Molecular Force Fields of Some XY₆ Type Ions of O₈ Symmetry

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The L matrix approximation method has been applied to hexachlorides of Tin and Titanium of O₈ 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 O₈ symmetry have six normal modes of vibration. On group theoretical considerations,

\[ G_{\text{vib.}} = a_{1g} + e_g + 2 f_{1u} + f_{2u} + f_{2g} \]

Out of these six, the three gerade modes, \( v_1(a_{1g}) \), \( v_2(e_g) \) and \( v_3(f_{2g}) \) give rise to Raman active fundamentals; the two modes \( v_2 \) 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 \( v_3 \) are associated with essentially valence vibrations while \( v_4, v_5, \) and \( v_6 \) are essentially deformation vibrations.

A number of octahedral molecules of XY₆ type, particularly hexafluorides, belonging to O₈ symmetry, have been subjected to normal coordinate treatment by a number of workers. A good many of them have used different and almost arbitrary assumptions to evaluate force constants for \( f_{1g} \) type vibrations which must be normalized as well. The selection of internal 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 and \( G \) and \( F \) matrices used in the present work are as follows:

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

\[ G_{11} = \mu_y; \]

\[ F_{11} = f_r + 4 f_t + f'_r. \]

For \( e_g \) type vibration:

\[ G_{11} = \mu_y; \]

\[ F_{11} = f_r - 2 f_t + f'_r. \]

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

\[ G_{12} = 2 \mu_x + \mu_y; \]

\[ F_{12} = f_{1u} + f_{2u}. \]

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>( v_6 ) a</th>
<th>( X )</th>
<th>( Y )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₆²⁻</td>
<td>309</td>
<td>232</td>
<td>291</td>
<td>163</td>
<td>159</td>
<td>112</td>
<td>2.43</td>
<td>15</td>
<td>13, 14</td>
</tr>
<tr>
<td>SnBr₆²⁻</td>
<td>182</td>
<td>135</td>
<td>203</td>
<td>111</td>
<td>101</td>
<td>71</td>
<td>2.77</td>
<td>b</td>
<td>13, 14</td>
</tr>
<tr>
<td>TiCl₆²⁻</td>
<td>320</td>
<td>271</td>
<td>316</td>
<td>183</td>
<td>173</td>
<td>122</td>
<td>2.34</td>
<td>15</td>
<td>13, 14</td>
</tr>
<tr>
<td>TiBr₆²⁻</td>
<td>192</td>
<td>162</td>
<td>244</td>
<td>119</td>
<td>115</td>
<td>81</td>
<td>2.45</td>
<td>b</td>
<td>13, 14</td>
</tr>
</tbody>
</table>

Ref.

2 M. J. Reiffeld, J. Mol. Spectrosc. 29, 120 [1969].
5 J. Gaunt, Trans. Faraday Soc. 49, 1122 [1953]. (Referred at page 1125.)

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

For \( e_g \) type vibration:

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

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For $f_{2g}$ type vibration:

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

For $f_{2u}$ type vibration:

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

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 \[ |G - E\lambda| = 0. \] 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 method to evaluate all the seven force constants. These are given in Table 2.

### Table 2. Force Constants in 10^5 dyne cm⁻¹.

<table>
<thead>
<tr>
<th>Ions</th>
<th>$f_s$</th>
<th>$f_{rr}$</th>
<th>$f_{rr}$</th>
<th>$f_{rr} - f'_{ss}$</th>
<th>$f_a - f'''_{as}$</th>
<th>$f_{as} - f''_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₆⁻²</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>SnBr₆⁻²</td>
<td>1.05</td>
<td>0.04</td>
<td>0.12</td>
<td>0.08</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>TiCl₆⁻²</td>
<td>1.40</td>
<td>0.33</td>
<td>0.10</td>
<td>0.10</td>
<td>0.16</td>
<td>0.00</td>
</tr>
<tr>
<td>TiBr₆⁻²</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>

### Trends in Force Constants

A comparison of the same type of force constants for SnCl₆⁻² and SnBr₆⁻² on the one hand and TiCl₆⁻² and TiBr₆⁻² on the other hand indicates interesting decrease as expected from hexachlorides to hexabromides. The main force constants $f_s$ and $f_a - f'''_{as}$ 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 $f'_{ss}$ for SnCl₆⁻² and TiCl₆⁻² and for SnBr₆⁻² and TiBr₆⁻² shows that the force constants increase from tin halide to titanium halide ions.

### Mean Amplitude of Vibration

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 \[ \Sigma G^{-1} - \Delta E = 0 \] at 0 K and 298 K, where $\Sigma$ is the symmetrized mean square amplitude matrix, $G^{-1}$ is the K.E. matrix and $\Delta_k$ is related to the normal mode of vibration $\nu_k$ by

\[ \Delta_k = \frac{\hbar}{8 \pi^2 \nu_k c} \coth \frac{\hbar \nu_k c}{2 kT}. \]

Factorisation, of the secular equation on group theoretical considerations, though giving one dimensional equations for the $a_{1g}$, $e_g$, $f_{2g}$ 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.

### Table 3. Mean Amplitude of Vibration $u$ in Å.

<table>
<thead>
<tr>
<th>Ions</th>
<th>$T=0^\circ\text{K}$</th>
<th>$T=298^\circ\text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$u(\text{X} - \text{Y})$</td>
<td>$u(\text{Y}...\text{Y})$</td>
</tr>
<tr>
<td>SnCl₆⁻²</td>
<td>0.047</td>
<td>0.0613</td>
</tr>
<tr>
<td>SnBr₆⁻²</td>
<td>0.0440</td>
<td>0.0534</td>
</tr>
<tr>
<td>TiCl₆⁻²</td>
<td>0.0519</td>
<td>0.0697</td>
</tr>
<tr>
<td>TiBr₆⁻²</td>
<td>0.0999</td>
<td>0.0581</td>
</tr>
</tbody>
</table>

### Acknowledgements

The authors wish to thank Professor A. MÜLLER for consultation and to Prof. S. LOKANATHAN for the interest taken by him during the progress of this work. One of us (M. L. M.) is also grateful to the U. G. C. (India) for the grant of Postgraduate Research Scholarship.

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