NQR Relaxation Studies on Halogenomethyl Groups in Halogenoacetates*

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The effect of temperature on the chlorine NQR spin-lattice relaxation times in $CsH(ClH_2CCOO)_2$, $KH(Cl_3CCOO)_2$ and $N(CH_3)_4H(ClF_2CCOO)_2$ has been studied in the temperature range 77 K to room temperature. The results were discussed on the basis of NQR relaxation theory.

Key words: NQR; Spin-lattice Relaxation

Introduction

The acidic monocarboxylic acids salts (2:1) contain anions consisting of two crystallographically equivalent acid radicals, linked to one another by a very short hydrogen bond involving an acid hydrogen [$RCCOO-H\cdots OOCCR^-$ [1]. In recent years this family of salts has been extensively investgated by us, and the results were discussed in the ligth of the ferroelectric properties, crystal structure and the hydrogen bond symmetry of the dimeric carboxylic acid unit. The NQR technique has been applied in order to examine the symmetry of the dimeric hydrogen bond potential as well as the pressure and isotope effects on it [2 - 4]. In our present investigation we have studied the temperature dependence of the ^{13}Cl NQR frequency and the quadrupole spin-lattice relaxation time T_{1Q} in order to monitor the molecular dynamics in the truly symmetrical acid salts. The problem of the hydrogen bond symmetry has been excluded form the considerations. The studied salts contain different CX_3 type sub-groups, i. e. $-CH_2Cl$, $-CCl_3$, and $-CClF_2$. They were chosen to represent different types of lattice motion. Especially, the $CClF_2$ type sub-groups are interesting from the dynamic point of view, because an unsymmetric potential can be expected for the reorientation about their three-fold axis [5, 6].

Experimental

Polycrystalline samples were prepared and identified by the conventional elementary analysis.

The ^{35}Cl NQR spectra were recording using an NQR Fourier transform pulse spectrometer FT-NQS 150. The ^{35}Cl spin-lattice relaxation time T_{1Q} was measured by employing the conventional (180° - τ - 90°) pulse sequence. The error of the T_{1Q} measurements did not exeed 10%. The temperature of the sample was stabilized to within 0.1 K by using an Oxford flow cryostat.

Results

The NQR spectrum of caesium hydrogen bis-monochloroacetate shows only a single resonance, so that the both chlorine atoms must be crystallographically equivalent. On deuteration of the hydrogen bond no significant shift of the chlorine resonance frequency was observed. Therefore, a symmetrical type of the anion is indicated, and the proton is either symmetrically located or is rapidly tunneling between two equivalent asymmetrical proton positions [2]. The observed negative temperature coefficient of the NQR frequency may be interpreted as the averaging effect on the electric field gradient caused by torsional oscillations of the CH_2Cl-group. The temperature dependence of the chlorine spin-lattice relaxation time T_{1Q} in $CsH(ClH_2CCOO)_2$ is shown in Figure 1. In the temperature range studied the experimental T_{1Q} data can be described by the relation

$$T_{1Q}^{-1} = aT^n. \qquad (1)$$

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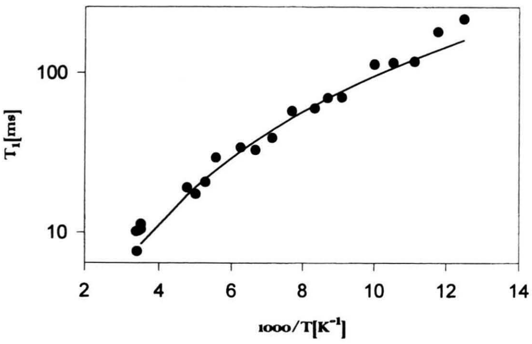

Fig. 1. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time of CsH(ClF$_2$CCOO)$_2$. The solid line represents the best fitted theoretical values.

The theoretical fit (standard deviation: 0.993) to the experimental plot yielded the parameters $a = 2.6 \cdot 10^{-4}$ [$K^{-2}s^{-1}$], $n = 2.3$.

The relaxation theory based on the analysis of thermal vibrations or torsional oscillations in a crystalline lattice [7, 8] shows that, when the temperature is high enough ($T > 0.1\ \Theta$ where Θ is the Debye temperature) i. e. for the effective phonons , one can use the approximation

$$T_{1Q}^{-1} = aT^2. \tag{2}$$

In the whole temperature region studied, the temperature dependence of T_{1Q} in CsH(ClH$_2$CCOO)$_2$ can be interpreted in terms of the quadrupolar mechanism due to the random fluctuations of the electric field gradient caused by lattice vibrations or torsional oscillations of -CH$_2$Cl groups.

