Chapter 3

NORMAL COORDINATE ANALYSIS OF THE INFRARED AND RAMAN INTERNAL VIBRATIONS OF DIBORON TETRAFLUORIDE CRYSTAL.
ABSTRACT

The optically active internal vibrations belonging to both infrared and Raman species of diboron tetrafluoride crystal have been studied using F.G. matrix method as modified by Shimanouchi. A general valence force field, considering the various intramolecular interactions, has been employed. The force field in the crystal is fixed entirely from a new angle using a parameter technique, incorporating the isotopic frequencies. In this formalism the dynamical matrix is expressed in terms of a parameter c. The value of the parameter is obtained by making use of the constraint that the force constants remain invariant under isotopic substitution. The F elements have been evaluated using the parameter c and the masses of the atoms in the crystal. The valence force constants obtained indicate that the principal B-B stretching and B-F stretching force constants remain the same as that in molecules. It has been found from the force constant study that diboron tetrafluoride retains its molecular nature in the crystal.
3.1 INTRODUCTION.

Diboron tetrafluoride compound has been studied in detail because of its structural transformation while going from molecule to crystal. Treffonas and Lipscomb have shown by X-ray diffraction studies that the crystal is planar with the molecular symmetry $D_{2h}$. It has a bimolecular unit cell with the space group $C_{2h}^5$; the molecules occupying sites of $C_1$ symmetry.

Gayles and Self have studied the infrared spectrum in both solid and gaseous states and interpreted the changes in the spectrum as that due to the symmetry transformation from $D_{2h}$ in crystal to $D_{2d}$ in molecule. Arthur Finch, Hyanas and Settelle have also reported the infrared spectrum of $B_2F_4$.

The matrix isolated $B_2F_4$ has been investigated in the infrared.
by Nimon, Sheshadri, Taylor and White. They have observed some of the frequencies corresponding to the infrared active modes of $^{11}B^{10}F_4$ crystal also. Recently, Durig, Thompson, Witt and Odom reported the Raman spectra of $B_2F_4$ crystal for the first time and have assigned the fundamentals.

The normal coordinate analysis of the infrared active internal vibrations of the crystal has been carried out by Padmaja and Aruldhas using Green's function method. A detailed analysis including both infrared and Raman active internal vibrations has so far not been attempted. In this chapter an analysis of all the optically active internal vibrations of the crystal using FG matrix method as modified by Shimanouchi et al is given. To fix the force field in the crystal, a different formalism is employed using isotopic frequencies in a parametric technique.

3.2 THEORY.

The motion of the atoms in the crystal in the harmonic approximation at zero wave vector can be summarised by the matrix equation

$$4 \pi^2 \nu^2 m U = F U$$

(3.1)

$m$ is a diagonal matrix specifying the atomic masses, $F$ is the matrix incorporating forces between atoms and $U$ is a vector representing the individual atomic displacements of a normal
mode with frequency \( \nu \). The dynamical matrix \( D \) specifying the motion of atoms in a lattice is written as

\[
D = m^{-1/2} F m^{-1/2}
\]  

(3.2)

\( m^{-1/2} \) is a diagonal matrix containing the reciprocal of the square root of the atomic masses. The dynamical matrix can also be expressed in terms of an orthogonal matrix \( W \) as

\[
D = W \Lambda W^{-1}
\]  

(3.3)

The matrix \( W \) can be selected in different ways in terms of different parameters\(^9\). For a vibrational problem of order \( n \), the \( F \) matrix contains \( \sqrt{2} n(n+1) \) distinct elements and therefore the \( W \) matrix requires \( \sqrt{2} n(n-1) \) parameters. Thus for a vibrational species of order 2 it depends only on a single parameter, say \( c \). In the present analysis, we employ a \( W \) matrix of the form

\[
W = \frac{1}{\sqrt{1 + c^2}} \begin{pmatrix} 1 & c \\ -c & 1 \end{pmatrix}
\]  

(3.4)

The orthogonal matrix \( W \) expressed in this form has been found to work very well in molecules \(^{10, 11} \). Using equation (3.3) in (3.2), the \( F \) matrix can be written as

\[
F = m^{1/2} W \Lambda W^{-1} m^{1/2}
\]  

(3.5)

