THE VIBRATIONAL SPECTRA

AND

THE NORMAL CO-ORDINATE ANALYSIS

OF

THIOCARBONYL HALIDES
THE VIBRATIONAL SPECTRA AND THE
NORMAL CO-ORDINATE ANALYSIS OF
THIOCARBONYL HALIDES

THESIS
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C. R. SUBRAMANIAM B.Sc., M. Sc.

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AUTHOR: C. R. Subramaniam

SUPERVISOR: Dr. D. C. Moule

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ABSTRACT: The infrared and the Raman spectra of CSF₂ has been obtained for the first time and has been analysed to give the in-plane normal vibrational frequencies of the molecule, in the ground state. A normal co-ordinate analysis has been carried out for the molecules CSF₂, CSClF and CSCl₂ using a Urey-Bradley type of potential function and the elements of the \([L]\) matrix elements, the distribution of the potential energy in Urey-Bradley space, and the displacement vector diagrams for the normal modes of vibration for these molecules, have been obtained.

The bond force constants obtained through the normal co-ordinate analysis, have given some interesting results. The stretching force constant, \(K_{CS}\), varies markedly with halogen substitution and the force constants \(K_{CF}\) and \(K_{CCl}\) also vary with substitution.
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CHAPTER I
INTRODUCTION

The study of the infrared and Raman spectra of a molecule enables one to determine the frequencies of the normal modes of vibrations and through a normal co-ordinate analysis, the bond force constants. This information helps one to understand the nature of the forces between the atoms in a molecule. Information about the excited electronic states of a molecule is obtained from an analysis of the electronic spectrum. Prior to the analysis of the electronic spectrum, it is usually necessary to have some information about the vibrational and rotational dynamics of the molecular ground state. Moreover, in order to obtain information about the geometry of the excited state from the vibronic band intensities through a Frank-Condon analysis, a knowledge of the elements of the $[L]$ matrix, which represents a transformation between the normal co-ordinates and the internal co-ordinates, is required.

The study of the vibrational spectrum of thiophosgene, CSCl$_2$ and its normal co-ordinate analysis have been carried out by many authors.(1-6) The electronic spectrum in absorption of thiophosgene has been analysed in considerable detail. (6) The infrared spectrum of thiocarbonyl fluoride has been recorded by Downs, the result of which was employed by Krishna Pillai and Ramaswamy (8) in a normal co-ordinate analysis.

In the present work, thiocarbonyl chloro-fluoride has been synthesised and its infrared and Raman spectra obtained for the first time and the vibrational bands assigned.

In order to carry out a normal co-ordinate analysis for CSClF, certain force constants were transferred from CSCl$_2$ and CSF$_2$. The potential field chosen was that of Urey-Bradley type. In the earlier work on CSF$_2$ by Pillai and Ramaswamy, an empirical valence force field was used which involved an
arbitrary transfer or estimate of the general valence force field constants. Again, data regarding the $[L]$ matrix and the potential energy distribution have not been reported. Hence, the normal co-ordinate analysis of CSF$_2$ was also carried out using the Urey-Bradley force field. In order to follow systematically the variation of the force constants with halogen substitution, the normal co-ordinate analysis of CSCl$_2$ was repeated using a similar procedure.

The normal co-ordinate analysis of CSClF was carried out and a set of Urey-Bradley force constants was obtained which gave a good agreement between the experimental and the calculated values. The potential energy distribution in the Urey-Bradley space has been calculated for all the three molecules and their normal modes expressed in terms of the mass-weighted cartesian displacement vectors.
CHAPTER II
EXPERIMENTAL

1. PREPARATION OF THIOCARBONYL CHLOROFLUORIDE

General methods for the preparation of fluoro thioketones, fluoro thioacyl halides and fluoro thioesters are described by Middleton, Howard and Sharkey. Methods are also described by which a chlorine atom of an acyl-chloride is exchanged for a fluorine atom by sodium fluoride. Thiocarbonyl fluoride, \( \text{CF}_2 = \text{S} \), has been prepared very conveniently by first converting thiophosgene, \( \text{CSCl}_2 \), into its dimer, fluorinating the dimer with antimony trifluoride, \( \text{SbF}_3 \), to give 2,2,4,4-tetra fluoro-1,3-dithietane, followed by pyrolysis at 475-500°C. In the fluorination step, small amounts of the chlorofluoro dithietane, \( \text{ClFC} = \text{S} \rightarrow \text{CF}_2 \), are formed which on pyrolysis at 450°C is cleaved to give a mixture of thiocarbonyl chlorofluoride and the difluoride.

In the present experiment, thiophosgene was fluorinated using \( \text{SbF}_3 \) in a non-aqueous solvent of high dielectric constant, tetrahydrothiophene-1,1-dioxide. The vacuum system used for the synthesis is shown in the Fig. 2.1. Approximately 5 ml of thiophosgene, 25-30 gms. of \( \text{SbF}_3 \) and 50 gms. of the solvent were taken and the mixture kept constantly stirred with a magnetic stirrer. The mixture was refluxed at atmospheric pressure for more than 48 hours at 78-80°C. After the reaction, all the products were condensed in traps surrounded by liquid \( \text{N}_2 \). These were fractionated by trap to trap distillation using different low temperature baths. The liquid \( \text{N}_2 \) trap was replaced by a bath at -95°C (Toluene-liquid \( \text{N}_2 \)) and the volatile products pumped off. The remaining material was subjected to a further separation by passing it through traps at -86°C (solid \( \text{CO}_2 \)-acetone) and -186°C. The trap at -86°C retained most of the high boiling materials (mainly \( \text{CSCl}_2 \)) while the
desired product was collected in the liquid N\textsubscript{2} trap. The sample was further subjected to low temperature fractional distillation at atmospheric pressure. The sample thus obtained still contained small amounts of COS, CCl\textsubscript{3}F and CS\textsubscript{2}. A gas chromatographic separation proved to be unsuccessful. Thiocarbonyl chlorofluoride is bright yellow in colour and boils at 67°C.

The impurities and thiocarbonyl chlorofluoride were identified by their mass spectrum. Fig. 2.2 shows the mass-spectrum of the sample obtained in a Bendix Time-of-Flight Mass Spectrometer (Basic Model 12). Table 2.1 shows the assignment of the various peaks.

2. INFRARED SPECTRUM

The infrared spectra of the samples for survey purposes were obtained on a Perkin-Elmer model 237B double beam spectrophotometer.

The high resolution spectra were obtained on a Perkin-Elmer model 225 double beam spectrophotometer.\textsuperscript{(12)} This instrument can cover the range from 5000 cm\textsuperscript{-1} to 200 cm\textsuperscript{-1} and is provided with a dry air purging unit which removes the absorption bands due to water vapour in the region 450 cm\textsuperscript{-1} to 200 cm\textsuperscript{-1}. The fore-monochromator consists of a KBr prism for the region 5000-450 cm\textsuperscript{-1}, and a filter-scatter plate combination for the region below 450 cm\textsuperscript{-1}. Two gratings with 150 and 30\textsuperscript{-lines/mm} respectively, are used in both the first and second orders to cover the region 5000-200 cm\textsuperscript{-1}. The instrument was provided with a Golay detector as well as with a thermocouple detector. The thermocouple proved to be superior to the Golay detector. The instrument was calibrated in the range 4000-200 cm\textsuperscript{-1} using the standard spectra of H\textsubscript{2}O, CH\textsubscript{4}, NH\textsubscript{3} and CO\textsubscript{2} \textsuperscript{(12, 13)}. With the slit program used, the approximated spectral slit widths were about 0.41, 0.59 and 1.65 cm\textsuperscript{-1} at 1500, 750 and 250 cm\textsuperscript{-1} respectively.

The infrared spectrum of the sample was obtained in the gaseous phase using gas cells of path length 10 cms and with NaCl, KBr and polythene windows.
Fig. 2.1  The Vacuum System for the synthesis of CSCI\textsubscript{F}.

Fig. 2.2  The Mass Spectrum of the sample containing CSCI\textsubscript{F}, obtained in a Bendix Time-of-Flight Mass spectrometer (Basic Model 12).
TABLE 2.1

Observed mass-spectrum and their assignments.

<table>
<thead>
<tr>
<th>No.</th>
<th>m/e</th>
<th>Assignment</th>
<th>Relative Intensity</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>CF</td>
<td>13.6</td>
</tr>
<tr>
<td>2</td>
<td>47</td>
<td>$^{35}$Cl</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>49</td>
<td>$^{37}$Cl</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>63</td>
<td>$^{32}$S</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>$^{34}$S</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>66</td>
<td></td>
<td>8.7</td>
</tr>
<tr>
<td>7</td>
<td>76</td>
<td>$^{32}$S$_2$</td>
<td>34.2</td>
</tr>
<tr>
<td>8</td>
<td>77</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>9</td>
<td>78</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>79</td>
<td>$^{35}$C$_2$S$_2$ (?)</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>$^{34}$S$_2$</td>
<td>1.75</td>
</tr>
<tr>
<td>12</td>
<td>81</td>
<td>$^{32}$F$_3$ (?)</td>
<td>73.6</td>
</tr>
<tr>
<td>13</td>
<td>82</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>14</td>
<td>96</td>
<td></td>
<td>12.2</td>
</tr>
<tr>
<td>15</td>
<td>98</td>
<td>$^{32}$SCF$^{35}$Cl</td>
<td>38.6</td>
</tr>
<tr>
<td>16</td>
<td>100</td>
<td>$^{32}$SCF$^{37}$Cl and $^{34}$SCF$^{35}$Cl</td>
<td>14</td>
</tr>
<tr>
<td>17</td>
<td>101</td>
<td>$^{35}$Cl$_2$</td>
<td>51.75</td>
</tr>
<tr>
<td>18</td>
<td>103</td>
<td>$^{35}$Cl$^{37}$Cl</td>
<td>31.5</td>
</tr>
<tr>
<td>19</td>
<td>105</td>
<td>$^{37}$Cl$_2$</td>
<td>5.2</td>
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A one-metre multiple reflection cell with CsI windows was also used.

3. RAMAN SPECTRUM

The Raman spectrum of liquid CsClF was obtained by using a Laser Raman Spectrophotometer. The sample was contained in a capillary tube of outer diameter 1.8 mm and of length 3 cms. The wave/length of the exciting line was 6328 Å.

For polarization measurements, a polarizer was introduced between the condensing lens and the entrance slit. The spectrum was recorded with the polarizer arranged in such a way that the polarized light was parallel to the direction of the electric vector of the incident light. The spectrum was also recorded with the polarizer at 90° for measurements at right angles to the incident electric vector direction. The maximum theoretical extent of depolarization with this set-up is 3/4.
CHAPTER III
THEORETICAL

The total energy of a molecule is given by the sum of the kinetic energy and potential energy of all the electrons and the nuclei present. The Hamiltonian operator $H$, corresponding to the internal energy, has eigenfunctions, $\Psi_T$, and eigenvalues, $E_T$.  

$$H\Psi_T = E\Psi_T \quad (3.1)$$

where $H = (K.E) + (P.E) = T_E + T_N + V_{EN} + V_{NN} + V_{EE}$

where $T_E$ and $T_N$ are the kinetic energy operators of the electrons and the nuclei respectively, $V_{EN}$, the operator for the coulombic attractions between electrons and nuclei, and $V_{NN}$ and $V_{EE}$ are the internuclear and interelectronic repulsion operators.

To a first approximation, the motion of the electrons at any given instant is very rapid compared to the motion of the nuclei. So, the nuclei can be assumed to be in fixed positions. Hence, $T_N=0$ and $V_{NN}=$constant. Therefore,

$$H_E = T_E + V_{EN} + V_{EE} \quad (3.2)$$

If $\Psi_E$ varies only slowly as a function of $R$, the nuclear co-ordinates, under the Born-Oppenheimer approximation we can write the molecular Hamiltonian as a sum of two components,

$$H = H_E + H_N \quad \text{and} \quad \Psi_T = \Psi_E \Psi_N \quad (3.3)$$

Hence,

$$H_E \Psi_E (r_i, R_i) = E_E \Psi_E (r_i, R_i) \quad (3.4)$$

where the electronic co-ordinates $r_i$ ($x_i, y_i, z_i$) are referred to a set of molecule-fixed cartesian co-ordinates with center of mass as the origin and $R_i$, the nuclear co-ordinates consist of the displacement co-ordinates, $S_i$, with origin at the equilibrium position of the nuclei.

Similarly,

$$(T_N + V_{NN} + E_E) \Psi_N = E \Psi_N \quad (3.5)$$
The nuclear wave function, $\Psi_N$, can be further resolved under the rigid rotor approximation as

$$\Psi_N (R_i) = \Psi_V (S_i) \Psi_R (\theta, \varphi, \chi) \quad (3.6)$$

where the Eulerian angles, $(\theta, \varphi, \chi)$, define the orientation in a space-fixed axes and $\Psi_V$ and $\Psi_R$ represent the vibrational and rotational wave functions, respectively.

