Symmetry Coordinates and Force Field Analysis of a Heptamolybdate, Mo_7O_{24}, Model

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A complete vibrational analysis is performed for a heptamolybdate, Mo_7O_{24}, model of C_{2v} symmetry. The symmetry coordinates are classified into those of (a) framework vibrations, (b) ligand vibrations, (c) framework-ligand couplings, and (d) interligand vibrations. A simple valence force field is estimated, and a relative scale for the force constants of the angles is presented. Vibrational frequencies are calculated and the influence of inclusion of redundancies is investigated. The final result is compared with experimental data from infrared and Raman. In the calculation of species A_1 a correlation is found to all except one of the polarized Raman frequencies.

Introduction

The heptamolybdate anion $Mo_7O_{24}{}^{6-}$ is well established in both the solid state and aqueous solution [1—4], and a great number of experimental vibrational spectra is reported [5—11].

The assignments of the infrared and Raman spectra are incomplete [10—11], since sufficient experimental data are mostly not available for such large complexes. There is thus need for a theoretical treatment which can increase the knowledge of the vibrational features. No normal coordinates analysis for the whole heptamolybdate anion has been published so far.

In the present work a successful analysis of symmetry coordinates was achieved for the Mo_7O_{24} group. The analysis was difficult due to the very condensed structure, until the idea of treating fragments of the molecule as separate units was applied.

The method was originally used by Cyvin et al. for some metal-ligand complexes [12—13] and has later proved to be successful even for complexes where the ligand concept is chemically inadequate [14—16].

The word ligand will be used sometimes in accordance with the earlier terminology, even if the word fragment is more adequate.

Theory

The heptamolybdate anion is assumed to have a C_{2v} symmetry. This assumption agrees closely with the X-ray structure determination [1]. A central framework MoO_2 is assumed to have four ligands of two different types. There are thus two ligands (A, B) of each type, L1 and L2, respectively. The type labelled L1 is a MoO_5 fragment having a $C_s(yz)$ symmetry, and the other type L2 is a Mo_2O_6 fragment having a $C_s(xz)$ symmetry. The vibrational modes are then classified into (a) framework vibrations, *F*, (b) ligand vibrations of two types; L1 and L2, (c) framework-ligand couplings of two types; F-L1 and F-L2, and (d) interligand vibrations, L1-L2. This is an extension from the original work [12—13], where only one type of ligand was at the hand.

Molecular and Fragmental Models

A schematic figure of a Mo_7O_{24} unit is shown in Fig. 1a. The symmetry is assumed to be C_{2v}. The cartesian coordinates were deduced on the basis of single crystal data [1], and values of bond lengths are shown in the upper left part of Figure 1b. The geometrical parameters for a certain symmetrically equivalent set are means of the experimental values belonging to the specific set. The numbering and the structures of the framework, ligand L1A and ligand L2A, are shown in Figs. 2, 3 and 5, respectively. The bonds involved in coupling coordinates are dotted. A key for the numbering and identification of the atoms is given in Table 1.

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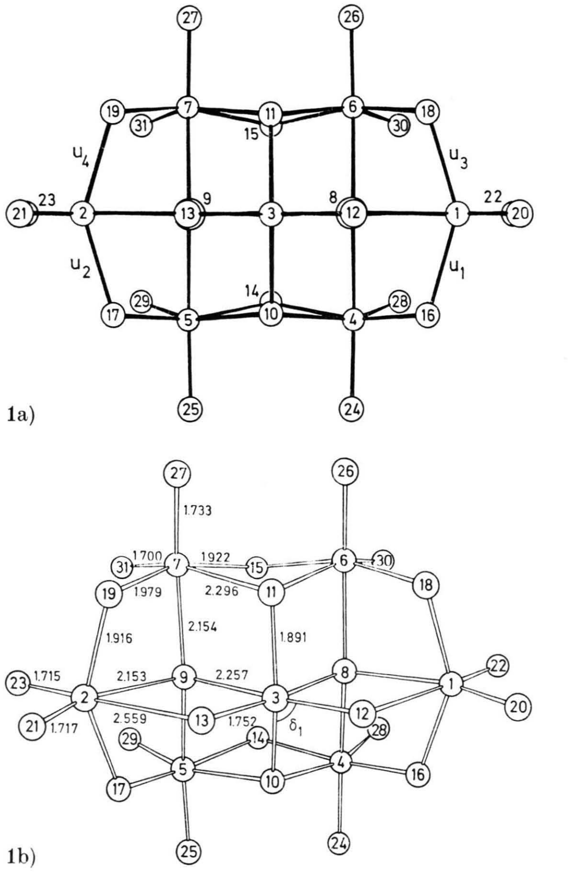

Fig. 1. a) A top view of the Mo_7O_{24} model. b) The Mo_7O_{24} structure, with the bond lengths in Å.

