Temperature dependence of chlorine NQR in 2-chloro 5-nitrobenzoic acid and 4-chloro 3-nitrobenzoic acid

V S S SASTRY and J RAMAKRISHNA

Department of Physics, Indian Institute of Science, Bangalore 560012

Abstract. Temperature dependence of chlorine nuclear quadrupole resonance in 2-chloro 5-nitrobenzoic acid and 4-chloro 3-nitrobenzoic acid has been investigated in the region 77° K to room temperature. No phase transition has been observed. The results are analysed to obtain the torsional frequencies and their temperature dependence. A nonlinear temperature dependence is obtained for the torsional frequencies.

Keywords. NQR; temperature dependence; internal motions.

1. Introduction

In this paper we report the results obtained from a study of the temperature dependence of ^{35}Cl NQR frequency in two chlorine derivatives of benzoic acid, namely; 2-chloro 5-nitrobenzoic acid (substance-I) and 4-chloro 3-nitrobenzoic acid (substance II). Their NQR frequencies at 77° K are already known (Bray 1957). Even though the quadrupole coupling constant for a good number of chlorine derivatives of benzoicacid are known, not much seems to have been done in these compounds with regard to the temperature dependence of NQR, which is sensitive to internal motions, especially the low lying librations (torsional oscillations) and phase transitions if any.

A Dean's type self-quenched super-regenerative spectrometer (Das and Hahn 1958) was used to observe the resonances, and the frequencies were measured with a BC 221 frequency meter. A home-made solid state lock-in-amplifier was used to record the signals. The signal-to-noise ratio could be improved, typically by a factor of 50, using this lock-in-system with a time constant of 4 seconds. The sample was kept in a low temperature cell and the temperature was varied from 77° K to about 300° K. The temperature was measured with a copper-constantan thermocouple and a Pye potentiometer. The temperature stability and accuracy of measurement were better than $\pm 0.5°$ K. Both the substances were obtained from Sigma Chemicals Company, USA and powder samples were used in the present work. While substance-I gave a visual signal-to-noise ratio (S/N) of about 5 at 77° K and remained almost the same up to 300° K, substance-II gave a weak signal at 77° K (visual S/N $\sim$ 2) and the signal weakened considerably with the increase of temperature. At 300° K, this signal could only be recorded with a S/N ratio of 6 to 10.

146

2. Method of calculation

The results from the experiments have been analysed by two methods, one with a view to evaluate the temperature coefficient, g, of torsional frequencies, using Brown's approach (Brown 1960) and the other to evaluate numerically f_x and f_y and hence g, using Bayer's equation (Bayer 1951). The two methods are summarised briefly here. On the basis of Bayer's theory, the temperature dependence of NQR frequency, for axially symmetric field gradients, is given by

$$\frac{\nu_T}{\nu_0} = 1 - \frac{3h}{8\pi^2 A_x f_x} \frac{1}{\exp(hf_x/kT) - 1} - \frac{3h}{8\pi^2 A_y f_y} \frac{1}{\exp(hf_y/KT) - 1}. \tag{1}$$

Here it is assumed that the NQR frequency of the stationary molecule is equal to that (ν_0) at $0°$ K. f_x and f_y are the torsional frequencies of the molecules about the principal X and Y axes of the EFG tensor. A_x and A_y are the corresponding moments of intertia. This equation as generalised by Kushida (1955) becomes

$$\frac{\nu_T}{\nu_0} = 1 - \frac{3kT}{8\pi^2} \sum_i \frac{1}{A_i f_i^2} - \frac{h^2}{32\pi^2 kT} \sum_i \frac{1}{A_i} \tag{2}$$

where $hf_i/kT \ll 1$ (high temperature approximation).

The effect of volume change with temperature, in the case of molecular solids, has been introduced by Brown (1960) through the temperature dependence of the torsional frequencies. He assumed a linear temperature dependence for the torsional frequencies on the basis of the observations of Ichishima (1950). Thus

$$f_i = f_i^0(1 - g_i t) \tag{3}$$

where t is the temperature measured from any reference point. Fixing the origin at some point in the high temperature region, say $T_0°$ K and neglecting the $1/T$ term in eq. (2), Brown showed that

$$\frac{\dfrac{d\nu}{dt}\bigg|_{T_0}}{\dfrac{d^2\nu}{dt^2}\bigg|_{T_0}} = \frac{1 + 2T_0 g}{4g + 6T_0 g^2} \tag{4}$$

where

$$g = \langle g \rangle = \left(\sum_i \frac{g_i}{A_i f_i^2}\right) \bigg/ \left(\sum_i \frac{1}{A_i f_i^2}\right) \tag{5 a}$$

and

$$g^2 = \langle g^2 \rangle = \left(\sum_i \frac{g_i^2}{A_i f_i^2}\right) \bigg/ \left(\sum_i \frac{1}{A_i f_i^2}\right). \tag{5 b}$$

The average value of the temperature coefficient g of the torsional frequencies can be evaluated using eqs (3) and (4). The method adopted in the present case

to evaluate f_o and f_y is similar to the one described by Vijaya and Ramakrishna (1970).