The vibrational and rotational motions can be separated under this approximation, and we have

$$H_V \Psi_V (S_i) = E_V \Psi_V (S_i)$$
$$H_R \Psi_R (\theta, \varphi, \chi) = E_R \Psi_R (\theta, \varphi, \chi) \quad (3.7)$$

Hence the total energy can be resolved into electronic, vibrational, and rotational energies.

$$E_T = E_e + E_V + E_R \quad (3.8)$$

and the corresponding wave function

$$\Psi_T = \Psi_e \Psi_V \Psi_R \quad (3.9)$$

Energy is absorbed or emitted when a transition takes place between two states with energies $E'$ and $E''$, where single primes and double primes represent the upper and lower states respectively, the difference appearing as radiation with a frequency, in cm$^{-1}$,

$$\sigma = (E' - E'')/hc \quad (3.10)$$

where $h$ is the Planck constant and $c$ is the velocity of light.

An electric dipole transition occurs between two states, $\Psi'$ and $\Psi''$ only if the transition moment, $\vec{M}$, given by

$$\vec{M} = \int \Psi'^* \vec{\mu} \Psi'' d\tau \quad (3.11)$$

where $\vec{\mu}$ is the dipole moment, is non-zero.

INFRARED AND RAMAN SPECTRA

Absorption in the infrared region is observed when a transition takes place between two vibrational levels associated with the ground electronic state. Hence, $\Psi'_e = \Psi''_e$ and, if $\Psi'_R = \Psi''_R$ (that is, for a simple vibra-
The dipole moment, \( \vec{\mu}_x \), which is a component of \( \vec{\mu} \), can be expanded as a power series in the co-ordinates, \( S_i \), of the atoms with the result

\[
\vec{\mu}_x = (\mu_{x0}) + \sum_i \left( \frac{\partial \mu_x}{\partial S_i} \right) S_i + \cdots \tag{3.13}
\]

where \( (\mu_{x0}) \) is the \( x \) component of the permanent dipole moment of the molecule.

Hence, from Eq. (3.11)

\[
\int \psi''^* \vec{\mu}_x \psi'' d\tau = (\mu_{x0}) \int \psi''^* \psi'' d\tau + \int \sum_i \left( \frac{\partial \mu_x}{\partial S_i} \right) \psi'' S_i \psi'' d\tau \tag{3.14}
\]

The first term vanishes because \( \psi'' \) and \( \psi'' \) are orthogonal. Hence, it is the change in dipole moment which determines the intensity of the vibrational transition. Replacing the displacement co-ordinates, \( S_i \), by \( Q_i \), the normal co-ordinates, we have

\[
\int \psi''^* Q_i \psi'' d\tau = \int \psi''^* (Q_1) \psi''^* (Q_1) dQ_1 \int \psi''^* (Q_2) \psi'' (Q_2) dQ_2 \cdots \nonumber
\]

\[
\times \int \psi''^* (Q_1) Q_1 \psi'' (Q_1) dQ_1 \tag{3.15}
\]

since, \( \psi = \psi(Q_1) \psi(Q_2) \cdots \psi(Q_{3N-6}) \cdots \)

All the integrals would vanish unless \( V_1 = V_1'' \), \( V_2 = V_2'' \), etc., with the exception of \( V_1 \) and \( V_1'' \). Hence,

\[
\int \psi''^* \mu_x \psi'' d\tau = \frac{\partial \mu_x}{\partial Q_1} \int \psi''^* (Q_1) Q_1 \psi'' (Q_1) dQ_1 \tag{3.16}
\]

For the transition moment to be non-zero, \( \psi'_{V_1} - \psi''_{V_1} = \pm 1 \), so that in harmonic oscillator approximation, only vibrational transitions in which the quantum number \( V_1 \) changes by unity are allowed. Transitions with \( \Delta V = \pm 2, \pm 3, \ldots \) have non-zero probability when the vibrations are anharmonic.

The Raman spectra also give information about the vibrational levels of the molecule in the ground state. The activity of Raman spectrum is determined by the induced dipole moment due to vibration and rotation and is given by

\[
\vec{\mu} = \Delta \vec{\xi} \tag{3.17}
\]
where $\mu$ is the induced dipole moment, $\vec{E}$ is the electric vector associated with the incident radiation and $\lambda$ is a constant called the polarizability. This is a tensor quantity. In a manner analogous to the selection rules for the infrared spectra, for a transition to occur the transition moment
\[
\int \psi_V^* \mu_o \psi_V \neq 0
\]  
where $\mu_o$ is the time-independent part of the induced dipole moment.

**ELECTRONIC SPECTRA**

The spectra observed in the visible or ultraviolet spectral region result from transitions which take place between the vibrational-rotational levels of two electronic states, $\psi_e'$ and $\psi_e''$. The vibronic wave function is given by
\[
\psi = \psi_e \psi_V
\]  
The electric dipole moment $\vec{P}$ can be separated into a component $\vec{P}_e$ due to electrons and a component $\vec{P}_N$ due to the nuclei. Hence, $\vec{R}$, the transition moment for vibronic transition, can be written as,
\[
\vec{R} = \int \psi_e^* \psi_V^* (\vec{P}_e + \vec{P}_N) \psi_e \psi_V \, d\tau
\]  
$\vec{P}_N$ and $\psi_V$ are functions of nuclear co-ordinates. Hence, Eq. (3.20) can be rearranged to give
\[
\vec{R} = \int \psi_V^* (\psi_e^* \vec{P}_e \psi_e \, d\tau_e) \psi_V^* \, dq + \int \psi_V^* \vec{P}_N (\psi_e^* \psi_e \, d\tau_e) \psi_V^* \, dq
\]  
Because of the orthogonality of wave functions belonging to different electronic states, the last term of (3.21) reduces to zero.

If,
\[
\vec{R}_e = \int \psi_e^* \vec{P}_e \psi_e \, d\tau_e
\]  
Then,
\[
\vec{R} = \int \psi_V^* \vec{R}_e \psi_V \, dq
\]  
Treating $\vec{R}_e$ as a constant, in a first approximation
\[
\vec{R} = \vec{R}_e \int \psi_V^* \psi_V \, dq
\]  
Therefore, the transition moment depends on the overlap integral, $\int \psi_V^* \psi_V \, dq$. 
The magnitude of the overlap integral is determined by the potential curves in the combining states. The Condon overlap integral, \( \int \psi'_V \psi''_V \, d\mathbf{q} \), determines the relative intensities of the bands in a progression.

In general, from group theoretical considerations, integrals of the form
\[
\int \psi'_f \psi''
\]
where \( f \) is an operator corresponding to either dipole moment or some other physical quantity, will differ from zero only if the direct product representation \( \Gamma(\psi') \otimes \Gamma(\psi'') \) transforms like \( \Gamma_f \). In other words, the representation generated by the integrand must be either totally symmetric or have a totally symmetric component.

**THE VIBRATIONS OF POLYATOMIC MOLECULES**

A molecule with \( N \) atoms has \( 3N-6 \) (3N-5 for linear molecules) vibrational, three translational and three rotational degrees of freedom. By using a molecule-fixed system of co-ordinates with the center of mass as origin, one can separate the vibrations from rotations and translations. Using the generalized co-ordinates
\[
\xi_1, \xi_2, \ldots, \xi_{3N}
\]
(3.26)
to represent the displacement co-ordinates, we have for \( f_i \), one of the components of the restoring force acting on the \( i \)th nucleus when displaced from the equilibrium position,
\[
f_i = -\frac{\partial V}{\partial \xi_i}
\]
(3.27)
where \( V \), the potential energy, is a function of \( (\xi_1, \xi_2, \ldots, \xi_{3N}) \). The equations of motion for the \( N \) nuclei consist of the 3N Lagrangian equations
\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\xi}_i} \right) - \frac{\partial L}{\partial \xi_i} = 0 \quad (i = 1, 2, \ldots, 3N)
\]
(3.28)
where \( L = T - V \). In terms of the mass-weighted co-ordinates, \( \eta_i = \sqrt{m_i} \xi_i \), the kinetic energy is given by
\[
2T = \sum_i \eta_i^2
\]
(3.29)
For small displacements, \( V \) can be expanded in \( \xi_i \) about the equilibrium position...
23

\[ V = V_0 + \sum_i \left( \frac{\partial V}{\partial \xi_i} \xi_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right) \xi_i \xi_j \right) + \ldots \]  

(3.30)

When the potential energy is measured with respect to the equilibrium configuration, \( V_0 = 0 \). Again, at equilibrium configuration, \( \xi_i \)'s are at a minimum. Hence,

\[ \left( \frac{\partial V}{\partial \xi_i} \right) = 0 \]  

(3.31)

For small displacements, neglecting higher terms in (3.30), we have

\[ 2V = \sum_{i,j=1}^{3N} f_{ij} \xi_i \xi_j \quad \text{where} \quad f_{ij} = \left( \frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right) \]  

(3.32)

From equations (3.28), (3.29) and (3.32), we have

\[ \ddot{\eta}_i + \sum_{j=1}^{3N} f_{ij} \eta_j = 0 \quad \text{(i = 1, \ldots, 3N)} \]  

(3.33)

This set of 3N homogeneous second-order differential equations possesses a solution of the form

\[ \eta_i = \eta_i^0 \sin \left( t\sqrt{\lambda} + \delta \right) \quad (i = 1, \ldots, 3N) \]  

(3.34)

where \( \eta_i, \lambda \) and \( \delta \) are constants. Substitution of Eq. (3.34) in Eq. (3.33) gives

\[ \sum_j f_{ij} \eta_j^0 = -\lambda \eta_i^0 \quad (i = 1, \ldots, 3N) \]  

(3.35)

which, on rearrangement, gives

\[ \sum_i \left( f_{ij} - \delta_{ij} \lambda \right) \eta_i^0 = 0 \quad (i = 1, \ldots, 3N) \]  

(3.36)

where \( \delta_{ij} = 0 \) when \( i \neq j \) and \( \delta_{ij} = 1 \) when \( i = j \).

The Equations 3.36 are a set of simultaneous homogeneous linear algebraic equations in the amplitudes, \( \eta_i^0 \). The condition for this set of equations to have non-vanishing solutions is that the determinant formed by the coefficients of \( \eta_i^0 \), called the secular equation, should be equal to zero.

\[
\begin{vmatrix}
    f_{11} - \lambda & f_{12} & f_{13} & \ldots & f_{1,3N} \\
    f_{21} & f_{22} - \lambda & f_{23} & \ldots & f_{2,3N} \\
    f_{3N,1} & f_{3N,2} & f_{3N,3} & \ldots & f_{3N,3N-\lambda}
\end{vmatrix} = 0
\]  

(3.37)

This equation has 3N roots which correspond to the 3N normal modes of vibration, called the normal frequencies or fundamental frequencies, representing for each mode the simple harmonic vibration of all the atoms with the same frequency and phase but different amplitudes. The frequencies are given by
\[ \lambda = 4\pi^2 \nu^2 \text{ (sec}^{-1}) \text{ or } \lambda = 4\pi^2 c^2 \nu^2 \text{ (cm}^{-1}) \] (3.38)

Six of these roots, corresponding to translational and rotational motion, would be zero. If \( n \) vibrations of the same frequency occur, \( n \)-fold degenerate frequencies occur. If \( \lambda_k \) is one of the roots, substitution in 3.36 gives 3N equations from which the ratio of the amplitudes, \( \eta_{1,k}', \eta_{2,k}', \ldots, \eta_{3N,k}' \) corresponding to the \( k \)th normal frequency, can be calculated. We can construct a set of 3N coefficients, \( \ell_{1k} \), proportional to \( \eta_{1k} \), satisfying the relation

\[ \sum \ell_{1k}^2 = 1 \] (3.39)

\( \eta_{1k}' \) and \( \ell_{1k} \) are related by

\[ \eta_{1k}' = K_k \ell_{1k} \quad (i = 1, 2, \ldots, 3N) \] (3.40)

Using matrix formulation

\[ 2V = [\eta]^t [F] [\eta] \] (3.41)

where \([\eta]\) represents a column vector with the 3N mass-weighted cartesian co-ordinates as elements and \([\eta]^t\), its transpose.

