Vibrational spectra of α-molybdic acid-MoO₃·H₂O

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Abstract. The IR and Raman spectra of molybdenum trioxide—monohydrate are studied assuming an effective tetrahedral Mo-O coordination and isolated water molecules, although the crystallographic coordination is six-fold with two long Mo-O distances. Based on C_i symmetry, the group theoretical analysis has been carried out and a vibrational assignment is proposed. The nature of hydrogen bonding and the librational modes of water molecules are discussed. The factor group splitting for ν_3, the asymmetric stretching mode of $MoO_4^=$ ion, is large indicating strong inter-chain coupling.

Keywords. Raman spectra; molybdic acid; librational modes; infrared spectra.

1. Introduction

The structural investigation of the different forms of molybdic acids (molybdenum trioxide-hydrates) was started by Lindqvist (1950, 1956). Recent investigations (Guntur 1972; Oswald *et al* 1975) revealed three different forms of $MoO_3 \cdot H_2O$— a white α-form, a white β-form and an yellow form. It has been established that the α-form has the oxygens 6-fold coordinated around molybdenum, of which the oxygen of the water molecule being the one, forming octahedral double chains (Oswald *et al* 1975). Further, from the O..O distances of the water oxygen there is evidence for hydrogen bonding between the octahedral double chains.

Guntur (1972) recorded the infrared spectra of $MoO_3 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ (yellow form) to study the coordination of water molecules. Maricic and Smith (1958) reported the infrared spectra of $MoO_3 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ and Krauss and Huber (1961) reported the spectrum of $MoO_3 \cdot 2H_2O$. However, no mention about the forms was made. The infrared and Raman spectra studies of the α-form of molybdenum trioxide-monohydrate could throw light on the nature and strength of hydrogen bonding, the librational modes of water molecules and the wide range of molybdenum-oxygen distances present in it.

2. Experimental

White molybdic acid (Analar grade) was used for the investigation. The far infrared spectrum (10-400 cm⁻¹) (figure 1) was recorded in an FIR 30 Polytec. The infrared spectrum (400–4000 cm⁻¹) using KBr pellet was recorded using spectrophotometer (Perkin Elmer).
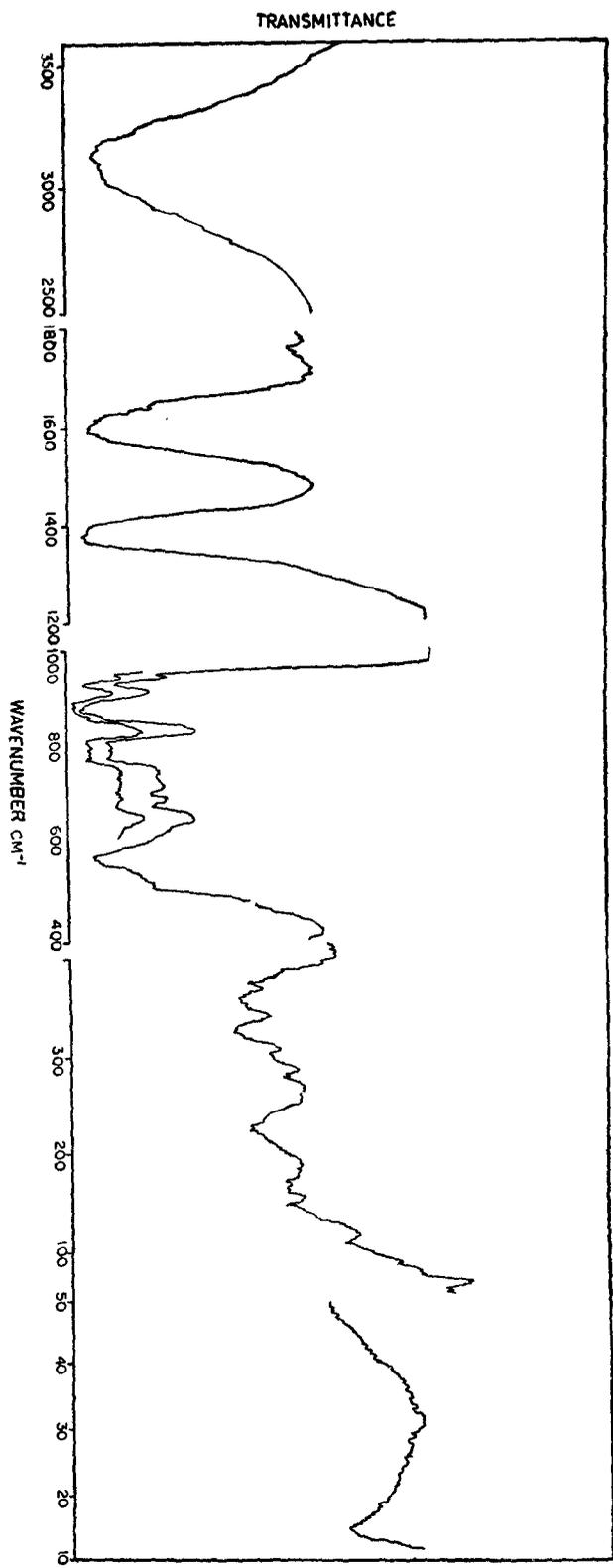
Figure 1. Far IR and IR spectra of α-molybdic acid.

