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Nuclear Quadrupole Resonance Study of Chloral Hydrate

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Three nuclear quadrupole resonance lines were observed in chloral hydrate at temperatures 20—300K, the frequencies being 38.2863±0.0004 MHz(ν_1), 39.5415±0.0002(ν_2), and 39.6252±0.0002(ν_3) at 20.3K. Their temperature dependence was measured below 77K, showing monotonous decrease with increasing temperature. The difference in frequency between ν_1 and ν_2(or ν_3) is probably due to a crystal field effect rather than OH···Cl hydrogen bonding as has been suggested. The spin-lattice relaxation time for all the lines, determined by pulse techniques, coincides with each other and tends to decrease rapidly above 250K. The decrease was interpreted as arising from hindered internal rotation of the CCl_3 group with the activation energy of 8.8 kcal mol^{-1}.

It is known that O–H···Cl type hydrogen bond exists in a few crystalline solids.[1] Chloral hydrate has been considered to have this type of hydrogen bond. Existence of the hydrogen bond was first predicted by Kondo and Nitta on the basis of their X-ray crystal structure analysis.[2] Allen found that one of the three ^{35}Cl nuclear quadrupole resonance (NQR) lines was much lower in frequency than the other two and interpreted the low frequency in terms of a hydrogen bond between an O–H group and the chlorine atom.[3] The crystal structure of chloral hydrate was later redetermined by Ogawa by an X-ray method and the possibility of a bifurcated hydrogen bond of the type $\text{O–H}\langle^{\text{Cl}}_{\text{O}}$ was suggested on the basis of the short intermolecular O–Cl and O–O distances.[4]

The structural data of Ogawa was further refined and all the hydrogen atoms were located with a neutron diffraction method by Brown.[5] The hydrogen atoms of the two crystallographically non-equivalent hydroxyl groups were found between two oxygen atoms of different molecules, O–H···O type hydrogen bonds being rather long in the crystallographic *ac*-plane.

Recently a question was raised by Biedenkapp and Weiss[6] as to whether or not the large NQR frequency shift is due really to the hydrogen bonding to chlorine. They examined the temperature range 77—323K and found that only a small change occurs in the ^{35}Cl NQR spectra upon deuteration; the observation led them to conclude that the "crystal field effects" rather than the OH···Cl hydrogen bond could account for the spectra.

The purpose of the present paper is to examine the existence and nature of the possible O–H···Cl hydrogen

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[1] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond" Freeman (1960).

[2] S. Kondo and I. Nitta, *X-rays*, **6**, 53 (1950).

[3] H. C. Allen, Jr., *J. Amer. Chem. Soc.*, **74**, 6074 (1952).

[4] K. Ogawa, This Bulletin, **36**, 610 (1963).

[5] G. M. Brown, private communication to Prof. K. Ogawa.

[6] D. Biedenkapp and H, Weiss, *Z. Naturforsch.*, **22a**, 1124 (1967),

bonding in chloral hydrate by means of the single crystal NQR method.

Experimental

Chloral hydrate (Merck) was recrystallized from chloroform solution by evaporation at 25°C. A single crystal (approximately $1\times1\times0.7$ cm^3) was grown also in the chloroform solution.

The ^{35}Cl NQR frequencies were measured at temperatures 20—80K by using a Dean-type super-regenerative spectrometer on a powdered specimen. Single crystal Zeeman effect experiment was carried out at liquid nitrogen temperature. The spin-lattice relaxation times were measured by the 180°—90° method[7] at 77—300K using a pulsed spectrometer. Details of the experimental methods were described elsewhere.[8]

Results and Discussion

Description of Crystal Structure. Chloral hydrate crystallizes in a monoclinic system with the space group $P2_1/c$ and contains four molecules in a unit cell. Figure 1 shows the crystal structure which was determined by Brown.[5] There are two relatively long O–H···O hydrogen bonds (H···O=1.908 and 1.933 Å). There is a somewhat short H···Cl distance of 2.643 Å between the hydrogen H_1 and the chlorine Cl_1 to be compared with the sum of the van der Waals radii of H and Cl atoms (3.0 Å).

