

The infrared spectra of tutton salts 1. A comparative study of $(\text{NH}_4)_2 \text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M}'' = \text{Ni}, \text{Co}$ or Mg)

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Abstract. The infrared spectra of $(\text{NH}_4)_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ has been analysed in the region $4000\text{--}250\text{ cm}^{-1}$. The dynamics of each crystal has been discussed in terms of 234 phonon modes, including 3 acoustical ones, using the unit cell approximation. The ambiguity in the assignments of the bands in the region $900\text{--}500\text{ cm}^{-1}$ has been removed by assigning the bands in this region to the libratory modes of H_2O molecules. It has been concluded that the NH_4^+ and SO_4^{2-} ions have a symmetry lower than T_d and also the complex $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ has a symmetry lower than O_h . The hydrogen bonding is the strongest in the Ni-salt and the weakest in the Mg-salt.

Keywords. Infrared spectra; tutton salts; optical phonons; libratory modes; metal-aquo complex.

1. Introduction

The infrared and Raman spectra of SO_4^{2-} ion in crystalline double sulphates, $\text{M}'_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (where $\text{M}' = \text{K}$ or NH_4 and $\text{M}'' = \text{Mg}, \text{Zn}, \text{Ni}$ or Co) have been reported by Ananthanarayanan (1961, 1962, 1968). He also theoretically calculated the force constants and the frequencies of the internal modes of vibrations of the complex $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ and has assigned the bands in the region $900\text{--}500\text{ cm}^{-1}$ to the overtones and combination bands (Ananthanarayanan 1963, 1970). In the IR reflection spectra of these salts, Eucken and Hellwege (1955) reported only a few prominent bands. Theimer (1950) reported only five prominent bands in the Raman spectra of the Mg-salt in the powder form. Recently, the infrared spectra of isotopically isolated NH_3D^+ and HDO species in seven ammonium tutton salts have been examined by Oxtan and Knop (1978).

A critical literature survey shows that the factor group analysis given by Ananthanarayanan (1961) is in error. It also appears that the ν_2^S and ν_4^S internal modes of SO_4^{2-} ion were wrongly assigned and the assignments of some overtones and combination bands were questionable. A closer look at the IR spectra of these salts shows that the bands in the region $900\text{--}500\text{ cm}^{-1}$ cannot be assigned to the overtone or combination bands of the weakly observed internal modes of the complex. But they actually appear to belong to the libratory modes of the three types of water molecules in these crystals in analogy with the results of their parent bivalent metal sulphates (Jain 1976; Janik *et al* 1969 and Jager and Schaack 1973) and other studies on double sulphates (Peytavin *et al* 1972). Moreover, a large number of bands were left unassigned, which may as well be due to different modes of H_2O molecules along

with their overtones and combination bands. In the present paper we report an exhaustive and comparative study of the IR spectra of $(\text{NH}_4)_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (where $\text{M}'' = \text{Ni}, \text{Co}$ or Mg) in the region $4000\text{--}250\text{ cm}^{-1}$.

2. Crystal structure

The crystals are isomorphic with space group $C_{2h}^5 (P2_1/a)$ (Grimes *et al* 1963; Margulis and Templeton 1962; Montgomery and Lingafelter 1964; Halla and Mehl 1931) with two formula units per unit cell. The bivalent metal cations (Ni, Co or Mg) occupy the inversion centres whereas all other atoms and molecular groups are placed in general positions. The bivalent cations are surrounded octahedrally by six water molecules. There are three types of water molecules which sit at three crystallographically non-equivalent C_1 sites. For convenience, we have designated them as $\text{H}_2\text{O I}$, $\text{H}_2\text{O II}$ and $\text{H}_2\text{O III}$ in the increasing order of their hydrogen bond strengths. The bond lengths and orientations of $\text{M}''\text{-H}_2\text{O}$ and S-O are different in all the three salts.

