A STUDY OF INTRAMOLECULAR FORCE FIELDS FOR TETRAHEDRAL TRANSITION METAL OXYANIONS

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The orbital valence force field (OVFF), Urey-Bradley force field (UBFF) and general valence force field (GVFF) have been employed to evaluate the force constants for 28 transition metal oxyanions: MO_4^{n-} (M = Ti, V, Cr, Mn, Fe, Co, Zr, Nb, Mo, Tc, Ru, Hf, Ta, W, Re, Os; n = 0, 1, 2, 3 or 4) in different oxidation states using the most reliable frequencies obtained from IR and Raman spectra. The results have been utilized to discuss the relative stability of the metal-oxygen bonding and the nature of forces between non-bonded atom pairs. The usefulness of the OVFF model in understanding valence forces has been examined and empirical equations have been used to estimate the metal-oxygen bond order and bond length. On the basis of the results the contribution of π-interaction in metal-oxygen bonding is briefly discussed.

1. Introduction

The study of bond properties of oxygen-bonded compounds using infrared and Raman spectroscopic techniques has attracted considerable attention in recent years. The bond strength manifested quantitatively by vibrational spectroscopic data, i. e., stretching frequencies or force constants, is a convenient measure of the strength of a chemical bond, and empirical relationships between the force constants, bond length and bond order have been suggested by many authors. These bond properties provide valuable information about the nature of chemical bond. Recently Jeżowska-Trzebiatowska and coworkers [1–10], Cotton and Wing [11], Griffith and coworkers [12–17] and Müller et al. [18, 19] have systematically studied the bond properties of metal-oxygen bond relating to the π-interactions in oxy-species using spectroscopic data. In the present paper it is aimed to extend such study to some more tetrahedral oxyanions of transition metals MO_4^{n-} (M = Ti, V, Cr, Mn, Fe, Co, Zr, Nb, Mo, Tc, Ru, Hf, Ta, W, Re, Os; n = 1, 2 3 or 4) using infrared and Raman spectroscopic data [19, 20] which have been recently reported in literature and can now be considered to be more reliable than previous results.

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2. Method of computation

The tetrahedral oxyanions of the type MO_4^{n-} possessing T_d symmetry give rise to four normal modes of vibration which are classified as (A_1+E+2F_2). All of them are Raman-active, but only $\nu_3(F_2)$ and $\nu_4(F_2)$ are infrared active. Wilson's FG matrix method [21] has been followed to compute the force constants using orbital valency force field (OVFF), Urey-Bradley force field (UBFF) and general valency force field (GVFF). F and G matrix elements are taken from literature [22]. The two dimensional secular determinant appearing in F_2 species for GVFF model has been solved by using L–F approximation method [23, 24].

A second set of OVFF constants have also been calculated by incorporating Lennard-Jones potential [25] in OVFF model to understand the nature of forces existing between non-bonded atom pairs.

The metal-oxygen bond order (N) has been calculated from the equations given by Siebert [26] as

$$N = 0.69(f_r/f_{MO})+0.37 \quad \text{if } (f_r/f_{MO}) > 1.5$$

and

$$N = (f_r/f_{MO}) \quad \text{if } (f_r/f_{MO}) < 1.5, \tag{1}$$

where f_r is the stretching force constant and f_{MO} is covalent bonding force constant given by the relation as

$$f_{MO} = 7.2\,\frac{Z_M Z_O}{n_M^3 n_O^3}. \tag{2}$$

Here Z_M and Z_O are the atomic numbers of the transition metal M and oxygen atom O, respectively, and n_M and n_O are the principal quantum numbers of valence electrons for M and O atoms, respectively.

Empirical Badger equation which relates bond length R_{MO} and force constant f_r, assumes the following linear form for oxyanions:

$$R_{M-O} = 1.08 f_r^{-1/3}+\beta. \tag{3}$$

Following Hanuza et al. [8] in the present work, the value of β has been taken as 1.19 for third row transition metal oxyanions and 1.14 for the first and second row transition metal oxyanions.

