CHAPTER-V
CHANGES IN FORCE CONSTANTS OF CHROMATE IN VARIOUS LATTICES

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5.7. REFERENCES.
5.1. INTRODUCTION:

The normal modes of vibration of a molecule of the type \( XY_4 \) having tetrahedral symmetry and their activity in IR and Raman spectrum has been investigated by many workers \([1-12]\).

Out of nine independent modes of vibrations of which one is totally symmetrical, single another is doubly degenerate and two others are triply degenerate. That is to say there are only four distinct normal frequencies of vibration of the molecule. However, depending on the reduction in symmetry of the molecule one can observe split components of these degenerate modes.

The frequency of the normal vibration is determined by kinetic and potential energies of molecules. The kinetic energy is determined by masses of individual atoms and their geometric arrangements, while the potential energy arises from interaction between the individual atoms and is described by individual force constants. As the potential energy provides valuable information about the nature of interatomic forces, it is desirable to obtain force constant from the observed frequencies. To calculate normal mode frequencies in case of
polyatomic molecules it becomes absolutely necessary to employ simple models. In order to test these various model force fields it is customary to carry out normal coordinate calculations in which the force field is constrained to fit the model under trial. The test is considered satisfactory if the following are found to apply.

1. With appropriate values of parameters in the model it is possible to fit all observable data.

2. The values of the parameters are characteristic of chemical group to which they refer, and are transferable from one molecule to another.

3. The values of the parameters are at least reasonably consistent with any theoretical expectations that may be implied by the model.

However, it is rather difficult to find a single model which could incorporate all these tests. It becomes therefore necessary to choose a simple model and see how best it can account for the various observations. There are many models suggested starting from a single valence force field (SVVF) model to a most general valence force field (GVVF) model. It
would be difficult to discuss these models in detail, and therefore potential functions used in these models are given along with the assumptions made therein.

A method for calculations of force constants for free \( \text{CrO}^{2-}_4 \) ion has been given, briefly, by employing Wilson's FG matrix method [3]. The structure of the tetrahedral \( \text{XY}_4 \) type ion (molecule) is displayed in Fig.5.1. This type of ion having symmetry of a tetrahedron belongs to point group \( T_d \). The symmetry elements being:

1) An identity element \( E \),
2) Eight three fold axis of symmetry \( C_{3v} \),
3) Three two fold axis of symmetry \( C_{2v} \),
4) Six diagonal planes of symmetry \( \sigma_d \) and
5) Six four-fold rotation-reflection axis of symmetry \( S_4 \).

The character table for the \( T_d \) point group is given in Table 3.10 along with the normal modes of vibration of the \( \text{CrO}^{2-}_4 \) ion.
Fig. 5.
5.2. POTENTIAL ENERGY MODELS:

Initially Bjerrum used two simple potential models for the calculation of force constants namely central force field and simple valence force field (SVFF). In the former, an assumption is made that, the forces are acting only along the lines joining the atoms. Here non-bonded forces are considered and bending forces are neglected. This model is used to calculate force constants of molecules like purely ionic molecule, simple X-Y type molecule and linear X-Y-Z type of molecules. The potential function is given by [4]

\[ 2V = f_r \left( \sum r_1^2 \right) + f_r \left( \sum r_i \right) + f_q \left( \sum q_i^2 \right) + f_q \left( \sum q_i \right) \]  

where the \( q_i \) are the changes in distances between non-bonded atoms.

In the latter case (SVFF) direct stretch and direct bond forces are used while non-bonded forces are neglected. The potential function for \( XY_4 \) type molecule belonging to \( T_d \) symmetry is given by,
When the simple valence force (SVFF) or central force field is used as the potential function, the vibration frequencies of polyatomic molecules often cannot be calculated satisfactorily \[4\]. In such cases Urey and Bradly \[5\] combined both the fields mentioned above. This improved UBFF model contains both force constants related to changes in the distances between non-bonded atoms and force constants associated with changes in bond lengths and bond angles. The UBFF model includes both linear and quadratic terms. The UBFF type of potential function for the \(XY_4(T_d)\) type molecule is expressed as

\[
V = 2V = f_r \left( \sum r_i^2 \right) + f_\alpha \left( \sum \alpha_i^2 \right) \tag{5.2}
\]

where \(f_r\) and \(f_\alpha\) are stretching and bending force constants respectively, \(r_i\) and \(\alpha_i\) being bond lengths and bond angles.

