Chlorine NQR on Derivatives of Chloral

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The ^{35}Cl-NQR spectrum of several derivatives of chloral, Cl_3CCHO, was studied in the range $77\ \mathrm{K} \leqq T \leqq T_\mathrm{m}$. By use of the spin echo double resonance technique a relative assignment of the resonances to different Cl_3C-groups within one crystallized compound was possible. The solid compounds studied are: High temperature phase of chloral hydrate, $Cl_3CCH(OH)_2$; parachloral, $(Cl_3CCHO)_3$, (α- and β-isomer); the two phases of chloral hemihydrate $Cl_3CCHO \cdot 1/2\ H_2O$; chloralide (II); chloralhemithiohydrate, $Cl_3CCHO \cdot 1/2\ H_2S$. The structure of the molecules in the solid state and the fade out of the NQR resonances are discussed.

Introduction

A simple compound carring a trichloromethyl group, CCl_3, is trichloroacetaldehyde (chloral), CCl_3CHO. It was prepared for the first time and extensively studied by Liebig [1]. The chemistry of chloral was recently reviewed by Luknitskii [2]. In course of studies of chloral hydrate, $CCl_3CH(OH)_2$ [3, 4] and of several trichloromethyl derivatives [5, 6] the relative intramolecular configuration of different CCl_3 groups within one molecule or within one crystallographically asymmetric unit was of interest. It has been shown that Spin Echo Double Resonance, SEDOR [7], offers an experimental way to contribute to the problem [8, 9]. Here SEDOR is applied besides wide line Nuclear Quadrupole Resonance (NQR) for the study of the relative configuration of the following compounds: high temperature phase of chloral hydrate, $CCl_3CH(OH)_2$(I), the two solid phases (I) and (II) of chloral hemihydrate, $CCl_3CHO \cdot 1/2\ H_2O$, the ester chloralide, $CCl_3\underline{CHOCOCHO}CCl_3$ (which shows a solid state phase transformation above room temperature), the two isomers of trimeric chloral, $(CCl_3CHO)_3$, known as α-parachloral and β-parachloral, and chloral hemithiohydrate, $CCl_3CHO \cdot 1/2\ H_2S$.

The application of NQR is of particular advantage in the study of solid trichloromethyl derivatives where in numerous examples solid state transformations have been observed. By means of Cl – NQR it is possible to follow up the transformation process and the onset of hindered rotation of the CCl_3 groups which results in a "fade-out" of the NQR lines.

Experimental

Preparation of the Compounds

The high temperature phase of chloral hydrate, $CCl_3CH(OH)_2$(I), and trichloroethylidene trichlorolactic ester (chloralide), $CCl_3\underline{CHOCOCHO}CCl_3$, were obtained as described previously [3, 4, 6]. Chloral hemithiohydrate, $CCl_3CHO \cdot 1/2\ H_2S$, was synthesized from chloral hydrate and H_2S according to Chattaway and Kellett [10]. α-parachloral and β-parachloral, $(CCl_3CHO)_3$, were prepared from chloral hydrate and sulphuric acid by the method given by Chattaway and Kellett [11]. Chloral hemihydrate, $CCl_3CHO \cdot 1/2\ H_2O$, was synthesized from CCl_3CHO and $CCl_3CH(OH)_2$ in the following way: One mole of $CCl_3CH(OH)_2$ (solid) was mixed with one mole of CCl_3CHO (liquid). The mixture was warmed up to ca. 330 K to dissolve the solid part thoroughly. To the liquid thereafter a trace of sulphuric acid was added and by annealing at ca. 295 K the liquid solidified completely within one hour. The compound can be recrystallized from $HCCl_3$. The results of chemical analysis are (calc/found): C(15.360%/15.10%); H(1.289%/1.15%). The existence of chloral hemihydrate has been proposed by van Rossen [12] and Shill [13]. Immediately after solidification $Cl_3CCHO \cdot 1/2\ H_2O$ showed at 77 K a very weak, six line ^{35}Cl-NQR spectrum. Within a few days the signals became relatively strong. The same spectrum was observed

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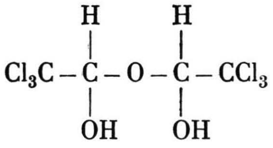
for a specimen recrystallized from $HCCl_3$. The polycrystalline substance obtained in that way was sealed in a glass ampoule and kept at room temperature. Within several weeks a different set of ^{35}Cl-NQR signals appeared for this sample. The new signals became more intense day by day at the expense of the six line spectrum and after three months a new spectrum consisting of twelve ^{35}Cl-NQR lines of fairly good signal to noise ratio was observed. These two crystalline phases are designated as phase I (six lines) and phase II (twelve lines), respectively. The IR spectrum of the compound (KBr-disk) shows the presence of an ether bond, suggesting the following structure:



$$Cl_3C-\underset{OH}{\overset{H}{C}}-O-\underset{OH}{\overset{H}{C}}-CCl_3$$

NQR Spectroscopy

The search for the ^{35}Cl-NQR lines was done with a superregenerative Zeeman modulated spectrometer (Decca). For the SEDOR experiments a two channel pulse spectrometer [9] was employed. The temperature measurements (thermocouple at the sample) are accurate to ±1 K, the error in the frequency measurements is ±3 kHz and only due to the line width. Theory and experiment of SEDOR have been developed by Emshwiller, Hahn, and Kaplan [7]. For a SEDOR experiment the sample must contain at least two crystallographically inequivalent nuclei with spin $I \geqq 1$, which we call A- and B-nuclei. During the experiment the echo amplitude of the A-nuclei is monitored by a 90°-τ-180° pulse sequence. At the time τ a third pulse with length $n \cdot 180^\circ$ is applied to the sample and the frequency of this rf-pulse is varied in steps while the whole pulse program is repeated. If the frequency of the third pulse matches one of the resonance frequencies of the B-nuclei, that part of the local magnetic field at the site of the A-nuclei which originates from the magnetic moments of the B-nuclei, changes its sign:

$$h_{AB} \to -h_{AB}; \quad h_{AB} = \mu_B / r_{AB}^3 . \tag{1}$$

This leads to a disturbance of the phase memory of the A-spins, and consequently the echo amplitude of the A-nuclei is lowered. Following Emshwiller et al. the decrease of the A-echo amplitude ΔE can be formulated as

$$\Delta E = \frac{1}{3} \gamma_A^2 \gamma_B^2 T_{AA} I_B (I_B + 1) \tau^2 \hbar^2 \sum_k g_{jk} r_{jk}^{-6} . \tag{2}$$

γ_A, γ_B are the gyromagnetic ratios of the A- and B-spins; T_{AA} is the relaxation time of the A-spins due to A-A interaction only, I_B the spin quantum number of the B-system, g_{jk} a geometrical factor and r_{jk} the distance between the nuclei A_j and B_k.

In our experiments the width of the 90° pulse for the A-spin system was 15 μsec in all cases. The time intervall τ in the sequence 90°-τ-180° was around 1000 μsec at 77 K and 600 μsec for measurements close to room temperature. For the length of the $n \cdot 180^\circ$ pulse applied to the B-system 400 μsec were choosen in order to avoid broadening of the B-spin resonance line through Fourier components of the B-pulse.

By heteronuclear double resonance it is possible to detect very weak NQR signals of the B-spin system via their influence on the A-signal, and the $1/r^6$ dependence offers a way to determine relative distances between A and B nuclei. For this purpose heteronuclear [7], homonuclear [9] and isotopic double resonance can be used. The last two techniques have been applied to study the relative intramolecular configuration of chlorine nuclei in trichloroacetic acid and other compounds [9] and homonuclear double resonance was applied in this work, too.

Results

In Fig. 1 – 5 the ^{35}Cl-NQR frequencies are shown as a function of temperature. A normal Bayer type behaviour [14] is found for all five compounds, and in Table 1 the coefficients of the polynominals

$$\nu(T) = A + B/T + C\,T + D\,T^2 \tag{3}$$

are given. This function describes the temperature dependence of $\nu(^{35}Cl)$ in the range $77\,K \leqq T \leqq T_m$ (T_m = melting point) adequately within the limits of experimental error in ν and T.

Table 2 lists the resonance frequencies $\nu(^{35}Cl)$ of the compounds measured at 77 K, together with T_m and the "fade-out" temperatures T_f. The fade-out temperature is defined as that temperature at which the ^{35}Cl-NQR signals disappear in the noise (see [6]). Some of the signals fade out at temperatures far below the respective melting point, while others could be observed till the compound melted. No

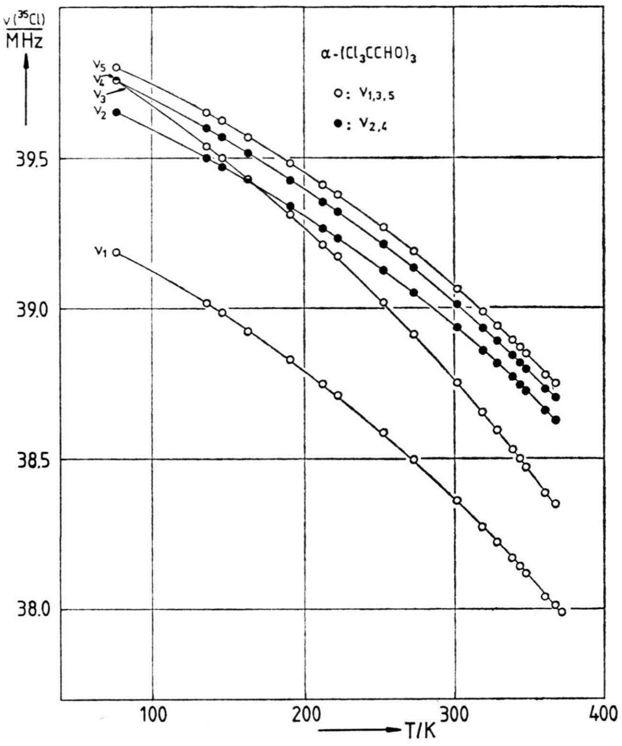


Fig. 1. Temperature dependence of the ^{35}Cl-NQR frequencies in α-parachloral, α-($Cl_3CCHO)_3$.

