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Force Constants and Mean Amplitudes of Vibration of the Metal-Hexahalo Species of Group IV–VI

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The general valence force constants and vibrational amplitudes have been evaluated for the metal hexahalo species of groups IV–VI elements using recent infrared and Raman spectral data. The results are employed to study the trend of variation among different species as well as the influence of cations on the relative stiffness of the chemical bonds. It has been found that the chemical bonds in the environment of a cesium cation are stronger than those of a tetraethylammonium cation.

Recently Bronswyk et al.[1] have recorded the infrared and laser Raman spectra of the metal-hexahalo species $R_2M^{IV}X_6$, $RM^{V}X_6$ [$R = (C_2H_5)_4N$ or Cs; M^{IV} = Ti, Zr or Hf; M^{V} = Nb, Ta; X = Cl or Br] and WCl_6 and interpreted the fundamental frequencies on the basis of octahedral symmetry. They have also reported the force constants using the modified Urey-Bradley force field (MUBFF) and the generalized valence force field (GVFF). In order to calculate the complete set of force constants in the GVFF model they have set a few interactions equal to zero and $f_{rr'} = 4/3\, f_{rr}$. In the present paper it is aimed to compute a complete set of force constants employing the GVFF model without the above constraints and the mean amplitudes of vibration. The results will be used to study the trend of variation in force constants as well as the influence of cations on the relative stiffness of the chemical bonds.

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The anions of the type MX_6 possessing octahedral symmetry give rise to six fundamental frequencies which are distributed among different species as

$$1\, a_{1g} + 1\, e_g + 2\, f_{1u} + 1\, f_{2g} + 1\, f_{2u}$$

where $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(f_{2g})$ are Raman active, $\nu_3(f_{1u})$ and $\nu_4(f_{1u})$ are infrared active and $\nu_6(f_{2u})$ is inactive in both. The inactive $\nu_6(f_{2u})$ is permitted as binary combination bands. The only fundamental to show appreciable dependence on the cation is $\nu_3(f_{1u})$.

Wilson's GF matrix method[2] was employed to calculate the force constants in the GVFF model. The mean amplitudes of vibration were evaluated at 0 °K, 298 °K and 500 °K using Cyvin's secular equation[3] $|\Sigma G^{-1} - \Delta E| = 0$, where the symbols have their usual meaning. F and G matrix elements, and analytical expressions for mean amplitudes of vibration were taken from Cyvin's book[3]. The two dimensional equations occuring in f_{1u} species were solved by Müller's method[4, 5, 6]. The fundamental fre-

Table 1. General Valence Force constants for some halogenated XY_6 type ions (in mdyne/Å). (* A = $[(C_2H_5)_4N]$; B = Cs.)

* Ions	f_r	f_{rr}	$f_{rr'}$	$(f_\alpha - f_{\alpha\alpha'''})$	$(f_{\alpha\alpha} - f_{\alpha\alpha''})$	$(f_{\alpha\alpha'} - f_{\alpha\alpha'''})$	$(f_{r\alpha} - f_{r\alpha''})$
A_2TiCl_6	1.169	0.101	0.567	0.157	0.001	0.001	0.095
B_2TiCl_6	1.301	0.116	0.594	0.217	0.007	0.018	0.103
A_2ZrCl_6	1.248	0.141	0.339	0.124	0.002	0.003	0.056
B_2ZrCl_6	1.417	0.154	0.186	0.139	0.004	0.002	0.064
A_2HfCl_6	1.316	0.140	0.344	0.133	0.003	0.003	0.040
B_2HfCl_6	1.403	0.149	0.318	0.138	0.006	−0.004	0.042
$ANbCl_6$	1.605	0.180	0.487	0.161	0.007	−0.010	0.064
$BNbCl_6$	1.613	0.183	0.498	0.141	−0.006	−0.013	0.066
$ATaCl_6$	1.757	0.188	0.474	0.155	0.004	0.006	0.046
$BTaCl_6$	1.786	0.197	0.475	0.137	0.015	−0.020	0.047
WCl_6	2.289	0.240	0.263	0.154	0.007	0.007	0.047
A_2TiBr_6	1.086	0.134	0.078	0.128	0.002	0.002	0.101
A_2ZrBr_6	1.172	0.133	0.069	0.116	0.001	0.005	0.074
A_2HfBr_6	1.018	0.146	0.224	0.122	0.002	0.001	0.060
$BNbBr_6$	1.312	0.139	0.492	−0.166	−0.006	−0.005	0.082
$BTaBr_6$	1.405	0.159	0.490	0.149	−0.005	−0.005	0.065

quencies used in the present computation were taken from Bronswyk et al. [1].

The results of the force constant calculations are collected in Table 1. The GVFF model includes, f_r bond stretching constant, f_α angle bending force constant and the following interaction constants: f_{rr} and $f_{rr'}$ which represent cis and trans bond stretching interactions respectively; $f_{\alpha\alpha}$, $f_{\alpha\alpha'}$, $f_{\alpha\alpha''}$, and $f_{\alpha\alpha'''}$ angle bending interactions; and $f_{r\alpha}$ and $f_{r\alpha''}$ interactions involving an angle and one of the bonds. It is seen from Table 1 that for each anion the value of the stretching force constant for tetraethylammonium salts is less than that for cesium salts. This is in accordance with the dimensions of the sites. The average value of f_r for each group increases wth the oxidation state of the central atom [viz.: M(iv)

Table 2. Mean amplitudes of Vibration u (in Å)) for halogenated ions of metals. (* A = $[(C_2H_5)_4N]$; B = Cs.)

