BOND PROPERTIES OF ANTIMONY PENTA CHLORIDE
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(Reçu le 27.11.84, accepté le 31.1.85)

ABSTRACT

A new study of harmonic potential constants, compliance constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants has been attempted in Antimony pentachloride molecule and ion. The values of these molecular constants evaluated in the present work are, in general, in the expected range. It is also shown that ionization of the molecule brings about a lowering of the stretching potential constant while the other potential constants are affected characteristically.

RESUME

Nouvelle étude de constantes du potentiel harmonique, de constantes de compliance, d'amplitudes vibratoires moyennes, de constantes de Coriolis et de constantes de distorsion centrifuge, dans le cas du pentachlorure d'antimoine moléculaire et ionique. Les valeurs calculées dans ce travail sont proches de ce que peut être attendu. On montre aussi que l'ionisation de la molécule abaisse les constantes du potentiel d'élongation tandis que les autres constantes de potentiel sont affectées de manière caractéristique.

1. Introduction

Many of the hexatomic molecules have structures in which all bonds emerge from a central atom. Two such arrangements that commonly exist are the trigonal bipyramidal and the tetragonal pyramidal structures. Molecules of the formulae XY₅ and XY₂Z are known for both arrangements. The interesting molecule SbCl₅ was studied by Condrate and Nakamoto (1), Gaunt and Ainscough (2), Krishnapillai (3) and Olle (4) and Carlson (5). SbCl₅ in the molecular form belongs to XY₅ type molecule of D₅w symmetry.

It is interesting to note that SbCl₅ in the ionic state does not fall under D₅w symmetry. The X-ray studies of SbCl₅ has shown its structure to be tetragonal pyramidal type (6). Szymanski (7) assigned SbCl₅ to C₁ point group. This interesting variation tempted us to examine the bond properties of antimony pentachloride molecule and ion. An examination of all the molecular constants of SbCl₅ molecule and ion on the basis of kinetic constants attempted in the present study, leads to interesting results in molecular vibrations.

2. Theoretical Considerations

2.1. SbCl₅ molecule

The trigonal bipyramidal molecule SbCl₅ (XY₅ type) belongs to the D₅w point group. Vibrational frequencies are distributed among the following species:

2σ₁ + 2σ₂ + 3σ₃ + 1σ⁰

Of these eight normal modes σ₁, σ₂ and σ⁰ are Raman active while σ₂ and σ⁰ are infrared active. The orientation of the Cartesian coordinate axes and the numbering of modes are shown in Figure 1. The symmetry coordinates in the present investigation are the same as used by 'omek et al. (6).

The elements of the kinetic energy matrix have been obtained using Wilson's method (1) and they are utilised to evaluate kinetic constants. The F-matrix elements evaluated using the most general quadratic potential energy function are given below:

\[
\begin{align*}
\sigma_1 \text{ type} \\
F_{\text{II}} &= f_\sigma + 2 f_{\omega} \\
F_{\text{III}} &= \sqrt{2} f_{\omega} \\
F_{\text{IV}} &= f_\sigma + f_{\omega} \\
\sigma_2 \text{ type} \\
F_{\text{V}} &= f_\sigma - f_{\omega} \\
F_{\text{VI}} &= \frac{1}{2} D d (f_\sigma - f_{\omega}) \\
F_{\text{VII}} &= \frac{1}{2} D d (f_\sigma - f_{\omega}) \\
\sigma_0 \text{ type} \\
F_{\text{VIII}} &= f_\sigma - f_{\omega} \\
F_{\text{IX}} &= d (f_\sigma - f_{\omega}) \\
F_{\text{X}} &= -\sqrt{2} D d (f_\sigma - f_{\omega}) \\
F_{\text{XI}} &= d (f_\sigma - f_{\omega}) \\
F_{\text{XII}} &= \sqrt{2} D d (f_\sigma - f_{\omega}) \\
F_{\text{XIII}} &= \frac{1}{2} D d (f_\sigma - f_{\omega}) \\
\end{align*}
\]

σ and d are the apical and the basal bond distances respectively. The primes indicate the interactions between the bond-distant bond or angle-distant angle.

2.2. SbCl₅ ion

The tetragonal pyramidal molecules of the XY₂Z type belong to the C₁ point group and are characterised by
nine fundamental frequencies distributed among the various species as

\[ 3a_r + 2b_r + b_u + 3e \]

of the nine modes \( a_r \) and \( e \) are both Raman and infrared active whereas \( b_r \) and \( b_u \) are Raman active.

The orientation of the Cartesian coordinate axes and the numbering of the atoms are shown in Figure 1. The symmetry coordinates employed in the present work are the same as those given by Begun et al. \(^{(1)}\). Using the vector method \(^{(2)}\) the \( G \) matrix is constructed for the SbCl\(_4^+\) ion. The elements of Wilsons inverse \( G \) matrix are used to calculate the kinetic constants. Using the most general quadratic potential energy function the \( F \) matrix elements are calculated. They are:

\[
\begin{align*}
F_{11} &= f_1 \\
F_{12} &= f_2 + 2f_3 + f_4 \\
F_{13} &= N_1(f_1 + 2f_4 + f_3) - 4N_2(f_{12} + f_{13}) \\
&+ N_1(f_1 + 2f_3 + f_4) \\
F_{14} &= 2f_{14} \\
F_{15} &= 2(N_1 f_{15} - N_2 f_{16}) \\
F_{16} &= 2N_1(f_4 + f_{15}) - N_1(f_{16} + 3f_{17}) \\
\end{align*}
\]

\[
\begin{align*}
b_u \text{ type} \\
F_{12} &= f_4 - 2f_{14} + f_{15} \\
F_{13} &= f_4 - f_{14} + 3f_{17} \\
\end{align*}
\]

\[
\begin{align*}
b_r \text{ type} \\
F_{12} &= f_4 - 2f_{14} + f_{15} \\
F_{13} &= f_4 - f_{14} + 3f_{17} \\
F_{14} &= f_4 - 2f_{14} + f_{15} \\
\end{align*}
\]

\[
\begin{align*}
ea \text{ type} \\
F_{12} &= f_4 - f_{14} \\
F_{13} &= f_4 - f_{14} \\
F_{14} &= f_4 - 2f_{14} + f_{15} \\
\end{align*}
\]

where \( N_1 = \frac{1}{\sqrt{1 + K^2}} \) and \( N_2 = \frac{K}{\sqrt{1 + K^2}} \) with \( K = -\cos \left(\frac{\beta}{2}\right)\). The primes indicate the bond-distant bond or angle-distant angle interactions.

2.3.

The secular equations relating to the potential constants have been solved by the method of kinetic constants \(^{(1,4)}\) which provides the required number of additional data through the symmetry kinetic constants and the corresponding symmetry force constants. The compliance constants are also evaluated for both the cases by Decius method \(^{(5)}\).

2.4.

The mean square amplitude matrix elements may be obtained using the normal coordinate transformation matrix \( L \).

2.5.

The Coriolis coupling constants which are useful in the interpretation of vibrational spectra may be evaluated theoretically from a reliable set of potential constants.

In SbCl\(_4^+\) molecule the vibration-rotation interactions arise from the couplings

\[ a' \times a', a'' \times e', e'' \times e'' \text{ and } e'' \times a'' \]

while in SbCl\(_4^+\) ion the following couplings are effective:

\[ a' \times a', b_1 \times a', b_2 \times e, b_1 \times b_2 \text{ and } e \times e. \]

In both the cases the first three interactions possess rotation about \( x \) and \( y \) axes and the remaining two about \( z \)-axis. The Coriolis matrix elements \( C_\alpha(\alpha = x,y,z) \) are obtained by the vector method of
Bond properties of antimony pentoxide

Meal and Polo (10), and the zeta matrix elements may be evaluated from the relation:

\[ \zeta = L^{-1} C (L')^{-1}. \]

2.6

The determination of the exact rotational levels of a non-rigid molecule requires the knowledge of centrifugal distortion constants. Following Kivelson and Wilson (11), the centrifugal distortion constants of both SbCl₆⁺ ion and SbCl₆⁻ molecule have been evaluated in the present investigation.

3. Results and Discussion

The structural parameters and the frequencies employed in the present work are presented in Table I.

The kinetic constants, potential constants, compliance constants and the mean amplitudes of SbCl₆⁻ molecule and SbCl₆⁺ ion are presented in Table II and Table III respectively. From Tables II and III the following observations may be made. The kinetic constants of the SbCl₆⁻ molecule and the ion studied here may be grouped under three heads. Based on the properties of these constants they may be grouped as complementary kinetic constant or supplementary kinetic constants.

The bond-angle interaction kinetic constants form the first group of kinetic constants, as they vanish among themselves, when added together. Second group of kinetic constants is provided by the bending kinetic constants \( k_a \) (\( k_b \) in SbCl₆⁺ ion) and the six angle-angle interaction kinetic constants in as much as they also become zero when added together. The remaining kinetic constants, namely, the stretching kinetic constants \( k_o \) and \( k_v \) and bond-bond kinetic constants: \( k_{oo} \), \( k_{ov} \), and \( k_{vv} \) are together called supplementary kinetic constants as they lead to characteristic constants 25 of this molecule concerned, that is

\[ 5 \mu v \Sigma k_v = 5 \mu (2k_v + \Sigma k_v + \Sigma k_{ov} + \Sigma k_{ov} + \Sigma k_{oo}) = 25. \]

As expected the stretching kinetic constants \( k_o \) and \( k_v \) are nearly the same in both cases. Regarding the stretching force constants \( k_o \) and \( f_{oo} \) for ionic bonds (SbCl₆) are less than those for SbCl₆ molecule. There is similar decrease in the bond-angle and the angle-angle interaction constants for SbCl₆⁺ ions. Further the stretching force constant \( f_a \) is about half of the force constant \( f_v \) for the SbCl₆⁻ ions. This indicates that the electron-electron interaction between antimony and basal chlorine ions is much stronger than that between antimony and apical ion.

The compliance constants are invariant to the choice of coordinates defining the force field and they may be used as a measure of bond strengths and interactions instead of potential constants (11). The Coriolis coupling coefficients which may be experimentally determined can also be evaluated from a reliable set of potential constants. The zeta elements for the molecule and the ion under study are given in Table IV. The high values of \( \zeta_{oo} \) and \( \zeta_{ov} \) in SbCl₆⁻ molecule, show the coupling \( \epsilon \times \epsilon \) is stronger than other couplings. In SbCl₆⁺ ion the zeta values \( \zeta_{oo}, \zeta_{ov}, \zeta_{vv} \) are high, suggesting that the concerned couplings are strong.

Further it is observed that, the relation

\[ \theta + \zeta_{oo} + \zeta_{ov} = 1/2\mu \]

is obeyed.

The centrifugal distortion constants of SbCl₆⁺ (ion) and SbCl₆⁻ (molecule) are presented in Table V. The values of \( D_e \) and \( D_v \) for the concerned ion are being much greater than those of the molecule, indicating the increase in the rotational energy levels. This inference is due to the fact that \( D_e, D_v \), etc. are significant only at higher energy levels. But no attempt is made for the energy calculation in the present investigation.

