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Vibrational spectroscopic studies of $FeClMoO_4$, Na_2MoO_4 and $Na_2MoO_4 \cdot 2H_2O/D_2O$

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Abstract

FTIR and Raman spectra of $FeClMoO_4$ single crystal and polycrystalline Na_2MoO_4, $Na_2MoO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2D_2O$ are recorded and analysed. The band positions for different modes suggest that MoO_4 tetrahedron is more distorted in $FeClMoO_4$. The larger splitting observed for the bending modes and partial retention of degeneracy of the asymmetric stretching mode indicate that angular distortion is greater than liner distortion in MoO_4^{2-} ion in $FeClMoO_4$ confirming x-ray data. The non-appearance of the v_1 and v_2 modes in the IR and partial retention of the degeneracies of various modes show that MoO_4^{2-} ion retains T_d symmetry in Na_2MoO_4. Wavenumber values of the v_1 mode indicate that the distortion of MoO_4 tetrahedra in the four crystals are in the order $FeClMoO_4 > Na_2MoO_4 \cdot 2H_2O > Na_2MoO_4 \cdot 2D_2O > Na_2MoO_4$. The water bands suggest the presence of two crystallographically distinct water molecules in $Na_2MoO_4 \cdot 2H_2O$. They form strong hydrogen bonds. © 1997 Elsevier Science B.V.

Keywords: Deuteration; Hydrogen bonding; Infrared spectra; Raman spectra; Single crystal spectra

1. Introduction

The anhydrous and hydrated molybdates constitute a large class of inorganic compounds and they have been the subject of various investigations including IR and Raman spectroscopic studies. The crystal structure and magnetism of $FeClMoO_4$, a new two dimensional antiferromagnet with O–Mo–O super exchange pathways have been investigated by Torardi et al. [1,2]. Its structure is built from $FeMoO_4Cl$ layers stacked along the c axis and is closely related to α-$VOPO_4$ type compounds. Individual layers consist of corner-sharing MoO_4 tetrahedra and $FeClO_4$ square pyramids.

The crystal structure of $Na_2MoO_4 \cdot 2H_2O$ (abbreviated as NaMH) has been investigated by several workers [3,4]. It is isostructural with $Na_2WO_4 \cdot 2H_2O$. The oxygen coordination around the two crystallographically distinct Na atoms is remarkably different. The first Na^+ ion is surrounded by six oxygen atoms, two from the water molecules and four from the MoO_4^{2-} ions, forming a distorted octahedron. The second Na^+ is

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surrounded by five oxygen atoms, two from water molecules and three from MoO_4^{2-} ions forming a distorted trigonal bipyramid. This kind of coordination surrounding Na^+ is very rare in other sodium compounds.

Busey and Keller [5] have carried out a preliminary analysis of the IR and Raman spectra of $Na_2MoO_4 \cdot 2H_2O$ and Na_2MoO_4. In continuation of our studies on the structure of MoO_4^{2-} ions in different crystalline environment, a detailed vibrational analysis of the FTIR and Raman spectra of $FeClMoO_4$ single crystal and polycrystalline Na_2MoO_4, $Na_2MoO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2D_2O$ have been carried out.

2. Experimental

The single crystals of $FeClMoO_4$ (abbreviated as FeM) were grown [1] and provided by Dr C.C. Torardi, Central Research and Development Department, E.I. Du Pond de Nemours and Company, USA. Commercially available $Na_2MoO_4 \cdot 2H_2O$ (BDH, AR grade) was used for the investigation. $Na_2MoO_4 \cdot 2D_2O$ (abbreviated as NaMD) was prepared by dissolving a small quantity of $Na_2MoO_4 \cdot 2H_2O$ in excess of pure heavy water and then evaporated inside a vacuum desiccator. The process was repeated several times to increase the percentage of deuteration. The anhydrous Na_2MoO_4 (abbreviated as NaM) was prepared [5,6] by heating $Na_2MoO_4 \cdot 2H_2O$ in an oven at a temperature of 373 K for about 8 h.

