CHAPTER III

INTRAMOLECULAR FORCE FIELD OF CARBONYL CYANIDE

ABSTRACT

The general quadratic valence force field has been applied to Carbonyl cyanide, using molecular kinetic constants and Wilson's F.G. matrix method. The potential constants, compliance constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants are reported here for the molecule for the first time. The character of the bonds is briefly discussed. It is also shown that the present method leads to acceptable sets of characteristic constants for Carbonyl cyanide.

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3.1 INTRODUCTION

Carbonyl cyanide is a planar molecule belonging to the $C_{2v}$ point group with $C - C = N$ chain being linear. Trammer and Weirzchowski (1, 2) have reported Raman and infrared spectra of this compound. They have also determined an approximate set of force constants on the basis of general valence force field assuming bond lengths from theoretical values (2). The geometrical parameters of $CO(CN)_2$ have been reported by Westerkamp (3) from microwave data. Prochorow et al (4) reinvestigated the infrared spectrum of $CO(CN)_2$ and made some refinements on the fundamental frequencies. Yet, another independently published assignment which seems to be more reasonable is available in the literature due to Bates et al (5).

The most interesting aspect about $CO(CN)_2$ is the presence of the $C \equiv N$ bonds and one $C = O$ bond which are responsible for the distinct properties of the compound. Unnikrishnan Nayar et al (6) have used the general valence and Urey-Bradley force field for the determination of the force constants of Carbonyl cyanide.

The most general quadratic valence field using molecular kinetic constants has been attempted in the present investigation to obtain characteristic constants of this molecule. The values of the molecular constants obtained in the present work are satisfactory and confirms
Fig. 1

Internal co-ordinates and the orientation of the case of

$\text{C}_2 \text{(C N)}_2$ molecule
the validity of the method. Further the vibrational - rotational coupling constants and the rotational distortion constants of \( \text{CO(CN)}_2 \) are available for the first time in the present work.

3.2 THEORETICAL CONSIDERATIONS

3.2.1 Structure, symmetry coordinates and frequency distribution

The \( \text{CO(CN)}_2 \) molecule of the \( WX(YZ)_2 \) model is characterized by twelve fundamental frequencies distributed among the four species as

\[
5 A_1 + 4 B_1 + 1 A_2 + 2 B_2
\]

The geometry and the internal coordinates of the molecule are shown in figure 1. The symmetry coordinates used in the present investigation are given below. (6).

Symmetry coordinates

\( A_1 \) species:

\[
S_1 = \frac{(\Delta R_1 + \Delta R_2)}{\sqrt{2}}
\]

\[
S_2 = \Delta d
\]

\[
S_3 = \frac{(\Delta r_1 + \Delta r_2)}{\sqrt{2}}
\]

\[
S_4 = r \Delta \zeta
\]

\[
S_5 = \sqrt{(Rr/2)} \left( \Delta \beta_1 + \Delta \beta_2 \right)
\]
B\textsubscript{1} species:

\begin{align*}
S_6 &= (\Delta R_1 - \Delta R_2)/\sqrt{2} \\
S_7 &= (\Delta r_1 - \Delta r_2)/\sqrt{2} \\
S_8 &= \sqrt{(rd/2)} (\Delta \gamma_1 - \Delta \gamma_2) \\
S_9 &= \sqrt{(Rr/2)} (\Delta \phi_1 - \Delta \phi_2)
\end{align*}

\begin{align*}
A\textsubscript{2} \text{ species:} \\
S_{10} &= \sqrt{(Rr/2)} (\Delta \sigma_1 - \Delta \sigma_2) \\
B\textsubscript{2} \text{ species:} \\
S_{11} &= \sqrt{(Rr/2)} (\Delta \sigma_1 + \Delta \sigma_2) \\
S_{12} &= \sqrt{(rd)} \Delta \phi
\end{align*}

where C=\text{N} Bond distance = R, \\
C-C Bond distance = r, \\
C=\text{O} Bond distance = d, \\
C\overset{\wedge}{C}C Bond angle = \phi, \\
C\overset{\wedge}{C}O Bond angle = \gamma, \\
C\overset{\wedge}{C}N Bond angle = \beta, \\

The out of plane C=\text{O} \overset{\bigcirc}{\bigcirc} bending coordinate \overset{\bigcirc}{\bigcirc} = \phi, \\
and the out of plane C-C\overset{\bigcirc}{\bigcirc}N bending coordinate \overset{\bigcirc}{\bigcirc} = \delta.
3.2.2 F matrix:

The most general quadratic potential function has been considered to obtain the F matrix elements in the present investigation. The following are the F matrix elements for the species concerned.