4. Conclusion

A comparative study between SbCl₆⁻ ion and molecule has been attempted for the first time in the present investigation. The results of such an investigation are

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural parameters and frequencies used in investigation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System</th>
<th>Species</th>
<th>Frequency (cm⁻¹)</th>
<th>Bond Distances (Å)</th>
<th>Bond Angles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbCl₆⁻</td>
<td>( \alpha_1 )</td>
<td>377,307</td>
<td>2.31</td>
<td>2.43</td>
<td>( \alpha = 120° )</td>
</tr>
<tr>
<td>(Molecule)</td>
<td>( \alpha_2 )</td>
<td>371,154</td>
<td></td>
<td></td>
<td>( \beta = 90° )</td>
</tr>
<tr>
<td>( \alpha_3 )</td>
<td>397,177,66</td>
<td>165</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbCl₆⁺</td>
<td>( \beta_1 )</td>
<td>445,285,180</td>
<td>2.49</td>
<td>2.37</td>
<td>( \beta = 90° )</td>
</tr>
<tr>
<td>(ion)</td>
<td>( \beta_2 )</td>
<td>420,174</td>
<td></td>
<td></td>
<td>( \gamma = 95.8° )</td>
</tr>
<tr>
<td>( \beta_3 )</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
<td>117</td>
</tr>
<tr>
<td>( \beta_4 )</td>
<td>300,255,90</td>
<td></td>
<td></td>
<td></td>
<td>117</td>
</tr>
</tbody>
</table>
TABLE II

Kinetic constants, force constants, compliance constants, and mean amplitude of vibration of SbCl₆ (Molecule)

<table>
<thead>
<tr>
<th></th>
<th>Kinetic constants k</th>
<th>Force constants f</th>
<th>Compliance constants n</th>
<th>Mean amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10² cm⁻¹)</td>
<td>(10⁻⁵ dynes/cm)</td>
<td>(10⁻⁵ cm²/dynes)</td>
<td>(Å)</td>
</tr>
<tr>
<td>d</td>
<td>5.1191</td>
<td>2.4930</td>
<td>0.4112</td>
<td>0.0464</td>
</tr>
<tr>
<td>Dd</td>
<td>0.7366</td>
<td>1.9008</td>
<td>0.5359</td>
<td>(Sb-Cl basal)</td>
</tr>
<tr>
<td>D</td>
<td>1.0605</td>
<td>0.0409</td>
<td>0.1427</td>
<td>0.0516</td>
</tr>
<tr>
<td>D</td>
<td>0.0000</td>
<td>0.0949</td>
<td>0.1427</td>
<td>(Sb-Cl apical)</td>
</tr>
<tr>
<td></td>
<td>-0.5902</td>
<td>-0.0559</td>
<td>-0.0714</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III

Kinetic constants, force constants, compliance constants, and mean amplitude of vibration of SbCl₆ (ion)

<table>
<thead>
<tr>
<th></th>
<th>Kinetic constants k</th>
<th>Force constants f</th>
<th>Compliance constants n</th>
<th>Mean amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10² cm⁻¹)</td>
<td>(10⁻⁵ dynes/cm)</td>
<td>(10⁻⁵ cm²/dynes)</td>
<td>(Å)</td>
</tr>
<tr>
<td>d</td>
<td>5.1195</td>
<td>2.3002</td>
<td>1.2168</td>
<td>0.0561</td>
</tr>
<tr>
<td>Dd</td>
<td>0.6957</td>
<td>0.1489</td>
<td>0.4918</td>
<td>(Sb-Cl basal)</td>
</tr>
<tr>
<td>D</td>
<td>3.0920</td>
<td>0.5908</td>
<td>16.5880</td>
<td>0.0516</td>
</tr>
<tr>
<td>D</td>
<td>0.0000</td>
<td>0.0513</td>
<td>1.1090</td>
<td>(Sb-Cl apical)</td>
</tr>
<tr>
<td></td>
<td>0.2616</td>
<td>0.0000</td>
<td>0.1991</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7195</td>
<td>0.0000</td>
<td>-0.2654</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1991</td>
<td>0.0000</td>
<td>-0.2654</td>
<td></td>
</tr>
</tbody>
</table>

Journal de chimie physique, 1985, 82, n° 7-8
TABLE IV
Coriolis Coupling Constants
SbCl₅ molecule

<table>
<thead>
<tr>
<th>•,* B •**</th>
<th>4*8</th>
<th>-0.5459</th>
<th>1.45*</th>
<th>0.7454</th>
</tr>
</thead>
<tbody>
<tr>
<td>4*8</td>
<td>-0.4396</td>
<td>1.25*</td>
<td>0.3726</td>
<td></td>
</tr>
<tr>
<td>4*8</td>
<td>0.2772</td>
<td>1.35*</td>
<td>0.2756</td>
<td></td>
</tr>
<tr>
<td>4*8</td>
<td>-0.0702</td>
<td>1.45*</td>
<td>0.7125</td>
<td></td>
</tr>
</tbody>
</table>

TABLE V
Centrifugal Distortion Constants (KHz)

<table>
<thead>
<tr>
<th>SbCl₅ (Molecule)</th>
<th>SbCl₅ (Ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0185</td>
<td>0.0480</td>
</tr>
<tr>
<td>0.0166</td>
<td>0.0357</td>
</tr>
<tr>
<td>-0.0116</td>
<td>-0.0791</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-0.0015</td>
<td>0.0141</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Acknowledgement
The authors are thankful to Dr S. Sathikht, Director, Madras Institute of Technology, for his kind permission and encouragement to pursue this investigation.

References

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References
Dynamical model of molecular constants on the vibrational analysis of trimethyl antimony dihalides

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Abstract: The general quadratic valence force field has been applied to the trimethyl antimony dihalides belonging to the \( D_{3h} \) point group using molecular kinetic constants and Wilson's \( F-G \) matrix method. The molecular character of the bond is briefly discussed. Other molecular characteristic constants such as compliance constants, vibrational mean amplitudes, Coriolis coupling constants and the rotational distortion constants are reported for these molecules in the present investigation. The results are interesting from the point of view of molecular dynamics. It is also shown that the kinetic constants method leads to acceptable set of molecular constants.

1. Introduction
The kinetic constants relating to molecules have been studied at length. Their role and significance has been estimated earlier (Mohan et al. 1982). Such kinetic constants have been advantageously utilised in solving the secular equations governing the potential constants.

The present investigation is to obtain a reasonable set of potential constants for four molecules viz. trimethyl antimony dihalides. Added to this the compliance constants. Coriolis coupling constants, vibrational mean amplitudes and rotational distortion constants have been calculated using kinetic constants.

2. Theoretical considerations
The trimethyl antimony dihalides are analysed on the basis of \( D_{3h} \) point group. It is assumed that the methyl groups behave as point mass. The normal modes of vibration of these molecules are distributed among the four symmetry species as \( 2\alpha_1^1 + 2\alpha_2^2 + 3\alpha_3^3 + \varepsilon \). The symmetry coordinates used are the same as those given by Wood and Long (1971):

The structure, nomenclature of the parameters and the orientation of the principal axes are given in Figure 1.

The most general quadratic potential energy function in terms of internal coordinates has been considered and hence \( F \) matrix elements have been obtained. Following Ford and Thomas (1967) the redundancy constrains are utilised to...
reduce the general $F$ matrix. The reduced $F$ matrix is of the following form for various species

$$a'_1: \left[ \frac{f_a + \sqrt{3} f_{aa}}{f_a + f_{aa}} \right]$$

$$a''_1: \left[ \frac{f_a - f_{aa} + 2 \sqrt{3} f_{as}}{2f_a + 4f_{sp}} \right]$$

$$a'_2: \left[ f_{dd} - \frac{3}{\sqrt{2}} f_{ds} - 3 f_{ds} \right]$$

$$a''_2: \left[ f_{dd} - f_{dd} - \frac{3}{\sqrt{2}} f_{dd} - 3 f_{dd} \right]$$

$$e': \left[ \frac{f_{dd} - f_{dd} - \frac{3}{\sqrt{2}} f_{dd} - 3 f_{dd}}{f_{dd}} \right]$$

The notation of force constants and kinetic constants are given below:

<table>
<thead>
<tr>
<th>Nature of the constants</th>
<th>Force constants</th>
<th>Kinetic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb - R stretching</td>
<td>$f_D$</td>
<td>$k_D$</td>
</tr>
<tr>
<td>Sb - X stretching</td>
<td>$f_A$</td>
<td>$k_A$</td>
</tr>
</tbody>
</table>
Dynamical model of molecular constants etc. 403

Sb - R/Sb - X interaction $f_{DA}$ $k_{DA}$
Sb - R/Sb - R interaction $f_{DD}$ $k_{DD}$
Sb - X/Sb - X interaction $f_{xx}$ $k_{xx}$
R - Sb - R bending $f_a$ $k_a$
R - Sb - X bending $f_b$ $k_b$
Sb - R/R - Sb - R interaction $f_{DA}$ $k_{DA}$
Sb - R/R - Sb - X interaction $f_{DB}$ $k_{DB}$
Sb - X/R - Sb - R interaction $f_{DA}$ $k_{DA}$
Sb - X/R - Sb - X interaction $f_{DB}$ $k_{DB}$
R - Sb - R/R - Sb - X interaction $f_{AB}$ $k_{AB}$
R - Sb - X/R - Sb - X interaction $f_{AB}$ $k_{AB}$

The kinetic constants are derived from a knowledge of $G$ matrix elements using Wilson's expression $2\mathbf{T} = \mathbf{S} = G^{-1}\mathbf{S}$. The method of kinetic constants for evaluating the force constants is as mentioned in the earlier works (Thirugnanasambandam and Mohan 1974, 1975, Mohan 1977 and Mohan and Ravikumar 1983). The procedure of kinetic constants relate the off-diagonal elements to the diagonal elements of the $F$-matrix as

$$ F_{ij}F_{H} = {K}_{ij}{K}_{H} \ (i,j = 1, 2, 3) $$

Thus the equations involving $a_{1x}$, $a_{2x}$ and $e'$ species are solved.

Vibrational mean amplitudes:
Utilizing Cyvin's equation (Cyvin 1968) $\Sigma = L\mathbf{L}$, the symmetrized mean square amplitudes and hence the valence mean square amplitudes for both the bonded and non-bonded distances are evaluated at 296.16 K, using the force constants obtained.

Compliance constants:
Compliance constants are evaluated by the Decius (1963) method.

Coriolis coupling constants:
The Coriolis vibration rotation constants $\zeta^e(\kappa = x, y, z)$ in this type of molecules arise from the couplings $a'_i \times e_i^x$, $a''_i \times e_i^x$, $e' \times e'$ and $e'' \times e''$. The Coriolis matrix elements $C^e_{ij}$ are obtained by the vector method of Meal and Polo (1956). These matrices are related to $\zeta^e$ by an expression $\zeta^e = L^{-1}C^eL^{-1}$ where $L$ is the normal coordinate transformation matrix.

Centrifugal distortion constants:
Cyvin et al (1968) have reformulated the theory of centrifugal distortion
by introducing $T_{*,a}$ instead of partial derivatives of the inertia tensor components $J_{*,a}$ of Kivelson and Wilson (1953). Using $T_{*,a}$ matrix elements the centrifugal distortion constants have been calculated.

