

SPECTROSCOPIC STUDIES OF ROOT-MEAN-SQUARE AMPLITUDES
FOR SOME TETRAHEDRAL OXYANIONS OF GROUPS VB, VIB,
AND VIIB ELEMENTS

BY V. ANANTHA NARAYANAN

Department of Mathematics and Physics, Savannah State College*

AND

G. NAGARAJAN

Department of Physics and Astronomy, Valdosta State College**

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A brief description of the vibrational and structural analysis of a few oxyanions of group VB, VIB, and VIIB elements, such as VO_4^{3-} , CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , MnO_4^- , MnO_4^{2-} , MnO_4^{3-} , TcO_4^- , and ReO_4^- possessing a regular tetrahedral structure with the symmetry point group T_d has been made. On the basis of group-theoretical considerations, the mean-square amplitudes, generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products), and root-mean-square amplitudes for both bonded and nonbonded atom pairs have been evaluated for these oxyanions at the temperatures $T = 298^\circ\text{K}$ and $T = 500^\circ\text{K}$. The behaviour of the root-mean-square amplitudes for both bonded and nonbonded atom pairs has been explained in terms of the electronegativities of the central atoms. The results have been discussed on the chemical significance of the characteristic bonds for all the oxyanions.

Introduction

All the existing molecules and ions of the type XY_4 having highly symmetrical configurations may be classified into four groups, namely, a tetragonal square plane with the symmetry point group D_{4h} , a tetragonal pyramid belonging to the point group C_{4v} , a slightly distorted tetrahedral configuration with the point group D_{2d} , and a regular tetrahedron with the symmetry point group T_d . For the first of these, four coplanar bonds directed toward the corners of a square are formed by dsp^2 hybridization and these configurations

* Address: Department of Mathematics and Physics, P. O. Box 20473, Savannah State College, Savannah, Georgia 31404, USA.

** Address: Department of Physics and Astronomy, Valdosta State College, Valdosta, Georgia 31601, USA.

are well known for the tetra-coordinated derivatives of the type XY_4 of Ni^{2+} , Pd^{2+} , Pt^{2+} , Cu^{2+} , Ag^{2+} , Au^{2+} , and other elements. For the second of these, four tetragonal pyramidal bonds are formed from a d^4 configuration, and molecules of this class possessing a spatial arrangement are still unknown, but the boron skeleton of stable pentaborane may be cited under this symmetry. For the third of these, the d orbitals of X and the appropriate orbitals of Y are formed and the molecule is slightly deformed by compressing or stretching it along one of the axes; molecules of this class are still unknown. Among the considerable number of vibrational and structural studies, the largest and thoroughly investigated group is of the fourth one involving the sp^3 hybridization.

Theoretical investigations on the vibrations of a tetragonal square planar model of D_{4h} symmetry, and computations of root-mean-square amplitudes for many ions and molecules have been carried out by many investigators [1-7]. A method has been theoretically developed earlier for the determination of root-mean-square amplitudes for a tetragonal pyramid with C_{4v} symmetry, and applied to boron skeleton of stable pentaborane [8]. Similarly, a method has been theoretically developed very recently for the determination of root-mean-square amplitudes for a slightly distorted tetrahedral configuration with D_{2d} symmetry, and applied to a phosphate ion [9]. Among the considerable number of vibrational spectra and molecular structures, the largest and thoroughly investigated group is the last of these series involving the sp^3 hybridization. Cyvin [7] has developed a theoretical method for the determination of root-mean-square amplitudes for this regular tetrahedral model with T_d symmetry, and several investigators [7] have extended this theory to many molecules. Such investigations have been, due to the lack of reliable vibrational assignments, limited only to a few ions of regular tetrahedral symmetry. In the present study, a few oxyanions of groups VB, VIB, and VIIB elements, such as VO_4^{3-} , CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , MnO_2^- , MnO_4^{2-} , MnO_4^{3-} , TcO_4^- , and BeO_4^- have been chosen for the evaluation of mean-square amplitudes, generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products), and root-mean-square amplitudes at the temperatures $T = 298^\circ K$ and $T = 500^\circ K$ such that the results of the present investigation would be very useful in future for the evaluation of normal frequencies in other related oxyanions and molecules having similar chemical bonds, for the interpretation of the results of electron diffraction studies, and for the determination of ionic and molecular structures.

