

## Multicomponent Polyaniions. 33. Single Crystal Raman Spectra of $\text{Na}_6\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})_{14}$

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Polarized Raman spectra of an  $\text{Na}_6\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})_{14}$  single crystal, containing the anion  $\text{Mo}_7\text{O}_{24}^{6-}$ , have been measured. Spectra in the ranges 40–1000 and 2900–3600  $\text{cm}^{-1}$  are presented for all the species of point group  $C_{2v}$ . Different vibrational activity was observed depending on the geometrical orientation of measurement. Tentative assignments of the vibrational modes are performed by comparing structure and orientation of the  $\text{Mo}_7\text{O}_{24}$  groups within the unit cell. The descriptions of the vibrational modes are also compared with assignments of other Mo-oxo-complexes. From the O–H vibrational modes (1500–1700, 2900–3600  $\text{cm}^{-1}$ ) two main types of water of crystallization were found, and furthermore that the waters have fixed orientations.

In acidic aqueous solution of Mo(VI) several polynuclear species exist. The complexes established are hepta- and octanuclear species, e.g.  $\text{Mo}_7\text{O}_{24}^{6-}$ ,  $\text{H}_n\text{Mo}_7\text{O}_{24}^{(6-n)-}$  ( $n=1-3$ ) and  $\text{Mo}_8\text{O}_{26}^{4-}$ .<sup>1-4</sup> Molybdenum(VI) thus easily forms large polyaniions with different compositions and structures. Great interest has been shown in identification and characterization of isopolymolybdate complexes using vibrational spectroscopy.<sup>5-12</sup> The Raman technique is particularly useful for obtaining information on species in aqueous solution, since water has only a weak Raman spectrum. An identification method used is to compare the spectrum of a complex in solution with the spectrum of a powdered solid sample.<sup>5,9,11</sup> The interpretation of spectra will, however, become difficult, since spectra of such large complexes in

general are incomplete. In order to obtain complementary information, a Raman investigation of a single crystal containing the anion  $\text{Mo}_7\text{O}_{24}^{6-}$  was undertaken. Furthermore, the single crystal spectra will show shifts when transferring the  $\text{Mo}_7\text{O}_{24}^{6-}$  anion from an aqueous solution into the crystal field. It would also be profitable to investigate the extent of correlation splitting effects. Moreover, spectra of single crystals are very valuable, especially for group theoretical interpretations and in theoretical calculations of vibrational modes.<sup>13-16</sup>

### EXPERIMENTAL

Polarized single crystal spectra of an  $\text{Na}_6\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})_{14}$  phase were recorded with a Spex Ramalog 1401/14018 at the Institute of Inorganic Chemistry, University of Bielefeld, BRD. The Raman spectrophotometer was equipped with a Coherent Radiation Ar<sup>+</sup> laser, and the blue line at 488.0 nm was used for excitation. The scattered light was detected at 90° from that of illumination.

The crystal had natural faces perpendicular to the crystal axes, so no cutting was necessary. After polishing, the size of the crystal was  $3 \times 8 \times 11 \text{ mm}^3$ . A goniometer system for the orientation of the crystal was used. The crystal axes were also identified with X-ray diffraction Weissenberg techniques.<sup>17</sup> Since the crystal belongs to an orthorhombic space group  $P2_1ab-C_{2v}^2$  (No. 29)<sup>18</sup> the optical and crystal axes coincide,<sup>19</sup> which facilitates the experimental work. Spectra of 12 different scattering geometries were recorded, and the wavenumber ranges 40–1000, 1500–1700 and 2900–3600  $\text{cm}^{-1}$  were covered.

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## METHOD

An advantage of modern Raman spectroscopy is the use of lasers. The laser beam commonly used is coherent and has a very small cross section, which are useful attributes in investigations of single crystals. There are three ways to orientate the crystal with respect to the laser beam and the spectrometer slit in analyzing the scattered light, and two ways of detection, either parallel or perpendicular to the electric vector of the exciting beam ( $E$ ). This gives 12 different geometrical orientations of measurement. However, the polarizability tensor  $\alpha(I = \alpha \cdot E)$  of an orthorhombic class has only 6 unique components, since  $\alpha_{ij} = \alpha_{ji}$ .<sup>20</sup> (A rotation of the crystal  $180^\circ$  along each axis gives in all 24 spectra; however, the 12 new orientations are only replicas of the former, but can be used as a control.) In Fig. 1 four different geometrical orientations of the crystal are shown. The equations of the scattered light intensities for the different observations are also given in Fig. 1.

