

A STUDY OF INTRAMOLECULAR FORCE FIELDS AND DEPENDENCE OF FORCE CONSTANTS ON CRYSTAL-FIELD STABILIZATION ENERGY FOR SOME OCTAHEDRAL IONS AND MOLECULES OF SECOND- AND THIRD-ROW TRANSITION AND NON-TRANSITION METALS

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The general valence force field (GVFF), the modified Urey-Bradley force field (MUBFF) and the modified orbital valence force field (MOVFF) have been employed to compute the force constants for MCl_6^{2-} ($M = Hf, Re, Os, Ir, Pt, Tl$ or Pb); MBr_6^{2-} ($M = Hf, Re, Os, Ir$ or Pt); SnX_6^{2-} ($X = F, Cl, Br$ or I), $PdCl_6^{2-}$, PtX_6^{2-} ($X = F$ or I), MF_6 ($M = Mo, Tc, Ru, Rh, Pd, W, Re, Os, Ir$ or Pt) octahedral ions and molecules of second- and third-row transition and non-transition metals. The force constants have been utilized to study the relative strength of the chemical bonds. A study of dependence of force constants on the number of non bonding valence electrons and crystal field stabilization energies have been made. Definite trends regarding force constants dependence on c.f.s.e. have been discussed briefly.

1. Introduction

In recent years a number of workers have employed the most reliable vibrational data to understand the nature of intramolecular forces by using different potential energy function models. La Bonville et al. [1] have applied five force fields to twenty seven hexafluorides, twenty three hexachlorides eleven hexabromides and one hexaiodide. The calculations of force constants for octahedral hexahalogen species considered were done on an IBM 360 computer using Schachtschneiders force constants adjust programme [2], and large discrepancy occurs between observed and calculated frequencies for some hexa-

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halides. Recently, Bosworth and Clark [3] have recorded the Raman spectra for some octahedral ions of second- and third- row transition and non transition metals using a spex 1401 spectrometer in conjunction with Coherent Radiation Ltd. Ar⁺ and Kr⁺ lasers. As these data are more reliable than previous results, therefore it was thought worthwhile to use these for computing force constants using different potential energy function models. For this purpose three force fields have been selected. These are the general valence force field (GVFF) with seven force constants and modified Urey-Bradley force field (MUBFF) suggested by Venkateswarlu and Malathy Devi [4] which uses seven force constants. The MOVFF involving six force constants has been recently successfully applied by Ramaswamy and Muthusubramanian [5], Pandey et al. [6] and Sharma et al. [7] to some octahedral molecules and anions. The same potential energy function has also been used in the present work. These three force fields (GVFF, MUBFF and MOVFF) have been employed to compute the force constants for MCl_6^{2-} ($M = \text{Hf, Re, Os, Ir, Pt, Tl or Pb}$); MBr_6^{2-} ($M = \text{Hf, Re, Os, Ir or Pt}$); SnX_6^{2-} ($X = \text{F, Cl, Br or I}$), $PdCl_6^{2-}$, PtX_6^{2-} ($X = \text{F or I}$); MF_6 ($M = \text{Mo, Tc, Ru, Rh, Pd, W, Re, Os, Ir or Pt}$) octahedral ions and molecules of second and third row transition and non transition metals.

Kim et al. [8] have discussed the dependence of the non-bonded interaction constant F and bending constant D in simple OVFF model on the number (n) of non-bonding valence electrons (upto $n = 4$). Therefore, the results of the present study have been employed to discuss the dependence of force constants on the number of non-bonding valence electrons and crystal field stabilization energies for the octahedral ions and molecules.

2. Method of computation

The hexahalide anions of the type MX_6^{n-} possessing octahedral symmetry give rise to six fundamental frequencies which are distributed among different symmetry species as follows:

$$\Gamma_{\text{vib}} = 1a_{1g} + 1e_g + 2f_{1u} + 1f_{2g} + 1f_{2u}$$

of these frequencies $\nu_1(a_{1g})$, $\nu_2(e_g)$ 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 or can be computed with the help of the relation $\nu_5 = \sqrt{2}\nu_6$.

