Isotope Effect of the Pure ^{35}Cl and ^{37}Cl Quadrupole Resonance Spectra in $CHCl_2COOH$ and $CDCl_2COOD$

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The temperature dependence of the pure nuclear quadrupole resonance of ^{35}Cl and ^{37}Cl in solid $CHCl_2COOH$ and $CDCl_2COOD$ has been measured. The spectra are doublets according to two different sites, Cl(I) and Cl(II), of the chlorine atoms in the $CXCl_2$ group (X = H, D). In $CHCl_2COOH$ and $CDCl_2COOD$ the ^{37}Cl spectra became unobservable above 198 K and 175 K and the ^{35}Cl spectra vanished at 238 K and 226 K, respectively. The temperature dependence was calculated using the Bayer-Kushida theory which gives a satisfactory approach in the case of the compounds investigated here. A small difference has been found in the temperature dependence of the resonance frequencies for Cl(I) and Cl(II) in both the $CHCl_2$ and $CDCl_2$ group, which is probably due to differences in the bond lengths of Cl(I) and Cl(II). Furthermore, there is a different temperature dependence of the resonance frequencies of the chlorine isotopes at the sites Cl(I) and Cl(II). This gives evidence for the so-called isotope effect: i. e. there are slightly different thermal motions for the chlorine isotopes which are involved in the averaging of the electric field gradient tensor. The replacement of protons by deuterons gave a shift of the resonance frequencies of about 20 kHz to lower values. This may be primarily caused by effects of deuteration on the electronic structure.

1. Introduction

As pointed out by Wang[1] the ratio of the quadrupole coupling constants of the chlorine isotopes $(e^2 q Q)_{^{35}\mathrm{Cl}}/(e^2 q Q)_{^{37}\mathrm{Cl}}$ varies with temperature. This was attributed to zero-point and thermal vibrations of the molecule in which the ^{35}Cl and ^{37}Cl nuclei are contained. It decreases with a decrease of temperature. Since the ratio of the quadrupole moments Q_{35}/Q_{37} is constant, only the ratio of the electric field gradient (EFG) tensors q_{35}/q_{37} will vary with temperature due to slightly different effects of vibrations for the different chlorine isotopes.

One would expect larger differences in the thermal vibrations for the chlorine isotopes in molecules containing protons and deuterons since the relative difference in masses for hydrogen and deuterium is the largest. Thus, we measured the temperature dependence of the ^{35}Cl and ^{37}Cl quadrupole resonance frequencies in dichloro acetic acid ($CHCl_2COOH$) and dichloro acetic acid-d_2 ($CDCl_2COOD$). The work was undertaken in the hope that information could be obtained on the $CXCl_2$ (X = H, D) group torsional motion and its effect on the averaging of the EFG tensor due to different isotopic composition.

2. Experimental Procedure and Results

The nuclear quadrupole resonance (NQR) spectra were observed with a super-regenerative spectrometer[2]. The spectrometer is self-quenched (quench frequency about 30 kHz) and frequency modulated (30 Hz). A rf coil of seven turns silvered copper was used to cover the frequency range from 40 MHz to 28 MHz.

At lower temperatures the NQR signals were observed on the oscilloscope whereas at higher temperatures the quadrupole absorption lines were recorded after narrow band amplification and phase sensitive detection. To measure the NQR frequencies the signal of an external frequency meter (Rhode & Schwarz, BN 4140) was superimposed with the NQR signal. The NQR frequencies are accurate within an error of ± 3 kHz which is due to the NQR line width.

The temperature control was achieved for ± 0.5 K via a gas flow cryostat. No temperature gradient was observed over the sample. The temperature was monitored with copper-constantan thermocouples. Commercial samples of $CHCl_2COOH$ (Merck, Darmstadt, Germany) and of $CDCl_2COOD$ (Merck, Sharp & Dohme, Kirkland, Canada) were used. At room temperature both are liquid. All samples were sealed in glass tubes. Sample volumes were of about 5 cm^3 (glass tube diameter 17 mm). The results of the NQR measurements are given in Figures 1 and 2.

