

## Libratory modes of water molecules in tutton salts

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**Abstract.** The existence of rocking, wagging and twisting librations of different types of water molecules in tutton salts has been established from their ir spectra. These bands have been identified, following the intensity criterion of Miyazawa. The present assignments indicate that the bands due to libratory motion of  $\text{H}_2\text{O}$  III in  $\text{NH}_4\text{Mn-}$ ,  $\text{KNi-}$ ,  $\text{KCo}$  and  $\text{KMn-}$  and of  $\text{H}_2\text{O}$  I in  $\text{KMn-}$  and  $\text{KCu-}$  tutton salts are out-of-plane H-bonded. The strength of the hydrogen bonding is the weakest in the  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

**Keywords.** Infrared spectra; tutton salts; libratory modes of water; double sulfates.

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### 1. Introduction

The tutton salts (Hoffmann 1930, 1931, 1932) under investigation are of the type  $M'_2 M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  where  $M' = \text{NH}_4, \text{K}$  and  $M'' = \text{Ni, Co, Fe, Mn}$  and  $\text{Cu}$ . A large number of infrared (Ananthanarayanan 1968; Brown and Ross 1970; Singh *et al* 1980) and Raman (Ananthanarayanan 1962; Singh *et al* 1982) studies have already been made on these salts. It has been shown through infrared studies on the internal modes of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  ions (Gupta *et al* 1984; Gupta and Khanna 1986) in these salts, that the spectral features associated with  $\text{Ni-}$ ,  $\text{Co-}$  and  $\text{Fe-}$  tutton salts are quite similar to each other whereas those of  $\text{Mn-}$  and  $\text{Cu-}$  salts differ not only among themselves but also from others. Extending these studies to the libratory modes of water molecules which have been classified into three types according to their coordination, it was considered necessary to study the systematics, if any, in their spectra.

Further, a study of librational modes of water molecules would be useful for a clear understanding of the nature of librational force fields in the crystal hydrates because these salts provide a large number of controlled environments in terms of crystal structure, number of water molecules per unit cell, strength of H-bonds and metal coordination etc. The librational modes of water can contribute significantly towards the thermodynamic properties of these crystals (Price and Stuart 1973) and a better understanding of phase transition, if any, along with the evaluation of order parameters (Caterford and Niniv 1974; Fawcett *et al* 1975; Savatinova and Anachkova 1977; Anachkova *et al* 1981). Generally the librational modes show up large variations in frequency, intensity and half-width on lowering the sample temperature. They are, therefore, easy instruments for detecting the phase transition in hydrated systems.

Towards this end, the infrared spectra of tutton salts  $M'_2 M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at room as well as at low temperatures have been recorded in the  $900\text{--}400\text{ cm}^{-1}$  region.

Partially-deuterated infrared spectrum of  $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  has also been recorded. H-bonding associated with the three types of water molecules in these salts is expected crystallographically (Montgomery and Linga Fetter 1964, 1966; Montgomery *et al* 1967) to be almost of the same strength but it would be interesting to monitor and compare the magnitudes of these bond strengths from our spectral data.

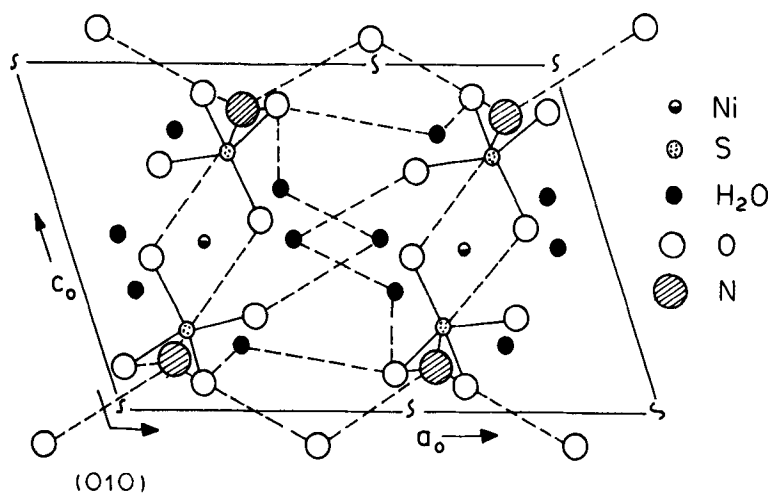
## 2. Crystal structure

The bimolecular unit cell of the tutton salts belongs to the monoclinic class of space group  $C_{2h}$  (P21/a). All the atoms and polyatomic units, except the bivalent metal cation ( $M''$ ) which lies at the centre of inversion, are placed at general positions. Each  $M''$  metal cation is centrosymmetrically coordinated to three non-equivalent pairs of water molecules thereby forming a complex  $[M''(\text{H}_2\text{O})_6]^{2+}$ . The water molecules are connected to oxygens of different  $\text{SO}_4^{2-}$  ions and also with each other through H-bonding. The structure of  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Grimes *et al* 1963), a member of isomorphous series of tutton salts, is depicted in figure 1.