Wilson's FG matrix method [9] has been followed to calculate the force constants. F and G matrix elements are taken from literature [5, 10]. There are seven force constants in GVFF and MUBFF models, i. e. more than the observed fundamentals. Therefore, in order to calculate the complete set of force constants the method suggested by Pandey et al. [11] has been used to solve the two-dimensional secular equations occurring in f_{1u} species which gives results with reasonable accuracy for molecules of the type XY_n where $M_X < M_Y$ or $M_X > M_Y$. The six force constants, appearing in MOVFF model have been calculated by employing the six vibrational frequencies.

3. Results and discussion

The vibrational frequencies used in the present computations are listed in Table I. The Raman active frequencies of the $\nu_1(a_{1g})$, $\nu_2(e_g)$, $\nu_5(f_{2g})$ fundamentals for the octahedral ions MF_6^{2-} ($M = Pt$ or Sn); MCl_6^{2-} ($M = Re, Os, Ir, Pd, Pt, Sn$ or Pb); MBr_6^{2-} ($M = Os, Ir, Pt$, or Sn) and MI_6^{2-} ($M = Pt$ or Sn) are taken from Bosworth and Clark [3]. It is worth mentioning that Raman spectrum of the PtI_6^{2-} ion and $\nu_6(f_{2g})$ fundamental for $IrBr_6^{2-}$ and $OsBr_6^{2-}$ ions has been reported for the first time in Ref. [3]. The infrared active fundamentals for the other ions are the same as used by Labonville et al. [1].

TABLE I

Observed frequencies in (cm^{-1}) for octahedral molecules and ions of second- and third-row transition and non-transition metals

Hexahalides	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	Ref.
SnF_6^{2-}	582	465	556	300	249	170*	[1, 3]
$SnCl_6^{2-}$	313	229	303	166	157	112*	[1, 3]
$SnBr_6^{2-}$	185	138	215	114	94	73*	[1, 3]
SnI_6^{2-}	136	113	161	84	78	55*	[1, 3]
$PbCl_6^{2-}$	285	206	258	137	141	(76)	[1, 3]
$TiCl_6^{2-}$	264	192	230	146	135	95*	[1]
$\dagger PdF_6$	590	525	711	280	258	191	[1]
$PdCl_6^{2-}$	317	293	358	175	154	116*	[1, 3]
PtF_6	656.4	601	705	273	242	(211)	[1]
PtF_6^{2-}	600	576	571	281	210	149*	[1, 3]
$PtCl_6^{2-}$	343	319	345	183	160	(78)	[1, 3]
$PtBr_6^{2-}$	210	192	244	90	95	69*	[1, 3]
PtI_6^{2-}	150	131	186	46	69.5	54*	[1, 15]
RhF_6	634	592	724	283	269	(189)	[1]
IrF_6	701	645	719	276	258	(206)	[1]
$IrCl_6^{2-}$	346	293	335	168	160	135*	[1, 3]
$IrBr_6^{2-}$	210	174	223	124	97	68.5*	[1, 3]
RuF_6	675	624	735	275	283	(186)	[1]
OsF_6	730.7	668	720	268	276	(205)	[1]
$OsCl_6^{2-}$	345	245	314	177	160	117*	[1, 3]
$OsBr_6^{2-}$	211	169	227	122	100	71*	[1, 3]
TcF_6	712.9	639	748	275	297	(145)	[1]
ReF_6	753.7	671	715	257	295	(147)	[1]
$ReCl_6^{2-}$	346	275	313	172	156	112*	[1, 3]
$ReBr_6^{2-}$	213	174	217	118	104	74*	[1]
MoF_6	741	643	741	262	312	(122)	[1]
WF_6	771	677	711	258	320	(127)	[1]
$HfCl_6^{2-}$	333	237	288	145	157	(80)	[1]
$HfBr_6^{2-}$	201	157	193	112	116	82*	[1]

*Calculated from Eq. $\nu_6 = \nu_5/\sqrt{2}$.

