

Vibrational analysis of $\text{NaM}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2/\text{D}_2\text{O}$ [M = Ni, Zn]

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MS received 8 August 1994; revised 6 February 1995

Abstract. The infrared and Raman spectra of $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and their partially deuterated analogues are recorded and analysed on the basis of vibrations of MoO_4^{2-} tetrahedra and H_2O molecules. The MoO_4^{2-} groups are found to be more distorted in $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ than in the other compound. Bands indicating the presence of H_3O^+ ions are not observed in $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$, ruling out the possibility of the formulation of $\text{NaZn}_2\text{OHO}(\text{MoO}_3\text{OH})_2$. Hydrogen bonds of medium strength are present in both the compounds.

Keywords. Infrared spectrum; Raman spectrum; hydrogen bonding.

PACS No. 78·30

1. Introduction

The simple and mixed metal molybdate phases, formed by the reaction of metal molybdates with salts of transition metals are of great importance because of their catalytic and magnetic properties and their spectral features ([1, 2]. X-ray diffraction studies on such phases show that $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ is isostructural with $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ [3, 4]. The Raman and infrared spectra of compounds containing MoO_4^{2-} ions have been investigated by several workers [5–8]. However, there is considerable disagreement in the assignments of the fundamental bending modes, $\nu_2(\text{E})$ and $\nu_4(\text{F}_2)$ of these ions. In view of the above facts, IR and Raman spectra of $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$, $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and their deuterated analogues have been studied to elucidate the dynamics of the crystal and to understand the nature of hydrogen bonding in them.

2. Experimental

The polycrystalline sample of $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ (abbreviated as NNHM) was prepared by adding $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (2 M, 100 ml) dropwise to a well stirred boiling solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2 M, 100 ml) and refluxing it for 15 h [3]. $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ (hereafter referred to as NZHM) was prepared by adding $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ (1 M, 100 ml) in a similar way to $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1 M, 100 ml) and refluxing it for 24 h [4]. The deuterated analogues (NNDM and NZDM) were prepared by dissolving the final products in heavy water. The infrared spectra were recorded using a Perkin-Elmer 577 spectrophotometer using KBr pellet method. A Spex 1401 double monochromator equipped with a Spectra Physics model 165 argon

Table 1. Summary of the factor group analysis of $\text{NaM}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ [M = Ni, Zn].

Factor group species C_{2h}	$2\text{MoO}_4^{2-}(C_3)$		$\text{H}_2\text{O}(C_{2h})$		O (C_{2h})	H (C_{2h})	2 $(\text{Ni}_2^{2+}/\text{Zn}^{2+})$ (C_1)	Na^+ (C_{2h})	Optical Acoustic modes
	Internal modes	External modes	Internal modes	External modes					
A_g	6	2T, 1R	2	1R	—	—	—	—	12
B_g	3	1T, 2R	1	2R	—	—	—	—	9
A_u	3	1T, 2R	—	1T	1T	1T	3T	1T	12
B_u	6	2T, 1R	—	2T	2T	2T	3T	2T	18
	18	6T, 6R	3	3R, 3T	3T	3T	6T	3T	51
									3

Table 2. Correlation scheme for the internal vibrations of MoO_4^{2-} in $\text{NaM}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ [M = Ni, Zn].

Free ion symmetry		Site symmetry	Factor group symmetry	
T_d		C_s	C_{2h}	
2	(ν_1) A_1	A'	A_g	6
4	(ν_2) E	A''	B_g	3
			A_u	3
12	(ν_3, ν_4) $2F_2$		B_u	6

ion laser was used to record the Raman spectra in the Stokes region with a resolution better than 3 cm^{-1} .

3. Factor group analysis

$\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ crystallizes in the monoclinic system with space group $C2/m$ (C_{2h}^3) having one formula unit per Bravais cell [3, 9]. There are two crystallographically unique H atoms with one of them occupying half of the available sites, resulting in the presence of water and hydroxyl groups on alternate sites. The MoO_4 units form a tetrahedron with three short Mo-O bonds and the fourth one relatively longer. The coordination of O atoms around Ni atom represents a slightly distorted octahedral arrangement.

