^{35}Cl NQR and Molecular Motion in Solid C_6X_5Cl (X = H, F)*

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The ^{35}Cl NQR frequency and spin-lattice relaxation time of solid chlorobenzene and chloropentafluorobenzene at temperatures from 77 K to the melting points have been measured and explained by thermoactivated librations and reorientations of the molecules around the normal to their plane. The activation energies of these motions have been estimated.

Key words: NQR spectroscopy, Molecular motion, Benzene derivatives.

In crystalline benzene, hexafluorobenzene, hexachlorobenzene, and hexamethylbenzene the molecules are able to reorient around their hexad axis.The motion is activated with energies which are listed in Table 1. The E_a values were obtained from NMR and NQR studies [1–16].

In this paper we report on the molecular motion in crystalline chlorobenzene, C_6H_5Cl ($T_{mp} = 227$ K) and chloropentafluorobenzene, C_6F_5Cl ($T_{mp} = 258$ K), at temperatures from 77 K up to the melting points, as studied with ^{35}Cl NQR techniques using a standard pulse spectrometer.

The ^{35}Cl NQR spectra in crystalline C_6H_5Cl and C_6F_5Cl at 77 K were measured earlier [17]. The temperature dependences of the ^{35}Cl resonance frequencies obtained by us are shown in Fig. 1 (the C_6H_5Cl dependence $\nu(T)$ coincides with that described in [18, 19]). The curves $\nu(T)$ are approximated by the equation [20]

$$\nu(T) = \nu_0 - AT - BT^2, \quad (1)$$

where ν_0, A, and B are parameters listed in Table 2.

Figure 1 shows that the experimental data of $\nu(T)$ correspond well to the curves calculated from (1). Consequently, in C_6H_5Cl and C_6F_5Cl crystals the thermal librations of the molecules are quasi-harmonic (see [21]).

In addition to the librational motion there is a thermoactivated motion of the C_6H_5Cl and C_6F_5Cl molecules. On heating, the ^{35}Cl resonance lines tend to fade, and in the C_6F_5Cl crystal the NQR signal disappears about 100 K below the melting point (in the C_6H_5Cl crystal the resonance line broadens up to the melting point and the NQR signal becomes weak). This NQR line phenomenon in accompanied by an exponential shortening of the relaxation time T_1 of the ^{35}Cl nuclei with decreasing T^{-1} (Fig. 1), indicating an Arrhenius type thermoactivated jump motion. The jump motion apparently is a reorientation of the molecules around the axis which is perpendicular to the plane of the benzene ring.

As is seen from Fig. 1, the ^{35}Cl dependences $T_1(T)$ consists of two parts, indicating two independent spin-lattice relaxation mechanisms: librational and reorientational ones (the former dominates at lower temperatures). Accordingly, the ^{35}Cl relaxation rate may

Table 1. The values of the activation energy E_a of the molecular hexad reorientations in solid benzene and its hexa-substituted derivatives.

Compound	E_a, kJ mol^{-1}
C_6H_6	16–18 [2–9]
C_6F_6	12–14 and 29–31 [10–12]*
C_6Cl_6	53–61 [13–15]
$C_6(CH_3)_6$	27–28 [5, 16, 17]

* Two crystallographically non-equivalent molecular sites.

Table 2. ^{35}Cl NQR spectra and the parameters of (1) for crystalline C_6H_5Cl and C_6F_5Cl.

Compound	ν at 77 K (MHz)	ν_0 (MHz)	$A \cdot 10^4$ (MHz K^{-1})	$B \cdot 10^5$ (MHz K^{-2})
C_6H_5Cl	34.621	34.7490	4.848	1.602
C_6F_5Cl	39.410	39.5212	3.172	1.379

