

## C H A P T E R - 5

### CALCULATION OF TORSIONAL FREQUENCIES AND THEIR TEMPERATURE DEPENDENCE USING NQR DATA

The torsional frequency of molecules is calculated on the basis of Bayer's theory (1951) and Brown's method (1960) using the experimental data of NQR frequency from the present work and the crystal structure data from the literature. The torsional frequencies in the temperature range 77K to 300K are calculated for five of the chlorine compounds - mono chloro acetic acid, sodium chloro acetate, 2,4-dichloro phenoxy acetic acid, 3,5-dichloro phenol and 2,6-dichloro phenol and the results obtained are reported in this chapter.

#### 5.1. METHOD OF CALCULATION:

The Bayer-Kushida theory for the temperature dependence of NQR frequency is already described in detail in Chapter 2. Bayer considered the torsional motions about the principal X and Y axes only (of the electric field gradient tensor), as the torsional motion about the Z axis does not affect the resonance frequency except through the asymmetry parameter (which is a second-order effect). The principal Z axis is taken along the direction of C-Cl bond, the principal

X axis is taken perpendicular to the plane of the (benzene ring) molecule and the principal Y axis is taken in the plane of the molecule (benzene ring) and perpendicular to the Z-axis (C-Cl bond). The principal Z component of the field gradient at a temperature T is given by (Das and Hahn, 1958)

$$q_T = q_Q \left[ 1 - \frac{3}{2} ( \langle \theta_X^2 \rangle + \langle \theta_Y^2 \rangle ) - \frac{1}{2} ( \langle \theta_X^2 \rangle - \langle \theta_Y^2 \rangle + (1/2)(3 - \eta) \langle \theta_X^2 \rangle \langle \theta_Y^2 \rangle ) \right] \dots (5.1)$$

where  $q_T$  and  $q_Q$  are the averaged field gradients at the quadrupolar nucleus of the oscillating (at TK) and stationary molecules respectively.  $\theta_X$  and  $\theta_Y$  are the torsional amplitudes at TK about the X and Y axes respectively and  $\eta$  is the asymmetry parameter. Bayer approximated the torsional motions to a corresponding quantum mechanical oscillators as

$$\langle A_i \omega_i^2 \langle \theta_i^2 \rangle \rangle = \hbar \omega_i \left( \frac{1}{2} + \frac{1}{\exp(\hbar \omega_i / k_B T) - 1} \right) \dots (5.2)$$

where  $i = X$  or  $Y$ ,  $\omega_i$  is the torsional frequency and  $A_i$  is the corresponding moment of inertia. Substituting equation (5.2) in equation (5.1) for  $I = 3/2$  and  $\eta = 0$

$$q_T = q_Q \left[ 1 - \frac{3\hbar}{16\pi^2} \left( \frac{1}{A_X I_X} + \frac{1}{A_Y I_Y} \right) - \frac{3\hbar}{8\pi^2} \left( \frac{1}{A_X I_X [\exp(\hbar \omega_X / k_B T) - 1]} + \frac{1}{A_Y I_Y [\exp(\hbar \omega_Y / k_B T) - 1]} \right) \right] \dots (5.3)$$

where  $\omega_X = 2\pi f_X$  and  $\omega_Y = 2\pi f_Y$ .  $\nu_T$  is the resonance frequency at TK and  $\nu_Q$  is that of the stationary molecule obtained by extrapolating the ( $\nu_T$  Vs T curve) experimental curve to OK. The temperature-independent term in equation (5.3), viz.

$$\nu_Q \left[ 1 - \frac{3h}{16\pi^2} \left( \frac{1}{A_X f_X} + \frac{1}{A_Y f_Y} \right) \right]$$

represents the resonance frequency at OK and is denoted by  $\nu$ .

Thus

$$\nu_T = \nu_0 - \nu_Q \cdot \frac{3h}{8\pi^2} \left( \frac{1}{A_X f_X [\exp(hf_X/k_B T) - 1]} + \frac{1}{A_Y f_Y \exp(hf_Y/k_B T) - 1} \right) \dots (5.4)$$

The effect of zero-point vibrations, being very small, can be neglected and one can approximate  $\nu_Q = \nu_0$  and hence obtain

$$\frac{\nu_T}{\nu_0} = 1 - \frac{3h}{8\pi^2} \left( \frac{1}{A_X f_X [\exp(hf_X/k_B T) - 1]} + \frac{1}{A_Y f_Y [\exp(hf_Y/k_B T) - 1]} \right) \dots (5.5)$$

This equation represents Bayer's theory for  $I = 3/2$  and  $\eta = 0$ . The moments of inertia  $A_X$  and  $A_Y$  are calculated from the molecular structure data.

Bayer's theory of motional averaging of the electric field gradient was later generalized by Kushida (1955) who took into consideration all of the normal modes. Kushida's equation is given by

$$\nu_T = \nu_0 \left[ 1 - \frac{3h}{8\pi^2} \sum_i \frac{A_i^*}{f_i} \left( \frac{1}{2} + \frac{1}{\exp(hf_i/k_B T) - 1} \right) \right] \dots (5.6)$$

$A_1^*$  has no simple physical significance (though  $A_1^{*-1}$  has the dimensions of moment of inertia) and  $f_1$  represents the frequency of the corresponding normal mode. This equation is simplified under the high-temperature approximation ( $hf_1/k_B T \ll 1$ ) as

$$\gamma_T = a (1 + bT + c/T) \quad \dots (5.7)$$

where  $a = \gamma_0$ ,  $b = - (3/8 \pi^2) k_B \sum_i (A_1^*/f_1^2)$ , and  $c = - (h^2/8k_B) \sum_i A_1^*$ .

There are practical difficulties in applying Kushida's equations as the frequencies of the normal modes and also  $A_1^*$  values are not always known. He had shown, however, that the rotary modes are the most important, the others contributing about 10% only. Kushida et al. (1956) later took into account the effects of volume change but again this requires a knowledge of parameters like the coefficient of thermal expansion, Gruneisen constant etc. Brown suggested that the effects of volume change could be taken into account by making the lattice frequencies temperature-dependent. On the basis of Ichishima's work (1950) Brown assumed a linear temperature-dependence for  $f_1$  as

$$f_1 = f_1^0 (1 - g_1 T')$$

where  $T'$  is the temperature measured from any reference temperature  $T_0$ ,  $f_1$  is the torsional frequency at any temperature  $T$ ,  $g_1$  is the corresponding temperature coefficient of the torsional frequency, and  $f_1^0$  is the lattice

frequency at  $T' = 0$  (at  $T_0$ ). Substituting this temperature-dependence for  $f_i$  in equation (5.7) the relationship between the first and second derivatives of  $\delta$  are given by

$$\left(\frac{d\delta}{dT'}\right)_{T'=0} / \left(d^2\delta/dT'^2\right)_{T'=0} = (1 + 2T_0 g) / (4g + 6T_0 g^2) \quad \dots (5.8)$$

where

$$g = \langle g \rangle = \frac{\sum_i \left(\frac{A_i}{\omega_i^2}\right) g_i}{\sum_i \left(\frac{A_i}{\omega_i^2}\right)}$$

$$g^2 = \langle g^2 \rangle = \frac{\sum_i \left(\frac{A_i}{\omega_i^2}\right) g_i^2}{\sum_i \left(\frac{A_i}{\omega_i^2}\right)}$$