The different types of water molecules, located at three non-equivalent  $C_1$  sites, have been designated as  $\text{H}_2\text{O I}$ ,  $\text{H}_2\text{O II}$  and  $\text{H}_2\text{O III}$  in the decreasing order of their hydrogen bond strengths. The bond lengths ( $\text{O}-\text{H}\dots\text{O}'$ ), determined crystallographically, refer to two different hydrogen bond linkages associated with a particular water molecule and are shown in table 1.

## 3. Experimental

The crystals of hexa-hydrated double sulphates were grown by slow evaporation of aqueous saturated solution of the respective hydrated metal sulphates  $M''\text{SO}_4 \cdot n\text{H}_2\text{O}$  ( $M'' = \text{Ni, Co, Fe, Mn, Cu}$ ) and ammonium/potassium sulphates of analar grade in



**Figure 1.** (010) project of  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  with origin shifted to  $1/4a, -1/2c$  showing proposed H-bonding at broken lines. (Grimes *et al* 1963).

**Table 1.** Crystallographically determined (O-H...O) bond lengths (in Å) in  $(\text{NH}_4)_2M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $M'' = \text{Ni, Co, Fe, Mn, Cu}$ ).

	$\text{NH}_4\text{Ni-}$ (14)	$\text{NH}_4\text{Co-}$ (16)	$\text{NH}_4\text{Fe-}$ (16)	$\text{NH}_4\text{Mn-}$ (15)	$\text{NH}_4\text{Cu-}$ (15)
$\text{H}_2\text{O I}$	2.78	2.71	2.72	2.71	2.72
	2.62	2.76	2.76	2.78	2.76
mean	2.70	2.73	2.74	2.74	2.74
$\text{H}_2\text{O II}$	2.71	2.71	2.73	2.72	2.71
	2.80	2.76	2.76	2.78	2.74
mean	2.75	2.73	2.74	2.75	2.72
$\text{H}_2\text{O III}$	2.81	2.79	2.78	2.79	2.82
	2.80	2.83	2.83	2.86	2.84
mean	2.80	2.81	2.80	2.82	2.83

\*Two values of (O-H...O) bond lengths refer to two hydrogen bonded distances associated with a particular type of water molecule.

the equimolar ratios at room temperature (27°C). The crystals thus grown were ground and polished to well-developed faces and used as such.

The IR spectra were recorded on a PE-521 IR double beam spectrophotometer in the 900–400  $\text{cm}^{-1}$  region using pressed disc (KBr pellet) and nujol mull techniques at room temperature and on a PE-580 instrument at low temperature (–185°C). Since Cu-salt undergoes anion exchange with KBr, its spectra have, therefore, been recorded as a single thin crystalline plate or in the pellet form. The results were found to be identical.

#### 4. Results and discussion

The assignments of the bands in the spectra of tutton salts in the region 900–400  $\text{cm}^{-1}$  had been rather ambiguous. Ananthanarayanan (1963) assigned these bands as overtones and combinations of the internal modes of the complex  $[M''(\text{H}_2\text{O})_6]^{2+}$  in his Raman study whereas Campbell *et al* (1970) attributed them to the libratory modes of water molecules in his infrared spectra. The bands observed in the present ir study in the 900–400  $\text{cm}^{-1}$  region are of appreciable intensities and thus cannot be explained due to the multiphonon processes. The Raman spectra in this region associated with the libratory modes of water molecules in these salts are expected to be quite weak and this might have wrongly prompted Ananthanarayanan (1961, 1962, 1963) to assign them as overtones and combinations of the complex  $[M''(\text{H}_2\text{O})_6]^{2+}$ . In a detailed infrared study of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , Jain (1976) attributed the bands falling in the region 900–400  $\text{cm}^{-1}$  to the libratory modes of  $\text{H}_2\text{O}$  molecules. Since the spectra of the salts under discussion resemble closely with their parent bi-valent metal sulphates  $M''\text{SO}_4 \cdot n\text{H}_2\text{O}$  ( $M'' = \text{Ni, Cu, ...}$ ), we are justified in assigning these bands to the libratory modes of  $\text{H}_2\text{O}$  molecules. Similar studies carried out on different crystal hydrates (Montgomery and Linga Fetter 1966; Jain *et al* 1974) as well as on hydrated metal sulphates (Berger 1976; Nakagawa and Shimanouchi 1964) also corroborate our viewpoint.