() Value obtained from site splitting, overtones or combination bands.

† Theoretical molecule.

The GVFF model [10] includes bond stretching constant f_r , angle bending constant f_{α} , 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 $f'_{r\alpha}$ interaction involving an angle and one of the bonds. The MOVFF [5] model employs bond stretching constant K , angle bending constant D and interaction constants F , F' , k and h . In the MUBFF [4] K , H , F and F' represent the stretching, bending and non-bonded interaction force constants and the following interaction constants h , k and g represent interaction between two angles in two perpendicular planes, interaction between two bonds in the same diagonal and interaction between two angles in the same plane respectively.

Tables II-VI collect the results of the calculations made for the GVFF, MUBFF and MOVFF force fields. It is interesting to study a number of trends in force constants in the light of present data.

TABLE II

GVFF constans (in mdyne/Å) for some octahedral ions of second- and third-row transition and non-transition metals

Ion	f_r	f_{rr}	$f_{\alpha}-f'''_{\alpha\alpha}$	f'_{rr}	$f_{r\alpha}-f'_{r\alpha}$	$f_{\alpha\alpha}-f''_{\alpha\alpha}$	$f'_{\alpha\alpha}-f'''_{\alpha\alpha}$
SnF ₆ ²⁻	2.780	0.228	0.250	0.098	0.072	0.044	0.038
SnCl ₆ ²⁻	1.328	0.159	0.148	0.082	0.047	0.009	0.010
SnBr ₆ ²⁻	1.098	0.118	0.134	0.040	0.070	0.004	0.015
SnI ₆ ²⁻	0.923	0.070	0.112	0.169	0.063	0.000	0.000
PbCl ₆ ²⁻	1.109	0.135	0.095	0.048	0.029	0.017	-0.004
TiCl ₆ ²⁻	0.922	0.114	0.121	0.075	0.032	0.013	0.013
PdCl ₆ ²⁻	1.792	0.050	0.159	0.105	0.063	0.009	0.018
PtF ₆ ²⁻	3.449	0.053	0.229	0.366	0.049	0.052	0.053
PtCl ₆ ²⁻	2.055	0.054	0.145	0.182	0.053	0.041	0.006
PtBr ₆ ²⁻	1.727	0.055	0.106	0.119	0.041	-0.003	0.000
PtI ₆ ²⁻	1.292	0.068	0.073	0.126	0.019	-0.018	0.009
IrCl ₆ ²⁻	1.893	0.116	0.191	0.137	0.046	0.000	0.029
IrBr ₆ ²⁻	1.515	0.107	0.150	0.126	0.074	0.020	0.020
OsCl ₆ ²⁻	1.607	0.206	0.178	0.060	0.050	0.017	0.022
OsBr ₆ ²⁻	1.512	0.123	0.150	0.083	0.072	0.016	0.016
ReCl ₆ ²⁻	1.707	0.155	0.165	0.180	0.048	0.017	0.019
ReBr ₆ ²⁻	1.481	0.118	0.150	0.181	0.068	0.021	0.011
HfCl ₆ ²⁻	1.414	0.190	0.103	0.139	0.035	0.018	-0.013
HfBr ₆ ²⁻	1.213	0.123	0.155	0.194	0.061	-0.001	-0.001

From the variation of bond stretching constant f_r (GVFF), K (MUBFF) and K (MOVFF), it is inferred that the relative strength of the chemical bonds is in the order $M-F > M-Cl > M-Br > M-I$ (where M represent metal) which is in accordance with the decrease in electronegativity from fluorine to chlorine, chlorine to bromine and bromine to iodine. A comparison of the effects of mass made by keeping the halogen constant is demon-

