Force Constants and Mean Amplitudes of Vibration of Hexahalo Species of Groups IVA and VIA

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The GVFF constants and mean amplitudes of vibration have been calculated for 21 hexahalo species of group IV A and VI A elements. The influence of the cation on these constants is discussed. It has been found that the chemical bonds in the environment of a light cation are relatively stronger than in that of a heavy cation in case of inorganic cations while the situation is opposite in case of organic cations.

Introduction

In a previous paper[1] we have studied the influence of the cations on the force constants as well as on the mean amplitudes of vibration for the hexahalo species of group IVB – VIB elements. In continuation of our systematic program, we have now extended such study to the hexahalo species of IVA and VIA group elements whose complete vibrational analysis has been reported in the literature[2, 3] on the basis of octahedral symmetry. The systems under present study are: $M_2^I[MCl_6]$ $M^I = K$, NH_4, Rb, Cs, NMe_4, NEt_4, $AsPh_4$ and IPh_2; M = Sn and Pb and $M_2[TeX_6]$ (X = Cl or Br). The general valence force field (GVFF) constants and mean amplitudes of vibration are calculated for these systems.

Method of Computation

The species under present study belong to the O_h point group and the fundamental frequencies are distributed 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 $_6(f_{2g})$ is inactive in both. The general valence force field model was employed to calculate the force constants using Wilson's GF matrix method[4]. The expressions for F and G matrices were taken from literature[5]. Müller's method[6–8] was followed for the solution of the 2×2 secular determinant of species f_{1u}. The mean amplitudes of vibration were computed following Cyvin's method[5] and the L matrix approximation method by Müller[6–8]. The required expressions for these computations were taken from current literature[2, 3].

Results and Discussion

The GVFF constants are presented in Table 1. The GVFF model includes, f_r bond stretching constant, f_α angle bending constant and the following interaction constants: f_{rr} and f'_{rr} which represent cis

Table 1. General valance force constants for some halogenated XY_6 type ions (in mdyne/Å).

Ion	f_r	f_{rr}	f'_{rr}	$f_\alpha - f''_{r\alpha}$	$f_{\alpha\alpha} - f''_{\alpha\alpha}$	$f'_{\alpha\alpha} - f'''_{\alpha\alpha}$	$f_{r\alpha} - f''_{r\alpha}$
A_2 $SnCl_6$	1.50	0.16	0.11	0.17	0.00	0.00	0.07
B_2 $SnCl_6$	1.47	0.13	0.10	0.16	0.01	0.00	0.07
C_2 $SnCl_6$	1.44	0.14	0.07	0.15	0.01	0.00	0.07
D_2 $SnCl_6$	1.42	0.13	0.07	0.14	0.02	0.00	0.06
$SnCl_6^{2-}$	1.82	0.19	0.43	0.16	0.01	0.15	0.03
B_2 $PbCl_6$	1.26	0.14	0.02	0.12	0.02	0.00	0.04
C_2 $PbCl_6$	1.27	0.13	0.00	0.10	0.01	0.00	0.03
D_2 $PbCl_6$	1.20	0.12	0.02	0.10	0.02	0.00	0.04
E_2 $PbCl_6$	1.13	0.12	0.03	0.09	0.02	0.00	0.04
F_2 $PbCl_6$	1.18	0.11	0.01	0.10	0.02	0.00	0.03
G_2 $PbCl_6$	1.07	0.12	0.09	0.09	0.02	0.00	0.03
H_2 $PbCl_6$	1.17	0.09	0.12	0.10	0.01	0.00	0.03
A_2 $TeCl_6$	1.19	0.09	0.33	0.11	0.00	0.00	0.04
B_2 $TeCl_6$	1.20	0.10	0.30	0.10	0.01	0.00	0.04
C_2 $TeCl_6$	1.33	0.09	0.19	0.09	−0.03	0.00	0.01
D_2 $TeCl_6$	1.14	0.08	0.28	0.09	−0.03	0.00	0.01
E_2 $TeCl_6$	1.05	0.07	0.32	0.09	−0.01	0.00	0.02
F_2 $TeCl_6$	1.13	0.07	0.24	0.08	−0.03	0.00	0.01
$TeCl_6^{2-}$	1.20	0.08	0.23	0.12	0.01	0.01	0.05
A_2 $TeBr_6$	1.05	0.05	0.15	0.06	0.00	0.00	0.04
B_2 $TeBr_6$	1.12	0.07	0.15	0.08	0.02	0.00	0.07
E_2 $TeBr_6$	0.98	0.05	0.16	0.10	0.01	0.00	0.07
F_2 $TeBr_6$	0.91	0.06	0.18	0.11	−0.06	−0.03	0.03
$TeBr_6^{2-}$	1.14	0.05	0.16	0.12	0.00	0.00	0.06