A well developed single crystal of $FeClMoO_4$ of size $3 \times 3 \times 1$ mm was selected and crystallographic axes were determined by using a polarizing microscope. The sides of the crystal were cut parallel to the crystallographic a, b and c axes. The crystal was finely polished and properly aligned on the goniometer to record the Raman spectra in the 90° scattering geometry. The polarized Raman spectra of the FeM single crystal (Fig. 1) were recorded for six crystal orientations viz., $z(xx)y$, $z(yy)x$, $x(zz)y$, $z(yx)y$, $z(yz)y$ and $z(xz)y$. Raman spectra of the polycrystalline samples of FeM, NaM, NaMH and NaMD were also recorded by taking the samples in capillary tubes. A 1401 Spex Raman spectrometer equipped with

a Spectra Physics model 165.08 Ar^+ ion laser was used and the spectra were recorded using 514.5 nm radiation at a resolution better than 3 cm^{-1}. The FTIR spectra of the compounds were recorded on a Bruker IFS-66V-FTIR spectrometer with the samples taken as polyethylene pellets and KBr pellets in the far-IR and mid-IR regions respectively. The IR spectra of FeM and NaMH in the 200–4000 cm^{-1} region were also recorded on a Perkin Elmer model 882 spectrophotometer in the KBr pellet method.

3. Factor group analysis

$FeClMoO_4$ crystallizes in the tetragonal system, with space group P4/nmm having two molecular units per unit cell. In the crystal, MoO_4^{2-} ions occupy D_{2d} sites, and Fe and Cl atoms occupy C_{4v} sites. Factor group analysis of the compound has been carried out using correlation method developed by Fately et al. [7]. Excluding acoustic modes at $k = 0$, 39 optical modes are distributed as

$$\Gamma = 4A_{1g} + A_{2g} + 3B_{1g} + 1B_{2g} + 6E_g + A_{1u} + 4A_{2u} + B_{1u} + 2B_{2u} + 5E_u$$

$Na_2MoO_4 \cdot 2H_2O$ crystallizes in the orthorhombic system with the space group Pbca having eight formula units per unit cell [4]. MoO_4^{2-} ions, water molecules and Na atoms occupy the general sites C_1 in the crystal. Excluding acoustic modes at $k = 0$, the 309 optical modes are obtained as

$$\Gamma = 39A_g + 39B_{1g} + 39B_{2g} + 39B_{3g} + 39A_u + 38B_{1u} + 38B_{2u} + 38B_{3u}$$

Na_2MoO_4 crystals has a spinel type structure. It is cubic in nature with space group Fd3m and has two formula units per Bravais unit cell [8,9]. In the crystal, MoO_4^{2-} ions occupy, T_d sites and Na atoms occupy D_{3d} sites. The 39 optical modes are, excluding acoustic modes at $k = 0$, are given by