3. Experimental

The crystals of the tutton salts in the present investigation were grown by slow evaporation of the aqueous saturated solution of analar grade $(\text{NH}_4)_2\text{SO}_4$ and $\text{M}''\text{SO}_4 \cdot x\text{H}_2\text{O}$, obtained from the British Drug House, Bombay in equimolar ratios at room temperature (25°C). The infrared spectra of the microcrystalline samples were recorded at room temperature using KBr pellet and nujol mull techniques on PE- 521 Grating infrared spectrophotometer working in the range $4000\text{--}250\text{ cm}^{-1}$. The calibration of the instrument was checked by the usual procedure (Singh *et al* 1977).

4. Results and discussion

4.1. Phonon modes in the crystals

The dynamics of these crystals has been described in terms of 234 phonon modes, including 3 acoustical ones. Different modes have been attributed respectively to the internal (i ; 36, 36, 36, 30) and libratory (l ; 36, 12, 12, 6) modes of H_2O , NH_4^+ , SO_4^{2-} and the complex $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ and the translatory (t ; 12, 12, 6) modes of the last three units. The translatory modes of H_2O and bivalent metal cation $(\text{M}'')^{2+}$ have been accounted for by the modes of the complex.

A correlation between different species of C_{2v} for H_2O , T_d for NH_4^+ and SO_4^{2-} ions and O_h for $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ complex in free state with those of the space group C_{2h}^5 of the crystals *via* their site symmetries is displayed in figure 1. The symmetry classification of different modes under the site symmetry approach (Halford 1946; Hornig 1948) is given in table 1 and under the factor group approach (Bhagavantam and Venkatarayudu 1939) is summarised in table 2. Different modes belonging to H_2O , NH_4^+ , SO_4^{2-} and $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ have been distinguished by using the super-

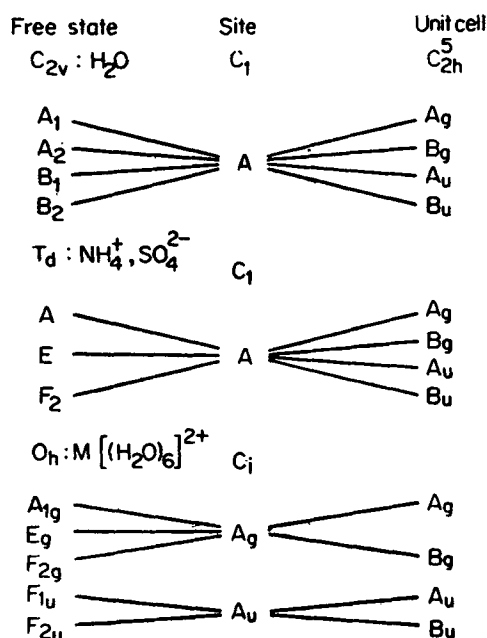


Figure 1. A correlation between different species of C_{2v} for H_2O , T_d for NH_4^+ and SO_4^{2-} ions and O_h for $[M(H_2O)_6]^{2+}$ complex in free state with those of the factor group C_{2h}^5 via their site symmetries.

scripts w , n , s and c respectively. Here only F_2 under T_d , F_{1u} under O_h and A_1 , B_1 and B_2 under C_{2v} are infrared active.

4.2. Observed spectra and assignments

The infrared spectra of the Ni-, Co- and Mg-salts recorded at room temperature by the KBr pellet technique is shown in figure 2. The frequencies (ν cm^{-1}) of the bands observed in these spectra and their assignments have been given in table 3. For the calculation of the relative intensities of different bands and also for the determination of the positions of few badly overlapped and obscured bands, the spectra have been resolved into an optimum number of Lorentzian shaped bands (not shown in figure 2). The values are accurate within ± 2 cm^{-1} for well-developed and sharp bands and within ± 10 cm^{-1} for broad, diffuse and manually resolved bands.