The factor group analysis has been carried out on the basis of the correlation method developed by Fateley *et al* [9] to get the irreducible representations. The molybdate ion contributes to 18 internal and 12 external modes, distributed among four factor group species. Water molecules contribute to 3 internal modes. The remaining vibrational degrees of freedom are made up of translational and rotational modes of different ions. The Ni^{2+} and Na^+ ions contribute only to the IR active species A_u and B_u . The results are summarized in tables 1 and 2. The irreducible representations of the title compound in C_{2h} factor group, excluding acoustic modes are:

$$\Gamma_{\text{NNHM}} = 12A_g + 9B_g + 12A_u + 18B_u$$

$\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ is isostructural with the nickel compound and the Zn atoms occupy the positions of Ni atoms [4].

4. Results and discussion

4.1 MoO_4^{2-} vibrations

A free MoO_4^{2-} ion has a tetrahedral symmetry with four normal modes of vibrations: a non-degenerate symmetric stretching mode ν_1 (A_1) at 894 cm^{-1} , a doubly degenerate symmetric bending mode ν_2 (E) at 318 cm^{-1} , triply degenerate asymmetric stretching ν_3 (F_2) and asymmetric bending ν_4 (F_2) modes at 833 and 381 cm^{-1} respectively [10]. All these modes are Raman active whereas ν_1 and ν_2 are IR inactive.

The most intense band in the Raman spectrum of NNHM (table 3) observed at 917 cm^{-1} with a shoulder at 896 cm^{-1} and split components at 942 and 880 cm^{-1} are

Table 3. Spectral data (cm⁻¹) and band assignments of NaNi₂OH(H₂O)(MoO₄)₂/D₂O and NaZn₂OH(H₂O)(MoO₄)₂/D₂O.

NaNi ₂ OH(H ₂ O)(MoO ₄) ₂		NaNi ₂ OD(D ₂ O)(MoO ₄) ₂		NaZn ₂ OH(H ₂ O)(MoO ₄) ₂		NaZn ₂ OD(D ₂ O)(MoO ₄) ₂		Assignments	
Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR
3498 wbr	3480 – 2878 sbr		3520 – 2860 sbr	3350 mbr	3380 – 2820 mbr	3356 mbr	3351 – 3138 mbr		v ₃ , v ₁ H ₂ O
3290 wbr		3386 wbr		3115 wbr		3119 wbr			
3016 wbr		3292 wbr				2510 wbr	2660 –		
		3119 wbr				2327 wbr	2565 wbr		v ₃ , v ₁ D ₂ O
		2474 wbr	2240 –						
		2448 wbr	2030 mbr	1618 wbr	1610 w	1590 wbr	1620 wbr		v ₂ H ₂ O
1604 wbr	1618 mbr	2347 wbr	1625 mbr		1570 mbr	1348 wbr	1560 mbr		
		1608 wbr					1389 wbr		v ₂ D ₂ O
		1333 wbr	1380 w						
1271 w	1200 m	1094 m	1110 m	1136 m	1129 mbr		1026 wbr		δMo-O-H/D
				1125 w	1112 mbr				
942 w		922 w	920 vs	919 sbr	908 s	918 s	918 s		v ₁ MoO ₄ ²⁻
917 vs	912 vs	911 vs							
896 sh		908 s							
880 vw		893 w							
855 s	849 –	852 s		857 mbr	850 –	857 s	857 s		
823 sh	771 sbr	823 sh	863 –	820 mbr	720 sbr	818 m	840 s		v ₃ MoO ₄ ²⁻
773 m		770 m	760 sbr	794 w			782 m		
743 m		747 w		768 w		748 wbr			
726 w		737 w							
		721 m							

assigned to the symmetric stretching (ν_1) mode of the molybdate ion. In NZHM, only a single strong band is observed in this region (*ca.* 919 cm^{-1}). This IR inactive mode appears as an intense band at 912 cm^{-1} in the IR spectrum of NNHM and at 908 cm^{-1} in NZHM. The appearance of the IR inactive mode may be due to the lowering of symmetry of the molybdate ion from T_d to C_1 . In the deuterated compounds also, these bands are observed without much change (figures 1 and 2).

