Ultra Scientist Vol. 24(1)B, 19-28 (2012).

Investigation of vibrational constants of some metals

R. SINGH[1], K. K. VERMA[2], D. K. GANGWAR[3], D. SINGH[4], A. GUPTA[5] and L. DIXIT[6]

[1,2,3]Department of Applied Science & Humanities, R.I.M.T., Bareilly (INDIA)
[4]Department. of Physics, S.I.E.M.T., Mathura (INDIA)
[5]Department of Physics, V.C.T.M., Aligarh (INDIA)
[6]Scientist, I.I.P.A., Dehradoon (INDIA)
Corresponding Author: rajputrsingh@gmail.com

(Acceptance Date 14th December, 2011)

Abstract

The vibrational constants namely, force constants, compliance constants, coriolis coupling constants and mean amplitudes of vibration have been computed for the octahedral hexa-halogeno anions of 8-10 groups belonging 3d, 4d and 5d series of transition metals using latest vibrational wave numbers. Three modified force fields such as **GVFF, MUBFF** and **MOVFF** but we are selected one of them **GVFF** to compute the force constants. In addition to this compliance constants have been evaluated using the force constants. The mean amplitudes of vibrations are investigated at three temperatures. The trends among the force constants are examined and the results are logically discussed and some useful conclusions are drawn.

Introduction

Modified force fields play a vital role in the understanding of the nature of intra-molecular force. One the reliable force field in terms of force constants is established. The related vibrational constants such as coriolis coupling constant, compliance constant and mean amplitudes can be studied with fair degree of accuracy. LaBonville *et al.*[1] and Pandey *et al.*[2-4] successfully applied the modified force fields to understand the molecular properties for the octahedral hexahalides. Since the more accurate and reliable vibrational data for the hexahalogeno-anions of the transition metals of the group VIII in comparison to the earlier vibrational data are available in literature,[5-10] therefore it was thought timely to investigate different vibrational constants for MX_6^{n-} [M= Fe, Rh, Ir, Pd, Ni, Pt, Os], [X= F, Cl, Br, I] n = 0, -2, -3 type hexahalogeno-anions using latest vibrational data. Such study is intended to throw new light in understanding the bond properties of the anions under present investigation.

The hexahalogeno-anions of the type MX_6^{n-} (n = 0, 1, 2, 3) belonging to O_h symmetry point group give to six fundamental frequencies, which are distributed under different species as under:

$$\Gamma(Vibrational) = A_{1g}\left(R_{ip}\right) + E_g\left(R_j dp\right)$$

$$+ 2 f_{1u}(1R,11) + 2F_{2g}\left(R_j dp\right) + F_{2u}(inactive)$$

Where R, IR, p, dp and 11 in parenthesis stand for Raman active, Infrared active, fundamentals, polarized, de-polarized and parallel components, respectively.

Methods of computation :

Wilson's FG-matrix[11] method has been employed to frame the secular equations. The two dimensional secular equation in F_{2g} species has been solved by L-F approximation method.[12] three modified force fields namely, general valency force field (GVFF) modified Urey-Bradly force field (MUBFF) and modified orbital valency force field (MOVFF) but we are selected (GVFF) to construct the elements of F-matrices.

The computed force constants have been used in turn to compute the coriolis coupling constants following the method of Meal and Pole[13] the compliance constants are evaluated by solving the secular equation method of Cyvin[14] has been used to calculate the mean amplitudes of vibration at three temperatures. The vibrational wavenumbers and structural data used in the present computations are collected in Table 1.

Results and Discussion

The force constants computed for the hexahalogeno-anions of the elements of the transition metals of the group VIII are summarized in Table 2.

Perusal of these table shows that the bond stretching force constant $\left(f_r/K\right)$ varies in the sequence M-F > M-Cl > M-Br > M-I. This trend is in accordance with the variation in electro negativities[15] of the ligand atoms and the metal ligand bond distances Table 1.

A comparison of the effects of mass made by keeping the halogen constant is demonstrated by comparing the stretching force constants in transmission series $\left(f_r/K\right)$ FeF_6^{3-} (1.708/1.400), OsF_6 (5.049/4.096)[4], RhF_6 (4.250/3.958), IrF_6 (4.902/4.702), NiF_6^{2-} (3.155/2.640), PtF_6^{2-} (3.476/3.279), PdF_6^{2-} (1.737/1.416), $PtCl_6^{2-}$ (2.046/1.831), $RhBr_6^{2-}$ (1.374/0.999), $IrBr_6^{2-}$ (1.560/1.420), $PdBr_6^{2-}$ (1.468/1.115) and $PtBr_6^{2-}$ (1.759/1.355).

