Narrowing of the ^{35}Cl NQR Lines of Trichloroacetamide Caused by Its Ferroelectric Phase Transition *

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Dielectric measurements on single crystals and DSC of the title compound (monoclinic, space group $P2_1$) revealed a ferroelectric transition at ca. 355 K ($\Delta H \approx 0.5$ kJ mol^{-1}). Powder x-ray diffraction indicated that the high temperature phase is also monoclinic and the change in volume at the transition is very small. A displacement of hydrogen atoms is considered as responsible for the appearance of ferroelectricity. The ^{35}Cl NQR signals at ca. 77 K were considerably broad, but a drastic narrowing took place after the compound had once experienced the phase transition. A tentative assignment of the NQR spectrum was made from a calculation of the NQR frequencies based on the CNDO/2 method. Another phase transition was evidenced by a small drift of the DSC curve and a slight anomaly of the dielectric behavior around 358 K. The present ^1H NMR experiments gave no indication of the onset of torsional motion of the NH_2 group reported to occur at ca. 210 K.

Key words: NQR, Phase transition, Ferroelectricity, Hydrogen bond, Disordered structure.

Introduction

Trichloroacetamide (TCAA) undergoes a phase transition at $T_c \approx 355$ K [1]. Since the crystal is monoclinic, space group $P2_1$ [1], it is likely that the room temperature phase shows spontaneous polarization. Unfortunately, the phase transition cannot be studied directly by ^{35}Cl NQR because the resonance lines disappear for $T \gtrapprox 220$ K [2]. But we found that the linewidths and the central frequencies of the NQR signals at 77 K were changed after the compound had been annealed at $T > T_c$. This suggests that some sort of lattice imperfection contributes to the broadening and the frequency shift, and that the imperfection is removed to a certain extent by the phase transition.

In the present work, the effect of annealing on the NQR spectrum was examined to investigate the nature of the imperfection which affects the NQR lines. Furthermore, the phase transition was studied extensively by means of thermal analysis, dielectric measurements, powder x-ray diffraction, vibrational spectra, and ^1H NMR.

Experimental

TCAA, purchased from Nacalai Tesque, was purified by recrystallizations from ethyl ether. The last crystallization was carried out under two different conditions; 1) Crystal R: a saturated solution at the boiling point of the solvent (34.5 °C) was rapidly cooled by an ice bath to obtain the crystals; 2) Crystal S: a saturated solution at room temperature was cooled at a rate of ca. 1.5 °C/day down to 9 °C to crystallize TCAA slowly. For the dielectric measurements, large single crystals of TCAA were grown from ethanolic solutions by slow cooling. The crystal axes of them were determined by means of x-ray oscillation photographs.

DSC was carried out with a diffractional scanning calorimeter (Rigaku DSC 8058) in the range $77 \leqq T/\mathrm{K} \leqq 414$ (m.p.).

A transformer bridge (Ando Denki TR-1 C) was employed for dielectric measurements in the frequency range $0.11 \leqq f/\mathrm{kHz} \leqq 10^3$ on single crystals. For the

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electrode assembly cf. [3]. Single crystals with faces perpendicular to the *a*-axis were easily obtained by cleavage. To obtain specimens with faces perpendicular to the *b* (or *c*) axis, a large single crystal was cut in several pieces. The specimens were placed between platinum electrodes.

X-ray powder patterns were observed at $300 \leqq T/\mathrm{K} \leqq 363$ by means of an x-ray diffractometer (Rigaku RAD-RC).

IR and Raman spectra were recorded on a Hitachi-EPI-G2 IR and a Spex Ramalog 5 M Raman spectrometer with a 488 nm Ar^+ laser source. Nujol mulls and the sample in a glass ampoule were used for the IR and Raman experiments, respectively. The spectra at higher temperatures were observed by using high-temperature thermostats with suitable beam-transparent windows.

The ^{35}Cl NQR spectra were recorded at liquid N_2 temperature by using a regenerative spectrometer controlled by a micro-computer [4]. From the digital records of the spectra, the linewidth ($\Delta\nu$) and the central frequency (ν_0) were calculated by means of a least squares method assuming Gaussian line shape. The accuracy of the frequency measurements was within ± 0.1 kHz. The NQR experiments were carried out on the crystals R and S. In order to examine the changes of the NQR spectrum due to annealing, we observed $\Delta\nu$ and ν_0 of crystal R annealed at various temperatures.