$$\Gamma = A_{1g} + E_g + F_{1g} + 3F_{2g} + 2A_{2u} + 2E_u + 4F_{1u} + 2F_{2u}$$
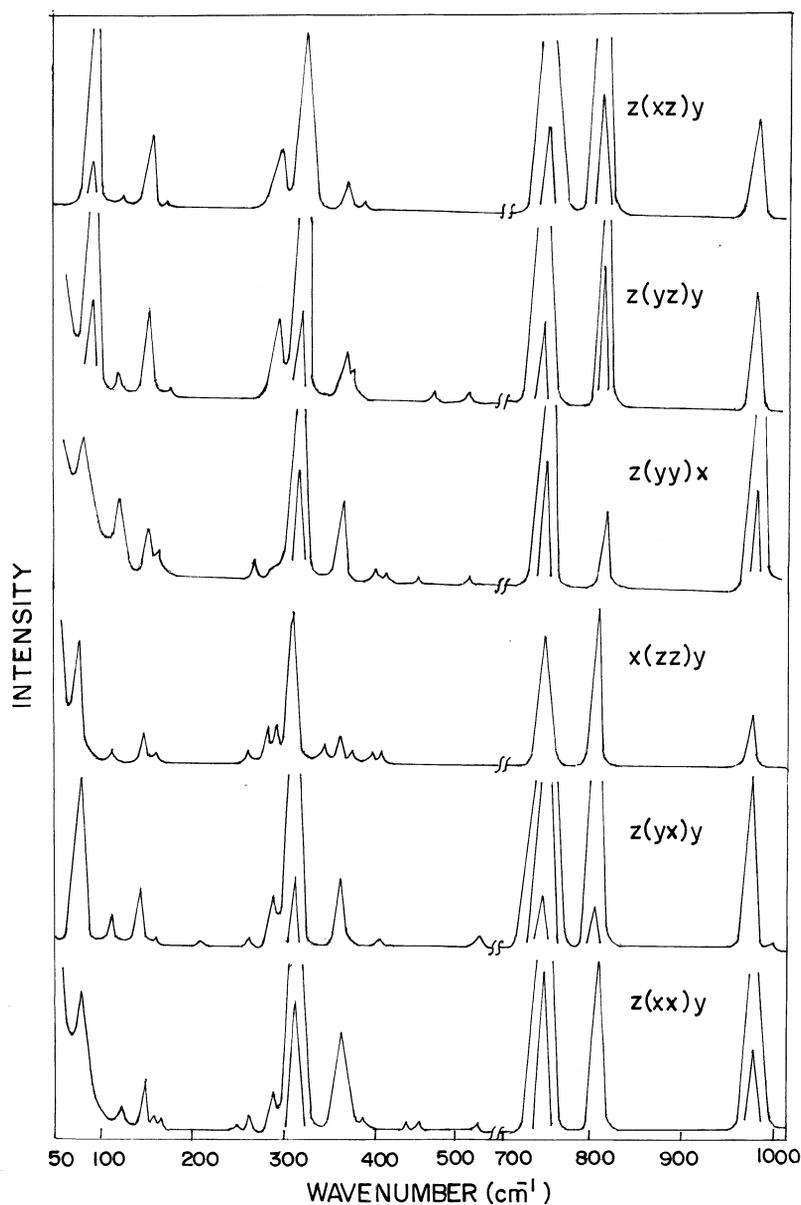
Fig. 1. Polarized Raman spectra of FeClMoO$_4$.

4. Results and discussion

The correlation diagram for the MoO$_4^{2-}$ ion in Table 1 maps out the site splitting and factor group splitting in the crystals. The wavenumbers of the observed bands, in the infrared and Raman spectra (Figs. 1–5) and their assignments are presented in Tables 2 and 3.

Table 1

Correlation of the internal vibrational modes of MoO_4^{2-} ions in (a) $FeClMoO_4$, (b) $Na_2MoO_4 \cdot 2H_2O$ and (c) Na_2MoO_4

(a) $FeClMoO_4$

Free ion symmetry T_d	Site symmetry D_{2d}	Factor group symmetry D_{4h}	
		$A_{1g}(\nu_1, \nu_2)$	2
2 $A_1(\nu_1)$	A_1 (ν_1, ν_2)	$B_{1g}(\nu_3, \nu_4)$	2
4 $E(\nu_2)$	B_1 (ν_2)	$B_{2g}(\nu_2)$	1
		$E_g(\nu_3, \nu_4)$	2
		$A_{1u}(\nu_2)$	1
12 $F_2(\nu_3, \nu_4)$	B_2 (ν_3, ν_4)	$A_{2u}(\nu_3, \nu_4)$	2
	E (ν_3, ν_4)	$B_{2u}(\nu_1, \nu_2)$	2
		$E_u(\nu_3, \nu_4)$	2

(b) $Na_2MoO_4 \cdot 2H_2O$

Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry D_{2h}	
8 $A_1(\nu_1)$		$A_g(\nu_1, \nu_2, \nu_3, \nu_4)$	9
		B_{1g} "	9
16 $E(\nu_2)$	A $(\nu_1, \nu_2, \nu_3, \nu_4)$	B_{2g} "	9
		B_{3g} "	9
		A_u "	9
48 $F_2(\nu_3, \nu_4)$		B_{1u} "	9
		B_{2u} "	9
		B_{3u} "	9

(c) Na_2MoO_4

Free ion symmetry T_d	Site symmetry T_d	Factor group symmetry O_h	
2 $A_1(\nu_1)$	$A_1(\nu_1)$	$A_{1g}(\nu_1)$	1
		$A_{2u}(\nu_1)$	1
4 $E(\nu_2)$	$E(\nu_2)$	$E_g(\nu_2)$	1
		$E_u(\nu_2)$	1
12 $F_2(\nu_3, \nu_4)$	$F_2(\nu_3, \nu_4)$	$F_{2g}(\nu_3, \nu_4)$	2
		$F_{1u}(\nu_3, \nu_4)$	2

Fig. 2. Raman spectra of (a) $Na_2MoO_4 \cdot 2H_2O$, (b) $Na_2MoO_4 \cdot 2D_2O$, (c) Na_2MoO_4 in the 50–1200 cm^{-1} region.