3. Results and discussion

The observed variation of NQR frequency with temperature (v_T versus T curve) for both the substances is shown in figures 1 a and 1 b. The values of f_o and f_y at each temperature are estimated using the method mentioned earlier and the
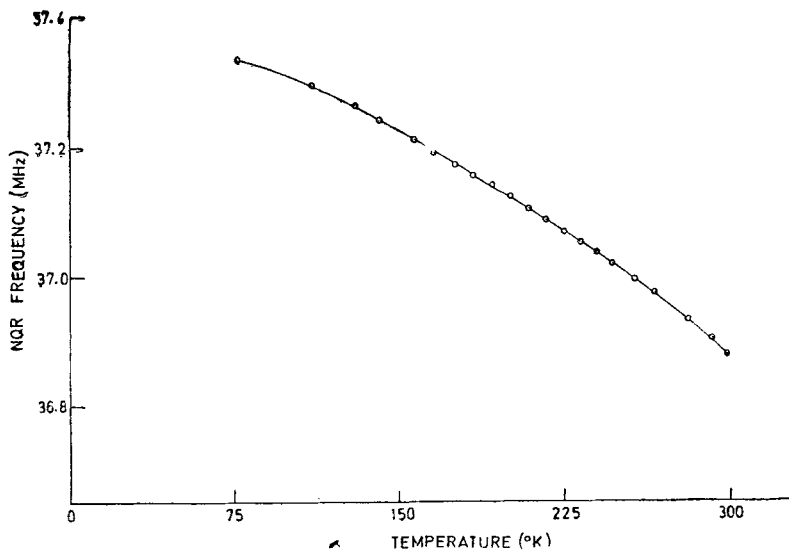

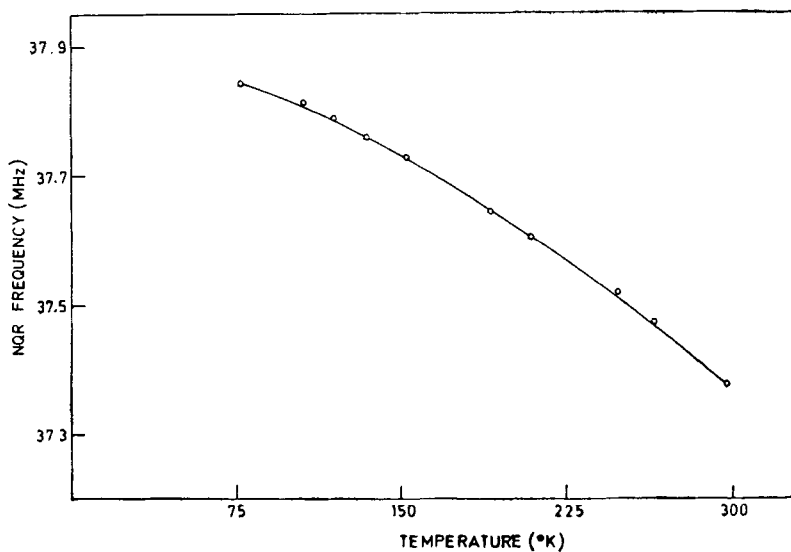**Figure 1 a.** Temperature variation of NQR frequency in 2-chloro 5-nitrobenzoic acid.

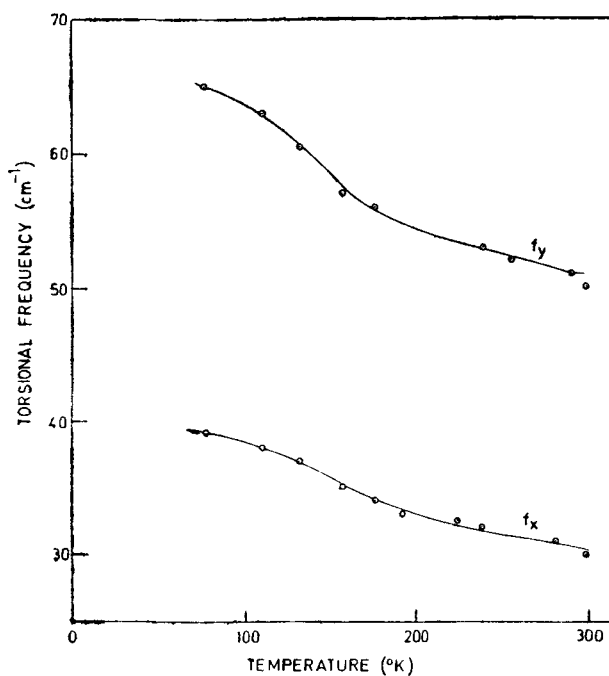**Figure 1 b.** Temperature variation of NQR frequency in 4-chloro 3-nitrobenzoic acid.

