CHAPTER-V
VIBRATIONAL ANALYSIS OF SOME MIXED BORON HALIDES

Abstract

The kinetic constant method has been used along with the Wilson's F-G matrix method to evaluate the force constants of some planar $XYZ_2$ molecules belonging to $C_{2v}$ symmetry. These force constants have been used to evaluate the other molecular constants namely vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants. The values obtained in the present investigation agree well with the literature values.
5.1 Introduction

This chapter gives a brief account of the investigation of the molecular constants of six molecules of planar \( \text{XYZ}_2 \) structure. Many authors have already investigated about the structure, spectra and molecular constants of planar \( \text{XYZ}_2 \) type molecules. As with boron halides, their monosubstituted derivatives have been fully studied. All the compounds where \( Z \) is hydrogen or deuterium and \( Y \) is F,Cl (or) Br have been investigated by Lynds and coworkers (1,2,3) and some of the mixed halides have been studied by Lindemann and Wilson (4) and Goubeau (5). The vibrational spectra of boron halides have been studied by Müller et al (6). A more complete study of boron halides has recently appeared (7). Lindemann et al (4) have also evaluated the force constants using a general harmonic force field. Meisigseh (8) and Toyki (9) have calculated the force constants of boron halides using Urey-Bradley force field. Wolfe et al (7) have determined the force constants of all the binary mixtures of boron halides by transferring the force constants evaluated for pure boron halides. Further they have found that the transfer of valence force constants give better coincidence with the observed frequencies than the transfer of symmetry force constants. Nagarajan et al (10) have
reported the vibrational mean amplitudes of boron halides by assuming $C^{2v}$ point group. Ford and Orville-Thomas (11) have calculated the force constants of boron halides and also reported the redundancy constraints for this type of molecules.

The purpose of the present investigation is to establish the role of kinetic constants in the evaluation of molecular constants of mixed boron halides. Here the kinetic constants have been advantageously used to evaluate the force constants and other molecular constants of mixed boron halides. The results indicate the importance of kinetic constants employed in the analysis of molecular vibrations.

5.2 Theoretical considerations

5.2.1 Structure and normal modes of vibration

The structure, bond angles and bond distances of the planar $X Y Z_2$ type molecules together with the orientation of the principal axes is shown in fig. 1. These $X Y Z_2$ planar type molecules belong to $C^{2v}$ point group and hence has six non-degenerate normal modes of vibrations which are classified as

$$
\Gamma = 3A_1 + 2B_1 + B_2
$$
5.2.2 **Symmetry coordinates**

The symmetry elements relating to this point group are the same as used by Oka and Morino (12) and Ford and Orville-Thomas (11) and are given below:

\[ S_1(\alpha_1) = \Delta D \]

\[ S_2(\alpha_1) = \left(\frac{1}{2}\right)^{\frac{1}{2}} \left[ \Delta d_1 + \Delta d_2 \right] \]

\[ S_3(\alpha_1) = \left(\frac{1}{2}\right)^{\frac{1}{2}} \Delta \alpha \left[ \Delta \mu_1 - \Delta \mu_2 \right] \]

\[ S_r(\alpha_1) = \left(\frac{1}{2}\right)^{\frac{1}{2}} \Delta \mu \left[ \Delta \nu_1 + \Delta \nu_2 \right] \equiv 0 \]

\[ S_4(B_1) = \left(\frac{1}{2}\right)^{\frac{1}{2}} \left[ \Delta d_1 - \Delta d_2 \right] \]

\[ S_5(B_1) = \left(\frac{1}{2}\right)^{\frac{1}{2}} \Delta \nu \left[ \Delta \nu_1 - \Delta \nu_2 \right] \]

\[ S_6(B_2) = \Delta \delta . \]

The internal coordinates used in framing the symmetry coordinates are defined as follows:

\( \Delta D \) is the change in \( X-Y \) bond distance

\( \Delta d \)'s are the changes in \( X-Z \) bond distances

\( \Delta \alpha \) is the change in \( ZXZ \) bond angle

\( \Delta \nu \)'s are the changes in \( YXZ \) bond angles

\( \Delta \delta \) is the change in the angle relating to the out of plane bending mode.
FIG. I. THE STRUCTURE AND NOMENCLATURE OF THE PARAMETERS AND THE ORIENTATION OF THE PRINCIPAL AXES OF XYZ$_2$ TYPE MOLECULES.
Potential energy expression