4.3 Internal modes of SO_4^{2-} and NH_4^+ ions

These modes have been assigned on the basis of the knowledge of their frequencies in the free state SO_4^{2-} and NH_4^+ ions (Herzberg 1960). Under the perfect T_d symmetry only ν_3 (F_2) and ν_4 (F_2) are IR active whereas all ν_i ($i = 1-4$) are Raman active. But in these crystals, SO_4^{2-} ion sites at C_1 site and thus one expects all the internal modes of vibrations to show up both in the IR and Raman spectra. But the symmetries of IR active modes (A_u , B_u) are different from those of the Raman modes (A_g , B_g) and thus 'the mutual exclusion rule' in these centrosymmetric crystals is

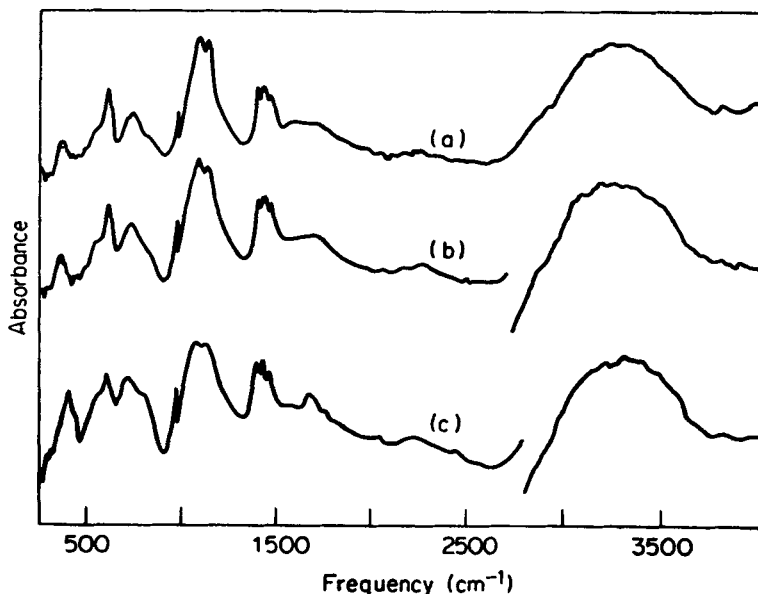
Table 1. Classification of phonons in $(\text{NH}_4)_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M}'' = \text{Mg, Ni or Co}$) (The site symmetry approach).

Modes	Species under C_{2h}^5				N^x	Modes	Species under C_{2h}^5				N^x
	A_g	B_g	A_u	B_u			A_g	B_g	A_u	B_u	
1	2	3	4	5	6	1	2	3	4	5	6
(1) Internal modes of H_2O						(4) Internal modes of NH_4^+					
(C_{2v}) : Site C_1						(T_d) : Site C_1					
Symmetric						$\nu_1^s(A_1)$					
stretching $\nu_1^w(A_1)$						1 1 1 1 4					
Bending $\nu_2^w(A_1)$						2 2 2 2 8					
Asymmetric						$\nu_2^s(F_2)$					
stretching $\nu_3^w(B_2)$						3 3 3 3 12					
						$\nu_3^s(F_2)$					
						3 3 3 3 12					
Total internal modes						Total					
3 3 3 3 12						9 9 9 9 36					
(2) Librational modes of H_2O						(5) Internal modes of $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$					
(C_{2v}) : Site C_1						(O_h) : Site C_i					
Rocking $\nu_\gamma^w(B_2)$						$\nu_1^c(A_{1g})$					
1 1 1 1 4						1 1 0 0 2					
Wagging $\nu_\delta^w(B_1)$						$\nu_2^c(E_g)$					
1 1 1 1 4						2 2 0 0 4					
Twisting $\nu_1^w(A_2)$						$\nu_3^c(F_{1u})$					
1 1 1 1 4						0 0 3 3 6					
						$\nu_4^c(F_{1u})$					
						0 0 3 3 6					
						$\nu_5^c(F_{2g})$					
						3 3 0 0 6					
						$\nu_6^c(F_{2u})$					
						0 0 3 3 6					
Total libratory modes						Total					
9 9 9 9 36						6 6 9 9 30					
(3) Internal modes of SO_4^{2-}						(6) External modes					
(T_d) : Site C_1						Rotations					
$\nu_1^s(A_1)$						of $\text{SO}_4^{2-}(F_1)$					
1 1 1 1 4						3 3 3 3 12					
$\nu_2^s(E)$						Rotations					
2 2 2 2 8						of $\text{NH}_4^+(F_1)$					
$\nu_3^s(F_2)$						3 3 3 3 12					
3 3 3 3 12						Rotations of					
$\nu_4^s(F_2)$						$[\text{M}''(\text{H}_2\text{O})_6]^{2+}(F_{1g})$					
3 3 3 3 12						3 3 0 0 6					
						Optical					
						translations					
						6 6 8 7					
						Acoustical					
						translations					
						0 0 1 2					
Total						Total					
9 9 9 9 36						15 15 15 15 60					
						Grand total					
						57 57 60 60 234					

