

^{17}O AND ^{14}N QUADRUPOLE COUPLING AND THE MECHANISM OF THE FERROELECTRIC TRANSITION IN DIGLYCINE NITRATE[†]

JANEZ SELIGER, VESELKO ŽAGAR, ROBERT BLINC

J. Stefan Institute, E. Kardelj University of Ljubljana, 61000 Ljubljana, Yugoslavia

A. NOVAK

Laboratoire de Spectrochimie Infrarouge et Raman, C.N.R.S.,
2 rue Henri Dunant, 94320 Thiais,

and

S. RODIN^x

Radioengineering Institute, Minsk, USSR

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Abstract. The ^{14}N and ^{17}O quadrupole couplings in diglycine nitrate have been determined by proton- ^{14}N and proton- ^{17}O double resonance. The O—H—O bonded proton is moving between two off-centre sites in the H—bond above T_c and is frozen out in an off-centre site below T_c . The results show that the basic phase transition mechanism is a biasing of the flipping of the $-\text{NH}_3$ groups around the C—N bond between two equilibrium orientations separated by $\sim 60^\circ$ connected with a corresponding rotation of the NO_3^- ions, an exchange of the ionic character of the two glycine molecules and a transfer of the O—H—O bonded proton.

I. INTRODUCTION

Diglycine nitrate (DGN) is known¹ to undergo a paraelectric—ferroelectric phase transition at $T_c = -67^\circ\text{C}$. The high temperature space group² is monoclinic $\text{P}2_1/a$ with $a = 9.459 \text{ \AA}$, $b = 5.172 \text{ \AA}$, $c = 9.225 \text{ \AA}$, $\beta = 97.19^\circ$ and two formula units per unit cell ($z = 2$). Below T_c the two fold screw axis disappears and the space group is again monoclinic Pa with $z = 2$ and only slightly changed unit cell parameters². Structural studies^{2,3,4} have suggested

^xTemporary address: E. Kardelj University, Department of Physics, Ljubljana, Yugoslavia

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that the basic asymmetric unit is $\text{NH}_3^+\text{CH}_2\text{COO}^- \cdot \text{NH}_3^+\text{CH}_2\text{COOH} \cdot \text{NO}_3^-$. The glycine zwitter-ion and the monoprotonated glycinium ion are connected by a short O—H—O hydrogen bond with an O—O distance of $2.449 \pm 0.013 \text{ \AA}$. Neutron diffraction data² seem to show that the proton is not located at the centre of the H—bond but should be located closer to the oxygen of the glycinium ion. The O—H bond length should be 1.13 \AA and the H—O distance $\approx 1.35 \text{ \AA}$ whereas the O—H—O bond angle is $\approx 160^\circ$. This result is in contrast to C—O bond length determination which showed that the C—O bond lengths for the two O—H—O bonded glycine molecules are practically equal, $\approx 1.28 \text{ \AA}$, as expected for the case that the proton would be located at the centre of the H—bond or that it would be moving between two equivalent off-centre sites at a rate fast compared to the time of the X-ray experiment. The static asymmetric position of the proton is also hard to reconcile with the fact² that both glycine ions in DGN are nearly planar in contrast to⁵ tri-glycine sulfate (TGS) where the non-planar glycine zwitter ion and the planar glycinium ion are as well connected by a rather short O—H—O bond with a length less than 2.45 \AA .

The absence of an isotope effect in the ferroelectric transition temperature T_c on deuteration⁶ has been interpreted as suggesting that the H—bond in DGN is effectively of the symmetric single minimum type and cannot play a role as a trigger in the phase transition mechanism.

In order to throw some additional light on the microscopic nature of this transition and in particular on the role of the O—H—O bond, we decided to study the temperature dependence of the ^{14}N and ^{17}O quadrupole couplings via proton—nitrogen and proton— ^{17}O double resonance experiments in the laboratory frame⁷. The ^{17}O —proton dipolar fine structure was determined as well.