and trans interactions respectively; $f_{\alpha\alpha}$, $f'_{\alpha\alpha}$, $f''_{\alpha\alpha}$ and $f'''_{\alpha\alpha}$ bending interactions; and $f_{r\alpha}$ and $f''_{r\alpha}$ interactions involving an angle and one bond. The force constants obtained by the present method are compared with the values reported by other workers [9, 10]. It is found that the agreement is resonably good in case of hexahalogenotellurates while in case of chlorostannate, it is not so. This discrepancy may be due to the use of vibrational data under different crystal fields.

The force constants are a convenient measure of the strength of a chemical bond and, therefore, it is interesting to study the trend of variation among force constants for understanding the influence of cations on the relative strength of the chemical bonds in the anions having different environments. For this purpose, the most valuable information is contained in the bond stretching force constant, f_r. The comparison of the stretching force constants f_r shows a general decrease with increase of the size of the cation in the complexes where the anion is in the environment of inorganic cations (K, NH_4, Rb, Cs) while in the presence of organic cations (NMe_4. NEt_4, $AsPh_4$, IPh_2) in general an opposite trend has been noticed. The strength of the chemical bonds also vary in the same way. From this variation it is generally inferred that in the presence of inorganic cations the stiffness of the chemical bonds in anions decreases with the increase of the mass of the cation while in presence of organic cations it increases with the increase of the mass of the cation. Such variation has also been noticed by Pandey et al. [1] The bond-bond interaction constants vary as $f_{rr} > f'_{rr}$ in the hexachloro species of IVA group elements while the opposite trend $f_{rr} < f'_{rr}$ was noticed in the hexachloro species of IVB group elements [1]. It is also noted from the Table 1 that in case of hexahalogeno tellurates, $f_{rr} < f'_{rr}$ in general. The angle

Table 2. Mean amplitudes of vibration (in Å) for halogenated ions of metals.

