Coordination Chemistry Reviews, 11 (1973) 21–69

A STUDY OF FORCE FIELDS FOR TETRAHEDRAL MOLECULES AND IONS*

L.J. BASILE, J.R. FERRARO*, P. LaBONVILLE** and M.C. WALL, S.M.C.‡
Argonne National Laboratory, Argonne, Illinois 60439 (U.S.A.)

(Received December 4th, 1972)

CONTENTS

A. INTRODUCTION

Six years have elapsed since Müller et al.[1,2] presented their study of the Normal Coordinate Treatment (NCT) of some 67 tetrahedral molecules and ions. In this period of time, the laser technique in Raman spectroscopy has become a valuable tool. More and more tetrahedral molecules and ions (some highly colored) have now been studied by this method. Certainly, the frequency assignments can now be considered to be more reliable than previous results. Thus a re-examination of this problem seemed in order.

In this study 146 entries appear. The most recent experimental data have been used wherever possible. The number of studies in this field has proliferated immensely, and during the course of our preparation of this paper, new studies have appeared. We have used these newest data in the cases where significant differences in frequency assignments from the older data existed. Our results present the nature of the experiment performed, and

---

* Work performed under auspices of the U.S. Atomic Energy Commission.

* To whom correspondence should be addressed.

** Resident Associate under AUA-ANL Fellowship Program from the University of Detroit, Detroit, Michigan, July 1969–December 1970.

‡ Resident Associate under Faculty Research Participation Program from Rosemont College, Rosemont, Pa., June–August 1971.

whether the frequencies used were obtained from Raman or infrared data. In order to keep the size of this manuscript within a reasonable length, we have chosen to ignore hydrogenic tetrahedral molecules for the present.

Our objective has been to compare the three force fields commonly used for T_d molecules – the Urey–Bradley (UBFF), orbital valence (OVFF), and general valence force fields (GVFF). We have also examined and compared the force constants obtained from these force fields, and cited trends wherever any existed.

The molecules studied included 7 tetrafluorides, 37 tetrachlorides, 21 tetrabromides, 18 tetraiodides, 44 oxygenated ions ($MO_4{}^n$), 8 thio ions ($MS_4{}^n$), 5 seleno ions ($MSe_4{}^n$), and 6 miscellaneous compounds.

B. MOLECULAR FORCE FIELDS FOR TETRAHEDRAL MOLECULES

Several monographs and review articles have recently appeared in the literature on the theory of molecular force fields; hence for the sake of brevity, we shall not dwell at length on this subject[3-8].

In dealing with a tetrahedral molecule four frequencies are found to be vibrationally allowed, $\Gamma_{vib} = A_1(R) + E(R) + 2F_2(IR,R)$. One is confronted with the problem of finding the force field which best accounts for the forces within the molecule and has fewer force constants than the observed frequencies. Both the UBFF[9-11] and the OVFF[12] offer a solution to the problem. In the UBFF the force constants are K (force constant for stretching along a bond); H (force constant for angle deformation ($\Delta\alpha$)); F and F' (force constants for interactions between non-bonded atoms). In the case of the OVFF the symbol D replaces H, and corresponds to the Heath and Linnett[12] angle based on overlap of orbitals ($\Delta\beta$); otherwise, the remaining force constants are the same. Although four force constants are required by both fields, one of the force constants F' is usually taken as $-\frac{1}{10}F$ for T_d molecules. This reduces the number of force constants to three, and allows a degree of freedom for the least-squares analysis. We recognize that we might have chosen other values for F'. However, for many of the molecules studied in this paper the use of a Lennard–Jones potential failed because of the steepness in the repulsive portion of the curve. Thus, a meaningful value of F' in terms of F was unavailable from this method.

The potential energy functions for T_d molecules using the UBFF and the OVFF may be expressed as

UBFF:

$$2V = (K + 2F + F') \sum_{i}^{4} \Delta r_i{}^2 + r_0{}^2(H + \tfrac{1}{3}F - \tfrac{5}{3}F') \sum_{i,j}^{6} (\Delta\alpha_{i,j})^2$$

$$+ 2(\tfrac{2}{3}F - \tfrac{1}{3}F') \sum_{i,j}^{6} \Delta r_i \Delta r_j + 2r_0 \left[\frac{\sqrt{2}}{3}(F + F') \sum_{i,i,j}^{12} \Delta r_i \Delta\alpha_{i,j}\right]$$

$$+ 2r_0{}^2(-\tfrac{2}{3}F') \sum_{i,j,k}^{12} \Delta\alpha_{i,j}\Delta\alpha_{i,k} \qquad (1)$$

Here Δr and $\Delta\alpha$ are the changes in bond lengths and bond angles between non-bonded atoms. The symbols K, H, F and F' have been previously defined. The symbol r_0 refers to the bond distance at the equilibrium position.

OVFF:

$$2V = (K + 2F + F')\sum_{i}^{4}\Delta r_i^2 + r_0^2(\tfrac{1}{2}D + \tfrac{1}{3}F - \tfrac{5}{3}F')\sum_{i,j}^{6}\Delta\beta_{ij}^2$$

$$+ 2(\tfrac{2}{3}F - \tfrac{1}{3}F')\sum_{i,j}^{6}\Delta r_i\Delta r_j + 2r_0\,[\frac{\sqrt{2}}{3}(F + F')\sum_{i,i,j}^{12}\Delta r_i\Delta\beta_{ij}]$$

$$+ 2r_0^2(\tfrac{1}{2}D - \tfrac{2}{3}F')\sum_{i,j,k}^{12}\Delta\beta_{ij}\Delta\beta_{ik} \qquad (2)$$

The symbolism is equivalent to that used in the UBFF expression above except that $\Delta\beta$ replaces $\Delta\alpha$.

The differences between the UBFF and the OVFF relate to the fact that the UBFF expresses the bending force constant H in terms of $\Delta\alpha$, a change in the angle between two bonds, while the OVFF expresses the bending constant D in terms of $\Delta\beta$, a change in the position of the axis of the bonding orbital associated with the bending vibration. This change in the position of the axis is due to a rehybridization[13] of the bonding orbitals that takes place during the bending motion of the molecule.

The GVFF for T_d molecules requires seven force constants to describe the forces taking place in the T_d molecule. In the GVFF the force constants are: f_r (force constant for stretching along a bond); f_{rr} (force constant for stretching interaction along two bonds); f_α (force constant for angle deformation); $f_{\alpha\alpha}$ (force constant for interaction between two adjacent angle deformations); $f_{\alpha\alpha'}$ (force constant for interaction between angle deformations having no common bond); $f_{r\alpha}$ (force constant for interaction between a stretch and an adjacent angle deformation); $f_{r\alpha'}$ (force constant for interaction between a stretch and an angle deformation having no common bond). Even then, repulsion forces between non-bonded atoms are neglected. Since we observe only four frequencies, the number of force constants must be reduced so that one degree of freedom is allowed for the least-squares analysis. Certain approximations can be made. The usual practice is to reduce the number of force constants to five by assuming that the force constants associated with the stretch–bend ($f_{r\alpha'}$) and angle–angle ($f_{\alpha\alpha'}$) interactions are zero since the two internal coordinates do not share a common bond. However, we have used the multiple regression analysis of Schachtschneider and Snyder[14] to find those starting force constants for the T_d field to which the calculated frequencies are most sensitive. The constants f_α and f_r for the pair of compounds SiH_4 and SiD_4 were used and were refined by the perturbation technique, while all other constants were held fixed at zero. The multiple regression analysis added those interaction constants which gave the greatest improvement of fit between the observed and calculated frequencies. The regression analysis was not carried out directly on the halide species since isotopic data for these were not readily available. The results indicated that for the GVFF, four constants were necessary, and since we are dealing with four frequencies this obviously gave a perfect fit between the observed and calculated frequencies. In addition to the diagonal constants f_r and f_α, the necessary interaction terms chosen by the regression technique were f_{rr} and $f_{\alpha\alpha}$.

The potential energy function for a T_d molecule for the constrained GVFF is therefore, given by the expression

$$2V = f_r \sum_{i}^{4} \Delta r_i^2 + r_0^2 f_\alpha \sum_{i,j}^{6} (\Delta\alpha_{i,j})^2 + f_{rr} \sum_{i,j}^{6} \Delta r_i \Delta r_j + 2r_0(f_{r\alpha}) \sum_{i,i,j}^{12} \Delta r_i \Delta\alpha_{ij}$$

$$+ 2r_0^2(f_{\alpha\alpha}) \sum_{i,j,k}^{12} \Delta\alpha_{ij}\Delta\alpha_{ik} \tag{3}$$

It should be emphasized that other force constant interactions which we have failed to consider might have proved to be more important for certain families of compounds. However, an exhaustive search for such interactions was beyond the scope of this paper.

C. CALCULATIONS OF FORCE CONSTANTS

In the calculations the force constants were adjusted until the calculated frequencies gave the best fit with the observed frequencies. The calculations were performed on an IBM 360 computer using Yeranos's[15] NCT and Schachtschneider and Snyder's[14] FADJ programs. The systems converged with about 4–5 perturbations for all force fields (with some small number of exceptions for the GVFF). Molecules in which the cation was smaller than the anion resulted in 15 cases which were found to diverge for the GVFF only, and no adjustment corrections were possible. Similar observations have been previously made[16]. This divergence is undoubtedly due to our neglect of interaction constants to account for the large Coriolis interactions commonly exhibited by these lighter molecules.

The final results 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 the force constants and frequencies. The F and G matrices appear in Table 1.

The method included a refinement in χ where

$$\chi = \delta\lambda' \cdot W\delta\lambda \tag{4}$$

obtained a minimum, and changes in the F matrix were made so small that the changes in the frequencies were negligible, i.e.

$$L_{NN-1} G_0(F_0 + \Delta F_{NN}) L_{NN} = \Lambda_{NN} \cong \Lambda_{NN-1} \tag{5}$$

TABLE 1

F and *G* matrices obtained for UBFF, OVFF and GVFF for AB_4 molecules and ions

		F matrix		
Mode	*G* matrix	UBFF [a]	OVFF [a]	GVFF
A_1	$G_{11} = \mu_B$	$F_{11} = K + 4F$	$F_{11} = K + 4F$	$F_{11} = (f_r + 3f_{rr})$
E	$G_{22} = 3\mu_B$	$F_{22} = H + \frac{1}{3}F - \frac{1}{3}F'$	$F_{22} = \frac{1}{3}D + \frac{1}{3}F - \frac{1}{3}F'$	$F_{22} = (f_\alpha - 2f_{\alpha\alpha})$
F_2	$G_{33} = \frac{4}{3}\mu_A + \mu_B$	$F_{33} = K + \frac{4}{3}(F + F')$	$F_{33} = K + \frac{4}{3}F + \frac{4}{3}F'$	$F_{33} = (f_r - f_{rr})$
	$G_{34} = G_{43} = -\frac{8}{3}\mu_A$	$F_{34} = F_{43} = \frac{2}{3}(F + F')$	$F_{34} = F_{43} = -\frac{2}{3}(F + F')$	$F_{34} = F_{43} = 0$
	$G_{44} = \frac{16}{3}\mu_A + 2\mu_B$	$F_{44} = H + \frac{1}{3}F - \frac{5}{3}F'$	$F_{44} = \frac{1}{2}D + \frac{1}{3}F - \frac{5}{3}F'$	$F_{44} = f_\alpha$

[a] For the UBFF and the OVFF the assumption $F' = -\frac{1}{10}F$ was used.

T_d symmetry coordinates

A_1 vibration

$R_1 \quad = \frac{1}{2}(\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4)$

$R_2 \quad = \frac{1}{\sqrt{6}}(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\alpha_{14} + \Delta\alpha_{24} + \Delta\alpha_{34}) = 0$

E vibration

$R_{3a} \quad = \frac{1}{\sqrt{12}}(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{14} - \Delta\alpha_{24} + 2\Delta\alpha_{34})$

$R_{3b} \quad = \frac{1}{2}(\Delta\alpha_{14} - \Delta\alpha_{31} + \Delta\alpha_{23} - \Delta\alpha_{24})$

F vibrations

$R_{4a} \quad = \frac{1}{\sqrt{12}}(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} + \Delta\alpha_{14} + \Delta\alpha_{24} - 2\Delta\alpha_{34})$

$R_{4b} \quad = \frac{1}{\sqrt{6}}(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\alpha_{14} - \Delta\alpha_{24} - \Delta\alpha_{34})$

$R_{4c} \quad = \frac{1}{2}(\Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{14} + \Delta\alpha_{24})$

$R_{5a} \quad = \frac{1}{\sqrt{6}}(\Delta d_1 + \Delta d_2 - 2\Delta d_3)$

$R_{5b} \quad = \frac{1}{\sqrt{12}}(\Delta d_1 + \Delta d_2 + \Delta d_3 - 3\Delta d_4)$

$R_{5c} \quad = \frac{1}{\sqrt{2}}(\Delta d_2 - \Delta d_1)$

where *NN* denotes the iteration number. The weighting element W was used, where $W = 1/\lambda$, according to Mann et al.[17] to ensure a fit on a percentage basis.

D. RESULTS AND DISCUSSION

(i) Comparison of force fields

A comparison of the OVFF and UBFF is made for the main-family and transition-metal tetrahalides and for the main-family and transition-metal oxy-, thio and seleno-anions (e.g. MO_4^n, MS_4^n, MSe_4^n). This comparison is made in Tables 2—13. Also included in these tables are the average percent deviation of the stretching modes (ν_1, ν_3) and the bending modes (ν_2, ν_4). The tables contain experimental details and references. The source of the data relating to observed frequencies (for example Raman and/or IR) is also indicated.

In the case of tetrahedral molecules one is dealing with four experimental frequencies and three force constants in the OVFF and UBFF. With so few parameters to work with, any modification of these force fields without corollary data would not be very significant. A comparison with the GVFF was not possible since this field involved four experimental frequencies and four force constants, and a perfect fit of theoretical frequencies with the experimental frequencies was obtained. (Since the frequencies calculated by the GVFF agree with those observed, they are not included in the tables.) However, the GVFF was included in this study because it provided a third set of force constants.

(a) Main-family tetrahalides

Tables 2—5 include the experimental frequencies and those calculated from the OVFF and the UBFF for the main-family tetrahalides. It may be observed that the OVFF gives a better fit in 34 of 40 cases where a clear-cut distinction may be made. In 6 cases no distinction may be observed, and both fields appear to fit equally well. In 9 cases one force field gives a better fit for ν_1, ν_3 stretching modes, and the other field a better fit for the ν_2, ν_4 bending vibrations. In the case of 11 gaseous molecules in this group, both fields appear to determine the forces within the molecule equally well.

