Temperature Dependence of ^{35}Cl NQR in Benzotrichloride[+]

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Abstract A precise measurement of the temperature dependence of NQR frequencies in benzotrichloride crystal was carried out. The fade-out phenomenon of the resonance lines was ascribed to the reorientational motion of $-CCl_3$ group. Owing to the crystal field effect, two kinds of molecular conformation exist. The torsional frequency and its temperature behavior were analyzed.

Introduction

In order to investigate the torsional vibration of $-CCl_3$ group in molecular crystals, a precise measurement was carried out on the temperature dependence of ^{35}Cl NQR frequency in benzotrichloride (ω-trichlorotoluene). Preliminary works were reported by McCall and Gutowsky[1] and Bray[2], who found six lines at 77 K, and by Ainbinder et al.[3], who found the existance of the thermally different non-equivalent positions of $-CCl_3$ group in the crystal.

Experimental

The NQR signal was detected by means of a regenerative spectrometer[4] to avoid the side-band interference in a super-regenerative detector. The sample was a commercial product of GR grade, and was used without further purification. The least-squares calculation for the determination of the fitting parameters was carried out on a computer of FACOM 230-35 at Kanazawa University.

Results and Discussion

Six resonance lines with equal intensity were observed at 77 K and the resonance frequencies of these lines decreased monotonously with increase in temperature, as
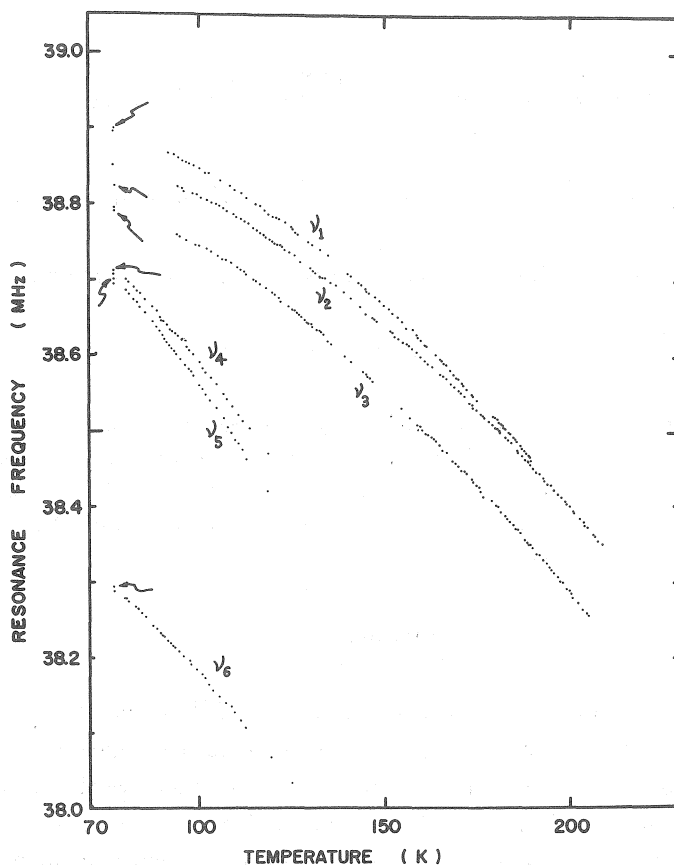

Fig. 1. Temperature dependence of NQR frequencies in benzotrichloride.
Previous data by McCall and Gutowsky are shown by arrows.

shown in Fig. 1. The lines, ν_4, ν_5, and ν_6, showed large temperature variation than the others and faded out at 120–125 K, which was considerably below the melting point (268 K). In contrast, for ν_1, ν_2, and ν_3 lines, the fade–out phenomenon was also found at 205–210 K; the temperature range of which was also below the melting point, although Gutowsky and McCall[1] reported that the resonance was found to disappear at 172 K, even by the use of a super–regenerative spectrometer. Similar phenomena were found in trichloroacetamide[5] and some derivatives of benzotrichloride[6]. Especially, in p– and o–chlorobenzotrichlorides, the resonance due to the Cl atom attached to the benzene ring can be observed near the melting point, although the resonance due to the $-CCl_3$ group is beyond the detection considerably below the melting point. These facts indicate that these fade–out phenomena originate from a characteristic motion (e.g., reorientational motion) of $-CCl_3$ group rather than the librational motion of the molecule as a whole.