N^x Total phonon modes originating from a particular mode of a unit.

Table 2. Factor group analysis of $(\text{NH}_4)_2 \text{M}'' (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

	C_{2h}				Total
	A_g	B_g	A_u	B_u	
Translations { Acoustical	0	0	1	2	3
	6	6	8	7	27
Librations ($l^s + l^w + l^n + l^c$)	18	18	15	15	66
Internal ($\nu_1^s + \nu_1^w + \nu_1^n + \nu_1^c$)	33	33	36	36	138
Total	57	57	60	60	234

Figure 2. The infrared spectra of (a) $(\text{NH}_4)_2 \text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (b) $(\text{NH}_4)_2 \text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and (c) $(\text{NH}_4)_2 \text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in KBr pellet at room temperature.

still obeyed. A sharp and weak band at 983, 983 and 984 cm^{-1} respectively in the spectra of the Ni-, Co- and Mg- salts has unambiguously been assigned to the IR forbidden (under perfect T_d symmetry), non-degenerate ν_1^s mode. The triply degenerate ν_3^s mode splits into two components falling at 1145 and 1095 cm^{-1} in the Ni-salt and at 1140 and 1092 cm^{-1} in the Co-salt. But in the Mg- salt there is an indication of three components at 1140, 1100 and 1080 cm^{-1} . Moreover, the whole envelope of ν_3^s modes in the Mg- salt is broader as compared to that of the other salts. These observations indicate that the crystalline field strength perturbing the symmetry of the SO_4^{2-} ion in the Mg- salt is different from that in the Ni- and Co-salts. In addition to the above noted components of ν_3^s , a weak band has also been observed respectively at 1060, 1065 and 1050 cm^{-1} in the spectra of Ni-, Co- and Mg- salts in the same envelope. But this band shows a behaviour quite different from these components and has thus been assigned to the $\nu_2^s + \nu_4^s$ combination mode.

Table 3. Frequencies observed in the infrared spectra of the $(\text{NH}_4)_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M}'' = \text{Ni, Co or Mg}$) and their assignments

$(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	Assignments
3520	3520	3530	$\nu_1^w + \nu_L$
3460	3475	3470	ν_3^w III
3425	3430	3400	ν_1^w III
3330	3355	3355	ν_3^w II
3250	3300	3305	ν_1^w II/ ν_3^w I
3220	3235	3255	ν_1^w I
3170	—	3205	$2\nu_2^w$
3120	3175	3140	$\nu_1^w - \nu_L/\nu_3^w + \nu_L$
3070	3085	3080	ν_3^n
—	3025	3035	ν_1^n
2980	2950	2975	$2\nu_4^n$
2855	2870	2870	
—	2420	2430	$\nu_2^w + \nu_r^w$ II
2220	2230	2240	$2\nu_5^s$
2115	2120	2120	$\nu_1^s + \nu_3^s$
2050	2045	2045	$\nu_3^n + \nu_6^n$
1810	1820	1815	$\nu_4^n + \nu_6^n$
1765	1760	1765	$\nu_3^s + \nu_4^s$
1715	1710	1715	ν_2^n
1680	1680	1690	
—	1645	1645	ν_2^w
1590	—	1590	
1466	1475	1470	ν_4^n
1432	1438	1435	
1405	1407	1404	$\nu_1^s + \nu_2^s$
1200	1200	1200	$2\nu_4^s$
1145	1140	1140	ν_3^s
1095	1092	1100	
—	—	1080	
1060	1065	1050	$\nu_2^s + \nu_4^s$

Table 3. (Contd.)

