CHAPTER VIII

FORCE FIELD STUDY OF Xe O F₄

ABSTRACT

The general quadratic valence force field has been applied to the molecule Xe O F₄ of X Y Z type on the basis of C₄ᵥ point group. All the molecular constants such as potential constants, compliance constants, the vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants have been reported. The values reported in the present investigation agree quite well with the earlier reported values.

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8.1 INTRODUCTION

The tetragonal pyramidal molecules like XeOF₄, IF₅, BrF₅ and ClF₅ have been studied by various investigators (15). They have analysed both Raman and infrared spectra on the basis of C₄ᵥ point group. Nuclear magnetic shielding experiments by Gutowsky et al (6) and the investigations of Burke et al (3) and Stephenson et al (5) have confirmed a square pyramidal structure, for iodine pentafluoride (IF₅) and Bromine penta fluoride molecules.

In the case of Xenon oxy tetrafluoride molecule, the Xe – O bond distance is shorter than Xe – F distance (31). The electron diffraction studies (7) have revealed that Xe atom is slightly above the plane containing the fluorine atoms. The angle F – Xe – O is slightly greater than 90°, indicating that the repulsive effect of Xe = O is greater than that of the lone pair electron (8). Several normal coordinate treatments have previously been attempted for this molecule using general valence force field (2), Urey Bradley force field (9) and orbital valence force field (10). In the present investigation the author has employed the method of kinetic constants (11, 12) to study the force field of XeO F₄, by applying the general quadratic valence force field.
8.2 THEORETICAL CONSIDERATIONS

8.2.1 Symmetry coordinates and frequency distribution:

The tetragonal pyramidal \( \text{Xe}_4 \text{F}_4 \) molecule belonging to \( C_{4v} \) point group, has nine fundamental frequencies distributed among the species as

\[
3a_1 + 2b_1 + b_2 + 3e
\]

Of these nine modes \( a_1 \) and \( e \) are both Raman and infrared active whereas \( b_1 \) and \( b_2 \) are Raman active. The \( e \) species are doubly degenerate.

The symmetry coordinates used in the present work are the same as those given by Begun et al. (2).

8.2.2 \( F \) matrix:

The most general quadratic potential energy function is employed to obtain the force constant matrix elements of \( \text{Xe}_4 \text{F}_4 \) molecule. The \( F \) matrix elements are as follows.

\( a_1 \) species:

\[
\begin{align*}
F_{11} &= f_D \\
F_{22} &= f_d + 2f_{dd} + f_{dd}^d \\
F_{33} &= N^2 (f + 2f_f + f_f') - 4N N (f + f_f') + 2 (f_{f} + f_f') \\
&\quad + N^2 (f_f + 2f_f + f_f') \\
F_{12} &= 2f_Dd \\
F_{13} &= 2 (N_f f_D - N_f f_D) \\
F_{23} &= 2N (f + f_f') - N (f + f') + 3f_f'
\end{align*}
\]
\( b_1 \) species:

\[
F_{44} = f_d - 2f_{dd} + f'_d
\]
\[
F_{55} = f'_{\gamma} - 2f_{\gamma} + f''_{\gamma}
\]
\[
F_{45} = f_d + f'_{d\gamma}
\]

\( b_2 \) species:

\[
F_{66} = f_B - 2f_{BB} + f'_{BB}
\]

e species:

\[
F_{77} = f_d - f'_d
\]
\[
F_{88} = f'_{\gamma\gamma}
\]
\[
F_{99} = f_B - f'_{BB}
\]
\[
F_{78} = f_{d\gamma} - f'_{d\gamma}
\]
\[
F_{79} = \sqrt{2} (f_{\phi B} - f'_{\phi B})
\]
\[
F_{89} = \sqrt{2} (f_{\gamma B} - f'_{\gamma B})
\]

where \( N_1 = (1 + K^2)^{-1/2} \); \( N_2 = K (1 + K^2)^{-1/2} \)

\[
K = - \cos(\phi/2)/\sqrt{2} \cos\gamma,
\]
\[
D = (Xe - O) \text{ bond distance},
\]
\[
d = (Xe - F) \text{ bond distance},
\]
\[
\beta = (F - Xe - F) \text{ bond angle},
\]
\[
\gamma = (F - Xe - O) \text{ bond angle},
\]
\( f_d, f_D, f_B \) and \( f_\gamma \) are the stretching and bending force constants respectively, while \( f_{dd}, f_{BB} \) and \( f_{\gamma\gamma} \), etc. are the interaction force constants. The prime denotes the distant interactions.
8.2.3 G matrix:

Using the Vector $S(13)$ the G matrix is constructed.

The G matrix elements for the Xe O F$_4$ molecule are as follows.

A$_1$ species:

$G_{11} = \mu_{xe} + \mu_e$

$G_{12} = 2b \mu_{xe}$

$G_{13} = 4\xi \mu_{xe}$

$G_{22} = \mu_F + 4b^2 \mu_{xe}$

$G_{23} = 2(Xa + \xi b) \mu_F + 8\xi b \mu_{xe}$

$G_{33} = 4(X^2 + \xi^2) \mu_F + 16\xi^2 \mu_{xe}$

B$_1$ species:

$G_{44} = \mu_F$

$G_{45} = 0$

$G_{55} = p^2 \mu_F$

B$_2$ species:

$G_{66} = 4a^2 \mu_F$

E species:

$G_{77} = \mu_F + 2a^2 \mu_{xe}$

$G_{78} = -2a(q - pb) \mu_{xe}$
\[ G_{79} = -\sqrt{2} b^2 \mu_F - 2 \sqrt{2} a^2 \mu_x \]
\[ G_{88} = p^2 \mu_F + 2 (q - pb)^2 \mu_x + 2q^2 \mu_0 \]
\[ G_{99} = \sqrt{2} a \left[ pb \mu_F + 2 (q - pb) \mu_x \right] \]
\[ G_{99} = 2 \mu_F + 4a^2 \mu_x \]

where \( a = \sin \phi \); \( b = \cos \phi \);
\( p = \sqrt{(D/d)} \); \( q = \sqrt{(d/D)} \);
\[ \xi = (N_p a - N_q b); \quad \chi = -N_p pb/2 \]

8.2.4 Kinetic constants and the method of calculations:

The kinetic constants are generally referred to as the elements of Wilson's \( G^{-1} \) matrix. The secular equation relating to the potential constants are solved by the method of kinetic constants which provides the required number of additional data through the symmetry kinetic constants and the corresponding symmetry force constants i.e. \( F_{ij}/F_{jj} = K_{ij}/K_{jj} \) (i<j).

The \( k \) matrix elements are related exactly in the same manner as the \( F \) matrix elements.

8.2.5 Compliance constants:

Compliance constants are evaluated by Decius method (14).

8.2.6 Mean square amplitudes:

The mean square amplitude matrix elements are obtained using the normal coordinate transformation matrix.
L from the relation \( \Sigma = L \Delta \Sigma' \). The valence mean square amplitude elements are related to the symmetrized mean square amplitude elements as follows.

\[
\begin{align*}
\sigma_D &= \Sigma_{11} \\
\sigma_d &= (\Sigma_{22} + \Sigma_{44} + 2 \Sigma_{77})/4 \\
\sigma_p &= \frac{(\Sigma_{66} + \Sigma_{99}) + \sigma_{\beta\beta}}{2} \\
\sigma_y &= (\Sigma_{55} + \Sigma_{88})/2 \\
\sigma_{dd} &= (\Sigma_{22} - \Sigma_{44})/4 \\
\sigma_{\gamma\gamma}' &= (\Sigma_{22} + \Sigma_{44} - 2 \Sigma_{77})/4 \\
\sigma_{Dd} &= \Sigma_{12}/2 \\
\sigma_{\gamma\beta}' &= (\Sigma_{55} - \Sigma_{88})/2 \\
\sigma_{\gamma\beta} &= \Sigma_{89}/\sqrt{2} \\
\sigma_{d\gamma} &= -\sigma_{d\gamma}' = (\Sigma_{45} + \Sigma_{78})/2 \\
\sigma_{d\beta} &= \frac{(\Sigma_{23} + \Sigma_{79})/2}{2N_1} + \frac{\Sigma_{12}}{\sqrt{2}} \\
\sigma_{d\beta}' &= \frac{(\Sigma_{23} + \Sigma_{79})/2}{2N_1} - \frac{\Sigma_{12}}{\sqrt{2}} \\
\sigma_{\beta\beta} &= \frac{1}{4} \left[ \Sigma_{33} + 2 \sqrt{2} \frac{N_1 N_2 \Sigma_{89} - N_2^2 \Sigma_{55}}{N_1^2} - \Sigma_{66} \right]
\end{align*}
\]
The non bonded mean square amplitudes are given by the following expressions.

