Chapter 2

NORMAL COORDINATE ANALYSIS OF THE INFRARED INTERNAL VIBRATIONS OF CRYSTALLINE CYANOGEN HALIDES.
ABSTRACT

Normal coordinate analysis of the optically active internal vibrations of cyanogen halide XCN (X = Cl, Br, I) crystals has been carried out using a general valence force field. The C–N stretching force constant in these crystals has values between 18.35 and 18.65 (m.dynes/Å). The corresponding C–X values are found to vary from 2.02 to 2.85. A decrease in the C–X stretching force constant and an increase in the corresponding C–N values are observed as the substances get transformed from the molecular to crystalline state. The C–X stretching force constant is not found to vary much between halides unlike in molecules.

The frequencies of the optically active internal vibrations of the isotopic analogues of these cyanogen halides have been predicted. It has been found that the predicted frequencies for the C–N stretching mode in X^13CN and X^15CN crystals are in excellent agreement with the experimentally observed values.
2.1 INTRODUCTION

The study of compounds containing C – X (X = Cl, Br, I) and C≡N bonds are of interest, since the variation of the C≡N and C – X force constants with different X atoms leads to information about their bond character.

The crystal structure of cyanogen halides XCN (X = Cl, Br, I) is known. The X-ray study of Katellair and Zwartensberg reveals that cyanogen iodide crystal is built up of parallel linear chains with ICN molecules on sites of C₃ᵥ symmetry. The crystal is unimolecular and belongs to the trigonal system with the space group C₃ᵥ. However, cyanogen chloridă and bromide crystals have an orthorhombic bimolecular unit cell with the space group D¹₃h. The molecules are strictly linear and are closely packed in one direction within the crystals. These structures have been confirmed by Bandy, Frederich and Person from an absolute intensity study of the fundamental absorption
bands in the infrared and by Savoie and Pezolet\(^4\) from a longitudinal modes study in the Raman spectra.

The infrared spectra of these halides at \(-180^\circ\) C have been analysed by Freitag and Nixon\(^5\). They have also observed the C-N stretching frequencies in \(X\text{CN}^1\) and \(X\text{C}^\text{15}\text{N}\) crystals. A detailed infrared and Raman study of crystalline ICN carried out by Savoie et al\(^6\) agrees with that of Freitag et al\(^5\).

The force constant analysis of cyanogen halide molecules has been carried out by a number of authors\(^7\text{-}13\). Bahnick and Person\(^7\) have studied the complexes of ICN with various organic donor solvents and have evaluated the force constants for the ICN molecules in these systems. Ramaswamy and Ranganathan\(^10\) have used the Green's function method of analysis to evaluate the force constants of XCN molecules.

However, a normal coordinate analysis of the cyanogen halide crystals has not been attempted so far. In this chapter the force constants corresponding to the optically active internal vibrations of cyanogen halide crystals have been evaluated using FG matrix method\(^14\) as formulated by Shimanouchi, Tsuboi and Miyazawa\(^15\) for crystals.

2.2 THE METHOD

The analysis of the optically active lattice vibrations by Shimanouchi et al\(^15\) incorporates the symmetrised inverse kinetic energy matrix \(G^S\) and potential energy matrix \(F^S\). The optically active internal vibrational frequencies are calculated by
solving the secular equation

\[
\begin{vmatrix}
G_{op}^s & F_{op}^s \\
F_{op}^s & -\Lambda E
\end{vmatrix} = 0
\] (2.1)

The method of evaluating the \( G_{op}^s \) and \( F_{op}^s \) matrices are outlined in chapter I (Section 1.2). The \( F_{op}^s \) matrix can be expressed in terms of the \( B_{op}^s \) matrix as:

\[
F_{op}^s = \sum_{\text{op}} B_{op}^s F_{op} B_{op}^s
\] (2.2)

The crystals being molecular in nature, the interactions considered in the \( B_{op}^s \) matrix are of those coordinates to which the chosen internal coordinates get transformed during the symmetry operations. The \( F_{op}^s \) matrix is the sum of the potential energy matrix due to the chosen Bravais cell \((i, j, k)\) and those due to the surrounding inter-Bravais interaction matrices.

In molecular crystals, the intermolecular interactions being vanishingly small\(^{16}\), the inter-Bravais interactions are expected to be extremely weak and therefore, these interactions have not been considered. The \( G_{op}^s \) matrix can be expressed as:

\[
G_{op}^s = U M^{-1} U
\] (2.3)

here \( M^{-1} \) is a diagonal inverse mass matrix. \( U \) is matrix of transformation to the symmetry coordinates from internal valence coordinates. The force constants can be evaluated using the experimentally observed vibrational frequencies in equation (2.1).

