

Temperature Dependence of ^{35}Cl NQR in 3,4-Dichlorophenol

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NQR frequencies in 3,4-dichlorophenol are investigated in the temperature range 77 K to room temperature. Two resonances have been observed throughout the temperature range, corresponding to the two chemically inequivalent chlorine sites. Using Bayer's theory and Brown's method torsional frequencies and their temperature dependence in this range are estimated.

Chloro-substituted phenols form an interesting class of compounds and have been the subject of several studies employing nuclear quadrupole resonance (1). In this paper, we report the results of our measurements on the temperature dependence of the chlorine NQR frequency in 3,4-dichlorophenol in the range 77 to 298 K. The resonance frequencies in 3,4-dichlorophenol were reported earlier by Pies and Weiss (1) at 77 K, 195 K, and room temperature. Two lines are present throughout the temperature range studied, indicating that there are two chemically inequivalent chlorines.

In this work, a frequency modulated, self-quenched superregenerative spectrometer was used for detecting the resonances. The resonance frequencies were measured with a BC-221 frequency meter with an accuracy of ± 1 kHz and the temperatures were measured with a copper-constantan thermocouple with an accuracy of ± 0.5 K.

METHOD OF CALCULATION

According to Bayer's theory (2), the temperature dependence of an NQR frequency (for $I = 3/2$ and $\eta = 0$) is given by

$$\nu_T = \nu_0 \left[1 - \frac{3\hbar}{8\pi^2} \sum_i \frac{1}{A_i f_i} \left(\frac{1}{2} + \frac{1}{e^{\hbar f_i/kT} - 1} \right) \right], \quad [1]$$

where $i = X, Y, Z$ denote the principal EFG axes, the Z axis is taken along the C–Cl direction, the Y axis is taken perpendicular to the Z axis and lies in the plane

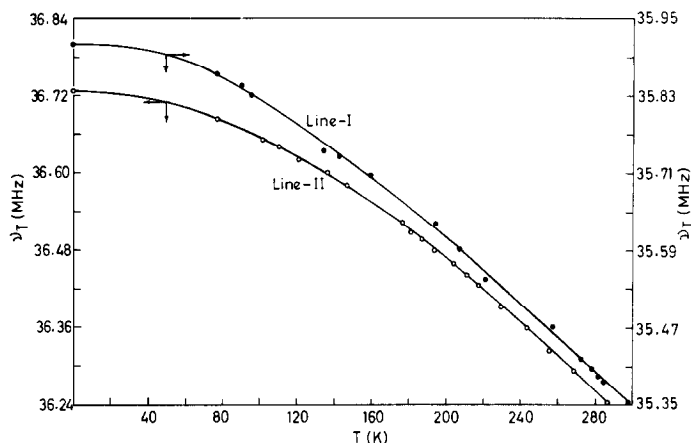


FIG. 1. Variation of resonance frequency (ν_T) with temperature (Lines I and II).

of the molecule, the X axis is perpendicular to the plane of the molecule, A_i 's are the moments of inertia, and f_i 's are the corresponding torsional frequencies. Bayer assumed that the torsional motions about the principal axes of the EFG tensor are harmonic. This is generally not true except when the moment of inertia axes coincide with the EFG axes.

However, when the moment of inertia axes differ from the principal EFG axes, the modification of Tatsuzaki *et al.* (3) seems to be relevant and this has been employed in the present case. Bayer's expression for the temperature dependence of NQR frequency then takes the form

$$\nu_T = \nu_0 \left[1 - \frac{3h}{8\pi^2} \sum_i \frac{\sin^2 \alpha_i}{A_i f_i} \left(\frac{1}{2} + \frac{1}{e^{hf_i/kT} - 1} \right) \right], \quad i = X, Y, Z, \quad [2]$$

where the expansion is over the three torsional motions about the moment of inertia axes, and the α_i 's are the angles made by the axes of motion with the principal Z axis of the EFG tensor. In principle, a three-mode calculation would be ideal for evaluating the torsional frequencies but the numerical analysis becomes complicated. Instead, a two-mode analysis has been carried out neglecting the mode corresponding to the highest component of the moment of inertia tensor and the torsional frequencies are evaluated by the numerical method (4).

