# The Motion of the OH Group in p-Chlorophenol and its Influence on the $^{35}$Cl NQR Parameters*, **

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The $^{35}$Cl NQR transition frequencies and the spin-lattice relaxation times, $T_1$, for both lines in p-chlorophenol have been measured in the temperature range 90–310 K. The frequency difference and the temperature derivatives for both lines clearly show the existence of two temperature intervals with distinct lattice contributions to the EFG. Similarly, $T_1$ data show a normal behaviour due to spin-phonon interactions up to 240 K. Above this temperature $T_1$ begins to shorten in an exponential manner. The hindered motions of the OH group are proposed as responsibles of these effects, and an activation energy of 26 kJ mol$^{-1}$ is determined.

## Introduction

Crystalline p-chlorophenol in the stable $\alpha$ phase has two $^{35}$Cl nuclear quadrupole resonances (NQR) [1] due to the existence of two crystallographically non-equivalent chlorine sites. The temperature dependence of both resonances looks normal, and the splitting between the two lines exhibits a slight change over a wide temperature range. Previous Zeeman effect studies [2, 3] reveal that the higher frequency line $\nu^+$ corresponds to resonant nuclei located such that the Cl–O vector makes a small angle with the (010) plane (Type II molecules according to Perrin and Michel's notation, [4]), and the low frequency line $\nu^-$ is associated with chlorines such that its Cl–O vector makes a large angle with the (010) plane (Type I molecules). In this paper the temperature dependence of the NQR frequency, $\nu_Q(T)$, for both resonance lines, and the spin-lattice relaxation time, $T_1(T)$, are reported and the possibility of hindered reorientational motion of the OH groups is examined.

## Experimental

A powder p-chlorophenol sample, provided by Fluka (catalog number 25850), was used.

The $^{35}$Cl NQR frequency was measured by means of a super-regenerative type spectrometer with an error of about +/– 300 Hz. The spin-lattice relaxation time was measured using both continuous pulse (for $T_1 > 30$ ms) and $\pi/2 - \pi/2$ pulse (for $T_1 < 30$ ms) sequences in a conventional pulsed spectrometer.

## Temperature Dependence of the NQR Frequency

The $^{35}$Cl NQR frequency, $\nu_Q(T)$, was measured in the temperature range 90 to 310 K. The data are shown in Figure 1.

Figure 2 shows the frequency difference $\Delta\nu_Q = \nu^+ - \nu^-$ vs. $T$. A change in the curvature of $\Delta\nu_Q$ is observed at about 240 K, which is correlated to a marked change in the shape of $T_1(T)$, Fig. 4, for both lines. Therefore, the analysis of $\nu_Q(T)$ is restricted to the low temperature range by means of Bayer's expression [5]

$$\nu_Q(T) = \nu_0 \left[1 - 3/2 \langle\theta^2\rangle\right], \tag{1}$$

where $\nu_0$ is the static lattice resonance frequency. The asymmetry parameter has been neglected since its value was shown to be about 0.08 (3). $\langle\theta^2\rangle$ is given by [6]

$$\langle\theta^2\rangle = \frac{\hbar}{2} \sum_j \frac{1}{I_j\,\omega_j} \coth\left(\frac{\hbar\,\omega_j}{2kT}\right), \tag{2}$$

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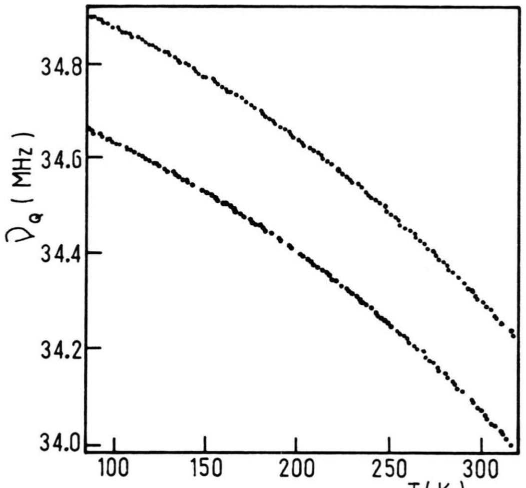

Fig. 1. Temperature dependence of the lower ($\nu^-$) and upper ($\nu^+$) NQR frequencies.

