^{35}Cl NQR AND MOBILITY OF PARTLY CHLORINATED METHYL GROUPS IN CRYSTALS

I.A. KJUNTSEL, V.A. MOKEEVA, G.B. SOIFER, and I.G. SHAPOSHNIKOV
Radiospectroscopy Laboratory, Perm University, Perm (USSR)

ABSTRACT

The temperature dependence of the ^{35}Cl NQR frequencies, their temperature coefficients, and spin-lattice relaxation times was studied for crystalline compounds $Cl_xH_{3-x}C-R$ with $R=C_6H_5$, COOH, and $CONH_{2-y}(CH_3)_y$ ($x=1,2$ and $y=0,1,2$) in the temperature range from 77 K to the sample melting points. It is found that for the mono- and dichloromethyl groups the shape of the experimental curves on the upper part of the temperature range often differs essentially from that predicted by the Bayer theory. These deviations may be interpreted as due to the appearance of the considerable anharmonicity of the autonomous librations of the groups mentioned.

Due to the configuration of partly **chlorinated** methyl groups in molecular crystals and the character of their interaction with the molecule framework, autonomous librations of these groups may be possible. In this paper, the mobility of the mono- and dichloromethyl groups is studied by NQR experiments in some $Cl_xH_{3-x}C-R$ - type crystals with $R = C_6H_5$, COOH, and $CONH_{2-y}(CH_3)_y$ with $x = 1,2$ and $y = 0,1,2$. The temperature dependence of the resonance frequencies γ, their temperature coefficients $\alpha \equiv (1/\gamma_{77})(\Delta\gamma/\Delta T)$, and spin-lattice relaxation times T_1 is obtained for ^{35}Cl in the temperature range from 77 K to the sample melting points.

It is well known that to describe the temperature dependence in question the Bayer theory (ref. 1) with different generalizations (see the review ref. 2) is often used successfully if the temperature is not very low, the following approximate theoretical formulae being utilized:

$$- \alpha(T) = p + qT, \tag{1}$$

$$T_1^{-1}(T) = a\,T^n \tag{2}$$

with $1 < n < 3$ (see, for example, refs. 3, 4 and refs. 5, 6 respectively). On the other hand, if the temperature becomes high enough this approach ceases to be satisfactory.

The Table gives the experimental results for all the compounds investigated. These results reveal essential deviations from (1) and (2), especially for the dichloromethyl groups: beginning with some temperature region, the rate of the change
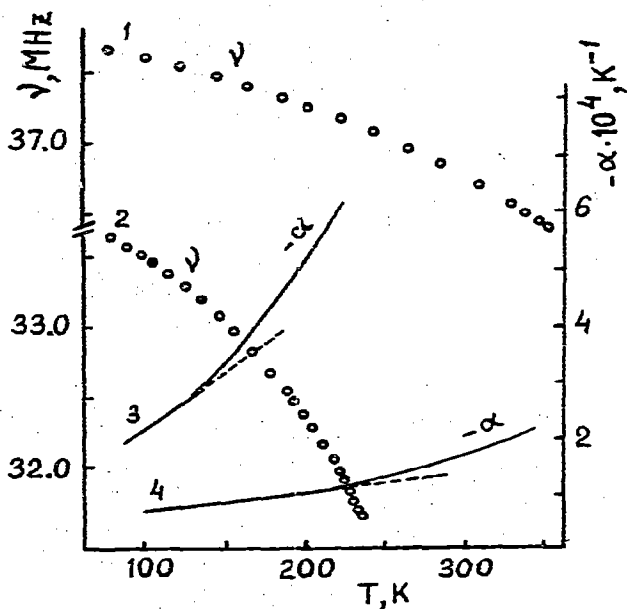

Fig. 1. The temperature dependence of the NQR frequencies ν (curves 1 and 2) and their temperature coefficients $\alpha \cdot (1/\nu_{77})(\Delta\nu/\Delta T)$ (curves 3 and 4) for the chlorine-35.
1,4 – $CHCl_2CONHCH_3$; 2,3 – $CH_2ClC_6H_5$.

of $|\alpha|$ becomes greater than given by Eq. (1), and Eq. (2) holds with the greater values of n[x]. Figures 1 and 2 present examples of the deviations discussed.

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[x] For the dichloromethyl group this character of $T_1(T)$ has been reported formerly in refs. 7, 8.