4.1. MoO_4^{2-} vibrations

The MoO_4^{2-} ion with T_d symmetry has four normal modes of vibration and are at $v_1(A_1)$, 894 cm^{-1}; $v_2(E)$, 318 cm^{-1}; $v_3(F_2)$, 823 cm^{-1} and $v_4(F_2)$, 381 cm^{-1} [10] respectively.

4.2. FeClMoO₄ (FeM)

In the Raman spectra, the nondegenerate v_1 mode appears as a polarized band at 973 cm^{-1} in all orientations. This mode appears with very large intensity in the $z(xx)y$ and $z(yy)x$ orientations and its intensity is less in other orientations. The bands in the $x(zz)y$ orientation are generally less intense for all the modes. From the correlation diagram (Table 1), v_1 mode belongs to

phonons of A_{1g} and B_{2u} symmetries. The band at 973 cm^{-1} has larger intensity in A_{1g} orientations and hence this mode belongs to A_{1g} species. In the powder spectrum this mode is observed as an intense band at 972 cm^{-1}. In the FTIR spectrum, this inactive mode appears with medium intensity at 964 cm^{-1} which belongs to B_{2u} species. In $MnMoO_4$ [11] where Mo–O bond length is 1.73 Å, the v_1 mode is observed at 959 cm^{-1} and in $Tb_{1.8}Eu_{0.2}(MoO_4)_3$ with Mo–O bond length 1.76 Å, it is obtained at 960 cm^{-1} [12]. In $FeClMoO_4$ the short Mo–O bond is of length 1.756 Å. Hence the value obtained for the v_1 mode in the present study is slightly high.

The v_1 mode has polarizability components α_{xx}, α_{yy} and α_{zz} in T_d symmetry, which belongs to the A_{1g} and B_{1g} species of D_{4h} factor group. Hence, this mode is expected to appear in A_{1g} orientations without any distortion of the MoO_4 tetrahedra. According to Bhattacharjee's criteria [13], the appearance of this mode in B_{2g} and E_g species indicates the distortion of MoO_4 tetrahedra contributing to α_{xy}, α_{xz} and α_{yz} polarizability tensor components. Therefore, this IR inactive mode also appears in the IR spectrum.

The correlation diagram shows that Raman phonons of the triply degenerate v_3 mode belongs to E_g and B_{1g} symmetries. This mode appears with a partial lifting of degeneracies in all orientations of the Raman spectra, as two bands around
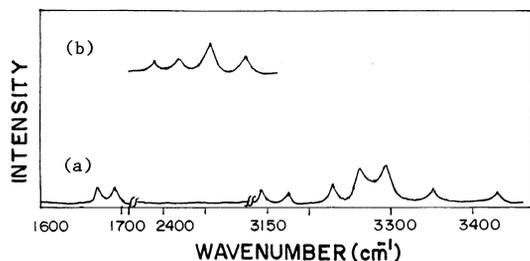

