

Pulsed Double Resonance Study of the Nuclear Quadrupole Interactions of ^{14}N in Paraelectric Tri-glycine Sulfate

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The technique of nuclear magnetic pulsed double resonance in the rotating frame has been used to study the quadrupole interactions of ^{14}N in a single crystal of paraelectric $(\text{NH}_3^+\text{CH}_2\text{COO}^-)\cdot(\text{NH}_3^+\text{CH}_2\text{COOH})_2\cdot\text{SO}_4$. The ^{14}N quadrupole coupling tensors of glycine II and glycine III are chemically equivalent ($e^2qQ/h = 989$ kHz, $\eta = 0.108$), demonstrating the existence of fast exchange of glycinium-glycine roles due to proton transfer between the two equilibrium sites in the short $\text{O}-\text{H}\cdots\text{O}$ bond. The ^{14}N quadrupole coupling tensor of the glycinium ion I has a somewhat smaller quadrupole coupling constant ($e^2qQ/h = 906$ kHz) and a larger asymmetry parameter, $\eta = 0.693$. The largest principal axes of the ^{14}N EFG tensors of all three glycine groups are found to lie in the mirror plane perpendicular to the crystal b axis.

It is well known that tri-glycine sulfate $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ - abbreviated TGS - becomes ferroelectric¹ below $T_c = 49^\circ\text{C}$.

The microscopic nature of the ferroelectric transition and in particular the role of the various glycine groups is, however, still not completely understood. It has been suggested that the compound should be properly called glycine di-glycinium sulfate $(\text{NH}_3^+\text{CH}_2\text{COO}^-)(\text{NH}_3^+\text{CH}_2\text{COOH})_2\cdot\text{SO}_4^{2-}$, and that in the polar phase, the glycine groups I and III are completely planar, whereas the glycine group II is only partially planar with the nitrogen atom being displaced from the plane of the two carbons and two oxygens of the same molecule.² The transition to the paraelectric phase is, according to this model, connected with the onset of flipping of the C - N axes of all three glycine groups between two equilibrium sites, symmetrically arranged above and below the mirror plane, which is perpendicular to the monoclinic b axis, and with the dynamic exchange of the glycine-glycinium roles of glycines III and II. The transition would thus be of the order-disorder type. Recently, however, a different model has been suggested,^{3,4} according to which the transition is of the displacive type, at least as far as glycine I is concerned.

To solve this discrepancy, a knowledge of the ^{14}N ($I=1$) electric field gradient (EFG) tensors of the various glycine units in TGS is needed. Such a knowledge might in addition be of some biochemical interest in view of the role of glycine in biological macromolecules.

Since pure quadrupole resonance was found not to be sufficiently sensitive to allow the detection of ^{14}N signals in TGS, we decided to study this problem with the help of pulsed proton-nitrogen double resonance in the rotating frame, as first introduced by Hartmann and Hahn.⁵ This method is known to be particularly suitable for the observation of the spectra of nuclei, which cannot be detected by ordinary techniques. The proton spin system is first prepared in a state of low spin temperature by adiabatic demagnetization into the rotating frame, whereas the nitrogen spin system is heated by an r.f. magnetic field, and then made to interact with the proton spin system by means of dipolar coupling in such a way that order can be transferred from the "cool" to the "hot" system. This process is made continuously for the time of the dipolar spin-lattice relaxation time T_{1D} of the protons. The protonic signal is finally monitored, and order transfer is detected as an anomalous decrease in the proton magnetization. Order transfer occurs only⁵ if the "double resonance" condition

$$\gamma_{\text{H}}(H_{\text{L}})_{\text{H}} = 2\gamma_{\text{N}}(H_{\text{L}})_{\text{N}} \langle a|S_x|b \rangle \quad (1)$$

and

$$\nu_{\text{N}} = (E_a - E_b)/h \quad (2)$$

are simultaneously fulfilled. Here H_{L} is the local protonic dipolar field, $(H_{\text{L}})_{\text{N}}$ is the second radiofrequency field with a frequency ν_{N} , which should be equal to the frequency of one of the nitrogen transitions between the energy levels E_a and E_b , corresponding to eigenstates $|a\rangle$ and $|b\rangle$ of the combined ^{14}N Zeeman and quadrupole Hamiltonian. In practice, ν_{N} is varied so long that the condition (2) is fulfilled. The matrix element $2 \langle a|S_x|b \rangle$ is of the order of $\sqrt{2}$, if the ^{14}N Zeeman energy is small, compared to the ^{14}N quadrupole energy level splitting. If the Zeeman and quadrupole terms are of the same magnitude, the value of $\langle a|S_x|b \rangle$ varies, as one rotates the crystal with respect to the static magnetic field H_0 .

