

# Temperature dependence of external modes of water in infrared spectra of monohydrates of some divalent transition metal sulfates

V. P. TAYAL AND D. P. KHANDELWAL

*H. B. Technological Institute, Kanpur*

AND

H. D. BIST

*Indian Institute of Technology, Kanpur*

The IR spectra of  $MSO_4 \cdot H_2O$  ( $M = Mn, Co, Ni$ ) which are isomorphous have been recorded in the region  $1000-250 \text{ cm}^{-1}$  at liquid nitrogen temperature (LNT). The overlapping contours have been analyzed into Lorentzian components and the positions half-widths and integrated intensities have been reported for different components of external modes of water. All components show an increase in intensity and a shift towards higher frequency at LNT over their room temperature (RT) values. In the region around  $300 \text{ cm}^{-1}$  one dominant temperature sensitive band is attributed to  $M-O_w$  stretch. Correlation curves are given for  $H_2O$  (rock),  $H_2O$  (Wag) and  $M-O_w$  stretch frequency against  $M-O_w$  distances.

## 1. INTRODUCTION

The hydrates  $MSO_4 \cdot H_2O$  ( $M = Mn, Co, Ni$ ) are isostructural belonging to the space group  $C_{2h}^{62}$  having four formula units per unit cell<sup>(1,2)</sup>. Infrared studies of these salts have been reported in the past<sup>(3,4)</sup> at room temperature (RT) above  $600 \text{ cm}^{-1}$ . In a previous paper by the authors<sup>(5)</sup> an analysis of the overlapping bands with half widths and relative integrated intensities of the internal and librational modes of water along with the internal modes of  $SO_4^{2-}$  at room temperature were reported and a linear correlation of the frequency of the rocking mode of  $H_2O$  with  $M-O_w$  distance was given,  $O_w$  being the oxygen of the water. In the present paper the effect of changing the temperature from room temperature to liquid nitrogen temperature (LNT) on the water librational and  $M-O_w$  stretch bands is presented, and the correlation with  $M-O_w$  distance is extended to  $H_2O$  wag and  $M-O_w$  stretching frequencies (at LNT) also.

## 2. EXPERIMENTAL.

The monohydrates of Mn and Co salts were prepared by crystallization from aqueous solution at  $\sim 80^\circ\text{C}$  and drying the precipitate in an oven at  $100^\circ\text{C}$ , while that of Ni was prepared by baking the hexahydrate at  $\sim 120^\circ\text{C}$ . The hydration level was checked by the weight loss method. Spectra were recorded in Nujol mull on Perkin-Elmer 521 spectrophotometer. For low temperatures (LT) a modified Wagner Hornig type cell was used, which could be directly inserted in the sample beam without any material change of the optical path. Prior to cooling the cell was evacuated to  $\sim 10^{-5}$  cm of Hg. The temperatures were measured by a thermocouple and the spectra at different temperatures were recorded without disturbing the geometry.

## 3. RESULTS AND DISCUSSION

## (a) Analysis of the Spectra

Figure 1 gives the spectra in region  $250\text{-}1000\text{ cm}^{-1}$  at RT and LNT for the three salts. Considerable overlapping of the bands will at once be observed. The contours were subjected to analysis into Lorentzian components, which is justified when band widths are much larger than instrumental resolution. The

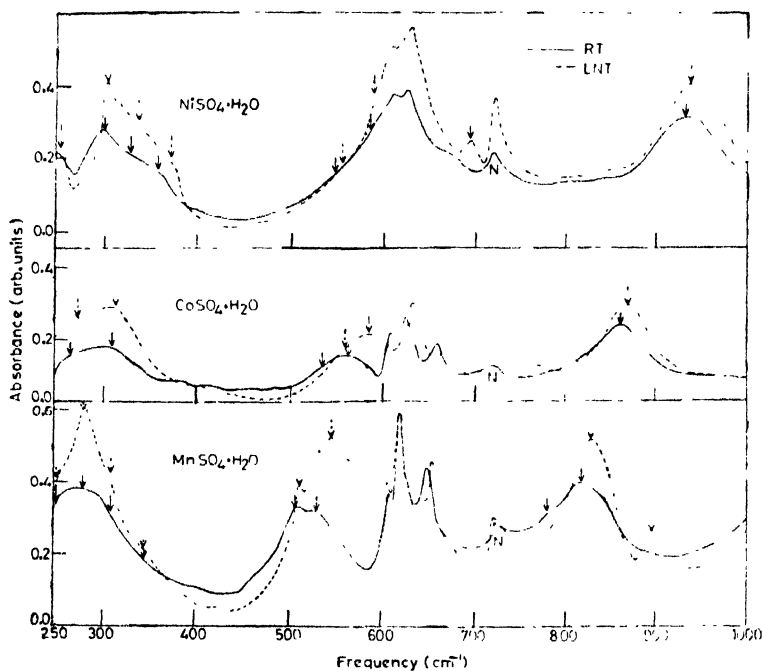


Fig. 1. Infrared absorption spectra at room temperature (RT) and Liquid Nitrogen Temperature (LNT) of (a)  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (b)  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$  (c)  $\text{NiSO}_4 \cdot \text{H}_2\text{O}$  in Nujol mull. N denotes bands due to nujol.