For the sake of simplicity, it is assumed that all  $\xi_i$  values are equal, i.e., all the normal modes exhibit the same temperature dependence. Thus  $g$  describes the weighted average of the temperature coefficient for the internal motions. The numerical value of  $g$  depends on the reference temperature chosen, since the derivatives in equation (5.8) are determined at  $T' = 0$  by fitting the experimental data in the high-temperature region (since equation (5.7) is valid in the high-temperature region only) to a parabola of the type

$$\delta = a + bT' + cT'^2$$

The experimental data are analysed by means of Bayer's equation (5.5). The moment of inertia  $A_X$  and  $A_Y$  are calculated

from the molecular structure data of each compound. The resonance frequency at 0K (i.e.  $\nu_0$ ) is determined by fitting the experimental data to a polynomial of order four in absolute temperature. The torsional frequency  $f_x$  and  $f_y$  at each temperature was calculated by the numerical method of Vijaya and Ramakrishna (1970) by solving equation (5.5). The left hand side of equation (5.5) was calculated at each temperature using the experimental value of  $\nu_T$  and the extrapolated value of  $\nu_0$ . According to Kushida (1955) the intra-molecular vibrations which occur at much higher frequencies than the torsional frequencies, do not contribute appreciably to the temperature dependence of NQR. The torsional frequencies of molecules usually lie below 100 or 150  $\text{cm}^{-1}$  (Stidham, 1968). Therefore, it was assumed that  $f_x$  and  $f_y$  are less than 150  $\text{cm}^{-1}$ . The RHS of equation (5.5) was calculated for all possible combinations of  $f_x$  and  $f_y$  each taking values from 1 to 150  $\text{cm}^{-1}$  in steps of 1  $\text{cm}^{-1}$ . The fifteen thousand values so obtained for the RHS, for a given temperature, were then compared with the experimentally obtained LHS for the corresponding temperature. The calculations were made using IBM 360/44 computer. The programmes used are given in Appendix II.

The method employed to choose the proper pairs of  $f_x$  and  $f_y$  values that fit the Bayer's equation is the following. Keeping  $f_x$  constant,  $f_y$  was increased, in steps of 1  $\text{cm}^{-1}$ , the difference (LHS-RHS) was found to decrease and change its sign at a particular value of  $f_y$ . Later the difference was found to increase with increasing  $f_y$ .

The exact fit is expected for a value of  $f_Y$  lying between the two successive  $f_Y$  values for which there is a change in the sign. The variation of the difference (LHS-RHS) was assumed to be linear in this interval of  $1 \text{ cm}^{-1}$  and the value of  $f_Y$  for the exact fit (i.e., LHS-RHS = 0) was calculated. The value of  $f_Y$  and the corresponding  $f_X$  value was taken as the pair giving the exact fit with Bayer's equation. More than one pair exists at each temperature. The following criteria was employed to choose the proper pair at each temperature.

1.  $f_X$  is less than  $f_Y$  or viceversa as  $A_X$  is  $>$  than  $A_Y$  or  $A_X$  is  $<$   $A_Y$ .

2. Brown's theory (1960) assumes a linear temperature dependence for torsional frequencies on the basis of Ichishima's work (1950) on Raman Spectroscopy.

Brown further assumed that the temperature dependence of both  $f_X$  and  $f_Y$  are similar. The temperature dependence of  $f_X$  and  $f_Y$  may be written as

$$f_X = f_X^{\circ} (1 - g_X T') \quad \dots (5.9)$$

$$f_Y = f_Y^{\circ} (1 - g_Y T') \quad \dots (5.10)$$

where  $T'$  is the temperature measured from any fixed reference temperature,  $f_X^{\circ}$  and  $f_Y^{\circ}$  are the torsional frequencies at  $T' = 0$  and  $g_X$  and  $g_Y$  are the temperature coefficients of torsional frequencies. The reference temperature  $T'$

was chosen some where in the region 200 to 300 K. Using Brown's (1960) assumption  $g_X = g_Y = g$ , we get

$$\frac{f_X}{f_Y} = \frac{f_X^0}{f_Y^0} \quad \text{for all } T \quad \dots (5.11)$$

Among the pairs of  $(f_X, f_Y)$  values that fit Bayer's equation, those that satisfy criteria (1) were chosen. The ratio  $f_X/f_Y$  was calculated for each pair at all temperatures. The ~~pairs~~ pairs that had a constant ratio  $f_X/f_Y$  (to better than 1%) at all temperatures were taken as the proper pairs of  $f_X$  and  $f_Y$ .

$f_X$  and  $f_Y$  values so obtained were plotted against temperature and the points are fitted to a straight line by the method of least squares. From the graphs of  $f_X$  and  $f_Y$  VS  $T$ ,  $g_X$ ,  $g_Y$  and hence  $g$  was calculated. The value of  $g$  obtained by this numerical method was compared with that obtained by Brown's method using a IBM 360/44 Computer. The programme used is given in Appendix II.

## 5.2. TEMPERATURE VARIATION OF TORSIONAL FREQUENCY IN MONO CHLORO ACETIC ACID:

In order to calculate the moment of inertia  $A_X$  and  $A_Y$ , crystal-structure data must be known or if the low frequency Raman spectroscopy data is known, using equation (5.5) moment of inertia can be calculated. Since both of them were not available for mono chloro acetic acid, an



approximation has been made that the crystal structure of  $\text{CH}_2\text{ClCOOH}$  is the same as that of  $\text{CH}_2\text{FCOOH}$  but for the fact that the fluorine atom is replaced by the chlorine atom. Using the crystal structure data of  $\text{CH}_2\text{FCOOH}$  (Kanters and Kroon, 1972) and the appropriate bond-lengths and bond-angles,  $A_X$  and  $A_Y$  for  $\text{CH}_2\text{ClCOOH}$  are estimated and found to be nearly equal (405.69 and 436.69  $\text{gm cm}^2$ ) having a mean value of  $421.19 \times 10^{-40} \text{ gm. cm}^2$ . (Error in this approximation is between 5 and 10%). Since  $A_X \approx A_Y$ , it is reasonable to assume that  $f_X \approx f_Y$ . Thus, the equation (5.5) is simplified when average values of  $A_X$  and  $A_Y$  (i.e.,  $A_X = A_Y = A_t$ ) and of  $f_X$  and  $f_Y$  (i.e.  $f_X = f_Y = f_t$ ) are considered and takes the form

$$\frac{\partial f}{\partial T} = \left\{ 1 - \frac{3h}{4\pi^2 A_t f_t} \frac{1}{\left\{ \exp(h f_t / kT) - 1 \right\}} \right\} \dots (5.12)$$

Using the experimental data from Table (4.1),  $\partial f / \partial T$  and  $A_t$  in equation (5.12) the variation of torsional frequency at each temperature in the range 77 to 300 K has been calculated for the two lines observed in monochloro acetic acid. The calculated values of torsional frequencies at various temperature are given in Table (5.1) and the temperature variation of the torsional frequency is shown in Fig. (5.1). The variation of  $f_t$  with temperature is not linear for both the resonance lines,  $f_t$  decreasing with increase in temperature more rapidly at lower temperatures than at higher temperatures. The value of  $f_t$  increases from  $45.82 \text{ cm}^{-1}$  at 300 K to  $63.68 \text{ cm}^{-1}$  at 77 K for the first line and from  $51.15 \text{ cm}^{-1}$  to  $76.54 \text{ cm}^{-1}$  for the second