Figure 2 *a*. Temperature variation of f_x and f_y in 2-chloro 5-nitrobenzoic acid
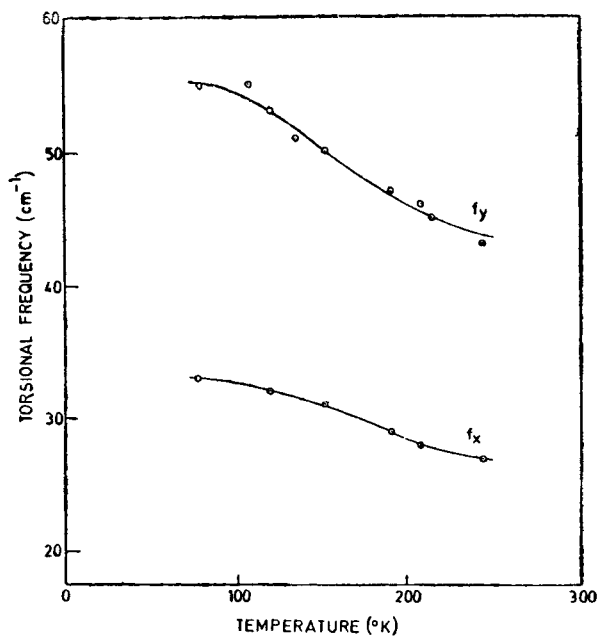
Figure 2 *b*. Temperature variation of f_x and f_y in 4-chloro 3-nitrobenzoic acid

results are presented in figures 2 *a* and 2 *b*. The values of A_x, A_y, v_0, for both the substances are presented in table 1. The values of g_x and g_y are evaluated in the region 250° K–300° K (high temperature region) and the value of g is obtained using eq. (5 *a*). The value of g has also been evaluated using Brown's approach. For this, data in the region 250° K–300° K is fitted to a parabolic equation using the method of least squares. The values of g_x, g_y, and g obtained from the numerical method and also the value of g obtained from Brown's method are shown in table 2. The maximum error in the estimation of g using the latter method is expected to be $\pm\, 0\cdot0001$, corresponding to a mean square deviation of about 5 $(\text{KHz})^2$ in the parabolic fit of the experimental data. It is found that the value of the temperature coefficient of torsional frequencies obtained using Brown's method compares well with the one obtained by the numerical method in the case of 4-chloro 3-nitrobenzoic acid, while the agreement is not so good in the case of 2-chloro 5-nitrobenzoic acid.

It may be pointed out from figures 2 *a* and 2 *b* that the variations of the torsional frequencies are not quite linear with temperature. The values of the torsional frequencies tend to level off at lower and higher temperatures and this behaviour is more pronounced in the case of 2-chloro 5-nitrobenzoic acid. We have recently studied (under publication) the temperature dependence of ^{35}Cl NQR in *o*-chloro and *m*-chlorobenzoic acids and found that the numerical method and Brown's method give comparable results in the case of *m*-chlorobenzoic acid, while in the case of *o*-chlorobenzoic acid the agreement was not so good. Also the torsional frequencies showed a tendency to level off at lower and higher temperatures, this behaviour being more pronounced in *o*-chlorobenzoic acid. A Raman study of the low lying liberational motions may throw more light on this peculiar behaviour of the frequencies.

Table 1. Molecular constants used in Bayer's equation.

Substance	A_x $\times\ 10^{-40}$ gm cm²	A_y $\times\ 10^{-40}$ gm cm²	v_0 MHz
2-chloro 5-nitrobenzoic acid	2100·3	1320·5	37·424
4-chloro 3-nitrobenzoic acid	2513·7	1728·1	37·946

Table 2. Temperature coefficients of torsional frequencies

Substance	Numerical method (° C⁻¹) g_x	g_y	g	Brown's method (°C⁻¹) g
2-chloro 5-nitrobenzoic acid	0·0007	0·0006	0·0007	0·0018
4-chloro 3-nitrobenzoic acid	0·0009	0·0010	0·0010	0·0008

Acknowledgement

References

Bayer H 1951 *Z. Physik.* **130** 227
Bray P 1957 *J. Chem. Phys.* **27** 551
Brown R J C 1960 *J. Chem. Phys.* **32** 116
Das T P and Hahn E L 1958 *Nuclear Quadrupole Resonance Spectroscopy* Solid State Phys.
    Suppl. 1 p 90, eds F Seitz and D Turnbull (Academic Press)
Ichishima I 1950 *J. Chem. Soc. Japan* '*/1* 607
Kushida T 1955 *J. Sci. Hiroshima Univ. Ser A Phys. Chem.* **19** 327
Vijaya M S and Ramakrishna J 1970 *Mol. Phys.* **19** 131