Fig. 3. Raman spectra of (a) $Na_4MoO_4 \cdot 2H_2O$, (b) $Na_2MoO_42D_2O$ in the 1600–3500 cm^{-1} region.
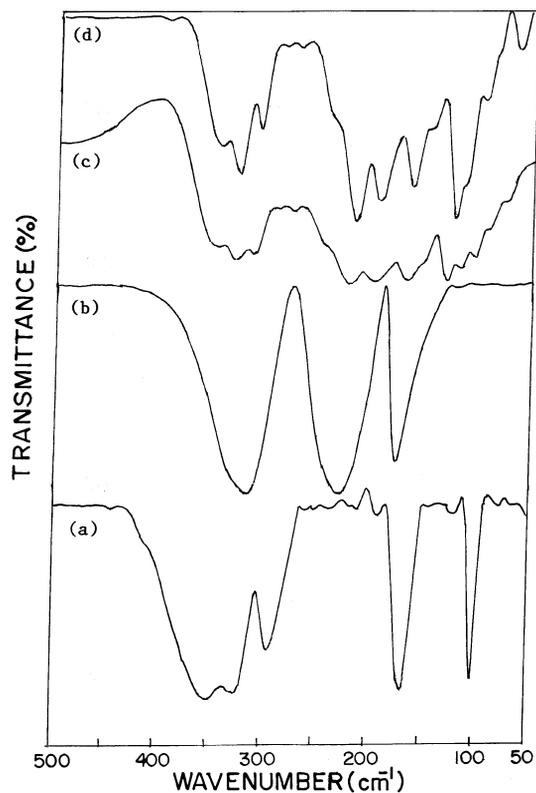
Fig. 4. FTIR spectra of (a) FeClMoO$_4$, (b) Na$_2$MoO$_4$, (c) Na$_2$MoO$_4$·2H$_2$O, (d) Na$_2$MoO$_4$·2D$_2$O in the 50–500 cm^{-1} region.

747 and 804 cm^{-1}. The band at 804 cm^{-1} shows larger intensity in the E_g orientations whereas the band at 747 cm^{-1} shows considerable intensity in most of orientations. In the powder sample spectrum, both these bands appear with equal intensity and the intensity is more than that of the v_1 mode. At the same time, this mode appears in the FTIR spectrum as a very intense band at 845 cm^{-1} without the lifting of the degeneracy. Wienstock et al. [14] have shown that the v_1 mode in a tetrahedral ion is of large intensity in the Raman spectrum, and of weak intensity in the IR spectrum, while v_3 mode is of weak intensity in the Raman and large intensity in the IR. In FeM, the intensity of the v_3 mode is found to be more than that of the v_1 mode in the Raman spectra.

Controversies exist in the assignments of v_2 and v_4 modes of the MoO$_4^{2-}$ ion, $v_2 > v_4$ or $v_4 > v_2$. But, from intensity calculations and the IR and

Raman data of various tetrahedral ions, it has been conclusively proved that $v_4 > v_2$. Moreover, v_2 has higher intensity than v_4 in the Raman spectrum. A very intense band around 314 cm^{-1} and a medium intense band around 288 cm^{-1} in Raman are assigned to the doubly-degenerate v_2 mode. In $z(yy)x$, the band at 288 cm^{-1} is not observed and in $x(zz)y$ it appears as two weak bands at 283 and 288 cm^{-1}. The band at 314 cm^{-1} has very large intensity in $z(xx)y$ orientation and slightly lesser intensity in $z(yy)x$, $z(yx)y$ and $z(yz)y$ orientations. The intensity of this band is the least in $z(xz)y$ and $x(zz)y$ orientations. The intense band around 360 cm^{-1} and the weak bands in the 340–410 cm^{-1} region in the Raman spectrum are assigned to the asymmetric bending mode v_4. In the FTIR spectrum a very intense band is observed at 350 cm^{-1} for this vibration.

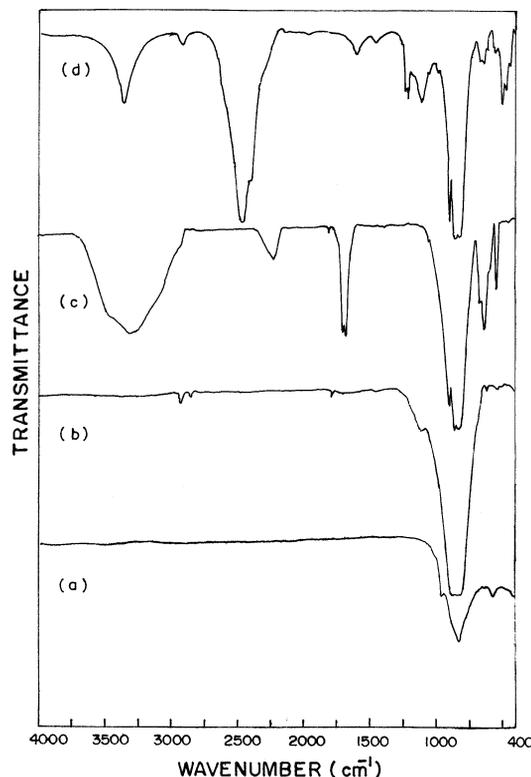The lifting of degeneracies of the v_2, v_3 and v_4 modes, appearance of v_1 and v_2 modes in the IR