The oxygen atoms 12 and 13 (Fig. 2) were decided to belong to the framework instead of the atoms 8 and 9 (Figs. 2, 3) due to the shorter bond lengths, ~ 1.75 Å vs. ~ 2.25 Å. Furthermore, it seems more suitable that atom 8 belongs to the ligand L1A instead of atom 12, also on the basis of bond lengths which are ~ 2.15 Å and ~ 2.55 Å, respectively.

Table 1. Numbering of the atoms in the Mo_7O_{24} unit, arranged according to the different fragments; O_t = terminal oxygens.

Fragment	MoO_2	MoO_5		Mo_2O_6	
Atom	F	L1A	L1B	L2A	L2B
Mo	3	1	2	4, 5	6, 7
O	 12, 13	8 16, 18	9 17, 19	10 14	11 15
O_t		20, 22	21, 23	24, 25 28, 29	26, 27 30, 31

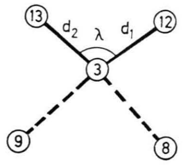

Fig. 2. MoO_4 part of the Mo_7O_{24} model showing the MoO_2 (F) fragment; symmetry C_{2v} (Couplings dashed lines.)

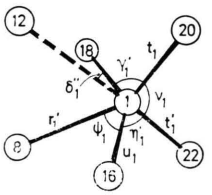

Fig. 3. A MoO_6 part of the Mo_7O_{24} model, showing the MoO_5 (L1A) fragment; symmetry $C_s(yz)$.

Valence Coordinates

(a) Framework Vibrations (F)

For the framework MoO_2 the valence coordinates, d and λ, are defined in Figure 2.

(b) Ligand Vibrations (L1, L2)

L1: For the ligand MoO_5 (L1A) the stretching (r', u, t, t') and bending (γ', η', ψ, ν) coordinates are illustrated in Figure 3. The bending η is shown in Fig. 4, where the two coplanar rings formed by the two L1 ligands and the framework are also illustrated. The order of numbering is that for the u coordinate, shown in Fig. 1a, i.e. the ligand A corresponds always with odd numbers.

L2: The stretching (u'', s, t'', t''') and bending (ω, ω', ζ, η''', ε, ν', γ''') coordinates for the ligand Mo_2O_6 (L2A) are shown in Figure 5. For the two ligands L2 (A, B) we have also defined four torsions o, with the numbering o_1 (14-5-10-4), o_2 (14-4-10-5) for L2A and analogously o_3 and o_4 for L2B.

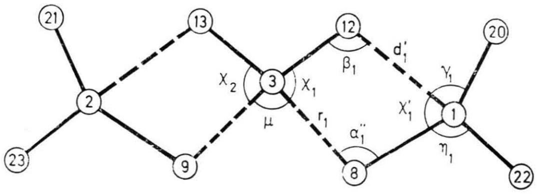

Fig. 4. The coplanar Mo_2O_2 rings made up from the couplings of the F and L1 fragments.

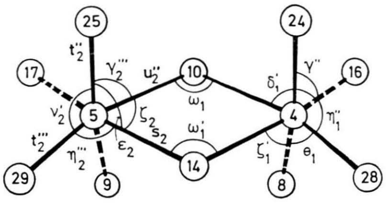

Fig. 5. A Mo_2O_{10} part of the Mo_7O_{24} model, showing the Mo_2O_6 (L2A) fragment; symmetry $C_s(xz)$.

(c) Framework Ligand Couplings (F-L1-L2)

(i) For the stretch coupling F-L1 the coordinates r, d' are shown in Figure 4. The bendings α'', β, γ, μ, χ and χ' for the planar Mo_2O_2 ring are also illustrated in Fig. 4, and δ'' in Figure 3. In addition two torsions are defined, viz. τ_1 (1-8-3-9) and τ_2 (2-9-3-8).

(ii) For the coupling F-L2 the stretching d'' and bending β'' is shown in Fig. 6, the bending δ is illustrated in Figure 1b. Here we have defined four torsions, τ'; τ_1' (4-10-3-13), τ_2' (5-10-3-12), τ_3' (6-11-3-13) and τ_4' (7-11-3-12), see Figure 1b.

