Transition-metal Tetra-oxo-complexes and their Vibrational Spectra

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The vibrational spectra of a number of transition metal tetra-oxo-complexes are reported for the first time, including those of salts containing the anions $[RuO_4]^-$; $[MO_4]^{2-}$ (M = Mn, Fe, or Ru); $[MO_4]^{3-}$ (M = Cr, Mn, Re, or Fe); and $[MO_4]^{4-}$ (M = Ti, V, Cr, Mo, W, Fe, or Co). From these measurements and published data on the fundamental frequencies of other such ions we calculate force constants for most of the known transition-metal tetra-oxo-anions. Raman data on $[Cr^{18}O_4]^{2-}$ and $[W^{18}O_4]^{2-}$ are also presented

THERE have been a number of reports on the vibrational spectra of the tetra-oxo tetrahedral complexes, $[MO_4]^{n-}$, of transition metals, and these have recently been reviewed;[1] there have also been several force-constant calculations on the basis of these results using various force fields.[1,2] The two most recent studies, and probably the best, have been concerned with $Os^{16}O_4$ and $Os^{18}O_4$ [3] and on RuO_4.[4] In this paper we present results of the Raman (200—1200 cm^{-1}) and i.r. (200—1200 cm^{-1}) measurements on the salts of the many hitherto unstudied $[MO_4]^{n-}$ ions, particularly those involving the metal in lower oxidation states. The aim has been to establish the fundamental vibrational modes, to test the modified valence force field which is said to be the most suitable for tetra-oxo species,[2] and to attempt some correlation of the results in terms of the metal–oxygen bonding in the complexes. Many of the salts studied were either insoluble or were attacked by solvents and so had to be studied in the solid state; it was possible to

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[1] W. P. Griffith, *Co-ordination Chem. Rev.*, 1970, **5**, 459.

[2] A. Müller and B. Krebs, *J. Mol. Spectroscopy.*, 1967, **24**, 180; A. Müller and A. Fadini, *Spectrochim. Acta*, 1966, **22**, 1523.

[3] R. S. McDowell and M. Goldblatt, *Inorg. Chem.*, 1971, **10**, 625.

[4] I. W. Levin and S. Abramowitz, *J. Chem. Phys.*, 1969, **50**, 4860.

obtain Raman spectra in aqueous solution only of $[MnO_4]^{2-}$, $[RuO_4]^{2-}$, $[VO_4]^{3-}$, $[CrO_4]^{3-}$, and $[FeO_4]^{2-}$.

For an undistorted tetrahedron (T_d symmetry) there are four fundamental vibrational modes ($A_1 + E + 2F_2$; all Raman-active with the A_1 mode polarised; only the F_2 modes are i.r. active). Two of the modes are predominantly of the stretching type, ν_1 (A_1) and ν_3 (F_2), and the other two are deformations, ν_2 (E) and ν_4 (F_2). In Table 1 we list the assignments for these four modes for all the ions studied here together with published data [1] on other transition-metal tetra-oxo-anions. In Table 2 we give the results of our studies on the spectra of $[MO_4]^{n-}$ species; the assignment from the bands observed of the four modes presents a number of difficulties, especially where solid-state results have to be used. In general the site symmetry of the $[MO_4]^{n-}$ ion in a crystal lattice is lower than T_d; such site symmetries are usually obtainable from X-ray data and the use of correlation diagrams allows us to predict the consequent splitting of the four fundamental 'free ion' modes (although a factor group analysis is more appropriate in such cases, we have shown that for a wide variety of $[MO_4]^{n-}$ species a simple site symmetry approach is adequate for assignment purposes [5]). The expected splittings for ν_2, ν_3, and ν_4 for different site symmetries have been listed.[5] The totally symmetric MO_4 stretch ν_1 is easily identified by its intensity in the Raman of $[MO_4]^{n-}$ species; in solutions of the ions, it is the only polarised Raman mode. The asymmetric stretch ν_3 is normally very strong in the i.r. but usually weak or even absent in the Raman; being triply degenerate (like ν_4) it is frequently split in i.r. spectra of the solids. The assignment of ν_2 and ν_4 is difficult in some cases; we assume that ν_4 will be stronger than ν_2 in the i.r. (in the free ions ν_2 is Raman-active only) and ν_4 is usually more split in the solid salts than ν_2, since it is triply degenerate and ν_2 doubly degenerate. Nevertheless these assignments may sometimes be tentative and it is quite possible that in some cases our assignments for ν_2 and ν_4 in Table 1 should be reversed. In some cases also, particularly for the heavier metals, the deformations may coincide. No corrections for anharmonicity have been made for any of the frequencies given.

