^{35}Cl NQR in Solid Trichloroacetyl Halides *

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By ^{35}Cl NQR the temperature dependences of the resonance frequencies and spin-lattice relaxation times for the ^{35}Cl nuclei have been studied in solid CCl_3COHal (Hal = F, Cl, Br, I). A linear correlation between the average ^{35}Cl NQR frequencies of the CCl_3 groups and the electronegativities of the halogen atoms in the COHal groups has been discovered. The temperature-dependent NQR data reveal thermoactivated reorientations of the CCl_3COHal molecules as a whole in the crystal lattice. The activation energies of this motion are found to lie in the range 31–37 kJ mol^{-1}.

Key words: NQR spectroscopy, Molecular motion, Trichloroacetyl halides.

Introduction

This paper present the results of a ^{35}Cl NQR study of CCl_3COHal compounds (Hal = F, Cl, Br, I) in which the NQR parameters of the CCl_3 group are used as an indicator of both the "Hal" atom intramolecular effect and the peculiarities of librational and thermoactivated molecular motions. The halogen atom of the COHal segment influences the ^{35}Cl NQR of the CCl_3 group, in that the resonance frequency of quadrupole nuclei depends on the electronegativity of the neighbour atoms [1]. The molecular mobility shows the typical temperature behaviour of the NQR spectral and relaxation parameters in the case of molecular librations or reorientations in crystals [2]. In the present work, a complete temperature-dependent ^{35}Cl NQR study has been performed for all four trichloroacetyl halides (at 77 K the ^{35}Cl NQR frequencies of CCl_3COCl have previously been measured by Allen [3]).

Experimental

The ^{35}Cl NQR spectra of the title compounds were obtained with a pulsed NQR spectrometer. The temperature dependences of the NQR frequencies ν and spin-lattice relaxation times T_1 for the ^{35}Cl nuclei were measured using a nitrogen gas flow cryostat from 77 K to the samples melting points, giving an accuracy of ± 0.5 K. The error of the ^{35}Cl NQR frequencies was about ± 5 kHz. The values of T_1 were measured by means of the "progressive saturation" pulsed method with an error of about 10%. The temperature-dependent data were processed using a standard least squares procedure.

Results and Discussion

In solid CCl_3COHal compounds (Hal = F, Cl, Br, I) the ^{35}Cl NQR spectra of the CCl_3 group consist of three lines due to the molecular and crystal nonequivalence of the chlorine atoms (see Table 1). That is why we have characterized the CCl_3 groups by the average NQR frequency values. There is a correlation between the average ^{35}Cl NQR frequencies $\nu_{Av}^{CCl_3}$ (at 77 K) of the CCl_3 groups and the electronegativities X_{Hal} of the halogen atoms [4] of the COHal segments (Figure 1). The least squares analysis gives

$$\nu_{Av}^{CCl_3}(\mathrm{MHz}) = 38.964 + 0.456 \cdot X_{Hal}, \qquad (1)$$

the correlation coefficient is $r = 0.999 \pm 0.001$, and the standard deviation is $\sigma = 0.011$ MHz.

The character of the temperature variation of the ^{35}Cl NQR frequencies of the CCl_3 groups is the same in the four investigated crystals (see Figure 2). The temperature dependences of the resonance frequencies of all the ^{35}Cl nuclei can be approximated by [5]

$$\nu(T) = a_0 - a_1 T - a_2 T^2, \qquad (2)$$

where a_0, a_1, and a_2 are listed in Table 1. Good agreement between the experimental NQR frequencies and

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Table 1. ^{35}Cl NQR spectra and the parameters of (2) for crystalline CCl_3COHal (Hal = F, Cl, Br, I).