$(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	Assignments
983	983	984	ν_1^s
865	830	805	ν_r^w I
825	800	770	ν_r^w II
760	740	745	ν_w^w I
735	720	715	ν_w^w II
695	690	680	ν_r^w I
660	660	655	ν_r^w II
635	630	635	ν_4^s
616	613	614	
570	570	580	ν_r^w III
550	550	550	ν_w^w III
497	500	510	ν_r^w III
460	458	455	ν_2^s
428	432	—	
400	380	425	ν_3^c
370	365	405	
365	350	390	
330	350	350	†
305	310	320	
290	290	310	
255*	253*	245*	ν_4^c

ν_4^s represents the libratory mode of NH_4^+ ion.

†overtones and combination bands of lattice modes.

*The values taken from the spectra recorded on PE-580 infrared spectrophotometer.

The IR active triply degenerate ν_4^s mode of this ion in the free state appears around 612 cm^{-1} . In the spectra of the Ni-, Co- and Mg- salts, we observe a sharp band respectively at 616, 613 and 614 cm^{-1} along with a shoulder at 635, 630 and 635 cm^{-1} in the same envelope in the respective spectra. Except these bands, all other bands falling in this region are broad which is the characteristic of the libratory modes of H_2O molecule. Hence only these two bands may be assigned to the split components of ν_4^s mode. On the basis of factor group analysis, the IR forbidden doubly degenerate ν_2^s mode is also made IR active. But such a mode must appear with a weak intensity unless there is an interaction with the other modes falling

nearby. In our spectra of the Ni- and Co- salts, two weak bands have appeared respectively at 460 and 428 and at 458 and 432 cm^{-1} whereas in that of the Mg-salt only one band at 455 cm^{-1} could be observed. The other mode might have been obscured by the internal modes of the complex which have appeared very intense in this spectrum. Here the higher frequency band may unambiguously be assigned to the ν_2^s mode. It is surprising that even in the Raman spectra of the single crystal of these compounds we could not get ν_2^s as a doublet. However, the sharp structure of these bands compels us to assign this lower frequency band also to ν_2^s mode only and not to any overtone and combination mode. The splitting may be explained as arising due to the correlation field splitting.

The appearance of ν_2^s mode in our spectra indicates that the sulphate-tetrahedron is angularly distorted and that of ν_1^s predicts that it does have a linear distortion. The comparison of the corresponding intensities of ν_1^s and ν_2^s in the respective spectra shows that the SO_4^{2-} tetrahedron in the Mg-salt^t, which shows more intense bands, is more distorted as compared to those of the Ni- and Co- salts.

While coming to the internal modes of NH_4^+ ion which also has a T_d symmetry in free state, we observe that the N-H stretching and ν_2^n mode regions give a complicated appearance due to the overlapping with the OH stretching and ν_2^n (bending) modes respectively. The stretching region has been resolved into an optimum number of Lorentzian-shaped bands (not shown in figure 2). The N-H stretching (ν_1^n and ν_3^n) and the ν_2^n modes in these spectra have been sorted out by a comparison of the IR spectra of the corresponding isostructural $\text{K}_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ salts (Singh *et al*, unpublished) and their parent metal sulphate $\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Jain 1976; Janik *et al* 1969; Jager and Schaack 1973) and help has also been taken of their free state values. Therefore, the bands at 3085 and 3025 cm^{-1} and at 3080 and 3035 cm^{-1} respectively in the spectra of the Co- and Mg- salts have been assigned respectively to the ν_3^n and ν_1^n modes and a band at 3070 cm^{-1} in the spectrum of the Ni-salt to the ν_2^n mode. The bands at 1715 and 1680 cm^{-1} , 1710 and 1680 cm^{-1} and 1715 and 1690 cm^{-1} respectively in the spectra of the Ni-, Co- and Mg- salts have been assigned to the ν_2^n mode.