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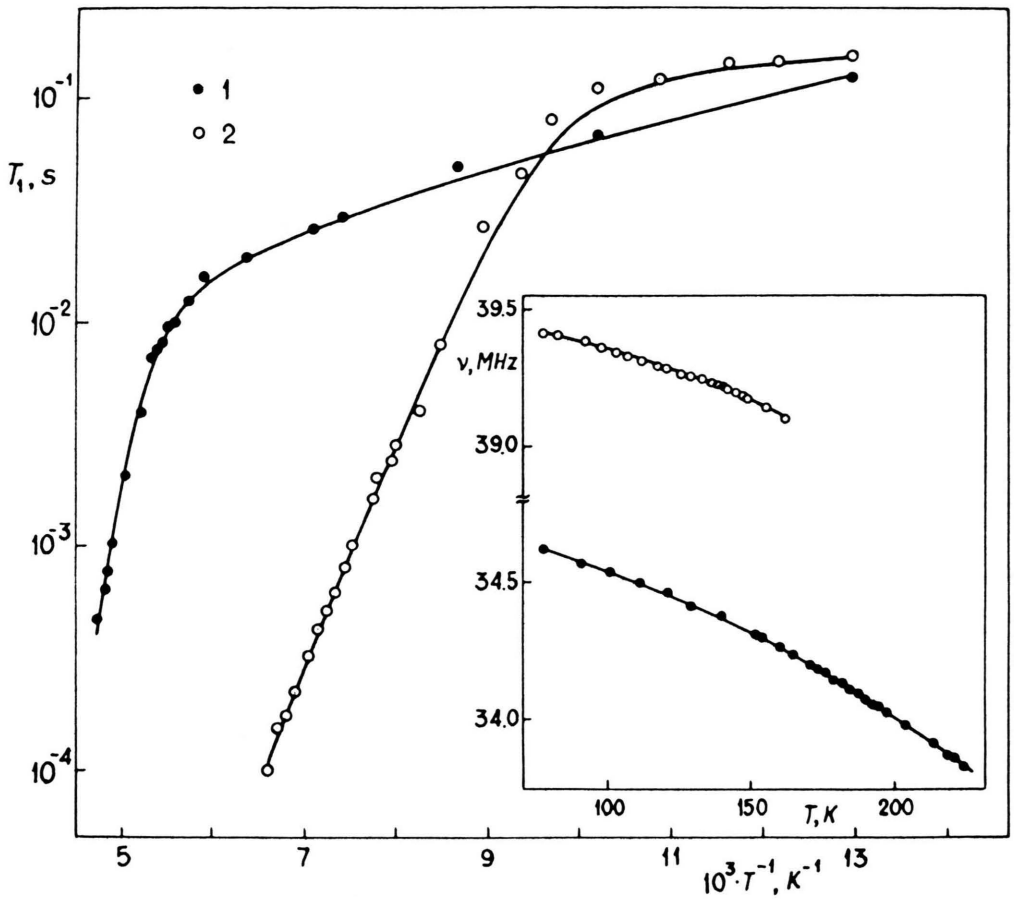

Fig. 1. Temperature dependence of the ^{35}Cl NQR T_1 and ν (inset) in crystalline C_6H_5Cl (•) and C_6F_5Cl (○). The solid curves were calculated from (1) and (2) by using the parameters listed in Tables 2 and 3, respectively.

Table 3. The parameters of (2) for crystalline C_6H_5Cl and C_6F_5Cl.

Compound	a ($s^{-1}K^{-n}$)	n	b (s^{-1})	E_a (kJ mol^{-1})
C_6H_5Cl	$8.67 \cdot 10^{-5}$	2.63	$7.47 \cdot 10^{13}$	41.8
C_6F_5Cl	$4.05 \cdot 10^{-2}$	1.17	$3.40 \cdot 10^{10}$	18.7

be presented as [22]

$$T_1^{-1}(T) = (T_1^{-1})_{libr} + (T_1^{-1})_{reor} = a\,T^n + b\exp(-E_a/RT). \quad (2)$$

Here a, n, b, and E_a (the activation energy of the molecular reorientations) are parameters which are obtained by least squares fitting and are given in Table 3.

Thus the NQR method reveals reorientations of molecules that are asymmetric with respect to the motion axis. In solids such molecular motion occurs between unequal potential wells. In our case the activation energies E_a (41.8 and 18.7 kJ mol^{-1} in C_6H_5Cl and C_6F_5Cl, respectively) describe motions from a metastable orientation into a stable one [23]. It should be noted that the E_a values found for C_6H_5Cl and C_6F_5Cl crystals lie in the range of the values listed in Table 1.

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