The most general quadratic potential energy function written in terms of internal coordinates is,

\[
2V = f_D (\Delta d)^2 + f_d \left[ (\Delta d_1)^2 + (\Delta d_2)^2 \right]
\]

\[
+ 2f_D \left[ (\Delta d) (\Delta d_1 + \Delta d_2) \right]
\]

\[
+ 2f_d \left[ (\Delta d_1) (\Delta d_2) \right] + d^2 f_\alpha (\Delta \alpha)^2
\]

\[
+ D_d f_\beta (\Delta \beta_1)^2 + (\Delta \beta_2)^2
\]

\[
+ 2d (Dd)^{1/2} f_{\alpha \beta} \left[ (\Delta \alpha)(\Delta \beta_1 + \Delta \beta_2) \right]
\]

\[
+ 2D_d f_{\alpha \beta} \left[ (\Delta \alpha)(\Delta \beta_2) \right] + 2d f_D \left[ (\Delta D)(\Delta \alpha) \right]
\]

\[
+ 2D_d^{1/2} f_{D \beta} \left[ (\Delta D)(\Delta \beta_1 + \Delta \beta_2) \right]
\]

\[
+ 2d f_{\beta \alpha} \left[ (\Delta d_2 + \Delta \alpha_2) \Delta \sigma \right]
\]

\[
+ 2(Dd)^{1/2} f_{d \beta} \left[ (\Delta d_1)(\Delta \beta_1) + (\Delta d_2)(\Delta \beta_2) \right]
\]

\[
+ 2(Dd)^{1/2} f_{d \beta} \left[ (\Delta d_1)(\Delta \beta_2) + (\Delta d_2)(\Delta \beta_1) \right]
\]

\[
+ Dd f_d \left[ (\Delta \delta)^2 \right]
\]

5.2.3 G matrix

The G matrix elements evaluated by using Wilson's expression (13) are given below:
\( \Lambda_1 \) species:

\[
G_{11} = \mu_x + \mu_y \\
G_{12} = (2)^{\frac{3}{2}} C \mu_x \\
G_{13} = (6)^{\frac{3}{2}} S \mu_x \\
G_{22} = 2C^2 \mu_x + \mu_z \\
G_{23} = (12)^{\frac{3}{2}} CS \mu_x \\
G_{33} = 3.25^2 \mu_x + \mu_z
\]

\( \Pi_1 \) species:

\[
G_{44} = 2S^2 \mu_x + \mu_z \\
G_{55} = 2(r - C)^2 \mu_x + 2r^2 \mu_y + \mu_z \\
G_{45} = -2S(r - C) \mu_x
\]

\( \Omega_2 \) species:

\[
G_{66} = (r - C^{-1})^2 \mu_x + r^2 \mu_y + (2C^2)^{-1} \mu_z
\]

where \( S = \sin \beta = \sin \alpha / 2 \)

\[
C = \cos \beta = -\cos \alpha / 2
\]

\[
r = d/D
\]

\( \mu_x, \mu_y \) and \( \mu_z \) represent the reciprocal masses of \( X, Y \) and \( Z \) atoms respectively.
5.2.4 Kinetic constants

The expressions for the symmetrized kinetic energy matrix elements are given below:

\[ A_1 \text{ species:} \]

\[ K_{11} = k_D \]

\[ K_{22} = k_d + k_{dd} \]

\[ K_{33} = \left( \frac{3}{\rho} \right) (k \rho^2 + k_{d\rho}^2) \]

\[ K_{12} = (2)^{1/2} k_{dd} \]

\[ K_{13} = (3)^{1/2} k_{d\alpha} \]

\[ K_{23} = -\left( \frac{3}{\rho} \right)^{1/2} (k_{d\rho} + k_{d\rho}^\prime) \]

\[ B_1 \text{ species:} \]

\[ K_{44} = k_d - k_{dd} \]

\[ K_{55} = (1/\rho) (k \rho^2 - k_{d\rho}) \]

\[ K_{45} = -\left( \frac{1}{\rho} \right)^{1/2} (k_{d\rho}^\prime - k_{d\rho}^\prime) \]

\[ B_2 \text{ species:} \]

\[ K_{66} = (1/\rho) k \]

