

Molecular dynamics in chloronitrobenzenes using NQR data

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Abstract. The torsional frequencies have been rigorously evaluated in the compounds 1,2,4,5-tetrachloro-3,6-dinitrobenzene and 1,3,5-trichloro-2,4-dinitrobenzene over an extended temperature range (77 K–392 K) using the experimental results of NQR and crystal structure data. The values have been compared with those obtained by using the X-ray thermal parameters.

Keywords. Quadrupole resonance; chloronitrobenzenes.

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1. Introduction

Many poly nitro-substituted aromatic compounds show distortion from planarity. The chlorine atoms exert a steric effect on the nitro groups resulting in its tilting out of the benzene ring plane. The electronegative nitro groups also influence the charge distribution in the molecule. Chloronitro benzenes are suitable to study such changes by ^{35}Cl and by ^{14}N NQR spectroscopy. The temperature dependence of NQR in molecular solids gives useful information about the molecular dynamics (torsional oscillations) and phase transitions.

The temperature dependence of NQR frequency of ^{35}Cl in the range 77 to 400 K were investigated by Wigand *et al* [1] in the compounds 1,2,4,5-tetrachloro-3,6-dinitrobenzene and 1,3,5-trichloro-2,4-dinitrobenzene. The tetrachloro compound, a centrosymmetric one, gives a single resonance line indicating that all the four chlorine atoms are chemically equivalent. Whereas the trichloro compound answers for three resonance lines due to three chemically inequivalent lattice sites.

In the present paper, the torsional vibration frequencies have been evaluated over an extended range (77 K to 392 K) using the NQR results and the crystal structure data [1] of the compounds. The torsional vibration frequencies have also been evaluated from the mean square angular displacements of various C–Cl bond directions and the available data of X-ray thermal parameters [1].

2. Theory

2.1 The temperature dependence of NQR interaction is mostly due to low frequency torsional vibrations. According to Bayer's [2] theory, the temperature dependence of NQR frequency for the case $l = 3/2$ and $\eta = 0$ is given by

$$\frac{\nu_T}{\nu_0} = 1 - \frac{3h}{8\pi^2} \left[\frac{1}{A_x f_x \{ \exp(hf_x/KT) - 1 \}} + \frac{1}{A_y f_y \{ \exp(hf_y/KT) - 1 \}} \right] \quad (1)$$

where ν_T is the NQR frequency at T K, ν_0 that at 0 K. f_x and f_y are the torsional frequencies about X and Y axes of the EFG tensor. A_x and A_y are the moments of inertia of the molecule about X and Y axes respectively. Bayer's theory was later modified by Kushida [3] by taking into consideration all the normal modes. Kushida's equation is given by

$$\nu_T = \nu_0 \left[1 - \frac{3h}{8\pi^2} \sum_i \frac{1}{A_i f_i} \left\{ \frac{1}{2} + \frac{1}{\exp(hf_i/KT) - 1} \right\} \right] \quad (2)$$

where $i = X, Y$.

Under high temperature approximation $hf_i/kT \ll 1$,

$$\nu_T = a(1 + bT + cT^{-1}) \quad (3)$$

where

$$a = \nu_0, \quad b = -\frac{3k}{8\pi^2} \sum_i \frac{1}{A_i f_i^2}, \quad c = -\frac{h^2}{32\pi^2 k} \sum_i \frac{1}{A_i}.$$

The temperature variation of torsional frequencies f_x and f_y was analysed by following Brown [4]. Assuming a linear temperature dependence for f_i as

$$f_i = f_i^0(1 - g_i T') \quad (4)$$

where T' is the temperature measured from any reference temperature T_0 , g_i is the corresponding temperature coefficient of torsional frequency and f_i^0 is the torsional frequency at $T' = 0$ (i.e., at T_0). Introducing the temperature dependence of f_i in (3), the relationship between the first and second derivatives of ν is given by

$$\left[\frac{d\nu}{dT'} \right]_{T'=0} / \left[\frac{d^2\nu}{dT'^2} \right]_{T'=0} = \frac{1 + 2T_0 \langle g \rangle}{4 \langle g \rangle + 6T_0 \langle g^2 \rangle} \quad (5)$$

where,

$$\langle g \rangle = \sum_i \left[\frac{A_i}{\omega_i^0} \right] g_i / \sum_i \left[\frac{A_i}{\omega_i^2} \right]$$

and

$$\langle g^2 \rangle = \sum_i \left[\frac{A_i}{\omega_i^0} \right] g_i^2 / \sum_i \left[\frac{A_i}{\omega_i^2} \right].$$

Here it is assumed that all g_i values are equal. Thus g describes the weighted average of the temperature coefficient for the internal motions. The g values were estimated from the above equation by curve fitting the experimental points to Brown's parabolic equation and calculating the derivatives of ν versus T' curve.