It is observed from these data and table 1 that an increase of v_1 and the stretching force constant $\left(f_r/K\right)$ occurs as one proceeds from first to third and from second to third row transition series. The suggestion to use ν_1 as a measure of the bond strength has been made by Brown *et al*.[16] this may be justified since the heavy central atom remains stationary during vibration.

To compare the covalent character of the metal-chlorine and metal-bromine bonds in various compounds, Hiraishi *et al*.[17] computed the ratio. $f_r\,(M\text{-}B_r)/f_r(M\text{-}Cl)$. This ratio was 0.79 for a large number of non-hexahalides but 0.83 and 0.86 for PyX_6^{2-} and SnX_6^{2-} (X=Cl, Br), respectively. In the present study the ratio comes out to be 0.84, 0.91, 0.94 and 0.86 for PdX_6^{2-} OsX_6^{2-}, IrX_6^{2-} and PtX_6^{2-} anions, respectively. Form this data it is inferred that difference in covalent character between M-Br and M - Cl bonds becomes larger for hexahalogeno-species.

It is interesting to study the trend in K, H and F force constants in MUBFF with number of non-bonding electrons (n) for MY_6^{n-} (M = Os, Ir, Pt), (X = F, Cl, Br, I) of the third row transition metal hexahalides. The respective force constants K, H and F are for IrF_6 [4.704, 0.136, 0.192], PtF_6^{2-} [3.279, 0.146, 0.126], $OsCl_6^{2-}$ [1.404, 0.003, 0.256], $IrCl_6^{2-}$ [1.01, -0.02, 0.41], $PtCl_6^{2-}$ [1.831, 0.085, 0.123], $OsBr_6^{2-}$ [1.182, 0.067, 0.184], $IrBr_6^{2-}$ [1.220, 0.043, 0.181], $PtBr_6^{2-}$ [1.355, 0.170, 0.174], OsI_6^{2-} [0.752, 0.116, 0.106], and PtI_6^{2-} [1.215, 0.005, 0.087][4].

For hexachloro-anions and hexabromo-anions, the trend in general, among or between the stretching, bending and non-bonded interaction force constants are in line with the crystal field stabilization energies with respect to non-bonding electrons. This trend is further supported by the variation in coordinate bond stregths[18] which are (in $KJmol^{-}$) for Os - Cl = 1496, Ir - Cl = 1478, Pt - Cl = 1577, Os - Br = 1480, Ir - Br = 1454 and Pt - Br = 1565. It is also evident that in case of the hexaiodo-anions, the starching forces constant increases with the increase in the number of non-bonding electrons while the bending and interaction force constants (H, F) show opposite trend.

The trend among the bending and interaction force constants between the hexafluoro-anions and other hexahalogeno-anions may be deduce to the decreased ionicity as one moves from F^- to $Cl^- \rightarrow Br^- \rightarrow I^-$

The compliance constants (Table 3) are in line with the trend among force constants.

A comparison of the stretching force constants (in mdyne/Å) table 2 among the isostructural series: PtF_6^{2-} (3.476), PtF_6^{2-}(3.658)[2] and PtF_6^{2-}(4.494)[4] exhibits that higher oxidation state is more stable

Regarding the trend in the stretching force constants among the hexahalogeno-anions of the transition metals belonging to second and third rows of the periodic table, an inspection of the results displayed in table 2, shows that as one moves from left to right side of the periodic table in the rows, the stretching force constants show increasing tendency.

Form this trend it is inferred that the strength of the chemical bonds also varies the similar way.

A survey of the magnitude interaction force constants included in the table 2, shows that these influence the principal force constants and hence the bond properties.

It is interesting to investigate the trend in force constants (in mdyne/Å)[19,20] with respect to coordination number and oxidation state. The force constants are given here in tabular form as under:

Anions	f_r	$f_{(\alpha\text{-}\alpha''')}$	K	H
$PdCl_6^{2-}$	1.737	0.199	1.416	0.138
$PdCl_4^{2-}$	1.558	0.193	1.312	0.096
$PtCl_6^{2-}$	2.046	0.154	1.831	0.085
$PtCl_4^{2-}$	1.822	0.230	1.627	0.118
$PdBr_6^{2-}$	1.488	0.149	1.115	0.085
$PdBr_4^{2-}$	1.381	0.159	1.195	0.073
$PtBr_6^{2-}$	1.759	0.242	1.355	0.170
$PtBr_4^{2-}$	1.642	0.204	1.443	0.116

A close examination of the above results exhibits that in general the stretching force constant increases with the increase of the coordination number from four to six. This is further supported by our expectation that the higher state is more stable. The bonding force constants do not show regular trend. The compliance constants displayed in table 3 favors the trend among force constants.

