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

Masao Hashimoto, Takahiro Isono, Haruo Niki[a], and Takuya Higa[b]
Department of Chemistry, Faculty of Science, Kobe University, Nadaku Kobe 657, Japan

Z. Naturforsch. **45a**, 472–476 (1990); received August 26, 1989; in revised form December 1, 1989

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}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_2^* of about 10 μs, 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 μs, probably having a minimum in between. The short T_2 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 μs) at that temperature.

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

Introduction

The ^{35}Cl NQR spectra of a series of chloral hemiacetals ($Cl_3CCH(OH)O \cdot R$) 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, $Cl_3CCH(OH)O \cdot C_4H_9$) was the most remarkable compound; the ^{35}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}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°–τ–90° pulse sequences above 170 K and by echo sequences (90°–τ–90°–180°) below 120 K. T_2 was obtained by a conventional spin echo method ($90°–\tau–\tau_e–180°$). 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 μs. 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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* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

[a] Department of Physics, Division of General Education, University of Ryukyus, Nishihara, Okinawa 903-01, Japan.

[b] Department of Physics, College of Science, University of Ryukyus, Nishihara, Okinawa 803-01, Japan.

Reprint requests to Dr. M. Hashimoto, Department of Chemistry, Faculty of Science, Kobe University, Nadaku, Kobe 657, Japan.

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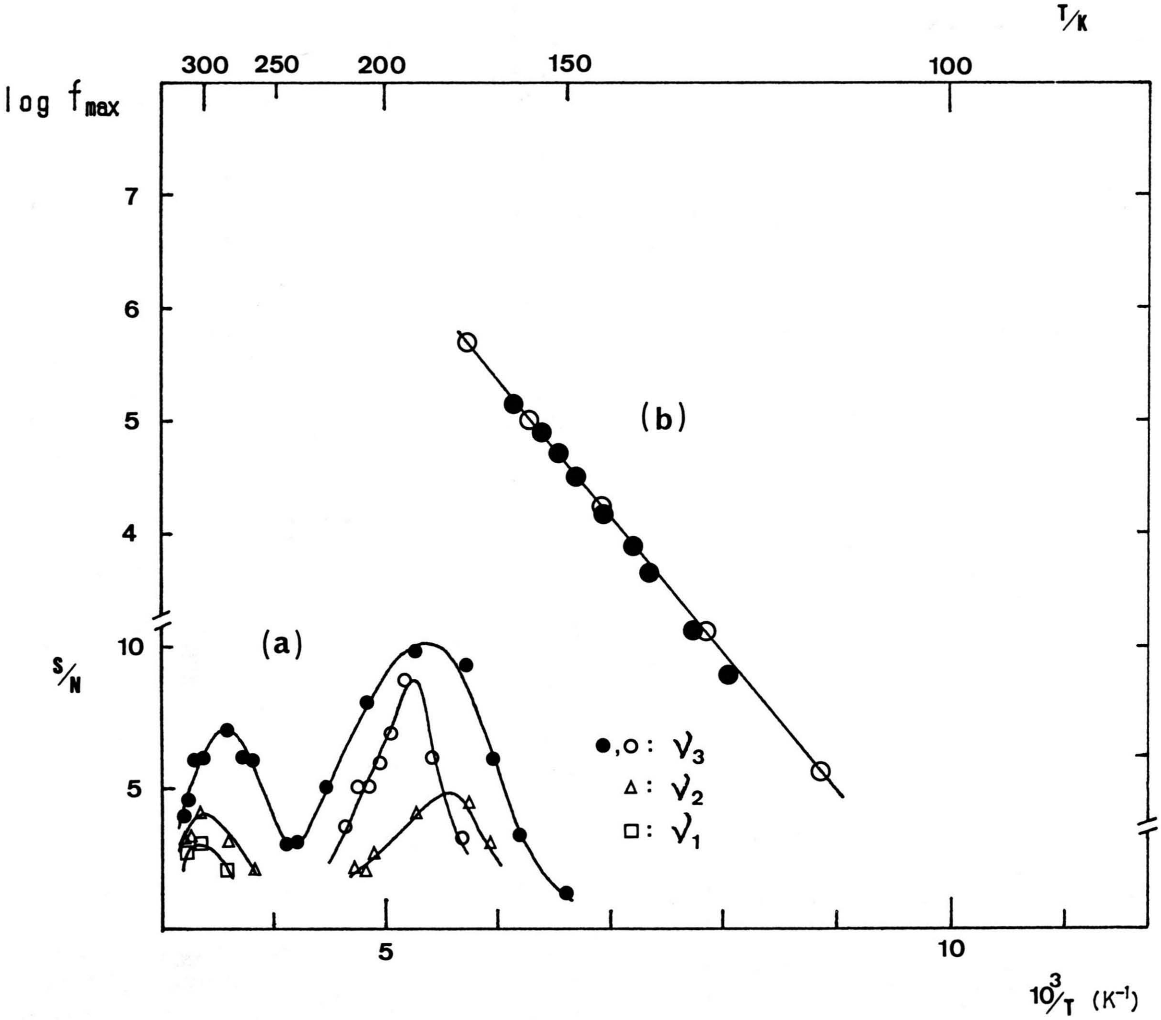