Here \( \rho = d/D \)

The notation of the force constants and the corresponding
kinetic constants is indicated below:

<table>
<thead>
<tr>
<th>Nature of the constant</th>
<th>Force constant</th>
<th>Kinetic constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>XY stretching</td>
<td>f_D</td>
<td>k_D</td>
</tr>
<tr>
<td>XZ stretching</td>
<td>f_d</td>
<td>k_d</td>
</tr>
<tr>
<td>XY/XZ interaction</td>
<td>f_Dd</td>
<td>k_Dd</td>
</tr>
<tr>
<td>XZ/XZ interaction</td>
<td>f_dd</td>
<td>k_dd</td>
</tr>
<tr>
<td>ZXZ bending</td>
<td>f_α</td>
<td>k_α</td>
</tr>
<tr>
<td>YXZ bending</td>
<td>f_ν</td>
<td>k_ν</td>
</tr>
<tr>
<td>XY/ZXZ interaction</td>
<td>f_Dα</td>
<td>k_Dα</td>
</tr>
<tr>
<td>XZ/ZXZ interaction</td>
<td>f_dα</td>
<td>k_dα</td>
</tr>
<tr>
<td>XZ_1/XXZ interaction</td>
<td>f_d′α</td>
<td>k_d′α</td>
</tr>
<tr>
<td>Out of plane bending</td>
<td>f_δ</td>
<td>k_δ</td>
</tr>
</tbody>
</table>

5.2.5 \( F \) matrix

Using the relation \( F = uu' \), the \( F \) matrix elements of different species have been evaluated using the redundancy constraint for \( A_1 \) species given by Ford and Orville-Thomas (11), the \( F \) matrix elements reduced to the following form:

\( A_1 \) species:

\[
F_{11} = f_D \\
F_{12} = (2)^{\frac{1}{2}} f_{Dd}
\]
\[ F_{22} = f_d + f_{dd} \]
\[ F_{33} = \left( \frac{3}{5} \right) (f_{\rho} + f_{\rho \rho}) \]
\[ F_{13} = \left( \frac{3}{2} \right) f_d \]
\[ F_{23} = -\left( \frac{3}{4} \right) (f_{d \rho} + f_{d \rho}) \]

\[ F_{44} = f_d - f_{dd} \]
\[ F_{55} = \frac{1}{c} (f_d + f_{dd}) \]
\[ F_{45} = \frac{1}{c} (f_{d \rho} - f_{d \rho}) \]

\[ F_{66} = \frac{1}{c} f_s \]

where \( P = \frac{d}{\beta} \)

The redundancy constraints used to reduce the \( F \) matrix elements are

\[ (c) f_d + 2f_{d \rho} = 0 \]
\[ (P) f_{d \alpha} + f_{d \rho} + f_{d \rho} = 0 \]
\[ (P) f_{d \alpha} + 2f_{d \rho} = 0 \]
\[ P f_{d \alpha} - 2 \left[ f_{d \rho} + f_{d \rho} \right] = 0 \]

**Method of kinetic constants**

The method of kinetic constants for the determination of force constants have been successfully applied.
for different types of molecules (14-18). In this method, the off diagonal elements are related to the diagonal elements of the $F$ matrix by the relation,

$$\frac{F_{ii}}{F_{jj}} = \frac{K_{ii}}{K_{jj}} \quad (i < j, i, j = 1, 2, 3)$$

Thus equations of $A_1$ species and $B_1$ species are solved quite easily.

5.2.6 **Compliance constants**

Using Decius method (19) the compliance constants which are invariant to the choice of coordinates can be evaluated. Compliance constants can be obtained from the relation $N = F^{-1}$.

