Fade-Out of $^{35}\text{Cl}$ NQR in Chloral n-Butylhemiacetal *

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Continuous wave and pulsed NQR, dielectric absorption and infrared (IR) measurements were carried out to investigate the origin of the peculiar temperature dependence of the S/N ratio of the $^{35}\text{Cl}$ NQR in the title compound. The dielectric and IR experiments evidenced a thermally activated jumping motion of the H atom participating in O–H⋯O H-bonds. As $T_1$ and $T_2$ below 120 K were much longer than $T_1^*$ of about 10 $\mu$s, the line broadening in this temperature region was attributed to static lattice defects. A random freezing of the jumping motion may be the origin of the defects. In the range 120–170 K, S/N was extremely low and $T_2$ was less than 10 $\mu$s, probably having a minimum in between. The short $T_1$ is considered to be responsible for the low S/N. A minimum of S/N at about 240 K is attributed to a $T_1$ minimum (less than 10 $\mu$s) at that temperature.

**Key words:** NQR, Relaxation times, Hydrogen bond, Dielectric absorption, Disordered structure.

**Introduction**

The $^{35}\text{Cl}$ NQR spectra of a series of chloral hemiacetals (Cl\(_2\)CCH(OH)O·R) have been investigated in [1]. An unusual finding was the absence of an increase of the signal to noise ratio (S/N) of the NQR lines with decreasing temperature. In this respect, chloral n-butylhemiacetal (nB-CH, Cl\(_2\)CCH(OH)O·C\(_2\)H\(_4\)O) was the most remarkable compound; the $^{35}\text{Cl}$ NQR signals disappeared at several temperatures between 77 K and the melting point (324 K).

In the present work, the temperature dependence of the NQR spectrum of nB-CH was studied by continuous wave (cw) and pulsed methods to find the origin of the line broadening. The dielectric properties and the vibrational spectrum were also investigated.

**Experimental**

nB-CH was prepared and purified by the methods described in [1].

The $^{35}\text{Cl}$ NQR signals were detected by a home-made, frequency modulated, superregenerative spectrometer [2]. A pulsed NQR spectrometer (Matec 5100-525) was employed for the measurements of the spin-lattice relaxation time ($T_1$), the spin-phase memory time ($T_2$) and the apparent inverse linewidth parameter ($T_2^*$). The induced magnetization was monitored with a digital oscilloscope (Hitachi VC-6275) having the function of signal-averaging up to 256 times. $T_1$ was determined by 90°–$\tau$–90° pulse sequences above 170 K and by echo sequences (90°–$\tau$–90°–180°) below 120 K. $T_2$ was obtained by a conventional spin echo method (90°–$\tau$–90°–180°). $T_2^*$ 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 traces of the induction tails following single pulses, and also from the shapes of individual echoes. The length of the 90° pulse was about 5 $\mu$s. The pulsed NQR measurements were carried out in the range 90–300 K with the aid of a cryostat described in [3].

The dielectric measurements were performed on a compressed disk of the compound and on polycrystalline specimen grown from the melt in a conventional cell for liquid samples. The electrode assembly for the disk has been reported in [4]. A transformer bridge (Ando Denki TR-1C) was employed for the experiment in the range 0.11–10\(^3\) kHz.

The spectra of solid nB-CH were recorded on a Hitachi EPI-G2 IR spectrometer with a resolution less than 2 cm\(^{-1}\). The spectra were measured in the range 117–300 K with the aid of a low-temperature cryostat described in [5].

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Results

nB-CH shows three $^{35}$Cl NQR signals at 297 K; $v_1 = 37.500$ MHz, $v_2 = 37.650$ MHz and $v_3 = 38.083$ MHz [1]. The temperature variation of S/N for $v_3$ obtained by the present cw method is illustrated in Fig. 1a (open circles), together with the data taken from [1], in which work a commercial, Zeeman modulated cw spectrometer (Decca) was used. The lower $v_1$ and $v_2$ lines were too weak to be detected.

$T_1$, $T_2$, and $T_2^*$ could be determined only for $v_3$, as S/N of the other lines was too low to give reliable NQR signals. The temperature variation of the relaxation times of $v_3$ is shown in Figure 2. In the range 90–120 K, $T_2^*$ was determined from echo envelopes. Free induction decay (FID) signals were difficult to observe because of the line broadening. On the contrary, in the range 170–300 K, the echo could not be detected, probably due to short $T_2$, although at 180 K the echo could be observed with difficulty. So $T_2^*$ in this temperature region was determined from the shape of the FID. At 220 and 280 K the determination of $T_1$ was possible, while at temperatures in between it was impossible. Although the values of $T_1$ obtained at
280 and 220 K were approximate ones, they are plotted in Fig. 2 as they suggest the occurrence of a \( T_1 \) minimum.

The dielectric absorption of nB-CH was observed in ca. 110–180 K. The data are interpreted satisfactorily by a normal Debye type absorption. The activation energy for the absorption \( (\Delta E) \) was calculated by [6]

\[
f_{\text{max}} = A \exp \left[ -\frac{\Delta E}{RT} \right],
\]

where \( f_{\text{max}} \) is the frequency at which the absorption becomes maximum and \( A \) is a constant. The values of \( \Delta E \) were 23.1 ± 0.2, 23.4 ± 0.2 and 24.6 ± 0.1 kJ mol\(^{-1}\) for the compressed disk, the melt-grown sample and partially deuterated nB-CH, respectively. In the deuterated nB-CH about 65\% of H in the OH group was replaced by D. The difference in \( \Delta E \) between the normal and the deuterated compound is similar to that reported for \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) [7]. Figure 1 b shows log \( (f_{\text{max}}) \) vs. \( 10^3/T \) plots for the melt-grown sample and the deuterated one.