3. Results and discussion

The fundamental frequencies and the structural parameters used in the present work are taken from Nevett and Perry (1970) and Wells (1938). These are presented in Table 1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$D_{AU}$</th>
<th>$d$</th>
<th>$a^s_a$ species</th>
<th>$a^s_b$ species</th>
<th>$c^s_a$ species</th>
<th>$c^s_b$ species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_3SbF_3$</td>
<td>2.13</td>
<td>2.14</td>
<td>545</td>
<td>655</td>
<td>484</td>
<td>215</td>
</tr>
<tr>
<td>$R_3SbCl_3$</td>
<td>2.13</td>
<td>2.49</td>
<td>358</td>
<td>272</td>
<td>282</td>
<td>196</td>
</tr>
<tr>
<td>$R_3SbBr_3$</td>
<td>2.13</td>
<td>2.63</td>
<td>296</td>
<td>215</td>
<td>172</td>
<td>179</td>
</tr>
<tr>
<td>$R_3SbI_3$</td>
<td>2.13</td>
<td>2.88</td>
<td>192</td>
<td>144</td>
<td>173</td>
<td>556</td>
</tr>
</tbody>
</table>

The kinetic constants of the Trimethyl antimony dihalides are given in Table 2. The primary kinetic constants $k_a$ and $k_b$ increase from $R_3SbF_3$ to $R_3SbI_3$, whereas the bond-bond interaction constants $k_{DD}$ decreases in the same order. Similarly the bending kinetic constants $k_a$ and $k_b$ and the angle-angle interaction constants $k_{aa}$ and $k_{bb}$ also increase from $R_3SbF_3$ to $R_3SbI_3$. The interaction constants $k_{db}$ and $k_{ab}$ are zero.

The evaluated force constants are listed in Table 3. The values of stretching force constants $f_D$ and $f_B$ decrease due to the decrease in electronegativity Cl, to I. Similar trend may also be noticed with respect to bending force constant $f_B$.

The compliance constants detailed in Table 4 exhibit trends opposed to that of force constants. The valence mean square amplitudes are given in Table 5. The mean square amplitude for Sb–X bond, $(\sigma_d)$ increases from F to I, due to decrease in the corresponding electronegativity.

The Coriolis coupling constants are given in Table 6. The values $\xi_{ab}$, $\xi_{ba}$, $\xi_{ac}$ and $\xi_{ca}$ are high showing the strong coupling between the species concerned. It is found that the zeta element obey the following sum rule:

$$|\xi_{aa}+\xi_{ba}+\xi_{ac}| = 1$$ for $e' \times e'$ coupling

$$88 = f_D/2f_B(e' \times e')$$

The distortion constants are given in Table 7. $D_2$ is positive and shows a
Dynamical model of molecular constants etc.  

<table>
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<tr>
<th>Molecule</th>
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<th>I1</th>
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Table 2. Kinetic constants ($10^{-10} s$)

Table 3. Force constants ($10^9$ dyn/cm)

---

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### Table 4. Compliance constants (Å/m dynes).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\sigma_D$</th>
<th>$\sigma_d$</th>
<th>$\sigma_{DD}$</th>
<th>$\sigma_{DD}$</th>
<th>$\sigma_{D\sigma}$</th>
<th>$\sigma_{\sigma\sigma}$</th>
<th>$\sigma_{D\sigma}$</th>
<th>$\sigma_{\sigma\sigma}$</th>
<th>$\sigma_{DD}$</th>
<th>$\sigma_{D\sigma}$</th>
<th>$\sigma_{\sigma\sigma}$</th>
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</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SiF}_6$</td>
<td>2.5093</td>
<td>2.5429</td>
<td>-0.0548</td>
<td>-0.0548</td>
<td>82.2735</td>
<td>159.9046</td>
<td>-0.3802</td>
<td>-0.4869</td>
<td>-0.3487</td>
<td>1.0699</td>
<td>-72.4933</td>
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<tr>
<td>$\text{H}_2\text{SiCl}_4$</td>
<td>2.5655</td>
<td>3.8221</td>
<td>-0.0715</td>
<td>-0.0715</td>
<td>75.9561</td>
<td>18.6978</td>
<td>-0.3165</td>
<td>-0.5948</td>
<td>-0.7791</td>
<td>1.8379</td>
<td>-1.4712</td>
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<tr>
<td>$\text{H}_2\text{SiBr}_4$</td>
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<td>-0.0602</td>
<td>-0.0602</td>
<td>125.9876</td>
<td>16.6792</td>
<td>-0.4177</td>
<td>-0.6494</td>
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<td>2.0400</td>
<td>0.4165</td>
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<tr>
<td>$\text{H}_2\text{SiI}_4$</td>
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<td>3.9201</td>
<td>-0.0491</td>
<td>-0.0491</td>
<td>103.9042</td>
<td>15.4166</td>
<td>-0.4467</td>
<td>-0.7165</td>
<td>-2.5061</td>
<td>2.0913</td>
<td>1.9254</td>
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### Table 5. Vibrational mean square amplitudes ($10^{-4}$ Å$^2$) at 298.15K.

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<th>$\sigma_d$</th>
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<th>$\sigma_{\sigma\sigma}$</th>
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<td>125.9876</td>
<td>16.6792</td>
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<td>$\text{H}_2\text{SiI}_4$</td>
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<td>-2.5061</td>
<td>2.0913</td>
<td>1.9254</td>
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</table>
Dynamical model of molecular constants etc.

Decreasing trend from $R_a SbF_4$ to $R_a SbI_4$. $D_K$ increases steadily in the same direction. Decrease in $D_J$ can be explained as follows. The centrifugal forces increase the moment of inertia and hence reduce the distortion constant. From $R_a SbF_4$ to $R_a SbI_4$ the mass of the atoms increases and hence there is a decrease in $D_J$. Since the molecules are of symmetric rotor type, $\delta_J$, $R_a$ and $R_e$ and zero.

Acknowledgment
The authors wish to express their thanks to Prof. S. Sathikh, Director, Madras Institute of Technology for his encouragement.

References
Cyvin S J 1968 Molecular vibrations and mean square amplitudes (Amsterdam : Elsevier)
Cywin S J, Cyvin B N and Hagen G 1968 Z. Naturforsch. 23A 1696
Decius J 1963 J. Chem. Phys. 21 3126

Table 6. Coriolis coupling constants.

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Table 7. Centrifugal distortion constants (KHz)

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<th>$D_{JK}$</th>
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<td>0.0317</td>
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<td>0.0746</td>
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<td>0.0086</td>
<td>+0.2235</td>
<td>0.0277</td>
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</table>
Nevett and Perny 1977 Spectrochim. Acta 33A 759
Thirugnanasambandam P and Mohan S 1974 J. Chem. Phys. 61 270
Wells A F 1938 Z. Krist. A99 867
FORCE FIELD STUDY OF Xe OF₄

S. Monan and S. Durais

Division of Applied Sciences, Anna University
Madras Institute of Technology Campus, Chromepet, Madras-600044 India.

ABSTRACT

The general quadratic valence force field has been applied to the molecule Xe OF₄ of XY₄Z type, on the basis of C₄ᵥ point group. All the molecular constants, such as the potential constants, compliance constants, 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.

Introduction

The kinetic constants are generally referred to as the elements of Wilson's G⁻¹ matrix. The kinetic constants method has been successfully employed in the earlier works (Mohan et al 1977, 1984). Their role in molecular dynamics is of great significance.

The purpose of the present paper is to obtain all the molecular characteristic constants and to discuss the nature of the chemical bonds.

Theoretical Considerations

The tetragonal bipyramidal molecules like XeOF₄, IF₅, BrF₅ and CIF₅, belonging to the point group C₄ᵥ have been studied extensively (Szymanski et al 1967; Begun et al 1965). The tetrafluoride molecule XeOF₄ has its Xe-O equatorial distance, shorter than Xe-F axial distance. The electron diffraction studies (Martin et al 1968) have revealed that Xe atom is slightly above the plane containing the fluorine atoms. The nine fundamental frequencies are distributed as

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

Methods of Calculations

The elements of kinetic energy matrix (Wilson 1955) are used to calculate the kinetic constants. The secular equations 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., \( F_{ij}/F_{ij} = K_{ij}/K_{ij} \) (i j). The compliance constants are evaluated for this molecule by Decius method (Decius 1963). The mean square amplitude matrix elements (Cyvin 1968) may be obtained using the normal coordinate transformation matrix L from the relation \( \Sigma = L \Delta L^T \). From
this the valence mean square amplitudes and mean amplitudes of vibration at 298.15 K are evaluated. The Coriolis coupling constants are calculated from the potential constants. The Coriolis matrix elements $C_{i j}(x=x, y, z)$ are evaluated by the vector method (Meal et al 1956) and hence the zeta elements are obtained from the relation $\zeta_i = L_{-i} C_{i j}(L^{-1}j)$. With the reformulated theory of Cyvin et al (Cyvin 1968) the $T_{\alpha, \beta}$ matrix is evaluated. From the $T_{\alpha, \beta}$ values the distortion constants $x_{\alpha, \beta}$ can be obtained.

Results and Discussion

The structural parameters and the vibrational frequencies employed in the present work are taken from Willet et al (Willet et al 1975). The calculated kinetic constants, potential constants, compliance constants and vibrational mean square amplitudes and the mean amplitudes are presented in Table 1. It is observed that Xe-F bond is only half as strong as the Xe-O bond, which is consistent with Rundle $3e^{-4e}$ type bonding (Azaroff 1960). The bending force constant $f_\beta$ is found to be more than the bending force constant $F_\beta$, where $\beta$ is the F-Xe-F bond angle and $\beta$ is the F-Xe-O bond angle. In this table the prime indicates the interaction between the bond-distant bond or angle-distant angle.

The compliance constants are a measure of bond strengths and exhibit trends opposite to that of potential constants. The mean amplitudes are in good agreement with the literature values.

The Coriolis coupling coefficients and centrifugal distortion constants are given in Table 2. The Coriolis coupling constants obey the quadratic sum rules. In addition, the following relation is also satisfied:

$$\epsilon_{\alpha i} + \epsilon_{\beta i} + \epsilon_{\gamma i} = \epsilon_{i i}/2$$

The centrifugal distortion constant, agrees with the observed value.

The molecular constants obtained in the present investigation have been compared with the literature values wherever possible. The reasonable agreement confirms the validity of the method adopted.

References

S. Mohan and S. Durai

<table>
<thead>
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<th>Kinetic constants, Potential constants, compliance constants, vibrational mean square amplitudes (at 298.16 K) and vibrational mean amplitudes of Xe OF₄</th>
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<tr>
<td><strong>D</strong></td>
</tr>
<tr>
<td>d</td>
</tr>
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<tr>
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<tr>
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* Electron diffraction data - (Jews 1971)
### Force Field Study of Xe OF*  

#### Table 2  

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**Centrifugal Distortion Constants of XeOF* (KHz)**  

| $D_J$ | 0.5292 ($^{*0.32\pm0.1}$) | $R_J$ | 0.0000 |  
| $D_J$ | 0.4220 | $R_J$ | 0.1437 |  
| $D_{3J}$ | -0.8645 | $\delta_J$ | 0.0000 |  

*Observed value (Martin et al 1968).