2.2 The NQR motional averaging has been shown to arise from temperature dependent tilting of the Z -axis of the EFG tensor. One can therefore estimate the mean square angular displacements $\langle \theta^2 \rangle$ for the various C—Cl bond directions which define the respective EFG Z -direction. Using the high temperature approximation, the expression for $\langle \theta^2 \rangle$ is given by

$$\langle \theta^2 \rangle = \frac{kT}{4\pi^2 c^2 A f_i^2}.$$

The torsional mode frequency

$$f_t = \left(\frac{kT}{4\pi^2 c^2 A \langle \theta^2 \rangle} \right)^{1/2} \quad (6)$$

where $A = (A_x + A_y)/2 =$ average value of the moment of inertia.

The mean square angular displacement $\langle \theta^2 \rangle$ is evaluated using the thermal parameters in the following manner. Suppose the mean square displacements of two atoms forming a bond are given by $\langle u_1^2 \rangle$ and $\langle u_2^2 \rangle$ and the length of the bond is l_{12} , then the mean square angular displacement of the bond direction would be approximately given by

$$\langle \theta^2 \rangle = \frac{\langle u_1^2 \rangle + \langle u_2^2 \rangle}{l_{12}^2}. \quad (7)$$

3. Method of calculation

3.1 The moment of inertia A_x and A_y were evaluated using the crystal structure data of both the compounds. The principal Z-axis is taken along the C—Cl direction in the centrosymmetric tetrachloro compound whereas it has been taken parallel to C—Cl direction in the other compound. The results are given in table 1. The torsional frequencies f_x and f_y at each temperature were found by solving (2) using the numerical method of Vijaya *et al* [5]. The temperature coefficients of torsional frequencies g are calculated with $T' = 0$ at $T_0 = 200$ K.

3.2 The mean value of $\langle \theta^2 \rangle$ for the three directions of the ellipsoid of thermal vibrations of each atom has been evaluated from thermal parameter data of Wigand *et al* [1] using (7) and is given in table 2. Using these values of $\langle \theta^2 \rangle$ the torsional frequencies have been calculated and shown in table 2.

Table 1. Parameters used in the calculation.

Compound	ν_0 MHz	A_x 10^{-47} kgm ²	A_y 10^{-47} kgm ²	g
1,2,4,5-tetrachloro- 3,6-dinitro benzene	39-185	4198-903	1965-744	0-0031167 ^a 0-0032900 ^b
1,3,5-trichloro- 2,4-dinitro benzene				
Line I	39-210	3527-036	1331-487	0-0035 ^a 0-00365 ^b
Line II	38-082	3521-356	1989-477	0-0034 ^a 0-00362 ^b
Line III	37-880	3505-022	1945-985	0-00341 ^a 0-00330 ^b

^aby Brown's Method

^bby numerical method

Table 2. Estimated values of $\langle \theta^2 \rangle$ and f_i at $T = 300$ K.

Compound	Atom	C-Cl bond length (pm)	$\langle \theta^2 \rangle$ rad ²	Torsional frequency f_i	
				X-ray data	NQR data
				cm ⁻¹	
1,2,4,5-tetrachloro-3,6-dinitro benzene	Cl	170.9	0.00695	23	20
1,3,5-trichloro-2,4-dinitro benzene					
Line I	Cl(2)	171.5	0.00453	32	27
Line II	Cl(1)	171.5	0.00927	21	21
Line III	Cl(3)	172.2	0.00874	22	22