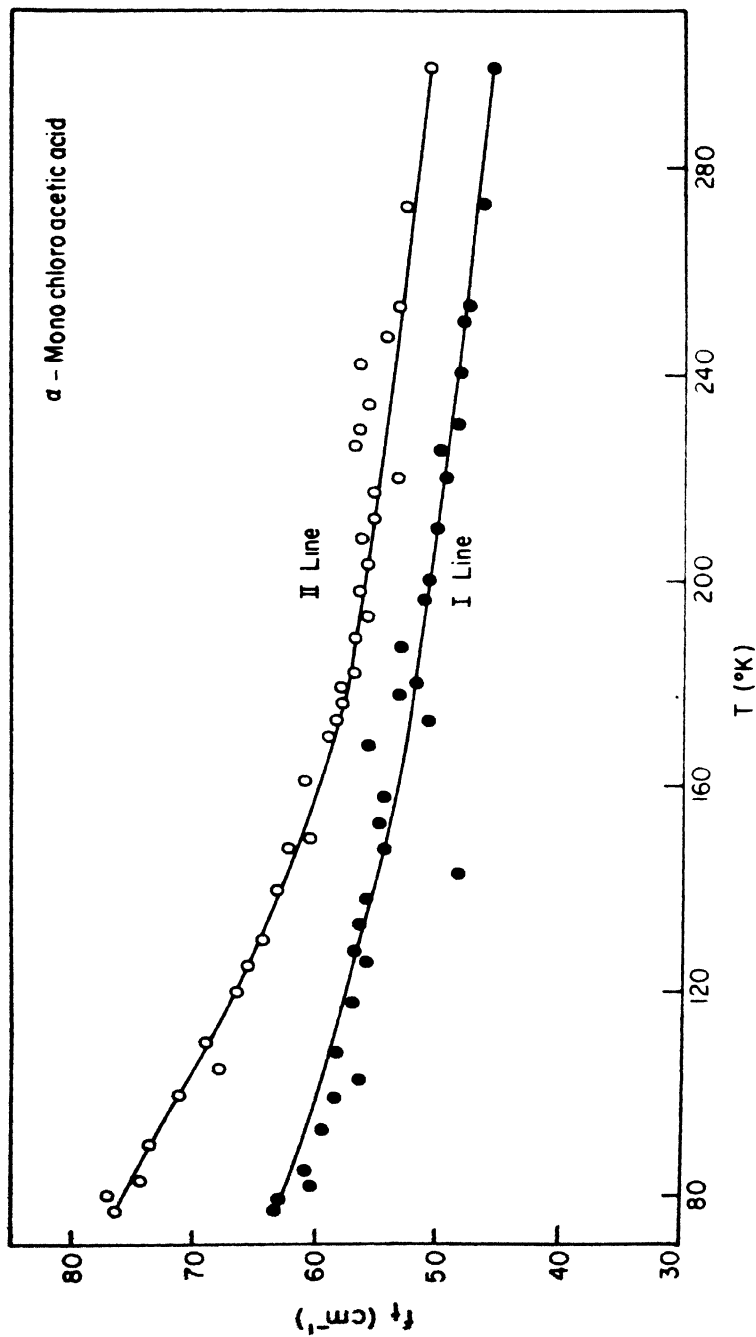


Fig 5 | Variation of  $f_t$  with temperature in  $\alpha$  -  $\text{CH}_2\text{Cl COOH}$  ( Line I & Line II )

line in the same temperature range.

### 5.3. TEMPERATURE VARIATION OF TORSIONAL FREQUENCY IN SODIUM CHLORO ACETATE:

The moments of inertia  $A_X$  and  $A_Y$  in this case are calculated on the basis of the available crystal structure data of the compound (Kennard et al., 1960-65), and are found to be  $467.90 \times 10^{-40}$  gm cm<sup>2</sup> and  $615.10 \times 10^{-40}$  gm cm<sup>2</sup> respectively. At OK,  $\nu_0$  is 34.875 MHz. Equation (5.5) was solved for  $f_X$  and  $f_Y$  at each temperature by the numerical method of Vijaya and Ramakrishna (1970). The values of the torsional frequencies obtained at various temperatures are given in Table (5.2) and the variation of the torsional frequencies with temperature from 77 to 300 K is shown in Fig. (5.2). The variation of  $f_Y$  with temperature is very small and linear for most of the temperature region studied, though at lower temperatures the variation is slightly larger. The resonance frequency (at any temperature) was not found to be sensitive to small changes in the value of  $f_X$  ( $f_X$  being larger than  $f_Y$  and greater than  $100$  cm<sup>-1</sup>) and this resulted in some difficulty in choosing the proper values for  $f_X$  and hence in some scatter of points. However, it can be seen that the variation of  $f_X$  is also essentially linear. The temperature coefficients  $g_X$  and  $g_Y$  of  $f_X$  and  $f_Y$  are calculated from these data using equations (5.9) and (5.10) with  $T' = 0$  at  $T = 200$  K, (high-temperature approximation, so that the values may be compared with those

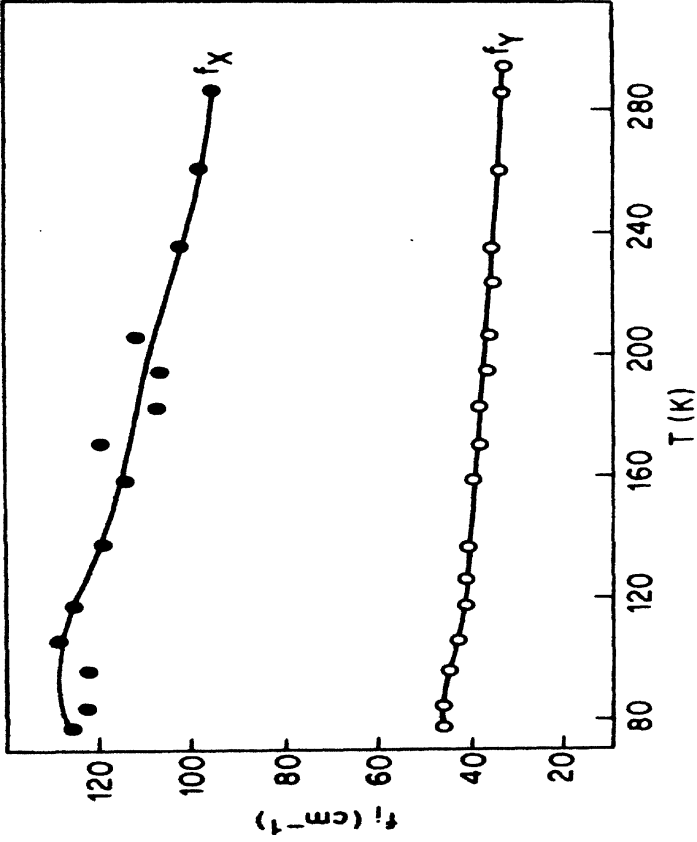


Fig. 5.2. Variation of  $f_X$  &  $f_Y$  with temperature in sodium chloroacetate

obtained from Brown's method-equation (5.8)).  $g_X$  and  $g_Y$  are obtained as 0.0017 and 0.0014 respectively so that  $g$  is 0.00146.