TABLE 1

Fundamental vibrational modes and MVFF constants for tetra-oxo-complexes

	ν_1 (A_1)	ν_2 (E)	ν_3 (F_2)	ν_4 (F_2)	f_d	f_{dd}	f_α	$f_{\alpha\alpha}$
RuO_4 [a]	883	338	918	332	6·714	0·21	0·39	0·02
OsO_4 [b]	965	333	961	329	8·03	0·225	0·43	0·04
$[MnO_4]^-$ [c]	838	355	921	429	5·79	0·28	0·59	0·10
$[TcO_4]^-$ [d]	912	325	912	325	6·75	0·38	0·37	0·02
$[ReO_4]^-$ [e]	971	332	916	332	7·50	0·45	0·43	0·04
$K[RuO_4]$	830	339	845	312	5·75	0·25	0·34	0·02
$[CrO_4]^{2-}$ [f]	847	348	884	368	5·48	0·43	0·42	0·02
$[MoO_4]^{2-}$ [d]	897	318	841	318	5·94	0·55	0·35	0·02
$[WO_4]^{2-}$ [e]	931	324	833	324	6·42	0·58	0·41	0·04
$[MnO_4]^{2-}$ *	812	325	820	332	4·88	0·45	0·35	0·07
$[FeO_4]^{2-}$ *	832	340	790	322	4·73	0·59	0·32	0·01
$[RuO_4]^{2-}$ *	840	331	804	336	5·39	0·42	0·40	0·03
$[VO_4]^{3-}$ *	827	337	780	341	4·53	0·64	0·36	0·00
$[CrO_4]^{3-}$ *	834	260	860	324	5·25	0·44	0·38	0·06
$K_3[MnO_4]$	810	324	838	349	5·01	0·39	0·38	0·02
$Li_3[ReO_4]$	808	264	853	319	6·13	0·01	0·27	0·01
$K_3[FeO_4]$	776	265	805	335	4·63	0·45	0·35	0·06
$Ba_2[TiO_4]$	761	306	770	371	4·09	0·52	0·42	0·07
$Li_4[ZrO_4]$	792	332	846	387	5·51	0·14	0·52	0·09
$Li_4[HfO_4]$	796	325	800	379	5·51	0·16	0·56	0·11
$Ba_2[VO_4]$	818	319	780	368	4·49	0·60	0·42	0·00
$Ba_2[CrO_4]$	806	353	855	404	5·02	0·37	0·53	0·07
$Ba_2[MoO_4]$	792	328	808	373	5·19	0·24	0·53	0·10
$Ba_2[WO_4]$	821	323	840	367	6·04	0·11	0·58	0·13
$Ba_2[FeO_4]$	762	257	857	314	5·05	0·14	0·31	0·05
$Ba_2[CoO_4]$	790	300	855	340	5·17	0·21	0·36	0·04

[a] Ref. 4. [b] Ref. 3. [c] P. J. Hendra, *Spectrochim. Acta*, 1968, **24A**, 125; S. Pinchas, D. Samuel, and E. Petreanu, *J. Inorg. Nuclear Chem.*, 1967, **29**, 335. [d] Ref. 23. [e] Ref. 21. D. Bassi and O. Sala, *Spectrochim. Acta*, 1958, **12**, 403.

Spectra measured in aqueous solution for ions (or * aqueous alkali) RuO_4 measured in pure liquid phase, ref. 4; OsO_4 in vapour phase; other data from Table 2. Frequencies in cm^{-1}; no corrections made for anharmonicity. Force constants in mdyn/Å.

ASSIGNMENT OF MODES

$M^{VIII}O_4$ *Complexes*.—In Table 1 we quote the most recent values for osmium [3] and ruthenium [4] tetroxides; isotopic data are available for both.[3,4]

$[M^{VII}O_4]^-$ *Complexes*.—We could obtain solid-state data only for $K[RuO_4]$ since this (and other perruthenate salts) disproportionate in water. X-Ray data on $K[RuO_4]$ indicate a scheelite structure with a Ru–O bond length of 1·79 Å and S_4 site symmetry for the anion;[6] in agreement with this we find ν_3 and ν_4 to be split into doublets. We assign ν_4 to the intense Raman band at 312 cm^{-1} and ν_2 to the Raman band at 339 cm^{-1}.