The concept of the invariance of the force field under isotopic substitution can be employed as the basic criteria in choosing the parameter \( c \). Denoting isotopic substitution
by an asterisk, the condition
\[ F = F^* \] (3.6)
leads to
\[ m^{1/2} \Lambda m^{-1} = m^* \Lambda m^* \] (3.7)

Multiplication of (3.7) by \( m^* \) from left and right yields
\[ m^{1/2} \Lambda m^{-1} m^{1/2} m^* = m^* \Lambda m^* \] (3.8)

Since the matrices \( m^{1/2} \) and \( m^* \) are diagonal, its product is the diagonal matrix
\[ g = m^{1/2} m^* \] (3.9)

Introducing equations (3.4) and (3.9) in (3.8) and equating the elements
\[ \frac{(-\Lambda_i + \Lambda_j) g_{ii} g_{jj} c}{1 + c^2} = \frac{-*(\Lambda_i + \Lambda_j) c^*}{1 + c^{*2}} \] (3.10)
\[ g^2_{ii} (\Lambda_i + \Lambda_j c^2) \frac{1}{1 + c^2} = \frac{* \Lambda_i + \Lambda_j c^*}{1 + c^{*2}} \] (3.11)
\[ g^2_{jj} (\Lambda_i c^2 + \Lambda_j) \frac{1}{1 + c^2} = \frac{\Lambda_i c^{*2} + \Lambda_j}{1 + c^{*2}} \] (3.12)
The value of $c^2$ can be obtained by adding (3.11) and (3.12):

$$
c^2 = \frac{(\Lambda_i + \Lambda_j) - g_{ii}^2 \Lambda_i - g_{jj}^2 \Lambda_j}{g_{ii}^2 \Lambda_j - g_{jj}^2 \Lambda_i - (\Lambda_i + \Lambda_j)}
$$  \hfill (3.13)

The $F$ elements are computed by substituting (3.13) in (3.5):

$$
F_{ii} = \frac{m_{ii} (\Lambda_i + \Lambda_j c^2)}{1 + c^2}
$$  \hfill (3.14)

$$
F_{jj} = \frac{m_{jj} (\Lambda_j + \Lambda_i c^2)}{1 + c^2}
$$  \hfill (3.15)

$$
F_{ij} = \frac{-m_{ii}^{1/2} m_{jj}^{1/2} (\Lambda_i - \Lambda_j) c^2}{1 + c^2}
$$  \hfill (3.16)

Thus, knowing the atomic masses and vibrational frequencies the values of the $F$ elements can be evaluated. Two values are possible for $c$ from equation (3.13). This leads to two sets of values for $F$ elements which differ only in the interaction term $F_{ij}$ as $F_{ii}$ and $F_{jj}$ depend on $c^2$ and $F_{ij}$ on $c$. 
The $F$ elements can be expressed in terms of the valence force constants by evaluating the $B^S_{op}$ matrix as described in section 1.2. The symmetrised $F^S_{op}$ elements are expressed in terms of the $B^S_{op}$ and $F^S_{op}$ matrices as

$$F^S_{op} = B^S_{op} F^S_{op} B^S_{op}$$  \hspace{1cm} (3.17)

The $F^S_{op}$ matrix contains the valence force constants. The $B^S_{op}$ matrix is constructed taking into consideration all the internal coordinates taking part in the symmetry transformations of the crystal. The expressions for the $F^S_{op}$ elements so obtained can be equated to the corresponding value in equations (3.14) to (3.16) and the valence force constants can be evaluated.

3.3 APPLICATION TO DIBORON TETRAFLUORIDE CRYSTAL

Diborane tetrafluoride in the solid state has twelve intramolecular fundamentals. Excluding the optically inactive $A_u$ mode, the eleven optically active normal vibrations span the representations

$$T^S_{op} = 3 A_g (R) + 2 B_{1g} (R) + 1 B_{2g} (R)$$

$$+ 1 B_{1u} (IR) + 2 B_{2u} (IR) + 2 B_{3u} (IR)$$  \hspace{1cm} (3.18)

The Bravais cell with the internal coordinates of $B_2F_4$...
crystal is shown in Figure 3.1(a). The symmetry coordinates for all the above species of vibrations are given below.

