us to reveal a complex cation motion and derive the respective activation parameters. In the low-temperature phase a proton motion in the hydrogen bond has been demonstrated and characterized. A convergence of two reorientational correlation times of the guanidinium cation has been discovered at the first-order phase transition.

1. Introduction

Ionic motion in a number of guanidinium salts has been extensively studied in our laboratory by nuclear magnetic resonance (NMR) techniques [1–6]. It was particularly interesting to examine a role of the cation–anion interaction and hydrogen bonding, contributing essentially to a potential barrier that hindered the considered ionic reorientation. In all the compounds studied we found evidence for the existence of the reorientation of the whole guanidinium cation around its C_3 symmetry axis, accompanied by motion of one or two NH_2 groups. In the fluorinated guanidinium salts it was possible to describe the molecular dynamics of both ionic sublattices and reveal an interesting interaction of cations and anions, leading to a coupling of the reorientational frequencies at a first-order phase transition [7].

The molecular dynamics of guanidinium nitrate has been studied by Gima *et al* [8]. The NMR results obtained in a limited temperature range were interpreted in terms of a simple C_3 reorientation of the cation. More recently guanidinium nitrate was reported to exhibit two solid–solid phase transitions [9], not revealed by Gima *et al*. The compound undergoes a first-order phase transition T_{III-II} at 296 K and a second one T_{II-I} at 384 K. The melting point was found to be 487 K. Noteworthy is an abrupt change in the crystal dimensions at T_{III-II} , namely an elongation of the crystal needle by about 45%, with simultaneous reduction in its transversal dimensions [9]. Other interesting properties of the crystal connected with the phase transitions were observed in calorimetric, dilatometric and dielectric studies [9].

Katrusiak and Szafranski [10] have recently succeeded in resolving the crystal structure of the compound in phase III. Guanidinium nitrate crystallizes in the monoclinic space group Cm , with $a = 12.930$ (3), $b = 7.274$ (2), and $c = 3.646$ (1) Å; $\beta = 120.29$ (2)° and $Z = 2$. The crystal is built of sheets of guanidinium and nitrate ions linked by hydrogen bonds $N-H \cdots O$ of 2.956 (6), 2.981 (6) and 3.022 (8) Å in length. Significant changes in the crystal shape at the first-order phase transition at 296 K are connected with shear shifts of these sheets in the crystal lattice.

The present NMR study has been undertaken to examine the reorientation of the guanidinium cation in all three phases and provides an insight into the mechanism of the phase transitions. Especially interesting was the low-temperature phase (III) wherein our preliminary measurements revealed a flat and barely visible T_1 minimum that could be explained by proton motion in a hydrogen bond.

2. Experimental

The guanidinium nitrate obtained by allowing guanidinium carbonate to react with nitric acid was recrystallized three times from an ethanol/water solution. The product was then ground to a powder, degassed by the usual freeze-pump-thaw technique and sealed under vacuum in a glass ampoule.

Measurements of proton NMR second moments (M_2) and linewidths (ΔH) were carried out over a wide range of temperature, using a home-made wide-line spectrometer, operating for protons at a Larmor frequency of 28 MHz. The second-moment values were calculated by numerical integration of the first derivative of an absorption line and corrected for the finite modulation amplitude. Mean values were obtained for about twenty curves registered at each temperature.

Measurements of the proton spin-lattice relaxation time T_1 were performed as a function of temperature with a 60 MHz home-made spectrometer and a 12 MHz Bruker SXP 4100 spectrometer, by the saturation recovery method. The relaxation time $T_{1\rho}$ was measured at 70 MHz in a rotating field of 9×10^{-4} T by a spin-locking method in the temperature range 330–480 K. This could not be measured at lower temperatures, since the local field criterion was not fulfilled there.

3. Results

The results for proton NMR second-moment and linewidth studies performed over a wide temperature range are shown in figure 1. The second moment observed at lower temperatures (18.5×10^{-8} T²) starts to decrease at about 280 K to a value of 3.3×10^{-8} T², achieved above 440 K. The linewidth changes from 6×10^{-4} T registered below 310 K to 2.1×10^{-4} T above 385 K. Figure 1 shows also the shapes of resonance line derivatives registered at different temperatures. At low temperatures a narrow, small component appears in the centre of the spectrum, which disappears above 330 K. At temperatures higher than 390 K the lineshape resembles Pake's doublet changing with temperature.

The temperature variations of the spin-lattice relaxation times T_1 and $T_{1\rho}$ are shown in figure 2. T_1 values measured at 60 and 12 MHz show broad minima of 803 s at 267 K and 238 s at 225 K, respectively. The rotating frame relaxation time $T_{1\rho}$ displays a minimum of 130 μ s at 357 K and a change in its slope at 384 K. The proton magnetization decay was one-exponential at all temperatures studied.