$A_1$ species:

$F_{11} = f_R + f_{RR}$

$F_{22} = f_d$

$F_{33} = f_r + f_{rr}$

$F_{44} = r^2 f_o$

$F_{55} = 2 C_1^2 (f_\beta + f_{\beta\beta})$

$F_{12} = \sqrt{2} f_{dR}$

$F_{13} = f_{RR} + f'_{RR}$

$F_{14} = \sqrt{2} r f_{R\alpha}$

$F_{15} = \sqrt{2} C_1 (f_{R\beta} + f'_{R\beta})$

$F_{23} = \sqrt{2} f_{dR}$

$F_{24} = r f_{d\alpha}$

$F_{25} = 2 C_1 f_{d\beta}$

$F_{34} = \sqrt{2} r f_{R\alpha}$

$F_{35} = \sqrt{2} C_1 (f_{\beta} + f'_{\beta})$

$F_{45} = 2 C_1 r f_{o\alpha\beta}$
\[ B_1 \text{ species:} \]
\[ F_{66} = f_R - f_{RR} \]
\[ F_{77} = f_r - f_{rr} \]
\[ F_{88} = c_2^2 (f_y - f_{yy}) \]
\[ F_{99} = 2c_1^2 (f_\beta - f_{\beta\beta}) \]
\[ F_{67} = f_{Rr} - f'_{Rr} \]
\[ F_{68} = c_2 (f_{Ry} - f'_{Ry}) \]
\[ F_{69} = \sqrt{2} c_1 (f_{R\beta} - f'_{R\beta}) \]
\[ F_{78} = c_2 (f_{ry} - f'_{ry}) \]
\[ F_{79} = \sqrt{2} c_1 (f_{r\beta} - f'_{r\beta}) \]
\[ F_{89} = \sqrt{2} c_1 c_2 (f_{\beta\gamma} - f'_{\beta\gamma}) \]

\[ A_2 \text{ species:} \]
\[ F_{10 \ 10} = 2 c_1^2 (f_\delta - f_{\delta\delta}) \]

\[ B_2 \text{ species:} \]
\[ F_{11 \ 11} = 2 c_1^2 (f_\phi + f_{\delta\phi}) \]
\[ F_{12 \ 12} = c_2^2 f_\phi \]
\[ F_{11 \ 12} = 2 c_1 c_2 f_\delta f_\phi \]

where \[ c_1 = \sqrt{Rr/2} \]
\[ c_2 = \sqrt{r_d} \]

\( f_\delta, f_r, f_R \) are the stretching force constants of the
C = O bond, C - C bond and C = N bond respectively, while
\( f_\alpha, f_\beta, f_\gamma, f_\delta, \) and \( f_\phi \) are the bending force constants. The interaction force constants are \( f_{RR}, f_{rr}, f_{\alpha\beta}, f_{\delta\phi}, \) etc.

3.2.3 G matrix:

On the basis of Wilson's formula (7) using \( S_k^t \) vectors
the G matrix for a general \( WX(YZ)_2 \) type molecule has been constructed. The same results have been also arrived at by using the orthogonal B matrix using the relation

\[
G = B \mu B^t
\]

where \( \mu \) is the diagonal matrix of reciprocal masses of the atoms. The B matrix is given in Table 1. The evaluated G matrix elements are given below.

\( A_1 \) species:

\[
\begin{align*}
G_{11} &= \mu_Y + \mu_Z \\
G_{22} &= \mu_W + \mu_X \\
G_{33} &= (1 + \cos \alpha C) \mu_X + \mu_Y \\
G_{44} &= \frac{2(1 - \cos \alpha C)}{r^2} \mu_X + \frac{2}{r^2} \mu_Y \\
G_{55} &= \frac{2}{r^2} \mu_X + \left( \frac{1}{r^2} + \frac{1}{R^2} \right)^2 \mu_Y + \frac{1}{R^2} \mu_Z \\
G_{12} &= 0 \\
G_{13} &= -\mu_Y
\end{align*}
\]
\[ G_{14} = 0. \]
\[ G_{15} = -\left( \frac{1}{r} + \frac{1}{R} \right) \cos \left( \frac{\alpha_c}{2} \right) \mu_y - \frac{1}{R} \cos \left( \frac{\alpha_c}{2} \right) \mu_z \]
\[ G_{23} = \sqrt{2} \cos \gamma \mu_x \]
\[ G_{24} = -\left[ \frac{1 - \cos \alpha_c}{r} \cdot 2 \cos \gamma \right] \mu_x \]
\[ G_{25} = -\frac{\sqrt{2}}{r} \mu_x \]
\[ G_{34} = -\frac{\sqrt{2}}{r} \sin \alpha \mu_x \]
\[ G_{35} = \frac{2}{r} \cos \left( \frac{\alpha_c}{2} \right) \mu_x + \left( \frac{1}{r} + \frac{1}{R} \right) \cos \left( \frac{\alpha_c}{2} \right) \mu_y \]
\[ G_{45} = -2 \frac{\sqrt{2}}{r} \left( \frac{1 - \cos \alpha_c}{r} \right) \cos \left( \frac{\alpha_c}{2} \right) \mu_x \]
\[ \quad + \frac{\sqrt{2}}{r} \sin \alpha \left( \frac{1}{r} + \frac{1}{R} \right) \cos \left( \frac{\alpha_c}{2} \right) \left( \cos \alpha_c - 1 \right) \mu_y \]