Fig. 1. (a): Temperature dependence of S/N of the ^{35}Cl NQR signals of chloral n-butylhemiacetal (data are taken from [1] except for those of ν_3 drawn by open circles). – (b): log (f_{max}) as a function of reciprocal temperature ($10^3/T$); f_{max} in Hz. Open signs: melt-grown sample; full circles: compressed disk of the deuterated one.

Results

nB-CH shows three ^{35}Cl NQR signals at 297 K; $\nu_1 = 37.500$ MHz, $\nu_2 = 37.650$ MHz and $\nu_3 = 38.083$ MHz [1]. The temperature variation of S/N for ν_3 obtained by the present cw method is illustrated in Fig. 1 a (open circles), together with the data taken from [1], in which work a commercial, Zeeman modulated cw spectrometer (Decca) was used. The lower ν_1 and ν_2 lines were too weak to be detected.

T_1, T_2, and T_2^* could be determined only for ν_3, as S/N of the other lines was too low to give reliable NQR signals. The temperature variation of the relaxation times of ν_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 (ΔE) was calculated by [6]

$$f_{\max}=A\exp[-\Delta E/(RT)], \qquad (1)$$

where $f_{\max}$ is the frequency at which the absorption becomes maximum and A is a constant. The values of ΔE 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 ΔE between the normal and the deuterated compound is similar to that reported for H_2O and D_2O [7]. Figure 1 b shows log ($f_{\max}$) vs. $10^3/T$ plots for the melt-grown sample and the deuterated one.

Figure 3 shows IR bands assigned to OH stretching vibrations ($\tilde{\nu}_{OH}$) 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 $\tilde{\nu}_{OD}$ band of the deuterated sample showed a splitting corresponding to that of the $\tilde{\nu}_{OH}$ band.

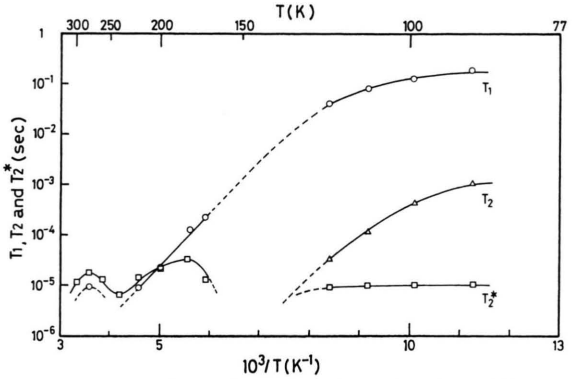

Fig. 2. T_1, T_2, and T_2^* of ν_3 as functions of reciprocal temperature ($10^3/T$).

