

# Lattice Imperfections and Relaxation of Cl NQR in Chloral Iso-Butylhemiacetal\*

Haruo Niki and Ryokan Igei

Department of Physics, Division of General Education, University of the Ryukyus, Nishihara, Okinawa 903-01, Japan

Takuya Higa

Department of Physics, College of Science, University of the Ryukyus, Nishihara, Okinawa 903-01, Japan

Masao Hashimoto and Takahiro Isono

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan

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The temperature dependence of the S/N ratios of three  $^{35}\text{Cl}$  NQR lines ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ) in chloral iso-butylhemiacetal shows interesting features in the range 77–300 K.  $^{35}\text{Cl}$   $T_1$  indicates that above 220 K reorientation of  $\text{CCl}_3$  is excited, and this results in a gradual decrease in S/N. The activation energy calculated from  $^{35}\text{Cl}$  NQR  $T_1$  results is  $30 \text{ kJ mol}^{-1}$  for  $\nu_1$  and  $\nu_2$  but  $25 \text{ kJ mol}^{-1}$  for  $\nu_3$ . The difference seems to be attributable to the motion of H in the OH group. A minimum of  $^{35}\text{Cl}$  NQR  $T_2$  is found around 180 K but  $^{35}\text{Cl}$   $T_1$  shows no anomaly.  $^{35}\text{Cl}$   $T_2$  determines the S/N ratios in the range between 130–220 K. The line broadening below 130 K is attributable to an inhomogeneity of the electric field gradient at resonant nuclei produced by lattice defects.

**Key words:** NQR, Lattice imperfections, Magnetic relaxation, Hydrogen bonding.

## Introduction

In trichloromethyl derivatives the onset of reorientation of the  $\text{CCl}_3$  group causes a decrease in the chlorine NQR spin-lattice relaxation time ( $T_1$ ) [1, 2]. The signal to noise ratios (S/N) turn out to be poor when they are measured by the cw method. In addition, if lattice imperfections exist, S/N becomes poor because of the line broadening due to the inhomogeneity of the electric field gradient (efg) at the chlorine nuclei [3]. In this case, S/N is expected to be improved by annealing provided the imperfections are not originating from chemical impurities [4]. Thus S/N of NQR signals can be used for studying the onset of motions and/or the presence of imperfections.

In course of our NQR study on chloral hemiacetals ( $\text{Cl}_3\text{CCH}(\text{OH})\text{OR}$ ) [5] it was found that S/N's of the  $^{35}\text{Cl}$  NQR signals in chloral iso-butylhemiacetal (isoB-CH) are weak at 77 K. Moreover, the tempera-

ture dependence of S/N did not exhibit the usually observed behavior. S/N decreases remarkably in two temperature regions. The decrease at temperatures near the melting point is probably caused by the reorientation of the  $\text{CCl}_3$  group, but the one observed in the region  $\sim 150 \leq T/\text{K} \leq \sim 200$  seems to be very interesting. In the present work, the temperature dependence of the NQR spectrum is investigated by cw and pulsed methods to clarify this peculiarity.

## Experimental

Chloral iso-butylhemiacetal was prepared by the method described in [5]. The crystals obtained were purified by recrystallizations from n-hexane; m.p. = 304 K (31 °C).

$^{35}\text{Cl}$  NQR signals were detected by a frequency modulated super-regenerative spectrometer. A pulsed NQR spectrometer (Matec 5100-525) was employed for the measurements of  $T_1$ , the spin phase memory time ( $T_2$ ), and the apparent inverse line width parameter ( $T_2^*$ ).

$^{35}\text{Cl}$   $T_1$  was determined by  $90^\circ - \tau - 90^\circ$  pulse sequences above 170 K and by echo sequences ( $90^\circ - \tau -$

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Reprint requests to Dr. H. Niki, Department of Physics, Division of General Education, University of the Ryukyus, Nishihara, Okinawa 903-01, Japan.