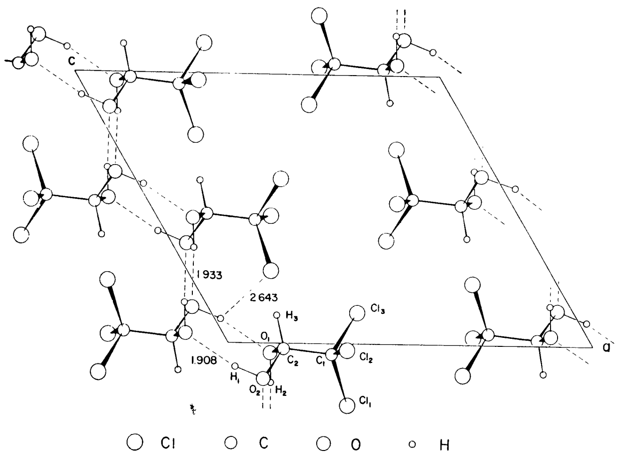

Fig. 1. Crystal structure of chloral hydrate projected along the crystalline *b* axis. (Ref. 5)

Figure 2 shows the position of the zero-splitting loci for four of the six independent C–Cl bond directions in a laboratory coordinate system. The direction of principal *Z*-axis and the asymmetry parameter η of the electric field gradient of ^{35}Cl in each C–Cl bond were calculated by using a NEAC-2200 computer from the observed zero-splitting loci by means of the relation[9]

$$\sin^2\theta = 2/(3-\eta\cos 2\varphi),$$

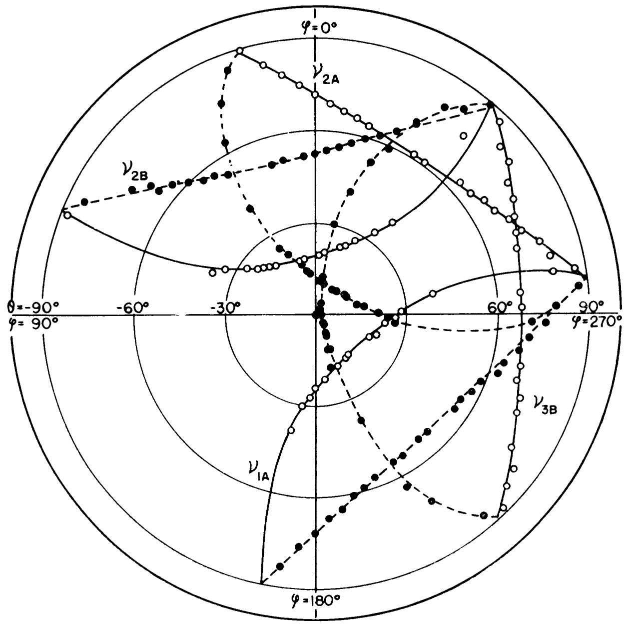

Fig. 2. Zero-splitting loci of four C–Cl bonds at 77K.
—○— locus projection from above the plane of paper,
--●-- locus projection from below the plane of paper.

where θ and φ are respectively the polar and azimuthal angles of the Zeeman field direction that gives zero splitting in the coordinate system fixed to the principal EFG tensor axes. The number of data collected was 40 for Cl_{1A}, 40 for Cl_{2A}, 43 for Cl_{2B} and 46 for Cl_{3B}. The results are given in Table 1, with the direction cosines of the other two unobserved cones[10] (Cl_{1B} and Cl_{3A}), which were calculated by utilizing the fact that there is a glide plane perpendicular to the crystalline *b*-axis. From an examination of the relative directions of the six C–Cl bonds (assumed to coincide with the *Z*-axes of EFG) we can unambiguously assign each NQR frequency to a particular chlorine atom in Fig. 1, *viz.*, ν_1, ν_2, and ν_3 correspond to Cl_1, Cl_3 and Cl_2, respectively. It is noticeable that ν_1, which is anomalously lower than the other two, corresponds to the Cl_1 atom which has a close hydrogen neighbor.

Interactions between Chlorine Cl_1 and Other Atoms. We now attempt to find the possible interactions that make the ν_1 frequency lower than ν_2 or ν_3. The geometry of the CCl_3 group as determined by diffraction methods is quite normal in that every C–Cl distance (1.760 to 1.765 Å) is typical of a single bond length and that the angles between the three C–Cl bonds are close to the tetrahedral angle (see Table 2). Thus there seems to be no interaction of intramolecular origin through σ bonds that will be responsible for the difference between ν_1 and ν_2 (or ν_3). The fact that the asymmetry parameters for the three chlorines are small and about the same in magnitude also supports such a view.