II. EXPERIMENTAL RESULTS

The ^{14}N nucleus has a spin one and thus three allowed NQR transitions in zero magnetic field:

$$\nu_{\pm} = (1/4) e^2 q Q / h (3 \pm \eta) \quad (1)$$

$$\nu_0 = \nu_+ - \nu_- = (1/2) \eta \cdot e^2 q Q / h \quad (2)$$

Here $e^2 q Q / h$ is the ^{14}N quadrupole coupling constant and η the asymmetry parameter.

The temperature dependence of the ^{14}N transition frequencies ν_+ and ν_- is shown in Fig. 1. The narrow lines in the 500 kHz range are due to the NO_3^- and those in the 800 – 900 kHz range – which are broadened by the N–H dipolar coupling – are due to the glycine – NH_3^+ nitrogens. The corresponding ^{14}N quadrupole coupling constants and asymmetry parameters are presented in Fig. 2.

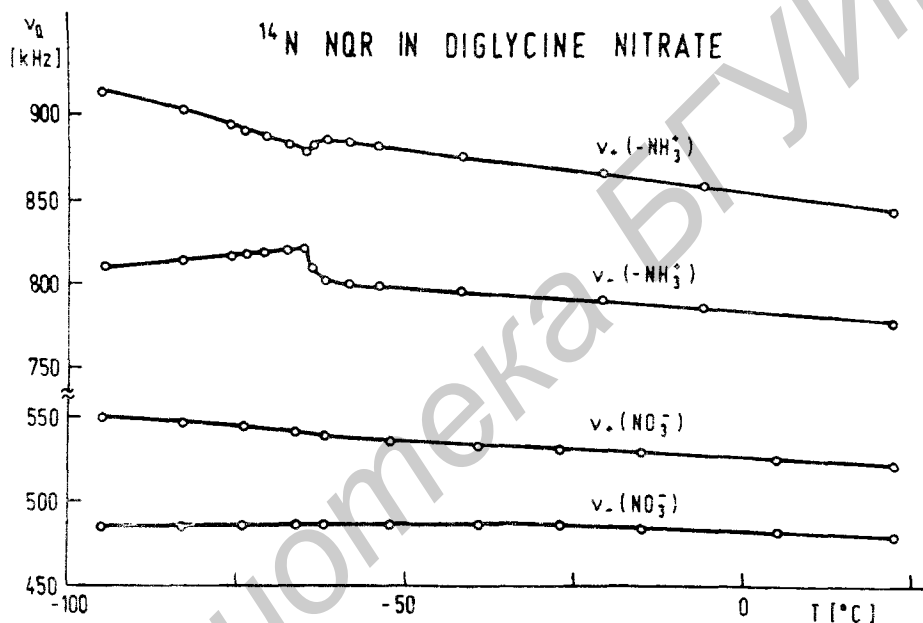


FIGURE 1 Temperature dependence of the ν_+ and ν_- ^{14}N nuclear quadrupole resonance transition frequencies in diglycine nitrate

The surprising result is that all glycine $-\text{NH}_3^+$ groups and NO_3^- ions in the unit cell are chemically equivalent both above and below T_c .

To check on this result we decided to determine the ^{17}O ($I = 5/2$) quadrupole coupling tensor and the ^{17}O –proton dipolar fine structure⁸ in the ^{17}O –H—O bond via a proton– ^{17}O double resonance experiment.

The temperature dependences of the ^{17}O quadrupole transition frequencies are shown in Fig. 3 and the corresponding quadrupole coupling constants and asymmetry parameters in Fig. 4.