In benzotrichloride, if the $-CCl_3$ group in a molecule rotates freely, the three

chlorine atoms are chemically equivalent, and therefore only one resonance line should be observed.

One stable conformation is that one of the Cl atom of $-CCl_3$ group is located in a mirror plane perpendicular to the benzene ring and another two should be in the equivalent positions, as shown in Fig. 2–a. This case was found for p–chlor~ and 2,4-dichloro benzotrichlorides[6], in which two resonance lines due to the $-CCl_3$ group were observed. However, this configuration does no explain the six lines consisted of the two kinds of the triplet line in benzotrichloride.

If the temperature change of the resonance frequency is predominantly due to the torsional oscillation of $-CCl_3$ group, the resonance lines for the $-CCl_3$ group in a molecule should exhibit the same temperature dependence. Hence, the higher three lines ($\nu_1 \sim \nu_3$: Group I) and the lower ones ($\nu_4 \sim \nu_6$: Group II) must be assigned to each of the $-CCl_3$ groups in the different molecules, because of their distinct temperature behaviors. In addition to this, it is reasonable to consider that if the small deviation of the orientation of the $-CCl_3$ group relative to benzene ring, as shown in Fig. 2–b, occurs by the effect of the crystal field, three Cl atoms in a $-CCl_3$ group are not mutually equivalent; three resonance lines being expected to be observed. From these considerations, the experimental results of NQR in benzotrichloride crystal are clearly explained.

The $-CCl_3$ group of Group II can moves vigorously than that of Group I, for the larger temperature coefficients and the lower fade–out temperature are observed for the resonance lines assigned to Group II. In any event, it is suggessted that the torsional oscillation of these $-CCl_3$ groups turns into the reorientational motion (or hindered rotation) above the fade–out temperature. In fact, the measurements[7] of the temperature dependence of T_1 and T_{1AD} for the proton NMR in this compound give a suggestion for the presence of such a motion of $-CCl_3$ group near 120 K and also give a possibility of the same motion of another $-CCl_3$ group above 180 K.

PLANE OF BENZENE RING

(a)   (b)
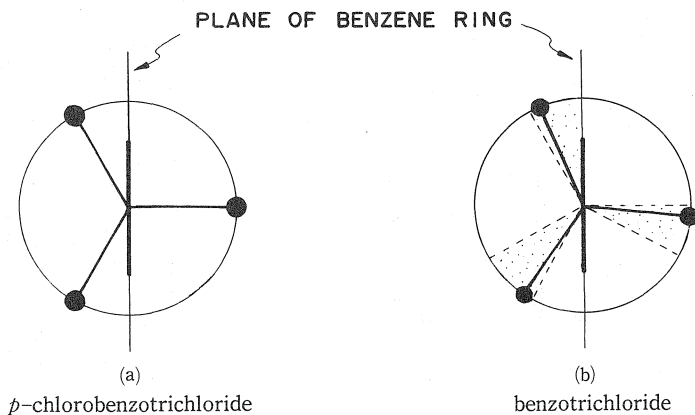p-chlorobenzotrichloride   benzotrichloride

Fig. 2. Orientation of $-CCl_3$ group relative to the plane of benzene ring.

Table 1. Methods of analysis for temperature dependence of NQR frequency.

