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A STUDY OF FORCE FIELDS FOR OCTAHEDRAL HEXAHALOGEN MOLECULES *

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CONTENTS

A. INTRODUCTION

The objective of this study was to make a systematic comparison of five force fields applied to several octahedral hexahalogen species. Molecules considered were those for which assignments of Raman and infrared spectra were available, the most recent data being used. Kim et al. [1] have made such a study for fifteen hexafluorides using two force fields, but only limited and scattered studies have been made of the corresponding chloride, bromide and iodide compounds.

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The five force fields examined were the Urey-Bradley Force Field (UBFF), with four force constants, the Orbital Valence Force Field (OVFF), which also employs four force constants, the modification of the UBFF made by Shimanouchi (MUBFF), which involves five force constants, a modified Orbital Valence Force Field (MOVFF) with five force constants, and the General Valence Force Field (GVFF) which uses seven force constants (reduced to five with certain assumptions).

The molecules studied include twenty-seven hexafluorides, twenty-three hexachlorides, eleven hexabromides and one hexaiodide. Of the six fundamental frequencies for molecules with octahedral symmetry, three are active in the Raman and two in the infrared spectrum; the sixth vibration is inactive in both Raman and infrared. In many cases the frequency of this sixth vibration has been obtained from assignments of overtones, combinations and site splitting in the solid spectra. In cases where there was no such value recorded in the literature, an estimated value [2] was obtained using the formula $\nu_\varepsilon = \nu_s/\sqrt{2}$.

B. THEORY OF MOLECULAR FORCE FIELDS

Each of the force fields used gives an expression for the potential energy in which the force constants appear as coefficients. In representing a molecule containing n atoms, $3n$ coordinates will be needed to describe their motions; for non-linear molecules, six of these describe the translations and rotations of the system whilst for linear molecules only five are needed, since these have one less degree of rotational freedom. For a general molecule the kinetic energy (T) and the potential energy (V) can be expressed as functions of these coordinates: $q_1, q_2, \ldots, q_{3n-6}$ (or q_{3n-5} for linear molecules).

$$T = \sum_i \tfrac{1}{2} m_i (\dot{q}_i)^2 \tag{1}$$

where $\dot{q}_i = \mathrm{d}q_i/\mathrm{d}t$, and, making the harmonic approximation,

$$V = \sum_i \tfrac{1}{2} f_{ij} q_i q_j \tag{2}$$

The frequencies of the vibrations may be thought of as due to small displacements from the equilibrium position of the molecule and can be expressed in terms of the mass of the atoms and the restoring forces. The restoring forces are approached through the concept of the potential force field which to a good approximation can be written as

$$V = \tfrac{1}{2} \sum_{i,j=1}^{3n-C} F_{ij} q_i q_j \tag{3}$$

where C is 5 or 6 depending on whether the molecule is linear or not. This general quadratic potential function for most molecules contains more force constants (F_{ij}) than there are fundamental frequencies. Thus, all of the force constants cannot be calculated from the values of the observed frequencies. There have been a number of approximations introduced to reduce the number of coefficients F_{ij} in eqn. (3). The Central Force Field (CFF) includes only forces in molecules between atoms along the lines joining them, whether the atoms are bonded or not, and is unrealistic because it neglects bending inter-

actions. The Simple Valence Force Field (SVFF) considers bending of molecules as well as stretching along bonds. There are only two types of force constants needed, and there is no consideration of interactions between non-bonded atoms. The General Valence Force Field (GVFF) includes, besides the bending and stretching constants of the SVFF, all cross terms involving stretch–stretch, bend–bend, and bend–stretch. It generally has more force constants than frequencies and hides the interaction between non-bonded atoms in the species in cross terms.

Several assumptions can be made to reduce the number of force constants. For the GVFF, seven force constants are necessary for a hexacoordinated molecule of O_h symmetry, and these must be reduced to five or less than the number of observed frequencies. The usual practice is to assume that force constants associated with a stretch–bend and a bend–bend interaction are zero if the two internal coordinates do not share a common bond. The GVFF includes the stretching constant f_r, the bending constant f_α, the stretching interaction constants f_{rr} and $f_{rr'}$, the angle interaction constants $f_{\alpha\alpha}$ and $f_{\alpha\alpha'}$ and the stretch-angle interaction constant $f_{r\alpha}$. These can be reduced to five by assuming that $f_{\alpha\alpha} = f_{\alpha\alpha'}$ and $f_{rr'} = {}^4/_3 f_{rr}$ as has been done by Van Bronswyk et al. [3]. The first of these assumptions necessitates that $\nu_6 = \nu_5\sqrt{2}$. The number of such assumptions is quite large and most probably no one set would fit all molecules. We have chosen this set only as an example of what can be done with the GVFF to reduce the number of force constants and wish to emphasize that the procedure is completely arbitrary.

Two general methods to reduce the number of force constants while including in the potential energy function the interaction between non-bonded atoms are the UBFF and the OVFF mentioned earlier. The function for the potential energy in the UBFF was proposed by Urey and Bradley [4]. It includes two repulsion force constants between non-bonded atoms and may be expressed as

$$V = \sum_i [K'_i(r_i)_0 \Delta r_i + \tfrac{1}{2}K(\Delta r_i)^2] + \sum_{i<j} [H'_{ij}(r_{ij})_0^2 (\Delta\alpha_{ij}) + \tfrac{1}{2}H_{ij}(r_{ij_0}\Delta\alpha_{ij})^2]$$

$$+ \sum_{i<j} [F'_{ij}(q_{ij})_0 \Delta q_{ij} + \tfrac{1}{2}F_{ij}(\Delta q_{ij})^2] \qquad (4)$$

where

$$q_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos\alpha_{ij} \qquad (5)$$

This latter expression makes it possible to express the potential function (V) in terms of Δr_i, Δr_j and $\Delta\alpha_{ij}$, the bond lengths and bond angles. The subscript zero refers to the equilibrium state.

In the case of the octahedral system with six identical ligand atoms, the UBFF requires only four force constants: K, F, H, F'. K is the force constant for stretching along a bond, H for an angle deformation, and F and F' are force constants for interactions between non-bonded atoms. The value for F' will generally be much smaller than that for F. Thus, the UBFF combines a small number of force constants with the inclusion in the potential function of interactions between non-bonded atoms. This was a very attractive function, has been used extensively, and has been found to be adequate for many systems. However,

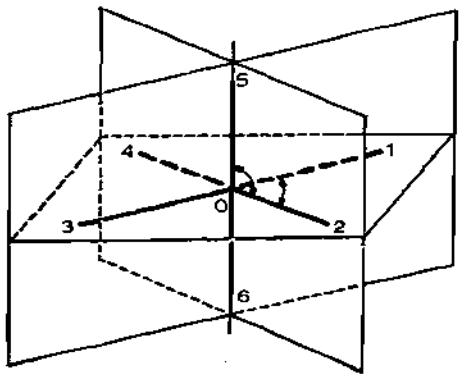

Fig. 1. Urey–Bradley field correction term.

it has failed to represent adequately the forces in a number of molecules studied. As a result, Shimanouchi and coworkers borrowed from the GVFF and introduced first one additional force constant which involved interactions between stretches along the same diagonal [5] (k), and later another involving the interaction of two angles having a common side and lying in perpendicular planes [6] (h) (see Fig. 1). The F' constant of the UBFF is assumed to be $-1/10$ of the F constant and so there are still only 5 force constants to be determined from the six vibrational frequencies. This represents the MUBFF.

A second type of special force field which has been used less extensively but which has been receiving some attention of late [1,7] is the OVFF proposed by Heath and Linnett [8]. It considers the bending vibration in the light of theories of directed valence. At first, Heath and Linnett questioned the emphasis which the UBFF placed on repulsions between non-bonded atoms [9]. As they worked with more complicated molecules, they recognized the importance of these repulsions and added them to their potential function as a Lennard–Jones term of the form

$$V \cong b/R^{12} \tag{6}$$

They found that this outweighed the attractive term in the Lennard–Jones function. A second difference between their potential field and that of the SVFF and UBFF is that instead of the angle of deformation between two bonds ($\Delta\alpha$), they used the angle which represents the distortion of the bond from the axis of the bonding orbital ($\Delta\beta$). Hence the name given was Orbital Valence Force Field. The contribution of this to the potential energy function is given as

$$V = \tfrac{1}{2}k'_{\beta}(\Delta\beta_{ij})^2 \tag{7}$$

The over-all OVFF potential energy function is

$$2V = 2B' \sum_{j} \Delta r_{ij} + k_i \sum_{j} (\Delta r_{ij})^2 + k'_{\beta} \sum_{j} (\Delta\beta_{ij})^2 - 2B \sum_{jk} \Delta R_{jk} + 2A \sum_{jk} (\Delta R_{jk})^2 \tag{8}$$

where $\Delta\beta_{ij}$ is the angle the line from the central atom to atom j makes with the line in which the particular orbital has its maximum value, and it measures the movement of the atom away from the direction in which the orbitals of the two atoms show the maximum overlap; k_i = OVFF stretching force constant; k'_β = OVFF bending force constant; B, A = force constants for repulsions between non-bonded atoms expressed by $V = -B\Delta R + A(\Delta R)^2 \ldots$; where $B = -(dV/dR)$; $A = \frac{1}{2}(d^2V/dR^2)$. Heath and Linnett proposed their angular distortion force constant on the basis of their assumption that the bond-forming orbitals of the central atom are at definite fixed angles to each other and the equilibrium state is the one in which they have maximum overlap with the bond-forming orbitals of the ligands. Hence, when a molecule undergoes a bending vibration, the bonding orbitals will seek to return to a position of maximum overlap. Therefore, differences between calculations based on the SVFF (or UBFF) and those based on the OVFF will differ primarily in this third term of eqn. (8). If the difference between $(\Delta\alpha)$ and $(\Delta\beta)$ is small, the potential fields give similar results. They further suggest that the central atom may even change its hybridization to allow the molecule to undergo a given bending vibration with greater facility and thus lower the potential energy. They used methane and its deuterated derivatives and found that such changes of hybridization were feasible for some vibrations and not for others. They included this in their OVFF potential expression wherever appropriate. We have modified the OVFF by adding the fifth force constant (k) and obtained the MOVFF. (The constant k has the same meaning as that in the MUBFF.)