Root-mean-square amplitudes

The normal modes of oscillation for a molecule or ion of the present study has already been given by Herzberg [10]. According to the relevant symmetry considerations and selection rules [10], a molecule or ion of the present study with the symmetry point group T_d would give rise to nine vibrational degrees of freedom constituting only four fundamental frequencies. They are distributed under the various irreducible representations as follows: $A_1 + E + 2F_2$. The frequency ν_1 corresponds to a totally symmetrical stretching mode under the symmetry species A_1 ; ν_2 corresponds to a bending mode under the symmetry species E ; and ν_3 and ν_4 correspond to an asymmetrical stretching mode and a bending

mode, respectively under the symmetry species F_2 . The A_1 , E and F_2 type vibrations represent the nondegenerate, doubly degenerate, and triply degenerate modes, respectively. All the vibrations are allowed in the Raman spectrum but only the F_2 vibrations are allowed in the infrared absorption spectrum.

TABLE I
Fundamental frequencies in cm^{-1} for some tetrahedral oxyanions of groups VB, VIB, and VIIB elements

Ion	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
VO_4^{3-}	827	340	790	340
CrO_4^{2-}	847	348	884	368
MoO_4^{2-}	894	381	833	318
WO_4^{2-}	931	373	833	320
MnO_4^-	845	355	910	395
MnO_4^{2-}	810	328	862	328
MnO_4^{3-}	863	348	770	348
TcO_4^-	912	347	912	325
ReO_4^-	972	332	916	332

The analytical expressions for the mean-square amplitudes, generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products), and root-mean-square amplitudes for both bonded and nonbonded atom pairs for a molecule or ion of the present study have been generated by Cyvin [11–13]. Many investigations were carried out to assign the vibrational frequencies for the anions VO_4^{3-} , CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , MnO_4^- , MnO_4^{2-} , MnO_4^{3-} , TcO_4^- , and ReO_4^- . The vibrational frequencies in cm^{-1} for these anions are given in Table I from the recent Raman and infrared spectral studies as well as theoretical investigations [14–21]. The basic equation $|\Sigma G^{-1} - \Delta E| = 0$ generated by Cyvin [22] has been adopted here for constructing and solving the secular equations, where Δ has been related to the normal frequency ν in the form $\Delta_i = \left(\frac{h}{8\pi^2\nu_i} \right) \text{Coth} \left(\frac{h\nu_i}{2kT} \right)$ and E is the unity matrix. Here, h is the Planck's constant, k the Boltzmann constant, and T the temperature in degrees Kelvin. The secular equations giving the normal frequencies in terms of the mean-square amplitudes were constructed at the temperatures $T = 298^\circ\text{K}$ and $T = 500^\circ\text{K}$ with help of the fundamental frequencies in cm^{-1} given in Table I. Since the secular equations are singular under the symmetry species A_1 and E , the symmetrized mean-square amplitude matrices Σ_{11} and Σ_{22} were readily obtained. There are three unknowns, namely, Σ_{33} , Σ_{44} , and Σ_{34} , with only two secular equations under the symmetry species F_2 . When the off-diagonal element Σ_{34} was neglected, the secular equations resulted to imaginary values for the diagonal elements. Hence, the off-diagonal element was taken into consideration, and the secular equations were then solved by the method of Torkington [23].

