

Infrared and Raman spectra of aquamolybdenum (VI) oxide hydrate ($\text{MoO}_3 \cdot 2\text{H}_2\text{O}$)

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Abstract. The infrared and Raman spectra of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ are recorded and analysed on the basis of vibrations due to MoO_6 octahedra and H_2O molecules. Considerable changes in the frequencies of the octahedra have been observed due to strong distortion in the octahedral arrangement. The inactive ν_6 vibration of O_h symmetry became active in the Raman spectrum. Co-ordinated (aquated) and hydrated (interlayer) water molecules give rise to different frequencies.

Keywords. Raman spectrum; infrared spectrum; hydrogen bond; anisotropic crystal field effect.

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1. Introduction

The structural investigation of hydrates of molybdenum trioxide (molybdic acids) has been reported earlier (Lindquist 1950; Asbrink and Brandt 1971; Guntur 1972; Krebs 1972; Boschen and Krebs 1974; Oswald *et al* 1975; Crouch Baker and Dickens 1984a, b, 1986). The dihydrate consists of infinite layers of vertex sharing $\text{MoO}_5\text{-H}_2\text{O}$ octahedra. Every octahedron shares a corner with each of the four neighbouring octahedra within the layers (Krebs 1972). The remaining water molecule assumes the interlayer position and the layers are linked by a system of hydrogen bonds involving all the four hydrogen atoms. Three H atoms participate in the normal H bonds whereas the fourth enters into bifurcated ones (Asbrink and Brandt 1971). Vibrational spectrum of the α form of the monohydrate was studied by Saleem and Aruldas (1983) assuming Mo-O co-ordination to be tetrahedral. The present investigation deals with vibrational spectroscopic studies of molybdenum trioxide dihydrate, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$.

2. Experimental

Analar grade $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ was used for the investigation. The Raman spectrum (figure 1) of the powder sample was recorded in the Stokes region of the green line 5145 \AA (laser power, 50 mW) using a double monochromator (Spex Ramalog 1401

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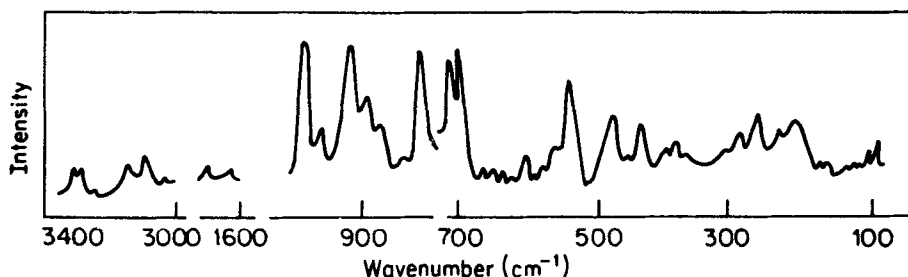


Figure 1. Raman spectrum of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$.

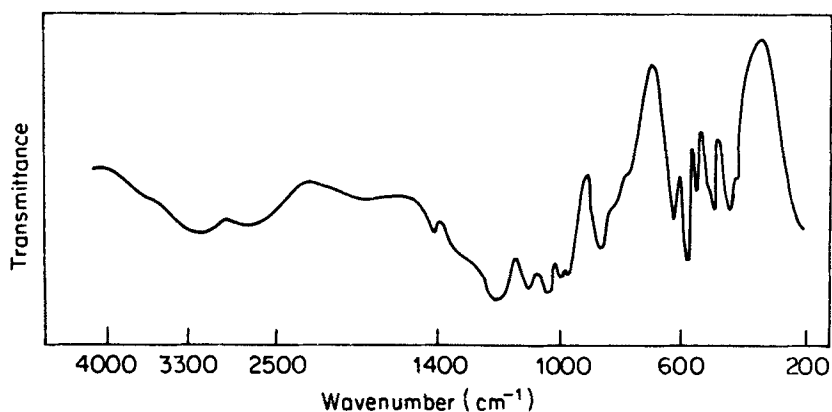


Figure 2. Infrared spectrum of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$.

having a resolution of 2 cm^{-1} equipped with a laser (Spectra Physics model 165 Ar^+). The photomultiplier tube C31034 has a high efficiency and uniform response. Signal to noise ratio is between 10 and 50. The IR spectrum (figure 2) in the region $200\text{--}4000\text{ cm}^{-1}$ was obtained on a spectrophotometer (Perkin-Elmer 983) with KBr pellet as the sample.

3. Factor group analysis

$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ —the first example of an aquoxide (Krebs 1972) with both co-ordinated and hydrated water molecules crystallizes in the monoclinic system-space group $P2_1/n$ (C_{2h}^2)-with 16 formula units per unit cell. All the atoms are in general site C_1 . The MoO_6 octahedron is strongly distorted with six alternating short and long Mo-O distances (1.694, 2.054, 1.766, 2.288, 1.800 and 2.056 Å). The group theoretical analysis developed by Fateley *et al* (1972) gives the distribution of fundamentals amongst the irreducible representations of the space group C_{2h} as follows

$$\Gamma\text{MoO}_3 \cdot 2\text{H}_2\text{O} = 120A_g^{(R)} + 120B_g^{(R)} + 119A_u^{(IR)} + 118B_u^{(IR)}.$$

4. Vibrational analysis

The vibrational assignments (table 1) were carried out on the basis of vibrations due to MoO_6 octahedra and water molecules.

