CHLORINE NQR IN 4-CHLORO-2-NITROBENZOIC ACID

By S. P. Basavaraju and N. Devaraj

Department of Physics, Bangalore University*

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The nuclear quadrupole resonance frequency of ^{35}Cl in 4-chloro-2-nitrobenzoic acid has been measured in the range 77K to room temperature. A single resonance line has been observed. The torsional frequencies of the molecule about the principal X and Y axes are evaluated in the above temperature range following Bayer's theory and Brown's method. The temperature coefficient of the torsional frequency has also been evaluated.

1. Introduction

Nuclear Quadrupole Resonance (NQR) spectroscopy deals with the electrostatic interaction between the nuclear quadrupole moment and the electric field gradient at the site of the nucleus. The electric field gradient at the site of the nucleus is very sensitive to the details of the charge distribution in the molecule. Due to the torsional motion of the molecules, what the nucleus experiences is a net temperature dependent averaged field gradient. Hence a study of NQR frequency as a function of temperature reveals information about phase transitions, nature of chemical bonding and internal motions. Chlorine NQR in 4-chloro-2-nitrobenzoic acid was detected for the first time and the NQR frequency at 77 K and room temperature was reported by the authors [1]. In this paper we report the results of our measurements on the temperature dependence of NQR frequency of ^{35}Cl in this compound over the wide range of temperature, 77 to 301 K. A single line has been observed throughout this temperature range. Using our experimental results and the molecular structure data of Ferguson and Sim [2] we have calculated the torsional frequencies of the molecule in the above temperature range following Bayer [3] and Brown [4].

2. Experimental

A home made, frequency modulated and self-quenched superregenerative spectrometer of Dean's type [5] has been used for detecting the resonances. A superregenerative oscillator--detector of this type has the advantage of high rf power output and high sensitivity.

* Address: Department of Physics, Bangalore University, Bangalore 560 001, India.

Polycrystalline samples of 4-chloro-2-nitrobenzoic acid taken in glass envelopes were studied in these experiments. For low temperature studies, the rf coil containing the sample was immersed in a bath of low boiling petroleum ether and liquid nitrogen was used as the coolant. The temperatures were measured by an iron-constantan thermocouple with an accuracy of ± 1K. The resonance frequencies were measured with a digital frequency counter accurate to ± 1 KHz and the signal to noise ratio was about 4, as observed on the oscilloscope throughout the temperature range studied.

3. Results and discussions

The variation of the NQR frequency with temperature is shown in Fig. 1. The frequency decreases with the increase in temperature, as expected, and no phase transition is present in the temperature range studied. The resonance frequency varies from 36.114 MHz at 77K to 35.531 MHz at 301K. The temperature coefficient of the NQR frequency is

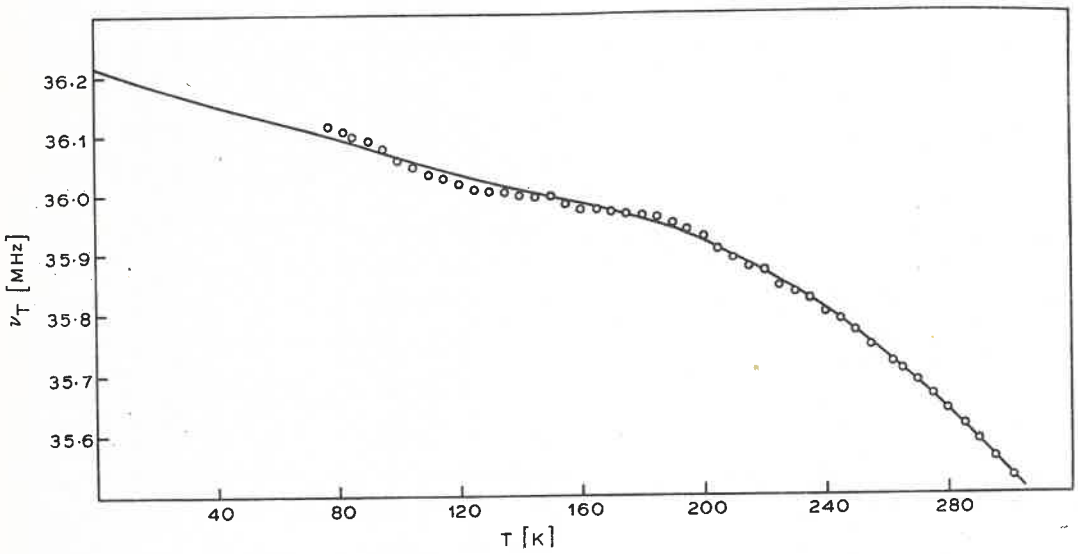

Fig. 1. Temperature variation of chlorine NQR frequency in 4-chloro-2-nitrobenzoic acid