\[ \sigma_p (Y....Z) = \rho^{-2} \left[ A^2 \sigma_D^2 + B^2 \sigma_d^2 + 2 A B \sigma_{dd} + 2 A \epsilon a \sigma_{dy} + 2 B \epsilon a \sigma_{dy} + 2 \rho \epsilon a \sigma_{dy} \right] \]

\[ \sigma_q (Y....Y) = 2s^2 (\sigma_d^2 + \sigma_{dd}^2) + 4sc \sigma_{dp}^2 + c^2 \sigma_p^2 \]

\[ \sigma_r (Y....Y) = 2s^2 (\sigma_d^2 + \sigma_{dd}^2) + 4qab (\sigma_{dy}^2 + \sigma_{dy}^2) + 2q^2b^2 (\sigma_{dy}^2 + \sigma_{dy}^2) \]

where:

- \( s = \sin(\beta/2) \)
- \( c = \cos(\beta/2) \)
- \( a = \sin \gamma \)
- \( b = \cos \gamma \)
- \( p = \sqrt{D/d} \)
- \( q = \sqrt{d/D} \)
- \( \epsilon^2 = \frac{Dd}{D} \)
- \( A = (D - bd) \)
- \( B = (d - bD) \)

8.2.7 Coriolis coupling constants:

The following types of interactions arise among the vibrational species:

- \( a_1 \times e, b_1 \times e, b_2 \times e, b_1 \times b_2 \) and \( e \times e \)

The first three types possess rotation about \( x \) and \( y \) axes and the last two about \( z \) axis. The non-vanishing Coriolis matrix elements \( C^{OE} \) calculated by the Vector method (16) are listed below:

- \( a_1 \times e (C^X) \)

\[ C_{17} = - a \mu X_e \]

\[ C_{18} = (q - pb) \mu X_e + q \mu_0 \]

\[ C_{19} = \sqrt{2} a \mu X_e \]
\[ C_{27} = -2ab \mu_Xe \]
\[ C_{28} = -\frac{p}{2} \mu_F + 2b(q - pb) \mu_Xe \]
\[ C_{29} = 2\sqrt{2}ab \mu_Xe \]
\[ C_{37} = (x_b - \xi a) \mu_F - 4a \xi \mu_Xe \]
\[ C_{38} = -p(xa + \xi b) \mu_F + 4\xi(q - pb) \mu_Xe \]
\[ C_{39} = -\sqrt{2}(x_b - \xi a) \mu_F + 4\sqrt{2}\xi a \mu_Xe \]
\[ b_1 \times e (C^x) \]
\[ C_{47} = 0 \]
\[ C_{43} = -\frac{p}{2} \mu_F \]
\[ C_{49} = -\sqrt{2}ab \mu_F \]
\[ C_{57} = \frac{p}{2} \mu_F \]
\[ C_{58} = 0 \]
\[ C_{59} = \frac{b}{\sqrt{2}}(a^2 - b^2) \mu_F \]
\[ b_2 \times e (C^x) \]
\[ C_{67} = -ab \mu_F \]
\[ C_{68} = pa^2 \mu_F \]
\[ C_{69} = \sqrt{2}ab \mu_F \]
Using these elements the zeta elements are evaluated from the relation $\zeta^{\alpha} = \mathbf{I}^{-1} \mathbf{C}^{\alpha} (\mathbf{I}^{-1})^T$.

