Molecular Force Fields of Some Selenium and Tellurium Hexahalide Ions
M. N. AVASTHI and M. L. MEHTA
Department of Physics, University of Jodhpur, Jodhpur, India

Wilson's GF matrix method has been used to evaluate all the seven independent force constants of some XY₆ type ions using Müller's mathematical constraint. Mean amplitudes of vibration and Bastiansen-Morino shrinkages have also been calculated for these ions.

1. Introduction

XY₆ type molecules and ions, generally are found to possess Oh symmetry or are most likely to possess it. Group theoretical considerations lead to the fact that the symmetry distribution of vibration of these molecules or ions in this point group is given by

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

Out of the six normal modes of vibrations, the three gerade modes \( v_1(a_{1g}) \), \( v_2(e_g) \) and \( v_2(f_{1u}) \) give rise to Raman active fundamentals; the two \( v_3(f_{1u}) \) modes are the permitted fundamentals in the infrared while the remaining \( v_6(f_{2u}) \) mode is forbidden in Raman effect and infrared. The vibrations \( v_1 \), \( v_2 \) and \( v_3 \) primarily involve stretching of the \( X-Y \) bond while the remaining vibrations \( v_4 \), \( v_5 \) and \( v_6 \) are associated with skeletal deformations arising from \( Y-X-Y \) bending modes.

Normal coordinate analysis for the molecules and ions of XY₆ type using various force fields, has been made by different workers. Recently the fundamental frequencies of SeCl₆⁻², SeBr₆⁻², TeCl₆⁻² and TeBr₆⁻² ions have been reported by HENDRA and JOVIC and WARE for the first time. These are reported in Table 1. The former authors have also made a normal coordinate analysis using U.B.F.F. It was thought desirable, therefore, to evaluate all the seven force constants with the help of given frequency data for these ions. Naturally the force constants, as evaluated here, must be nearer to the actual values. The present investigation may basically be considered as an extension of the work of HENDRA and JOVIC and an almost full theoretical analysis of the vibrational data.

Using latest available frequency and structural data for these ions the mean amplitudes of vibration and Bastiansen-Morino shrinkages were also calculated.

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Table 1. Fundamental frequencies in cm⁻¹ and interatomic distances \( X-Y \) in Å.

<table>
<thead>
<tr>
<th>IONS</th>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_3 )</th>
<th>( r_4 )</th>
<th>( r_5 )</th>
<th>( r_6 )</th>
<th>( X-Y ) Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeCl₆⁻²</td>
<td>286</td>
<td>257</td>
<td>280</td>
<td>159</td>
<td>165</td>
<td>(117)</td>
<td>2.39 17,26</td>
</tr>
<tr>
<td>SeBr₆⁻²</td>
<td>179</td>
<td>159</td>
<td>225</td>
<td>122</td>
<td>105</td>
<td>(75)</td>
<td>2.54 17,27</td>
</tr>
<tr>
<td>TeCl₆⁻²</td>
<td>280</td>
<td>247</td>
<td>260</td>
<td>150</td>
<td>159</td>
<td>(98)</td>
<td>2.541 17,18,28</td>
</tr>
<tr>
<td>TeBr₆⁻²</td>
<td>179</td>
<td>159</td>
<td>200</td>
<td>102</td>
<td>105</td>
<td>(75)</td>
<td>2.71 17,29</td>
</tr>
</tbody>
</table>

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Reprints request to Dr. M. N. AVASTHI, 807, Chopasani Road, Saradpur (Jodhpur), India.

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In order to determine the inactive fundamental \( r_4 \), Wilson's rule (mentioned on page 1125 in Ref. 1) has been applied in our calculation and these calculated values are given in parentheses. It may be added that \( r_5 \) calculated, using UBFF, was the same as got by Wilson's rule.
2. Evaluation of Force Constants

Within the framework of Wilson's GF matrix method, the normal coordinate analysis has been carried out. The first problem involved in the evaluation of the force constants is the choice of the suitable set of symmetry coordinates. These coordinates are the linear combinations of the internal coordinates of the molecules or ions concerned. These internal coordinates usually are the bond length displacements $\Delta r_i$ and the internal bond displacements $\Delta z_{ij}$ ($i \neq j$). The symmetry coordinates belonging to each representation must be normalized and orthogonalized as well. In our investigation these are the same as used by Pistorius. The next step is the choice of a suitable force field. In general, it resolves itself to the use of either the general quadratic function or a Urey Bradley type potential. We have used the former which is given by the expression

$$2V = \sum_i F_i S_i + 2 \sum_{ij} \sum_k F_{ij} S_i S_j,$$

where $F_i$ are the valence type force constants, $S_i$ are the valence type internal displacement coordinates and $F_{ij}$ are the interaction constants. The $G$ and $F$ matrix elements used in our work are as follows:

For $a_{1g}$ type vibration:

$$G_{11} = \mu_y, \quad F_{11} = f_r + 4f_{rr} + f_{rr}'.$$

For $e_g$ type vibration:

$$G_{11} = \mu_y, \quad F_{11} = f_r - 2f_{rr} + f_{rr}'.$$

For $f_{1u}$ type vibration:

$$G_{11} = 2\mu_x + \mu_y, \quad F_{11} = f_r - f_{rr}',$$

$$G_{12} = G_{21} = 4\mu_x, \quad F_{12} = F_{21} = -2(f_{rr} - f_{rr}'''),$$

$$G_{22} = 8\mu_x + 2\mu_y, \quad F_{22} = f_{so} + 2f_{oa} - 2f_{ax} - f_{ax}'''.$$

For $f_{2g}$ type vibration:

$$G_{11} = 4\mu_x, \quad F_{11} = f_r - 2f_{ax} + f_{ax}'.$$

For $f_{2u}$ type vibration:

$$G_{11} = 2\mu_y, \quad F_{11} = f_r - 2f_{oa} + 2f_{ax} - f_{ax}'',$$

where $\mu_x$ and $\mu_y$ are reciprocals of atomic masses of metal and halide atoms respectively. The valence force constants used here are: $f_r$ — the bond stretching constant for the metal-halide bond; $f_{rr}$ — the constant for the interaction between a bond being stretched and an adjacent bond; $f_{rr}'$ — the constant for interaction between a bond being stretched and a bond opposite to it; $f_{ra}$ — is the interaction constant between an angle and one of the bond forming it's side; $f_{ra}''$ — is the interaction constant between an angle and a bond in its plane but not forming one of it's sides; $f_a$ — is the bending force constant; $f_{oa}$ — the interaction constant between an angle and an adjacent angle in the same plane; $f_{ax}$ — the interaction constant between an angle and an angle when one bond is common to both bending pairs and others are opposite; $f_{ax}''$ — the interaction constant between an angle and an angle in the adjacent plane but with no bond in common and $f_{ax}'''$ — the interaction constant between an angle and an angle when bending angles are opposite to each other.

A scrutiny of the above expressions shows that there are more than six independent force constants to be evaluated while using the secular equation $|GF - E \lambda | = 0$. This is precisely what has been done by many of the earlier authors. No reasons have been advanced by them — except that of computational convenience. Further, different authors have made different assumptions which do not allow a comparative study of these force constants for a sequence of similar molecules or ions. It was, particularly, from this point of view of comparative study for a series of $XY_6$ type molecules and ions that these have been taken up for investigation — out of these some have already been reported, four are reported in this paper and further work is in progress in this direction.

Very recently, additional mathematical constraints have been used to overcome the above mentioned difficulty. Out of all these, to the present authors, MÜLLER's method seems to be most practical for species with a heavy central atom. We have, therefore, used it-leading to a unique evaluation of all the seven force constants. The force constants along with symmetry force constants for the $f_{1u}$ mode are given in Table 2.

3. Trends of Force Constants

(i) The stretching force constants $f_r$ decrease as the Y-atom is changed from chlorine to bromine.
when the X-atom remains unchanged. The same is true when the Y-atom remains as it is while the X-atom is changed from Se to Te.

These facts are consistent both
a) with the decrease in the electronegativity, as we go from chlorine to bromine, and
b) the internuclear distance involved.

4. Mean Amplitudes of Vibration

Using the latest available fundamentals, the mean amplitudes of vibration have been evaluated from the secular equation \(|\Sigma G^{-1} - \Delta E| = 0\) at two different temperatures 0 °K and 298 °K. Here \(\Sigma\) is the mean square amplitude matrix, \(G^{-1}\) is the inverse of the kinetic energy matrix and \(\Delta E\) is related to the observed fundamental \((v_k)\) according to the expression

\[
\Delta E = -\frac{\hbar}{8\pi^2 v_k c} \coth \frac{\hbar v_k c}{2kT}.
\]

Utilizing group theory, except for the \(f_{1u}\) mode, which led to a two dimensional equation, all other modes led to a one dimensional equation. For the unique solutions, again the method of MÜLLER\(^{25}\) has been used with great advantage. The calculated values of mean amplitudes of vibration \(u\) for \(X - Y\), \(Y...Y\) short and \(Y...Y\) long distances are given in Table 3.

