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Structural features and spectroscopic and energy characteristics of alkali metal molybdates and tungstates

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ABSTRACT. The results of X-ray structural, i.r. and Raman spectroscopic, and thermodynamic studies of alkali metal molybdates and tungstates $A_2M_nO_{3n+1}$ (A = Li, Na, K, Rb, Cs; M = Mo, W) are reviewed and analysed. The dependence of the vibrational spectra, activation energies, and crystal lattice energies on features of the structures of these compounds is discussed.

The bibliography comprises 51 references.

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I. Introduction

In recent decades there has been increased interest in the study of molybdates and tungstates of various compositions. The range of compounds whose structures have been determined using precision techniques has expanded considerably. It has been found that molybdates and tungstates can form a large number of fundamentally different structures, the number of structure types running to dozens. Molybdenum and tungsten have the ability to form various oxygen coordination polyhedra which have a tendency to condensation at appropriate cation ratios.

The general crystal-chemical principles of molybdates and tungstates are set out in two monographs[1,2] but there is not a great deal of discussion of the alkali metal compounds.

There are many publications devoted to studies of molybdates and tungstates by vibrational spectroscopic methods (i.r. and spontaneous Raman).[3–5] However no serious attempts have so far been made to collect together the available data and to review them together with X-ray structural data.

The present work aims to fill this gap. We have interpreted the vibrational spectra of the alkali metal molybdates and tungstates on the basis of an analysis of their crystal structures and proposed explanations for the variation in the spectroscopic and thermodynamic characteristics along this series of compounds. However information on the thermodynamics of molybdates and tungstates is disconnected and very meagre. Some values (atomisation energies and crystal lattice energies) have been calculated by the authors using known experimental data. Such information, and to such an extent, is not present in any of the available publications.

The compounds under discussion have structures with discrete tetrahedral or octahedral oxygen coordination polyhedra and also various types of linking of these to form chain or block structures. However alkali metal cations introduce very small perturbations into the energetics of molybdenum-oxygen or tungsten-oxygen ensembles compared to the cations of other elements. There is no mixing of the vibrations of the cationic sublattices with the vibrations of the molybdenum-oxygen or tungsten-oxygen systems. Lithium compounds form an exception. The frequencies of lithium cation vibrations appear in the deformation region of the oxygen polyhedra but they can be fairly safely distinguished in experiments using specimens in which the lithium is isotopically substituted ($^6Li-^7Li$).

Thus structural features of the molybdenum-oxygen and tungsten-oxygen systems and the type of interatomic interactions in them are controlling factors affecting the energy characteristics (vibration frequencies, thermodnamic values) of the molybdates and tungstates under discussion. The correlations obtained for them can be used successfully to interpret the results of studies of molybdates and tungstates of elements which form stronger cation–oxygen bonds with appreciable covalent contributions.

II. Crystal chemistry of the alkali metal molybdates and tungstates

Alkali metal molybdates and tungstates can be divided into four structural series depending on the types of molybdenum-oxygen and tungsten-oxygen polyhedra and the way in which they are joined together:[1]

structures with isolated tetrahedral MO_4 anions;

structures with chain-type anions composed of MO_4 tetrahedra (or MO_5 pyramids) and MO_6 octahedra;

polygon-network structures based on MO_6 octahedra sharing corners;

block structures formed by MO_6 octahedra sharing edges.

The first series comprises compounds with the general formula A_2MO_4 (A = Li, Na, K, Rb, Cs; M = Mo, W) in which the $MO_3:A_2O$ ratio is equal to one. They have structures formed by isolated MO_4 tetrahedra. The type of coordination polyhedron of the alkali metal depends on its ionic radius and varies along the series from lithium to caesium as the coordination number (CN) of the cation A increases from 4 to 10 (Table 1).

For example, in the structures of Li_2MoO_4 and Li_2WO_4 [6,7] the lithium has close tetrahedral coordination (hexagonal phenacite Be_2SiO_4 structure type[7]). On moving to Na_2MoO_4 and Na_2WO_4 [8,9] a spinel structure with octahedral coordination of the sodium cations by oxygen is found. As the size of the alkali metal cation increases further its CN rises to 8 in K_2MoO_4 and K_2WO_4, and also in

Rb_2MoO_4 and Rb_2WO_4 [10,11] while caesium, the largest cation in this series, has two types of coordination polyhedra, with CN's of 6 and 10, in Cs_2MoO_4 and Cs_2WO_4.[12]

Table 1. Changes in structural features in the alkali metal molybdates and tungstate series.

Compound	Structural series	Space group	Z	CN_A	r_{A-O}	CN_M	r_{M-O}*	Refs.
Li_2MoO_4	structure with tetrahedral MO_4^{2-} complexes	$R\bar{3}$	6	4				[7]
Li_2WO_4	ditto	$R\bar{3}$	6	4	1.96(8)	4	1.79(8)	[6]
Na_2MoO_4	»	$Fd3m$	8	6				[8]
Na_2WO_4	»	$Fd3m$	8	6	2.378(8)	4	1.819(8)	[9]
K_2MoO_4	»	$C2/m$	4	8	2.74(1)–3.21(1)	4	1.76(1)	[10, 11]
K_2WO_4	»	$C2/m$	4	8				[10, 11]
Rb_2MoO_4	»	$C2/m$	–	–				[10, 11]
Rb_2WO_4	»	$C2/m$	–	–				[10, 12]
Cs_2MoO_4	»	$Pnam$	4	4,10				[12]
Cs_2WO_4	»	$Pnam$	4	4,10				[12]
$Li_2W_2O_7$	structure with octahedral complexes	$P\bar{1}$	2	4	1.90(5)–2.11(4)	6	1.74(2)–2.30(1)	[14]
$Na_2Mo_2O_7$	chain structure with tetrahedra and octahedra	$Cmca$	8	6	1.2–1.75	4 6	1.71; 1.75; 1.69; 1.90; 2.26	[15]
$Na_2W_2O_7$	ditto	$Cmca$	8	6	2.35(2)–2.56(1)	4 6	1.76; 1.807(9) 1.725; 1.921; 2.252	[16]
$K_2Mo_2O_7$	»	$P\bar{1}$	2	9	2.59–3.64	4 6	1.75–1.80 1.75; 1.76; 1.83; 2.10; 2.17; 2.27	[17]
$K_2Mo_3O_{10}$	chain structures with trigonal bipyramids and octahedra	$C2/c$	4	10	2.64–3.47	5 6	1.64–2.08 1.69; 1.99; 2.11	[18]
$Rb_2Mo_3O_{10}$	ditto	$C2/c$	4	10				[19]
$Cs_2Mo_3O_{10}$	»	$C2/c$	4	10				[19]
$K_2W_3O_{10}$	polygon-network	$P2/c$	6	9,13	2.58(4)–3.55(4)	6	1.68(5)–2.21(3)	[20]
$Li_2Mo_4O_{13}$	block structure	$P\bar{1}$	3	6	1.91(3)–2.58(3)	6	1.68(1)–2.47(1)	[21]
$Na_2W_4O_{13}$	polygon-network	$P\bar{1}$	1	5	2.16–2.65	6	1.71–2.28	[22]
$K_2Mo_4O_{13}$	chain structure with octahedra	$P\bar{1}$	2	8	2.67(3)–3.37(4)	6	1.67(3)–2.39(3)	[25]
$K_2W_4O_{13}$	polygon-network structure with octahedra	$P\bar{3}$	3	14,18	2.72(3)–3.75(4)	6	1.75(3)–2.12(4)	[23, 24]
$Rb_2Mo_4O_{13}$	ditto	$P\bar{1}$	2	8				[25]
$Rb_2Mo_5O_{16}$	block structures	$C2/c$	4	10				[26]
$Cs_2Mo_5O_{16}$	ditto	$C2/c$	4	10	2.96–3.41	6	1.70–2.51	[27]
$Rb_2Mo_7O_{22}$	»	$C2/c$	4	10				[26]
$Cs_2Mo_7O_{22}$	»	$C2/c$	4	10	2.94–3.53	6	1.70–2.51	[26]

*For the set of compounds with chain structures formed from tetrahedra and octahedra all the r_{M-O}(oct) values are listed in the order: r_{M-O}(terminal), r_{M-O}(bridging, *trans*), r_{M-O}(bridging, *cis*).