TABLE

The temperature dependence of the α and T_1^{-1} for the ^{35}Cl in the mono- and dichloromethyl groups

Substance (Melting point)	$\nu^{35}Cl$, MHz (77 K)	Parameters in the Eq. (1)			Parameters in the Eq. (2)		
		p, K^{-1}	q, K^{-2}	Temperature range, K	a, $s^{-1}K^{-n}$	n	Temperature range, K
$CH_2ClC_6H_5$ (234 K) a)	33.628	$1.9 \cdot 10^{-5}$	$2.0 \cdot 10^{-6}$	$77 \div 120$	$3.79 \cdot 10^{-5}$ $2.82 \cdot 10^{-7}$	2.87 ± 0.02 3.87 ± 0.05	$77 \div 110$ $150 \div T_{m.p.}$
$CHCl_2C_6H_5$ (256 K) b)	36.519 (1) c) 36.383 (2) 35.831 (1) 35.734 (1) 35.622 (1)						
$CH_2ClCOOH$ α-phase (336 K) d)	36.427 36.131	$5.0 \cdot 10^{-5}$ $3.7 \cdot 10^{-5}$	$3.8 \cdot 10^{-7}$ $6.3 \cdot 10^{-7}$	$77 \div T_{m.p.}$ $77 \div T_{m.p.}$	$1.54 \cdot 10^{-4}$ $1.48 \cdot 10^{-20}$ $4.37 \cdot 10^{-4}$ $2.29 \cdot 10^{-19}$	2.25 ± 0.03 8.8 ± 0.7 2.27 ± 0.05 8.4 ± 0.6	$77 \div 260$ $320 \div T_{m.p.}$ $77 \div 260$ $320 \div T_{m.p.}$
$CHCl_2COOH$ (279 K) e)	38.806 37.976	$5.4 \cdot 10^{-5}$ $5.0 \cdot 10^{-5}$	$6.4 \cdot 10^{-7}$ $5.2 \cdot 10^{-7}$	$77 \div 180$ $77 \div 180$			

TABLE (continued)

Substance (Melting point)	$\nu^{35}Cl$, MHz (77 K)	Parameters in the Eq. (1)			Parameters in the Eq. (2)		
		β, K^{-1}	q, K^{-2}	Temperature range, K	a, s^{-1}K^{-n}	n	Temperature range, K
CH$_2$ClCONH$_2$ f) (392 K)	34.884	$1.4 \cdot 10^{-5}$	$3.9 \cdot 10^{-7}$	77÷260	$2.54 \cdot 10^{-4}$ $1.70 \cdot 10^{-8}$	2.02 ± 0.03 $3.8^+ \pm 0.3$	77÷220 280÷T$_{m.p.}$
CHCl$_2$CONH$_2$ f) (371 K)	37.814	$5.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-6}$	77÷240	$5.89 \cdot 10^{-2}$ $8.04 \cdot 10^{-2}$	1.5 ± 0.2 4.6 ± 0.4	77÷140 180÷300
	37.261	$3.8 \cdot 10^{-5}$	$1.1 \cdot 10^{-6}$	77÷240	$5.89 \cdot 10^{-9}$ $8.04 \cdot 10^{-9}$	1.5 ± 0.2 4.6 ± 0.4	77÷140 180÷300
CH$_2$ClCONHCH$_3$ (315 K)	34.671	$3.6 \cdot 10^{-5}$	$6.4 \cdot 10^{-7}$	77÷260	$1.64 \cdot 10^{-4}$ $8.39 \cdot 10^{-6}$	2.30 ± 0.03 2.8 ± 0.2	77÷250 280÷T$_{m.p.}$
	34.543	$4.4 \cdot 10^{-5}$	$5.2 \cdot 10^{-7}$	77÷260	$1.64 \cdot 10^{-4}$ $8.39 \cdot 10^{-6}$	2.30 ± 0.03 2.8 ± 0.2	77÷250 280÷T$_{m.p.}$
CHCl$_2$CONHCH$_3$ (354 K)	37.646	$3.6 \cdot 10^{-5}$	$3.5 \cdot 10^{-7}$	77÷200	$3.05 \cdot 10^{-2}$ $2.48 \cdot 10^{-8}$	1.26 ± 0.08 3.9 ± 0.1	77÷160 260÷T$_{m.p.}$
CH$_2$ClCON(CH$_3$)$_2$ (291 K)	35.351	$8.0 \cdot 10^{-6}$	$6.4 \cdot 10^{-7}$	77÷T$_{m.p.}$	$2.59 \cdot 10^{-3}$	1.92 ± 0.02	77÷T$_{m.p.}$

TABLE (continued)