The Raman spectrum (figure 2) was recorded using double monochromator, (Cary 82 and Spex Ramalog), both equipped with argon ion laser (Spectra Physics) operating at 4880 Å. The sample was placed in a metal cone of diameter 4-5 mm and a capillary tube of diameter 1.1 mm for Spex Ramalog.

3. Factor group analysis

The α-form molybdenum trioxide-monohydrate belonged to the triclinic system with the space group $\bar{P}1$ (C_i^1) (Oswald *et al* 1975). The oxygens are 6-fold coordinated around molybdenum forming an infinite double chain of edge-linked [$MoO_5(H_2O)$] octahedra perpendicular to the *b*-axis. The Mo-O distances range between 1·66 and 2·37 Å. Hence as an approximation, if the two ligands with the largest Mo-O distances are neglected, the structure may be alternatively described as built up from chains (perpendicular to *b*-axis) of corner-linked distorted MoO_4-tetrahedra and isolated water molecules. This approximation is similar to the one by Kihlborg (1963) to characterize the structure of MoO_3 as a transitional state between octahedral and tetrahedral coordination. Using a similar approximation Blasse (1975) succeeded in explaining the vibrational spectra and the luminiscent properties of $HgMoO_4$.

The crystal has two formula units per unit cell and all atoms are located on the general positions. The symmetry of a free molybdate ion is T_d. However, in the crystal, it occupies a general site of C_1 symmetry. The anisotropic crystal field lifts the degeneracies of the normal modes. For such a configuration, the number of internals to be expected can be derived as indicated in table 1. Coupling between the vibrating ions produces further splitting of each crystal mode into components equal to the number of ions in the primitive unit cell (Davydov 1969).

4. Assignments

The internal modes of the molybdate ion are expected to occur in the region 775–950 cm^{-1} (stretching) 275–425 cm^{-1} (bending) irrespective of its environment. For the external modes, the frequency strongly depends on the type of motion (translation or rotation) and on the nature of the cation. Further, interactions could occur between rotational, translational and low-lying internal modes. It is difficult to explain the observed spectra of powdered samples due to the complex nature of the metal-oxygen