Since molybdenum and tungsten in higher oxidation states have fairly similar ionic radii[5] molybdates and tungstates with the same alkali metal cation are expected to be isomorphous. However, this assumption is valid only for the low-temperature modifications of A_2MO_4. As the $MO_3:A_2O$ ratio is increased diferences appear in the structure of isopolymolybdates and isopolytungstates. Nevertheless in both instances systems of condensed MO_n (n = 4, 5, 6) polyhedra are formed.

The structure of $Li_2W_2O_7$, which forms triclinic crystals,[6] is composed of LiO_4 tetrahedra and distorted WO_6 octahedra linked by shared edges to form $(W_2O_7)^{2-}$ anions, which in turn form infinite chains. Moving to the larger sodium cation in $Na_2Mo_2O_7$ [7] and $Na_2W_2O_7$ [8] leads to changes in the coordination of both the alkali metal and the molybdenum or tungsten. Here the $(M_2O_7)^{2-}$ anions, which form infinite chains, are composed of MO_4 tetrahedra and MO_6 octahedra with shared corners. This combination of different coordination polyhedra is typical of the stereochemistry of molybdenum and, to a significant extent, tungsten. The sodium has octahedra coordination in $Na_2Mo_2O_7$ but occupies two sets of positions, in oxygen octahedra and pentagonal pyramids, in the structure $Na_2W_2O_7$.

A further increase in the size of the alkali metal cation is accompanied by an increase in the CN to 9. The structure of $K_2Mo_2O_7$,[9] like that of $Na_2Mo_2O_7$, is composed of chains of molybdenum-oxygen tetrahedra and octahedra but their mutual arrangement is different. A pair of octahedra has a shared edge and is linked by means of two tetrahedra, via shared corners, to the next pair. Each tetrahedron and octahedron has two free vertices.

Increasing the $MO_3:A_2O$ ratio to three leads, in the structure of $K_2Mo_3O_{10}$,[10,11] to the production of a new type of chain which is formed from square-pyramidal MoO_5 polyhedra and MoO_6 octahedra. The chain unit comprises an octahedron and two pyramids but each octahedron is linked via corners to four pyramids.

Thus there is a general tendency to a change in the chain structure on going from $Na_2Mo_2O_7$ to $K_2Mo_2O_7$ and $K_2Mo_3O_{10}$. In $Na_2Mo_2O_7$ the octahedra share corners and are also linked in pairs by tetrahedra. In $K_2Mo_2O_7$ two neighbouring octahedra share edges and each pair is joined to the next pair via the corners of two tetrahedra; the relative number of tetrahedrally coordinated molybdenum atoms is greater than in $Na_2Mo_2O_7$. In the structure of $K_2Mo_3O_{10}$ all the octahedra are linked by pairs of tetrahedra with a change in the latter to distorted tetragonal pyramids due to the formation of a fifth, longer Mo–O bond with the tetrahedra drawn appreciably closer together.

A comparison of the MoO_6 octahedra in these structures reveals a number of trends in the Mo–O bond lengths:

(i) there is a tendency to form two long, two short, and two medium-length bonds between the central atom and oxygen;

(ii) in the *trans* position to a short bond there is a long bond and this is usually longer (weaker), the shorter (stronger) is the short bond;

(iii) the mean Mo–O distances are fairly similar (~1.94 Å) in compounds with different compositions.

These rules are also valid for the WO_6 octahedra in the structure of $Na_2W_2O_7$.[8]

In all cases a decrease in the Mo_{tetr}–O bond lengths is accompanied by lengthening of the associated O–Mo bonds, the tetrahedron becoming quasi-free (the bonds in the octahedron nearest to it are weakened while the bonds in the tetrahedron itself are strengthened).

Although the molybdenum-oxygen distances differ considerably the lengths of the O...O edges of the octahedra lie within a fairly narrow range, 2.75 ± 0.1 Å. The preference of the oxygen atoms to be spaced at equilibrium distances from each other influences the magnitude and form of the angular distortions. The electron density is increased at one, two, or three *cis*-located Mo–O bonds but decreased at the others. This phenomenon can be likened to a *trans* effect.

The polymolybdates $K_2Mo_3O_{10}$, $Rb_2Mo_3O_{10}$, and $Cs_2Mo_3O_{10}$ are isostructural.[11] The structure of $K_2W_3O_{10}$ [12] differs considerably from that of the molybdates of similar composition. Among the compounds under discussion it provides the simplest example of a polygon-network structure with planar nets made up of ensembles of WO_6 octahedra linked to form infinite chains and channels running through the whole structure. The potassium cations occupy positions in the channels with coordination numbers of 9 and 13.

When the $MO_3:A_2O$ ratio is increased to 4 or more the molybdenum or tungsten atoms change to exclusively octahedral coordination. Thus on going from simple molybdates to di-, tri-, and tetra-molybdates the coordination of molybdenum by oxygen changes from tetrahedral with octahedral, square pyramidal with octahedral, and finally pure octahedral.

An oxygen atom deficiency in the tetramolybdates necessitates appreciable joining together with the edges and/or corners of the octahedra. For example, $Li_2Mo_4O_{13}$ has a three-dimensional block structure.[13] The structure of $Na_2W_4O_{13}$ [14] is composed of groups of four WO_6 octahedra sharing edges and linked to form an infinite chain, also via shared edges, whereas the tunnel structure of $K_2W_4O_{13}$ [15,16] contains WO_6 octahedra linked by shared contents to form six-membered rings. The reason for this is that the larger potassium ion requires a larger number of neighbours and the rigid unit chain of octahedra present in $Na_2W_4O_{13}$ cannot be distorted to such an extent.

The triclinic potassium and rubidium tetramolybdates are isomorphous.[17] Caesium tetramolybdate probably has a similar structure.[17] In the structure of $K_2Mo_4O_{13}$ groups of four MoO_6 octahedra with almost coplanar central atoms have shared edges and are joined to similar groupings, by shared edges, to form infinite chains. The latter do not have shared oxygen atoms but are held together by potassium ions in eight-coordinate positions.

With this mutual arrangement of the MoO_6 octahedra the molybdenum atoms are drawn closer together, leading to their mutual repulsion from the centres of the octahedra. This in turn causes differences between the molybdenum–oxygen interatomic distances which is typical of many structures of compounds containing molybdenum in a high oxidation state.

