^{35}Cl and ^{37}Cl Pure Quadrupole Resonance in α-$CH_2ClCOOH$: Hydrogen Bonding and Chlorine Isotope Effect

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The temperature dependence of the pure nuclear quadrupole resonance of ^{35}Cl and ^{37}Cl in solid α-$CH_2ClCOOH$ has been measured from 77 K to 298 K. The NQR spectrum consists of a doublet arising from the two nonequivalent chlorine atoms in the unit cell. The temperature dependence was calculated using the Bayer-Kushida theory which gives a satisfactory fit to the NQR spectra in the temperature range investigated. From the NQR data evidence of an isotope effect was found for both nonequivalent chlorine atoms. The isotope effect depends on the C-Cl bond length and its direction probably on the state of binding of the chlorine atoms. The NQR results and their interpretation are consistent with the crystal structure of α-$CH_2ClCOOH$.

1. Introduction

In a previous paper [1] the temperature dependence of the ^{35}Cl and ^{37}Cl nuclear quadrupole resonance (NQR) frequencies in $CHCl_2COOH$ and $CDCl_2COOD$ was investigated in connection with the so-called chlorine isotope effect [2, 3]. This effect has been shown to exist in $CHCl_2COOH$ whereas in $CDCl_2COOD$ no significant difference between the ^{37}Cl and ^{35}Cl shifts has been found [1]. It is possible that the effect of deuteration on the electronic structure is responsible for masking the chlorine isotope effect in $CDCl_2COOD$.

Here, we report the chlorine isotope effect in α-$CH_2ClCOOH$. The NQR spectrum of α-monochloro acetic acid is a doublet indicating two nonequivalent chlorine atoms in the unit cell. From the splitting of the doublet it follows that the chlorine atoms are in equivalent positions in the free molecules but the interaction between neighboring molecules destroys their equivalence when introduced into the solid state. Recently the crystal structure of α-$CH_2ClCOOH$ was described as a hydrogen-bonded tetramer. The structure reported by Kalyanaraman et al. [4] allows for the presence of two nonequivalent chlorine atoms. The nonequivalence is demonstrated by the difference in the C—Cl distances. The large C—Cl distance with 1.789(6) Å is assumed to be due to a hydrogen bond of the chlorine atom while the C—Cl distance with 1.725(6) Å is not involved in hydrogen bonding.

Roelofsen and Kanters [5] describe the structure of α-monochloro acetic acid as a centrosymmetric tetramer formed by hydrogen bonds between carboxyl groups of two independent dimeric $CH_2ClCOOH$ molecules, I and II. The C—Cl bond distances of 1.765(5) Å in molecule I and of 1.759(4) Å in molecule II are very similar in contrast to the data given by Kalyanaraman et al [4]. However, using the fractional coordinates of the atomic positions given by Kanters and Roelofsen [5] we found that the distance between the chlorine atom Cl(I) of molecule I and the nearest hydrogen, H(3) II in molecule II, is 2.756 Å. The bond angle C—Cl(I) ... H(3) II is 89.7°. The distance of the chlorine atom Cl(II) of molecule II to the nearest hydrogen, H(3) I in molecule I, is 3.02 Å. The bond angle C—Cl(II) ... H(3) I is also 89.7°. Thus, taking the van der Waals radii of 1.2 Å for hydrogen and of 1.8 Å for chlorine into account it seems to be reasonable to assume that the chlorine atom Cl(I) participates in a hydrogen bond whereas Cl(II) does not. Therefore, α-$CH_2ClCOOH$ should be suitable to study the dependence of the chlorine isotope effect on different spacings and bondings of the chlorine nuclei.

2. Experimental Procedure and Results

The experimental procedure which was employed to determine the chlorine NQR frequencies has been described elsewhere [1]. The results of the NQR measurements on a commercial sample of α-$CH_2ClCOOH$ (Merck, Darmstadt Germany) are summarized in Figure 1. The accuracy of the frequency measurements is ± 3 kHz and the temperature was determined within an error of ± 0.5 K.

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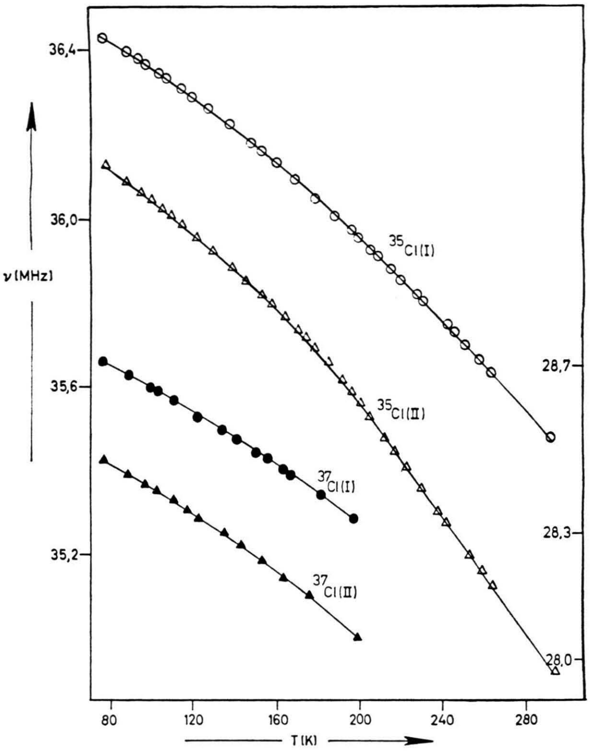

Fig. 1. Temperature dependence of the pure NQR frequencies in α-$CH_2ClCOOH$. The solid curves were calculated from Equation (1) using the parameters listed in Table 1.