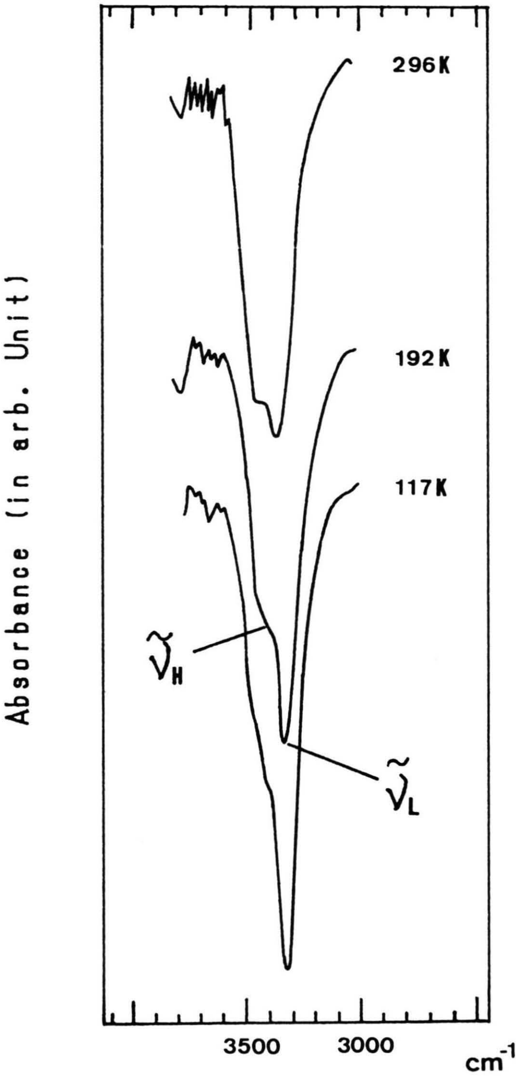

Fig. 3. Temperature variation of the IR band corresponding to the OH stretching vibration (ν_{OH}). ν_H and ν_L: higher and lower wavenumber component, respectively.

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 ($O_2 \cdots O_1' = 297$ pm and $O_2 \cdots O_2' = 323$ 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 $\tilde{\nu}_{OH}$ IR band (Figure 3). The lower-wavenumber band ($\tilde{\nu}_L$) is assignable to the stronger hydrogen bond between $O_2 \cdots O_1'$ because of the shorter O ··· O distance [8]. The rise of the relative intensity of $\tilde{\nu}_L$ with decreasing temperature indicates

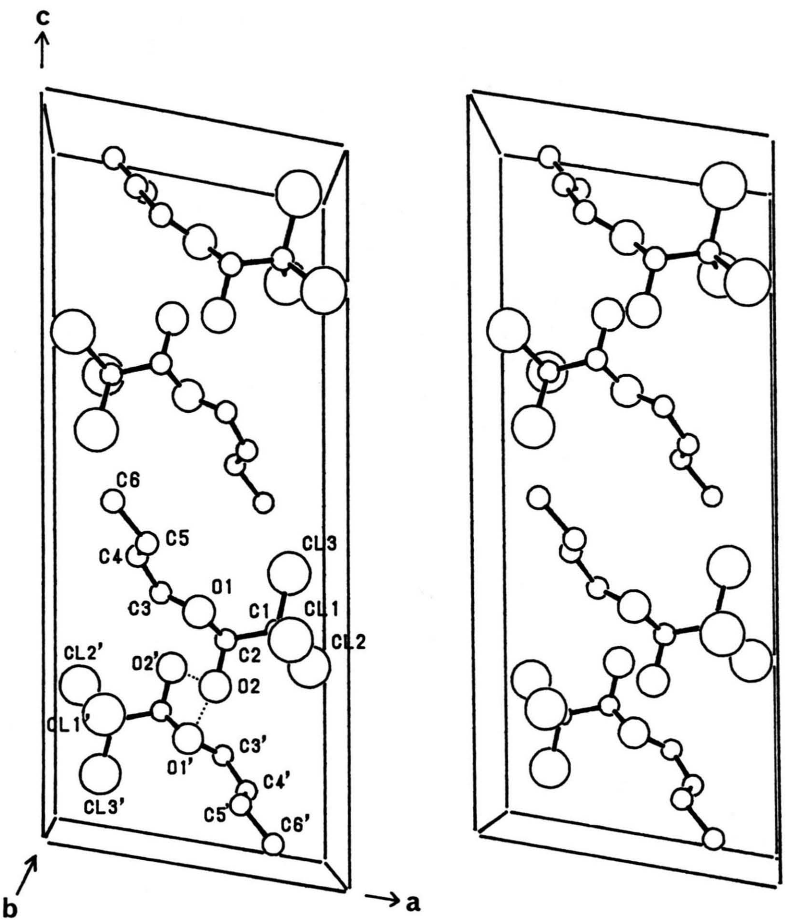

Fig. 4. A stereographic view of the crystal structure of chloral n-butylhemiacetal. The molecules connected by the O–H ··· O H-bonds (drawn by dotted lines) are related to the 2_1 axis in a monoclinic cell of space group $P2_1/c$.

that the population of the more stable site increases at lower temperatures.

Since ΔE 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 ΔE 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 ca. 110–180 K, 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 ν_3 exhibited a much better S/N than ν_1 and ν_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 μs above ca. 120 K. Above 170 K, however, it is probably longer than 10 μs 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.

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