The ^{35}Cl NQR spectrum of KH(Cl$_3$CCOO)$_2$, consisting of three widely spaced and strong lines having equal intensity at 77 K, confirms the symmetry of the anion. The temperature dependence of the chlorine spin-lattice relaxation time T_{1Q} for the NQR line corresponding to the lowest frequency in KH(Cl$_3$CCOO)$_2$ is shown in Figure 2. Evidently there are two temperature regions corresponding to two relaxation mechanisms. Between 77 K and ca. 170 K, the relaxation process is determined by small amplitude torsional oscillations of the CCl$_3$ groups. The same relaxation mechanism was observed in CsH(ClH$_2$CCOO)$_2$. On increasing the temperature above 170 K, the experimental T_{1Q}^{-1} values exhibit an exponential behaviour and fit well to a simple random reorientation of the CCl$_3$ groups about its C$_3$ symmetry axis. A gradual broadening of the NQR lines and decrease of the signal amplitude were also observed. The NQR signal vanishes at a fade-out temperature of about 200 K.

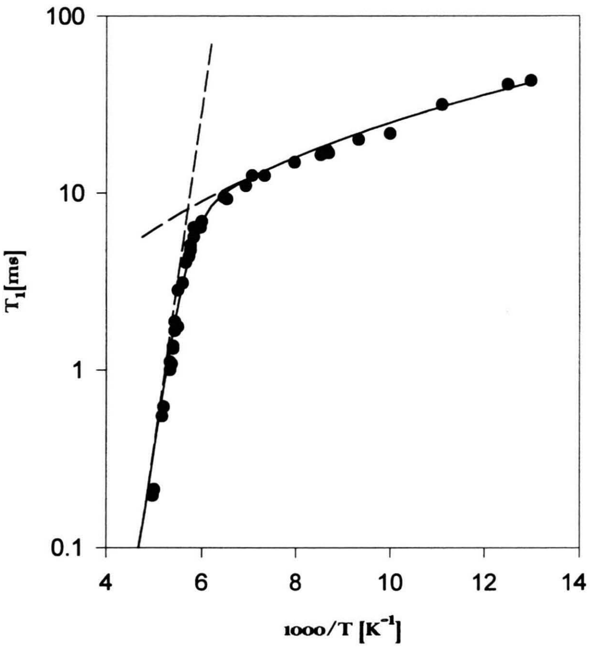

Fig. 2. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} of KH(Cl$_3$CCOO)$_2$. The solid line represents the best fitted theoretical values. The broken lines indicate the contributions to T_{1Q} from the components $(T_{1Q})_{\mathrm{vibr}}$ and $(T_{1Q})_{\mathrm{reor}}$.

When the contribution of lattice vibrations is taken into account, the experimental T_{1Q} may be represented by the equation

$$(T_{1Q})^{-1} = (T_{1Q})^{-1}{}_{\mathrm{vibr}} + (T_{1Q})^{-1}{}_{\mathrm{reor}}, \tag{3}$$

provided that the lattice vibrations and the reorientation do not couple. Assuming an Arrhenius relationship between the correlation time τ_c and the activation energy E_a for the CCl$_3$ group motion, the general form of the relaxation rate may be expressed by [7, 8]

$$T_{1Q}^{-1} = aT^n + b\exp(-E_a/RT) \tag{4}$$

Fitting calculations to the observed relaxation rates of KH(Cl$_3$CCOO)$_2$ were performed using above formula. The best fitted curve is shown in Fig. 2 by the solid line (standard deviation: 0.996). The broken lines indicate the contributions to T_{1Q}^{-1} from each relaxation mechanism $(T_{1Q})^{-1}{}_{\mathrm{vibr}}$ and $(T_{1Q})^{-1}{}_{\mathrm{reor}}$. The following motional parameters were obtained from the fitting procedure:

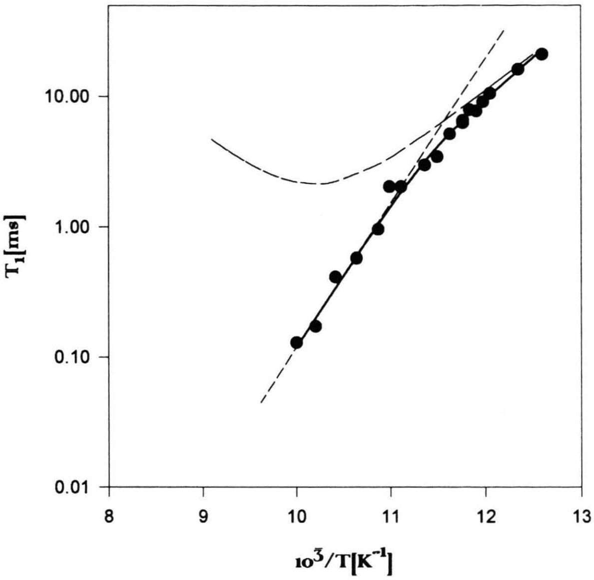

Fig. 3. Temperature dependence of ^{35}Cl spin-lattice relaxation time T_{1Q} of $N(CH_3)_4H(ClF_2CCOO)_2$. The solid line represents the best fitted theoretical values. The broken lines indicate the contributions to T_{1Q} from the components $(T_{1Q})_{reor}$ and $(T_{1Q})_{mod}$.

$$a = 4 \cdot 10^{-3}\ [s^{-1}K^{-2}],\ n = 2,\ b = 6.5 \cdot 10^{12}\ [s^{-1}],$$
$$E_a = 35\ [kJ/mol],$$

which may be compared with the parameters of other compounds containing reorienting CCl_3 groups [9].