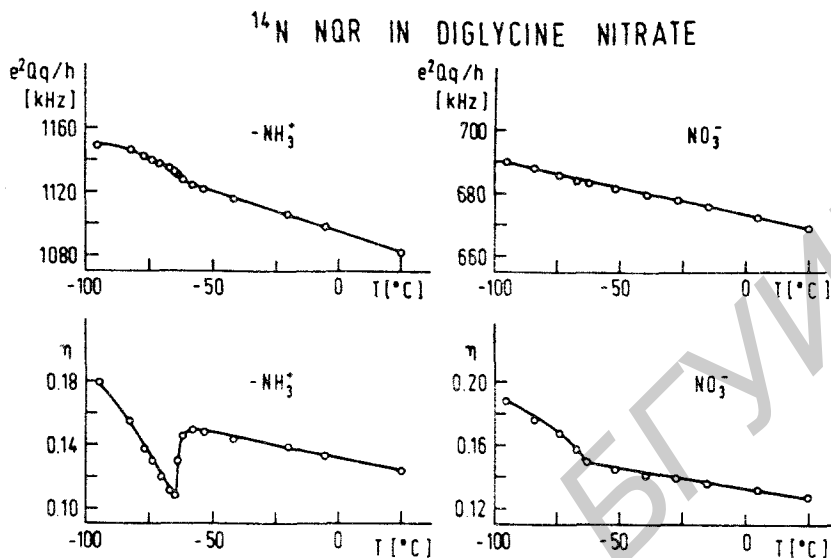


FIGURE 2 Temperature dependence of the $-\text{NH}_3^+$ and the NO_3^- quadrupole coupling constants e^2qQ/h and asymmetry parameters η in diglycine nitrate

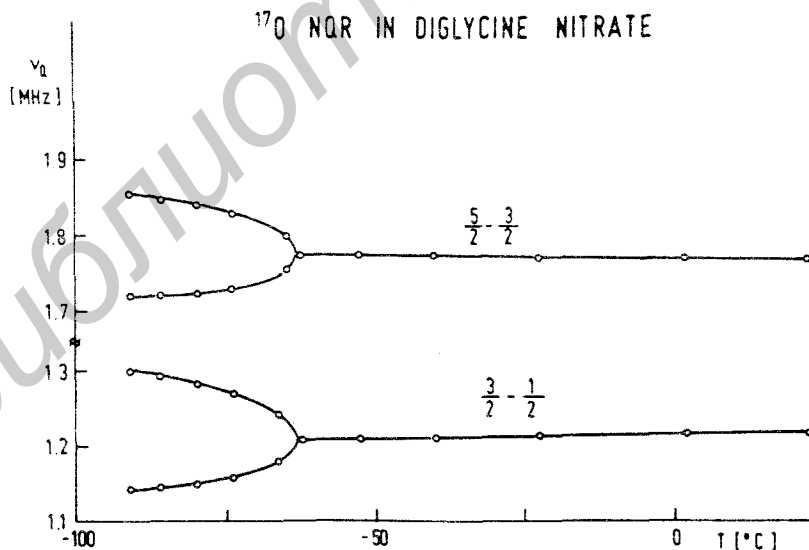


FIGURE 3 Temperature dependence of the $\text{O}-\text{H}\cdots\text{O}$ ^{17}O ($I = 5/2$) quadrupole resonance frequencies in diglycine nitrate

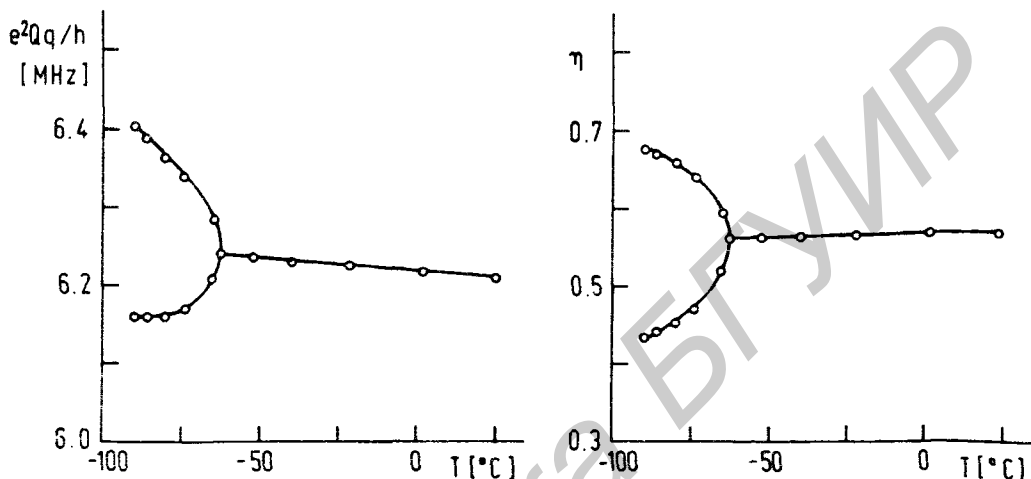
^{17}O NQR IN DIGLYCINE NITRATE

FIGURE 4 Temperature dependence of the O—H—O ^{17}O electric quadrupole coupling constant e^2qQ/h and asymmetry parameter η in diglycine nitrate