According to Pauling, the bond number m (which is equivalent to bond order for molecules), is given by

$$R = R(A-B)-0.6 \log m, \tag{4}$$

where R is the interatomic distance and $R(A-B)$ is the interatomic distance of a single bond. The value of $R(A-B)$ is given by the relation

$$R(A-B) = r_A+r_B-C|X_A-X_B|. \tag{5}$$

Where r_A and r_B are the radii and X_A and X_B the Pauling electronegativities of atoms A and B, C is the Schomker-Stevenson coefficient. For ionic systems m is not equivalent to the bond order.

Recently we have proposed a relation (*Monatshefte für Chemie* (in press)) between bond number m, and bond order N, for ionic systems of the type $(A^{z+}B_n)^{z-n}$, which is of the form

$$N = m\,z/n. \tag{6}$$

Where z is the oxidation number of the central atom A and n is the number of ligands B. Inclusion of equation (6) in equation (4) gives

$$R = R(A-B) - 0.6 \log N - 0.6 \log (n/z) \tag{7}$$

This equation has also been used to calculate the value of bond order N.

3. Results and discussion

The vibrational frequencies, used in the present computations, are collected in Table I. The results of force constant calculation using OVFF and UBFF models are presented in Table II in standard notations. An inspection of Table II shows that the evaluated UBFF

TABLE I

Vibrational wavenumbers (in cm^{-1}) for transition metal oxyanions

Molecule	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
TiO_4^{4-}	761	306	770	371
VO_4^{3-}	826	336	804	336
VO_4^{4-}	818	319	780	368
CrO_4^{2-}	846	349	890	378
CrO_4^{3-}	834	260	860	324
CrO_4^{4-}	806	353	855	404
MnO_4^{-}	839	360	914	430
MnO_4^{2-}	812	325	820	332
MnO_4^{3-}	810	324	833	349
FeO_4^{2-}	832	340	790	322
FeO_4^{3-}	776	265	805	335
FeO_4^{4-}	762	257	857	314
CoO_4^{4-}	790	300	855	340
ZrO_4^{4-}	792	332	846	387
NbO_4^{3-}	816	340	650	420
MnO_4^{2-}	897	317	837	317
MnO_4^{4-}	792	328	808	373
TcO_4^{-}	912	325	912	336
RuO_4	818.8	322.4	912.9	333
RuO_4^{-}	830	339	845	312
RuO_4^{2-}	840	331	804	336
HfO_4^{4-}	796	325	800	379
TaO_4^{3-}	818	330	660	420
WO_4^{2-}	931	325	838	325
WO_4^{4-}	821	323	840	367
ReO_4^{-}	971	331	920	331
ReO_4^{3-}	808	264	853	319
OsO_4	965.2	333.1	960.1	322.7

