Nuclear Quadrupole Resonance Study of ^{35}Cl in Chloral Hydrate, $CCl_3CH(OH)_2$, and Chloral Deuterate, $CCl_3CH(OD)_2$

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The nuclear quadrupole resonance (NQR) spectra of ^{35}Cl in chloral hydrate and chloral deuterate were investigated in the temperature range between 77 °K and 323 °K. Two modifications have been found for each substance. One of the modifications is unstable at room temperature and changes within a few weeks into the stable modification. The NQR spectrum can be explained in terms of crystal field effects.

In 1952, Allen [1] has studied the nuclear quadrupole resonance (NQR) spectrum of chloral hydrate, $CCl_3CH(OH)_2$. In the temperature range between 77 °K and room temperature he found a three line spectrum for ^{35}Cl. The three lines have equal intensity. At 77 °K the NQR frequencies of ^{35}Cl in $CCl_3CH(OH)_2$ are 39.515 MHz, 39.429 MHz, and 38.190 MHz. The large splitting in this spectrum ($|\Delta\nu|_{max} = 1.3$ MHz) was interpreted by Allen in terms of the crystal structure of chloral hydrate. At room temperature the crystal structure as determined by Kondo and Nitta [2] shows three different C – Cl-distances (1.72 Å; 1.78 Å; and 1.79 Å) within one CCl_3-group. Kondo and Nitta proposed that the two Cl-atoms within a CCl_3-group, which belong to the longer C – Cl-distances 1.78 Å and 1.79 Å are bonded by hydrogen bridge bonds to the OH-groups of the next nearest molecules. This argument was used by Allen in interpreting the NQR spectrum: The two upper frequencies belong to the two chlorine atoms bonded to the next nearest molecules by hydrogen bridge bonds; the lower NQR frequency belongs to the third Cl atom with the C – Cl-distance of 1.72 Å. In a later paper, Allen [3] argues that by theoretical arguments the Cl atoms involved in a hydrogen bridge bond should show up a lower NQR frequency than the non-bonded atoms. This argument, however, introduces some difficulties into the discussion of the NQR spectrum in terms of the crystal structure. An interesting experimental fact was mentioned by Allen [1]: Freshly prepared chloral hydrate (by reaction of chloral and water or by crystallising from a melt) has to be kept at room temperature over a period of about three months until NQR on ^{35}Cl may be observed.

In course of investigations [4] of the crystal field influence on NQR spectra of ^{35}Cl in molecular compounds and salts of trichloroacetic acid, CCl_3COOH, we have also looked for the ^{35}Cl resonance in chloral hydrate. Chloral deuterate, $CCl_3CH(OD)_2$, was also investigated by NQR. The chloral deuterate was synthesized by reaction of chloral with deuterium oxide:

$$CCl_3CHO + D_2O \rightarrow CCl_3CH(OD)_2 .$$

For the NQR work a simple superregenerative spectrometer was used and the resonances were observed on the oscilloscope.

Results

Chloral hydrate from chloral and water freshly prepared or immediately after crystallisation from a melt shows no ^{35}Cl signal at room temperature. The same observation was made for $CCl_3CH(OD)_2$. At 77 °K the two substances show ^{35}Cl spectra, each of which consists of 12 lines. The lines were found in the frequency range between 38.5 MHz and 39.8 MHz. This modification of chloral hydrate (deuterate, respectively) is called modification (I). In Table 1 the resonance frequencies of $CCl_3CH(OH)_2$ (I) and $CCl_3CH(OD)_2$ (I) are listed. After the substances are kept at room temperature for a time of about two weeks from preparation or crystallisation from a melt both the chloral hydrate and the chloral deuterate show a three line ^{35}Cl NQR spec-

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[1] H. C. Allen jr., J. Am. Chem. Soc. **74**, 6074 [1952].

[2] S. Kondo and I. Nitta, Struct. Repts. **13**, 448 [1950].

[3] H. C. Allen jr., J. Phys. Chem. **57**, 501 [1953].

[4] D. Biedenkapp and A. Weiss, Ber. Bunsenges. Physik. Chem. **70**, 788 [1966].

	ν_H MHz	ν_D MHz	$\nu_D - \nu_H$ kHz
a) **77**°K			
Modification (I)	39.806	39.816	10
	39.769	39.783	14
	39.450	39.465	15
	39.302	39.306	4
	39.184	39.194	10
	39.131	39.141	10
	38.979	38.991	12
	38.946	38.956	10
	38.697	38.711	14
	38.530	38.550	20
	38.508	38.538	30
	38.498	38.519	21
Modification (II)	39.515	39.527	12
	39.429	39.441	12
	38.190	38.209	19
b) **23**°*C*			
Modification (II)	38.791	38.796	5
	38.706	38.713	7
	37.518	37.533	15

Table 1. ^{35}Cl NQR frequencies of chloral hydrate (ν_H) and chloral deuterate (ν_D).

trum. The spectrum can be easily observed between 323 °K and 77 °K. This second modification which in case of $CCl_3CH(OH)_2$ was observed by ALLEN is called modification (II). The resonance frequencies of this modification are given in Table 1. The temperature dependence of the NQR frequencies of ^{35}Cl in this modification is shown in Fig. 1. In the scale of Fig. 1 the difference in the ^{35}Cl NQR frequencies of the two substances $CCl_3CH(OH)_2$ (II) and $CCl_3CH(OD)_2$ (II) is not visible. The temperature dependence follows the theory of BAYER[5]:

$$\nu = a - b / (e^{c/T} - 1) . \qquad (1)$$

In Table 2 the parameters a, b, and c are given.

	a MHz	b MHz	c °K
$CCl_3CH(OH)_2$ (II)	39.525	1.396	315.0
	39.435	1.477	327.2
	38.195	1.337	322.2
$CCl_3CH(OD)_2$ (II)	39.551	1.453	317.5
	39.462	1.529	328.4
	38.231	1.355	319.1

Table 2. Parameters a, b, and c in Eq. (1).