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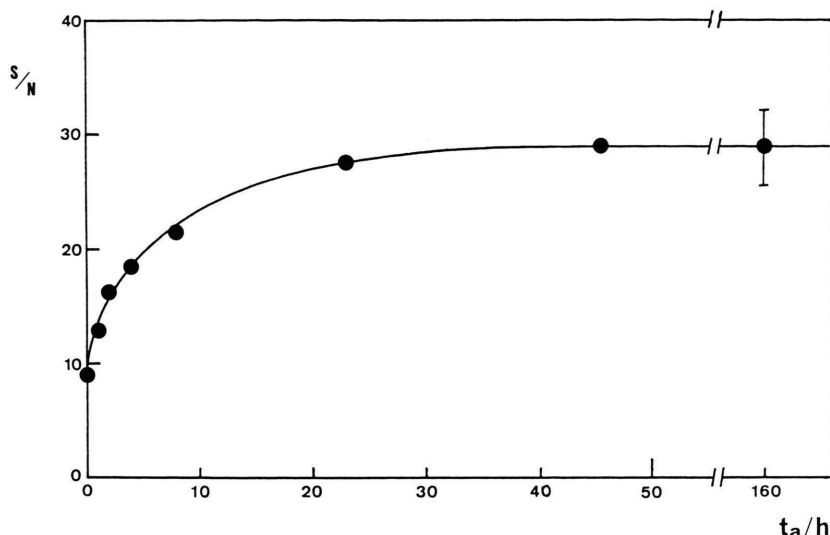


Fig. 1. S/N of  $^{35}\text{Cl}$  NQR signals versus annealing period  $t_a$  in chloral iso-butylhemiacetal (annealing temperature: 24 °C).

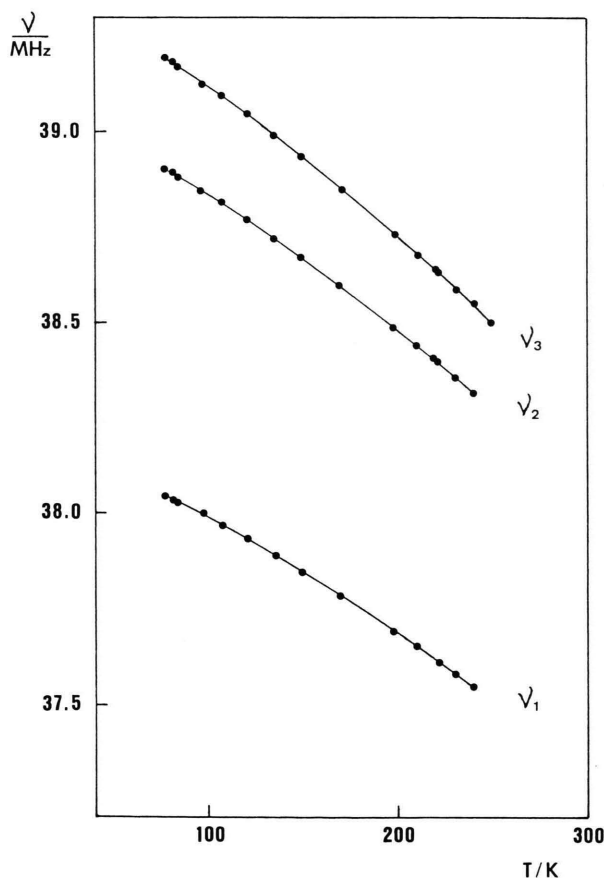


Fig. 2. Temperature dependence of  $^{35}\text{Cl}$  NQR frequencies in chloral iso-butylhemiacetal.

$90^\circ - \tau' - 180^\circ$ ) below 120 K.  $^{35}\text{Cl}$   $T_2$  was measured by a conventional spin echo method ( $90^\circ - \tau - 180^\circ$ ).

$^{35}\text{Cl}$   $T_2^*$  was determined as the time required for a given induction signal to decay to  $1/e$  of its maximum value. Experimental values for  $T_2^*$  were found from digital-oscilloscope traces of the free induction tails following pulses and also from the shapes of individual echoes. The width of the  $90^\circ$  pulse was about 5  $\mu\text{s}$  throughout.

## Results

Although the melting point of isoB-CH is 304 K, the compound is usually liquid at room temperature, its supercooled state being rather stable. At room temperature it was not easy to crystallize the compound from the liquid state. Immediately after crystallization, the specimen gives three  $^{35}\text{Cl}$  NQR lines at 77 K, but the S/N ratios are poor. However, they are much improved by annealing the specimen at temperatures below the melting point. To determine the period within which S/N reaches a constant value,  $\nu_2$  was observed at 77 K after various annealing times ( $t_a$ ) at 297 K. Fig. 1 shows S/N as a function of  $t_a$ . The linewidth after prolonged annealing was about 6 kHz, while it was 10 kHz or more for  $t_a = 1$  h. The results given below were obtained for specimens annealed for a sufficiently long period just below the melting point.