8.2.8 Centrifugal distortion constants:

With the reformulated theory of Cyvin et al. (17), the $T_{\alpha \beta s}$ matrix is worked out. The non vanishing elements to $T_{\alpha \beta s}$ matrix are provided in Table 1. From the $T$ matrix, the matrix elements and hence the distortion constants $\tau$ are evaluated.

8.3 RESULTS AND DISCUSSION

The structural parameters and the vibrational frequencies employed in the present work are taken from Willet et al. (18). The kinetic constants, potential constants
and the compliance constants are presented in Table 2. It is observed that the Xe - F bond is only half as strong as the Xe - O bond, which is consistent with Rundle 3e - 4e type bonding. The bending force constant $f_B$ is found to be more than the bending force constant $f_Y$.

The compliance constants are a measure of bond strength and exhibit trends opposite to that of the potential constants. Table 3 brings out the mean square amplitudes and mean amplitudes of vibration. A comparison with electron diffraction data shows a good agreement between the calculated and experimental values.

Table 4 presents the Coriolis coupling coefficients and the centrifugal distortion constants. The coupling coefficients obey the quadratic sum rules. In addition, the following relation is also satisfied.

$$I_{77}^Z + I_{88}^Z + I_{99}^Z = I_{zz}/2 I_{xx}$$

where $I_{zz}$ and $I_{xx}$ are the moments of inertia about the axes $z$ and $x$.

The centrifugal distortion constants are in the expected range, and $D_{JK}$ is negative as in most of the molecules.
8.4 CONCLUSION

The molecular constants of Xe O F$_4$ obtained in the present investigation have been compared with the experimental or literature values wherever possible. The close fit of the present values of the vibrational mean amplitudes to the corresponding observed values clearly establishes the role of kinetic constants in the understanding of molecular dynamics.

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<table>
<thead>
<tr>
<th>TABLE 1</th>
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<tr>
<td>$T_5$ matrix elements for Xe O F$_4$</td>
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<table>
<thead>
<tr>
<th>$T$</th>
<th>$xx$</th>
<th>$yy$</th>
<th>$zz$</th>
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<tbody>
<tr>
<td>$T_1$</td>
<td>2D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_2$</td>
<td>2$d(1 + b^2)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_3$</td>
<td>4$a^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_4$</td>
<td>2$da^2$</td>
<td></td>
<td></td>
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<tr>
<td>$T_5$</td>
<td>2$dab$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_6$</td>
<td>4$da^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_7a$</td>
<td>2$2dab$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_8a$</td>
<td>$pd(a^2 - b^2) + qD$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_9a$</td>
<td>$2\sqrt{2}dab$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_7b$</td>
<td>2$2dab$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_8b$</td>
<td>$pd(a^2 - b^2) + qD$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_9b$</td>
<td>$2\sqrt{2}dab$</td>
<td></td>
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<tr>
<td>TABLE - 2</td>
<td></td>
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<tr>
<td>---</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetic constants, potential constants and compliance constants of Xe O F₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>d</td>
<td>Md</td>
<td>Dd</td>
</tr>
<tr>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>D</td>
<td>d</td>
<td>dd</td>
<td>γ</td>
</tr>
<tr>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>D</td>
<td>d</td>
<td>dd</td>
<td>γ</td>
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<tr>
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</table>