(b) Transition-metal tetrahalides

Tables 6—8 include the experimental frequencies and those calculated by the OVFF and the UBFF for the transition-metal tetrahalides. Only slight differences in the calculated force fields are noted.

(c) Main-group oxygenated anions (MO_4^n)

Table 9 compiles data for the main-group MO_4^n oxyanions. Of the ten anions represented, the OVFF gives by far the best fit with the experimental frequencies.

(d) Transition-metal oxygenated anions (MO_4^n)

Table 10 lists the data for the transition-metal oxyanions. In 22 of 29 cases, the UBFF

TABLE 2

Observed and calculated fundamental frequencies for main-family tetrahalides (cm^{-1}). I. Fluorides

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
BeF_4^{2-}	Obs.	547(R)	255(R)	800(R)	385(R)			Li_2BeF_4 (melt) at 487°C – Raman – 4880 A exciting line – Ar^+ laser	34
	OVFF	548	275	801	364	0.15	6.7		
	UBFF	553	267	798	369	1.38	4.4		
BF_4^- (solid)	Obs.	769(R)	353(R)	984(R)[a]	524(R)			$NaBF_4$(solid) – Raman – 4358 A exciting line – Hg arc	43, 44
	OVFF	770	359	984	519	0.06	1.4		
	UBFF	774	365	983	510	0.39	3.0		
BF_4^- (melt)	Obs.	777(R)	360(R)	1070(R)	533(R)			$NaBF_4$(melt) at 414°C – Raman – 4880 A exciting line – Ar^+ laser	45
	OVFF	777	385	1071	508	0.05	5.8		
	UBFF	784	375	1068	514	0.93	2.5		
CF_4	Obs.	908(R)	435(R)	1283(IR/R)	632(IR/R)			Infrared (gas); Raman spectrum (gas) – 4358 A exciting line – Hg arc	46–48
	OVFF	909	442	1283	625	0.08	1.3		
	UBFF	918	457	1280	605	0.64	4.3		
SiF_4	Obs.	801(R)	264(R)	1032(IR/R)	389(IR/R)			Infrared (gas); Raman spectrum (gas) – 4358 A exciting line – Hg arc	46–48
	OVFF	801	278	1032	377	0.03	4.1		
	UBFF	811	291	1025	356	0.92	9.4		
GeF_4	Obs.	738(R)	205[b]	800(IR)	260(IR)			Infrared spectrum (gas); Raman spectrum (gas) – 4358 A, 4046 A exciting lines – Hg arc	48, 49
	OVFF	737	212	801	254	0.11	2.8		
	UBFF	743	219	796	242	0.62	6.9		
TiF_4(gas)	Obs.	712(R)	185(R)	793(R)	209(R)			Raman spectrum (gas) at 300°C; Ar^+ laser	50
	OVFF	709	190	795	206	1.5	1.6		
	UBFF	709	177	795	216	1.5	3.4		

[a] Average of observed doublet.

[b] Estimated to give best fit.

(R) Frequency obtained from Raman data. (IR) Frequency obtained from infrared data.

TABLE 3

Observed and calculated fundamental frequencies for main-family tetrahalides (cm^{-1}). II. Chlorides

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$MgCl_4^{2-}$	Obs.	252(R)	100(R)	330(R)	142(R)			K_2MgCl_4(melt) – Raman; frequencies < 100 cm^{-1} – 5682 A, 6471 A exciting lines; frequencies > 100 cm^{-1} – 4880 A, 5145 A exciting lines	51
	OVFF	252	100	330	142	0.00	0.0		
	UBFF	251	106	331	138	0.35	2.8		
BCl_4^-	Obs.	405(R)	190(R)	670(IR)	274(R)			IR: $(C_2H_5)(i\text{-}C_3H_7)_2NHBCl_4$ in CH_2Cl_2; $(CH_3)_4NBCl_4$ soln. in liq. SO_2; Raman: 4358 A – Hg arc	52
	OVFF	405	198	670	266	0.00	3.6		
	UBFF	406	191	670	273	0.01	0.45		
$AlCl_4^-$	Obs.	351(R)	121(R)	490(R)	186(R)			$AlCl_3$–NaCl melt (225°C) – Raman 5145 A, 4880 A exciting lines	53, 54
	OVFF	351	126	490	182	0.00	3.3		
	UBFF	354	129	489	178	0.49	5.3		
$GaCl_4^-$	Obs.	346(R)	114(R)	386(R)	149(R)			$HGaCl_4$ aqueous soln. – Raman – 4358 A – Hg arc	55–57
	OVFF	346	115	386	148	0.02	0.55		
	UBFF	347	118	385	145	0.23	2.9		
$InCl_4^-$	Obs.	321(R)	89(R)	337(R)	112(R)			$HInCl_4$ aqueous soln. – Raman – 4358 A – Hg arc	56, 57
	OVFF	321	92	337	110	0.14	2.5		
	UBFF	322	92	336	108	0.26	3.5		
$TlCl_4^-$	Obs.	312(R)	60(R)	296(R)	78(R)			$(C_6H_5)_4AsTlCl_4$ soln. in acetonitrile – Raman – 4358 A – Hg arc	32
	OVFF	308	68	299	69	1.1	12.6		
	UBFF	312	62	296	76	0.11	2.6		
CCl_4(liq.)	Obs.	458(R)	218(R)	776(R)[a]	314(R)			Liquid – Raman – 4358 A – Hg arc	46, 58, 59
	OVFF	458	217	776	315	0.03	0.52		
	UBFF	460	222	776	309	0.25	1.8		
CCl_4(solid)	Obs.	456(R)	217(R)	791(R)	315(R)			CCl_4(solid) – 77°K – Raman – 4880 A Ar^+ laser	60, 61
	OVFF	457	227	791	305	0.11	3.2		
	UBFF	459	223	790	308	0.40	2.2		

CCl_4(gas)	Obs.	460(R)	214(R)	793(R)	313(R)			Vapor–Raman– 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	461	225	793	303	0.11	4.2		
	UBFF	463	220	792	306	0.39	2.5		
$SiCl_4$(liq.)	Obs.	424(R)	150(R)	621(IR)	221(R)			Liquid –Raman – 4358 A – Hg arc, IR–vapor	46, 58, 59
	OVFF	424	152	621	219	0.01	1.2		
	UBFF	427	159	619	212	0.51	5.2		
$SiCl_4$(gas)	Obs.	423(R)	145(R)	616(R)	220(R)			Vapor–Raman–4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	421	157	617	210	0.30	6.4		
	UBFF	427	156	614	209	1.06	6.3		
$SiCl_4$(solid)	Obs.	419(R)	152(R)	612(R)	221(R)			Solid – Raman at 80°K – 4880, 5280, 4280 A exciting lines	61
	OVFF	418	160	613	214	0.31	4.2		
	UBFF	421	160	611	212	0.45	6.3		
$GeCl_4$(liq.)	Obs.	396(R)	134(R)	453(R)	172(R)			Liquid–Raman–4358 A – Hg arc	46, 55, 58, 59
	OVFF	396	133	453	173	0.01	0.53		
	UBFF	397	139	452	167	0.30	3.3		
$GeCl_4$(gas)	Obs.	396(R)	125(R)	459(R)	171(R)			Vapor–Raman–4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	393	134	461	163	0.44	6.7		
	UBFF	399	134	457	161	0.44	6.5		
$GeCl_4$(solid)	Obs.	392(R)	134(R)	457(R)	171(R)			Solid – Raman at 80°K – 5682, 6471 A exciting lines	61
	OVFF	391	138	458	168	0.24	2.4		
	UBFF	394	139	456	165	0.36	3.6		
$SnCl_4$(liq.)	Obs.	366(R)	104(R)	403(R)	134(R)			Liquid–Raman–4358 A – Hg arc	46, 58, 59
	OVFF	366	107	403	131	0.10	2.6		
	UBFF	369	111	401	125	0.62	6.9		
$SnCl_4$(gas)	Obs.	369(R)	95(R)	408(R)	126(R)			Vapor–Raman–4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	365	103	411	119	0.40	6.9		
	UBFF	372	103	406	116	0.62	8.2		
$SnCl_4$(solid)	Obs.	364(R)	108(R)	405(R)	130(R)			Solid – Raman at 80°K – 5280, 5682 A exciting lines	61 [b]
	OVFF	363	111	406	128	0.26	2.2		
	UBFF	366	113	404	124	0.35	4.6		
$PbCl_4$(liq.)	Obs.	327(R)	90(R)	348(R)	90(R)			Liquid–Raman–0°C –4358 A Hg arc	62
	OVFF	328	83	347	95	0.29	6.6		
	UBFF	327	89	348	91	0.07	0.78		

TABLE 3 (continued)

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
	Obs.	325(R)	90(R)	345(R)	116(R)			Solid – Raman at 80°K– 5682, 6471 A exciting lines	61
$PbCl_4$(solid)	OVFF	322	97	348	109	0.90	6.9		
	UBFF	329	99	342	102	1.1	11.0		
	Obs.	458(R)	171(IR/R)	658(R)	251(IR/R)			PCl_5(solid) – Raman – 4358 A – Hg arc; IR – solid deposition at 90°C	63
PCl_4^+	OVFF	458	175	658	248	0.01	1.6		
	UBFF	462	183	656	238	0.65	6.2		
	Obs.	422(R)	156(R)	500(R)	187(R)			AsF_3Cl_2(solid) – Raman – 4358 A Hg arc	64
$AsCl_4^+$	OVFF	422	148	500	193	0.07	4.1		
	UBFF	423	159	499	184	0.22	1.8		
	Obs.	353(R)	143(R)	399(R)	153(R)			$SbCl_4F$ in CCl_4 and $CHCl_3$ soln.–Raman – 4358 A – Hg arc	65
$SbCl_4^+$	OVFF	354	131	399	161	0.12	7.0		
	UBFF	353	144	399	152	0.10	0.87		

[a] Average of doublet.

[b] The most recent data on solid $SnCl_4$ appear in ref. 111.

(R) Frequency obtained from Raman data.

(IR) Frequency obtained from infrared data.

TABLE 4

Observed and calculated fundamental frequencies for main-family tetrahalides (cm^{-1}). III. Bromides

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$MgBr_4^{2-}$	Obs.	150(R)	61(R)	290(R)	90(R)			K_2MgBr_4(melt) – Raman; frequencies < 100 cm^{-1}: 5682 A, 6471 A exciting lines; frequencies > 100 cm^{-1}: 4880 A, 5145 A exciting lines	51
	OVFF	150	62	290	89	0.00	1.4		
	UDFF	150	64	290	88	0.00	3.6		
BBr_4^-	Obs.	243(R)	117(R)	605(IR)	166(R)			Raman and IR of $(C_2H_5)(i\text{-}C_3H_7)_2NHBBr_4$ in CH_2Cl_2; Raman: 4358 A exciting line – Hg arc	52
	OVFF	242	114	605	169	0.17	2.0		
	UBFF	243	117	605	166	0.01	0.00		
$AlBr_4^-$	Obs.	214(R)	76(R)	405(IR)	118(R)			Raman of $(CH_3)_4NAlBr_4$(solid) with He–Ne excitation; IR Nujol mull and solution in nitromethane or acetonitrile	54, 66
	OVFF	214	77	405	117	0.01	1.2		
	UBFF	215	79	405	115	0.30	3.3		
$GaBr_4^-$	Obs.	210(R)	71(R)	278(R)	102(R)			$HGaBr_4$ in aqueous solution – Raman – 4358 A exciting line – Hg arc	67
	OVFF	210	72	278	102	0.01	0.58		
	UBFF	211	73	278	100	0.17	2.0		
$InBr_4^-$	Obs.	197(R)	55(R)	239(R)	79(R)			$HInBr_4$ in aqueous solution – Raman – 4358 A, 4046 A exciting lines – Hg arc	68
	OVFF	197	58	239	77	0.12	3.6		
	UBFF	198	58	238	76	0.35	4.4		
$TlBr_4^-$	Obs.	190(R)	51(R)	209(R)	64(R)			$TlBr_3$ in alcohol – Raman – 4358 A, 5460 A – Hg arc	67, 69
	OVFF	190	52	209	64	0.00	1.0		
	UBFF	190	52	209	63	0.00	1.8		
CBr_4	Obs.	267(R)	123(R)	672(R)	183(R)			CBr_4 (solid) in CCl_4 solution – Raman – 4358 A exciting line – Hg arc	46, 58, 59, 70
	OVFF	267	123	672	183	0.00	0.00		
	UBFF	269	126	672	179	0.33	2.4		

TABLE 4 (continued)

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$SiBr_4$(liq.)	Obs.	249(R)	90(R)	487(R)	137(R)			Liquid – Raman – 4358 A exciting line – Hg arc	46, 58, 59, 70
	OVFF	249	91	487	137	0.01	0.38		
	UBFF	251	94	486	136	0.37	3.9		
$SiBr_4$(gas)	Obs.	246(R)	85(R)	494(R)	134(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	245	91	494	129	0.20	5.4		
	UBFF	248	91	493	127	0.51	6.4		
$GeBr_4$(liq.)	Obs.	235(R)	79(R)	327(R)	112(R)			Liquid – Raman – 4358 A exciting line – Hg arc	46, 58, 59, 70
	OVFF	235	79	327	112	0.00	0.17		
	UBFF	236	82	326	109	0.29	3.1		
$GeBr_4$(gas)	Obs.	236(R)	75(R)	332(R)	111(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	235	81	333	106	0.36	6.3		
	UBFF	238	80	331	106	0.57	5.6		
$SnBr_4$(liq.)	Obs.	220(R)	64(R)	279(R)	88(R)			Liquid – Raman – 4358 A exciting line – Hg arc	58, 59, 68, 70
	OVFF	220	65	279	88	0.01	0.87		
	UBFF	221	67	278	84	0.42	4.6		
$SnBr_4$(gas)	Obs.	222(R)	59(R)	284(R)	86(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	47
	OVFF	220	64	285	82	0.63	6.6		
	UBFF	224	64	283	80	0.63	7.7		
PBr_4^+	Obs.	227(R)	72(R)	474(R)	140(R)			PBr_5(solid) – Raman – 4358 A exciting line – Hg arc	71
	OVFF	228	84	474	126	0.32	13.6		
	UBFF	234	87	471	117	1.86	18.8		

(R) Frequency obtained from Raman data. (IR) Frequency obtained from infrared data.