2.3 APPLICATION TO CYANOGEN IODIDE

The factor group analysis\(^6\) of the cyanogen iodide crystal yields
the optically active internal vibrational modes.

\[ \gamma_{\text{vib}}^{\text{op}} = 2A_1 + E \]  

(2.4)
since the crystal is a non centrosymmetric one, all the frequencies are present both in the Raman and infrared spectra.
The unit cell of the crystal containing a single Bravais cell is shown in Figure 2.1.
During the symmetry operations under the \( C_{3v} \) group the ICN molecule gets transformed to some of the surrounding Bravais cells to which the transformation takes place, which are considered in constructing the \( B_{\text{op}} \) matrix. The complete \( B_{\text{op}} \) matrix is reproduced in Table 2.2. \( R_2, R_3, R_4 \) and \( r_2, r_3, r_4 \) are the respective C-N and C-I distances measured along the direction of the bond in the neighbouring Bravais cells (Table 2.1) to which the distances \( R_1 \) and \( r_1 \) get transformed during symmetry operations. The angle ICN measured in two perpendicular directions are denoted as \( \beta_a \) and \( \beta_b \).
\( \theta \) is the angle made by the linear ICN in the Bravais cell with the X-axis.
The symmetry coordinates associated with the various optically active internal vibrational modes can be written as:

\( A_1 \) species.

\[ S_1 = \frac{1}{2\sqrt{3}} (3r_1 + r_2 + r_3 + r_4) \]

\[ S_2 = \frac{1}{2\sqrt{3}} (3R_1 + R_2 + R_3 + R_4) \]
\[ \begin{align*}
S_{3a} & = \sqrt{\pi R} \beta_a \\
S_{3b} & = \sqrt{\pi R} \beta_b
\end{align*} \]

A valence force field is employed and the potential energy matrix is derived by taking into account all the intramolecular interactions in the chosen Bravais cell. The elements of the symmetrized force constant matrix are:

\[ F_{11} = 2(1 + 2 \sin \phi + \cos \phi) f_x \] (2.5)

\[ F_{12} = - \left[ \frac{1}{6} + \sin \phi \left( \frac{4}{3} \sin \phi + 1 \right) \cos \phi \right] f_x + \left[ 1 + \sin \phi \right] f_{xR} \] (2.6)

\[ F_{22} = \frac{1}{3} \left( \frac{1}{2} + \sin \phi + \cos \phi \right)^2 f_x + \left[ \frac{2}{3} \sin \phi \left( 1 + \cos \phi \right) + \frac{1}{6} - \frac{2}{3} \sin^2 \phi \right] f_{xR} + \left( \sin \phi + \cos \phi \right) f_{R} \] (2.7)

\[ F_{33} = \frac{\tau}{R} f_{\beta} \] (2.8)

\( \phi \) is half the angle between \( I - C \) bonds among neighbouring Bravais cells. The structural parameters\(^\text{17}\) (Table 2.3)
have been used to calculate $\phi$. For ICN crystal it is found to be 44° 31'. Substitution of the value of $\phi$ reduces the expressions (2.5), (2.6) and (2.7) to

$$F_{11} = 6.2314 f_T$$

$$F_{12} = -2.2047 f_T + 4.1831 f_{TR}$$

$$F_{22} = 1.222 f_T - 0.025 f_{TR} + 0.8364 f_R$$

The symmetrised $G$ matrix elements for cyanogen iodide crystal are:

$$G_{11} = \frac{\mu}{I}$$

$$G_{12} = 0$$

$$G_{22} = \frac{\mu}{C} + \frac{\mu}{N}$$

$$G_{33} = \frac{\mu}{I} + \frac{\mu}{C} + \frac{\mu}{N}$$

$\mu$ represents the reciprocal mass of the individual atom. The vibrational frequencies used in the analysis are those of Freitag et al.\(^5\) (Table 2.4).

The symmetrised force constants obtained using equation (2.1) have the following values (in m. dyne/Å):

$$F_{11} = 15.24$$

$$F_{22} = 17.98$$
The interaction constant $F_{12} = 0$ (equation 1.24 in chapter 1). Using these symmetrised $F$ values in equations (2.8) and (2.9 to 2.11) the valence force constants $f_T$, $f_{TR}$, $f_R$ and $f_\beta$ have been evaluated and are given in Table 2.5.