Because the NQR measurements were carried out by immersing the specimen in a liquid N_2 bath, the NQR frequency was found to fluctuate from time to time depending on the atmospheric pressure. The NQR frequencies given in the text are the values reduced to the ordinary pressure (101, 300 $p_a = 760$ mm Hg).

The ^1H NMR spectra were measured with a conventional bridge spectrometer [5] by modulating and sweeping an external magnetic field of 7.75 kOe.

Results

The thermal analysis (Fig. 1) revealed anomalies at 354.6 ± 0.5 K and 357.5 ± 0.5 K. The enthalpy change (ΔH) corresponding to the sharp endothermic peak was ca. 0.5 kJ mol^{-1}. ΔH of fusion was ca. 22 kJ mol^{-1}. The deuterated TCAA showed the same thermal behavior (the dotted curve in Fig. 1), except for slight shifts of the T_c's (ca. 1 K) due to deuteration.

Figure 2 shows the temperature dependence of the dielectric constants parallel to the crystal axis *b* in the vicinity of the T_c's. The dielectric constant could be determined only approximately because the precise estimation of the sample size was difficult and sub-

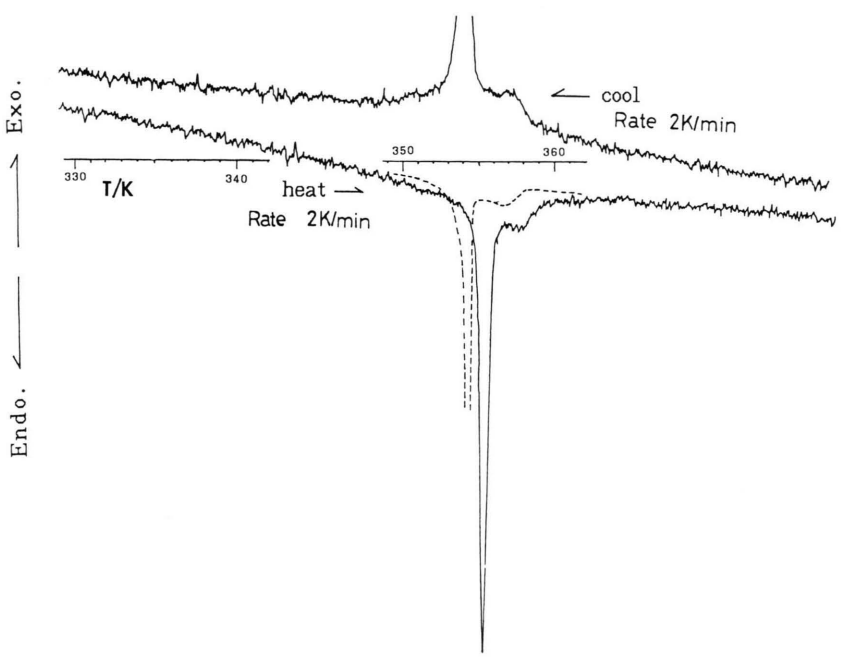

Fig. 1. DSC curves of trichloroacetamide (solid line) and its deuterated analogue (broken line) in the vicinity of the phase transitions.