The frequencies observed in the 720 to 860 cm^{-1} region in both the compounds are assigned to the triply degenerate asymmetric stretching (ν_3) vibrations of the MoO_4^{2-} ion [11]. The degeneracy of this mode is lifted in both the compounds and additional splitting is observed. NNHM exhibits a larger splitting (around 129 cm^{-1}) than that in NZHM (89 cm^{-1}).

When the Mo-O bond length is 1.759 \AA , the MoO_4 tetrahedron is considered to be perfect and Mo-O correlation yields symmetric stretching frequencies at 858 cm^{-1} [12]. But in NNHM the Mo-O bond lengths vary from 1.751 to 1.833 \AA whereas in NZHM Mo-O bond lengths vary from 1.737 to 1.839 \AA . In both the compounds, the symmetric stretching mode ν_1 shows a shift to higher wavenumbers from the free state values. These higher frequencies for the ν_1 mode and large splitting of ν_3 mode are due to the interaction between the stretching motions of the tetrahedral ions [13].

Discrepancies exist in the assignment of the symmetric bending mode ν_2 and asymmetric bending mode ν_4 . Polarization studies by Miller *et al* [14] and comparative study of various potential functions for the MoO_4 species [15] have conclusively proved that $\nu_4 > \nu_2$. Further, from the intensity calculations for ν_2 and ν_4 Muller *et al* [16] have shown that ν_2 has a higher intensity than ν_4 in Raman while ν_4 has a higher intensity in the infrared. The assignment of the internal modes $\nu_2(\text{E})$ and $\nu_4(\text{F}_2)$ is however complicated by the presence of lattice modes in the same region.

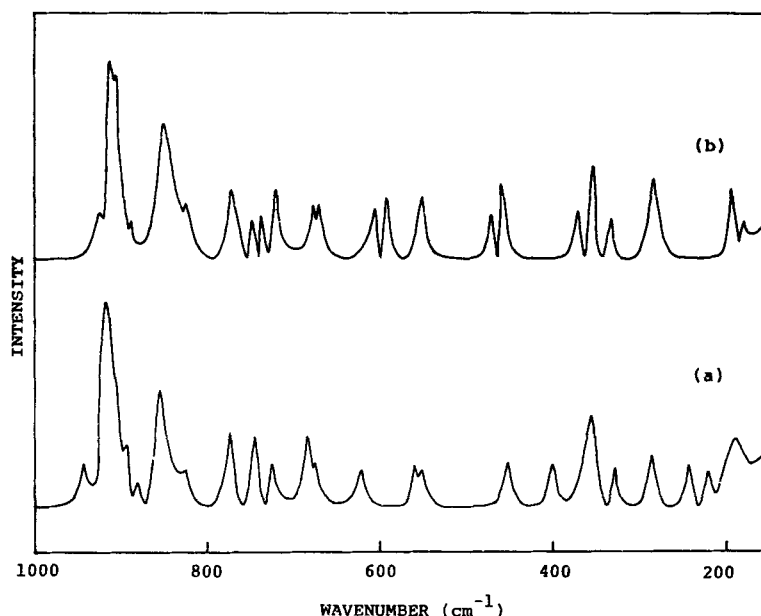


Figure 1. Raman spectra of the internal modes of (a) $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and (b) $\text{NaNi}_2\text{OD}(\text{D}_2\text{O})(\text{MoO}_4)_2$ in the 150 – 1000 cm^{-1} region.