Torsional frequencies f_1 and f_2 in the 3,4-dichlorophenol molecule were calculated at each temperature by means of Eq. [2]. The procedure followed for the actual calculations of f_1 and f_2 is the same as that used by Chandramani *et al.* (5). The temperature variation of torsional frequencies (f_i) is also analyzed following Brown (6). Assuming a linear temperature dependence for f_i as

$$f_i = f_i^0 (1 - g_i T'),$$

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 (6), we get

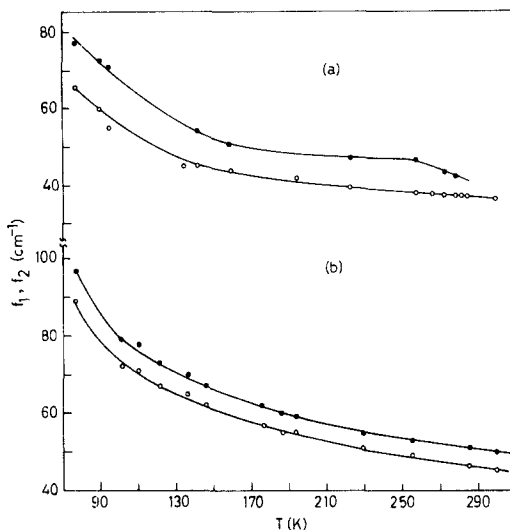


FIG. 2. (a) Variation of f_1, f_2 with temperature for Line I. (b) Variation of f_1, f_2 with temperature for Line II.

$$\left(\frac{d\nu}{dT'}\right)_{T'=0} \bigg/ \left(\frac{d^2\nu}{dT'^2}\right)_{T'=0} = (1 + 2T_0g)/(4g + 6T_0g^2),$$

where

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

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 and calculating the derivatives of ν versus T' curves.

RESULTS AND DISCUSSION

The variation of NQR frequency with temperature for the two resonance lines is shown in Fig. 1. The resonance frequency decreases with an increase in temperature as expected and no phase transition is observed in the temperature range studied. The present values of NQR frequency agree well with the earlier results (1).

The torsional frequencies are evaluated at various temperatures in the range 77 to 298 K and the variation with temperature is shown in Fig. 2. It may be seen from Fig. 2, that the variation of both f_1 and f_2 is almost linear in the temperature range 130 K to room temperature, but below this temperature both f_1 and f_2 increase quite rapidly with a decrease in temperature. The temperature coefficients g_1 and g_2 of f_1 and f_2 and the average g are calculated and given in Table 1.

The results are also analyzed by Brown's method (6) by fitting the experimental data in the high-temperature region to a parabola centered at $T_0 = 200$ K and the values of g obtained for both the lines are given in Table 1. The values of g ob-

TABLE 1
PARAMETERS USED IN THE CALCULATION OF TORSIONAL FREQUENCIES

Compound	ν_0 (MHz)	A_1 (10^{-40} g cm ²)	A_2 (10^{-40} g cm ²)	g_1	g_2	g
3,4-Dichlorophenol						
Line I	35.911	865.5	455.0	0.0008	0.0010	0.0008 ^a 0.0005 ^b
Line II	36.729	865.5	455.0	0.0013	0.0012	0.0012 ^a 0.0010 ^b

^a Value obtained by the numerical method.

^b Value obtained by Brown's method.

tained by Brown's method compare quite well with those obtained by the numerical method.

The values obtained for the torsional frequencies seem to be reasonable (7). It would be interesting to compare these values of torsional frequency with Raman and ir data when they become available.

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