Eq. 3.29 becomes

\[ 2T = [\dot{\eta}]^t [\dot{\eta}] \] (3.42)

It is necessary to use normal co-ordinates \( Q_k, k=1, 2, \ldots, 3N \), in terms of which the kinetic and potential energies have the form

\[ 2T = [\dot{Q}]^t [Q] \quad \text{and} \quad 2V = [Q]^t [\Lambda] [Q] \] (3.43)

The normal co-ordinates are defined in terms of the mass-weighted cartesian co-ordinates by the linear equation

\[ Q_k = \sum_{i=1}^{3N} \ell_{ki} \eta_i \] (3.44)

In the Eq. 3.43, \([\Lambda]\) is a diagonal matrix. The advantage in using the normal co-ordinates is that the expression for potential energy is also reduced into a sum of squares of \( Q_k \)'s like the expression for the kinetic energy.

\[ 2T = \sum_{k=1}^{3N} \dot{Q}_k^2 \quad 2V = \sum_{k=1}^{3N} \lambda_k Q_k^2 \] (3.45)

The Lagrangian equation, in terms of \( Q_k \)'s, is

\[ [\ddot{Q}] + [\lambda] [Q] = 0 \] (3.46)
where \[ 2L = 2(T-V) = \mathbf{Q}^t \mathbf{Q} - \mathbf{Q}^t \mathbf{A} \mathbf{Q} \] (3.47)

Eq. 3.46 has solutions of the form

\[ Q_i = Q_i^0 \sin (t \sqrt{\lambda} + \delta) \] (3.48)

and the secular equation has the diagonal form

\[ |[\mathbf{A}] - \lambda \mathbf{E}| = 0 \] (3.49)

The normal co-ordinates are obtained from another set of co-ordinates by a linear transformation given by

\[ [\gamma] = [L] [Q] \] (3.50)

where [L] reduces the potential energy into a sum of squares and hence is orthogonal. The inverse transformation is

\[ [Q] = [L]^{-1} [\gamma] = [L]^t [\gamma] \] (3.51)

since

\[ [L]^{-1} = [L]^t \] (3.52)

The 3N-6 (3N-5 for a linear molecule) internal co-ordinates, consisting of changes in interatomic distances and changes in bond angles in a molecule, could be used to describe the potential energy and kinetic energy of the system. In terms of these co-ordinates, the potential energy of the molecule becomes physically more significant. In terms of the internal co-ordinates, \( S_i \), the potential energy is written as

\[ 2V = [S]^t [F] [S] \] (3.53)

where [S] is a column vector with \( S_i \) as elements and [F], the potential energy matrix. The elements of [F] are the force constants,

\[ f_{ij} = \left( \frac{\partial^2 V}{\partial S_i \partial S_j} \right) \] (3.54)

Again, the normal co-ordinates and internal co-ordinates are related by

\[ [S] = [L] [Q] \] (3.55)

The expression for kinetic energy in terms of internal co-ordinates is not simple. Eq. 3.42 gives the kinetic energy in terms of \( \mathbf{\gamma}_i \). A relation connecting the \( \mathbf{\gamma}_i \)'s and \( S_i \)'s of the form

\[ [\mathbf{\gamma}] = [R] [S] \] (3.56)

From the geometry of the molecule, the [D] matrix, representing the inverse
transformation, can be obtained.

\[ [S] = [D][\gamma] \]  

(3.57)

Matrix \([D]\) has 3N-6 rows and 3N columns, and hence \([D]^{-1}\) cannot be formed. As \([D][D]^t\) is a square matrix of order (3N-6), therefore

\[ 2T = [S]^t[G]^{-1}[S] \]  

(3.58)

where \([G] = [D][D]^t\). In the F - G symbolism, the secular equation assumes the form

\[ |[F] - \lambda[G]^{-1}| = 0 \]  

(3.59)

Eq. 3.59 has 3N-6 (3N-5 for linear molecules) roots. Multiplying through by \(G\), we have the secular equation in the familiar Wilson FG matrix form(7).

\[ |[G][F] - \lambda[E]| = 0 \]  

(3.60)

**SYMMETRY OF VIBRATIONAL WAVE FUNCTIONS AND APPLICATION OF GROUP THEORY.**

The equilibrium configuration of a molecule possesses certain symmetry elements which form a point group. The symmetry operations performed on a molecule leave the potential energy unchanged. Applying group theory, it is possible to determine the normal modes of vibration and classify them according to their symmetry properties. Using the symmetry of the molecule, it is also possible to set up a co-ordinate system, called symmetry co-ordinates, which are a linear combination of internal co-ordinates, in terms of which the order of the secular equation is reduced. This also enables one to separate vibrations belonging to different symmetry species. When a symmetry operation \(W\) is carried out on the co-ordinates \(q_i\), a different set of co-ordinates \(q'_i\) which are related by a linear transformation, is obtained.

\[ W[q] = q' = [C][q] \]  

(3.61)

Associated with each symmetry operation \(W^{(i)}\), we have the square matrix \([C^{(i)}]\). The set of matrices

\[ [C^{(1)}], [C^{(2)}], ... \]  

(3.62)
form a representation of the point group. In general, it is possible to find a matrix \([S]\) such that
\[
[S] \begin{bmatrix} c^{(1)} \end{bmatrix} = [S]^{-1}
\]
(3.63)
factors every \([C^{(1)}] \) into matrices of smaller order, along the diagonal. The operation in Eq. 3.63 is called similarity transformation and the reduced matrices of \([C^{(1)}] \) are called the irreducible representations.

Each of the normal co-ordinates, and hence the normal vibrations, can be assigned to an irreducible representation of the group. These irreducible representations are called the symmetry species.

In terms of the normal co-ordinates \(Q_i\), the transformation matrix, \([C]\) in 3.61, has elements (± 1) along the diagonal for a non-degenerate vibration. For a degenerate vibration, the symmetry operation transforms \(Q_i\) and \(Q_j\) into a linear combination of \(Q_i\) and \(Q_j\). The representation generated is of the same dimension as the degree of degeneracy.

The total vibrational energy of a molecule in terms of \(Q_i\) is given by
\[
E = \frac{1}{2} \sum_{i=1}^{3N-6} \hat{Q}_i^2 + \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2
\]
(3.64)
\(\hat{Q}_i\) is the momentum conjugate of \(Q_i\) and is replaced by the operator \(-i\hbar(\partial/\partial Q_i)\).

The quantum mechanical vibrational operator is
\[
\hat{H}_V = -\frac{\hbar^2}{2} \sum_{i=1}^{3N-6} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i \hat{Q}_i^2
\]
(3.65)
Substituting in the wave equation
\[
\hat{H}_V \psi = E \psi
\]
(3.66)
we can separate Eq. 3.65 into \(3N-6\) equations, one for each normal mode.

\[
E_i = E_1 + E_2 + \ldots + E_{3N-6}
\]
(3.67)
and
\[
\psi = \psi(Q_1) \psi(Q_2) \ldots \psi(Q_{3N-6})
\]
(3.68)
We can write down \(3N-6\) equations of the form
\[
\frac{\partial^2 \psi(Q_i)}{\partial Q_i^2} + \frac{2}{\hbar^2} (E_i - \frac{1}{2} \lambda_i \hat{Q}_i^2) \psi(Q_i) = 0
\]
(3.69)
where \(i=1, 2, \ldots, 3N-6\), which are wave equations for the harmonic oscillator expressed in \(Q_i\). The eigenvalues for Eq. 3.69 are
E = (v + \frac{1}{2}) \hbar \nu \text{ where } v = 0, 1, 2, ... \hspace{1cm} (3.70)

and the eigenfunctions are given by

\[ \mathcal{V}_{v1}^{\nu} (Q_1) = N_{v1} H_{v1} (\xi_1) e^{-\xi_1^2 / 2} \hspace{1cm} (3.71) \]

where \( H_{v1} (\xi_1) \) is the Hermite polynomial of degree \( v_1 \) and \( \xi_1 = Q_1 \sqrt{\lambda_1 / \hbar} \).

The total vibrational energy is given by

\[ E_v = (v_1 + \frac{1}{2}) \hbar \nu_1 + (v_2 + \frac{1}{2}) \hbar \nu_2 + \ldots + (v_{3N-6} + \frac{1}{2}) \hbar \nu_{3N-6} \hspace{1cm} (3.72) \]

and the total vibrational wave function by

\[ \mathcal{V}_v = N H_{v1} (\xi_1) H_{v2} (\xi_2) \ldots H_{v_{3N-6}} (\xi_{3N-6}) \exp \left\{ -\frac{1}{2} (\xi_1^2 + \xi_2^2 + \ldots + \xi_{3N-6}^2) \right\} \hspace{1cm} (3.73) \]

In general,

\[ E_v = \sum_{i=1}^{3N-6} \left( v_i + \frac{d_i}{2} \right) \hspace{1cm} (3.74) \]

where \( d_i \) is the degree of degeneracy of the \( i \)th normal vibration.

**SYMMETRY OF VIBRATIONAL WAVE FUNCTION**

In Eq. 3.73, the exponential part is invariant with respect to symmetry operation and hence the representation of \( \mathcal{V}_v \) is determined by the transformations of the Hermite polynomials \( H_{v1} (\xi_1) \) under group operations. Thus, in the ground vibrational state with \( v_1 = v_2 = \ldots = 0 \), the vibrational wave function generates a totally symmetric representation.

We have,

\[ \Gamma(\mathcal{V}_v) = \Gamma(\mathcal{V}_{v1}) \Gamma(\mathcal{V}_{v2}) \ldots \Gamma(\mathcal{V}_{v_{3N-6}}) \hspace{1cm} (3.75) \]

where the representation of the total wave function has been expressed as the direct product of the irreducible representations of the 3N-6 non-degenerate wave functions.

The Hermite polynomials, \( H_{vk} (\xi_k) \), for \( v_k = 0, 2, 4, \ldots \) are invariant under symmetry operation. Hence, when an even number of quanta \( v_k \) are excited, a totally symmetric representation is generated.

For odd \( v_k = 1, 3, 5, \ldots \), \( H_{vk} (\xi_k) = -H_v (-\xi_1) \hspace{1cm} (3.76) \)

and therefore

\[ \Gamma(H_{vk} (\xi_k)) = \Gamma(Q_k) \hspace{1cm} (3.77) \]
For the $k^{th}$ non-degenerate vibration in which $v_k$ quanta are excited, the representation generated by $\psi_V$ is

$$\Gamma_{v_k} = \Gamma_{Q_1} \otimes \Gamma_{Q_2} \otimes \Gamma_{Q_3} \cdots = (\Gamma_{Q})^{v_k} \quad \text{(3.78)}$$

For a combination level with $v_1$ quanta of $l^{th}$ vibration and $v_m$ quanta of the $m^{th}$ vibration, the representation of the level is

$$\Gamma \left( \psi_{v_1}, \psi_{v_m} \right) \neq \Gamma(\psi_{v_l}) \otimes \Gamma(\psi_{v_m}) \quad \text{(3.79)}$$
CHAPTER IV

THE VIBRATIONAL SPECTRA OF THIOCARBONYL CHLOROFLUORIDE

The vibrational spectra of SCCl₂ and SCF₂ have been studied by many authors. The spectrum of thiocarbonyl chlorofluoride has not been reported earlier. As part of a systematic investigation of the spectra of thiocarbonyl dihalides and the mixed halides, a study of the vibrational spectra of CSClF was undertaken.

Thiocarbonyl chlorofluoride was synthesised and the spectra were obtained as outlined earlier. The infrared spectrum of CSClF in the region 1400 cm⁻¹ to 250 cm⁻¹ is shown in Fig. 4.1. Fig. 4.2 shows the infrared spectrum of CSClF recorded at a higher resolution. The Raman spectrum of the sample is shown in Fig. 4.3.

Though the microwave spectra for CSCl₂ and CSF₂ have not been reported and the electron-diffraction data inconclusive, both the molecules are presumably planar and belong to the C₂ᵥ point group. CSClF is also assumed to be planar and since the geometrical parameters were not available, the parameters were transferred from similar molecules. The assumed parameters are r(CS) = 1.63 Å, r(CF) = 1.32 Å, r(CCl) = 1.746 Å, θ(ClCF) = 111° 54', θ(SCCl) = 124° 18' and θ(SCF) = 123° 48', where r and θ are the interatomic distance and the bond angle respectively. The molecule CSClF belongs to the point group Cₛ. The molecule will have 3N-6 i.e., 6 normal modes of vibrations. The number of vibrations belonging to any symmetry species can be calculated from the equation.

\[ n(\gamma) = \frac{1}{h} \sum_{\gamma} \chi^*_{R} \chi_{\gamma} \]

where \( n(\gamma) \) is the number of vibrations belonging to the species \( \gamma \), \( h \) is the order of the group, and \( \chi_{\gamma} \), the character of various irreducible representations of the group, and \( R \), the number of operations of the group. Table 4.1 gives the character table for the point group Cₛ.
The infrared spectrum of CSC1F in the region 1400 cm\(^{-1}\) to 250 cm\(^{-1}\) with pressures of 6 and 12.35 mm of Hg and a path length of 10 cms.

The infrared spectrum of CSC1F obtained with a higher resolution with pressures of 1, 2.45 and 60 cms and a path length of 10 cms.
The Raman spectrum of liquid CsClF obtained using the 6328 Å line of the He-Ne laser as the exciting line. The intensities given in Table 4.5 have not been corrected for the non-linear response of the photomultiplier tube.

Upper trace was recorded with polarizer perpendicular to incident vector direction, lower trace parallel to incident vector direction.
TABLE 4.1

SYMMETRY TYPES AND CHARACTERS FOR
THE NORMAL MODES OF CSCLF. (POINT GROUP C_s)

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>S_h</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A''</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Dr. Number of Fundamentals and their Activity

- 5 R(p) and I
- 1 R(d) and I

The character $\chi_R$ for the reducible representation in terms of the cartesian co-ordinates of the system can be calculated. (7) They are given below.

$$\chi_R = \begin{bmatrix} E & S_h \\ 12 & 4 \end{bmatrix}$$

From the value of $\chi_R$ and $\chi_r$, we have 8 vibrations belonging to $A'$ species and 4 vibrations belonging to $A''$ species which include the six non-genuine vibrations. The symmetry species of the overtones and combination bands are obtained by the direct product of the species to which the fundamentals belong and are given in Table 4.2.