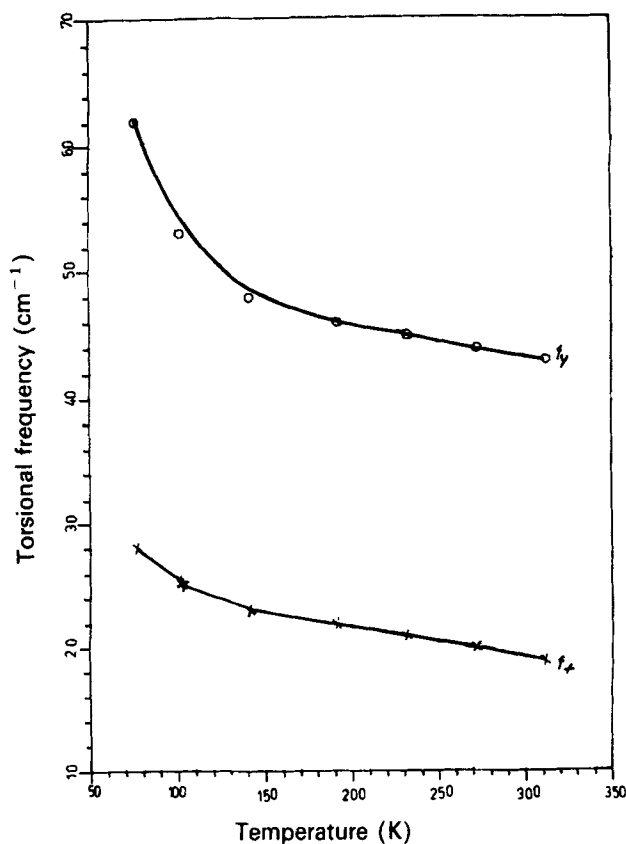


Figure 1. Temperature dependence of torsional frequencies in 1,2,4,5-tetrachloro-3,6-dinitro benzene.

4. Results and discussion

The variation of torsional frequency with temperature is shown in figure 1 for the centrosymmetric tetrachlorobenzene compound. Variation of f_x and f_y with temperature is small and is linear for most of the temperature region studied except at very low temperatures where the variation is slightly larger. For trichloro compound

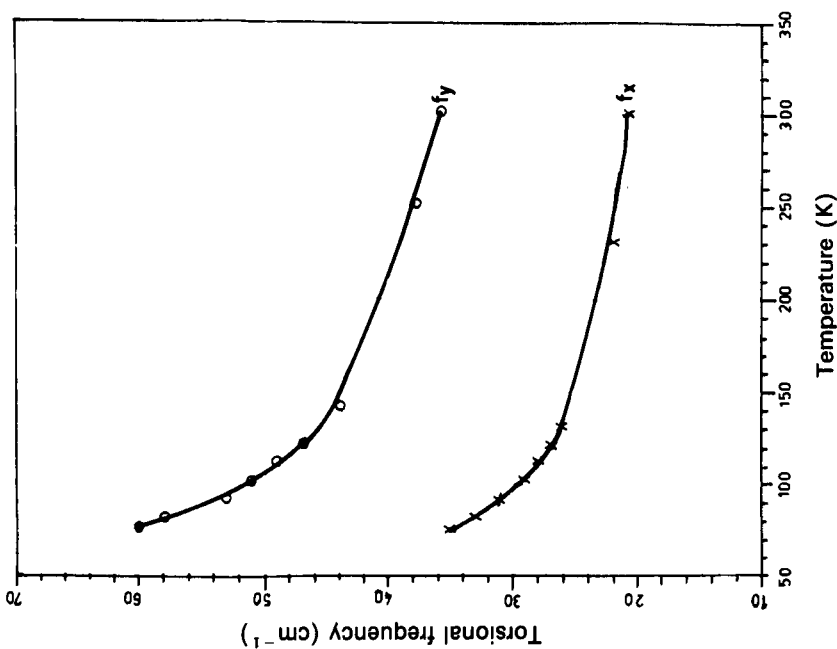


Figure 3. Temperature dependence of torsional frequencies in 1,3,5-trichloro-2,4-dinitro benzene (line II).