Ions	Distance	*Mean Amplitudes of Vibration* $T = 0$ °K	$T = 298.16$ °K	$T = 500$ °K
A_2SnCl_6	(X−Y)	0.0457	0.0581	0.0725
	(Y..Y) linear	0.0592	0.0788	0.0981
	(Y..Y) non-linear	0.0687	0.1071	0.1378
B_2SnCl_6	(X−Y)	0.0459	0.0591	0.0731
	(Y..Y) linear	0.0595	0.0791	0.0985
	(Y..Y) non-linear	0.0695	0.1103	0.1400
C_2SnCl_6	(X−Y)	0.0461	0.0596	0.0738
	(Y..Y) linear	0.0603	0.0811	0.1012
	(Y..Y) non-linear	0.0708	0.1147	0.1458
D_2SnCl_6	(X−Y)	0.0462	0.0598	0.0740
	(Y..Y) linear	0.0603	0.0811	0.1011
	(Y..Y) non-linear	0.0717	0.1180	0.1502
B_2PbCl_6	(X−Y)	0.0462	0.0623	0.0777
	(Y..Y) linear	0.0629	0.0876	0.1099
	(Y..Y) non-linear	0.0750	0.1313	0.1677
C_2PbCl_6	(X−Y)	0.0461	0.0620	0.0774
	(Y..Y) linear	0.0630	0.0878	0.1101
	(Y..Y) non-linear	0.0766	0.1367	0.1747
D_2PbCl_6	(X−Y)	0.0467	0.0634	0.0792
	(Y..Y) linear	0.0635	0.0891	0.1119
	(Y..Y) non-linear	0.0768	0.1373	0.1755
E_2PbCl_6	(X−Y)	0.0475	0.0693	0.0874
	(Y..Y) linear	0.0646	0.0918	0.1155
	(Y..Y) non-linear	0.0803	0.1566	0.2008
F_2PbCl_6	(X−Y)	0.0469	0.0639	0.0800
	(Y..Y) linear	0.0638	0.0900	0.1130
	(Y..Y) non-linear	0.0776	0.1402	0.1793
G_2PbCl_6	(X−Y)	0.0482	0.0671	0.0842
	(Y..Y) linear	0.0644	0.0913	0.1148
	(Y..Y) non-linear	0.0797	0.1470	0.1882
H_2PbCl_6	(X−Y)	0.0471	0.0641	0.0801
	(Y..Y) linear	0.0622	0.0856	0.1071
	(Y..Y) non-linear	0.0776	0.1391	0.1778
A_2TeCl_6	(X−Y)	0.0491	0.0668	0.0835
	(Y..Y) linear	0.0597	0.0794	0.0988
	(Y..Y) non-linear	0.0753	0.1283	0.1637
B_2TeCl_6	(X−Y)	0.0488	0.0659	0.0823
	(Y..Y) linear	0.0599	0.0801	0.0997
	(Y..Y) non-linear	0.0769	0.1359	0.1736
C_2TeCl_6	(X−Y)	0.0465	0.0606	0.0752
	(Y..Y) linear	0.0596	0.0793	0.0987
	(Y..Y) non-linear	0.0858	0.1814	0.2332
D_2TeCl_6	(X−Y)	0.0489	0.0662	0.0827
	(Y..Y) linear	0.0606	0.0815	0.1016
	(Y..Y) non-linear	0.0862	0.1825	0.2345
E_2TeCl_6	(X−Y)	0.0506	0.0704	0.0883
	(Y..Y) linear	0.0611	0.0828	0.1035
	(Y..Y) non-linear	0.0797	0.1435	0.1836
F_2TeCl_6	(X−Y)	0.0488	0.0661	0.0825
	(Y..Y) linear	0.0612	0.0829	0.1035
	(Y..Y) non-linear	0.0867	0.1806	0.2321
A_2TeBr_6	(X−Y)	0.0431	0.0672	0.0854
	(Y..Y) linear	0.0514	0.0851	0.1085
	(Y..Y) non-linear	0.0694	0.1643	0.2119
B_6TeBr_6	(X−Y)	0.0421	0.0667	0.0846
	(Y..Y) linear	0.0509	0.0836	0.1060
	(Y..Y) non-linear	0.0671	0.1628	0.2100
E_2TeBr_6	(X−Y)	0.0447	0.0717	0.0913
	(Y..Y) linear	0.0522	0.0876	0.1118
	(Y..Y) non-linear	0.0627	0.1314	0.1692
F_2TeBr_6	(X−Y)	0.0449	0.0723	0.0921
	(Y..Y) linear	0.0528	0.0896	0.1144
	(Y..Y) non-linear	0.0660	0.1463	0.1885

where A = K, B = NH_4, C = Rb, D = Cs, E = NMe_4, F = NEt_4, G = $AsPh_4$, H = IPh_2.

bending force constant $(f_\alpha - f'''_{\alpha\alpha})$, in general, shows a slight decreasing tendency with the increase in the mass of the cations. The other interaction force constants do not show regular variation but $(f'_{\alpha\alpha} - f'''_{\alpha\alpha})$ comes out to be zero for most of the anions. Comparison of the force constants from the Table 1 among chlorostannates and plumbates containing similar cations shows that the force constants f_r, f_{rr}, f'_{rr} and $(f_\alpha - f'''_{\alpha\alpha})$ decrease in going from Sn to Pb complexes and therefore, the stiffness of the chemical bond is in the order $Sn-Cl > Pb-Cl$. On comparison of the stretching force constants in halogenotellurates in the presence of a similar environment it is found that $f_r(TeCl_6^{2-}) > f_r(TeBr_6^{2-})$. Therefore, stability of the bonds is in the order $Te-Cl > Te-Br$. This is consistent with the decrease in electronegativity from Cl to Br.

The mean amplitudes of vibration for bonded as well as for non-bonded atom pairs at $T = 0\ ^\circ K$, $T = 298.16\ ^\circ K$ and $T = 500\ ^\circ K$ are summarized in Table 2. It is seen from Table 2 that the mean amplitude values for bonded and non-bonded atom pairs are in the order $M-X < X\ldots X$ (linear) $< X\ldots X$ (non-linear). From the observation of mean amplitudes of vibration it is found that the values are approximately the same.

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