4.1 MoO_6 vibrations

For a free MoO_6 octahedron, the internal modes are expected to occur in the regions $600\text{--}800\text{ cm}^{-1}$ (stretching) and $300\text{--}450\text{ cm}^{-1}$ (bending) (Leigeois-Duyckaerts and Tarte 1974; Blasse and Corsmit 1973). Since the MoO_6 octahedra are strongly distorted, a large shift of the internal modes is expected. As the octahedra occupy sites (C_1) of lower symmetry than the free octahedral symmetry O_h , the resulting anisotropic crystal field may cause inactive modes to become active, removal of degeneracies of normal modes and shifting of the frequencies of non-degenerate modes.

In the Raman spectrum, two strong bands at 957 and 929 cm^{-1} have been observed for $\nu_1(A_{1g})$ symmetric stretching mode. The splitting of this non-degenerate mode may be due to correlation field effect. The corresponding IR bands are observed at 1000 and 985 cm^{-1} . The appearance of five Raman bands for $\nu_3(F_{1u})$ in the region $800\text{--}900\text{ cm}^{-1}$ is due to both site symmetry and correlation field effects. In IR only

Table 1. Vibrational assignments.

Raman (cm^{-1})	IR(cm^{-1})	Assignments
3350	—	$\nu_3\text{H}_2\text{O(I)}$
3342	—	$\nu_3\text{H}_2\text{O(II)}$
3327	3300	C
3167	—	$\nu_1\text{H}_2\text{O(I)}$
3120	—	$\nu_1\text{H}_2\text{O(II)}$
3024	—	C
1648	—	$\nu_2\text{H}_2\text{O(II)}$
1607	1610	$\nu_2\text{H}_2\text{O(I)}$
	1395	O—H...O
957	1000	
929	985	$\nu_1\text{MoO}_6$
891, 868, 854	879, 860	$\nu_3\text{MoO}_6$
822, 803	810	
720, 696	—	$\nu_2\text{MoO}_6$
649, 636	620	Rr H_2O
616, 607	—	C
593, 582, 561	590, 575	$\nu_5\text{MoO}_6$
544, 532	542	
511, 464, 441	500, 489, 440	$\nu_4\text{MoO}_6$
420	425, 410	
374		$\nu_6\text{MoO}_6$
358, 336, 302	310	C
285, 246, 235, 224		
196, 187, 149, 140		External modes
133, 126, 119, 108		
81, 73, 64		

$\text{H}_2\text{O(I)}$, co-ordinated water molecule; $\text{H}_2\text{O(II)}$, hydrated water molecule; C, combination; Rr, rotational rocking.

three bands are observed at 897, 860 and 810 cm^{-1} . The large splitting of about 90 cm^{-1} for ν_3 mode both in IR and Raman is indicative of the octahedral co-ordination (Miller 1971). The observation of two bands at 720 and 696 cm^{-1} for $\nu_2(E_g)$ in Raman may be due to the lower site symmetry.

The bands observed in the regions 600–530 cm^{-1} and 525–400 cm^{-1} are assigned to $\nu_5(F_{2g})$ and $\nu_4(F_{1u})$ modes respectively (table 1). The appearance of Raman (ν_4) and IR (ν_5) inactive modes may be due to the crystal field effect. Moreover, the large shifting of ν_5 and ν_4 modes indicates that the octahedra are highly distorted. Though $\nu_6(F_{2u})$ mode is inactive under O_h symmetry, it is observed at 374 cm^{-1} in Raman spectrum in agreement with Wilson's rule (Gaunt 1953).

4.2 Vibrations of H_2O

The mean O...O distance for the co-ordinated water molecule is 1.729 Å and for the hydrated one 1.824 Å. Hence, two sets of frequencies are expected for the internal modes of water. The observed wavenumbers in Raman are assigned on this basis. In IR, only a broad band centred around 3300 cm^{-1} for stretching modes and a medium intense band at 1610 cm^{-1} for bending mode are observed. The medium intense IR band at 1395 cm^{-1} is probably due to O—H...O deformation mode (Pezerat 1979; Vinogradov and Linnel 1970). Although the librational modes of water fall within the region (500–900 cm^{-1}) of the internal modes of molybdate ion, one can distinguish the weak, broad bands due to the water molecule (Nakagawa and Shimonouchi 1964). Assignment of bands due to external modes is difficult in a powder spectrum.

5. Conclusion

The observed splitting of the asymmetric stretching modes is due to strong distortion in the octahedral arrangement. The observation of Raman inactive mode $\nu_4(F_{1u})$ and IR inactive mode $\nu_5(F_{2g})$ and the shifting of these modes to high wavenumbers also support this. The co-ordinated and hydrated water molecules differ in their hydrogen bond strengths. The inactive ν_6 mode of MoO_6 became active in the Raman spectrum.

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