$[M^{VI}O_4]^{2-}$ *Complexes*.—Unequivocal assignments for ν_1 (polarised) and ν_3 (depolarised) are provided by the solution Raman data for potassium manganate and ruthenate. For the former, the 325 cm^{-1} Raman band is assigned to ν_2 and that at 332 cm^{-1} to ν_4 (since in solid $K_2[MnO_4]$ there is a strong band at 333 cm^{-1} presumably due to ν_4). The X-ray crystal structure of $K_2[MnO_4]$ shows a site symmetry of C_s for the anion, hence the complex splitting of ν_3 and ν_4 modes; the Mn–O distance of 1·659 Å is, as expected, slightly longer than that in $K[MnO_4]$ (1·629 Å).[7] In $K_2[RuO_4]$ the 336 cm^{-1} band is assigned to ν_4 and that at 331 cm^{-1} to ν_2 (solid $Ba[RuO_4]$ has a single i.r. band at 330 cm^{-1} presumably due to ν_4).

Potassium ferrate, $K_2[FeO_4]$, is isomorphous with $K_2[CrO_4]$ and has C_s site symmetry for the anion; we reverse the literature assignments of ν_1 and ν_3 based on the solid-state i.r. spectrum of this salt [8] from the state of polarisation of lines in the Raman spectrum of the alkaline solution. For the deformations, ν_4 is assigned as having a slightly lower frequency than ν_2 as the solid salt has a strong i.r. band at 319 cm^{-1}.

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[5] W. P. Griffith, *J. Chem. Soc. (A)*, 1970, 286.

[6] M. D. Silverman and H. A. Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3317.

[7] G. J. Palenik, *Inorg. Chem.*, 1967, **6**, 507.

[8] P. Tarte and G. Nizet, *Spectrochim. Acta*, 1964, **20**, 503.