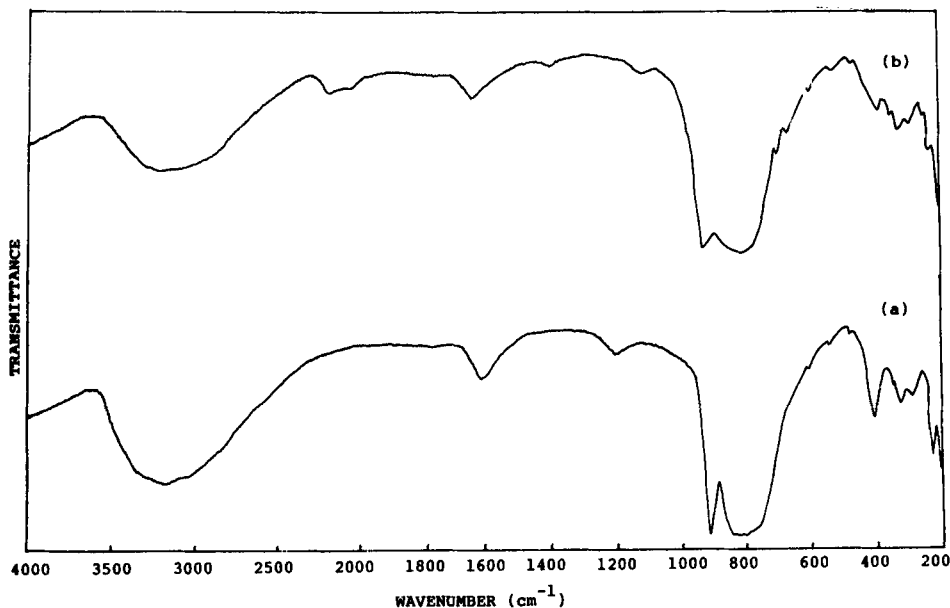


Figure 2. Raman spectra of the internal modes of (a) $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and (b) $\text{NaZn}_2\text{OD}(\text{D}_2\text{O})(\text{MoO}_4)_2$ in the $100\text{--}1000\text{ cm}^{-1}$ region.

In NZHM, two medium intense broad bands are observed in Raman spectrum in the symmetric bending region (ν_2). The corresponding IR band is a weak line at 310 cm^{-1} . Moreover, asymmetric bending mode ν_4 is observed as a weak band around 418 cm^{-1} in Raman and a medium intense band around 374 cm^{-1} in the IR spectrum in agreement with the intensity criteria suggested by Muller *et al* [16]. But, in NNHM, only a weak band is observed in the symmetric bending mode in the Raman spectrum, while a medium intense band is obtained in the infrared spectrum. The asymmetric bending mode gives a medium intense band at 353 cm^{-1} in the Raman spectrum along with a weak one at 401 cm^{-1} . The corresponding IR band is observed as a medium intense band at 400 cm^{-1} with a weak line at 350 cm^{-1} . Intensity criteria are found to be not obeyed in the nickel compound. Spectra of the deuterated compounds do not show much variation in this region. In both NNHM and NZHM a partial lifting of degeneracy is observed for the bending modes while the degeneracy of the asymmetric stretching mode ν_3 is lifted completely and additional splitting is observed in both the compounds. In addition, the non-degenerate ν_1 mode shows additional weak bands in NNHM. The splitting of the ν_1 mode in NNHM and the departure from the intensity criteria suggested by Muller *et al* [16] show that the distortion of the MoO_4^{2-} ion is more in NNHM than in NZHM.

4.2 $\text{H}_2\text{O}/\text{D}_2\text{O}$ vibrations

The vibrational frequencies of a free water molecule usually occur at 3756 (ν_3), 3652 (ν_1) and 1595 (ν_2) cm^{-1} . Depending on the hydrogen bond strength, the stretching modes will shift to lower wavenumbers and bending mode to higher wavenumbers [17].

In the Raman spectrum of NNHM, three weak bands are obtained in the stretching mode region of water while a medium intense band at 3350 cm^{-1} and a weak band at

3115 cm^{-1} are observed in NZHM for the corresponding region. The infrared spectrum of the nickel compound shows a strong broad absorption ranging from 2878 to 3480 cm^{-1} while the zinc compound gives medium intense broad band from 2820 to 3380 cm^{-1} in this region. On deuteration, these IR bands are reduced in intensity, showing partial deuteration and a medium intense band is obtained in the 2030 – 2240 cm^{-1} region for NNDM and in 2565 – 2660 cm^{-1} region for NZDM. This is assigned to the D_2O stretching modes.

Infrared spectra show a broad band of medium intensity at 1618 cm^{-1} in NNHM and two bands at 1610 (weak) and 1570 (broad, medium intense) cm^{-1} in NZHM for the H_2O bending modes. Corresponding Raman bands are of weak intensity. On deuteration new bands appears in the D_2O bending region. The degree of deuteration is found to be 42% for the nickel compound and 58% for the zinc compound (figures 3–5).