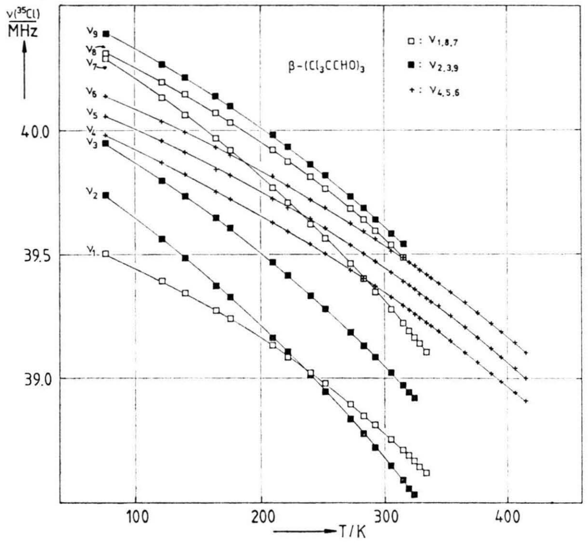


Fig. 2. Temperature dependence of the ^{35}Cl-NQR frequencies in β-parachloral, β-($Cl_3CCHO)_3$.

anomaly was found in the $\nu(^{35}Cl) = f(T)$ curves except for chloralide, which compound shows a reversible phase transformation, chloralide (I) ⇌ chloralide (II) [6].

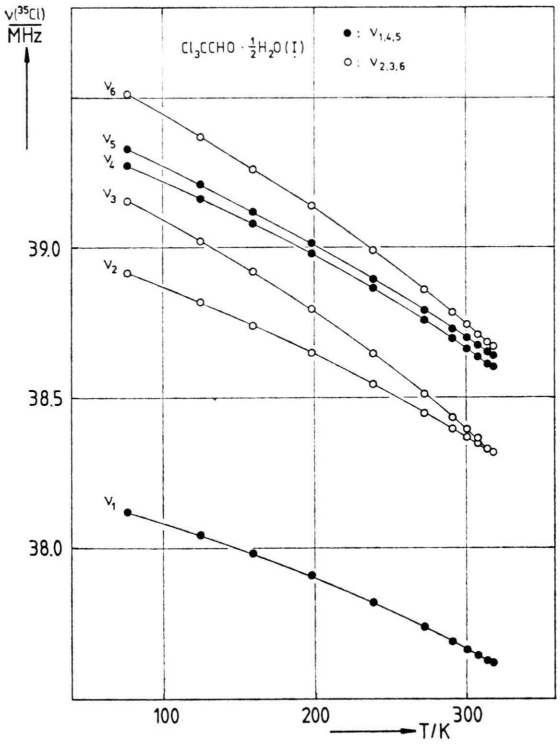


Fig. 3. Temperature dependence of the ^{35}Cl-NQR frequencies in chloral hemihydrate (phase I), $Cl_3CCHO \cdot 1/2\ H_2O$(I).

Discussion

All compounds studied here by ^{35}Cl-NQR are derivatives of chloral, CCl_3CHO, and by the chemical treatment of the compounds the CCl_3 group was not affected. Each of the compounds shows more than three ^{35}Cl-NQR lines at 77 K, an observation which proves that more than one CCl_3 group must exist within the asymmetric unit of the crystallographic unit cell. By the SEDOR technique it was possible to decide which of the ^{35}Cl-NQR lines (the number n of lines at 77 K is $5 \leqq n \leqq 12$ in the compounds studied) belongs to the same CCl_3 group. The relative intramolecular assignment found in this way is shown in Table 3, together with the frequency splitting within one CCl_3 group.

α- and β-parachloral

From ^{1}H-NMR Novak and Walley [15] concluded, that α- and β-parachloral in chloroform solution have C_s and C_3 symmetry, respectively.