The evaluated values of the symmetrized mean-square amplitude matrices in \AA^2 for all the anions are given in Table II at the temperatures $T = 298^\circ\text{K}$ and $T = 500^\circ\text{K}$. The mean-square amplitudes were calculated from the symmetrized mean-square amplitudes

TABLE II

Symmetrized mean-square amplitude matrices in \AA^2 for some tetrahedral oxyanions of groups VB, VIB, and VIIB elements

Ion	Element	Symmetrized mean-square amplitude matrix	
		$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$
VO_4^{3-}	Σ_{11}	0.0013223	0.0015345
	Σ_{22}	0.0137676	0.0205043
	Σ_{33}	0.0021310	0.0024455
	Σ_{44}	0.0135479	0.0206872
	Σ_{34}	-0.0000319	-0.0000568
CrO_4^{2-}	Σ_{11}	0.0012870	0.0014827
	Σ_{22}	0.0132389	0.0196391
	Σ_{33}	0.0018551	0.0020595
	Σ_{44}	0.0118869	0.0178545
	Σ_{34}	-0.0000398	-0.0000640
MoO_4^{2-}	Σ_{11}	0.0012110	0.0013739
	Σ_{22}	0.0114347	0.0166272
	Σ_{33}	0.0016254	0.0018719
	Σ_{44}	0.0138188	0.0209560
	Σ_{34}	-0.0001106	-0.0001642
WO_4^{2-}	Σ_{11}	0.0011578	0.0012990
	Σ_{22}	0.0118311	0.0172852
	Σ_{33}	0.0014620	0.0016948
	Σ_{44}	0.0123390	0.0185672
	Σ_{34}	-0.0002913	-0.0003704
MnO_4^{2-}	Σ_{11}	0.0012905	0.0014878
	Σ_{22}	0.0128215	0.0189295
	Σ_{33}	0.0017755	0.0019511
	Σ_{44}	0.0104190	0.0154380
	Σ_{34}	-0.0000327	-0.0000587
MnO_4^{3-}	Σ_{11}	0.0013544	0.0015815
	Σ_{22}	0.0146191	0.0219231
	Σ_{33}	0.0018360	0.0020703
	Σ_{44}	0.0144973	0.0221010
	Σ_{34}	-0.0000584	-0.0000899
MnO_4^{3-}	Σ_{11}	0.0012599	0.0014438
	Σ_{22}	0.0132389	0.0196391
	Σ_{33}	0.0021462	0.0024852
	Σ_{44}	0.0127929	0.0194326
	Σ_{34}	-0.0000665	-0.0000572

Table II (continued)

Ion	Element	Symmetrized mean-square amplitude matrix	
		$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$
TeO_4^-	Σ_{11}^*	0.0011836	0.0013364
	Σ_{22}^*	0.0133111	0.0197440
	Σ_{33}^*	0.0014531	0.0016328
	Σ_{44}^*	0.0132836	0.0200575
	Σ_{34}^*	-0.0001303	-0.0002013
ReO_4^-	Σ_{11}^*	0.0011045	0.0012252
	Σ_{22}^*	0.0143251	0.0214336
	Σ_{33}^*	0.0013137	0.0014831
	Σ_{44}^*	0.0115776	0.0172032
	Σ_{34}^*	-0.0002931	-0.0001114

TABLE III

Mean-square amplitude quantities in \AA^2 for some tetrahedral oxyanions of groups VB, VIB, and VIIB elements