3. Analysis and Discussion of the Results

In all cases the resonance frequencies decrease with increasing temperature. The ^{35}Cl spectra in

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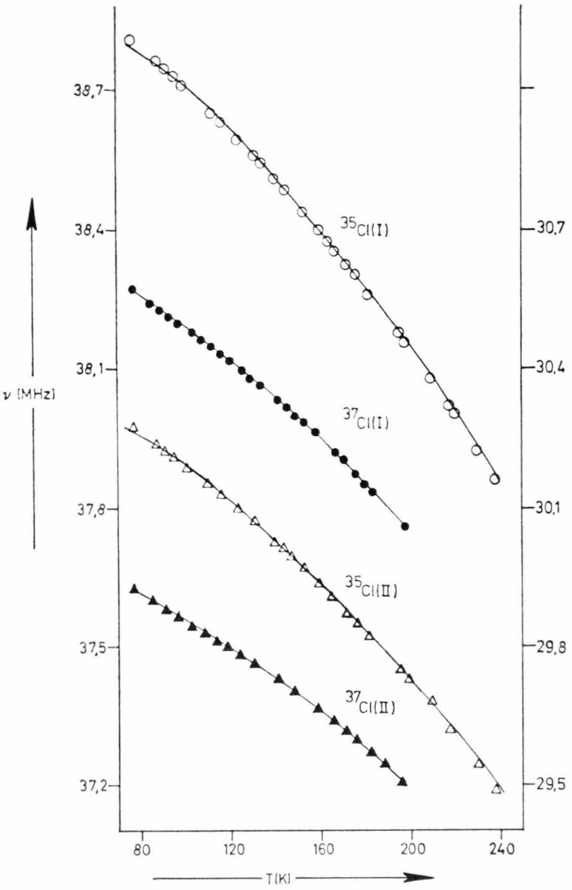

Fig. 1. Temperature dependence of the pure NQR frequencies in $CHCl_2COOH$. The solid curves were calculated from Eq. (2) using the parameters listed in Table 1.

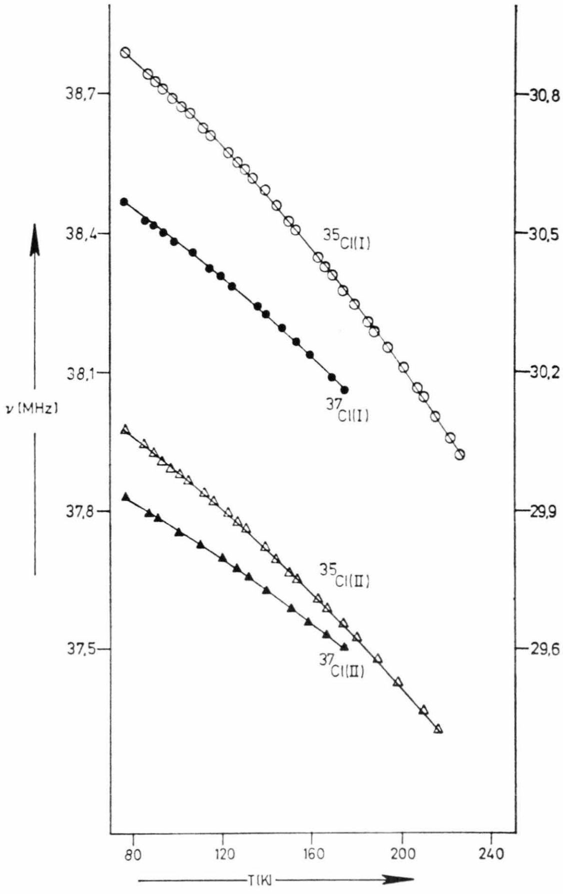

Fig. 2. Temperature dependence of the pure NQR frequencies in $CDCl_2COOD$. The solid curves were calculated from Eq. (2) using the parameters listed in Table 1.

$CHCl_2COOH$ could be observed up to 238 K, in $CDCl_2COOD$ up to 226 K. The ^{37}Cl spectra vanished even at 198 K and 175 K. At 77 K the ^{35}Cl NQR frequencies in $CHCl_2COOH$ agree with those reported by Chihara and Nakamura[3]. In both compounds the ^{35}Cl and ^{37}Cl spectra consist of two NQR lines which are due to different chlorine sites, Cl(I) and Cl(II).

The NQR frequency vs T curves show a small but clearly different temperature dependence for the sites Cl(I) and Cl(II) in the $CXCl_2$ group. This is probably due to differences in the bond lengths of Cl(I) and Cl(II). Further, the frequency ratio $\nu(^{35}\mathrm{Cl})/\nu(^{37}\mathrm{Cl})$ of the chlorine isotopes at Cl(I) and Cl(II) is temperature dependent. Therefore, from the measured data evidence may be found for the chlorine isotope effect: i. e. the chlorine isotopes may undergo slightly different effects of thermal vibrations which are involved in the averaging of the EFG tensor.

