Molecular Force Fields of Some XY_6 Type Ions of O_h Symmetry

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The L matrix approximation method has been applied to hexachlorides and hexabromides of Tin and Titanium of O_h 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 XY_6 type belonging to O_h symmetry have six normal modes of vibration. On group theoretical considerations,

$$\Gamma_{\text{vib.}} = a_{1g} + e_g + 2\,f_{1u} + f_{2g} + f_{2u}\,.$$

Out of these six, the three gerade modes, $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(f_{2g})$ give rise to Raman active fundamentals; the two modes ν_3 and $\nu_4(f_{1u})$ are permitted in the infrared, while the last $\nu_6(f_{2u})$ mode is forbidden in both, Raman effect and infrared, though it may appear in combination. ν_1, ν_2 and ν_3 are associated with essentially valence vibrations while ν_4, ν_5, and ν_6 are essentially deformation vibrations.

A number of octahedral molecules of XY_6 type, particularly hexafluorides, belonging to O_h symmetry, have been subjected to normal coordinate treatment by a number of workers [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. [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. [13] have recently reported the fundamental frequencies for hexachlorides $SnCl_6^{-2}$ and $TiCl_6^{-2}$ and hexabromides $SnBr_6^{-2}$ and $TiBr_6^{-2}$ 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.

Ions	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6 [a]	$X-Y$	Ref.
$SnCl_6^{-2}$	309	232	291	163	159	112	2.43 [15]	13, 15
$SnBr_6^{-2}$	182	135	203	111	101	71	2.775 [b]	13, 16
$TiCl_6^{-2}$	320	271	316	183	173	122	2.34 [15]	13, 15
$TiBr_6^{-2}$	192	162	244	119	115	81	2.45 [b]	13, 16

Table 1. Fundamental Frequencies in cm^{-1} and Interatomic Distances in Å. [a] The inactive fundamental $\nu_6(f_{1u})$ has been calculated by Wilson's rule [14]. It may not be out of place to mention that this calculated ν_6 is the same as if evaluated by U. B. F. F. — [b] Calculated by BADGER's rule [16].

Force Constants Evaluation

The normal coordinate treatment using $G-F$ matrix method [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 [3]. G and F matrices used in the present work are as follows:

For a_{1g} type vibration:

$$G_{11} = \mu_y; \qquad F_{11} = f_r + 4\,f_{rr} + f'_{rr}.$$

For e_g type vibration:

$$G_{11} = \mu_y; \qquad F_{11} = f_r - 2\,f_{rr} + f'_{rr}.$$

For f_{1u} type vibration:

$$G_{11} = 2\,\mu_x + \mu_y; \qquad F_{11} = f_r - f'_{rr};$$
$$G_{12} = G_{21} = 4\,\mu_x; \qquad F_{12} = F_{21} = -2\,(f_{r\alpha} - f''_{r\alpha});$$
$$G_{22} = 8\,\mu_x + 2\,\mu_y; \qquad F_{22} = f_\alpha + 2\,f_{\alpha\alpha} - 2\,f''_{\alpha\alpha} - f'''_{\alpha\alpha}.$$

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For f_{2g} type vibration:

$$G_{11} = 4\,\mu_y; \qquad F_{11} = f_a - 2\,f'_{\alpha\alpha} + f'''_{\alpha\alpha}.$$

For f_{2u} type vibration:

$$G_{11} = 2\,\mu_y; \qquad F_{11} = f_a - 2\,f_{a\alpha} + 2\,f''_{\alpha\alpha} - f'''_{\alpha\alpha}.$$

Here μ_x and μ_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 $|\,G\,F - E\,\lambda\,| = 0$. It is not surprising, therefore, to find that earlier authors have either neglected less important constants or made not very logical assumption. Recently some authors have tried to overcome the uncertainity in force constant calculations by the use of additional mathematical constraints [18–21]. The present authors have used MÜLLER's method [12] to evaluate all the seven force constants. These are given in Table 2.

Ions	f_r	f'_{rr}	f_{rr}	$f_{r\alpha} - f''_{r\alpha}$	$f_\alpha - f'''_{\alpha\alpha}$	$f_{a\alpha} - f'_{\alpha\alpha}$	$f'_{\alpha\alpha} - f'''_{\alpha\alpha}$
$SnCl_6^{-2}$	1.30	0.11	0.14	0.06	0.14	0.01	0.01
$SnBr_6^{-2}$	1.05	0.04	0.12	0.08	0.13	0.00	0.00
$TiCl_6^{-2}$	1.40	0.33	0.10	0.10	0.16	0.00	0.00
$TiBr_6^{-2}$	1.18	0.22	0.08	0.10	0.14	−0.01	−0.01

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 hexabromi-implications. The main force constants f_r and $f_\alpha - f'''_{\alpha\alpha}$ des 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 $f_\alpha - f'''_{\alpha\alpha}$ 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.

Mean Ampliude 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 [22] secular equation $|\,\Sigma\,G^{-1} - \Delta E\,| = 0$ at 0 °K and 298 °K, where Σ is the symmetrized mean square amplitude matrix, G^{-1} is the K.E. matrix and Δ_k is related to the normal mode of vibration ν_k by

$$\Delta_k = \frac{h}{8\,\pi^2\,\nu_k\,c}\,\mathrm{Coth}\,\frac{h\,\nu_k\,c}{2\,K\,T}.$$

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 [12] was used to give the solution for the above mentioned two dimensional equation, giving all symmetrized mean square amplitude matrices Σ, whose elements are also connected to mean amplitudes of vibration [23]. The calculated mean amplitudes of vibration are given in Table 3.

Ions	$T = 0$ °K $u(X-Y)$	$u(Y\ldots Y)$ short	$u(Y\ldots Y)$ long	$T = 298$ °K $u(X-Y)$	$u(Y\ldots Y)$ short	$u(Y\ldots Y)$ long
$SnCl_6^{-2}$	0.047	0.0722	0.0613	0.0599	0.1171	0.0758
$SnBr_6^{-2}$	0.0440	0.0606	0.0534	0.0696	0.1177	0.0929
$TiCl_6^{-2}$	0.0519	0.0697	0.0577	0.0656	0.1098	0.0748
$TiBr_6^{-2}$	0.0499	0.0581	0.0497	0.0667	0.1115	0.0797

Table 3. Mean Amplitude of Vibration u in Å.

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