Table 2

Raman (R) and i.r. frequencies for tetra-oxo-complex salts

	$\nu_1(A_1)$		$\nu_2(E)$		$\nu_3(F_2)$		$\nu_4(F_2)$		Other strong bands	
	R	i.r.	R	i.r.	R	i.r.	R	i.r.	R	i.r.
$[MO_4]^-$ salts										
$K[RuO_4]$	830(10)		339(1)		840w	846s 835m	317w 312(4)	316m 305s		
$[MO_4]^{2-}$ salts										
$K_2[MnO_4]$ *	812(10)p		325(3)		820(3)dp		332(2)			
$K_2[MnO_4]$	813(10)	810w	325(3)	327w 322w	841w 836w	844m 835v	339($\frac{1}{2}$)	333s 326m 321m	860(1)	301m
$Ba[MnO_4]$	803(10)		330($\frac{1}{2}$)	330w	840w 824w	857s 838m 828m	338(2)	336s 326m 321m	875(1) 660(3)b	690m 620m 301s
$K_2[FeO_4]$ *	832(10)p		340(3)		790(6)dp		322(5)			
$K_2[FeO_4]$	830(10)		336($\frac{1}{2}$)	340m	796(6) 786(1)	816w 796vs 780m	318(2) 312(3) 307(1)	324w 319vs 311w	840(2)	620s 297w
$K_2[RuO_4]$ *	840(10)p		331(3)		804(2)p		336(6)			
$Ba[RuO_4]$						818m 812vs 806m		330s		
$[MO_4]^{3-}$ salts										
$K_3[CrO_4]$ *	834(10)p		260(1)		860(2)dp		324(4)			
$Ba_3[CrO_4]_2$	828(10)	824w	276(1)	280w		868m 855vs 844w	319(6)	319s 309w	763(5) 676(2) 276(1)	762vs
$K_3[MnO_4]$	810(10)	810m	324(4)		839(2)	860w 838vs 826w	349(2)			
$Cs_3[MnO_4]$	810(10)	805w	328($\frac{1}{2}$)		836(2)	843m 831vs 819w	364(2)	368w 364vs 362w	736(1)	460w
$Li_3[ReO_4]$	808(10)	800w	264(1)	264m	863w 848w	869m 853vs 836m	333(3) 320(3) 317(1)	332m 319vs	700(3) 505(4) 474(4)	680b
$K_3[FeO_4]$	776(10)	780m	265(2)	264w	818(5)	820m 805s 798m	347($\frac{1}{2}$) 335(3)	339w 335vs 331w	870(4)	856m 617s
$[MO_4]^{4-}$ salts										
$Ba_2[TiO_4]$	761(10)	761w	315($\frac{1}{2}$) 306(4)	319m 310w	775(2)	780m 770vs 765m	384($\frac{1}{2}$) 373($\frac{1}{2}$)	371s	692(2) 255(3)	698s 500m 338m
$Li_4[ZrO_4]$	792(10)		342(2) 332(2)	320w	851(1) 835(3)	846s	389(1) 380(4)	392w 387vs 380m	616(1) 596(7) 474(3)	740s 520s
$Li_4[HfO_4]$	796(10)		332(1) 325(1)	320w		800s 772m	384(6) 366(2)	390w 386m 368m	636(3) 592(8)	608s 510m 477s
$Ba_2[VO_4]$	818(10)	820w	319w	333s 324m	788w 776($\frac{1}{2}$) 762(2)	808m 780s	379(2) 368(4) 361($\frac{1}{2}$)	367m 364s 360w		672s 573m 471m
$Mg_2[VO_4]$	816(10)	820vw	333(2)	333w	788($\frac{1}{2}$) 764(4)	766vs	380(1) 368(4) 361w	367m 364s 360w		574s 480s
$Ba_2[CrO_4]$	806(6)		361(4) 353(6)	373m 369w		873m 855vs 825m	404(3)	416s 412w 390s	862(10) 464(1)	890m 768m 692s
$Ba_2[MoO_4]$	792(10)	790w	328(5)	325m 327s		824w 808vs	398(3) 352(4)	373s	891(5) 704(1) 666(1)	510b 293w
$Ba_2[WO_4]$	821(10)	820w	323(6)	329m		850w 840vs 784w	398(5) 367(4)	371s 365sh	410(2)	682s
$Ba_2[FeO_4]$	762(10)		257(3)		846(1)	892m 857m 823w	324w 320w	320m 314s 308m	688(8) 500(9)	692m 500s
$Na_4[FeO_4]$	796(10)	798w	280w			878s 853m	338w 332(4)		716(4) 415(2)	693m 633s 464s
$Ba_2[CoO_4]$	790(10)		303(2) 296(2)	301m 295w	850(2) 830(2)	855s 840m	340($\frac{1}{2}$)	340s 335m	720(2) 690(6) 600(6)	768m 732m 692w

Raman (R) and i.r. spectra on sosid salts.

* Aqueous solutions; spectra 200—1200 cm^{-1}.

We also report the Raman spectra of aqueous solutions of $[Cr^{18}O_4]^{2-}$ and $[W^{18}O_4]^{2-}$; the values of the fundamentals are used to provide a check for the calculation of force constants (see below).

$[M^{V}O_4]^{3-}$ *Complexes*.—For $K_3[CrO_4]$ polarisation data for the alkaline aqueous solution allow unambiguous assignment of ν_1 and ν_3, and we assign ν_4 to 324 cm^{-1} as the barium salt $Ba_3[CrO_4]_2$ (which is known to contain $[CrO_4]^{3-}$ tetrahedra [9]), and solid $K_3[CrO_4]$ have i.r. bands near this frequency. There are no structural data on $K_3[CrO_4]$, but the Cr–O bond length in $Ca_5[CrO_4]_3OH$ has been shown to be 1·66 Å.[9]

Several salts of the very unstable ' hypomanganate ' ion $[MnO_4]^{3-}$ were made; all had similar spectra, but reliable solution data could not be obtained. For the solid salts examined, comparison of Raman and i.r. spectra suggested that ν_4 is higher than ν_2 (no structural data for these salts are reported). Although the salt $Li_3[ReO_4]$ is reported in the literature [10] no synthetic details are supplied, so we used a preparative method similar to that employed for $Li_3[MnO_4]$.[11] For $K_3[FeO_4]$ the only far-i.r. band is at 335 cm^{-1} which is accordingly assigned to ν_4; *X*-ray studies show that the salt contains tetrahedral anions.[12]