TABLE II

OVFF and UBFF constants (in mdyn/Å) for transition metal oxyanions

Molecule	K_1 (K)	K'_α ($3H$)	A ($F/2$)	B/R ($-F'$)
TiO_4^{4-}	3.477 (3.505)	0.350 (0.314)	0.248 (0.244)	0.037 (0.081)
VO_4^{3-}	3.720 (3.769)	0.440 (0.402)	0.339 (0.333)	−0.054 (−0.003)
VO_4^{4-}	3.511 (3.533)	0.217 (0.198)	0.350 (0.347)	0.043 (0.068)
CrO_4^{2-}	4.839 (4.912)	0.728 (0.657)	0.238 (0.229)	0.056 (0.032)
CrO_4^{3-}	4.596 (4.603)	0.080 (0.072)	0.245 (0.244)	0.067 (0.077)
CrO_4^{4-}	4.476 (4.537)	0.791 (0.706)	0.206 (0.198)	−0.028 (0.072)
MnO_4^{-}	5.298 (5.361)	0.882 (0.784)	0.167 (0.159)	0.005 (0.119)
MnO_4^{2-}	4.089 (4.145)	0.520 (0.473)	0.266 (0.259)	−0.056 (0.005)
MnO_4^{3-}	4.297 (4.352)	0.555 (0.501)	0.236 (0.229)	−0.037 (0.030)
FeO_4^{2-}	3.604 (3.657)	0.424 (0.390)	0.365 (0.359)	−0.065 (−0.017)
FeO_4^{3-}	4.119 (4.141)	0.207 (0.188)	0.195 (0.192)	0.065 (0.089)
FeO_4^{4-}	4.827 (4.862)	0.447 (0.399)	0.081 (0.076)	0.014 (0.071)
CoO_4^{4-}	4.774 (4.827)	0.590 (0.529)	0.139 (0.132)	−0.019 (0.055)
ZrO_4^{4-}	5.271 (5.369)	0.860 (0.772)	0.080 (0.068)	0.018 (0.131)
NbO_4^{3-}	2.456 (2.440)	−0.084 (−0.079)	0.478 (0.479)	0.218 (0.210)
MoO_4^{2-}	4.700) (4.735)	0.210 (0.195)	0.361 (0.356)	0.016 (0.040)
MoO_4^{4-}	4.738 (4.830)	0.701 (0.636)	0.147 (0.135)	0.020 (0.108)
TcO_4^{-}	5.968 (6.050)	0.546 (0.500)	0.234 (0.223)	−0.018 (0.048)
RuO_4	6.139 (6.243)	0.726 (0.662)	0.149 (0.136)	−0.044 (0.046)
RuO_4^{-}	5.093 (5.223)	0.849 (0.779)	0.175 (0.159)	−0.116 (−0.014)

TABLE II (continued)

Molecule	K_1 (K)	K'_α (3H)	A (F/2)	B/R (−F′)
RuO_4^{2-}	4.465 (4.545)	0.501 (0.463)	0.273 (0.263)	−0.015 (0.044)
HfO_4^{4-}	5.255 (5.379)	0.739 (0.674)	0.090 (0.074)	0.078 (0.173)
TaO_4^{3-}	3.030 (3.018)	−0.076 (−0.070)	0.410 (0.411)	0.283 (0.275)
WO_4^{2-}	5.104 (5.140)	0.169 (0.159)	0.383 (0.379)	0.061 (0.079)
WO_4^{4-}	5.853 (5.991)	0.824 (0.741)	0.062 (0.045)	0.047 (0.152)
ReO_4^-	6.500 (6.583)	0.414 (0.386)	0.298 (0.288)	0.022 (0.070)
ReO_4^{3-}	6.208 (6.308)	0.610 (0.556)	0.007 (0.019)	−0.060 (−0.140)
OsO_4	7.362 (7.501)	0.735 (0.680)	0.177 (0.160)	−0.044 (0.046)

UBFF constants are given in parentheses.

constants K, $3H$ and $F/2$ are in good agreement with the corresponding values of OVFF constants K_1, K'_α and A. If one compares these values with those reported by other workers [20, 28–30], it is found that these are well comparable. A notable change is observed only in cases where the vibrational wavenumbers listed in Table I are quite different than those used by previous workers. It is also apparant from Table II that the present calculations lead to negative values of B/R for a few oxyanions. Many workers [27–30] have reported the negative values of B/R in case of anions. A negative value itself does not carry any physical significance as explained by Krebs and Müller [27].

In order to understand the nature of forces acting between non-bonded atom pairs, the Lennard-Jones potential has been incorporated in OVFF model. This gives a relation of the type $A = 6.5\,B/R$ between non-bonded interaction force constants. The force constants thus obtained are listed in Table III alongwith the calculated and experimentally observed frequencies of F_2 species. As seen from Table III that the calculated frequencies compare fairly with the experimental data in case of metal oxyanions where the metal exists in IV oxidation state. It is, therefore, inferred that Lennard-Jones potential is fairly adequate to take into account the interaction between non-bonded atom pairs in these oxyanions. Similar conclusion has also been drawn by Basile et al. [20] for six cases out of nine in MO_4^{4-} type oxyanions on the basis of OVFF model in which the non-bonded interaction has been approximated by the term $F' = -F/10$ instead of $B/R = (2/13)A$, which is applicable to nine metal oxyanions possessing fourth oxidation state. For other systems the vander Waals forces alone, in general, cannot represent the interaction between