The three types of chain structure known at present for di-, tri-, and tetra-molybdates remain stable in the presence of alkali metal cations of a certain size. The lower limit of the cation size is determined by the arrangement of the chains but the upper limit depends on the way in which the polyhedra are joined together to form a chain and also their potentiality for ensuring coordination of large cations. For example, the helical chain structure of the trimolybdate may remain stable in the presence of potassium, rubidium, or caesium due to it ability to rotate and to extend somewhat whereas the dimolybdate chain structure is not in a position to be extended and is therefore not found with cations larger than sodium.

The tetramolybdate chain structure is the most compact of those discussed and even with its greater rigidity it proved possible to retain it for potassium and rubidium cations. The structure of caesium tetramolybdate is however different from those of $K_2Mo_4O_{13}$ and $Rb_2Mo_4O_{13}$.[17]

The occurrence of polymolybdates with the largest $MoO_3:A_2O$ ratio for rubidium and caesium is evidently due to the ability of these large cations to be combined effectively with the largest number of molybdenum-oxygen fragments.

III. Vibrational spectra

The study of the vibrational spectra of alkali metal molybdates and tungstates has received great attention. However most of the research has been concerned with the compounds in the A_2MO_4 (A = Li, Na, K, Rb, Cs; M = Mo, W) series which have comparatively simple structures. Their i.r. spectra in the region down to 70 cm^{-1} [3,4] and Raman spectra of polycrystalline specimens[28–31] have been obtained.

A group-theoretical analysis of the distribution of the vibrations of MO_4^{2-} anions, which form the basis of the crystal structure of these compounds, among the irreducible representations of the point group T_d gives

$$\Gamma_{vib} = A_1(\text{Raman}) + E(\text{Raman}) + 2T_2(\text{IR, Raman}).$$

Hence the Raman spectrum of "free" tetrahedral MO_4^{2-} anions will contain one line due to the totally symmetric stretch $\nu_1(A_1)$, one line due to the triply degenerate vibration $\nu_3(T_2)$, and two lines due to the deformations $\nu_2(E)$ and $\nu_4(T_2)$. Only the two triply degenerate vibrations $\nu_3(T_2)$ and $\nu_4(T_2)$ will be i.r.-active.

The values of the vibrational wavenumbers of "free" MoO_4^{2-} and WO_4^{2-} ions have been obtained from measurements of the spectra of aqueous solutions[29] in polarised light and of ions isolated in an inert-gas matrix,[31–34] in conjunction with a theoretical analysis of the wavenumbers and modes of the normal vibrations.[35]

Table 2. Wavenumbers (cm^{-1}) of the vibrations of the free tetrahedral ions.[35]

Ion	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(T_2)$	$\nu_4(T_2)$
MoO_4^{2-}	896	381	833	318
WO_4^{2-}	931	373	833	320

The effect of the alkali metal cations on the vibrations of MoO_4^{2-} and WO_4^{2-}, as functions of their concentration, was considered. The presence of lithium and sodium cations in the solution increases the vibrational wavenumbers of the anions, the effect being more marked in the case of lithium. The introduction of potassium, rubidium, and caesium cations into the system leads to a reduction in the vibrational wavenumbers due to enhancement of the effective polarisability of the water molecules surrounding the anions. The perturbation recorded was more appreciable for the tungstate ion. Extrapolation of the experimental data to infinite dilution gives values of the symmetric vibration ν_1 of 931 cm^{-1} for WO_4^{2-} and 896 cm^{-1} for MoO_4^{2-}.

The data given in Table 2 provide a basis for analysing the vibrations of crystalline specimens. Such vibrations are described not only by the wavenumbers of the internal vibrations of the oxo-anions but also by the wavenumbers of the external vibrations — the librations of the anions and the translational vibrations of the anions and cations.

The changes in the wavenumbers in the vibrational spectra of Na_2MoO_4 and Na_2WO_4 on moving from liquid to crystalline specimens have been analysed.[36] The Raman lines at 928 and 892 cm^{-1} were assigned (by analogy with the spectra of the solutions) to the symmetric stretches $\nu_1(A_1)$. Lines at 813 and 808 cm^{-1} were assigned to $\nu_3(T_2)$. The fact that, if the anion symmetry is T_d, only the T_2 mode can appear in the i.r. spectra of crystalline Na_2MoO_4 and Na_2WO_4 enables the two remaining wavenumbers to be safely assigned to the deformations $\nu_2(E)$ and $\nu_4(T_2)$.

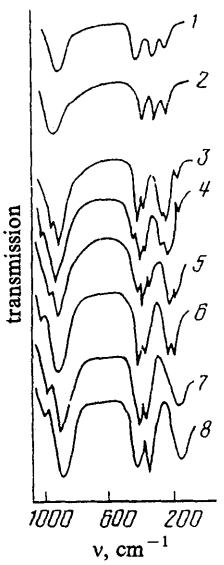


Figure 1. Ir spectra of alkali metal monomolybdates and monotungstates:[25] *1*, Na_2MoO_4; *2*, Na_2WO_4; *3*, K_2MoO_4; *4*, K_2WO_4; *5*, Rb_2MoO_4; *6*, Rb_2WO_4; *7*, Cs_2MoO_4; *8*, Cs_2WO_4.

It was found that $\nu_2(E) > \nu_4(T_2)$ for both the free ions and the anions in a crystal field, so that there is inversion of these wavenumbers in the spectra of Na_2MoO_4 and Na_2WO_4 compared to those in the spectra of the tetrahedral anions ClO_4^-, SO_4^{2-}, PO_4^{3-}, and CrO_4^{2-}, for which $\nu_4(T_2) > \nu_2(E)$. Similarly $\nu_1(A_1) > \nu_3(T_2)$ which is also in the reverse order compared to the wavenumbers for the other tetrahedral ions. The Raman lines at 116 and 93 cm^{-1} in the spectra of crystalline Na_2MoO_4 and Na_2WO_4 relate to external lattice vibrations. Similar results were obtained from a study of the i.r. and Raman spectra[4] of anhydrous mono-molybdates and -tungstates of the whole series of alkali metals, with the exception of lithium in the region down to 70 cm^{-1} (Table 3, Figs. 1 and 2). The spectra were interpreted using the results of a group-theoretical analysis of the vibrations of Na_2MoO_4 crystals which have a spinel structure composd of MoO_4 tetrahedra and NaO_6 octahedra.[8] The bands in the spectra of the other alkali metal compounds were assigned by analogy with Na_2MoO_4. All the vibrations are active in both the Raman and i.r. spectra. This, and also the considerable difference between the wavenumbers observed in these spectra, is due to interaction between the vibrations of crystallographically equivalent tetrahedral anions and their distortion in the crystal field.

For all the compounds under discussion the vibrations of the tetrahedral oxo-anions were found to occur in the regions shown in Table 2.

In the molybdates and tungstates the vibrations of the alkali metal cations with octahedral coordination occur below 230 cm^{-1}. The two i.r. bands at 230 and 170 cm^{-1} and the Raman line at 120 cm^{-1} in the spectrum of Na_2MoO_4 are assigned to T_{1u} and T_{2g} type vibrations. The wavenumbers of the vibrations of the cations decrease in the order Na > K > Rb > Cs and show little change on going from molybdates to tungstates. The proposed assignment is fully consistent with the results of a calculation of the vibrational wavenumbers and modes of K_2WO_4 and K_2MoO_4.[37]

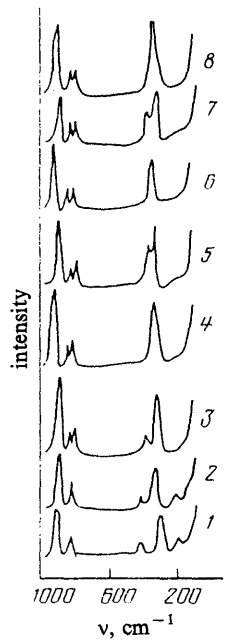


Figure 2. Raman spectra of alkali metal monomolybdates and monotungstates:[25] *1*, Na_2WO_4; *2*, Na_2MoO_4; *3*, K_2MoO_4; *4*, K_2WO_4; *5*, Rb_2MoO_4; *6*, Rb_2WO_4; *7*, Cs_2MoO_4; *8*, Cs_2WO_4.