TABLE III

MUBFF constants (in mdyne/Å) for some octahedral ions of second- and third-row transition and non-transition metals

Ion	K	F	F'	H	k	h	g
SnF ₆ ²⁻	2.490	0.300	-0.155	0.022	0.098	-0.033	0.038
SnCl ₆ ²⁻	1.140	0.206	-0.122	-0.011	0.082	-0.047	0.010
SnBr ₆ ²⁻	0.819	0.180	-0.049	0.015	0.040	-0.020	0.015
SnI ₆ ²⁻	0.670	0.134	-0.007	0.042	0.169	-0.040	0.000
PbCl ₆ ²⁻	0.994	0.164	-0.106	-0.040	0.048	-0.036	-0.004
TlCl ₆ ²⁻	0.794	0.146	-0.082	0.006	0.075	-0.028	0.013
PdCl ₆ ²⁻	1.540	0.113	0.013	0.109	0.105	0.016	0.018
PtF ₆ ²⁻	3.253	0.102	-0.005	0.175	0.366	0.050	0.053
PtCl ₆ ²⁻	1.841	0.108	0.000	0.092	0.182	0.041	0.006
PtBr ₆ ²⁻	1.562	0.097	-0.014	0.051	0.119	0.010	0.000
PtI ₆ ²⁻	1.215	0.087	-0.048	0.005	0.126	-0.042	-0.009
IrCl ₆ ²⁻	1.709	0.162	-0.071	0.074	0.137	-0.035	0.029
IrBr ₆ ²⁻	1.220	0.181	-0.033	0.043	0.126	0.003	0.020
OsCl ₆ ²⁻	1.406	0.256	-0.155	-0.028	0.060	-0.035	0.022
OsBr ₆ ²⁻	1.222	0.196	-0.051	0.027	0.083	-0.009	0.016
ReCl ₆ ²⁻	1.516	0.201	-0.105	0.011	0.180	-0.036	0.019
ReBr ₆ ²⁻	1.208	0.186	-0.050	0.181	0.031	-0.015	0.002
HfCl ₆ ²⁻	1.273	0.226	-0.155	-0.087	0.139	-0.059	-0.013
HfBr ₆ ²⁻	0.969	0.185	-0.062	0.032	0.194	-0.033	-0.001

TABLE IV

MOVFF constants (in mdyne/Å) for some octahedral ions of second- and third-row transition and non-transition metals

Ion	K	F	F'	D	k	$h/2$
SnF ₆ ²⁻	2.735	0.209	-0.247	0.070	0.218	-0.072
SnCl ₆ ²⁻	1.033	0.248	-0.070	-0.019	0.023	0.026
SnBr ₆ ²⁻	0.828	0.182	-0.055	0.032	0.056	-0.028
SnI ₆ ²⁻	0.601	0.180	0.039	0.090	0.054	0.021
PbCl ₆ ²⁻	0.860	0.206	-0.064	-0.074	0.014	-0.013
TlCl ₆ ²⁻	0.773	0.158	-0.071	0.013	0.052	-0.022
PdCl ₆ ²⁻	1.525	0.121	0.021	0.218	0.089	0.020
PtCl ₆ ²⁻	1.888	0.091	-0.017	0.185	0.202	0.033
PtBr ₆ ²⁻	1.413	0.159	0.048	0.110	0.020	0.023
PtI ₆ ²⁻	1.003	0.185	0.050	0.037	-0.054	0.013
IrCl ₆ ²⁻	1.624	0.191	-0.042	0.150	0.108	0.020
OsCl ₆ ²⁻	1.392	0.260	-0.151	-0.056	0.056	-0.058
OsBr ₆ ²⁻	1.272	0.168	-0.079	0.062	0.145	-0.021
ReCl ₆ ²⁻	1.498	0.208	-0.100	0.021	0.173	-0.033
ReBr ₆ ²⁻	1.087	0.271	-0.021	0.045	0.066	0.004
HfCl ₆ ²⁻	1.064	0.293	-0.088	-0.159	0.983	-0.022
HfBr ₆ ²⁻	0.766	0.265	0.017	0.087	0.077	0.013