The ν_4^n mode of this ion falls in an isolated frequency region 1480–1400 cm^{-1} . In all the three spectra, we have observed three bands in this region. A band at 1405, 1407 and 1404 cm^{-1} in the respective spectra shows an abnormal behaviour on changing the concentration of the sample in the pellet and has thus been assigned to the combination of ν_1^n with ν_2^s . The remaining bands at 1466 and 1432 cm^{-1} , 1475 and 1438 cm^{-1} and at 1470, 1435 cm^{-1} in the respective spectra may unambiguously be assigned to the two split components of the ν_4^n mode. These assignments are further supported by the bands observed very nearly at the same frequencies and separations in their Raman spectra (Ananthanarayanan 1962).

The appearance of IR forbidden ν_1^n and ν_2^n modes predicts that the T_d symmetry of NH_4^+ ion is distorted linearly as well as angularly. Simply on the basis of their intensities it cannot be concluded as to which type of distortion is more prominent as ν_1^n has more enhanced intensity than expected due to some kind of interaction with the nearby bands whereas ν_2^n has no such interaction. The splitting of ν_4^n mode

into two components also confirms the distortion of NH_4^+ tetrahedron. On the basis of the relative intensities, it has also been inferred that the tetrahedron is more distorted in the Mg- salt. These observations are consistent with the crystal structure data.

The broadness and smaller peak intensity of most of the bands of NH_4^+ ion as compared to those of the corresponding modes of SO_4^{2-} ion can be understood in terms of the anharmonicities of the force fields of NH_4^+ and SO_4^{2-} ions of which the former being more anharmonic than the latter.

4.4 Internal modes of H_2O molecules

In these spectra the OH and NH stretching regions overlap with each other. The bands due to NH_4^+ ion have already been sorted out. The remaining bands may be attributed to H_2O molecules including their overtones and combination bands. There are three types of water molecules in each salt and the hydrogen bonding is different in all the three types of water molecules in a particular salt. Thus the bands belonging to different types of water molecules have been assigned on the basis of the relation between the $O^W\text{-H}\dots O'$ (where O^W belongs to the H_2O molecule and O' to the SO_4^{2-} ion) distance and the OH stretching frequency given by Nakamoto *et al* (1955). In these salts the water molecules (H_2O III) with largest $O^W\text{-H}\dots O'$ distance i.e., with the weakest hydrogen bond strength are symmetric (Grimes *et al* 1963; Margulis and Templeton 1962; Montgomery and Lingafelter 1964). Thus the OH stretching modes due to this type of water molecules will have the smallest frequency shift from their respective free state values. The symmetric type of water molecule will also obey Glew's relation (Glew 1968) between ν_3^w and ν_1^w frequencies. In the spectra of the Ni-, Co- and Mg-salts, we have observed the bands respectively at 3460, 3425 cm^{-1} ; 3475, 3430 cm^{-1} and 3470, 3400 cm^{-1} which have the lowest frequency shift from their free state values and also satisfy Glew's relation. Therefore, these bands may unambiguously be assigned respectively to the ν_3^w and ν_1^w modes of the symmetric type of water molecule (H_2O III). The remaining two types of H_2O molecules are asymmetric, the one with the smallest $O\text{-H}\dots O'$ distance has been denoted by H_2O I while the remaining type of molecule by H_2O II.* The bands corresponding to the ν_1^w and ν_3^w modes of these water molecules (H_2O I and H_2O II) have been assigned on the basis of the characteristic downward shift of their frequencies, from their free state values, on increasing the strength of hydrogen bonding (table 3).

