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BRIEF COMMUNICATIONS

Temperature Dependence of ^{35}Cl NQR in 2,6-Dichloropyridine

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Chlorine NQR in 2,6-dichloropyridine has been investigated in the temperature range 77 K to room temperature and a single resonance line has been observed throughout. Using this data, torsional frequencies of the molecule have been evaluated on the basis of both the Bayer theory and the modified Bayer theory incorporating Tatsuzaki correction.

Introduction

The NQR frequency of ^{35}Cl in 2,6-dichloropyridine has been measured by previous workers both at 77 K (*1*) and at room temperature (*2*, *3*). We have measured ^{35}Cl NQR frequencies in this solid over the temperature range 77 K to room temperature. A single resonance line has been observed throughout the range. The temperature dependence of NQR interaction in molecular solids is due mostly to low frequency torsional vibrations. For analyzing our experimental results we have employed three of the well-known theoretical treatments of this temperature dependence, viz. Bayer (*4*), Tatsuzaki (*5*), and Brown (*6*).

Polycrystalline samples of 2,6-dichloropyridine were studied in these experiments. A homemade NQR spectrometer with a solid state lock-in-detection system was used to record the signals and the NQR frequencies were measured with a BC 221 frequency meter to an accuracy of ±1 kHz. A low temperature cell was used for the slow variation of temperature of the sample. The temperatures were measured with an iron-constantan thermocouple with an accuracy of ±1 K.

Results and Discussion

The present values of NQR frequencies, both at 77 K and at room temperature agree well with the earlier results. The observed temperature dependence of the NQR frequency is shown in Fig. 1. The resonance frequency decreases with the increase of temperature as expected and no phase transition is observed in the temperature region studied. The difference between the resonance frequency at 77 K and that at 298 K is

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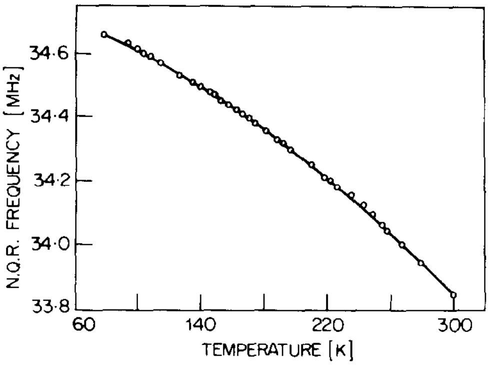

FIG. 1. Temperature dependence of NQR frequency in 2,6-dichloropyridine.

803 kHz. The temperature coefficient γ of the NQR frequency is calculated at three temperatures, 77, 210, and 290 K, and the values obtained are $0.688 \times 10^{-4}\ K^{-1}$, $1.135 \times 10^{-4}\ K^{-1}$, and $1.505 \times 10^{-4}\ K^{-1}$, respectively.

The torsional frequencies of the molecule have been evaluated by the Bayer method and the modified Bayer method incorporating Tatsuzaki correction, as follows.

(*a*) *The Bayer Method*

Torsional frequencies f_X and f_Y of the molecule about the principal X and Y axes of the electric field gradient tensor have been evaluated following Bayer (*4*) and Brown (*6*). Since the torsional vibration about the Z axis does not affect the NQR frequency except through the asymmetry parameter which is a second order effect, it is not considered. The calculated moments of inertia, A_X and A_Y of the molecule about the principal X and Y axes of the electric field gradient are given in Table I. The value of the resonance frequency ν_0 at 0 K is obtained by the least square fitting of the experimental data of NQR frequency to a polynomial of order four in absolute temperature and is given in Table I. The torsional frequencies at various temperatures in the region 77 to 300 K are calculated by the numerical method of Vijaya and Ramakrishna (*7*) using the DEC-10 computer.