\( B_1 \) species:

\[ G_{66} = \mu_y + \mu_z \]
\[ G_{77} = (1 - \cos \alpha_c) \mu_x + \mu_y \]
\[ G_{88} = \frac{1}{\sigma^2} \left( 1 - \cos \alpha_c \right) \mu_w + \left( \frac{r - d \cos \gamma}{r \sin \gamma} \right)^2 \left( \frac{r - d \cos \gamma}{r \sin \gamma} \right) \mu_x \]
\[ G_{99} = \left( \frac{1}{r} + \frac{1}{R} \right)^2 \mu_y + \frac{1}{R^2} \mu_z \]
\[ G_{67} = -\mu_y \]
\[ G_{68} = 0 \]
\[ G_{69} = -\left( \frac{1}{r} + \frac{1}{R} \right) \cos \left( \frac{\alpha_0}{2} \right) \mu_Y - \frac{1}{R} \cos \left( \frac{\angle_0}{2} \right) \mu_Z \]

\[ G_{78} = -\sqrt{2} \frac{(r - d \cos \gamma)}{r \sin \gamma} (1 - \cos \alpha) \mu_X \]

\[ G_{79} = \left( \frac{1}{r} + \frac{1}{R} \right) \cos \left( \frac{\alpha_0}{2} \right) \mu_Y \]

\[ G_{89} = 0 \]

\( A_2 \) species:

\[ G_{10\, 10} = \left( \frac{1}{r} + \frac{1}{R} \right)^2 \mu_Y + \frac{1}{R^2} \mu_Z \]

\( B_2 \) species:

\[ G_{11\, 11} = \frac{2}{r^2} \mu_X + \left( \frac{1}{r} + \frac{1}{R} \right)^2 \mu_Y + \frac{1}{R^2} \mu_Z \]

\[ G_{12\, 12} = \frac{1}{d^2} (\mu_W + \mu_X) \]

\[ G_{11\, 12} = 0 \]

where \( W, X, Y, Z \) correspond to O, C, C and N atoms respectively.

3.2.4 \( K \) matrix:

The kinetic energy matrix elements are calculated from the \( G \) matrix. The kinetic constants are the vibrational inertial coefficients. The symmetrised kinetic constant elements are related to the valence kinetic elements (given below).
\[ k_R = \frac{(k_{11} + k_{66})}{2} \]
\[ k_{RR} = \frac{(k_{11} - k_{66})}{2} \]
\[ k_d = k_{22} \]
\[ k_r = \frac{(k_{33} + k_{77})}{2} \]
\[ k_{rr} = \frac{(k_{33} - k_{77})}{2} \]
\[ k_{dr} = \frac{k_{23}}{\sqrt{2}} \]
\[ k_{RR} = \frac{(k_{13} + k_{67})}{2} \]
\[ k_{RR} = \frac{(k_{13} - k_{67})}{2} \]
\[ k_{dR} = \frac{k_{12}}{\sqrt{2}} \]
\[ k_{\alpha \alpha} = k_{44}/x^2 \]
\[ k_{\beta} = \frac{(k_{55} + k_{99})}{4} c_1^2 \]
\[ k_{\beta \beta} = \frac{(k_{55} - k_{99})}{4} c_1^2 \]
\[ k_{\alpha \beta} = k_{45}/2 c_1 r \]
\[ k_{\gamma \gamma} = k_{88}/c_2^2 \]
\[ k_{\beta \gamma} = k_{89}/\sqrt{2} c_1 c_2 \]
\[ k_{d} = \frac{(k_{10} + k_{11} + k_{11})}{4} c_1^2 \]
\[ k_{\delta \delta} = \frac{(k_{11} - k_{10} + k_{10})}{4} c_1^2 \]
\[ k_{\phi} = k_{12}/c_2^2 \]
3.2.5 Role of kinetic constants:

The kinetic constants have been advantageously employed to obtain acceptable sets of molecular constants in polyatomic molecules. The secular equation is solved in a straightforward manner using the constraint

\[ F_{ij}/F_{jj} = \frac{k_{ij}}{k_{jj}} \quad (i \neq j) \]

The theoretical aspects have been discussed in detail recently \((8, 9)\). This method has been applied by Mohan et al. \((10 - 13)\) earlier in different types of polyatomic molecules concerning lower order problems. The method
has been applied successfully to 5 x 5 vibrational problem in the present work.

3.2.6 Compliance constants:

The compliance constants are invariant to the choice of coordinates and they can be used to measure bond strengths. They have been evaluated by Decius (14) method. The compliance matrix \( N \) is related to the force constant matrix \( F \) as \( N = F^{-1} \).

3.2.7 Vibrational mean amplitudes:

The symmetrized mean square amplitude elements have been calculated using Cyvin's relation (15)

\[
\Xi = L \Delta L^t
\]

where \( L \) is the normal coordinate, transformation matrix.