Various criteria (Vander-Elsken and Robinson 1961; Lutz *et al* 1974; Miyazawa

1961) have been formulated by different workers to help us in identifying rocking, wagging and twisting librations in the spectra of such salts but no single method has been universally followed. We are, however, making use of the criterion enunciated by Miyazawa (1961) stating that the wagging modes were expected to be generally stronger than the corresponding rocking modes. Twisting modes being IR-forbidden will either be absent or will appear in the IR spectra with very weak intensity. In addition, the suggestion of Jain (1975), that for in-plane-bent or in-plane-linear H-bonding, the rocking modes fall at higher frequency side than the corresponding wagging modes, has also been considered. Help has also been sought from the established criterion that an increase in the H-bond strength is associated with the increase of librational mode frequencies of water molecules. Since H<sub>2</sub>O I, H<sub>2</sub>O II and H<sub>2</sub>O III have been arranged in the descending order of their H-bond strengths, the respective bands due to various librations will also appear in decreasing order of frequencies.

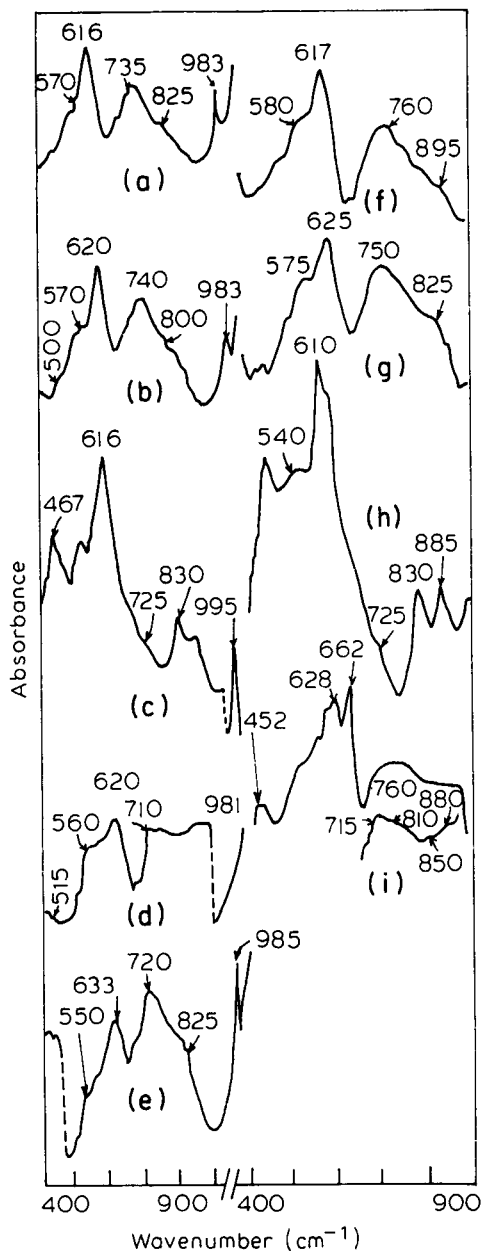
## 5. Assignments

### 5.1 $M'_2 M''(SO_4)_2 \cdot 6H_2O$ ( $M' = NH_4/K$ ; $M'' = Ni, Co, Fe$ )

The spectral features due to libratory modes of H<sub>2</sub>O in the NH<sub>4</sub>Ni-, NH<sub>4</sub>Co- and NH<sub>4</sub>Fe tutton salts resemble very much with each other as well as with the corresponding ones for the K-tutton salts (figure 2). The observed bands are grouped into two distinct broad band profiles and have been resolved manually as optimum number of Lorentzian-shaped bands. The closeness of H-bond strengths of H<sub>2</sub>O I and H<sub>2</sub>O II molecules (table 1) while a comparatively weaker H-bonding for H<sub>2</sub>O III molecules has led us to assign the bands falling in the first band profile to the libratory modes of H<sub>2</sub>O I and H<sub>2</sub>O II molecules whereas those falling in the lower frequency envelope to those of H<sub>2</sub>O III molecules.