Analysis of the vibrations modes and the displacements of the atoms shows that the Raman line at 926 cm^{-1} and the i.r. band at 925 cm^{-1} in the spectra of K_2WO_4 are due to vibrations of the WO_4 tetrahedron with the predominant change in the shortest W—O bond (1.76 Å); the Raman line at 829 cm^{-1} and the i.r. band at 830 cm^{-1} are due to the longest bond (1.81 Å). The wavenumbers in the 357—298 cm^{-1} region are assigned to deformations of the tetrahedron. The bands at 164, 145, 132, and 100 cm^{-1} in the spectrum of K_2WO_4 can be assigned to the predominant vibrations of the potassium cations involving the oxygen neighbours and the tungsten atoms.

Table 3. Vibrational wavenumbers (i.r. and Raman) (cm^{-1}) of A_2MO_4 and their assignment

Na_2MoO_4	Na_2WO_4	K_2MoO_4	K_2WO_4	Rb_2MoO_4	Rb_2MoO_4	Cs_2MoO_4	Cs_2WO_4	Assignment	Type of vibration	Symmetry type*
897	932	890	926	893	924	888	922	$\nu_{1,T}$	ν(M–O)	A_{1g}
		889	925	892	923	889	923			
		852	853	855	847	840	840			
840	840	835	830	830	828	826	826	$\nu_{3,T}$	ν(M–O)	T_{1u}
810	810	824	829	834	824	820	820			T_{2g}
387	379	357	357	335		328	338	$\nu_{4,T}$	δ(O–M–O)	T_{2g}
317	309									T_{1u}
307	313	318	331	315	329	311	322	$\nu_{2,T}$	δ(O–M–O)	E_g
			338	345	333		338			
		333	319	325	317	338	315	$\nu_{2,T} + \nu_{4,T}$		
		311	298	305	300	321	301			
		168	164							
230	228	147	145	132	138	110	110—95	$\nu_{3,o}$	ν(A–O)	T_{1u}
		138	132	115	115	95				
178	168	100	100					$\nu_{4,o}$	δ(O–A–O)	T_{1u}
120	98							$\nu_{5,o}$	δ(O–A–O)	T_{2g}

* The assignment to symmetry types is given only for Na_2MoO_4 and Na_2WO_4.

Table 4. I.r. wavenumbers (cm^{-1}) and their assignment for $A_2M_nO_{3n+1}$ (A = Na, K, Rb, Cs; M = Mo, W).[5]

$N_2W_2O_7$	$K_2Mo_2O_7$	$K_2W_2O_7$	$Rb_2Mo_2O_7$	$Cs_2Mo_2O_7$	$K_2W_3O_{10}$	$Rb_2Mo_3O_{10}$	$Cs_2Mo_3O_{10}$	$Na_2Mo_4O_{13}$	$K_2W_4O_{13}$	$K_2W_4O_{13}$	$Rb_2Mo_4O_{13}$	$Cs_2Mo_4O_{13}$	Assignment
							992	970	960		955	955	
957	930					940	941	960	945		945	945	$\nu_{3,o}$; $\nu_{1,T}$
949			925	930			932	940	935	955	932	932	
911	905	908	912	919	920	910	910	925	919		915	910	
			890	908	870		900	910	901		900	900	
882	870	840	882	888	840	890	890	895	890	870	890	890	$\nu_{3,T}$
865			877	870	820		870	870	868		860	858	
			860	855			856						
			840	820			830	835					
820			809		798		820			790			
770			765	782									$\nu_{1,o}$; $\nu_{2,o}$
		740		755	760		750	745	755		752	752	
	720		721			722	725			730		730	
	705	670			650	705	710	650	700		700	700	
		620							622	640	628	625	
640				580		560	570		580		575	570	
						535			552		550	550	
458	480				465				518		515	515	
		441	453	452	450	480	480		470	470	470	470	ν_4O; $\nu_{4,T}$
			420		437		432	438	431	440	431	431	
420	402			402	410			405	405	420	405	408	
		390	380	395	390	385	390		390		391	391	
372	375	370	372				380	382	372		372	372	
361	362			362	370	361	365		360		360	359	
			355	351	350	355	355			352			
		346						348					
342			335	335	330	330	332	335					
	321		330	320		325			328	330	328	330	$\nu_{5,o}$; $\nu_{6,o}$; $\nu_{2,T}$
308		322	310					320					
		307	305		300		305					305	
		285	300				285	295	292	290	295	295	
280		275			270	265	260	272	270		270	265	
	242		242	255				255					
			230			230	230	220	222			227	
	220		220								220		
				215		210	210				212	210	
			205			205	205						

Lithium molybdates and tunsgate Li_2MO_4, whose crystal structures contain almost undistorted MO_4^{2-} tetrahedra, have simple i.r. spectra the interpretation of which causes no difficulties.[38]

The analysis of the vibrational spectra of alkali metal polymolybdates and polytungstates is an incomparably more serious problem due to the complex structure of the anions which are composed to condensed molybdenum or tungsten coordination polyhedra. This makes it impossible to interpret the vibrational spectra using the "free" ion approximation.

Nevertheless such attempts were made in some of the earlier papers. From studies of the i.r. spectra of $Na_2Mo_2O_7$, $Na_2W_2O_7$, and $Na_2W_4O_{13}$ the existence of $(O_3M-O-MO_3)^{2-}$ ions was proposed[39,40] by analogy with ions like $P_2O_7^{4-}$, $S_2O_7^{2-}$, $Cr_2O_7^{2-}$. It was found that in the vibrational spectra of molybdates and tungstates, and also vanadates, and in contrast to the spectra of phosphates, sulphates, and chromates, the wavenumbers of the M–O symmetric stretches are always higher than those of the antisymmetric vibrations. Tarte[40] showed that the wavenumbers of the M–O stretches increase as the number of oxygen atoms coordinated to the molybdenum or tungsten decreases. Further, the higher the degree of condensation of the molybdenum–oxygen or tungsten–oxygen groups, the higher are the wavenumbers of the stretches of the polyhedra.[40]

The vibrational spectra of alkali metal polymolybdates and polytungstates have been analysed.[5] The i.r. spectra of the compounds $A_2M_nO_{3n+1}$ (A = Na, K, Rb, Cs; M = Mo, W) in the 4000–200 cm^{-1} region were studied (Table 4). An interpretation of the observed spectra was proposed on the assumption that in the structures of these compounds distorted MO_6 octahedra and MO_4 tetrahedra are linked by shared corners. It was shown by spectroscopy that there is a similarity between the structures of potassium, rubidium, and caesium tetramolybdates on one hand, and rubidium and caesium tritungstates on the other.

The vibrational wavenumbers of polymolybdates isotopically substituted with lithium ($^6Li-^7Li$) and molybdenum ($^{92}Mo-^{100}Mo$),[37,41,42] supplemented with our own previously unpublished data for tungstates, are given in Table 5.