The valence mean square amplitude elements are given below:

\[
\begin{align*}
\sigma_{RR} & = (\Xi_{11} + \Xi_{66})/2 \\
\sigma_{d} & = \Xi_{22} \\
\sigma_{r} & = (\Xi_{33} + \Xi_{77})/2 \\
\sigma_{rr} & = (\Xi_{33} - \Xi_{77})/2 \\
\sigma_{dr} & = \Xi_{23}/\sqrt{2} \\
\sigma_{Rr} & = (\Xi_{13} + \Xi_{67})/2
\end{align*}
\]
\[
\begin{align*}
\sigma_{\text{Rr}}' &= (\Sigma_{13}^1 - \Sigma_{67}^1)/2 \\
\sigma_{\text{dR}} &= \Sigma_{12}/\sqrt{2} \\
\sigma_{\alpha} &= \Sigma_{4+}/r^2 \\
\sigma_\beta &= (\Sigma_{55}^1 + \Sigma_{99}^1)/4 \, C_1^2 \\
\sigma_{\beta'\beta'} &= (\Sigma_{55}^1 - \Sigma_{99}^1)/4 \, C_1^2 \\
\sigma_{\alpha'\beta'} &= \Sigma_{45}/2 \, C_1 \, r \\
\sigma_{\gamma} - \sigma_{\gamma'} &= \Sigma_{88}/C_2^2 \\
\sigma_{\rho'} - \sigma_{\rho''} &= \Sigma_{89}/\sqrt{2} \, C_1 \, C_2 \\
\sigma_{\delta} &= (\Sigma_{10}^{'}10 + \Sigma_{11}^{'}11)/4 \, C_1^2 \\
\sigma_{\delta'\delta'} &= (\Sigma_{11}^{'}11 - \Sigma_{10}^{'}10)/4 \, C_1^2 \\
\sigma_{\phi} &= \Sigma_{12}/C_2^2 \\
\sigma_{\rho} &= \Sigma_{12}^{'}12/2 \, C_1 \, C_2 \\
\sigma_{\gamma} = \Sigma_{14}^{}/\sqrt{2} \, r \\
\sigma_{\beta} &= (\Sigma_{15}^{'}15 + \Sigma_{69}^{'}69)/2 \sqrt{2} \, C_1 \\
\sigma_{\beta} &= (\Sigma_{15}^{'}15 - \Sigma_{69}^{'}69)/2 \sqrt{2} \, C_1 \\
\sigma_{\alpha} &= \Sigma_{24}^{}/r \\
\sigma_{\beta} &= \Sigma_{25}^{}/2 \, C_1 \\
\sigma_{\gamma} &= \Sigma_{34}^{}/\sqrt{2} \, r
\end{align*}
\]
3.2.8 Coriolis coupling constants:

According to Jahn's rule (16), the Coriolis coupling constants in the present case arise from the couplings:

- $A_1 \times B_2$ and $B_1 \times A_2$ corresponding to $\zeta_x^x$
- $A_1 \times B_1$ and $B_2 \times A_2$ corresponding to $\zeta_y^y$
- $A_1 \times A_2$ and $B_1 \times B_2$ corresponding to $\zeta_z^z$

The Coriolis matrix elements ($C^C_{ij}$) are obtained by the vector method of Meal and Polo (17), and they are given below.

Coupling $A_1 \times B_2$:

\[
C_{11}^{x} = -\left[ \frac{\mu_y (\frac{1}{r} + \frac{1}{R}) + \mu_z}{r} \right] c \alpha
\]

\[
C_{21}^{x} = \frac{\mu_x \sqrt{2}}{r}
\]

\[
C_{31}^{x} = \left[ \frac{2 \mu_x + \mu_y (\frac{1}{r} + \frac{1}{R})}{r} \right] c \alpha
\]

\[
C_{41}^{x} = -\left[ \frac{2 \mu_x + \mu_y (\frac{1}{r} + \frac{1}{R})}{r} \right] \sqrt{2} c \alpha \left( \frac{1 - \cos \alpha}{r \sin \alpha} \right)
\]
\[ C_{11}^x = \frac{2 \mu_x + \mu_y (1 + \frac{1}{R})^r + \frac{\mu_z}{R^2}}{r^2} \]

\[ C_{12}^x = 0 \]

\[ C_{21}^x = - (\mu_w + \mu_x) \]

\[ C_{31}^x = \frac{\sqrt{2} \mu_x c \alpha}{d} \]

\[ C_{41}^x = - \frac{2 \mu_x (1 - \cos \alpha)}{r \sin \alpha} \]

\[ C_{51}^x = \frac{\sqrt{2} \mu_x}{r d} \]

**Coupling B_1 \times A_2:**

\[ C_{610}^x = - \left[ \frac{\mu_x (1 + \frac{1}{R}) + \frac{\mu_z}{R}}{r} \right] c \alpha \]

\[ C_{710}^x = \mu_y \left( \frac{1 + \frac{1}{R}}{R} \right) c \alpha \]

\[ C_{810}^x = 0 \]

\[ C_{910}^x = \mu_y \left( \frac{1 + \frac{1}{R}}{R} \right) + \frac{\mu_z}{R} \]

**Coupling A_1 \times B_1:**

\[ C_{16}^y = C_{17}^y = C_{18}^y = 0 \]
\[
\begin{align*}
C_{19}^y &= - \left[ \mu_y \left( \frac{1}{r} + \frac{1}{R} \right) + \frac{\mu_z}{R} \right] s \alpha \\
C_{26}^y &= C_{29}^y = 0 \\
C_{27}^y &= \sqrt{2} \mu_x s \alpha \\
C_{28}^y &= - \left[ \sqrt{2} \mu_x + 2 \mu_x \frac{(r - d \cos \gamma)}{r \sin \gamma} \right] s \alpha \frac{d}{d}
\end{align*}
\]