The results are also analysed by means of Brown's method, by fitting the experimental data in the high-temperature region to a parabola centered at  $T_0 = 200$  K and a value of 0.0011 is obtained for  $g$ . This value compares well with that obtained from Bayer's theory by the numerical method. Also Brown's assumption that the  $g_1$  values are all equal seems to be quite reasonable in the present case, in view of the nearly equal values obtained for  $g_X$  and  $g_Y$ . The values obtained for  $f_X$  and  $f_Y$  lie in the range 105 to 130 and 40 to 50  $\text{cm}^{-1}$  respectively in the temperature range 300 K to 77 K .

#### 5.4. TEMPERATURE VARIATION OF TORSIONAL FREQUENCY IN 2,4-DICHLOROPHENOXY ACETIC ACID:

The moments of inertia  $A_X$  and  $A_Y$  in this case are calculated from the crystal-structure data (Kennard et al., 1960-65) and are found to be  $3407.4 \times 10^{-40}$   $\text{gm cm}^2$  and  $2813.0 \times 10^{-40}$   $\text{gm cm}^2$  respectively for line I and  $3212.00 \times 10^{-40}$  and  $1422.00 \times 10^{-40}$   $\text{gm cm}^2$  respectively for line II. At OK,  $\nu_0$  is 35.24 MHz and 36.33 MHz for the two resonance lines observed. The values of  $f_X$  and  $f_Y$  are calculated following the numerical method of Vijaya et al. (1970). The temperature variation of the torsional frequency obtained for the two lines is shown in Fig. (5.3) and the values of torsional frequencies at various temperatures are given in

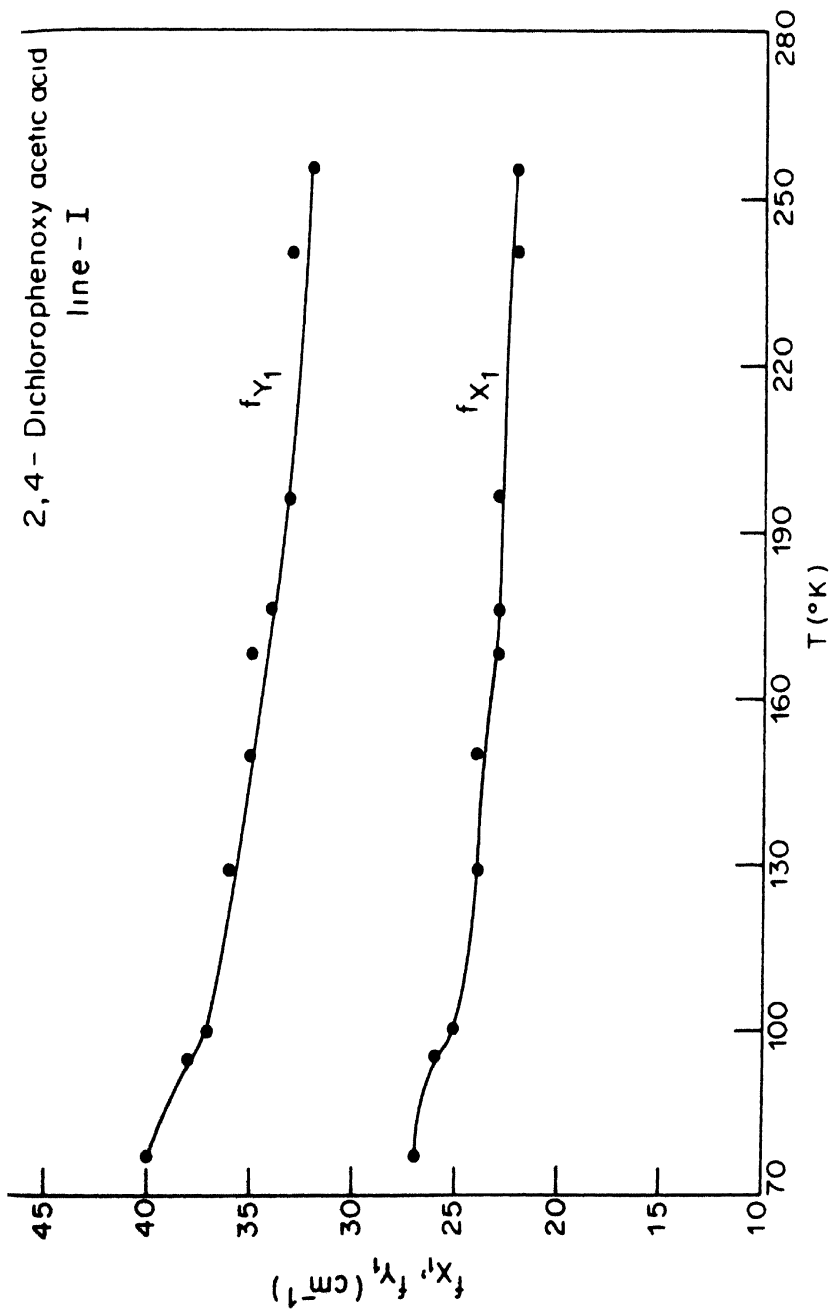


Fig 5.3 Variation of  $f_X$  &  $f_Y$  with temperature in 2,4-dichlorophenoxy acetic acid (Line - I)