2.4 APPLICATION TO CYANOCYANIDE CHLORIDE AND BROMIDE

The optically active normal vibrations have been classified into

$$T_{\text{vib}}^\text{op} = 2 \Sigma^+ + \pi^+$$  \hspace{1cm} (2.16)

The bimolecular unit cell of these crystals is shown in Figure 2.2. The $B_{op}$ matrix derived for these crystals is given in Table 2.6. As all the symmetry operations are contained in the bimolecular unit cell itself, those coordinates alone are considered in constructing the $B_{op}$ matrix.

The symmetry coordinates associated with the optically active internal vibrations are:

$\Sigma^+$ vibrations

$$s_1 = \frac{1}{\sqrt{2}} (r_1 + r_2)$$

$$s_2 = \frac{1}{\sqrt{2}} (R_1 + R_2)$$

$\pi$ vibrations

$$s_{3a} = \sqrt{\frac{FR}{5}} (\beta_1 - 2\beta_2)$$

$$s_{4a} = \sqrt{\frac{FR}{5}} (\beta_1 + 2\beta_2)$$
using a general valence force field, the following symmetrised force constant matrix elements have been obtained.

\[
F_{11} = (f_{rr} - f_{rr}) \quad (2.17)
\]

\[
F_{12} = (f_{rr} - 1/2 (f_{rR} - f_{rr}) \quad (2.18)
\]

\[
F_{22} = (f_{rr} - f_{rr}) + (f_{rR} - f_{rr}) \quad (2.19)
\]

\[
F_{33} = 2/5 rR (f_{p} + f_{pp}) \quad (2.20)
\]

The symmetrised $G$ matrix elements for these crystals are

\[
G_{11} = \mu_X + \mu_C \quad (2.21)
\]

\[
G_{12} = 0 \quad (2.22)
\]

\[
G_{22} = \mu_C + \mu_N \quad (2.23)
\]

\[
G_{33} = \mu_X + \mu_C + \mu_N \quad (2.24)
\]

The structural parameters and the vibrational frequencies used in the calculation are summarised in Tables 2.3 and 2.4 respectively. The symmetrised force constants have been obtained from equation (2.1).

For cyanogen chloride

\[
F_{11} = 2.85 \text{ m. dynes/Å}
\]

\[
F_{22} = 21.50 \text{ m. dynes/Å and}
\]
For cyanogen Bromide

\[ F_{11} = 2.02 \text{ m. dynes/Å} \]
\[ F_{22} = 20.37 \text{ m. dynes/Å} \]

As the interaction \( F_{12} = 0 \) by the present analysis, equations (2.17) to (2.20) allows one to calculate the valence force constants. These are tabulated in Table 2.7.

2.5 RESULTS AND DISCUSSION.

Tables 2.5 and 2.7 give the valence force constants calculated for the halides. For comparison, the values obtained for the halide molecules by Ramaswamy et al.\(^\text{10}\) and for ICN by Bahnick et al.\(^\text{7}\) are also given.

An inspection of Tables 2.5 and 2.7 clearly indicates that the C-X stretching force constant decreases and C-N stretching force constant increases as the substances get transformed from the molecular to crystalline state. This is in conformity with the results for HCN crystals\(^\text{18}\), where C-H force constant decreases and C-N force constant increases from the corresponding molecular values.

In XCN molecules, the C-X stretching force constant varies from 6.16 m. dynes/Å in ClCN to 4.38 m. dynes/Å in BrCN to 3.06 m. dynes/Å in ICN. These force constant values are found to have a linear relation with the electronegativity of the X atom. However, the variation of the C-X stretching force constant in crystals is not found to be much. The C-N stretching force
constant does not show a variation between these halides. The stretching force constant for a pure triple C-N bond is around 18 m. dyne/Å. Since in these crystals the C-N stretching force constant is between 18.35 and 18.65 m. dyne/Å, the C-N bond is a triple one. The force constant values $f_\tau$ and $f_R$, thus indicate the probable structure $X-C\equiv N$ in these crystals unlike a resonant structure $X^+ = C = N\equiv X - C\equiv N$ in molecules.

The interaction force constant $f_R$ has been found to be higher than that in molecules. Such a high interaction value indicates a stronger association between the two bonds. The bending force constant $f_\phi$ in these halides is also found to be higher than their corresponding molecular counterparts.