In the two interesting temperature regions, that is for  $T/\text{K} \geq \sim 250$  and  $\sim 170 \leq T/\text{K} \leq \sim 200$ , the  $^{35}\text{Cl}$

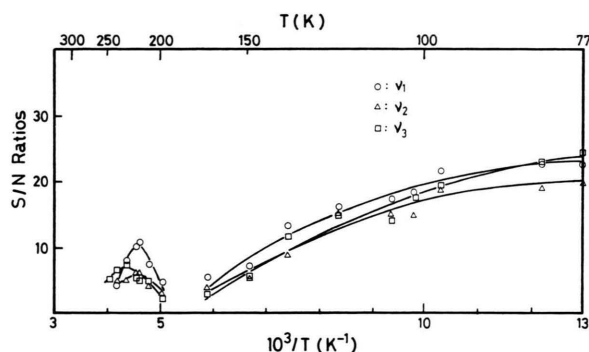


Fig. 3. Temperature dependence of the S/N ratios of  $^{35}\text{Cl}$  NQR signals in chloral iso-butylhemiacetal.

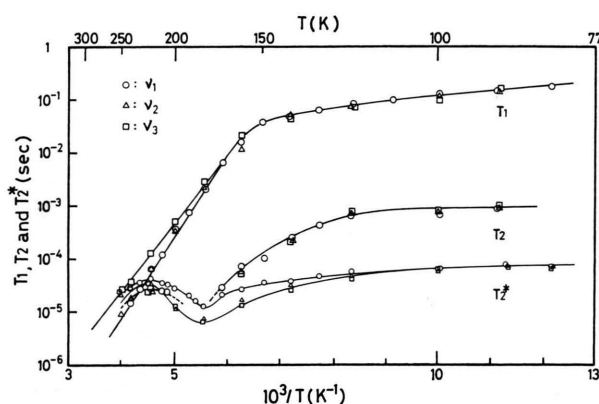


Fig. 4. Temperature dependence of  $^{35}\text{Cl}$  NQR  $T_1$ ,  $T_2$ , and  $T_2^*$  in chloral iso-butylhemiacetal.

NQR signals are too weak to be detected by the cw method. Figure 2 shows the temperature dependence of the NQR frequencies. The temperature dependence of the S/N ratios is illustrated in Figure 3. As a general trend, S/N of  $\nu_1$  is always larger than that of the other two lines.

In Fig. 4,  $^{35}\text{Cl}$   $T_1$ ,  $T_2$ , and  $T_2^*$  are plotted against the inverse of  $T$ . The  $T_2^*$  values were found from echo envelopes below 170 K and from free induction tails following pulses above 170 K.  $T_2^*$  is longer for  $\nu_1$  than for  $\nu_2$  and  $\nu_3$  at all temperatures. Therefore S/N for  $\nu_1$  in the cw method is largest among the three lines. In the two ranges of  $\sim 170 \leq T/K \leq \sim 200$  and  $T/K \geq \sim 230$ ,  $T_2$  is too short to be determined under the present experimental conditions, and they seem to have minimum values at a certain temperature within the former range. Moreover, the magnitudes of  $T_2^*$  are apparently larger than those of  $T_2$  in the range of

$\sim 170 \leq T/K \leq \sim 220$  as well as those of  $T_1$  in the range of  $T/K \geq \sim 240$ . But it is probable that  $T_2^*$  is comparable to  $T_2$  or  $T_1$ , when one takes account of the systematic errors which originate from the present experimental conditions of measuring the extremely short  $T_2^*$  from free induction tails immediately after pulses put out. When  $T/K \geq \sim 250$ , the determination of  $^{35}\text{Cl}$   $T_1$ ,  $T_2$ , and  $T_2^*$  is again difficult.

## Discussion

It has often been observed that the inhomogeneity of the efg dominates the linewidth of NQR signals [3]. The inhomogeneity can be caused by chemical impurities and also by lattice defects not due to impurities. In the latter case, the defects can be partially removed by thermal annealing. This decreases the linewidth. In the present case the S/N of the three NQR signals is improved remarkably by annealing. So it is clear that the crystal of isoB-CH contains lattice defects at least before annealing. Even after annealing,  $T_2^*$  is relatively short and hence the linewidths are relatively wide. As  $T_1$  and  $T_2$  are much longer than  $T_2^*$ , the effect of lattice defects on linewidths persists even after sufficient annealing.