S. Mohan and S. Durai


Molecular Constants of some Mixed Phosphorous Halides

S. Mohan, Division of Applied Sciences, Anna University, Madras Institute of Technology, Madras-600 044

A detailed study of the potential constants and the vibrational mean amplitudes have been attempted in the case of mixed phosphorous halides using the fresh procedure involving kinetic constants.

The method of kinetic constants has led to highly reasonable and interesting results in the study of the polyatomic molecules (1–3). The pyramidal $XYZ_a$ type mixed halides belong to $C_s$ point group, having six fundamental frequencies under two species ($4A'+2A''$). The aim of this investigation is to obtain the reasonable set of molecular constants using the most general quadratic valence force field. In addition to potential constants the vibrational mean amplitudes (4) of bonded as well as the non-bonded distances are evaluated at 298.16K. The symmetry coordinates used in the present work are taken from Ref 5. The most general quadratic potential energy function has been considered and the $F$-matrix elements have been obtained as follows:

$A' Type$:

$$
\begin{bmatrix}
f_{0} & f_{0} & 4f_{0} & 4f_{0} \\
4f_{0} & 4f_{0} & f_{0} & f_{0} \\
f_{0} & f_{0} & f_{0} & f_{0} \\
4f_{0} & 4f_{0} & f_{0} & f_{0}
\end{bmatrix}
$$

The elements of the kinetic energy matrix are used to calculate the kinetic constants of these molecules.

The method of kinetic constants relates the off-diagonal elements to the diagonal elements of the $F$ matrix through the relation

$$F_{ij}/F_{ii} = K_{ij}/K_{ii} = (i < j; i - j = 1, 2, 3, 4)$$

using Cyvin's equation $\Sigma = \Delta \Delta ^*$ the symmetrized mean square amplitudes and the valence mean square amplitudes are evaluated at 298.16K.

The structural parameters and the frequencies are taken from literature (6, 7, 8). The potential constants of the mixed halides are presented in Table 1. As the mass of the $Z$ atom increases the major stretching constant $f_{0}$ increases. The interaction force constants $f_{0}$ is negative for all cases. The vibrational mean amplitudes evaluated as mentioned earlier are given in Table 2.

References:

4. S. J. Cyvin, Molecular vibrations and Mean-square amplitudes, (Elsevier, Amsterdam 1969)
| Table 1 |
|------------------|------------------|-----------------|------------------|
| Potențial       | Constante [10^3 N/m] |
| $f_{0x}$         | $f_x$            | $f_{0x}$         | $f_x$            |
| $f_{0y}$         | $f_y$            | $f_{0y}$         | $f_y$            |

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<td>Bonded $^1d(x-z)$</td>
<td>Non Bonded Bonded $^1p(z...z)$</td>
<td>Non Bonded $^1q(y...z)$</td>
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SPECTROSCOPIC STUDIES OF SOME PYRAMIDAL $XY_3$ MOLECULES

S. Mohan and S. Durai
Division of Applied Sciences, Anna-University,
Madras Institute of Technology, Chrompet, Madras-600044 India.

ABSTRACT

A new look at molecular vibrations, developed in relation to pyramidal $XY_3$ molecules, resulted in fresh results with respect to molecular constants. Extending this study to twelve more molecules in this paper, it is found that the new procedure leads to interesting results in these cases as well. The potential constants, compliance constants, vibrational mean amplitudes, Coriolis coupling constants and rotational distortion constants are reported here for the molecules for the first time. It is also shown that the kinetic constant method leads to acceptable sets of characteristic constants for these molecules.

Introduction

Wilson's group theoretical method has been a powerful tool in the evaluation of potential constants of Polyatomic molecules. However there have been some imperfections in as much as some internal coordinates have not been taken into account so far. Additional internal coordinates naturally mean additional potential constants but it is possible to separate secondary potential constants from primary potential constants and the latter potential constants may be evaluated from spectral frequencies. Further, the evaluation of these primary potential constants may be carried out easily through an understanding and application of the kinetic constants of molecules. Such a comprehensive application of the group theoretical method has led to satisfactory results which was presented under the title "A new look at molecular vibrations". This procedure is now extended to twelve more cases of the pyramidal type of molecules in this paper. The symmetry coordinates, the $F$ matrix, the $G$ matrix, the $K$ matrix and other details of the procedure are the same as those given in earlier papers 1, 2, 3.

The results of the present investigation are once again interesting and confirm the potentialities of the new procedure in leading to satisfactory results in the study of molecular vibrations. The validity of the force field has also been tested by evaluating the mean square amplitudes of vibration, Coriolis coupling constants and centrifugal distortion using the present values of the potential constants. The evaluated molecular constants seem to be reasonable and they are in the expected range. It may be added that all the molecular constants for the molecules under...
Spectroscopic studies of some pyramidal XY₃ Molecules

study are reported here for the first time.

Theoretical Considerations

Using the G matrix and F matrix, the kinetic constants and the force constants of the XY₃ (r = 3) Pyramidal type (X = Pr, S, Se, Ge, Sn, Te and Y = F, Cl, Br, I) have been calculated. Using the force constants in Cyvin's secular equation the symmetrized mean square amplitude elements are obtained.

The Coriolis matrix elements - C*µ (r = 3) are obtained by the vector method of Meal and Polo² and Zeta matrix elements are evaluated from the relation Cµ = L⁻¹ C (L')⁻¹ making use of the kinetic constants. Cyvin et al.³ have formulated the theory of centrifugal distortion by introducing Cµ. The quantities Cµ have been obtained using Cyvin's relation and the non vanishing Cµ matrix elements have been evaluated. The centrifugal distortion constants of eleven molecules have been calculated using the force constants.

Results and Discussion

Results relating to twelve pyramidal XY₃ halides are discussed here. Table 1 gives the structural parameters and the vibrational frequencies of these molecules.

Table 2 gives the kinetic constants. The stretching kinetic constant and bond-bond interaction kinetic constant from a group known as Supplementary kinetic constants while the bending kinetic constant, angle-angle interaction kinetic constants from the complementary kinetic constants.

From Table 2, the following observation are made regarding the behaviour of kinetic constants.

1. The kinetic constant Kµ assume negative sign in all molecules.
2. The bond-bond interaction kinetic constant Kµ is positive in all the cases.
3. The angle-angle interaction kinetic constant Kµ is positive in some cases and negative in the other cases depending upon the molecule.
4. When the mass of the X atom increases (for the same Y atom), the stretching kinetic constant Kµ increases while the Kµ value decreases.
5. For the tribromides and tri iodide, |K'µ| values are quite large due to the increase in the mass of the halogen atoms.

From Table 3, the following observations are made.

1. The stretching force constant fµ and the interaction force constant fµ are positive in all cases.
2. The bending force constant fµ and the interaction force constant fµ are positive in all cases except in PrF₃ where fµ is negative.
3. The bond-angle interaction force constant f'µ is positive in SCl₃, SnBr₅, SnCl₅, and TeCl₅ where-as it is negative in PrF₃, SnCl₅, GeCl₅, SnF₅, SnBr₅, TeCl₅ and TeBr₅. Further it may be noticed that decrease of electronegativity of halogen
atom decreases the value of major potential constants viz., $f_a$ and $f_b$.

4. The bond-angle interaction force constant between a bond and the adjacent angle is greater than that between a bond and the distant angle. $f'_{ab}$ is the interaction between the bond and the distant angle and $f'_{ba}$ is the interaction between the bond and adjacent angle. This accounts for the fact that $|f'_{ab}| > |f'_{ba}|$. This observation is in line with the observation made in our earlier papers (1-3).

Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>Frequency $d(A')$, $v_1$ (A)</th>
<th>$Cm_{2-4}(A)$</th>
<th>$v_2$ (E)</th>
<th>$v_4$ (E)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sn $F_2^-$</td>
<td>2.30</td>
<td>458</td>
<td>188</td>
<td>394</td>
<td>150</td>
</tr>
<tr>
<td>2.</td>
<td>Sn $F_2^-$</td>
<td>2.30</td>
<td>429</td>
<td>152</td>
<td>382</td>
<td>129</td>
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<tr>
<td>3.</td>
<td>Pr $F_2$</td>
<td>-</td>
<td>525</td>
<td>86</td>
<td>458</td>
<td>99</td>
</tr>
<tr>
<td>4.</td>
<td>S $Cl_2^-$</td>
<td>2.00</td>
<td>519</td>
<td>284</td>
<td>543</td>
<td>214</td>
</tr>
<tr>
<td>5.</td>
<td>Ge $Cl_2^-$</td>
<td>2.35</td>
<td>320</td>
<td>162</td>
<td>253</td>
<td>139</td>
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<tr>
<td>6.</td>
<td>Se $Cl_2^-$</td>
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<td>437</td>
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<td>350</td>
<td>168</td>
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<td>Sn $Cl_2^-$</td>
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<td>297</td>
<td>128</td>
<td>256</td>
<td>163</td>
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<td>8.</td>
<td>Te $Cl_2^+$</td>
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<td>412</td>
<td>170</td>
<td>385</td>
<td>150</td>
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<td>9.</td>
<td>$^{*}$Te $Cl_2^+$</td>
<td>2.33</td>
<td>363</td>
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<td>83</td>
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<td>11.</td>
<td>$^{*}$Te$Br_2^+$</td>
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<td>240</td>
<td>110</td>
<td>222</td>
<td>87</td>
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<tr>
<td>12.</td>
<td>$^{*}$Te$I_2^+$</td>
<td>2.60</td>
<td>172</td>
<td>88</td>
<td>140</td>
<td>62</td>
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b - Univalent Cation  
c - Bivalent Cation  
$^{*}$ - Molecules which are considered to exist as ionic TeX$_2^+$X$^-$ molecules.
Spectroscopic studies of some pyramidal \textit{XY}_5 Molecules

Table 2

<table>
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<tr>
<th>No.</th>
<th>Molecule</th>
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<th>$K_{uv}$</th>
<th>$K_{ab}$</th>
<th>$K_{ab}$</th>
<th>$K_{dv}$</th>
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<td>0.0131</td>
<td>0.0242</td>
<td>0.0957</td>
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<td>2.</td>
<td>SnF$_5$</td>
<td>2.1139</td>
<td>0.0723</td>
<td>0.3405</td>
<td>0.0131</td>
<td>0.0242</td>
<td>0.0957</td>
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<td>-0.0167</td>
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<td>9.</td>
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<td>0.2057</td>
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<td>1.6095</td>
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</table>

The compliance constants of the molecules are listed in Table 4. The compliance constants are a measure of the bond strength, and interactions instead of force constants which are pointed by Decius$^7$ and Jones$^8$. It may be seen that the compliance constants exhibit trends opposite to that of force constants. The stretching compliance constant $W$ and the bending compliance constant $K_{dv}$ increase with the increase in the mass of the halogens.