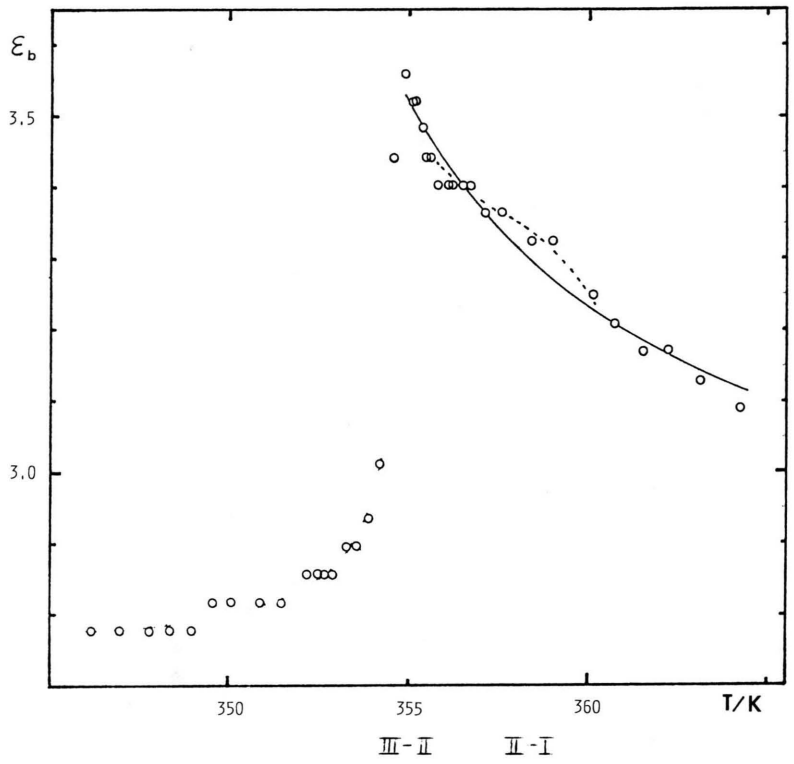

Fig. 2. The temperature dependence of dielectric constant of trichloroacetamide parallel the *b*-axis (ε_b) in the vicinity of the phase transitions (frequency used = 1 kHz). The solid line corresponds to (1) in the text. The dotted line shows the slight deviation near the phase transition II–I.

limation was considerably fast around the T_c's. The dielectric constant parallel to the *a* and *c* axes did not show any significant change at the T_c's. Appreciable dielectric dispersion was not observed in any direction. No ferroelectric hysteresis loop was observed by a simple Sawyer-Tower circuit.

A few of the vibrational bands of crystalline TCAA were found to vary significantly with temperature. Figure 3 shows the temperature variation of the NH_2 stretching (ν) and the out of plane (π) vibrations (for the assignment of the vibrational bands of TCAA, see [6]). Figure 4 shows the temperature dependence of the Raman spectra in the lower wavenumber region.

The x-ray powder patterns taken at 303, 343, 357, and 363 K were the same as that at 287 K. The lattice parameters (a_0, b_0, c_0, and β) at higher temperatures were calculated from the powder patterns by assuming a constant β of 107.61° [1]. The temperature dependence of the lattice parameters thus obtained indicated that at $T_c \approx 355$ K c_0 exhibits a slight jump (1.5%), while a_0 and b_0 are almost continuous.

Table 1 lists the ^{35}Cl NQR frequencies and their linewidths obtained before and after annealing at 358 K for 2 h of the crystals R and S. Figure 5 shows the effect of the annealing temperature (T_a) on $\Delta\nu$ of the NQR line A_3. A similar behavior was observed for the other lines. When the specimen was annealed at temperatures higher than 355 K, a time dependence of the narrowing could not be observed.

The peak-to-peak linewidth of the ^1H NMR spectrum was found to be constant in the temperature range studied: 10.0 ± 0.5 Oe at 77 and 300 K, 10 ± 1 Oe at 348, 357 and 363 K.

Discussion

Phase Transitions

The thermal analysis and the dielectric measurements evidenced that TCAA undergoes two phase transitions within the temperature range investigated: one at ca. 355 K and the other at around 358 K. The phases found are designated hereafter as I, II, and III in the order of decreasing temperature. Figs. 1 and 2 show that the III–II transition is characterized by a sharp DSC peak and a distinct rise of ε_b, but the II–I

