Mean Amplitudes of Vibration of Some Octahedral MF_6^- Anions

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The mean amplitudes of vibration of the hexafluoroanions of the groups 5 and 15 of the Periodic System have been calculated from known spectroscopic data between 0 and 1000 K. Bond peculiarities of these compounds are discussed, and some comparisons with related species are made.

Key words: Hexafluoroanions; Mean Amplitudes of Vibration; Bond Properties.

It is well known that chlorine oxide trifluoride, $ClOF_3$, exhibits amphoteric properties. It forms adducts with Lewis acids or bases according to [1 – 5]:

$$ClOF_3 + AF_n \rightarrow ClOF_2^+ + [AF_{n+1}]^-, \qquad (1)$$

$$ClOF_3 + BF_m \rightarrow ClOF_4^- + [BF_{m-1}]^+, \qquad (2)$$

(AF_n and BF_m stand for acid and base molecules, respectively).

Using the pentafluorides of the elements of groups 5 (V,Nb,Ta) and 15 (P,As,Sb,Bi) of the Periodic System as Lewis acids, it was possible to generate a number of adducts of $ClOF_3$ and investigate their vibrational spectra [5].

On the basis of this spectroscopic information, and as a continuation of our studies on vibrational properties of simple inorganic molecules and ions, the mean amplitudes of vibration for these octahedral fluoranions were now calculated.

To perform these calculations we have employed the method of the characteristic vibrations of Müller et al. [6] (cf. also [7, 8]) which, as we have demonstrated earlier, leads to excellent results in the case of octahedral molecules and ions [9]. The necessary vibrational data were taken from the paper of Bougon et al. [5], and a perfect octahedral geometry was assumed for all the calculated species.

The calculated mean amplitudes of vibration for the four hexafluoroanions of group 15 at 0 – 1000 K are shown in Table 1.

Table 1. Calculated mean amplitudes of vibration (in Å) of the group 15 hexafluoroanions.

T (K)	PF_6^-			AsF_6^-		
	u_{P-F}	$u_{F\cdots F}$ (sh.)	$u_{F\cdots F}$ (lg.)	u_{As-F}	$u_{F\cdots F}$ (sh.)	$u_{F\cdots F}$ (lg.)
0	0.0450	0.060	0.053	0.0414	0.066	0.054
100	0.0450	0.060	0.053	0.0414	0.066	0.054
200	0.0453	0.062	0.054	0.0418	0.071	0.055
298.16	0.0467	0.066	0.056	0.0433	0.078	0.057
300	0.0467	0.066	0.056	0.0433	0.078	0.057
400	0.0489	0.072	0.059	0.0457	0.086	0.061
500	0.0516	0.077	0.063	0.0485	0.094	0.064
600	0.0545	0.083	0.067	0.0514	0.102	0.069
700	0.0575	0.089	0.071	0.0544	0.109	0.073
800	0.0605	0.094	0.075	0.0573	0.116	0.077
900	0.0634	0.099	0.078	0.0602	0.122	0.081
1000	0.0663	0.104	0.082	0.0629	0.129	0.084

T (K)	SbF_6^-			BiF_6^-		
	u_{Sb-F}	$u_{F\cdots F}$ (sh.)	$u_{F\cdots F}$ (lg.)	u_{Bi-F}	$u_{F\cdots F}$ (sh.)	$u_{F\cdots F}$ (lg.)
0	0.0404	0.073	0.055	0.0415	0.080	0.057
100	0.0404	0.075	0.055	0.0415	0.084	0.057
200	0.0409	0.084	0.055	0.0422	0.098	0.058
298.16	0.0425	0.095	0.058	0.0444	0.114	0.061
300	0.0425	0.095	0.058	0.0444	0.114	0.061
400	0.0450	0.107	0.062	0.0474	0.129	0.066
500	0.0478	0.118	0.066	0.0508	0.142	0.071
600	0.0508	0.128	0.070	0.0542	0.155	0.075
700	0.0538	0.137	0.074	0.0575	0.167	0.080
800	0.0567	0.146	0.078	0.0608	0.178	0.085
900	0.0597	0.154	0.083	0.0640	0.188	0.089
1000	0.0623	0.162	0.086	0.0670	0.198	0.094

As can be seen, the mean amplitudes for the X-F bonds diminish from PF_6^- to AsF_6^- and SbF_6^- and increase again in going from SbF_6^- to BiF_6^-. This trend agrees with the corresponding force constants, which show the inverse trend (*i.e.*, they increase from PF_6^- to SbF_6^- and diminish again for BiF_6^-) [5]. Interestingly, above 700 K the amplitudes for BiF_6^- are even higher than those of PF_6^-.

