$^{35}\text{Cl} \text{ NQR and Molecular Motion in Solid } \text{C}_6\text{X}_5\text{Cl} (X = \text{H, F})$

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The $^{35}\text{Cl} \text{ NQR frequency and spin-lattice relaxation time of solid chlorobenzene and chloro-

pentafluorobenzene 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, hexa-
chlorobenzene, 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, $\text{C}_6\text{H}_5\text{Cl}$ ($T_{mp} = 227 \text{ K}$) and 
chloropentafluorobenzene, $\text{C}_6\text{F}_5\text{Cl}$ ($T_{mp} = 258 \text{ K}$), at temperatures from 77 K up to the melting points, as studied with $^{35}\text{Cl} \text{ NQR techniques using a standard 
pulse spectrometer.}$

The $^{35}\text{Cl} \text{ NQR spectra in crystalline } \text{C}_6\text{H}_5\text{Cl}$ and 
$\text{C}_6\text{F}_5\text{Cl}$ at 77 K were measured earlier [17]. The tempera-
ture dependences of the $^{35}\text{Cl} \text{ resonance frequen-
ties obtained by us are shown in Fig. 1 (the } \text{C}_6\text{H}_5\text{Cl} 
dependence } v(T) \text{ coincides with that described in 
[18, 19]). The curves } v(T) \text{ are approximated by the 
equation [20].}

$$v(T) = v_0 - AT - BT^2,$$

(1)

where $v_0$, $A$, and $B$ are parameters listed in Table 2.

Figure 1 shows that the experimental data of $v(T)$ 
correspond well to the curves calculated from (1). 
Consequently, in $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{F}_5\text{Cl}$ crystals the thermal librations of the molecules are quasi-har-
monic (see [21]).

In addition to the librational motion there is a ther-
moactivated motion of the $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{F}_5\text{Cl}$
molecules. On heating, the $^{35}\text{Cl}$ resonance lines tend 
to fade, and in the $\text{C}_6\text{F}_5\text{Cl}$ crystal the NQR signal 
disappears about 100 K below the melting point (in 
the $\text{C}_6\text{H}_5\text{Cl}$ 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 
$^{35}\text{Cl}$ nuclei with decreasing $T$ (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 $^{35}\text{Cl}$ dependences $T_1(T)$ 
consists of two parts, indicating two independent spin-
lattice relaxation mechanisms: librational and reori-
entational ones (the former dominates at lower tem-
peratures). Accordingly, the $^{35}\text{Cl}$ relaxation rate may

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_5\text{Cl}$</td>
<td>16–18 [2–9]</td>
</tr>
<tr>
<td>$\text{C}_6\text{F}_5\text{Cl}$</td>
<td>12–14 and 29–31 [10–12]</td>
</tr>
<tr>
<td>$\text{C}_6\text{Cl}_6$</td>
<td>53–61 [13–15]</td>
</tr>
<tr>
<td>$\text{C}_6(\text{CH}_3)_6$</td>
<td>27–28 [5, 16, 17]</td>
</tr>
</tbody>
</table>

* Two crystallographically non-equivalent molecular sites.

Table 2. $^{35}\text{Cl} \text{ NQR spectra and the parameters of (1) for 
crystalline } \text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{F}_5\text{Cl}.$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$ at 77 K (MHz)</th>
<th>$v_0$ (MHz)</th>
<th>$A \cdot 10^4$ (MHz K$^{-1}$)</th>
<th>$B \cdot 10^5$ (MHz K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_5\text{Cl}$</td>
<td>34.621</td>
<td>34.7490</td>
<td>4.848</td>
<td>1.602</td>
</tr>
<tr>
<td>$\text{C}_6\text{F}_5\text{Cl}$</td>
<td>39.410</td>
<td>39.5212</td>
<td>3.172</td>
<td>1.379</td>
</tr>
</tbody>
</table>

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be presented as [22]

\[ T_1^{-1}(T) = (T_1^{-1})_{\text{libr}} + (T_1^{-1})_{\text{reor}} = a T^n + b \exp(-E_a/R T). \]  

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\(_6\)H\(_5\)Cl and C\(_6\)F\(_5\)Cl, respectively) describe motions from a metastable orientation into a stable one [23]. It should be noted that the \( E_a \) values found for C\(_6\)H\(_5\)Cl and C\(_6\)F\(_5\)Cl crystals lie in the range of the values listed in Table 1.

**Table 3.** The parameters of (2) for crystalline C\(_6\)H\(_5\)Cl and C\(_6\)F\(_5\)Cl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a ) (s(^{-1}) K(^{-n}))</th>
<th>( n )</th>
<th>( b ) (s(^{-1}))</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)H(_5)Cl</td>
<td>8.67 ( \cdot ) 10(^{-5})</td>
<td>2.63</td>
<td>7.47 ( \cdot ) 10(^{13})</td>
<td>41.8</td>
</tr>
<tr>
<td>C(_6)F(_5)Cl</td>
<td>4.05 ( \cdot ) 10(^{-2})</td>
<td>1.17</td>
<td>3.40 ( \cdot ) 10(^{10})</td>
<td>18.7</td>
</tr>
</tbody>
</table>

Fig. 1. Temperature dependence of the \(^{35}\)Cl NQR \( T_1 \) and \( v \) (inset) in crystalline C\(_6\)H\(_5\)Cl (•) and C\(_6\)F\(_5\)Cl (○). The solid curves were calculated from (1) and (2) by using the parameters listed in Tables 2 and 3, respectively.