The behaviour shown in Fig. 2 is explainable by the Bayer theory [6]. The S/N's, however, exhibit an interesting temperature dependence; they are extremely poor above  $\sim 250$  K and in the range  $\sim 170 \leq T/K \leq \sim 200$ . Another interesting point is that the S/N's have maxima around 220 K. A comparison between Figs. 3 and 4 indicates that the behaviour of S/N is correlated with that of  $T_2^*$ .

Similarly, an unusual temperature dependence of S/N was found for chloral n-butylhemiacetal (nB-CH), an isomer of isoB-CH [7]. As in the case of nB-CH, the origin of the line broadening seems to change with temperature, and thus we have three different characteristic temperature regions:

### 1) $T/K \geq \sim 220$

In trichloromethyl derivatives the reorientation of the  $\text{CCl}_3$  group takes place at temperatures well below their melting point [1, 2, 8]. The excitation of the motion results in a gradual decrease in  $T_1$  with increasing temperature [9]. In this case, when NQR signals are observed by the cw method, broadening of the signals and hence a decrease in S/N will be observed

with increasing temperature. The activation energy ( $\Delta E$ ) calculated from the slope of the  $\log T_1$  vs.  $10^3/T$  plots is  $30 \text{ kJ mol}^{-1}$  for  $\nu_1$  and  $\nu_2$ , while  $25 \text{ kJ mol}^{-1}$  for  $\nu_3$ . Although the values for  $\nu_1$  and  $\nu_2$  are larger than that for  $\nu_3$ , their magnitudes are in the order of values reported so far for the reorientation of  $\text{CCl}_3$  groups in any trichloromethyl derivatives [2]. In the case of isoB-CH, the excitation of the reorientation of the  $\text{CCl}_3$  group is probably responsible for the decrease in  $T_1$  and hence for the decrease in S/N found in this temperature range.

Since the difference in  $\Delta E$  mentioned above seems to be too large to be attributable to experimental errors,  $\nu_1$  and  $\nu_2$  must be affected by another relaxation mechanism in addition to the reorientation of the  $\text{CCl}_3$  group. Although the crystal structure of isoB-CH is unknown, one may refer to the structure of nB-CH, for which a similar feature has been observed [7]. In the case of nB-CH, the H atom in an OH group is involved in two different types of  $\text{O}-\text{H}\cdots\text{O}$  H-bonds, and moreover the H atom is in close proximity to two of the three chlorine atoms in the  $\text{CCl}_3$  group. This results in a difference in the extent of interaction between H in the OH group and the Cl atoms. The effect of thermal motion of the H atom, which causes a fluctuating electric or magnetic field capable of inducing relaxation of the chlorine NQR, is different for the three Cl atoms. By this idea, the difference in  $\Delta E$  mentioned above seems to be qualitatively

accounted for if the motion of the proton affects the  $^{35}\text{Cl}$   $T_1$  as in the case of nB-CH.

## 2) $\sim 130 \leq T/\text{K} \leq \sim 220$

The most interesting feature of  $T_2$  in this temperature region is its minimum around 180 K. It is clear that the temperature dependences of  $T_2^*$  and S/N are dominated by that of  $T_2$  in this region. The rather strong temperature dependence of  $T_2$  is probably due to thermal motion of the molecule. It is evident, however, that the motion does not affect  $T_1$ . Therefore, one may assume that the maximum of the motion arises not at about the NQR frequency but in a lower frequency region. Judging from the case of nB-CH, the motion of the H atom is one of the possible reasons.

## 3) $T/\text{K} \leq \sim 130$

In this temperature region  $T_2^*$  is considerably shorter than  $T_1$  and  $T_2$ , and the line broadening is clearly attributable to the inhomogeneity of the efg produced by lattice defects. As in the case of nB-CH [7], random freezing of the disordered H atoms of OH groups is a probable mechanism to produce the inhomogeneity of the efg.  $T_2^*$  of isoB-CH is much longer than that of nB-CH, indicating that the amount of defects in the former is smaller than that in the latter compound. This seems to explain why in the whole temperature range investigated, S/N of the NQR signals (cw method) in isoB-CH is better than in nB-CH.

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