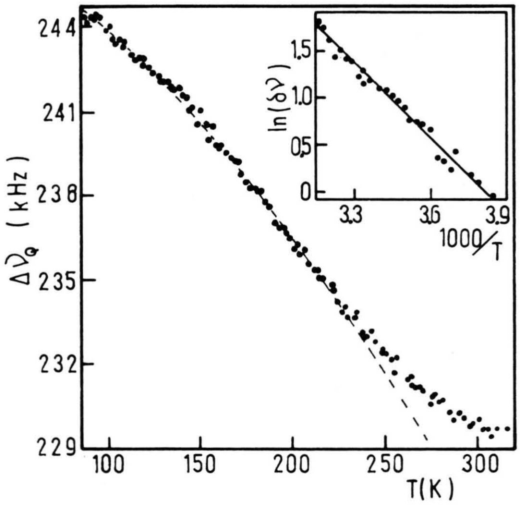

Fig. 2. Frequency difference between $\nu^+$ and $\nu^-$ ($\Delta\nu_Q$). Dashed line corresponds to a fit with a second degree polynomial. The insert shows the difference between the $\Delta\nu_Q$ data and the dashed line ($\delta\nu$ in kHz) as a function of $1000/T$ ($T$ in K).

where the sum is taken including all the internal bending of the Cl−C bond and the torsional lattice modes. In order to evaluate the contribution of the internal modes to $\langle\theta^2\rangle$ we use the eigen-vectors and frequencies given by Varsanyi [7], and following O'Leary [8] to calculate the $I_{j\text{'s}}$ we may write

$$\begin{aligned}\langle\theta^2\rangle = {} & 3.72\cdot 10^{-4}\coth\left(\frac{312.2}{T}\right)\\ & + 7.05\cdot 10^{-4}\coth\left(\frac{238.1}{T}\right)\\ & + 6.69\cdot 10^{-4}\coth\left(\frac{118.0}{T}\right)\\ & + 4.05\cdot 10^{-4}\coth\left(\frac{195.0}{T}\right)\\ & + \frac{\hbar}{2 I_e\,\omega_e}\coth\left(\frac{\hbar\,\omega_e}{2kT}\right), \end{aligned} \tag{3}$$

where the four first terms are internal mode contributions and the last accounts for the lattice contribution. $\omega_e$ is an effective lattice librational frequency related to $\omega_x$ and $\omega_y$ by

$$\frac{1}{I_e} = \frac{1}{I_x} + \frac{1}{I_y}; \quad \frac{1}{I_e\,\omega_e^2} = \frac{1}{I_x\,\omega_x^2} + \frac{1}{I_y\,\omega_y^2} \tag{4}$$

with $I_x$, $\omega_x$ and $I_y$, $\omega_y$ being the molecular moments of inertia and the librational frequencies about the $x$ and $y$ axes of the Electric Field Gradient (EFG), respectively. The $z$-axis is along the Cl−C direction and the $x$-axis is perpendicular to the benzene ring.

In order to take into account thermal expansion effects on the lattice frequencies a linear temperature behaviour is adopted as proposed by Brown [9]:

$$\omega_e = \omega_{e0}\,(1 - C_e T)\,. \tag{5}$$

Equations (3), (4) and (5) permit us to fit the frequency data for $T < 240$ K. The following values are obtained:

$\nu_0^+ = (35\,173.6 \pm 0.4)$ kHz, $\omega_{e0}^+ = (60.6 \pm 0.2)\ \text{cm}^{-1}$,
$C_e^+ = (8.08 \pm 0.04)\ 10^{-4}\ \text{K}^{-1}$,
$\nu_0^- = (34\,923.3 \pm 0.4)$ kHz, $\omega_{e0}^- = (61.6 \pm 0.2)\ \text{cm}^{-1}$
and $C_e^- = (8.13 \pm 0.04)\ 10^{-4}\ \text{K}^{-1}$,

Note that the temperature dependences of the effective frequency, $\omega_e$, obtained for both $\nu^+$ and $\nu^-$ are similar. Fitting the frequency data in the whole temperature range yields effective torsional frequencies differing by about 10% for the two lines.