The potential energy function for molecules of octahedral symmetry corresponding to the force fields used in this study can be represented by the following equations where K is the force constant for a stretch along a bond, F and F' are force constants for interactions between non-bonded atoms, and H corresponds to the usual concept of angle deformation $(\Delta\alpha)$, while D corresponds to Heath and Linnett's angle based on overlap or orbitals $(\Delta\beta)$. In the GVFF, the force constant f_r is a stretching constant and the constant f_α is a bending constant. The bond interaction constant f_{rr} corresponds to an interaction of a bond with a bond at right angles to it, while $f_{rr'}$ corresponds to an interaction of a bond with an opposite bond. The angle interaction constant, $f_{\alpha\alpha}$, is the interaction of an angle with an angle adjacent and in the same plane while $f_{\alpha\alpha'}$ is an interaction of an angle with an angle in a perpendicular plane having a bond in common. The stretch–angle interaction constant $f_{r\alpha}$ corresponds to an interaction of an angle with one of the bonds forming its sides. The Δr_i and ΔR_{ij} terms relate to the internal coordinates as used by Kim et al. [1].

UBFF:

$$2V = K\sum_{i}^{6}(\Delta r_i)^2 + r_0^2 H\sum_{ij}^{12}(\Delta\alpha_{ij})^2 + F\sum_{ij}^{12}(\Delta R_{ij})^2 + 2R_0F'\sum_{ij}^{12}(\Delta R_{ij}) + 2r_0f'\sum_{i}^{6}(\Delta r_i) \quad (9)$$

OVFF:

$$2V = K\sum_{i}^{6}(\Delta r_i)^2 + r_0^2 D\sum_{i}^{6}(\Delta\beta_i)^2 + F\sum_{ij}^{12}(\Delta R_{ij})^2 + 2R_0F'\sum_{ij}^{12}(\Delta R_{ij}) + 2r_0f'\sum_{i}^{6}(\Delta r_i) \quad (10)$$

GVFF:

$$2V = f_r \sum_{i}^{6} (\Delta r_i)^2 + 2f_{rr} \sum_{ij}^{12} (\Delta r_i)(\Delta r_j) + 2f_{rr'} \sum_{ij}^{3} (\Delta r_i)(\Delta r_j) + r_0^2 f_\alpha \sum_{i}^{12} (\Delta\alpha_i)^2$$
$$+ 2r_0^2 f_{\alpha\alpha} \sum_{ij}^{12} (\Delta\alpha_i)(\Delta\alpha_j) + 2r_0^2 f_{\alpha\alpha'} \sum_{ij}^{24} (\Delta\alpha_i)(\Delta\alpha_j) + 2r_0 f_r \sum_{i}^{24} (\Delta r_i)(\Delta\alpha_j) \qquad (11)$$

The MUBFF includes the above UBFF terms and the modifications indicated on p. 260. The MOVFF includes the above OVFF terms and the modifications indicated on p. 261.

C. CALCULATIONS OF FORCE CONSTANTS

The calculations of force constants was one of adjustment until the calculated frequencies gave the best fit with the observed frequencies. The calculations were done on an IBM 360 computer using Schachtschneider's force constant adjust program [10]. The systems converged with about 5 perturbations for all force fields. A few of the fluorides were found to diverge or oscillate between two sets of force constants. When this occurred, the mean of both sets finally resulted in convergence. The logical sequence in the calculations for molecules of octahedral symmetry is [11,12]

(1) determine internal coordinates;

(2) choose orthonormal coordinates of O_h symmetry and form U, the matrix of coefficients;

(3) derive the f matrix of the force constants;

(4) form the F matrix corresponding to the potential energy function from U f U' where U' is the transpose of U (Table 1);

(5) form the G matrix corresponding to the kinetic energy using the methods of Wilson et al.[13], and others [14] (Table 1);

(6) set up the secular determinant,

$$GF - E\lambda = 0 \qquad (12)$$

where E is the unit matrix and

$$\lambda = 4\pi^2 c^2 \nu^2 \qquad (13)$$

where ν is the frequency in cm^{-1}.

The F and G matrices used appear in Table 1. Fortran programs FADJ and EIGV coded by Schachtschneider were used for the calculations. The final calculations gave the calculated frequencies, the converged force constants, the L matrix (transformation from symmetry coordinates to normal coordinates), and the potential energy distribution (PED) of force constants to frequencies. (To save space the L matrix and the PED matrix are not printed, but are available from the authors.)

If brief, the method includes a refinement in χ where

$$\chi = \delta\lambda' \cdot W\delta\lambda \qquad (14)$$

TABLE 1

F and *G* matrices obtained for UBFF, MUBFF, OVFF, MOVFF, and GVFF for AB_6 molecules

Mode	*G* matrix	*F* matrix				
		UBFF [1]	MUBFF ** [4,5]	OVFF [1]	MOVFF	GVFF
A_{1g}	$G_{11} = \mu_B$	$F_{11} = K + 4F$	$F_{11} = K + 4F + k$	$F_{11} = K + 4F$	$F_{11} = K + 4F + k$	$F_{11} = f_r + 5.33 f_{rr}$
E_g	$G_{22} = \mu_B$	$F_{22} = K + F + 3F'$	$F_{22} = K + 0.7F + k$	$F_{22} = K + F + 3F'$	$F_{22} = K + F + 3F' + k$	$F_{22} = f_r - 0.667 f_{rr}$
F_{1u}	$G_{33} = \mu_B(1+2\mu_A/\mu_B)$	$F_{33} = K + 2F + 2F'$	$F_{33} = K + 1.8F - k$	$F_{33} = K + 2F + 2F'$	$F_{33} = K + 2F + 2F' - k$	$F_{33} = f_r - 1.33 f_{rr}$
	$G_{34} = -4\mu_A$	$F_{34} = F + F'$	$F_{34} = 0.9F$	$F_{34} = F + F'$	$F_{34} = F + F'$	$F_{34} = 2f_{r\alpha}$
	$G_{44} = 2\mu_B(1+4\mu_A/\mu_B)$	$F_{44} = H + F/2 - 3/2F'$	$F_{44} = H + 0.65F + 2h$	$F_{44} = D/2 + F/2 - 3/2F'$	$F_{44} = D/2 + F/2 - 3/2F'$	$F_{44} = f_\alpha + 2f_{\alpha\alpha}$
F_{2g}	$G_{55} = 4\mu_B$	$F_{55} = H + 1/2F - 1/2F'$	$F_{55} = H + 0.55F$	$F_{55} = D/4 + F/2 - F'/2$	$F_{55} = D/4 + F/2 - F'/2$	$F_{55} = f_\alpha - 2f_{\alpha\alpha}$
	$G_{66} = 2\mu_B$	$F_{66} = H + 1/2F + 1/2F'$	$F_{66} = H + 0.45F - 2h$	$F_{66} = D/2 + F/2 + F'/2$	$F_{66} = D/2 + F/2 + F'/2$	$F_{66} = f_\alpha - 2f_{\alpha\alpha}$

** For MUBFF the assumption $F' = -(1/10)F$ was used.

TABLE 2

Observed and calculated frequencies and force constants for several MF_6 and MF_6^{n-} complexes[a]

Hexafluorides		Frequencies (cm^{-1})						Force constants (mdyne/A)					Ave. % deviation		Ref.
		$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	K f_r	F f_{rr}	$H(D)$ f_α	$k(F')$ $f_{\alpha\alpha}$	h $f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)	
SF_6	Obs.	773.5	641.7	939	614	525	(347)								20
	MUBFF	789	633	943	591	543	342	3.66	0.75	0.41	0.28	0.04	1.3	2.9	
	UBFF	801	612	959	581	536	349	3.70	0.87	0.31	−0.12		3.4	2.6	
	OVFF	814	603	960	605	503	354	3.59	0.95	0.60	−0.16		4.5	2.5	
	MOVFF	813	618	948	599	510	352	3.55	0.80	0.82	−0.24	0.63	3.2	2.4	
	GVFF	774	642	939	614	525	371	4.84	0.35	0.96	0.09	0.34	0.0		
SeF_6	Obs.	708	661	780	437	403	(262)								1
	MUBFF	713	657	780	423	420	258	4.40	0.26	0.35	0.24	0.05	0.5	3.0	
	UBFF	720	630	803	418	418	259	4.44	0.34	0.26	−0.11		3.1	3.0	
	OVFF	739	620	795	442	385	265	4.26	0.47	0.45	−0.14		4.1	2.2	
	MOVFF	739	635	779	448	381	264	4.35	0.38	0.56	−0.15	0.25	2.8	3.0	
	GVFF	708	661	780	437	403	285	4.97	0.12	0.55	0.05	0.19	0.0		
TeF_6	Obs.	701	674	752	325	313	(195)								20
	MUBFF	703	672	752	316	325	192	4.81	0.14	0.22	0.15	0.04	0.2	2.7	
	UBFF	706	656	767	315	324	193	4.90	0.17	0.17	−0.09		1.8	2.7	
	OVFF	727	645	758	327	306	196	4.62	0.32	0.20	−0.09		2.9	1.1	
	MOVFF	729	648	752	328	305	196	4.61	0.32	0.21	−0.10	0.06	2.6	1.3	
	GVFF	701	674	752	325	313	221	5.13	0.07	0.34	0.03	0.14	0.0		
$[PoF_6]$	Estd.	700	682	747	253	243	144								19
	MUBFF	700	682	747	242	255	142	5.15	0.08	0.14	−0.01	0.03	0.0	3.6	
	UBFF	706	677	747	242	255	142	5.25	0.08	0.11	−0.07		0.5	3.7	
	OVFF	718	669	743	254	241	144	5.07	0.18	0.14	−0.08		1.7	0.5	
	MOVFF	716	667	747	254	241	144	5.08	0.18	0.14	−0.08	−0.05	1.5	0.5	
	GVFF	700	682	747	253	243	172	5.23	0.05	0.22	0.03	−0.06	0.0		

TABLE 2 (continued)