TABLE V

GVFF constants (in mdyne/Å) for some octahedral molecules of second- and third-row transition and non-transition metals

Molecule	f_r	f_{rr}	$f_a - f''_{aa}$	f'_{rr}	$f_{ra} - f'_{ra}$	$f_{aa} - f''_{aa}$	$f'_{aa} - f''_{aa}$
MoF ₆	4.802	0.253	0.164	0.331	0.065	0.040	-0.054
TcF ₆	4.770	0.186	0.195	0.172	0.070	0.039	-0.026
RuF ₆	4.535	0.123	0.234	0.070	0.070	0.020	0.005
RhF ₆	4.236	0.096	0.245	-0.121	0.073	0.023	0.022
(PdF ₆)	3.796	0.135	0.246	-0.441	0.070	0.020	0.030
WF ₆	5.178	0.254	0.184	0.460	0.045	0.047	-0.051
ReF ₆	5.130	0.220	0.198	0.349	0.044	0.039	-0.022
OsF ₆	5.049	0.166	0.268	0.228	0.047	0.016	0.028
IrF ₆	4.900	0.141	0.279	0.038	0.049	0.021	0.046
PtF ₆	4.494	0.130	0.282	-0.191	0.048	0.016	0.059

TABLE VI

MUBFF constants (in mdyne/Å) for some octahedral molecules of second- and third-row transition metals

Molecule	K	F	F'	H	k	h	g
MoF ₆	4.541	0.318	-0.188	-0.089	0.331	-0.053	-0.054
TcF ₆	4.488	0.257	-0.116	0.008	0.172	-0.019	-0.025
RuF ₆	4.256	0.193	-0.054	0.110	0.070	-0.007	0.005
RhF ₆	3.945	0.169	-0.023	0.149	-0.121	0.011	0.022
(PdF ₆)	3.516	0.205	-0.065	0.110	-0.441	-0.012	0.030
WF ₆	4.999	0.298	-0.209	-0.070	-0.460	-0.080	-0.051
ReF ₆	4.954	0.264	-0.176	0.021	0.349	-0.060	-0.033
OsF ₆	4.906	0.211	-0.116	0.105	0.228	-0.042	0.028
IrF ₆	4.752	0.190	-0.091	0.138	0.033	-0.001	0.046
PtF ₆	4.303	0.178	-0.082	0.152	-0.191	0.011	0.059

strated by comparing the stretching force constant (Table V) of MoF₆, WF₆; TcF₆, ReF₆; RuF₆, OsF₆; RhF₆, IrF₆; (PdF₆), PtF₆; PdCl₆²⁻, PtCl₆²⁻. It may be observed from Tables I, V, VI, that an increase in ν_1 and stretching force constant (K or f_r) occurs as one proceeds from the second to third row transition series. The suggestion made by Brown et al. [12] to use ν_1 as a measure of bond strength may be justified since the heavy central atom remains stationary during the vibration.

To compare the covalent character of the metal chlorine and the metal bromine bonds in various compounds, Hiraishi et al. [13] computed the ratio of the stretching force constants $f_r(M-Br)/f_r(M-Cl)$. This ratio comes out to be 0.79 for a large number of non-hexahalide molecules and 0.83 and 0.86 for PtX₆²⁻ and SnX₆²⁻ ($X = Cl$ or Br), respectively. In the present work, the ratio $f_r(M-Br)/f_r(M-Cl)$ is found to have values of 0.83, 0.84,

0.80, 0.86 and 0.85 for SnX_6^{2-} , PtX_6^{2-} , IrX_6^{2-} , ReX_6^{2-} , and HfX_6^{2-} species, respectively. From this it is concluded that the difference in covalent character between $M\text{-Br}$ and $M\text{-Cl}$ bonds becomes larger in hexahalogeno species.

