Molecular Force Fields of Some XY₆ Type Ions of Oh Symmetry

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The L matrix approximation method has been applied to hexachlorides and hexabromides of Tin and Titanium of Oh symmetry. All the seven independent force constants have been evaluated using Wilson’s G — F matrix method. Mean amplitudes of vibration have been computed using latest fundamental frequencies.

Octahedral molecules or ions of XY₆ type belonging to Oh symmetry have six normal modes of vibration. On group theoretical considerations,

\[ F_{\text{n}} = a_{1g} + e_{g} + 2 f_{1u} + f_{2g} + f_{2u}. \]

Out of these six, the three gerade modes, \( v_1 (a_{1g}) \), \( v_2 (e_{g}) \), and \( v_5 (f_{2g}) \) give rise to Raman active fundamentals; the two modes \( v_3 \) and \( v_4 (f_{1u}) \) are permitted in the infrared, while the last \( v_6 (f_{2u}) \) mode is forbidden in both, Raman effect and infrared, though it may appear in combination. \( v_1, v_2 \), and \( v_5 \) are associated with essentially valence vibrations while \( v_3, v_4 \), and \( v_6 \) are essentially deformation vibrations.

A number of octahedral molecules of XY₆ type, particularly hexafluorides, belonging to Oh symmetry, have been subjected to normal coordinate treatment by a number of workers \(^\text{1-11}\). A good many of them have used different and almost arbitrary assumptions to evaluate force constants for \( f_{1u} \) type of vibrations which has rendered their comparative study almost impossible. Recently MÜLLER et al. \(^\text{12}\) have published papers about the evaluation of force constants with the matrix method. This method has been fruitfully employed to evaluate all the seven force constants uniquely (using GVFF). CLARK et al. \(^\text{13}\) have recently reported the fundamental frequencies for hexachlorides SnCl₆ \(^{2-}\) and TiCl₆ \(^{2-}\) and hexabromides SnBr₆ \(^{2-}\) and TiBr₆ \(^{2-}\) ions. These are given in Table 1. It was thought desirable, therefore, to evaluate all the seven force constants. Mean amplitudes of vibration for these ions have also been evaluated.

### Table 1. Fundamental Frequencies in cm\(^{-1}\) and Interatomic Distances in Å

<table>
<thead>
<tr>
<th>Ions</th>
<th>( v_1 )</th>
<th>( v_2 )</th>
<th>( v_3 )</th>
<th>( v_4 )</th>
<th>( v_5 )</th>
<th>( X-Y )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₆ (^{2-})</td>
<td>309</td>
<td>232</td>
<td>291</td>
<td>163</td>
<td>159</td>
<td>112</td>
<td>2.43 (^\text{13})  (^\text{15})</td>
</tr>
<tr>
<td>SnBr₆ (^{2-})</td>
<td>182</td>
<td>135</td>
<td>203</td>
<td>111</td>
<td>101</td>
<td>71</td>
<td>2.775 (^\text{13})  (^\text{16})</td>
</tr>
<tr>
<td>TiCl₆ (^{2-})</td>
<td>320</td>
<td>271</td>
<td>316</td>
<td>183</td>
<td>173</td>
<td>122</td>
<td>2.34 (^\text{13})  (^\text{15})</td>
</tr>
<tr>
<td>TiBr₆ (^{2-})</td>
<td>192</td>
<td>162</td>
<td>244</td>
<td>119</td>
<td>115</td>
<td>81</td>
<td>2.45 (^\text{13})  (^\text{15})</td>
</tr>
</tbody>
</table>

The normal coordinate treatment using G — F matrix method \(^\text{17}\) has been carried out. The symmetry coordinates which are constructed from the linear combination of internal coordinates must transform according to the character of the vibration type concerned and must be normalized as well. The selection of internal coordinates, and construction of symmetry coordinates are the same as used by Pistorius. \(^\text{9}\) C and F matrices used in the present work are as follows:

For \( a_{1g} \) type vibration:

\[ G_{11} = \mu_{yg}; \]

For \( e_{g} \) type vibration:

\[ G_{11} = \mu_{yg}; \]

For \( f_{1u} \) type vibration:

\[ \begin{align*}
G_{11} &= 2 \mu_{x}; \\
G_{12} &= 2 \mu_{x} + \mu_{y}; \\
G_{22} &= 8 \mu_{x} + 2 \mu_{y}; 
\end{align*} \]

\[ F_{11} = f_{x} + 4 f_{rr} + f_{rr}'; \]

\[ F_{11} = f_{x} - 2 f_{rr} + f_{rr}'; \]

\[ F_{12} = F_{21} = -2 (f_{xx} - f_{rs}'); \]

\[ F_{22} = f_{x} + 2 f_{xx} - 2 f_{rs}'; \]

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\(^{9}\) B. Krebs and A. Müller, Spectrochim. Acta 22, 1532 [1966].