The obtained effective torsional frequencies are in agreement with previous measurements [10] and the temperature coefficient $C_e$ is similar to the corresponding one for other substituted benzene compounds [11].

Since $\Delta\nu_Q$ reflects the difference between the lattice contributions to each resonant site, namely Cl (I) and Cl (II), the change of $\Delta\nu_Q$ may be associated with the onset of a neighbouring OH molecular group motion. Two temperature zones are distinguished for the data, i.e. $T < 240$ and $T > 240$, as may be seen from Figure 2. For each zone the data are best fitted by means of a second degree polynomial:

$$\Delta\nu^{\mathrm{I}}(\mathrm{kHz}) = 247.9 - 0.025\,T - 1.60\cdot 10^{-4}\,T^2, \qquad T < 240\,\mathrm{K}. \tag{6}$$

$$\Delta\nu^{\mathrm{II}}(\mathrm{kHz}) = 271.8 - 0.247\,T + 3.53\cdot 10^{-4}\,T^2, \qquad T > 240\,\mathrm{K}.$$

Taking the difference between the $\Delta\nu_Q$ data, for $T > 240$, and the analytical fit corresponding to the low temperature zone, and plotting the logarithm of this difference vs. $1/T$ (insert in Fig. 2), a linear behaviour is found. The slope of the plotted difference $\delta\nu$ is $E_d = (23.3 \pm 1.7)\,\mathrm{kJ\,mol^{-1}}$, which shows that the contribution to $\nu_Q$ by the OH group is given by

$$\delta\nu^{\mathrm{OH}} = A + C\,e^{-E_d/kT}.$$

Although this equation is obtained by means of the above mentioned data manipulation, presently there are no basic principles available from which to deduce such a temperature behaviour of $\delta\nu^{\mathrm{OH}}$. Also, the temperature derivatives for both lines clearly depict the existence of two temperature intervals evidencing the two different lattice contributions to the EFG, Figure 3. The obtained value for $E_d$ is close to the activation energy determined from the $T_1(T)$ data.

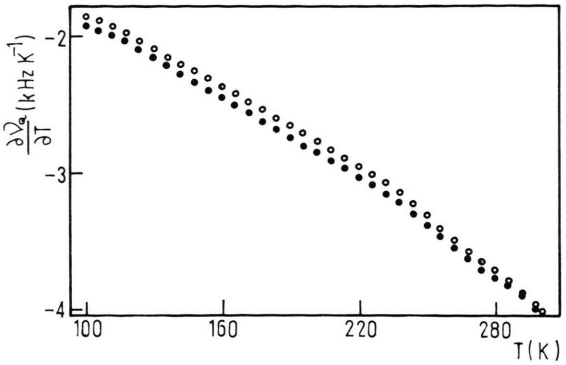

Fig. 3. Temperature derivatives ($\partial\nu_Q/\partial T$) for $\nu^+$ (open circles) and $\nu^-$ (solid circles).