Of the intermolecular interactions, the hydrogen

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[7] D. E. Woessner and H. S. Gutowsky, *J. Chem. Phys.*, **39**, 440 (1963).

[8] T. Kiichi, N. Nakamura, and H. Chihara, *J. Magn. Reson.*, **6**, 516 (1972).

[9] C. Dean, *Phys. Rev.*, **96**, 1053 (1954).

[10] These lines could not be observed because of unfavorabel orientations of the EFG *Z*-axes with respect to the orientation of the rf-coil.

TABLE 1. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES, QUADRUPOLE COUPLING CONSTANTS, ASYMMETRY PARAMETERS AND THE DIRECTION COSINES OF PRINCIPAL Z-AXIS OF ELECTRIC FIELD GRADIENT TENSORS IN A LABORATORY FIXED COORDINATE SYSTEM (77K). THE STANDARD DEVIATIONS ARE SHOWN IN PARENTHESES

Resonance line	Frequency (MHz)	e^2Qq/h (MHz)	η	Direction cosines		
				X_L	Y_L	Z_L
ν_{1A}	38.1894	76.373	0.022(0.010)	−7002(22)	−6429(23)	3105(69)
ν_{2A}	39.4330	78.858	0.025(0.008)	7548(17)	−4913(23)	−4346(39)
ν_{3A}	39.5189			3426	4781	8088*
ν_{1B}	38.1894			−5826	−1410	8005*
ν_{2B}	39.4330	78.837	0.048(0.013)	9273(14)	2443(47)	2836(63)
ν_{3B}	39.5189	79.021	0.035(0.013)	0267(36)	8452(14)	5337(23)

TABLE 2. RELATIVE ORIENTATIONS OF PRINCIPAL Z-AXIS OF ELECTRIC FIELD GRADIENT TENSORS. THE RELATIVE ORIENTATIONS OF C–Cl BONDS CALCULATED BY USING THE NEUTRON DIFFRACTION DATA (Ref. 5) ARE GIVEN IN PARENTHESES

	$\nu_{1A}(Cl_1)$	$\nu_{2A}(Cl_3)$	$\nu_{3A}(Cl_2)$	$\nu_{1B}(Cl_1')$	$\nu_{2B}(Cl_3')$
$\nu_{2A}(Cl_3)$	110.3 (109.5)				
$\nu_{3A}(Cl_2)$	107.2 (109.2)	109.1 (109.2)			
$\nu_{1B}(Cl_1')$	41.7 (41.6)	135.9	67.6		
$\nu_{2B}(Cl_3')$	135.9	62.8 (62.2)	48.4	110.3 (109.5)	
$\nu_{3B}(Cl_2')$	69.0	48.1	145.6 (147.5)	108.9 (109.2)	109.4 (109.2)

bonding between O_2–H_1 and Cl_1 is an obvious possibility which could account for the NQR frequency of Cl_1. Two models of hydrogen bond, electrostatic and charge-transfer, will now be studied in turn.

In an electrostatic model, we consider that a net positive charge δ is produced on the proton H_1 as a result of the formation of the hydrogen bond O_2–H···O_1 and this charge interacts with the effective negative charge on Cl_1. The additional electrostatic interaction makes the system more stable. This model corresponds to the bifurcated hydrogen bond $\text{O–H}\langle^{\text{Cl}}_{\text{O}}$ suggested by Ogawa4). An excess EFG Δq should be produced by the charge δ, at the position of the Cl_1 nucleus. This is given by

$$\Delta q = \delta\left(\frac{3\cos^2\theta - 1}{r^3}\right)(1-R),$$

where θ is the angle between the C–Cl_1 axis and the Cl···H direction, r the Cl···H distance and R the shielding or antishielding coefficient of covalently bonded chlorine atom. If we put $\delta=+0.1e$,11) $\theta=122.5°$, and $r=2.64$ Å, R is required to be as large as 10^3 in order to explain $\Delta\nu=1.3$ MHz. This is mainly because the angle θ is close to the magic angle (54°44′ or 125°16′), and therefore the electrostatic part of the hydrogen bond alone, if any, is not sufficient to account for $\Delta\nu$.