(iii) Couplings F-L1-L2 in which both of the ligands take part are the bendings α' and χ'', which are shown in Figure 6. We have in addition defined 6 torsions p for each of the four puckered Mo_3O_3 rings. For the F-L1A-L2A coupling the notation is p_1 (16-1-12-3), p_2 (1-12-3-10), p_3 (12-3-10-4), p_4 (3-10-4-16), p_5 (10-4-16-1) and p_6 (4-16-1-12) etc. for the other 18 torsions.

(d) Interligand Vibrations (L1-L2)

The interligand couplings are supposed to be important in this case. The condensed structure will lead to a great number of such couplings, which in turn give a stiffness to the structure. The stretchings u_1' and r_1'' are shown in Figure 6. The numbering follows that for u. The bendings γ'', δ', ζ', η'' and θ are shown in Fig. 5 and the bendings α, β', ψ' and ψ'' in Figure 6. We have in addition defined 8 torsions τ'' for the four-membered Mo_2O_2 rings, formed by the bonds denoted u, u', r'' and r' shown in Figure 6. There are four such rings and two torsions are constructed for each ring in the same manner as the torsion o, i.e. τ_1'' (16-1-8-4) and τ_2'' (16-4-8-1) for example.

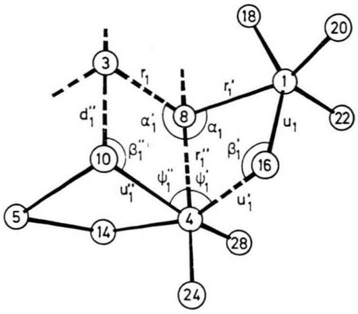

Fig. 6. A fragment of the Mo_7O_{24} model showing the couplings F-L1, F-L2 and L1-L2. χ_1'' is the $\wedge$ 10-3-8.

Classification and Symmetry of the Normal Modes

The whole complex of 31 atoms has 87 normal modes of vibration, which are distributed into the different species of the C_{2v} group according to

$$\Gamma(Mo_7O_{24}) = 26\,A_1(\mathrm{IR, R}) + 18\,A_2(\mathrm{R}) + 20\,B_1(\mathrm{IR, R}) + 23\,B_2(\mathrm{IR, R})\,. \tag{1}$$

As mentioned, the Mo_7O_{24} unit is divided into different fragments, and the normal modes of vibration for each of the fragments have to be derived.

(a) For the framework MoO_2, which has a C_{2v} symmetry, the species are

$$\Gamma(MoO_2) = 2\,A_1 + 1\,B_2\,. \tag{2}$$

(b) The ligand MoO_5 (L1) has a $C_s(yz)$ symmetry, and the 12 normal modes of vibration are distributed into the species according to

$$\Gamma(MoO_5) = 8\,a' + 4\,a''\,. \tag{3}$$

The two ligands L1 and the correlation between the symmetry species of the $C_s(yz)$ and C_{2v} groups [17] (cf. Table 2) gives the following C_{2v} representation

$$\Gamma(\mathrm{L1}) = 8\,A_1 + 4\,A_2 + 4\,B_1 + 8\,B_2\,. \tag{4}$$

For the ligand Mo_2O_6(L2) the 18 normal modes of vibration are distributed into the following species of the $C_s(xz)$ group

$$\Gamma(Mo_2O_6) = 10\,a' + 8\,a''\,. \tag{5}$$

Table 2. Correlation table for the species of the C_{2v} group and its subgroups $C_s(xz)$ and $C_s(yz)$[17].

C_{2v}	A_1	A_2	B_1	B_2
$C_s(yz)$	a'	a''	a''	a'
$C_s(xz)$	a'	a''	a'	a''

A transformation of the species into the C_{2v} group (cf. Table 2) for two ligands gives the representation

$$\Gamma(\mathrm{L2}) = 10A_1 + 8A_2 + 10B_1 + 8B_2 . \quad (6)$$

The total number of vibrational modes for the framework and all the ligands L1 and L2 is thus the sum of Eqs. (2), (4) and (6), which is

$$\Gamma(\mathrm{F, L1, L2}) = 20A_1 + 12A_2 + 14B_1 + 17B_2 . \quad (7)$$

The difference between Eqs. (1) and (7) is

$$\Gamma = 6A_1 + 6A_2 + 6B_1 + 6B_2 . \quad (8)$$

(c, d) Equation (8) gives totally 24 normal modes of vibration which are classified as different types of couplings. The distribution of the six modes for each species, Eq. (8), is made in such an even manner as possible, see Table 3. Moreover, the pattern shall be so that the correlations in Table 2 remain valid. The F-L1 couplings shall have about half the number of modes in species A_2 and B_1 compared with those in species A_1 and B_2, cf. Equation (4). These considerations give the distribution shown in Table 3.