Symbol	$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$	$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$
	VO_4^{3-}		CrO_4^{2-}	
σ_r	0.0019289	0.0022174	0.0017130	0.0019153
σ_{rr}	-0.0002022	-0.0002277	-0.0001420	-0.0001442
σ_θ	0.0113632	0.011784	0.0103564	0.0154736
$\sigma_{\theta\theta}$	-0.0022946	-0.0034174	-0.0022065	-0.0032732
$\sigma_{\theta\theta'}$	-0.0021847	-0.0035088	-0.0015305	-0.0023809
$\sigma_{r\theta}$	-0.0000113	-0.0000201	-0.0000141	-0.0000226
$\sigma_{r\theta'}$	0.0000113	0.0000201	0.0000141	0.0000226
σ_d	0.0060687	0.0083416	0.0055203	0.0074767
σ_{dd}	0.0001167	-0.0001161	0.0001225	-0.0001026
$\sigma_{dd'}$	-0.0012460	-0.0017390	-0.0008693	-0.0011355
σ_{rd}	0.0014033	0.0016132	0.0012746	0.0014330
$\sigma_{rd'}$	-0.0003236	-0.0003603	-0.0002238	-0.0002224
	MoO_4^{2-}		WO_4^{2-}	
σ_r	0.0015218	0.0017474	0.0013860	0.0015958
σ_{rr}	-0.0001036	-0.0001245	-0.0000761	-0.0000990
σ_θ	0.0107210	0.0160204	0.0101132	0.0150453
$\sigma_{\theta\theta}$	-0.0019058	-0.0027712	-0.0019718	-0.0028809
$\sigma_{\theta\theta'}$	-0.0030978	-0.0049356	-0.0022258	-0.0035219
$\sigma_{r\theta}$	-0.0000391	-0.0000580	-0.0001030	-0.0001310
$\sigma_{r\theta'}$	0.0000391	0.0000580	0.0001030	0.0001310
σ_d	0.0053909	0.0073945	0.0049234	0.0067640
σ_{dd}	0.0001721	-0.0000078	0.0001146	-0.0000943
$\sigma_{dd'}$	-0.0012351	-0.0018678	-0.0007506	-0.0011909
σ_{rd}	0.0011354	0.0012916	0.0010101	0.0011466
$\sigma_{rd'}$	-0.0001466	-0.0001698	-0.0000647	-0.0000860

Table III (continued)

Symbol	$T = 298^\circ\text{K}$		$T = 500^\circ\text{K}$	
	MnO_4^-		MnO_4^{3-}	
σ_r	0.0016543	0.0018352	0.0017156	0.0019481
σ_{rr}	-0.0001213	-0.0001158	-0.0001204	-0.0001222
σ_θ	0.0094833	0.0140289	0.0121268	0.0183582
$\sigma_{\theta\theta}$	-0.0021369	-0.0031549	-0.0024365	-0.0036539
$\sigma_{\theta\theta'}$	-0.0009357	-0.0014092	-0.0023756	-0.0037428
$\sigma_{r\theta}$	-0.0000116	-0.0000207	-0.0000206	-0.0000318
$\sigma_{r\theta'}$	0.0000116	0.0000207	0.0000206	0.0000318
σ_d	0.0051833	0.0069297	0.0061386	0.0084940
σ_{dd}	0.0001480	-0.0000598	0.0000908	-0.0001636
$\sigma_{dd'}$	-0.0006135	-0.0007395	-0.0010740	-0.0015136
σ_{rd}	0.0012450	0.0013919	0.0012905	0.0014725
$\sigma_{rd'}$	-0.0001913	-0.0001772	-0.0001847	-0.0001812

Symbol	MnO_4^{3-}		TcO_4^-	
	σ_r	0.0019246	0.0022248	0.0013857
σ_{rr}	-0.0002216	-0.0002604	-0.0000674	-0.0000741
σ_θ	0.0103094	0.0162627	0.0110788	0.0166101
$\sigma_{\theta\theta}$	-0.0022065	-0.0032732	-0.0022185	-0.0032907
$\sigma_{\theta\theta'}$	-0.0019835	-0.0031699	-0.0022048	-0.0034474
$\sigma_{r\theta}$	-0.0000235	-0.0000202	-0.0000461	-0.0000712
$\sigma_{r\theta'}$	0.0000235	0.0000202	0.0000461	0.0000712
σ_d	0.0058295	0.0080020	0.0053638	0.0073819
σ_{dd}	0.0001044	-0.0001286	0.0000495	-0.0000206
$\sigma_{dd'}$	-0.0012077	-0.0017128	0.0008277	-0.0012126
σ_{rd}	0.0013770	0.0015923	0.0010498	0.0011711
$\sigma_{rd'}$	-0.0003483	-0.0004135	-0.0000834	-0.0000799