Fig. 5. FTIR spectra of (a) FeClMoO$_4$ (b) Na$_2$MoO$_4$ (c) Na$_2$MoO$_4$·2H$_2$O (d) Na$_2$MoO$_4$·2D$_2$O in the 400–4000 cm^{-1} region.

Table 2
Spectral data (cm^{-1}) and band assignments for FeClMoO$_4$

FTIR	IR	Raman							Assignments
		z(xx)y	z(yy)z	x(zz)y	z(xz)y	z(yz)y	z(yx)y	Powder	
		A$_{1g}$+B$_{1g}$	A$_{1g}$+B$_{1g}$	A$_{1g}$	E$_g$	E$_g$	B$_{2g}$		
51 vw		81 m	76 m	82 s	82 vs	82 vs	81 vs		
79 vw			115 m	114 vw	114 vw	115 w	114 w		
102 w		125 vw			125 vw	125 vw			
120 w		146 m	146 m	145 m	145 s	145 s	144 m	142 m	
145 vw		155 w	155 vw	155 vw	159 vw	155 sh	155 w		External modes
167 m		165 w						170 m	
192 vw							210 vw	210 vw	
214 vw		245 vw				248 vw		248 vw	
251 vw		265 w	265 w			265 vw	264 w		
261 vw									
294 m	280 m	288 w	288 sh	283 w	288 s	288 s	288 m	283 m	
	300 m			288 w				288 m	v$_2$ MoO$_4$
326 m		314 vvs	313 vvs	314 s	314 vs	314 vs	314 vs	314 vvs	
350 m	345 m	360 s	361 s	345 vw	345 vw	340 w	340 vw	332 w	
		385 vw	390 vw	362 w	361 m	361 m	361 m	345 w	
		435 vw	405 w	370 vw	366 w	370 w	405 w	360 s	v$_4$ MoO$_4$
				395 vw	385 vw			370 w	
				405 vw				380 w	
								390 vw	
								420 w	
		445 vw	440 w					440 m	
		500 w	498 vw			460 vw		448 m	
575 m	550 m	585 vw	583 vw			490 vw		455 w	
								500 vw	FeO$_4$ modes?
								550 w	
								565 w	
								680 w	
845 vs	810 vsbr	747 vvs	747 vs	746 s	747 vvs	747 vs	747 vvs	746 vs	v$_3$ MoO$_4$
		801 vs	804 m	803 s	803 vvs	804 vs	803 vs	805 vs	
964 m	950 sh	973 vvs	973 vs	973 m	973 s	973 s	973 vs	972 s	v$_1$ MoO$_4$

v, very; s, strong; w, weak; m, medium; sh, shoulder; br, broad.

and the shifting of v_1 mode to higher wavenumbers indicate that MoO$_4^{2-}$ ion has linear and angular distortion in the crystal. The larger splitting observed for the bending modes and partial retention of degeneracy of the v_3 mode indicate that angular distortion is greater than the linear distortion, confirming the X-ray data [1,2].

4.3. Na$_2$MoO$_4$, Na$_2$MoO$_4$·2H$_2$O and Na$_2$MoO$_4$·2D$_2$O

In NaMH, the nondegenerate v_1 mode of MoO$_4$ is observed as a very intense band at 902 cm^{-1} with a shoulder at 912 cm^{-1}. In the FTIR spectrum, this mode is observed with medium intensity at 899 cm^{-1}. In NaM this mode is observed with very large intensity at 897 cm^{-1} in the Raman spectrum. However, it remains inactive in the FTIR spectrum. In the deuterated compound (hereafter referred to as NaMD) a very intense band is observed at 882 cm^{-1} with a shoulder at 899 cm^{-1} in Raman and a medium intense band at 900 cm^{-1} in the FTIR.