TABLE 5

Observed and calculated fundamental frequencies for main-family tetrahalides (cm^{-1}). IV. Iodides

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
MgI_4^{2-}	Obs.	107(R)	42(R)	259(R)	60(R)			K_2MgI_4 (melt) – Raman – frequencies < 100 cm^{-1} – 5682 A, 6471 A exciting lines; frequencies > 100 cm^{-1} 4880 A, 5145 A exciting lines	51
	OVFF	107	41	259	60	0.00	0.01		
	UBFF	107	42	259	60	0.00	0.00		
AlI_4^-	Obs.	146(R)	51(R)	336(R)	82(R)			AlI_3–CsI melt – 250°C – Raman – 5145 A, 4880 A exciting lines	16
	OVFF	146	58	337	69	0.15	14.8		
	UBFF	147	54	336	80	0.35	4.0		
GaI_4^-	Obs.	145(R)	52(R)	222(R)	73(R)			$HGaI_4$ aqueous soln. – Raman – 4358 A – Hg arc	73
	OVFF	145	50	222	74	0.01	2.5		
	UBFF	145	51	222	74	0.09	1.0		
InI_4^-	Obs.	139(R)	42(R)	185(R)	58(R)			$HInI_4$ aqueous soln. – Raman – 4358 A – Hg arc	73
	OVFF	139	42	185	58	0.00	0.00		
	UBFF	139	42	185	58	0.00	0.00		
CI_4	Obs.	178(R)	90(R)	555(R)	123(IR)			Solid CI_4; Raman: 6678 A exciting line; IR: Nujol mull	47, 72
	OVFF	177	87	555	126	0.33	2.9		
	UBFF	178	90	555	124	0.08	0.50		
SiI_4(solid)	Obs.	168(R)	63(R)	405(R)	94(R)			Solid – Raman – 4358 A – Hg arc	46
	OVFF	168	62	405	95	0.02	1.3		
	UBFF	169	65	405	92	0.25	2.6		
SiI_4(gas)	Obs.	166(R)	58(R)	405(R)	90(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting lines of Kr^+ laser	47
	OVFF	166	61	405	87	0.00	4.3		
	UBFF	167	61	405	87	0.30	4.3		

TABLE 5 (continued)

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
GeI_4(soln.)	Obs.	159(R)	60(R)	264(R)	81(R)			GeI_4 in cyclohexane soln. – Raman – 6471 A, 5682 A, 4880 A exciting lines	59, 74
	OVFF	159	57	264	83	0.03	4.3		
	UBFF	159	60	264	81	0.02	0.23		
GeI_4(gas)	Obs.	156(R)	52(R)	273(R)	77(R)			Vapor–Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting lines of Kr^+ laser	47
	OVFF	156	54	273	76	0.00	2.6		
	UBFF	157	56	272	73	0.50	6.5		
SnI_4(soln.)	Obs.	151(R)	43(R)	221(R)	63(R)			SnI_4 in cyclohexane soln. – Raman – 6471 A, 5682 A, 5145 A, 4880 A exciting lines	59
	OVFF	151	44	221	63	0.01	1.3		
	UBFF	152	46	220	60	0.52	5.7		
SnI_4(gas)	Obs.	148(R)	42(R)	210(R)	63(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting lines of Kr^+ laser	47
	OVFF	147	46	211	60	0.58	7.1		
	UBFF	149	45	209	60	0.58	6.0		

(R) Frequency obtained from Raman data.
(IR) Frequency obtained from infrared data.

TABLE 6

Observed and calculated fundamental frequencies for transition-metal tetrahalides (cm^{-1}). I. Chlorides

Compound		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$TiCl_4$(sol.)	Obs.	388(R)	120(R)	498(R)	136(R)			$TiCl_4$ in cyclohexane - Raman – 6764 A, 5682 A, 4880 A laser excitation	59, 75
	OVFF	389	106	497	144	0.24	8.7		
	UBFF	385	112	500	142	0.50	5.7		
$TiCl_4$(gas)	Obs.	389(R)	114(R)	498(R)	136			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	390	112	498	137	0.13	1.3		
	UBFF	387	109	499	140	0.36	3.7		
$TiCl_4$(solid)	Obs.	384(R)	123(R)	496(R)	136(R)			Solid – Raman at 80°K – 5145, 5280, 5682 A exciting lines	61
	OVFF	387	115	494	141	0.59	5.1		
	UBFF	381	114	498	143	0.59	6.3		
$ZrCl_4$	Obs.	377(R)	98(R)	418(R)	113(R)			Vapor – 220°C – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	379	101	419	110	0.38	2.9		
	UBFF	376	95	418	116	0.13	2.9		
$HfCl_4$	Obs.	382(R)	102(R)	390(R)	112(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	380	106	392	109	0.52	3.3		
	UBFF	382	102	390	112	0.00	0.00		
VCl_4	Obs.	385(R)	111(R)	483(R)	128(R)			VCl_4 in CCl_4 soln. – Raman – 6471 A, 5682 A, 5208 A excitations	77
	OVFF	386	109	483	129	0.13	1.3		
	UBFF	383	104	485	134	0.46	5.5		
$MnCl_4^{2-}$	Obs.	255(R)	78(R)	284(IR)	117(IR)			$[(C_2H_5)_4N]_2MnCl_4$(solid); Raman: He–Ne exciting line; IR: $[(CH_3)_4N]_2MnCl_4$ – Nujol mull	78
	OVFF	254	85	285	112	0.28	6.5		
	UBFF	257	84	283	110	0.45	6.5		

TABLE 6 (continued)

Compound		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$FeCl_4^{2-}$	Obs.	266(R)	82(IR)	286(IR)	119(IR)			$[(C_2H_5)_4N]_2FeCl_4$ – Raman – He–Ne exciting line	78
	OVFF	265	88	287	115	0.19	4.9		
	UBFF	267	86	286	115	0.29	3.6		
$FeCl_4^-$	Obs.	330(R)	114(R)	378(R)	136(R)			$[(C_2H_5)_4N]_2FeCl_4$(solid) – Raman – He–Ne laser	78
	OVFF	331	107	378	140	0.19	4.9		
	UBFF	329	109	379	140	0.29	3.6		
$CuCl_4^{2-}$	Obs.	297(R)	104(R)	252(R)	135(R)			Cs_2CuCl_4(single crystal) – Raman – 6328 A exciting line	79
	OVFF	295	111	254	131	0.75	4.6		
	UBFF	297	105	252	134	0.03	0.53		
$ZnCl_4^{2-}$	Obs.	275(R)	79(R)	306(R)	104(R)			Aqueous solution – $ZnCl_2$ + HCl Raman – Hg arc – 4358 A	78, 80
	OVFF	275	81	306	103	0.08	1.5		
	UBFF	275	80	306	103	0.06	0.89		
$CdCl_4^{2-}$ (soln.)	Obs.	259(R)	91(R)	282(IR/R)	98(IR)			ν_1, ν_2: Raman of aqueous and TBP solutions respectively; ν_3: Raman, IR of TBP solution – 5461, 4359 A lines; ν_4: IR – Nujol mull	81
	OVFF	260	84	281	103	0.25	6.4		
	UBFF	259	90	282	100	0.15	1.6		
$CdCl_4^{2-}$ (solid)	Obs.	265(R)	104 [a]	250(R)	104(R)			$(NEt_4)_2CdCl_4$(solid) – Raman – He–Ne gas laser	82
	OVFF	266	103	250	105	0.39	0.96		
	UBFF	264	95	251	111	0.39	7.7		
$HgCl_4^{2-}$	Obs.	267(R)	180(R)	276(R)	192(R)			$HgCl_2$ + KCl(melt) – Raman – 5461, 4358 A exciting lines	83
	OVFF	266	172	276	199	0.02	0.55		
	UBFF	269	187	274	183	0.23	2.9		

[a] Broad absorption including ν_4 and ν_2.

(R) Frequency obtained from Raman data. (IR) Frequency obtained from infrared data.

TABLE 7

Observed and calculated fundamental frequencies for transition-metal tetrahalides (cm^{-1}). II. Bromides

Compound		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$TiBr_4$ (soln.)	Obs.	231(R)	74(R)	389(R)	90(R)			$TiBr_4$ in cyclohexane – Raman – 5682 A, 5145 A, 4880 A, 6764 A, 6471 A exciting lines	59
	OVFF	231	64	389	95	0.00	9.5		
	UBFF	230	69	390	93	0.33	5.0		
$TiBr_4$(gas)	Obs.	232(R)	69(R)	393(R)	88(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	233	66	393	90	0.22	3.3		
	UBFF	231	67	394	90	0.34	2.6		
$ZrBr_4$	Obs.	226(R)	60(R)	315(R)	72(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	227	58	315	73	0.22	2.4		
	UBFF	225	58	316	74	0.38	3.1		
$HfBr_4$	Obs.	236(R)	63(R)	273(R)	71(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	236	63	273	71	0.00	0.00		
	UBFF	235	60	274	73	0.39	3.8		
$MnBr_4^{2-}$	Obs.	195(R)	65(R)	226(R)	81(R)			$[(C_4H_9)_4N]_2MnBr_4$ in $CHCl_3$ solution – Raman – 5876 A He laser exciting line	84
	OVFF	196	61	226	83	0.26	3.9		
	UBFF	194	55	226	87	0.26	10.2		
$ZnBr_4^{2-}$	Obs.	172(R)	66(R)	208(R)	88(R)			$ZnBr_2$ + HBr – aqueous soln. – Raman – He–Ne laser exciting line	78, 80
	OVFF	172	63	208	90	0.00	3.5		
	UBFF	171	63	208	90	0.29	3.5		
$CdBr_4^{2-}$	Obs.	166(R)	53(R)	183(R)	62(R)			$CdBr_2$ + KBr – aqueous soln. – Raman – 4358 A, 5461 A – Hg arc	68, 86
	OVFF	167	50	183	64	0.30	4.4		
	UBFF	165	48	184	66	0.58	7.9		

(R) Frequency obtained from Raman data.

TABLE 8

Observed and calculated fundamental frequencies for transition-metal tetrahalides (cm^{-1}). III. Iodides

Compound		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
TiI_4(soln.)	Obs.	162(R)	51(R)	323(R)	67(R)			TiI_4 in cyclohexane – Raman – 6471 A, 5682 A, 5145 A, 4880 A exciting lines	59
	OVFF	161	49	323	68	0.30	2.7		
	UBFF	161	49	323	69	0.30	3.5		
TiI_4(solid)	Obs.	162(R)	51(R)	322(IR)	67(IR)			Solid; Raman: 6471, 6764 A exciting lines; IR: paraffin wax disc	76, 87
	OVFF	162	49	322	68	0.00	0.27		
	UBFF	161	49	322	69	0.30	0.35		
ZrI_4	Obs.	158(R)	43(R)	254(R)	55(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	159	42	254	56	0.32	2.1		
	UBFF	158	42	254	56	0.00	2.1		
HfI_4	Obs.	158(R)	55(R)	224(R)	63(R)			Vapor – Raman – 4880 A, 5145 A exciting lines of Ar^+ laser and 6471 A exciting line of Kr^+ laser	76
	OVFF	159	49	223	67	0.52	8.8		
	UBFF	158	55	224	63	0.00	0.00		
MnI_4^{2-}	Obs.	116(R)	44(R)	190(IR)	56(R)			ν_1: $[(C_4H_9)_4N]_2MnI_4$ in $CHCl_3$ – Raman – 5676 A; ν_2: Raman – 6678 A; ν_4: $[(C_4H_9)_4N]_2MnI_4$ (solid) – Raman – 6678 A; ν_3: $[(C_2H_5)_4N]_2MnI_4$ – Nujol mull	84
	OVFF	116	39	190	59	0.00	8.4		
	UBFF	115	40	190	59	0.43	7.2		
ZnI_4^{2-}	Obs.	122(R)	44(R)	170(R)	62(R)			$ZnI + I^-$ – aqueous soln. – Raman – 5460 A exciting line of Hg	78, 85
	OVFF	122	43	170	63	0.00	1.9		
	UBFF	122	42	170	64	0.00	3.9		
CdI_4^{2-}	Obs.	117(R)	36(R)	145(R)	44(R)			$CdI + I^-$ – aqueous soln. – Raman – 5460 A exciting line of Hg	86
	OVFF	117	33	145	45	0.00	5.3		
	UBFF	116	32	146	47	0.77	9.0		

(R) Frequency obtained from Raman data. (IR) Frequency obtained from infrared data.

TABLE 9

Observed and calculated fundamental frequencies for main-family anions MO_4^{n} (cm^{-1})

Anion		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
SiO_4^{4-}	Obs.	819	340	956	527				88
	OVFF	820	373	956	493	0.09	8.1		
	UBFF	834	386	946	461	1.5	13.00		
PO_4^{3-}	Obs.	938(R)	420(R)	1017(IR)	567(IR)			Na_3PO_4 in NaOH soln. – IR;	88, 89
	OVFF	938	428	1017	560	0.01	1.6	Raman: 4358 A – Hg arc	
	UBFF	946	448	1012	534	0.67	6.3		
AsO_4^{3-}	Obs.	837	349	878	463				88
	OVFF	836	371	879	441	0.12	5.6		
	UBFF	848	389	869	402	1.2	12.3		
SO_4^{2-}	Obs.	983	450	1105	611				88, 89
	OVFF	983	462	1105	601	0.02	2.1		
	UBFF	994	486	1098	566	0.89	7.6		
SeO_4^{2-}	Obs.	833	335	875	432				88
	OVFF	832	352	876	416	0.11	4.4		
	UBFF	843	370	866	380	1.1	11.2		
TeO_4^{2-}	Obs.	647	298[a]	624	357				88
	OVFF	646	309	625	346	0.17	3.4		
	UBFF	652	325	620	317	0.76	10.1		
ClO_4^-(soln.)	Obs.	928(R)	459(R)	1119(R)	625(R)			$HClO_4$(aqueous soln.) –	88, 90
	OVFF	930	476	1118	608	0.11	3.3	Raman – 4358 A – Hg arc	
	UBFF	945	506	1107	559	1.4	10.4		
ClO_4^-(melt)	Obs.	954(R)	462(R)	1118(R)	633(R)			$LiNO_3$–$LiClO_4$ melt – 350°C –	91
	OVFF	952	489	1120	606	0.20	4.0	Raman – 4880 A exciting line	
	UBFF	970	509	1107	569	1.3	10.2	of Ar^+ laser	

TABLE 9 (continued)

Anion		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
BrO_4^-	Obs.	798	331	883	410			3 *M* $HBrO_4$ aqueous soln. and $KBrO_4$(solid) – Raman – He–Ne source	92
	OVFF	798	340	883	402	0.02	2.4		
	UBFF	809	363	873	363	1.2	10.7		
IO_4^-	Obs.	791	268	851	306			$NaIO_4$(aqueous soln.)	93
	OVFF	791	270	852	305	0.05	0.53		
	UBFF	799	290	843	275	0.98	9.2		

[a] Calculated.