MnF_6^{2-}; Solid Cs_2MnF_6														
	Obs.	610	488	620	334	290	(232)							7
	MUBFF	597	495	621	311	318	217	2.34	0.38	0.07	0.13	−0.01	1.2	7.7
	UBFF	592	486	635	311	318	215	2.31	0.40	0.07	−0.02		2.0	7.9
	OVFF	581	487	639	328	300	231	2.35	0.36	0.26	−0.02		2.7	1.9
	MOVFF	587	500	620	331	297	230	2.36	0.33	0.28	−0.02	0.16	2.1	1.4
	GVFF	610	488	620	334	290	205	2.83	0.25	0.30	0.03	0.07	0.0	
NiF_6^{2-}; Solid K_2NiF_6														
	Obs.	562	520	658	345	310	220**							18
	MUBFF	568	516	659	330	328	214	2.74	0.19	0.19	0.10	0.01	0.6	4.4
	UBFF	571	504	669	327	327	215	2.74	0.23	0.17	−0.04		2.0	4.3
	OVFF	583	498	663	349	299	222	2.65	0.28	0.32	−0.05		2.9	1.8
	MOVFF	583	503	658	351	297	221	2.66	0.27	0.34	−0.06	0.06	2.4	2.2
	GVFF	562	520	658	345	310	220	3.08	0.08	0.32	0.03	0.09	0.0	0.0
MoF_6	Obs.	741	643	741	262	312	(122)							20
	MUBFF	797	604	727	270	286	124	3.29	0.92	−0.28	0.14	0.03	5.2	4.2
	UBFF	795	594	773	270	280	124	3.43	0.91	−0.30	−0.13		5.1	5.0
	OVFF	756	619	756	262	308	122	3.97	0.61	−0.34	−0.10		2.6	0.5
	MOVFF	763	628	741	263	308	122	3.95	0.60	−0.34	−0.10	0.15	1.8	0.6
	GVFF	741	643	741	262	312	221	4.79	0.25	0.26	−0.01	0.06	0.0	
TcF_6	Obs.	712.9	639	748	275	297	(145)							20
	MUBFF	739	620	745	274	274	148	3.89	0.55	−0.09	0.01	0.02	2.4	4.3
	UBFF	739	618	748	274	272	148	3.99	0.53	−0.10	−0.08		2.3	4.7
	OVFF	734	621	750	266	293	145	4.06	0.49	−0.18	−0.08		2.0	0.7
	MOVFF	735	623	748	266	293	145	4.05	0.49	−0.18	−0.08	0.02	1.9	0.7
	GVFF	713	639	748	265	297	210	4.69	0.19	0.25	0.00	0.01	0.0	
RuF_6	Obs.	675	624	735	275	283	(186)							20
	MUBFF	674	625	735	273	287	185	4.17	0.22	0.11	0.04	0.01	0.1	1.0
	UBFF	674	621	740	273	287	185	4.20	0.22	0.10	−0.04		0.4	0.0
	OVFF	693	612	731	276	279	187	3.97	0.35	0.08	−0.04		1.7	0.7
	MOVFF	692	610	735	276	279	189	3.98	0.35	0.08	−0.04	−0.03	1.6	0.6
	GVFF	675	624	735	275	283	200	4.44	0.12	0.25	0.01	−0.01	0.0	

TABLE 2 (continued)

RhF_6	Obs.	634	592	724	283	269	(189)							20
	MUBFF	633	593	724	271	285	183	3.94	0.17	0.13	−0.13	0.01	0.1	4.4
	UBFF	637	598	713	270	285	183	3.98	0.14	0.14	−0.04		1.0	4.5
	OVFF	652	590	706	285	265	190	3.80	0.24	0.21	−0.05		1.9	0.9
	MOVFF	647	582	724	284	266	190	3.84	0.25	0.20	−0.05	−0.17	1.3	0.6
	GVFF	634	592	724	283	269	190	3.98	0.10	0.27	0.03	−0.11	0.0	
$[PdF_6]$	Estd.	590	525	711	280	258	191							19
	MUBFF	585	528	711	261	279	182	3.44	0.21	0.10	−0.47	0.01	0.5	6.6
	UBFF	592	552	656	262	279	181	3.38	0.14	0.13	−0.03		4.4	6.6
	OVFF	601	547	653	283	255	191	3.30	0.18	0.27	−0.05		4.7	0.8
	MOVFF	588	526	711	280	258	191	3.47	0.21	0.23	−0.04	−0.46	0.2	0.1
	GVFF	590	525	711	280	258	182	3.17	0.14	0.34	0.08	−0.27	0.0	
WF_6	Obs.	771	677	711	258	320	(127)							20
	MUBFF	820	642	700	265	300	128	3.59	0.89	−0.24	0.40	0.04	4.4	3.3
	UBFF	809	616	735	266	292	129	3.79	0.88	−0.28	−0.14		5.8	4.5
	OVFF	777	641	741	258	317	127	4.32	0.61	−0.32	−0.11		3.4	0.4
	MOVFF	793	662	711	259	316	127	4.28	0.60	−0.31	−0.11	0.36	1.7	0.6
	GVFF	771	676	713	258	320	226	5.29	0.26	0.32	0.02	0.34	0.1	
ReF_6	Obs.	753.7	671	715	257	295	(147)							20
	MUBFF	773	657	713	262	284	148	4.18	0.56	−0.09	0.26	0.02	1.7	2.3
	UBFF	767	639	735	262	281	149	4.28	0.57	−0.11	−0.10		3.1	2.7
	OVFF	753	648	738	257	294	147	4.49	0.47	−0.14	−0.09		2.3	0.2
	MOVFF	765	663	715	257	293	147	4.45	0.46	−0.13	−0.09	0.27	0.9	0.3
	GVFF	754	671	715	257	295	209	5.18	0.22	0.26	0.01	0.14	0.0	
OsF_6	Obs.	730.7	668	720	268	276	(205)							20
	MUBFF	721	676	720	254	296	197	4.75	0.21	0.13	0.20	0.00	0.8	5.5
	UBFF	716	662	738	254	296	196	4.75	0.25	0.11	−0.03		1.8	5.6
	OVFF	721	659	737	268	277	205	4.68	0.28	0.22	−0.04		1.7	0.2
	MOVFF	729	669	720	268	276	205	4.65	0.28	0.23	−0.04	0.19	0.1	0.1
	GVFF	731	668	720	268	276	195	5.10	0.16	0.26	0.02	0.06	0.0	

TABLE 2 (continued)

IrF_6	Obs.	701	645	719	276	258	(206)								20
	MUBFF	690	653	719	247	287	190	4.62	0.17	0.14	0.03	0.01	0.9	9.8	
	UBFF	690	651	722	248	287	190	4.65	0.17	0.13	−0.03		1.0	9.8	
	OVFF	690	650	723	275	260	206	4.69	0.16	0.36	−0.04		1.0	0.4	
	MOVFF	692	652	719	275	259	206	4.68	0.16	0.36	−0.04	0.04	0.8	0.3	
	GVFF	701	645	719	276	258	182	4.75	0.14	0.27	0.04	−0.12	0.0		
PtF_6	Obs.	656.4	601	705	273	242	(211)								20
	MUBFF	645	610	705	232	275	186	4.25	0.15	0.13	−0.20	0.00	1.1	13.4	
	UBFF	650	620	685	233	275	186	4.22	0.13	0.14	−0.02		2.3	13.4	
	OVFF	644	622	689	272	244	210	4.35	0.07	0.46	−0.03		2.5	0.5	
	MOVFF	638	615	705	271	245	210	4.40	0.08	0.45	−0.03	−0.16	1.7	0.7	
	GVFF	656	601	705	273	242	171	4.13	0.13	0.31	0.07	−0.28	0.0		
PtF_6^{2-} *; Solid K_2PtF_6															
	Obs.	600	576	571	281	210	149 **								18
	MUBFF	598	578	573	222	237	138	3.32	0.08	0.11	0.37	0.02	0.3	13.7	
	UBFF	587	542	606	222	237	138	3.30	0.14	0.06	−0.05		4.7	13.7	
	OVFF	566	547	618	269	216	148	3.67	−0.02	0.37	−0.10		6.4	2.5	
	MOVFF	587	588	573	274	213	148	3.62	−0.14	0.52	−0.13	0.58	1.6	1.3	
	GVFF	603	556	589	281	210	149	3.53	0.10	0.25	0.06	0.22	2.3	0.0	
UF_6	Obs.	667	535	624	186	201	(140)								20
	MUBFF	630	553	627	178	214	135	3.28	0.31	−0.04	−0.07	0.00	3.2	4.8	
	UBFF	630	558	620	179	214	135	3.27	0.29	−0.03	−0.03		3.5	4.8	
	OVFF	612	565	620	185	205	139	3.45	0.19	0.05	−0.02		4.8	1.1	
	MOVFF	610	562	624	185	205	139	3.46	0.19	0.05	−0.02	−0.04	4.6	1.1	
	GVFF	667	535	624	186	201	142	3.40	0.30	0.22	0.05	−0.32	0.0		
NpF_6	Obs.	648	528	624	199	208	(165)								1
	MUBFF	611	547	627	184	228	154	3.30	0.25	0.01	−0.13	−0.01	3.3	7.9	
	UBFF	612	556	612	186	228	153	3.27	0.23	0.02	−0.02		4.2	7.9	
	OVFF	601	560	613	198	213	164	3.37	0.17	0.14	−0.01		5.0	1.2	
	MOVFF	596	554	624	198	213	164	3.41	0.17	0.14	−0.01	−0.10	4.3	1.2	
	GVFF	648	528	624	199	208	147	3.29	0.26	0.24	0.06	−0.03	0.0		

TABLE 2 (continued)