	VF_6^-			NbF_6^-			TaF_6^-		
T (K)	u_{V-F}	$u_{F\cdots F(sh)}$	$u_{F\cdots F(lg)}$	u_{Nb-F}	$u_{F\cdots F(sh)}$	$u_{F\cdots F(lg)}$	u_{Ta-F}	$u_{F\cdots F(sh)}$	$u_{F\cdots F(lg)}$
0	0.0442	0.074	0.056	0.0421	0.077	0.055	0.0405	0.076	0.055
100	0.0442	0.076	0.056	0.0421	0.079	0.055	0.0405	0.079	0.055
200	0.0447	0.085	0.057	0.0426	0.091	0.055	0.0411	0.091	0.055
298.16	0.0466	0.096	0.059	0.0445	0.104	0.058	0.0430	0.104	0.058
300	0.0466	0.096	0.059	0.0445	0.104	0.058	0.0430	0.104	0.058
400	0.0493	0.107	0.063	0.0472	0.117	0.061	0.0456	0.117	0.062
500	0.0525	0.118	0.068	0.0503	0.129	0.065	0.0487	0.129	0.066
600	0.0558	0.128	0.072	0.0535	0.141	0.070	0.0518	0.141	0.070
700	0.0591	0.138	0.077	0.0568	0.151	0.074	0.0549	0.151	0.074
800	0.0623	0.147	0.081	0.0599	0.161	0.078	0.0579	0.161	0.078
900	0.0654	0.155	0.086	0.0630	0.171	0.082	0.0609	0.171	0.082
1000	0.0685	0.163	0.090	0.0659	0.180	0.086	0.0638	0.180	0.086

Table 2. Calculated mean amplitudes of vibration (in Å) of the group 5 hexafluoroanions.

Although the fact that the bonding force constants do not follow a linear trend in the full series has been interpreted as a consequence of a higher ionic contribution to the X-F bonds in the case of BiF_6^- [5], it probably arises from relativistic effects. As has been demonstrated for the hydrogen halides, a relativistic bond contraction takes place from HF to HI, but an expansion is observed for HAt. This behavior has been explained in terms of a "competition" of scalar relativistic and spin-orbit effects [10]. Therefore one may expect that also in the case of bismuth (lying in the same period and close to astatine) similar effects become operative, causing a weakening of the Bi-F bonds.

Regarding the mean amplitudes of vibration of the non-bonded pairs, in all cases those of the shorter F···F distances are greater than those of the longer F···F distances and also show stronger temperature dependences. The values of these short F···F distances become continuously higher in the direction from PF_6^- to BiF_6^-, also in agreement with the decrease of the respective bending force constants in the same direction [5]. The amplitudes for the longer F···F distances are fairly similar in all cases but also show a slight increase in the direction from PF_6^- to BiF_6^-.

The calculated mean amplitudes of vibration for the group 5 hexafluoroanions are shown in Table 2. The trends observed for these species are similar to those found in the previous series. The amplitudes of the X-F bonds decrease from X = V to X = Ta, in agreement with the increase of the corresponding force constants in the same direction [5]. Also for this species the amplitudes of the short F···F distances are higher than those of the respective longer ones. However, interestingly, both groups of values are identical for NbF_6^- and TaF_6^-, despite the fact that the bending force constant is slightly higher for TaF_6^- (0.47 mdyn/Å for TaF_6^- ; 0.45 mdyn/Å for NbF_6^- [5]). Curiously, the F···F (short) amplitudes are lowest in VF_6^-, although this anion shows the lowest bending constant (0.38 mdyn/Å [5]). This may probably be related to some coupling effects between stretching and bending motions in this fluorocomplex, containing the lightest metal center.

Table 3. Comparison of the bond force constants, f_r, and mean amplitudes of vibration (at 298,16 K) of the investigated hexafluoroanions and its isoelectronic neutral molecules.

Species	f_r (mdyn/Å)	u(X-F) (Å)	Species	f_r (mdyn/Å)	u(X-F) (Å)
PF_6^-	2.66	0.0467	SF_6	3.59	0.0419
AsF_6^-	3.10	0.0433	SeF_6	4.25	0.0399
SbF_6^-	3.45	0.0425	TeF_6	4.62	0.0376
BiF_6^-	3.03	0.0444			
CrF_6		0.0416	VF_6^-	2.66	0.0466
MoF_6	3.97	0.0400	NbF_6^-	2.78	0.0445
WF_6	4.32	0.0385	TaF_6^-	2.90	0.0430

For some of the investigated species the related XF_5 pentafluorides are known, and their bond properties and geometrical characteristics are well established. This is the case of the triangular bipyramidal PF_5, AsF_5, and VF_5 molecules. The mean amplitudes of vibration for them are, as expected, slightly lower than those of the respective hexafluoroanions (*i.e.*, 0.0448 Å for the axial P-F and 0.0406 Å for the equatorial P-F bonds in PF_5 [11]; 0.0410 Å and 0.0386 Å for the same bonds in AsF_5 [11] and 0.0415 Å and 0.0405 Å for the corresponding bonds in VF_5 [12] (all values at 298 K)), confirming the somewhat stronger bonds for the neutral XF_5 species.

To conclude the analysis of the reported data, it seems also valuable to make some comparisons with the isoelectronic neutral hexafluorides. The mean amplitudes of vibration, and the related bonding force constants (when available), for the investigated anions and the corresponding isoelectronic molecules are compared in Table 3. The force constants were taken from [5], and the mean amplitudes of vibration of the neutral hexafluorides from [13]. As can be seen from the presented data, in each case the bond is strengthened on going from the anion to the corresponding isoelectronic molecule and, consequently, in each pair the mean amplitudes of vibration are lower in the molecules than in the anions. This is the trend usually expected for pairs of isoelectronic species, because the force constant increases with increasing positive charge of the central atom, and therefore the corresponding mean amplitude of vibration decreases [7].

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