From Figs. 1 and 2 it follows that the ^{35}Cl(I) and ^{37}Cl(I) NQR frequencies of $CDCl_2COOD$ are up to 20 kHz lower than the corresponding frequencies of $CHCl_2COOH$, whereas the ^{35}Cl(II) and ^{37}Cl(II) NQR frequencies of $CHCl_2COOH$ and $CDCl_2COOD$ are the same within the limit of experimental error. The fact that in $CDCl_2COOD$ only the $^{35/37}$Cl NQR frequencies of Cl(I) are shifted indicates that mainly Cl(I) is affected by deuteration.

As will be emphasized, the Cl(I) frequencies of the deuterated compound are found to be lower than the Cl(I) frequencies of the undeuterated one. This is in contrast to what one would expect if the difference in amplitudes of thermal motions was the dominant factor contributing to the hydrogen-deuterium shift. The shift is slightly temperature dependent and becomes smaller with increasing temperature. Allen [4] has measured the pure quadrupole spectra of $CH_2ClCOOH$ and $CH_2ClCOOD$. He reported that the NQR lines were shifted 20 kHz higher in the deuterated compound which was assumed to be due to the difference in the $O..H-O$ and $O...D-O$ bonds in the acid dimers. In the case reported here the shift of the NQR frequencies may be primarily dominated by the effects of deuteration on electronic structure whereas the small temperature dependence of the shift may be attributed to thermal motions.

Since torsional motions are usually most effective in averaging the EFG tensor, analysis of NQR data is commonly based on fitting the NQR frequency vs T curve to a model which contains the torsional frequency and moment of inertia as adjustable parameters. In the present case the formula for $\nu(T)$ is given by the Bayer-Kushida theory [5, 6]

$$\nu(T) = \nu_0\left(1-\sum_i \frac{3\,A_i\,\hbar}{2\,\omega_i}\,[\tfrac{1}{2}+1/(\exp\{\hbar\,\omega_i/k\,T\}-1)]\right) \tag{1}$$

where ν_0 is the NQR frequency at 0 K in absence of zero-point energy, ω_i is the angular frequency of the lattice vibration and A_i is the corresponding inertia factor equal to the reciprocal of the moment of inertia for one rotational mode. The summation has to be taken over all modes. Actually, the approximation [7]

$$\nu(T) = \chi_1-\chi_2[\tfrac{1}{2}+1/(\exp\{\Theta_1/T\}-1)] \tag{2}$$

of Eq. (1) was fitted to the measured NQR data by a least squares method using χ_1, χ_2, and Θ_1 as adjustable parameters. Here,

$$\chi_1 = \nu_0\,, \tag{3}$$

$$\chi_2 = 3\,A_1\,\hbar\,\nu_0\,N/2\,\omega_1\,, \quad \text{and} \tag{4}$$

$$\Theta_1 = \hbar\,\omega_1/k\,. \tag{5}$$

Θ_1 is the Einstein temperature of the first mode, χ_1 the NQR frequency of the perfectly static lattice, and N the degeneracy of the mode.

In doing so, it must be mentioned that Eqs. (1) and (2) are based on several assumptions:

i) The molecular vibration is represented by the Einstein model in the harmonic approximation. This leads to two consequences, firstly that $(\partial\nu/\partial T)$ is negative and approaches a constant value at high temperatures and secondly that $(\partial^2\nu/\partial T^2)$ is negative at all temperatures. Figs. 1 and 2 show these features clearly.

ii) The most effective molecular motions in averaging the EFG tensor are torsions of the $CXCl_2$ group about the $C-C$ axis assuming $CXCl_2COOX$ exists as a dimer in the solid state.

iii) In the compounds investigated intramolecular stretching vibrations are not taken into account. $C-Cl$ stretching vibration frequencies are of the order of hundreds of cm^{-1} which are much less effective in averaging the EFG tensor than torsional motions [8]. However, the change in the bond nature due to stretching and/or bending vibrations may have an effect.

The parameters χ_1, χ_2, and Θ_1 thus determined are listed in Table 1 and the best fit obtained is shown in Figs. 1 and 2 by solid lines. The maximum difference between the measured and calculated NQR frequencies is not larger than 20 kHz and is also listed in Table 1. Assuming there is only one non-degenerate vibration mode, approximate values for $1/A_1$ and ω_1 can be calculated from Eqs. (4) and (5). Although it has been argued that these values have no physical significance [9] quite reasonable estimates of the order of magnitude have been obtained. Therefore, we conclude that for the com-

Table 1. Parameters for the temperature dependence of the NQR frequencies in $CHCl_2COOH$ and $CDCl_2COOD$ according to Eq. (2) and maximum differences between calculated and measured NQR frequencies in the temperature range investigated.