According to a simple charge-transfer theory of hydrogen bond12) a fraction of $3p$ electrons in a Cl lone pair orbital has to be transferred to a vacant antibonding orbital of the O–H group.13) In this case the EFG tensor components can be analyzed by using the p-electron population numbers U_x, U_y, and U_z on the Cl atom.14) Here U_z is the population number in the C–Cl bonding orbital, U_x and U_y are those in the lone pair orbitals in the absence of charge transfer. If U_x is assumed to change to U_x' by the charge transfer interaction, the decrease in EFG Δq is given by

$$\Delta q = \frac{1}{2}(U_x - U_x')q_{at}$$

or, in terms of the frequency shift $\Delta\nu$,

$$\Delta\nu = \frac{1}{2}(U_x - U_x')\nu_{at}, \quad \nu_{at} = \frac{1}{2}e^2Qq_{at}$$

where q_{at} is the EFG in the atomic chlorine. The change in η is approximately given by

$$\Delta\eta \doteqdot \frac{3}{2}\frac{\nu_{at}}{\nu}(U_x' - U_x).$$

$\Delta\eta$ can be either positive or negative according to the sign of $(U_x - U_y)$ in the molecule without the charge transfer.

We can estimate the quantity $U_x - U_y$ and then η by assuming that $\Delta\nu$ is produced only by charge transfer: On substitution of $\Delta\nu=+1.29$ MHz and

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11) C. A. Coulson and O. Danielsson, *Arkiv Fysik*, **8**, 245 (1954).

12) R. S. Mulliken, *J. Amer. Chem. Soc.* **74**, 811 (1952).

13) The overlap integral between the hydrogen $1s$ and chlorine $3p$ lone pair orbital amounts to 0.07 if the Slater-type atomic orbitals are used.

14) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York (1958): H. Chihara and N. Nakamura, This Bulletin, **44**, 2676 (1971).

$\nu_{at}=+54.87$ MHz, we obtain $U_x-U_x'=0.046$ and $\Delta\eta=-0.096$. While the value of U_x-U_x' is not of an unacceptable magnitude, the difference in the experimental asymmetry parameter on different chlorine atoms is trivial as shown in Table 1.

The charge-transfer model does not satisfactorily account for observation.

We are now left with what is generally called a crystal field effect. From the crystal structure as depicted in Fig. 1, we find that both the Cl_2 and Cl_3 atoms have Cl···Cl intermolecular contacts whereas the Cl_1 atom has as close neighbors two oxygen atoms of the same molecule and two oxygen atoms of the neighboring molecules. In particular, the intramolecular Cl···O distances are short (3.06 and 3.09 Å) and the orientation of hydroxyl groups is such that the polarization of oxygen 2*p* lone-pair orbitals would affect the EFG at the Cl_1 site to some extent. The fact that the temperature coefficient of the three NQR lines are similar to each other (Fig. 3) also suggests that the intermolecular (including non-bonded intramolecular) interactions in which the chlorine atoms participate are of long range.

Molecular Motion. The temperature dependence of the NQR frequencies below 80K is shown in Fig. 3. NQR frequencies at 79K were in agreement with published results.[3,6] The resonance frequencies at 20.3K are ν_1, 38.2863±0.0004; ν_2 39.5415±0.0002; and ν_3, 39.6252±0.0002 MHz. These values are rather larger than those for the frequencies at 0K predicted by Biedenkapp and Weiss.[6] It is apparent that ν_1 shows no anomalous temperature dependence as is usually expected in the solid where intermolecular charge transfer exists.[15,16] This has already been discussed by Biedenkapp and Weiss on the experimental data above 77K. The normal behavior of ν_1 above 20K supports the view that the resonance frequency shift originates mainly from the polarization of lone pair orbitals of oxygen.