\[
V = \sum_{i=1}^{4} \left[ K'_i r_i \Delta r_i + \frac{1}{2} K_i (\Delta r_i)^2 \right] + \sum_{i<j} \left[ H'_{ij} r_{ij}^2 \Delta \alpha_{ij} \right] + \frac{1}{2} H_{ij} (r_{ij} \Delta \alpha_{ij})^2 + \sum_{i<j} [F'_{ij} q_{ij} \Delta q_{ij}] + \frac{1}{2} F_{ij} (\Delta q_{ij})^2 \tag{5.3}
\]
where \( r_0 \)'s are the equilibrium bond lengths, \( \alpha \)'s the equilibrium bend angles, \( q \)'s the equilibrium distances between atoms not-bonded directly, \( r \)'s bond lengths (X-Y), and \( r_{ij} \) represents \((r_i, r_j)^{1/2}\). \( K', K, H, H' \) are force constants, between the bounded atoms, while \( F' \) and \( F \) are the force constants between the non bonded atoms.

As the complexity of molecule increases the model is further improved by taking care of other forces like atomic non-coplanar repulsion, angle-angle, non-bonded bond and angle interactions. Force constants have significance only with respect to the potential field in which they appear. The SVFF was further improved by including the force constants like bending interactions between angle coordinates with and without a common side \( f_{aa} \) and \( f_{aa'} \), respectively, stretch bend interactions \( f_{r\alpha} \) and \( f_{r\alpha'} \), where the bond specified by the stretching coordinate is, or is not, a side of the angle specified by the bending coordinate, and is referred to as Generalised valance force field (GVFF).

The potential energy function for a \( XY_4 \) \((T_d)\) type molecule is given by,
\[ 2V = f_r \left( \sum r_i^2 \right) + d^2 f_{\alpha} \left( \sum \alpha_i^2 \right) + 2f_{rr} \left( \sum r_{ij} \right) + \]

\[ 2d^2 f_{\alpha\alpha} \left( \sum \alpha_i \right) + 2d^2 f_{\alpha\alpha'} \left( \sum \alpha'_i \right) + \]

\[ 2df_{r\alpha} \left( \sum r_{ij} \alpha_j \right) + 2df_{r\alpha'} \left( \sum r_{ij} \alpha'_j \right). \tag{5.4} \]

In majority of cases, the force constant determination using GVFF method seems to be satisfactory as it uses generalised coordinates. So in the present case GVFF model is used as potential function to calculate force constants. Potential function (5.4) in terms of f matrix is given in (Table 5.1).

5.3.1. INTERNAL CO-ORDINATES:

The set of coordinates which describe the internal configuration of the molecule without regard to its position as a whole in space are called as internal coordinates. They being changes in inter atomic distances and angles between chemical bonds. These coordinates are unaffected by translations or rotations of a molecule as a whole. These are most physically significant set in describing the potential
Table 5.1 The $f$ matrix.

<table>
<thead>
<tr>
<th></th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_4$</th>
<th>$r_4$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$a_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>$f_r$</td>
<td>$f_{rr}$</td>
<td>$f_{rr}$</td>
<td>$d_{f} a'$</td>
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<tr>
<td>$r_2$</td>
<td>$f_r$</td>
<td>$f_{rr}$</td>
<td>$f_{rr}$</td>
<td>$d_{f} a$</td>
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<tr>
<td>$r_3$</td>
<td>$f_r$</td>
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<td>$d_{f} a$</td>
<td>$d_{f} a'$</td>
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<tr>
<td>$r_4$</td>
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<tr>
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<td>$\alpha_2$</td>
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<td>$\alpha_3$</td>
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<tr>
<td>$\alpha_5$</td>
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<tr>
<td>$\alpha_6$</td>
<td>$d_{f}^2 a$</td>
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</table>
energy of a molecule. Referring to Fig. 5.1a internal coordinates for the $XY_4$ type molecule with $T_d$ symmetry are listed below:

$$XY_1 = r_1, \quad XY_2 = r_2, \quad XY_3 = r_3, \quad XY_4 = r_4$$

$$Y_2XY_3 = \alpha_1, \quad Y_3XY_4 = \alpha_2, \quad Y_4XY_1 = \alpha_3, \quad Y_1XY_2 = \alpha_4$$

$$Y_1XY_2 = \alpha_5, \quad Y_2XY_4 = \alpha_6, \quad Y_3XY_1 = \alpha_6$$

5.3.2. SYMMETRY CO-ORDINATES:

The kinetic energy is more easily expressed in terms of cartesian displacement of the atoms. The amplitudes of vibration are infinitesimal and all displacements are also infinitesimal. So by considering only first-order or linear terms, final expression gets simplified considerably. Displacements of atoms are described by vectors, which are the symmetry coordinates.

There are several types of symmetry coordinates. Out of them linear combination of internal coordinates i.e., changes in interatomic distances and angles within the molecule are considered in the present case. In internal symmetry coordinates, there are two kinds. First kind includes
changes in interatomic distances and simple bond angles, while the second includes the angle between a bond and plane initially containing bond and angle between two planes.

Internal symmetry coordinates for $X_4$ type ion with $T_d$ symmetry are listed below:

1. $S_1(A_1) = \frac{1}{2} (r_1 + r_2 + r_3 + r_4)$  
   **Stretching Coordinate**

2. \[
\begin{align*}
S_{2a}(E) &= (12)^{-1/2}(2\alpha_1 - \alpha_2 + 2\alpha_3 - \alpha_4 - \alpha_5 - \alpha_6) \\
S_{2b}(E) &= (1/2)(\alpha_2 + \alpha_4 - \alpha_5 - \alpha_6)
\end{align*}
\]
   **Bending Coordinates**

3. \[
\begin{align*}
S_{3a} &= (1/2) (r_1 + r_2 - r_3 - r_4) \\
S_{3b} &= (1/2) (r_1 - r_2 + r_3 - r_4) \\
S_{3c} &= (1/2) (r_1 - r_2 - r_3 + r_4)
\end{align*}
\]
   **Stretching coordinate**

4. \[
\begin{align*}
S_{4a} &= 2^{-1/2}(\alpha_4 - \alpha_2) \\
S_{4b} &= 2^{-1/2}(\alpha_6 - \alpha_5) \\
S_{4c} &= 2^{-1/2}(\alpha_3 - \alpha_1)
\end{align*}
\]
   **Bending coordinate**
5.4.1. G-MATRIX:

The elements of g matrix are obtained by the relation 
\[ g = S M^{-1} S' \] and the elements of G matrix are obtained from 
the relation \[ G = U g U' \] and are listed below.

\[ G_{11} (A_1) = \mu_y \]

\[ G_{22} (E) = 3\mu_y \rho^2 \]

\[
\begin{bmatrix}
G_{33} & G_{34} \\
G_{43} & G_{44}
\end{bmatrix}
= 
\begin{bmatrix}
\mu_y + (4/3)\mu_x & (-8/3)\rho \mu_x \\
(-8/3)\rho \mu_x & \rho^2 (2\mu_y + (16/3)\mu_x)
\end{bmatrix}
\]

Where \( \mu_x, \mu_y \) are the reciprocal masses of the atoms X and Y respectively and \( \rho = 1/r \)

Isotopic masses of Cr are 50, 51, 52, 53, 54 AMU

Isotopic masses of O are 16, 17, 18 AMU

In the present case most abundant atoms of Cr and O are considered.