PuF_6	Obs.	628	523	616	206	211	(173)							20
	MUBFF	597	540	618	188	234	159	3.25	0.22	0.03	−0.13	−0.01	2.9	9.0
	UBFF	598	550	603	190	233	158	3.22	0.20	0.05	−0.01		4.0	9.0
	OVFF	591	552	603	205	215	172	3.29	0.15	0.19	−0.01		4.5	1.1
	MOVFF	586	546	616	205	215	172	3.33	0.16	0.18	−0.01	−0.01	3.7	1.2
	GVFF	628	523	616	206	211	149	3.21	0.23	0.25	0.06	−0.31	0.0	
SiF_6^{2-}; Solid $(NH_4)_2SiF_6$; Raman spectra for aqueous solution														
	Obs.	655	474	740	458	395	279 **							21
	MUBFF	654	474	740	447	410	274	2.07	0.69	0.09	−0.03	−0.01	0.1	2.7
	UBFF	651	479	735	449	410	273	2.06	0.67	0.11	−0.05		0.8	2.7
	OVFF	654	477	736	461	394	279	2.03	0.69	0.24	−0.06		0.4	0.3
	MOVFF	655	474	740	458	395	279	2.02	0.71	0.22	−0.06	−0.05	0.0	0.0
	GVFF	655	474	740	458	395	279	2.77	0.38	0.56	0.06	0.18	0.0	0.0
GeF_6^{2-}; H_2GeF_6 solution for Raman and $(NH_4)_2GeF_6$, solid for IR														
	Obs.	627	454	600	350	318	225 **							22
	MUBFF	606	462	602	333	341	216	2.08	0.52	0.04	−0.06	0.01	1.8	5.4
	UBFF	609	465	596	336	341	215	2.10	0.51	0.04	−0.07		2.0	5.2
	OVFF	597	466	598	347	328	223	2.17	0.46	0.16	−0.06		2.6	1.7
	MOVFF	597	465	600	347	328	223	2.17	0.46	0.16	−0.06	−0.02	2.4	1.7
	GVFF	627	454	600	350	318	225	2.53	0.35	0.40	0.06	−0.03	0.0	0.0
SnF_6^{2-}; Solid $(Et_4N)_2SnF_6$														
	Obs.	585	470	556	300	241	170 **							38
	MUBFF	559	483	558	261	269	159	2.36	0.27	0.05	0.06	0.02	2.5	10.3
	UBFF	562	474	566	263	269	159	2.42	0.28	0.03	−0.06		2.2	10.2
	OVFF	539	478	575	290	252	169	2.64	0.15	0.25	−0.08		4.3	2.9
	MOVFF	545	490	556	292	250	169	2.65	0.13	0.28	−0.08	−0.16	3.7	2.5
	GVFF	585	470	556	300	241	170	2.62	0.23	0.27	0.06	−0.05	0.0	0.0
NbF_6^-; Solid $CsNbF_6$														
	Obs.	683	562	602	244	280	198 **							23
	MUBFF	675	567	603	242	285	196	2.83	0.46	−0.02	0.44	−0.02	0.7	1.1
	UBFF	653	531	645	241	288	195	2.69	0.52	−0.04	−0.02		5.7	1.9
	OVFF	639	535	646	242	285	198	2.80	0.44	0.00	−0.01		6.1	0.9
	MOVFF	666	571	602	244	283	197	2.82	0.42	0.02	−0.01	0.44	1.4	0.5
	GVFF	684	561	605	244	280	198	3.70	0.29	0.26	0.02	0.32	0.3	0.0

TABLE 2 (continued)

TaF_6^- ; Solid $CsTaF_6$														
	Obs.	692	581	560	240	272	(192)							24
	MUBFF	673	592	561	235	283	188	3.05	0.35	0.03	0.62	−0.00	1.6	2.8
	UBFF	636	537	615	234	284	187	2.92	0.40	0.01	−0.03		8.5	3.1
	OVFF	630	539	614	239	277	192	2.97	0.37	0.07	−0.03		8.6	0.9
	MOVFF	673	592	560	239	275	191	3.03	0.35	0.09	−0.03	0.63	1.6	0.6
	GVFF gave unreasonable eigenvalues													
PF_6^- ; Solid KPF_6 for ν_3 and ν_4, aqueous solution ν_1, ν_2, ν_5														
	Obs.	735	563	830	550	462	(317)							17
	MUBFF	741	560	830	531	482	311	2.82	0.80	0.21	0.14	0.01	0.4	3.2
	UBFF	746	550	841	526	480	313	2.81	0.85	0.17	−0.09		1.7	3.1
	OVFF	751	546	843	542	458	320	2.77	0.89	0.37	−0.11		2.3	1.0
	MOVFF	744	559	832	546	460	318	2.78	0.72	0.58	−0.17	0.51	0.7	0.5
	GVFF	735	563	830	550	462	327	3.82	0.42	0.77	0.09	0.28	0.0	
AsF_6^-; Solid $[(AsCl_4)(AsF_6)]$														
	Obs.	682	583	706	396	372	263 **							25
	MUBFF	680	584	706	382	391	256	3.38	0.41	0.20	0.15	0.01	0.2	3.8
	UBFF	680	571	721	381	391	257	3.38	0.45	0.17	−0.06		1.5	3.8
	OVFF	692	567	717	396	367	264	3.28	0.52	0.32	−0.07		2.0	0.6
	MOVFF	696	574	706	398	366	264	3.29	0.50	0.35	−0.07	0.11	1.2	0.9
	GVFF	682	583	706	396	372	263	3.96	0.23	0.46	0.04	0.08	0.0	0.0

[a] All spectroscopic data measured on gases except where indicated.
( ) Values obtained from overtones, combination bands or site splitting.
[ ] Theoretical molecule.
** Calculated from equation $\nu_6 = \nu_5/\sqrt{2}$.
* Oscillated slightly.

TABLE 3

Observed and calculated frequencies and force constants for several MCl_6^{n-} complexes

Hexachlorides	Frequencies (cm^{-1})						Force constants (mdyne/A)					Ave. % deviation		Ref.
	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	K f_r	F f_{rr}	$H(D)$ f_α	$k(F')$ $f_{\alpha\alpha}$	h $f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)	
$TiCl_6^{2-}$; $(Et_4N)_2TiCl_6$ (aq. solution)														
Obs.	331	284	330	193	194	(142)								27
MUBFF	331	284	330	193	194	142	1.13	0.18	0.10	0.42	−0.02	0.0	0.0	
UBFF	332	246	354	189	198	143	0.87	0.36	0.03	0.01		7.1	1.6	
OVFF	335	245	353	190	193	145	0.86	0.37	0.06	0.01		7.3	1.3	
MOVFF	346	274	330	194	186	144	0.98	0.32	0.10	0.01	0.24	2.7	2.0	
GVFF	331	284	330	193	194	137	1.75	0.10	0.29	0.05	0.34	0.0		
$ZrCl_6^{2-}$; Solid $(Et_4N)_2ZrCl_6$														
Obs.	321	250	293	152	151	107 **								3
MUBFF	316	252	294	150	155	105	1.00	0.23	0.00	0.17	−0.01	0.8	1.9	
UBFF	310	235	312	149	157	105	0.93	0.27	−0.01	−0.01		5.3	2.8	
OVFF	303	237	313	150	156	107	0.96	0.24	0.01	−0.01		6.0	1.5	
MOVFF	313	254	293	152	153	107	0.99	0.22	0.03	−0.01	−0.16	1.4	0.7	
GVFF	321	250	293	152	151	107	1.40	0.14	0.24	0.06	0.28	0.0	0.0	
$HfCl_6^{2-}$; Solid $(Et_4N)_2HfCl_6$														
Obs.	326	257	275	145	156	(80)								3,27,
MUBFF	332	254	274	146	153	80	0.96	0.29	−0.04	0.19	0.01	1.0	1.1	19
UBFF	322	233	296	147	150	81	0.99	0.29	−0.05	−0.05		6.0	2.0	
OVFF	314	237	297	144	157	80	1.05	0.25	−0.07	−0.04		6.4	0.4	
MOVFF	327	257	275	145	156	80	1.07	0.24	−0.06	−0.04	0.20	0.1	0.1	
GVFF	326	257	275	145	156	110	1.47	0.14	0.17	0.02	0.17	0.0		

TABLE 3 (continued)

$HfCl_6^{2-}$; Aq. solution; $(NH_4)_2HfCl_6$														
	Obs.	333	237	288	145	157	(80)							27
	MUBFF	333	237	288	145	157	80	0.86	0.35	−0.06	0.07	0.01	1.0	0.0
	UBFF	333	230	297	146	154	81	0.93	0.35	−0.08	−0.06		2.1	1.1
	OVFF	317	236	297	144	160	80	1.03	0.27	−0.09	−0.05		2.7	0.9
	MOVFF	321	241	288	144	160	80	1.02	0.27	−0.09	−0.05	0.06	1.9	0.9
	GVFF	333	237	288	145	156	111	1.30	0.19	0.28	0.08	0.26	0.0	
$NbCl_6^-$; Solid $(Et_4N)NbCl_6$														
	Obs.	367	288	333	162	179	(126)							3
	MUBFF	367	288	333	162	179	126	1.28	0.33	−0.01	0.22	−0.02	0.0	0.0
	UBFF	358	270	355	160	182	125	1.17	0.37	−0.02	−0.01		5.2	1.1
	OVFF	352	271	355	161	182	126	1.20	0.35	−0.01	−0.01		5.6	0.9
	MOVFF	363	290	333	162	180	126	1.24	0.33	0.01	−0.01	0.21	0.5	0.3
	GVFF	367	288	333	162	179	126	1.85	0.18	0.30	0.07	0.36	0.0	
$TaCl_6^-$; Solid $(Et_4N)TaCl_6$														
	Obs.	378	298	318	156	179	(119)							3
	MUBFF	376	299	318	156	181	119	1.38	0.33	−0.01	0.25	−0.01	0.4	0.5
	UBFF	362	278	343	155	181	119	1.34	0.35	−0.02	−0.02		6.2	0.7
	OVFF	358	280	343	155	181	119	1.37	0.33	−0.01	−0.02		6.4	0.6
	MOVFF	373	301	318	156	180	119	1.39	0.32	0.00	−0.02	0.25	0.8	0.4
	GVFF	378	298	318	156	179	126	1.98	0.19	0.20	0.02	0.21	0.0	
$InCl_6^{3-}$; Solid $[Co(NH_3)_6]InCl_6$														
	Obs.	277	193	250	157	149	105 **							30
	MUBFF	269	196	251	152	157	102	0.63	0.21	0.01	0.02	0.00	1.6	3.9
	UBFF	268	193	255	153	157	101	0.63	0.22	0.01	−0.02		1.8	3.9
	OVFF	265	194	255	156	153	104	0.64	0.21	0.04	−0.02		2.3	1.5
	MOVFF	267	197	250	156	153	104	0.63	0.20	0.04	−0.02	0.03	2.0	1.4
	GVFF	277	193	250	157	149	105	0.87	0.14	0.14	0.01	0.01	0.0	0.0

TABLE 3 (continued)