In analysing the spectra of complex systems containing octahedral, as well as tetrahedral, groupings it must be borne in mind that for an isolated, regular MO_6 octahedron with O_h symmetry six normal vibrations are possible:

$$\Gamma_{vib} = A_{1g}(\text{Raman}) + E_g(\text{Raman}) + 2T_{1u}(\text{IR}) + T_{2g}(\text{Raman}) + T_{2u}(\text{n.a.}),$$

of which only ν_3 and ν_4 with symmetry T_{1u} will be i.r.-active. On the basis of these ideas, and using known structural data for $Na_2Mo_2O_7$, $Na_2W_2O_7$, and $K_2Mo_3O_{10}$,[15,16,18] Caillet and Saumagnt[39]

Table 5. Wavenumbers (cm^{-1}) of the vibrations in the i.r. and Raman spectra of some polymolybdates and polytungstates (including specimens with isotopic substitution of the cations).

$Li_2W_2O_7$*				$Na_2Mo_2O_7$ (Ref.42)				$K_2Mo_3O_{10}$ (Ref.41)				$Rb_2W_3O_{10}$		$Cs_2W_3O_{10}$		$Na_2W_4O_{13}$	
IR		Raman		IR		Raman		IR		Raman							
^6Li	^7Li	^6Li	^7Li	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	IR	Raman	IR	Raman	IR	Raman
1015	1015			952	942					968	963	975		950			953
		955	955			939	935			958	953	944		942		950	
									955								
								958	942			932		938			
945	945								936								
				929	922					942	942		932		935		
		936	936								937						
		925	925			920	918			934	931						920
907	907			915	913					922	916		921				
					904					915	908		914		904		
				892	890					909	902						
855	855			874	882			904	904							882	
		852	852			875	869		893								
						836	828			897	890	872		867			
835	835				822			872	868			855		853			
		816	816			818	815			853	850	830		826		830	
				800	780			762	765			771		764			790
		765	765			774	765			769	755		747		759	775	
								733	728			742		732			774
755	755					741	739			724	722				731		
								715	710								
									672			686		667			674
665	665									671	668		681		653		
										634	630	637		625		620	
				600	590			620	620								
										610	610		613		612		

Table 5 (continued).

$Li_2W_2O_7$*				$Na_2Mo_2O_7$ (Ref.42)				$K_2Mo_3O_{10}$ (Ref.41)				$Rb_2W_3O_{10}$		$Cs_2W_3O_{10}$		$Na_2W_4O_{13}$	
IR		Raman		IR		Raman		IR		Raman							
^6Li	^7Li	^6Li	^7Li	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	^{92}Mo	^{100}Mo	IR	Raman	IR	Raman	IR	Raman
								575				585		580		578	
								572	562								
		551	551							568	568						
											550						
540	540							539	533								539
						526	525			510	505						
									503								
496	480			487	481					480	479						
472	470			470	465			479	477								
458	458					464	460			449	449					460	
448	442						454	439	447			453		455		450	
								421	430				436				445
419	419			417					405			407		408		418	
						411	411			392	388		405				369
389	383							390	389			395		395			360
		370	370					376	370			365		365		355	
						369	368			374	369						344
350	342			364	361			359	356							342	
321	321					340	336			340	338		339		354		336
					339			327	324			337		340			319
		305	305	315	314			299	290				301		299	312	
						296	294			278	276	283		309			310
286	284			276	270			267	267			274		294			280
				262	264					260	258	259		252			274
		237	237			245	245			240	239	250				265	
237	235					228	227			233	230		247		252		265
				227	228			232	228			224		220		252	
206	206					215	215			223	222		219		223	228	
		199	205	195	195			209	206				196		201		222
		183	185			199	199			205	202			190			208
181	179			184	184			185								198	
				182						167	164				166	182	
169	169			168	168			165	164			160		160			167
		162	162	153	152												
159	159		158		159												
		144	149	148	148							150		138		148	
						140	138			145	141						147
				138	138							130		118		130	
128	128				129												
				125	120												
						120	120			127	123						
				112	112			115	115			106					
				102	103					114	114						
						90	87			109	88						
88	88			86	78												
						84	84			84	82						
				79	75												
					71												
					66												
62	62				63							62		68			
						45	44			59	57						

*Our data.

[Ref. 4? (Ed. of Translation)] assigned the highest wavenumbers to the $\nu_3(T_{1u})$ vibrations of the MO_6 octahedra. Confirmation of the correctness of this assignment was evident in the splitting of the corresponding band in the i.r. spectra of many polymolybdates and polytungstates into three components due to removal of the degeneracy. The next highest wavenumber was assigned to $\nu_1(A_1)$ of the MO_4 tetrahedron. The $\nu_3(T_2)$ vibration of the same tetrahedron appears in the i.r. spectra as a strong triplet with its centre at $\sim$890 cm^{-1}. The i.r. bands in the 350–200 cm^{-1} region were assigned to deformations of the tetrahedron $[\nu_2(E)]$ and $[\nu_3(T_{1u})]$. The absence of simple criteria led to difficulties in interpreting the spectra in the 560–350 cm^{-1} region where bands due to the vibrations $\nu_4(T_{1u})$ or $\nu_5(T_{2g})$ of the octahedron and $\nu_4(T_2)$ of the tetrahedron are expected.

The proposed assignment is rather provisional and open to serious doubts in a number of aspects. For example, the wavenumbers of the stretches of the tetrahedral MO_4 groups will, because of the smaller interatomic distances and higher bond energies, be higher than those of the stretches of the MO_6 octahedra.

The structures of the other polymolybdates and polytungstates were established later and therefore a hypothetical assignment of their vibrational wavenumbers was made from a comparison with the spectra of the whole series of compounds, and also of $Na_2Mo_2O_7$ and $Na_2W_2O_7$ as described previously. In the 400–200 cm^{-1} region there are a number of i.r. bands with increased wavenumbers which were difficult to describe by considering only structural fragments formed from tetrahedra and octahedra. No analysis of the vibrations of the cationic sublattice was made in Ref. 35.

The i.r. spectra of $Na_2Mo_2O_7$ and $Na_2W_2O_7$, studied by Dupuis and Veltange,[39] were also found to be very similar. Antisymmetric stretches of the M–O–M bridges were assigned to the bands in the 600 cm^{-1} region for $Mo_2O_7^{2-}$ (a very strong band) and the 625–575 cm^{-1} region for $W_2O_7^{2-}$ (a doublet of strong bands). It is likely[39] that the symmetric vibrations of the bridges occur at 465 cm^{-1} for $Mo_2O_7^{2-}$ and 455 cm^{-1} for $W_2O_7^{2-}$. The antisymmetric stretch of MO_3 groups appears as a doublet in the 825–780 cm^{-1} region for $Na_2Mo_2O_7$ and the 825–775 cm^{-1} region for $Na_2W_2O_7$. Deformations were recorded at 360, 333, and 315 cm^{-1} for $Mo_2O_7^{2-}$ and 418 and 360 cm^{-1} for $W_2O_7^{2-}$. Thus it was shown that the i.r. spectra of sodium dimolybdate and ditungstate can be interpreted and satisfactorily in terms of the vibrations of a model $M_2O_7^{2-}$ anion with symmetry C_{2v} and containing two symmetrical MO_3 groups linked by an M–O–M bridge, as in pyrophosphates, pyrosulphates, and dichromates. The wavenumbers of the stretches of the M–O–M bridges decrease as the atomic weight of M increases.