Symbol	ReO_4^-	
	σ_r	0.0012614
σ_{rr}	-0.0000523	-0.0000644
σ_θ	0.0105636	0.0157461
$\sigma_{\theta\theta}$	-0.0023875	-0.0035723
$\sigma_{\theta\theta'}$	-0.0010138	-0.0014570
$\sigma_{r\theta}$	-0.0001036	-0.0000394
$\sigma_{r\theta'}$	0.0001036	0.0000394
σ_d	0.0049380	0.0069799
σ_{dd}	-0.0000595	-0.0003739
$\sigma_{dd'}$	0.0002820	-0.0005833
σ_{rd}	0.0009274	0.0010829
$\sigma_{rd'}$	-0.0000256	-0.0000825

TABLE IV

Generalized mean-square amplitudes in \AA^2 for some tetrahedral oxyanions of elements of groups VB, VIB, and VIIB

Ion	Mean-square amplitude	Bonded atom pair		Nonbonded atom pair	
		$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$	$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$
VO_4^{3-}	$\langle \Delta z^2 \rangle$	0.0019289	0.0022174	0.0060687	0.0083416
	$\langle \Delta x^2 \rangle$	0.0036875	0.0055876	0.0039679	0.0056385
	$\langle \Delta y^2 \rangle$	0.0036875	0.0055876	0.0050313	0.0073859
CrO_4^{2-}	$\langle \Delta z^2 \rangle$	0.0017130	0.0019153	0.0055203	0.0074767
	$\langle \Delta x^2 \rangle$	0.0033320	0.0049843	0.0035986	0.0050528
	$\langle \Delta y^2 \rangle$	0.0033320	0.0049843	0.0046661	0.0067915
MoO_4^{2-}	$\langle \Delta z^2 \rangle$	0.0015218	0.0017474	0.0053909	0.0073945
	$\langle \Delta x^2 \rangle$	0.0035439	0.0053149	0.0034792	0.0049349
	$\langle \Delta y^2 \rangle$	0.0035439	0.0053149	0.0044131	0.0064029
WO_4^{2-}	$\langle \Delta z^2 \rangle$	0.0013860	0.0015958	0.0049234	0.0067640
	$\langle \Delta x^2 \rangle$	0.0032995	0.0049218	0.0032059	0.0045722
	$\langle \Delta y^2 \rangle$	0.0032995	0.0049218	0.0042603	0.0061985
MnO_4^-	$\langle \Delta z^2 \rangle$	0.0016543	0.0018352	0.0051833	0.0069297
	$\langle \Delta x^2 \rangle$	0.0030221	0.0044720	0.0033546	0.0046597
	$\langle \Delta y^2 \rangle$	0.0030221	0.0044720	0.0043942	0.0063424
MnO_4^{2-}	$\langle \Delta z^2 \rangle$	0.0017156	0.0019481	0.0061386	0.0084940
	$\langle \Delta x^2 \rangle$	0.0039365	0.0059708	0.0040252	0.0057717
	$\langle \Delta y^2 \rangle$	0.0039365	0.0059708	0.0052545	0.0077676
MnO_4^{3-}	$\langle \Delta z^2 \rangle$	0.0019246	0.0022248	0.0058295	0.0080020
	$\langle \Delta x^2 \rangle$	0.0035019	0.0052802	0.0038167	0.0054204
	$\langle \Delta y^2 \rangle$	0.0035019	0.0052802	0.0048256	0.0070629
TcO_4^-	$\langle \Delta z^2 \rangle$	0.0013857	0.0015587	0.0053638	0.0073819
	$\langle \Delta x^2 \rangle$	0.0036000	0.0054061	0.0035429	0.0050587
	$\langle \Delta y^2 \rangle$	0.0036000	0.0054061	0.0047279	0.0069344
ReO_4^-	$\langle \Delta z^2 \rangle$	0.0012614	0.0014186	0.0049380	0.0069799
	$\langle \Delta x^2 \rangle$	0.0033646	0.0050118	0.0033317	0.0049026
	$\langle \Delta y^2 \rangle$	0.0033646	0.0050118	0.0046966	0.0069793