2.6 PREDICTION OF FREQUENCIES OF ISOTOPIC CYANOCEN HALIDES.

The valence force constants given in Table 2.5 and 2.7 have been used to calculate the frequencies of the vibrational modes of the isotopic cyanogen halide crystals and are given in Tables 2.8, 2.9, and 2.10. The frequencies for the $C\equiv N$ stretching mode in $X^{13}CN$ and $X^{15}CN$ crystals are the only available experimental values which are also given in the tables. The predicted frequencies are in excellent agreement with the experimentally available values, supporting the model employed in the present calculation.
### TABLE 2.1

**INTERACTIONS CONSIDERED IN THE $b_{op}$ MATRIX FOR CYANOGEN IODIDE**

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>Bravais cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(r_1 ; R_1)$</td>
<td>$(i, j, k)$</td>
</tr>
<tr>
<td>$(r_2 ; R_2)$</td>
<td>$(i, j-1, k)$</td>
</tr>
<tr>
<td>$(r_3 ; R_3)$</td>
<td>$(i-1, j, k)$</td>
</tr>
<tr>
<td>$(r_4 ; R_4)$</td>
<td>$(i-1, j-1, k-1)$</td>
</tr>
<tr>
<td>Internal Coordinates</td>
<td>Cartesian Coordinates</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>$r_1$</td>
<td>0 0 -1 0 0 +1 0 0 0</td>
</tr>
<tr>
<td>$r_2$</td>
<td>$\sin\theta$ 0 $-\cos\theta$ $-\sin\theta$ 0 $\cos\theta$ 0 0 0</td>
</tr>
<tr>
<td>$r_3$</td>
<td>$-\sin\theta$ 0 $-\cos\theta$ $\sin\theta$ 0 $\cos\theta$ 0 0 0</td>
</tr>
<tr>
<td>$r_4$</td>
<td>0 0 +1 0 0 -1 0 0 0</td>
</tr>
</tbody>
</table>
**TABLE 2.3**

**STRUCTURAL PARAMETERS OF CYANOGEN HALIDES**

<table>
<thead>
<tr>
<th>Parameters*</th>
<th>ICN</th>
<th>Br CN</th>
<th>Cl CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.44</td>
<td>6.02</td>
<td>5.68</td>
</tr>
<tr>
<td>b</td>
<td>4.44</td>
<td>4.12</td>
<td>3.98</td>
</tr>
<tr>
<td>c</td>
<td>4.44</td>
<td>5.80</td>
<td>5.74</td>
</tr>
<tr>
<td>α</td>
<td>101° 24'</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>r</td>
<td>2.03</td>
<td>1.79</td>
<td>1.57</td>
</tr>
<tr>
<td>R</td>
<td>1.18</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>β</td>
<td>180°</td>
<td>180°</td>
<td>180°</td>
</tr>
</tbody>
</table>

* includes only those parameters which are used in the calculation.
The distances are in Angstroms and angles are in degrees.
### Table 2.4

**Frequencies of optically active internal vibrations of cyanogen halides.**

<table>
<thead>
<tr>
<th>Species and modes</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICN</td>
</tr>
<tr>
<td>( A_1 / \Sigma^+ )</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 )</td>
<td>451.5</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>2176.0</td>
</tr>
<tr>
<td>( E / \Pi^+ )</td>
<td></td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>328.5</td>
</tr>
</tbody>
</table>
TABLE 2.5

VALENCE FORCE CONSTANTS OF ICN

<table>
<thead>
<tr>
<th>Valence force Constants</th>
<th>Values (m. dyne/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present study on crystal</td>
</tr>
<tr>
<td></td>
<td>Ref. 7</td>
</tr>
<tr>
<td>( f_R )</td>
<td>2.47</td>
</tr>
<tr>
<td>( f_{RR} )</td>
<td>18.62</td>
</tr>
<tr>
<td>( f_{RR} )</td>
<td>1.30</td>
</tr>
<tr>
<td>( f_P )</td>
<td>0.32</td>
</tr>
</tbody>
</table>
### TABLE 2.6