The Raman spectra of polycrystalline $K_2W_3O_{10}$ and $K_2W_4O_{13}$, and also polytungstates with a higher tungsten content, have been published and discussed.[43] In the opinion of the authors the vibrations of terminal W–O bonds appear in the Raman spectra of these compounds as a pair of lines at 962 and 902 cm^{-1}.

The external vibrations of the alkali metal tungstates and molybdates have not been studied in detail. However precision studies of the i.r. and Raman spectra of a number of lanthanide molybdates, where the greatest attention was paid to the external vibrations,[44] confirm the assignment, proposed from an analysis of the spectra of compounds with the scheelite structure,[45] of the wavenumbers 140–110 cm^{-1} to translational, and 260–200 cm^{-1} to librational, vibrations of the molybdate ions. It seems that these values are general, remaining valid for the alkali metal molybdates (and with small adjustments tungstates also) provided, of course, that the structure of the compound contains tetrahedral anions.

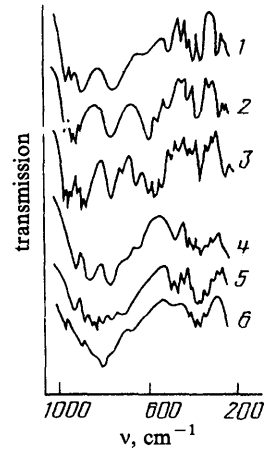


Figure 3. I.r. spectra of potassium polymolybdates and polytungstates: *1*, $K_2Mo_2O_7$; *2*, $K_2Mo_3O_{10}$; *3*, $K_2Mo_4O_{13}$; *4*, $K_2W_2O_7$; *5*, $K_2W_3O_{10}$; *6*, $K_2W_4O_{13}$.

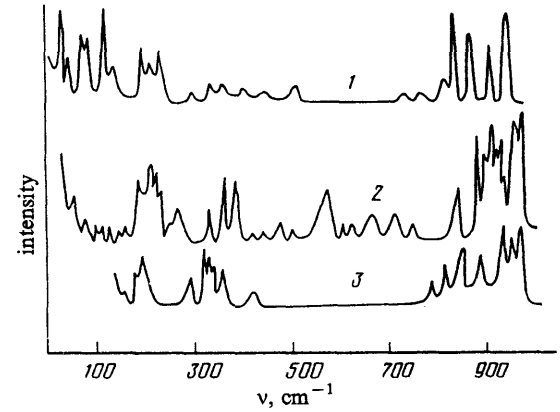


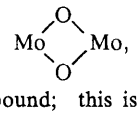
Figure 4. Raman spectra of alkali metal polymolybdates: *1*, $Na_2Mo_2O_7$; *2*, $K_2Mo_3O_{10}$; *3*, $K_2Mo_2O_7$.

The appearance in print of Refs. 15, 18, and 19 with a description of the structures of a large number of molybdates stimulated studies of their vibrational spectra.

A number of recent papers[37,41,42] have been concerned with a detailed study of the vibrational spectra of potassium and sodium molybdates including a factor-group analysis of the vibrations of the crystals and a theoretical calculation of the normal vibrational modes and wavenumbers using the valence-force field approximation, with the aim of demonstrating the relationship between the type of spectrum and the structure. The compounds K_2MoO_4, $K_2Mo_2O_7$,[37] $K_2Mo_3O_{10}$,[41] and $Na_2Mo_2O_7$ [42] were chosen as models for the calculation because of the diversity of their crystal structures [including structures with isolated tetrahedral anions (K_2MoO_4), chain structures with tetrahedra and octahedra ($Na_2Mo_2O_7$, $K_2Mo_2O_7$), and chain structures with trigonal bipyramids and octahedra ($K_2Mo_3O_{10}$)] and hence the presence of

different types of Mo—O—Mo bridging bonds, to the vibrations of which particular attention was paid. The range of Mo—O bond lengths in the compounds studied was 1.64—2.27 Å, so enabling the effect of the interaction at "long" Mo—O bonds on the vibrational spectrum to be investigated.

In Refs. 37, 41, and 42 experimental data are given on the i.r. and Raman spectra in the 4000—50 cm^{-1} region (Figs. 3 and 4) of specimens isotopically substituted with molybdenum ($^{92}Mo-^{100}Mo$) and an assignment of the vibrations of the different sublattices in the crystal is made. These data were supplemented by the results of studies of some alkali metal tungstates by the authors of the present review.

The lengthening of the Mo—O bonds in $K_2Mo_2O_7$ crystals to 2.27 Å leads to a reduction of the wavenumbers of the vibrations involving these bonds to 600—480 cm^{-1}.[37] In this region the coordinates of the change in the O—Mo—O angles also make a substantial contribution to the vibrational modes. An analysis of the normal vibrations of $K_2Mo_3O_{10}$ [41] shows that the vibrations in the system with the highest wavenumbers (970—900 cm^{-1}) are accounted for by the coordinates of the change in length of the very short terminal Mo—O bonds and the vibrations of the Mo—O—Mo bridging bonds occur over a broad spectral range (860—480 cm^{-1}). A single vibration is not found for the closed grouping , which is present in the crystal structure of this compound; this is evidently due to the considerable different between the bond angles at the bridging oxygen atoms.

The vibrations of the tetrahedral MoO_4^{2-} grouping in $Na_2Mo_2O_7$ [45] occur over a broader spectral range (910—770 cm^{-1}) than is the case for the isolated tetrahedra in the A_2MoO_4 structures or for the free MoO_4^{2-} ion.[4] The coordinates of the bonds in the octahedral grouping make the predominant contribution to the vibrations in the 940—460 cm^{-1} region which is considerably broader than the wavenumber range for stretches of isolated MoO_6 octahedra.[5] The reasons for these discrepancies are both the presence in the structure of long Mo—O bonds (up to 2.26 Å) and the formation of Mo—O—Mo bridging bonds between a tetrahedron and an octahedron and between two octahedra. The broadening of the range for deformation of the molybdenum-oxygen polyhedra to 420—240 cm^{-1} is also due to condensation of the coordination polyhedra.

The analysis of the vibrations for the series of alkali metal molybdates enabled the assignment of the wavenmbers in their i.r. and Raman spectra to be improved and also the effect of the bridging bonds on the crystal lattice dynamics to be found. A comparison of the geometrical and spectroscopic characteristics of the bridging groups (Table 6) shows that an increase in the Mo—O interatomic distances is accompanied by a decrease in the wavenumbers of the vibrations of these groups and that an increase in the bond angles at the oxygen atoms leads to an increase in the wavenumbers of their antisymmetric vibrations and a decrease in those of the symmetric vibrations. The latter occupy the wavenumber region between the stretches and deformations of the coordination polyhedra and this complicates the interpretation of the spectra. The values of the force constants of the Mo—O bonds which we obtained in these calculated show a correlation with the interatomic distances.

We obtained similar results for $Li_2W_2O_7$ and $Na_2W_4O_{13}$. In these compounds we are faced with a more complex structure for the set of condensed polyhedra. In addition to W—O—W bridging bonds formed by pairs of tungsten coordination octahedra, the structures of these compounds contain oxygen nodes shared between three tungsten octahedra.

Table 6. Characteristics of the M—O—M bonds.