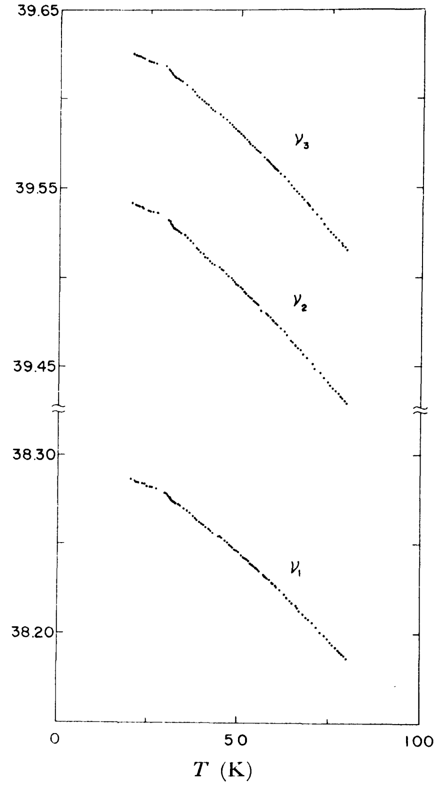

Fig. 3. Temperature dependence of ^{35}Cl nuclear quadrupole resonance frequencies.

The result of measurements of the spin-lattice relaxation time T_1 is shown in Fig. 4. Values of T_1 of ν_1, ν_2 and ν_3 coincide with each other within experimental error over the entire temperature range examined.

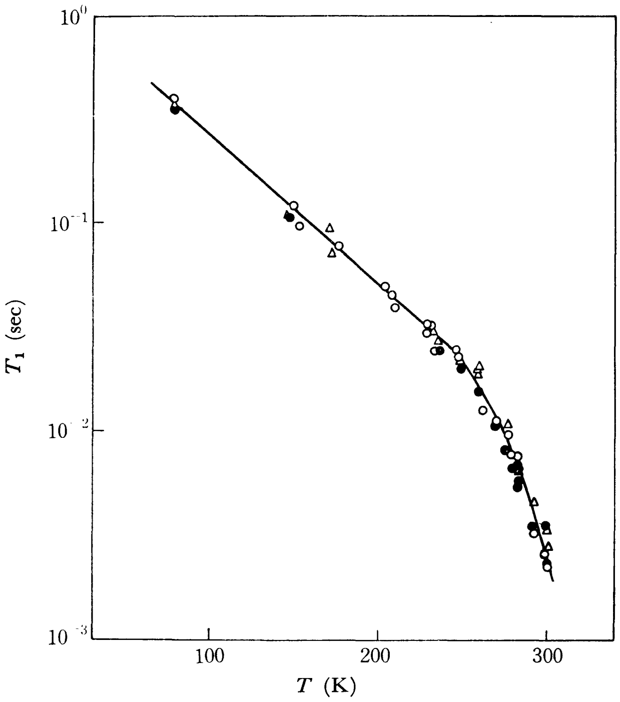

Fig. 4. Nuclear quadrupole spin-lattice relaxation time.
○: ν_1, ●: ν_2, △: ν_3

This suggests that there exists no excess electric quadrupolar or magnetic dipolar interaction between Cl_1 and its environment.

The T_1 value decreases rapidly above 250K. This phenomenon is interpreted as due to the excitation of the internal rotation of the CCl_3 group about the molecular C–C axis. The plot of ln $1/T_1$ against $1/T$ gives a straight line; thus, the relation $1/T_1=Ae^{-E_a/RT}$ holds. The slope of the line gives the activation energy $E_a=8.8+0.8$ kcal/mol.[17] This value is much larger than 4 kcal/mol for CCl_3COOH.[19] It may be reasonable to consider that the high potential barrier in chloral hydrate is attributed to large

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15) H. Chihara, N. Nakamura, and H. Okuma, *J. Phys. Soc. Jap.* **24**, 306 (1968).

16) H. Okuma, N. Nakamura, and H. Chihara, *ibid.*, **24**, 453 (1968).

17) Recently the T_1 measurement was carried out by Ainbinder *et al.*[18] Their rigorous analysis gives $V_0=11.4$ kcal/mol which is considerably larger than ours.

18) N. E. Ainbinder, B. F. Amirkhanov, I. V. Izmest'ev, A. N. Osipenko and G. B. Soifer, *Soviet Physics-Solid State*, **13**, 344 (1971).

19) M. Buyle-Bodin, *Ann. Phys.* (Paris), **10**, 533 (1955).

intramolecular steric hindrance due to short Cl···O distances. Such intramolecular origin as potential height has also been reported in the case of *p*-CCl_3-C_6H_4Cl.[8]

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