Figure 3 shows IR bands assigned to OH stretching vibrations \( (\tilde{\nu}_{\text{OH}}) \) observed at 296, 192 and 117 K. At every temperature the band has at least two components (designated as \( \tilde{\nu}_L \) and \( \tilde{\nu}_H \)). The \( \tilde{\nu}_{\text{OD}} \) band of the deuterated sample showed a splitting corresponding to that of the \( \tilde{\nu}_{\text{OH}} \) band.

**Discussion**

The crystal structure of nB-CH is shown in Fig. 4 (details of the crystal structure analysis will be given elsewhere). The crystal contains two kinds of disorders. First, there exists disorder associated with the position of H in the O–H ⋯ O H-bonds, since H in an OH group participates in two kinds of H-bonds \( (\text{O}_2 \cdots \text{O}_1 = 297 \text{ pm} \text{ and } \text{O}_2 \cdots \text{O}_2 = 323 \text{ pm}) \). Secondly, \( C_5 \) and \( C_6 \) in the n-butyl group exhibit another disorder.

The first kind of disorder seems to manifest itself in the splitting of the \( \tilde{\nu}_{\text{OH}} \) IR band (Figure 3). The lower-wavenumber band \( (\tilde{\nu}_L) \) is assignable to the stronger hydrogen bond between \( \text{O}_2 \cdots \text{O}_1 \) because of the shorter O–O distance [8]. The rise of the relative intensity of \( \tilde{\nu}_L \) with decreasing temperature indicates

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Fig. 3. Temperature variation of the IR band corresponding to the OH stretching vibration \( (\tilde{\nu}_{\text{OH}}) \). \( \tilde{\nu}_H \) and \( \tilde{\nu}_L \): higher and lower wavenumber component, respectively.
that the population of the more stable site increases at lower temperatures.

Since $\Delta E$ obtained from the temperature dependence of the dielectric absorption is in the order of the ordinary H-bond energy [9] and consistent with the values of $\Delta E$ reported for a series of alcohols [10], the dielectric absorption is attributable to a jumping of the H atom between the two H sites.

A comparison of Fig. 1a and Fig. 2 indicates that the temperature dependence of S/N follows closely that of $T_{2^*}$. The anomalous behavior of $T_{2^*}$ cannot be explained by phase transitions because the temperature dependence of the NQR frequencies showed no indication of them [1].

It is well known for trichloromethyl derivatives that broadening of Cl NQR lines occurs near the melting point because of the decrease in $T_1$ caused by the reorientation of the CCl$_3$ group [11–13]. Therefore, in nB-CH (mp = 324 K) the line broadening above 300 K can be interpreted by the reorientation.

A $T_{2^*}$ minimum found at ca. 240 K corresponds to that of S/N observed at the same temperature. A $T_{1}$ minimum which is likely to exist at some temperature around 240 K seems to be responsible for the $T_{2^*}$ minimum. In the 110–180 K range, the jumping motion of H in the O–H … O group was evidenced by the dielectric absorption. Since there is no phase transition above 180 K, thermal motion with a higher jumping rate may be assumed at 240 K. Then, fluctuation of the electric field gradient (EFG) and/or that of the magnetic field due to the jumping motion is considered to be the origin of the $T_{1}$ minimum. The crystal structure of nB-CH indicates that, among the three Cl atoms in the CCl$_3$ group, Cl$_1$ and Cl$_2$ are closer to the H of the OH group than Cl$_3$. Therefore, the NQR lines of Cl$_1$ and Cl$_2$ are expected to be the most affected ones by
the thermal motion of H. This consideration is consistent with the observation that \( v_3 \) exhibited a much better S/N than \( v_1 \) and \( v_2 \).

The decrease in \( T_1 \) due to the reorientation of the CCl\(_3\) group takes place in a rather wide temperature range determined by its activation energy \([12, 13]\). Therefore, the reorientation can be also responsible for the decrease in \( T_1 \) of nB-CH observed in the range 170–220 K.

An extrapolation of the \( T_2 vs. 10^3/T \) curve to the range >120 K suggests that \( T_2 \) is shorter than 10 \( \mu \)s above ca. 120 K. Above 170 K, however, it is probably longer than 10 \( \mu \)s provided that it is approximately equal to \( T_2^* \). Then, a \( T_2 \) minimum seems to exist in the range 120–170 K. The extremely short \( T_2 \) will be responsible for the line broadening in the range 120–150 K. The relationship between the temperature dependence of \( T_2 \) and the rather slow jumping motion of H evidenced by the dielectric absorption is not clear at present. For chloral iso-butylhemiacetal a similar minimum of \( T_2 \) and that of \( T_2^* \) were found at ca. 180 K \([14]\).

In the range 90–120 K, both \( T_1 \) and \( T_2 \) are much longer than \( T_2^* \). Therefore it is clear that the cause of the line broadening is the static inhomogeneity of the EFG at the Cl nuclei. A possible origin of the inhomogeneity is a random freezing of the jumping motion of H and/or that of the disorder of C\(_5\) and C\(_6\) in the n-butyl group.