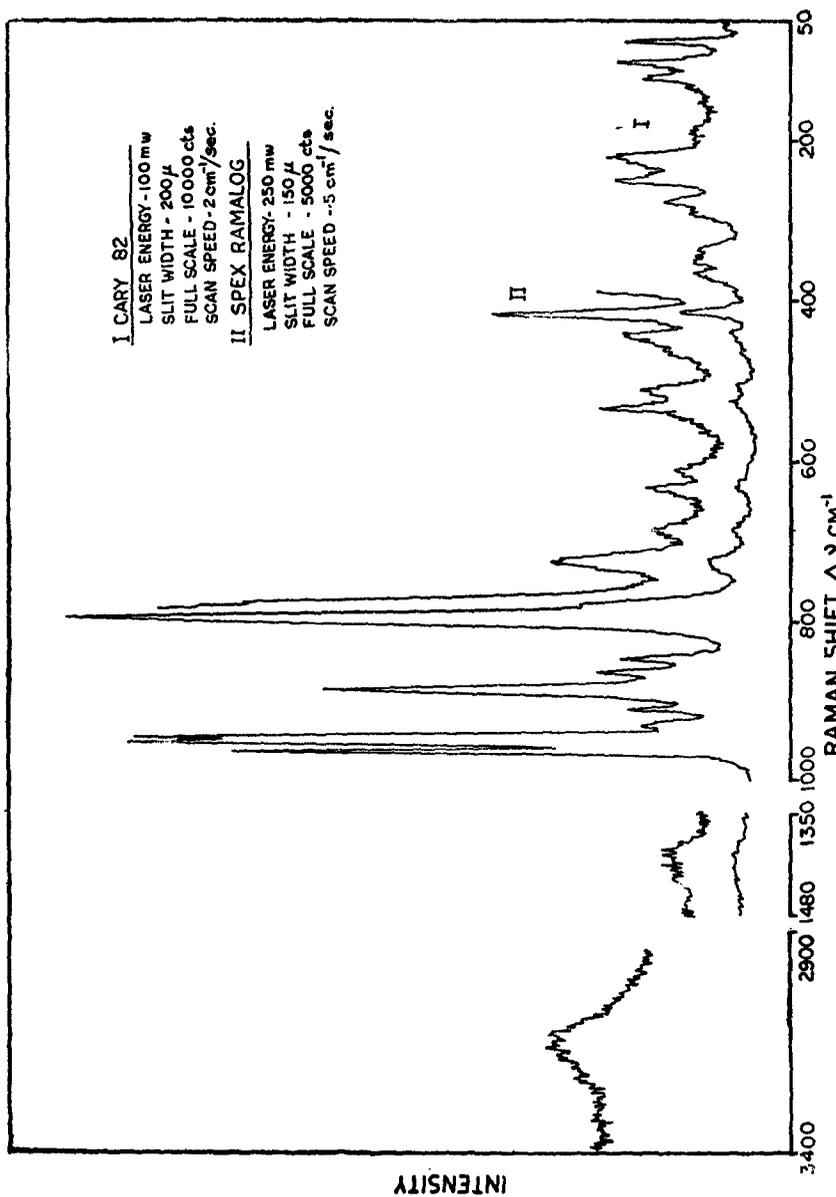**Table 1.** Correlation table for the normal modes of the MoO_4 group with site symmetry C_1.

T_d symmetry[a]	Site symmetry	Two groups under C_i symmetry[b]
ν_1 A (R)	A	$A_g + A_u$
ν_2 E (R)	2A	$2A_g + 2A_u$
$\nu_3, \nu_4 F_2$ (i. r, R)	3A	$3A_g + 3A_u$

[a] (R) — Raman active; (i. r.) — infrared active
[b] *g* modes Raman active; *u* modes infrared active

Figure 2. Raman spectra of α-molybdic acid

linkages and the distortions present in the metal-oxygen polyhedra. However, it is possible to make symmetry assignments by comparison with the normal modes of free molecules.

4.1 *O-H vibrations*

The octahedral double chains are linked through possible hydrogen bonds. The distances from the water oxygen O(4) to oxygen atoms $O(1^{iv})$, $O(3^i)$, $O(3^{vii})$ of neighbouring octahedral double chain are respectively 2.76, 2.85 and 3.14Å. These values indicate medium and weak strength for the hydrogen bonding. Oswald *et al* (1975) have assumed that if $O(1^{iv})$ is definitely bonded it remains open which of the other two $[O(3^i), O(3^{vii})]$ contacts represents the second water hydrogen bridge and the most probable hydrogen bonds are indicated by them (figure 3).

The strong bands at 3215, 3185, 3172 and 3155 cm^{-1} in Raman, and the strong broad band centred around 3140 cm^{-1} in infrared indicate hydrogen bonding of medium strength. Since the site symmetry of the water molecule is C_1, the two O-H bonds should be of unequal strength and the presence of four lines in Raman indicates this. These are the symmetric and asymmetric stretching of the hydrogens bonded to the $O(1^{iv})$ and $O(3^i)$ with $O(4)-O(1^{iv})$ and $O(4)-O(3^i)$ distance of 2·76 and 2.85 Å respectively. These O-H frequencies fall in the region of intermediate hydrogen bond strength (Novak 1979) and this clearly excludes the possibility of the hydrogen bonding with the $O(3^{vii})$ with an $O(4)-O(3^{vii})$ distance of 3.14 Å which is a distance indicative of a weak hydrogen bond.