The anion  $\text{Mo}_7\text{O}_{24}^{6-}$  itself has a symmetry very close to  $C_{2v}$ ,<sup>18</sup> and this point group will therefore be

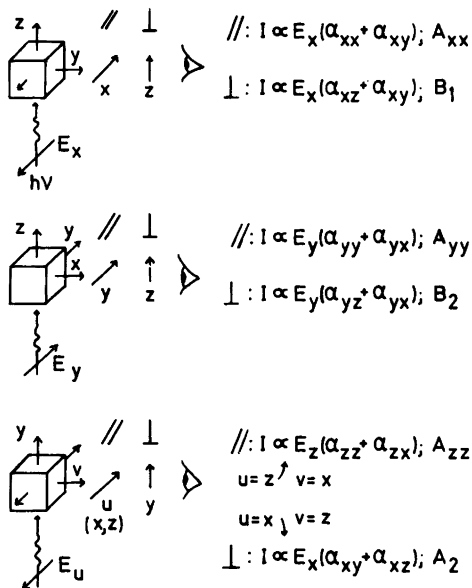


Fig. 1. Different geometrical orientations of the crystal with respect to the exciting laser beam. For each orientation two ways of observation is possible, parallel (//) and perpendicular ( $\perp$ ). The first polarizability factor ( $\alpha$ ) is the main term of the scattered light intensity ( $I$ ), and thus given the point group notation.

adopted. Since the factor group also is  $C_{2v}$  and the site symmetry is  $C_1$ , there will be a complete correlation splitting of each internal fundamental mode into the four Raman active components  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$ . The interactions between molecules are, however, weak compared with those within molecules.<sup>21</sup>

The notation of Damen *et al.*<sup>22</sup> is used to indicate the directions of excitation, observation and polarization. The expression  $i(xy)j$  thus means that the incident light travels along the  $i$  axis and has its electric vector along  $x(E_x)$ , and the  $y$  component of the scattered light is observed along the  $j$  axis. Phonons of the symmetric representation  $A_1$  ( $C_{2v}$  symmetry) can be observed when the directions of polarization are the same for illumination and observation. For different directions of polarization  $A_2$ ,  $B_1$  and  $B_2$  phonons can be observed. Thus, using combinations of polarization in different directions, spectra representing the phonons  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  can be measured, see Fig. 1.

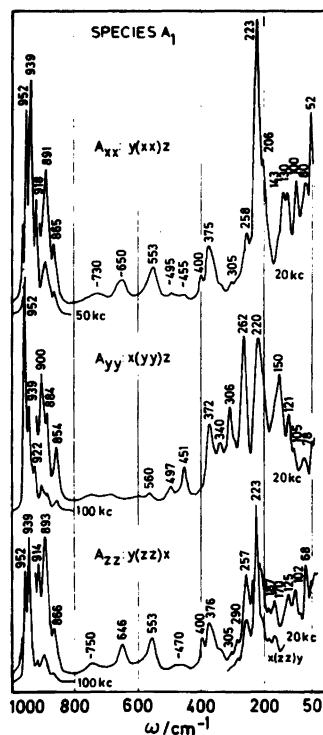


Fig. 2. Polarized Raman spectra of the  $\text{Na}_6\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})_{14}$  single crystal, representing the three "symmetric spectra" ( $A_1$ ) of the anion  $\text{Mo}_7\text{O}_{24}^{6-}$  (kc means 1000 counts).

## SPECTRA

## Spectral measurements

Spectra of the four different species  $A_1$  ( $A_{xx}$ ,  $A_{yy}$ ,  $A_{zz}$ ),  $A_2$ ,  $B_1$  and  $B_2$  were recorded in the wavenumber ranges 40–1000, 1500–1700 and 2900–3600  $\text{cm}^{-1}$ . In the first range, spectra were taken for all the 12 possible orientations, *i.e.* two independent spectra for each of the 6 different types of representations. Highly reproducible spectra were obtained for each corresponding spectra type. There was sometimes, however, a noticeable change in the intensity of the scattered light, due to a more or less successful alignment of the crystal and the optical devices. Owing to the good reproducibility, it was sufficient to record the 6 spectra types only once within the other wavenumber ranges.