basis was to fit the minimum number of components warranted by the observed contours and in most cases the positions were reproducible within  $5\text{ cm}^{-1}$  and intensities within 10%. In those cases where the choice was between one component slightly departing from Lorentzian shape and two components with good Lorentzian shapes the first was preferred, unless there was other evidence favouring the second alternative. Figure 2 gives the typical resolution of a contour into Lorentzian components in the latter category. In the cases of Co and Mn salts the  $\text{SO}_4^{2-}$  ( $\nu_1$ ) bands have Lorentzian shapes and two water librations are found well separated. Hence in this spectrum of Ni salt the  $\text{SO}_4^{2-}$  bands were kept in Lorentzian shapes and the residue led necessarily to two components on the lower frequency tail.

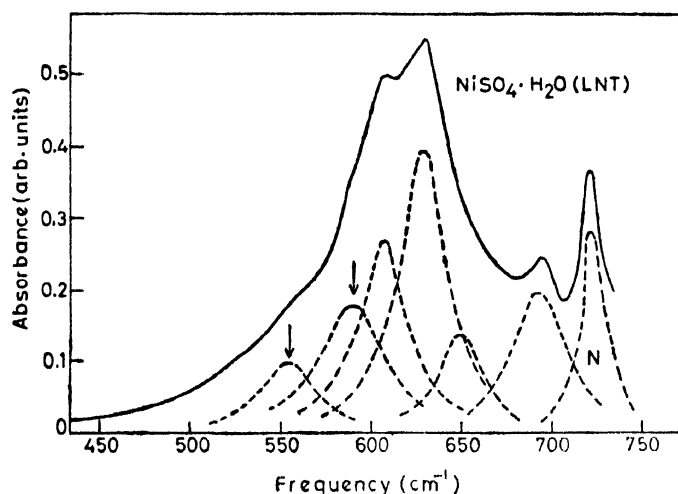


Fig. 2 Typical analysis of the absorption band contour in the region  $500\text{--}750\text{ cm}^{-1}$  (solid curve) into Lorentzian components (broken curves) for  $\text{NiSO}_4 \cdot \text{H}_2\text{O}$  spectrum LNT. The water wagging components at low frequency tail are marked by arrows

Table 1 gives the results of analysis excluding the internal modes of  $\text{SO}_4^{2-}$ . Band positions, half widths and integrated intensities are given.

#### (b) Librational Modes of Water

Amongst the librational modes of water, the rocking mode has lowest frequency  $820\text{ cm}^{-1}$  in the Mn salt which increases to  $860\text{ cm}^{-1}$  in the Co salt and  $930\text{ cm}^{-1}$  in the Ni salt. In all the three cases the lowering of temperature results in an increase in peak intensity and shift towards higher frequency. The observed curves cannot be resolved into components in the case of Co and Ni salts but in the case of Mn salt the contour shows the presence of an additional component at both RT and LNT. In this spectrum a new sharp band ( $\Delta\nu_{\frac{1}{2}} = 20\text{ cm}^{-1}$ ) appears at  $892\text{ cm}^{-1}$  at LNT. Spectra

Table 1. Infrared absorption bands of external modes of water of mono-hydrates of Mn, Co and Ni sulfates at room temperature (RT) and at liquid nitrogen temperature (LNT)

MnSO <sub>4</sub> ·H <sub>2</sub> O			CoSO <sub>4</sub> ·H <sub>2</sub> O			NiSO <sub>4</sub> ·H <sub>2</sub> O			Assignment
RT	LNT		RT	LNT		RT	LNT		
$\nu$ $\Delta\nu_j$ I	$\nu$ $\Delta\nu_j$ I		$\nu$ $\Delta\nu_j$ I	$\nu$ $\Delta\nu_j$ I		$\nu$ $\Delta\nu_j$ I	$\nu$ $\Delta\nu_j$ I		?
	892* 20 2								
820 80 25	830 50 28		860 80 20	865 80 23		930 100 25	935 100 40		H <sub>2</sub> O Rock
770 60 8	790 50 5						695* 35 7		
530 80 16	547 70 35		560 80 10	585 60 12		585 40 6	590 40 7		H <sub>2</sub> O Wag
510 30 6	516 20 2		535 40 2	560 30 2		545 40 3	555 40 3		
345 40 3	345 40 4					360 40 6	374 24 3		M-O <sub>s</sub> Stretch
310 40 5	310 50 6								
290* 80 25	290* 50 28		310* 80 13	315* 80 20		312* 30 3	338* 40 10		
						302 40 10	304 30 10		
250 30 2	250 40 6		265 40 3	275 40 5		250 30 6	254 20 4		