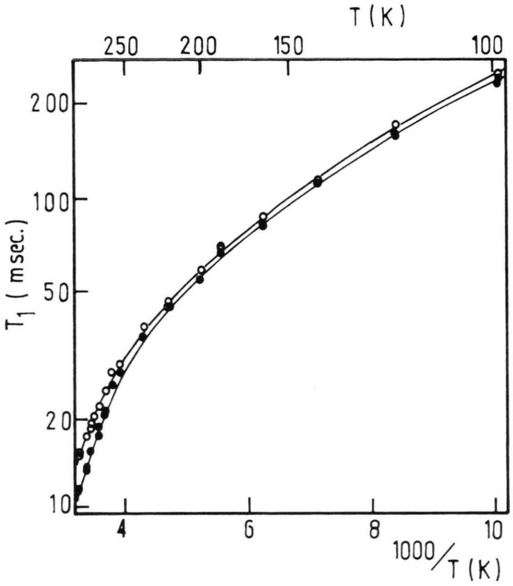

Fig. 4. Spin-lattice relaxation time for $\nu^+$ (open circles) and $\nu^-$ (solid circles). Solid lines correspond to fit with Equation (9).

## Spin-Lattice Relaxation Time

Spin lattice relaxation times were measured in the temperature range 100 to 310 K for each line, and depicted in Figure 4. From the data two temperature zones are clearly distinguished, i.e. $T < 240$ K and $T > 240$ K. In the low temperature zone, $T_1$ behaves as $T_1 = A\,T^{-\lambda}$ with $\lambda \cong 2.2$, indicating a relaxation mechanism mainly governed by torsional oscillations [12]. In the high temperature zone, $T_1(T)$ decreases faster than for low temperatures, also the rate of decrease of $\nu^-$ is larger. This is associated with a reorientational motion of the OH group belonging to a neighbouring molecule. The change in the contribution to the EFG created at the resonant site by reorientational motion of a neighbouring atomic group should modulate the EFG at this nucleus and give rise to an effective spin-lattice relaxation mechanism with a rate [12]

$$\left(\frac{1}{T_1}\right)_{\mathrm{mod}} = \frac{1}{12}\left(\frac{e^2 Q q'}{\hbar}\right)^2 \frac{\tau_c}{1+\omega_Q^2\tau_c^2}, \tag{7}$$

where $q'$ is that part of the EFG at the nucleus which changes with the reorientational motion and whose correlation time is

$$\tau_c = \tau_0 \, e^{E_a/kT} , \tag{8}$$

where $E_a$ is the potential barrier hindering reorientation. The $T_1$ ($T$) data were fitted by means of

$$\left(\frac{1}{T_1}\right) = \left(\frac{1}{T_1}\right)_{\text{libr}} + \left(\frac{1}{T_1}\right)_{\text{mod}} = a\,T^{\lambda} + B\,e^{-E_a/kT} , \tag{9}$$

where the exponential in (9) is obtained from (7) when slow reorientational motion is assumed, i.e. $\omega_Q \tau_c \gg 1$. The fitting for both lines gives

$$\lambda = 2.24 \pm 0.02 , \quad E_a = (26.2 \pm 1.3) \text{ kJ mol}^{-1} .$$

A similar behaviour of $T_1$ as that given by (7) could be obtained by modulations of the dipole-dipole interaction between the Cl and the H nuclei. However, such a possibility is discarded since the observed $T_1$'s yield Cl$-$H distances of the order of 0.1 Å. Besides, the change of curvature of $\Delta\nu_Q$ at 240 K corroborates the above conclusion.

The parameter $B$ from (9) allows to determine the ratio of the OH contributions to $\nu_Q$

$$\frac{B^{(+)}}{B^{(-)}} = \left(\frac{\nu_Q^-}{\nu_Q^+}\right)^2 \left| \frac{\delta\nu_{(+)}^{\text{OH}}}{\delta\nu_{(-)}^{\text{OH}}} \right|^2 , \quad \delta\nu_{(-)}^{\text{OH}} = 1.4\,\delta\nu_{(+)}^{\text{OH}}$$

which clearly shows that the OH group contributes more to the resonant Cl in type I molecules, giving rise to $\nu^-$. This is also plausible since type I molecules are arranged in loose dimers, and it may be this which causes a lowering of the Cl (I) NQR frequency relative to Cl (II) [13].

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