TABLE 4.2

SELECTION RULES FOR THE COMBINATION
AND OVERTONE BANDS. (C_s Symmetry)

- $A'$ and $A''$
- $A'$ and $A''$
- $A'$ and $A''$
- $A'$ and $A''$

Since both $A'$ and $A''$ are both infrared and Raman active, all the combinations and overtones of $A'$ and $A''$ are allowed.

The moments of inertia of CSCLF were calculated using the parameters shown in Fig. 4.4. The molecule is planar and hence the axes of two of the
moments of inertia lie on the plane and the third, perpendicular to the plane.

The centre of mass was determined by arbitrarily choosing a system of co-ordinates, like the one shown in Fig. 4.1 and using the condition that \( \sum m_i x_i = 0 \) and \( \sum m_i y_i = 0 \) about the center of mass. The principal moments of inertia with the center of mass as origin were determined with masses of S and Cl as 32 and 35 A.M.U respectively and are shown in Table 4.3.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>I_A (10^-40 gm cm^2)</th>
<th>I_B (10^-40 gm cm^2)</th>
<th>I_C (10^-40 gm cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSCIF</td>
<td>149.8</td>
<td>268.1</td>
<td>417.8</td>
</tr>
</tbody>
</table>

From Table 4.3 it is seen that CSCIF is an asymmetric top. The direction of \( I_A \) and \( I_B \) with reference to the assumed co-ordinate system is shown in Fig. 4.1. The transitions between the rotational levels associated with each of the vibrational levels, are superimposed on the vibrational transitions. These rotational lines are not resolved and hence only a band contour is observed. The shape of the vibration-rotational band contour depends upon the direction of the transition moment during a normal vibration. They are classified as type A, B or C when the dipole moment change is parallel to a, b or c axes respectively. For CSCIF, belonging to \( C_S \), symmetry, the translations \( T_x \) and \( T_y \) belong to the same representation and hence the direction of transition moment in the plane of the molecule (xy), cannot be uniquely determined.

ASSIGNMENT OF THE FUNDAMENTALS

The infrared spectra of the sample of CSCIF contained certain impurities like CCl_3F, CS_2, COS, etc. After eliminating the bands due to these impurities, the bands at 1257.7, 1014.7, 611.9, 427.0 and 322.6 cm\(^{-1}\) were identified as the frequencies due to CSCIF.\(^{(14-16)}\) The C-S stretch appears at 1139 cm\(^{-1}\) in CSCl_2 and at 1368 cm\(^{-1}\) in CSF_2. Hence, it is logical to assign the most intense band at 1257 cm\(^{-1}\) with a PR separation of 12.5 to 13 cm\(^{-1}\) to the CS stretch. The
intense band at 1014 cm\(^{-1}\), which has a PQR structure similar to the 1257 band, and has a PR separation of 13 cm\(^{-1}\), is assigned to CF stretch.

The band at 612 cm\(^{-1}\) shows a complicated structure. This band displays four to five sharp maxima and a PR separation of 16-18 cm\(^{-1}\). This behaviour is difficult to understand. This band is assigned as CCl\(_2\) stretch. The band at 427 cm\(^{-1}\) has the anticipated PQR structure whereas the band at 323 cm\(^{-1}\) has a different contour. These two bands can be assigned as the other two a' fundamentals.

The out-of-plane mode for CSCl\(_2\) and CSF\(_2\) have been found to be 471 and 622 cm\(^{-1}\) respectively.\(^{2,3}\) The out-of-plane vibration belonging to the a'' species for CSClF is expected to lie in the region around 540 cm\(^{-1}\). At least two impurity bands are present in this region and for this reason it is difficult to assign the a'' mode. However, the absorption spectrum in the visible region suggests a value of 540 cm\(^{-1}\) for the out-of-plane mode of vibration. Table 4.4 lists all the observed infrared bands in the region 1400-250 cm\(^{-1}\).

A preliminary study of the Raman spectrum showed frequency shifts of 1242, 992, 608, 426 and 326 cm\(^{-1}\) respectively. All these lines were found to be polarized with depolarization ratios ranging from approximately 0.03 to 0.54. Thus, they supplement the infrared data. In principle, it should have been possible to identify the unassigned out-of-plane vibration from the Raman spectrum since it would have a depolarization ratio of 3/4. The two intense Raman lines with 536 and 569 cm\(^{-1}\) shifts are polarized. The 536 cm\(^{-1}\) shift may be assigned to CCl\(_3\)F \(^{16}\) which is present as impurity. Hence, the out-of-plane vibration could not be identified in the Raman spectrum. The observed Raman lines are listed in Table 4.5.

Only a few overtone and combination bands were assigned because of the interference from impurity bands. The observed bands of CSClF with their frequencies and intensities are shown in Table 4.6.
## TABLE 4.4

Observed Infrared Bands and their Assignment

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>2260</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>2060</td>
<td>CS O</td>
</tr>
<tr>
<td>1829</td>
<td>—</td>
</tr>
<tr>
<td>1618</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>1528</td>
<td>CS₂</td>
</tr>
<tr>
<td>1357</td>
<td>CS F₂</td>
</tr>
<tr>
<td>1258</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>1154</td>
<td>—</td>
</tr>
<tr>
<td>1082</td>
<td>CCl₃ F</td>
</tr>
<tr>
<td>1040</td>
<td>—</td>
</tr>
<tr>
<td>1015</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>921</td>
<td>CCl₃ F</td>
</tr>
<tr>
<td>850</td>
<td>CS O, CCl₃ F</td>
</tr>
<tr>
<td>612</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>520</td>
<td>CS O</td>
</tr>
<tr>
<td>427</td>
<td>CS Cl F</td>
</tr>
<tr>
<td>397</td>
<td>CS₂</td>
</tr>
<tr>
<td>323</td>
<td>CS Cl F</td>
</tr>
</tbody>
</table>
## TABLE 4.5

Observed Raman Bands and their Assignment

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1242</td>
<td>CSC1F</td>
</tr>
<tr>
<td>1074</td>
<td>CCl$_3$F</td>
</tr>
<tr>
<td>992</td>
<td>CSC1F</td>
</tr>
<tr>
<td>857</td>
<td>CCl$_3$F</td>
</tr>
<tr>
<td>804</td>
<td>CS$_2$</td>
</tr>
<tr>
<td>797</td>
<td>CS$_2$</td>
</tr>
<tr>
<td>659</td>
<td>CS$_2$</td>
</tr>
<tr>
<td>648</td>
<td>CS$_2$</td>
</tr>
<tr>
<td>608</td>
<td>CSC1F</td>
</tr>
<tr>
<td>569</td>
<td></td>
</tr>
<tr>
<td>536</td>
<td>CCl$_3$F</td>
</tr>
<tr>
<td>426</td>
<td>CSC1F</td>
</tr>
<tr>
<td>394</td>
<td>CCl$_3$F</td>
</tr>
<tr>
<td>352</td>
<td>CCl$_3$F</td>
</tr>
<tr>
<td>326</td>
<td>CSC1F</td>
</tr>
<tr>
<td>241</td>
<td>CCl$_3$F</td>
</tr>
</tbody>
</table>
### TABLE 4.6

Observed Vibrational Frequencies of CSCIF

<table>
<thead>
<tr>
<th>Infrared Gas (in cm⁻¹)</th>
<th>Intensity a</th>
<th>Raman Liquid (in cm⁻¹)</th>
<th>Intensity b</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>0.1</td>
<td></td>
<td></td>
<td>2ν₁</td>
</tr>
<tr>
<td>2260</td>
<td>0.8</td>
<td></td>
<td></td>
<td>ν₁ + ν₂</td>
</tr>
<tr>
<td>1618</td>
<td>0.3</td>
<td></td>
<td></td>
<td>ν₂ + ν₃</td>
</tr>
<tr>
<td>1257</td>
<td>100</td>
<td>1242</td>
<td>32 (P)</td>
<td>ν₁</td>
</tr>
<tr>
<td>1014</td>
<td>75</td>
<td>992</td>
<td>8 (P)</td>
<td>ν₂</td>
</tr>
<tr>
<td>612</td>
<td>28</td>
<td>608</td>
<td>100 (P)</td>
<td>ν₃</td>
</tr>
<tr>
<td>427</td>
<td>4</td>
<td>426</td>
<td>10 (P)</td>
<td>ν₄</td>
</tr>
<tr>
<td>323</td>
<td>2</td>
<td>326</td>
<td>50 (P)</td>
<td>ν₅</td>
</tr>
</tbody>
</table>

P = Polarized

a The intensity of the band at 1257 cm⁻¹ was arbitrarily taken as 100 and the other band intensities are normalized with respect to this band.

b The Raman line at 608 is the most intense and is taken as of intensity 100.
CHAPTER V
NORMAL CO-ORDINATE ANALYSIS

The motion of a molecule can be described in terms of $3N$ displacement co-ordinates. If cartesian co-ordinates are used, the displacement of the nucleus is represented by $\vec{r}$ whose components along one of the mass-weighted cartesian co-ordinate is given by $\eta_i$. Using a simple harmonic oscillator approximation, the potential energy becomes,

$$V = \frac{1}{2} \sum_{i,j=1}^{3N} f_{ij} \eta_i \eta_j$$

where $f_{ij} = \left( \frac{-\partial^2 V}{\partial \eta_i \partial \eta_j} \right)$. (5.1)

and the kinetic energy, $T$, is given by

$$T = \frac{1}{2} \sum_{i=1}^{3N} \dot{\eta}_i^2$$

It was seen in Chapter III that in the simple harmonic oscillator approximation, a set of normal co-ordinates $Q_i$, could be constructed so that

$$2V = \left[ Q \right]^t [\Lambda] [Q]$$

and

$$2T = \left[ \dot{Q} \right]^t [\dot{Q}]$$

Since, it is the normal co-ordinates that have to be determined, in the present calculation internal co-ordinates were used. In terms of these

$$2V = \left[ S \right]^t [F] \left[ S \right]$$

and

$$2T = \left[ \dot{S} \right]^t [G] \left[ \dot{S} \right]$$

The internal co-ordinates are related to the normal co-ordinates by

$$[S] = \left[ L \right] [Q]$$

The frequencies of normal modes of vibrations are a function of the force-constants, $f_{ij}$, which are not known in advance. But it is possible to transfer certain force-constants from similar molecules. The experimentally observed frequencies are the roots $\lambda_i$ of the secular equation,

$$\left[ [C] - \Lambda [E] \right] = 0$$

where $\lambda = 4\pi c^2 \nu^2 (\text{cm}^{-1})$ (5.8)

An initial set of force constants are assumed, which are adjusted systematically until the calculated frequencies agree with the experimental values.
The \( [F] \) matrix in 3.5 would contain \((3N-6)^2 = 36\) elements \(f_{ij}\). But, since \(f_{ij} = f_{ji}\), the number of independent force-constants would be 21. If the potential energy is of the most general form

\[
2V = \sum_{i,j=1}^{3N-6} f_{ij} S_i S_j \tag{5.9}
\]

The number of force-constants required would be much larger than the observed frequencies, i.e., 6. Hence the force-constants cannot be determined uniquely. The central force field, which reduces the number of force-constants required, assumes that forces holding the atoms in their equilibrium positions act only along the lines joining pairs of atoms and a force-constant could be associated with every pair of atoms. This force field has not proved very successful in practice.

In the valence force field approximation, the forces are due to changes in bond distances and bond angles. This force field is found to be better than the central force field but is still only a rough approximation. The advantage in this force field is that the normal modes could be assigned in terms of the valence bonds. The force-constants are roughly characteristic of the bonds involved.