Table 2 shows the frequencies (in cm<sup>-1</sup>), peak intensities ( $I'$ ) and FWHM intensity ( $\Delta\nu$  in cm<sup>-1</sup>) of each of the manually-resolved band in the spectra of the salts under discussion. The values are accurate up to  $\pm 2$  cm<sup>-1</sup> for sharp bands and up to  $\pm 10$  cm<sup>-1</sup> for broad and diffuse bands. The integrated intensities ( $I$ ), determined by multiplying peak absorbance with FWHMI, of the bands observed at 760 and 735 cm<sup>-1</sup>; 740 and 720 cm<sup>-1</sup> and 750 and 720 cm<sup>-1</sup> in the respective spectra of NH<sub>4</sub>Ni-, NH<sub>4</sub>Co- and NH<sub>4</sub>Fe- salts are greater than the intensities of the bands at 865 and 825 cm<sup>-1</sup>; 830 and 800 cm<sup>-1</sup> and 825 and 800 cm<sup>-1</sup> respectively. The corresponding bands in the KNi salt appear at 795, 760 cm<sup>-1</sup> and 895, 850 cm<sup>-1</sup> and in KCo salt they appear at 785, 750 cm<sup>-1</sup> and 872, 825 cm<sup>-1</sup> respectively. Following Miyazawa's intensity criterion (Miyazawa 1961), the former pair of bands associated with the H<sub>2</sub>O I and H<sub>2</sub>O II molecules respectively have been attributed to the wagging modes whereas the later pair of bands to the corresponding rocking modes in each of the salts. The two very weak bands observed in the same envelope in each of the NH<sub>4</sub>Ni-, NH<sub>4</sub>Co-, NH<sub>4</sub>Fe-, KNi- and KCo- salts at 715 and 695 cm<sup>-1</sup>; 690 and 660 cm<sup>-1</sup>; 695 and 680 cm<sup>-1</sup>; 730 and 710 cm<sup>-1</sup> and 715 and 695 cm<sup>-1</sup> have been assigned tentatively to the twisting modes of H<sub>2</sub>O I and H<sub>2</sub>O II molecules respectively.

In the second band profile (contour) of the respective spectra observed in the



**Figure 2.** Infrared spectra of microcrystalline hexa hydrated double sulphates. (a)  $\text{NH}_4\text{Ni-}$  (b)  $\text{NH}_4\text{Co-}$  (c)  $\text{NH}_4\text{Mn-}$  (d)  $\text{NH}_4\text{Cu-}$  (e)  $\text{NH}_4\text{Fe-}$  (f)  $\text{KNi-}$  (g)  $\text{KCo-}$  (h)  $\text{KMn-}$  (i)  $\text{KCu-}$ .

$\text{NH}_4\text{Ni-}$   $\text{NH}_4\text{Co-}$  and  $\text{NH}_4\text{Fe-}$  salts, three bands at  $570$ ,  $550$  and  $497 \text{ cm}^{-1}$ ;  $570$ ,  $550$  and  $500 \text{ cm}^{-1}$  and  $757$ ,  $550$  and  $510 \text{ cm}^{-1}$ , ignoring the bands due to  $\text{SO}_4^{2-}$  ions, (Gupta 1984) have been observed. Of these three bands in each case, the first two are almost of equal and moderate intensities whereas the last one is very weak. On the basis of the intensity criterion (Miyazawa 1961), we have assigned the first band in

**Table 2.** Infrared librational mode frequencies (in  $\text{cm}^{-1}$ ) of  $\text{H}_2\text{O}$  molecules, peak intensities ( $I'$ ) and full widths at half the maximum intensity ( $\Delta\nu\text{cm}^{-1}$ ) of micro-crystalline  $M_2M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  for  $M' = \text{NH}_4$  and  $M'' = \text{Ni, Co, Fe, Mn}$  and  $\text{Cu}$  alongwith their assignments.