Hal	X_{Hal}*	Assignment	NQR line No	77 K		Parameters of (2)			
				ν (MHz)	$\nu_{Av}^{CCl_3}$ (MHz)	a_0 (MHz)	$a_1 \cdot 10^3$ (MHz K^{-1})	a_2 (MHz K^{-2})	$\sigma_\nu \cdot 10^3$** (MHz)
F	4.0	CCl_3	1	41.273		41.4807	1.584	$1.389 \cdot 10^{-5}$	3.9
			2	40.928	40.79	41.1634	1.971	$1.387 \cdot 10^{-5}$	3.9
			3	40.167		40.3596	1.464	$1.295 \cdot 10^{-5}$	3.2
Cl	3.2	CCl_3	1	40.614		40.9260	3.307	$9.605 \cdot 10^{-6}$	3.0
			2	40.473	40.41	40.7080	2.410	$8.156 \cdot 10^{-6}$	2.9
			3	40.132		40.3943	2.498	$1.181 \cdot 10^{-5}$	2.8
		COCl	4	33.720		33.9986	2.785	$1.122 \cdot 10^{-5}$	2.6
Br	3.0	CCl_3	1	40.647		40.8852	1.884	$1.550 \cdot 10^{-5}$	3.1
			2	40.336	40.34	40.6215	3.364	$4.267 \cdot 10^{-6}$	3.6
			3	40.023		40.3191	3.100	$9.548 \cdot 10^{-6}$	4.3
I	2.6	CCl_3	1	40.720		40.9946	2.947	$8.873 \cdot 10^{-6}$	4.5
			2	40.015	40.15	40.2998	3.184	$7.554 \cdot 10^{-6}$	4.4
			3	39.713		39.9071	1.825	$1.001 \cdot 10^{-5}$	4.7

* X_{Hal} is the electronegativity of the halogen atoms. ** σ_ν is the standard deviation of the experimental points.

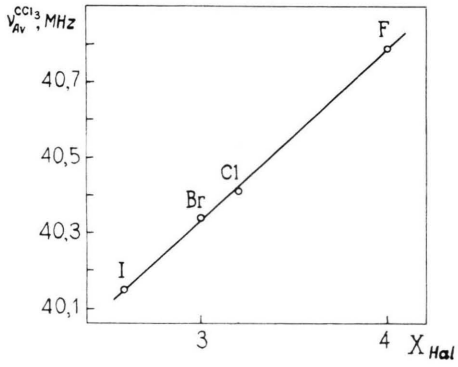

Fig. 1. Dependence of the average ^{35}Cl NQR frequencies $\nu_{Av}^{CCl_3}$ (at 77 K) of the CCl_3 groups on the halogen atom electronegativity X_{Hal} in CCl_3COHal compounds (Hal = F, Cl, Br, I). The solid straight line corresponds to (1).

their approximation (2) is evidence of the quasi-harmonic character of the thermal molecular librations [5, 6] in crystalline CCl_3COHal compounds.

In all four solid trichloroacetyl halides, in addition to the librational molecular motion there is a thermoactivated motion which leads to the fading of the ^{35}Cl NQR signals at temperature T_f (see Table 2). At temperatures preceding the signal disappearance, an exponential shortening of the relaxation time T_1 with

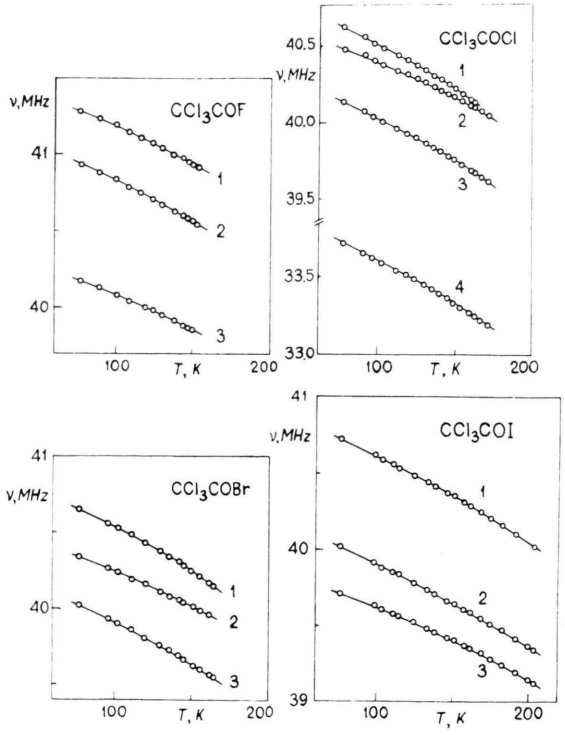

Fig. 2. Temperature dependences of the ^{35}Cl NQR frequency ν in crystalline CCl_3COHal (Hal = F, Cl, Br, I). The solid curves were calculated from (2) by using the parameters listed in Table 1.