The molecular structure of α-parachloral is a six membered ring having chair conformation with one

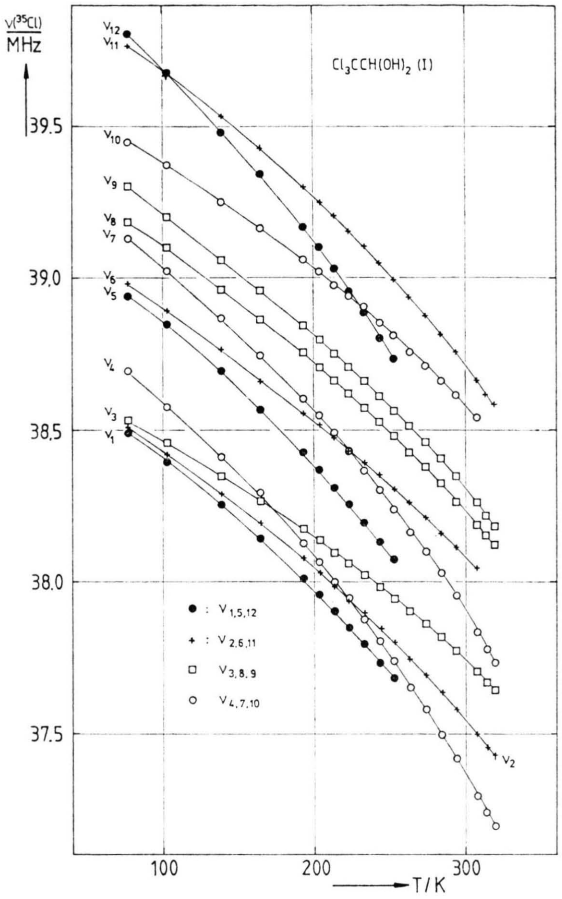


Fig. 4. Temperature dependence of the ^{35}Cl-NQR frequencies in chloral hydrate (phase I), $Cl_3CCH(OH)_2$(I).

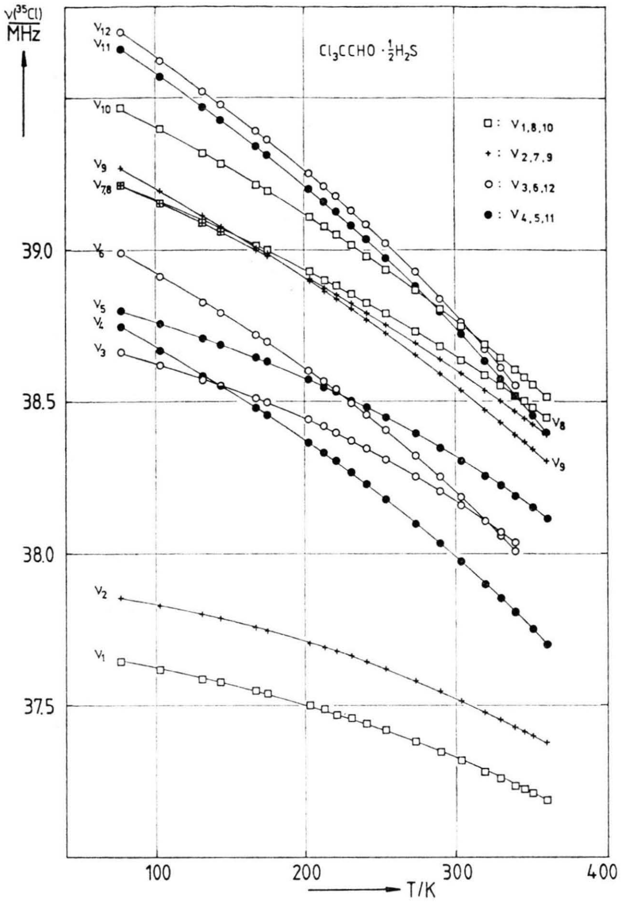


Fig. 5. Temperature dependence of the ^{35}Cl-NQR frequencies in chloral hemithiohydrate, $Cl_3CCHO \cdot 1/2\ H_2S$.

axial and two equatorial CCl_3 groups. In Fig. 6 the structure of the molecule α-parachloral is sketched. Thus a molecule of α-parachloral has nine chlorine atoms, while the solid compound showed a five line ^{35}Cl-NQR spectrum in the temperature range investigated. At 77 K four lines were observed (see Table 2 and Figure 1). This is due to an accidental coalescence of the two lines ν_3, ν_4 to an unresolved doublet at 39.755 MHz. The superposition of two lines at 77 K is confirmed by the $\nu(^{35}\text{Cl}) = f(T)$ measurements (see Fig. 1) and by SEDOR experiments at 77 K and 274.8 K.

The ^{35}Cl-NQR spectrum (SEDOR) indicates that ν_1, ν_3, ν_5 (see Table 3 and Fig. 1) belong to the two equatorial CCl_3 groups and that the two equatorial CCl_3 groups are crystallographically equivalent. The line group b, which consists of two lines (ν_2 and ν_4) is assignable to the axial CCl_3 group. Two of the three chlorine atoms in the axial group are also equivalent. So the molecule must have C_s symmetry in the crystalline state, the same symmetry as in the solution.

Since the intensity of the ^{35}Cl-NQR line ν_2 is two times weaker than that of ν_4, ν_2 belongs to the chlorine atom located on the symmetry plane.