*Spectral description.* In Fig. 2 the three  $A_1$  spectra ( $A_{xx}$ ,  $A_{yy}$ ,  $A_{zz}$ ) are shown up to 1000  $\text{cm}^{-1}$ , and in Fig. 3 the  $A_2$ ,  $B_1$  and  $B_2$  spectra. These spectra mainly reflect the detectable vibrational modes for the polyanion  $\text{Mo}_7\text{O}_{24}^{6-}$ , which will be the main topic of this paper. In Fig. 4 the spectra of the water of crystallization in the range 2900–3600  $\text{cm}^{-1}$  are shown. One must, however, be aware that the spectra presented are of the molecules in a crystal

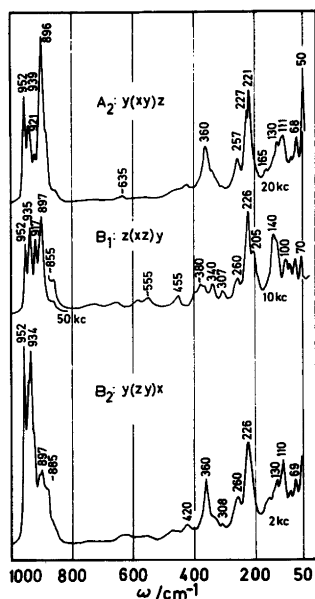


Fig. 3. Polarized Raman spectra of  $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot (\text{H}_2\text{O})_{14}$ , representing the "non symmetric spectra" of the anion  $\text{Mo}_7\text{O}_{24}^{6-}$ .

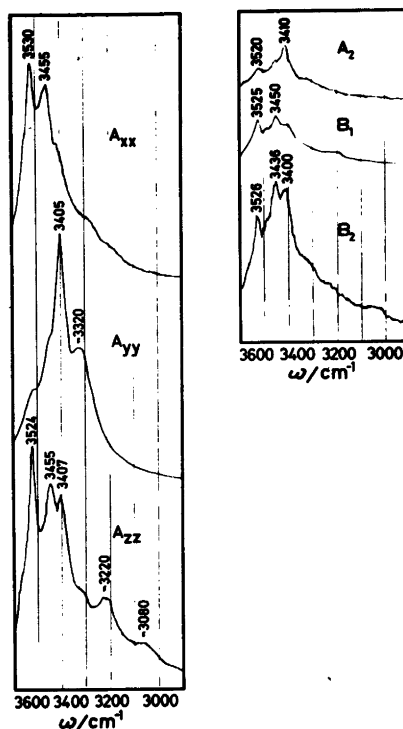


Fig. 4. Polarized Raman spectra of the  $\text{Na}_6\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})_{14}$  single crystal, representing the O–H stretch vibrational modes of the water of crystallization.

field, and that solid state effects may occur.

The difference between the spectra of  $A_1$  phonons ("symmetric spectra") in Fig. 2 and the "nonsymmetric spectra" in Fig. 3 is the greater intensities of the former. The number of peaks is, however, very nearly the same ( $\sim 15$ – $8$ ) in all the spectra. Owing to the lack of automatic intensity measurements, no depolarization ratio has been calculated. The great similarity of the  $A_1$  to the other spectra thus indicates an almost complete correlation splitting of each fundamental mode of a free anion into the four Raman active components  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$ . Most of the peaks thus seem to represent  $A_1$ , *i.e.* symmetrical vibrational modes, since they in general have the highest intensity.

If we compare the  $A_1$  species spectra in Fig. 2 the following observations can be made: (i) that the  $A_{xx}$  and  $A_{zz}$  have great similarities and thus differ from the  $A_{yy}$  spectrum, (ii) that the  $A_{yy}$  spectrum has many peaks of high intensity in the range 150–300, where

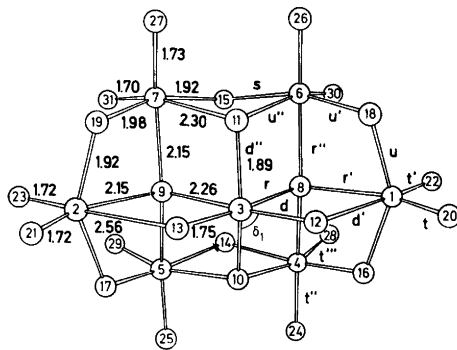


Fig. 5. The structure of the anion  $\text{Mo}_7\text{O}_{24}^{6-}$  with an idealized  $C_{2v}$  symmetry. The bond lengths are given in Å, and defined as internal coordinates. The atoms 1–7 are Mo, and the other oxygen atoms.

$A_{xx}$  and  $A_{zz}$  have only one strong band, (iii) that the  $A_{xx}$  and  $A_{zz}$  spectra have broad low intensity bands in the range 500–800, where  $A_{yy}$  shows almost no activity.