\( M_o = 16 \) AMU and \( M_{cr} = 52 \) AMU
5.4.2 F-MATRIX:

The symmetrised F matrix elements have been obtained using the relation $F = U f U'$. The simplified forms of F matrix elements [4] are:

i. $F_{11}(A_1) = f_r + 3f_{rr}$

ii. $F_{22}(E) = d^2(f_\alpha + f_{\alpha\alpha'}) - 2f_{\alpha\alpha}$

iii. $\begin{bmatrix} F_{33} & F_{34} \\ F_{43} & F_{44} \end{bmatrix} = \begin{bmatrix} f_r - f_{rr} & (\frac{1}{2})d(f_{r\alpha} - f_{r\alpha'}) \\ (\frac{1}{2})d(f_{r\alpha} - f_{r\alpha'}) & 2d(f_{\alpha\alpha} - f_{\alpha\alpha'}) \end{bmatrix}$

From F and G matrices secular equation is set up

$|FG - \lambda| = 0$

Secular equations for the three types of vibrations are,

for $A_1$ type, $\lambda_1(A_1) = F_{11}G_{11} = 0$

for $E$ type, $\lambda_2(E) - F_{22}G_{22} = 0$
and for $T_2$ type,

$$
\begin{bmatrix}
F_{33}G_{33} - \lambda & F_{34}G_{34} \\
F_{43}G_{43} & F_{44}G_{44} - \lambda
\end{bmatrix} = 0
$$

Expanding the secular determinant, we have

$$
\left\{ \lambda^2 - (F_{33}G_{33} + 2F_{34}G_{34} + F_{44}G_{44})\lambda + F_{33}F_{44}G_{33}G_{44} + F_{34}^2G_{34}^2 - F_{33}F_{44}G_{33}^2 - F_{44}^2G_{34}^2 \right\} = 0
$$

Substituting the proper values of the wavenumbers and masses in the above, one can obtain the force constants of the ion.

5.5. CHANGES IN FORCE CONSTANTS FOR XY TYPE MOLECULE DUE TO LOWERING OF SYMMETRY FROM $T_d$ TO $C_{2v}$:

The IR spectra of $\text{CrO}_4^{2-}$ ion in alkali halide crystal have been analysed by Jain, Warriar and Agarwal [11], where in they add $\text{Ca}^{2+}$ as an additional divalent cationic impurity. The position of the divalent cation $\text{Ca}^{2+}$ decides the symmetry of...
When $T_d$ (XY$_4$) is distorted to $C_{2v}$, the total symmetric stretching vibration, forbidden in the IR spectrum in the $T_d$ group, becomes active and the triply degenerate stretching vibration $\nu_3^o(T_2)$ splits into three components belonging to $A_1$, $B_1$, and $B_2$ symmetry modes respectively.

Correlation of symmetries of $T_d$ with $C_{2v}$ and description of normal modes of XY$_4$ type ion.

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1^o$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$\nu_2^o$</td>
<td>$E$</td>
</tr>
<tr>
<td>$\nu_3^o, \nu_4^o$</td>
<td>$T_2$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The individual components of $\nu_3$ (X-O stretching modes) have been identified through a perturbation calculation [10-12] which neglects interaction with the lower-frequency bending modes, $\nu_2$ and $\nu_4$. The assumption is made that for the $C_{2v}$ model, two of the bonds (those nearest $M^{2+}$) suffer a decrease in force constant by an amount $-\Delta f_1$, while the remaining two bonds enjoy an increase in force constant by an amount $+\Delta f_2$.

One can express the symmetry coordinates of $T_d$ ($XY_4$) in various ways because of the degeneracy, for the present purpose

\[ S_1(a_1) = (1/2)(r_1 + r_2 + r_3 + r_4) \]

\[ S_2(a_1) = (1/2)(r_1 + r_2 - r_3 - r_4) \]

\[ S_3(b_1) = (1/\sqrt{2})(r_1 - r_2) \]

\[ S_3(b_2) = (1/\sqrt{2})(r_3 - r_4) \]

One may express the G matrix for the stretching modes in terms of these coordinates; on the assumption that the geometry of the tetrahedral molecular ion is not sufficiently
distorted from its $T_d$ symmetry, one finds

$$G = \begin{bmatrix} G_{11} & 0 & 0 & 0 \\ 0 & G_{33} & 0 & 0 \\ 0 & 0 & G_{33} & 0 \\ 0 & 0 & 0 & G_{33} \end{bmatrix}$$

where $G_{11} = \mu_y$ and $G_{33} = \mu_y + (4/3)\mu_x$.