(43)
Table 3
Potential Constants (10^4 dynes/cm) of the XY₃ molecules

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
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<th>f₂₀</th>
<th>f₃₀</th>
<th>f₄₀</th>
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<td>0.0069</td>
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<tr>
<td>7.</td>
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<td>0.0040</td>
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<td>10.</td>
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<td>11.</td>
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Table 5 presents the values of the valence mean-square amplitudes of vibration at 298.16K. The mean-square amplitudes (and hence mean amplitudes) \( \alpha_x \) and \( \alpha_y \) corresponding to the bonded and non-bonded distances respectively, are found to increase with the increase in mass of the Y atom. The vibrational mean amplitudes evaluated in the present investigation are in the expected range. These results are useful in the interpretation of electron diffraction date of these molecules.

Table 6 and 7 deal with the evaluated values of the Coriolis Coupling constants and the centrifugal distortion constants of the molecules. The Zeta values in table 6 obey the following sum rules given by Oka:

\[
(\omega_x'^2 + \omega_y'^2) + (\omega_x''^2 + \omega_y''^2) = 1
\]

\[
2(\omega_x'^2 + \omega_y'^2) + 2(\omega_x''^2 + \omega_y''^2) = 0
\]

They also further obey the relation

\[
(\omega_x'^2 - \omega_y'^2) = 0
\]

It is to be mentioned that the magnitudes of \( \omega_x'^2 \) and \( \omega_y'^2 \) are of the same order in all cases.

Further the high value of \( \omega_y'^2 \) in these cases suggest the strong coupling between the modes \( \nu_2 \) (A) and \( \nu_4 \) (E). The vibrational rotational coupling constants for the molecules in the present investigation are useful for bond assignments analysis of rotational structure and prediction of bond shapes.

The determination of the exact energy levels of the non-rigid molecules requires the knowledge of centrifugal distortion constants.

In Table 7 the decrease of \( D_M \) values and increase of \( D_J \) values with increase in the mass of the Y atom, may be observed in all the cases.

The centrifugal distortion constants obtained in the present investigation are in the expected range. Since the experimental results are not available for these molecules, to the authors knowledge the centrifugal constants are not compared.

Conclusion

All the molecular constants have been evaluated for the twelve molecules of \( XY_2 \) pyramidal system using kinetic constants. Uniform trends have also been seen in the values of the molecular constants of these molecules. It may be added that a systematic set of molecular constants relating to these molecules are available in the present work for the first time.
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Spectroscopic studies of some pyramidal \( XY_3 \) Molecules

Table 5
Valence Mean Square amplitudes \( (10^{-4} \text{A}^2) \) and Mean amplitudes \( (\text{A}^*) \) at 298.16K of the \( XY_3 \) Molecules

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<th>( \sigma_{d'd} )</th>
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(47)
Table 5 (Contd.)
Valence Mean Square amplitudes (10⁻⁸Å²) and Mean amplitudes (Å⁻¹)
at 298.16K of the XY₃ Molecules

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<th>bᵧ</th>
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Spectroscopic studies of some pyramidal \( XY_3 \) Molecules

### Table 6

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<td>10.</td>
<td>&quot;TeCl(^+)_2</td>
<td>0.2382</td>
<td>0.4819</td>
<td>0.8009</td>
<td>0.3491</td>
<td>0.1916</td>
<td>0.1239</td>
<td>0.7632</td>
<td>0.4936</td>
</tr>
<tr>
<td>11.</td>
<td>&quot;TeBr(^+)_1</td>
<td>0.4137</td>
<td>0.5848</td>
<td>0.7682</td>
<td>0.2925</td>
<td>0.3472</td>
<td>0.2469</td>
<td>0.7657</td>
<td>0.5445</td>
</tr>
<tr>
<td>12.</td>
<td>&quot;TeBr(^+)_2</td>
<td>0.5315</td>
<td>0.6806</td>
<td>0.7210</td>
<td>0.2540</td>
<td>0.4500</td>
<td>0.2165</td>
<td>0.7445</td>
<td>0.3504</td>
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</table>

### Acknowledgement

The authors wish to express their thanks to Dr. Sethikh, Director, Madras Institute of Technology, for his encouragement to pursue this investigation.

### References


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<th>-D</th>
<th>D</th>
</tr>
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<td></td>
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<td>0.4743</td>
<td>0.6534</td>
<td>0.2598</td>
</tr>
<tr>
<td>3</td>
<td>SeCl₄⁺</td>
<td>0.1378</td>
<td>0.1592</td>
<td>0.0544</td>
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<tr>
<td>4</td>
<td>GeCl₅⁻</td>
<td>0.2811</td>
<td>0.3064</td>
<td>0.0996</td>
</tr>
<tr>
<td>5</td>
<td>SnF₅⁻ᵇ</td>
<td>0.7898</td>
<td>0.7705</td>
<td>0.2227</td>
</tr>
<tr>
<td>6</td>
<td>SnF₅⁻ᶜ</td>
<td>0.9523</td>
<td>0.9876</td>
<td>0.3393</td>
</tr>
<tr>
<td>7</td>
<td>SnCl₅⁻</td>
<td>0.2603</td>
<td>0.2821</td>
<td>0.0607</td>
</tr>
<tr>
<td>8</td>
<td>SnBr₅⁻</td>
<td>0.0515</td>
<td>0.0674</td>
<td>0.0260</td>
</tr>
<tr>
<td>9</td>
<td>TeCl₅⁺</td>
<td>0.1298</td>
<td>0.1320</td>
<td>0.0484</td>
</tr>
<tr>
<td>10</td>
<td>*TeCl₄⁺</td>
<td>0.1485</td>
<td>0.1381</td>
<td>0.0425</td>
</tr>
<tr>
<td>11</td>
<td>*TeBr₄⁺</td>
<td>0.0368</td>
<td>-0.0023</td>
<td>0.0038</td>
</tr>
<tr>
<td>12</td>
<td>*Tel₂⁺</td>
<td>0.0309</td>
<td>-0.2908</td>
<td>0.0409</td>
</tr>
</tbody>
</table>

PARAMETRIC APPROACH TO THE FORCE FIELD STUDY OF SOME XY\(_2\) PLANAR MOLECULES

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(Received October 9, 1984)

The force field study of six XY\(_2\)\(_{\text{type}}\) molecules has been attempted using the parametric representation method. Experimental data such as frequencies and the vibrational mean amplitudes have been used to fix the unique force field for these cases. The compliance constants, Coriolis coupling constants and the centrifugal distortion constants have also been calculated and compared with the literature values.

PACS numbers: 33.10.Gx

1. Introduction

The determination of symmetry force constants from the vibrational frequencies alone is a mathematically undetermined problem. This is so because \(n\) vibrational frequencies of a given species are not sufficient for estimating the \(n(n+1)/2\) force constant elements \(F_{ij}\) in general. In the parametric approach the additional \(n(n-1)/2\) data for the determination of force constants are imposed on the parameter matrix which may be expressed in terms of trigonometrical functions of angle parameters. In the present work the vibrational amplitudes are retorted to these parameters. Using the relation and the experimentally observed mean amplitude values a determination of the parameters is possible.

2. Parametric approach

The internal coordinates \(S\) and the normal coordinates \(Q\) in molecules are related through the transformation \(S = LQ\). In the parametric method the transformation matrix \(L\) is written as

\[ L = L_A A, \]

where \(A\) is an orthogonal matrix. The matrix \(L_A\) is a triangular matrix and its elements can be obtained from \(L_A L_Q = G\). The orthogonal matrix \(A\) consists of only one parameter.

(14)
The elements of the symmetrized mean square amplitude matrix $\mathcal{S}$ are obtained from the expression (1)

$$\mathcal{S} = \mathcal{A} \mathcal{D} \mathcal{A}^T.$$

Here $\mathcal{A}$ is a diagonal matrix with the elements

$$A_i = \frac{h}{8\pi^2 \gamma_i^2} \coth \left( \frac{h \gamma_i}{2kT} \right),$$

where $\gamma_i$ is the wave number, $h$ is the Planck constant, $k$ is the Boltzmann constant, and $T$ is the absolute temperature.

The planar $XY_3$ molecules with $D_{3h}$ point group symmetry have the frequency distribution $1A'$, $1A''$, and $2E'$. The symmetrised mean square amplitudes are $\mathcal{S}_{11}$, $\mathcal{S}_{22}$, $\mathcal{S}_{44}$, $\mathcal{S}_{33}$ for the species respectively.

Substitution of equations (1), (2) and (4) in equation (3) leads to the following relations:

$$\mathcal{S}_{11} = \frac{(L_0)_{11}d_1}{1 + r^2},$$

$$\mathcal{S}_{22} = \frac{(L_0)_{22}d_2}{1 + r^2},$$

$$\mathcal{S}_{33} = \frac{(L_0)_{33}d_3}{1 + r^2} + \frac{(L_0)_{33}d_3}{1 + r^2},$$

$$\mathcal{S}_{44} = \frac{(L_0)_{44}d_4}{1 + r^2} + \frac{(L_0)_{44}d_4}{1 + r^2},$$

$$\mathcal{S}_{34} = \frac{(L_0)_{34}d_3 + (L_0)_{34}d_4}{1 + r^2} + \frac{(L_0)_{34}d_3 + (L_0)_{34}d_4}{1 + r^2} + \frac{(L_0)_{34}d_3 + (L_0)_{34}d_4}{1 + r^2}.$$

The vibrational mean amplitudes in molecules are related to the elements of $\mathcal{S}$ matrices. Corresponding to the bonded and non-bonded atom pairs, for the type of molecules under consideration the following relations (2) are significant

$$\sigma_a = (\mathcal{S}_{11} + 2\mathcal{S}_{33})/3,$$

$$\sigma_p = \mathcal{S}_{11} + \mathcal{S}_{22} + \mathcal{S}_{44} - \mathcal{S}_{33}/\sqrt{3}. $$
From a knowledge of the experimental values $\sigma_\alpha$ and $\sigma_\beta$, the parameter $t$ may be calculated. The equations being quadratic lead to two values of $t$. Of these two values one is eliminated by ordering the assignment of frequencies. This can be achieved by considering further experimental data viz. Coriolis coupling constants and centrifugal distortion constants. That is the value that can reproduce the experimental values of Coriolis coupling constants and rotational distortion constants.