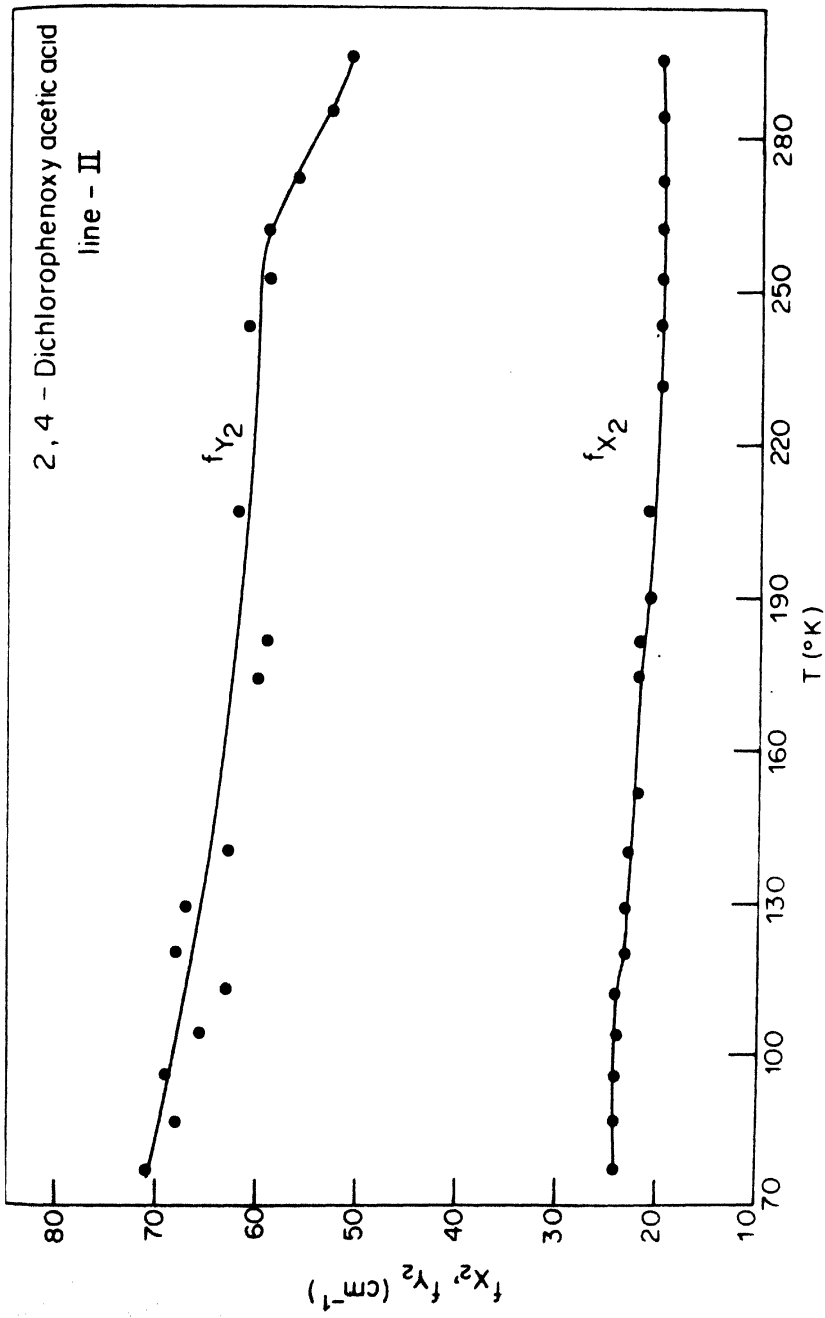


Fig. 5.3 a. Variation of  $f_X$  &  $f_Y$  with temperature in 2,4 - dichlorophenoxyacetic acid ( Line-II )

Table 5.3. The variation of  $f_{X_1}$  and  $f_{X_2}$  is small and is linear for most of the temperature region studied. The variation of  $f_{Y_1}$  and  $f_{Y_2}$  is also linear in most of the temperature region except in the region close to 300 K. The temperature coefficients  $g_X$  and  $g_Y$  of  $f_X$  and  $f_Y$  for both the lines are calculated from these data using equations (5.9) and (5.10) with  $T' = 0$  at  $T = 275$  K (high-temperature approximation) and are obtained as 0.0004 and 0.0004 respectively for the I line and as 0.0006 and 0.0006 respectively for the II line. The average  $g$  value for the I and II lines are 0.0004 and 0.0007 respectively.

The results are also analysed by Brown's method by fitting the experimental data in the high-temperature region to a parabola centered at  $T_0 = 275$  K using the method of least squares and the  $g$  values are obtained as 0.00046 and 0.00065 for the I and II resonance lines respectively. The values of  $g$  obtained by the numerical method compare well with the values of  $g$  obtained by Brown's method. Also Brown's assumption that the  $g_1$  values are all equal seems to be quite reasonable in the present case, for both the lines. The values obtained for  $f_X$  and  $f_Y$  lie in the range 20 to 30  $\text{cm}^{-1}$  and 30 to 40  $\text{cm}^{-1}$  respectively for the I line and 20 to 30  $\text{cm}^{-1}$  and 55 to 70  $\text{cm}^{-1}$  respectively for the II line in the temperature range 300 K to 77 K.



### 5.5. TEMPERATURE VARIATION OF TORSIONAL FREQUENCY IN 2,6-DICHLOROPHENOL:

The moments of inertia  $A_X$  and  $A_Y$  are calculated using the crystal structure data of 2,6-dichloro phenol (Bavoux and Thozet, 1974) for the two lines observed, one due to the ortho (H) chlorine and the other due to the ortho chlorine. The values of  $A_X$  and  $A_Y$  obtained are  $1283.958 \times 10^{-40}$  gm cm<sup>2</sup> and  $753.556 \times 10^{-40}$  gm cm<sup>2</sup> respectively for the ortho (OH) line (i.e., the line due to the chlorine involved in intramolecular hydrogen bonding) and  $1306.088 \times 10^{-40}$  gm cm<sup>2</sup> and  $787.538 \times 10^{-40}$  gm cm<sup>2</sup> respectively for the line due to the ortho chlorine. The resonance frequency,  $\nu_0$ , at 0K is obtained by extrapolating the  $\nu_T$  versus T curve, as 35.315 MHz and 35.880 MHz respectively for the ortho (H) and ortho chlorine lines.

The temperature variation of the torsional frequency obtained for the two lines using the numerical method is shown in Fig. (5.4) and the values of torsional frequencies at various temperatures are given in Table(5.4). The variation of  $f_X$  and  $f_Y$  is almost linear for most of the temperature region for both the lines except around 77 K. The temperature coefficients  $g_X$  and  $g_Y$  for both the lines are calculated using equations (5.9) and (5.10) with  $T' = 0$  at  $T = 200$  K (high-temperature approximation). The values of  $g_X$  and  $g_Y$  are obtained as 0.00126 and 0.0015 respectively for the I line and as 0.0010 and 0.0007 respectively for the

2, 6 - Dichlorophenol  
(Line-I)

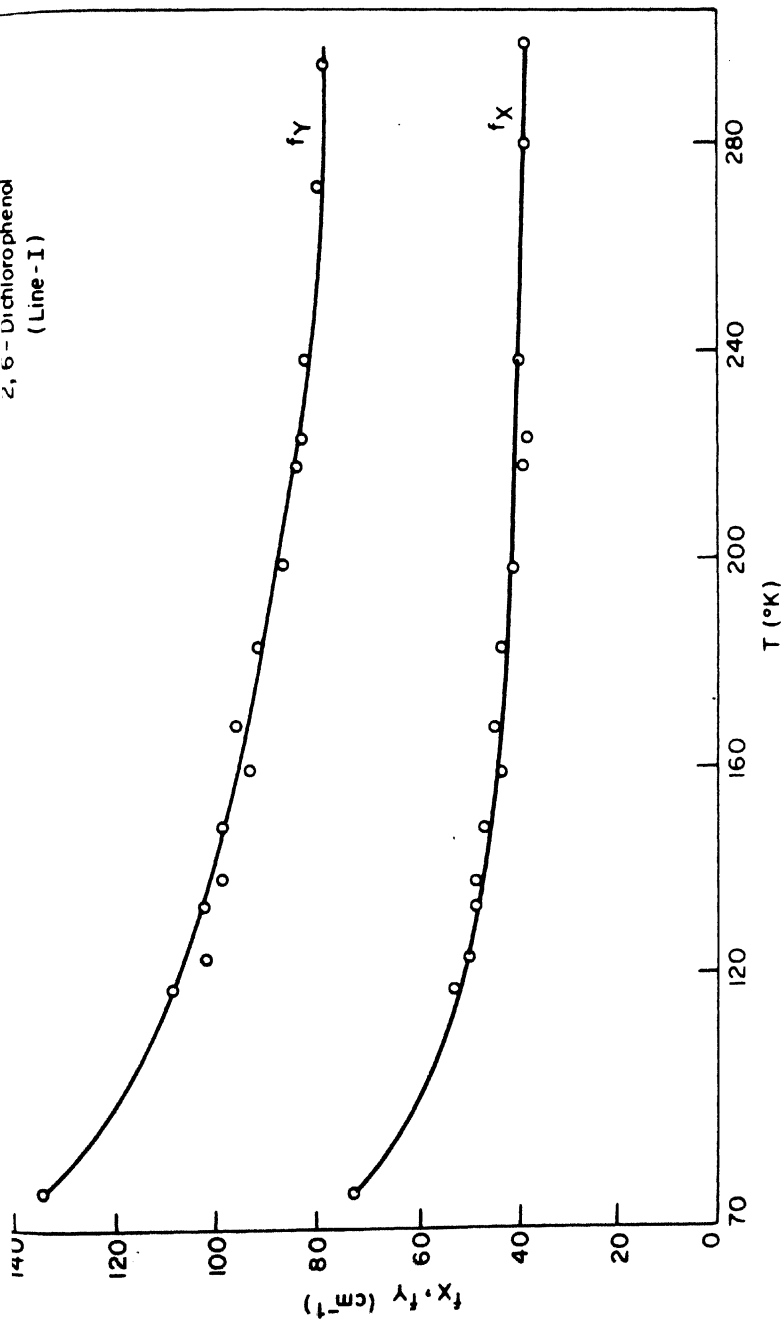


Fig. 5.4. Variation of  $f_X$  and  $f_Y$  with temperature in 2,6-Dichlorophenol (Line-I)