The ^{35}Cl spectrum at 77 K agrees with those reported by several authors [6, 7, 8, 9]. The NQR frequencies decrease with increasing temperature and the ^{35}Cl NQR lines were still observed at room temperature whereas the ^{37}Cl lines vanished above 200 K. The ^{35}Cl and ^{37}Cl spectra are doublets. At 77 K the splitting of the doublet amounts to about 300 kHz in the case of ^{35}Cl and to about 230 kHz in the case of ^{37}Cl. In both cases the splitting increases with increasing temperature.

3. Analysis and Discussion of Results

The temperature dependence of the ^{35}Cl and ^{37}Cl NQR frequencies was described using the Bayer-Kushida theory [10, 11] where the assumptions have been outlined [1]. The equation [12]

$$\nu(T) = \chi_1 - \chi_2 \times \left(\tfrac{1}{2} + 1/(\exp(\theta_1/T) - 1)\right) \tag{1}$$

was fitted to the experimental NQR frequency vs. T curves by a least-squares method. χ_1, χ_2, and θ_1 were used as adjustable parameters where

$$\chi_1 = \nu_0\,, \tag{2}$$

$$\chi_2 = \frac{3\,A_1\,\hbar\,\nu_0\,N}{2\,\omega_1}\,, \tag{3}$$

$$\theta_1 = \frac{\hbar\,\omega_1}{k}\,. \tag{4}$$

θ_1 is the Einstein temperature of the first mode, N is the degeneracy of the mode, ω_1 is the angular frequency of the lattice vibration and A_1 is the corresponding inertia factor equal to the reciprocal of the moment of inertia for one rotational mode and lastly χ_1 is the NQR frequency of the perfectly static lattice. The parameters χ_1, χ_2, and θ_1 thus determined are listed in Table 1 and the best fit obtained is shown by solid lines in Figure 1. The maximum difference between the measured and calculated NQR frequencies is not larger than 15 kHz and is generally less than 5 kHz. Thus, Eq. (1) adequately describes the temperature dependence of the NQR spectra in the temperature range investigated.

Table 1. Parameters for the temperature dependence of the NQR frequencies in α-$CH_2ClCOOH$ according to Equation (1).

Isotope	χ_1/MHz	χ_2/MHz	θ_1/K
^{35}Cl(I)	37,244 ±0,015	1,557 ±0,055	280,75 ±8,1
^{35}Cl(II)	37,326 ±0,128	2,330 ±0,161	314,13 ±11,6
^{37}Cl(I)	29,137 ±0,021	0,741 ±0,034	198,40 ±3,8
^{37}Cl(II)	29,094 ±0,030	1,151 ±0,045	248,48 ±7,6

Then, from equation (1) the temperature coefficient of the NQR frequencies follows as

$$\frac{\partial \nu}{\partial T} = -\,\chi_2 \cdot \frac{\theta_1}{T^2} \cdot \frac{\exp(\theta_1/T)}{(\exp(\theta_1/T) - 1)^2}\,. \tag{5}$$

Taking the parameters of Table 1 the coefficients at 77 K were calculated and listed in Table 2. The values of the coefficients for ^{35}Cl and ^{37}Cl do not differ very much but it should be noted that the value for ^{37}Cl(I) is large. Further, from the parameters χ_1 in Table 1 it follows that the ^{35}Cl(I) frequencies must cross the ^{35}Cl(II) fre-

Table 2. ^{35}Cl(I, II) and ^{37}Cl(I, II) temperature coefficients at 77 K and experimental and calculated shifts Δ at constant temperature.

	^{35}Cl(I)	^{35}Cl(II)	^{37}Cl(I)	^{37}Cl(II)
$\dfrac{\left(\dfrac{\partial\gamma}{\partial T}\right)_{T=77K}}{\left(\dfrac{\text{kHz}}{\text{K}}\right)}$	$-2{,}03$	$-2{,}16$	$-2{,}21$	$-2{,}07$
Δ_{exp}	0,01271	0,01586	0,01348	0,01510
Δ_{cal}	0,01261	0,01582	0,01289	0,01473
T/K	198,7	200,0	198,4	200,0

quencies at temperatures far below 77 K whereas the ^{37}Cl frequencies do not cross. Of course, this holds true provided that no phase transition occurs and the Bayer-Kushida theory is able to describe the temperature dependence of the NQR frequencies below 77 K. No measurements were made so far to prove this. However, the opposite behavior of the temperature coefficients i.g.

$$\frac{\partial\nu}{\partial T}(^{35}\text{Cl(II)}) > \frac{\partial\nu}{\partial T}(^{35}\text{Cl(I)})$$

whereas

$$\frac{\partial\nu}{\partial T}(^{37}\text{Cl(II)}) < \frac{\partial\nu}{\partial T}(^{37}\text{Cl(I)})$$

gives an indication of the chlorine isotope effect in α-CH$_2$ClCOOH.