5.2.7 **Vibrational mean amplitudes**

Using Cyvin's relation (20), $\Sigma = L \Delta L'$, and the values of force constants, the symmetrized mean square amplitudes and the valence mean square amplitudes for both the bonded and non-bonded distances are evaluated at 298.16 °K. The relations are given below:

**Bonded:**

- $\sigma_D = \Sigma_{11}$
- $\sigma_{dd} = 1/2 \left( \Sigma_{22} + \Sigma_{44} \right)$
- $\sigma_{dd} = 1/2 \left( \Sigma_{22} - \Sigma_{44} \right)$
\[\sigma_{d} = \frac{p}{6} \left[ \Sigma_{33} - 6 \Sigma_{55} \right] \]

The redundancy constraints used to reduce \( \Sigma \) expressions, are,

\[\sigma_{D\alpha} + 2 (r)^{\frac{1}{2}} \sigma_{d\alpha} = 0\]

\[\sigma_{d\alpha} + (r)^{\frac{1}{2}} \left[ \sigma_{d\rho} + \sigma_{d\nu} \right] = 0\]

\[\sigma_{\alpha} + 2 (r)^{\frac{1}{2}} \sigma_{\alpha} = 0\]

\[\sigma_{\alpha} - 2r \left[ \sigma_{\rho} + \sigma_{\nu} \right] = 0\]

**Non-bonded:**

\[\sigma_{p} = p^{-2} \left[ a^{2} \sigma_{D} + b^{2} \sigma_{d} + Dd S^{2} \sigma_{\rho} + 2ab \sigma_{D\rho} - DS \left( a \sigma_{D\alpha} - 2b \left( r \sigma_{d\nu} \right) \right) \right] \]

\[\sigma_{d} = 2s^{2} \left[ \sigma_{d} + \sigma_{d\rho} \right] + c^{2} \sigma_{\alpha} - 4cs \sigma_{d\alpha} \]

where \( p \) is the Y...Z distance.
and \( q \) is the \( Z \ldots Z \) distance
\[
a = D - dC
\]
\[
b = d - DC
\]
\[
p = (D^2 + d^2 - 2DdC)^{1/2}
\]

Thus the vibrational mean amplitudes of Boron halides have been determined from the mean square amplitude quantities.

5.2.8 Coriolis coupling constants

By applying Jahn's rule (21), the non-vanishing Coriolis couplings arise for the planar \( XYZ_2 \) type molecules are given below:

1) \( A_1 \times B_2 \) along \( X \) axis,

2) \( A_1 \times B_1 \) along \( Y \) axis and \( B_1 \times B_2 \) along \( Z \) axis.

The Coriolis coupling elements \( C_{ij}^\alpha (\alpha = x,y,z) \) have been determined by applying the vector method of Meal and Polo (22). The \( C_{ij}^\alpha \) elements are listed below:

**\( C_{ij} \) elements:**

**\( A_1 \times B_2 \) coupling:**

\[
C_{i16}^X = - \left[ (r - C^{-1}) \mu_x + r \mu_y \right]
\]
\[
C_{26}^X = \left( \frac{1}{2} \right)^{\frac{1}{2}} \left[ 2(1 - rC) \mu_x + \mu_z \right]
\]
\[ C_{36}^X = \left( \frac{3}{2} \right)^3 t \left[ 2(1 - r) \mu_x + \mu_z \right] \]

**A1 x B1 coupling:**

\[ C_{14}^Y = - (2)^{\frac{1}{2}} S \mu_x \]

\[ C_{24}^Y = - 2 CS \mu_x \]

\[ C_{34}^Y = - (3)^{\frac{1}{2}} S^2 \mu_x + \mu_z \]

\[ C_{15}^Y = (2)^{\frac{1}{2}} \left[ (r - C) \mu_x + r \mu_y \right] \]

\[ C_{25}^Y = 2C(r - C) \mu_x - \mu_z \]

\[ C_{35}^Y = (12)^{\frac{1}{2}} S(r - C) \mu_x \]

**B1 x B2 coupling**

\[ C_{46}^Z = \left( \frac{1}{2} \right)^3 t \left[ 2(1 - r) \mu_x + \mu_z \right] \]

\[ C_{56}^Z = \left( \frac{1}{2} \right)^3 \left[ 2(r - C)(r - C^{-1}) \mu_x + 2r^2 \mu_y + \mu_z \right] \]

The zeta matrix elements have been evaluated by using the relation

\[ \mathbf{C}^Z = L^{-1} C^Z (L^{-1})' \]

where \( L^{-1} \) is the inverse of normal coordinate transformation matrix \( L \).