(R) Frequency obtained from Raman data.

(IR) Frequency obtained from infrared data.

TABLE 10

Observed and calculated frequencies for transition-metal oxyanions MO_4^{n} (cm^{-1})

Anion		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
TiO_4^{4-}	Obs.	761(R)	306(R)[a]	770(IR)	371(IR)			Infrared of solid Ba_2TiO_4 – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown, and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
	OVFF	757	318	773	362	0.45	3.4		
	UBFF	763	316	768	360	0.25	3.1		
ZrO_4^{4-}	Obs.	792(R)	332(R)	846(IR)[a]	387(IR)			Li_4ZrO_4 (solid) (details as for TiO_4^{4-}, above)	33
	OVFF	791	336	847	384	0.12	1.0		
	UBFF	800	356	834	354	1.2	7.9		
HfO_4^{4-}	Obs.	796(R)	325(R)	800(IR)	379(IR)[a]			Li_4HfO_4 (solid) (details as for TiO_4^{4-}, above)	33
	OVFF	791	340	804	365	0.75	4.2		
	UBFF	804	354	793	332	0.93	10.7		
VO_4^{3-}	Obs.	827(R)	340[b]	780(R)	340(R)			K_3VO_4(aqueous soln.) – Raman – no reference to exciting line	22
	OVFF	834	307	775	360	0.75	7.7		
	UBFF	824	314	782	363	0.34	7.2		
VO_4^{4-}	Obs.	818(R)	319(R)	780(IR)[a]	368(IR)			Infrared of solid Ba_2VO_4 – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown, and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
	OVFF	812	333	784	358	0.60	3.1		
	UBFF	818	319	780	368	0.00	0.00		
CrO_4^{2-} (aqueous soln.)	Obs.	847(R)	348(R)	884(R)	368(R)			K_2CrO_4 (aqueous soln.) – Raman – 5876 A exciting line – He–Ne laser	22, 33, 94, 95
	OVFF	850	317	882	387	0.30	7.1		
	UBFF	845	339	886	376	0.22	2.4		

TABLE 10 (continued)

Anion		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
CrO_4^{2-} (melt)	Obs.	840(R)	348(R)	880(R)	378(R)			K_2CrO_4 in molten LiF–NaF–KF– Raman – 6328 A – He–Ne laser	96
	OVFF	843	338	878	385	0.30	2.3		
	UBFF	839	345	881	381	0.12	0.83		
CrO_4^{3-}	Obs.	834(R)	260(R)	860(R)	324(R)			Infrared of solid – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
	OVFF	825	280	867	307	0.56	6.5		
	UBFF	837	270	858	312	0.30	3.8		
CrO_4^{4-}	Obs.	806(R)	353(R)	855(IR)	404(R)			Ba_2CrO_4 (details as for CrO_4^{3-}, above)	33
	OVFF	807	349	854	407	0.12	0.93		
	UBFF	808	361	853	395	0.24	2.2		
MoO_4^{2-}	Obs.	897(R)	318 [b]	841(R)	318(R)			Na_2MoO_4(aqueous soln.) – Raman – 4358 A – Hg arc	33,98 [c]
	OVFF	901	302	838	329	0.40	4.1		
	UBFF	895	309	842	328	0.15	3.0		
MoO_4^{4-}	Obs.	792(R)	328(R)	808(IR)	373(IR) [a]			Infrared of solid Ba_2MoO_4 – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown, and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
	OVFF	790	333	809	369	1.1	1.3		
	UBFF	797	347	804	349	0.56	6.1		
WO_4^{2-}	Obs.	931(R)	324 [b]	833(R)	324(R)			Na_2WO_4(aqueous soln.) – . Raman – 4358 A – Hg arc	33, 98
	OVFF	932	322	832	326	0.11	0.62		
	UBFF	931	325	833	322	0.00	0.46		

WO_4^{4-}	Obs.	821(R)	323(R)	840(IR)	367(IR)			Infrared of solid Ba_2WO_4 – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
	OVFF	818	332	843	358	0.36	1.4		
	UBFF	829	350	832	325	0.96	9.9		
MnO_4^-	Obs.	838(R)	355(R)	921(R)	429(R)			$KMnO_4$(aqueous soln.) – Raman – He–Ne laser exciting lines	22, 33, 95
	OVFF	838	351	921	432	0.00	0.49		
	UBFF	845	377	916	402	0.69	6.3		
MnO_4^{2-}	Obs.	810(IR)	328^b	862(IR)	328(IR)			K_2MnO_4(solid) – IR – Nujol mull	22
	OVFF	814	288	859	351	0.42	9.6		
	UBFF	806	314	865	341	0.42	4.2		
MnO_4^{3-}	Obs.	863(IR)	348^b	770(IR)	348(IR)			Na_3MnO_4(solid) – IR – Nujol mull	22
	OVFF	870	322	764	362	0.80	5.8		
	UBFF	862	321	770	370	0.05	7.1		
TcO_4^-	Obs.	912(R)	$(347)^d$	912(R)	325(R)			NH_4TcO_4(aqueous soln.) – Raman – 4358 A – Hg arc	100, 101
	OVFF	917	310	907	348	0.55	9.0		
	UBFF	908	333	915	339	0.37	4.2		
ReO_4^- (aqueous soln.)	Obs.	971(R)	332^b	916(R)	332(R)			$KReO_4$(aqueous soln.) – Raman – 4358 A – Hg arc	22, 33
	OVFF	973	324	914	339	0.18	2.2		
	UBFF	972	325	915	328	0.07	1.1		
ReO_4^- (solid)	Obs.	952(R)	334(R)	925(R)	374(R)			$NaReO_4$(single crystal) – Raman – 77°K – 5145 A – Ar^+ laser	99
	OVFF	945	350	931	359	0.69	4.4		
	UBFF	958	356	920	342	0.48	7.6		
ReO_4^{3-}	Obs.	808(R)	264(R)	853(IR)	319(IR)			Infrared of solid – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown, and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
	OVFF	804	276	857	307	0.49	3.4		
	UBFF	820	293	842	270	1.4	13.7		

TABLE 10 (continued)

Anion		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
FeO_4^-	Obs.	912(R)	325^b	912(R)	325(R)			$KFeO_4$(aqueous soln.) – Raman – 4358 A – Hg arc	22
	OVFF	918	294	908	343	0.55	7.6		
	UBFF	907	302	916	345	0.46	6.7		
FeO_4^{2-}	Obs.	778(IR)	320^b	800(IR)	320(IR)			K_2FeO_4(solid) – IR – Nujol mull	22
	OVFF	784	301	795	331	0.56	4.7		
	UBFF	774	304	803	335	0.45	5.0		
FeO_4^{3-}	Obs.	776(R)	265(R)	805(IR)	335(IR)			Infrared of solid – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown and purple solids, 5648 A for chromate, 5145 A for blue and colorless solids)	33
	OVFF	769	283	810	319	0.75	5.8		
	UBFF	780	281	802	315	0.44	6.0		
FeO_4^{4-}	Obs.	762(R)	257(R)	857(IR)	314(IR)			Ba_2FeO_4 (details as for FeO_4^{3-}, above)	33
	OVFF	761	261	858	310	0.12	1.4		
	UBFF	768	274	852	293	0.68	5.9		
RuO_4^-	Obs.	826(IR)	282^b	848(IR)	282(IR)			$KRuO_4$(solid) – IR – Nujol mull	22, 97
	OVFF	830	273	845	288	0.36	2.6		
	UBFF	826	281	848	284	0.00	0.53		
RuO_4^{2-} (K salt)	Obs.	808(R)	323^b	790(R)	323(R)			K_2RuO_4(solid) – Raman – He–Ne laser – 6328 A exciting line	97
	OVFF	811	301	787	338	0.38	5.8		
	UBFF	807	320	791	326	0.08	0.98		
RuO_4^{2-} (aqueous soln.)	Obs.	810(R)	330^b	836(R)	330(R)			K_2RuO_4(aqueous soln.) – Raman – He–Ne laser – 6328 A exciting line	22, 97
	OVFF	812	304	834	348	0.27	6.7		
	UBFF	810	331	836	329	0.04	0.4		
RuO_4^{2-} (Ba salt)	Obs.	811(R)	335(R)	840(R)	330(R)			$BaRuO_4$(solid) – Raman – He–Ne laser – 6328 A exciting line	97
	OVFF	814	305	838	350	0.30	14.5		
	UBFF	811	335	840	331	0.00	0.15		

	Obs.	883(R)	338(R)	918(R)	332(R)			Liquid – He–Ne laser exciting line	98
RuO_4(liq.)	OVFF	886	308	915	352	0.33	7.5		
	UBFF	883	337	918	334	0.00	0.45		
	Obs.	878(R)	332(R)	921(R)	328(R)			Solid – Ne–He laser exciting line	102
RuO_4(solid)	OVFF	881	303	919	348	0.28	7.4		
	UBFF	878	332	921	328	0.00	0.00		
	Obs.	965(R)	333(R)	960(R)	323(R)			Vapor – Raman – 5145 A, 6328 A exciting lines	103
OsO_4(gas)	OVFF	968	325	951	329	0.31	2.1		
	UBFF	966	337	959	319	0.10	0.12		
	Obs.	965(R)	338(R)	954(R)	335(R)			Liquid – Raman – 4358 A – Hg arc; also 4046 A, 5461 A used	22, 24, 97
OsO_4(liq.)	OVFF	966	323	951	346	0.22	3.9		
	UBFF	966	344	951	326	0.22	2.3		
	Obs.	961(R)	340(R)	951(R)	327(R)			Solid – Raman – 4358 A, 5461 A, 5790 A exciting lines – Cary 81	102
OsO_4(solid)	OVFF	964	319	948	342	0.31	5.4		
	UBFF	962	342	950	324	0.11	0.75		
	Obs.	790(R)	300(R)[a]	855(IR)	340(IR)			Infrared of solid Ba_2CoO_4 – Nujol mull; Raman of solid – Cary 81 with Ar–Kr laser (6471 A for red, brown and purple solids, 5648 A for chromate, 5145 A for green solids, 4880 A for blue and colorless solids)	33
CoO_4^{4-}	OVFF	791	297	854	342	0.25	1.9		
	UBFF	793	308	853	330	0.12	1.2		

---

[a] Average of two bands.

[b] Broad absorption including ν_4 and ν_2.

[c] Recent assignments based on the isotopic shift technique have appeared recently for the MoO_4^{2-} ion (see ref. 112).

[d] Estimated.

(R) Frequency obtained from Raman data.

(IR) Frequency obtained from infrared data.

TABLE 11

Observed and calculated fundamental frequencies for transition-metal anions MS_4^{n} (cm^{-1})

Compound		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
VS_4^{3-}	Obs.	404(IR)	200[a]	470(IR)	200(IR)			$(NH_4)_3VS_4$ – IR – Nujol mull	104, 106
	OVFF	405	163	470	218	0.13	13.6		
	UBFF	399	179	473	215	1.02	9.1		
NbS_4^{3-}	Obs.	408(R)	163[a]	421(IR)	163(IR/R)[b]			Tl_3NbS_4 – IR Nujol mull; Raman – He–Ne exciting line	105
	OVFF	411	154	419	168	0.61	4.3		
	UBFF	405	151	423	173	0.61	6.8		
TaS_4^{3-}	Obs.	424(R)	170[a]	399(IR/R)[b]	170(IR/R)[b]			Tl_3TaS_4 – IR – Nujol mull; Raman – He–Ne laser exciting line	105
	OVFF	425	169	399	171	0.12	0.58		
	UBFF	423	166	400	174	0.24	2.4		
MoS_4^{2-}	Obs.	460(IR)	195[a]	480(IR)	195(IR)			Cs_2MoS_4 – IR – Nujol mull	104–106[c]
	OVFF	464	181	477	203	0.75	3.6		
	UBFF	457	183	482	206	0.53	5.8		
WS_4^{2-}	Obs.	485(R)	185[a]	465(R)	185(R)			Cs_2WS_4 – Raman – laser excitation line not specified	104–106
	OVFF	486	183	464	186	0.21	0.81		
	UBFF	484	181	466	190	0.21	2.5		
ReS_4^{-}	Obs.	501(R)	200[a]	486(IR)[d]	200(IR)			$(C_6H_5)_4PReS_4$ – Raman – exciting line not mentioned; $(C_6H_5)_4PReS_4$ and $(CH_3)_4NReS_4$ – IR – Nujol mull	105
	OVFF	503	196	485	203	0.30	1.8		
	UBFF	500	197	487	204	0.20	1.8		

[a] Broad absorption including ν_4 and ν_2.
[b] Average of Raman and IR measurements.
[c] Recent assignments based on the isotopic shift technique have appeared recently for the MoS_4^{2-} ion (see Ref. 66).
[d] Average of IR runs.

TABLE 12

Observed and calculated fundamental frequencies for transition-metal anions MSe_4^{n} (cm^{-1})

Compound		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
VSe_4^{3-}	Obs.	232[a]	121[b]	365(IR)	121(IR)			Tl_3VSe_4 – Nujol mull	105
	OVFF	234	98	364	132	0.56	14.1		
	UBFF	227	104	367	133	1.3	11.5		
$NbSe_4^{3-}$	Obs.	239(R)	100[b]	316(IR)	100(IR/R)[c]			Tl_3NbSe_4 – Nujol mull; Raman – He–Ne laser exciting line	105
	OVFF	242	85	314	107	0.38	11.0		
	UBFF	236	87	318	109	0.38	11.0		
$TaSe_4^{3-}$	Obs.	249(R)	103[a]	277(IR/R)[c]	103(IR/R)[c]			Tl_3TaSe_4 – Nujol mull; Raman – He–Ne laser exciting line	105
	OVFF	252	93	275	108	0.96	7.3		
	UBFF	247	95	279	110	0.75	7.3		
$MoSe_4^{2-}$	Obs.	255(R)	120[b]	340(IR)	120(IR)			$(NH_4)_2MoSe_4$ – Nujol mull; Raman – He–Ne laser exciting line	105
	OVFF	258	100	338	130	0.88	12.5		
	UBFF	251	107	342	129	1.1	9.2		
WSe_4^{2-}	Obs.	281(R)	107[b]	309(R)	107(R)			Cs_2WSe_4 – Raman – He–Ne laser exciting line	105
	OVFF	284	99	307	112	0.86	6.1		
	UBFF	279	97	311	115	0.68	8.4		

[a] Estimated.