$[M^{IV}O_4]^{4-}$ *Complexes*.—Most of these were studied as the solid barium salts since no aqueous solutions of $[MO_4]^{4-}$ transition-metal species are stable. It has been shown by an *X*-ray crystal study that $Ba_2[TiO_4]$ contains discrete $[TiO_4]^{4-}$ tetrahedra (Ti–O = 1·70 Å); the anion has C_s site symmetry,[13] and it has been shown that all the other $Ba_2[MO_4]$ salts in Table 1 are isomorphous with $Ba_2[TiO_4]$.[14,15] † The splitting of bands which we assign to ν_3 and ν_4 into triplets, and ν_2 into doublets, is consistent with C_s site symmetry. There is no direct evidence that $Li_4[ZrO_4]$ or $Li_4[HfO_4]$ contain tetrahedra, but the appearance of their Raman and i.r. spectra suggests that this is the case.

In a number of cases quoted in Table 2, bands were observed in the i.r. and Raman spectra of the salts which could not be assigned with confidence to any of the four fundamental vibrational modes; these occur most frequently for the barium salts and are found *ca.* 600 cm^{-1}. These we believe to arise from Ba–O stretching modes; bands below 250 cm^{-1} may arise from deformation modes.

TABLE 3

Fundamental modes of vibration and force constants for $[M^{16}O_4]^{n-}$ and $[M^{18}O_4]^{n-}$ complexes

	ν_1	ν_2	ν_3	ν_4	F_{11}	F_{22}	F_{33}	F_{34}	F_{44}	f_d	f_{dd}	$(f_\alpha - f_{\alpha\alpha})$	$(f_{\alpha\alpha} - f_{\alpha\alpha'})$	$(f_{d\alpha} - f_{d\alpha'})$
$[Cr^{16}O_4]^{2-}$	847	348	884	368	6·76	0·38	5·05	0·08	0·40	5·48	0·43	0·39	0·01	0·06
$[Cr^{18}O_4]^{2-}$	799	330	850	353										
$[Cr^{18}O_4]^{2-}$ *	798	328	851	355										
$[W^{16}O_4]^{2-}$	931	324	833	324	8·17	0·33	5·82	−0·1	0·35	6·42	0·56	0·34	0·01	−0·07
$[W^{18}O_4]^{2-}$	879	309	791	309										
$[W^{18}O_4]^{2-}$ *	878	305	791	309										
$Os^{16}O_4$ [a]	965	333	961	329	8·70	0·35	7·80	0·04	0·42	8·03	0·22	0·37	0·05	0·03
$Os^{18}O_4$ [a]	910	316	912	313										
$Os^{18}O_4$ *	910	314	912	313										

* Calculated frequencies using MVFF of Table 1.

[a] From ref. 3, using uncorrected frequencies; force constants in mdyn/Å.

FORCE CONSTANTS

A number of force fields have been applied to tetra-oxo-species [1,2] these include a general valence (GVFF),[3] Urey–Bradley,[16] orbital valency [17] and modified valency force field (MVFF).[2]

Since there are only four frequencies to calculate the five symmetry force constants F_{ij} for $[MO_4]^{n-}$ molecules we have to fix one of these values; we have chosen to place $F_{34} = 0$, and so to use the MVFF approximation. This appears from previous work [2] to provide reasonable force constants for transition-metal tetra-oxo-complexes, and its extension to a large number of other species of this type is one of the main objectives of this work. As a check on the validity of the MVFF we have measured the four fundamental modes for solutions of $[Cr^{18}O_4]^{2-}$ and for $[W^{18}O_4]^{2-}$ and calculated F_{34} for these molecules; the results in Table 3 show that for both molecules F_{34} is very small. Isotopic data, Coriolis constants, and mean amplitudes of vibration have also shown that F_{34} is small (0·1 ± 0·1 for OsO_4,[3] −0·3 ± 0·3 for RuO_4 [4]). A further justification for use of the MVFF is the closeness of the calculated and observed frequencies for $[Cr^{18}O_4]^{2-}$ and $[W^{18}O_4]^{2-}$; the calculated frequencies (in Table 3)

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† Recently, $Ba_2[CoO_4]$ has been shown to contain discrete $[CoO_4]^{4-}$ tetrahedron of C_s symmetry (Co–O = 1·76 Å) (M. Mattausch and H. Mueller-Buschbaum, *Z. anorg. Chem.*, 1971, **386**, 1)

[9] K. A. Wilhelmi and O. Jonsson, *Acta Chem. Scand.*, 1965, **19**, 177.