The mean amplitudes of vibration at three temperatures are collected in table 4. A comparison of the mean amplitudes [U (M-X)] from this table at temperature T=298.15^{o}K among the hexahalide anions shows slightly decreasing tendency with the increase of mass of the central atom on one hand and on the other hand the corresponding stretching force constants show opposite trend. This trend is favor of the variation in the mean amplitudes.

Acknowledgement

We are extremely thankful to Shri Rajendra Kr. Agarwal, Chairmen, Prof. R.P. Shukla, Director, Shri Saket Agarwal, Dean, Rajshree Inst. of Mgnt. & Technology, Bareilly, Prof. Rajendra Sharma, Formerly Director, Vision Inst. of Tech. Aligarh and Prof. G.N. Pandey, Formerly Director, IET, Lucknow for his keen interest and encouragement.

Table 1. VIBRATIONAL WAVENUMBERS (in cm-1) for XY_6 TYPE OCTAHEDRAL ANIONS

Anions	ν_1 (A_{1g})	ν_2 (E_g)	ν_3 (F_{1u})	ν_4 (F_{1u})	ν_5 (F_{1g})	ν_6 (F_{2u})	Bond Length (Å)
FeF_6^{3-}	511	368	447	268	252	178.2	1.93
RhF_6	634	595	724	283	269	192	
IrF_6	702	645	719	276	267	206	1.830
NiF_6^{2-}	562	520	658	345	310	220	
PtF_6^{2-}	611	576	571	281	210	143	
$OsCl_6^{2-}$	345	245	314	177	160	140	2.40 (2.35)
$IrCl_6^{2-}$	352	225	333	184	190	134.3	2.31(2.35)
$PdCl_6^{2-}$	318	289	346	200	178	125.86	2.32
$PtCl_6^{2-}$	348	318	342	183	171	88	2.35
$OsBr_6^{2-}$	210	172	217	122	107	86	2.50
$RhBr_6^{2-}$	185	164	253	130	136	96	
$IrBr_6^{2-}$	210	174	235	82	97	68.5	2.67
$PdBr_6^{2-}$	198	176	253	130	100	70.7	
$PtBr_6^{2-}$	213	190	243	146	137	96.87	2.49
OsI_6^{2-}	128	118	165	95	70	60	2.70

Table 2. GVFF CONSTANTS (in mdyne / Å) FOR XY_6 TYPE OCTAHEDRAL HEXA-HALOGENO ANIONS

Anions	f_r	f_{rr}	$f_{rr}^{'}$	$f_{\alpha} - f_{\alpha\alpha}^{'''}$	$f_{\alpha\alpha} - f_{\alpha\alpha}^{''}$	$f_{\alpha\alpha}^{'} - f_{\alpha\alpha}^{'''}$	$F_{r\alpha} - f_{r\alpha}^{''}$
FeF_6^{3-}	1.708	0.234	0.276	0.200	0.011	0.011	0.077
RhF_6	4.250	0.089	-0.108	0.249	0.021	0.023	0.073
IrF_6	4.902	0.143	0.040	0.279	0.021	0.039	0.049
NiF_6^{2-}	3.155	0.085	0.041	0.322	0.026	0.026	0.128
PtF_6^{2-}	3.476	0.077	0.393	0.223	0.055	0.050	0.049
$OsCl_6^{2-}$	1.605	0.205	0.059	0.208	0.002	0.037	0.050
$IrCl_6^{2-}$	1.655	0.255	-0.087	0.209	0.010	0.103	0.054
$PdCl_6^{2-}$	1.737	0.061	0.130	0.199	0.017	0.017	0.080
$PtCl_6^{2-}$	2.046	0.069	0.205	0.154	0.036	0.001	0.053
$OsBr_6^{2-}$	1.470	0.112	0.156	0.179	0.002	0.022	0.072
$RhBr_6^{2-}$	1.374	0.057	0.007	0.198	-0.009	-0.009	0.093
$IrBr_6^{2-}$	1.560	0.108	0.082	0.097	-0.007	-0.007	0.035
$PdBr_6^{2-}$	1.488	0.065	0.099	0.149	0.016	0.016	0.093
$PtBr_6^{2-}$	1.759	0.072	0.084	0.242	0.011	0.011	0.101
OsI_6^{2-}	1.056	0.031	0.046	0.147	0.006	0.027	0.076