The HOH deformation (ν_2) of a free water molecule occurs around 1600 cm^{-1} and will be strong in infrared and very weak in Raman. Usually the bending mode (ν_2) of water increases in wavenumber with increased strength of hydrogen bonding. However, this correlation does not always hold (Scherer 1978). Pezerat (1979) reported the bending vibration at low frequencies from a study of hydrogen bonded biological systems. In yellow molybdic acid ($MoO_3.2H_2O$) Sreenivasan (1979)
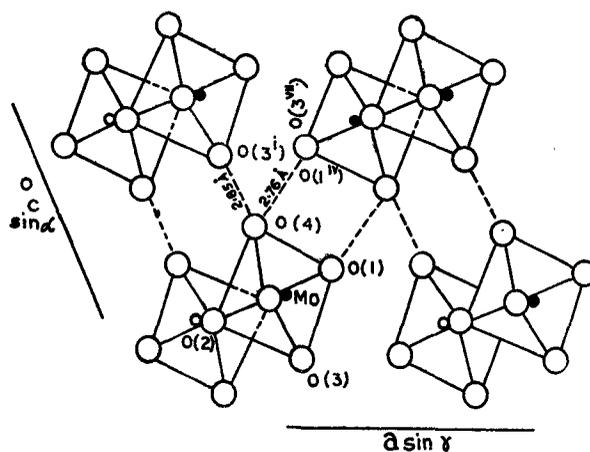

Figure 3. Projection of crystal structure parallel to [010]. Dotted lines indicate probable hydrogen bonds (after Oswald *et al* 1975).

observed the bending frequency around 1400 cm^{-1} which shifts to $\sim$ 1100 cm^{-1} on partial deuteration. In the present investigation, the infrared spectrum presents strong broad bands centred at 1600 and 1385 cm^{-1}. In Raman spectrum there is only a weak band in the region 1390-1445 cm^{-1} with distinct peaks at 1406 and 1436 cm^{-1} and no band could be observed around 1600 cm^{-1}. These observed frequencies are perhaps not HOH modes but OHO ones, one of a strongly bonded and the other that of a weakly bonded.

4.2 *Molybdate ion*

The molybdate ions are in a crystal field of low symmetry. Hence a large splitting of the degenerate vibrational modes is expected. Table 1 predicts four Raman active A_g modes and four infrared active A_u modes for the Mo-O stretchings. The frequency observed at 960 cm^{-1} in Raman and at 950 cm^{-1} in infrared is assigned to the symmetric stretching ν_1 of the molybdate ion. Such a high frequency for an Mo-O stretching is due to the Mo-O bond of 1·654 Å which is the shortest ever found in molybdenum-oxygen compounds. The frequencies 883 and 792 cm^{-1} correspond to two of the three predicted asymmetric frequencies of the molybdate ion. The third has split into a doublet (940 and 948 cm^{-1}) due to vibrational interaction with the neighbouring ions. The shoulder at 778 cm^{-1} may also be due to this interaction. The splitting of about 150 cm^{-1} for the triply degenerate ν_3 mode is unusually large. The complementary infrared frequencies are found at 927, 875 cm^{-1} and a broad band centred at 790 cm^{-1} with peaks at 770 and 805 cm^{-1}. Here again, the large splitting is maintained ($\sim$ 150 cm^{-1}). A similar type of splitting observed in MgMoO$_4$ (Miller 1971) and HgMoO$_4$ (Blasse 1975) is attributed to the strong interactions between the stretching motions of the tetrahedra and Mg-O, Hg-O interactions. The wide range of Mo-O distances present in the crystal can also give rise to such large splittings. Another possibility seems to be a strong interchain coupling.

The intensity of the symmetric stretching ν_1 is strong in Raman and weak in infrared whereas ν_3 is strong in both. Also the intensity ratio of ν_1/ν_3 is < 1 in both infrared and Raman. For tetrahedral ions Wienstock *et al* (1973) have established that ν_1 is strong in Raman and weak in infrared whereas ν_3 is strong in infrared and weak in Raman. It may be pointed out here that the above conclusion is based on the assumption that the crystal contains distorted MoO$_4$ tetrahedra and isolated water molecules. In the actual case, the oxygens are 6-fold coordinated with molybdenum and the Mo-O network is in an intermediate state between octahedral and tetrahedral coordination. The observed large splittings of ν_3 and the departure from Wienstock *et al's* (1973) intensity criteria may be due to this.