In the present treatment, the potential function used is that of Urey-Bradley force field.\(^{(17,18)}\) This function is basically of the valence type and it also takes into account the interaction between the non-bonded atoms. The function is of the form,

\[
V = \sum_{i} K' r_i (\Delta r_i) + \frac{1}{2} \sum_{i} K_i (\Delta r_i)^2 + \sum_{i<j} H'_{ij} r_{ij} \cdot \alpha_{ij} (r_{ij}) + \frac{1}{2} \sum_{i<j} F'_{ij} (\Delta q_{ij})^2 + \frac{1}{2} \sum_{i<j} F_{ij} (\Delta q_{ij})^2 \tag{5.10}
\]

where \(K'\) and \(K\) are the stretching force-constants, \(H'\) and \(H\) are the bending force-constants and \(F'\) and \(F\) are the repulsive force-constants. In 5.10, \(r_{ij} = (r_i r_j)^{1/2}\), \(r_i, \phi_{ij}\) and \(q_{ij}\) are the \(i^{th}\) interatomic distance, the angle between bonds \(r_i\) and \(r_j\) and the non-bonded distance between \(i^{th}\) and \(j^{th}\) atoms respectively. The co-ordinates \(r_i, q_{ij}\) and \(\phi_{ij}\) are not independent and so the
but the redundant co-ordinates \( \Delta q_{ij}^{(9)} \) can be removed by the substitution

\[
q_{ij}^2 = r_i^2 + r_j^2 - 2 r_i r_j \cos \phi_{ij}
\]  

(5.11)

and \( \Delta q_{ij} = s_{ij} \Delta r_i + s_{ji} \Delta r_j + (t_{ij} t_{ji})^{1/2} (r_{ij} \Delta \phi_{ij}) + \frac{1}{2q_{ij}} \left( t_{ij}^2 (\Delta r_i)^2 + t_{ji}^2 (\Delta r_j)^2 - s_{ij} s_{ji} (r_{ij} \Delta \phi_{ij})^2 (r_j/r_i) - 2 t_{ij} t_{ji} (\Delta r_i \Delta r_j) + 2 t_{ij} s_{ji} (\Delta r_i \Delta \phi_{ij}) (r_j/r_i) + 2 t_{ji} s_{ij} (\Delta r_i \Delta \phi_{ij}) \right) \]  

(5.12)

where, \( s_{ij} = (r_i^2 - r_j \cos \phi_{ij})/q_{ij} \) and \( t_{ij} = (r_j \sin \phi_{ij})/q_{ij} \) (5.13)

Now, the potential energy is expressed in an independent set of co-ordinates and hence \( \frac{\partial V}{\partial r_i} = 0 \) but \( \frac{\partial V}{\partial \phi_{ij}} \neq 0 \).

Hence, substitution of Eq. 5.12 introduces the linear force-constant \( F_{ij} \).

Now the potential energy is expressed as

\[
2V = [S][F'][S] \tag{5.14}
\]

where the elements of \([F']\) are a linear combination of the Urey-Bradley force-constants.

\[
f'_{ij} = \sum_k a_{jk} \phi_k \tag{5.15}
\]

In Eq. 5.5, \([F]\) is symmetrical about the diagonal and hence it's upper triangular half can be numbered as shown below.

\[
[F] = \begin{bmatrix}
  f_1 & f_2 & f_4 \\
  f_3 & f_5 \\
  & f_6 \\
  & & \ddots \\
  & & & f_{n_s(n_s+1)/2}
\end{bmatrix}
\]  

(5.16)

where \( n_s \) is the total number of internal co-ordinates. The transpose of the column vector consisting of the internal co-ordinates is

\[
[S]^t = [S_1 \ S_2 \ S_3 \ \ldots \ldots \ S_{n_s}] \tag{5.17}
\]
The element \( f_n \) of the matrix \([F]\) in 5.16 is related to the square matrix of Eq. 5.5, \( f_{ij} \) by the relation

\[
\begin{align*}
n = \begin{cases} 
  j \frac{j-1}{2} + i & \text{if } i < j \\
i \frac{i+1}{2} & \text{if } i = j \\
i \frac{i-1}{2} + j & \text{if } j < i
\end{cases}
\]
\]

(5.18)

where \( i \) and \( j \) are also indices of \( S_i \) and \( S_j \).

Writing the Urey-Bradley force-constants as a column vector (which is written horizontally for convenience)

\[
[\phi] = (\phi_1, \phi_2, \ldots, \phi_n)
\]

(5.19)

we can define the \( Z \) matrix as

\[
[F] = [Z] [\phi]
\]

(5.20)

where the elements of \([Z]\) matrix depend on the geometry of the molecule and are the coefficients of the Urey-Bradley force-constants obtained by substituting relations of the type Eq. 5.12 for each \( \Delta q_{ij} \).

In nonmatrix notation,

\[
f_n = Z_{nk} \phi_k
\]

(5.21)

Substitution of Eq. 5.12 for \( \Delta q_{ij} \), gives for the coefficient of the diagonal force-constants a value of unity. The coefficients for the \( F_{ij} \) and \( F'_{ij} \) terms are given in Table 5.1.

<table>
<thead>
<tr>
<th>( S_i S_j )</th>
<th>( F_{ij} )</th>
<th>( F'_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta r_i \Delta r_i )</td>
<td>( s_{ij}^2 )</td>
<td>( t_{ij}^2 )</td>
</tr>
<tr>
<td>( \Delta r_j \Delta r_j )</td>
<td>( s_{ji}^2 )</td>
<td>( t_{ji}^2 )</td>
</tr>
<tr>
<td>( (r_i \Delta \alpha_{ij})^2 )</td>
<td>( t_{ij} t_{ji} (r_j/r_i) )</td>
<td>( -s_{ij} s_{ji} (r_j/r_i) )</td>
</tr>
<tr>
<td>( (\Delta r_i \Delta r_j) )</td>
<td>( s_{ij} s_{ji} )</td>
<td>( -t_{ij} t_{ji} )</td>
</tr>
<tr>
<td>( (\Delta r_i \Delta \alpha_{ij}) )</td>
<td>( s_{ij} (t_{ij} t_{ji})^{\frac{1}{2}} (r_j/r_i)^{\frac{1}{2}} )</td>
<td>( t_{ij} s_{ji} (r_j/r_i) )</td>
</tr>
<tr>
<td>( (\Delta r_j \Delta \alpha_{ij}) )</td>
<td>( s_{ji} (t_{ij} t_{ji})^{\frac{1}{2}} (r_j/r_i)^{\frac{1}{2}} )</td>
<td>( t_{ji} s_{ij} )</td>
</tr>
</tbody>
</table>
Eq. 5.10 still contains twelve independent force-constants and with the approximation that \( F' = -0.1F \) \(^{(20)}\) the number is reduced to nine. The number of Urey-Bradley force-constants required for describing the in-plane vibrations of the molecules CSF\(_2\) and CSCl\(_2\) are six, and Tables 5.2 and 5.3 tabulate the initial set of force-constants used for CSClF and CSX\(_2\) where \( X = F \) or Cl. Table 5.4 tabulates the \([Z]\) matrix elements for CSF\(_2\). The majority of \([Z]\) matrix elements are zeros.

**TABLE 5.2**

<table>
<thead>
<tr>
<th></th>
<th>K(_{CS})</th>
<th>K(_{CF})</th>
<th>K(_{CCl})</th>
<th>H(_{SCF})</th>
<th>H(_{FCCl})</th>
<th>H(_{ClCS})</th>
<th>F(_{SF})</th>
<th>F(_{FFCl})</th>
<th>F(_{SCl})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSF(_2)</td>
<td>5.44(^a)</td>
<td>4.35(^b)</td>
<td>2.30(^c)</td>
<td>0.261(^c)</td>
<td>0.321(^c)</td>
<td>0.08(^a)</td>
<td>1.554(^c)</td>
<td>0.821(^c)</td>
<td>0.69(^a)</td>
</tr>
</tbody>
</table>

**TABLE 5.3**

<table>
<thead>
<tr>
<th></th>
<th>K(_{CS})</th>
<th>K(_{CX})</th>
<th>H(_{XCX})</th>
<th>H(_{SCX})</th>
<th>F(_{SX})</th>
<th>F(_{XX})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSF(_2)</td>
<td>5.44(^a)</td>
<td>4.35(^c)</td>
<td>0.425(^c)</td>
<td>0.261(^c)</td>
<td>1.0045</td>
<td>0.67(^c)</td>
</tr>
<tr>
<td>CSCl(_2)</td>
<td>5.44</td>
<td>2.30(^c)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.69</td>
<td>0.74</td>
</tr>
</tbody>
</table>

The superscripts \(^a\), \(^b\) and \(^c\) refer to the references (6) (5) and (19) respectively, from which the initial values were taken.

The changes in \( i \)th bond length and \( i \)th bond angle are represented by \( \Delta r_i \) and \( \Delta \alpha_i \) respectively. The \( F \) matrix is of the form,

\[
\begin{array}{ccccccc}
\Delta r_1 & \Delta r_2 & \Delta r_3 & \Delta \alpha_1 & \Delta \alpha_2 & \Delta \alpha_3 \\
\Delta r_1 & F_{11} & F_{12} & F_{13} & F_{14} & F_{15} & F_{16} \\
\Delta r_2 & F_{21} & F_{22} & F_{23} & F_{24} & F_{25} & F_{26} \\
\Delta r_3 & F_{31} & F_{32} & F_{33} & F_{34} & F_{35} & F_{36} \\
\Delta \alpha_1 & F_{41} & F_{42} & F_{43} & F_{44} & F_{45} & F_{46} \\
\Delta \alpha_2 & F_{51} & F_{52} & F_{53} & F_{54} & F_{55} & F_{56} \\
\Delta \alpha_3 & F_{61} & F_{62} & F_{63} & F_{64} & F_{65} & F_{66} \\
\end{array}
\]
The indices \( i, j \) of Eq. 5.22 are related to the index \( n \) of Eq. 5.16 by the relations given in Eq. 5.18. In Tables 5.4 and 5.5, the index \( n \) of the triangular form of \( [F] \) in Eq. 3.16 are listed along the first column.

The \( [Z] \) matrix elements of \( \text{CS}_2 \) are shown in Table 5.5. A general program was written for evaluating the \( [Z] \) matrix elements for \( \text{CS}_2 \) type of molecules for the GE-235 computer in Fortran II language.

THE \([G]\) MATRIX

The internal co-ordinates \( S_i \) are related to the mass-weighted cartesian co-ordinates by the transformation,

\[
[S] = [D][F] \quad (5.23)
\]

and

\[
[G] = [D][D]^T \quad (5.24)
\]

If the vibrations are assumed to be of infinitesimal amplitude we can write

\[
S_t = \sum_{i=1}^{3N} B_{ti} \tilde{S}_i \quad \text{where} \quad t = 1, 2, \ldots, 3N-6 \quad (5.25)
\]

The constants \( B_{ti} \) are determined by the geometry of the molecule. The three cartesian displacements of atom \( \alpha \) could be considered as the components of a vector \( \mathbf{r}_\alpha \). Similarly the three coefficients for a given \( S_t \), like \( B_{ti}, B_{ti}', B_{ti}'' \) being associated with a given atom \( \alpha \), can be considered as the components of a vector \( s_{t\alpha} \). Then Eq. 5.25 takes the form

\[
S_t = \sum_{\alpha=1}^{N} s_{t\alpha} \mathbf{r}_\alpha \quad (5.26)
\]

where the dot represents the scalar product of the two vectors. The magnitude \( |s_{t\alpha}| \) of \( s_{t\alpha} \) is equal to the increase in \( S_t \) produced by unit displacement of the atom in the most effective direction. The direction of \( s_{t\alpha} \) is the direction in which the greatest increase of \( S_t \) is produced for a given displacement of atom \( \alpha \) when the other atoms are in the equilibrium position. The \( s_{t\alpha} \) vectors are given for different types of internal co-ordinates by Wilson, Decius and Cross. (21)

The elements of the \( [G] \) matrix can be obtained in terms of these \( s_{t\alpha} \) vectors.

\[
G_{tt'} = \sum_{\alpha=1}^{N} \mu_{t\alpha} s_{t\alpha} \cdot s_{t'\alpha} \quad (5.27)
\]
TABLE 5.4

[2] MATRIX ELEMENTS FOR CSF₂

<table>
<thead>
<tr>
<th>n</th>
<th>K₁</th>
<th>K₂</th>
<th>H₁</th>
<th>H₂</th>
<th>F₁</th>
<th>F₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td>1.6097</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.7965</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td></td>
<td>0.7024</td>
<td>0.6604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.7965</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>0.7222</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td></td>
<td>0.7024</td>
<td>0.6604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>0.5487</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>0.5487</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.7424</td>
<td></td>
<td></td>
<td></td>
<td>0.5751</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5094</td>
<td></td>
</tr>
<tr>
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TABLE 5.5

\textbf{\[^{2}\] Matrix Elements for CSCl\textsubscript{2}}

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<th>(K_2)</th>
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<td>0.8416</td>
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</tr>
</tbody>
</table>
where $\mu = 1/m$, the reciprocal of the mass of atom, and the dot represents the dot product. There is one element for each pair of internal co-ordinates. Wilson, Decius and Cross\textsuperscript{(21)} have tabulated the $[G]$ matrix elements which commonly occur. They can be calculated once the geometrical parameters of the molecule are known. The kinetic energy in terms of the internal co-ordinates $S_t$ is given by

$$2T = \sum_{tt'} (G^{-1})_{tt'} S_t S_{t'} \quad \text{where} \quad (G^{-1})_{tt'} \quad \text{and} \quad G_{tt'}(5.28)$$

are related by:

$$\sum_t G_{tt'} (G^{-1})_{tt'} = \delta_{tt'}$$

and

$$\sum_t G_{tt'} (G^{-1})_{t't''} = \delta_{tt'}$$

where $\delta_{tt'} = 0$ if $t \neq t'$ and $\delta_{tt'} = 1$ if $t = t'$.

(5.29) (5.30)

In the same internal co-ordinates the potential energy is given by

$$2V = \sum_{tt'} F_{tt'} S_t S_{t'} \quad (5.31)$$

In the present calculation the $[G]$ matrix elements were calculated using the above mentioned tabulations.