\[
\begin{align*}
C_{36}^y &= 0 \\
C_{37}^y &= - 2 \mu_x s \alpha c \alpha \\
C_{38}^y &= 2 \sqrt{2} \mu_x \frac{(r - d \cos \gamma)}{r d \sin \gamma} s \alpha c \alpha \\
C_{39}^y &= \mu_y \left( \frac{1}{r} + \frac{1}{R} \right) s \alpha \\
C_{46}^y &= - \left[ \mu_y s \alpha c \alpha \right] = \sqrt{2} \frac{r}{\sin \alpha} \\
C_{47}^y &= 2 \sqrt{2} \left[ \mu_x (1 - \cos \alpha) + \mu_y \right] s \alpha c \alpha \frac{1}{r \sin \alpha} \\
C_{48}^y &= - 4 \mu_x s \alpha c \alpha \frac{(1 - \cos \alpha)(r - d \cos \gamma)}{r^2 d \sin \alpha \sin \gamma} \\
C_{49}^y &= \sqrt{2} \frac{\mu_y s \alpha (1 + \cos \alpha)(1 + l)}{r \sin \alpha}
\end{align*}
\]
\[ \mu_Y \left( \frac{1}{r} + \frac{1}{R} \right) + \frac{\mu_Z}{R} \right] s_0 \]

\[ \frac{\mu_X}{r} + \frac{\mu_Y (1 + \frac{1}{r})}{R} \right] s_0 \]

\[ \sqrt{2} \frac{\mu_X (r - d \cos \gamma)}{r^2 d \sin \gamma} s_0 \]

\[ 0 \]

Coupling \( A_1 \times A_2 \):

\[ \mu_Y \left( \frac{1}{r} + \frac{1}{R} \right) s_0 \]

\[ \mu_Y \left( \frac{1}{r} + \frac{1}{R} \right) s_0 \]

\[ \sqrt{2} \frac{\mu_Y s_0 (1 + \cos \alpha) (1 + \frac{1}{r})}{r \sin \alpha} \frac{1}{r} \frac{1}{R} \]

\[ 0 \]

Coupling \( B_1 \times B_2 \):

\[ \mu_Y (\frac{1}{r} + \frac{1}{R}) s_0 \]

\[ \frac{2 \mu_X + \mu_Y (\frac{1}{r} + \frac{1}{R})}{r} \right] s_0 \]
The Coriolis coupling coefficients are calculated using the relation
\[ \tau_{\alpha} = L^{-1} \alpha (L^{-1}) \]
where \( L \) is the normal coordinate transformation matrix and \( \alpha = x, y, z \).

### 3.2.9 Centrifugal distortion constants:

From the reformulated theory of Cyvin (18), the centrifugal distortion constants are evaluated. The non-vanishing \( T_{\alpha \beta}, s \) elements in terms of the symmetry coordinates are given in Table 2. The \( t_{\alpha \beta, s} \) quantities are evaluated using the relation
\[ t_{\alpha \beta, s} = J_{\alpha \beta, s} J_{\alpha \beta, s} N_{\alpha \beta, s} \]
where \( J_{\alpha \beta, s} = G_{\alpha \beta, s}^{-1} T_{\alpha \beta, s} \)
The centrifugal distortion constants $D_j$, $D_k$, etc. are calculated from the general expressions

\[
D_j = -\left(\frac{1}{32}\right) \hbar^4 \left[ 3 \tau_{xxxx} + 3 \tau_{yyyy} + 2 (\tau_{xyy} + 2 \tau_{xyx}) \right]
\]

\[
D_k = D_j - \left(\frac{1}{4}\right) \hbar^4 \left[ \tau_{zzzz} - (\tau_{xxzz} + 2 \tau_{xz})x(\tau_{xxzz} + 2 \tau_{yz}) \right]
\]

\[
D_{jk} = -D_j - D_k - \left(\frac{1}{4}\right) \hbar^4 \tau_{zzzz}
\]

\[
R_a = -\left(\frac{1}{32}\right) \hbar^4 \left[ \tau_{xxxx} - \tau_{yyyy} + 2 (\tau_{xxzz} + 2 \tau_{zyzz}) + 2 (\tau_{yyyy} + 2 \tau_{yyzz}) \right]
\]

\[
R_b = -\left(\frac{1}{64}\right) \hbar^4 \left[ \tau_{xxxx} + \tau_{yyyy} - 2 (\tau_{xyyy} + 2 \tau_{xyxy}) \right]
\]

\[
\delta_j = -\left(\frac{1}{16}\right) \hbar^4 \left[ \tau_{xxxx} - \tau_{yyyy} \right]
\]