5.2.9 Centrifugal distortion constants

The \( t_{a',a} \) quantities have been evaluated using Cyvin's relation (23) and \( T_{a',a} \) matrix elements.
determined in terms of symmetry coordinates are tabulated below:

$T$ matrix elements for the planar $XYZ_2$ molecules:

<table>
<thead>
<tr>
<th>$t_{\alpha \beta, \delta}$</th>
<th>XX</th>
<th>YY</th>
<th>ZZ</th>
<th>T</th>
<th>ZX</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1(A_1)$</td>
<td>2D</td>
<td>2D</td>
<td>0</td>
<td>$S_4(R_1)$</td>
<td>$\sqrt{6} \ dCS$</td>
</tr>
<tr>
<td>$S_2(A_1)$</td>
<td>$\sqrt{3} \ dC^2$</td>
<td>$\sqrt{3} \ dC$</td>
<td>$\sqrt{3} dS^2$</td>
<td>$S_1(R_1)$</td>
<td>$-\sqrt{6} \ dS$</td>
</tr>
<tr>
<td>$S_3(A_1)$</td>
<td>$\sqrt{2} \ dC$</td>
<td>0</td>
<td>$-\sqrt{2} \ dC$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The elements are obtained from the relation

$t_{\alpha \beta, \delta} = -2I_{\alpha \alpha} \ I_{\beta \delta} \ I_{\gamma \gamma} \ I_{\lambda \lambda} \ t_{\alpha \beta, \delta}$

Here the expressions for moment of inertia for this type of molecules are,

$I_{XX} = M^{-1} \left[ D^2 m_y(m_x + 2m_z) + 2D^2 C^2 m_z(m_x + m_y) - 4DdC m_y m_z \right]$

$I_{ZZ} = 2d^2 S^2 m_z$

where $m_x$, $m_y$, $m_z$ and $M$ are the masses of $X, Y, Z$ atoms and the mass of the molecule respectively.

Results and discussion

The structural parameters and the vibrational
frequencies used in the present investigation are given in Table-I.

**Kinetic Constants**

The evaluated kinetic constants of some mixed boron halides taken for investigation are given in Table-II. The features exhibited by these constants as observed from the table are:

1. It is interesting to note that the bond-bond interaction constant $k_{db}$ and the bond-angle interaction constants $k_{db}$, $k_{dca}$ and $k_{dc}$ are uniquely negative for all the cases taken for investigation.

2. The algebraic sum of the bond angle interaction kinetic constants of these molecules vanishes.

3. Again the sum of the bending and the angle-angle interaction kinetic constants also vanishes.

4. These complimentary kinetic constants are found to satisfy the following redundancy constraints:

$$
\begin{align*}
\frac{d}{dt}k_{db} + 2k_{dca} &= 0 \\
\frac{d}{dt}k_{dca} + k_{dc} - k_{dca} &= 0 \\
\frac{d}{dt}k_{dc} + 2k_{dca} &= 0 \\
\frac{d}{dt}k_{dca} - 2(k_{dc} + k_{dca}) &= 0.
\end{align*}
$$

These results are analogous to the results obtained in other molecules of this type (23-25).
Foroe constants

The force constants evaluated for mixed boron halides are reported in table III. The features exhibited by these constants as noticed in table are:

1. The stretching force constant B-I in BI Br₂ is lesser than that in BI Cl₂ which may be due to the effect of electronegativity of bromine and chlorine atoms. The same trend can be observed in B-I stretching force constants of BIF, BICl, and BIBr, where the electronegativity of fluorine, chlorine and bromine atoms influence over B-I force constant.

2. In the case of X-Z stretching constants (λₐ) the observed order is B-F > B-Cl > B-Br. This is perhaps due to the influence of electronegativity of the accompanying halogen atom over the stretching force constants.