On the other hand β-parachloral loses its C_3 symmetry by the solid state interactions. It becomes totally asymmetric (C_1) as evidenced by the ^{35}Cl-NQR spectrum:

a) Nine lines are observed and
b) SEDOR reveals three CCl_3 groups, each of which is in itself asymmetric (Table 3).

Chloral Hemihydrate

Chloral hemihydrate, $Cl_3CCHO \cdot 1/2\ H_2O$, appears with two crystalline phases. Nothing is known about

Table 1. Coefficients of the power series $\nu(^{35}\mathrm{Cl}) = f(T) = A + B/T + CT + DT^2$. For numbering of ν see Table 2.

Compounds	No of lines	$\frac{A}{\mathrm{MHz}}$	$\frac{B}{\mathrm{K\cdot MHz}}$	$\frac{C\cdot 10^3\,\mathrm{K}}{\mathrm{MHz}}$	$\frac{D\cdot 10^5\,\mathrm{K}^2}{\mathrm{MHz}}$	Temperature range $\Delta T/\mathrm{K}$
α-parachloral	ν_1	39.1793	8.353	− 0.7596	− 0.6783	77−361
	ν_2	39.6555	7.212	− 0.8130	− 0.5516	77−361
	ν_3	39.7907	8.904	− 1.4123	− 0.7040	77−361
	ν_4	39.7602	7.392	− 0.8685	− 0.5617	77−361
	ν_5	39.8022	6.770	− 0.6921	− 0.6058	77−361
β-parachloral	ν_1	39.5342	5.666	− 0.8423	− 0.5789	77−329
	ν_2	39.8956	4.481	− 2.3646	− 0.5819	77−325
	ν_3	39.9965	7.509	− 1.4269	− 0.6056	77−329
	ν_4	40.0715	3.579	− 1.5293	− 0.3112	77−415
	ν_5	40.1327	3.047	− 1.2401	− 0.3597	77−415
	ν_6	40.2191	3.260	− 1.3015	− 0.3337	77−415
	ν_7	40.3934	5.588	− 1.7907	− 0.6287	77−329
	ν_8	40.3024	7.110	− 0.6057	− 0.6486	77−315
	ν_9	40.4446	5.027	− 1.1097	− 0.5771	77−315
Chloralhemihydrate phase I	ν_1	38.1184	4.450	− 0.3977	− 0.3832	77−317
	ν_2	38.9306	5.416	− 0.8261	− 0.3643	77−317
	ν_3	39.1858	6.662	− 1.7000	− 0.5421	77−317
	ν_4	39.3601	2.132	− 1.1861	− 0.3813	77−317
	ν_5	39.3880	5.165	− 1.3957	− 0.3159	77−317
	ν_6	39.5412	6.900	− 1.1894	− 0.5116	77−317
Chloral hydrate phase I	ν_1	38.5016	9.573	− 0.9057	− 0.9798	77−253
	ν_2	38.4560	11.299	− 0.5513	− 0.8779	77−318
	ν_3	38.5185	8.591	− 0.7775	− 0.6403	77−318
	ν_4	38.5797	15.807	− 0.0550	− 1.3968	77−318
	ν_5	39.1385	1.739	− 2.1169	− 0.8391	77−253
	ν_6	39.1221	3.981	− 2.0943	− 0.4770	77−306
	ν_7	38.9697	17.435	0.2542	− 1.3490	77−318
	ν_8	39.1676	10.862	− 1.0042	− 0.7471	77−318
	ν_9	39.2105	15.054	− 0.6569	− 0.8472	77−318
	ν_{10}	39.4191	9.564	− 0.6093	− 0.7696	77−306
	ν_{11}	39.6395	15.901	− 0.1581	− 1.0416	77−318
	ν_{12}	39.6887	18.247	− 0.4354	− 1.4364	77−253
Chloral hemithiohydrate	ν_1	37.6172	3.439	0.0551	− 0.3546	77−361
	ν_2	37.8540	2.021	− 0.0411	− 0.3592	77−361
	ν_3	38.5769	7.512	0.3060	− 0.5801	77−340
	ν_4	38.7532	7.586	− 0.9707	− 0.5536	77−361
	ν_5	38.7529	6.229	− 0.0681	− 0.4837	77−361
	ν_6	38.9472	10.062	− 0.6307	− 0.6523	77−340
	ν_7	39.3068	2.936	− 1.4155	− 0.3167	77−361
	ν_8	39.2323	5.935	− 0.9180	− 0.3620	77−361
	ν_9	39.2897	8.065	− 1.2689	− 0.4235	77−361
	ν_{10}	39.5554	4.290	− 1.5571	− 0.3761	77−361
	ν_{11}	39.6434	10.494	− 1.0267	− 0.6985	77−361
	ν_{12}	39.6424	13.171	− 0.6677	− 0.7816	77−340

their crystal structure; also the relations between $\mathrm{Cl_3CCHO\cdot 1/2\,H_2O(I)}$ and $\mathrm{Cl_3CCHO\cdot 1/2\,H_2O(II)}$ are not clear yet. From the crystallographic point of view the six ^{35}Cl-NQR lines of chloral hemihydrate (I) can be accounted for by one of the two following models: the unit cell contains (1) one molecule in the asymmetric unit with two crystallographically inequivalent $\mathrm{CCl_3}$ groups or (2) two molecules in the asymmetric unit, each having C_s (or C_2) symmetry *. Both models are in accordance with SEDOR experiments and no decision between (1) and (2) is possible on the basis of ^{35}Cl-NQR. Model (1) seems to be the more likely one in accordance with an ether bridged molecular structure. In Fig. 7 the