Method (Approximation)	Temperature Expansion of NQR frequency[d]	of torsional frequency[e]	Theoretical expression for NQR frequency[f]
A Bayer[a] (Harmonic)	$\nu(T)=a_0+a_1T$	$\omega_i=\text{constant}$	$\dfrac{1}{\nu_{(0)}}\left(\dfrac{d\nu}{dT}\right)=b_0$
B-1 Brown[b] (Quasi-harmonic)	$\nu(t)=a_0+a_1t+a_2t^2$	$\omega_i(t)=\omega_{i0}(1-\alpha_it)$	$\dfrac{1}{\nu_{(0)}}\left(\dfrac{d\nu}{dt}\right)_{t=0}=(1+2t_0\alpha)b_0$
			$\dfrac{1}{\nu_{(0)}}\left(\dfrac{d^2\nu}{dt^2}\right)_{t=0}=(4\alpha+6t_0\alpha^2)b_0$
B-2 Extended Brown[c] (Quasi-harmonic)	$\nu(t)=a_0+a_1t+a_2t^2+a_3t^3$	$\omega_i(t)=\omega_{i0}(1-\alpha_it-\beta_it^2)$	$\dfrac{1}{\nu_{(0)}}\left(\dfrac{d\nu}{dt}\right)_{t=0}=(1+2t_0\alpha)b_0$
			$\dfrac{1}{\nu_{(0)}}\left(\dfrac{d^2\nu}{dt^2}\right)_{t=0}=(4\alpha+2t_0\beta+6t_0\alpha^2)b_0$
			$\dfrac{1}{\nu_{(0)}}\left(\dfrac{d^3\nu}{dt^3}\right)_{t=0}=(24t_0\alpha^3+18\alpha^2+36t_0\alpha\beta+12\beta)b_0$

(a) H. Bayer, *Z.Physik*, **130**, 227(1951). (b) R.J.Brown, *J.Chem.Phys.*, **32**, 116(1960). (c) C.V.Ramanohan and J.Sobhanadri, *Mol.Phys.*, **22**, 575(1971). (d) Observed frequency is expressed as a function of temperature measured from a fixed temperature t_0 ; $t=T-t_0$. (e) Torsional frequency of i-th mode is assumed to be a function of temperature. (f) The expressions at $t_0=300$ K were given in the previous works[b,c]. α and β are the weighted averages of α_i and β_i. $b_0=(-3k/2\omega_{t_0}^2)\sum_i(\sin^2\theta_i/I_i)$, where k is the Boltzman constant, ω_{t_0} the average value of ω_i at $t=t_0$, and θ_i are the angles between principal axes of the EFG tensor and those of the moment of inertia I_i for i-th torsional mode. θ_i was not taken into account in the original methods.[a,b,c] The fitting parameters α, β, and ω_{t_0}(or b_0) were calculated by equating the theoretical expressions with the corresponding derivatives obtained from the temperature expansion of NQR frequency.

Table 2.   Values of the torsional frequencies and various fitting parameters.

	Method A	Method B-1			Method B-2			
	ω	ω_{t_0}	α	b_0	ω_{t_0}	α	β	b_0
	cm^{-1}	cm^{-1}	K^{-1}	K^{-1}	cm^{-1}	K^{-1}	K^{-2}	K^{-1}
ν_1	65	81	0.213×10^{-2}	-0.704×10^{-4}	73	0.112×10^{-2}	-0.160×10^{-5}	-0.873×10^{-4}
ν_2	66	83	0.182×10^{-2}	-0.683×10^{-4}	75	0.956×10^{-3}	-0.121×10^{-5}	-0.830×10^{-4}
ν_3	63	77	0.170×10^{-2}	-0.786×10^{-4}	70	0.934×10^{-3}	-0.194×10^{-5}	-0.956×10^{-4}
ν_4	55	65	0.196×10^{-2}	-0.111×10^{-3}	60	0.942×10^{-3}	0.148×10^{-5}	-0.131×10^{-3}
ν_5	52	59	0.273×10^{-2}	-0.117×10^{-3}	54	0.128×10^{-2}	0.512×10^{-5}	-0.142×10^{-3}
ν_6	58	66	0.159×10^{-2}	-0.106×10^{-3}	62	0.877×10^{-3}	-0.203×10^{-5}	-0.121×10^{-3}