2,6-Dichlorophenol  
(Line- II)

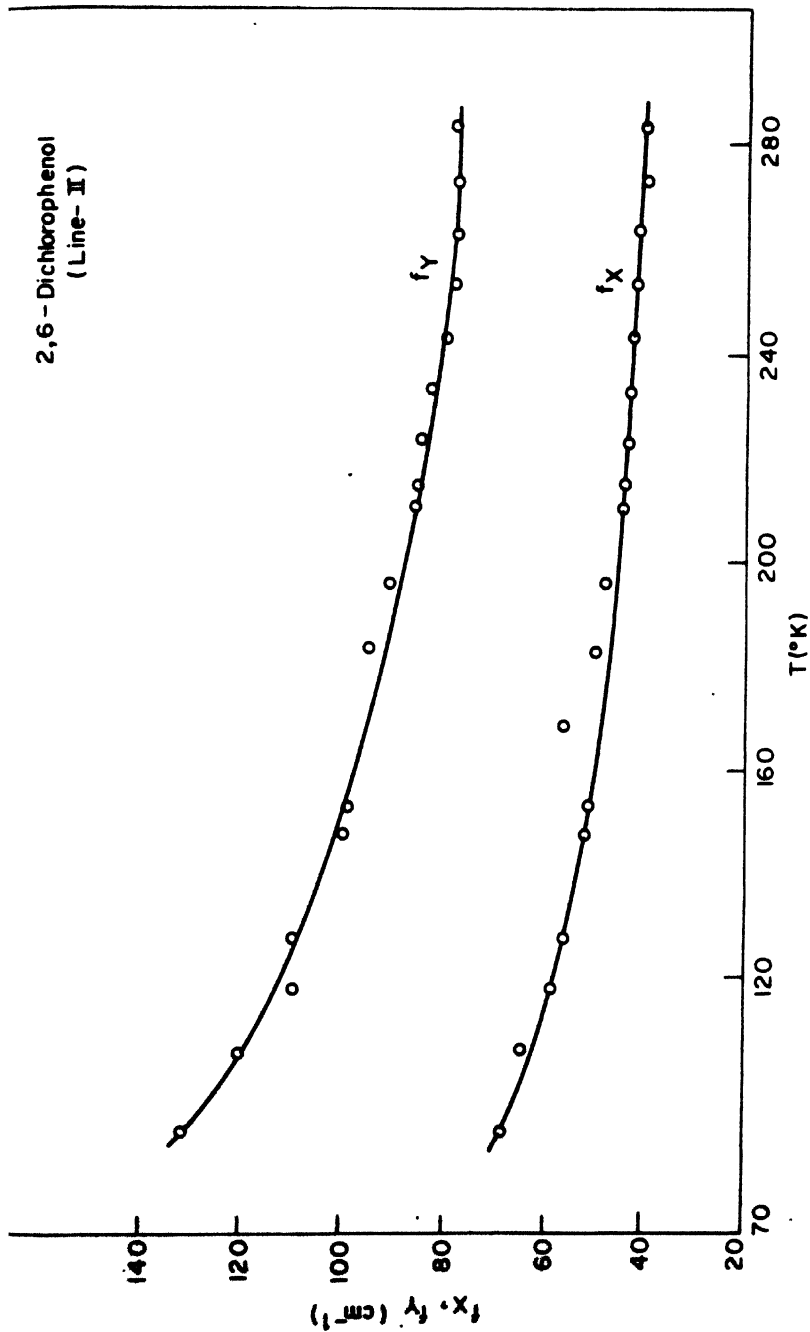


Fig. 5.4 a. Variation of  $f_X$  and  $f_Y$  with temperature in 2,6-dichlorophenol (Line-I)

II line. The average  $g$  values for the I and II lines are 0.00134 and 0.0009 respectively.

The results are also analysed by Brown's method by fitting the experimental data in the high-temperature region to a parabola centered at  $T_0 = 200$  K using the method of least squares and values of  $g$  obtained are 0.0013 and 0.0006 respectively for the I and II lines. The value of  $g$  obtained by the numerical method for the I line compares very well with that obtained by Brown's method whereas there is a little difference between the two values for the II line. The values of  $f_x$  and  $f_y$  lie in the range 40 to 70  $\text{cm}^{-1}$  and 70 to 140  $\text{cm}^{-1}$  respectively for the I line and 40 to 70  $\text{cm}^{-1}$  and 75 to 130  $\text{cm}^{-1}$  respectively for the II line in the temperature range 300 to 77 K.

#### 5.6. TEMPERATURE VARIATION OF TORSIONAL FREQUENCY IN 3,5-DICHLOROPHENOL:

The moments of inertia  $A_x$  and  $A_y$  are calculated using the crystal structure data of 3,5-dichlorophenol (Bavoux and Thozet, 1973) and are obtained as  $1505.00 \times 10^{-40}$  and  $863.897 \times 10^{-40}$   $\text{gm cm}^2$  respectively for the two resonance lines. The resonance frequency  $\nu_0$ , at OK is 35.445 and 35.790 MHz respectively for the I and II line.

Sashikala et al. (1971) have reported earlier the torsional frequency ( $f_t$ ) at 218 K as 43.99 and 53.20  $\text{cm}^{-1}$  respectively for the I and II lines, assuming that  $f_x = f_y = f_t$ . We have studied the temperature variation of torsional

frequencies  $f_X$  and  $f_Y$  in the temperature range 77 to 300 K using the numerical method of Vijaya et al. (1970). The values of torsional frequencies obtained at various temperatures are given in Table (5.5) and the temperature variation of the torsional frequency for the two lines is shown in Fig. (5.5). The variation of  $f_X$  and  $f_Y$  is almost linear for both the lines except near 77 K. The temperature coefficients  $g_X$  and  $g_Y$  are calculated using equations (5.9) and (5.10) with  $T' = 0$  at  $T = 200$  K. The values of  $g_X$  and  $g_Y$  are obtained as 0.00146 and 0.00144 for the I line and as 0.0012 and 0.00129 for the II line leading to an average value of 0.0014 and 0.0012 respectively for the I and II lines.

The results are also analysed by Brown's method by fitting the experimental data in the high-temperature region to a parabola centered at  $T_0 = 200$  K using the method of least squares and the values of  $g$  for the I and II lines are obtained as 0.0013 and 0.0009. The value of  $g$  obtained by the numerical method for the I line compares very well with that obtained by Brown's method whereas for the II line there is a little difference between the two values. The values of  $f_X$  and  $f_Y$  lie in the range 40 to 90  $\text{cm}^{-1}$  and 60 to 140  $\text{cm}^{-1}$  for the I line and for the II line in the range 40 to 90  $\text{cm}^{-1}$  and 60 to 130  $\text{cm}^{-1}$  in the temperature range 300 to 77 K.