Symmetry Coordinates

The symmetry coordinates for the whole $Mo_7O_{24}^{6-}$ complex are constructed by means of the intermediate coordinates for the individual fragments F, L1 and L2.

Table 3 shows the correlations between the overall symmetry coordinates under the symmetry group C_{2v} and those of the ligand and coupling vibrations.

Table 3. Classification of the normal modes and a compilation of the correlation for the species of the groups C_s and C_{2v}.

Type		C_s	C_{2v}	Number of modes
a Framework vibrations			$2A_1 + B_2$	3
b Ligand vibrations	L1	$2 \cdot 8a'$	$8A_1 + 8B_2$	24
		$2 \cdot 4a''$	$4A_2 + 4B_1$	
	L2	$2 \cdot 10a'$	$10A_1 + 10B_1$	36
		$2 \cdot 8a''$	$8A_2 + 8B_2$	
c Framework ligand couplings	F-L1		$2A_1 + A_2 + 2B_2$	5
	F-L2		$2A_1 + 2A_2 + 3B_1 + 2B_2$	9
d Interligand couplings	L1-L2		$2A_1 + 3A_2 + 3B_1 + 2B_2$	10

The 87 symmetry coordinates are constructed out of 30 internal coordinates. All of the 87 symmetry coordinates are not given explicitely, although most of them are included. A compilation of the chosen coordinates and of the distribution into different species in the C_{2v} group is given in Table 4.

The MoO_2 unit. The two valence coordinates d and λ take part in the symmetry coordinates given below,

$$S_1(A_1) = 2^{-1/2}(d_1 + d_2) ,$$
$$S_2(A_1) = D \cdot \lambda ,$$
$$S_1(B_2) = 2^{-1/2}(d_1 - d_2) .$$

The MoO_5 unit. The 24 ($2 \cdot 12$) symmetry coordinates [Eqs. (3), (4)] for the two MoO_5 units were constructed in the following way;

$$S_3(A_1) = \tfrac{1}{2}(u_1 + u_2 + u_3 + u_4) ,$$
$$S_4(A_1) = 2^{-1/2}(r_1' + r_2') ,$$

Table 4. A compilation of the basic set of symmetry coordinates and their occurance in the different species.

Type	Species A_1	A_2	B_1	B_2	
d	+			+	F
λ	+				
u	+	+	+	+	L1
r'	+			+	
t	+			+	
t'	+			+	
γ'	+	+	+	+	
η'	+	+	+	+	
ν	+			+	
ψ	+	+	+	+	
u''	+	+	+	+	L2
s	+	+	+	+	
t''	+	+	+	+	
t'''	+	+	+	+	
γ'''	+	+	+	+	
ε	+	+	+	+	
ν'	+	+	+	+	
ω	+		+		
η'''	+	+	+	+	
o	+		+		
r	+			+	F-L1
d'	+			+	
τ		+			
d''	+		+		F-L2
β''	+	+	+	+	
τ'		+	+	+	
u'	+	+	+	+	L1-L2
γ''	+	+	+	+	
τ''		+	+		
	26	18	20	23	

$$S_5(A_1) = 2^{-1/2}(t_1 + t_2)\,,$$
$$S_6(A_1) = 2^{-1/2}(t_1' + t_2')\,,$$
$$S_7(A_1) = \tfrac{1}{2}(TU)^{1/2}(\gamma_1' + \gamma_2' + \gamma_3' + \gamma_4')\,,$$
$$S_8(A_1) = \tfrac{1}{2}(T'U)^{1/2}(\eta_1' + \eta_2' + \eta_3' + \eta_4')\,,$$
$$S_9(A_1) = \tfrac{1}{2}(R'U)^{1/2}(\psi_1 + \psi_2 + \psi_3 + \psi_4)\,,$$
$$S_{10}(A_1) = (TT'/2)^{1/2}(\nu_1 + \nu_2)\,,$$
$$S_1(A_2) = \tfrac{1}{2}(u_1 - u_2 - u_3 + u_4)\,,$$
$$S_2(A_2) = \tfrac{1}{2}(TU)^{1/2}(\gamma_1' - \gamma_2' - \gamma_3' + \gamma_4')\,,$$
$$S_3(A_2) = \tfrac{1}{2}(T'U)^{1/2}(\eta_1' - \eta_2' - \eta_3' + \eta_4')\,,$$
$$S_4(A_2) = \tfrac{1}{2}(R'U)^{1/2}(\psi_1 - \psi_2 - \psi_3 - \psi_4)\,.$$