Table 2. The parameters of (3) for crystalline CCl_3COHal (Hal = F, Cl, Br, I).

Hal	NQR line No	T_f* (K)	a ($s^{-1}K^{-n}$)	n	b (s^{-1})	E_a (kJ mol^{-1})
F	1, 2, 3	155	$5.14 \cdot 10^{-4}$	2.31	$3.76 \cdot 10^{14}$	35.4
Cl	1, 3	175	$8.29 \cdot 10^{-2}$	1.38	$2.91 \cdot 10^{13}$	36.0
	2	175	$3.98 \cdot 10^{-3}$	1.92	$1.37 \cdot 10^{14}$	38.4
	4	175	$3.95 \cdot 10^{-2}$	1.50	$4.84 \cdot 10^{13}$	36.6
Br	1, 3	170	$2.08 \cdot 10^{-3}$	2.17	$9.91 \cdot 10^{11}$	30.9
	2	170	$3.65 \cdot 10^{-4}$	2.41	$1.21 \cdot 10^{12}$	31.6
I	1, 2, 3	205	$5.59 \cdot 10^{-4}$	2.31	$1.22 \cdot 10^{12}$	33.8

* T_f is the fading temperature of the ^{35}Cl NQR signal.

decreasing reciprocal temperature T^{-1} is observed for the ^{35}Cl nuclei. This indicates that the chlorine atoms of the CCl_3COHal crystals participate in an Arrhenius type thermoactivated jump motion.

The observed temperature dependence of the ^{35}Cl spin-lattice relaxation rate can be described by an equation including two contributions which express the effects of two independent relaxation mechanisms connected with the librational molecular motion and the thermally activated molecular motion (the former dominates at lower temperatures) [2, 7]:

$$(T_1^{-1})_{obs} = (T_1^{-1})_{libr} + (T_1^{-1})_{t.a.} = a\,T^n + b\exp(-E_a/R\,T). \quad (3)$$

The parameters a, b, n, and E_a (the activation energy of the thermoactivated motion) obtained by standard fitting of the experimental data are given in Table 2.

In the case of crystalline CCl_3COCl the ^{35}Cl dependence $T_1(T)$ shows that all the chlorine atoms of the molecule perform an Arrhenius type termoactivated jump motion (see Figure 3). The shortening of the time T_1 is followed by the fading of the ^{35}Cl NQR lines of all four chlorine atoms at the same temperature $T_f = 175$ K. The activation energies (E_a) of 37.2 and 36.6 kJ mol^{-1} (Table 2) have been estimated by means of $T_1(T)$ data processing for the CCl_3 group and the COCl segment, respectively. The E_a values have been obtained from (3) with an uncertainty of 5–7%, therefore the above-mentioned activation energies are practically equal. All these results, together with the shape of the $T_1(T)$ curves in Fig. 3 demonstrate that