The values of  $J_0$ ,  $A_X$ ,  $A_Y$ ,  $g_X$ ,  $g_Y$  and  $g$  obtained

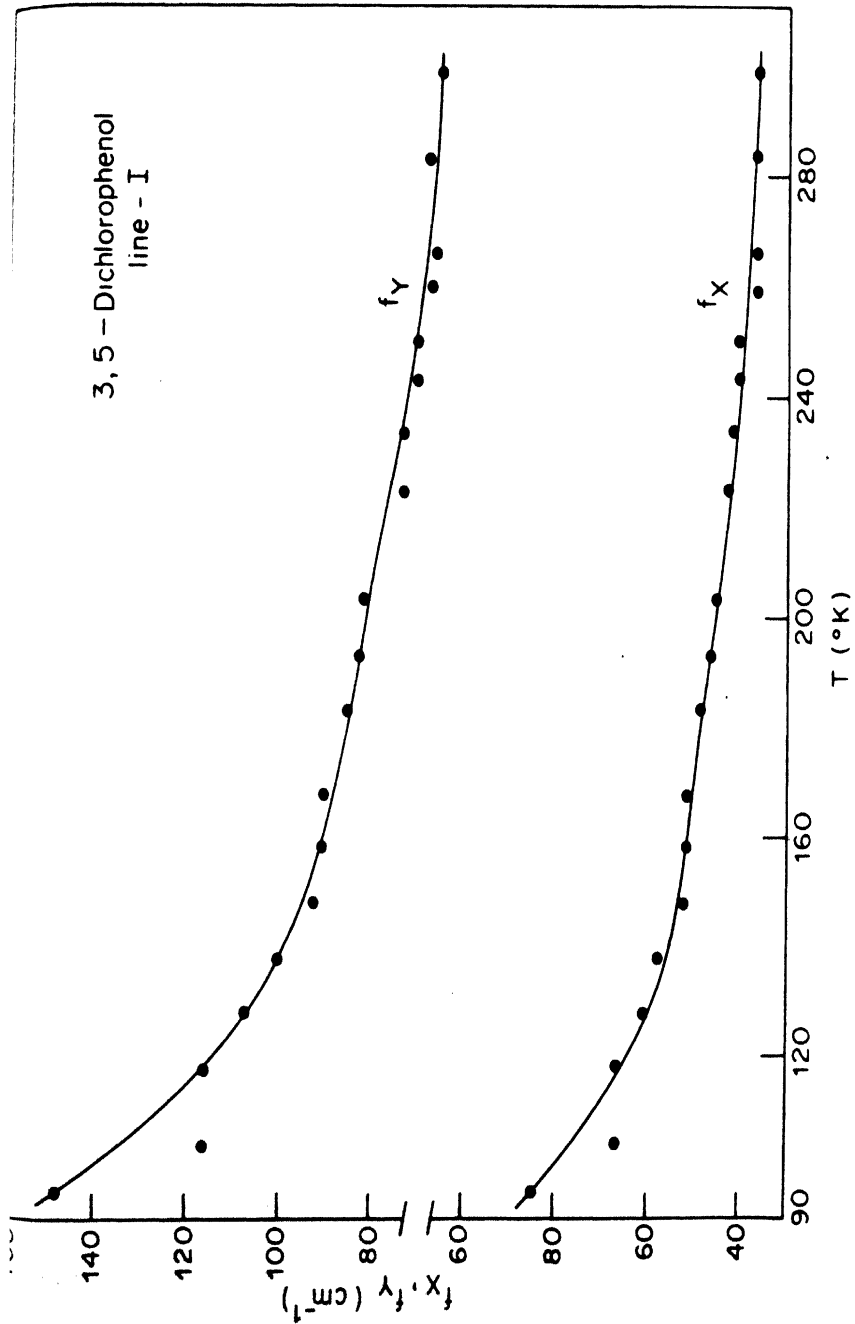


Fig. 5.5. Variation of  $f_X$  &  $f_Y$  with temperature in 3, 5 - dichlorophenol ( Line-I )

3, 5 - Dichlorophenol  
line - II

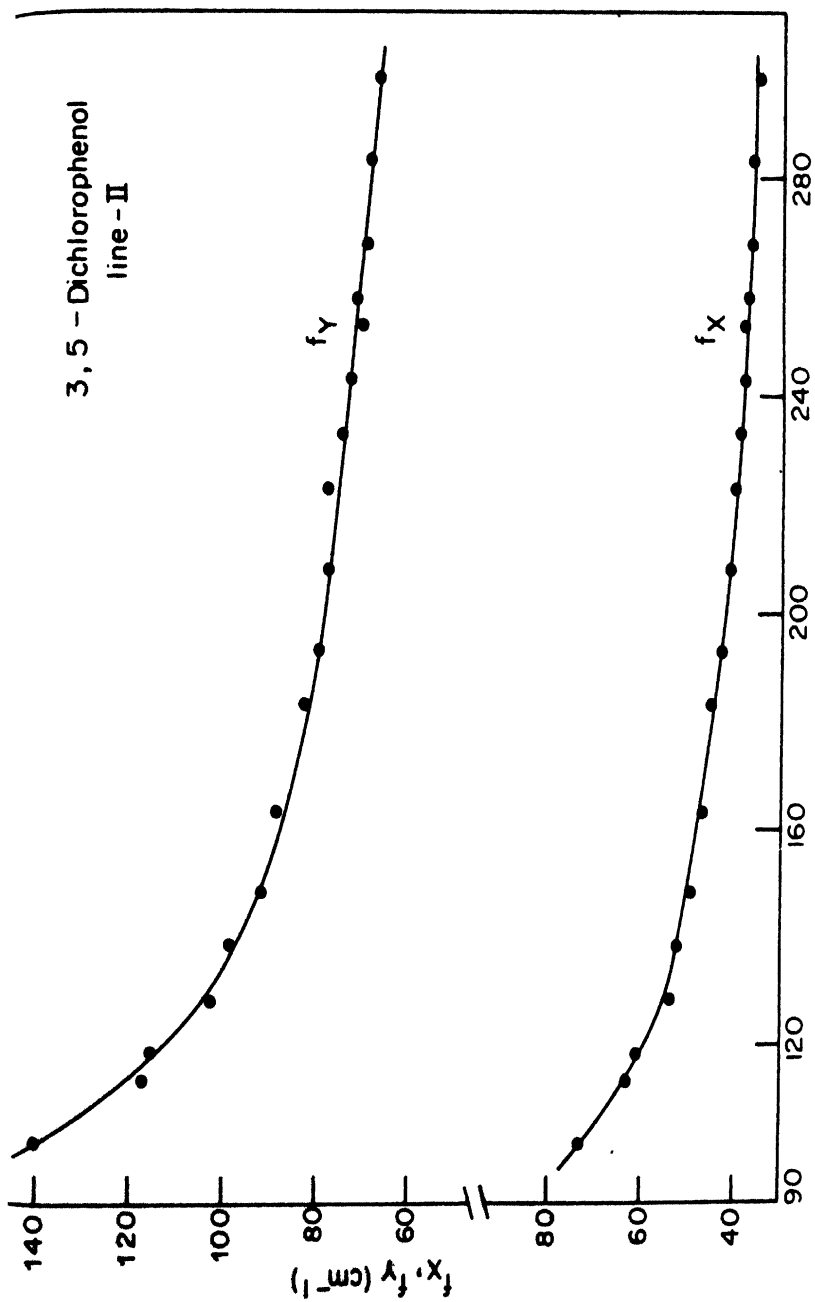


Fig. 5 a. Variation of  $f_X$  &  $f_Y$  with temperature in 3, 5-dichlorophenol (Line-II)

for all the resonance lines in the five compounds studied are given in Table (5.6).