In the bending mode region of H_2O , two weak bands besides the bands due to ν_2^n mode have been observed at 1765 and 1590 cm^{-1} in the Ni-salt and at 1760 and 1645 cm^{-1} in the Co-salt and three bands at 1765, 1645 and 1590 cm^{-1} in the Mg-salt. In view of the strength of hydrogen bonding and the metal-oxygen coordination, only the band at 1590 cm^{-1} in the Ni-salt and at 1645 cm^{-1} in the Co-salt and the

*In the Ni-salt the average hydrogen bond lengths for H_2O I, H_2O II and H_2O III are respectively 2.7505, 2.7605 and 2.320 Å due to Montgomery and Lingafelter (1964) and 2.700, 2.755 and 2.805 Å due to Grimes *et al* (1963) and those in the Mg-salt for H_2O I, H_2O II and H_2O III are 2.739, 2.745 and 2.818 Å respectively (Margulis and Templeton 1962).

bands at 1645 and 1590 cm^{-1} in the Mg-salt have been assigned to the ν_2^w mode and the higher frequency band to the $\nu_3^s + \nu_4^s$ combination. It seems that the bands due to the ν_2^w mode of the three types of water molecules have got overlapped with each other. If not they have appeared so weakly that they were lost in the background of the noise. The modes have appeared weakly due to the coordination of the six water molecules with M^{2+} ion in the formation of the complex $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ and thus a small change in dipole moment might have associated with the bending motion of water molecules. This point may further be substantiated with the appearance of a strong ν_2^w band in the IR spectra of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Gupta 1979) due to seventh water molecule which does not take part in the formation of the octahedron, whereas in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Jain 1976), in which all the water molecules are coordinated to form an octahedron, the ν_2^w mode appears very weakly.

4.5 The libratory modes of H_2O molecules

The assignments of the bands in the region 900-500 cm^{-1} of the spectra of these salts is rather ambiguous. In the Raman and IR studies of the salts, Ananthanarayanan (1963) has assigned the bands observed in this region to the combination bands of the internal modes of the complex, $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$. In the spectra of the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, Jager and Schaack (1973), Janik *et al* (1969) and Jain (1974, 1976) have assigned the bands falling in this region to the libratory modes of H_2O molecules. The spectra of the salts in the present investigation resemble very much with their parent bivalent metal sulphates. Therefore, we are inclined to assign these bands to the libratory modes of H_2O molecules. It is likely that due to scattering losses (low scattering power of H_2O molecule), these bands might have appeared with weak intensity in the previous Raman experiments and had prompted Ananthanarayanan to assign them as overtones and combination bands.

In our spectra, the bands in this region have appeared in two isolated envelopes. A close proximity of the hydrogen bond strengths of H_2O I and H_2O II molecules along with the weak hydrogen bonding for H_2O III molecule have prompted us to assign the libratory modes falling in the first envelope to belong to H_2O I and H_2O II whereas those falling in the lower frequency envelope to the H_2O III molecules. Many criteria are in vogue for the assignments of bands due to rocking and wagging motion of the H_2O molecules. Miyazawa (1961) has shown that the intensity of the wagging mode of H_2O must be about 2.7 times the intensity of the rocking mode. This view gets further support from Srivastava *et al* (1978) who have shown that the above intensity is still larger (≥ 3.0). Jain (1975) showed that in the inorganic salt hydrates with linear or in-plane bent H-bonds, the rocking mode has a frequency greater than that of the wagging mode whereas the reverse is the case with the bifurcated H-bonds. Many authors (Tayal *et al* 1978; Lutz *et al* 1971; Nakagawa and Shimanouchi 1964) have corroborated this view and have ascertained $\nu_{\text{rock}} > \nu_{\text{wag}}$ in the spectra of many hydrates. From the crystal structure data of these salts, we see that none of the hydrogen bonds is bifurcated. Therefore, the rocking mode of each H_2O molecule will have a frequency greater than the corresponding wagging mode frequency. In our spectra of the Ni-, Co- and Mg-salts, we have observed that the bands at 760, 735 cm^{-1} ; 740, 720 cm^{-1} and 745, 715 cm^{-1} are about twice as intense as the bands at 865, 825 cm^{-1} ; 830, 800 cm^{-1} and 805, 770 cm^{-1} respectively in the spectra of the corresponding salts. Thus taking into consideration the

above criteria, we have assigned the higher frequency bands, i.e., 865, 825 cm^{-1} ; 830, 800 cm^{-1} and 805, 770 cm^{-1} to the rocking modes and the lower frequency bands to the wagging modes of the H_2O molecules in the respective salts of which the first band in each group will belong to H_2O I in view of the strength of H-bonding. A weak band observed at 695, 690 and 680 cm^{-1} respectively in the spectra of the Ni-, Co- and Mg-salts has been assigned to the twisting mode of H_2O I while that at 660, 660 and 655 cm^{-1} in the respective spectra to the twisting mode of H_2O II molecule.