3.3 RESULTS AND DISCUSSIONS

The structural parameters and the vibrational frequencies used in the present investigation are given in Table 3. Table 4 presents the kinetic constants and the force constants of Carbonyl cyanide. The $C=\overset{\frown}{N}$ stretching force constant $f_R$ is $19.4143 \times 10^2$ N/m and close to the earlier values \((18.5 \times 10^2 \text{ N/m in } CO \overset{\frown}{C}N_2)\) (6), \((18.68 \times 10^2 \text{ N/m in } HC\overset{\frown}{N}, 17.92 \text{ in } F\overset{\frown}{C}N, 18.51 \text{ in } Br\overset{\frown}{C}N \text{ and } 17.88 \text{ in } C_3H\overset{\frown}{C}N(19 \text{ and } 20))]. \text{ } This high value shows the strong triple bond character as expected. The $C=O$ stretching force constant $f_d$ is $12.88 \times 10^2$ N/m. This compares well with the literature values \((11.7 \times 10^2 \text{ N/m (6) \text{ and } 12.1 \times 10^2 \text{ N/m of a pure bond of } C=O \text{ in } CO \overset{\frown}{D}_2 \text{ (21).}}\)
The most interesting value is the C - C stretching force constant $f_r$ which is $4.6402 \times 10^2$ N/m $[4.5 \times 10^2$ N/m $(6)]$. This is less than the value to be expected for an sp$^2$ - sp hybridized C - C bond $(22)$. The value of $f_{C - C}$ is $5.6272 \times 10^2$ N/m in diacetylene $(23)$. This reduction in the value of $f_r$ may be attributed to the elongated C - C bond that is 1.46 Å. Further, the inductive influence of C ≡ N group increases the effective positive charge on the central atom. This may increase the ionic character of the C - C bond which in turn reduces the value of $f_{C - C}$. The high chemical reactivity of Carbonyl cyanide is due to this weakening of the C - C bond. The bending force constants $f_{\alpha_C}$, $f_{\beta}$, $f_{\gamma}$, and $f_{\delta}$ are $0.4215$, $0.1064$, $0.2242$ and $0.1460$ (10$^2$) N/m and they agree well with the earlier values $0.385$, $0.185$, $0.174$, and $0.140$ $(6)$ 10$^2$ N/m respectively.

The compliance constants 'n' and the vibrational mean square amplitudes $\sigma$ of Carbonyl cyanide are given in Table 5. The compliance constants exhibit trends opposite to the force constants. The vibrational mean amplitudes 'l' are also provided in the same table. The values obtained in the present investigation are within the expected range. They are $l_{C \equiv N} = 0.0342$ Å, $l_C = 0 = 0.0233$ Å and $l_{C - C} = 0.0485$ Å. The present values compare well with diacetylene $(l_{C - C} = 0.0475$ Å), Carbon suboxide $(l_{C = O} = 0.0367$ Å) and Sulfur dicyanide $(l_{C \equiv N} = 0.0346$ Å) molecules. Thus, it is clear that the mean amplitudes of C ≡ N,
C = 0 and C - C bonds are characteristic.

The Coriolis coupling coefficients and the centrifugal distortion constants are presented in Table 6. The values of $\gamma_{10}$ and $\gamma_{80}$ are high, indicating the strong couplings. $\gamma$ values of allowed coupling $A_2 \times B_2$ are zero. It is because of the fact that both the species concerned are related to out of plane bendings. The centrifugal distortion constants of the molecule have been calculated using potential constants obtained in the present investigation $D_J$, $D_K$ and $D_{JK}$ values are in the expected range and they seem to be reasonable. To the author's knowledge, no experimental data seems to be available for comparing the distortion constants.

3.4 CONCLUSION

The method of kinetic constants thus is able to account for the behaviour of the chemically active Carbonyl cyanide. Further it is added that a systematic set of molecular constants is presented for this molecule for the first time.

* * *

C = 0 and C - C bonds are characteristic.
TABLE-1

B-matrix for planar \( W X(YZ)_2 \) molecule

<table>
<thead>
<tr>
<th></th>
<th>( W )</th>
<th>( X )</th>
<th>( Y_1 )</th>
<th>( Y_2 )</th>
<th>( Z_1 )</th>
<th>( Z_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x )</td>
<td>( y )</td>
<td>( z )</td>
<td>( x )</td>
<td>( y )</td>
<td>( z )</td>
</tr>
<tr>
<td>( s_1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(-b_1)</td>
<td>0</td>
<td>( b_2)</td>
</tr>
<tr>
<td>( s_2 )</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>(-1)</td>
</tr>
<tr>
<td>( s_3 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(2b_2)</td>
</tr>
<tr>
<td>( s_4 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(2b_3)</td>
</tr>
<tr>
<td>( s_5 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(-2b_5)</td>
</tr>
<tr>
<td>( s_6 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( s_7 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(-2b_1)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( s_8 )</td>
<td>(-2b_1)</td>
<td>( \frac{d}{d} )</td>
<td>0</td>
<td>0</td>
<td>( b_7)</td>
<td>0</td>
</tr>
<tr>
<td>( s_9 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(-b_5-b_6)</td>
</tr>
</tbody>
</table>
\[
\begin{bmatrix}
S_{10} & 0 & 0 & 0 & 0 & 0 & 0 & (b_5+b_6) & 0 & 0 & (-b_5-b_6) & 0 & 0 & -b_6 & 0 & 0 & b_6 & 0 \\
S_{11} & 0 & 0 & 0 & -2b_5 & 0 & 0 & (b_5b_6) & 0 & 0 & (b_5b_6) & 0 & 0 & -b_6 & 0 & 0 & -b_6 & 0 \\
S_{12} & 0 & \frac{1}{d} & 0 & 0 & -\frac{1}{d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\]

\[
b_1 = \frac{s}{\sqrt{2}} ; \quad b_2 = \frac{c}{\sqrt{2}} \\
b_3 = \frac{s}{r} ; \quad b_4 = \frac{c}{r} \\
b_5 = \frac{1}{\sqrt{(\gamma^2 r)}} ; \quad b_6 = \frac{1}{\sqrt{(\gamma^2 R)}} \\
b_7 = \frac{\sqrt{2}}{r} \frac{s (r - d \cos \gamma)}{r d \sin \gamma} \\
c = \cos(\alpha/2) ; \quad s = \sin(\alpha/2)
\]
### TABLE - 2