The decrease in frequencies of stretching modes and increase in frequencies of bending mode of water molecules from the free state values show the presence of hydrogen bonds of medium strength in these compounds [17].

In $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ Clearfield *et al* [4] have suspected the presence of H_3O^+ ions considering a formulation $\text{NaZn}_2\text{OHO}(\text{MoO}_3\text{OH})_2$. But later Moni *et al* [3] have confirmed the structure of $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$. In the present study, bands indicating the presence of H_3O^+ ions are not observed in these compounds confirming the structure as suggested in manganese and nickel compounds [18, 19].

The librational modes of water viz. wagging, rocking and twisting, fall in the region of 452 – 490 cm^{-1} . These modes are assigned in the order $\nu_r > \nu_t > \nu_w$ [20]. The Mo-O-H bending modes are observed at 1200 cm^{-1} in the IR and at 1271 cm^{-1} in the Raman spectrum of NNHM [21]. But, in NZHM, the Raman spectrum gives a medium intense

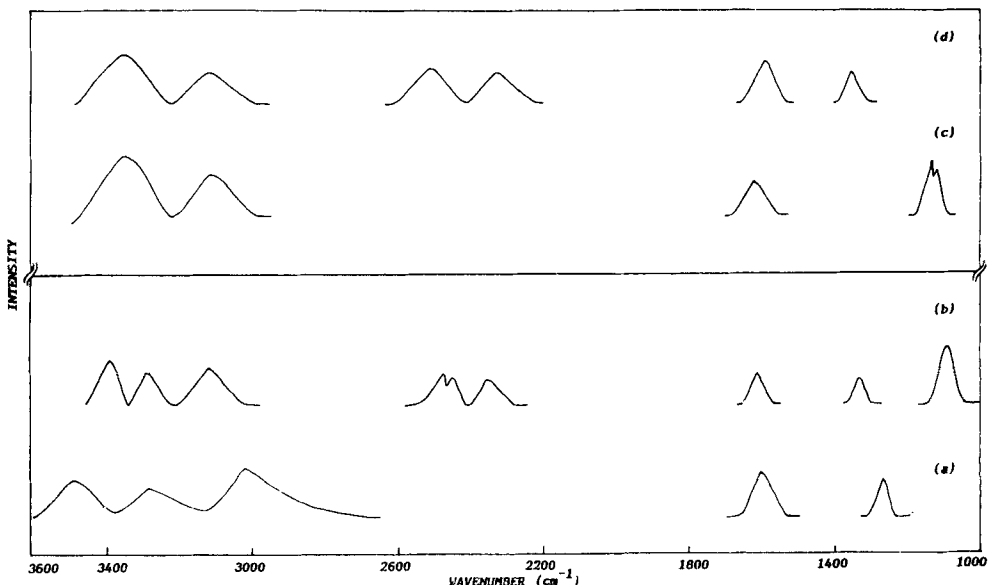


Figure 3. Raman spectra of (a) $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$, (b) $\text{NaNi}_2\text{OD}(\text{D}_2\text{O})(\text{MoO}_4)_2$, (c) $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and (d) $\text{NaZn}_2\text{OD}(\text{D}_2\text{O})(\text{MoO}_4)_2$ in the 1000 – 3600 cm^{-1} region.

Vibrational analysis of $\text{NaM}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$