[b] Broad absorption including ν_4 and ν_2.

[c] Average of Raman and IR measurements.

TABLE 13

Observed and calculated frequencies for several miscellaneous tetrahedral molecules (cm^{-1})

Molecule		$A_1(\nu_1)$	$E(\nu_2)$	$F_2(\nu_3)$	$F_2(\nu_4)$	Average % deviation		Experimental details	Ref.
						ν_1, ν_3	ν_2, ν_4		
$B(OH)_4^-$	Obs.	754(R)	379(R)	947(R)	533(R)			Aqueous soln. – Raman – no exciting line reported	107
	OVFF	755	396	948	516	0.12	3.8		
	UBFF	758	337	946	522	0.32	2.1		
$Al(OH)_4^-$	Obs.	615(R)	310 [a]	720 [b]	310(R)			Aqueous soln. – Raman – 4358 A – Hg arc	108
	OVFF	616	252	720	338	0.08	13.9		
	UBFF	607	279	725	333	1.0	8.8		
$Zn(OH)_4^-$	Obs.	470(R)	300 [a]	570(R)	300(R)			Aqueous soln. – Raman – 4358 A – Hg arc	108
	OVFF	471	304	569	296	0.22	1.3		
	UBFF	467	269	571	322	0.40	8.7		
XeO_4(solid)	Obs.	767(R)	277(R)	867(R)	303(R)			XeO_4(solid) – Raman – 6328 A, 5145 A exciting lines	107
	OVFF	767	271	867	309	0.02	2.1		
	UBFF	777	300	858	270	1.2	9.3		
XeO_4(gas)	Obs.	776(R)	267 [b]	879(IR)	306(IR)			Raman – 5145 A exciting line of Ar^+ laser; IR of vapor	110
	OVFF	777	262	878	310	0.12	0.17		
	UBFF	788	294	867	265	1.5	11.3		
UF_4	Obs.	614(R)	340(R)	420(IR)	180(IR)			UF_4(solid) – CsI pellet – IR; Raman – 6328 A exciting line	109
	OVFF	608	336	431	179	1.8	0.85		
	UBFF	608	338	430	180	1.7	0.51		
AsS_4^{3-}	Obs.	386(R)	171(R)	419(R)	216(R)			Raman – solution – no details on exciting line	90, 106
	OVFF	386	169	419	217	0.01	0.29		
	UBFF	388	179	417	206	0.49	4.6		
SbS_4^{3-}	Obs.	366(R)	156(R)	380(R)	178(R)			Raman – solution – no details on exciting line	90, 106
	OVFF	366	151	380	182	0.09	2.9		
	UBFF	367	161	379	173	0.29	3.1		

[a] Broad absorption including ν_4 and ν_2.
[b] Calculated.

is preferred. In five cases the two fields are either equal or one gives a better fit with the ν_1, ν_3 vibrations while the other is better for the ν_2, ν_4 vibration.

(e) Transition-metal thio- and seleno-anions (MS_4^n, MSe_4^n)

Tables 11 and 12 list the computer results for the OVFF and UBFF for six thio-anions (MS_4^n) and five seleno-anions (MSe_4^n). In three out of six cases for the thio-anions the OVFF is slightly preferred, while in the five cases involving the seleno-anions the fields are essentially equivalent.

(f) Miscellaneous tetrahedral molecules

Table 13 compiles the data for several other tetrahedral molecules.

(g) Summary

A number of difficulties in making a choice of force fields for tetrahedral molecules exist. Several approximations had to be made for both the UBFF and the OVFF to ensure that the number of force constants would be less than the frequencies observed. No anharmonicity corrections were made, and a good deal of the spectroscopic data were obtained for solids, where local perturbations become more important. Added to this is the complication that certain structures distorted from T_d are possible. Recent publications[18,19] indicate that in the A_2MCl_4 series (A = Cs and M = Fe, Co, Cu and Zn), distorted MCl_4^{2-} tetrahedra are known to exist. The extent of distortion varies, but is greatest for the copper complex. Similarly, doubt has been raised concerning the tetrahedral species MgX_4^{2-} in the melt[20]. Recent molecular dynamics calculations have indicated that the predominant structure is trigonal $MgCl_3^-$.

It is to be noted that except for the main-family oxyanions, only small differences existed between the results obtained from the OVFF and UBFF for tetrahedral molecules. For the main-family oxy-anions the OVFF is definitely superior to the UBFF. Heath and Linnett[21] made similar observations for these anions when they compared the OVFF with a simple valence force field.

Several force fields have previously been applied to some transition-metal oxyanions. These include the GVFF, UBFF, OVFF and a modified valence force field (MVFF)[1,22-26]. Since most of the results obtained for these anions relate to solids, there is some serious question as to the possibility of finding a force field that can adequately explain the forces involved. Krebs and Müller[26] have indicated that the interactions between non-bonded atoms cannot be explained by van der Waals forces alone, and that Coulombic forces must be taken into account. In this work, the UBFF does appear to demonstrate some advantage over the OVFF, except for the highly charged (–4) anions, where the OVFF seems to be preferred in six out of nine cases.

A comparison of force fields may prove to be helpful for assignment purposes. The case of $TlCl_4^-$ may be cited. In the original assignments[32] the 78 cm^{-1} absorption was assigned as ν_2 and the lowest absorption at 60 cm^{-1} was assigned as ν_4. When the computations are made based on these assignments, the UBFF gives extremely poor fits, and only the OVFF gives a reasonable fit. If one reverses the assignments, excellent results are obtained from both force fields. It appears then that ν_4 should be assigned at 78 cm^{-1} and ν_2 at 60 cm^{-1}. This is reasonable since for most main-family tetrahalides of T_d symmetry reported in this paper, the value of ν_4 is greater than ν_2, in agreement with conclusions reached by others[26,30,33].

(ii) Discussion of force constants

Various correlations between vibrational frequencies and the properties of molecules have been made[26-30]. It would be of more significance to use fundamental quantities such as force constants rather than vibrational frequencies in making such correlations. In this paper we make such correlations of the primary stretching force constant with the oxidation of the central atom and with the atomic number of M and X in $MX_4{}^n$-type molecules. This approach can be justified on two counts — no orderly trends are observed for the frequencies of many of these molecules and the primary stretching force constants as calculated from three different force fields (K in the OVFF and UBFF and f_r in the GVFF), appear to give similar trends for all fields. The smaller magnitude of the other force constants (H and F in the OVFF, D and F in the UBFF and f_{rr}, f_α and $f_{\alpha\alpha}$ in the GVFF) prevents one from making any additional meaningful comparisons.

The difficulties which present themselves in the case of tetrahedral molecules have been discussed in a previous section. Additional problems may be cited. For example, in some cases ν_2 is assumed to be equal to ν_4, since a broad absorption is found experimentally and both absorptions are considered to be coincidental. Alternatively, one of these absorptions may be so weak in intensity that it cannot be observed. Coupling of the low-frequency modes with lattice vibrations is an added complication in the solid state[31]. These difficulties contribute to the uncertainty of the force constants for T_d molecules. However, the values obtained for the primary stretching force constant appear to be reasonable in most cases, and, where comparisons are possible, agree with results obtained by other workers. Certainly the force constants would have more significance if corollary data, such as isotope shifts, Coriolis coupling constants and centrifugal distortions, could be used. In most cases, such additional data are either not available or in the case of solids and liquids impossible to obtain.

(a) Trends

The relationship between the primary stretching force constant with the physical properties in $MX_4{}^n$-type molecules has been previously cited[34-37]. However, most of the previous comparisons have been based on a limited number of data. Some of these relationships have now been substantiated using the large body of results reported in this paper. In addition, some new trends are suggested.

1. Oxidation state. The primary stretching force constants involving the MX stretch (K in the OVFF and UBFF, and f_r in the GVFF) are observed to be sensitive to the oxidation

TABLE 14

Force constants for main-family tetrahalides. I. Fluorides.
All force constants in this paper are in the units mdyne/A. An asterisk after the formula of a compound in the tables means that there is one or more additional entry for that compound.

Force field	IIA	IIIA	IVA	IVB
	BeF_4^{2-}	BF_4^- *(solid)*	CF_4	
OVFF	1.42, 0.31, 0.48	2.39, 0.27, 1.06	4.39, 0.84, 1.27	
UBFF	1.40, 0.08, 0.50	2.46, 0.10, 1.06	4.59, 0.33, 1.21	
GVFF	Diverges	Diverges	Diverges	
			SiF_4	
OVFF			5.86, 0.50, 0.33	
UBFF			5.83, 0.17, 0.38	
GVFF			7.11, 2.39, 0.46, 0.10	
			GeF_4	TiF_4 *(gas)*
OVFF			5.11, 0.24, 0.24	4.44, 0.07, 0.30
UBFF			5.03, 0.07, 0.29	4.44, 0.01, 0.30
GVFF			5.45, 0.22, 0.25, 0.05	4.81, 0.29, 0.15, 0.01
		BF_4^- *(melt)*		
OVFF		2.98, 0.62, 0.94		
UBFF		2.95, 0.16, 0.98		
GVFF		Diverges		

TABLE 14 (continued). II. Chlorides

Force field	IIA	IIIA	IVA	VA
		BCl_4^-	CCl_4^* *(liq.)*	
OVFF		1.32, 0.24, 1.63	1.79, 0.27, 0.65	
UBFF		1.26, 0.05, 0.54	1.87, 0.11, 0.64	
GVFF		Diverges	Diverges	
	$MgCl_4^{2-}$	$AlCl_4^-$	$SiCl_4^*$ *(liq.)*	PCl_4^+
OVFF	0.68, 0.06, 0.16	1.64, 0.08, 0.23	2.71, 0.20, 0.26	3.19, 0.31, 0.30
UBFF	0.67, 0.01, 0.16	1.65, 0.03, 0.24	2.72, 0.08, 0.27	3.22, 0.12, 0.31
GVFF	Diverges	1.70, 0.29, 0.20, 0.05	2.81, 0.31, 0.27, 0.06	3.29, 0.36, 0.36, 0.08
		$GaCl_4^-$	$GeCl_4^*$ *(liq.)*	$AsCl_4^+$
OVFF		1.73, 0.06, 0.19	2.43, 0.14, 0.21	3.01, 0.26, 0.18
UBFF		1.72, 0.02, 0.20	2.43, 0.05, 0.22	3.02, 0.11, 0.18
GVFF		1.94, 0.19, 0.14, 0.12	2.63, 0.22, 0.09, –0.02	3.22, 0.17, 0.22, 0.02

TABLE 14 (continued) II. Chlorides

Force field	IIA	IIIA	IVA	VA
		$InCl_4^-$	$SnCl_4^*$ *(liq.)*	$SbCl_4^+$
OVFF		1.54, 0.02, 0.14	2.33, 0.12, 0.11	2.29, 0.27, 0.08
UBFF		1.57, 0.00, 0.15	2.30, 0.04, 0.14	2.30, 0.12, 0.08
GVFF		1.77, 0.13, 0.08, 0.02	2.48, 0.10, 0.12, 0.02	2.40, 0.07, 0.16, 0.01
		$TlCl_4^-$	$PbCl_4^*$ *(liq.)*	
OVFF		1.39, −0.07, 0.15	1.99, 0.07, 0.06	
UBFF		1.33, −0.04, 0.18	2.01, 0.04, 0.05	
GVFF		1.62, 0.14, 0.05, 0.11	2.09, 0.05, 0.06, 0.003	
			CCl_4^* *(solid)*	
OVFF			1.97, 0.42, 0.60	
UBFF			1.95, 0.12, 0.61	
GVFF			Diverges	
			CCl_4^* *(gas)*	
OVFF			2.02, 0.39, 0.60	
UBFF			2.00, 0.11, 0.62	
GVFF			Diverges	
			$SiCl_4^*$ *(gas)*	
OVFF			2.71, 0.24, 0.25	
UBFF			2.69, 0.07, 0.28	
GVFF			2.70, 0.32, 0.24, 0.06	
			$SiCl_4^*$ *(solid)*	
OVFF			2.64, 0.26, 0.25	
UBFF			2.64, 0.08, 0.27	
GVFF			2.72, 0.32, 0.27, 0.06	
			$GeCl_4^*$ *(gas)*	
OVFF			2.55, 0.18, 0.17	
UBFF			2.49, 0.05, 0.21	
GVFF			2.72, 0.19, 0.18, 0.04	
			$GeCl_4^*$ *(solid)*	
OVFF			2.50, 0.21, 0.17	
UBFF			2.48, 0.06, 0.19	
GVFF			2.68, 0.17, 0.18, 0.03	
			$SnCl_4^*$ *(gas)*	
OVFF			2.45, 0.13, 0.84	
UBFF			2.36, −0.02, 0.13	
GVFF			2.55, 0.10, 0.11, 0.02	

TABLE 14 (continued) II. Chlorides

Force field	IIA	IIIA	IVA	VA
			$SnCl_4^*$ *(solid)*	
OVFF			2.37, 0.15, 0.09	
UBFF			2.34, 0.05, 0.11	
GVFF			2.50, 0.09, 0.11, 0.02	
			$PbCl_4^*$ *(solid)*	
OVFF			2.01, 0.16, 0.04	
UBFF			1.91, 0.04, 0.09	
GVFF			2.06, 0.05, 0.10, 0.02	