The $F$ matrix is then expressed in terms of its unperturbed part, $F^0$, plus a correction $F'$ in which $F'_{11} = F'_{22} = -\Delta f$ and $F'_{33} = F'_{44} = \Delta f'$ where the indices refer to the four bonds as defined above.

$$U = \begin{bmatrix} 1/2 & 1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & -1/2 & -1/2 \\ 1/4 & -1/4 & 0 & 0 \\ 0 & 0 & 1/4 & -1/4 \end{bmatrix} \quad U' = \begin{bmatrix} 1/2 & 1/2 & 1/4 & 0 \\ 1/2 & 1/2 & -1/4 & 0 \\ 1/2 & -1/2 & 0 & 1/4 \\ 1/2 & -1/2 & 0 & -1/4 \end{bmatrix}$$

$$F = \begin{bmatrix} f_r - \Delta f_1 & f_{rr} & f_{rr} & f_{rr} \\ f_{rr} & f_r - \Delta f_1 & f_{rr} & f_{rr} \\ f_{rr} & f_{rr} & f_r + \Delta f_2 & f_{rr} \\ f_{rr} & f_{rr} & f_{rr} & f_r + \Delta f_2 \end{bmatrix}$$
Upon transformation to the symmetry coordinates, the $F$ matrix gets factored according to symmetry

$$
F' = \begin{bmatrix}
(1/2)(f_{r}-f_{1}+3f_{rr}) & (1/2)(f_{r}-f_{1}-f_{rr}) & (1/2)(f_{r}-f_{1}-f_{rr}) & 0 \\
(1/2)(f_{r}-f_{1}-3f_{rr}) & (1/2)(f_{r}-f_{1}-f_{rr}) & (1/2)(f_{r}-f_{1}-f_{rr}) & 0 \\
(1/2)(f_{r}+f_{2}+3f_{rr}) & (1/2)(f_{rr}-f_{r}-f_{2}) & 0 & (1/2)(f_{r}+f_{2}-f_{rr}) \\
(1/2)(f_{r}+f_{2}+3f_{rr}) & (1/2)(f_{rr}-f_{r}-f_{2}) & 0 & (1/2)(f_{r}+f_{2}-f_{rr}) \\
\end{bmatrix}
$$

$$
U F U' = \begin{bmatrix}
f_r + 3f_{rr} - (\Delta f_1 - \Delta f_2)/2 & - (\Delta f_1 + \Delta f_2) & 0 & 0 \\
-(\Delta f_1 + \Delta f_2)/2 & f_r - f_{rr} - (\Delta f_1 - \Delta f_2)/2 & 0 & 0 \\
0 & 0 & (f_r - f_{rr} - \Delta f_1) & 0 \\
0 & 0 & 0 & (f_r - f_{rr} - \Delta f_2) \\
\end{bmatrix}
$$

in which the abbreviations are $\varepsilon = (-\Delta f + \Delta f')/2$ and $\eta = -(\Delta f + \Delta f')/2$. By solving the secular determinant given below and by
using the relation $\lambda = 4\pi^2 c^2 \nu^2$ one can determine the values of $\lambda$.

$$\begin{bmatrix} G_1(F_1+\varepsilon) - \lambda & G_1\eta & 0 & 0 \\ G_3\eta & G_3(F_3+\varepsilon) - \lambda & 0 & 0 \\ 0 & 0 & G_3(F_3-\Delta f) - \lambda & 0 \\ 0 & 0 & 0 & G_3(F_3+\Delta f') - \lambda \end{bmatrix} = 0$$

$A_1$: 

$$\begin{bmatrix} \lambda_1 + G_1\varepsilon - \lambda & G_1\eta \\ G_3\eta & \lambda_3 + G_3\varepsilon - \lambda \end{bmatrix} = 0$$

$B_1$: $\lambda_3 - G_3\Delta f = \lambda_3(b_1)$

$B_2$: $\lambda_3 + G_3\Delta f' = \lambda_3(b_2)$

The two roots of the $A_1$ factors are $\lambda_1(a_1)$ and $\lambda_3(a_1)$.