\( A_g \) species

\[ \begin{align*}
S_1 &= D \\
S_2 &= \frac{1}{2} (d_1 + d_3 + d_6 + d_8) \\
S_3 &= \frac{d}{2 \sqrt{2}} (\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)
\end{align*} \]

\( B_{1g} \) species

\[ \begin{align*}
S_4 &= \frac{1}{2} (d_1 - d_3 - d_6 + d_8) \\
S_5 &= \frac{1}{2} (\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4)
\end{align*} \]

\( B_{2g} \) species

\[ \begin{align*}
S_6 &= \frac{1}{2} (\theta_1 + \theta_2 - \theta_3 - \theta_4)
\end{align*} \]

\( B_{1u} \) species

\[ \begin{align*}
S_7 &= \frac{1}{2} (\theta_1 - \theta_2 - \theta_3 + \theta_4)
\end{align*} \]

\( B_{2u} \) species

\[ \begin{align*}
S_8 &= \frac{1}{2} (d_1 + d_3 - d_6 - d_8) \\
S_9 &= \frac{1}{2} (\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4)
\end{align*} \]
\( \text{B}_{3u} \) species

\[
S_{10} = \frac{1}{2} (d_1 - d_3 + d_5 - d_8)
\]

\[
S_{11} = \frac{1}{2} (\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)
\]

D and d are respectively the B - B and B - F distances and \( \alpha \) is the F - B - F angles. \( \gamma \) is the BF\textsubscript{2} rocking coordinate, \( \theta \) is the out of plane wagging angle involved in the vibration and is shown in Figure 3.1 (b).

The \( B_{op} \) matrix is constructed by considering all the internal coordinates within the Bravais cell, as the symmetry operations are contained in the bimolecular Bravais cell. The elements of the \( B_{op} \) matrix are given in Table 3.1. In calculating the potential energy matrix \( F_{op} \), a general valence force field has been used and all the intramolecular interactions have been taken into account. As the crystal being molecular the intermolecular interactions are expected to be extremely weak and therefore, they are not considered.

Using equation (3.17) the expressions for the \( F_{op} \) elements are derived. The structural parameters used in the calculation are from Wyckoff\textsuperscript{13}. The simplified expressions for the \( F_{op} \) elements in terms of the valence force constants are
\[ F_{11} = f_D + f_{DD} \quad (3.18) \]

\[ F_{22} = 0.43 (f_d + f_{dd}) - 0.86 f_{dd} - 0.55 f_{d\alpha} \\
+ 3.87 f_{d\alpha} + 0.88 (f_\alpha + f_{\alpha\alpha}) \quad (3.19) \]

\[ F_{23} = 0.15 (f_d + f_{dd}) + 1.5 f_{dd} + 0.66 f_{d\alpha} \\
- 0.66 f_{d\alpha} + 1.9 (f_\alpha + f_{d\alpha}) \quad (3.20) \]

\[ F_{33} = 0.10 (f_d + f_{dd}) - 0.63 f_{d\alpha} \\
- 0.08 f_{d\alpha} + 0.76 f_\alpha \quad (3.21) \]

\[ F_{44} = 0.88 (f_d + f_{dd}) + 1.27 f_{dd} + 1.76 f_{d\gamma} \\
+ 1.04 f_{d\gamma} + 1.10 (f_\gamma + f_{\gamma\gamma}) \quad (3.22) \]

\[ F_{45} = 0.69 f_{d\gamma} + 0.42 f_{d\gamma} + 0.16 (f_\gamma + f_{\gamma\gamma}) \quad (3.23) \]

\[ F_{55} = -0.13 f_{d\gamma} + 0.29 f_\gamma - 0.14 f_{\gamma\gamma} \quad (3.24) \]

\[ F_{66} = f_\theta + f_{\theta\theta} \quad (3.25) \]

\[ F_{77} = f_\theta - f_{\theta\theta} \quad (3.26) \]

\[ F_{88} = (f_d + f_{dd}) - 1.47 f_{dd} + 0.1 f_{d\gamma} \\
+ 0.17 f_{d\gamma} + 0.61 (f_\gamma + f_{\gamma\gamma}) \quad (3.27) \]
\[ F_{89} = -0.43 (f_d + f_{dd}) + 0.87 f_{dd} - 0.76 f_d\gamma - 0.15 f_d\gamma + 0.91 (f_\gamma + f_{\gamma\gamma}) \tag{3.28} \]