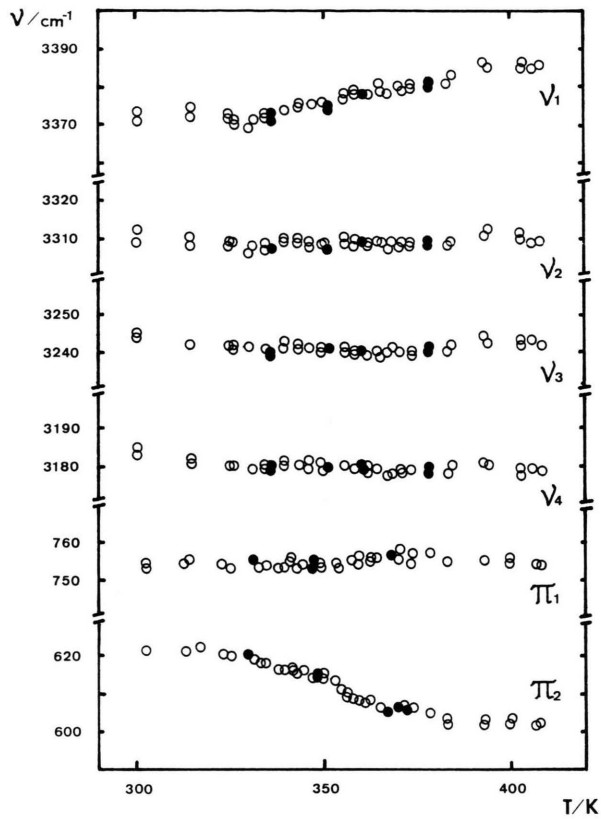

Fig. 3. The temperature dependence of the wavenumbers of the NH_2 stretching vibrations (ν_{1-4}) and the NH_2 out of plane vibrations ($\pi_{1,2}$).

Table 1. The ^{35}Cl NQR frequencies (ν_0) and linewidths ($\Delta\nu$) of the crystals R and S at liquid N_2 temperature before (initial) and after annealing (annealed).

Line no. *	Initial		Annealed	
	ν_0/MHz	$\Delta\nu$/kHz	ν_0'/MHz	$\Delta\nu'$/kHz
Crystal R				
A_1	39.4795	5.0	39.4806	3.2
A_2	39.6685	5.5	39.6680	4.1
A_3	40.0069	4.8	40.0082	3.1
B_1	38.8588	6.8	38.8567	4.4
B_2	39.6046	5.6	39.6051	4.9
B_3	39.8176	5.6	39.8182	4.4
Crystal S				
A_1	39.4805	2.1	39.4807	1.7
A_2	39.6684	2.4	39.6682	1.8
A_3	40.0081	1.9	40.0083	1.6
B_1	38.8576	2.4	38.8573	1.8
B_2	39.6055	2.6	39.6056	2.1
B_3	39.8185	2.3	39.8185	1.8

* A_{1-3} and B_{1-3} correspond to CCl_3 of molecule A and B, respectively.

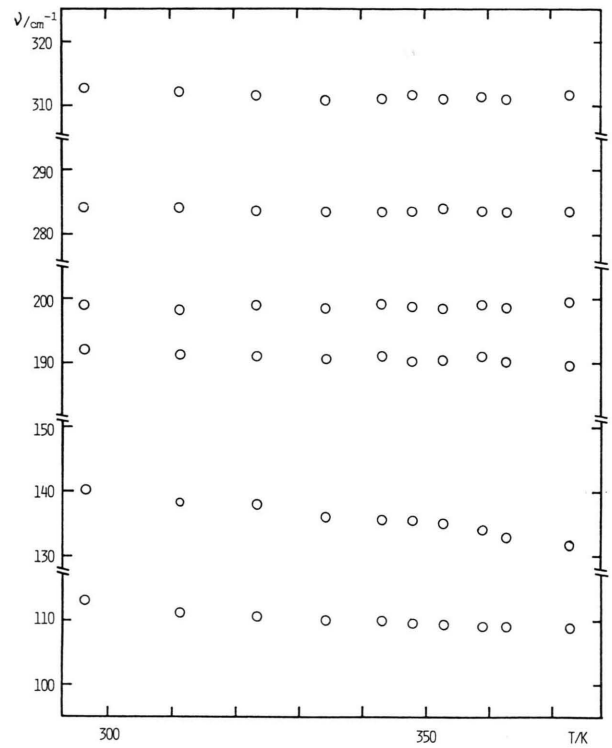

Fig. 4. The temperature dependence of Raman spectra of trichloroacetamide in the lower wavenumber region.

one appears as only a slight anomaly both in the thermal and dielectric behavior.

The ε_b vs. temperature curve for $T > T_{III,II}$ is well reproduced by the Curie-Weiss relation

$$\varepsilon_b = \varepsilon_0 + C/(T - T_0), \quad (1)$$

where $\varepsilon_0 = 2.8$, $C = 6.4$ K and $T_0 = 347$ K (solid line in Figure 2). This suggests that the III–II transition is ferroelectric and, because $T_0 < T_{III,II}$, it appears to be of first order [7]. Although a hysteresis loop was not observed, reversal of the direction of the pyroelectric current parallel to the crystal *b* axis could be observed when the direction of the polarizing field was reversed [8]. This also indicates that the III–II transition is ferroelectric. In connection with the possible ferroelectricity of TCAA it should be mentioned that a temperature dependence of vibrational spectra similar to that shown in Fig. 3 has been reported for the ferroelectric transition of thiourea [9].