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* If the molecule maintains the C_3 symmetry in the crystalline state, there must be three independent molecules in the unit cell, to account for a nine line NQR spectrum. This is, however, crystallographically difficult.

Table 2. The ^{35}Cl-NQR frequencies, $\nu(^{35}\mathrm{Cl})$, at 77 K, signal to noise ratios[a], S/N, fade out temperatures, T_f, and melting points, T_m, of some chloral derivatives.

Compounds		ν/MHz	(S/N)	T_f/K	T_m/K
α-parachloral	ν_1	39.188	(53)	370–380 (all of the lines)	389
	ν_2	39.653	(24)		
	$\nu_{3,4}$	39.755	(70)		
	ν_5	39.800	(43)		
β-parachloral	ν_1	39.508	(14)	420 (ν_4, ν_5, ν_6)	425
	ν_2	39.736	(14)		
	ν_3	39.948	(16)		
	ν_4	39.981	(11)	320–335 (the other lines)	
	ν_5	40.054	(10)		
	ν_6	40.141	(15)		
	ν_7	40.290	(12)		
	ν_8	40.309	(8)		
	ν_9	40.390	(15)		
Chloral hemihydrate phase I	ν_1	38.123 [38.123][b]	(11)		321
	ν_2	38.916 [38.904]	(16)		
	ν_3	39.158 [39.160]	(19)		
	ν_4	39.274 [39.280]	(7)		
	ν_5	39.329 [39.327]	(11)		
	ν_6	39.509 [39.508]	(20)		
Chloral hemihydrate phase II	ν_1	38.591 [38.601]	(4)		
	ν_2	38.878 [38.879]	(4)		
	ν_3	38.890 [38.886]	(6)		
	ν_4	39.000 [39.003]	(3)		
	ν_5	39.038 [39.036]	(4)		
	ν_6	39.049 [39.045]	(4)		
	ν_7	39.067 [39.071]	(2)		
	ν_8	39.145 [39.153]	(5)		
	ν_9	39.354 [39.355]	(5)		
	ν_{10}	39.453 [39.451]	(7)		
	ν_{11}	39.741 [39.752]	(6)		
	ν_{12}	39.882 [39.888]	(5)		
Chloral hydrate[c] phase I	ν_1	38.498 [38.519]	(10)	255 (ν_1, ν_5, ν_{12})	328
	ν_2	38.508 [38.538]	(7)		
	ν_3	38.530 [38.550]	(4)		
	ν_4	38.697 [38.711]	(8)		
	ν_5	38.946 [38.956]	(8)		
	ν_6	38.979 [38.991]	(8)		
	ν_7	39.131 [39.141]	(8)		
	ν_8	39.184 [39.194]	(8)		
	ν_9	39.302 [39.306]	(8)		
	ν_{10}	39.450 [39.465]	(8)		
	ν_{11}	39.769 [39.783]	(6)		
	ν_{12}	39.806 [39.816]	(7)		
Chloral hemithiohydrate	ν_1	37.645	(5)	345 (ν_3, ν_6, ν_{12})	411
	ν_2	37.856	(7)		
	ν_3	38.663	(9)		
	ν_4	38.743	(12)		
	ν_5	38.800	(9)		
	ν_6	38.989	(12)		
	$\nu_{7,8}$	39.217[d]	(15)		
	ν_9	39.270	(7)		
	ν_{10}	39.469	(11)		
	ν_{11}	39.660	(13)		
	ν_{12}	39.713	(12)		
Chloralide[e] phase II	ν_1	38.870	(17)	350–360 (ν_1, ν_4, ν_6)	388
	ν_2	38.910	(17)		
	ν_3	39.298	(17)		
	ν_4	39.695	(22)		
	ν_5	39.831	(17)		
	ν_6	40.178	(20)		

[a] S/N measured with lock in technique and a time constant $\tau = 10$ sec.

[b] The frequencies in the paranthese, [ ], correspond to the deuterate.

[c] The data were taken from ref. [3].

[d] The superposition of two lines was confirmed by the frequency vs. temperature relationships.