The u coordinate is used to show the pattern in the B_1 and B_2 species, i.e.;

$$S_1(B_1) = \tfrac{1}{2}(u_1 + u_2 - u_3 - u_4)\,,$$
$$S_2(B_2) = \tfrac{1}{2}(u_1 - u_2 + u_3 - u_4)\,,$$

The symmetry coordinates $S_2(B_1) - S_4(B_1)$ and $S_7(B_2) - S_9(B_2)$ for γ', η' and ψ are constructed in the same manner.

In addition the r', t, t' and ν coordinates are represented in the B_2 species, $S_3(B_2) - S_6(B_2)$ (cf. Table 4); for example $S_3(B_2) = 2^{-1/2}(r_1' - r_2')$.

The Mo_2O_6 unit. The 36 (2 · 18) symmetry coordinates [Eqs. (5), (6)] for the two Mo_2O_6 units were constructed in the following way:

$$S_{11}(A_1) = \tfrac{1}{2}(u_1'' + u_2'' + u_3'' + u_4'')\,,$$
$$S_{12}(A_1) = \tfrac{1}{2}(s_1 + s_2 + s_3 + s_4)\,,$$
$$S_{13}(A_1) = \tfrac{1}{2}(t_1'' + t_2'' + t_3'' + t_4'')\,,$$
$$S_{14}(A_1) = \tfrac{1}{2}(t_1''' + t_2''' + t_3''' + t_4''')\,,$$
$$S_{15}(A_1) = \tfrac{1}{2}(ST'')^{1/2}(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4)\,,$$
$$S_{16}(A_1) = \tfrac{1}{2}(T''U'')^{1/2}(\gamma_1''' + \gamma_2''' + \gamma_3''' + \gamma_4''')\,,$$
$$S_{17}(A_1) = \tfrac{1}{2}(T''\,T''')^{1/2}(\nu_1' + \nu_2' + \nu_3' + \nu_4')\,,$$
$$S_{18}(A_1) = 2^{-1/2}\,U''(\omega_1 + \omega_2)\,,$$
$$S_{19}(A_1) = \tfrac{1}{2}(ST''')^{1/2}(\eta_1''' + \eta_2''' + \eta_3''' + \eta_4''')\,,$$
$$S_{20}(A_1) = \tfrac{1}{2}(SU'')^{1/2}(o_1 - o_2 + o_3 - o_4)\,,$$

$$S_5(A_2) = \tfrac{1}{2}(u_1'' - u_2'' - u_3'' + u_4'')\,,$$
$$S_6(A_2) = \tfrac{1}{2}(s_1 - s_2 - s_3 + s_4)\,,$$
$$S_7(A_2) = \tfrac{1}{2}(t_1'' - t_2'' - t_3'' + t_4'')\,,$$
$$S_8(A_2) = \tfrac{1}{2}(t_1''' - t_2''' - t_3''' + t_4''')\,,$$
$$S_9(A_2) = \tfrac{1}{2}(ST'')^{1/2}(\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4)\,,$$
$$S_{10}(A_2) = \tfrac{1}{2}(T''\,U'')^{1/2}(\gamma_1''' - \gamma_2''' - \gamma_3''' + \gamma_4''')\,,$$
$$S_{11}(A_2) = \tfrac{1}{2}(T''\,T''')^{1/2}(\nu_1' - \nu_2' - \nu_3' + \nu_4')\,,$$
$$S_{12}(A_2) = \tfrac{1}{2}(ST''')^{1/2}(\eta_1''' - \eta_2''' - \eta_3''' + \eta_4''')\,.$$

The same valence coordinates as used in A_1(11-20) are used for $S_5(B_1) - S_{14}(B_1)$, and those in A_2(5-12) are used for $S_{10}(B_2) - S_{17}(B_2)$, cf. Table 4. The expression may be derived from the u'' examples given below,

$$S_5(B_1) = \tfrac{1}{2}(u_1'' + u_2'' - u_3'' - u_4'')\,,$$
$$S_9(B_2) = \tfrac{1}{2}(u_1'' - u_2'' + u_3'' - u_4'')\,.$$

The $S_{14}(B_1)$ coordinates shall contain the torsions o which are written in the following way;

$$S_{14}(B_1) = \tfrac{1}{2}(SU'')^{1/2}(o_1 - o_2 - o_3 + o_4)\,.$$

Coupling and interligand vibrations. There are 6 symmetry coordinates for coupling and interligand vibrations for each of the species A_1, A_2, B_1 and B_2, Equation (8).