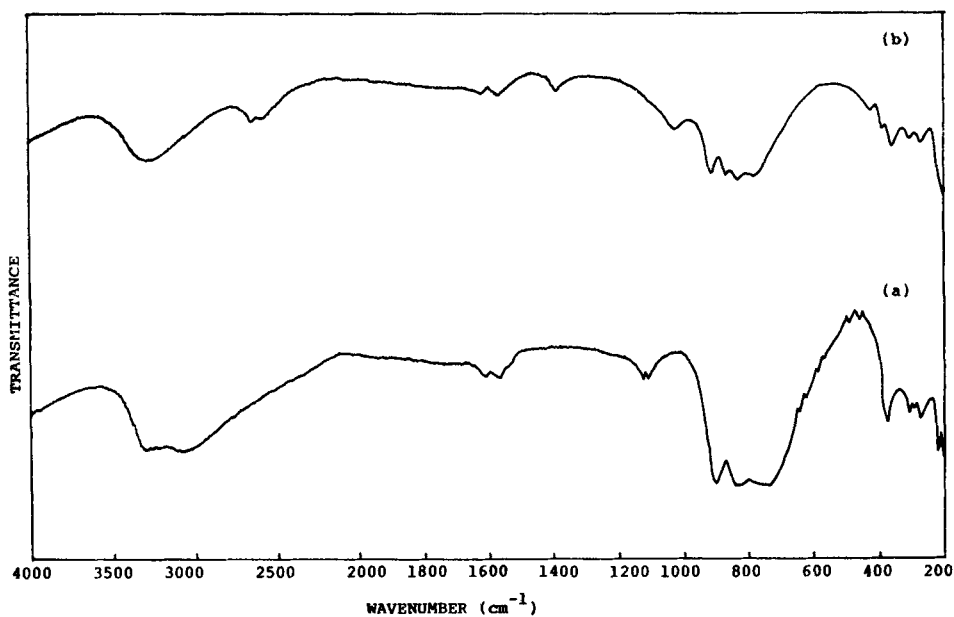


Figure 4. Infrared spectra of (a) $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and (b) $\text{NaNi}_2\text{OD}(\text{D}_2\text{O})(\text{MoO}_4)_2$ in the $200\text{--}4000\text{ cm}^{-1}$ region.

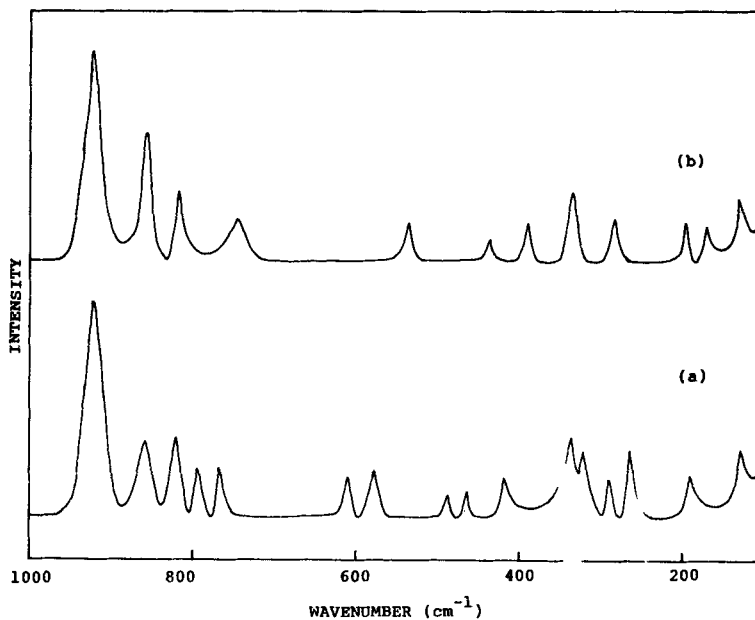


Figure 5. Infrared spectra of (a) $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ and (b) $\text{NaZn}_2\text{OD}(\text{D}_2\text{O})(\text{MoO}_4)_2$ in the $200\text{--}4000\text{ cm}^{-1}$ region.

band at 1136 cm^{-1} and a weak band at 1125 cm^{-1} in this region. The infrared spectrum gives a doublet with medium intensity.

4.3 External modes

The region below 291 cm^{-1} is complicated due to the external modes of the MoO_4^{2-} ion, lattice modes of water and metal oxygen stretching modes. Hence, an unambiguous assignment of the observed bands to each of these modes is not possible. However, Ni-O and Zn-O stretching modes are assigned tentatively taking into account the octahedral coordination of these atoms [22].

5. Conclusions

The MoO_4^{2-} groups in $\text{NaNi}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ are found to be more distorted than that in $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$. Bands indicating the presence of H_3O^+ ions are not observed in $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ ruling out the possibility of the formulation of $\text{NaZn}_2\text{O}(\text{MoO}_3\text{OH})_2$. The decrease in frequencies of the stretching modes and the increase in frequencies of the bending mode of water molecules from the free state values show the presence of hydrogen bonds of medium strength in these compounds.

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