[e] This compound has a phase transition at 344 K (Ref. [6])

NQR line groups are shown in form of a stick diagram. Twelve ^{35}Cl-NQR lines are found for $Cl_3CCHO\cdot 1/2\,H_2O$ (II). A comparison of the assignment of the frequencies to different CCl_3 groups in phase I and phase II leads to the assumption that the line group a in phase I corresponds to the groups a and a′ in phase II and group b to b and b′. This proposal is based on (1) the large frequency splitting of line group a in phase I and II; and (2) the fact that both groups b show nearly the same frequencies in phase I and phase II. Thus on the basis of the SEDOR experiments one can suggest that the twelve NQR-lines belong to two crystallographically nonequivalent molecules.

Table 3. Line groups as determined by SEDOR and frequency splittings, $\Delta\nu$, of each line group at $T = 77$ K.

Compounds	Line Group	Components	$\Delta\nu$/MHz
α-parachloral *	a	ν_1, ν_2, ν_5	0.61
	b	ν_2, ν_4	0.10
β-parachloral	a	ν_1, ν_7, ν_8	0.80
	b	ν_2, ν_3, ν_9	0.65
	c	ν_4, ν_5, ν_6	0.16
Chloral hemihydrate phase I	a	ν_1, ν_4, ν_5	1.21
	b	ν_2, ν_3, ν_6	0.59
Chloral hemihydrate phase II	a	ν_1, ν_9, ν_{12}	1.29
	a′	ν_3, ν_5, ν_{11}	0.85
	b	ν_2, ν_8, ν_{10}	0.58
	b′	ν_4, ν_6, ν_7	0.07
Chloral hydrate phase I	a	ν_1, ν_5, ν_{12}	1.31
	a′	ν_2, ν_6, ν_{11}	1.26
	b	ν_3, ν_8, ν_9	0.77
	b′	ν_4, ν_7, ν_{10}	0.75
Chloralide phase II	a	ν_1, ν_4, ν_6	1.31
	b	ν_2, ν_3, ν_5	0.92
Chloral hemithiohydrate	a	ν_1, ν_8, ν_{10}	1.82
	a′	ν_2, ν_7, ν_9	1.41
	b	ν_3, ν_6, ν_{12}	1.05
	b′	ν_4, ν_5, ν_{11}	0.92

* Complete assignment by SEDOR has been carried out at $T = 274.8$ K. For the other compounds the assignment to the different line groups was done by SEDOR technique at 77 K.

Chloral Hydrate (I)

SEDOR divides the twelve ^{35}Cl-NQR lines of chloralhydrate (phase I) into four line groups, which correspond to four crystallographically inequivalent CCl_3 groups. Therefore the unit cell of this solid must contain four molecules within the asymmetric unit. In Fig. 7 the spectrum divided up into the different groups is shown. It is noted that the splitting pattern of the line groups a and a′ (and b and b′ also) are strikingly similar to each other. Although four nonequivalent molecules in the solid evidently exist as mentioned above, there seems to be a pseudosymmetry which makes the molecules pairwise almost equivalent.

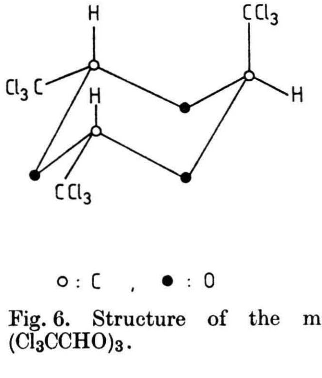


Fig. 6. Structure of the molecule α-parachloral, α $(Cl_3CCHO)_3$.

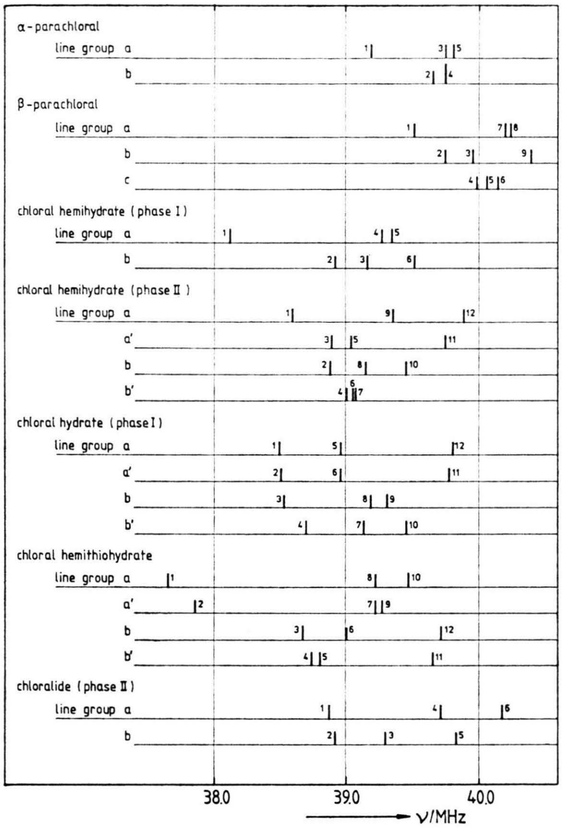
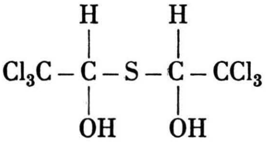


Fig. 7. Stick diagram of the ^{35}Cl-NQR frequencies in several derivates of chloral, CCl_3CHO.