The mean amplitudes of vibration have a definite trend for all these ions at both temperatures — \(u(Y...Y)\) short > \(u(Y...Y)\) long > \(u(X-Y)\) and increase with it.

5. Bastiansen-Morino Shrinkages

The interatomic distances for SeBr\(_6\)^{2-}, TeCl\(_6\)^{2-} and TeBr\(_6\)^{2-} ions are known experimentally\(^{27-29}\) while those of SeCl\(_6\)^{2-} ion has been calculated by summing covalent radii\(^{26}\). These interatomic distances have been used to evaluate Bastiansen-Morino shrinkages\(^3\) for the \(Y...Y\) short and \(Y...Y\) long distances at 0 °K and 298 °K. These are given in Table 4.

The Bastiansen-Morino shrinkages\(^3\) for the \(Y...Y\) long distance are greater than for the \(Y...Y\) short distance for all the ions at both temperatures and increase with it.

The small but real Bastiansen-Morino shrinkages are added to the experimentally observed nonbonded distances to get real nonbonded distances.

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Table 2. Symmetry force constants for \(f_{1u}\) mode and force constants (in mdyne/Å).

<table>
<thead>
<tr>
<th>IONS</th>
<th>Symmetry force constants for (f_{1u}) mode</th>
<th>(f_r)</th>
<th>(f_{rr})</th>
<th>(f_{rr} - f_{rr}')</th>
<th>(f_{ss} - f_{ss}')</th>
<th>(f_{ss} - f_{ss}'')</th>
<th>(f_{ss} - f_{ss}''')</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeCl(_6)^{2-}</td>
<td>0.984 0.064</td>
<td>1.24</td>
<td>0.25</td>
<td>0.05</td>
<td>0.06</td>
<td>0.14</td>
<td>−0.00</td>
</tr>
<tr>
<td></td>
<td>0.064 0.136</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SeBr(_6)^{2-}</td>
<td>1.056 1.000</td>
<td>1.17</td>
<td>0.11</td>
<td>0.06</td>
<td>0.10</td>
<td>0.14</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>0.100 0.150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TeCl(_6)^{2-}</td>
<td>0.977 0.049</td>
<td>1.20</td>
<td>0.23</td>
<td>0.08</td>
<td>0.05</td>
<td>0.12</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>0.049 0.137</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TeBr(_6)^{2-}</td>
<td>0.979 0.064</td>
<td>1.14</td>
<td>0.16</td>
<td>0.05</td>
<td>0.06</td>
<td>0.12</td>
<td>−0.00</td>
</tr>
<tr>
<td></td>
<td>0.064 0.116</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Mean amplitudes of vibration \(u\) in Å.

<table>
<thead>
<tr>
<th>IONS</th>
<th>(u(X-Y))</th>
<th>(T = 0^\circ K)</th>
<th>(u(Y...Y))</th>
<th>(T = 298^\circ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>short</td>
<td>long</td>
<td>short</td>
<td>long</td>
</tr>
<tr>
<td>SeCl(_6)^{2-}</td>
<td>0.0501</td>
<td>0.0723</td>
<td>0.0598</td>
<td>0.0657</td>
</tr>
<tr>
<td>SeBr(_6)^{2-}</td>
<td>0.0453</td>
<td>0.0591</td>
<td>0.0505</td>
<td>0.0674</td>
</tr>
<tr>
<td>TeCl(_6)^{2-}</td>
<td>0.0484</td>
<td>0.0758</td>
<td>0.0605</td>
<td>0.0649</td>
</tr>
<tr>
<td>TeBr(_6)^{2-}</td>
<td>0.0427</td>
<td>0.0604</td>
<td>0.0505</td>
<td>0.0659</td>
</tr>
</tbody>
</table>

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\(^{27}\) J. L. HOARD and B. N. DICKINSON, Z. Kristallogr. 84, 436 [1933].


T = 0°K  T = 298°K
IONS  \( \partial(Y\ldots Y) \)  \( \partial(Y\ldots Y) \)  \( \partial(Y\ldots Y) \)  \( \partial(Y\ldots Y) \)  
short  long  short  long  
SeCl\(_6^2\)  0.00072  0.0024  0.0018  0.0069  
SeBr\(_6^2\)  0.00070  0.0018  0.0019  0.0069  
TeCl\(_6^2\)  0.00052  0.0022  0.0014  0.0076  
TeBr\(_6^2\)  0.00051  0.0016  0.0019  0.0068

Table 4. Bastiansen-Morino shrinkages effect in Å.

* The Bastiansen-Morino shrinkages effect for SeCl\(_6^2\) are less reliable because the interatomic distance (Se–Cl) is not known experimentally but for the sake of comparison we have calculated here.

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