Compound	nucleus	χ_1 MHz	χ_2 MHz	Θ_1 K	$\nu_{exp}-\nu_{cal}$ kHz
$CHCl_2COOH$	^{35}Cl (I)	40.070 ±0.068	2.451 ±0.210	301.5 ±16.8	17
	^{35}Cl (II)	38.938 ±0.017	1.851 ±0.016	283.1 ±5.4	18
	^{37}Cl (I)	31.325 ±0.008	1.411 ±0.013	252.8 ±3.7	8
	^{37}Cl (II)	30.448 ±0.072	0.945 ±0.166	219.6 ±25.5	8
$CDCl_2COOD$	^{35}Cl (I)	39.885 ±0.065	2.119 ±0.119	276.9 ±8.7	10
	^{35}Cl (II)	38.839 ±0.013	1.655 ±0.041	266.6 ±5.4	10
	^{37}Cl (I)	31.300 ±0.042	1.371 ±0.217	245.6 ±27.0	5
	^{37}Cl (II)	30.478 ±0.009	1.012 ±0.001	229.6 ±2.1	4

Table 2. Temperature coefficients and their ratios at 77 K for ^{35}Cl(I, II) and ^{37}Cl(I, II) in $CHCl_2COOH$ and $CDCl_2COOD$. * These ratios were obtained from Equation (7).

Compound	$\frac{(\partial\nu/\partial T)}{\text{kHz/K}}$ ^{35}Cl(I)	$\frac{(\partial\nu/\partial T)}{\text{kHz/K}}$ ^{35}Cl(II)	$\frac{(\partial\nu/\partial T)}{\text{kHz/K}}$ ^{37}Cl(I)	$\frac{(\partial\nu/\partial T)}{\text{kHz/K}}$ ^{37}Cl(II)
$CHCl_2COOH$	−2.60	−2.35	−2.44	−2.28
$CDCl_2COOD$	−2.87	−2.49	−2.54	−2.21

	$(\partial\nu/\partial T)\,^{35}$Cl(I) / $(\partial\nu/\partial T)\,^{35}$Cl(II)	$(\partial\nu/\partial T)\,^{37}$Cl(I) / $(\partial\nu/\partial T)\,^{37}$Cl(II)
$CHCl_2COOH$	1.11 1.03 *	1.07 1.03 *
$CDCl_2COOD$	1.15 1.03 *	1.15 1.03 *

pounds investigated here Eq. (2) is adequate to describe the temperature dependence of the chlorine NQR frequencies.

Then, from Eq. (2) it follows as an expression for the temperature coefficient of the NQR frequencies

$$\frac{\partial\nu}{\partial T} = -\chi_2\cdot\frac{\Theta_1}{T^2}\,\frac{\exp\{\Theta_1/T\}}{(\exp\{\Theta_1/T\}-1)^2}\,. \qquad (6)$$

Taking the parameters of Table 1 at 77 K the values were calculated and listed in Table 2. In the approximation of the Bayer-Kushida theory the value of χ_2 is given by Equation (4). Assuming only torsional motions of the $CXCl_2$ group about the C – C axis, χ_2 should be the same for Cl(I) and Cl(II). Thus, the ratio of the temperature coefficients can be written as

$$\frac{\left(\dfrac{\partial\nu}{\partial T}\right)_{z_{\mathrm{Cl(I)}}}}{\left(\dfrac{\partial\nu}{\partial T}\right)_{z_{\mathrm{Cl(II)}}}} = \frac{(\chi_1)_{z_{\mathrm{Cl(I)}}}}{(\chi_1)_{z_{\mathrm{Cl(II)}}}}\,, \quad z = 35, 37\,. \qquad (7)$$

The ratios calculated by relation (7) are also given in Table 2. They show a disagreement with the ratios obtained from Equation (6). This is not very surprising in view of the assumptions made above. It confirms that effects other than torsional motions are also effective in averaging the EFG tensor at the chlorine sites. As pointed out Chihara and Nakamura [3] there are special interactions in or between molecules contributing to the NQR temperature dependence. The discussion of these interactions would need some more experimental knowledge such as the exact crystal structure, Raman measurements etc.