$TlCl_6^{2-}$; Solid $[Co(NH_3)_6]TlCl_6$														
	Obs.	264	192	230	146	135	95 **							30
	MUBFF	252	197	231	137	146	91	0.67	0.16	0.03	0.03	0.01	2.5	6.5
	UBFF	252	192	237	138	146	90	0.69	0.16	0.02	−0.03		3.5	6.2
	OVFF	248	193	237	144	140	94	0.71	0.14	0.07	−0.03		3.1	2.0
	MOVFF	251	197	230	144	140	94	0.71	0.14	0.07	−0.03	0.04	2.5	1.8
	GVFF	264	192	230	146	135	95	0.85	0.11	0.20	0.05	0.15	0.0	0.0
$GeCl_6^{2-}$; Solid Cs_2GeCl_6														
	Obs.	309	211	310	213	198	140 **							26
	MUBFF	307	212	310	210	204	138	0.74	0.31	0.05	−0.03	−0.01	0.3	2.0
	UBFF	306	215	304	212	204	137	0.73	0.31	0.05	−0.02		1.6	2.0
	OVFF	311	215	303	215	196	140	0.70	0.33	0.10	−0.02		1.5	0.6
	MOVFF	310	211	310	213	197	140	0.70	0.34	0.09	−0.02	−0.05	0.2	0.2
	GVFF	309	211	310	213	198	140	1.05	0.18	0.26	0.03	0.07	0.0	0.0
$SnCl_6^{2-}$; Aq. solution														
	Obs.	310	235	303	166	158	112 **							38
	MUBFF	304	238	304	161	166	109	1.01	0.23	0.02	0.01	−0.00	1.1	3.6
	UBFF	304	237	305	162	166	109	1.00	0.23	0.02	−0.02		1.2	3.6
	OVFF	301	237	306	165	161	112	1.01	0.22	0.06	−0.02		1.5	1.0
	MOVFF	302	238	303	165	161	111	1.01	0.22	0.06	−0.02	−0.02	1.3	0.9
	GVFF	310	235	303	166	158	112	1.25	0.14	0.16	0.01	0.00	0.0	0.0
$PbCl_6^{2-}$; Solid, frequencies average for M_2PbCl_6 where M = Me_4N^+, n-Bu_4N^+, $AsPh_4^+$, IPh_2^+														
	Obs.	281	206	258	137	141	(76)							31
	MUBFF	279	207	258	136	142	76	0.74	0.22	−0.02	−0.01	0.01	0.3	0.5
	UBFF	276	208	258	137	143	76	0.83	0.19	−0.03	−0.04		1.0	0.6
	OVFF	282	206	258	137	140	76	0.79	0.22	−0.03	−0.04		0.2	0.3
	MOVFF	276	208	258	137	143	76	0.83	0.19	−0.03	−0.04	0.00	1.0	0.6
	GVFF	281	206	258	137	141	100	0.97	0.13	0.14	0.02	−0.04	0.0	

TABLE 3 (continued)

PCl_6^-; ν_1 and ν_5 solution; others solid														
	Obs.	378	275	444	285	238	168 **							26
	MUBFF	382	273	444	278	245	165	1.07	0.45	0.07	0.17	−0.01	0.6	2.4
	UBFF	384	267	452	276	245	167	1.03	0.51	0.05	−0.02		2.1	2.2
	OVFF	385	266	451	280	238	170	1.02	0.52	0.10	−0.02		2.3	1.0
	MOVFF	380	274	444	284	237	168	1.00	0.43	0.21	−0.05	0.29	0.3	0.2
	GVFF	378	275	444	285	238	168	1.73	0.23	0.35	0.03	0.19	0.0	0.0
PCl_6^-; $pyHPCl_6$(CH_3CN solution)														
	Obs.	378	262	454	284	238	170 **							19
	MUBFF	380	261	454	278	246	167	1.04	0.48	0.05	0.05	−0.01	0.2	2.4
	UBFF	378	262	454	279	247	167	1.02	0.49	0.06	−0.02		0.1	2.3
	OVFF	379	261	454	284	238	170	1.00	0.50	0.13	−0.02		0.2	0.1
	MOVFF	379	262	454	284	237	170	1.00	0.50	0.13	−0.03	−0.01	0.1	0.1
	GVFF	378	262	454	284	238	170	1.61	0.26	0.39	0.05	0.20	0.0	0.0
$AsCl_6^-$; Solid $(Et_4N)AsCl_6$														
	Obs.	337	289	333	220	202	143 **							26
	MUBFF	340	287	333	215	209	141	1.26	0.21	0.11	0.32	0.00	0.5	2.5
	UBFF	339	257	356	211	209	143	1.10	0.33	0.06	−0.02		5.9	2.6
	OVFF	343	256	354	216	200	145	1.07	0.35	0.11	−0.02		6.2	1.5
	MOVFF	350	281	333	223	194	144	1.18	0.28	0.18	−0.02	0.25	2.2	2.1
	GVFF	337	289	333	220	202	143	1.81	0.10	0.33	0.06	0.33	0.0	0.0
$SbCl_6^-$; Solid $TlSbCl_6$														
	Obs.	333	285	349	180	176	124 **							32
	MUBFF	332	286	349	177	182	122	1.50	0.18	0.07	0.08	0.00	0.2	2.2
	UBFF	332	279	357	176	182	122	1.47	0.21	0.06	−0.02		1.5	2.3
	OVFF	339	277	354	180	174	125	1.41	0.25	0.10	−0.02		2.0	0.7
	MOVFF	341	280	349	181	173	125	1.41	0.24	0.10	−0.02	0.04	1.3	0.9
	GVFF	333	385	349	180	176	124	1.76	0.10	0.18	0.01	0.05	0.0	0.0

TABLE 3 (continued)

$SbCl_6^-$; CH_3CN solution; $[AsCl_4][SbCl_6]$														
	Obs.	329	280	348	182	170	120 **							26
	MUBFF	328	281	348	176	178	117	1.46	0.18	0.07	0.06	0.00	0.2	3.4
	UBFF	328	276	354	176	178	117	1.46	0.20	0.06	−0.20		1.2	3.4
	OVFF	332	274	353	182	169	120	1.42	0.22	0.11	−0.02		1.4	0.3
	MOVFF	333	277	348	183	168	120	1.43	0.21	0.11	−0.03	−0.04	0.8	0.5
	GVFF	329	280	348	182	170	120	1.71	0.10	0.18	0.01	0.03	0.0	0.0
$SeCl_6^{2-}$; Solid Rb_2SeCl_6														
	Obs.	290	248	280	159	164	117 **							28
	MUBFF	290	248	280	159	164	117	0.96	0.14	0.06	0.23	−0.01	0.0	0.2
	UBFF	289	223	299	156	166	117	0.80	0.23	0.03	0.00		5.9	1.1
	OVFF	293	222	298	158	162	119	0.78	0.25	0.04	0.00		6.0	1.0
	MOVFF	301	241	280	160	159	118	0.83	0.23	0.06	0.00	0.15	2.3	1.6
	GVFF	290	248	280	159	164	116	1.34	0.08	0.17	0.01	0.18	0.0	0.0
$TeCl_6^{2-}$; Solid Cs_2TeCl_6														
	Obs.	289	247	260	150	139	98 **							28,37
	MUBFF	286	249	260	145	146	95	0.99	0.13	0.04	0.21	0.00	0.5	3.8
	UBFF	279	222	283	143	147	95	0.90	0.18	0.01	−0.02		7.5	4.4
	OVFF	276	222	283	147	142	98	0.91	0.17	0.05	−0.02		7.8	1.7
	MOVFF	290	246	260	150	139	98	0.97	0.14	0.08	−0.02	0.21	0.2	0.1
	GVFF	290	242	265	150	139	98	1.28	0.09	0.14	0.02	0.15	1.5	0.0
$PdCl_6^{2-}$; Solid K_2PdCl_6														
	Obs.	317	292	358	175	164	116 **							29
	MUBFF	319	291	358	170	171	114	1.57	0.11	0.09	0.12	0.00	0.3	3.0
	UBFF	319	281	368	169	170	114	1.54	0.15	0.07	−0.02		2.5	2.9
	OVFF	328	278	364	176	160	117	1.47	0.19	0.11	−0.02		3.3	1.2
	MOVFF	329	282	358	177	159	117	1.47	0.18	0.12	−0.02	0.06	2.5	1.6
	GVFF	317	292	358	175	164	116	1.82	0.05	0.16	0.01	0.08	0.0	0.0

TABLE 3 (continued)

WCl_6; Solid WCl_6														
	Obs.	410	315	364	158	164	(97)							3,32
	MUBFF	402	319	365	156	168	96	1.71	0.38	−0.06	0.14	0.01	1.2	1.4
	UBFF	397	308	379	156	167	96	1.73	0.39	−0.07	−0.05		3.2	1.3
	OVFF	380	314	381	157	168	97	1.89	0.29	−0.05	−0.04		4.2	1.3
	MOVFF	388	325	364	157	167	97	1.88	0.27	−0.04	−0.04	0.17	2.9	1.1
	GVFF	410	315	364	158	164	116	2.23	0.24	0.16	0.01	−0.01	0.0	
$ReCl_6^{2-}$; ν_1,ν_2,ν_5 solution of H_2ReCl_6; ν_3,ν_4 solid														
	Obs.	346	275	313	172	159	112 **							29
	MUBFF	335	280	314	162	171	108	1.37	0.21	0.04	0.12	0.01	1.8	5.7
	UBFF	332	269	328	163	171	107	1.38	0.23	0.02	−0.03		3.7	5.8
	OVFF	326	270	329	169	164	112	1.42	0.20	0.09	−0.03		4.2	1.6
	MOVFF	333	281	313	171	162	111	1.42	0.19	0.11	−0.03	0.14	2.0	1.1
	GVFF	346	275	313	172	159	112	1.68	0.15	0.17	0.02	0.03	0.0	0.0
$OsCl_6^{2-}$; Solid K_2OsCl_6														
	Obs.	345	274	314	177	165	117 **							29
	MUBFF	335	279	315	167	177	112	1.36	0.22	0.04	0.11	0.01	1.7	5.7
	UBFF	332	269	327	168	177	112	1.37	0.23	0.03	−0.03		3.3	5.7
	OVFF	328	269	328	175	169	117	1.40	0.22	0.11	−0.03		3.7	1.4
	MOVFF	335	279	314	176	168	116	1.40	0.20	0.12	−0.04	0.13	1.6	1.0
	GVFF	345	274	314	177	165	117	1.67	0.15	0.18	0.02	0.02	0.0	0.0
$IrCl_6^{2-}$; Solid K_2IrCl_6														
	Obs.	352	225	335	168	190	135 **							29
	MUBFF	341	228	338	164	199	132	1.01	0.41	−0.02	−0.21	−0.01	1.7	3.1
	UBFF	350	236	308	164	202	129	0.86	0.43	−0.02	−0.04		4.6	4.3
	OVFF	340	239	305	167	200	133	0.90	0.38	0.02	−0.03		6.3	2.5
	MOVFF	332	230	336	167	197	133	1.02	0.37	0.02	−0.02	0.22	2.8	1.9
	GVFF	352	225	355	168	190	135	1.23	0.26	0.46	0.14	0.29	0.0	0.0

