CHAPTER 5

MOLECULAR CONSTANTS OF SOME $XY_3$ ($D_{3h}$ POINT GROUP) MOLECULES BY HIGH FREQUENCY AND LOW FREQUENCY SEPARATION METHOD (HFLS)

ABSTRACT

Pseudo exact force constants of some $XY_3$ type compounds viz., $BF_3$, $BCl_3$, $BBr_3$, $BI_3$, $NO_3^-$, $BO_3^-$ and $CO_3^{2-}$ of $D_{3h}$ point group by high frequency and low frequency separation method (HFLS).
CHAPTER 5

MOLECULAR CONSTANTS OF SOME XY₃ (D₃h POINT GROUP) MOLECULES BY HIGH FREQUENCY AND LOW FREQUENCY SEPARATION METHOD (HFLS)

5.1 INTRODUCTION

The formalism "Approximation Separation of High and Low Frequencies" developed by Crawford and Edsall [51] and Wilson et al., [43] enables one to reduce the order of secular determinant describing the vibrations of the molecules by factoring out the vibrations corresponding to the higher or low frequencies.

The secular equation (1.5.27)

\[ | G F - \Lambda I | = 0 \quad \ldots (5.1.1) \]

can be written also in the form (1.5.28)

\[ | F - G^{-1} \Lambda | = 0 \quad \ldots (5.1.2) \]

Following the details as explained in Section 1.5.1 of Chapter 1, one arrives the equations 1.5.34 and 1.5.35 one arrives for (2 x 2) order

\[ F_{44} = \frac{\Lambda G_{11}}{|G|} \quad \ldots (5.1.3) \]
Modes of Vibrations of $XY_3$ Type Molecules
for high frequency separation (HFS) technique and

\[ F_{33} = \frac{\Lambda}{G_{11}} \]  \hspace{1cm} \ldots \ (5.1.4) 

for low frequency separation (LFS) technique.

This HFLS method is adopted in this chapter for six
XY\textsubscript{3} type compounds belonging to D\textsubscript{3h} point group.

5.2 \ XY\textsubscript{3} COMPOUNDS (D\textsubscript{3h} POINT GROUP)

The four modes of vibration of planar XY\textsubscript{3} molecules are shown in Fig. (5.1). \( \nu_2, \nu_3 \) and \( \nu_4 \)
(vibrational frequencies) are infrared active and \( \nu_1, \)
\( \nu_3 \) and \( \nu_4 \) are Raman active.

The irreducible representations are

\[ A'_1 + A''_2 + 2E' \]  \hspace{1cm} \ldots \ (5.2.1) 

5.3 INVERSE KINETIC ENERGY AND POTENTIAL ENERGY MATRIX ELEMENTS (G AND F)

Only doubly degenerate E' species and A'_1 species are used.

\( A'_1 \) Species:

\[ G_{11} = \mu_Y \]
E' Species:

\[ G_{33} = \mu_Y + \frac{3}{2} \mu_X \]

\[ G_{44} = \frac{3}{2} [2\mu_Y + 3\mu_X] \]

\[ G_{34} = \frac{3\sqrt{3}}{2} \mu_X \]

\[ |G| = G_{33} G_{44} - G_{34}^2 \] \hspace{1cm} (5.3.1)

where \( \mu = \frac{N}{\text{Avagadro No.}} = \frac{N}{\text{At wt}} = \frac{N}{\text{Atomic weight}} \)

5.4 STRUCTURE AND SPECTRA

The structure and modes of vibrations are shown in Fig. 5.1.

5.5 FORCE CONSTANTS

Force constants are evaluated by HFLS method using the equations (5.1.3 and 5.1.4). Potential energy matrix elements are expressed in terms of valence force constants \( f \) as

\[ F_{11} = \frac{\mu_Y}{G_{11}} = \frac{11}{11} = f_d + 2f_{dd} \] \hspace{1cm} (5.5.1)

\[ F_{33} = f_d - f_{dd} \] \hspace{1cm} (5.5.2)
The vibrational frequencies used in the present work are taken from the reports of Ginn et al., [196] and Ramaswamy et al [197] and given in Table I.