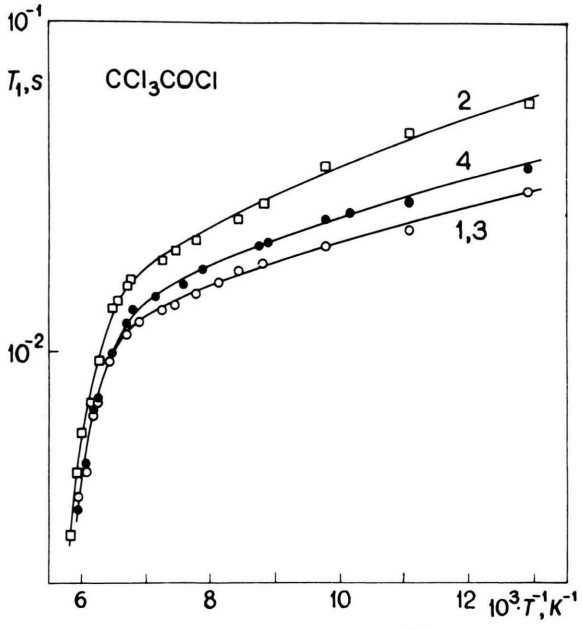

Fig. 3. Temperature dependence of T_1 of ^{35}Cl in crystalline CCl_3COCl. The notations 1, 2, 3 (CCl_3 group) and 4 (COCl segment) correspond to the ^{35}Cl NQR line numbers in Table 1. The solid curves were calculated from (3) by using the parameters listed in Table 2.

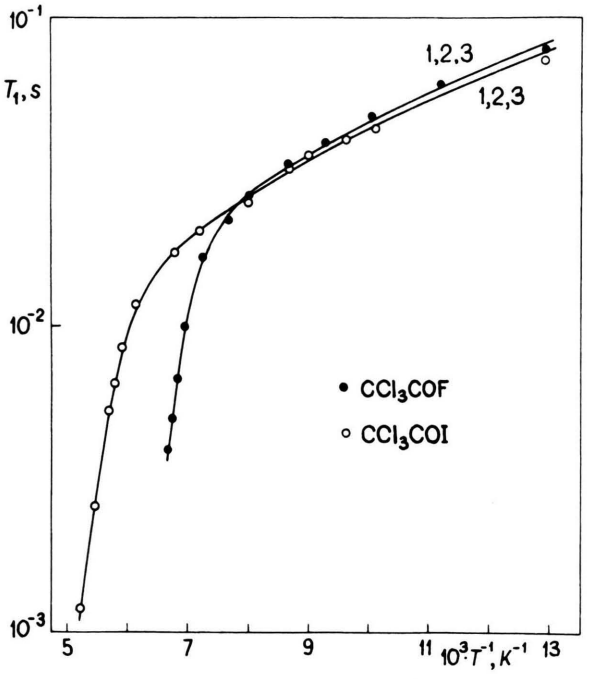

Fig. 4. Temperature dependence of T_1 of ^{35}Cl in crystalline CCl_3COF (•) and CCl_3COI (○). The values of T_1 are averages for the ^{35}Cl NQR lines No 1, 2, 3 (see Table 1) of these compounds. The solid curves were calculated from (3) by using the parameters listed in Table 2.

both the CCl_3 group and the COCl segment take part in the same motion, which is reorientation of the CCl_3COCl molecule as a whole in the crystal lattice.

As is seen from Fig. 4 in solid CCl_3COF and CCl_3COI the dependences $T_1(T)$ of ^{35}Cl demonstrate the presence of thermoactivated motions in these crystals, too. The E_a values of the motions are listed in Table 2.

In solid CCl_3COBr the temperature dependence of T_1 is analogous to the one of the other trichloroacetyl halides. Also the activation energy of the motion in this crystal is similar to the E_a values in the other CCl_3COHal compounds (see Table 2).

Thus there are reasons to believe that in all solid trichloroacetyl halides the thermoactivated molecular motion occurs in a similar manner, i.e. as the reorientations of the molecules as a whole with almost the same E_a values.

As is known, the CCl_3 groups can in solids reorient about their respective C_3 pseudosymmetry axes, and this motion can be strongly hindered by intra- or intermolecular interactions (a role of the latter can be significant [7]). The situation concerning the CCl_3-reorientations becomes clear from the temperature NQR behaviour of the "check" chlorine nuclei placed in the other molecular segment of CCl_3COCl. Apparently in the case of the CCl_3COHal crystals the E_a values corresponding to the motions of the compact molecules are smaller than those corresponding to the CCl_3 group reorientations.

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