The "Hahn" condition — eqn. (1) — means that in the rotating frame, the energy level splittings of the protonic and the nitrogen system are equal, so that resonant energy transfer is possible. This effect can, however, only be detected if, in addition, the nitrogen spin system is heated to an infinite spin temperature by irradiating it with a resonant — eqn. (2) — radiofrequency field.

In this communication we wish to present a brief report on the results obtained in the high temperature paraelectric phase of TGS.

EXPERIMENTAL DETAILS

The experiment was performed on a home-built double resonance spectrometer, using a somewhat modified Bruker B—KR 304 s pulsed spectrometer for the detection of the proton magnetization.

The equilibrium proton magnetization in a high magnetic field H_0 ($\nu_{\text{L}} = 18$ MHz) was spin locked along an effective field $[(H_{\text{L}})_{\text{H}}^2 + (H_{\text{L}})_{\text{N}}^2]^{1/2}$ in the rotating frame, where

$(H_1)_H$ was adiabatically decreased to zero. During the period $t_s \leq T_{1D}$ of spin-locking, a second radiofrequency field $(H_1)_N$ was applied for a time $t_d \approx 20 - 50 \times 10^{-3}$ s. To maintain the nitrogen spins at a high spin temperature, so that the cold proton spins are continuously heated through the double resonance interaction, $(H_1)_N$ was modulated by changing its phase by 180° every τ seconds, where $\tau \approx 3 \times 10^{-3}$ s is of the order of the proton-nitrogen spin flip-flop time. After the double resonance irradiation period was over, $(H_1)_N$ was removed, and $(H_1)_H$ was adiabatically turned on. Finally, $(H_1)_H$ was suddenly removed, and the remaining proton magnetization

$$M_H = (M_0)_H \exp[-(Wt_d + t_s/T_{1D})] \quad (3)$$

was monitored as a function of the frequency ν_N of $(H_1)_N$. The double resonance rate W is

$$W = (C_N/C_H) W_{NH} \quad (4)$$

where C_N/C_H is the ratio of the magnetic heat capacities of the nitrogen and hydrogen spin reservoirs ($C_N/C_H \propto n_N/n_H$ with n being the number of the corresponding spins per unit volume), and W_{NH} is the intrinsic double resonance cross relaxation rate which is proportional to the second moment of the dipolar interaction between the two spin reservoirs. It should be noted that W is practically zero if conditions (1) and (2) are not satisfied. The optimum signal to noise ratio S with which the nitrogen spectra can be measured by this method may be expressed for $T_{1D} > W^{-1}$ as

$$(S)_N \approx (S)_H (WT_{1D})^{-1/WT_{1D}} \quad (5)$$

where $(S)_H$ is the signal to noise ratio of the proton system.

The single crystals used were grown from water solution at IJS in Ljubljana.

RESULTS

A typical double resonance spectrum which shows the normalized value of the proton magnetization in TGS as a function of the frequency ν_N of the radiofrequency field $(H_1)_N$ is presented in Fig. 1. The angular dependences

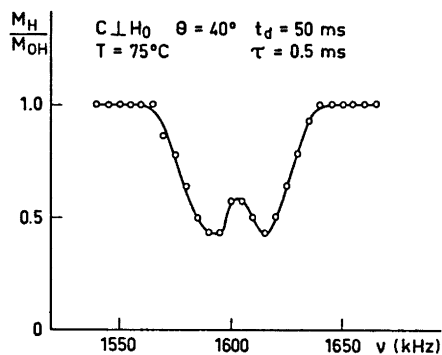


Fig. 1. Normalized values of the proton magnetization M_H/M_{0H} in TGS plotted as a function of the frequency ν_N of the radiofrequency field, applied in the vicinity of the ^{14}N transitions. M_H is the proton magnetization with, and M_{0H} the proton magnetization without double resonance irradiation.

of the double resonance spectra have been measured for three mutually orthogonal rotations of the TGS crystals with respect to H_0 . Both the $\Delta m = 1$ and $\Delta m = 2$ nitrogen transitions have been investigated. The double resonance rotation pattern for $\vec{C} \perp \vec{H}_0$ is shown in Fig. 2. All measurements have been performed at $T = 75 \pm 2^\circ\text{C}$.

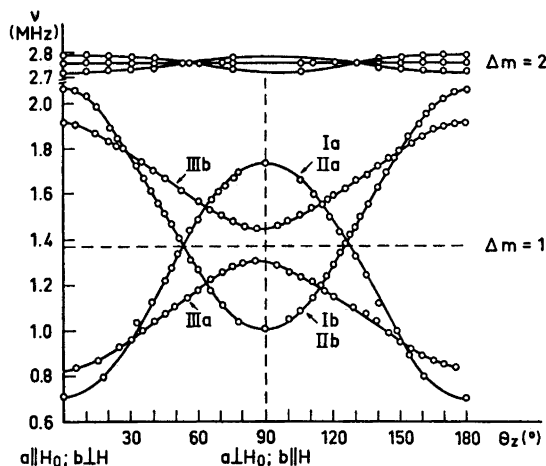


Fig. 2. Angular dependence of the ^{14}N transition frequencies in paraelectric TGS for $\vec{C} \perp \vec{H}_0$ and $H_0 = 4228$ Gauss.