Knowing $t$ the $L$-matrix is determined. Using the $L$-matrix the force constants may be directly computed from the vibrational frequencies of the molecule [3]

$$F = \tilde{L}^{-1} \tilde{J} \tilde{L}^{-1}.$$ 

The Coriolis coupling coefficients are evaluated by the method of Meal and Polo [3], using the relation

$$\zeta = L^{-1} (\tilde{L}^{-1}).$$

Cyvin et al. [5] have reformulated the theory of centrifugal distortion constant introducing quantities $t^{*}_{ij}$. The centrifugal distortion parameters $t^{*}_{ij}$ are calculated from

$$t^{*}_{ij} = \frac{h^2}{32\pi^2 I \omega_i \omega_j \omega_j}.$$ 

The centrifugal distortion constants $D_J$, $D_K$ and $D_{JK}$ for the planar molecules are given by

$$D_J = -\frac{t^{*}_{xxx}}{4},$$

$$D_K = -\frac{t^{*}_{yyz} - 3t^{*}_{zzx}}{4},$$

$$D_{JK} = -\frac{3}{2} (D_J + 2D_K).$$

3. Results and discussion

The experimental frequencies and the structural parameters used in the present calculation are reported in Table 1. The experimental values of vibrational amplitudes which are used for the evaluation of the parameter $t$ are presented in Table II. The evaluated force constants are given in

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>Bond distance [Å]</th>
<th>$v_1(\Delta)$</th>
<th>$v_2(\Delta)$</th>
<th>$v_3(\Delta)$</th>
<th>$v_4(\Delta)$</th>
<th>$v_5(\Delta)$</th>
<th>$v_6(\Delta)$</th>
<th>$v_7(\Delta)$</th>
<th>$v_8(\Delta)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^{10}$BF$_2$</td>
<td>1.3516</td>
<td>888</td>
<td>901</td>
<td>1454</td>
<td>440</td>
<td>[6, 7]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$^{10}$BCl$_2$</td>
<td>1.7421</td>
<td>471</td>
<td>460</td>
<td>936</td>
<td>243</td>
<td>150</td>
<td>[9, 10]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$^{10}$BBr$_2$</td>
<td>1.4932</td>
<td>375</td>
<td>375</td>
<td>375</td>
<td>106</td>
<td>102</td>
<td>[11]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$^{10}$BI$_2$</td>
<td>2.1000</td>
<td>190</td>
<td>336</td>
<td>704</td>
<td>100</td>
<td>100</td>
<td>[12, 13]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The interaction force constant $f_{ij}$ is negative in all the molecules. The bond bond interaction force constant $f_{ij}$ is negative in some cases and positive in other cases. It may also be noticed that an increase in the electronegativity of the central X atom is found to be associated with an increase in the values of all the force constants. These observations clearly indicate that the ionic character of the bond is an important factor.

### Table II

Mean amplitudes of vibration (experimental values) for planar $XY_2$ molecules [Å]

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>$(\alpha_0)^2[(\overline{X}-\overline{Y})]^2$</th>
<th>$(\alpha_0)^2[(\overline{Y}-\overline{Y})]^2$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF$_2$</td>
<td>0.0420 ± 0.02</td>
<td>0.0588 ± 0.003</td>
<td>[14]</td>
</tr>
<tr>
<td>2</td>
<td>BCl$_2$</td>
<td>0.0505 ± 0.0023</td>
<td>0.0700 ± 0.0023</td>
<td>[15]</td>
</tr>
<tr>
<td>3</td>
<td>BB$_2$</td>
<td>0.0514 ± 0.0063</td>
<td>0.0759 ± 0.0031</td>
<td>[9]</td>
</tr>
<tr>
<td>4</td>
<td>Bi$_2$</td>
<td>0.0559</td>
<td>0.0824</td>
<td>[9]</td>
</tr>
<tr>
<td>5</td>
<td>FeCl$_2$</td>
<td>0.060 ± 0.005</td>
<td>0.180 ± 0.0010</td>
<td>[16]</td>
</tr>
<tr>
<td>6</td>
<td>GaI$_2$</td>
<td>0.076</td>
<td>0.185</td>
<td>[17]</td>
</tr>
</tbody>
</table>

### Table III

Force constants [$10^4$ dynes/cm] of $XY_2$ molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$f_{12}$</th>
<th>$f_{13}$</th>
<th>$f_{23}$</th>
<th>$f_{11}$</th>
<th>$f_{22}$</th>
<th>$f_{33}$</th>
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</thead>
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<tr>
<td>BF$_2$</td>
<td>9.08159</td>
<td>3.88415</td>
<td>4.84746</td>
<td>2.56199</td>
<td>2.5862</td>
<td>1.86760</td>
</tr>
<tr>
<td>BCl$_2$</td>
<td>-0.04543</td>
<td>0.34407</td>
<td>-0.58636</td>
<td>0.0639</td>
<td>-0.06749</td>
<td>-0.11187</td>
</tr>
<tr>
<td>BB$_2$</td>
<td>0.38948</td>
<td>0.14890</td>
<td>0.25300</td>
<td>0.0853</td>
<td>0.04034</td>
<td>0.03439</td>
</tr>
<tr>
<td>Bi$_2$</td>
<td>-0.95329</td>
<td>-0.7025</td>
<td>-0.78926</td>
<td>-0.16549</td>
<td>-0.14276</td>
<td>0.15502</td>
</tr>
<tr>
<td>FeCl$_2$</td>
<td>0.28411</td>
<td>0.13807</td>
<td>0.09977</td>
<td>0.07908</td>
<td>0.03255</td>
<td>0.01544</td>
</tr>
<tr>
<td>GaI$_2$</td>
<td>0.076</td>
<td>0.185</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

### Table IV

Coriolis coupling constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>$\zeta_{12}$</th>
<th>$\zeta_{13}$</th>
<th>$\zeta_{23}$</th>
<th>$\zeta_{11}$</th>
<th>$\zeta_{22}$</th>
<th>$\zeta_{33}$</th>
<th>Ref.</th>
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<td>0.5086</td>
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<td>0.8692</td>
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<tr>
<td>2</td>
<td>BCl$_2$</td>
<td>0.9617</td>
<td>0.2754</td>
<td>0.8488</td>
<td>-0.8488</td>
<td>0.5288</td>
<td>PW</td>
<td>[15]</td>
</tr>
<tr>
<td>3</td>
<td>BB$_2$</td>
<td>0.9397</td>
<td>0.3812</td>
<td>0.7167</td>
<td>-0.7163</td>
<td>0.6948</td>
<td>PW</td>
<td>[16]</td>
</tr>
<tr>
<td>4</td>
<td>Bi$_2$</td>
<td>0.9045</td>
<td>0.1764</td>
<td>0.9382</td>
<td>-0.9382</td>
<td>0.3464</td>
<td>PW</td>
<td>[17]</td>
</tr>
<tr>
<td>5</td>
<td>FeCl$_2$</td>
<td>0.8028</td>
<td>0.6068</td>
<td>0.2731</td>
<td>-0.2731</td>
<td>0.9616</td>
<td>PW</td>
<td>[18]</td>
</tr>
<tr>
<td>6</td>
<td>GaI$_2$</td>
<td>0.8413</td>
<td>0.4897</td>
<td>0.5285</td>
<td>-0.5285</td>
<td>0.8488</td>
<td>PW</td>
<td>[19]</td>
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PW - present work
in the determination of the force field. The present values of the force constants are in good agreement with those determined uniquely using additional data such as Coriolis coupling constants and centrifugal distortion constants.

The Coriolis coupling constants obtained in the present investigation are given in Table IV. An increase in the mass of the central atom is associated with a decrease in the value of \( \zeta_2 \) and a corresponding increase in \( \zeta_{24} \) as seen in BCl—FeCl₃ and B₁₅—Ga₁₅. The constant \( \zeta_2 \) increases while \( \zeta_{24} \) decreases with the increasing mass of the \( Y \)-atom in boron trihalides. The zeta elements obey the following sum rules

\[
\zeta_2 - \zeta_{24} = 1,
\]

\[
\zeta_2 \zeta_{24} + \zeta_{24} = -1,
\]

\[
\zeta_2 + \zeta_{24} = 0.
\]

The calculated values of the Coriolis coupling constants of the molecules and ions fit the curves of mass dependence well. The excellent agreement between the calculated and observed values in the case of boron trihalides brings out the significance of the method of parametric representation.

The centrifugal distortion constants are presented in Table V.

The Coriolis coupling constants and the centrifugal distortion constants evaluated in the present work agree very well with the earlier works. This is in support of the significance of the method of parametric representation.

The authors are thankful to Prof. S. Sathik, Director, Madras Institute of Technology, Madras and Anna University for the facilities given to carry out this research work.

**TABLE V**

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>( D_J )</th>
<th>( -D_{JX} )</th>
<th>( D_E )</th>
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<td>BF₃</td>
<td>11.0297</td>
<td>12.6575</td>
<td>8.7930</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12.0643)</td>
<td>(21.8950)</td>
<td>(9.7892)</td>
</tr>
<tr>
<td>2</td>
<td>BCl₃</td>
<td>1.4412</td>
<td>2.5616</td>
<td>1.2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.4195)</td>
<td>(2.5180)</td>
<td>(1.1700)</td>
</tr>
<tr>
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<td>BBr₃</td>
<td>0.1871</td>
<td>0.3282</td>
<td>0.1526</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.2095)</td>
<td>(0.3656)</td>
<td>(0.1706)</td>
</tr>
<tr>
<td>4</td>
<td>BiCl₃</td>
<td>0.0606</td>
<td>0.1077</td>
<td>0.0505</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.0612)</td>
<td>(0.1090)</td>
<td>(0.0511)</td>
</tr>
<tr>
<td>5</td>
<td>FeCl₃</td>
<td>1.4820</td>
<td>2.7848</td>
<td>1.3476</td>
</tr>
<tr>
<td>6</td>
<td>GaCl₃</td>
<td>0.1001</td>
<td>0.1916</td>
<td>0.0957</td>
</tr>
</tbody>
</table>

Values in parentheses: Ref. [20].
REFERENCES

Infrared Far infrared Spectra and Normal Coordinate analysis of Chromium Trifluoride

S. Mohan, S. Durai and K. G. Ravikumar, Division of Applied Sciences, Anna University, MIT, Madras-600 044
(Received 29 March 1983)

Infrared and Fourier for infrared spectra of chromium tri-fluoride has been recorded and the vibrational frequencies are assigned to $C_{3v}$ point group. Further, based on the present assignment, a complete vibrational analysis has been arrived out for this molecule.

Introduction:

$XY_3$ type molecules fall under two categories (i) Planar type belonging to $D_{3h}$ symmetry such as $BF_3$ (i) and (ii) pyramidal type belonging to $C_{3v}$ symmetry such as $PF_3$ (2). The present study is initiated towards the assignment of $C_{3v}$ symmetry point group to $CrF_3$ and also to evaluate the molecular constants.
Chromium trifluoride was obtained from A. G. Chemische Fabrik, Schweiz. The far red spectrum of CrF$_3$ has been recorded in Perkin Elmer IR-257 double beam grating spectrophotometer in the region 625 to 4000 cm$^{-1}$. The Fourier far IR spectrum has also been recorded on Polytec FIR-30 in the region 100-650 cm$^{-1}$. The observed frequencies are listed in Table 1. The frequencies for all sharp bands are expected to be accurate to $\pm 1$ cm$^{-1}$.

**Results and Discussion:**

Planar XY$_3$ type molecules belonging to D$_{3h}$ point group are represented as $\Gamma = A_1 + A_2 + 2E$, which only three frequencies ($A_1$, $B_1$, and $2E$) are infrared active whereas pyramidal XY$_3$ type molecule belong to C$_2v$ point group has 2$A_1$ and 2E species both which are infrared and Raman active. Further $\nu_4$ frequencies corresponding to stretching modes are expected to be higher than $\nu_3$ and $\nu_4$ bending modes. The appearance of two prominent peaks at 382 and 450 cm$^{-1}$ suggests the Cs$_1$ molecular symmetry for this molecules which is in consistent with those concluded by Hiroto et al in the case of $\text{C}_2$. (2). It has been observed recently that for slightly non-planar molecules, the symmetric frequency was found to be higher than $\nu_3$ and $\nu_4$, whereas for planar molecules the symmetric frequency was found to be higher than the asymmetric frequency. We assign the band at 682 cm$^{-1}$ to $\nu_3(A_2)$ and $\nu_4(E)$ bands most difficult to assign as no definite guidelines were followed in assigning the bending frequencies. Following the above criteria for non-planar molecules, the bands at 382 and 450 cm$^{-1}$ are assigned to $\nu_3(A_2)$ and $\nu_4(E)$ respectively.