$\text{NH}_4\text{Ni}-$ ( $I', \Delta\nu$ )	$\text{NH}_4\text{Co}-$ ( $I', \Delta\nu$ )	$\text{NH}_4\text{Fe}-$ ( $I', \Delta\nu$ )	$\text{KNi}-$ ( $I', \Delta\nu$ )	$\text{KCo}-$ ( $I', \Delta\nu$ )	$\text{NH}_4\text{Mn}-$ ( $I', \Delta\nu$ )	$\text{KMn}-$ ( $I', \Delta\nu$ )	$\text{NH}_4\text{Cu}-$ ( $I', \Delta\nu$ )	$\text{KCu}-$ ( $I', \Delta\nu$ )	Assignments
865 (5,80)	830 (12,50)	825 (12,40)	895 (16,55)	872 (18,50)	880 (10,50)	830 (15,40)	850 (w, br)	850 (4,35)	R <sup>w</sup> I
825 (9,95)	800 (14,60)	800 (15,50)	850 (18,45)	825 (22,60)	—	—	850 (w, br)	—	R <sup>w</sup> II
—	—	—	—	—	830 (15,48)	885 (20,45)	—	880 (5,50)	W <sup>w</sup> I
760 (12,75)	740 (22,58)	750 (22,45)	795 (25,40)	785 (28,45)	—	—	740 (10,55)	—	W <sup>w</sup> I
735 (16,60)	720 (18,45)	720 (25,55)	760 (32,55)	750 (32,60)	—	—	710 (8,45)	—	W <sup>w</sup> II
715 (8,45)	690 (8,38)	695 (10,38)	730 (12,20)	715 (Sh)	770 (vw)	—	680 (5,25)	—	T <sup>w</sup> I
—	—	—	—	—	725 (9,45)	725 (7,60)	—	760 (10,40)	R <sup>w</sup> II
—	—	—	—	—	680 (15,55)	670 (15,40)	—	810 (8,60)	W <sup>w</sup> II
695 (6,55)	660 (7,45)	680 (8,42)	710 (10,15)	695 (vw)	580 (20,7)	685 (Sh, Br)	680 (5,25)	715 (vw)	T <sup>w</sup> II
570 (11,40)	570 (17,45)	575 (8,40)	500 (25,30)	515 (20,42)	467 (32,30)	470 (40,22)	655 (8,30)	570 (10,28)	R <sup>w</sup> III
550 (9,55)	550 (16,55)	550 (7,50)	580 (34,40)	575 (30,55)	540 (30,50)	540 (30,60)	560 (10,50)	550 (8,35)	W <sup>w</sup> III
497 (5,42)	500 (8,40)	510 (vw)	540 (w)	550 (vw)	500 (br, Sh)	480 (Sh)	515 (w)	520 (5,20)	T <sup>w</sup> III

each of the salts to the rocking mode of H<sub>2</sub>O III molecule whereas the second one to its wagging mode. The last band can be identified unambiguously to the twisting mode.

In the IR spectrum of KNi salt, the band observed at 580 cm<sup>-1</sup> is stronger than the band at 500 cm<sup>-1</sup> whereas in KCu- salt, the band at 575 cm<sup>-1</sup> is stronger than that at 515 cm<sup>-1</sup>. On the basis of the intensity criterion, we have assigned the bands at 580 and 575 cm<sup>-1</sup> in the respective spectra of KNi- and KCo- salts to the wagging mode whereas those at 500 and 515 cm<sup>-1</sup> to the rocking mode of H<sub>2</sub>O III molecule respectively. The fact that the wagging mode of this group of water molecules (H<sub>2</sub>O III) has been identified at a higher frequency than the corresponding rocking mode led us to believe that the H-bonding associated with the H<sub>2</sub>O III molecule is out-of-plane in these two salts (KNi- and KCo-) whereas H<sub>2</sub>O I and H<sub>2</sub>O II water molecules are in-plane H-bonded in these salts.

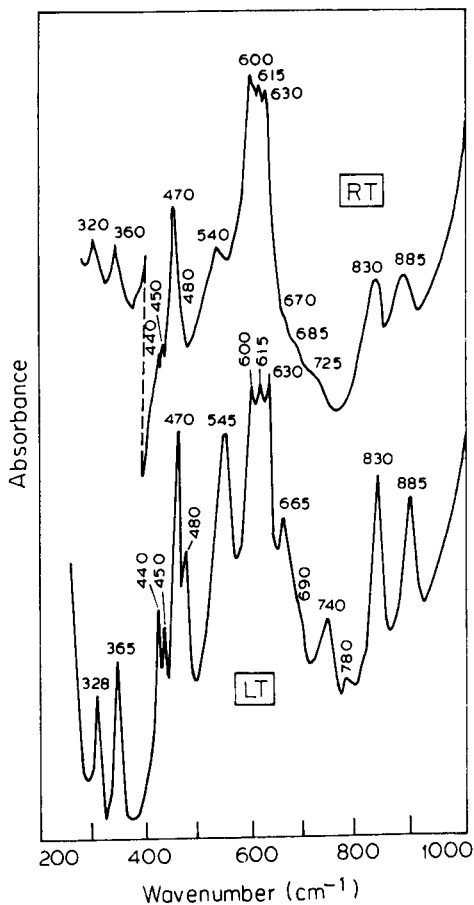
### 5.2 $M'_2Mn(SO_4)_2 \cdot 6H_2O$ ( $M' = NH_4$ and K)