**$T_s$ - matrix**

<table>
<thead>
<tr>
<th></th>
<th>$S_{1}$</th>
<th>$S_{2}$</th>
<th>$S_{3}$</th>
<th>$S_{4}$</th>
<th>$S_{5}$</th>
<th>$S_{6}$</th>
<th>$S_{7}$</th>
<th>$S_{8}$</th>
<th>$S_{9}$</th>
<th>$S_{10}$</th>
<th>$S_{11}$</th>
<th>$S_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x x$</td>
<td>$2 \sqrt{2} , R c^2$</td>
<td>$2 \sqrt{2} , R$</td>
<td>$2 \sqrt{2} , R s^2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$y y$</td>
<td>$2 \sqrt{2} , R c^2$</td>
<td>$2 \sqrt{2} , R$</td>
<td>$2 \sqrt{2} , R s^2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$z z$</td>
<td>$2 \sqrt{2} , R c^2$</td>
<td>$2 \sqrt{2} , R$</td>
<td>$2 \sqrt{2} , R s^2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$y z$</td>
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<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$z x$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$x y$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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</tbody>
</table>

$s = \sin(\alpha/2) \quad c = \cos(\alpha/2)$
### Structural parameters and the vibrational frequencies of Carbonyl cyanide

<table>
<thead>
<tr>
<th>Bond distances</th>
<th>Bond angles (Ref. 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C – C)</td>
<td>1.460 Å</td>
</tr>
<tr>
<td>(C ≡ N)</td>
<td>1.156 Å</td>
</tr>
<tr>
<td>(C = O)</td>
<td>1.220 Å</td>
</tr>
</tbody>
</table>

### Vibrational frequencies (Ref. 5)

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2242, 1712, 715, 495, 127.</td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2234, 1131, 456, 244.</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>298.</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>557, 208.</td>
</tr>
</tbody>
</table>
**TABLE - 4**

Kinetic constants $k \left( 10^6 \text{ kg}^{-1} \text{ s}^{-1} \right)$ and force constants $f \left( 10^2 \text{ N/m} \right)$ of $\text{CO}$(CN)$_2$.

<table>
<thead>
<tr>
<th>Description</th>
<th>$k$</th>
<th>$f$</th>
<th>Description</th>
<th>$k$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R (C \equiv N)$</td>
<td>2.6348</td>
<td>19.4143</td>
<td>$\beta \beta^*$</td>
<td>0.6539</td>
<td>-0.0021</td>
</tr>
<tr>
<td>$d (C = O)$</td>
<td>2.1527</td>
<td>12.8844</td>
<td>$\delta \delta$</td>
<td>0.0457</td>
<td>0.1021</td>
</tr>
<tr>
<td>$r (C - C)$</td>
<td>3.2535</td>
<td>4.6402</td>
<td>$\gamma - \gamma'$</td>
<td>0.5576</td>
<td>0.4391</td>
</tr>
<tr>
<td>$RR$</td>
<td>0.4633</td>
<td>-0.7289</td>
<td>$\beta \gamma - \beta \gamma'$</td>
<td>0.0565</td>
<td>-0.0119</td>
</tr>
<tr>
<td>$rr$</td>
<td>0.1177</td>
<td>0.1777</td>
<td>$R \alpha$</td>
<td>1.2089</td>
<td>0.1946</td>
</tr>
<tr>
<td>$dr$</td>
<td>0.6161</td>
<td>0.8135</td>
<td>$R \beta$</td>
<td>0.8537</td>
<td>0.0738</td>
</tr>
<tr>
<td>$dR$</td>
<td>-0.0153</td>
<td>-0.0917</td>
<td>$d \alpha$</td>
<td>-1.1065</td>
<td>-0.1781</td>
</tr>
<tr>
<td>$Rr$</td>
<td>1.6298</td>
<td>0.0755</td>
<td>$d \beta$</td>
<td>-0.4330</td>
<td>-0.0248</td>
</tr>
<tr>
<td>$'Rr$</td>
<td>0.0719</td>
<td>-2.3229</td>
<td>$r \alpha$</td>
<td>0.2757</td>
<td>0.0444</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>2.6181</td>
<td>0.4215</td>
<td>$r \beta$</td>
<td>-0.1526</td>
<td>-0.0213</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.1675</td>
<td>0.1064</td>
<td>$'R \beta$</td>
<td>0.5299</td>
<td>0.0054</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.3422</td>
<td>0.2242</td>
<td>$'r \beta$</td>
<td>0.0106</td>
<td>0.0132</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.9513</td>
<td>0.1460</td>
<td>$R \gamma - 'R \gamma$</td>
<td>0.5395</td>
<td>0.4248</td>
</tr>
<tr>
<td>$\alpha \beta$</td>
<td>1.3229</td>
<td>0.0757</td>
<td>$R \gamma - 'r \gamma$</td>
<td>1.0859</td>
<td>0.8551</td>
</tr>
</tbody>
</table>
### Table 5