Only one set of ^{17}O quadrupole frequencies — $\nu_{1/2 \rightarrow 3/2} = 1215$ kHz, $\nu_{3/2 \rightarrow 5/2} = 1765$ kHz and $\nu_{1/2 \rightarrow 5/2} = 2980$ kHz — was observed for $T > T_c$ and not two as expected if the proton would be located in an asymmetric single minimum type potential well, linking a zwitter ion and a glycinium ion. In this case separate signals should be obtained from the $^{17}\text{O}-\text{H}-^{16}\text{O}$ and $^{16}\text{O}-\text{H}-^{17}\text{O}$ oxygens 17. The observed data show that for $T > T_c$ there is only one ^{17}O quadrupole coupling constant $e^2qQ/h = 6210 \pm 10$ kHz and a corresponding asymmetry parameter $\eta = 0.570 \pm 0.005$. The angle between the O—H bond and the largest principal axis of the ^{17}O electric field gradient (EFG) tensor is $\theta = 50 \pm 5^\circ$. The data further show that the O—H bond lies in the plane determined by the largest and the intermediate principal axes of the EFG tensor.

Below T_c the ^{17}O NQR lines split into two components demonstrating that now the O—H—O bonded proton is in an off-centre site. Because of signal to noise ratio problems, the O—H distance could not be determined

below T_c . It is however clear that below T_c one glycinium group is mono-protonated and the other forms a glycine zwitter ion. The fact that this does not result in a splitting of the $-\text{NH}_3$ coupling constants seems to demonstrate that the effective asymmetry of the H-bond below T_c is rather small.

$^{17}\text{O}-^1\text{H}$ NQDR LINESHAPES IN DIGLYCINE NITRATE

$T = 23^\circ\text{C}$

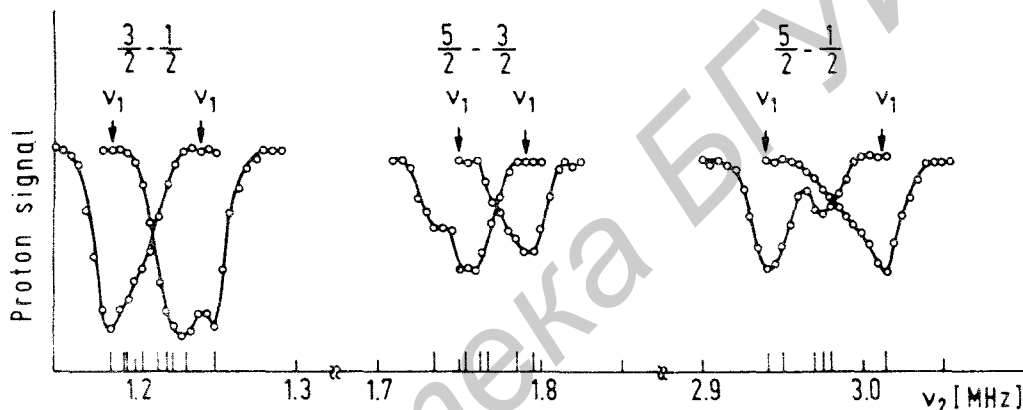


FIGURE 5 ^{17}O -proton dipolar fine structure of the $^{17}\text{O}-\text{H}-\text{O}$ bond in DGN obtained by the double frequency⁸ irradiation method. One of the irradiation frequencies (ν_1) was constant (arrow) while the other frequency (ν_2) has been swept. The corresponding dipolar perturbed ^{17}O resonance frequencies calculated with the parameters from the text are marked as vertical lines on the frequency scales.