4. Calculations and discussion

4.1. Second moment

To describe the nature of the motion occurring in the guanidinium nitrate, measured values for the second moment must be compared with the theoretical values. In view of a number

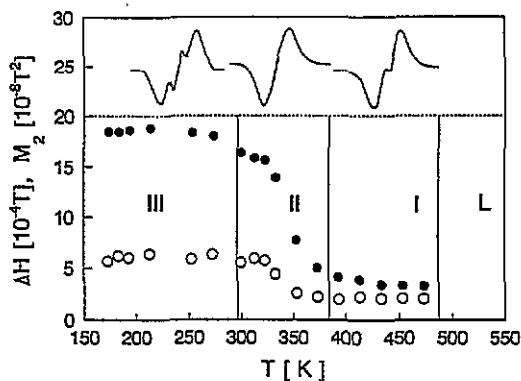


Figure 1. The temperature dependence of the NMR second moment M_2 (●), the linewidth ΔH (○) and the shapes of the resonance line derivatives.

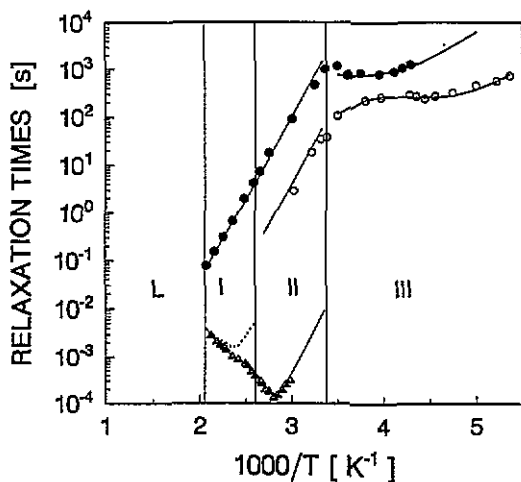


Figure 2. The temperature dependence of spin-lattice relaxation times T_1 at 60 MHz (●), 12 MHz (○) and $T_{1\rho}$ at $H_1 = 9 \times 10^{-4} T$ (Δ). The full and dotted curves are theoretical fits.

of studies made on related guanidinium salts [1-4] it seems needless to repeat all the details of the calculations in the present paper.

The value of $18.5 \times 10^{-8} T^2$ measured at the lowest temperature studied is found to correspond well to that expected for the rigid lattice ($18.8 \times 10^{-8} T^2$). The observed reduction of this value to $3.3 \times 10^{-8} T^2$ cannot be satisfactorily explained in terms of one simple motion, i.e. C_3 reorientation of the cation, contrary to that reported by Gima *et al* [8]. Such a motion would only reduce the second moment to a value not lower than $(5.0 \pm 0.5) \times 10^{-8} T^2$, which evidently exceeds the experimental value at the highest temperatures. Hence the reduction must result from a superposition of two simple motions, as we found in other guanidinium salts. It is probably the motion of one or two NH_2 groups which starts to influence the second-moment value and lineshape at low temperatures (phase III) and gives rise to the small narrow component observed in the NMR spectrum (figure 1). At higher temperatures (phase II) C_3 reorientation of the guanidinium cation

appears effective, greatly reducing the dipolar interaction and second-moment value. It also narrows the linewidth and washes out the fine structure of the spectrum above 330 K.

Particularly noteworthy is a change in the lineshape observed above 380 K, i.e. in phase I. Although the line is already narrowed by the reorientations of the cation it takes the form of a double-peaked curve, as was usually observed for the rigid structure of the guanidinium salts. Such a shape results from a better separation of spin pairs in phase I than in the other phases. This can result from a change of ionic symmetry at the phase transition and/or from a change of NH_2 group geometry caused by their rotation around the C-N axis [11, 12].

4.2. NMR relaxation times

The low-temperature T_1 minima (phase III) evidently reflect the existence of cation motion of a frequency comparable to the Larmor frequency. Since the ratio of both minima (3.37) is not equal to the ratio of the respective resonance frequencies (5.00) the relaxation constant must depend on the temperature. Also, the high values for both minima suggest that the motion takes place between unequal potential wells. Since the guanidinium and nitrate ions are linked by a number of hydrogen bonds [10] it is reasonable to assume that there is the motion of a proton in an asymmetric two-well potential of the hydrogen bond $\text{N-H}\cdots\text{O}$. To interpret fully our relaxation data for such a model of proton motion we can apply the procedure presented in [13, 14].