The great similarity of  $A_{xx}$  and  $A_{zz}$  spectra will be discussed below.

### Vibrational modes and structure

The low site symmetry and the large extent of correlation splitting diminishes the possibilities for an interpretation of spectra by means of selection rules. Another method will therefore be attempted below.

In order to correlate the spectra of different symmetry with the orientation of the  $\text{Mo}_7\text{O}_{24}$

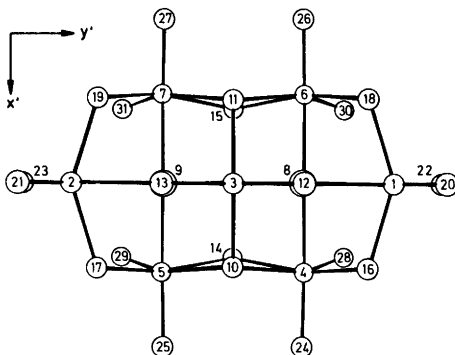


Fig. 6. A top view of the  $\text{Mo}_7\text{O}_{24}^{6-}$  anion, projected on the molecular  $x'y'$ -plane, i.e. the molecular  $z'$  axis is perpendicular to the plane of the paper.

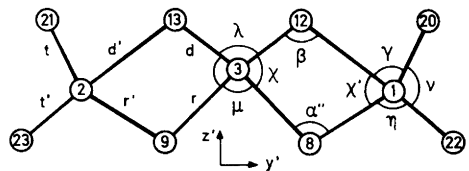


Fig. 7. An  $\text{Mo}_3\text{O}_8$  fragment, which is the central section of  $\text{Mo}_7\text{O}_{24}^{6-}$ , projected on the molecular  $y'z'$ -plane.

groups within the unit cell, some structural models are depicted in Figs. 5–10.

In Fig. 5 an idealized bond model of  $\text{Mo}_7\text{O}_{24}$  with  $C_{2v}$  symmetry is depicted, which in Fig. 6 is projected on the molecular  $x'y'$ -plane. In Fig. 7 the “central section”, a  $\text{Mo}_3\text{O}_8$  fragment of the anion, is projected on the  $y'z'$ -plane (to show the unit which primarily interacts with the  $y$  component of the exciting light, i.e. gives  $A_{yy}$  spectra). An overall view of several  $\text{Mo}_7\text{O}_{24}^{6-}$  anions linked by sodium ions is depicted in Fig. 8. The “central section” in the  $y$ -direction is recognized as the longest part of each polyhedron. This figure shows that the “central section” of a  $\text{Mo}_7\text{O}_{24}$  group is aligned almost parallel with the crystal  $y$ -axis, i.e. the  $y'$  and  $y$  axes are almost parallel. The molecular  $y'z'$  and crystal  $yz$  planes are, however, not parallel. The “molecule” is tilted throughout the crystals so that the angle between the  $y'z'$  and  $xy$  planes is respectively positive and negative every second time. The molecular  $x'$  and  $z'$  axes will thus alter while the  $y'$  axes will not, compared to the crystal axes. This geometrical phenomenon thus explains the great similarities between the  $A_{xx}$  and  $A_{zz}$  spectra. Spectral differences would have been expected with the  $x'$  and  $z'$  axes parallel with the crystal axes.

The  $\text{Mo}_7\text{O}_{24}$  spectra (Figs. 2–3) can now be examined in conjunction with the orientation of the anion (Figs. 5–8). For instance, the  $A_{yy}$  spectrum will be examined especially in combination with Fig. 7. The notation  $x(\gamma\gamma)z$  means that it is the  $y$  component of the laser beam which interacts with the anions in the crystal, and that the  $y$  component of the scattered light in the  $z$  direction is observed. In the spectra the peaks can be divided into three ranges, viz. below 400, 400–800 and above 800  $\text{cm}^{-1}$ .