\[ F_{99} = 0.15 (f_d - f_{dd}) + 0.52 f_d\gamma + 0.10 f_d\gamma + 0.29 f_\gamma - 0.14 f_{\gamma\gamma} \tag{3.29} \]

\[ F_{10,10} = 0.75 (f_d + f_{dd}) - 1.19 f_{dd} - 0.67 f_d\alpha + 0.68 f_d\alpha + 0.57 f_\alpha - 0.57 f_{\alpha\alpha} \tag{3.30} \]

\[ F_{10,11} = 0.12 (f_d + f_{dd}) - 0.66 f_d\alpha - 0.21 f_d\alpha + 0.29 (f_\alpha - f_{\alpha\alpha}) \tag{3.31} \]

\[ F_{11,11} = 0.18 f_d + 0.5 f_{dd} - 1.31 f_d\alpha + 0.29 f_\alpha \tag{3.32} \]

In fixing the values of the elements using the parametric approach outlined in section 3.2, the three A vibrations are split into 1 A (\(B - B\) stretch) and 2 A using Wilson's method. The frequencies of separation of high and low frequencies. The frequencies used in the calculation of \(F_{op}^2\) elements are given in Table 3.2. In the table some of the unobserved frequencies of \(11_{B_{op}}^{10}B\) are the calculated ones by the method of Ananthakrishnan and Aruldas. This method, found to be very good in the case of molecules, has been used here as \(B_{2}F_{4}\) being a molecular crystal. The value of the \(F_{op}^2\) elements evaluated are reproduced in Table 3.3 along with the value of parameter \(c^2\) for each species.
The interaction term $F_{ij} = 0$ (Section 1.2). Substituting the numerical values obtained from equations (3.14) and (3.15) and the result $F_{ij} = 0$ in equations (3.18) to (3.32) corresponding to each species, the valence force constants are evaluated.

3.4 RESULTS AND DISCUSSION

Table 3.4 contains the valence force constants calculated by the method outlined here. The value of $5.70 \text{ m. dynes/Å}$ obtained for the $B - F$ stretching force constant by this method is in complete agreement with the value $5.72 \text{ m. dynes/Å}$ obtained by Green's function analysis\(^6\) of the infrared active species. Ramaswamy, Swaminathan and Shanmugham\(^\text{16}\) obtained a value of $5.52 \text{ m. dynes/Å}$ for the molecule. The $B - B$ stretching force constant $f_D$ has a value of $6.39 \text{ m. dynes/Å}$ and this has a value of $6.67 \text{ m. dynes/Å}$ in the case of the molecule\(^\text{16}\). It can be seen from these values that the principal stretching force constants $f_D$ and $f_d$ remain practically the same when $B_2 F_4$ goes from molecule to crystal.

The $F - B - F$ angle deformation force constant $f_\alpha$ has a value of $0.46 \text{ m. dynes/Å}$. The rocking force constant $f_\gamma$ is $0.31 \text{ m. dynes/Å}$. The value obtained for the wagging force constant $f_\delta$ is $0.34 \text{ m. dynes/Å}$. All these values agree with the corresponding values for the molecule obtained by Ramaswamy et al\(^\text{16}\).
The high value for the constant $f_{dd}$ (0.68 m. dynes/A) indicates fairly strong interaction between the two B–F bonds attached to the same boron atom. The interaction between B–F bonds attached to two different boron atoms within the molecule is also not negligible as the $f_{dd}$ value for the crystal is found to be 0.34 m. dynes/A.

