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STUDY OF INTERNAL MOTIONS IN 2,5-DICHLORO-3,6-DIHYDROXY-P-BENZOQUINONE USING NQR

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Temperature dependence of chlorine pure quadrupole resonance frequency in 2,5-dichloro-3,6-dihydroxy-P-benzo-quinone (chloroanilic acid) is studied experimentally in the range 77–304 K. The data are analysed and torsional frequencies regarding internal motions in this molecule are evaluated in the above temperature range using Bayer's theory and Brown's method.

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1. *Introduction*

Temperature dependence of Nuclear Quadrupole Resonance (NQR) is useful to obtain information about librational motions (torsional oscillations) and phase transitions in solids. Bayer explained the temperature dependence as due to the motional averaging of the Electric Field Gradient (EFG) caused by the torsional oscillations of the molecule about the principal EFG axes. Further, he assumed that these oscillations are harmonic and derived an equation for the temperature dependence of NQR frequency for the case of spin $I = 3/2$ and axially symmetric EFG tensor (i.e. $\eta = 0$). Thus in favourable cases, where $\eta \approx 0$ and where the harmonic approximation is valid, Bayer's theory may be expected to yield reliable values for the torsional frequencies [1].

In this paper, we report the results of our measurements on the temperature dependence of chlorine NQR frequency in chloroanilic acid from 77 K to room temperature (304 K). As the centre of the molecule is also the centre of inversion symmetry (Fig. 1), the principal axes of moment of inertia coincide with the principal EFG axes and thus the harmonic

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approximation used in Bayer's equation is expected to hold good in this compound. NQR in chloroanilic acid was reported earlier by Bray et al. [2] at two temperatures, namely 77 K and 298 K. We have observed a single (rather broad) line throughout the temperature range, indicating that the two chlorines in the molecule are chemically equivalent in agreement with the crystal structure data [3]. The signal being rather broad (6 to 7 KHz) was barely visible on the oscilloscope and was recorded after lock-in detection. Using our experimental results and the crystal structure data of Anderson [3], we have analysed the temperature dependence of NQR frequencies following Bayer [4] and Brown [5] and estimated the torsional frequencies and their temperature coefficients.

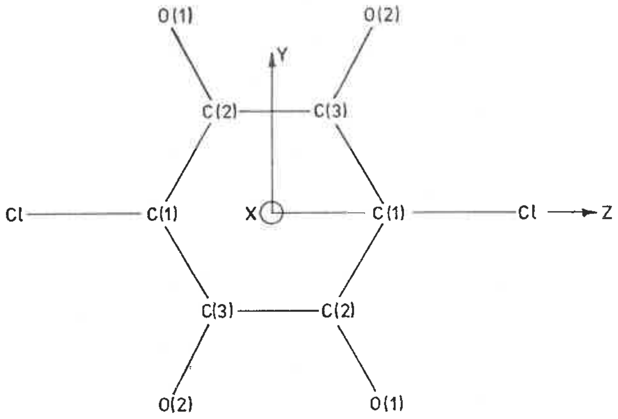

Fig. 1. Molecular structure of the compound 2,5-dichloro-3,6-dihydroxy-p-benzoquinone (chloranilic acid)

2. *Method of calculation*

The details of the method of calculation have already been reported [6]. Only the necessary equations are repeated here. The C—Cl bond direction is taken as the principal z direction. The electric field gradient at the chlorine nucleus is taken as having axial symmetry about the C—Cl bond direction, i.e. $\eta = 0$, and the torsional motions about the x and y axes only are considered since the torsional motion about the z axis does not contribute to the changes in the maximum component of an axially symmetric field gradient.

On the basis of Bayer's theory

$$\nu_T = \nu_0 - \nu_Q \left[\frac{3h}{8\pi^2 A_x f_x} \cdot \frac{1}{\exp(hf_x/kT - 1)} + \frac{3h}{8\pi^2 A_y f_y} \cdot \frac{1}{\exp(hf_y/kT - 1)} \right];$$

$$\nu_0 = \nu_Q \left(1 - \frac{3h}{16\pi^2 A_x f_x} - \frac{3h}{16\pi^2 A_y f_y} \right),$$

where ν_0 is the resonance frequency at $T = 0$ K, ν_Q is the resonance frequency of the stationary molecule, f_x and f_y are the torsional frequencies about the x and y axes, A_x and A_y

being the corresponding moments of inertia, k is the Boltzmann constant and T is the absolute temperature of the sample.

Bayer's equation was solved using numerical method [7] and the torsional frequencies at each temperature are evaluated. The temperature variation of torsional frequencies (f_i) is also analysed following Brown [5]. Assuming a linear temperature dependence for f_i as $f_i = f_i^0(1-g_iT')$ where T' is the temperature measured from any reference temperature T_0, g_i is the corresponding temperature coefficient and f_i^0 is the lattice frequency at $T' = 0$ (at T_0) and using the high temperature approximation, we get [5]

$$\frac{d\nu/.\ T'|_{T'=0}}{d^2\nu/dT'^2|_{T'=0}} = \frac{1+2T_0\langle g\rangle}{4\langle g\rangle+6T_0\langle g^2\rangle},$$

where

$$\langle g\rangle = \sum_i (A_i/\omega_i^{02})g_i/\sum_i (A_i/\omega_i^{02}), \quad \langle g^2\rangle = \sum_i (A_i/\omega_i^{02})g_i^2/\sum_i (A_i/\omega_i^{02}).$$

Here it is assumed that $g^2 = \langle g\rangle^2 = \langle g^2\rangle$. The average temperature coefficients for the torsional modes are estimated from the above equations by curve-fitting the experimental points to Brown's parabolic equation and calculating the derivatives.