The infrared spectral features due to Mn- salts in the libratory mode frequency region of H<sub>2</sub>O molecules are quite distinct from those of others (figure 2). In the NH<sub>4</sub>Mn- salt, the bands observed at 880 and 830 cm<sup>-1</sup> are of medium intensities and are well separated from other bands. The corresponding bands in the KMn- salt appear at 885 and 830 cm<sup>-1</sup> with respective FWHMI 45 and 40 cm<sup>-1</sup> (table 2). Such a pattern for the corresponding bands has not been observed in the infrared spectra of other salts under discussion (figure 2). These bands have been assigned as rocking and wagging modes of H<sub>2</sub>O I in the NH<sub>4</sub>Mn- salt and wagging and rocking modes in KMn- salt on the basis of intensity criterion proposed by Miyazawa (1961). In the infrared spectrum of K- salt at room temperature, there is no indication of a band corresponding to the twisting mode though it appears clearly at 780 cm<sup>-1</sup> (figure 3) at low temperature (-185°C). The weak and broad band at 725 cm<sup>-1</sup> in the IR spectrum of the K- salt becomes appreciably stronger in its peak intensity along with its shift towards higher frequency side (740 cm<sup>-1</sup>) when the spectrum is recorded at low temperature (table 3). This band has been associated with the rocking mode of H<sub>2</sub>O II. The corresponding wagging mode is comparatively stronger at room as well as at low temperatures. On the basis of the assignments that the band at 470 (470), 540 (545) and 480 (480) cm<sup>-1</sup> at room (low) temperature in the infrared spectrum of K- salt are due to the rocking, wagging and twisting modes of H<sub>2</sub>O III molecule, we may argue that this water molecule is out-of-plane H-bonded in this salt. The observed difference in the spectral features of the bands corresponding to three librations of H<sub>2</sub>O I, H<sub>2</sub>O II and H<sub>2</sub>O III molecules in the NH<sub>4</sub>Mn- and KMn- salts may, therefore, be explained due to different H-bonding linkages associated with them.

### 5.3 $M_2Cu(SO_4)_2 \cdot 6H_2O$ ( $M = NH_4/K$ )

The infrared spectrum of NH<sub>4</sub>Cu- as well as that of KCu- salt is quite broad and complex (figure 2) due to overlapping of bands resulting from the libratory modes of different types of water molecules.

However, some of the bands could be identified and their assignments made, taking recourse to the contour analysis of the band profiles, where Lorentzian line shape



**Figure 3.** Infrared spectra of microcrystalline  $K_2Mn(SO_4)_2 \cdot 6H_2O$  at  $27^\circ C$  (RT) and  $-185^\circ C$  (LT).

**Table 3.** Infrared librational mode frequencies ( $\nu$  in  $cm^{-1}$ ) of  $H_2O$  molecules, peak intensities ( $I'$ ) and FWHM intensity ( $\nu cm^{-1}$ ) of microcrystalline  $K_2Mn(SO_4)_2 \cdot 6H_2O$  at room and low temperature ( $-185^\circ C$ ) alongwith their assignments.

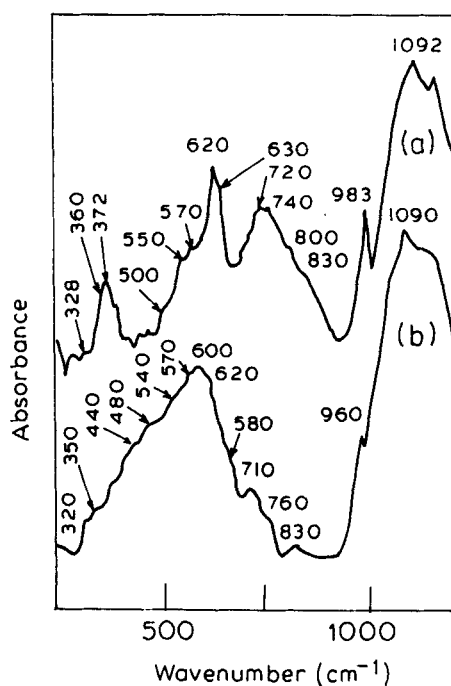
(27°C)			- 185°C)			Assignments
$\nu$	$I'$	$\Delta\nu$	$\nu$	$I'$	$\Delta\nu$	
830	15	40	830	45	18	R* I
—	—	—	780	15	20	T* I
885	20	45	885	40	25	W* I
725	7	60	740	20	25	R* II
685	sh	br	690	sh		T* II
670	15	40	665	40	25	W* II
540	30	60	545	55	30	W* III
480	sh		480	35	8	T* III
470	40	22	470	62	15	R* III



functions (Tobin 1971) were considered for the analysis. The basis of the assignment is the criterion of Miyazawa (1961) that the wagging modes are stronger than the corresponding rocking modes. Our analysis suggests that the H<sub>2</sub>O I and H<sub>2</sub>O II molecules are out-of-plane H-bonded in the K<sub>2</sub>Cu(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