The characteristic peaks from 150 to 300  $\text{cm}^{-1}$  in the  $A_{yy}$  spectrum are mainly due to bending vibrational modes, and the main cause is found within the co-planar  $\text{Mo}_2\text{O}_2$  rings (see Fig. 7). There

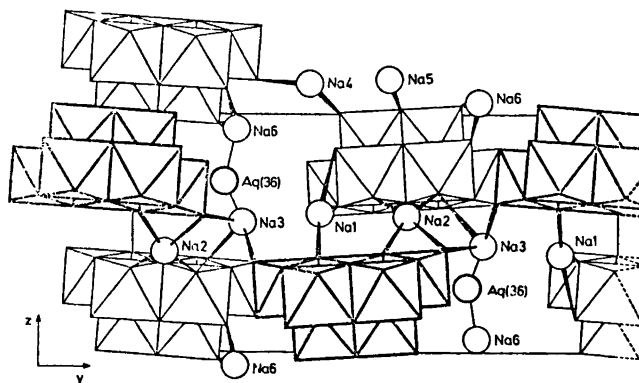


Fig. 8. A schematic drawing of the connection between  $\text{Mo}_7\text{O}_{24}^{6-}$  anions in a crystalline phase.

are, in addition to those in Fig. 7, two  $\text{Mo}_2\text{O}_2$  rings in Fig. 5 (4-10-5-14 and 6-11-7-15). It is especially the peaks  $150, 262$  and  $306\text{ cm}^{-1}$  which do not occur in the  $A_{zz}$  spectrum and they can thus be assigned to bendings such as  $\gamma, \eta, \beta, \chi, \alpha'$  and  $\mu$  (see Fig. 7). In this way peaks occurring only (or with large intensity) in one of the three  $A_1$  spectra can be assigned to a bending mode in one of the  $x$ -,  $y$ - or  $z$ -directions respectively. However, there are too great similarities in the  $A_{xx}$  and  $A_{zz}$  spectra in this case to completely allow such assignments. There are some peaks below  $150\text{ cm}^{-1}$ , which can be considered as lattice modes. The peak in common at about  $220\text{ cm}^{-1}$  for all three spectra must be due to bending of the angle between the terminal oxygen bonds ( $v, v'$  *i.e.*  $\angle 24\text{-}4\text{-}28$  *etc.*). These angles have the greatest changes in the  $x$ - and  $z$ -directions and the  $220$  peak is by far the most intense one in the  $A_{xx}$  and  $A_{zz}$  spectra. There is also a  $220\text{ cm}^{-1}$  band with a high intensity, however, little shifted in the three "non-symmetric spectra", see Fig. 3. Since the angles are made up of terminal bonds, the non-symmetric vibrational modes may also have relatively high intensities. It may be noticed that the shift is towards higher wavenumbers compared with the symmetric bendings.

Another band in common is that at about  $370\text{ cm}^{-1}$ , which may be a depolarized band. This band can be considered as a "trade mark" of condensed polymolybdates, since it occurs in most other Mo-containing polyanions, even heteropolymolybdates.<sup>11</sup> Since this band occurs in so many different compounds and there is no difference regarding the geometry of detection for  $\text{Mo}_7\text{O}_{24}^{6-}$ , this band cannot be due to a single type of

vibrational mode, *i.e.* one specific bond or angle. One fragment commonly occurring in most polymolybdates is a puckered  $\text{Mo}_3\text{O}_3$  ring (see Fig. 9). There are four such rings in the  $\text{Mo}_7\text{O}_{24}^{6-}$  anion, which can be considered to give rise to the  $370\text{ cm}^{-1}$  band. It is not easy to decide which kind of vibrational mode gives the main contribution to this peak. Most probably there are combinations of bendings and torsions and perhaps even stretchings. The large intensity for the  $370$  peak in the "non-symmetric spectra" in Fig. 3 supports the idea that it is not a single type of vibrational mode causing this peak.

The  $451$  peak in the  $A_{yy}$  spectrum can be assigned to a bending in the  $y$ -direction. The most probable candidates are the angles  $12\text{-}3\text{-}13(\lambda)$  and  $8\text{-}3\text{-}9(\mu)$ . In a theoretical calculation of vibrations, the angle  $\lambda$  obtained the value  $554\text{ cm}^{-1}$ .<sup>13</sup> This high value was obtained because the bending force constant was adjusted to give a wavenumber as close as possible to the experimental value at about  $555\text{ cm}^{-1}$ .<sup>8, 11, 12</sup> These single crystal spectra ( $A_{xx}$  and  $A_{zz}$ ) show that the  $555$  peak cannot be a bending in the  $y$ -direction. The theoretical calculation and assignment is thus incorrect in this sense.