TABLE III

OVFF constants (in mdyn/Å) using Lennard-Jones potential to represent the interaction between non-bonded atoms

Molecule	K_1	K'_α	A	B/R	calc. and exp. frequencies	
					ν_3	ν_4
TiO_4^{4-}	3.475	0.349	0.248	0.038	768 (770)	372 (371)
VO_4^{3-}	3.436	0.258	0.375	0.058	777 (804)	394 (336)
VO_4^{4-}	3.482	0.198	0.353	0.054	777 (780)	373 (368)
CrO_4^{2-}	4.591	0.568	0.270	0.042	844 (890)	422 (378)
CrO_4^{3-}	4.674	0.167	0.235	0.036	867 (860)	316 (324)
CrO_4^{4-}	4.318	0.689	0.226	0.035	842 (855)	430 (404)
MnO_4^{-}	5.244	0.847	0.174	0.026	909 (914)	423 (430)
MnO_4^{2-}	3.834	0.355	0.298	0.046	796 (820)	384 (332)
MnO_4^{3}	4.104	0.429	0.260	0.040	816 (833)	387 (349)
FeO_4^{2-}	3.286	0.218	0.405	0.062	758 (790)	370 (322)
FeO_4^{3-}	4.211	0.267	0.183	0.028	812 (805)	315 (335)
FeO_4^{4-}	4.830	0.450	0.080	0.012	857 (857)	314 (314)
CoO_4^{4-}	4.670	0.522	0.152	0.023	846 (855)	360 (340)
ZrO_4^{4-}	5.285	0.870	0.078	0.012	847 (846)	384 (387)
NbO_4^{3-}	2.784	0.149	0.437	0.067	688 (650)	352 (420)
MoO_4^{2-}	4.611	0.147	0.372	0.057	827 (837)	341 (317)
MoO_4^{4-}	4.731	0.696	0.148	0.023	807 (808)	374 (373)
TcO_4^{-}	5.848	0.459	0.249	0.038	902 (912)	361 336
RuO_4	5.991	0.619	0.167	0.026	900 (912.9)	364 (333)
RuO_4^{-}	4.776	0.621	0.215	0.033	816 (845)	380 (312)

TABLE III (continued)

Molecule	K_1	K'_α	A	B/R	calc. and exp. frequencies	
					ν_3	ν_4
RuO_4^{2-}	4.338	0.410	0.289	0.045	798 (804)	363 (336)
HfO_4^{4-}	5.378	0.836	0.074	0.011	811 (800)	354 (379)
TaO_4^{4-}	3.451	0.258	0.357	0.055	709 (660)	329 (420)
WO_4^{2-}	5.108	0.172	0.383	0.059	838 (838)	324 (325)
WO_4^{4-}	5.925	0.881	0.054	0.008	846 (840)	354 (367)
ReO_4^-	6.454	0.378	0.304	0.047	916 (920)	341 (331)
OsO_4	7.228	0.628	0.194	0.030	949 (960.1)	353 (322.7)

Experimental frequencies are given in parentheses.

non-bonded atom pairs but a potential which includes Coulomb alongwith dispersion forces seems plausible as suggested by Krebs and Müller [27] and Sanyal et al. [28, 30].

To study the usefulness of OVFF model in understanding valence forces, we have calculated the symmetrized force constants using OVFF constants from Table II. These in turn have been used to calculate the GVFF constants. The results are summarized in Table IV and compared with the GVFF constants, calculated the following L–F approximation method. The most reliable values of stretching force constant computed utilizing additional data for CrO_4^{2-}, MoO_4^{2-}, RuO_4 and OsO_4 are also included, in this Table IV. It is apparent from this Table that the stretching force constants are well comparable with the corresponding GVFF constants calculated by using OVFF constants and L–F approximation method. It is, therefore, inferred that the OVFF model is a reasonably good approximation to GVFF model in case of metal oxyanions. Similar conclusions have also been drawn by Mohan et al. [31] for $XY_4(T_d)$ and $XY_3(O_{3h})$ systems.