$\nu$  = Position of the band,  $\Delta\nu_j$  = Full band width at half the intensity

I = Integrated Intensity, \* = Temperature dependent.

at intermediate temperatures show that this band appears suddenly at  $\sim -100^\circ\text{C}$  and increases in intensity as the temperature is progressively lowered to LNT. The origin of this band is at present not clear.

The wagging mode region also has frequencies in the increasing order  $\text{Mn} \rightarrow \text{Co} \rightarrow \text{Ni}$ . One result of this is that while this region is well separated from the region of  $\nu_1$  of  $\text{SO}_4^{2-}$  in the Mn salt it penetrates into the tail of the  $\nu_1$  region of  $\text{SO}_4^{2-}$  in the case of Ni salt. The main wagging component in RT spectra falls at 530, 560 and 585  $\text{cm}^{-1}$  in Mn, Co and Ni salts respectively. At LNT each of them shifts by about 20  $\text{cm}^{-1}$  towards higher frequency and also increases in intensity. A low frequency component occurs at 510  $\text{cm}^{-1}$  in the Mn salt, not shifting with change of temperature. The analysis of the corresponding bands in Co and Ni salts is less certain due to heavy overlapping. At low temperature a band at 695  $\text{cm}^{-1}$  appears distinctly in the Ni salt. If the corresponding band exist for the Mn and Co salts, they would fall in the region of  $\nu_1$  of  $\text{SO}_4^{2-}$  and would not be observed because of overlapping.

#### (d) M-O Stretching

In the region around 300  $\text{cm}^{-1}$  there are four components for Mn and Ni salts and two in the case of Co salt at RT. As there are three types of oxygens ( $\text{O}_1$  and  $\text{O}_2$  of the sulfate group and  $\text{O}_w$  of the water) and three different M-O distances in the coordination octahedra around  $\text{M}_6^{(1)(2)}$ , one would expect three bands due to M-O stretch in this region. Besides these, bands due to combination with low lying lattice modes can also occur. It is noticed that one component (falling at 290, 310 and 332  $\text{cm}^{-1}$  in case of

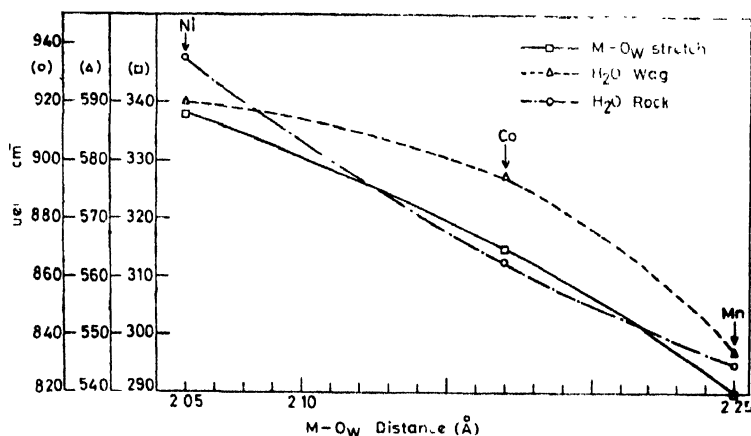


Fig. 3. Correlation of IR Frequencies at INT of M-O<sub>w</sub> stretch, H<sub>2</sub>O Wag, and H<sub>2</sub>O Rock with M-O<sub>w</sub> distance in  $\text{MSO}_4 \cdot \text{H}_2\text{O}$  ( $\text{M} = \text{Mn, Co, Ni}$ ).

Mn, Co and Ni respectively) shows the greater temperature variation in intensity or half-width while the others show marginal changes. As the

bands associated with internal modes of  $\text{SO}_4^{2-}$  are affected to much lesser degree by lowering of temperature, it may be inferred that the components showing marked dependence on temperature are associated with  $\text{M-O}_w$  stretch. These are also the dominant bands in the region.

*(e) Correlation of Frequencies with  $\text{M-O}_w$  distances*

Correlation of  $\nu$  (rock) with  $\text{M-O}_w$  distances has already been reported earlier<sup>(5)</sup>. Now we find that such correlation applies also to  $\nu$  (wag) and  $\nu$  ( $\text{M-O}_w$ ) stretch. Figure 3 gives the correlation curves using the low temperature data.

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