Compliance constants $n \left(10^{-2} \text{ m/N}\right)$, mean square amplitudes $\sigma \left(10^{-3} \text{ A}^2\right)$ and mean amplitude $l \left(\text{Å}\right)$ of CO(CN)$_2$

<table>
<thead>
<tr>
<th>Description</th>
<th>$n$</th>
<th>$\sigma$</th>
<th>Description</th>
<th>$n$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R(C≡N)$</td>
<td>0.0533</td>
<td>1.1689</td>
<td>$\beta\beta$</td>
<td>0.6565</td>
<td>1.5465</td>
</tr>
<tr>
<td>$d(C≡O)$</td>
<td>0.0802</td>
<td>1.5446</td>
<td>$\delta\delta$</td>
<td>-0.8984</td>
<td>-2.4988</td>
</tr>
<tr>
<td>$r(C-C)$</td>
<td>0.2878</td>
<td>2.3471</td>
<td>$\gamma_1\gamma_2$</td>
<td>1.0968</td>
<td>7.3061</td>
</tr>
<tr>
<td>$rr$</td>
<td>-0.0023</td>
<td>-0.0012</td>
<td>$\beta\gamma_1\beta\gamma_1$</td>
<td>0.1045</td>
<td>0.3445</td>
</tr>
<tr>
<td>$dr$</td>
<td>-0.0417</td>
<td>-0.4382</td>
<td>$R\alpha$</td>
<td>-0.0093</td>
<td>-0.0196</td>
</tr>
<tr>
<td>$dR$</td>
<td>-0.0161</td>
<td>-0.3721</td>
<td>$R\beta$</td>
<td>-0.0157</td>
<td>0.5319</td>
</tr>
<tr>
<td>$Rr$</td>
<td>0.0020</td>
<td>0.0188</td>
<td>$d\alpha$</td>
<td>0.0183</td>
<td>0.6131</td>
</tr>
<tr>
<td>$'Rr$</td>
<td>0.0279</td>
<td>-0.6202</td>
<td>$d\beta$</td>
<td>-0.0076</td>
<td>-0.3839</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.8763</td>
<td>2.4796</td>
<td>$r\beta$</td>
<td>0.0206</td>
<td>0.7492</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.9114</td>
<td>16.6993</td>
<td>$'R\beta$</td>
<td>0.0059</td>
<td>0.0208</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1.9741</td>
<td>9.3251</td>
<td>$'r\beta$</td>
<td>0.0288</td>
<td>0.3046</td>
</tr>
<tr>
<td>$\phi$</td>
<td>2.1584</td>
<td>9.6490</td>
<td>$R\gamma$</td>
<td>0.0005</td>
<td>0.0007</td>
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<tr>
<td>$\kappa\beta$</td>
<td>-0.6515</td>
<td>-2.2166</td>
<td>$R\gamma$</td>
<td>-0.3450</td>
<td>-2.6786</td>
</tr>
</tbody>
</table>

Mean amplitudes

$1_R = 0.0342$

$1_d = 0.0393$

$1_r = 0.0485$
**TABLE - 6**

a) Coriolis coupling coefficients and (b) centrifugal distortion constants (KHz) of CO(CN)\(_2\)

**a)**

<table>
<thead>
<tr>
<th>Coupling</th>
<th>(A_1 \times B_1)</th>
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</thead>
<tbody>
<tr>
<td>(\zeta^y)</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>0.0067</td>
</tr>
<tr>
<td>2</td>
<td>0.0154</td>
</tr>
<tr>
<td>3</td>
<td>-0.0631</td>
</tr>
<tr>
<td>4</td>
<td>0.6746</td>
</tr>
<tr>
<td>5</td>
<td>0.7907</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling</th>
<th>(A_1 \times A_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\zeta^z)</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>-0.0621</td>
</tr>
<tr>
<td>3</td>
<td>0.1374</td>
</tr>
<tr>
<td>4</td>
<td>-0.4997</td>
</tr>
<tr>
<td>5</td>
<td>-0.2704</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling</th>
<th>(A_1 \times B_2)</th>
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</thead>
<tbody>
<tr>
<td>(\zeta^x)</td>
<td>11</td>
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<tr>
<td>1</td>
<td>-0.4024</td>
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<tr>
<td>2</td>
<td>-0.4342</td>
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<tr>
<td>3</td>
<td>0.3002</td>
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<tr>
<td>4</td>
<td>-0.7187</td>
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<tr>
<td>5</td>
<td>0.4192</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling</th>
<th>(B_1 \times A_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\zeta^x)</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>0.4997</td>
</tr>
<tr>
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<td>0.3002</td>
</tr>
<tr>
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</tr>
<tr>
<td>5</td>
<td>0.4192</td>
</tr>
</tbody>
</table>

b) \(D_J = 12.6392\); \(D_K = 17.6315\); \(D_{JK} = -30.4219\)
REFERENCES

15. S. J. Cyvin, Molecular vibrations and mean square amplitudes, Amsterdam, (1968).

***