The number of each category (F-L1, F-L2, L1-L2) and the type of valence coordinates are illustrated in Table 4. These coordinates are combined in the following way:

$$S_{21}(A_1) = 2^{-1/2}(r_1 + r_2)\,,$$
$$S_{22}(A_1) = 2^{-1/2}(d_1' + d_2')\,,$$
$$S_{23}(A_1) = 2^{-1/2}(d_1'' + d_2'')\,,$$
$$S_{24}(A_1) = \tfrac{1}{2}(D''\,U'')^{1/2}(\beta_1'' + \beta_2'' + \beta_3'' + \beta_4'')\,,$$
$$S_{25}(A_1) = \tfrac{1}{2}(u_1' + u_2' + u_3' + u_4')\,,$$
$$S_{26}(A_1) = \tfrac{1}{2}(T''\,U')^{1/2}(\gamma_1'' + \gamma_2'' + \gamma_3'' + \gamma_4'')\,.$$

The combination for the other species is the same as for u'', and will therefore not be given. The torsions τ, τ' and τ'' are not so easily combined and these symmetry coordinates are given below:

$$S_{13}(A_2) = (DD'/2)^{1/2}(\tau_1 + \tau_2)\,,$$
$$S_{15}(A_2) = \tfrac{1}{2}(DU'')^{1/2}(\tau_1' + \tau_2' + \tau_3' + \tau_4')\,,$$
$$S_{18}(A_2) = N(\tau_1'' - \tau_2'' + \tau_3'' - \tau_4'' + \tau_5'' - \tau_6'' + \tau_7'' - \tau_8'')\,,$$
$$S_{15}(B_1) = (DD'/2)^{1/2}(\tau_1 - \tau_2)\,,$$
$$S_{20}(B_1) = N(\tau_1'' - \tau_2'' - \tau_3'' + \tau_4'' + \tau_5'' - \tau_6'' - \tau_7'' + \tau_8'')\,,$$
$$S_{21}(B_2) = \tfrac{1}{2}(DU'')^{1/2}(\tau' + \tau_2' - \tau_3' - \tau_4')\,,$$

where $N = (R'\,R''\,U\,U'/8)^{1/2}$.

Force Field Calculations

A diagonal valence force constant matrix was used in all the presented calculations. Redundancies were, however, allowed and incorporated successively in a manner described below. The Mo-O stretching force constants were produced by means of the empirical correlations to bond lengths given by

Cotton et al. [18]. In this valuation the experimental X-Ray values of the bond lengths were used instead of the mean values, because of the non-linear relationship between the force constants and the atomic distances, $f_{\text{Mo-O}} = g(r_{\text{Mo-O}})$. This emphasizes that the physical features are more important here than in the earlier geometrical treatment. For bending and torsional force constants there are no general or simple empirical formulas to use.

Classification of Angles

The angles O_i–Mo–O_j were divided into sets according to the number of bonds to the O_i atoms. The oxygens with the same i value thus form a set where the other oxygens O_j have different j values, so that $i \leqq j$; i.e. $j = i, i+1, i+2, \ldots$. There are thus four such sets as $1 \leqq i \leqq 4$. The force constants are increased within a set with increasing j value, as well as between the sets with increasing i value. The angles Mo–O_i–Mo, where $i = 2, 3, 4$, form a fifth set.

Such a relative scale makes an adjustment of the force constants easier and more relevant because a change in the values for one or several angles will then perhaps lead to adjustments of other force constants of related angles. As starting values for some preliminary calculations the values for the $PMo_{12}O_{40}^{3-}$ ion were used [15]. The final values for the angles are shown in Table 5. As seen in the table some angles assume values which differ from the others on the same line. This is due to the fact that the bonds involving the atoms 12 and 13 differ considerably in length from the rest on the same line. A separation of the angles and the corresponding values is made by a semicolon (;) in Table 5.

Table 5. Classification and valence force constants for the angles.