5.6. CHANGES IN FORCE CONSTANTS $XY_4$ TYPE MOLECULE DUE TO LOWERING OF SYMMETRY FROM $T_d$ TO $C_s$:

When $T_d(XY_4)$ is perturbed to $C_s$ symmetry, the totally symmetric mode $\nu_1(A')$ becomes IR active [1-4]. In case of
triply degenerate mode $\nu_3$ splits into three ($2A'+A''$) components.

Correlation of symmetries of $T_d$ with $C_s$ and description of normal modes of $XY_4$ ion.

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$C_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1^0$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$\nu_2^0$</td>
<td>$E$</td>
</tr>
<tr>
<td>$\nu_3^0, \nu_4^0$</td>
<td>$T_2$</td>
</tr>
</tbody>
</table>

2$\nu_4(A')$ and $\nu_4(A'')$

The nature and extent of splitting of the $\nu_3$ mode of $XY_4$ ion in $C_s$ symmetry can be determined by a perturbation calculation [11]. In the $C_s$ symmetry, two of $X$-$Y$ bonds symmetrically situated with respect to the mirror plane experience equal increase $\Delta f$ in the force constants.
The force constant of the expanded bond decreases by $\Delta f_1$ and that of contracted bond increases by $\Delta f_2$. The force constant matrix becomes

$$
F = \begin{pmatrix}
  f_r - \Delta f_1 & f_{rr} & f_{rr} & f_{rr} \\
  f_{rr} & f_r + \Delta f_2 & f_{rr} & f_{rr} \\
  f_{rr} & f_{rr} & f_r + \Delta f & f_{rr} \\
  f_{rr} & f_{rr} & f_{rr} & f_r + \Delta f
\end{pmatrix}
$$

Where $f_r$ is the unperturbed X-Y stretching force constant and the interaction force constant between the neighbouring X-Y bonds. The $G$ and $F$ matrices by the transformation becomes $UGU'$ and $UFU'$ by using symmetry coordinates of matrix $U$ and are given below:

$$
U = \begin{pmatrix}
  1/2 & 1/2 & 1/2 & 1/2 \\
  -1/2 & -1/2 & 1/2 & 1/2 \\
  1/4 & -1/4 & 0 & 0 \\
  0 & 0 & 1/2 & -1/4
\end{pmatrix}, \quad U' = \begin{pmatrix}
  1/2 & -1/2 & 1/4 & 2 & 0 \\
  1/2 & -1/2 & -1/2 & 0 \\
  1/2 & 1/2 & 0 & 1/2 \\
  1/2 & 1/2 & 0 & -1/4
\end{pmatrix}
$$

$$
FU' = \begin{pmatrix}
  (1/2)(f_r - \Delta f_1 + 3f_{rr}) & (1/2)(f_{rr} - f_r + \Delta f_2) & (1/4)(f_r - \Delta f_1 - f_{rr}) & 0 \\
  (1/2)(f_r + \Delta f_2 + 3f_{rr}) & (1/2)(f_{rr} - f_r - \Delta f_2) & (1/4)(f_r - \Delta f_2 - f_{rr}) & 0 \\
  (1/2)(f_r + \Delta f + 3f_{rr}) & (1/2)(f_r + \Delta f - f_{rr}) & 0 & (1/4)(f_r + \Delta f - f_{rr}) \\
  (1/2)(f_r + \Delta f + 3f_{rr}) & (1/2)(f_r + \Delta f - f_{rr}) & 0 & (1/4)(f_r + \Delta f - \Delta f_1)
\end{pmatrix}
$$
\[
UFU' = \begin{pmatrix}
(1/4)(4f_r + 12f_{rr} - \Delta f_1 - \Delta f_2 + 2\Delta f) & (1/4)(\Delta f_1 + \Delta f_2 - 2\Delta f) \\
(1/4)(\Delta f_1 + \Delta f_2 + 2\Delta f) & (1/4)(4f_r - 4f_{rr} - \Delta f_1 + \Delta f_2 + 2\Delta f) \\
(1/2)(-\Delta f_1 - 2\Delta f_2) & (1/2)(\Delta f_1 + \Delta f_2) \\
0 & 0 \\
(1/2)(-\Delta f_1 - \Delta f_2) & 0 \\
(1/2)(\Delta f_1 - \Delta f_2) & 0 \\
(1/2)(2f_{rr} - 2f_{r} - \Delta f_1 + \Delta f_2) & 0 \\
0 & (1/2)(2f_{rr} - 2f_{r} + 2\Delta f)
\end{pmatrix}
\]