Table 3. COMPLAINCE CONSTANTS (in Å / mdyne) FOR XY_6 TYPE OCTAHEDRAL HEXA-HALOGENO ANIONS

Anions	C_r	C_{rr}	C'_{rr}	$C_\alpha - C'''_\alpha$	$C_{\alpha\alpha} - C''_{\alpha\alpha}$	$C'_{\alpha\alpha} - C'''_{\alpha\alpha}$	$C_{r\alpha} - C''_{r\alpha}$
FeF_6^{3-}	0.654	0.053	-0.110	5.236	-0.195	-0.195	0.260
RhF_6	0.238	-0.005	0.004	4.170	-0.339	-0.304	0.058
IrF_6	0.215	0.011	0.008	3.675	-0.268	-0.669	0.032
NiF_6^{2-}	0.270	0.021	-0.070	3.265	--0.213	-0.226	0.117
PtF_6^{2-}	0.293	-0.005	-0.034	5.883	-1.427	-1.110	0.048
$OsCl_6^{2-}$	0.666	-0.065	-0.001	4.874	-0.006	-1.303	0.158
$IrCl_6^{2-}$	0.675	-0.093	0.083	4.895	-0.206	-0.205	0.140
$PdCl_6^{2-}$	0.604	0.017	-0.064	5.331	-0.359	-0.356	0.230
$PtCl_6^{2-}$	0.503	-0.013	-0.055	8.435	-1.965	0.942	0.131
$OsBr_6^{2-}$	0.733	-0.038	-0.099	5.850	0.052	-0.787	0.327
$RhBr_6^{2-}$	0.793	-0.028	-0.059	5.532	0.461	0.469	0.443
$IrBr_6^{2-}$	0.666	-0.037	-0.038	10.804	0.875	0.887	0.297
$PdBr_6^{2-}$	0.737	-0.024	-0.099	7.438	-0.531	-0.529	0.429
$PtBr_6^{2-}$	0.603	-0.020	-0.055	4.343	-0.095	-0.092	0.251
OsI_6^{2-}	1.034	-0.024	-0.122	7.397	-0.018	-1.761	0.554

Table 4. MEAN AMPLITUDES OF VIBRATION (in Å) FOR OCTA HEDRAL HEXA-HALOGENO ANIONS

Anions	Distance	$T=0^0K$	$T=298.15^0K$	$T=500^0K$
FeF_6^{3-}	(M - X)	0.0525	0.0598	0.0711
	(M ----X) linear	0.0661	0.0768	0.0921
	(M----X) non-linear	0.0937	0.1198	0.1472
RhF_6	(M - X)	0.0396	0.0413	0.0460
	(M ----X) linear	0.0540	0.0570	0.0645
	(M----X) non-linear	0.0779	0.0991	0.1209
IrF_6	(M - X)	0.0375	0.0389	0.0431
	(M ----X) linear	0.0517	0.0539	0.0601
	(M----X) non-linear	0.0738	0.0942	0.1152
NiF_6^{2-}	(M - X)	0.0441	0.0467	0.0529
	(M ----X) linear	0.0577	0.0263	0.0718
	(M----X) non-linear	0.0809	0.0967	0.1156
PtF_6^{2-}	(M - X)	0.0410	0.0436	0.0497
	(M ----X) linear	0.0549	0.0583	0.0663
	(M----X) non-linear	0.0819	0.1149	0.1432
$OsCl_6^{2-}$	(M - X)	0.0427	0.0564	0.0698
	(M ----X) linear	0.0592	0.0789	0.0982
	(M----X) non-linear	0.0758	0.1146	0.1446
$IrCl_6^{2-}$	(M - X)	0.0437	0.0567	0.0702
	(M ----X) linear	0.0609	0.0836	0.1046
	(M----X) non-linear	0.0742	0.1089	0.1371
$PdCl_6^{2-}$	(M - X)	0.0441	0.0545	0.0668
	(M ----X) linear	0.0565	0.0720	0.0889
	(M----X) non-linear	0.0797	0.1158	0.1454