**SYMMEHY INTERNAL CO-ORDINATES**

The molecules CSCl\textsubscript{2} and CSF\textsubscript{2} belong to the $C_{2v}$ point group. To attain simplification, made possible by the symmetry, the 3N-6 internal co-ordinates are combined into symmetry co-ordinates. The symmetry co-ordinates transform according to the characters of the vibrations concerned. The symmetry co-ordinates are normalized and orthogonal.

For CSF\textsubscript{2} and CSCl\textsubscript{2}, there are 3 $A_1$ and 2 $B_2$ in-plane vibrations and one $B_1$ out-of-plane vibration. Hence the symmetry co-ordinates would be

$A_1: \quad R_1 = \Delta r_{CS}$

$$R_2 = \frac{1}{\sqrt{2}} \left( \Delta r_{CX_1} + \Delta r_{CX_2} \right)$$

$$R_3 = \frac{1}{\sqrt{6}} \left( 2\Delta \alpha_{X_1X_2} - \Delta \alpha_{SX_1} - \Delta \alpha_{SX_2} \right)$$

$B_2: \quad R_4 = \frac{1}{\sqrt{2}} \left( \Delta r_{CX_1} - \Delta r_{CX_2} \right)$

$$R_5 = \frac{1}{\sqrt{2}} \left( \Delta \alpha_{SX_1} - \Delta \alpha_{SX_2} \right)$$

and the redundant co-ordinate

$$R_6 = \frac{1}{\sqrt{3}} \left( \Delta \alpha_{X_1X_2} + \Delta \alpha_{SX_1} + \Delta \alpha_{SX_2} \right) \quad \text{where} \quad X=Cl,F. \quad (5.32)$$
In matrix notation we can write
\[
[R] = [U][F]
\]  
(5.33)
where
\[
[U] = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{2}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\
0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\
0 & 0 & 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}
\end{bmatrix}
\]
(5.34)
When this co-ordinate transformation is applied, we have,
\[
\mathcal{F} = [U][F][U]^t
\]
(5.35)
\[
\mathcal{G} = [U][C][U]^t
\]
(5.36)
the secular equation of the form
\[
\mathcal{G} \mathcal{F} \lambda_i = \lambda_i \mathcal{G}_i
\]
(5.37)
where \([\mathcal{G}_i]\) is the eigenvector matrix and \(\lambda_i\), the eigenvalues.

**Calculation of Force Constants from Observed Frequencies.**

When the initial set of Urey-Bradley force constants \([\phi]\), such as those given in Tables 5.2 and 5.3, are used to obtain the elements of \([F]\) and the secular equation solved, the calculated roots \(\lambda_i^c\) may not agree with the observed value, \(\lambda_i^o\). Hence, correction has to be found for \([\phi]\) so that \(\lambda_i^c - \lambda_i^o = 0\).

For \((i - 1)\)th set of force constants, the difference between the observed and calculated roots is \((22)\)
\[
[E^{i-1}] = [\Lambda^o] - [\Lambda^{i-1}]^c
\]
(5.38)
A set of corrections to the force constants, \([\Delta \phi^{i-1}]\), is sought such that
\[
[J^\phi][\Delta \phi^{i-1}] = [E^{i-1}]
\]
(5.39)
where \([J^\phi]\) is called the Jacobian matrix whose elements are
\[
J^\phi_{ik} = \frac{\partial \lambda_i}{\partial \phi_k}
\]
(5.40)
In Eq. 5.39, for small changes in \(\Delta \lambda_i\) and \(\Delta \phi_k\), the relationship between \(\lambda_i\) and \(\phi_k\) is assumed to be linear. It may require several cycles of refinement,
if \( [\Delta \phi^{i-1}] \) is large, for the calculated value to approach the experimental value.

For each cycle, a set of residuals is defined by,

\[
[r] = [J^T] [\Delta \phi] - [\varepsilon]
\]

(5.41)

The sum of the squares of the residuals is given by

\[
X = [r]^T [W] [r]
\]

(5.42)

where \([W]\) is a diagonal matrix with elements \( W_i \), the weighting factors.

From 5.41 and 5.42 we have,

\[
X = [\Delta \phi]^T [J^T] [W] [J] [\Delta \phi] - [\varepsilon]^T [W] [J^T] [\Delta \phi]
\]

(5.43)

To minimize \( X \), with respect to \([\Delta \phi]\), we have

\[
\frac{\partial X}{\partial \Delta \phi} = 0
\]

(5.44)

From Eq. 5.44, we have

\[
[\Delta \phi^{i-1}] = [J^T] [W] [J] [\Delta \phi] - [\varepsilon]^T [W] [J^T] [\Delta \phi]
\]

(5.45)

where the superscripts have been reinstated. The set of corrections \([\Delta \phi]\) thus obtained, are added to the previous set of \( \phi \)'s so that another set of \( \phi \)'s are calculated for which \([\varepsilon^{i-I}] \leq [\varepsilon^{i-1}] \). The process of reiteration is continued until the sum of the squares of the residuals, \( X \), is a minimum.

The elements of \([W]\), the weight matrix are given by (23)

\[
W_i = \left( \frac{1}{\lambda_i^2} \right)
\]

(5.46)

When a frequency was not observed experimentally, it was given a weight, \( W_i = 0 \) in the calculation.

If the \([\phi]\) matrix is perturbed by an amount \([\Delta \phi]\), the change \( \Delta \lambda_i \) in the \( \ell \)th eigenvalue of the secular equation is given by (53)

\[
[L^T] [\Delta \phi] [L] = \Delta \lambda_i
\]

(5.47)

and since \([\phi]\) is linearly related to \([\phi]\),

\[
[L^T] [Z] [L] [\Delta \phi] = \Delta \lambda_i
\]

(5.48)

Comparing Eq. 5.39 and Eq. 5.48 we have,

\[
[L^T] [Z] [L] = [J^T]
\]

(5.49)
A typical element of the Jacobian $[J^\phi]$ matrix is given by

$$J^\phi_{\ell k} = \sum_{i=1}^{n_s} \sum_{j=1}^{n_s} \ell_{\ell i} \ell_{j \ell} Z_{nk}$$

(5.50)

where $n$ is given by Eq. 5.18.

**POTENTIAL ENERGY DISTRIBUTION**

The potential energy is given by

$$2V = [Q]^T [L]^T [F] [L] [Q]$$

(5.51)

The contribution to the potential energy by the normal vibration is given by

$$2V_{\ell} = [L_{\ell}]^T [F] [L_{\ell}] = \lambda_{\ell}$$

(5.52)

or

$$\lambda_{\ell} = [L_{\ell}]^T [Z] [L_{\ell}] [\phi]$$

(5.53)

$$\lambda_{\ell} = [J^\phi_{\ell}] [\phi]$$

(5.54)

The contribution of each $\phi_k$, the Urey-Bradley force constant, to the potential energy is given by

$$\lambda_{\ell k} = (J^\phi_{\ell k}) \phi_k$$

(5.55)

Expressing Eq. 5.54 in non-matrix notation

$$\lambda_{\ell} = \sum_{k=1}^{n_{\phi}} J^\phi_{\ell k} \phi_k$$

(5.56)

If $\lambda_{\ell}$ is normalized to unity, we have

$$\frac{1}{\lambda_{\ell}} \sum_{k=1}^{n_{\phi}} J^\phi_{\ell k} \phi_k = 1$$

(5.57)

Each element $\frac{1}{\lambda_{\ell}} J^\phi_{\ell k} \phi_k$ is an element of the potential energy distribution matrix $[V^\phi]$. Writing $[\phi]$ in diagonal form $[\phi^*]$, from Eq. 5.57, we have,

$$[V^\phi] = [J^{\phi^*}] [\Lambda]^{-1} [\phi^*]$$

(5.58)

The number of force constants to be determined in CSCIF and CSF$_2$ was nine and six respectively for the in-plane vibrations. The number of observed in-plane frequencies are five for both the molecules. In order to follow the least squares procedure, the number of frequencies should be greater than $n$, the force constants to be determined, or at least be equal to $n$. In the case of CSF$_2$, the force constants $H_{FCF}$ and $F_{FF}$ could be transferred from the similar molecule COF$_2$. (19)

In order to see the variation of the Urey-Bradley force constants as a
function of the constrained force constants, the latter were varied over a reasonable range and the other force constants calculated. Each of these sets reproduced the experimental values. Table 5.6 through Table 5.9 give these sets of force constants. Fig. 5.1 to Fig. 5.4 show the variation graphically.

Columns 4 in Tables 5.7 and 5.9 give the set for which two of the force constants, $H_{\text{FCF}}$ and $F_{\text{FF}}$ were constrained for $\text{CSF}_2$ and $H_{\text{ClCCl}}$ and $F_{\text{ClCl}}$ for $\text{CSCl}_2$. All the other sets were calculated with only one constrained value. Table 5.10 shows the calculated and observed in-plane fundamental frequencies for $\text{CSF}_2$ and $\text{CSCl}_2$.

**FORCE CONSTANTS FOR THIOCARBONYL CHLOROFLUORIDE.**

The $[G]$ matrix elements for $\text{CS}^{35}\text{ClF}$ and $\text{CS}^{37}\text{ClF}$ were calculated as mentioned earlier. For obtaining the $[F]$ matrix elements, it is necessary to know nine UBF constants even with the simplification, $F' = -0.1F$. Hence, some of the force constants were transferred from $\text{CSF}_2$, $\text{CSCl}_2$ and $\text{COCIF}$. Table 5.11 gives the $[Z]$ matrix elements for $\text{CSClF}$, which has a dimension of $(21, 9)$ since there are nine UBF constants. Tables 5.12 and 5.13 give the force constants and the calculated frequencies respectively. The process of reiteration to make the observed and calculated values agree was done in a way similar to that described before.

**CALCULATION OF THE DISTRIBUTION OF POTENTIAL ENERGY IN UREY-BRADLEY SPACE.**

The distribution of vibrational potential energy in the Urey-Bradley space was calculated by evaluating the matrix $[V^\phi]$ in Eq. 5.58. Tables 5.14, 5.15 and 5.16 show the contribution of the Urey-Bradley force constants to the normal modes of vibration of $\text{CSF}_2$, $\text{CSCl}_2$ and $\text{CSFCl}$ respectively. Figures 5.5, 5.6 and 5.7 give the pictorial representation of the normal co-ordinates for these three molecules. Fig. 5.8 and Fig. 5.9 show schematically the various steps that are carried out by the computer for the force constant calculations. A time sharing GE-235 computer was used and the data were fed and received
### TABLE 5.6

The set of force-constants obtained for different constrained values of $H_{\text{FCF}}$ in CSF$_2$. (in $\text{md/Å}$)

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<th>4</th>
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</thead>
<tbody>
<tr>
<td>$K_{\text{CS}}$</td>
<td>6.27</td>
<td>6.256</td>
<td>6.240</td>
<td>6.206</td>
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<tr>
<td>$K_{\text{CF}}$</td>
<td>4.495</td>
<td>4.508</td>
<td>4.522</td>
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<td>$H_{\text{FCF}}$</td>
<td>0.45</td>
<td>0.475</td>
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<tr>
<td>$H_{\text{SCF}}$</td>
<td>0.1345</td>
<td>0.114</td>
<td>0.094</td>
<td>0.097</td>
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<tr>
<td>$F_{\text{SF}}$</td>
<td>1.038</td>
<td>1.082</td>
<td>1.12</td>
<td>1.163</td>
</tr>
<tr>
<td>$F_{\text{FF}}$</td>
<td>1.056</td>
<td>0.991</td>
<td>0.93</td>
<td>0.878</td>
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</table>
### TABLE 5.7

The set of force constants obtained for different constrained values of $F_{FF}$ in $CSF_2$. (in $md/\AA$)

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<tr>
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<td>6.295</td>
<td>6.292</td>
<td>6.275</td>
<td>6.27</td>
</tr>
<tr>
<td>$K_{CF}$</td>
<td>4.465</td>
<td>4.447</td>
<td>4.427</td>
<td>4.483</td>
</tr>
<tr>
<td>$H_{FCF}$</td>
<td>0.388</td>
<td>0.363</td>
<td>0.342</td>
<td>0.425</td>
</tr>
<tr>
<td>$H_{SCF}$</td>
<td>0.183</td>
<td>0.211</td>
<td>0.241</td>
<td>0.157</td>
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<tr>
<td>$F_{SF}$</td>
<td>0.896</td>
<td>0.812</td>
<td>0.722</td>
<td>0.969</td>
</tr>
<tr>
<td>$F_{FF}$</td>
<td>1.243</td>
<td>1.343</td>
<td>1.443</td>
<td>1.143</td>
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</table>
The set of force constants obtained for different constrained values of $H_{ClCCl}$ in $CSCl_2$ (in $\text{md Å}$)

<table>
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<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$K_{CS}$</td>
<td>5.34</td>
<td>5.293</td>
<td>5.269</td>
</tr>
<tr>
<td>$K_{CCl}$</td>
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<td>2.366</td>
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<tr>
<td>$H_{ClCCl}$</td>
<td>0.06</td>
<td>0.1</td>
<td>0.12</td>
</tr>
<tr>
<td>$H_{SCl}$</td>
<td>0.108</td>
<td>0.096</td>
<td>0.091</td>
</tr>
<tr>
<td>$F_{SCl}$</td>
<td>0.657</td>
<td>0.687</td>
<td>0.701</td>
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<tr>
<td>$F_{ClCCl}$</td>
<td>0.819</td>
<td>0.729</td>
<td>0.686</td>
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</table>
TABLE 5.9

The set of force constants obtained for different constrained values of $F_{\text{ClCl}}$ in CCl$_2$. (in $\text{md/Å}$)

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</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{CS}}$</td>
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<td>5.392</td>
<td>5.327</td>
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<td>$K_{\text{CCl}}$</td>
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<td>2.342</td>
<td>2.317</td>
<td>2.352</td>
</tr>
<tr>
<td>$H_{\text{C1CCl}}$</td>
<td>0.14</td>
<td>0.052</td>
<td>0.012</td>
<td>0.08</td>
</tr>
<tr>
<td>$H_{\text{SCl}}$</td>
<td>0.086</td>
<td>0.110</td>
<td>0.126</td>
<td>0.101</td>
</tr>
<tr>
<td>$F_{\text{SCl}}$</td>
<td>0.715</td>
<td>0.649</td>
<td>0.612</td>
<td>0.6808</td>
</tr>
<tr>
<td>$F_{\text{ClCl}}$</td>
<td>0.64</td>
<td>-0.84</td>
<td>0.94</td>
<td>0.74</td>
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</table>
Fig. 5.1. The variation of the Urey-Bradley force constants of CSF$_2$, as a function of the constrained force constant H$_{FF}$.