As shown in Fig. 1, the T_c's of TCAA decreased slightly by deuteration. This seems to be anomalous, if the displacement of the H atom is considered as associated with the phase transition. In the cases of the

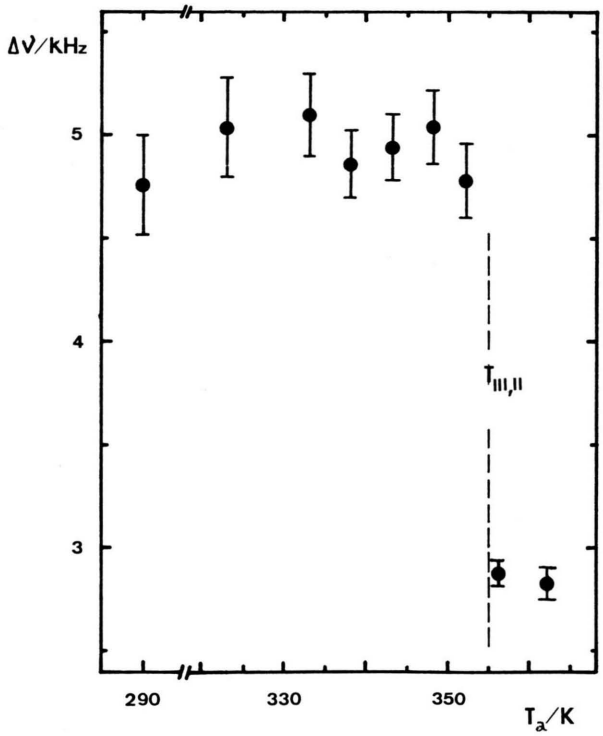

Fig. 5. Correlation between the annealing temperature (T_a) and the linewidth ($\Delta\nu$) of the NQR signal (A_3) of trichloroacetamide at liquid nitrogen temperature.

ferroelectrics of H-bonded crystals, T_c of the deuterated crystal is higher in general than that of the normal one, although there are exceptions such as Rochelle salt, where one of the T_c's is depressed by a few degrees on deuteration [10]. The rise of T_c due to deuteration has been interpreted by the H-tunneling model [11]. Recently it was proposed for the KH_2PO_4-type ferroelectrics that the isotope effect on T_c should be attributed to a change in the H-bond length on deuteration [12]. According to this idea, the very slight lowering of T_c found in TCAA could be explained by assuming that the H-bond lengths remain almost unchanged on deuteration.

The asymmetric unit cell of the room temperature phase of TCAA contains two crystallographically independent molecules (designated as A and B) [1]. They lie on a local pseudo 2-fold axis and form a dimer through two kinds of NH ··· O H-bonds as shown in Figure 6. In crystalline TCAA, ν_{NH_2} and π_{NH_2} appear as four and two well-resolved bands, respectively, while liquid TCAA gives two ν_{NH_2} bands at 3480 and 3350 cm^{-1} and one π_{NH_2} band at 680 cm^{-1} [6]. The splittings of the ν_{NH_2} and π_{NH_2} bands in the crystalline state are undoubtedly due to the presence of two independent molecules. Since the splittings persist even in the high temperature phases (see Fig. 3), it is evident