For guanidinium nitrate we have to consider the relaxation matrix for a two-spin system (^1H and ^{14}N):

$$\mathbf{R} = \begin{bmatrix} R_{\text{HH}} & R_{\text{HN}} \\ R_{\text{NH}} & R_{\text{NN}} \end{bmatrix}. \quad (1)$$

For any motion taking place between equivalent potential wells, diagonal (R_{II}) and off-diagonal (R_{IS}) elements of the relaxation matrix are defined by the formulae:

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

$$R_{\text{IS}} = \frac{1}{2}\gamma_{\text{S}}^2\Delta M_2^{\text{SI}}g_3(\omega_{\text{I}}, \omega_{\text{S}}, \tau)N_{\text{S}}/N_{\text{I}} \quad (3)$$

where

$$g_1(\omega_{\text{I}}, \tau) = \tau/(1 + \omega_{\text{I}}^2\tau^2) + 4\tau/(1 + 4\omega_{\text{I}}^2\tau^2) \quad (4)$$

$$g_2(\omega_{\text{I}}, \omega_{\text{S}}, \tau) = \tau/[1 + (\omega_{\text{I}} - \omega_{\text{S}})^2\tau^2] + 3\tau/(1 + \omega_{\text{I}}^2\tau^2) + 6\tau/[1 + (\omega_{\text{I}} + \omega_{\text{S}})^2\tau^2] \quad (5)$$

$$g_3(\omega_{\text{I}}, \omega_{\text{S}}, \tau) = -\tau/[1 + (\omega_{\text{I}} - \omega_{\text{S}})^2\tau^2] + 6\tau/[1 + (\omega_{\text{I}} + \omega_{\text{S}})^2\tau^2]. \quad (6)$$

In the case of proton motion in the hydrogen bond described by an inequivalent two-well potential (phase III) the first term of formula (2) must be replaced by the expression

$$R_{\text{H}} = C_{\text{HH}}\{[a/(1+a)^2]g_1(\omega_{\text{H}}, \tau)\} \quad (7)$$

where the correlation time τ is defined by

$$\tau = [a/K(1+a)]\exp(E_{\text{B}}/RT) \quad (8)$$

and

$$C_{\text{HH}} = \gamma_{\text{H}}^2 \Delta M_2^{\text{HH}} \quad (9)$$

$$1/\tau = W_1 + W_2. \quad (10)$$

The probability rates W_1 and W_2 for transitions between different wells, characterized by a higher E_A and a lower E_B energy barrier, respectively, are defined by

$$W_1 = K \exp(-E_A/RT) \quad (11)$$

$$W_2 = K \exp(-E_B/RT) \quad (12)$$

while the population parameter a is defined by

$$a = \exp(\Delta/RT) \quad (13)$$

where

$$\Delta = E_A - E_B. \quad (14)$$

K is a frequency factor independent of temperature.

Table 1. Activation parameters.

Type of motion	Phase	Activation energy (kJ mol ⁻¹)	K (s ⁻¹)	τ_0 (s)
H	III	$E_B = 17.2 \pm 1.4$ $\Delta = 5.7 \pm 0.5$	$(2.1 \pm 0.2) \times 10^{12}$	
NH ₂	III	34.0 ± 4.1		$(9.7 \pm 1.2) \times 10^{-12}$
	I, II	43.6 ± 2.6		$(9.9 \pm 0.6) \times 10^{-12}$
C ₃	I, II	66.9 ± 3.3		$(3.3 \pm 0.2) \times 10^{-16}$

The inverses of the calculated eigenvalues λ_{H} for the relaxation matrix were fitted to the T_1 experimental data. C_{HH} , E_A , Δ and K were used as fitting parameters. The best-fit activation parameters in the low-temperature phase are presented in table 1. A good agreement between experimental and theoretical T_1 values confirms the justness of the assumed model for proton motion in the hydrogen bond. The nitrate is the first guanidinium salt wherein such a motion has been revealed. The motion is fast enough to modulate the relaxation process producing a T_1 minimum in phase III. However an expected change of the second moment corresponding to such high T_1 minima ($\Delta M_2 \simeq 0.01 \times 10^{-8} \text{ T}^2$) is too small to be observed in the wide-line experiment.

A motion which evidently modulates a dipolar interaction and reduces the second moment and linewidth value is the reorientation of the guanidinium cation around its C₃ axis. The motion strongly affects the relaxation mechanism in phases II and I, which is reflected in a linear decrease of log T_1 values. However the log T_1 plot at 60 MHz does not reach a minimum before the melting point. Fortunately, a log $T_{1\rho}$ versus $1/T$ plot displays

the minimum expected for C_3 reorientation of the cation. The experimental $T_{1\rho}$ data can be described by the following expression, considering only the proton–proton interaction:

$$T_{1\rho} = C'_{\text{HH}} g_{\rho}(\omega_0, \omega_1, \tau) \quad (15)$$

where

$$g_{\rho}(\omega_0, \omega_1, \tau) = \frac{5}{2} \frac{\tau}{1 + \omega_0^2 \tau^2} + \frac{\tau}{1 + 4\omega_0^2 \tau^2} + \frac{3}{2} \frac{\tau}{1 + 4\omega_1^2 \tau^2} \quad (16)$$

and

$$C'_{\text{HH}} = \frac{2}{3} \gamma_{\text{H}}^2 \Delta M_2^{\text{HH}}. \quad (17)$$