In both NaMD and NaMH, the degeneracy of the asymmetric stretching mode is lifted in the Raman spectra. However, only two bands each are obtained in the FTIR spectra for this mode,

Table 3
Spectral data (cm^{-1}) and band assignments

Na$_2$MoO$_4$·2H$_2$O			Na$_2$MoO$_4$·2D$_2$O		Na$_2$MoO$_4$		Assignments
FTIR	IR	Raman	FTIR	Raman	FTIR	Raman	
51 vw		65 m	67 w	59 m	58 vw		
73 m		75 w		66 m	71 w		
87 m		91 s	92 w	73 w	93 vw		
98 s				81 s			
				94 vw			
113 s		120 m	116 sh	110 w	120 vw	124 m	
125 s		130 m	125 m	118 m			External modes
164 s		145 w	148 m	136 m			
		155 w		146 w			
		175 w	165 m	165 w	177 vs	175 w	
195 s		181 vw	195 m	179 w		190 s	
		195 w		202 vw			
218 s		215 vw	218 m				
		242 vw		253 vw	230 vw		
		265 vw					
274 m			274 w	279 m			
288 m		290 m	287 w				ν_2 MoO$_4$
311 s	305 s						
328 s	320 s	327 s	309 m	317 s		311 s	
	330 s		329 m	323 s			
347 s	340 s	337 s	346 m	336 s	317 vsbr	338 w	
		345 s		361 sh		388 w	ν_4 MoO$_4$
		365 w					
		385 w					
570 m	540 s	410 w	471 w			410 w	
641 m	640 m	590 w	500 m			453 w	
675 m	660 m	610 w	548 vw			465 w	NaO$_6$ modes and librational modes H$_2$O
		680 w	645 w				
		690 w					
835 vs	801 vs	810 w	831 vs	801 m	816 vs	814 s	
859 vs	860 vs	833 sh	854 vs	831 s		849 w	ν_3 MoO$_4$
		840 s		839 s			
		849 s					
899 m	895 vs	902 vs	900 m	892 vs		897 vs	ν_1 MoO$_4$
		912 sh		899 sh			
1394 vw	1400 s		1053 vw	930 w			
			1115 m	1119 w			Combinations
			1479 w				
1677 m	1670 s	1650 w	1223 m				
1698 m	1690 s	1690 w	1240 m				ν_2 H$_2$O/D$_2$O
		1780 vw					
2226 m	2200 m	2615 vw					
		2640 w					
		2770 w					Combinations
		2890 w					
		3020 w					
3298 vsbr		3170 w	2417 vs	2390 vw			
	Broad band extending from 3000–3580 cm^{-1}	3260 m	2469 vs	2420 w			
		3290 m	3308 m	2456 m			ν_1, ν_2 H$_2$O/D$_2$O
		3350 w		2486 w			
		3450 w					

for both the compounds. In NaM, only a very intense band (816 cm^{-1}) is obtained in the FTIR spectrum while an intense band at 811 cm^{-1} and a weak band at 849 cm^{-1} are obtained in the Raman spectrum. The bending modes also exhibit complete lifting of degeneracies in the Raman spectrum for NaMH and NaMD. For both compounds, v_2 mode is observed in the FTIR spectra. However in NaM, the v_2 mode (E_u species) remains inactive in the IR and gives only a single band at 311 cm^{-1} in the Raman spectrum corresponding to E_g species (Table 1). v_4 mode retains degeneracy (in NaM) in the FTIR while it is partially lifted in the Raman spectrum.

The lifting of degeneracies of v_2, v_3 and v_4 modes and appearance of v_1 and v_2 modes in the IR are attributed to the lowering of the symmetry of the MoO$_4^{2-}$ ion in NaMH and NaMD. The non-appearance of the v_1 and v_2 modes in the IR and the partial retention of degeneracies of various modes indicate that MoO$_4^{2-}$ ion retains T_d symmetry in the Na$_2$MoO$_4$ crystal.