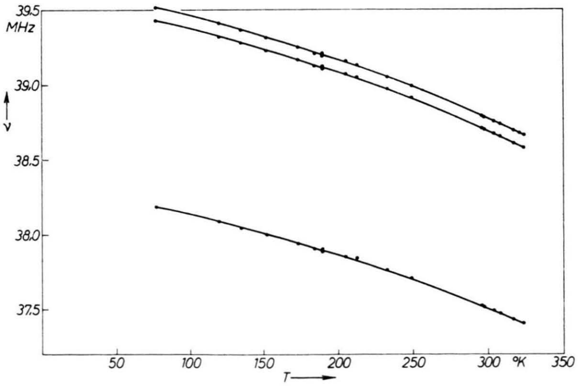

Fig. 1. The temperature dependence of ^{35}Cl NQR frequencies in $CCl_3CH(OH)_2$ (II).

Discussion

The NQR spectra of chloral hydrate and chloral deuterate reveal the existence of two modifications, (I) and (II). Modification (I) which appears first in course of synthesis from chloral and water or by crystallisation from a melt changes into modification (II) in 2 – 3 weeks. Modification (II) seems to be the stable phase at room temperature. From NQR spectra we cannot tell about the kinetics of the phase transformation. The 12 line spectrum of modification (I) shows that there are at least 4 crystallographically non-equivalent molecules in the elementary cell of $CCl_3CH(OH)_2$ (I) and $CCl_3CH(OD)_2$ (I). The transformation (I) → (II) cannot be due to a freezing in of internal rotations of the CCl_3-group in the molecules, since the NQR spectrum of phase (I) is observable at 77 °K. In the case of internal rotations the spectrum should not be observable up to the melting point of the phase (II).

All the ^{35}Cl NQR frequencies in the deuterated compound are a few kHz higher than the equivalent frequencies in the hydrated compound (Table 1). The maximum shift is 30 kHz. A comparable shift between a protonated and deuterated compound is known from monochloroacetic acid[3]. The strength of the hydrogen bridge bond is changed by going from hydrogen to deuterium. Therefore one expects that the NQR frequency of a chlorine atom bonded to an oxygen via a hydrogen bridge bond changes much more by isotopic substitution than the frequency of a Cl atom with a simple C – Cl-bond. The very small differences between the ^{35}Cl NQR spectra of $CCl_3CH(OH)_2$ (II) and $CCl_3CH(OD)_2$ (II) do not support ALLEN's explanation based on the crystal structure determination of KONDO and NITTA. A Cl–H–O or Cl–D–O bridge bond seems unlikely.

[5] H. BAYER, Z. Physik **130**, 227 [1951].

The large splitting of the ^{35}Cl NQR spectra of the modification (II) of the chloral hydrate and deuterate appears also in the spectra of the modifications (I). In the latter case the 12 lines of the spectrum are almost regularly scattered over the frequency range between the maximum frequency and the minimum frequency. There is no sign of two groups of frequencies belonging to hydrogen (deuterium) bonded chlorine atoms and to not hydrogen bonded atoms. In Fig. 2 a distribution curve of the ^{35}Cl NQR frequencies of 37 CCl_3COOH-compounds and -salts is given together with the NQR spectra of chloral hydrate (I) and (II). The figure shows that the large frequency spread of the ^{35}Cl NQR is within the distribution curve. Therefore we propose that the large splitting within the ^{35}Cl spectra of chloral hydrate and deuterate is due to crystal field effects.

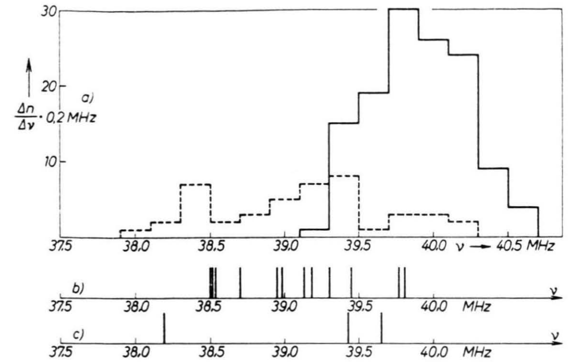

Fig. 2. The ^{35}Cl spectra of $CCl_3CH(OH)_2$ (I) and $CCl_3CH(OH)_2$ (II) in comparison with the ^{35}Cl NQR frequency distribution in 37 CCl_3COOH-molecular compounds and salts. a) $\Delta n/\Delta\nu$ (number of NQR frequencies within a range $\Delta\nu = 200$ kHz) as function of the resonance frequency ν at 77 °K. The curve — — — belongs to the salts, the curve ——— to the molecular compounds. b) ^{35}Cl NQR spectrum of $CCl_3CH(OH)_2$ (I) at 77 °K. c) ^{35}Cl NQR spectrum of $CCl_3CH(OH)_2$ (II) at 77 °K.

Conclusion

The ^{35}Cl NQR spectra of chloral hydrate and chloral deuterate have been investigated in the temperature range between 77 °K and 323 °K. The spectra show the existence of a stable and an unstable phase for each compound. The phase transformation is not due to the liberation of internal rotations of the CCl_3-group within the molecules. NQR does not support the assumption of hydrogen (deuterium) bridge bonds Cl–H–O or Cl–D–O in chloral hydrate and chloral deuterate. The large frequency splitting within the NQR spectra of these compounds is caused by crystal field effects.