The force constants, mean amplitudes of vibrations and Coriolis coupling constants evaluated for the seven compounds in this study according to the procedure explained in Section 1.7 and 1.8 are listed in Table I.

The force constants in our work agree well with the works of others [197,198]. Similarly mean amplitudes of vibrations are in good agreement with the report of others [197-200]. The zeta sum rule for Coriolis coupling constants is obeyed well in our work [75,198].

\[ F_{44} \approx f_d \] \hspace{1cm} ... (5.5.3)

\[ \zeta_3 + \zeta_4 = 0.5 \] \hspace{1cm} ... (5.5.4)
<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\nu_1$</th>
<th>$\nu_3$</th>
<th>$\nu_4$</th>
<th>$f_d$</th>
<th>$f_d(F_{44})$</th>
<th>$f_{dd}$</th>
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<tbody>
<tr>
<td>BF$_3$</td>
<td>888</td>
<td>1449</td>
<td>475.36</td>
<td>7.3054</td>
<td>0.4980</td>
<td>0.7606</td>
</tr>
<tr>
<td>BCl$_3$</td>
<td>471</td>
<td>956</td>
<td>243</td>
<td>3.7031</td>
<td>0.2248</td>
<td>0.4654</td>
</tr>
<tr>
<td>BBr$_3$</td>
<td>278</td>
<td>820</td>
<td>150</td>
<td>2.9867</td>
<td>0.1844</td>
<td>0.3259</td>
</tr>
<tr>
<td>Bi$_3$</td>
<td>190</td>
<td>704</td>
<td>100</td>
<td>2.2492</td>
<td>0.1278</td>
<td>0.2249</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1054.8</td>
<td>1383</td>
<td>715.6</td>
<td>7.9254</td>
<td>0.9861</td>
<td>1.2811</td>
</tr>
<tr>
<td>BO$_3^-$</td>
<td>939</td>
<td>1284.5</td>
<td>603.75</td>
<td>6.0290</td>
<td>0.6794</td>
<td>1.1411</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>1063</td>
<td>1415</td>
<td>680</td>
<td>7.7444</td>
<td>0.8717</td>
<td>1.4534</td>
</tr>
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</table>

[Contd.......]
### TABLE I [CONTINUED]

Mean square amplitude matrix elements \((10^{-4} \text{ A}^2)\) and Coriolis coupling constants

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\Sigma_{33})</th>
<th>(\Sigma_{44})</th>
<th>(\Sigma_{34})</th>
<th>(\zeta_3)</th>
<th>(\zeta_4)</th>
<th>(\zeta_3 + \zeta_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{BF}_3)</td>
<td>0.5322</td>
<td>2.5733</td>
<td>1.1342</td>
<td>-0.1989</td>
<td>0.6989</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{BCl}_3)</td>
<td>1.5772</td>
<td>6.6896</td>
<td>3.2403</td>
<td>-0.3165</td>
<td>0.8165</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{BBR}_3)</td>
<td>4.0913</td>
<td>14.7135</td>
<td>7.7567</td>
<td>-0.0434</td>
<td>0.5434</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{BI}_3)</td>
<td>9.2059</td>
<td>31.0999</td>
<td>16.9084</td>
<td>-0.1935</td>
<td>0.6935</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{NO}_3^{-1})</td>
<td>0.2944</td>
<td>1.3566</td>
<td>0.5668</td>
<td>-0.1505</td>
<td>0.6505</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{BO}_3^{-3})</td>
<td>0.4294</td>
<td>1.9779</td>
<td>0.8650</td>
<td>-0.1775</td>
<td>0.6775</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{CO}_3^{-2})</td>
<td>0.3467</td>
<td>1.6011</td>
<td>0.6891</td>
<td>-0.1675</td>
<td>0.6675</td>
<td>0.5</td>
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