The rotation patterns have been analyzed, using first and second order perturbation theory⁶ as well as by solving the secular equation exactly, and a good agreement between the two methods was found. The second order corrections were 10–15 % of the first order terms.

The high temperature paraelectric phase of TGS is monoclinic ($\beta = 110^\circ$) and belongs¹ to the centrosymmetrical class $2/m$. There are two formula units per unit cell, but in view of the crystal symmetry, only three physically non-equivalent ^{14}N EFG tensors, belonging to one asymmetric unit, can be seen.

The components of the ^{14}N quadrupole coupling tensors V_{ij} , expressed in the orthogonal $a \sin \beta$, b , c crystal fixed coordinate system, are presented in Table 1. After diagonalization, the eigenvalues and direction cosines of the

Table 1. Components of the ^{14}N quadrupole coupling tensors (in kHz) in paraelectric TGS, expressed in the crystal fixed coordinate system $a \sin \beta$, b , c .

	Glycine I			Glycines II and III		
	$a \sin \beta$	b	c	$a \sin \beta$	b	c
$a \sin \beta$	-740	30	208	-960	0	-208
b	30	-140	-36	0	480	± 52
c	208	-36	880	-208	± 52	480

principal axes of the three ^{14}N quadrupole coupling tensors are obtained. It is found (Table 2) that the directions of the largest principal axes of the ^{14}N EFG tensors of all three physically non-equivalent glycine groups in the

Table 2. Comparison between the direction cosines of the largest principal axes of the ^{14}N EFG tensors of glycines I, II, and III in paraelectric TGS, and the average of the two possible C–N bond directions² in the ferroelectric phase, as referred to the $a \sin \beta$, b , c crystal fixed coordinate system.

	Average C–N direction cosines	Direction cosines of the largest ^{14}N EFG tensor principal axis
G I	0.150 0 0.964	0.124 –0.031 0.992
G II G III	0.998 –0.032 0.046	0.990 ± 0.005 0.140

paraelectric phase agree with the average of the two possible C–N bond directions of the corresponding glycine groups in the ferroelectric phase. This fact makes it possible to assign the observed EFG tensors to the various glycine groups in a unique way. One thus finds that for glycine I, the quadrupole coupling constant e^2qQ/\hbar and asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ equal to

$$(e^2qQ/\hbar)_I = 906 \pm 10 \text{ kHz}, \eta_I = 0.69 \pm 0.02 \quad (6)$$

whereas the ^{14}N EFG tensors of glycine II and glycine III are chemically equivalent:

$$\left(\frac{e^2qQ}{\hbar}\right)_{\text{II,III}} = 990 \pm 10 \text{ kHz}, \eta_{\text{II,III}} = 0.10 \pm 0.02 \quad (7)$$

The fact that glycine II and glycine III are chemically equivalent, as far as the ^{14}N EFG tensor is concerned, demonstrates the fast exchange of glycinium-glycine roles of these two ions due to proton transfer between the two equilibrium sites in the short ($R_{\text{O}\cdots\text{O}} = 2.44 \text{ \AA}$) O–H \cdots O hydrogen bond. The frequency of proton transfer must be larger than the difference in the corresponding ^{14}N quadrupole coupling tensors, *i.e.* larger than 50 kHz. A similar deuteron motion has already been reported.⁴

It should be stressed that at 75°C, the $-\text{NH}_3^+$ groups of all three glycine groups are rotating around the C–N bond direction⁴ with a frequency which is large compared to the various ^{14}N transition frequencies, so that the above quadrupole coupling tensors represent an average over the $-\text{NH}_3$ rotation.

The fact that the directions of the largest principal axes of the ^{14}N EFG tensors of all three glycine groups are found to be in the mirror plane perpendicular to the monoclinic b axis, whereas they are arranged above or below this plane in the ferroelectric phase,² demonstrates that the disorder in the paraelectric phase is not static, but dynamic. The present data by themselves do not exclude the possibility that the crystallographic mirror plane above T_c is a true mirror plane, and not only a statistical one. In this case, the ferroelectric transition would be displacive rather than of the order-disorder type. This, however, seems to be hard to understand in view of the relatively large transition entropy.

The observed relatively large differences in e^2qQ/h and η between glycine I and glycines II and III, respectively, demonstrate that nitrogen nuclear quadrupole resonance measurements represent an extremely sensitive tool for the study of the electronic and structural characteristics of molecular solids. The use of field cycling nuclear double resonance *via* the laboratory frame which allows ^{14}N measurements in powders might therefore be of some importance in biology.

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