The assignments of ν_2 and ν_4 of the molybdate ion showed discrepancies before the work of Wienstock *et al* (1973) who proved from intensity calculations that $\nu_4 > \nu_2$ along with the Raman and infrared data of a variety of tetrahedral ions. The labelling of ν_2 and ν_4 as internal modes is only approximate as mixing is expected with the lattice modes. The frequencies observed at 414, 367, 350, 342 and 335 cm^{-1} in Raman and at 400, 375, 360, 350 and 325 cm^{-1} in infrared have been assigned to ν_4 and ν_2. The assignments are tentative owing to powder data.

The frequencies observed below 300 cm^{-1} may be due to rotational and translational modes. The possibility that some of the lines are lattice modes cannot be excluded. Further, it is difficult to distinguish between translational and rotational modes,

Table 2. Vibrational assignments of α-molybdic acid.

Infrared frequencies in cm^{-1} A_u symmetry	Raman frequencies in cm^{-1} A_g symmetry	Assignments
	3215	
3140	3185	OH stretching
	3172	
	3155	
1765		
1655		Combinations
1440–1360	1436	OHO bending
(broad band)	1406	
950	960	ν_1 MoO$_4$
927	948	ν_3 MoO$_4$
	940	
	908	Combination
875	883	ν_3 MoO$_4$
855	861	Combination
	846	Combination
805	792	ν_3 MoO$_4$
770	778	
	727·5	R_yH$_2$O
700		R_yH$_2$O
	689	R_yH$_2$O
675		R_yH$_2$O
	631	a
	610	a
570		R_tH$_2$O
	530	R_tH$_2$O
510	510	R_tH$_2$O
	461	R_rH$_2$O
	441	R_rH$_2$O
400	414	ν_4MoO$_4$
375	367	ν_4MoO$_4$
360	350	ν_4MoO$_4$
350	342	ν_2MoO$_4$
325	335	ν_2MoO$_4$
300	290	
280	274	
	246	R MoO$_4$
225	216	
165	188	
148	150	T MoO$_4$
114	120	
	116	
87	99	
78	74	
60		
50	52	Lattice modes
13		

a, coupled librations of H$_2$O; R_y, R_t, R_r, wag, twist and rock libration; R, Rotation; T, Translation

However, rotational modes in general have higher wavenumber and intensity than translational modes. A tentative assignment is shown in table 2.

4.3 *Librational modes of* H_2O

The three librational movements of H_2O are the wagging, twisting and rocking. Lutz *et al* (1979) tried to assign the librational modes of H_2O molecules which are in an asymmetric force field and the sequence of $\nu_{wag} > \nu_{twist} > \nu_{rock}$ within the region 300–775 cm^{-1} was preferred. The different librational modes have recently been studied by Singh *et al* (1980). They assigned the bands in the region 900–500 cm^{-1} to these modes in the order $\nu_{rock} > \nu_{wag} > \nu_{twist}$. All these studies show that the assignments of the librational modes are ambiguous. However, the frequencies observed in the region 750–450 cm^{-1} have been tentatively assigned. In infrared, the frequencies at 700 and 675 cm^{-1} have been assigned to the wagging vibration. The strong band at 570 cm^{-1} with a shoulder at 510 cm^{-1} has been assigned to the twisting vibration. The very high intensity for this band is suggestive of the coupling of some other vibrational modes. In infrared it is reasonable to assume that the rocking vibrations are mixed up with ν_2 and ν_4 of the molybdate ion. The weak broad line observed at 727·5 and 689 cm^{-1} and 441, 461 cm^{-1} in Raman, assigned to the wagging and rocking vibrations respectively. The lines at 530 and 510 cm^{-1} can be assigned to the twisting, since it has a higher intensity (Lutz 1979).

The proposed vibrational assignments are shown in table 2.

5. Conclusions

The approximation that molybdenum trioxide-monohydrate contains distorted MoO$_4$ tetrahedra and isolated water molecules can fairly explain the observed vibrational spectra. The number of modes predicted by group theoretical analysis and mutual exclusion of frequencies to be obeyed under C_i point group have been observed (table 2). The large splitting of the Mo-O asymmetric stretching and the failure to obey the intensity criteria indicate that the molybdenum-oxygen coordination is in an intermediate state between tetrahedral and octahedral. The splitting of about 150 cm^{-1} for the ν_3 asymmetric stretching vibrations is indicative of strong interchain coupling. The observed OH stretching frequency falls in the region of intermediate strength hydrogen bonding and hence it may be said that the hydrogen bridge is formed between O(4) and O(1^{iv}), O(3^i). Hence one can rule out the possibility of the hydrogen bonding with O(3^{vii}).

Acknowledgement

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