Set	Type	f/mdyn Å^{-1}
1. O_1–Mo–O_1	ν, ν'	0.15
–O_2	$\gamma; \gamma', \gamma'', \varepsilon, \eta', \eta'', \eta'''$	0.20; 0.25
–O_3	γ'''	0.27
–O_4	θ, η	0.30
2. O_2–Mo–O_2	$\delta''; \lambda$	0.27; 0.33
–O_3	$\delta; \delta', \zeta$	0.33; 0.32
–O_4	$\chi; \chi'; \psi, \psi', \zeta'$	0.36; 0.34; 0.35
3. O_3–Mo–O_3	—	
–O_4	χ'', ψ''	0.38
4. O_4–Mo–O_4	μ	0.40
5. Mo–O_2–Mo	β, β', ω'	0.40
–O_3–	β'', ω	0.42
–O_4–	$\alpha, \alpha', \alpha''$	0.44

Table 6. Calculated frequencies, ν/cm^{-1}, for the block A_1.

	I	II	III	IV	V
1	951	954	954	957	958
2	934	935	939	940	940
3	902	903	912	913	917
4	889	889	899	901	902
5	857	857	889	894	895
6	772	773	774	834	842
7	756	760	760	772	818
8	611	693	693	745	754
9	537	580	661	699	717
10	527	545	588	666	704
11	500	501	567	657	676
12	426	456	559	605	635
13	399	407	522	553	554
14	318	325	325	396	404
15	258	278	312	390	396
16	231	270	291	341	346
17	206	235	279	299	303
18	195	225	242	286	292
19	184	198	232	257	271
20	144	174	219	250	254
21	134	149	176	230	231
22	104	132	146	217	217
23	89	108	139	177	181
24	73	85	109	168	168
25	54	68	96	122	127
26	8	51	70	91	105

Redundants

A stepwise introduction of redundants was only performed for species A_1 and the result is shown in Table 6. The result for the basic set, i.e. no redundants except the stretching r'', is shown in column I and the results including additional redundants in columns II—V.

The angles for the ligands L1 and L2 were introduced as the first redundants (II). Then the couplings F-L1 and F-L2 were incorporated (III), and then the couplings L1-L2 (IV), and finally different combinations of the F-L1-L2 and L1-L2-L1 couplings (V). The torsions τ(F-L1) and τ'(F-L2) are introduced in the calculations III and the torsion τ''(L1-L2) in IV. All the torsions were given the force constant value 0.01 mdyn Å^{-1}.

Force Constants and Compliants

The valance diagonal force constant matrix was converted to a standard F matrix, i.e. symmetry force constants, and quite new values were obtained when redundants were incorporated. The diagonal terms, F_{ii}, are more interesting than the off-diagonal terms, so these are not discussed even if some of them are not small. There was no off-diagonal term greater than the greatest diagonal term. It must be noticed that only the whole block of the F matrix has a physical meaning with reference to the particular set of symmetry coordinates. The F_{ii} terms for the basic set (I) as well as including all redundants (II) are shown in Table 7 for species A_1. The values within parenthesis for the stretch coordinates are equal to the mean value of the set. The values for the angles and the torsions are equal within one symmetrical equivalent set. The change in the diagonal terms, F_{ii}, is large for some coordinates, cf. column I and II. The values for the terminal oxygens are, however, constant. The many high values cannot be interpreted as force constants for the related bendings, stretchings or torsions.

Table 7. The diagonal symmetry force constants, F /mdyn Å^{-1}/ and compliants, N/Å mdyn^{-1}/ for the species A_1, from two different calculations each. The values within parenthesis are means of the initial force constants.

		F_{ii}/mdyn Å^{-1}/		N_{ii}/Å mdyn^{-1}/	
		I	II	III	IV
r	(1.310)	1.585	4.995	0.763	0.373
r'	(1.925)	2.029	5.805	0.519	0.315
d	(6.000)	6.007	6.635	0.167	0.158
d'	(0.830)	0.941	2.574	1.205	0.688
d''	(4.125)	9.718	37.797	0.242	0.200
u	(3.850)	14.094	28.835	0.259	0.232
u'	(3.225)	3.596	6.556	0.310	0.276
u''	(1.288)	1.627	6.732	0.776	0.445
s	(3.773)	3.838	7.835	0.265	0.225
t	(6.675)	6.675	6.675	0.150	0.150
t'	(6.800)	6.800	6.800	0.147	0.147
t''	(6.380)	6.380	6.380	0.157	0.157
t'''	(7.170)	7.170	7.170	0.139	0.139
λ	(0.330)	0.383	1.789	3.030	1.058
γ'	(0.250)	0.253	62.020	4.000	0.848
γ'''	(0.270)	1.786	4.372	3.683	2.819
ε	(0.250)	13.153	33.695	3.791	2.494
η'	(0.250)	0.252	25.412	4.000	1.080
ν	(0.150)	0.150	5.224	6.667	3.146
ν'	(0.150)	0.150	0.570	6.667	3.119
ω	(0.420)	0.942	4.491	2.378	0.873
β''	(0.420)	2.208	3.377	2.371	1.005
ψ	(0.350)	0.720	49.956	2.854	0.744
γ''	(0.250)	11.926	30.553	3.811	2.611
η'''	(0.250)	0.250	0.533	4.000	2.434
o	(0.010)	8.743	23.909	11.768	2.923