Compound	Bond angle at oxygen atom, °	Interatomic distance M–O, Å	Force constant 10^{-6} K, cm^{-2}	Wavenumbers of vibrations, cm^{-1}		
				$\nu_{antisym}$	ν_{sym}	$\Delta\nu$*
K_2MoO_4**	–	1.74	9.45	852, 835,824	890, 889	
	–	1.78	8.8			
K_2WO_4**	–	1.82	9,7	835, 813	828	
$K_2Mo_3O_{10}$	101	2.08	2.7	620—610	540—510	93
		2.11	2.7			
$K_2Mo_2O_7$	101	1.83	6.1	720—570	570—560	150
		2.17	3.2			
$K_2Mo_3O_{10}$	114	1.88	7.5	870	630	240
		1.99	4.5			
$Na_2Mo_2O_7$	125	1.78	7.8	822—815	487—460	345
		2 26	2.8			
$K_2Mo_2O_7$	138	1,77	9.3	930	480	450
		2,27	2.8			
$Na_2Mo_2O_7$	141	1.90	6.4	952—942	600—525	390
		1.90	6.4			
$Li_2W_2O_7$	107	1.78	9,3	816	665	151
		2.29	3,0			
$Na_2W_4O_{13}$	112	1,88	7,0	790—774	674	108
		2.04	4,7			
$Li_2W_2O_7$	114	1.90	8.1	1015—852	700—698	234
		2,03	5.7			
$Li_2W_2O_7$		1.92	7.8			
	101, 106, 148	2.02	5.5	1015—852	700—698	234
		2.18	4.0			
$Na_2W_4O_{13}$***		1.92	6.0			
	96, 101, 157	2,09	4.4	920—882	578	323
		2.28	2.9			

*$\Delta\nu = \nu_{antisym} - \nu_{sym}$ was determined from the mean wavenumbers of the vibrations of the bridging oxygen atoms.

**The data given are for the terminal M—O bonds in the MO_4 tetrahedra.

***Oxygen atom in the field of three tungsten atoms (node). For $Li_2W_2O_7$ the vibrations of the bridging and nodal oxygen atoms are strongly mixed.

[*The units used for the force constant are not clear (Ed. of Translation)].

For lithium ditungstate the wavenumbers of the antisymmetric vibrations of the bridging and nodal oxygen atoms are mixed and lie in the fairly broad range 1015—852 cm^{-1}. In sodium tetratungstate

these vibrations are separated in mode and wavenumber. The wavenumber range 920–882 cm^{-1} is asigned to the vibrations of the nodal oxygen atoms and the range 790–774 cm^{-1} to vibrations of the bridging bonds. As in the molybdates, the symmetric vibrations of these structural fragments occur in the region of the spectrum adjacent to the high-wavenumber limit of the deformations of the tungsten-oxygen polyhedra.

The lithium isotope effect is well developed in the i.r. spectra of $Li_2W_2O_7$, $\Delta\nu$ reaching 16 cm^{-1}. The relatively high wavenumbers of the vibrations of the cations in the lithium sublattice (up to 500 cm^1) are consistent with tetrahedral coordination by oxygen and short lithium–oxygen interatomic distances.

In all the polymolybdates and polytungstates the antisymmetric vibrations of the M–O–M bridging atoms usually have higher wavenumbers than the vibrations of the terminal oxygen atoms, given that the interatomic distances are comparable.

IV. Stability of the crystals

Various thermodynamic quantities are used for comparing the stabilities of crystalline compounds: the enthalpies of formation of crystalline compounds from the elements under standard conditions $\Delta H^\circ_{f298.15}$ or $\Delta H^\circ_{ok\,298.15}$ [of representing formation of crystal (Ed. of Translation)], the melting point T_f, the crystal lattice energy U, or the energy of atomisation E_a. Urusov[46] showed that the most definitive characteristic of binding energy in a crystal is the energy of atomisation E_a which is released as a result of the formation of the crystal from an infinitely rarefied gas of individual atoms. However, the crystal lattice energy, which is used fairly frequently, is the energy released on formation of the crystal from individual gaseous ions at infinite distances from each other. For all compounds the energy of atomisation E_a is measured from the absolute zero level of the energy of interaction of a rarefied gas composed of atoms and it can therefore be used quite rigorously for comparison with various properties in a series of compounds of the same type. The greater the absolute value of the energy of the atomisation, the more stable is the structure.

The experimental determination of the lattice energy at 0 K[47] is based on use of the equation:

$$U_0 = \Delta H^0_{298} - \sum_M \Delta H^0_{298}(M) - \sum_X \Delta H^0_{298}(X) - \sum_M I + \sum_X F - \int_0^{298} C_p(MX)dT + \sum_{M,X} \int_0^{298} C_p(M,X)dT$$

where ΔH°_{298} is the enthalpy of formation of a crystalline compound from the elements under standard conditions

$$\sum_M \Delta H^0_{298}(M), \quad \text{and} \quad \sum_X \Delta H^0_{298}(X) —$$

are the sums of the enthalpies of formation of gaseous atoms of the metal (M) and metalloid (X) respectively from the elements under standard conditions, $\sum_M I$ — is the sum of the ionisation enegies of all the cations, $\sum_X F$ — the sum of the electron affinities of all the anions, and C_p the heat capacity at constant pressure.

The last two integrals allow for the enthalpy change on going from the standard temperature to 0 K; the first represents the enthalpy change of the crystal and the second that of a gas of individual ions.

The experimental value of the energy of atomisation is determined using the following cycle:

$$E^0_a = \Delta H^0_{298} - \sum_M \Delta H^0_{298}(M) - \sum_X \Delta H^0_{298}(X) — - \int_0^{298} C_p(M,X)dT + \sum_{M,X} \int_0^{298} C_p(M,X)dT.$$

Hence

$$U_0 - E_a = \sum_M I + \sum_X F.$$

We have calculated the crystal lattice energies and the energies of atomisation for the compounds A_2MoO_4 (A = Li, Na, K, Rb, Cs) (Table 7). Use was made of the enthalpies of formation of the crystalline compounds from the elements under standard conditions,[48] and enthalpies of formation of the gaseous atoms from the elements and the ionisation energies of the alkali metals[49] and the ionisation energy of molybdenum;[47] the affinity of oxygen for two electrons was taken to be −142 kcal.[50] An original method for calculating $-\Delta H^\circ_{298}$ using the thermal and energy characteristics of the compounds has been proposed.[51] The values of $-\Delta H^\circ_{298}$ so obtained are somewhat different from the experimental reference data[48] but the discrepancies are no more than 5%.

The calculated crystal lattice energies of A_2MoO_4 decrease as the atomic number of the alkali metal increases, indicating a decrease in the stabilities of the respective structures. The values of the energies of atomisation very similarly. This rule breaks down only for Cs_2MoO_4 (which has E_a = 793.6 kcal mol^{-1} whereas for Rb_2MoO_4 E_a = 790.9 kcal mol^{-1}). Thus Li_2MoO_4 has the most stable, and Rb_2MoO_4 the least stable, of these structures. The energy of atomisation of Li_2MoO_4 exceeds the corresponding values for the other members of the series by ~40 kcal mol^{-1}.

The particular stability of Li_2MoO_4 is evidently due to its structural peculiarities: the lithium has a tetrahedral environment of close packed oxygen atoms,[7] i.e. its CN is 4 whereas the CN of the other alkali metals is 6 in the structure of the Na_2MoO_4, 8 for potassium and rubidium, and 6 and 10 for caesium. These conclusions agree with results obtained by studying the perturbing effect of the alkali metal cation on the vibrations of the MoO_4^{2-} anion,[4] the effect being greatest for Li^+.