$PtCl_6^{2-}$	(M - X) (M ----X) linear (M----X) non-linear	0.0409 0.0539 0.0805	0.0500 0.0665 0.1290	0.0611 0.0814 0.1632
$OsBr_6^{2-}$	(M - X) (M ----X) linear (M----X) non-linear	0.0384 0.0482 0.0698	0.0570 0.0745 0.1223	0.0721 0.0946 0.1563
$RhBr_6^{2-}$	(M - X) (M ----X) linear (M----X) non-linear	0.0410 0.0497 0.0746	0.0596 0.0798 0.1198	0.0750 0.1016 0.1522
$IrBr_6^{2-}$	(M - X) (M ----X) linear (M----X) non-linear	0.0373 0.0478 0.0732	0.0546 0.0742 01426	0.0689 0.0942 0.1828
$PdBr_6^{2-}$	(M - X) (M ----X) linear (M----X) non-linear	0.0402 0.0480 0.0769	0.0575 0.0747 0.1342	0.0724 0.0949 0.1712
$PtBr_6^{2-}$	(M - X) (M ----X) linear (M----X) non-linear	0.0364 0.0463 0.0646	0.0520 0.0696 0.1048	0.0650 0.0881 0.1340
OsI_6^{2-}	(M - X) (M ----X) linear (M----X) non-linear	0.0472 0.0487 0.0763	0.0664 0.0879 0.1443	0.0849 0.1128 0.1854

References

1. Labonville, P., Ferraro, J. R., Wall, M.C., S. M. C. and Basile, L. *J. Coord. Chem. Rev. 7,* 257 (1972).
2. Pandey, A. N., Sharma, D. K. and Kumar, V., *Acta Ciencia Indica 63,* 63 (1975).
3. Sanyal, N. K., Goel, R. K. and Pandey, A. N., *Ind. J. Phys., 50,* 659 (1976).
4. Pandey, A. N., Sharma, D. K. and Verma, U. P., *acta Physica Pol. A51*, 475 (1977).
5. Nakamoto, K., "Infrared and Raman spectra of Inorganic and Coordination Compounds" [John Wiley and Sons, New

York] (1978).
6. Ferraro, J. R., "Low Frequency Vibrations of Inorganic and Coordination Compounds" [Plenum Pres, New York] (1971).
7. Ross, S.D. "Inorganic Infrared and Raman Spectra" [McGraw_ Hill, Landon] (1972).
8. Durig, J. R. (Ed.) "Vibrational Spectra and Structure" [Vols. 1-3 New York (1972, 1973, 1974) and Vol. 4, Elsevier, Amsterdam] (1975).
9. Schmidt, K.H. and Muller, A., Coord. Chem. Rev. 14, 115 (1974).
10. Pandey, A.N., Bhardwaj, S. and Gupta, E., " Proc. Fifteenth International Conf. on Raman Spectroscopy Eds. Sher, s. A. and Stcin, R., Pittsburgh PA (U. S. A.) [John, Wiley & Sons, New York] 568, (1996).
11. Wilson (Ir.), E. B., Decius, J. C. and Cross, P. C., "Molecular Vibrations" (McGraw _ Hill Book Co. Inc, New York) (1955).
12. Pandey, A.N., Sharma, D.K., Verma, U.P., Arora, L. D., Gupta, S. L. and Singh, B. P., *Indian J. Pure Appl. Phys. 14,* 815 (1977).
13. Meal, J. H. and Polo, S. R., *J. Chem. Phys. 24,* 1119, 1126 (1956).
14. Cyvin, S. J. "Molecular Vibrations and Mean - square Amplitudes" (Universitets Forlaget, Oslo, Elsevier Pub. Co. Amsterdam) (1968).
15. Pauling, L. *"The Nature of Chemical Bonds"* (Cornell Univ. Pres Ithaca) (1960).
16. Brown, T. L., Mc Dugle (Jr) W. G., and Kent, L. G., *J. Amer. Chem. Soc., 92,* 3645 (1970).
17. Hiraishi, T., Nakagawa, I. and Shimanouchi, T., *Spectrochim. Acta 20,* 819 (1964).
18. Jenkins, H. D. B. and Pratl, K. F. (Private Communication).
19. Pandey, A. N., Sharma, D. K., Verma, U. P. and Kumar, V., J. Raman Spectrosc. 6, 163 (1977).
20. Pandey, A. N. and Verma, U. P., *Mol. Structure. 42,* 171 (1977).