**B₂ Matrix of Cyanogen Chloride and Cyanogen Bromide**

<table>
<thead>
<tr>
<th>Internal Coordinates</th>
<th>Cartesian Coordinates</th>
<th>(x_1)</th>
<th>(y_1)</th>
<th>(z_1)</th>
<th>(x_2)</th>
<th>(y_2)</th>
<th>(z_2)</th>
<th>(x_3)</th>
<th>(y_3)</th>
<th>(z_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_1)</td>
<td></td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(r_2)</td>
<td></td>
<td>0</td>
<td>0</td>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(R_1)</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>+1</td>
</tr>
<tr>
<td>(R_2)</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>(\beta_a)</td>
<td></td>
<td>(\frac{1}{R})</td>
<td>0</td>
<td>0</td>
<td>(\frac{1}{R} + \frac{1}{r})</td>
<td>0</td>
<td>0</td>
<td>(\frac{1}{r})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\beta_b)</td>
<td></td>
<td>(\frac{1}{R})</td>
<td>0</td>
<td>0</td>
<td>(-\frac{1}{R} + \frac{1}{r})</td>
<td>0</td>
<td>0</td>
<td>(\frac{1}{r})</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
### TABLE 2.7

**VALENCE FORCE CONSTANTS OF C\textsubscript{3}CN AND Br\textsubscript{2}CN**

<table>
<thead>
<tr>
<th>Valence force Constants</th>
<th>C\textsubscript{3}CN Present study on crystal</th>
<th>Ref.10 (molecule)</th>
<th>Br\textsubscript{2}CN Present study on crystal</th>
<th>Ref.10 (molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_f )</td>
<td>2.85</td>
<td>6.16</td>
<td>2.02</td>
<td>4.38</td>
</tr>
<tr>
<td>( f_{rf} )</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>\ldots</td>
</tr>
<tr>
<td>( f_R )</td>
<td>18.65</td>
<td>15.34</td>
<td>18.35</td>
<td>15.76</td>
</tr>
<tr>
<td>( f_{RR} )</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>\ldots</td>
</tr>
<tr>
<td>( f_{R^R} )</td>
<td>1.42</td>
<td>0.69</td>
<td>1.01</td>
<td>0.43</td>
</tr>
<tr>
<td>( f_{p} )</td>
<td>0.51</td>
<td>0.21</td>
<td>0.47</td>
<td>0.18</td>
</tr>
<tr>
<td>( f_{pp} )</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>\ldots</td>
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</table>
### TABLE 2.8

**PREDICTED FREQUENCIES OF THE OPTICALLY ACTIVE INTERNAL VIBRATIONS OF ISOTOPOICALLY SUBSTITUTED ICN CRYSTALS.**

<table>
<thead>
<tr>
<th>Isotopic substitution</th>
<th>Frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td>$^{13}_1$ICN</td>
<td>449</td>
</tr>
<tr>
<td>$^{15}_1$ICN</td>
<td>449</td>
</tr>
<tr>
<td>$^{13}_1$ICN</td>
<td>449</td>
</tr>
<tr>
<td>$^{125}_1$ICN</td>
<td>455</td>
</tr>
</tbody>
</table>
TABLE 2.9
PREDICTED FREQUENCIES OF THE OPTICALLY ACTIVE INTERNAL VIBRATIONS OF ISOTOPICALLY SUBSTITUTED CICN CRYSTALS.

<table>
<thead>
<tr>
<th>Isotopic substitution</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td>Cl¹³CN</td>
<td>712.5</td>
</tr>
<tr>
<td>Cl⁻¹⁵C⁵N</td>
<td>734.0</td>
</tr>
<tr>
<td>Cl¹³C⁺¹⁵N</td>
<td>712.5</td>
</tr>
<tr>
<td>³⁷Cl⁻⁷C⁻⁷N</td>
<td>730.0</td>
</tr>
<tr>
<td>Isotopic Substitution</td>
<td>Frequencies (cm(^{-1}))</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Br(^{13})CN</td>
<td>553.4</td>
</tr>
<tr>
<td>Br(^{15})CN</td>
<td>572.5</td>
</tr>
<tr>
<td>Br(^{13})C(^{15})N</td>
<td>553.4</td>
</tr>
<tr>
<td>Br(^{81})CN</td>
<td>572.4</td>
</tr>
</tbody>
</table>
Figure 2.1

UNIT CELL OF ICN CRYSTAL

R - Carbon-nitrogen distance
r - Iodine-carbon distance
• - Iodine
△ - Carbon
○ - Nitrogen
UNIT CELL OF XCN (X = Cl, Br) CRYSTAL

- $R$ - Carbon nitrogen distance
- $r$ - Iodine Carbon distance
- $\bigcirc$ - X atom
- $\bullet$ - Carbon
- $\triangle$ - Nitrogen

Figure 2.2
REFERENCES