Substance (Melting point)	$\nu^{35}Cl$, MHz (77 K)	Parameters in the Eq. (1)			Parameters in the Eq. (2)		
		p, K^{-1}	q, K^{-2}	Temperature range, K	a, $s^{-1}K^{-n}$	n	Temperature range, K
$CHCl_2CON(CH_3)_2$ (312 K)	37.212	$1.1 \cdot 10^{-4}$	$5.2 \cdot 10^{-7}$	$77 \div 190$	$3.29 \cdot 10^{-1}$ $3.65 \cdot 10^{-8}$	1.1 ± 0.2 4.1 ± 0.8	$77 \div 140$ $250 \div 300$
	36.897	$1.0 \cdot 10^{-4}$	$5.2 \cdot 10^{-7}$	$77 \div 190$	$8.52 \cdot 10^{-1}$ $5.20 \cdot 10^{-7}$	0.9 ± 0.1 3.6 ± 0.3	$77 \div 140$ $250 \div 300$

[a] The temperature dependence of the chlorine-35 NQR frequency has been reported formerly in ref.9.

[b] There are peculiarities in $\nu(T)$ and $T_1(T)$ connected with a continuous phase transition which occurs at 94 K and is accompanied by a deep in $T_1(T)$; above the transition point, the number of the NQR lines decreases to two.

[c] In the brackets there are the relative intensities of the NQR lines.

[d] The temperature dependence of the Chlorine-35 NQR frequencies has been reported formerly in refs. 10, 11 in the range from 77 K to 300 K.

[e] The $T_1(T)$ is anomalous; the temperature dependence of the chlorine-35 NQR frequencies has been reported formerly in ref. 12 in the range from 77 K to 240 K.
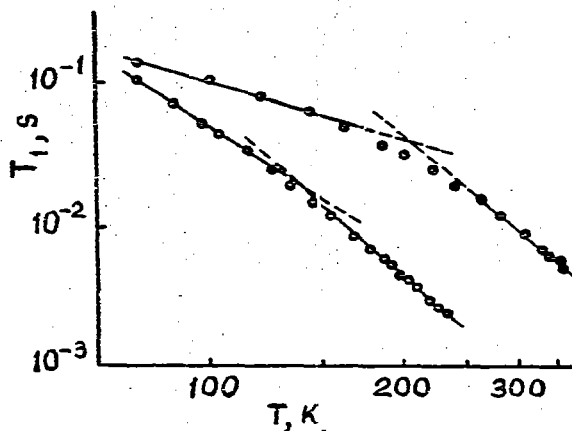
[f] The results from ref. 7.

Fig. 2. The temperature dependence of the quadrupole spin-lattice relaxation time T_1 for the chlorine-35.
1 - $CHCl_2CONHCH_3$;
2 - $CH_2ClC_6H_5$.

This failure of the Bayer approach in the high temperature region may be explained by the essential anharmonicity of the autonomous librations of the $CHCl_2$ and CH_2Cl groups due to the flexibility of the bond between these groups and the molecular framework. This interpretation is supported by the correlation between the effects in question and the anomalous behaviour of the thermal expansion coefficient of $CH_2ClCONH_2$ crystals (refs. 7, 13).

REFERENCES

1 H. Bayer, Z. Phys., 130 (1951) 227–238.
2 H. Chihara and N. Nakamura, in J.A.S. Smith (Ed.), Advances in Nuclear Quadrupole Resonance. Vol. 4. Heiden, London, 1980, pp. 1–69.
3 R.J.C.Brown, J.Chem.Phys., 32 (1960) 116–118.
4 V.A. Mokeeva, I.A. Kjuntsel, and G.B. Soifer, in Fiz.Metody Issled. Tverd. Tela, No.2, Sverdlovsk (USSR), 1977, pp.19–21.
5 T. Tokuhiro, J. Chem. Phys., 41 (1964) 1147–1152.
6 Yu.N. Gachegov, A.D. Gordeev, and G.B. Soifer, Fiz. Tverd. Tela (USSR), 23 (1981) 1490–1492.
7 I.V. Izmest'iev, G.B. Soifer, Optica i Spectroscopiya (USSR), 30 (1971) 893–896.
8 H. Chihara and N. Nakamura, J. Phys. Soc. Jap., 37 (1974) 156–162.
9 H.C. Meal, J. Amer. Chem. Soc., 74 (1952) 6121–6122.
10 R. Chandramani and N. Devaraj, J. Phys. C: Solid State Phys., 8 (1975) 1742–1744.
11 H. Rager, Z. Naturforsch., 33a (1978) 74–77.
12 H. Rager and A. Wergin, Z. Naturforsch., 32a (1977) 415–419.
13 M. Zdanowska and J. Stankowski, J. Magn. Reson., 31 (1978) 109–120.