calculated at three temperatures 77, 200 and 295K and the values obtained are 0.423×10^{-4}, 0.619×10^{-4}, and $1.555 \times 10^{-4} K^{-1}$, respectively.

The torsional frequencies (also called the rotary modes) f_X and f_Y in the molecule about the principal X and Y axes of the electric field gradient tensor are calculated following Bayer's theory and Brown's method. Only f_X and f_Y are considered since the torsional motion about the Z-axis does not affect the resonace frequency except through the asymmetry parameter which is a second order effect. The moments of inertia A_X and A_Y of the molecule about the X and Y axes, respectively, are calculated by the molecular structure data. For the calculation of moments of inertia A_X and A_Y one should have iether the molecular structure data of the low frequency Raman data; but these data are

not available in the literature for this compound. In the absence of such data, we have assumed, for the purpose of calculation of moments of inertia, that the values of bond lengths and bond angles for chlorine, nitro group, and COOH group in this compound to be the same as those for the corresponding groups in 2-chloro-5-nitrobenzoic acid for

TABLE I

Values of the parameters used in the calculations of torsional frequencies in the molecule 4-chloro-2-nitrobenzoic acid

ν_0 (MHz)	36.215
$10^{40}A_X$ (gm cm^2)	2339.42
$10^{40}A_Y$ (gm cm^2)	1645.08
g_X	0.0013
g_Y	0.0009
g	0.0012[a]
	0.0011[b]

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

which the molecular structure data is available [2]. The values obtained for A_X and A_Y are listed in Table I. The resonance frequency ν_0 at 0K is determined by extrapolation of the ν_T versus T curve and the value obtained is also given in Table I. The torsional frequencies f_X and f_Y are evaluated by the numerical method of Vijaya and Ramakrishna [6], using IBM 360/44 computer.

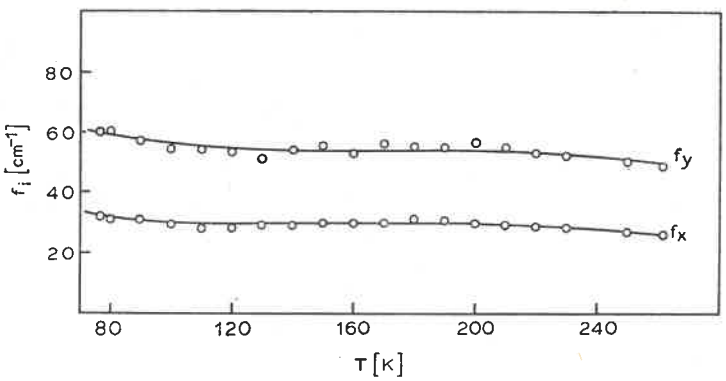

Fig. 2. Temperature variation of the torsional frequencies in the molecule 4-chloro-2-nitrobenzoic acid

The variation of torsional frequencies with temperature is shown in Fig. 2. The variation of both f_X and f_Y is almost linear throughout the region of temperature studied. The temperature coefficient g_X and g_Y of f_X and f_Y are calculated from these data by the equation

$$f_i = f_i^0(1-g_iT'),$$

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 $T = 200\,\mathrm{K}$ (high temperature approximation; Ichishima [7]) 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 NQR frequencies in the high temperature region to a parabola centered at $T_0 = 200\,\mathrm{K}$, and it is found that the value of g obtained by this method compares well with the value obtained by the numerical method (see Table I).

The values obtained for the torsional frequencies are in the range 25 to 60 cm^{-1} and these values appear to be reasonable in view of the fact that the rotary modes of molecules lie generally in the range 20 to 150 cm^{-1} [8]. It would be interesting to compare these values of torsional frequencies with the Raman and infrared data when they become available.

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