\[
F = \begin{pmatrix}
(F_{11} - \eta) & (\eta + \Delta f) & -\phi & 0 \\
(\eta + \Delta f) & (F_{33} - \eta) & \phi & 0 \\
-\phi & \phi & (F_{33} - \epsilon) & 0 \\
0 & 0 & 0 & (F_{33} + \Delta f)
\end{pmatrix}
\]

Here, \(\eta = (\Delta f_1 - \Delta f_2 - 2\Delta f)/4\), \(\epsilon = (\Delta f_1 - \Delta f_2)/2\) and \(\phi = (\Delta f_1 + \Delta f_2)/2\) as defined by Jain, Warrier and Agarwal [11].
\begin{align*}
G_{11} &= 1/\mu_y - \mu_y \quad \text{and} \quad G_{33} = \mu_y + 4/3\mu_x \\
\eta &= (\Delta f_1 - \Delta f_2 - 2\Delta f)/4 \\
\epsilon &= (\Delta f_1 - \Delta f_2)/2 \\
\eta &= (\Delta f_1 + \Delta f_2)/2 \\
G &= \begin{pmatrix}
G_{11} & 0 & 0 & 0 \\
0 & G_{33} & 0 & 0 \\
0 & 0 & G_{33} & 0 \\
0 & 0 & 0 & G_{33}
\end{pmatrix}
\end{align*}

The secular equation becomes

\begin{align*}
&\begin{pmatrix}
(\lambda^0_1 + \eta G_{11} - \lambda) & - (\eta - \Delta f) G_{11} & \phi G & 0 \\
- (\eta - \Delta f) G_{33} & (\lambda^0_3 + \eta G_{33} - \lambda) & - \phi G_{33} & 0 \\
\phi G_{33} & - \phi G_{33} & (\lambda^0_3 + \epsilon G_{33} - \lambda) & 0 \\
0 & 0 & 0 & (\lambda^0_3 + \epsilon G_{33} - \lambda)
\end{pmatrix} = 0
\end{align*}
and $\lambda^0_{3+} \Delta f G_{33} - \lambda_3(A''') = 0$

The three roots of the A factor are $\lambda_1(A')$, $\lambda_3(A')$, $\lambda_3(A')$.

As mentioned chapter in III, the IR spectra of chromate has been analysed assuming $C_s$, $C_{2v}$ and $T_d$ species of $CrO_4^{2-}$ in alkali halide crystals.

1. when only chromate is present the spectrum is analysed in terms of $C_s$ and $T_d$ symmetry species,

2. IR spectrum of crystals in case of crystals containing $CrO_4^{2-}$ with excess divalent cations ($M^{2+}$) has been analysed assuming $C_{2v}$ symmetry, while

3. the crystals containing divalent cation concentration lower than the concentration of chromate ions give rise to $C_s$, $C_{2v}$, $C_{3v}$ and $T_d$ species (see Fig.5.1).

The position of divalent cation can be either on the face centered position or on the corner of a unit cell alkali halides. Because of crystallographically (energetically) equivalent positions of $Ca^{2+}$ with respect to the substituent $CrO_4^{2-}$ ion can lead to $C_{2v}$, $C_{3v}$ or $C_s$ symmetries. Hence, to explain the observed spectrum authors have conveniently chosen the symmetry. Therefore, the analysis of the spectrum
of chromate in alkali halides and determining the changes in
force constants still remain to be incomplete.