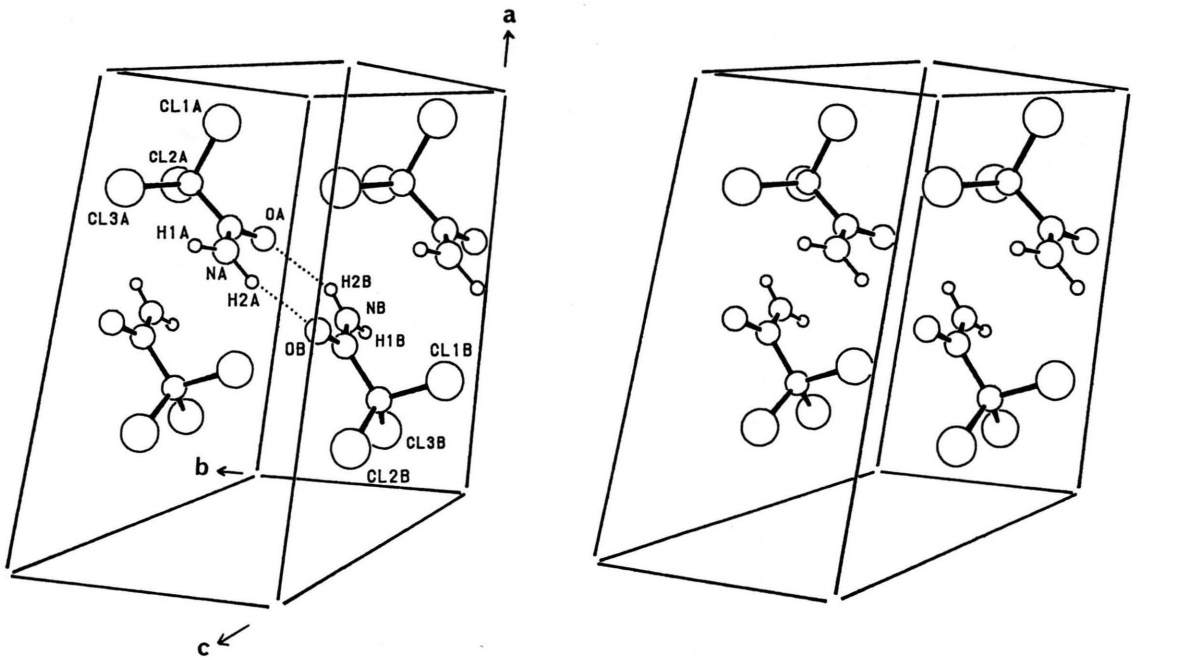

Fig. 6. A stereographic drawing of the crystal structure of trichloroacetamide. The molecules related by 2_1 symmetry operation are omitted in the figure for the sake of simplicity.

that the unit cell of II (or I) also contains two independent molecules. The vibrational spectra of the high temperature phases did not show any splittings characteristic of centrosymmetric cyclic dimers similar to those of most carboxylic acids [13]. This fact suggests that the dimer structure of TCAA is still present in the high temperature phases. According to powder x-ray experiments, the high temperature phases are also monoclinic with almost the same unit cell parameters as III. Because of the very small change of lattice constants at $T_{\mathrm{III-II}}$, it seems unlikely that the transition involves displacements of heavy atoms. This view is supported by the fact that the Raman spectra in the lower wavenumber region, where lattice vibrations appear, did not show any appreciable influence of the phase transitions (see Figure 4).

From the molecular geometry and bond moments [14], the dipole moments (μ_A and μ_B) for A and B are estimated as ca. 10×10^{-30} mC (ca. 3.1 Debye). In phase III, μ_A and μ_B are coupled almost antiparallely to give a very small net dipole moment ($\mu_{\parallel b}$) parallel to the b axis. $\mu_{\parallel b}$ is estimated to be of the order of 10^{-31} mC. A slight shift of any atom may cause the reversal of $\mu_{\parallel b}$. At this stage it is difficult to elucidate the mechanism of the ferroelectricity.

According to an H NMR study [15], TCAA undergoes a small change in linewidth at about 213 K; the linewidth above and below this temperature is 10 and about 11.8 Oe, respectively. The observation has been explained by an NH_2 large amplitude rotational oscillation. However, the motion of the NH_2 group seems to be doubtful because the present experiment showed no linewidth change even at $T_{\mathrm{III,II}}$.