4. Dependence of force constants on the crystal field stabilization energy and on the number of non-bonding valence electrons

Figs. 1 and 2 present plots of the K , H and F force constants in MUBFF as a function of the number of non bonding valence electrons (n) for $M\text{Cl}_6^{2-}$ ($M = \text{Hf, Re, Os, Ir, Pt, Tl}$ or Pb) and $M\text{Br}_6^{2-}$ ($M = \text{Hf, Re, Os, Ir}$ or Pt) of the third-row transition series. It may be observed that the plots of K and H vs n are similar and different from the F plot for these

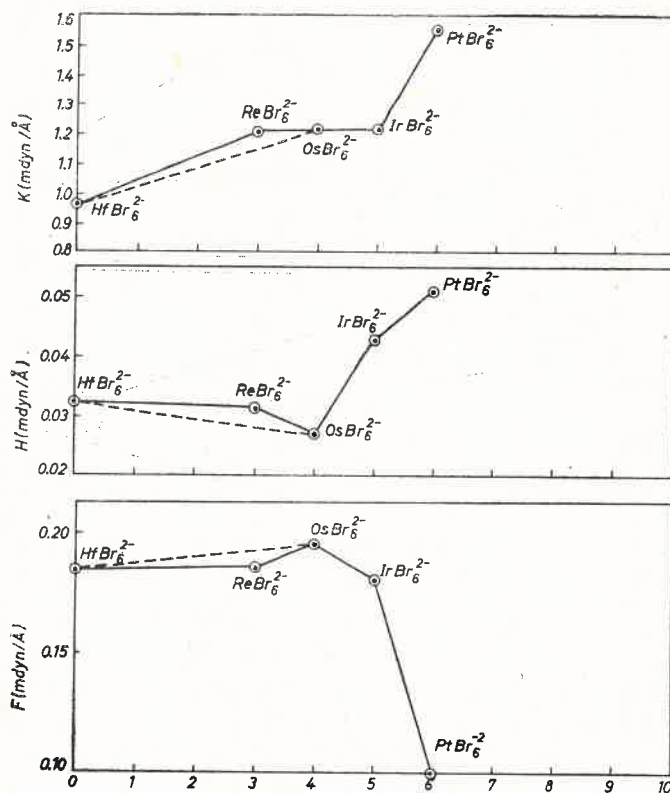


Fig. 1. Number of nonbonding d electrons

two series. For discussion, it is necessary to write first crystal field stabilization energies for d electron configurations. Following Figgis [14], the crystal field stabilization energies for d electron configuration for octahedral stereochemistry are as follows: $0 Dq$ for d^0 , d^5 and d^{10} configurations; $4 Dq$ for d^1 and d^6 configurations; $6 Dq$ for d^2 , d^4 , d^7 configurations and $12 Dq$ for d^3 and d^8 configurations, respectively. It may be observed from Figs. 1, 2

that K and H plots show a maximum point at $n = 3$ i. e. for the d^3 ions: ReCl_6^{2-} and ReBr_6^{3-} . This result appears to be consistent with the conception of weak ligand field and weak c. f. s. e. An increase in the stretching and bending constants (K , and H) for ReCl_6^{2-} and ReBr_6^{2-} (more stable ion) corresponds to a decreased force constant F . This trend of varia-