In the range  $500\text{--}800\text{ cm}^{-1}$ , the  $A_{yy}$  spectrum has only a small activity, while the  $A_{xx}$  and  $A_{zz}$  spectra have peaks at about  $550, 650$  and  $750\text{ cm}^{-1}$ . These peaks are to be explained by modes which have no analogues in the  $y$ -direction. The peaks can be described as being due to "breathings" of the anion, as was found for the anion  $\text{Mo}_5\text{P}_2\text{O}_{23}^{6-}$ .<sup>16</sup> It means that the dimensions of the anion are changing either in the  $x$  or the  $z$ , but not in the  $y$  direction. It also appears from the structure (see Figs. 5 and 8) that the anion is rather stiff in the  $y$  direction, while the

two octahedra, one on each side of the central  $\text{Mo}_3\text{O}_8$  section, are less "tightly bonded". In fact they are reminiscent of the wings of a bird. The low peak intensities also indicate some kind of "breathing" modes, which must have very small vibrational amplitudes.

The peaks in the range  $800-1000\text{ cm}^{-1}$  are due to stretch vibrational modes of short Mo—O bonds. It is obviously the short terminal oxygen bonds which give rise to the most intense peaks. In the  $A_{yy}$  spectrum the 952 peak is thus assigned to  $t$  and/or  $t'$ , and in  $A_{xx}$  and  $A_{zz}$  the 939 peak to  $t''$  and/or  $t'''$ . Vibrational modes involving the Mo—O bonds denoted  $d$  must be most intense in the  $A_{yy}$  spectrum.<sup>13</sup> Because of the short bond length (1.75 Å) the 922 peak is the most probable candidate. The other Mo—O bonds are not easy to assign without any guidance from isotope substituted spectra. The asymmetric spectra have also some high intensity peaks, e.g. at about 896, 934 and  $952\text{ cm}^{-1}$ . The bonds  $t$ ,  $t'$ ,  $d$  and  $r'$  are active only in  $B_2$  except  $A_1$ , and  $d''$  is active only in  $B_1$  except  $A_1$ .<sup>13</sup> The remainder of the short bonds are active in all four species. These selection rules thus confirm the 952 peak as a  $t$  and  $t'$  vibrational mode. The 934 peak ( $B_2$ ) can be an asymmetric vibrational mode of the  $d$  bond and the 917 peak ( $B_1$ ) can be assigned to the  $d''$  bond. The 896 peak appears somewhat shifted in all kinds of spectra, and is thus very difficult to assign. Owing to the very high intensity in  $A_2$  even asymmetric vibrational modes of terminal oxygen bonds ( $t''$ ,  $t'''$ ) may be involved. Most probably there are several non-resolved peaks in this region, which prevent a more complete description.

The spectra of the crystal waters in Fig. 4 also depend on the orientation of the crystal. In this case differences among all the spectra, and especially among the three  $A_1$  spectra, occur. All the peaks are due to O—H stretch vibrations. This implies that the waters of crystallization have fixed orientations.

The  $A_{zz}$  spectrum is the most detailed one, with several well-resolved peaks, and no new peak is found in any of the other spectra in Fig. 4. The two peaks in the  $A_{xx}$  spectrum originate most probably from only one type of water molecule, with two different O—H bond lengths. Support for this idea is that there is only one bending vibrational mode [ $\delta(\text{H}_2\text{O})$ , at  $1667\text{ cm}^{-1}$ ] for the  $A_{xx}$  orientation. The three  $A_1$  spectra can thus be considered to represent two different types of water molecules, one represented by the 3455 and 3520 peaks ( $A_{xx}$ ), and the other by the 3405 peak ( $A_{yy}$ ). The  $A_{zz}$  spectrum

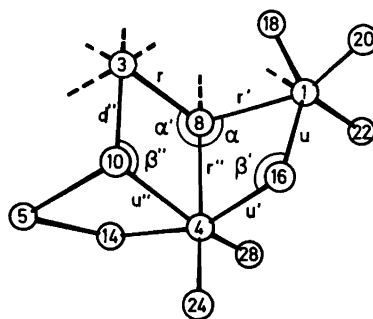


Fig. 9. A fragment of  $\text{Mo}_7\text{O}_{24}^{6-}$  showing one of the puckered  $\text{Mo}_3\text{O}_3$  rings, viz. 1-16-4-10-3-8.

has thus contributions from both types of waters. There are also two bending peaks (at 1602 and  $1668\text{ cm}^{-1}$ ) for the  $A_{zz}$  symmetry.

In Figs 8 and 10 one can find two types of waters, namely (i) waters coordinated to only one  $\text{Na}^+$ , and (ii) waters shared by  $\text{Na}^+$  ions. This classification is coarse and there are waters which differ from the two main types, as is also indicated by several shoulders and peaks at lower wavenumbers in the  $A_{zz}$  spectrum.