Compliance constants on the other hand possess the certain type of invariance properties which make it more feasible to associate them with the appropriate coordinates. We produced the compliance matrix for species A_1 by inverting the F matrix block. The compliants received reasonable values both when excluding (except r'', III) and including (IV) the redundants, see Table 7 column III and IV. It is pleasing to observe that the compliants for d'' and s coordinates are of the same magnitude in the two columns despite a factor of five between the d'' and s related F_{ii} values in column II. Corresponding compliants for the $PMo_{12}O_{40}^{3-}$ ion obtained values of the same order. The compliants for all the terminal oxygens are also very close to those obtained for the $PMo_{12}O_{40}^{3-}$ ion [15]. The obtainment of very similar values of the compliants in these two cases, despite different F matrices, is an indication of a correct treatment in both calculations.

Comparison with Observed Frequencies

In the present analysis the force constants for the angles are adjusted to suit the polarized Raman frequencies [9] as closely as possible. It is seen in Table 8 that only one of the polarized frequencies is missing (489 cm^{-1}) for the species A_1. The other 6 frequencies are very close, and differ by 3 cm^{-1} at most. The 554 peak was found to belong to the λ coordinate, and has served as a "calibration point" for the force constants of the angles. The calculated frequencies are distributed in the same ranges as the experimental, except for a range 450–500 cm^{-1} and for very low values. The very low frequencies are obtained for solids and may be due to solid state effects, and thus may not be genuine internal vibrations. It is interesting to see that in ranges where many peaks are observed, a great number of calculated frequencies are also obtained. A tentative description is given in the table and as expected, the terminal stretchings, $\nu_{Mo\text{-}O_t}$, correspond with the highest frequencies.

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Table 8. Calculated and observed frequencies, ν/cm^{-1}/ for the heptamolybdate anion.

Calculated				Tentative description	Observed				
					Raman				Infra-red
A_1	A_2	B_1	B_2		(aq)[9a]	(aq)[10]	(s)[9a]	(s)[10]	(s)[11]
								965	
958	957	960	957					955	
				Mo-O$_t$ stretch; t', t'''	944			950	
940			940		940 (p)		934	938	940
		925	926						924
916	918			Mo-O stretch; d	917		914	918	
902			904				907		
895			893	Mo-O$_t$ stretch; t, t''	892	900	902	895	900
							889		882
		876					880	880	872
	869	870					861	865	
								852	
842	842		842				839		841
818		815							
	807								
			777	Mo-O stretch + combinations with bendings					
754									770
754									
			741					745	
		726							
717			711		717 (p)		715		720
704									
	688								
676		675	671						
			652	Mo-O$_3$-Mo bendings; (β'', ω)				645	
635	635	638							635
					628	630	630		
					580		574		
554				O$_2$-Mo-O$_2$ bending λ	554 (p)	555			555
							547	550	
			505	torsion τ'					
					489 (p, sh)		484	490	490
							462		
					444	445	444	450	450
		431							
	422			O$_t$-Mo-O$_2$ bendings; (ε, η')					
404			403				411	405	
396		400			398 (p)			395	
								378	
	364						362	370	
					360	360		360	

Table 8 (continued).

Calculated				Tentative description	Observed				
					Raman				Infra-red
A_1	A_2	B_1	B_2		(aq)[9]a	(aq)[10]	(s)[9]a	(s)[10]	(s)[11]
346		341							
	337		335		334		335	340	
	314					320			
303		310			302		308	304	
292	294	291	296	O_t-Mo-O_x bendings; (ν, ν')					
	281		283						
271			274						
		261	265						
254	250				251 (p)			260	
	242		247			245	249		
231		239							
	224	224	229				221	222	
217		215			215	218			
			205						
181	186			bendings, "bridge stretchings" and torsions			200		
		173					175		
168			165						
	158								
							134	140	
127		125			124 (p)			127	
			119		120	115			
105								105	
							92		
								84	
	79						76		
								68	
							55		
							47	47	
							40	38	
								25	
							15		

a frequencies for $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and its solution. p = polarized; sh = shoulder.

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