The valence force constants obtained for the crystal indicate that diboron tetrafluoride retains its molecular nature in the crystal.
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<td>$-\frac{1}{R}$</td>
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<td>$-\frac{1}{2d}$</td>
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<td>$-E$</td>
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<td>$\frac{1}{R}$</td>
<td>$\sqrt{3}$</td>
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<td>0</td>
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<td>0</td>
<td>$-C$</td>
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<td>$-C$</td>
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<td>$-C$</td>
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<td>$\frac{1}{d}$</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

$A = \cos \beta$ \quad $B = \sin \beta$ \quad $C = \left(\frac{1}{D} + \frac{2}{d}\right)$ \quad $E = \frac{R + 2d}{2Rd}$
**TABLE 3.2**

OPTICALLY ACTIVE INTERNAL VIBRATIONAL FREQUENCIES OF DIBORON TETRAFLUORIDE CRYSTAL

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequencies (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11(_B) 11(_BF_4)(^{(a)})</td>
<td>11(_B) 10(_BF_4)(^{(b)})</td>
</tr>
<tr>
<td>(A_g)</td>
<td>1404</td>
<td>1430</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>694.5*</td>
</tr>
<tr>
<td></td>
<td>319</td>
<td>329.0*</td>
</tr>
<tr>
<td>(B_{1g})</td>
<td>1308</td>
<td>1348.0*</td>
</tr>
<tr>
<td></td>
<td>326</td>
<td>330.0*</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>392</td>
<td>...</td>
</tr>
<tr>
<td>(B_{1u})</td>
<td>646</td>
<td>688</td>
</tr>
<tr>
<td>(B_{2u})</td>
<td>1332</td>
<td>1353</td>
</tr>
<tr>
<td></td>
<td>154</td>
<td>164*</td>
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<tr>
<td>(B_{3u})</td>
<td>1138</td>
<td>1155</td>
</tr>
<tr>
<td></td>
<td>537</td>
<td>542</td>
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</table>

(a) All frequencies are from ref. 12
(b) The infrared frequencies are from ref. 1
* These frequencies are calculated by the method outlined in ref. 15.
<table>
<thead>
<tr>
<th>Species</th>
<th>Parameter $c^2$</th>
<th>Symmetrised force constants</th>
<th>Values in m. dynes/Å</th>
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</thead>
<tbody>
<tr>
<td>$A_g$</td>
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<td>$F_{11}$</td>
<td>6.39</td>
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<td></td>
<td>0.2232</td>
<td>$F_{22}$</td>
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<td>$F_{33}$</td>
<td>0.76</td>
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<tr>
<td>$B_{1g}$</td>
<td>0.0475</td>
<td>$F_{44}$</td>
<td>0.67</td>
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<td></td>
<td></td>
<td>$F_{55}$</td>
<td>0.35</td>
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<tr>
<td>$B_{2g}$</td>
<td></td>
<td>$F_{66}$</td>
<td>0.18</td>
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<tr>
<td>$B_{1u}$</td>
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<td>$F_{77}$</td>
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<tr>
<td>$B_{2u}$</td>
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<td>$F_{88}$</td>
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<tr>
<td></td>
<td></td>
<td>$F_{99}$</td>
<td>0.19</td>
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<tr>
<td>$B_{3u}$</td>
<td>0.0864</td>
<td>$F_{10,10}$</td>
<td>5.30</td>
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<tr>
<td></td>
<td></td>
<td>$F_{11,11}$</td>
<td>0.16</td>
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</table>
TABLE 3.4
VALENCE FORCE CONSTANTS OF DIBORON TETRAFLUORIDE CRYSTAL

<table>
<thead>
<tr>
<th>Valence force constants</th>
<th>Values in m. dynes/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>f_D</td>
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<tr>
<td>f_δ</td>
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<tr>
<td>f_δδ</td>
<td>0.68</td>
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<tr>
<td>f_δδδ</td>
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<td>f_δκκ</td>
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<tr>
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<tr>
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<td>0.04</td>
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<tr>
<td>f_κκκκκκκκ</td>
<td>0.34</td>
</tr>
<tr>
<td>f_κκκκκκκκκ</td>
<td>-0.16</td>
</tr>
</tbody>
</table>
Figure 3.1

a) **BRAVAIS CELL OF $B_2F_4$ CRYSTAL**

- $\bigcirc$ .... Boron atom
- $\bullet$ .... Fluorine atom
- $D$ .... $B-B$ distance
- $d$ .... $B-F$ distance
- $\alpha$ .... $F-B-F$ angle

b) **OUT OF PLANE WAGGING ANGLE**

$\theta$ .... The angle between $B-B$ bond and $BF_2$ group.
REFERENCES


3. A. Finch, J. Hyamas and D. Settelle, Spectrochimica Acta, 21A 1423 (1965)