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For $f_{2g}$ type vibration:

$$ G_{11} = 4 \mu_y; \quad F_{11} = f_a - 2 f'_{as} + f'''_{as}. $$

For $f_{2u}$ type vibration:

$$ G_{11} = 2 \mu_y; \quad F_{11} = f_a - 2 f'_{as} + 2 f''_{as} - f''''_{as}. $$

Here $\mu_x$ and $\mu_y$ are the respective reciprocals of atomic masses of metal and halide atoms.

Using six fundamental frequencies, only six and not all the force constants can be evaluated using the secular equation $|G F - E^2| = 0$. It is not surprising, therefore, to find that earlier authors have either neglected less important constants or made not very logical assumptions. Recently some authors have tried to overcome the uncertainty in force constant calculations by the use of additional mathematical constraints. The present authors have used MÜLLER'S second method to evaluate all the seven force constants. These are given in Table 2.

<table>
<thead>
<tr>
<th>Ions</th>
<th>$f_r$</th>
<th>$f'_{rs}$</th>
<th>$f''_{rs}$</th>
<th>$f_{as} - f'_{as}$</th>
<th>$f''_{as}$</th>
<th>$f_{as} - f''_{as}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl$_6^{-2}$</td>
<td>1.30</td>
<td>0.11</td>
<td>0.14</td>
<td>0.06</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>SnBr$_6^{-2}$</td>
<td>1.05</td>
<td>0.04</td>
<td>0.12</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiCl$_6^{-2}$</td>
<td>1.40</td>
<td>0.33</td>
<td>0.10</td>
<td>0.16</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiBr$_6^{-2}$</td>
<td>1.18</td>
<td>0.22</td>
<td>0.08</td>
<td>0.10</td>
<td>0.14</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 2. Force Constants in $10^5$ dyne cm$^{-1}$.

**Trends in Force Constants**

A comparison of the same type of force constants for SnCl$_6^{-2}$ and SnBr$_6^{-2}$ on the one hand and TiCl$_6^{-2}$ and TiBr$_6^{-2}$ on the other hand indicates interesting decrease as expected from hexachlorides to hexabromides. The main force constants $f_r$ and $f_{as} - f''_{as}$ for both the pairs of ions. A look at Table 1 will show that the interatomic distance $X - Y$ for chlorides is smaller than that of bromides resulting in stronger bonding for the chloride ions as compared to the bromide ions under the influence of the similar type of chemical bonding involved. Again comparison of $f_r$ and $f_{as} - f''_{as}$ for SnCl$_6^{-2}$ and TiCl$_6^{-2}$ and for SnBr$_6^{-2}$ and TiBr$_6^{-2}$ shows that the force constants increase from tin halide to titanium halide ions.

The mean amplitudes of vibration for the hexahalide ions of tin and titanium have been evaluated from the available fundamentals, using CYVIN'S secular equation $|G F - E^2| = 0$ at 0°K and 298°K, where $\Sigma$ is the symmetrized mean square amplitude matrix, $G^{-1}$ is the K.E. matrix and $A_k$ is related to the normal mode of vibration $v_k$ by

$$ A_k = \frac{\hbar}{8 \pi^2 v_k} \frac{1}{\cosh \frac{\hbar v_k c}{2 K T}}. $$

Factorisation, of the secular equation on group theoretical considerations, though giving one dimensional equations for the $a_{1g}$, $e_{2g}$, $f_{2g}$ and $f_{2u}$ types of vibration, give a two dimensional equation for the $f_{1u}$ type of vibration. Again the same method was used to give the solution for the above mentioned two dimensional equation, giving all symmetrized mean square amplitude matrices $\Sigma$, whose elements are also connected to mean amplitudes of vibration. The calculated mean amplitudes of vibration are given in Table 3.

**Acknowledgements**

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22. S. J. CYVIN, Molecular Vibration and Mean Square Amplitude, Universitetsforlaget, Oslo 1968.