Fig. 5.2. The variation of the Urey-Bradley force constants of CSF$_2$, as a function of F$_{FF}$.

Fig. 5.3. The variation of the Urey-Bradley force constants of CSCl$_2$, as a function of H$_{ClCl}$.

Fig. 5.4. The variation of the Urey-Bradley force constants of CSCl$_2$, as a function of F$_{ClCl}$. 
FIG. 5.1

FIG. 5.2
### TABLE 5.10

Calculated and observed in-plane fundamental frequencies of CSF$_2$ and CS$^{35}$Cl$_2$ (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Frequency</th>
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<th>CSF$_2$</th>
<th>OBS.-CAL.</th>
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<td>OBS.</td>
<td>CAL.</td>
<td>OBS.</td>
</tr>
<tr>
<td>$a_1$ $\nu_1$</td>
<td>1139</td>
<td>1139</td>
<td>1368</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>502</td>
<td>501.3</td>
<td>787</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>292</td>
<td>288.4</td>
<td>526</td>
</tr>
<tr>
<td>$b_2$ $\nu_5$</td>
<td>818</td>
<td>818.3</td>
<td>1189</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>292</td>
<td>292</td>
<td>417</td>
</tr>
<tr>
<td>n</td>
<td>$K_1$</td>
<td>$K_2$</td>
<td>$K_3$</td>
</tr>
<tr>
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<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
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<td>2</td>
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<tr>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td></td>
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</tr>
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<td>7</td>
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<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
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<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial force constants</td>
<td>Source of the constrained force constants</td>
<td>Final calculated force constants</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------</td>
<td></td>
</tr>
<tr>
<td>1 $K_{CS}$</td>
<td></td>
<td>5.739</td>
<td></td>
</tr>
<tr>
<td>2 $K_{CF}$</td>
<td></td>
<td>3.936</td>
<td></td>
</tr>
<tr>
<td>3 $K_{CCl}$</td>
<td></td>
<td>2.6324</td>
<td></td>
</tr>
<tr>
<td>4 $HFCl$</td>
<td>$COClF^{a)}$</td>
<td>0.321</td>
<td></td>
</tr>
<tr>
<td>5 $HFSCF$</td>
<td>$CSF_2^{b)}$</td>
<td>0.157</td>
<td></td>
</tr>
<tr>
<td>6 $HC1CS$</td>
<td>$CSCl_2^{b)}$</td>
<td>0.101</td>
<td></td>
</tr>
<tr>
<td>7 $F_{FCI}$</td>
<td></td>
<td>0.761</td>
<td></td>
</tr>
<tr>
<td>8 $FSF$</td>
<td>$CSF_2^{b)}$</td>
<td>0.9697</td>
<td></td>
</tr>
<tr>
<td>9 $F_{SCl}$</td>
<td>$CSCl_2^{b)}$</td>
<td>0.6808</td>
<td></td>
</tr>
</tbody>
</table>

a) From reference (10).

b) Values transferred from the previous calculation.
<table>
<thead>
<tr>
<th>Frequency</th>
<th>OBS.</th>
<th>$\text{CS}^{35}\text{ClF}$</th>
<th>$\text{CS}^{37}\text{ClF}$</th>
<th>$\Delta\nu$</th>
<th>Calculated Isotope Shift (cm$^{-1}$) $\text{CS}^{35}\text{ClF} - \text{CS}^{37}\text{ClF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>1257.7</td>
<td>1257.6</td>
<td>1257.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1014.7</td>
<td>1014.7</td>
<td>1013.9</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>611.9</td>
<td>611.8</td>
<td>608.3</td>
<td>0.1</td>
<td>3.5</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>427.1</td>
<td>426.9</td>
<td>423.3</td>
<td>0.2</td>
<td>3.6</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>322.6</td>
<td>323.5</td>
<td>320.4</td>
<td>0.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>
### TABLE 5.14

Potential Energy Distribution of Thiocarbonylfluoride in Urey-Bradley Space (in percent).

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>K(_{CS})</th>
<th>K(_{CF})</th>
<th>H(_{FCF})</th>
<th>H(_{SCF})</th>
<th>F(_{SF})</th>
<th>F(_{FF})</th>
</tr>
</thead>
<tbody>
<tr>
<td>787</td>
<td>19.23</td>
<td>41.31</td>
<td>0.44</td>
<td>0.10</td>
<td>19.69</td>
<td>19.19</td>
</tr>
<tr>
<td>526</td>
<td>7.32</td>
<td>0.12</td>
<td>30.84</td>
<td>7.03</td>
<td>21.33</td>
<td>33.30</td>
</tr>
<tr>
<td>1368</td>
<td>57.72</td>
<td>28.64</td>
<td>8.21</td>
<td>1.87</td>
<td>0</td>
<td>3.50</td>
</tr>
<tr>
<td>417</td>
<td>0</td>
<td>2.66</td>
<td>0</td>
<td>31.61</td>
<td>65.61</td>
<td>0.04</td>
</tr>
<tr>
<td>1189</td>
<td>0</td>
<td>89.97</td>
<td>0</td>
<td>5.52</td>
<td>5.88</td>
<td>1.41</td>
</tr>
<tr>
<td>[(\psi)'(\text{md}/\text{Å})]</td>
<td>6.27</td>
<td>4.483</td>
<td>0.425</td>
<td>0.157</td>
<td>0.969</td>
<td>1.143</td>
</tr>
</tbody>
</table>
TABLE 5.15

Potential Energy Distribution of Thiocarbonylchloride in Urey-Bradley Space (in percent).

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>$K_{CS}$</th>
<th>$K_{CCl}$</th>
<th>$H_{ClCCl}$</th>
<th>$H_{ClCS}$</th>
<th>$F_{ClS}$</th>
<th>$F_{ClCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>502</td>
<td>9.65</td>
<td>48.60</td>
<td>0.41</td>
<td>0.24</td>
<td>27.82</td>
<td>13.24</td>
</tr>
<tr>
<td>292</td>
<td>1.06</td>
<td>0.63</td>
<td>14.43</td>
<td>8.50</td>
<td>17.35</td>
<td>58.00</td>
</tr>
<tr>
<td>1139</td>
<td>77.89</td>
<td>15.65</td>
<td>1.96</td>
<td>1.16</td>
<td>0.79</td>
<td>2.52</td>
</tr>
<tr>
<td>292</td>
<td>0</td>
<td>5.97</td>
<td>0</td>
<td>26.55</td>
<td>67.58</td>
<td>-0.11</td>
</tr>
<tr>
<td>818</td>
<td>0</td>
<td>83.99</td>
<td>0</td>
<td>9.65</td>
<td>8.03</td>
<td>-1.68</td>
</tr>
<tr>
<td>$[\phi]$ (md/Å)</td>
<td>5.327</td>
<td>2.352</td>
<td>0.08</td>
<td>0.101</td>
<td>0.6808</td>
<td>0.74</td>
</tr>
<tr>
<td>Frequency (cm$^{-1}$)</td>
<td>$K_{CS}$</td>
<td>$K_{CF}$</td>
<td>$K_{CCl}$</td>
<td>$H_{FCl}$</td>
<td>$H_{SF}$</td>
<td>$H_{CIs}$</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------</td>
<td>---------</td>
<td>----------</td>
<td>----------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>1257.7</td>
<td>63.16</td>
<td>22.23</td>
<td>4.02</td>
<td>6.81</td>
<td>0.59</td>
<td>0.83</td>
</tr>
<tr>
<td>1014.7</td>
<td>5.87</td>
<td>50.42</td>
<td>28.22</td>
<td>1.01</td>
<td>4.85</td>
<td>1.96</td>
</tr>
<tr>
<td>611.9</td>
<td>14.06</td>
<td>9.72</td>
<td>32.72</td>
<td>1.56</td>
<td>3.23</td>
<td>0.77</td>
</tr>
<tr>
<td>427.1</td>
<td>1.47</td>
<td>0.31</td>
<td>11.13</td>
<td>25.53</td>
<td>8.11</td>
<td>0.27</td>
</tr>
<tr>
<td>322.6</td>
<td>1.43</td>
<td>0.56</td>
<td>2.82</td>
<td>6.88</td>
<td>7.52</td>
<td>17.36</td>
</tr>
<tr>
<td>$\phi$ (md/Å)</td>
<td>5.739</td>
<td>3.936</td>
<td>2.6324</td>
<td>0.321</td>
<td>0.157</td>
<td>0.101</td>
</tr>
</tbody>
</table>
Fig. 5.5. Normal Co-Ordinate Diagrams of Thiocarbonyl Difluoride, \( \text{S} \text{F} \text{F} \).

Fig. 5.6. Normal Co-Ordinate Diagrams of Thiocarbonyl Dichloride, \( \text{S} \text{C} \text{Cl} \text{Cl} \).

Fig. 5.7. Normal Co-Ordinate Diagrams of Thiocarbonyl Chlorofluoride, \( \text{S} \text{C} \text{Cl} \text{F} \).
FIG. 5.5

- $786 \text{ cm}^{-1}$
- $1368 \text{ cm}^{-1}$
- $527 \text{ cm}^{-1}$
- $1189 \text{ cm}^{-1}$
- $417 \text{ cm}^{-1}$
FIG. 5.6
FIG. 5.7
FIGURE 5.8

COMPUTER PROGRAM FOR FORCE-CONSTANT CALCULATION OF CS\textsubscript{12} OR CSF\textsubscript{2}.

\[
\begin{align*}
[F] & = [Z][\phi] \\
[U] & = [U][F][U]^T \\
\left[\Lambda^e\right]^{-1} & = [B][B]^T[2] \\
\left[\Lambda^e\right]^{-1}[\phi^*] \\
\end{align*}
\]

OMIT COLUMNS OF \([J^e_k]\) CORRESPONDING TO THE CONSTRAINED UBF CONSTANTS

\[
\begin{align*}
[v^e_\lambda] & = [\Lambda^e]^{-1}[J^e_k][\phi^*] \\
\end{align*}
\]

\[
\begin{align*}
[e] & = [\Lambda^e] - [\Lambda^e] \\
[J^e_k][e] \\
[J^e_k][e][J^e_k]^T \\
[J^e_k][e][J^e_k]^T \left[ [L^e_k][w][J^e_k]^T \right]^{-1} \\
[\Delta^e][e][J^e_k][e][J^e_k]^T \left[ [L^e_k][w][J^e_k]^T \right]^{-1} \\
\end{align*}
\]

\[
[\phi] + [\Delta^e]
\]
FIGURE 5.9
COMPUTER PROGRAM FOR FORCE-CONSTANT CALCULATION OF CSCIF.

[Diagram with mathematical expressions and flowchart]
through the No. 33 Automatic Sending and Receiving Teletypewriter on Teletype-writer Exchange Service. Approximately three hundred seconds of central processing time was required for each least-square refinement.

THE NORMAL CO-ORDINATE DIAGRAM.