The effect was found for both chlorine atoms, Cl(I) and Cl(II), and is shown in Figure 2. The relative shift Δ of the NQR frequencies is expressed by

$$\Delta = \frac{\nu_{77} - \nu_T}{\nu_{77}}\,. \tag{6}$$

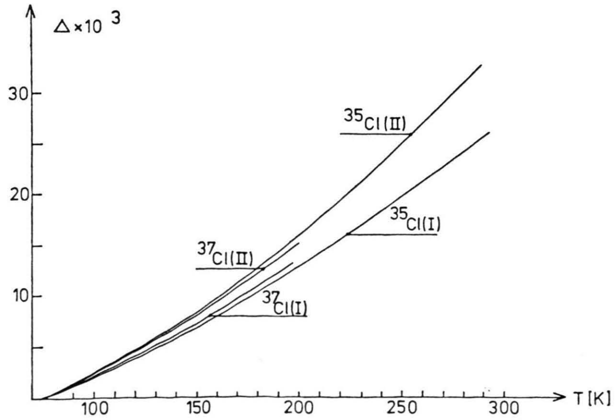

Fig. 2. Temperature dependence of the shift Δ of the ^{35}Cl(I, II) and ^{37}Cl(I, II) NQR frequencies in α-CH$_2$ClCOOH.

ν_{77} is the frequency at 77 K and ν_T at T K. Under the assumption that primarily torsional motions would be effective in averaging the electric field gradient tensor at the chlorine sites the Bayer-Kushida theory gives the following expression for the shift

$$\Delta = 1 - \frac{\chi_1 - \chi_2(\frac{1}{2} + 1/(\exp(\theta_1/T) - 1))}{\chi_1 - \chi_2(\frac{1}{2} + 1/(\exp(\theta_1/77) - 1))}\,. \tag{7}$$

Using the parameters in Table 1 the Δ values are given in Table 2. They agree satisfactorily with the experimental ones indicating that the Bayer-Kushida theory is a good approach in the case investigated here. The direction of the isotope effect may be defined by the difference of the respective shifts as $\Delta(^{35}\text{Cl(I, II)}) - \Delta(^{37}\text{Cl(I, II)})$. We found the direction of the shift for Cl(I) is just opposite to the direction for Cl(II). Thus, the nonequivalence of the two chlorine atoms can be also clearly recognized by the opposite direction of the isotope effect.

Duchesne [13] has pointed out that an increase in the length of the C—Cl bond (due to a hydrogen bond for example) leads to a decrease in the ionic character. Therefore, based on the structure reports given above one would expect the chlorine atom which forms a hydrogen bond to exhibit a larger quadrupole coupling constant than the one that does not form a hydrogen bond. From this point of view the higher NQR frequencies may be attributed to the hydrogen bonded chlorine atom Cl(I) whereas the lower frequencies are connected with the non hydrogen bonded chlorine atom Cl(II).

Furthermore, employing basic principles of the chemical bonding an increasing C—Cl bond length leads to a decreasing bending force constant. This is equivalent with a decrease of the vibration frequency of the C—Cl bonding. The bond length of C—Cl(I) is longer than the one of C—Cl(II). Therefore, it is expected that the C—Cl(I) vibration frequency is smaller than the C—Cl(II) vibration frequency. Using Eq. (4) this suggests θ_1(Cl(I)) is smaller than θ_1(Cl(II)). This is in agreement with the parameters in Table 1 and valid for both chlorine isotopes. Thus, the assignment of the higher NQR frequencies to Cl(I) and the lower ones to Cl(II) is consistent with the results of the Bayer-Kushida theory and the structure of α-CH$_2$ClCOOH.

The splitting of the NQR doublets amounts to about 300 kHz. This value gives an estimate of the strength of the hydrogen bonding. In comparison to the strength of the chlorine hydrogen bonding in $CCl_3CH(OH)_2$ [14] which results in a NQR frequency shift of about 1 MHz the chlorine hydrogen bonding in α-$CH_2ClCOOH$ seems to be rather weak. This would be in agreement with the crystal structure reported by Kalyanaraman et al. [4] where the hydrogen bonded chlorine atom is assumed to participate in a three-center hydrogen bond with two oxygen atoms.

4. Conclusion

The temperature dependence of the NQR frequencies in α-$CH_2ClCOOH$ was described satisfactorily with the aid of the Bayer-Kushida theory. The analysis resulted in the assignment of the higher Cl-NQR frequencies to the hydrogen bonded chlorine atom. Further, it was shown that the isotope effect depends on the C—Cl bond length and its direction probably on the state of binding of the chlorine atoms.

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