TABLE 14 (continued) III. Bromides

Force field	IIA	IIIA	IVA	VA
		BBr_4^-	CBr_4	
OVFF		1.04, 0.14, 0.43	1.49, 0.20, 0.47	
UBFF		1.09, 0.06, 0.42	1.57, 0.08, 0.46	
GVFF		Diverges	Diverges	
	$MgBr_4^{2-}$	$AlBr_4^-$	$SiBr_4^*$ *(liq.)*	PBr_4^+
OVFF	0.62, 0.07, 0.11	1.36, 0.06, 0.20	2.02, 0.14, 0.22	2.04, 0.22, 0.10
UBFF	0.62, 0.02, 0.11	1.37, 0.02, 0.20	2.05, 0.06, 0.23	2.10, 0.08, 0.12
GVFF	Diverges	1.25, 0.30, 0.21, 0.06	1.96, 0.32, 0.24, 0.06	1.86, 0.19, 0.36, 0.09
		$GaBr_4^-$	$GeBr_4^*$ *(liq.)*	
OVFF		1.32, 0.03, 0.19	1.88, 0.10, 0.18	
UBFF		1.33, 0.01, 0.19	1.89, 0.04, 0.18	
GVFF		1.43, 0.22, 0.13, 0.03	1.99, 0.20, 0.15, 0.03	
		$InBr_4^-$	$SnBr_4^*$ *(liq.)*	
OVFF		1.33, 0.02, 0.12	1.84, 0.08, 0.11	
UBFF		1.32, 0.01, 0.13	1.83, 0.03, 0.12	
GVFF		1.44, 0.13, 0.08, 0.02	1.94, 0.11, 0.10, 0.02	
		$TlBr_4^-$		
OVFF		1.29, 0.01, 0.10		
UBFF		1.28, 0.003, 0.11		
GVFF		1.42, 0.01, 0.06, 0.01		

TABLE 14 (continued) III. Bromides

Force field	IIA	IIIA	IVA	VA
			$SiBr_4^*$ *(gas)*	
OVFF			2.11, 0.20, 0.18	
UBFF			2.13, 0.06, 0.18	
GVFF			2.05, 0.27, 0.22, 0.05	
			$GeBr_4^*$ *(gas)*	
OVFF			1.97, 0.14, 0.15	
UBFF			1.96, 0.03, 0.18	
GVFF			2.05, 0.19, 0.15, 0.03	
			$SnBr_4$ *(gas)*	
OVFF			1.94, 0.10, 0.08	
UBFF			1.90, 0.02, 0.11	
GVFF			2.01, 0.10, 0.09, 0.02	

TABLE 14 (continued) IV. Iodides

Force field	IIA	IIIA	IVA	VA
			CI_4	
OVFF			0.94, 0.18, 0.35	
UBFF			1.01, 0.08, 0.34	
GVFF			Diverges	
	MgI_4^{2-}	AlI_4^-	SiI_4^* *(solid)*	
OVFF	0.54, 0.05, 0.08	1.08, 0.17, 0.08	1.48, 0.11, 0.16	
UBFF	0.54, 0.01, 0.08	1.02, 0.02, 0.15	1.50, 0.05, 0.16	
GVFF	Diverges	Diverges	1.40, 0.24, 0.18, 0.04	
		GaI_4^-	GeI_4^* *(soln.)*	
OVFF		0.98, 0.02, 0.15	1.39, 0.10, 0.12	
UBFF		0.98, 0.01, 0.15	1.41, 0.05, 0.12	
GVFF		1.01, 0.19, 0.11, 0.02	1.92, 0.63, 0.12, 0.02	
		InI_4^-	SnI_4^* *(soln.)*	
OVFF		0.98, 0.00, 0.12	1.42, 0.07, 0.07	
UBFF		0.98, 0.00, 0.12	1.42, 0.02, 0.08	
GVFF		1.06, 0.13, 0.06, 0.01	1.47, 0.08, 0.07, 0.01	

TABLE 14 (continued) IV. Iodides

Force field	IIA	IIIA	IVA	VA
			SiI_4^* (gas)	
OVFF			1.52, 0.13, 0.13	
UBFF			1.53, 0.04, 0.14	
GVFF			1.46, 0.20, 0.16, 0.04	
			GeI_4^* (gas)	
OVFF			1.52, 0.14, 0.07	
UBFF			1.53, 0.05, 0.08	
GVFF			1.54, 0.09, 0.11, 0.02	
			SnI_4^* (gas)	
OVFF			1.30, 0.07, 0.08	
UBFF			1.28, 0.02, 0.09	
GVFF			1.34, 0.10, 0.07, 0.02	

Key to Table 14 and subsequent tables (compounds MX_4^n)

Force field	Force constants
OVFF	K, H, F
UBFF	K, D, F
GVFF	$f_r, f_{rr}, f_\alpha, f_{\alpha\alpha}$

state (or ionic charge) of the central metal atom in the various tetrahedral molecules and anions studied in this paper. Tables 14–19 list the force constants obtained from the three force fields used. For the main-family tetrahalides the primary stretching force constant is observed to increase as the oxidation state increases (Table 14). For example

$BeF_4^{2-} < BF_4^- < CF_4$
$BCl_4^- < CCl_4$
$MgCl_4^{2-} < AlCl_4^- < SiCl_4 < PCl_4^+$
$GaCl_4^- < GeCl_4 < AsCl_4^+$
$InCl_4^- < SnCl_4 \approx SbCl_4^+$
$TlCl_4^- < PbCl_4$
$BBr_4^- < CBr_4$
$MgBr_4^{2-} < AlBr_4^- < SiBr_4 < PBr_4^+$
$GaBr_4^- < GeBr_4$
$InBr_4^- < SnBr_4$
$MgI_4^{2-} < AlI_4^- < SiI_4$
$GaI_4^- < GeI_4$
$InI_4^- < SnI_4$

Although not nearly as many examples are available for the transition-group tetrahalides, the same trend prevails (e.g. the primary stretching force constant for $TiCl_4 \simeq VCl_4 >$

TABLE 15

Force constants for transition-metal tetrahalides. I. Chlorides (mdyne/A)

Force field	IVB	VB	VIB	VIIB
	$TiCl_4^{*}$ *(soln.)*	VCl_4		$MnCl_4^{2-}$
OVFF	2.50, 0.08, 0.17	2.32, 0.01, 0.19		0.84, 0.01, 0.13
UBFF	2.31, 0.03, 0.15	2.37, 0.03, 0.15		0.83, −0.002, 0.14
GVFF	2.67, 0.17, 0.11, 0.05	2.52, 0.18, 0.09, −0.01		0.95, 0.14, 0.08, 0.02
	$ZrCl_4$			
OVFF	2.32, 0.04, 0.15			
UBFF	2.31, 0.004, 0.16			
GVFF	2.05, 0.15, 0.08, 0.007			
	$HfCl_4$			
OVFF	2.41, 0.07, 0.15			
UBFF	2.37, 0.01, 0.17			
GVFF	2.63, 0.14, 0.09, 0.01			
	$TiCl_4^{*}$ *(gas)*			
OVFF	2.50, 0.08, 0.17			
UBFF	2.51, 0.03, 0.15			
GVFF	2.67, 0.17, 0.10, 0.005			
	$TiCl_4^{*}$ *(solid)*			
OVFF	2.46, 0.09, 0.16			
UBFF	2.49, 0.04, 0.13			
GVFF	2.63, 0.15, 0.10, −0.002			

TABLE 15 (continued) II. Bromides

Force field	IVB	VB	VIB	VIIB
	$TiBr_4^{*}$ *(soln.)*			$MnBr_4^{2-}$
OVFF	2.08, 0.07, 0.11			0.78, −0.11, 0.26
UBFF	2.09, 0.04, 0.10			0.77, −0.04, 0.25
GVFF	2.15, 0.12, 0.09, 0.001			0.93, 0.29, 0.09, 0.01
	$ZrBr_4$			
OVFF	2.08, 0.06, 0.09			
UBFF	2.10, 0.03, 0.07			
GVFF	2.16, 0.08, 0.06, 0.003			

VII		IB	IIB
$FeCl_4^{2-}$	$FeCl_4^-$	$CuCl_4^{2-}$	$ZnCl_4^{2-}$
0.85, −0.01, 0.15	1.50, 0.02, 0.20	0.61, −0.08, 0.30	1.07, −0.01, 0.13
0.84, −0.01, 0.16	1.51, 0.01, 0.19	0.59, −0.04, 0.31	1.06, −0.01, 0.13
1.00, 0.16, 0.09, 0.02	1.70, 0.19, 0.11, 0.01	0.92, 0.31, 0.13, 0.03	1.21, 0.12, 0.06, 0.01
			$CdCl_4^{2-}$* *(soln.)*
			1.10, 0.06, 0.08
			1.11, 0.03, 0.07
			1.21, 0.06, 0.06, 0.00
			$HgCl_4^{2-}$
			1.17, 0.53, 0.08
			1.16, 0.21, 0.09
			1.27, 0.07, 0.15, −0.04
			$CdCl_4^{2-}$* *(solid)*
			0.80, 0.03, 0.17
			0.81, 0.03, 0.16
			1.03, 0.14, 0.07, 0.00

VII	IB	IIB
		$ZnBr_4^{2-}$
		0.69, −0.01, 0.18
		0.69, 0.00, 0.17
		0.74, 0.22, 0.12, 0.03
		$CdBr_4^{2-}$
		0.75, −0.04, 0.14
		0.75, −0.01, 0.13
		0.89, 0.14, 0.05, 0.002

TABLE 15 (continued) II. Bromides

Force field	IVB	VB	VIB	VIIB
	$HfBr_4$			
OVFF	2.12, 0.05, 0.13			
UBFF	2.13, 0.01, 0.12			
GVFF	2.27, 0.12, 0.07, 0.004			
	$TiBr_4$ (gas)*			
OVFF	2.14, 0.09, 0.10			
UBFF	2.15, 0.04, 0.09			
GVFF	2.22, 0.11, 0.08, 0.04			

TABLE 15 (continued). III. Iodides

Force field	IVB	VB	VIB	VIIB
	TiI_4 (soln.)*			*MnI_4^{2-}*
OVFF	1.61, 0.08, 0.09			0.60, 0.00, 0.10
UBFF	1.60, 0.03, 0.08			0.60, 0.00, 0.10
GVFF	1.64, 0.11, 0.07, 0.004			0.63, 0.13, 0.06, 0.007
	ZrI_4			
OVFF	1.62, 0.06, 0.06			
UBFF	1.63, 0.02, 0.06			
GVFF	1.66, 0.07, 0.05, 0.003			
	HfI_4			
OVFF	1.82, 0.16, 0.002			
UBFF	1.84, 0.07, 0.006			
GVFF	1.85, 0.005, 0.08, 0.002			
	TiI_4 (soln.)*			
OVFF	1.60, 0.07, 0.09			
UBFF	1.60, 0.03, 0.09			
GVFF	1.63, 0.11, 0.07, 0.004			

VII	IB	IIB

VII	IB	IIB
		ZnI_4^{2-}
		0.55, –0.02, 0.14
		0.55, –0.01, 0.14
		0.63, 0.16, 0.06, 0.007
		CdI_4^{2-}
		0.60, -0.04, 0.11
		0.60, –0.01, 0.10
		0.68, 0.11, 0.04, 0.002

TABLE 16

Force constants for main-family oxygenated tetrahedral anions (mdyne/A)

Force field	IVA	VA	VIA	VIIA
	SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^{-*} (soln.)
OVFF	4.30, 0.75, 0.51	5.03, 0.83, 0.82	6.06, 1.17, 0.76	6.51, 1.70, 0.41
UBFF	4.29, 0.26, 0.57	5.03, 0.32, 0.85	6.06, 0.44, 0.81	6.52, 0.63, 0.47
GVFF	4.41, 0.64, 0.91, 0.27	5.56, 0.91, 1.04, 0.24	6.56, 0.85, 1.18, 0.27	6.73, 0.46, 1.24, 0.29
		AsO_4^{3-}	SeO_4^{2-}	BrO_4^-
OVFF		5.33, 0.96, 0.32	5.39, 0.86, 0.28	5.63, 0.99, 0.09
UBFF		5.16, 0.32, 0.41	5.23, 0.29, 0.37	5.47, 0.35, 0.17
GVFF		5.74, 0.29, 0.73, 0.17	5.78, 0.25, 0.63, 0.14	5.75, 0.08, 0.57, 0.11
			TeO_4^{2-}	IO_4^-
OVFF			2.90, 0.62, 0.26	5.80, 0.67, 0.02
UBFF			2.81, 0.22, 0.30	5.63, 0.23, 0.10
GVFF			3.30, 0.22, 0.48, 0.10	5.83, 0.02, 0.34, 0.06
				ClO_4^{-*} (melt)
OVFF				6.56, 1.72, 0.50
UBFF				6.49, 0.59, 0.59
GVFF				6.78, 0.60, 1.28, 0.31

$MnCl_4^{2-}$; $FeCl_4^{2-} < FeCl_4^-$; $TiBr_4 > MnBr_4^{2-}$; $TiI_4 > MnI_4^{2-}$) as seen from Table 15. Similar trends are noted for the main-family oxyanions (Table 16), and the transition metal oxy-, thio- and seleno-anions (Tables 17, 18) (for example, the primary stretching force constant for $SiO_4^{4-} < PO_4^{3-} < SO_4^{2-} < ClO_4^-$; $AsO_4^{3-} < SeO_4^{2-} < BrO_4^-$; $TeO_4^{2-} < IO_4^-$; $ReO_4^{3-} < ReO_4^-$; $MnO_4^{3-} < MnO_4^{2-}$; $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$; $MoO_4^{2-} < TcO_4^- < RuO_4$; $WO_4^{2-} < ReO_4^- < OsO_4$; $MoO_4^{4-} < MoO_4^{2-}$; $RuO_4^{2-} < RuO_4^- < RuO_4$; $NbS_4^{3-} < MoS_4^{2-}$; $TaS_4^{3-} < WS_4^{2-} < ReS_4^-$; $NbSe_4^{3-} < MoSe_4^{2-}$; $TaSe_4^{3-} < WSe_4^{2-}$). Some minor defections for these trends are observed. For example, the primary stretching force constants for $CrO_4^{4-} \simeq CrO_4^{3-} < CrO_4^{2-}$; $FeO_4^{4-} > FeO_4^{3-} \simeq FeO_4^{2-} < FeO_4^-$; $WO_4^{4-} > WO_4^{2-}$.

2. *Atomic number effect.* The effects of increasing the atomic number of the X atom on the primary stretching force constant (keeping the oxidation state and the central atom M constant) for the main-family and the transition-metal tetrahalides are also apparent. For example, the primary force constant shows a decrease as one increases the atomic number of the halogen atom (for example, the primary stretching force constant for $MgCl_4^{2-} > MgBr_4^{2-} > MgI_4^{2-}$; $CF_4 > CCl_4 > CBr_4 > CI_4$; $AlCl_4^- > AlBr_4^- > AlI_4^-$; $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$; $GaCl_4^- > GaBr_4^- > GaI_4^-$; $GeCl_4 > GeBr_4 > GeI_4$; $PCl_4^+ > PBr_4^+$; $InCl_4^- > InBr_4^- > InI_4^-$; $SnCl_4 > SnBr_4 > SnI_4^-$; $TiCl_4 > TiBr_4 > TiI_4$; $MnCl_4^{2-} > MnBr_4^{2-} > MnI_4^{2-}$; $ZrCl_4 > ZrBr_4 > ZrI_4$; $HfCl_4 > HfBr_4 > HfI_4$; $ZnCl_4^{2-} > ZnBr_4^{2-} > ZnI_4^{2-}$; $CdCl_4^{2-} > CdBr_4^{2-} > CdI_4^{2-}$).