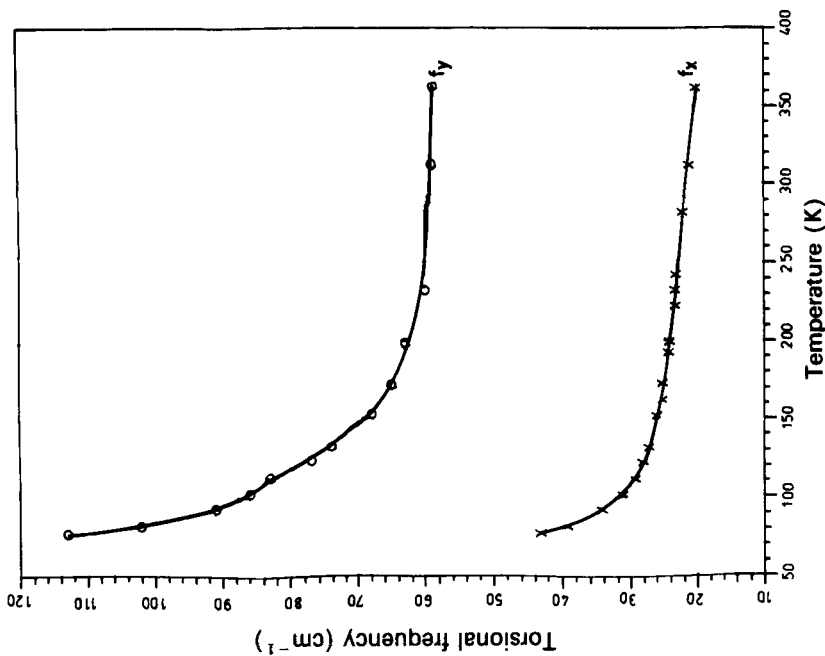


Figure 2. Temperature dependence of torsional frequencies in 1,3,5-trichloro-2,4-dinitro benzene (line I).

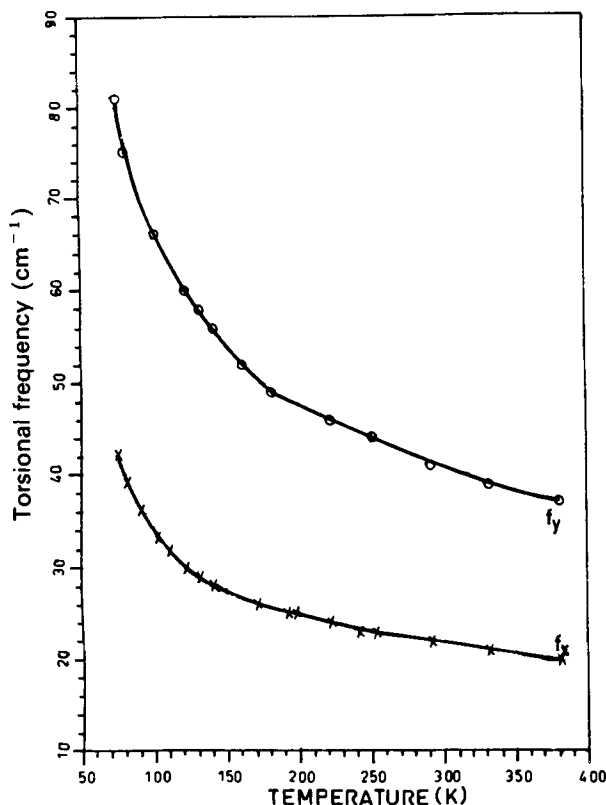


Figure 4. Temperature dependence of torsional frequencies in 1,3,5-trichloro-2,4-dinitro benzene (line III).

the variation of torsional frequencies with temperature for the three lines are shown in figures 2–4. The variation is comparatively more and is linear in most of the temperature region studied. The temperature coefficients g_x , g_y of f_x and f_y and also g , calculated by numerical method are given in table 1. The g value compares well with that obtained by Brown's method. The mean square angular displacements of the C—Cl bond directions and the order of magnitude estimation of the torsional wave numbers are in close agreement with the estimation made on the basis of NQR temperature dependence in both the compounds, as shown in table 2.

5. Conclusion

Generally the torsional frequencies of molecules lie in the range 20 to 100 cm^{-1} [6]. It is also interesting to compare these values with Raman and infrared data. In the present case, good agreement is observed on comparing the values with that obtained by using the X-ray thermal parameters.

The above approach is a good illustration of the supplementary nature of the data from X-ray studies in relation to NQR studies of compounds in the solid state.

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