There are several factors which influence the magnitude of force constants. The present discussion is limited only to the mass effect and oxidation effect. For transition metal oxyanions the third transition series representative show a higher stretching force constant f_r (K_1 or K) than that of second or first transition series ($WO_4^{2-} > MoO_4^{2-} > CrO_4^{2-}$; $ReO_4^- > TcO_4^- > MnO_4^-$; $OsO_4 > RuO_4$; $RuO_4^{2-} > FeO_4^{2-}$; $ReO_4^{3-} > MnO_4^{3-}$; $WO_4^{4-} > > MoO_4^{4-} \simeq CrO_4^{4-}$; $HfO_4^{4-} \leqslant ZrO_4^{4-} > TiO_4^{4-}$). A similar trend in stretching force constant has also been observed by Basile et al. [20]. This may be on account of greater amount of π-bonding occurring for the third row compared with second row or first row transition metal compounds [11, 32]. This trend is not followed by the oxyanions of VB group metals. This demands the reinvestigation of the spectra of these oxyanions, particularly for NbO_4^{3-} and TaO_4^{3-} in solution phase.

TABLE IV

GVFF constants (in mdyn/Å) for tetrahedral metal oxyanions

Molecule	f_r	f_{rr}	$f_{r\alpha}-f'_{r\alpha}$	$f_\alpha-f'_{\alpha\alpha}$	$f_{\alpha\alpha}-f'_{\alpha\alpha}$
TiO_4^{4-}	4.355	0.368	0.157	0.402	0.054
	(4.431)	(0.343)	(0.216)	(0.402)	(0.054)
VO_4^{3-}	4.900	0.510	0.128	0.335	−0.010
	(5.129)	(0.434)	(0.345)	(0.356)	(0.001)
VO_4^{4-}	4.691	0.539	0.151	0.401	0.041
	(4.866)	(0.480)	(0.309)	(0.413)	(0.047)
CrO_4^{2-}	5.747	0.333	0.161	0.426	0.022
	5.609*				
	(5.848)	(0.299)	(0.251)	(0.429)	(0.023)
CrO_4^{3-}	5.415	0.380	0.120	0.313	0.050
	(5.509)	(0.349)	(0.199)	(0.315)	(0.051)
CrO_4^{4-}	5.294	0.276	0.180	0.486	0.047
	(5.328)	(0.265)	(0.207)	(0.486)	(0.047)
MnO_4^{-}	6.018	0.206	0.102	0.549	0.071
	(5.962)	(0.225)	(0.155)	(0.561)	(0.077)
MnO_4^{2-}	5.044	0.390	0.122	0.333	0.001
	(5.208)	(0.336)	(0.277)	(0.343)	(0.005)
MnO_4^{3-}	5.160	0.341	0.133	0.368	0.019
	(5.278)	(0.302)	(0.240)	(0.373)	(0.021)
FeO_4^{2-}	4.885	0.547	0.113	0.315	−0.024
	(5.129)	(0.465)	(0.375)	(0.348)	(−0.007)
FeO_4^{3-}	4.799	0.292	0.123	0.341	0.060
	(4.832)	(0.281)	(0.153)	(0.342)	(0.060)
FeO_4^{4-}	5.185	0.096	0.109	0.299	0.045
	(5.136)	(0.112)	(0.070)	(0.300)	(0.046)
CoO_4^{4-}	5.329	0.185	0.124	0.356	0.037
	(5.347)	(0.178)	(0.139)	(0.356)	(0.037)
ZrO_4^{4-}	5.761	0.051	0.333	0.529	0.091
	(5.573)	(0.113)	(0.067)	(0.514)	(0.084)
NbO_4^{3-}	4.003	0.758	0.096	0.610	0.123
	(4.148)	(0.710)	(0.347)	(0.640)	(0.138)
MoO_4^{2-}	5.978	0.536	0.083	0.347	0.016
	5.856*				
	(6.126)	(0.486)	(0.332)	(0.372)	(0.028)
MoO_4^{4-}	5.293	0.207	0.112	0.481	0.071
	(5.305)	(0.202)	(0.129)	(0.481)	(0.071)
TcO_4^{-}	6.830	0.337	0.092	0.393	0.031
	(6.922)	(0.306)	(0.229)	(0.399)	(0.033)
RuO_4	6.728	0.200	0.090	0.388	0.030
	6.797*				
	(6.778)	(0.184)	(0.160)	(0.389)	(0.031)