Similar trends are observed in the thio and seleno series (e.g. $VO_4^{3-} > VS_4^{3-} > VSe_4^{3-}$; $NbS_4^{3-} > NbSe_4^{3-}$; $MoS_4^{2-} > MoSe_4^{2-}$; $TaS_4^{3-} > TaSe_4^{2-}$; $WS_4^{2-} > WSe_4^{2-}$).

The effects of atomic number on the primary stretching force constants as the atomic number of M is increased and the atomic number of X is kept constant (oxidation state also constant) do not show systematic changes. For the main-family tetrahalides an increase in the force constant occurs from the carbon tetrahalides to the silicon tetrahalides followed by a decrease in going to Ge, Sn, and Pb. Similar effects are noted with the B, Al, Ga, In and Tl series. The same results were observed by Heath and Linnett[38], who accounted for the results in terms of increased repulsive forces occurring in the carbon and boron halides which cause a distortion in the central atom—halogen bond which weakens it to a greater extent than when the central atom is larger (for example, the primary stretching force constants for $BCl_4^- < AlCl_4^- < GaCl_4^- > InCl_4^- > TlCl_4^-$; $CCl_4 < SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$; $PCl_4^+ > AsCl_4^+ > SbCl_4^+$; $CBr_4 < SiBr_4 > GeBr_4 > SnBr_4$; $CI_4 < SiI_4 \simeq GeI_4 \simeq SnI_4$). As one proceeds to the transition-metal tetrahalides some evidence exists that the primary stretching force constant is greater for the third transition series than for the second or first transition series (for example, the primary stretching force constant for $HfCl_4 > ZrCl_4$; $HfBr_4 > ZrBr_4 \simeq TiBr_4$; $HfI_4 > ZrI_4 \simeq TiI_4$; $TaS_4^{3-} > NbS_4^{3-} > VS_4^{3-}$; $WS_4^{2-} > MoS_4^{2-}$; $TaSe_4^{3-} > NbSe_4^{3-} > VSe_4^{3-}$; $WSe_4^{2-} > MoSe_4^{2-}$). Similar results were recently reported[26] for the octahedral hexahalogen molecules. This is consistent with observations that more stable complexes are found in the order of third transition series > second transition series > first transition series. The behavior previously reported for Group IIB compounds[39] is also observed in this work for the zinc family chlorides (e.g. $HgCl_4^{2-} > CdCl_4^{2-} > ZnCl_4^{2-}$).

The effect of the transition series is also demonstrated in the transition-metal oxyanions. In the case of the transition-metal oxyanions the third transition series representatives show a higher primary stretching force constant than that of the second or first transition series (the primary stretching force constant for $WO_4^{2-} > MoO_4^{2-} > CrO_4^{2-}$; $ReO_4^- > TcO_4^- > MnO_4^-$; $OsO_4 > RuO_4$; $RuO_4^- > FeO_4^-$; $RuO_4^{2-} > FeO_4^{2-}$; $WO_4^{4-} > MoO_4^{4-} > CrO_4^{4-}$; $ReO_4^{3-} > MnO_4^{3-}$; $HfO_4^{4-} > ZrO_4^{4-} > TiO_4^{4-}$). These trends may be due to the greater amount of π-bonding occurring for the third-row compared with the second-row or first-row transition metal compounds[40,41].

In the main-family oxyanion series the primary stretching force constant is observed to behave erratically as the atomic number of the central atom increases, although a tendency toward a decrease is observed in Group IIA (the primary stretching force constants for $SO_4^{2-} > SeO_4^{2-} > TeO_4^{2-}$).

3. Physical state of matter. For several molecules a comparison of the primary stretching force constant with the state of matter is possible (using K in the OVFF or UBFF). It is observed that the force constant (gas) > force constant (liquid) $\simeq$ force constant (solid) in the case of CCl_4, $SiCl_4$, $GeCl_4$, and $SnCl_4$. For $SiBr_4$, $GeBr_4$, $SnBr_4$, and GeI_4 the force constant (gas) > force constant (liquid). For SiI_4 the force constant (gas) > force constant (solid). For $PbCl_4$ the force constant (liquid) $\simeq$ force constant (solid). SnI_4 appears to be the only compound that does not follow this trend.

TABLE 17

Force constants for transition-metal oxyanions (mdyne/A)

Force field	IVB	VB	VIB
	TiO_4^{4-}	VO_4^{3-*}	CrO_4^{2-*} *(aqueous soln.)*
OVFF	3.53, 0.44, 0.47	3.42, 0.02, 0.78	4.79, 0.39, 0.51
UBFF	3.47, 0.13, 0.50	3.55, 0.05, 0.71	4.86, 0.19, 0.47
GVFF	4.10, 0.45, 0.42, 0.07	4.52, 0.64, 0.36, -0.003	5.48, 0.43, 0.42, 0.02
	ZrO_4^{4-}		MoO_4^{2-*}
OVFF	5.29, 0.90, 0.15		4.77, 0.06, 0.72
UBFF	5.16, 0.32, 0.22		4.87, 0.05, 0.67
GVFF	5.50, 0.13, 0.52, 0.09		5.94, 0.55, 0.35, 0.02
	HfO_4^{4-}		WO_4^{2-*}
OVFF	5.27, 0.92, 0.16		5.01, 0.10, 0.79
UBFF	5.01, 0.29, 0.27		5.03, 0.04, 0.79
GVFF	5.51, 0.15, 0.56, 0.11		6.42, 0.58, 0.41, 0.04
		VO_4^{4-*}	CrO_4^{2-*} *(melt)*
OVFF		3.61, 0.32, 0.65	4.75, 0.54, 0.49
UBFF		3.53, 0.06, 0.69	4.80, 0.20, 0.46
GVFF		4.46, 0.61, 0.42, 0.05	5.40, 0.41, 0.44, 0.03
			CrO_4^{3-*}
OVFF			4.70, 0.27, 0.43
UBFF			4.55, 0.04, 0.51
GVFF			5.25, 0.43, 0.32, 0.05
			CrO_4^{4-*}
OVFF			4.50, 0.70, 0.41
UBFF			4.50, 0.26, 0.41
GVFF			5.02, 0.37, 0.51, 0.06
			MoO_4^{4-*}
OVFF			4.77, 0.24, 0.28
UBFF			4.67, 0.26, 0.33
GVFF			5.19, 0.24,.0.49, 0.08
			WO_4^{4-*}
OVFF			5.87, 0.93, 0.11
UBFF			5.62, 0.31, 0.21
GVFF			6.03, 0.11, 0.53, 0.10
OVFF			
UBFF			
GVFF			

VIIB	VIII		
MnO_4^{-*} 5.41, 0.83, 0.30 5.36, 0.32, 0.34 5.80, 0.27, 0.58, 0.09	FeO_4^{-*} 5.10, 0.03, 0.71 5.25, 0.06, 0.62 8.17, 2.61, 0.33, −0.002	CoO_4^{4-} 4.79, 0.53, 0.28 4.78, 0.19, 0.29 5.17, 0.24, 0.36, 0.04	
TcO_4^- 5.93, 0.35, 0.50 6.11, 0.19, 0.41 6.75, 0.36, 0.37, −0.004	RuO_4^{-*} 5.28, 0.37, 0.30 5.36, 0.15, 0.27 5.77, 0.22, 0.28, 0.015		
ReO_4^{-*} *(aqueous soln.)* 6.43, 0.30, 0.62 6.46, 0.13, 0.61 7.53, 0.45, 0.43, 0.04			
MnO_4^{2-*} 4.69, 0.36, 0.39 4.79, 0.19, 0.33 5.24, 0.32, 0.33, −0.002	FeO_4^{2-*} 3.96, 0.35, 0.46 4.08, 0.14, 0.39 4.66, 0.78, 0.38, 0.00		
MnO_4^{3-*} 3.22, −0.11, 0.98 3.33, −0.01, 0.92 4.66, 0.79, 0.38, 0.00	FeO_4^{3-*} 4.20, 0.38, 0.34 4.06, 0.09, 0.42 4.63, 0.35, 0.35, 0.07		
ReO_4^{-*} *(solid)* 6.96, 0.76, 0.36 6.64, 0.21, 0.50 7.54, 0.35, 0.55, 0.10	FeO_4^{4-*} 4.85, 0.48, 0.15 4.76, 0.16, 0.20 5.04, 0.14, 0.31, 0.05		
ReO_4^{3-*} 6.23, 0.76, 0.04 5.87, 0.23, 0.11 6.14, 0.01, 0.40, 0.09	RuO_4^{2-*} *(K salt)* 4.41, 0.36, 0.45 4.49, 0.17, 0.41 5.14, 0.34, 0.37, 0.02	RuO_4^{2-*} *(aqueous soln.)* 5.15, 0.58, 0.27 5.19, 0.25, 0.25 5.58, 0.20, 0.38, 0.02	RuO_4^{2-*} *(Ba salt)* 5.21, 0.60, 0.26 5.26, 0.27, 0.23 5.63, 0.19, 0.38, 0.02
	RuO_4^* *(liq.)* 6.24, 0.58, 0.29 6.31, 0.26, 0.26 6.71, 0.21, 0.39, 0.02	RuO_4 *(solid)* 6.32, 0.60, 0.25 6.38, 0.26, 0.22 6.72, 0.18, 0.38, 0.02	
	OsO_4 *(gas)* 7.39, 0.60, 0.36 7.45, 0.23, 0.34 8.03, 0.25, 0.41, 0.03	OsO_4 *(liq.)* 7.27, 0.56, 0.38 7.28, 0.23, 0.38 10.59, 2.92, 0.44, 0.04	OsO_4 *(solid)* 7.22, 0.54, 0.38 7.29, 0.24, 0.36 7.91, 0.27, 0.43, 0.03

TABLE 18

Force constants for transition-metal thio and seleno tetrahedral anions (mdyne/A)

Force field	VB	VIB	VIIB
	VS_4^{3-}		
OVFF	2.03, 0.21, 0.26		
UBFF	2.08, 0.12, 0.23		
GVFF	2.30, 0.26, 0.22, −0.02		
	NbS_4^{3-}	MoS_4^{2-}	
OVFF	2.07, 0.14, 0.28	2.72, 0.25, 0.34	
UBFF	2.14, 0.05, 0.24	2.81, 0.11, 0.28	
GVFF	2.45, 0.23, 0.16, −0.004	3.18, 0.27, 0.23, −0.005	
	TaS_4^{3-}	WS_4^{2-}	ReS_4^-
OVFF	2.15, 0.19, 0.31	2.98, 0.23, 0.39	3.28, 0.31, 0.37
UBFF	2.17, 0.06, 0.30	3.01, 0.07, 0.35	3.32, 0.11, 0.35
GVFF	2.64, 0.25, 0.20, 0.009	3.56, 0.29, 0.24, 0.01	3.87, 0.29, 0.28, 0.01
	VSe_4^{3-}		
OVFF	1.75, 0.23, 0.20		
UBFF	1.75, 0.11, 0.16		
GVFF	1.86, 0.21, 0.18, −0.03		
	$NbSe_4^{3-}$	$MoSe_4^{2-}$	
OVFF	2.02, 0.14, 0.18	2.32, 0.26, 0.19	
UBFF	2.06, 0.07, 0.13	2.38, 0.13, 0.14	
GVFF	2.18, 0.16, 0.12, −0.02	2.51, 0.17, 0.18, −0.02	
	$TaSe_4^{3-}$	WSe^{2-}	
OVFF	2.07, 0.16, 0.22	2.60, 0.14, 0.29	
UBFF	2.14, 0.07, 0.17	2.69, 0.06, 0.23	
GVFF	2.34, 0.18, 0.15, −0.008	2.96, 0.24, 0.16, −0.009	

(b) Summary

Because the previously discussed difficulties involved for the tetrahedral molecules are so severe, it is suggested that the force constants obtained in this work are most useful only on a comparative basis.

The use of the primary stretching force constant as a measure of bond strength has been suggested[36,37]. We observe with a large number of data that the primary stretching force constant increases with an increase in oxidation state. Additionally, the primary stretching force constant decreases as the atomic number of the X atom increases in MX_4^n-type molecules or anions, where X = halogen, oxygen, sulfur or selenium. If X is kept constant

TABLE 19

Force constants for miscellaneous T_d molecules (mdyne/A)

Force field		
	$B(OH)_4^-$	
OVFF	2.11, 0.59, 0.90	
UBFF	2.08, 0.16, 0.92	
GVFF	Diverges	
	$Al(OH)_4^-$	
OVFF	2.52, 0.29, 0.32	
UBFF	2.58, 0.16, 0.28	
GVFF	2.84, 0.32, 0.28, -0.02	
	$Zn(OH)_4^-$	
OVFF	2.30, 0.32, -0.02	
UBFF	2.28, 0.76, -0.02	
GVFF	2.28, -0.02, 0.31, 0.006	
	XeO_4 *(solid)*	XeO_4 *(gas)*
OVFF	6.18, 0.88, -0.16	6.34, 0.84, -0.16
UBFF	6.00, 0.31, -0.08	6.13, 0.30 -0.07
GVFF	5.93, -0.13, 0.34, 0.05	6.09, -0.14, 0.35, 0.06
	UF_4	
OVFF	-0.07, 0.09, 1.05	
UBFF	-0.05, 0.04, 1.05	
GVFF	2.38, 0.61, 0.15, -0.14	
	AsS_4^{3-}	
OVFF	1.89, 0.29, 0.23	
UBFF	1.89, 0.11, 0.24	
GVFF	2.13, 0.23, 0.28, 0.05	
	SbS_4^{3-}	
OVFF	1.86, 0.24, 0.17	
UBFF	1.86, 0.10, 0.17	
GVFF	2.79, 0.84, 0.20, 0.03	

and the atomic number of the central atom is increased in main-family tetrahalides, the primary stretching force constant shows an initial increase from C → Si or B → Al, and then a decrease as one proceeds down the main group. For transition MX_4^{n}-type molecules and anions the primary stretching force constant is greatest for the third transition series and decreases in going to the second and first transition series. Similar observations are made for the transition-metal oxyanions.