Narrowing and Frequency Shift of the NQR Lines

As can be seen in Table 1, recrystallization considerably affects $\Delta\nu$ and ν_0; the linewidths of crystal R are ca. 5 to 8 kHz, while those of crystal S are 2 to 3 kHz. According to Izmest'ev and Soifer [2], T_2^* is 50 μs for $B_{1,2,3}$ and 90 μs for $A_{1,2,3}$ at 77 K. These values roughly correspond to the linewidths of R. Since T_1 is ca. 7 and 150 ms for $B_{1,2,3}$ and $A_{1,2,3}$, respectively, and T_2 is ca. 700 μs for both $A_{1,2,3}$ and $B_{1,2,3}$ [2], the line broadening is predominantly due to the inhomogeneity of the field gradient at Cl sites caused by lattice imperfections. Therefore, it is reasonable that crystal R exhibits broader lines, as the sample is considered to contain more imperfections because of rapid crystallization. The pronounced effect of annealing on the NQR spectrum seen in Table 1 confirms the contribution of lattice defects to the line broadening and frequency shift. Even after annealing, the linewidths of crystal R differ significantly from those of crystal S, indicating that the nature of defects is rather complicated. We will confine our discussion to those defects which were changed by the phase transition.

As shown in our previous work [16], a rise of annealing temperature results gradually in a faster rate of the intensity change of NQR lines, and the process during annealing can be analyzed by a kinetic treatment. In the present TCAA, however, this was not the case. Rather a distinct narrowing took place abruptly only when the annealing temperature exceeded $T_{\mathrm{III,II}}$ (see Figure 5). This observation clearly indicates that the narrowing is not a normal kinetic process, but a critical phenomenon closely related to some irre-

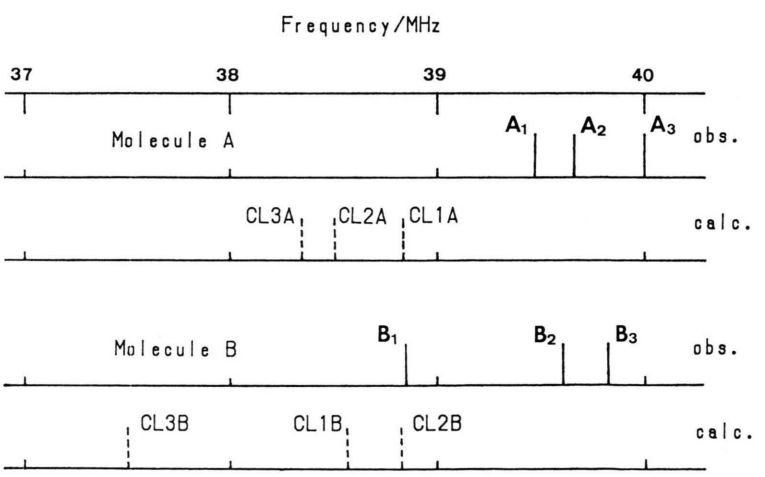

Fig. 7. Observed and calculated ^{35}Cl NQR spectra (solid and dotted lines respectively) of trichloroacetamide.

versible change in the crystal lattice associated with the phase transition.

In the ferroelectric phase of TCAA, the arrangement of the dipoles $\mu_{\parallel b}$ should possess long range order, but this can be disturbed by domain walls or lattice defects, both of which cause localized crystal strains. Since the dipoles in the paraelectric phase are distributed in a totally random fashion, it seems to be possible that the III–II transition eliminates those defects that pin domain walls in phase III. As a result, growth of larger domains and hence fewer Cl atoms under strain are expected after III–II transition. This accounts qualitatively the observation that the change of the linewidth of TCAA took place only when T_a exceeded $T_{III,II}$.

The broadening and the shift of the NQR lines observed for crystal R clearly differ from line to line, suggesting that the cause of the phenomena is of short range. The most remarkable effects are found for B_1. As an attempt to assign the NQR line to a definite chlorine atom, the NQR frequencies of TCAA were estimated from the 3p-orbital populations calculated by the MO (CNDO/2) method [17–19]. The calculated and observed NQR spectra of TCAA are shown in Figure 7. The overall feature of the NQR spectrum seems to be well reproduced except for the fact that the calculated frequencies are lower than the observed ones by ca. 1 MHz. The difference in the NQR spectrum of Molecule A and B seems to reflect the difference in the molecular geometry of the two molecules. From Fig. 7, B_1 can be tentatively assigned to Cl3B, though a complete assignment of the NQR spectrum must be done by a Zeeman NQR experiment on a single crystal. This assignment implies that the NQR of Cl3B is affected more seriously by the defects. If they are produced by a random distribution of hydrogen (s), the displacement of H1B is more favorable to account for the change of $\Delta\nu$ and ν_0 of B_1, because H1B is located very closely to Cl3B (H1B ... Cl3B distance $\approx$257 pm).

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