#### 5.4 Deuterated (NH<sub>4</sub>)<sub>2</sub>Co(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O

Figure 4 provides the infrared spectra of hydrated (NH<sub>4</sub>)<sub>2</sub>Co(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O salt in the libratory mode frequency region of water molecule (900–400 cm<sup>-1</sup>). There is an observable change in the respective spectral features of the bands associated with the libratory modes of water molecules involving hydrated and partially deuterated samples. The complexity of the spectrum of the partially deuterated Co-salt in this region is due to intermixing and overlapping of the libratory modes due to H<sub>2</sub>O, HDO and D<sub>2</sub>O molecular species (table 4). In addition, some bands due to SO<sub>4</sub><sup>2-</sup> ion and other molecular species also fall in the same region (Gupta 1984). Taking into account the criterion (Ichida *et al* 1972) that the rocking and wagging modes of HDO species should show downward frequency shifts in the ratio of 1:21 and 1:09 respectively with respect to the corresponding modes in the hydrated salt, the rocking mode frequencies of HDO species in the deuterated salt for H<sub>2</sub>O I, H<sub>2</sub>O II and H<sub>2</sub>O III molecules have been computed to lie around 686, 661 and 471 cm<sup>-1</sup> respectively. The corresponding computed wagging mode frequencies are expected to appear respectively at 679, 660 and 504 cm<sup>-1</sup>. These values have been obtained from the already assigned librational frequencies of H<sub>2</sub>O I, H<sub>2</sub>O II and H<sub>2</sub>O III in



**Figure 4.** Infrared spectra of microcrystalline (a) hydrated and (b) partially deuterated salt of (NH<sub>4</sub>)<sub>2</sub>Co(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

**Table 4.** Infrared librational mode frequencies ( $\nu \text{ cm}^{-1}$ ) of  $\text{H}_2\text{O}$  molecules, peak intensities ( $I'$ ) and FWHM intensity ( $\nu \text{ cm}^{-1}$ ) of microcrystalline hydrated and partially deuterated  $(\text{NH}_4)_2\text{CO}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  alongwith their assignments.

Hydrated			Partially deuterated			Assignments
$\nu$	$I'$	$\Delta\nu$	$\nu$	$I'$	$\Delta\nu$	
830	12	50	830	12	55	R* I
800	14	60	830	12	55	R* II
740	22	58	760	16	40	W* I
720	18	45	710	20	45	W* II
690	8	38	—	—	—	T* I
—	—	—	680	12	60	R <sup>D</sup> I/W <sup>D</sup> I(HDO)
660	7	45	—	—	—	T* II
570	17	45	570	30	48	R* III
550	16	55	540	35	50	W* III
500	8	40	—	—	—	T* III
—	—	—	480	30	60	R <sup>D</sup> III/W <sup>D</sup> III(HDO)

the hydrated Co- salt (table 4). Based on the calculated values, the bands observed at 680 and 480  $\text{cm}^{-1}$  in the deuterated Co- salt have been associated with the R<sup>D</sup> I or W<sup>D</sup> I and R<sup>D</sup> III or W<sup>D</sup> III of HDO species. The remaining bands of this region in this salt have either been attributed to the libratory modes of  $\text{H}_2\text{O}$  species or appear due to the modes of other molecular species (table 4).

## 6. Conclusions

### 6.1 H-Bonding

Based on the fact that for the in-plane H-bonded water molecules rocking modes should lie at higher frequencies than the corresponding wagging modes while reverse should be the case for out-of-plane hydrogen bonded water molecules, we have concluded from our assignments that the bands due to libratory motion of  $\text{H}_2\text{O}$  III in  $\text{NH}_4\text{Mn}$ ;  $\text{KNi}$ -;  $\text{KCo}$ -; and  $\text{KMn}$ - and of  $\text{H}_2\text{O}$  I in  $\text{KMn}$ - and  $\text{KCu}$ - salts are out of plane H-bonded. It has further been estimated that the strength of the H-bonding is the weakest in the  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . However, the potassium tutton salts have stronger bonding as compared to the corresponding ammonium tutton salts.

### 6.2 Distortion in symmetry

The presence of IR forbidden twisting mode in all the salts\* for all the three types of water molecules led us to conclude that the free state  $C_{2v}$  symmetry of  $\text{H}_2\text{O}$  molecules has been lowered in all the double sulphates under study.