**On the basis of C$_2v$ symmetry a normal coordinate analysis has been carried out for CrF$_3$ molecules using a general quadratic potential function and molecular kinetic constants.**

The experimental part of the work is the same as given in the earlier papers (3,4). The kinetic constants, the force constants, the compliance constants and the vibrational mean square amplitudes at 16 K are given in Table 1. As expected, the reaction potential constants $f_{xx}$, $f_{xy}$, and $f_{yy}$ are active for this type of molecule. The Cr-F stretch-potential constant $f_{\sigma}$ is in the expected range. The present set of potential constants have been used in evaluating compliance constants, valence mean square amplitudes, coriolis coupling constants and centrifugal distortion constants.

The compliance constants which are evaluated for this molecule by Decius method (5) show the opposite to that relating to the potential constants using the force constants in Cyvin's secular equation for the symmetrized mean square amplitude elements and hence the vibrational mean amplitudes at 298.16 K have been obtained. From Table 2, it may be seen that the mean amplitudes for both the bonded and non-bonded distances obtained in the present investigation are in the characteristic range. The present set of values will be useful in the interpretation of electron diffraction data relating to this molecule. The present set of values for the vibrational mean amplitudes once again confirms the correctness of our assignment.

The first order (EXE type) and the second order (A$_1 \times E$ type) Coriolis coupling constants have been evaluated using the matrix relation $\xi_{ij} = L^{-1} \xi_{ij} (L^{-1})^T$ making use of kinetic constants. The Ca ($a = x$, $y$, $z$) matrix elements have been obtained by the vector method of Meal & Polo (7). The Zeta values listed in Table 3 obey the sum rules given by Oka (8). Similar to XY$_3$ pyramidal molecules the Coriolis coupling constants, $\xi_{12}$, $\xi_{14}$, and $\xi_{44}$ of CrF$_3$ are negative. Further, the magnitude of $\xi_{12}$, $\xi_{14}$, and $\xi_{44}$ are of the same order. The high values of $\xi_{12}$, $\xi_{14}$, and $\xi_{44}$ shows that the coupling concerned is much stronger.

The centrifugal distortion constants of chromium trifluoride have been calculated by Kivelson and Vitek.

**Table 1 Assignment of fundamental infrared frequencies (cm$^{-1}$) of CrF$_3$**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Intensity*</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>VS</td>
<td>$\nu_1$ (Cr-F: Symmetric stretch)</td>
</tr>
<tr>
<td>220.5</td>
<td>VS</td>
<td>$\nu_2$ (&lt;FCrF Symmetric bending)</td>
</tr>
<tr>
<td>682</td>
<td>VS</td>
<td>$\nu_3$ (Cr-F asymmetric stretch)</td>
</tr>
<tr>
<td>298</td>
<td>VS</td>
<td>$\nu_4$ (&lt;FCrF asymmetric bending)</td>
</tr>
</tbody>
</table>

*VS = Very Strong.
The present investigation. They are reported in
Table 3. As expected, the value of $D_{JK}$ is negative
for this molecule.

Conclusion:

A complete vibrational analysis of CrF$_4$ using
the vibrational frequencies obtained from infrared
and Fourier far infrared spectra is available on the
basis of $C_4v$ symmetry in the present study.

Acknowledgement:
The authors are thankful to Prof. S. Sathikh,
Director of Madras Institute of Technology for his
encouragement and facilities given to carry out this
research work. One of the authors (KGR) is thank­
ful to CSIR for the award of JRF which enabled him
to pursue this investigation.

Table: Values of kinetic constants ($10^{-3}$ g); Force Constants ($10^8$ dynes/cm),
compliance constants (m dyne/A) and Mean Square amplitudes
(Both bonded and non bonded) ($10^{-3}$ A$^2$) at 298'16 K

<table>
<thead>
<tr>
<th>Constants</th>
<th>d(Cr-F)</th>
<th>dd</th>
<th>$\alpha$</th>
<th>$\alpha\alpha$</th>
<th>dz</th>
<th>$\delta z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic constants</td>
<td>0.1397</td>
<td>0.2986</td>
<td>-0.0040</td>
<td>-0.0511</td>
<td>0.1613</td>
<td></td>
</tr>
<tr>
<td>Force constants</td>
<td>-0.2824</td>
<td>0.0803</td>
<td>-0.0111</td>
<td>-0.0290</td>
<td>0.0379</td>
<td></td>
</tr>
<tr>
<td>Compliance constants</td>
<td>0.0582</td>
<td>0.6353</td>
<td>0.1484</td>
<td>0.0010</td>
<td>-0.0554</td>
<td></td>
</tr>
<tr>
<td>Bonded mean square amplitudes</td>
<td>0.2120</td>
<td>2.9767</td>
<td>0.6263</td>
<td>0.0396</td>
<td>-0.0378</td>
<td></td>
</tr>
<tr>
<td>Non-bonded mean square amplitudes</td>
<td>5.6034</td>
<td>2.4286</td>
<td>1.8662</td>
<td>0.3624</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table: Mean amplitudes ($10^{-4}$A) at 298'16 K, Coriolis coupling constants
and centrifugal distortion constants (MHz)

<table>
<thead>
<tr>
<th>Mean amplitudes</th>
<th>Coriolis coupling constants</th>
<th>Centrifugal distortion constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\zeta^2$ 3a3b</td>
<td>$\zeta^2$ 1a4a</td>
<td>$\zeta^2$ 2a4a</td>
</tr>
<tr>
<td>5.1602</td>
<td>-0.2982</td>
<td>-0.3297</td>
</tr>
<tr>
<td>7.4856</td>
<td>-0.5156</td>
<td>-0.2433</td>
</tr>
</tbody>
</table>

Reference:

Infrared Spectroscopic Investigations of Praseodymium Trichloride (PrCl₃)

S. Mohan, S. Durei
Division of Applied Sciences, Anna University, M.I.T. Campus,
Madras 600 044, India

Infrared spectroscopic studies of pyramidal molecules evoked interest in several workers in recent years. In the study of Lanthanide rare earth trifluorides (1) it was found that the spectra of most were consistent with planar \(D_4h\) conformation. The observation of two intense infrared stretching absorptions of \(\text{PrF}_3\) seemed best interpreted in terms of pyramidal structure for this molecule.

The complete vibrational frequencies of \(\text{PrCl}_3\) are not available in the literature. Hence our attention has been turned to \(\text{PrCl}_3\) to study its vibrational spectrum. In the present investigation, the far-infrared spectrum of \(\text{PrCl}_3\), has been reported. The vibrational frequencies of this molecule have been assigned on the basis of pyramidal \(C_{3v}\) symmetry.

2. Experimental

The far infrared spectrum of \(\text{PrCl}_3\) has been recorded in the region 600 - 70 cm\(^{-1}\) on Polytrock FIR - 30 spectrophotometer. The observations of the infrared studies of the molecule are given in Table 1.

3. Results and Discussion

Four fundamental absorption bands have been observed at 502, 346, 93 and 81 cm\(^{-1}\). The vibrational representation of a \(\text{XY}_3\) planar \(D_4h\) molecule is represented as \(t = 2A_1 + 2E\). Accordingly in a planar molecule only three frequencies \(2E\) and \(2E\) are infrared active, while in a pyramidal system all the four frequencies \(2A_1 + 2E\) should be active.

In both the systems the \(\nu_1\) and \(\nu_2\) stretching modes are expected to occur at frequencies higher than the \(\delta_1\) and \(\delta_2\) bending frequencies. The assignment of the infrared bands at 502 and 346 cm\(^{-1}\) suggests the \(C_{3v}\) molecular symmetry for the molecule which is consistent with those concluded by Hewitt et al (2). The assignment of the high frequency fundamentals (stretching modes) can be made on the basis of their relative intensity. For slightly non planar molecules, one expects the \(\nu_2(E)\) mode to be much more intense than \(\nu_1(A_1)\). On the basis we have assigned the band at 346 cm\(^{-1}\) to \(\nu_1(A_1)\) and that at 502 cm\(^{-1}\) to \(\nu_2(E)\). However the low frequency \(\nu_2(A_1)\) and \(\nu_1(E)\) bands are more difficult to assign, as no definite guidelines exist for intensity and relative magnitude of the frequencies. It has been observed that in the case of pyramidal systems \(\nu_2(A_1) < \nu_1(E)\), hence we have assigned \(\nu_2(A_1)\) mode at 81 cm\(^{-1}\) and \(\nu_1(E)\) to 93 cm\(^{-1}\) bands. Further these frequencies have been compared with the fundamental frequencies of \(\text{PrF}_3\).

A normal coordinate analysis of Praseodymium Trichloride has been carried out following Wilson's \(F-3\) matrix method, on the basis of \(C_{3v}\) point group. Using a general quadratic valence force field and molecular kinetic constants, a set of force constants and the other molecular constants have been reported for the first time. The evaluated constants are given in Table 2. The values seem to be reasonable and they are in the expected range.

The Coriolis coupling coefficients obey the following sum rules:

\[
(\chi^{13a}\beta)(\chi^{14a}\beta) - (\chi^{13a}\gamma)(\chi^{14a}\gamma) = 0
\]

\[
(\chi^{13a}\gamma)^2 + (\chi^{14a}\gamma)^2 + (\chi^{13a}\beta)^2 + (\chi^{14a}\beta)^2 = \frac{1}{3} \frac{\mu_{12}^2}{\mu_{11}^2}
\]

\[
(\chi^{13a}\gamma)^2 + (\chi^{14a}\gamma)^2 + (\chi^{13a}\beta)^2 + (\chi^{14a}\beta)^2 = 1
\]
The high value 0.8025 for $\chi^2_{344b}$ indicates the strong coupling between the species concerned.

### Conclusion

A complete vibrational analysis of PrCl$_3$ using the vibrational frequencies obtained from far-infrared spectra is available on the basis of C$_{3v}$ symmetry, in the present study, for the first time.

### References


### Table 1:

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency Assignments</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>55</td>
<td>64</td>
</tr>
<tr>
<td>95</td>
<td>95</td>
<td>103</td>
</tr>
<tr>
<td>170</td>
<td>170</td>
<td>180</td>
</tr>
<tr>
<td>180</td>
<td>180</td>
<td>202</td>
</tr>
<tr>
<td>202</td>
<td>202</td>
<td>250</td>
</tr>
<tr>
<td>346</td>
<td>346</td>
<td>502</td>
</tr>
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</table>

### Table 2:

<table>
<thead>
<tr>
<th>Force Constant</th>
<th>Coriolis Coupling Constants</th>
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</thead>
<tbody>
<tr>
<td>$f_a$</td>
<td>$r_a \times r_b$</td>
</tr>
<tr>
<td>$f_{dd}$</td>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>$f_{aa}$</td>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>$f_{ab}$</td>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>$f_{bc}$</td>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>$f_{cd}$</td>
<td>$\chi^2_{344b}$</td>
</tr>
</tbody>
</table>

### Table 3:

<table>
<thead>
<tr>
<th>Potential energy distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>100% $E_1$</td>
</tr>
<tr>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>100% $E_2$</td>
</tr>
<tr>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>100% $E_3$</td>
</tr>
<tr>
<td>$\chi^2_{344b}$</td>
</tr>
<tr>
<td>100% $E_4$</td>
</tr>
</tbody>
</table>
This paper presents the Infrared and Laser Raman Spectra of Potassium periodate from 625 to 4000 cm$^{-1}$, and 50 to 4000 cm$^{-1}$, respectively. The vibrational analysis has been made for the io$^{-}$ ion on the basis of tetrahedral $T_d$ symmetry and the General Quadratic Valence Force constants are reported. The fundamental frequencies of $IO_4^-$ are $A = 837$, $E = 330$ and $F = 850$, 340 cm$^{-1}$.