3. Results and discussion

The observed temperature variation of the resonance frequency is shown in Fig. 2. The other data on the molecule, such as the moments of inertia A_x and A_y, ν_0, g_x, g_y and mean g, are given in Table I.

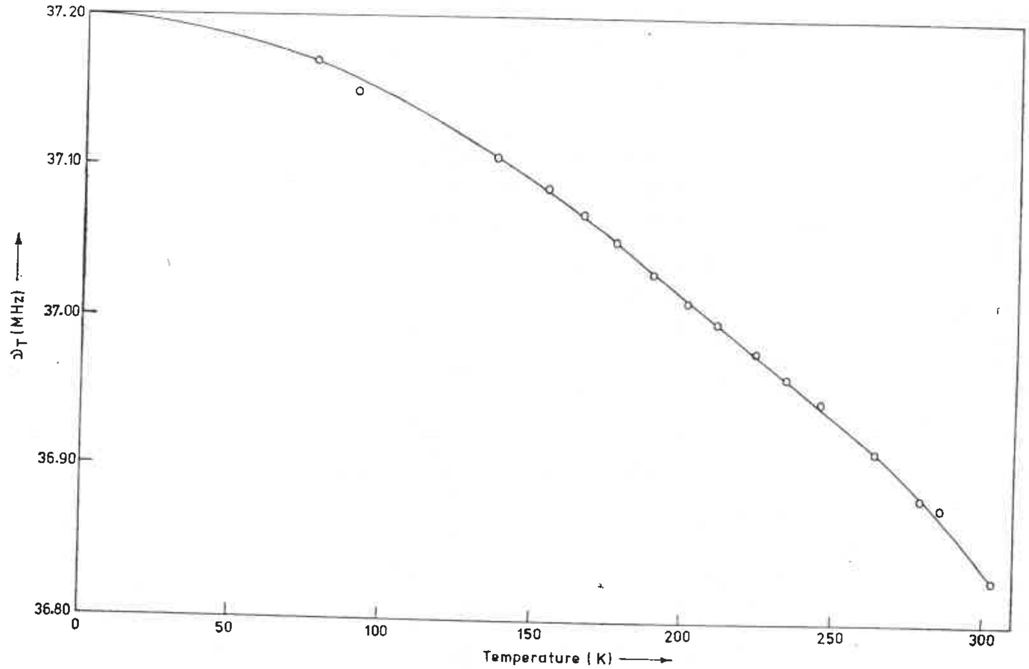

Fig. 2. Variation of ^{35}Cl resonance frequency (ν_T) with temperature

TABLE I

Parameters used in the calculation of torsional frequencies

Compound	ν_0 MHz	A_x 10^{-40} gm cm^2	A_y 10^{-40} gm cm^2	g_x	g_y	g
Chloroanilic acid	37.202	2210.28	1499.04	0.0022	0.0017	0.00134[a] 0.00137[b]

[a] Value obtained by the numerical method.

[b] Value obtained by Brown's method.

The variation of torsional frequencies f_x and f_y with temperature is shown in Fig. 3 and it is observed that in both cases the variation is almost linear in the range 90 to 304 K. But there are no experimental data available from the literature on the torsional frequencies and their temperature variation for this molecule. However, the values observed here lie in the expected range [8]. f_x varies from 38 to 55 cm^{-1} in the temperature range 304 K to 90 K whereas f_y takes values from 52 to 75 cm^{-1} in the same range of temperature. The value of g obtained by numerical method compares well with that obtained by Brown's method.

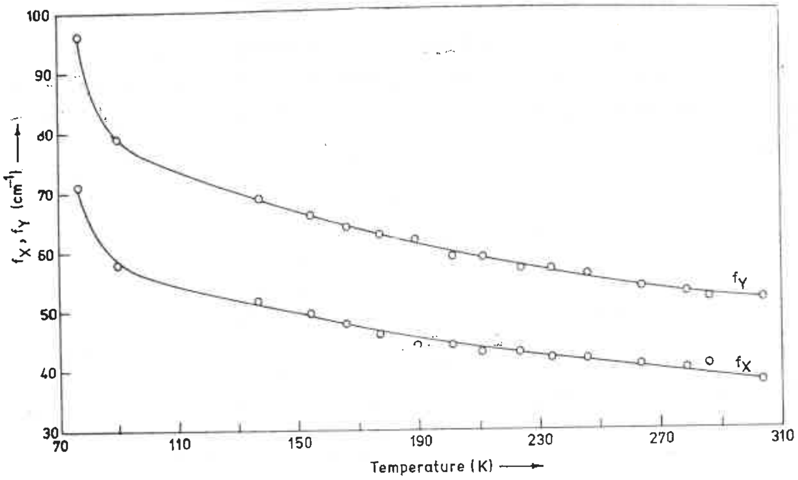

Fig. 3. Variation of f_x, f_y with temperature

It would be interesting to compare our data about librational frequencies of this molecule with infrared or Raman spectroscopic data when the latter become available.

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