3. The bond-angle interaction force constants f₄ and f₄₃ are uniquely negative in all cases.

4. The out of plane force constant f₅ seems to decrease with the decrease of electronegativity of the substituent halogen atom.

Vibrational mean amplitudes

The vibrational mean amplitudes are listed in table IV. The values obtained in the present investigation
appear to be reasonable and agree well with the values found in literature. This shows that the present method of evaluation of the force constants is highly reasonable.

The Coriolis coupling constants

The Coriolis coupling constants evaluated are reported in table V. They exhibit the following features as observed from the table:

1. $\zeta_{16}^x, \zeta_{36}^x, \zeta_{14}^y, \zeta_{34}^y, \zeta_{35}^y, \zeta_{46}^x$ are always negative for all the molecules under investigation.

2. The high values of the Coriolis coupling constants indicate the strong interaction between $A_1 x B_2$, $A_1 x B_1$ and $B_1 x B_2$ species.

3. Also zeta elements found to obey the sum rules of Oka (24) and Watson (25). They are:

$$\begin{align*}
(\zeta_{16}^x)^2 + (\zeta_{26}^x)^2 + (\zeta_{36}^x)^2 &= 1 \\
(\zeta_{14}^y)^2 + (\zeta_{24}^y)^2 + (\zeta_{34}^y)^2 &= 1 \\
(\zeta_{15}^x)^2 + (\zeta_{25}^x)^2 + (\zeta_{35}^x)^2 &= 1 \\
(\zeta_{46}^z)^2 + (\zeta_{56}^z)^2 &= 1.
\end{align*}$$

Centrifugal distortion constants

The centrifugal distortion constants evaluated for mixed boron halides are listed in table VI. They are within the expected range.
Table I: Structural parameters and vibrational frequencies (cm\(^{-1}\)) of some mixed boron halides

<table>
<thead>
<tr>
<th>Compound</th>
<th>(1^\text{st}B\text{F}_2)</th>
<th>(1^\text{st}B\text{Cl}_2)</th>
<th>(1^\text{st}B\text{Br}_2)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{B-F})</td>
<td>2.100 Å</td>
<td>1.295 Å</td>
<td>1.295 Å</td>
<td></td>
</tr>
<tr>
<td>(\gamma_1)</td>
<td>1280</td>
<td>835</td>
<td>766</td>
<td>7</td>
</tr>
<tr>
<td>(\gamma_2)</td>
<td>620</td>
<td>382</td>
<td>249</td>
<td></td>
</tr>
<tr>
<td>(\gamma_3)</td>
<td>270</td>
<td>185</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>(\gamma_4)</td>
<td>1455</td>
<td>937</td>
<td>652</td>
<td></td>
</tr>
<tr>
<td>(\gamma_5)</td>
<td>318</td>
<td>204</td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>(\gamma_6)</td>
<td>529</td>
<td>400</td>
<td>371</td>
<td></td>
</tr>
</tbody>
</table>
Table-III Force constants ($10^2$ N/m)

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$f_D$ (B-I) $f_{Dd}$</th>
<th>$f_{a}^*$</th>
<th>$f_{D a}$</th>
<th>$f_{d a}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}_{BIF_2}$</td>
<td>5.8202</td>
<td>0.2500</td>
<td>0.1515</td>
<td>0.3418</td>
</tr>
<tr>
<td></td>
<td>4.9062</td>
<td>0.9511</td>
<td>0.1520</td>
<td>0.3399</td>
</tr>
<tr>
<td></td>
<td>7.4997</td>
<td>0.8754</td>
<td>0.1743</td>
<td>0.0254</td>
</tr>
<tr>
<td>$^{11}_{BIF_2}$</td>
<td>4.5690</td>
<td>0.5917</td>
<td>0.1170</td>
<td>0.2998</td>
</tr>
<tr>
<td></td>
<td>4.5356</td>
<td>0.5833</td>
<td>0.1310</td>
<td>0.0342</td>
</tr>
<tr>
<td>$^{10}_{BICl_2}$</td>
<td>2.7057</td>
<td>0.5917</td>
<td>0.1170</td>
<td>0.2998</td>
</tr>
<tr>
<td></td>
<td>4.3939</td>
<td>1.3106</td>
<td>0.1142</td>
<td>0.0569</td>
</tr>
<tr>
<td>$^{11}_{BICl_2}$</td>
<td>2.7001</td>
<td>0.5833</td>
<td>0.1171</td>
<td>0.2485</td>
</tr>
<tr>
<td></td>
<td>4.5356</td>
<td>0.9858</td>
<td>0.0342</td>
<td>0.0987</td>
</tr>
<tr>
<td>$^{10}_{BIBr_2}$</td>
<td>1.8032</td>
<td>0.4238</td>
<td>0.1103</td>
<td>0.1891</td>
</tr>
<tr>
<td></td>
<td>4.3939</td>
<td>1.3106</td>
<td>0.1142</td>
<td>0.0569</td>
</tr>
<tr>
<td>$^{11}_{BIBr_2}$</td>
<td>1.8195</td>
<td>0.4253</td>
<td>0.1015</td>
<td>0.1887</td>
</tr>
</tbody>
</table>