and their values in \AA^2 are given in Table III at the temperatures $T = 298^\circ\text{K}$ and $T = 500^\circ\text{K}$, where σ is the mean-square amplitude due to the bonded atom pair X—Y, σ_θ the mean-square amplitude due to the bending $\widehat{\text{Y—X—Y}}$, σ_d the mean-square amplitude due to the nonbonded atom pair Y—Y, and σ_{rr} , $\sigma_{\theta\theta}$, $\sigma_{\theta\theta'}$, $\sigma_{r\theta}$, $\sigma_{r\theta'}$, σ_{dd} , $\sigma_{dd'}$, σ_{rd} , and $\sigma_{rd'}$ are the respective interaction quantities. One may refer to the earlier studies [11–13] for the detailed description of these quantities.

The generalized mean-square amplitudes (mean-square parallel amplitudes, mean-

TABLE V

Mean amplitudes of vibration in Å for some tetrahedral oxyanions of groups VB, VIB, and VIIB elements

Ion	Distance	Mean amplitude of vibration	
		$T = 298^\circ\text{K}$	$T = 500^\circ\text{K}$
VO_4^{3-}	V—O	0.0439	0.0471
	O-----O	0.0779	0.0913
CrO_4^{2-}	Cr—O	0.0414	0.0438
	O-----O	0.0743	0.0865
MoO_4^{2-}	Mo—O	0.0390	0.0418
	O-----O	0.0734	0.0860
WO_4^{2-}	W—O	0.0372	0.0400
	O-----O	0.0702	0.0822
MnO_4^-	Mn—O	0.0407	0.0428
	O-----O	0.0720	0.0833
$\text{Mn}_2\text{O}_4^{3-}$	Mn—O	0.0414	0.0441
	O-----O	0.0784	0.0922
$\text{Mn}_2\text{O}_4^{3-}$	Mn—O	0.0439	0.0472
	O-----O	0.0764	0.0895
TcO_4^-	Tc—O	0.0372	0.0935
	O-----O	0.0732	0.0859
ReO_4^-	Re—O	0.0355	0.0377
	O-----O	0.0703	0.0835

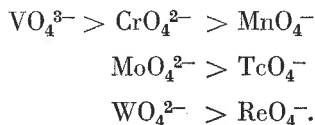
-square perpendicular amplitudes, and mean cross products) were then calculated from the symmetrized mean-square amplitudes and their values in Å² for both bonded and nonbonded atom pairs are given in Table IV for all the anions at the temperatures $T = 298^\circ\text{K}$ and $T = 500^\circ\text{K}$. The corresponding calculated values of the root-mean-square amplitudes in Å for both bonded and nonbonded atom pairs are given in Table V at the two temperatures studied for all the anions.

Results

The values of off-diagonal elements for most of the anions are much smaller in magnitude in comparison with those of the diagonal elements. However, they play an important role in solving the secular equations, because the diagonal elements were highly sensitive even to small changes in the off-diagonal elements. In general, the mean-square amplitude due to the nonbonded atom pair Y—Y is much greater than those of the bonded atom pair X—Y, and all other interaction quantities, but is much smaller than that of bending

$\widehat{Y-X-Y}$. The large value of the mean-square amplitude due to the bending and the small values of the mean-square amplitudes due to the bonded atom pairs, nonbonded atom pairs, and interaction quantities are exactly in reverse to the corresponding values of the valence and bonded force constants in many molecules and ions [3, 6, 24-26]. The mean-square amplitudes due to the interaction of bonded atom pairs and those due to the interaction of bonded and nonbonded atom pairs are generally smaller than those due to the interaction of bending and bonding. The mean-square amplitudes due to the interaction of bonded atom pair and bending, namely, $\sigma_{r,\theta}$ and $\sigma_{r,\phi}$, are, by symmetry of the ionic system, equal in magnitude but opposite in sign. The mean-square perpendicular amplitudes $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are, by symmetry of the ionic system, equal in magnitude in the case of bonded atom pair but different in the case of nonbonded atom pair (see Table V). The mean cross products, namely $\langle \Delta x \Delta y \rangle$, $\langle \Delta y \Delta z \rangle$, and $\langle \Delta z \Delta x \rangle$ vanish completely, by symmetry of the ionic system, for both the bonded and nonbonded atom pairs. As it is expected, the mean-square amplitudes due to the bonded atom pairs, nonbonded atom pairs, bending, and all other interaction quantities increase with increasing temperature.