In the present case however, the symmetry of \( \text{CrO}_4^{2-} \) in
\( \text{K}_2\text{SO}_4 \) and \((\text{NH}_4)_2\text{SO}_4\) is decisively proved to be \( C_s \) and this
reduction in symmetry is brought about by the structure of the
host lattice. The changes in force constants have been
calculated using \( C_s \) symmetry.

\[
F = \begin{pmatrix}
  f_r + \Delta f_1 & f_{rr} & f_{rr} & f_{rr} \\
  f_{rr} & f_r + \Delta f_2 & f_{rr} & f_{rr} \\
  f_{rr} & f_{rr} & f_r + \Delta f & f_{rr} \\
  f_{rr} & f_{rr} & f_{rr} & f_r + \Delta f
\end{pmatrix}
\]

\[
 UFU' = \begin{pmatrix}
  (1/4)(4f_r + 12f_{rr} + \Delta f_1 + \Delta f_2 + 2\Delta f) & (1/4)(-\Delta f_1 - \Delta f_2 + 2\Delta f) \\
  (1/4)(-\Delta f_1 - \Delta f_2 + 2\Delta f) & (1/4)(4f_2 - 4f_{rr} + \Delta f_1 + \Delta f_2 + 2\Delta f) \\
  (1/2)(\Delta f_1 - \Delta f_2) & (1/2)(\Delta f_1 - \Delta f_2) \\
  0 & 0
\end{pmatrix}
\]

\[
 \begin{pmatrix}
  (1/2)(\Delta f_1 - \Delta f_2) \\
  - (1/2)(\Delta f_1 - \Delta f_2) \\
  (1/2)(2f_r - 2f_{rr} + \Delta f_1 + \Delta f_2) \\
  0
\end{pmatrix} = 0
\]

\[
 (1/2)(2f_r - 2f_{rr} + 2\Delta f)
\]
UFU' = \begin{bmatrix}
\lambda_1^0 + \frac{1}{4}(\Delta f_1 + \Delta f_2 + 2\Delta f)G_{11} - \lambda \\
\frac{1}{4}(-\Delta f_1 - \Delta f_2 + 2\Delta f)G_{33} \\
\frac{1}{242}(\Delta f_1 - \Delta f_2)G_{33} \\
0
\end{bmatrix} \\
\begin{bmatrix}
\lambda_3^0 + \frac{1}{4}(\Delta f_1 + \Delta f_2 + 2\Delta f)G_{33} - \lambda \\
\frac{1}{4}(-\Delta f_1 - \Delta f_2 + 2\Delta f)G_{11} \\
\frac{1}{242}(\Delta f_1 - \Delta f_2)G_{33} \\
0
\end{bmatrix} = 0

By solving the secular equation, we have obtained values of change in force constant and are given in Table 5.2 along with those reported by Jain and Warrier and Agarwal [11] and Dem'yanenko et al. [10].
As can be seen from this table the changes in force constants are in line with those reported earlier. However, the numerical values differ considerably. This is probably due to the fact that in the calculations in case of CrO$_4^{2-}$ in alkali halides, the increase or decrease in force constant has been incorporated in writing the F matrix itself. A general procedure should take care of this and has been used in the present case. In the present calculation however, the values of $\nu_1^0$ and $\nu_3^0$ i.e., the values of total symmetric mode and triply degenerate mode in the unperturbed state (i.e., before
splitting of $v_3^0$ are difficult to estimate as these are not observed in the spectrum. The present calculation therefore is incomplete in view of this. The unperturbed values of $v_1^0$ and $v_3^0$ are taken from the laser Raman spectra of $\text{CrO}_4^{2-}$ in $\text{K}_2\text{CrO}_4$ crystals [13].

The calculation of changes in force constant using perturbation theory can therefore be considered as a simple extension of Wilson's FG matrix calculation.
5.7. REFERENCES:


10. V.P. Dem'yanenko, Yu.P. Tsyashchenko, and E.M. Verlan, 

11. S.C. Jain, A.V.R. Warrier and S.K. Agrawal, 


(1971).