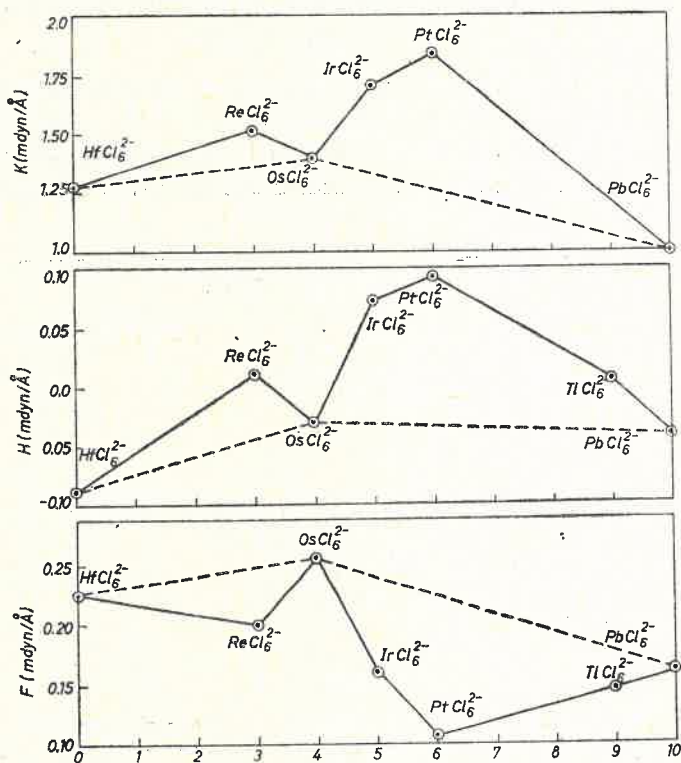


Fig. 2. Number of nonbonding d electrons

tion in force constants is also supported by GVFF and MOVFF force constant values for ReCl_6^{2-} and ReBr_6^{2-} . It is also observed from Figs. 1, 2 that stretching force constants K and bending constant H in MUBFF have minimum values for d^0 ions (HfCl_6^{2-} , HfBr_6^{2-}), and d^{10} ion (PbCl_6^{2-}). This decrease in the force constant K , and H value corresponds to a less stable ion and an increased value of interaction constant F . This result is consistent with c. f. s. e. values for d^0 and d^{10} octahedral anions. The trend of variation in force constants in MUBFF for HfCl_6^{2-} , HfBr_6^{2-} and PbCl_6^{2-} is also supported by GVFF and MOVFF force constant values.

The two series — MCl_6^{2-} and MBr_6^{2-} under present study also includes d^5 ions (IrCl_6^{2-} , IrBr_6^{2-}), d^4 ion (OsCl_6^{2-} , OsBr_6^{2-}) and d^6 ion (PtCl_6^{2-} and PtBr_6^{2-}). The K , H and F values for OsCl_6^{2-} , PtCl_6^{2-} and PtBr_6^{2-} are in accordance to c.f.s.e. concept. However, it is noted from Figs. 1, 2 that the K and H values in MUBFF vs n are not minimum as demanded by c.f.s.e. concept for d^5 configuration. This follows because the strong field

configuration with which the ground free ion term correlates lies $20 Dq$ above the ground strong field configuration. Thus we have $20 Dq$ energy gains for d^5 and d^6 configurations on reaching the strong fields configurations. Bosworth et al. [3] have also mentioned that IrCl_6^{2-} , IrBr_6^{2-} , OsBr_6^{2-} and PtI_6^{2-} have very complicated electronic spectra with many low-lying charge transfer bands and many relatively intense ligand bands through out the visible region. Therefore a high value of K and H and low value of F can be attributed

TABLE VII

Comparison of stretching force constants

Ion	n	$K(\text{MUBFF})$	$f_r(\text{GVFF})$	$K(\text{MOVFF})$
HfCl_6^{2-}	0	1.27	1.41	1.06
ReCl_6^{2-}	3	1.51	1.70	1.50
OsCl_6^{2-}	4	1.41	1.61	1.39
IrCl_6^{2-}	5	1.71	1.89	1.62
PtCl_6^{2-}	6	1.84	2.05	1.88
TlCl_6^{2-}	9	0.79	0.92	0.77
PbCl_6^{2-}	10	0.99	1.11	0.86
HfBr_6^{2-}	0	0.97	1.21	0.77
ReBr_6^{2-}	3	1.21	1.48	1.09
OsBr_6^{2-}	4	1.22	1.51	1.27
IrBr_6^{2-}	5	1.22	1.51	—
PtBr_6^{2-}	6	1.56	1.73	1.41