The temperature dependence of the chlorine quadrupole spin-lattice relaxation in $N(CH_3)_4H(ClF_2CCOO)_2$ is shown in Figure 3. With increasing temperature from 77 K to about 100 K the T_{1Q} values for the chlorine atoms decreased very sharply. Above 100 K the free induction decay signals became too week to obtain precise T_{1Q} values when T_{1Q} decreased below ca. 200 µs. The sharp decrease of T_{1Q} can be interpreted in terms of a thermal Arrhenius type. The temperature variations of the chlorine relaxation is two-exponential. This suggests that at least two different correlation times are responsible for the fluctuations of the EFG at the chlorine nuclei in the studied compound.

In order to explain the above results, the experimental $(T_{1Q})^{-1}$ values of chlorine nuclei observed for the present complex are assumed to be a sum of contributions from (i) the reorientation of the $CClF_2$ groups $(T_{1Q})^{-1}{}_{reor}$ involving the resonant nuclei and (ii) the modulation of the chlorine EFG due to the motion of the neighbouring $N(CH_3)_4{}^+$ cation $(T_{1Q})^{-1}{}_{mod}$. These motions are assumed to be independent. This suggestion was confirmed by the temperature dependence of the other NQR spectroscopy parameter, the line width [10]. The observed T_{1Q} can be written as

$$(T_{1Q})^{-1} = (T_{1Q})^{-1}{}_{reor} + (T_{1Q})^{-1}{}_{mod}. \qquad (5)$$

The recovery of the spin magnetisation was exponential over the whole temperature range investigated. Then, for $(T_{1Q})_{reor}$ one has [5]

$$(T_{1Q})^{-1}{}_{reor} = b \exp(-E_a/RT), \qquad (6)$$

where E_a represents the activation energy for the reorientation of the $CClF_2$ group in the crystal.

The relaxation rate $(T_{1Q})^{-1}{}_{mod}$ originating from the fluctuation of the external EFG due to the cationic motion can be written for chlorine nuclei with the nuclear spin $I = 3/2$ assuming a negligibly small asymmetry parameter η of the EFG as [7]

$$(T_{1Q})^{-1}_{mod} = (\omega_Q^2/3)(q'/q)^2\{\tau_m/(1 + \omega_Q^2\tau_m^2)\}, \qquad (7)$$

where (q'/q) is called an EFG-fluctuation fraction, ω_Q denotes the angular resonance frequency and τ_m is the correlation time for the cation motion which yields a fluctuating EFG at the resonant nuclei. τ_m can be expressed in terms of an Arrhenius relation:

$$\tau_m = \tau_{0m} \exp(E_{am}/RT) \qquad (8)$$

The fitting calculations to the observed ^{35}Cl T_{1Q} values of $N(CH_3)_4H(ClF_2CCOO)_2$ were performed using (5) - (8), in which $(\omega_Q/2\pi)$ of the ^{35}Cl nuclei was fixed at 35.59 MHz. The best fitted curve for the foregoing complex is shown in Fig. 3 by the solid line (standard deviation: 0.996). The broken lines indicate the contributions to T_{1Q} from the components $(T_{1Q})_{reor}$ and $(T_{1Q})_{mod}$. The following motional parameters were obtained from the fitting procedure:

$$E_a = 21.2\ [kJ/mol],\ b = 2.3 \cdot 10^{12}\ [s^{-1}],$$
$$E_{am} = 10.7\ [kJ/mol],\ \tau_{0m} = 9 \cdot 10^{15}\ [s^{-1}],$$

$q'/q = 0.09\%$. As seen from Fig. 3, the modulation of the quadrupolar interactions caused by thermal motion of $N(CH_3)_4{}^+$ groups was generally covered up by a more effective quadrupole relaxation mechanism such as the C_3 reorientation of $CClF_2$ groups. This is the reason why the modulation effect has not been observed clearly in the temperature dependence of the chlorine relaxation times. The NQR results did not give any evidence of the inequivalent local potential for $CClF_2$ group motion in $N(CH_3)_4H(ClF_2CCOO)_2$. The quadrupole spin-lattice relaxation due to the reorientation between inequivalent wells was first discussed by Ainbinder et al. [5]. Their most important conclusion is that the spin-lattice relaxiation process is described by two exponential decay curves with long and short relaxation times. The relaxation process in $N(CH_3)_4H(ClF_2CCOO)_2$ is practically determined by a single relaxation time, indicating that the situation corresponds to one of the two extremes: the potential is approximately symmetric or highly asymmetric [5]. In the present work we assumed the former case for simplicity.

The activation energy of the $CClF_2$ motion evaluated to be 21.2 kJ/mol for chlorines is larger than those reported for other salts of chlorodifluoroacetic acid [11, 12]. This suggests that the ions in the present compound are closely packed in the crystalline lattice. Since there are no structural data available, a detailed discussion of the dynamics in a broader context is presently not possible.

Acknowledgement

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