Further using the values of the present potential constants other molecular constants have also been evaluated.

Introduction

In the course of our investigation on the study of some characteristic constants of Tetrahedral molecules (1, 2) our attention has been turned to Potassium per iodate. The Vibrational $\nu$ frequencies of iodate ions have been assigned on the basis of Tetrahedral $T_d$ symmetry. The spectrum consists of four normal vibrations; two belonging to $A$ type symmetry species, one of doubly degenerate $E$ species and one of triply degenerate $F$ type symmetry species.

Experimental:

Potassium periodate was obtained from B.D.H. laboratory chemicals (England). The Infrared spectrum and the Laser Raman spectrum of $KIO_4$ have been recorded in Perkin Elmer IR 257 double beam grating spectrophotometer (625-4000 cm$^{-1}$ and Cary model 82 Spectrophotometer (50-4000 cm$^{-1}$) respectively. The observed frequencies are listed in Table 1. The frequencies of all sharp bands are expected to be accurate $\pm 1$ cm$^{-1}$.

Results and Discussion:

Four fundamental frequencies have been observed at 837, 850, 330 and 340 cm$^{-1}$ in Laser Raman spectrum and a sharp intense band at 858 cm$^{-1}$ in I.R. spectrum. The band at 837 is much stronger than that at 850 cm$^{-1}$. In this type of molecules the $\nu_3$ and $\nu_4$ stretching modes are expected to occur at high frequencies than the $\nu_1$ and $\nu_2$ bending deformation. Hence the high frequency bands at 837 and 850 are assigned to $\nu_1$ (A) and $\nu_2$ (F).

The low frequency $\nu_3$ (E) and $\nu_4$ (F) bands are assigned as 330 cm$^{-1}$ and 340 cm$^{-1}$ respectively.

A normal coordinate analysis of $IO_4^-$ ion has been carried out following Wilson's F. G - matrix (3) on the basis of $T_d$ point group, using a General Quadratic Valence Force Field and a set of potential constants has been reported.

The symmetry coordinate, theory and other details of the procedure are the same as those given in early paper (1-2). Table 2 gives the kinetic constants, force constants, compliance constants and the valence mean square amplitudes. Table 3 deals with the mean amplitudes for the bonded and non-bonded distances, Bastiansen-Morino Shrinkage constant $\beta$, Coriolis coupling coefficients and the centrifugal distortion constants.

The following observations are made from Table 2. There are two types of kinetic constants.

(i) The complementary kinetic constants consisting of bond-angle interaction, bending and angle-angle interaction kinetic constants.

(ii) The supplementary kinetic constants, consists of stretching and bond-bond interaction kinetic constants. As expected the interaction kinetic constants $k^{aa}$ and $k^{ab}$ are negative for this type of molecule and the algebraic sum of $k_4$ and $k_{ad}$ is equal to $4m_o$.

The interaction force constants $f^{aa}$ and $f^{ab}$ are also negative as expected.

The trend of the compliance constants is just opposed to that of force constants.
From Table 3 the following observations may be made. The coriolis Coupling Coefficients obey the linear and quadratic sum rules, $\zeta_{xx}$ is negative and the high value of $\zeta_{xx}$ & $\zeta_{yy}$ suggest that the coupling between the vibration concerned is more significant than others. The centrifugal distortion constants, $D_1$ and $D_2$ are positive while $D_{jk}$ and $R_4$ are negative. The constants evaluated in the present investigation are in the expected range. This once again confirms the validity of the assignment.

Table 1 Observed Frequencies (in cm$^{-1}$) and interatomic distance (Å) of KIO$_4$.

<table>
<thead>
<tr>
<th></th>
<th>$v_1(A_1)$</th>
<th>$v_1(E)$</th>
<th>$v_2(F_g)$</th>
<th>$v_4(F_u)$</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Raman Spectrum</td>
<td>837</td>
<td>3:10</td>
<td>850</td>
<td>340</td>
<td>1.79</td>
</tr>
<tr>
<td>Infra Red Spectrum</td>
<td>VS</td>
<td>S</td>
<td>VS</td>
<td>M</td>
<td></td>
</tr>
</tbody>
</table>

VS—Very Strong, S—Strong, M—Medium.

Table 2 Kinetic Constants ($10^{-2}$ A$^2$) Force Constants ($10^{8}$ dynes/cm) Compliance Constants (Å/mdyne) and Valence Mean Square amplitudes ($10^{-2}$ A$^2$).

<table>
<thead>
<tr>
<th></th>
<th>d</th>
<th>dd</th>
<th>a</th>
<th>$\sigma_a$</th>
<th>$\sigma_d$</th>
<th>$R_4 = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Constants</td>
<td>2.4333</td>
<td>0.0742</td>
<td>0.2027</td>
<td>0.0551</td>
<td>0.0525</td>
<td></td>
</tr>
<tr>
<td>Force Constants</td>
<td>5.9957</td>
<td>0.0202</td>
<td>0.0814</td>
<td>0.0244</td>
<td>0.0215</td>
<td></td>
</tr>
<tr>
<td>Compliance Constants</td>
<td>0.1665</td>
<td>0.0050</td>
<td>2.1638</td>
<td>0.2148</td>
<td>0.0175</td>
<td></td>
</tr>
<tr>
<td>Valence Mean Square</td>
<td>1.4489</td>
<td>-0.0482</td>
<td>10.5823</td>
<td>0.9627</td>
<td>0.1523</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 3 Mean amplitudes (Å), Shrinkage Constants ($10^{-3}$ Å), Coriolis Coupling coefficients, and Centrifugal Distortion Coefficients (KHZ).

<table>
<thead>
<tr>
<th></th>
<th>$\zeta_{xx}$</th>
<th>$\zeta_{yy}$</th>
<th>$\zeta_{xz}$</th>
<th>$\zeta_{yz}$</th>
<th>$\zeta_{zz}$</th>
<th>$\zeta_{xy}$</th>
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<tbody>
<tr>
<td>Coriolis Coupling</td>
<td>0.1439</td>
<td>0.3561</td>
<td>0.7425</td>
<td>0.7555</td>
<td>-0.6552</td>
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<tr>
<td>Coefficients</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Centrifugal distortion</td>
<td>$D_1$</td>
<td>$D_2$</td>
<td>$R_{jk}$</td>
<td>$R_4$</td>
<td>$R_4 = 0$</td>
<td>$R_4 = 0$</td>
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<tr>
<td>Constants</td>
<td>0.7706</td>
<td>0.9231</td>
<td>-0.7913</td>
<td>-0.0659</td>
<td></td>
<td></td>
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</tbody>
</table>

References:
Lattice dynamics of calcium oxide using three body force shell model* 

S Mohan, S Durai and O Vaidyanathan 

Abstract: The alkaline earth oxide crystals are predominantly ionic in character and their lattice dynamics can be studied on the basis of the same theoretical models which are applicable to alkali halides. The lattice vibrations of calcium oxide is studied on the basis of the three body force shell model. This model takes care of the effect of many-body interactions in the lattice potential. The aim of the present work is to treat the various interactions between the ions in a more general way without making them numerically equal.

The dispersion curves thus obtained agree well with the experiments.

Keywords: Lattice dynamics, alkaline earth oxide, calcium oxide.

1. Introduction

The dielectric properties of the alkali halides have been explained using the shell model developed by Dick and Overhauser (Dick and Overhauser 1939). Later this model has been suitably developed (Wood et al. 1963) for the study of vibrational properties of these solids. Further this model was improved by Verma and Singh (Verma and Singh 1969) by including the three body forces between ion pairs. This improved model was employed by Upadhyaya and Singh to calcium oxide (Upadhyaya and Singh 1972).

The original formulation of three body shell model suffered from a discrepancy in respect of the definition of shell, core charges and electronic polarizabilities of the ions which was later removed (Verma and Agarwal 1973). An application of the corrected theory to MgO has led to interesting results. But the electronic polarizability of Mg** is negligibly small, compared to that of O**. Hence MgO is more suited to one ion polarizable version of the TBM. But the polarizability of Ca** is sufficiently large for making CaO suitable for two ion polarizable version of TBM. Studies of CaO (Upadhyaya and Singh 1972) CoO, MnO and NiO (Gupta and Verma 1977) led to interesting results.

where \( \phi \) is a column matrix of elements \( U_1, U_2, W_1 \) and \( W_2 \) and \( B \) is a column matrix of elements:
\[
B = \begin{bmatrix}
M_1 & U_1 \\
M_2 & U_2 \\
0 & 0
\end{bmatrix}
\]

where \( M_1 \) and \( M_2 \) are the masses of the constituents. The solution of this equation is possible with appropriate substitutions of the values. The actual components to be substituted for each mode are as given by Cowley et al. (Cowley et al. 1963). The quadratic nature of the equation leads to two frequencies in each mode viz., optical and acoustical.

3. Results and Discussion

The input data presented in Table 1 are the elastic constants, lattice constant, the long wave optical frequencies and the polarizability.

Table 1. Input data (Agarwal and Verma 1975).

<table>
<thead>
<tr>
<th>Elastic constant ((10^4 \text{ dyn/cm}^2))</th>
<th>Lattice constant ((10^{-8} \text{ cm}))</th>
<th>Longwave optical frequency ((10^4 \text{ rad/sec}))</th>
<th>Molecular polarizability ((10^{-14} \text{ cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_1 )</td>
<td>51.94</td>
<td>2.6008</td>
<td>( \omega_1 ) 10.88</td>
</tr>
<tr>
<td>( G_2 )</td>
<td>5.91</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>( G_3 )</td>
<td>8.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The basic equations used for the calculation of the model parameters from the elastic constants are the same as given by Agarwal (Agarwal 1977). The calculated model parameters are given in Table 2.

Table 2.

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>( f_{\text{ag}} )</th>
<th>( A )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>21.48000</td>
<td>2.00000</td>
<td>1.00000</td>
</tr>
<tr>
<td>( B )</td>
<td>-8.28910</td>
<td>-1.00000</td>
<td></td>
</tr>
<tr>
<td>( (\cdot) )</td>
<td>-0.02814</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The vibration frequencies of CaO in the symmetry directions are given in Table 3. The experimental values of Vijayaraghavan and Iyengar (Agarwal and Verma 1973) as estimated from the graph are given in parenthesis. It is encouraging to note that the frequences evaluated using the present model are in reasonable agreement with the experimental values, wherever such data are available. This supports our approach to the problem of lattice vibrations.