\*The structure of band contours in  $\text{NH}_4\text{Cu}$ - and  $\text{KCu}$ - salts has not been resolved very distinctly and bands could not be identified unambiguously.

### 6.3 Anharmonicity

The comparatively broader spectral features associated with the librational modes of water molecules in the  $\text{NH}_4\text{Cu-}$  and  $\text{KCu-}$  tutton salts suggest that the force fields of water molecules are quite anharmonic in these salts.

### 6.4 Spectra-structure correlation

The infrared spectra of  $(\text{NH}_4)_2M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  resemble closely with the  $\text{K}_2M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $M'' = \text{Ni, Co and Fe}$ ) in the spectral region  $900\text{--}400\text{ cm}^{-1}$ . Therefore, the crystallographic data i.e. bond lengths, bond angles, environments and coordination of different groups (atomic and polyatomic) in these crystals are expected to be quite close. This feature predicts that the unknown crystallographic parameters for the potassium tutton salts  $\text{K}_2M''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  are expected to be quite close to those of the corresponding ammonium tutton salts. This aspect has also been corroborated from the IR and Raman studies of these salts in the spectral regions of fundamental modes of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and complex  $[M''(\text{H}_2\text{O})_6]^{2+}$ .

## References

- Anachkoa E, Ratajczak H and Savatinova I 1981 *Phys. Status Solidi* **B108** 65  
 Ananthanarayanan V 1961 *Z. Phys.* **163** 144  
 Ananthanarayanan V 1962 *Z. Phys.* **166** 318  
 Ananthanarayanan V 1963 *Z. Phys. Chem.* **222** 102  
 Ananthanarayanan V 1968 *J. Chem. Phys.* **48** 573  
 Brown R G and Ross S D 1970 *Spectrochim. Acta* **A26** 945  
 Campbell J A, Ryan D P and Semipson L M 1970 *Spectrochim. Acta* **A26** 2351  
 Caterford R P and Niniv F 1974 *Solid State Commun.* **15** 1451  
 Fawcett V, Long D A and Sankaranarayanan V N 1975 *J. Raman Spectrosc.* **3** 217  
 Grimes N W, Kay H F and Webb M W 1963 *Acta Crystallogr.* **16** 823  
 Gupta P 1984 *IR and Raman Spectra of some transition metal single and double sulphates* Ph D Thesis AMU, Aligarh, India  
 Gupta P and Khanna B N 1986 *Indian J. Phys.* **B60** 347  
 Gupta P, Singh B and Khanna B N 1984 *J. Mol. Struct.* **112** 41  
 Hoffmann W 1930 *Z. Kristallogr. Kristallogenom. Krystalphys. Kristallochem.* **75** 158  
 Hoffmann W 1931 *Z. Kristallogr. Kristallogenom. Krystalphys. Kristallochem.* **78** 279  
 Hoffmann W 1932 *Z. Kristallogr. Kristallogenom. Krystalphys. Kristallochem.* **82** 323  
 Ichida K, Kuroda Y, Nakamura D and Kubo M 1972 *Spectrochim. Acta* **A28** 2433  
 Jain Y S 1975 *Solid State Commun.* **17** 605  
 Jain Y S 1976 *J. Phys. Chem. Solids* **37** 641  
 Jain Y S, Bist H D and Verman A L 1974 *J. Raman Spectrosc.* **2** 326  
 Lutz H D, Kluppel H J, Robitschka W and Baasner 1974 *Z. Naturforsch.* **B26** 723  
 Montgomery H, Chashtain R V, Natt J J, Witkowska A M and Linga fether E C 1967 *Acta Crystallogr* **22** 275  
 Montgomery H and Linga fether E C 1964 *Acta Crystallogr.* **17** 1478  
 Montgomery H and Linga fether E C 1966 *Acta Crystallogr.* **20** 659, 731  
 Miyazawa T 1961 *Bull. Chem. Soc. Jpn.* **34** 202  
 Nakagawa I and Shimanouchi T 1964 *Spectrochim Acta* **20** 429  
 Price G C and Stuart W I 1973 *J. Chem. Soc. Faraday Trans.* **69** 1498  
 Savatinova I and Anachkova E 1977 *Phys. Status Solidi* **B84** 401  
 Singh B, Gupta Shashi P and Khanna B N 1980 *Pramana – J. Phys.* **14** 509  
 Singh B, Gupta Shashi P and Khanna B N 1982 *Pramana – J. Phys.* **18** 427  
 Tobin M C 1971 *Laser Raman spectroscopy* (New York: Wiley Interscience)  
 Vander-Elsken J and Robinson D W 1961 *Spectrochim. Acta* **17** 1249