ROTATIONAL MODES IN THE MOLECULE 2-AMINO-5-CHLOROPYRIDINE FROM CHLORINE NQR STUDIES

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Chlorine n. q. r. frequencies in 2-amino-5-chloropyridine have been measured in the temperature range 77 K to room temperature. A single resonance line has been observed. Rotational modes of the molecule have been evaluated in the above temperature range following Kushida, Benedek, and Bloembergen method. The temperature coefficient of the torsional frequency has also been evaluated.

1. Introduction

The nuclear quadrupole resonance frequency of ^{35}Cl in 2-amino-5-chloropyridine has been measured by Bray et al. [1] at 77 K only. Since these measurements are at 77 K only, we have measured the ^{35}Cl n. q. r. frequencies in this solid over a wide range of temperature, 77 K to room temperature. A single n. q. r. line has been observed. Using these values of n. q. r. frequencies and the molecular structure data of Vick and Backeus [2], the rotational modes in the molecule 2-amino-5-chloropyridine have been calculated following Kushida, Benedek and Bloembergen method [3]. The temperature coefficient of the torsional frequency has also been calculated and it is compared with the value obtained by Brown's method [4].

2. Experimental

Polycrystalline samples of 2-amino-5-chloropyridine were studied in these experiments. Frequency-modulated self-quenched superregenerative spectrometer of Dean's type [5] was used for detecting the resonance. The resonance frequencies were measured with a digital frequency counter with an accuracy of ± 1 KHz. Low boiling petroleum ether was used as the bath liquid and liquid nitrogen as the coolant. The temperatures were measured

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with an iron-constantan thermocouple with accuracy of ± 0.5 K. The signal to noise ratio was about 5 as observed on the oscilloscope throughout the temperature range studied. The resonance frequencies were measured at temperature intervals of about 5 K.

3. Results and discussion

The variation of n. q. r. frequency with temperature for the resonance line observed is s hown in Fig. 1. Resonance frequency decreases with the increase of temperature and no phase transition is observed in the temperature region studied. The present value of

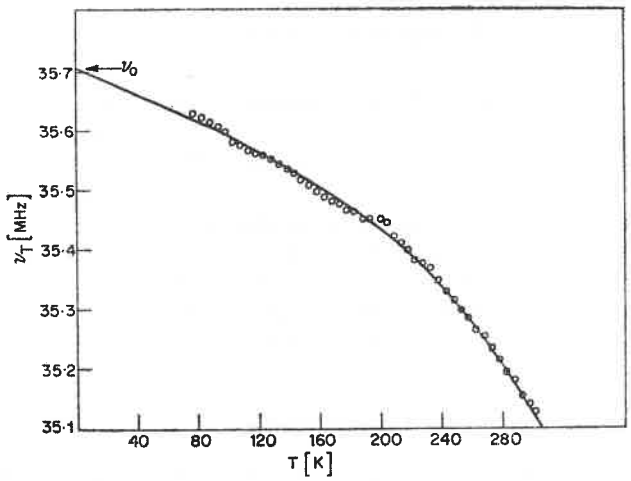

Fig. 1. Temperature variation of the n. q. r. frequency of ^{35}Cl line in 2-amino-5-chloropyridine

n. q.r. frequency at 77 K agrees well with the earlier result of Bray et al. 77 K, the only temperature at which they have measured the frequency. The difference between the frequency at 77 K and at 301 K is 504 KHz. The temperature coefficient, γ, of the n. q. r. frepuency is calculated at three temperatures 85, 210 and 290 K and the values obtained are 0.365×10^{-4}, 0.600×10^{-4}, and 1.168×10^{-4} K^{-1}, respectively.

Rotary modes f_X and f_Y in the molecule have been evaluated following Kushida, Benedek and Bloembergen method. Only f_X and f_Y about the principal X and Y axes of the electric field gradient tensor are considered because the rotary mode about the Z-axis does not affect the n. q. r. frequency except through the asymmetry parameter which is a second order effect. The moments of inertia A_X and A_Y of the molecule are calculated using the molecular structure data from Vick and Backeus and the values obtained are given in Table I. The value of the resonance frequency ν_0, at 0 K is obtained from the ν_T versus T curve by extrapolation and the value obtained is also given in Table I. The rotational modes at various temperatures in the region 77 to 300 K are calculated by the numerical method [6] using IBM 360/44 computer.

TABLE I

Values of the parameters used in the calculations of rotational modes in the 2-amino-5-chloropyridine molecule

ν_0 (MHz)	35.707
A_X (10^{-40} g cm^2)	978.96
A_Y (10^{-40} g cm^2)	839.93
g_X	0.0015
g_Y	0.0014
g	0.0015 [a]
	0.0015 [b]

[a] value obtained by numerical method, [b] value obtained by Brown's method.

The variation of the frequencies of rotational modes with temperature is shown in Fig. 2. It may be seen from the figure that the variation of both f_X and f_Y is almost linear in the temperature range 120 to 300 K, but below 120 K both f_X and f_Y increase rapidly with the decrease of temperature. The temperature coefficients g_X and g_Y of f_X and f_Y are

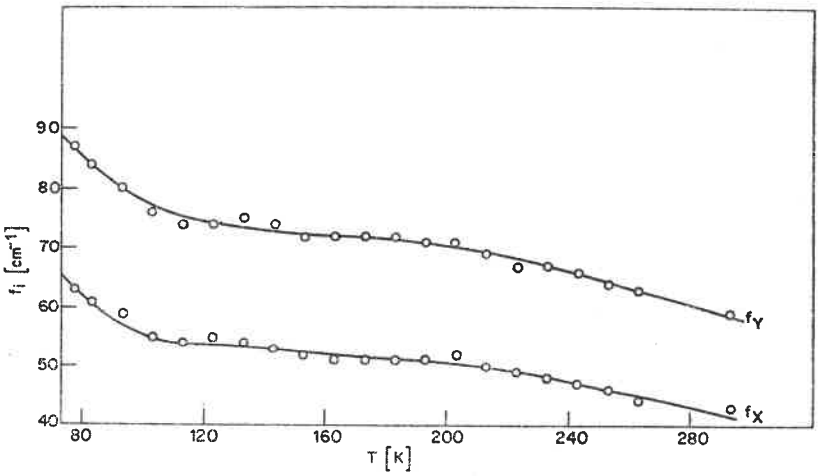

Fig. 2. Temperature variation of the frequencies of rotary modes in the 2-amino-5-chloropyridine molecule

calculated from the values of frequencies of rotational modes obtained 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 frequency of rotational mode 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 $T = 200$ K (high temperature approximation) and the values obtained for g_X, g_Y and their weighted average, g, are given in Table I.

The results are also analysed by Brown's method by fitting the experimental data of n. q. r. frequencies in the high temperature region to a parabola centered at $T_0 = 200$ K and the value of g obtained by this method compares well with that obtained by the numerical method (see Table I).

The values obtained for the frequencies of rotational modes in the 2-amino-5-chloropyridine molecule lie in the range 40 to 90 cm^{-1}, and these values appear to be reasonable in view of the fact that the rotational modes of molecule are generally in the range 20 to 150 cm^{-1} [7]. It would be interesting to compare these values of frequencies with Raman and infrared data when they become available.

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