[10] R. Scholder, *Angew Chem.*, 1958, **70**, 583.

[11] R. Scholder, D. Fischer, and H. Waterstradt, *Z. anorg. Chem.*, 1954, **277**, 234.

[12] W. Klemm, quoted by A. Carrington and M. C. R. Symons, *Chem. Rev.*, 1963, **63**, 443.

[13] J. A. Bland, *Acta Cryst.*, 1961, **14**, 875.

[14] R. Scholder and W. Klemm, *Angew. Chem.*, 1954, **66**, 461.

[15] R. Scholder and G. Sperka, *Z. anorg. Chem.*, 1956, **285**, 49.

[16] A. Müller, R. Ahrlich, and B. Krebs, *Z. Naturforsch.*, 1966, **21**, 719.

[17] B. Krebs and A. Müller, *J. Mol. Spectroscopy*, 1967, **22**, 290.

are obtained using the MVFF values obtained for $[Cr^{16}O_4]^{2-}$ and $[W^{16}O_4]^{2-}$. The equations for the G and F matrices for the MVFF are [2,18]

$$\begin{array}{ll} (\text{for } \nu_1)\ G_{11} = \mu_0 & F_{11} = f_d + 3f_{dd} \\ (\text{for } \nu_2)\ G_{22} = 3\mu_0 & F_{22} = f_\alpha - 2f_{\alpha\alpha} \\ (\text{for } \nu_3 \text{ and } \nu_4): & \end{array}$$

$$\begin{array}{ll} G_{33} = (4\mu_M/3) + \mu_0 & F_{33} = f_d - f_{dd} \\ G_{34} = -(8\mu_M/3) & F_{34} = 0 \\ G_{44} = (16\mu_M/3) + 2\mu_0 & F_{44} = f_\alpha \end{array}$$

(the notation used is that of Müller and Fadini [2]). In Table 1 we list values, using the MVFF, for f_d (stretching force constant), f_{dd} (stretch–stretch interaction), f_α (deformation constant), and $f_{\alpha\alpha}$ (interaction constant for adjacent angles). The MVFF [2] assumes that three further interaction constants have zero values ($f_{\alpha\alpha'}$, interaction of opposite angles; $f_{d\alpha}$, interaction of a bond with angles including the bond; and $f_{d\alpha'}$, interaction of the bond stretch with other angles). The general valence force field (GVFF) then has the same expressions for F_{11} and F_{33} as the MVFF, while for the other F values the following expressions hold: [2,18]

$$\begin{aligned} F_{22} &= f_\alpha + f_{\alpha\alpha'} - 2f_{\alpha\alpha} \\ F_{34} &= \sqrt{2}(f_{d\alpha} - f_{d\alpha'}) \\ F_{44} &= f_\alpha - f_{\alpha\alpha'} \end{aligned}$$

Although the use of ligand isotopes for determining F_{34} is a relatively approximate method, as the negative value of $(f_{d\alpha} - f_{d\alpha'})$ for tungstate shows, it is clear that the omission of F_{34} for MVFF calculations is not too serious. The calculations were performed on frequencies uncorrected for anharmonicity; ν_1 is taken directly from Table 2 and the ν_2, ν_3, and ν_4 frequencies are usually taken as the strongest components of the bands assigned to these modes in Table 2.

DISCUSSION

Owing to the approximations of the MVFF, the lack of anharmonicity corrections and the fact that solids had to be used for the spectra so that true 'free ion' values were not always obtainable, it is clear that the force constant figures are best used on a comparative basis only. It is evident that f_d drops with oxidation state for a given metal (*e.g.* $Ru^{VIII} > Ru^{VII} > Ru^{VI}$), an exception is $[MnO_4]^{3-}$ for which f_d is anomalously high. The same trend is seen within a series of isoelectronic species (*e.g.* $O^{VIII} > Re^{VII} > W^{VI}$; $Cr^{VI} > V^{V} > Ti^{IV}$); these effects clearly follow from the greater degree of $(\sigma + \pi)$ bonding in high oxidation states. The more effective $(\sigma + \pi)$ bonding of heavier elements in vertical Periodic triads is seen in the decrease of f_d from the third to first row in such groups (*e.g.* $Re^{VII} > Tc^{VII} > Mn^{VII}$; $W^{VI} > Mo^{VI} > Cr^{VI}$).