TABLE 3 (continued)

$PtCl_6^{2-}$; Solid K_2PtCl_6														
	Obs.	344	320	345	183	162	(78)							29
	MUBFF	345	320	345	180	165	78	1.86	0.11	0.08	0.19	0.03	0.1	1.3
	UBFF	347	295	364	179	164	78	1.89	0.15	0.02	−0.08		4.8	1.3
	OVFF	350	294	363	182	161	78	1.87	0.17	0.04	−0.08		5.1	0.6
	MOVFF	356	310	345	186	157	78	1.93	0.12	0.10	−0.09	0.23	2.2	1.6
	GVFF	344	318	347	183	162	115	2.15	0.06	0.22	0.04	0.22	0.4	
$CeCl_6^{2-}$; Solid $(Ph_2I)_2CeCl_6$														
	Obs.	295	265	268	117	120	86 **							33
	MUBFF	293	266	268	115	123	84	1.16	0.10	0.03	0.26	0.00	0.4	1.7
	UBFF	283	236	293	114	125	83	1.02	0.16	−0.01	−0.01		7.7	2.8
	OVFF	279	237	294	116	122	85	1.05	0.14	0.02	−0.01		8.5	1.1
	MOVFF	297	263	268	117	120	86	1.11	0.13	0.03	−0.01	0.24	0.5	0.2
	GVFF	gave unreasonable eigenvalues												
UCl_6^{2-}; CH_3CN solution														
	Obs.	299	237	262	114	121	(80)							35
	MUBFF	290	241	263	111	126	79	1.00	0.17	−0.01	0.10	0.00	1.7	2.7
	UBFF	285	232	275	112	126	79	1.00	0.17	−0.01	−0.02		4.0	2.7
	OVFF	278	234	276	113	124	80	1.05	0.14	0.01	−0.02		4.5	1.2
	MOVFF	285	244	262	113	123	80	1.04	0.14	0.01	−0.02	0.11	2.5	1.0
	GVFF	299	237	262	114	121	85	1.25	0.12	0.08	0.01	0.01	0.0	

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

( ) Values obtained from site splitting, overtones or combinations.

TABLE 4

Observed and calculated frequencies and force constants for several MBr_6^{n-} complexes

Hexabromides	Frequencies (cm^{-1})						Force constants (mdyne/A)					Ave. % deviation		Ref.
	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	K f_r	F f_{rr}	$H(D)$ f_α	$k(F')$ $f_{\alpha\alpha}$	h $f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)	
$TiBr_6^{2-}$; Solid $(Et_4N)_2TiBr_6$														26a,
Obs.	192	141	244	119	115	82 **								31
MUBFF	192	141	244	120	112	83	0.66	0.24	0.01	0.10	−0.02	0.1	1.5	
UBFF	193	140	244	119	114	83	0.61	0.29	0.01	0.01		0.4	0.7	
OVFF	196	140	243	120	113	82	0.61	0.30	0.01	0.01		1.0	1.0	
MOVFF	196	140	244	119	113	82	0.60	0.30	0.01	0.01	−0.01	1.0	0.8	
GVFF	192	141	244	119	116	82	1.02	0.13	0.32	0.08	0.28	0.1	0.0	
$ZrBr_6^{2-}$; Solid $[Et_4N]_2ZrBr_6$														
Obs.	194	144	223	106	99	69 **								3
MUBFF	194	144	223	106	100	69	0.70	0.24	−0.01	0.02	−0.01	0.1	0.3	
UBFF	193	145	222	106	100	69	0.76	0.25	−0.01	−0.01		0.4	0.7	
OVFF	190	145	224	106	100	69	0.77	0.23	−0.01	−0.01		1.0	0.7	
MOVFF	191	145	223	106	100	69	0.77	0.23	0.00	−0.01	0.01	0.9	0.6	
GVFF	194	144	223	106	98	69	1.06	0.13	0.31	0.10	0.30	0.0	0.0	
$HfBr_6^{2-}$; Solid $(Et_2NH_2)_2HfBr_6$														
Obs.	201	157	193	112	116	82 **								34
MUBFF	201	157	193	112	116	82	0.88	0.23	0.03	0.13	−0.01	0.0	0.1	
UBFF	199	150	202	111	117	82	0.79	0.27	0.03	0.00		3.3	0.8	
OVFF	202	149	201	112	115	83	0.77	0.29	0.04	0.00		3.2	0.7	
MOVFF	205	155	193	112	114	82	0.79	0.27	0.05	−0.01	0.09	1.1	0.8	
GVFF	201	157	193	112	116	82	1.24	0.12	0.28	0.06	0.27	0.0	0.0	

TABLE 4 (continued)

$ReBr_6^{2-}$; ν_1, ν_2, ν_5 H_2ReBr_6 solution; ν_3, ν_4 (solid)														
	Obs.	213	174	217	118	104	74 **							36
	MUBFF	211	175	217	114	109	72	1.16	0.20	0.03	0.14	0.00	0.5	3.9	
	UBFF	211	166	227	113	110	82	1.12	0.24	0.01	−0.02		3.3	4.2	
	OVFF	207	166	228	116	107	74	1.14	0.22	0.05	−0.02		4.0	1.6	
	MOVFF	211	175	217	118	105	74	1.16	0.20	0.08	−0.02	0.14	0.5	0.3	
	GVFF	213	174	217	118	104	74	1.50	0.12	0.15	0.01	0.08	0.0	0.0	
$PtBr_6^{2-}$; ν_1, ν_2, ν_5 solution Na_2PtBr_6 in HBr; ν_3, ν_4 solid														6,33
	Obs.	207	190	244	90	97	69 **							
	MUBFF	207	190	244	91	96	70	1.54	0.10	0.05	0.10	−0.01	0.0	0.9	
	UBFF	208	186	248	90	96	70	1.47	0.14	0.04	0.01		1.4	0.7	
	OVFF	215	184	243	90	95	70	1.38	0.20	0.02	0.00		2.6	1.2	
	MOVFF	215	183	244	90	95	69	1.38	0.20	0.02	0.00	−0.01	2.5	1.2	
	GVFF	207	190	244	90	97	69	1.73	0.05	0.11	0.00	0.06	0.0	0.0	
$PdBr_6^{2-}$ *; Solid K_2PdBr_6														
	Obs.	198	176	253	130	100	71 **							29
	MUBFF	202	173	253	121	107	68	1.16	0.15	0.05	0.14	0.01	1.3	5.9	
	UBFF	203	165	262	120	107	69	1.14	0.20	0.02	−0.02		4.2	5.4	
	OVFF	201	164	265	124	103	72	1.14	0.19	0.08	−0.02		4.3	2.6	
	MOVFF	200	174	255	125	102	71	1.16	0.11	0.18	−0.05	0.31	0.9	3.3	
	GVFF	198	176	253	130	100	71	1.50	0.06	0.15	0.02	0.09	0.0	0.0	
$SnBr_6^{2-}$; Solid $(Et_4N)_2SnBr_6$														
	Obs.	185	136	215	114	103	73 **							38
	MUBFF	184	136	215	113	106	72	0.76	0.22	0.01	−0.04	−0.01	0.2	1.7	
	UBFF	184	140	213	115	105	70	0.77	0.20	0.02	−0.02		1.7	2.4	
	OVFF	184	140	212	116	102	71	0.76	0.21	0.05	−0.02		1.7	1.7	
	MOVFF	184	137	215	114	104	73	0.74	0.23	0.03	−0.01	−0.05	0.4	0.3	
	GVFF	185	136	215	114	103	73	0.95	0.12	0.15	0.01	0.03	0.0	0.0	

TABLE 4 (continued)

$SeBr_6^{2-}$; Solid K_2SeBr_6														
	Obs.	179	157	225	122	105	74 **							28
	MUBFF	183	154	226	118	108	73	0.81	0.14	0.06	0.22	0.00	1.5	2.6
	UBFF	185	142	235	117	107	75	0.75	0.21	0.03	0.00		5.7	2.2
	OVFF	187	142	234	119	104	75	0.74	0.22	0.05	−0.01		5.9	1.8
	MOVFF	185	153	226	121	103	75	0.75	0.14	0.15	−0.03	0.31	2.2	1.2
	GVFF	179	157	225	122	105	74	1.20	0.06	0.14	0.01	0.11	0.0	0.0
$TeBr_6^{2-}$; Solid K_2TeBr_6														
	Obs.	178	155	200	102	90	64 **							28
	MUBFF	179	154	200	100	93	63	0.88	0.12	0.04	0.16	0.00	0.3	2.5
	UBFF	180	143	210	99	93	63	0.81	0.18	0.01	−0.01		4.5	2.8
	OVFF	179	143	210	100	91	64	0.82	0.17	0.03	−0.01		4.4	1.4
	MOVFF	182	152	200	103	86	64	0.85	0.14	0.06	−0.01	0.13	1.3	0.9
	GVFF	178	155	200	102	90	64	1.17	0.06	0.11	0.01	0.09	0.0	0.0
$NbBr_6^-$; Solid $CsNbBr_6$														
	Obs.	224	180	236	112	114	81 **							3
	MUBFF	225	179	236	113	112	82	1.09	0.26	0.00	0.23	−0.02	0.3	1.1
	UBFF	225	166	248	111	115	81	0.95	0.36	−0.02	0.00		4.3	0.9
	OVFF	221	167	249	110	116	81	0.97	0.33	−0.02	0.00		4.8	1.3
	MOVFF	226	179	236	112	113	81	1.02	0.30	−0.01	0.00	0.17	0.5	0.3
	GVFF	224	180	236	112	114	81	1.61	0.14	0.36	0.10	0.41	0.0	0.0
$TaBr_6^-$; Solid $CsTaBr_6$														
	Obs.	232	183	212	107	116	82 **							3
	MUBFF	232	183	212	107	116	82	1.15	0.29	0.00	0.23	0.00	0.0	0.2
	UBFF	239	177	213	106	115	84	1.21	0.23	0.05	0.01		1.8	1.4
	OVFF	237	176	212	108	114	84	1.22	0.22	0.10	0.00		2.1	1.7
	MOVFF	231	183	212	107	116	82	1.08	0.31	0.01	0.00	0.20	0.2	0.1
	GVFF	232	183	212	107	116	82	1.68	0.16	0.28	0.06	0.33	0.0	0.0

* Oscillated slightly.