* Ions	Distance	Mean Amplitudes of Vibration $T=$ 0°K	$T=$ 298°K	$T=$ 500°K
A_2TiCl_6	(X−Y)	0.0519	0.0656	0.0808
	(Y....Y) Linear	0.0577	0.0748	0.0927
	(Y....Y) Non-Linear	0.0965	0.1386	0.2105
B_2TiCl_6	(X−Y)	0.0509	0.0636	0.0780
	(Y....Y) Linear	0.0576	0.0798	0.0925
	(Y....Y) Non-Linear	0.0938	0.1300	0.1630
A_2ZrCl_6	(X−Y)	0.0482	0.0626	0.0777
	(Y....Y) Linear	0.0594	0.0789	0.0973
	(Y....Y) Non-Linear	0.0891	0.1390	0.1741
B_2ZrCl_6	(X−Y)	0.0472	0.0606	0.0749
	(Y....Y) Linear	0.0594	0.0788	0.0981
	(Y....Y) Non-Linear	0.0866	0.1319	0.1667
A_2HfCl_6	(X−Y)	0.0455	0.0597	0.0742
	(Y....Y) Linear	0.0586	0.0772	0.0959
	(Y....Y) Non-Linear	0.0817	0.1304	0.1653
B_2HfCl_6	(X−Y)	0.0449	0.0584	0.0724
	(Y....Y) Linear	0.0581	0.0760	0.0944
	(Y....Y) Non-Linear	0.0804	0.1264	0.1602
$ANbCl_6$	(X−Y)	0.0453	0.0558	0.0684
	(Y....Y) Linear	0.0554	0.0699	0.0860
	(Y....Y) Non-Linear	0.0831	0.1222	0.1538
$BNbCl_6$	(X−Y)	0.0450	0.0557	0.0683
	(Y....Y) Linear	0.0552	0.0696	0.0857
	(Y....Y) Non-Linear	0.0838	0.1259	0.1586

* Ions	Distance	Mean Amplitudes of Vibration $T=$ 0°K	$T=$ 298°K	$T=$ 500°K
$ATaCl_6$	(X−Y)	0.0422	0.0526	0.0646
	(Y....Y) Linear	0.0544	0.0679	0.0834
	(Y....Y) Non-Linear	0.0769	0.1175	0.1485
$BTaCl_6$	(X−Y)	0.0421	0.0523	0.0642
	(Y....Y) Linear	0.0543	0.0676	0.0830
	(Y....Y) Non-Linear	0.0776	0.1263	0.1544
WCl_6	(X−Y)	0.0400	0.0482	0.0586
	(Y....Y) Linear	0.0528	0.0645	0.0787
	(Y....Y) Non-Linear	0.0759	0.1131	0.1486
A_2TiBr_6	(X−Y)	0.0508	0.0747	0.0943
	(Y....Y) Linear	0.0527	0.0898	0.1148
	(Y....Y) Non-Linear	0.0969	0.1588	0.2018
A_2ZrBr_6	(X−Y)	0.0444	0.0674	0.0851
	(Y....Y) Linear	0.0517	0.0866	0.1106
	(Y....Y) Non-Linear	0.0839	0.1491	0.1905
A_2HfBr_6	(X−Y)	0.0416	0.0662	0.0842
	(Y....Y) Linear	0.0519	0.0873	0.1114
	(Y....Y) Non-Linear	0.0754	0.1409	0.1805
$BNbBr_6$	(X−Y)	0.0420	0.0596	0.0795
	(Y....Y) Linear	0.0468	0.0714	0.0905
	(Y....Y) Non-Linear	0.0799	0.1348	0.1724
$BTaBr_6$	(X−Y)	0.0384	0.0567	0.0716
	(Y....Y) Linear	0.0463	0.0700	0.0886
	(Y....Y) Non-Linear	0.0709	0.1255	0.1605

$= 1.31$; $M(\mathrm{v}) = 1.69$ and $M(\mathrm{vi}) = 2.29$]. The f_r values for hexachlorometalate ions are greater than those for hexabromometalate ions. From this variation it is inferred that the relative strength of the chemical bond is in the order M – Cl > M – Br which is in accordance with the decrease in electronegativity from chlorine to bromine.

The bond-bond interaction constants show that $f_{rr'} > f_{rr}$ for most of the anions which is consistent with previous findings [7]. The values of the bending force constant $(f_\alpha - f_{\alpha\alpha'''})$ are approximately the same in hexachloride and hexabromide ions respectively in which the central atom belongs to the same group of the periodic table. The other interaction constants are comparatively much smaller than the main force constants and do not show any regular variation.

The computed values of the mean amplitudes of vibration (u) at temperatures 0 °K, 298 °K and 500 °K are presented in Table 2. It is noted from this table that u for Y ... Y (nonlinear) is greater than for Y ... Y (linear) and X – Y (bonded) at all temperatures and increases with it. Similar results have also been reported for a number of octahedral ions of XY_6 type [3, 7, 8]. The u values for the X-Y bonded distance of tetraethyl ammonium salts are greater than that of cesium salts while the stretching force constants (from Table 1) show the reverse trend. The mean amplitudes of vibration for the X – Y bonded distance decrease as the chlorine atom is replaced by the bromine atom (the central atom remaining the same. The mean amplitudes show the expected trend of variation with temperature.

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