From the proton- ^{17}O dipolar fine structure⁸ above T_c we find $R_{\text{O}-\text{H}} = 1.22 \pm 0.02 \text{ \AA}$, i.e. an effectively symmetric H-bond, if the proton is assumed to be static. If however we allow for dynamic proton disorder between two equilibrium sites so that

$$\left\langle \frac{1}{R_{\text{OH}}^3} \right\rangle = \frac{1}{2} \left[\frac{1}{R_{\text{O}-\text{H}}^3} + \frac{1}{(R_{\text{O}-\text{---}\text{O}} - R_{\text{OH}})^3} \right]$$

the proton may well be off-centre above T_c . The limits for R_{OH} are in this case $1.10 \text{ \AA} \leq R_{\text{OH}} \leq 1.22 \text{ \AA}$, so that the maximum possible distance between the two equilibrium sites is 0.25 \AA .

III. DISCUSSION

The ^{17}O -proton dipolar fine structure data by themselves are thus compatible both with a protonic "order-disorder" transition with the proton moving fast on an NMR time scale (10^{-5} s) between two equivalent off-centre sites above T_c , or with a protonic "displacive" transition where the proton is at the centre of the H-bond above T_c and is displaced to an off-centre site below T_c .

The near temperature independence of the ^{17}O NQR transition frequencies above T_c is however easier to interpret in terms of an "order-disorder" than in terms of a "displacive" transition. For a displacive transition one would namely expect a strong parabolic T-dependence of the ^{17}O NQR transition frequencies above T_c due to critical fluctuations which was not observed.

The proton order-disorder model is also favoured by the infrared spectra which show above T_c - in addition to an O-H stretching vibration around 900 cm^{-1} as expected for a short O-H...O bond of about 2.45 \AA - separate bands for COO^- and COOH groups, i.e. they show the presence of the glycine zwitter ion and the monoprotonated glycinium ion on the vibrational time scale $\sim 10^{-13}$ s.

Our results demonstrate that the ^{14}N quadrupole coupling constant of the glycine $-\text{NH}_3^+$ groups practically does not change at T_c but that there is a significant change in the asymmetry parameter η which first decreases and then increases on further cooling below T_c . Since it is known from ^{14}N studies in other compounds⁷ that the largest principal axis of the EFG tensor of a $-\text{C}-\text{NH}_3^+$ groups points along the C-N bond, the above results *exclude* large amplitude flipping of the C-N groups above and below the molecular mirror plane² due to the zwitter ion - monoprotonated glycinium ion exchange² as the basic order-disorder phase transition mechanism in DGN.

The above experimental data are however compatible with a model where the $-\text{NH}_3^+$ groups flip *around* the C-N axis between two equilibrium orientations with respect to the $-\text{CH}_2$ groups and this flipping is accompanied by a 60° rotation of the NO_3^- ions which are linked to the glycine ions by N-H...O bonds. The flipping occurs between two equivalent equilibrium sites

above T_c and is accompanied by a reorientation of the NO_3^- ions, an exchange of the glycine-glycinium ionic character and a proton transfer from one site to another. Below T_c the two equilibrium configurations become non-equivalent giving rise to spontaneous polarization and lowering of crystal symmetry.

Within this model the EFG tensor of a given $-\text{NH}_3^+$ is flipping around its largest principal axis by $\pm \phi_0$ thus explaining the approximate temperature independence of e^2qQ/h and the temperature dependence of η . The argument goes as follows: In an isolated methyl-ammonium group the charge distribution will have trigonal (C_{3v}) symmetry about the C-N bond. The largest principal axis of the EFG tensor at the ^{14}N site will be parallel to the C-N bond and η will be zero. The formation of H-bonds of different lengths will destroy the trigonal symmetry and induce a small, but non zero value of the asymmetry parameter which we denote by η_0 . Let us designate the corresponding eigenvalues of the ^{14}N EFG tensor by

$$V_{\xi\xi} = -a + \Delta, \quad V_{\eta\eta} = -a - \Delta, \quad V_{\zeta\zeta} = 2a \quad (3a)$$

so that

$$\eta_0 = \Delta/a \quad (3b)$$

Let us further introduce a crystal fixed x, y, z frame where the two x and y axes are rotated by $\pm \phi$ with respect to the eigenframe around the z -direction which is parallel to the largest principal axis ($z \parallel \xi$). If the $-\text{NH}_3^+$ group now flips between these two equilibrium orientations with a high enough rate, the EFG tensor in the crystal fixed x, y, z frame \underline{V} will be an average of the EFG tensors \underline{V}_i at the two equilibrium sites

$$\langle \underline{V} \rangle = \sum_{i=1}^2 W_i \underline{V}_i \quad (4)$$

Here W_i denotes the occupation probability of the i -th site.