A least-squares fit (full curves in figure 2) to the experimental $T_{1\rho}$ and T_1 at 60 and 12 MHz ($\Delta M_2^{\text{HH}} = 10.95 \times 10^{-8} \text{ T}^2$) yielded the activation parameters for the C_3 reorientation presented in table 1.

The activation parameters derived at three different relaxation experiments characterize the motion in phase II. These are in good agreement with those found for this compound by Gima *et al* [8] in phase I.

Most noteworthy is that the $T_{1\rho}$ curve evidently changes its slope at 384 K, i.e. at the phase transition. The slope in phase I gives an activation energy much lower than that found for the C_3 reorientation in this phase. This can suggest the existence of another motion which can be separated by subtracting an experimental $T_{1\rho}$ plot from that simulated for the C_3 reorientation. Such a procedure yields a new $T_{1\rho}$ minimum of 1.5 ms at 425 K (dotted curve in figure 2) that could be related to an expected reduction in the second-moment value of $\Delta M_2 \simeq 0.7 \times 10^{-8} \text{ T}^2$. Activation parameters extracted for this motion are listed in table 1. It is interesting to note that the parameters are similar to those found for NH_2 group motion in guanidinium aluminate and gallate [5, 6]. The calculated relaxation constant, as well as the value for the pre-exponential factor, indicate the motion of a small fragment of the cation. This further confirms the existence of NH_2 group motion, which precedes the C_3 reorientation of the whole cation, as was found in the other guanidinium salts. The motion already starts to influence the relaxation behaviour in phase III by a shortening of T_1 values just before $T_{\text{III-II}}$. The activation energy obtained for NH_2 group motion corresponds well to the value found theoretically for a rotation of one amino group in the guanidinium cation [11, 12]. Since the rotation of another NH_2 group requires much higher energy it can affect the second moment in phase I but cannot be revealed in our relaxation experiment.

The activation parameters obtained for all the motions considered (table 1) enabled us to plot $\log \tau$ against $1/T$, as shown in figure 3. The temperature behaviour of the microscopic parameter τ gives a direct insight into the mechanism of motion. Hence it is interesting to note that the plots obtained for C_3 reorientation and NH_2 group motion converge at the phase transition $T_{\text{III-II}}$. This means that the correlation times for both motions derived in phase II tend with decreasing temperature to the same value of 10^{-3} s . This effect may represent a new kind of coupling of two internal modes in the guanidinium cation. A similar effect has been observed in the other guanidinium salts wherein a coupling between rotational modes of the cation and the anion has been discovered [7].

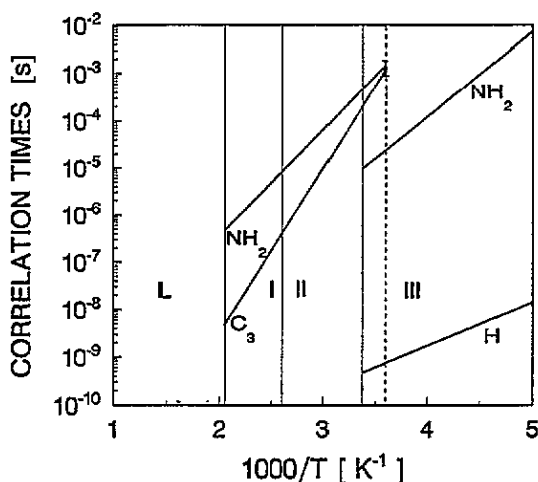


Figure 3. The temperature dependence of correlation times for the motions considered.

5. Conclusions

The guanidinium cation linked by hydrogen bonds with the nitrate anions undergoes a complex motion in all the solid phases detected. In the low-temperature phase III proton motion between two inequivalent potential wells of the hydrogen bonds has been discovered. This motion produces the most effective mechanism for spin-lattice relaxation. In phase II the relaxation is governed by C_3 reorientation of the whole cation, preceded by NH_2 group motion. In phase I, besides the latter motions, characterized by the same activation parameters as in phase II, one cannot exclude the motion of another NH_2 group. Activation parameters derived for all the motions considered enabled us to find the temperature behaviour of the respective correlation times. A convergence of two reorientational correlation times for the guanidinium cation has been discovered at the first-order phase transition.

Acknowledgments

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