Table 3. Measured and calculated shifts of the NQR frequencies in $CHCl_2COOH$ at 189 K and in $CDCl_2$ COOD at 175 K.

Compound	nucleus	Δ_{exp}	Δ_{cal}	
$CHCl_2COOH$	^{35}Cl(I)	0.0164	0.0164	$T = 198$ K
	^{37}Cl(I)	0.0171	0.0160	
	^{35}Cl(II)	0.0141	0.0141	
	^{37}Cl(II)	0.0146	0.0136	
$CDCl_2COOD$	^{35}Cl(I)	0.0133	0.0126	$T = 175$ K
	^{37}Cl(I)	0.0134	0.0127	
	^{35}Cl(II)	0.0111	0.0107	
	^{37}Cl(II)	0.0110	0.0106	

As will be noticed from Table 2, at both chlorine sites the temperature coefficients of ^{35}Cl are higher than the coefficients of ^{37}Cl in agreement with the temperature dependence of the measured NQR frequencies. This confirms the presence of different effects of thermal motions for the chlorine isotopes.

Blinc and coworkers [10] studied the chlorine isotope effect in trichloro acetic acid. They discussed the effect on the basis of the relative shift Δ of the NQR frequencies expressed by

$$\Delta = (\nu_{77} - \nu_T)/\nu_{77} \qquad (8)$$

where ν_{77} is the frequency at 77 K and ν_T at T K. In the approximation of the Bayer-Kushida theory the shift can be explicitly given by

$$\frac{\nu_{77}-\nu_T}{\nu_{77}} = 1 - \frac{\chi_1 - \chi_2\left(\dfrac{1}{2} + \dfrac{1}{\exp\{\Theta_1/T\}-1}\right)}{\chi_1 - \chi_2\left(\dfrac{1}{2} + \dfrac{1}{\exp\{\Theta_1/77\}-1}\right)}\,. \qquad (9)$$

The values obtained for $CHCl_2COOH$ at 198 K and for $CDCl_2COOD$ at 175 K are listed in Table 3. In $CHCl_2COOH$ a small isotope effect was found. It is shown in Figure 3. The measured shifts for ^{35}Cl(I) and ^{35}Cl(II) agree with the shifts calculated by Eq. (8) whereas the measured shifts for ^{37}Cl(I) and ^{37}C(II) are higher than the calculated ones. This indicates also that effects other than only torsional motions are responsible for the chlorine isotope effect, such as bond stretching and/or bending motions. However, at present no estimate can be given for the influence of the changes in the bond nature due to such motions on the EFG tensor.

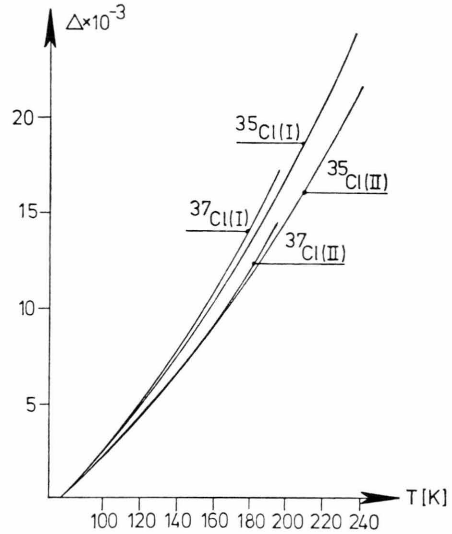

Fig. 3. Temperature dependent shift of the ^{35}Cl(I, II) and ^{37}Cl(I, II) NQR frequencies in $CHCl_2COOH$.

No significant difference has been found or calculated between the ^{37}Cl and ^{35}Cl shifts in $CDCl_2COOD$ (see Table 3). The reason is not yet clear. Probably the effect of deuteration on the electronic structure is responsible for masking the chlorine isotope effect in this compound.

4. Conclusion

We have measured the temperature dependence of the ^{37}Cl and ^{35}Cl NQR frequencies in $CHCl_2COOH$ and $CDCl_2COOD$. To analyze the measured NQR frequencies the Bayer-Kushida theory was used which considers torsional motions only. The analysis revealed that motions other than torsional ones are also effective in averaging the EFG tensor. However, with the aid of the Bayer-Kushida theory the temperature dependence of the NQR frequencies could be described satisfactorily within the experimental error. To get a more detailed picture of the motions which are involved in the averaging of the EFG tensor, NQR measurements down to liquid helium temperature and with higher accuracy, as well as Raman measurements, should be of advantage.

Acknowledgements

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