Two bands in the second envelope appear very close to each other with very nearly the same intensity at 570 and 550 cm^{-1} ; 570 and 550 cm^{-1} and 580 and 550 cm^{-1} . The former band in each pair may be assigned to the rocking and the latter to the wagging modes of H_2O III molecules. The first band which should otherwise have appeared with an intensity lower than that of the wagging mode, might have borrowed intensity from the ν_2^s mode and has shifted towards the lower frequency side due to the interaction with the ν_2^s mode. A very weak band in the corresponding spectra at 497, 500 and 510 cm^{-1} has been assigned to the twisting mode of H_2O III molecule.

4.6 Internal modes of the complex

The metal-aquo complex $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ occupies lattice positions like a single molecular unit in several crystal hydrates. Considering H_2O molecule as a single unit of mass 18 a.m.u. the complex may be regarded to belong to the O_h symmetry (Jain and Bist 1975). For the designation of the internal modes of the complex, we have used the customary notation (Herzberg 1960) rather than that used by Ananthanarayanan and Danti (1964). Therefore, only the ν_3^c and ν_4^c both belonging to F_{1u} will be IR active under the perfect O_h symmetry and ν_6^c (F_{2u}) will be made IR active under the site group analysis (table 1). Thus the complete assignment of ν_i^c 's for $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ on the basis of the theoretical analysis given by Ananthanarayanan and Danti (1964) will be

$$\nu_1^c (A_{1g}) 397, \nu_2^c (\text{Eg}) 221, \nu_3^c (F_{1u}) 410, \nu_4^c (F_{1u}) 257,$$

$$\nu_5^c (F_{2g}) 217 \text{ and } \nu_6^c (F_{2u}) 148.$$

In our IR spectra of the Ni-, Co- and Mg-salts, we have observed quite an intense band centered respectively at 370, 365 and 405 cm^{-1} with two more bands in the same envelope at 400 and 365 cm^{-1} , 380 and 350 cm^{-1} and 425 and 390 cm^{-1} . We have assigned all these three bands to the ν_3^c mode. Its degeneracy might have been lifted due to lowering in symmetry of the octahedron of the complex and it may also be expected due to coupled motion of different $[\text{M}''(\text{H}_2\text{O})_6]^{2+}$ ions in the unit cell. Three more bands observed at frequencies lower than those of the ν_3^c mode are very weak and may be assigned to the overtone and combination modes of some lattice modes. The ν_4^c falls around 250 cm^{-1} . Thus for a clear indication of any ν_4^c band one should go beyond the range of our instrument (250 cm^{-1}). We have therefore, recorded the spectra on PE-580 infrared spectrophotometer as well as on Polytech FIR-30 for the assignment of this mode in the region below 300 cm^{-1} . In the respective spectra we have observed this band at 255, 253 and 245 cm^{-1} respectively.

Various overtones and combination bands have also been dealt with and their assignments have been given in table 3. Some of them have appeared with an appreciable intensity which may be due to some sort of interaction of one of its factor group components with the corresponding component of a fundamental lying very close to it. The appearance of a medium strong band around 2045 cm^{-1} and an absorption around 1815 cm^{-1} in all the spectra under investigation (at room temperature), which have been assigned respectively to the combination modes $\nu_2^n + \nu_6^n$ and $\nu_4^n + \nu_6^n$ is a clear indication of the absence of rotation of NH_4^+ ion in these salts (Waddington 1958; Dunsmuir and Lane 1972). In each case the NH_4^+ ion is hydrogen bonded (Oxton *et al* 1975). These observations are consistent with the crystal structure data.

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