The type of water represented by the 3405 peak ( $A_{yy}$ ) has identical bond lengths, which should be longer than the bonds in the water represented by the  $A_{xx}$  spectrum. For the two-coordinated waters the bonds  $\text{Na}^+ - \text{O}(\text{Aq}) - \text{Na}^+$  are, in general, different in length, 0.18 Å at the most,<sup>18</sup> which can result in asymmetric O—H bonds, and thus give an  $A_{xx}$  type of spectrum. The single coordinated water [ $\text{Aq}(2)$ ,  $\text{Aq}(4)$ ],<sup>18</sup> being stronger bonded to  $\text{Na}^+$ , should thus give the 3405 peak.

The  $B_2$  spectrum has by far the greatest intensity of all the asymmetric spectra. The selection rules for a free water molecule with  $C_{2v}$  symmetry allows vibrational modes in  $B_2$ , only if the  $\text{H}_2\text{O}$  lies in the  $yz$ -plane.  $B_1$  activity corresponds to a molecule in the  $xz$ -plane. Accordingly most of the waters thus have the hydrogens orientated in the  $yz$ -plane.

## DISCUSSION AND CONCLUSION

The similarity of spectra in Figs. 2 and 3 suggests complete correlation splitting. On the other hand the differences in  $A_{xx}$  and  $A_{zz}$  compared to  $A_{yy}$  (Fig. 2) tend to rule out complete correlation splitting. The explanation of this is, as discussed earlier, that the molecular  $x'$  and  $z'$  axes have a different

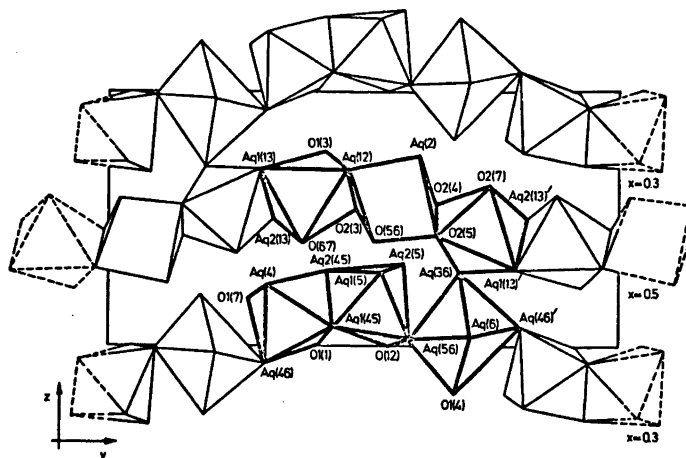


Fig. 10. A schematic drawing of the arrangement of  $\text{NaO}_x(\text{H}_2\text{O}_{6-x})$  octahedra.

direction than the crystal axes, while the  $y'$  and  $y$  axes are almost parallel. The observed correlation splitting is thus not due to intermolecular couplings in the unit cell, but to the geometrical facts mentioned.

Almost all the peaks obtained in this work have been reported for the Raman spectrum of the anion  $\text{Mo}_7\text{O}_{24}^{6-}$  in aqueous solution. However, the intensity relations of the peaks are quite different. Especially the "solution peaks" have much lower intensities than the corresponding peaks obtained

for the  $A_{yy}$  spectrum. However, the peak positions are not altered much when the anion is transferred from an aqueous to a crystal field. This implies that there exists a lattice of cations also in aqueous solution of high concentration, and that the aqueous and crystal fields are comparable, at least in their effects on  $\text{Mo}_7\text{O}_{24}^{6-}$ .

Some comparisons can be made, since several interpretations of vibrational modes of other Mo-oxo-complexes have been reported.<sup>23-25</sup> Table 1 contains a compilation of assignments for mono-

Table 1. A compilation of the assignments for Mo(VI)-oxo-complexes of different nuclearity.