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

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

TABLE 5

Observed and calculated frequencies and force constants for SnI_6^{2-} complex [38]

Hexaiodide	Frequencies (cm^{-1})						Force constants (mdyne/A)					Ave.% deviation	
	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	K f_r	F f_{rr}	$H(D)$ f_α	$k(F')$ $f_{\alpha\alpha}$	h $f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)
$[SnI_6^{2-}]$; Solid $(Et_4N)_2SnI_6$													
Obs.	122	93	161	84	78	55 **							
MUBFF	122	93	161	84	78	55	0.52	0.14	0.04	0.03	−0.01	0.0	0.1
UBFF	121	94	160	85	78	55	0.51	0.15	0.04	0.00		0.6	0.3
OVFF	123	94	168	86	74	55	0.50	0.17	0.06	0.00		1.9	3.0
MOVFF	126	91	161	85	75	56	0.48	0.19	0.04	0.00	−0.05	1.8	1.9
GVFF	122	93	161	84	78	55	0.70	0.08	0.12	0.00	0.05	0.0	0.0

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

attained a minimum, and changes in the F matrix were made so small that the changes in the frequencies were negligible. That is,

$$L_{NN-1}G_0(F_0+\Delta F_{NN})L_{NN}=\Lambda_{NN}\cong\Lambda_{NN-1} \tag{15}$$

where NN denotes the iteration number. The weighting elements W were used, where $W=1/\lambda^2$. These weighting elements W were used by Aldous and Mills [15] to give less weight to the higher frequencies, since the uncertainties in the frequencies arising from the uncertainties in the anharmonicity are larger for the higher frequencies.

D. RESULTS AND DISCUSSION

(i) Comparison of force fields

Tables 2–5 list the results of the calculations made for the MUBFF, UBFF, OVFF, MOVFF, and the GVFF force fields. These tables list the data for hexafluorides, hexachlorides, hexabromides and one hexaiodide respectively. The tables include the values of the observed frequencies and those calculated with each force field for the six fundamental frequencies occurring for an MX_6 molecule. The observed assignments are used as reported in the literature, and some of these could be in error. The percentage deviation of the calculated values from the observed values are included for the average of the three stretching vibrations (ν_1, ν_2, ν_3), and for the three bending vibrations (ν_4, ν_5, ν_6). The final set of converged force constants are also found in the tables.

When one compares the UBFF with the OVFF, one observes that OVFF is in better agreement with the observed bending frequencies than the UBFF. Only slight differences are noticed in making a similar comparison for the observed stretching frequencies. A modification of the UBFF and the OVFF improves the agreement for both fields, with the MOVFF showing better over-all agreement with the observed frequencies for both stretching and bending modes than the MUBFF. Hiraishi et al. [6] have observed that the calculated values obtained for ν_4 using the UBFF had lower values than those of ν_5 for several compounds, whereas ν_4 has been generally assigned at higher frequency than ν_5. The MUBFF fails to rectify this situation. Similarly, for the OVFF the calculated values of ν_1 are found to be at lower frequency than ν_3, although the assigned values are reversed. Where this discrepancy occurs, the MOVFF appears to correct the problem. Therefore, the MOVFF offers some definite advantages over the UBFF and the MUBFF.

In the case of the GVFF, the restriction that ν_6 must be calculated from the expression $\nu_6=\nu_5/\sqrt{2}$ means that a comparison of the value of this frequency with ν_6, as determined from combination bands, has little significance. For this force field, one adjusts five force constants to five frequencies in MX_6'' molecules, which allows for no degrees of freedom.

The improvement in the deviations of the bending and stretching vibrations from the observed values for the MOVFF is 100% for the fluorides, and appears to decrease as one goes to the heavier halogen compounds. Certain factors which may contribute to this difference in behavior between the hexafluoride and the other hexahalogen compounds are

(1) a difference in anharmonicity between the fluorides and other halides;

(2) decreased ionicity occurring as one goes from $F^- \rightarrow Cl^- \rightarrow Br^- \rightarrow I^-$ (refs. 16–19);

(3) increase in anion size from $F^- \rightarrow I^-$ causing increased repulsive forces;

(4) additional forces present in the solid MX_6^{2-} molecules (where X = Cl, Br, I) vs. the gaseous MF_6 molecules.

(ii) Trends observed

Several factors which contribute to the position at which a stretching metal–ligand vibration occurs were cited by Clark [39]. These factors were based on a limited amount of data and primarily on the metal–chlorine stretching vibration. With considerably more data, Ferraro [40] has recently cited that these trends are more general than originally believed and also hold for the metal–fluorine, metal–bromine, and metal–iodine vibrations. A number of these trends can be cited in light of the present data.

(a) Mass effect

A number of elements form at least two hexahalides. Keeping the other factors constant (such as oxidation effect, stereochemistry, CN and metal) it can be demonstrated that, as the mass of the halogen atom increases, all three stretching frequencies (ν_1, ν_2, and ν_3) decrease. This is additionally reflected in the force constants K (MUBFF and MOVFF) and f_I, which also decrease with a corresponding increase in MX bond distance. A similar trend is observed for the bending XMX vibrations ν_4 and ν_5. A comparison of the effects of mass made by keeping the halogen constant is demonstrated when one compares TcF_6, ReF_6; $PdCl_6^{2-}$, $PtCl_6^{2-}$; $PdBr_6^{2-}$ and $PtBr_6^{2-}$. It may be observed that an increase in ν_1 and K occurs as one proceeds from the first to the second and to the third transition series. The suggestion to use ν_1 as a measure of bond strength has been made [41] and may be justified since the heavy central metal atom remains stationary during the vibration. In a recent paper, ν_3 was found to increase as a function of mass of the central atom (across the periodic table) in MCl_6^{2-} species [41]. Where comparisons are possible, similar trends for ν_3 are observed in this paper for MCl_6^{2-} and MBr_6^{2-} ions.

(b) Oxidation effect

The oxidation effect is demonstrated by the decrease in ν_1, ν_2, and ν_3 and in K and f_I in decreasing the oxidation number of Pt from VI → IV ($PtF_6 \rightarrow PtF_6^{2-}$). In the series SiF_6^{2-}, PF_6^-, and SF_6, GeF_6^{2-}, AsF_6^- and SeF_6, and SnF_6^{2-}, TcF_6, ν_1, ν_2, ν_3 and K and f_I show increases indicating that the oxidation effect is more important than the mass effect.

(c) Dependence of F, K and H force constants (MUBFF and MOVFF) on the number of non-bonding valence electrons and the crystal-field stabilization energy

The dependence of the F and D force constants in the OVFF on the number (n) of non-bonding valence electrons (up to $n = 4$) has been discussed [1]. Figs. 2–4 present plots of the F, K, and H force constants in the MUBFF or the MOVFF as a function of the number of non-bonding valence electrons (n) for several transition series MF_6. For the plots of H and K vs. n, the results are reminiscent of plots of the ligand-field stabilization energy vs. n. The plot of F vs. n appears to be the reverse of the H and K plots.

The plot of the repulsion constant (F) for the MOVFF vs. n is recorded in Fig. 2. It may be observed that F is greatest for the $3d$ transition series and least with the $5d$ transi-

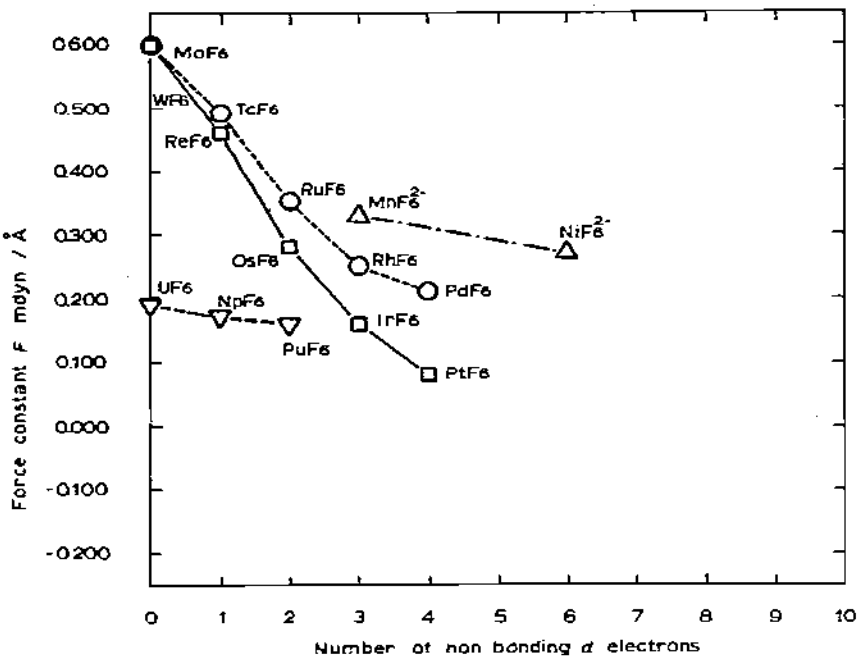

Fig. 2. Plot of F repulsion constant in MOVFF vs. number of non-bonding d electrons in MF_6^n compounds.