owing to strong field configurations for bond stretching constant K in IrCl_6^{2-} , IrBr_6^{2-} and OsBr_6^{2-} . A higher value for IrCl_6^{2-} , IrBr_6^{2-} , and OsBr_6^{2-} is also supported by f_r and K values obtained from GVFF and MOVFF. These are compared in Table VII.

From the above discussion it can be concluded that a dependence of F , K and H force constants from the MUBFF vs the number of non-bonding valence electrons and crystal field stabilization energy exists for MCl_6^{2-} and MBr_6^{2-} type anions. It is also significant to cite that f_r and K force constants obtained from GVFF, MUBFF and MOVFF reflects these trends clearly.

Figure 3 shows the plot of the stretching constant K in MUBFF vs n for $\text{MF}_6(M = \text{Mo, Tc, Ru, Rh, or Pd; W, Re, Os, Ir or Pt})$ transition series. It may be observed that at the maximum point $n = 3$ in the H Plot a minimum point is observed for F and for the minimum point $n = 0$ in the H plot a maximum point is observed for F . This result appears to be consistent with observations made for the ligand-field stabilization energy plots for transition-metal complexes when a maximum energy is obtained at $n = 3, 8$ and minimum at 0, 5 and 10 for complexes in a octahedral field. It is observed from Tables V, VI and Fig. 3, that the stretching force constant K decreases as the atomic mass of the central atom increases for $\text{MF}_6(M = \text{Mo, Tc, Ru, Rh, or Pd})$ and $\text{MF}_6(M = \text{W, Re, Os, Ir or Pt})$ transition series. The same trend is observed by GVFF calculations for these molecules.

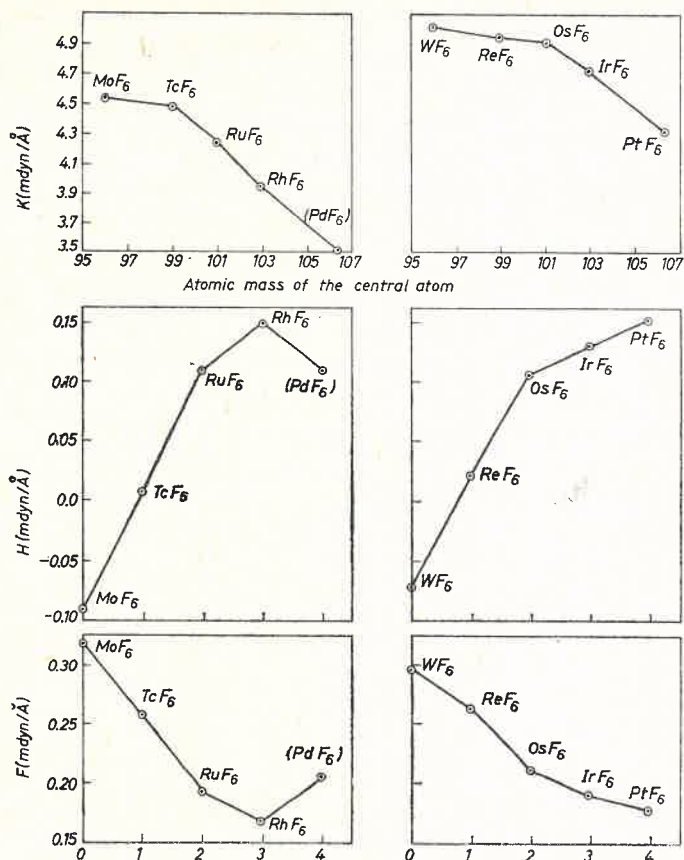


Fig. 3. Number of nonbonding d electrons

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