Modes	$\text{MoO}_2\text{F}_4$ Ref. 23	$\text{Mo}_2\text{O}_5(\text{ox})_2(\text{H}_2\text{O})_2^{2-}$ I, Ref. 23	$\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2^{2-}$ II, Ref. 23	$\text{Mo}_7\text{O}_{24}^{6-}$ Ref. 6	This work
$\nu^s [\text{Mo}(\text{O})_2]$	951	} 958 } R 919 }	971	} 900 }	} 952 (t, t')
$\nu^{as} [\text{Mo}(\text{O})_2]$	920		975		
$\delta [\text{Mo}(\text{O})_2]$	385	385		360	224 (v, v')
$\nu^s (\text{Mo}-\text{O}-\text{Mo})$		235		400-600	
$\nu^{as} (\text{Mo}-\text{O}-\text{Mo})$		851		750-840	
$\delta (\text{Mo}-\text{O}-\text{Mo})$		130 <sup>a</sup>		219	
$\nu^s (\text{Mo}_2\text{O}_2)$			499		} 850-900 (d, d', d'', r, r') <sup>a</sup> 120-300 (\gamma, \eta, \beta, \alpha'', \mu)
$\nu^{as} (\text{Mo}_2\text{O}_2)$			578		
$\delta (\text{Mo}_2\text{O}_2)$			224		
" $\text{Mo}_3\text{O}_3$ modes"					370
"Breathing modes" - Mo-O-Mo-					550-750

<sup>a</sup> Interpreted as Mo-O<sub>b</sub> stretches.

and dinuclear complexes as well as for the heptamolybdate complex given. The dinuclear Mo complexes found in the solids  $K_2Mo_2O_5(Ox)_2(H_2O)_2$  (I)<sup>26</sup> and  $BaMo_2O_4(Ox)_2(H_2O)_2$  (II),<sup>27</sup> have one and two oxygen bridges, respectively.

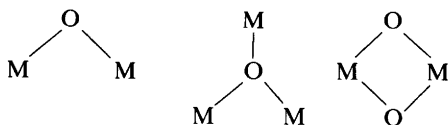
The stretches for the terminal oxygens ( $O_t$ ) seem to be independent of the nuclearity. There is thus no mixing with other vibrational modes. Griffith<sup>23</sup> assigns peaks at about  $360\text{ cm}^{-1}$  to  $Mo=O$  bends. The spectra in this work do not support the same assignment for  $Mo_7O_{24}^{6-}$ , and the 220 peak is assigned to  $Mo=O$  bends. It can, however, be noticed that for structures I and II there are peaks at 235 (I) and at 224 (II)  $\text{cm}^{-1}$ , respectively.

The stretch force constant,  $f$ , is dependent on the  $Mo-O$  bond length, especially for terminal oxygens.<sup>28</sup> Short bond lengths give high  $f$ -values, which will result in peaks at high wavenumbers. The bridging  $Mo-O_b$  bonds for structures I and II are in general shorter than those in  $Mo_7O_{24}^{6-}$ , viz. 1.88 Å (I); 1.88, 1.93 Å (II) compared with 1.75–2.56 Å for  $Mo_7O_{24}^{6-}$ . Despite this, the  $Mo_7O_{24}^{6-}$  anion has several peaks assigned to bridging oxygens at higher wavenumbers, cf.  $\nu(Mo_2O_2)$  in Table 1. In this case it is most probably the terms of the atomic masses, included in the kinetic energy ( $T = \frac{1}{2}mx^2$ ), which give rise to the peaks at high wavenumbers.

The assignments for the complexes I and II thus differ from those for the heptanuclear  $Mo_7O_{24}^{6-}$  complex. One conclusion is thus that one cannot compare large and very condensed structures with smaller ones. This was also clearly shown in a theoretical study of  $PMo_{12}O_{40}^{3-}$  and small fragments of the same anion.<sup>29</sup>

Another condensed anion with known structure is  $Mo_6O_{19}^{2-}$ , of which both Raman and IR spectra are recorded.<sup>25</sup> The reported assignments give  $Mo-O_b$  and  $Mo-O_t$  vibrational modes in the ranges 470–810 and 950–980  $\text{cm}^{-1}$ , respectively. In  $Mo_6O_{19}^{2-}$  each Mo has only one terminal oxygen ( $O_t$ ) and there are only three types of  $Mo-O$  bonds in all, whereas in  $Mo_7O_{24}^{6-}$  there are 14.<sup>13</sup> Despite that, the reported peaks and assignments are on the whole comparable with those given in this work.

Thus a conclusion is that it is not possible to isolate parts such as



and assign them to unique vibrational modes. The vibrational conditions and peak positions thus depend upon the way in which such units are bonded to the rest of the complex.

There is also a large mixing of the terms for the kinetic energy for multibonded atoms. It is therefore not possible to talk in terms of group frequencies for condensed complexes such as  $Mo_7O_{24}^{6-}$ . It is thus mostly the outermost atoms, or atoms with few bonds that do have quite assignable vibrational modes.

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