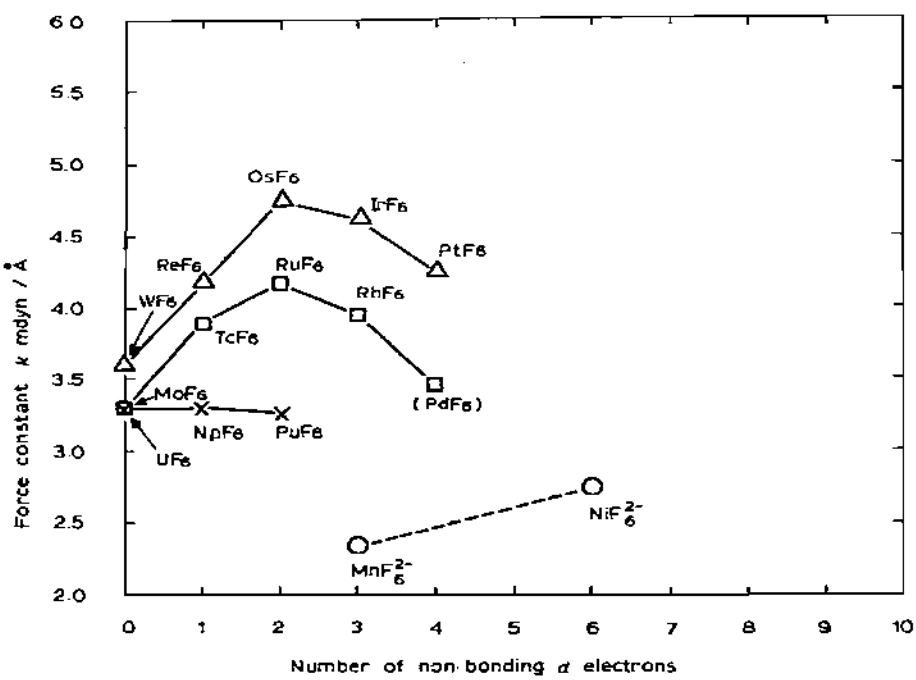

Fig. 3. Plot of K stretching force constant in MUBFF vs. number of non-bonding d electrons in MF_6^n compounds.

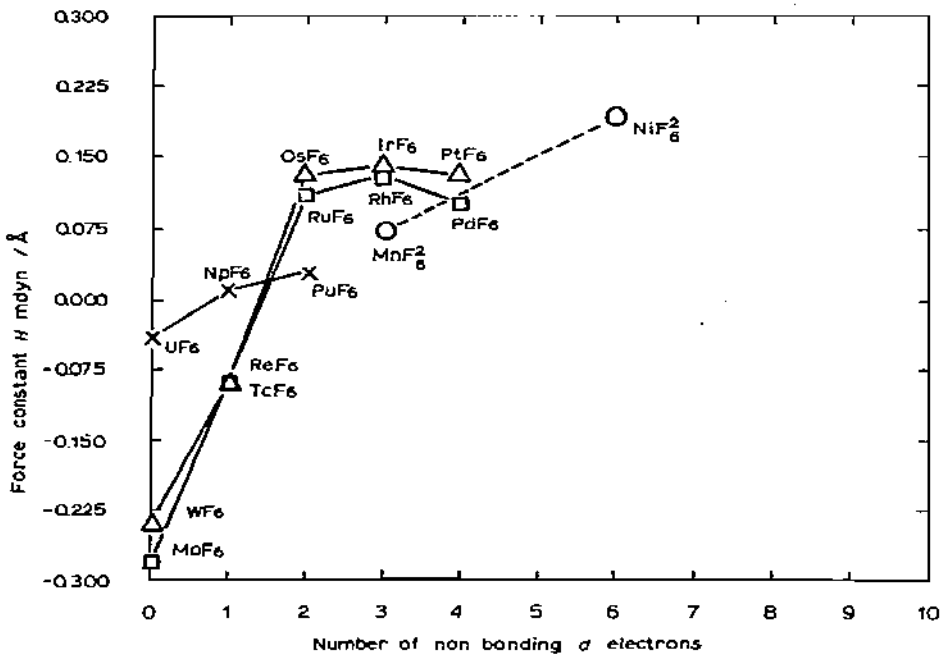

Fig. 4. Plot of H bending constant in MUBFF vs. number of non-bonding d electrons in MF_6^n compounds

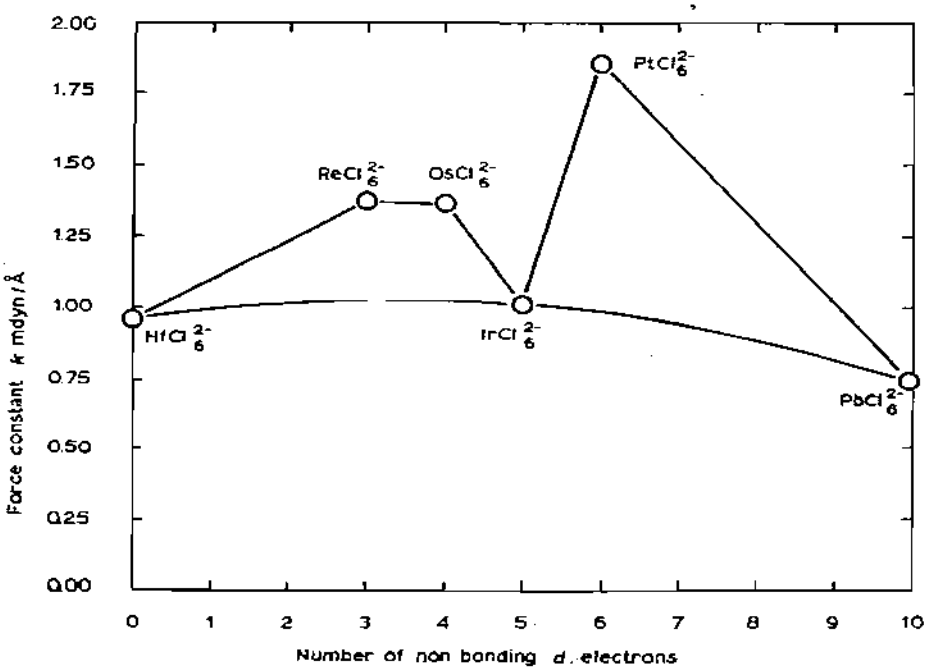

Fig. 5. Plot of K stretching constant in MUBFF vs. number of non-bonding d electrons in MCl_6^{2-} compounds.

tion series indicating an increase in stability of the complexes from the $3d$ series to the $5d$ series. For comparison, a plot of the $5f$ actinide series is also included.

Figure 3 shows the plot of the stretching constant, K, for the MUBFF vs. n for the various transition series. An initial increase in K is noted with a maximum at $n=2$ for the $4d$ and $5d$ series. The stretching constant appears to decrease in the direction $5d > 4d > 5f > 3d$, which is consistent with observations that the third transition series form more stable complexes than the second or first transition series. These trends may be explained on the basis that the π-bond effects caused by donation of fluorine p electrons into the metal orbitals are greater in the third-row than in the second-row transition series.

Figure 4 plots the bending constant (H) for the MUBFF vs. n. An initial increase occurs with a maximum at $n=3$. H decreases in the direction $5d > 4d > 3d > 5f$.

In comparing the three plots, it is observed that the plots of K and H vs. n are similar and different from the F plot. At the maxima points of $n=2$ or 3 in the K and H plots, a minimum point is observed for F. The results appear to be consistent with observations made for the ligand-field stabilization energy plots for transition-metal complexes where a maximum in energy is obtained at $n=3$ and 8 and a minimum at 5 for complexes in an octahedral field. An increase in the force constants for stretching and bending (K and H) at $n=2$ or 3 (more stable hexafluorides) corresponds to a decreased repulsion force constant, F. Likewise, a lowered force constant (K and H) corresponds to a less stable hexafluoride, which correlates with an increase in the repulsion constant, F.

TABLE 6

K (MUBFF), K (MOVFF) and f_r (GVFF) force constants for MF_6 and MCl_6^{2-} molecules

	n	K (MUBFF)	K (MOVFF)	f_r (GVFF)
MoF_6	0	3.29	3.95	4.79
TcF_6	1	3.89	4.05	4.69
RuF_6	2	4.17	3.98	4.44
RhF_6	3	3.94	3.84	3.98
(PdF_6)	4	3.44	3.47	3.17
WF_6	0	3.59	4.28	5.29
ReF_6	1	4.18	4.45	5.18
OsF_6	2	4.75	4.65	5.10
IrF_6	3	4.62	4.68	4.75
PtF_6	4	4.25	4.40	4.13
$HfCl_6^{2-}$	0	0.86	1.02	1.30
$ReCl_6^{2-}$	3	1.37	1.42	1.68
$OsCl_6^{2-}$	4	1.36	1.40	1.67
$IrCl_6^{2-}$	5	1.01	1.02	1.23
$PtCl_6^{2-}$	6	1.86	1.93	2.15
$PbCl_6^{2-}$	10	0.74	0.83	0.97

( ) Theoretical molecule.
n = number of non-bonding d electrons.

Table 6 tabulates the K and f_r for the second- and third-row transition series for MF_6 compounds, and for MCl_6^{2-} of the third-row transition series. Figure 5 shows a plot for six MCl_6^{2-} solid complexes of K for the MUBFF vs. the number of non-bonding d electrons. This group of compounds contains a d^5 compound ($IrCl_6^{2-}$) and illustrates a minimum at $n=5$. Figure 5 is very typical of curves obtained for crystal-field stabilization energy or heats of formation [42] vs. number of d electrons, where maxima are obtained at $n=3$ and $n=7$ or 8 and minima at $n=0$, 5 and 10. It is also significant to cite that the K force constant obtained from the MOVFF or the MUBFF reflects these trends more clearly than the f_r(GVFF) force constant.

E. POTENTIAL ENERGY DISTRIBUTION (PED)

The calculated potential energy distributions for all fields except the GVFF indicate ν_1 and ν_2 to be predominantly stretching vibrations, since they are determined by K. However, as one increases the size of the halogen, F or the repulsion force constant increases to the point at which for the bromides and the iodides, ν_1 mostly consists of the repulsion constant. The vibrations ν_5 and ν_6 are predominantly $H(D)$, and F, with F getting predominantly greater from F^- to I^-, but the fact that they can be identified as bending modes is unmistakable. The modes ν_3 and ν_4 are considerably more complex being a mixture of K, F and $H(D)$. However, ν_3 is weighted more by K while ν_4 is weighted by $H(D)$ and F, again repulsion increasing from F^- to I^-.

F. CONCLUSIONS

The following conclusions may be made from a consideration of the data obtained in this work.

(1) The MOVFF demonstrates several advantages over the other force fields, particularly because of the better over-all agreement found for the observed frequencies.

(2) Definite trends regarding mass and oxidation effects are observed for these compounds. Where both effects occur, the oxidation effect appears to be more important than the mass effect.

(3) A dependence of F, K and $H(D)$ force constants from the MUBFF and MOVFF vs. the number of non-bonding valence electrons and crystal-field stabilization energy exists for MF_6 and MCl_6^{2-}-type compounds.

(4) In studies of this type, it may be advisable to study several force fields, as was done in this work.

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