TABLE IV (continued)

Molecule	f_r	f_{rr}	$f_{r\alpha}-f'_{r\alpha}$	$f_\alpha-f'_{\alpha\alpha}$	$f_{\alpha\alpha}-f'_{\alpha\alpha}$
RuO_4^-	5.819	0.225	0.079	0.340	−0.010
	(5.909)	(0.194)	(0.220)	(0.348)	(−0.007)
RuO_4^{2-}	5.467	0.395	0.090	0.395	0.025
	(5.573)	(0.359)	(0.265)	(0.408)	(0.032)
HfO_4^{4-}	5.550	0.141	0.076	0.558	0.113
	(5.536)	(0.145)	(0.048)	(0.558)	(0.113)
TaO_4^{3-}	4.348	0.653	0.088	0.687	0.172
	(4.385)	(0.641)	(0.253)	(0.707)	(0.183)
WO_4^{2-}	6.502	0.556	0.056	0.412	0.040
	(6.577)	(0.531)	(0.333)	(0.441)	(0.055)
WO_4^{4-}	6.072	0.094	0.071	0.522	0.097
	(6.056)	(0.090)	(0.037)	(0.533)	(0.100)
ReO_4^-	7.602	0.428	0.058	0.428	0.042
	(7.672)	(0.405)	(0.271)	(0.442)	(0.049)
ReO_4^{3-}	6.165	−0.004	0.054	0.398	0.089
	(6.295)	(0.011)	(0.035)	(0.209)	(0.011)
OsO_4	8.066	0.238	0.055	0.408	0.030
	8.045*				
	(8.115)	(0.222)	(0.188)	(0.413)	(0.032)

First row of each oxyanions represents the GVFF constants evaluated using L–F approximation method. The values in parentheses are derived from OVFF constants listed in Table II.

* Most reliable values of stretching force constant.

Now we shall discuss the relative strength of the metal-oxide bonds in relation to the oxidation state of the metals. For this purpose, the most valuable constant is that involved in bond stretching i. e. $f_r(K_1$ or $K)$. A comparison of the stretching force constant (bond strength) from Table II and Table IV among isoelectronic and isostructural series reveals that it increases, in general, with the increase of oxidation state of the metal ($TiO_4^{4-} < VO_4^{3-} < CrO_4^{2-} < MnO_4^-$; $NbO_4^{3-} < MoO_4^{2-} < TcO_4^- \leqslant RuO_4$; $TaO_4^{3-} < WO_4^{2-} < ReO_4^- < OsO_4$; $VO_4^{4-} < VO_4^{3-}$; $CrO_4^{4-} < CrO_4^{3-} < CrO_4^{2-}$; $MnO_4^{3-} \simeq MnO_4^{2-} < MnO_4^-$; $FeO_4^{3-} < FeO_4^{2-}$; $MoO_4^{4-} < MoO_4^{2-}$; $RuO_4^{2-} < RuO_4^- < RuO_4$; $WO_4^{4-} < WO_4^{2-}$; $ReO_4^{3-} < ReO_4^-$). This trend is also supported by the increase of corresponding bonding force constants (K'_α) and decrease of non-bonded interaction constant (A) in Table II with the increase of oxidation state of the metal. A similar trend in stretching force constant has also been observed by Basile et al. [20] and Jeżowska-Trzebiatowska and coworkers [7, 8]. In case of a few metal oxyanions these trends are not observed in the stretching force constants K_1 (K) obtained for OVFF and UBFF models. For example the stretching force constants for $FeO_4^{4-} > FeO_4^{3-}$; $MoO_4^{4-} > MoO_4^{2-}$ and $WO_4^{4-} > WO_4^{2-}$.