$t_0=150$ K for ν_1, ν_2, and ν_3; $t_0=100$ K for others.
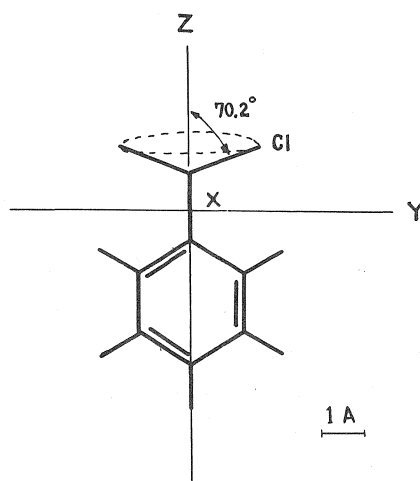

Fig. 3.   Assumed molecular geometry.
The reduced moment of inertia* of $-CCl_3$ group was   calculated as :
$I_r=I_{-CCl_3}\,[1-(I_{-CCl_3}/I_Z)]=11.1\times10^{-39}$ g $\cdot$ cm^2, where $I_{-CCl_3}=42.8\times10^{-39}$
g $\cdot$ cm^2 and $I_Z=62.2\times10^{-39}$ g $\cdot$ cm^2. (* See Ref.10)

    The temperature dependence of the resonace frequencies has been analyzed on the basis of the torsional motion of $-CCl_3$ groups.   The methods of the analysis are illustrated in Table 1.   The results are shown in Table 2. Fig. 3 shows the molecular geometry and the moment of inertia used.   The torsional frequencies, which can be refered, are 118 cm^{-1} obtained by Raman effect in benzotrichloride in liquid state[8], and 111 cm^{-1} (at $-180°$C) by IR spectroscopy or 96 cm^{-1} (liquid) by Raman effect in chloral[9].   The low values obtained from the analysis may be resulted from the neglect of the librational contribution.
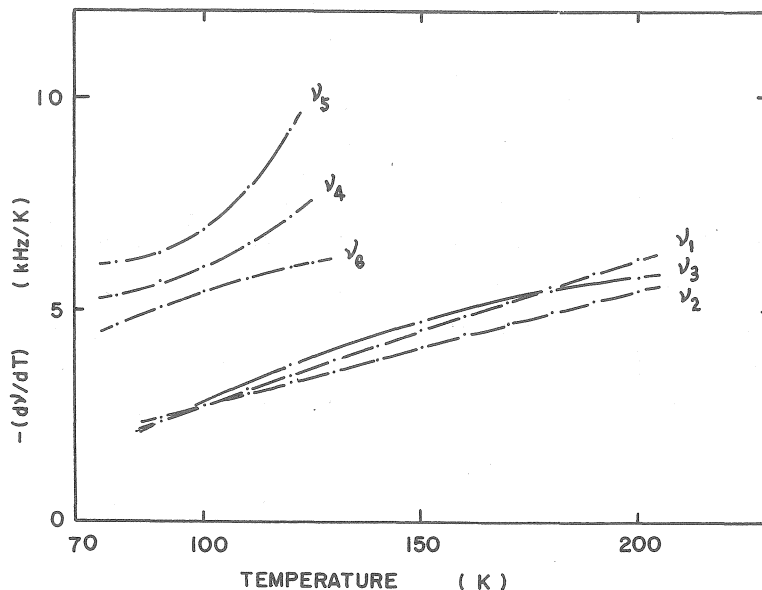
Fig. 4.   Temperature dependence of $-(d\nu/dT)$ in benzotrichloride.

The characteristic feature is the large temperature dependence of the torsional frequencies comparing with that of the librational one in *normal* compounds.   The positive β values for ν_4 and ν_5 lines is consistent with the divergent behaviors of $-(d\nu/dT)$ with an increase in temperature, as shown in Fig. 4.   The differences of the motion of the two kinds of $-CCl_3$ group are also clearly demonstrated.   From the parameters in Table 2, the average torsional frequency of Group I lines is larger than that of Group II lines by 20 cm^{-1} at 100 K.   It is clear that the potential barrier of the torsional motion for the $-CCl_3$ of Group II are lower than that of Group I.

Acknowledgements

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