Relationships between Force Constants and between Frequencies.—The observation [19] of an empirical relationship between f_d and the $(t_1 \longrightarrow 2e)$ electronic transition for groups of d^0 ions of the same oxidation states is found to hold, but the observation that the $f_{dd} : f_d$ ratio tends to be constant for species of the same oxidation state [20] holds only for the (VIII), (VII), and (VI) states. The deformation constant f_α remains fairly constant for most species, with a slight tendency to higher values for the lighter elements and for lower oxidation states, and the deformation interaction constant $f_{\alpha\alpha}$ remains remarkably low for all species.

Clearly the symmetric stretch ν_1 provides a better measure of f_d than does the asymmetric stretch ν_3. If our assignments are correct, for almost all species where ν_3 exceeds ν_1 then ν_4 exceeds ν_2 (and the reverse is also true in most cases: if $\nu_1 > \nu_3$, then $\nu_2 > \nu_4$). The expectation that $\nu_3 > \nu_1$ and $\nu_4 > \nu_2$ for lighter metals with equality or reversal for heavier metals [21,22] is generally found, though there are exceptions. In particular, $\nu_3 > \nu_1$ and $\nu_4 > \nu_2$ for highly charged ions, which is perhaps to be expected since the symmetric stretching and deformation modes will involve more O–O repulsions than the asymmetric modes if negative charge tends to be localised on the oxo-ligands. Although it has been claimed that ν_2 is too weak and broad to be observed for some ions (*e.g.* $[MnO_4]^{2-}$, $[WO_4]^{2-}$, $[TcO_4]^-$, and $[ReO_4]^-$),[23] the intensity of this mode in the other species studied by us suggests that, as has already been proposed,[1,21] ν_2 and ν_4 are simply coincident in these cases.

EXPERIMENTAL

The following salts were made by the standard literature methods: $K[RuO_4]$ [24]; $K_2[MnO_4]$ [25]; $K_2[FeO_4]$ [26]; $K_2[RuO_4]$ [24] (the aqueous solution only was prepared); $K_3[CrO_4]$ [27]; $Ba_3[CrO_4]_2$ [28]; $K_3[MnO_4]$ and $Cs_3[MnO_4]$ [11]; $Li_3[ReO_4]$ was made by a similar method; [11] $K_3[FeO_4]$ [27]; $Ba_2[TiO_4]$ [13]; $Li_4[ZrO_4]$ and $Li_4[HfO_4]$ [29]; $Ba_2[VO_4]$ [10]; $Ba_2[CrO_4]$ [15]; $Ba_2[MoO_4]$ and $Ba_2[WO_4]$ [14,30]; $Ba_2[FeO_4]$ and $Na_4[FeO_4]$ [31]; $Ba_2[CoO_4]$ [10,14]. The barium

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salts Ba[MnO_4] and Ba[RuO_4] were prepared by addition of barium chloride to solutions of K_2[MnO_4] and K_2[RuO_4] in potassium hydroxide solutions. The solutions of K_2[MnO_4], K_2[FeO_4], and K_3[CrO_4] were made by dissolving the solids in 10% aqueous potassium hydroxide solution under nitrogen.

I.r. spectra were measured as Nujol mulls between potassium bromide plates for the 400—1200 cm^{-1} region and as Vaseline mulls between Polythene plates in the 200—400 cm^{-1} region on a Perkin-Elmer 325 instrument. Raman spectra of aqueous solutions were measured in capillary tubes and of solids as microcrystalline powders on a Cary 81 instrument with a CRL 52MG mixed-gas (argon–krypton) laser; red excitation (6471 Å) was used for red, brown, and purple samples; the yellow 5648 Å lines for chromate; the green 5145 Å line for green samples; and the blue 4880 Å line for blue and for colourless samples.

Oxygen-18 enriched $[Cr^{18}O_4]^{2-}$ was made by addition of potassium dichromate (0·025 g) to a 20% solution of $Na^{18}OH$ in $H_2{}^{18}O$ (98% enrichment, 0·5 ml; the calculated percentage of $[Cr^{18}O_4]^{2-}$ in the product is 74·8% and of $[Cr^{18}O_3{}^{16}O]^{2-}$, 22·5%); $[W^{18}O_4]^{2-}$ was prepared by addition of solid tungsten hexachloride to 50% $Na^{18}OH$ in $H_2{}^{18}O$ (98% enrichment giving 92% of $[W^{18}O_4]^{2-}$).

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