<p>| Kinetic constants | 2.4661 | 0.0147 | 16.6612 | 17.7087 | 0.1598 |</p>
<table>
<thead>
<tr>
<th>k(10⁻²⁶kg⁻¹)</th>
<th>2.8873</th>
<th>-0.0011</th>
<th>2.1750</th>
<th>17.9642</th>
<th>0.4385</th>
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<tr>
<td>Potential constants</td>
<td>7.7631</td>
<td>0.0173</td>
<td>1.1978</td>
<td>1.0667</td>
<td>0.1003</td>
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<tr>
<td>f(10⁻²N/m)</td>
<td>3.3837</td>
<td>0.2308</td>
<td>0.4911</td>
<td>1.6779</td>
<td>0.1259</td>
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<td>---</td>
</tr>
<tr>
<td>Compliance constants</td>
<td>0.1293</td>
<td>-0.0007</td>
<td>5.1606</td>
<td>2.5726</td>
<td>0.0849</td>
</tr>
<tr>
<td>n(10⁻²m/N)</td>
<td>0.2950</td>
<td>-0.0085</td>
<td>2.1496</td>
<td>3.2785</td>
<td>0.1550</td>
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(Ref. 10) - 0.0065 - 0.0413
(Ref. 10) - 0.1078 - 0.0413
(Ref. 10) - 0.0065 - 0.0413
(Ref. 10) - 0.1078 - 0.0413
<table>
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<tr>
<th>$\sigma_d$</th>
<th>$\sigma_\beta$</th>
<th>$\sigma_{dp}$</th>
<th>1.3026</th>
<th>1.9511</th>
<th>0.0082</th>
<th>0.0364</th>
<th>0.1332</th>
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<td>$\sigma_d'$</td>
<td>$\sigma_{dp}$</td>
<td>$\sigma_{dp}'$</td>
<td>26.1434</td>
<td>10.4832</td>
<td>7.9048</td>
<td>10.0972</td>
<td>3.0018</td>
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<tr>
<td>$\sigma_{dd}'$</td>
<td>$\sigma_{dp}$</td>
<td>$\sigma_{dp}'$</td>
<td>0.5634</td>
<td>1.0334</td>
<td>0.2428</td>
<td>0.2428</td>
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<td>-</td>
</tr>
<tr>
<td>$\sigma_{dd}''$</td>
<td>$\sigma_{dp}$</td>
<td>$\sigma_{dp}'$</td>
<td>0.0361</td>
<td>0.0442</td>
<td>0.0702</td>
<td>0.0803*</td>
<td>0.0608</td>
<td>0.0610*</td>
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* Electron diffraction data (20)
**TABLE 4**

Coriolis coupling constants of Xe O F₄

<table>
<thead>
<tr>
<th>Coupling</th>
<th>Zeta elements</th>
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<tbody>
<tr>
<td>a₁ x e</td>
<td>( \zeta_{17}^x = -0.1150 )</td>
</tr>
<tr>
<td></td>
<td>( \zeta_{18}^x = 0.6108 )</td>
</tr>
<tr>
<td></td>
<td>( \zeta_{19}^x = 0.0831 )</td>
</tr>
<tr>
<td>b₁ x e</td>
<td>( \zeta_{47}^x = 0.0021 )</td>
</tr>
<tr>
<td></td>
<td>( \zeta_{48}^x = -0.2419 )</td>
</tr>
<tr>
<td></td>
<td>( \zeta_{49}^x = 0.0810 )</td>
</tr>
<tr>
<td>b₂ x e</td>
<td>( \zeta_{67}^x = 0.0271 )</td>
</tr>
<tr>
<td>b₁ x b₂</td>
<td>( \zeta_{46}^z = 0.9978 )</td>
</tr>
<tr>
<td>e x e</td>
<td>( \zeta_{77}^z = 0.2224 )</td>
</tr>
<tr>
<td></td>
<td>( \zeta_{78}^z = -0.1174 )</td>
</tr>
<tr>
<td></td>
<td>( \zeta_{79}^z = 0.9621 )</td>
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Centrifugal distortion constants (KHz) of Xe O F₄

<table>
<thead>
<tr>
<th>D_J</th>
<th>D_K</th>
<th>D_JK</th>
<th>R_5</th>
<th>R_6</th>
<th>( \delta_j )</th>
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<tr>
<td>0.5292</td>
<td>0.4220</td>
<td>-0.8645</td>
<td>0.0000</td>
<td>0.1437</td>
<td>0.0000</td>
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REFERENCES

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