The normal co-ordinate diagrams were obtained from the normalized eigenvector matrix \([L]\), which relates the internal co-ordinates \(S_i\) and the normal co-ordinates \(Q_k\).

\[
[S] = [L][Q]
\]  
(5.59)

In order to obtain the normal co-ordinates in terms of cartesian co-ordinates, the elements of \([B]\) matrix, which give the internal co-ordinates in terms of cartesian co-ordinates, were obtained.

\[
[S] = [B][q]
\]  
(5.60)

Eq. 5.26 gives the internal co-ordinates \(S_i\), in terms of \(s_{\alpha \beta}^\prime\) and \(\mathbf{p}_\alpha\) vectors

\[
\mathbf{p}_\alpha = \Delta x_{\alpha} \mathbf{i} + \Delta y_{\alpha} \mathbf{j} + \Delta z_{\alpha} \mathbf{k}
\]  
(5.61)

The \(s_{\alpha \beta}^\prime\) vectors are obtained in terms of unit vectors \(\mathbf{e}_{\alpha \beta}\) along the bond from atoms \(\alpha\) to \(\beta\). The \(s_{\alpha \beta}^\prime\) vectors for the end atoms and the apex atom are defined in Fig. 5.10 and given in Table 5.17. (21)

A vector \(\mathbf{e}_{\alpha \beta}\) is defined along the direction from atom \(\alpha\) to \(\beta\), given by

\[
\mathbf{e}_{\alpha \beta} = \left( x_{\beta} - x_{\alpha} \right) \mathbf{i} + \left( y_{\beta} - y_{\alpha} \right) \mathbf{j} + \left( z_{\beta} - z_{\alpha} \right) \mathbf{k}
\]  
(5.62)

The unit vector \(\mathbf{e}_{\alpha \beta}\) is then given by

\[
\mathbf{e}_{\alpha \beta} = \mathbf{e}_{\alpha \beta} / \left( \mathbf{e}_{\alpha \beta} \cdot \mathbf{e}_{\alpha \beta} \right)^{\frac{1}{2}}
\]  
(5.63)

The elements of the \([B]\) matrix are the coefficients of each cartesian co-ordinate obtained from Eq. 5.62, 5.63 and 5.26.

In order to obtain the internal co-ordinates in terms of mass-weighted cartesian co-ordinates, given by

\[
[S] = [D][\eta]
\]  
(5.64)

The \([D]\) matrix elements are obtained by the relation

\[
[D] = [B][m^2]^{\frac{1}{2}}^{-1}
\]  
(5.65)

where \([m^2]\) is a diagonal matrix with \(m_i^2\) as elements. Hence, the normal co-
Expressions for the $\vec{s}_{tk}$

**Internal Co-ordinate $S_t$**

$\Delta r_{\phi \rho}$

$\Delta \phi_{\rho \rho \rho}$

\[
\begin{align*}
\vec{s}_{td} &= \frac{\cos(\phi_{\rho \rho \rho}) \cdot \vec{e}_{\rho \rho} - \vec{e}_{\rho \rho}}{r_{\rho \rho} \cdot \sin \phi_{\rho \rho \rho}} \\
\vec{s}_{t\rho} &= (r_{\rho \rho} - r_{\rho \rho} \cos(\phi_{\rho \rho \rho})) \vec{e}_{\rho \rho} + (r_{\rho \rho} - r_{\rho \rho} \cos(\phi_{\rho \rho \rho})) \vec{e}_{\rho \rho} \\
\vec{s}_{tY} &= \frac{\cos(\phi_{\rho \rho \rho}) \cdot \vec{e}_{\rho \rho} - \vec{e}_{\rho \rho}}{r_{\rho \rho} \cdot \sin \phi_{\rho \rho \rho}}
\end{align*}
\]
ordinates $Q$'s are obtained in terms of the cartesian displacements by the relation,

$$[L]^{-1} [B][m^2]^{-1} [q] = [Q]$$  \hspace{1cm} (5.66)

In the case of CSF$_2$ and CSCL$_2$, we have

$$[L]^{-1} [U][B][m^2]^{-1} [q] = [Q]$$  \hspace{1cm} (5.67)

where $[Q]^{-1}$ is the symmetrized eigenvector matrix and $[U]$ the transformation matrix from internal co-ordinates to symmetry co-ordinates. The inverse transformation from internal co-ordinates $[S]$ to the normal co-ordinates is given by the relation,

$$([F]G - [P] \lambda \ [L]^{-1}) = 0$$  \hspace{1cm} (5.68)

The elements of the $[L]$ matrix for CSF$_2$, CSCL$_2$ and CSFCI are listed in Tables 5.18, 5.19 and 5.20 respectively.
TABLE 5.18
Elements of \([L]\) matrix for CSF\(_2\).

<table>
<thead>
<tr>
<th></th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_5)</th>
<th>(\nu_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta_{\text{CS}})</td>
<td>+.318578</td>
<td>+.105741</td>
<td>-.043700</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\delta_{\text{CF}(2)})</td>
<td>-.187675</td>
<td>+.129584</td>
<td>+.004818</td>
<td>+.289177</td>
<td>+.017435</td>
</tr>
<tr>
<td>(\delta_{\text{CF}(1)})</td>
<td>-.187675</td>
<td>+.129584</td>
<td>+.004818</td>
<td>-.289177</td>
<td>-.017435</td>
</tr>
<tr>
<td>(\delta_{\text{SCF(1)}})</td>
<td>+.349801</td>
<td>+.046810</td>
<td>+.260994</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\delta_{\text{SCF(2)}})</td>
<td>-.174900</td>
<td>-.023405</td>
<td>-.130497</td>
<td>+.261040</td>
<td>-.218827</td>
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</table>

Elements of symmetrised \([L]\) matrix CSF\(_2\).

<table>
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<tr>
<th></th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_5)</th>
<th>(\nu_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta_{\text{CS}})</td>
<td>+.318578</td>
<td>+.105741</td>
<td>-.043700</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\delta_{\text{CF}(2)})</td>
<td>-.265413</td>
<td>+.183260</td>
<td>+.006814</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\delta_{\text{CF}(1)})</td>
<td>+.428418</td>
<td>+.057330</td>
<td>+.319652</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\delta_{\text{FCF}})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+.408938</td>
<td>+.024657</td>
</tr>
<tr>
<td>(\delta_{\text{SCF(1)}})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+.369167</td>
<td>-.309468</td>
</tr>
</tbody>
</table>
### TABLE 5.19
Elements of $[L]$ matrix for CSCL₂.

<table>
<thead>
<tr>
<th></th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_5$</th>
<th>$\nu_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta r_{CS}$</td>
<td>+.334369</td>
<td>+.051796</td>
<td>-.009882</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta r_{CC1(1)}$</td>
<td>-.159544</td>
<td>+.123679</td>
<td>+.008128</td>
<td>+.265418</td>
<td>+.025317</td>
</tr>
<tr>
<td>$\delta r_{CC1(2)}$</td>
<td>-.159544</td>
<td>+.123679</td>
<td>+.008128</td>
<td>-.265418</td>
<td>-.025317</td>
</tr>
<tr>
<td>$\delta \theta_{C1CC1}$</td>
<td>+.248501</td>
<td>-.050171</td>
<td>+.170308</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta \theta_{SCCL(1)}$</td>
<td>-.124250</td>
<td>+.025085</td>
<td>-.085154</td>
<td>+.257365</td>
<td>-.152717</td>
</tr>
<tr>
<td>$\delta \theta_{SCCL(2)}$</td>
<td>-.124250</td>
<td>+.025085</td>
<td>-.085154</td>
<td>-.257365</td>
<td>+.152717</td>
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</tbody>
</table>

Elements of symmetrised $[L]$ matrix for CSCL₂

<table>
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<tr>
<th></th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_5$</th>
<th>$\nu_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta r_{CS}$</td>
<td>+.334369</td>
<td>+.051796</td>
<td>-.009882</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta r_{CC1(1)}$</td>
<td>-.225629</td>
<td>+.174908</td>
<td>+.011495</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta r_{CC1(2)}$</td>
<td>+.304351</td>
<td>-.061447</td>
<td>+.208583</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta \theta_{C1CC1}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+.375358</td>
<td>+.035803</td>
</tr>
<tr>
<td>$\delta \theta_{SCCL(1)}$</td>
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<td>0</td>
<td>0</td>
<td>+.363969</td>
<td>-.215975</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$</td>
<td>$\nu_2$</td>
<td>$\nu_3$</td>
<td>$\nu_4$</td>
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<td>$\delta r_{CS}$</td>
<td>-0.320219</td>
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<td>+0.073504</td>
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<td>+0.012399</td>
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<td>-0.278747</td>
<td>+0.073818</td>
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<td>-0.009401</td>
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<tr>
<td>$\delta r_{CCl}$</td>
<td>+0.119397</td>
<td>+0.255010</td>
<td>+0.165564</td>
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<td>+0.025730</td>
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<td>$\delta r_{ClCF}$</td>
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<td>$\delta r_{FCS}$</td>
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<td>-0.203710</td>
<td>-0.077091</td>
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<td>+0.193007</td>
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DISCUSSION

The Urey-Bradley force constants for the three thiocarbonyl halides studied, are shown in Table 5.21. It is difficult to attach great significance to small variations found in some of the bending and non-bonded interaction force constants because they depend on the nature of the constraints used. However, it is interesting to note the marked changes in the stretching force constants with halogen substitution which do not appear to depend very much on the value of the constrained force constants. In contrast with the variation of 2% of $K_{CO}$ in carbonyl halides, the value of $K_{CS}$ varies by about 18% between $CSF_2$ and $CSCl_2$.$^{(5,19)}$

The changes in the value of the stretching force constants can be understood in terms of the different possible bond structures that could be written for the thiocarbonyl halides. The possible resonance structures for $CSCl_2$ are

$$\begin{align*}
&\text{I}_a \quad \text{I}_b \quad \text{I}_c \\
&\begin{array}{c}
\text{Cl}^+ \quad \text{C-S} \leftrightarrow \\
\text{Cl} \quad \text{Cl}^- \\
\end{array}
\end{align*}$$

Similarly, the structures that can be written for $CSClF$ are

$$\begin{align*}
&\text{II}_a \quad \text{II}_b \quad \text{II}_c \\
&\begin{array}{c}
\text{F}^- \quad \text{C = S} \leftrightarrow \\
\text{Cl}^+ \quad \text{Cl}^- \\
\end{array}
\end{align*}$$

For $CSF_2$, structures equivalent to that of $I_a$ and $I_b$ of $CSCl_2$ would make very little contribution to the overall structure since it would require the presence of a positive charge on the fluorine atom and the prominent structure will be

$$\begin{align*}
&\text{III}_a \\
&\begin{array}{c}
\text{F}^- \quad \text{C = S} \\
\text{F}^- \\
\end{array}
\end{align*}$$

The work of Jensen$^{(24)}$ has shown from the infrared spectra of thioamides and amides that the structure of the form $X^- - \text{C} = \text{NH}_2^+$ has greater weight than the structure $X = \text{C} - \text{NH}_2$ when $X=S$, where as the reverse is true when $X=O$.

The LCAO/MO calculation by Richards$^{(25)}$ has also demonstrated that back
<table>
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<th>CSF$_2$</th>
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<tr>
<td>$K_{CS}$</td>
<td>6.27</td>
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<td>$K_{CF}$</td>
<td>4.483</td>
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<td>$K_{CCl}$</td>
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<td>$H_{FF}$</td>
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<tr>
<td>$H_{ClCl}$</td>
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<td>0.08</td>
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<tr>
<td>$H_{SF}$</td>
<td>0.158</td>
<td>0.158</td>
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<tr>
<td>$H_{SCl}$</td>
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<td>0.101</td>
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<td>$H_{FCl}$</td>
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<td>$F_{FF}$</td>
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<td>$F_{ClCl}$</td>
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<td>0.74</td>
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<tr>
<td>$F_{SF}$</td>
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<td>0.97</td>
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<tr>
<td>$F_{SCl}$</td>
<td></td>
<td>0.681</td>
<td>0.681</td>
</tr>
<tr>
<td>$F_{FCl}$</td>
<td></td>
<td>0.761</td>
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donation should be easier to CS than to CO group, in a complex formation with an inorganic ion. Thus, the ionic structures like $I_a$ and $I_b$ play a greater role in thiocarbonyl compounds than in carbonyl compounds. Now, the increase in the value of $K_{CS}$ from $CSCl_2$ to $CSF_2$ can be related to the extent of the contribution of ionic structures to the overall structure. The structures $I_a$ and $I_b$ together make a greater contribution in $CSCl_2$ than structure $II_b$ in $CSClF$ which in turn makes a greater contribution than the ionic structures in $CSF_2$. Thus, the bond order for CS will be lowest in $CSCl_2$ because of the presence of structures $I_a$ and $I_b$ and the value of $K_{CS}$ will be lower than either in $CSClF$ or $CSF_2$.

The variations of $K_{CCl}$ and $K_{CF}$ are more difficult to understand. One possible explanation for the increase in the value of $K_{CCl}$ from $CSCl_2$ to $CSClF$ is the presence of the structure $II_a$ in $CSClF$ which is not present in $CSCl_2$. Similarly, the increase in the value of $K_{CF}$ in $CSF_2$ over $CSClF$ can be attributed to the fact that in $CSF_2$, the structure $III_a$ is predominant and a structure similar to $II_a$ with a partial negative charge on the original F, does not exist.
REFERENCES


GENERAL REFERENCES