It is commonly assumed that there is a correlation between the variation in T_f and E_a.[47] However in the alkali metal molybdate series the variation in T_f, $\Delta H^\circ_{f298.15}$, and $\Delta G^\circ_{298.15}$ is not uniform. Rb_2MoO_4 has the highest T_f (1228 K) and Na_2MoO_4 the lowest (960 K) (see Table 7).

It was found[47] that $U - E_a$ is greater, the greater the deviation of the character of the A–O bond from the ionic type. However in the present A_2MoO_4 series the difference $U - E_a$ decreases as the ionisation energy of the alkali metal decreases. Thus on going from caesium to lithium the estimation of the stability of the molybdates using the ionic model introduces an ever increasing error in accordance with a greater deviation of the A–O bond from the ionic type as the ionisation energy of A increases.

For the alkali metal tungstates, owing to the paucity of reference data the energy of atomisation and crystal lattice energy can be calculated only for the first three members of the series: Li_2WO_4, Na_2WO_4, and K_2WO_4 (see Table 7). In the series A_2WO_4 (A = Li, Na, K) E_a and U very in the same way and, as with the molybdates, the lithium compound has the highest stability: the increase in the energy of atomisation from the potassium to the sodium compound

Table 7. Thermodynamic data for $A_2M_nO_{3n+1}$ (A = Li, Na, K, Rb, Cs; M = Mo, W).

Compound	T_fK (Ref.47)	$-\Delta H^0_{f298.15}$, (Ref.47)	$-\Delta G^0_{f298.15}$, (Ref.47)	E_a^*	U	$U-E_a$	E_a(add)=$E_a(A_2O)$+ $+nE_a(MO_3)$	E_a-E_a(add)
		kcal mol^{-1}						
Li_2MoO_4	975,65	353.53±0.18	336,318±0,91	834,9	6862,07	6027,1	792.4	42,5
$Li_2Mo_2O_7$	836	543.75±0,26	498,098±1.5	1350.8	13014,3	11663.5	1306,2	44,6
$Li_2Mo_3O_{10}$		723.92±0.24	659.977±1,8	1866.6	19166.5	17299.9	1820.0	46.6
$Li_2Mo_4O_{13}$	852	900,74±0,36	818,208±2,4	2379,1	25315.4	22936,3	2333,8	45 3
Na_2MoO_4	960	351.1±0.1	323,888	797,8	6813.2	6015.4		
$Na_2Mo_2O_7$	888	536.7±0.3	492.032	1319,1	12970,9	11651.8		
K_2MoO_4	1193	358.14±0,24	330.182±1.5	796,0	6774,6	5978,6	702.6	93,4
$K_2Mo_2O_7$	763	547,7±0.3	501.154±2.1	1321,2	12936,2	11615,0	1216.4	104,8
$K_2Mo_3O_{10}$	843	727.0±0.8	662,163±2,5	1836,2	19087,6	17251.4	1730,2	106.0
$K_2Mo_4O_{13}$	834	912,8±1,0	829.374±3.1	2357.6	25245.4	22887.8	2244,0	113,6
Rb_2MoO_4	1228	356.99±0.14	329.326±1.5	790,9	6762,0	5971.1		
Cs_2MoO_4	1208	362.0±0.1	336.314	793,6	6751.6	5958,0		
$Cs_2Mo_2O_7$	743	550.32±0.18	506.236±2.4	1317,6	12911,9	11594,5		
Li_2WO_4	1013	383.3	355.651	901.7	6196,2	5294,5		
Na_2WO_4	969	369,9	342.519	863.6	6146.4	5282,8		
$Na_2W_2O_7$	1013	574,9	529,925	1451,3	11637,9	10186,6		
K_2WO_4	1196	377,7	349,157	862,6	6108,6	5246,0		

* Our determination.

is only 1 kcal mol^{-1} but lithium tungstates has a value which is much higher (by 38.1 kcal mol^{-1}). As with the molybdates, the appreciable stabilisation of Li_2WO_4 compared to the other members of the series can be attributed to tetrahedral close packing of the oxygen atoms around the lithium cations.[6] In the light of this the slightly higher value of the energy of atomisation of Cs_2Mo[4] compared to Rb_2MoO_4 is understandable as being due to the placing of some of the caesium cations in positions with a smaller CN.

Turning to Na_2WO_4 and K_2WO_4 the CN's of the alkali metals increases to 6 and 8 respectively and less compact structures are formed. As with the alkali metal molybates, a comparison of the melting points of the tungstates does not lead to the correct conclusion regarding the relative stability of the compounds. K_2WO_4 which is the least stable compounds in the series $Li_2WO_4-Na_2WO_4-K_2WO_4$ has the highest T_f (1196 K). It is clear from Table 7 that the difference $U - E_a$ varies in the same way for A_2WO_4 as for A_2MoO_4. Hence the use of the crystal lattice energy to estimate the stability is the least reliable in the case of the lithium compounds.

Furthermore the standard enthalpies and Gibbs free energies of formation of the compounds do not match the variation of the energy of atomisation and the melting points in the A_2MO_4 (A = Li, Na, K, Rb, Cs; M = Mo, W) series.

To compare the stabilities of the crystals in the series $A_2MO_4-A_2M_2O_7-A_2M_3O_{10}-A_2M_4O_{13}$ is quite difficult because the calculation scheme presupposes the summation of the contributions of individual atoms and for comparison the values of the energy of atomisation quoted are required. One of the possible methods is to compare the E_a values obtained with the sum of the E_a values for the respective constitutent oxides. In the potassium molybdate series the differences obtained increase on moving from potassium molybdate to the dimolybdate, the trimolybdate, and then the tetramolybdate (Fig. 5). However the greatest increase in E_a is for $K_2Mo_2O_7$. This is likely to be the most stable of these compounds. The condensation of the coordination polyhedra in the structure of $K_2Mo_2O_7$ results in there being very short M–O bonds which have relatively high dynamic coefficients for bridging bonds.

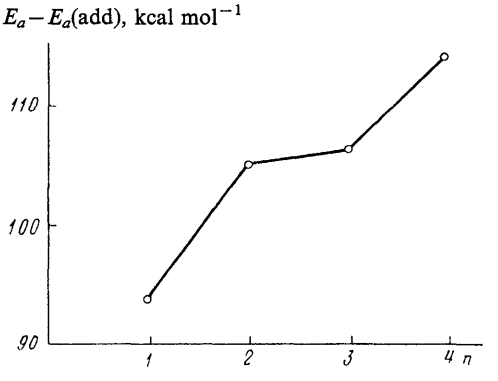


Figure 5. Variation of the activation energy ΔE_a for the potassium molybdates $K_2Mo_nO_{3n+1}$ (n = 1–4) with their composition.

The data for alkali metal molybdates and tungstates presented here and their analysis show that vibrational spectroscopy is a sensitive method enabling very small changes in the structures of the compounds to be recorded. However, because the vibrations of complex condensed systems are not characteristic, it is not always possible to interpret the results obtained unambiguously. Systematic changes in the crystal structure with the size of the alkali metal cation and the cation content in the system show correlations with the thermodynamic properties. Nevertheless the latter, being integrated quantities, are not responsive to the detailed features of the structure of the substance.

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