Chloralhemithiohydrate

Chloralhemithiohydrate is assumed to have a thioether structure [10]:



$$Cl_3C-\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}-S-\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}-CCl_3$$

Based on SEDOR, the twelve ^{35}Cl-NQR lines of chloralhemithiohydrate are divided into four line groups shown in Table 3 and Figure 7. The splitting pattern of line group a bears a striking resemblance to that of line group a′. Similarly the splitting patterns of line group b and b′ are quite alike. These facts suggest that line-group a and b belong to one crystallographically independent molecule and the line group a′ and b′ to another molecule. It is interesting to compare the NQR spectra of chloralhemithiohydrate and chloralhemihydrate. The two molecules have a common structure, the former being a thioether and the latter an ether. From this structural similarity one may expect a resemblance between their NQR spectra. In fact the two compounds show quite similar NQR spectra (see Figure 7). It is obvious that the line groups a and a′ of the hemithiohydrate correspond to the line groups α of chloralhemihydrate (I) and chloralhemihydrate (II). These four line groups are characterized by their large frequency splittings. Since this feature is common to the two compounds, the large frequency splitting is attributable to an intramolecular origin. Moreover, it will possibly be of steric nature, because the hemithiohydrate shows much larger splittings.

Frequency Splitting

The magnitude of the frequency splittings of α- and β-parachloral $((\Delta\nu)_\alpha = 0.61$ MHz, $(\Delta\nu)_\beta =$ 0.88 MHz at 77 K) is of the order of the crystal field splitting observed for ^{35}Cl-NQR on chlorine bonded to carbon [16]. In the line group a of chloralhemihydrate (I) the frequency ν_1 is strongly depressed compared to the other lines, whereby a large frequency splitting of $\Delta\nu = 1.21$ MHz results for this group. For sine group a in chloralhemihydrate(II) $\Delta\nu = 1.29$ MHz has been obtained (Table 3). Line groups a and a′ of chloralhydrate(I) exhibit splittings of similar magnitude ($\Delta\nu =$ 1.31 MHz and 1.26 MHz, respectively). Among the compounds studied here, chloralhemithiohydrate shows the largest splitting of almost 2 MHz (group a). The magnitude of these splittings is too large to be explained simply by crystal field effects, because for CCl$_3$ groups they do not exceed 1 MHz [5]. It is tempting to assume Cl . . . H type hydrogen bond formation in crystallized chloralhydrate(I) and chloralhemihydrate (I). However, this assumption should be excluded, at least for $Cl_3CCH(OH)_2$(I) and $Cl_3CCHO \cdot 1/2\ H_2O$(I) because no significant change in $\nu(^{35}Cl)$ was originated by deuteration, as shown in Table 1. For chloralhydrate(II) it has been shown by deuteration experiments that the frequency splitting $\Delta\nu = 1.43$ MHz at 77 K is not due to hydrogen bonds Cl . . . H [3, 17].

The origin responsible for the large $\Delta\nu$'s, in the compounds considered here is most probably intramolecular. In this connection it is interesting to note that the largest splitting observed was for $Cl_3CCHO \cdot 1/2\ H_2S$, a compound in which one of the neighbours of the CCl$_3$ group is the bulky sulfur atom.

Fade Out

It is well known that the Cl-NQR signals of CCl$_3$ groups often fade out at temperatures far below the melting point. This phenomenon has been ascribed to the occurance of reorientational motions of the group around its three fold axis [18]. In general T_f tends to rise with increasing magnitude of the potential barrier which hinders the reorientational motion [19 – 22]. For the compounds studied here, most of the T_f are higher than 320 K, except for the line group a of $Cl_3CCH(OH)_2$(I). $T_{f,max} = 420$ K was found for chloralide (II), line group a. These values are much higher than those found for CCl$_3$ groups in trichloroacetates [5]. In both cases a CCl$_3$ group has the configuration COO as neighbours, but the electronic configurations of the carbon attached to Cl$_3$C differ from each other. It is sp^3 (chloral derivatives) and sp^2 (trichloroacetates), respectively. Thus it can be seen that the reorientational motion of CCl$_3$ groups attached to C(sp^3) is much more hindered by a potential barrier higher than that of Cl$_3$C-C(sp^2).

One of the three CCl$_3$ groups of β-parachloral differs in T_f considerably from the two other groups. This difference is induced by intermolecular forces because in solution the three CCl$_3$ groups are equivalent. A detailed discussion on this point, however, rests on the knowledge of the crystal structure.

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