Values in parentheses refer to Wolfe and Humphrey (1969) values.
### Table IV: Vibrational mean amplitudes

<table>
<thead>
<tr>
<th>Molecules</th>
<th>( ^1 \mathbf{D}(X-Y) )</th>
<th>( ^1 \mathbf{P}(Z\ldots Y) )</th>
<th>( ^1 \mathbf{D}(X-Z) )</th>
<th>( ^1 \mathbf{q}(Z\ldots Z) )</th>
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<tbody>
<tr>
<td>(^{10}\text{SIF}_2)</td>
<td>5.2037</td>
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<td>5.1557</td>
<td>6.9412</td>
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<td>(^{11}\text{SIF}_2)</td>
<td>4.8603</td>
<td>6.0129</td>
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<td>(^{10}\text{BICl}_2)</td>
<td>7.6919</td>
<td>6.5011</td>
<td>6.4220</td>
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<td>(^{11}\text{BICl}_2)</td>
<td>7.0625</td>
<td>6.5085</td>
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<td>10.8116</td>
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<tr>
<td>(^{11}\text{BIFr}_2)</td>
<td>10.2966</td>
<td>6.6788</td>
<td>7.2218</td>
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Table-V: Coriolis coupling constants

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<th>$\Sigma^y_x$</th>
<th>$\Sigma^y_{24}$</th>
<th>$\Sigma^y_{34}$</th>
<th>$\Sigma^y_{46}$</th>
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<td>$^{10}$BIF$_2$</td>
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<td>0.6812</td>
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<td>$^{11}$BIF$_2$</td>
<td>0.8424</td>
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<td>$^{10}$BICl$_2$</td>
<td>0.9120</td>
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<td>0.3610</td>
<td>0.9839</td>
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<td>0.1915</td>
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<td>0.2576</td>
<td>0.4089</td>
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<td>0.2003</td>
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</table>
Table VI: Centrifugal distortion constants (KHz)

<table>
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<tr>
<th>Molecules</th>
<th>$\gamma_{xxxx}$</th>
<th>$\gamma_{yyyy}$</th>
<th>$\gamma_{zzzz}$</th>
<th>$\gamma_{xyy}$</th>
<th>$\gamma_{xxx}$</th>
<th>$\gamma_{yyz}$</th>
<th>$\gamma_{xzz}$</th>
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</thead>
<tbody>
<tr>
<td>$^{10}\text{BIF}_2$</td>
<td>1.4624</td>
<td>0.4576</td>
<td>112.3225</td>
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<td>8.6719</td>
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<td>$^{11}\text{BIF}_2$</td>
<td>1.4429</td>
<td>0.4714</td>
<td>113.7663</td>
<td>0.7818</td>
<td>8.3509</td>
<td>2.7569</td>
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<td>$^{10}\text{BICl}_2$</td>
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<td>7.9663</td>
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<td>0.1247</td>
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<td>0.0073</td>
<td>0.3540</td>
<td>-0.0032</td>
<td>0.4016</td>
</tr>
</tbody>
</table>
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