Revised Mean Amplitudes of Vibration for Some Octahedral Hexafluorides

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Mean amplitudes of vibration and related quantities for octahedral hexafluorides have been calculated from spectroscopic data by many workers.[1] Most of these works are based on different assumptions to determine all unknown force constants of the two-dimensional F_{1u} species. Only for two of the molecules, *viz.* SF_6 and TeF_6 more accurately determined data of mean amplitudes have been reported, [1] as based on calculations using experimental Coriolis constant values.[2] Since the recent appearance of an excellent paper by Kim *et al.*[3] it is now possible to perform similar calculations for a number of other octahedral hexafluorides. The purpose of the present work is to report the results of such calculations of mean amplitudes of vibration and Bastiansen-Morino shrinkage effects.[1]

Table 1 contains some results of previous calculations taken from Ref. 1, supplemented by those of the present work. The present results are found in the column of calculations based on observed ζ-values for all the listed molecules except SF_6 and TeF_6. In these calculations we have used ζ values from Kim *et al.*[3] We have retained the previously applied frequencies according to Weinstock and Goodman,[4] but the magnitudes of these frequencies are essentially the same as those from Kim *et al.*[3] The calculated results of mean amplitudes do not depend on the applied bond length. For the purpose of calculating the shrinkage effects we have adopted bond lengths from Kim *et al.*[3] For each of the molecules UF_6 and IrF_6 two ζ values are reported.[3] Since they closely obey the ζ sum rule, similar force fields were obtained when using each of these values individually. The results given in Table 1 were obtained after averaging the force constants from the separate computations.

Table 1. Mean amplitudes of vibration (u) and shrinkage effects (δ) in Å units for octahedral hexafluorides.

Molecule and quantity		Approximation [a] 0°K	Approximation [a] 298°K	From observed ζ 0°K	From observed ζ 298°K
SF_6	u(S—F)	0.0410	0.0419	0.0413	0.0423
	u(F...F short)	0.0554	0.0603	0.0560	0.0610
	u(F...F long)	0.0512	0.0532	0.0512	0.0532
	δ(F...F short)	0.00062	0.00063	0.00051	0.00050
	δ(F...F long)	0.00214	0.00262	0.00201	0.00245
SeF_6	u(Se—F)	0.0387	0.0399	0.0387	0.0399
	u(F...F short)	0.0617	0.0717	0.0616	0.0715
	u(F...F long)	0.0512	0.0533	0.0512	0.0533
	δ(F...F short)	0.00043	0.00050	0.00045	0.00052
	δ(F...F long)	0.00209	0.00315	0.00213	0.00322
TeF_6	u(Te—F)	0.0376	0.0388	0.0376	0.0389
	u(F...F short)	0.0681	0.0866	0.0680	0.0863
	u(F...F long)	0.0510	0.0529	0.0510	0.0529
	δ(F...F short)	0.00044	0.00060	0.00045	0.00061
	δ(F...F long)	0.00236	0.00451	0.00237	0.00452

Table 1. Continued.

Molecule and quantity		Approximation [a] 0°K	Approximation [a] 298°K	From observed ζ 0°K	From observed ζ 298°K
WF_6	u(W–F)	0.0372	0.0385	0.0372	0.0385
	u(F...F short)	0.0731	0.1038	0.0727	0.1032
	u(F...F long)	0.0503	0.0520	0.0503	0.0520
	δ(F...F short)	0.00041	0.00039	0.00043	0.00043
	δ(F...F long)	0.00310	0.00810	0.00311	0.00813
UF_6	u(U–F)	0.0400	0.0424	0.0403	0.0431
	u(F...F short)	0.0816	0.1222	0.0831	0.1250
	u(F...F long)	0.0557	0.0595	0.0557	0.0595
	δ(F...F short)	0.00068	0.00169	0.00059	0.00140
	δ(F...F long)	0.00315	0.00860	0.00307	0.00835
NpF_6	u(Np–F)	0.0402	0.0426	0.0402	0.0427
	u(F...F short)	0.0793	0.1140	0.0797	0.1147
	u(F...F long)	0.0562	0.0602	0.0562	0.0602
	δ(F...F short)	0.00066	0.00165	0.00062	0.00152
	δ(F...F long)	0.00282	0.00686	0.00279	0.00677
PuF_6	u(Pu–F)	0.0404	0.0430	0.0405	0.0431
	u(F...F short)	0.0784	0.1110	0.0795	0.1135
	u(F...F long)	0.0566	0.0608	0.0566	0.0608
	δ(F...F short)	0.00064	0.00158	0.00058	0.00138
	δ(F...F long)	0.00273	0.00642	0.00275	0.00659
RhF_6	u(Rh–F)	0.0397	0.0413	0.0397	0.0414
	u(F...F short)	0.0721	0.0946	0.0723	0.0950
	u(F...F long)	0.0541	0.0572	0.0541	0.0572
	δ(F...F short)	0.00111/R	0.00183/R	0.00059	0.00096
	δ(F...F long)	0.00488/R	0.00970/R	0.00265	0.00527
IrF_6	u(Ir–F)	0.0375	0.0389	0.0375	0.0389
	u(F...F short)	0.0709	0.0924	0.0707	0.0921
	u(F...F long)	0.0517	0.0539	0.0517	0.0539
	δ(F...F short)	0.00053	0.00098	0.00054	0.00100
	δ(F...F long)	0.00236	0.00458	0.00237	0.00460
PtF_6	u(Pt-F)	0.0384	0.0400	0.0384	0.0400
	u(F...F short)	0.0720	0.0945	0.0718	0.0941
	u(F...F long)	0.0536	0.0564	0.0536	0.0564
	δ(F...F short)	0.00052	0.00103	0.00056	0.00110
	δ(F...F long)	0.00225	0.00432	0.00236	0.00453

[a] From $F_{12}(F_{1u})/F_2(F_{1u}) = -4m_Y/(m_X+2m_Y)$; *cf.* Refs. 1 and 4.

The conclusion from this work is clear: The agreement between the two sets of calculated results is excellent for all the molecules studied here without exception. Many of the results are almost identical. Some of the larger discrepancies are found in the case of UF_6, but even in that case they are hardly significant. Hence the present work confirms the results of previous calculations quoted elsewhere,[1] and the conclusions from studies [5] in connection with electron-diffraction investigations [6–9] performed for some of the molecules, *viz.* UF_6, MoF_6, WF_6, and TeF_6.

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