(iii) Frequency trends

For > 90% of the molecules studied $\nu_3 > \nu_1$. The largest number of examples which showed $\nu_1 > \nu_3$ appeared for the transition-metal oxyanions. In most of the cases where $\nu_3 > \nu_1$ then $\nu_4 > \nu_2$. Only a few examples exist where $\nu_2 > \nu_4$, and these occur for the transition-metal oxyanions. It is apparent that ν_1 is a better measure of K or f_r than is ν_3 This has recently also been recognized by Gonzalez-Vilchez and Griffith[33] for the transition-metal oxyanions.

(iv) Potential energy distribution (PED)

(a) The tetrahalides

The calculated PED for the OVFF and the UBFF indicates that ν_1 is predominantly a stretching vibration due to the force constant K. However, as the mass of the central atom (M) is decreased, maintaining that of the halogen (X) constant, the importance of the repulsion constant F increases. When the mass of M is greater than the mass of X, ν_1 becomes predominantly due to the repulsion force constant. The degree of repulsion also increases from $F^- \rightarrow I^-$.

The ν_2 vibration is predominantly due to the repulsion force constant for all of the tetrahalides, decreasing as the mass of the halogen increases.

The ν_3 vibration is predominantly due to the stretching force constant K, although a slight mixture of F and H are present. The latter become insignificant as the mass of the halogen increases.

The ν_4 vibration is predominantly due to the repulsion force constant with a mixture of K and H, with H becoming more important as the mass of the halogen increases.

(b) The oxy-, thio- and seleno-anions

For these anions the vibrations appear to be purer than those found for the tetrahalides. The modes ν_1 and ν_3 are mainly stretch, and ν_2 and ν_4 are a mixture of repulsion and bend, with the bending force constant becoming more important as the mass of the ligand increases.

(c) The hydroxides – $M(OH)_4{}^n$

Some question concerning the validity of the symmetry involving these anions has been raised[42]. All modes seem to show a predominant dependence on the repulsion constants with the exception of ν_3, which is a mixture of K, F and H with K predominating.

REFERENCES

1 A. Müller and B. Krebs, *J. Mol. Spectrosc.*, 24 (1967) 180.

2 B. Krebs, A. Müller and A. Fadini, *J. Mol. Spectrosc.*, 24 (1967) 198.
3 T. Shimanouchi, in D. Henderson (Ed.), *The Molecular Force Field in Physical Chemistry – An Advanced Treatise*, Academic Press, New York, 1970.
4 J.R. Ferraro and J.S. Ziomek, *Introductory Group Theory and Its Application to Molecular Structure*, Plenum Press, New York, 1969.
5 L.H. Jones, *Inorganic Vibrational Spectroscopy*, M. Dekker, New York, 1971.
6 D. Steele, *Theory of Vibrational Spectroscopy*, W.B. Saunders, Philadelphia, 1971.
7 P. LaBonville, J.R. Ferraro, M.C. Wall and L.J. Basile, *Coord. Chem. Rev.*, 7 (1972) 257.
8 J.W. Linnett, in A.J. Downs, D.A. Long and A.K. Staveley (Eds.), Molecular force fields and valency, *Essays in Structural Chemistry*, Macmillan, London, 1971.
9 H.C. Urey and C.A. Bradley, *Phys. Rev.*, 38 (1931) 1969.
10 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 18 (1962) 89, 101.
11 T. Hiraishi, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 20 (1962) 819.
12 D.F. Heath and J.W. Linnett, *Trans. Faraday Soc.*, 44 (1948) 873, 878, 888; 45 (1949) 264.
13 J.W. Linnett and P.J. Wheatley, *Trans. Faraday Soc.*, 45 (1949) 33.
14 J.H. Schachtschneider and R.G. Snyder, *Spectrochim. Acta*, 19 (1963) 117.
15 W.A. Yeranos, *Bull. Soc. Chim. Belg.*, 74 (1965) 414.
16 G.M. Begun, C.R. Boston, G. Torsi and G. Mamantov, *Inorg. Chem.*, 10 (1971) 886.
17 D.E. Mann, T. Shimanouchi, J.J. Meal and L. Fano, *J. Chem. Phys.*, 27 (1957) 43.
18 J.T.R. Dunsmuir and A.P. Lane, *J. Chem. Soc. A*, (1971) 2781.
19 J.T.R. Dunsmuir and A.P. Lane, *J. Chem. Soc. A*, (1971) 404.
20 B.R. Sundheim and L.V. Woodcock, *Chem. Phys. Lett.*, 15 (1972) 191.
21 D.F. Heath and J.W. Linnett, *Trans. Faraday Soc.*, 44 (1948) 484.
22 W.P. Griffith, *Coord. Chem. Rev.*, 5 (1970) 459.
23 A. Müller and A. Fadini, *Spectrochim. Acta*, 22 (1966) 1523.
24 R.S. McDowell and M. Goldblatt, *Inorg. Chem.*, 10 (1971) 625.
25 A. Müller, R. Ahrlich and B. Krebs, *Z. Naturforsch. B*, 21 (1966) 719.
26 B. Krebs and A. Müller, *J. Mol. Spectrosc.*, 22 (1962) 290.
27 D.M. Adams, *Metal–Ligand and Related Vibrations*, E. Arnold, London, 1967.
28 R.J.H. Clark, in V. Gutmann (Ed.), *Halogen Chemistry*, Academic Press, New York, 1968.
29 J.R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, 1971.
30 H. Siebert, *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*, Springer-Verlag, Berlin, 1966.
31 P. Tarte and J. Preudhomme, *Spectrochim. Acta, Part A*, 26 (1970) 2207.
32 T.G. Spiro, *Inorg. Chem.*, 4 (1965) 1290.
33 F. Gonzalez-Vilchez and W.P. Griffith, *J. Chem. Soc. Dalton*, (1972) 1416.
34 A.S. Quist, J.B. Bates and G.E. Boyd, *J. Phys. Chem.*, 76 (1972) 78.
35 L.A. Woodward, *Trans. Faraday Soc.*, 54 (1958) 1271.
36 H. Siebert, *Z. Anorg. Allg. Chem.*, 274 (1953) 34.
37 I. Wharf and D.F. Shriver, *Inorg. Chem.*, 8 (1969) 914.
38 D.F. Heath and J.W. Linnett, *Trans. Faraday Soc.*, 44 (1948) 556.
39 D.A. Long and J.Y.H. Chan, *Trans. Faraday Soc.*, 58 (1962) 2325.
40 J.H. Canterford and R. Colton, *Halides of the Second and Third Row Transition Metals*, Wiley-Interscience, New York, 1968.
41 F.A. Cotton and R.M. Wing, *Inorg. Chem.*, 4 (1965) 867.
42 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1962.
43 J. Goubeau and W. Bues, *Z. Anorg. Allg. Chem.*, 268 (1952) 221.
44 N.N. Greenwood, *J. Chem. Soc. A*, (1959) 3811.
45 A.S. Quist, J.B. Bates and G.E. Boyd, *J. Chem. Phys.*, 54 (1971) 4896.
46 T. Shimanouchi, National Standard Reference Data Series, *Nat. Bur. Stand. (U.S.) 17*, NSRDS-NBS 17, March 1968.
47 R.J.H. Clark and D.M. Rippon, *Chem. Commun.*, (1971) 1295.

48 A.D. Caunt, L.N. Short and L.A. Woodward, *Trans. Faraday Soc.*, 48 (1952) 873.
49 A.D. Caunt, L.N. Short and L.A. Woodward, *Nature*, 168 (1951) 557.
50 L.E. Alexander and I.R. Beattie, *J. Chem. Soc. Dalton*, (1972) 1745.
51 V.A. Maroni, *J. Chem. Phys.*, 55 (1971) 4789.
52 J.A. Creighton, *J. Chem. Soc., London*, (1965) 6589.
53 G. Torsi, G. Mamantov and G.M. Begun, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 553.
54 R.H. Bradley, P.N. Brier and D.E.H. Jones, *J. Chem. Soc. A*, (1971) 1397.
55 L.A. Woodward and A.A. Nord, *J. Chem. Soc., London*, (1956) 3721.
56 L.A. Woodward and M.J. Taylor, *J. Chem. Soc., London*, (1956) 4473.
57 B.P. Singh, *J. Mol. Spectrosc.*, 33 (1970) 169.
58 D.A. Long, T.V. Spencer, D.N. Waters and L.A. Woodward, *Proc. Roy. Soc., Ser. A*, 240 (1957) 499.
59 R.J.H. Clark and C.J. Willis, *Inorg. Chem.*, 10 (1971) 1118.
60 H.F. Shurvell, *Spectrochim. Acta, Part A*, 27 (1971) 2375.
61 R.J.H. Clark and B.K. Hunter, *J. Chem. Soc. A*, (1971) 2999.
62 J.T. Neu and W.D. Gwinn, *J. Amer. Chem. Soc.*, 70 (1948) 3463.
63 G.L. Carlson, *Spectrochim. Acta*, 19 (1963) 1291.
64 J. Weidlein and K.Z. Dehnicke, *Z. Anorg. Allg. Chem.*, 337 (1965) 113.
65 K. Dehnicke and J. Weidlein, *Chem. Ber.*, 98 (1965) 1087.
66 A. Müller, N. Weinstock, N. Mohan, C.W. Schläpfer and K. Nakamoto, *Appl. Spectrosc.*, 27 (1973) 4.
67 L.A. Woodward and A.A. Nord, *J. Chem. Soc., London*, (1955) 2655.
68 L.A. Woodward and P.T. Bill, *J. Chem. Soc., London*, (1955) 1699.
69 M.L. Delwaulle, *C.R. Acad. Sci.*, 238 (1954) 2522.
70 T.E. Thomas and W.J. Orville-Thomas, *J. Inorg. Nucl. Chem.*, 34 (1972) 839.
71 H. Gerding and P.C. Nobel, *Rec. Trav. Chim. Pays-Bas*, 77 (1958) 472.
72 H. Stammreich, Y. Tavares and D. Bassi, *Spectrochim. Acta*, 17 (1961) 661.
73 L.A. Woodward and G.H. Singer, *J. Chem. Soc. A*, (1958) 716.
74 H. Stammreich, R. Forneris and Y. Tavares, *J. Chem. Phys.*, 25 (1956) 1278.
75 N.J. Hawkins and D.R. Carpenter, *J. Chem. Phys.*, 23 (1955) 1700.
76 R.J.H. Clark, B.K. Hunter and D.M. Rippon, *Inorg. Chem.*, 11 (1972) 56.
77 R.J.H. Clark, B.K. Hunter and P.D. Mitchell, *J. Chem. Soc. Faraday II*, (1972) 476.
78 J.S. Avery, C.D. Burbridge and D.M.L. Goodgame, *Spectrochim. Acta, Part A*, 24 (1968) 1721.
79 I.R. Beattie, T.R. Gilson and G.A. Ozin, *J. Chem. Soc. A*, (1969) 534.
80 D.F.C. Morris, E.L. Short and D.N. Waters, *J. Inorg. Nucl. Chem.*, 25 (1963) 975.
81 J.E.D. Davies and D.A. Long, *J. Chem. Soc. A*, (1968) 2054.
82 J.E.D. Davies and D.A. Long, *J. Chem. Soc. A*, (1971) 1273.
83 G.J. Jany and D.W. Janes, *J. Chem. Phys.*, 38 (1963) 905.
84 H.G.M. Edwards, M.J. Ware and L.A. Woodward, *Chem. Commun.*, (1968) 540.
85 M.L. Dewaulle, *Bull. Soc. Chim. Fr.*, (1955) 1294.
86 J.A. Rolfe, D.E. Sheppard and L.A. Woodward, *Trans. Faraday Soc.*, 50 (1954) 1275.
87 R.J.H. Clark and C.J. Willis, *J. Chem. Soc. A*, (1971) 838.
88 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn., Wiley-Interscience, New York, 1970, p. 111.
89 E. Steger and W. Schmidt, *Ber. Bunsenges. Phys. Chem.*, 68 (1964) 102.
90 H. Siebert, *Z. Anorg. Allg. Chem.*, 275 (1954) 225.
91 M.M. Brooker, A.S. Quist and G.E. Boyd, *Chem. Phys. Lett.*, 9 (1971) 242.
92 E.V. Appleman, *Inorg. Chem.*, 8 (1969) 223.
93 H. Siebert and G. Wieghardt, *Spectrochim. Acta, Part A*, 27 (1971) 1677.
94 H. Stammreich, D. Bassi and O. Sala, *Spectrochim. Acta*, 12 (1958) 403.
95 P.J. Hendra, *Spectrochim. Acta, Part A*, 24 (1968) 125.
96 F.L. Whitney, *Inorg. Chim. Acta*, 5 (1971) 260.
97 W.P. Griffith, *J. Chem. Soc. A*, (1968) 1663.
98 I.W. Levin and S. Abramowitz, *J. Chem. Phys.*, 50 (1969) 4860.
99 R.A. Johnson, M.T. Rogers and G.E. Leroi, *J. Chem. Phys.*, 56 (1972) 789.
100 A. Müller and B. Krebs, *Z. Naturforsch. B*, 21 (1966) 3.

101 R.H. Busey and O.L. Keller, *J. Chem. Phys.*, 41 (1964) 215.
102 I.W. Levin, *Inorg. Chem.*, 8 (1969) 1018.
103 J.L. Huston and H.H. Claassen, *J. Chem. Phys.*, 52 (1970) 5646.
104 A. Müller, B. Krebs, W. Rittner and M. Stockburger, *Ber. Bunsenges. Phys. Chem.*, 71 (1967) 182.
105 A. Müller, K.H. Schmidt and K.H. Tytko, *Spectrochim. Acta, Part A*, 28 (1972) 381.
106 N.K. Sanyal, A.N. Pandey and H.S. Singh, *J. Mol. Spectrosc.*, 30 (1969) 144.
107 J.O. Edwards, G.C. Morrison, V.F. Ross and J.W. Schultz, *J. Amer. Chem. Soc.*, 77 (1955) 266.
108 E.R. Lippincott, J.A. Psellos and M.C. Tobin, *J. Chem. Phys.*, 20 (1952) 536.
109 W. Krasser and H.W. Nurnberg, *Spectrochim. Acta, Part A*, 26 (1970) 1059.
110 R.S. McDowell and L.B. Asprey, *J. Chem. Phys.*, 57 (1972) 3062.
111 H.F. Shurvell, *Can. J. Spectrosc.*, 17 (1972) 109.