Hardcastle and Wachs [15] have studied the correlation between the Raman scattering frequencies of the Mo–O bonds and their respective bond lengths in various molybdates. They have related the stretching frequency v_1 with the bond distance R by a relation.

$$v_1 \text{ (cm}^{-1}) = 32895 \exp(-2.073R).$$

In FeClMoO$_4$, the shortest Mo–O bond length is 1.759 Å, and the formula gives a value of 858 cm^{-1} for the v_1 mode. In NaMH, the shortest Mo–O bond length is 1.752 Å, and this leads to a value of 871 cm^{-1}. The lower the stretching frequency for the shortest Mo–O bond, the more regular the tetrahedron is. The increase in the wavenumber values observed for the v_1 mode in NaMH and FeM indicate that the MoO$_4$ tetrahedron is distorted in both NaMH and FeM. In FeM, the shift is about 114 cm^{-1} and in NaMH it is only 31 cm^{-1}. Therefore MoO$_4$ tetrahedra is distorted more in FeClMoO$_4$ than in Na$_2$MoO$_4 \cdot$2H$_2$O. Wavenumber values of the v_1 mode indicate that the distortion of MoO$_4$ tetrahedron in the four crystals are in the order FeClMoO$_4$ > Na$_2$MoO$_4 \cdot$2H$_2$O > Na$_2$MoO$_4 \cdot$2D$_2$O > Na$_2$MoO$_4$. The distortion of MoO$_4$ tetrahedra in Na$_2$MoO$_4 \cdot$2H$_2$O and

Na$_2$MoO$_4 \cdot$2D$_2$O compared with that in Na$_2$MoO$_4$ can be attributed to the formation of hydrogen bonds with the oxygen atoms of the tetrahedra.

4.4. Water vibrations

In the H$_2$O stretching mode region, a very intense band extending from 3050 to 3500 cm^{-1} is observed in the FTIR spectrum in NaMH. Several weak to medium intense bands are also observed in the Raman spectrum. In the deuterated compound two very intense FTIR bands are observed at 2417 and 2469 cm^{-1} for these stretching modes. In the bending mode region, two very intense FTIR bands are observed at 1677 and 1698 cm^{-1} in NaMH and these are shifted to 1223 and 1240 cm^{-1} in NaMD. The deuteration of the compound is only partial as seen from the IR spectrum. The enhanced intensity for the stretching and bending modes in the IR and Raman spectra are due to the strong hydrogen bonds formed in the crystal and also due to the presence of large number of water molecules in the unit cell. The appearance of two distinct bands repeatedly in FTIR, IR and Raman spectra for the bending mode and the appearance of the broad FTIR band and more than two Raman bands in the stretching modes region indicate the presence of two crystallographically distinct water molecules in NaMH. The shifting of stretching modes to lower wavenumbers and bending modes to higher wavenumbers indicate that these water molecules form strong hydrogen bonds in the NaMH crystal.

A number of bands is observed in the FTIR spectrum in the 1800–2230 cm^{-1} region. These can be due to the combinations of bending and librational modes of water molecules. The observation of similar bands of medium intensity is obtained in the isostructural compound Na$_2$WO$_4 \cdot$2H$_2$O [16].

5. Conclusions

The appearance of the v_1 mode in B_{2g} and E_g species, contributing to α_{xy}, α_{xz} and α_{yz} polarizability tensor components, its appearance at higher wavenumber and the appearance of the v_1

and v_2 modes in the IR spectra suggest that MoO_4 tetrahedra is distorted in $FeClMoO_4$. The larger splitting observed for the bending modes and partial retention of degeneracy of the asymmetric stretching mode indicate that angular distortion is greater than linear distortion in MoO_4^{2-} ion, confirming the X-ray data.

The non-appearance of v_1 and v_2 modes in the IR and partial retention of the degeneracies of various modes indicate that MoO_4^{2-} ion retains T_d symmetry in Na_2MoO_4. Wavenumber values of the v_1 mode indicate that the distortion of MoO_4 tetrahedra in the four crystals are in the order $FeClMoO_4 > Na_2MoO_4 \cdot 2H_2O > Na_2MoO_4 \cdot 2D_2O > Na_2MoO_4$. The water bands indicate the presence of two crystallographically distinct water molecules in $Na_2MoO_4 \cdot 2H_2O$. They form strong hydrogen bonds.

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