For $T > T_c$ where $W_1 = W_2 = 1/2$ we find

$$\langle V_{zz} \rangle = 2a \quad (5a)$$

$$\langle V_{xx} \rangle = -a + \Delta \overline{\cos 2\phi} \quad (5b)$$

$$\langle V_{yy} \rangle = -a - \Delta \overline{\cos 2\phi} . \quad (5c)$$

$$\langle V_{xy} \rangle = 2\Delta \overline{\sin \phi \cos \phi} = 0 \quad (5d)$$

The new principal axes are thus $z \parallel \xi$, x and y so that the effective asymmetry parameter is

$$\eta = \eta_0 \overline{\cos 2\phi} , \quad T > T_c \quad (6)$$

whereas e^2qQ/h is independent of ϕ . The drop in η close to T_c could be the result of an increase in ϕ as expected if the transition would have some displacive character.

Below T_c the two $-\text{NH}_3^+$ orientations are not equivalent:

$$W(\phi_0) = \frac{1}{2} (1 + p) \quad (7a)$$

$$W(-\phi_0) = \frac{1}{2} (1 - p) \quad (7b)$$

where p stands for the long range order parameter, e.g. the reduced spontaneous polarization. This results in a non-zero value of $\langle V_{xy} \rangle$ and a change in the magnitude and direction of the two minor principal axes. The new EFG tensor eigenvalues are found from the secular equation:

$$(\lambda - 2a) [\lambda^2 + 2a\lambda + a^2 - \Delta^2 \cos^2(2\phi_0) - \Delta^2 p^2 \sin^2(2\phi_0)] = 0 \quad (7c)$$

leading to

$$\eta = \eta_0 \sqrt{1 - (1 - p^2) \sin^2(2\phi_0)} , \quad T < T_c \quad (8)$$

and a temperature independent value of e^2qQ/h . The weak residual temperature dependence of e^2qQ/h which is not affected by the ferroelectric transition is of course due to lattice vibrations and is not described by the present model. It should be also noted that expression(8) reduced to eq. (6) for $p=0$.

Let us now assume that ϕ_0 is temperature independent below T_c and that the temperature dependence of η is due to the temperature dependence of p . Spontaneous polarization measurements¹ have shown that $p \approx 0.72$ at $T = -100^\circ\text{C}$. From this and the fact that $p = 0$ at $T = T_c$ we find $\eta_0 \approx 0.24$ and $2\phi_0 \approx 60^\circ$ in good agreement with the 60° rotation² of the NO_3^- groups.

Using the above values of η_0 and ϕ_0 we can determine the T-dependence of ρ from the measured T-dependence of η . We obtain as expected a mean field – like critical exponent β for the T-dependence of the order parameter

$$\rho \propto (T_c - T)^\beta, \quad \beta = 0.5 \pm 0.05 \quad (9)$$

The above model thus explains the $-\text{NH}_3^+$ quadrupole coupling data in a satisfactory way.

The absence of an isotope effect⁶ in T_c on deuteration in DGN is thus not due to the fact that the O–H–O bond is of the “single minimum” type but rather due to the fact that the basic reorientable dipoles are the “heavy” $-\text{NH}_3^+$ and NO_3^- groups to which the proton motion is coupled and not the O–H–O bond by itself as in KH_2PO_4 type crystals. The proton is in DGN much closer to the centre of the H–bond than in KH_2PO_4 so that the change in the dipole moment connected with the proton transfer is negligible connected with the change induced by the $-\text{NH}_3^+$ group reorientation.

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