### 5.7. CONCLUSION:

The variation of  $f_x$  and  $f_y$  is almost linear in the temperature range 77 to 300 K in all the five compounds studied. The values of  $f_x$  and  $f_y$  in all the compounds studied lie in the range 20 to 150  $\text{cm}^{-1}$  between the temperatures 300 and 77 K. It is generally known that the rotary modes of molecules lie in the range 20 to 100 or 150  $\text{cm}^{-1}$  (Stidham, 1968). In view of this observation, the values obtained for  $f_x$  and  $f_y$  in all the compounds studied may be considered reasonable and it would be interesting to compare these values with Raman and infrared data when they become available. It would also be useful to have Raman and infrared data on the temperature-dependence of rotary modes in molecules; such data are not available at present or very meagre if available.



TABLE 5.1. VALUES OF TORSIONAL VIBRATION FREQUENCY IN MONO CHLORO  
ACETIC ACID AT VARIOUS TEMPERATURES

Line I		Line II	
Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )	Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )
77	63.68	77	76.54
79	63.17	80	77.14
82	60.46	90	73.72
85	61.02	100	70.94
93	59.41	110	69.04
98	58.24	120	66.56
108	58.35	130	64.74
113	56.70	140	63.14
118	56.97	148	62.30
123	56.16	150	60.39
128	56.85		
133	56.40	161	60.94
138	55.85	170	59.17
148	54.69	182	57.12
158	54.69	189	56.94
168	56.18	198	56.41
178	53.31	203	56.01
196	51.04	212	55.75
200	50.84	220	53.71
210	50.10	229	57.10
220	49.50	234	56.14
230	48.70	247	54.56
240	48.29	253	53.53
250	47.87	273	52.97
273	46.69	299	51.13
299	45.82		

TABLE 5.2. VALUES OF TORSIONAL FREQUENCY IN SODIUM  
CHLORO ACETATE AT VARIOUS TEMPERATURE

Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )	
	$f_X$	$f_Y$
77.0	126	46
83.5	123	46
95.5	122	45
117.0	125	42
137.0	119	41
158.0	114	40
170.0	119	39
194.0	107	38
206.0	113	37
223.5	113	36
234.5	103	36
260.6	98	35
285.5	96	34
294	89	34

TABLE 5.3. VALUES OF TORSIONAL FREQUENCY IN 2,4-DICHLOROPHENOLY ACETIC ACID AT VARIOUS TEMPERATURES

Line I			Line II		
Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )		Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )	
	$f_A$	$f_Y$		$f_X$	$f_Y$
77.0	27	40	77.0	24	70
95.0	26	38	86.5	24	69
100.0	25	37	95.5	24	68
129.0	24	36	104.0	24	67
149.5	24	35	119.5	23	66
168.0	23	35	128.5	23	66
176	23	34	151.0	22	65
196	23	33	189.5	21	65
240.5	22	33	243.0	20	62
255.0	22	32	261.5	20	58
288.0	22	32	284.5	20	53
299.0	22	31	295.0	20	51

TABLE 5.4. VALUES OF TORSIONAL FREQUENCY IN 2,6-DICHLOROPHENOL AT VARIOUS TEMPERATURES

Line I			Line II		
Temperature (K)	Torsional frequency (Cm <sup>-1</sup> )		Temperature (K)	Torsional frequency (Cm <sup>-1</sup> )	
	f <sub>X</sub>	f <sub>Y</sub>		f <sub>X</sub>	f <sub>Y</sub>
77.0	73	134	90.0	68	131
108.0	43	80	106.0	64	120
117.0	53	98	118.0	58	109
123.0	50	91	128	56	108
133.0	49	92	148.0	52	99
138.0	49	88	153.0	51	98
148.0	47	88	169.0	56	104
159.0	46	83	183.5	50	94
168.0	45	85	196.0	48	90
183.0	44	81	211.0	44	85
199.0	41	76	215.0	44	85
218.0	39	73	223.0	43	84
223.0	38	72	233.0	43	82
238.0	38	72	243.0	42	79
			253.0	42	77
			263.0	41	76
			273.0	40	77
			283.0	40	77

TABLE 5.5. VALUES OF TORSIONAL VIBRATION FREQUENCY IN 3,5-DICHLOROPHENOL AT VARIOUS TEMPERATURES

Line I			Line II		
Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )		Temperature (K)	Torsional frequency ( $\text{Cm}^{-1}$ )	
	$f_X$	$f_Y$		$f_X$	$f_Y$
95.0	85	148	101.0	73	140
104.0	67	116	112.5	63	117
118.0	67	116	118.0	61	115
128.0	61	107	128	54	102
138.0	58	100	138	52	98
148.0	52	92	148.0	49	91
158.0	52	90	163.0	47	88
168.0	52	90	183.0	45	82
183.0	49	85	193.0	43	79
193.0	47	83	208.0	41	77
203.0	46	81	223.0	40	77
223.0	43	73	233.0	39	74
233.0	42	73	243.0	38	72
243.0	41	70	253.0	38	70
250.0	41	70	258.0	37	71
259.5	37	67	268.0	36	69
266.0	37	66	283.0	36	68
298.0	37	65	298	35	60

TABLE 5.6. VALUES OF THE PARAMETERS  $\delta_0$ ,  $k_x$ ,  $k_y$ ,  $\epsilon_x$ ,  $\epsilon_y$  and  $\epsilon$

Name of the compound	$\delta_0$ (MHz)	$k_x$ in $10^{-2}$ gm cm	$k_y$ in $10^{-2}$ gm cm	$\epsilon_x$	$\epsilon_y$	$\epsilon$
Mono chloro acetic acid						
I line	36.32	405.69	436.69	-	-	-
II line	36.56	405.69	436.69	-	-	-
Sodium chloro acetate						
I line	34.875	467.90	615.10	0.0017	0.0014	0.0014 <sup>a</sup> 0.0011 <sup>b</sup>
2,4-dichloro phenoxy- acetic acid						
I line	35.24	3477.40	2818.0	0.0004	0.0004	0.0004 <sup>a</sup> 0.00046 <sup>b</sup>
II line	36.33	3212.00	1422.0	0.0006	0.0006	0.0007 <sup>a</sup> 0.00065 <sup>b</sup>
2,6-dichloro phenol						
I (Ortho-H) line	35.315	1283.958	753.556	0.00126	0.0015	0.0013 <sup>a</sup> 0.0013 <sup>b</sup>
II (Ortho) line	35.880	1316.088	787.538	0.0010	0.0007	0.0009 <sup>a</sup> 0.0006 <sup>b</sup>

(Contd.)

TABLE 5.6. (CONTD.)

	$\delta_0$	$\delta_X$	$\delta_Y$	$\delta_X$	$\delta_Y$	$\delta$
3,5-dichloro phenol						
I line	35.445	1505.0	863.897	0.00146	0.00144	0.0014 <sup>a</sup> 0.0013 <sup>b</sup>
II line	35.790	1505.0	863.897	0.0012	0.0012	0.0012 <sup>a</sup> 0.0009 <sup>b</sup>

a - Values obtained by the numerical method

b - Values obtained by Brown's method

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