Large values of stretching force constants obtained in the present study for transition metal-oxyanions may be accounted for the stability of such oxygen molecular systems

TABLE V

Correlation between force constant, bond length and bond order of the metal-oxygen bonding*

Molecule	f_r	Bond length R_{MO}	Bond order N by Eq. (1) and Eq. (2)	Bond order N by Eq. (6)	Ref. R_{MO}	Ref. N
TiO_4^{4-}	4.355	1.80	1.6	1.6		
VO_4^{3-}	4.900	1.78 (1.71)	1.7 (2.1)	1.5	[33]	[19]
VO_4^{4-}	4.691	1.79	1.6	1.1		
CrO_4^{2-}	5.747	1.74 (1.66)	1.9 (2.2)	2.2	[33]	[19]
CrO_4^{3-}	5.415	1.76	1.8	1.8		
CrO_4^{4-}	5.294	1.76	1.7	1.4		
MnO_4^{-}	6.018	1.73 (1.586)	1.9	2.5	[34]	
MnO_4^{2-}	5.044	1.77	1.6	1.9		
MnO_4^{3-}	5.160	1.77	1.6	1.6		
FeO_4^{2-}	4.885	1.77 (1.60)	1.5	2.0	[35]	
FeO_4^{3-}	4.799	1.78	1.5	1.7		
FeO_4^{4-}	5.185	1.76	1.6	1.4		
CoO_4^{4-}	5.329	1.76	1.6	1.4		
ZrO_4^{4-}	5.761	1.74	2.1	3.2		
NbO_4^{3-}	4.003	1.82	1.5	2.9		
MoO_4^{2-}	5.978	1.74 (1.77)	2.1 (2.4)	3.9	[33]	[19]
MoO_4^{4-}	5.293	1.76	1.9	2.4		
TcO_4^{-}	6.830	1.71 (1.75)	2.3 (2.25)	4.6	[36]	[36]
RuO_4	6.728	1.71 (1.705)	2.2	—	[37]	
RuO_4^{-}	5.818	1.74 (1.79)	2.0	4.2	[38]	
RuO_4^{2-}	5.467	1.75 (1.75)	1.9	3.3	[8]	
HfO_4^{4-}	5.550	1.80	2.0	3.6		
TaO_4^{3-}	4.348	1.85	1.6	2.5		
WO_4^{2-}	6.502	1.77 (1.79)	2.2 (2.7)	3.3	[33]	[19]
WO_4^{4-}	6.072	1.78	2.1	2.1		
ReO_4^{-}	7.602	1.74 (1.76)	2.5 (2.6)	2.3	[33]	[19]
ReO_4^{3-}	6.165	1.77	2.1	2.6		
OsO_4	8.066	1.73 (1.75)	2.6 (2.2)	—	[33]	[19]

* Experimental values are given in parentheses.

resulting form π-interaction between oxygen and metal. Besides stetching force constant, bond length and bond also provides valuable information about π-interactions. Therefore, a full correlation of the computed results i. e., stetching force constants (GVFF), bond lengths and bond orders, are given in Table V. In a few cases the experimental values of bond lengths and bond orders have also been included in Table V. It is observed from this Table that the calculated and experimental values are in fair agreement. An inspection of numerical values of bond orders, which are the measure of a total bonding effect ($\sigma+\pi$), from Table V, shows that it varies in order $MO_4^- < MO_4^{2-} < MO_4^{3-} < MO_4^{4-}$ in isoelectronic series. This trend leads us to conclusion that the contribution of π-electrons to the metal-oxygen bonding increases with the increase in oxidation state of the metal. The corresponding bond lengths also supports this trend.

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