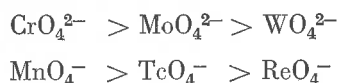
The atomic numbers of the central atoms increase in order by one unit, while those of the peripheral oxygen atoms remain fixed, as an example, for the anions VO_4^{3-} , CrO_4^{2-} , and MnO_4^- . There is an increase of all the four fundamental frequencies from the triply negatively charged anion to the singly negatively charged anion MnO_4^- (see Table I). The obtained values of the root-mean-square amplitudes in Å for the bonded atom pairs V—O, Cr—O, and Mn—O are 0.0439, 0.0414, and 0.0407, respectively. The same situation can be observed for the other values of mean-square amplitudes (see Tables III and V) for the following series of anions:



This shows that the change in the electronegativity of the central atom is very sensitive to the mean-square amplitude, though the difference in the atomic weights of the central atoms is significantly small.

For any molecular system, the replacement of one or more atoms with atom or atoms of higher atomic weights lowers the fundamental frequencies, thereby decreasing the magnitudes of the force constants and increasing the magnitudes of the mean-square amplitudes. But, in the present series of anions CrO_4^{2-} , MnO_4^{2-} and WO_4^{2-} , the magnitudes of the fundamental frequencies are in the irregular order (see Table I). However, there is a regular order in the magnitudes of the mean-square amplitudes. The values of root-mean-square amplitudes in Å for the bonded atom pairs Cr—O, Mo—O and W—O are 0.0414, 0.0390, and 0.0372, respectively. The same situation can be observed for the other values of the mean-square amplitudes and root-mean-square amplitudes for the doubly negatively charged anions CrO_4^{2-} , MoO_4^{2-} , and WO_4^{2-} . Similarly, the values of the root-mean-square amplitudes in Å for the bonded atom pairs Mn—O, Tc—O, and Re—O are 0.0407, 0.0372, and 0.0355, respectively. The same situation can be observed for the other values of the mean-square

amplitudes and root-mean-square amplitudes for the singly negatively charged anions MnO_4^- , TcO_4^- , and ReO_4^- . Thus, the values of the mean-square amplitudes are in the decreasing order for the same series of doubly negatively charged anions or for the same series of singly negatively charged anions.



This shows that the increase in atomic weight of the central atom causes a decrease in the mean-square amplitudes, and this situation in ionic systems is contrary to the result in molecular systems. Further, this can be understood from the irregular orders of the fundamental frequencies in a series of ionic systems in the same group of the periodic table.

The values of the mean-square amplitudes, generalized mean-square amplitudes, and root-mean-square amplitudes obtained here are very correct at the room temperature, only when the fundamental frequencies (symmetrical as well as asymmetrical stretchings) in wave numbers are in the range 200–1200 cm^{-1} . If the frequency is above 1200 cm^{-1} , the hyperbolic cotangent approaches unity near the room temperature and correspondingly the root-mean-square amplitude due to the respective atom pair is an independent function of temperature. If the frequency is below 200 cm^{-1} , the coth function gives merely approximate values, and correspondingly the root-mean-square amplitude is a function of temperature. In the present investigation, the stretching frequencies as well as the bending frequencies are above 200 cm^{-1} and below 1200 cm^{-1} for all the anions studied here, and hence the obtained values of the root-mean-square amplitudes for both bonded and nonbonded atom pairs are reliable and dependable. The results of the present study would be very useful in future for the evaluation of normal frequencies in other related oxyanions, for the structural studies, and for the interpretation of the results of electron diffraction studies.

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