The variation of the frequencies of torsional vibrations with temperature is shown in Fig. 2a. It may be seen from the figure that the variation of torsional frequencies with temperature is linear. The temperature coefficients g_X and g_Y of f_X and f_Y, respectively, are calculated from the values of torsional frequencies using the equation $f_i = f_i^0 (1 - g_i T')$ where T' is the temperature measured from any reference temperature T_0, $f_i (i = X, Y)$ is the torsional frequency at T' and f_i^0 at T_0, and g_i is the temperature coefficient. The calculations are made by choosing $T' = 0$ at $T = 225$ K (high temperature approximation) and the values obtained for g_X and g_Y are also given in Table I. The results are also analyzed by Brown's method by fitting the experimental data of NQR frequencies in the high temperature region to a parabola centered at $T_0 = 225$ K and the value of g obtained by this method agrees well with that obtained by the numerical method.

(*b*) *The Modified Bayer Type of Calculation Incorporating Tatsuzaki Correction*

In the Bayer theory, the torsional motion was assumed to take place about the principal axes of the electric field gradient (EFG) tensor. But, Tatsuzaki (*5*) suggested that torsional vibrations are to be considered as occurring about the principal axes of the moment of inertia. Taking the example of hexachloroethane, Tatsuzaki showed that a torsional mode about the *i*th axis of the

TABLE I

VALUES OF THE PARAMETERS USED IN THE CALCULATION OF TORSIONAL FREQUENCIES IN THE 2,6-DICHLOROPYRIDINE MOLECULE

ν_0 (MHz)	34.818	$A_1(10^{-40}$ g cm$^2)$	1292.5
$A_X(10^{-40}$ g cm$^2)$	1292.5	$A_2(10^{-40}$ g cm$^2)$	282.2
$A_Y(10^{-40}$ g cm$^2)$	854.6	α_1	90°
		α_2	62.5°
g_X	0.00087	g_1	0.0011
g_Y	0.0009	g_2	0.0011

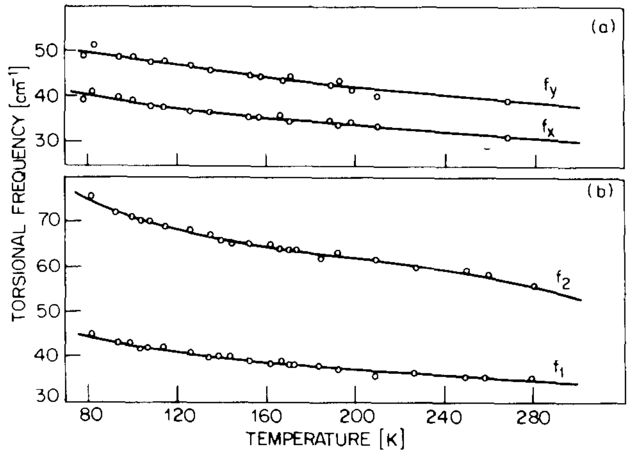

FIG. 2. Temperature dependence of torsional frequencies in 2,6-dichloropyridine following (a) Bayer method and (b) modified Bayer method incorporating Tatsuzaki correction.

principal moment of inertia modifies the Bayer expression through a weightage factor $\sin^2\alpha_i$, where α_i is the angle between the ith principal axis and the EFG Z axis (viz. C–Cl direction). Numerical evaluation of torsional frequencies about all the three principal axes would be ideal, but such an evaluation is quite difficult. Hence the motion of the molecule only about the two axes which make maximum contribution to the resonance frequency through the factor $(\sin^2 \alpha_i)/A_i$ were considered. The moments of inertia A_1 and $A_2(A_i;\ i = 1,2)$ of the molecule about these two principal axes and their corresponding angles α_1 and α_2 to the EFG Z axis were evaluated by using the substitutional structure method (*1*).

Using the above data, the torsional frequencies f_1 and f_2 $(f_i;\ i = 1,2)$ about the two principal axes were evaluated at various temperatures between 77 K and room temperature. The variation of torsional frequency with temperature is quite linear in both the cases as shown in Fig. 2b. The values of temperature coefficients g_1 and g_2 of f_1 and f_2, respectively, at $T = 225$ K are given in Table I.

The values obtained for torsional frequencies by the Bayer method lie in the range 30 to 50 cm^{-1} whereas those obtained by employing Tatsuzaki correction lie in the range 35 to 70 cm^{-1}. These values lie in the expected range of wave numbers for low frequency modes in molecular crystals (*8*), viz. 20–100 cm^{-1}. It would be interesting to compare these results with the Raman and infrared data when they become available.

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