

## The infrared and laser Raman spectra of $K_2Zn(SO_4)_2 \cdot 6H_2O$

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**Abstract.** The Raman spectra of the single crystal of  $K_2Zn(SO_4)_2 \cdot 6H_2O$  belonging to  $C_{2h}^{25}$  space group in the 40-1200  $cm^{-1}$  region in different scattering geometries and the IR spectra of the microcrystalline salt in the 1500-50  $cm^{-1}$  region have been reported. The dynamics of the crystal has been described in terms of 186 phonon modes under the unit cell approximation. The weak bands in the region 400-900  $cm^{-1}$  have been assigned to the libratory modes of  $H_2O$  molecules in contradiction to the assignments reported by Ananthanarayanan. The ambiguities existing in the literature about the assignments of  $\nu_2^g$  and  $\nu_3^g$  modes of  $[Zn(H_2O)_6]^{2+}$  have also been removed. The translatory and libratory modes of different units of the crystal have been identified and assignments are made using far IR and Raman data on various isomorphous tutton salts.

It has been inferred that both  $SO_4^{2-}$  tetrahedron and  $[Zn(H_2O)_6]^{2+}$  octahedron undergo linear as well as angular distortions from their free state symmetries in the crystal.

**Keywords.** Raman spectra; infrared spectra; tutton salts;  $K_2Zn(SO_4)_2 \cdot 6H_2O$ ; libratory modes; metal-aquo complex; lattice modes.

### 1. Introduction

The tutton salts have been a subject of many infrared (Ananthanarayanan 1968; Brown and Ross 1970; Campbell *et al* 1970; Singh *et al* 1980) and Raman studies (Ananthanarayanan 1961, 1962, 1963, 1968; Brown and Ross 1970) in the past. However, none of these studies is complete and the assignments of some of the bands are ambiguous. Ananthanarayanan has recorded the Raman spectra of some of the tutton salts in one geometry only on  $E_1$  quartz spectrograph using Hg arc as the source of excitation. A critical evaluation of his Raman study has led us to believe that he has wrongly assigned the bands falling in the region 400-900  $cm^{-1}$  to the multiphonon modes and also that his group theoretical analysis, giving the symmetry classification of phonon modes, is not correct. Some of his results and interpretation of the data dealing with the assignments of the bands pertaining to the  $SO_4^{2-}$  and  $[M''(H_2O)_6]^{2+}$  complex, where  $M''$  is a bivalent cation, are also at variance with those of Brown and Ross (1970). Campbell *et al* (1970) also could not resolve and distinguish fully the libratory modes of  $H_2O$  molecules. Therefore, the IR and laser excited single crystal Raman spectra of  $K_2Zn(SO_4)_2 \cdot 6H_2O$  (hereafter abbreviated as  $kzsh$ ) in the region 40-1200  $cm^{-1}$  have been reexamined.

## 2. Crystal structure and optical properties

The bimolecular unit cell of KZSH, a positive biaxial crystal (Canterford and Ninio 1975), belongs to  $C_{2h}^5$  space group of the monoclinic class. The bivalent metal cation, Zn, occupies the centre of inversion and is surrounded octahedrally by six water molecules to form a complex  $[Zn(H_2O)_6]^{2+}$  which behaves dynamically as a quasi-molecule (Ananthanarayanan 1963; Singh *et al* 1980). There are three types of inequivalent  $H_2O$  molecules at three different  $C_1$  sites of the crystal. These have been designated as  $H_2O$  I,  $H_2O$  II, and  $H_2O$  III in the decreasing order of their H-bond strengths for our convenience. All other atomic and molecular groups are at general positions.

As in the monoclinic class of crystals, the indicatrix —  $Y$  is  $\parallel$  to the crystallographic  $b$ -axis, the Loudon's (1964) Raman tensors developed with respect to the axes ( $OX_1$ ,  $OX_2$ ,  $OX_3$ ) defined by Nye (1957) may, therefore, be expressed in terms of the indicatrix axes simply by making the similarity transformations\* (Brenblut *et al* 1971). The desired Raman tensors thus come out to be

$$A_{g'} = \begin{bmatrix} a \cos^2 \theta + c \sin^2 \theta - d \sin 2\theta & 0 & (a-c) \sin \theta \cos \theta + d \cos 2\theta \\ 0 & b & 0 \\ (a-c) \sin \theta \cos \theta + d \cos 2\theta & 0 & a \sin^2 \theta + c \cos^2 \theta + d \sin 2\theta \end{bmatrix}$$

and

$$B_{g'} = \begin{bmatrix} 0 & e \cos \theta - f \sin \theta & 0 \\ e \cos \theta - f \sin \theta & 0 & e \sin \theta + f \cos \theta \\ 0 & e \sin \theta + f \cos \theta & 0 \end{bmatrix}.$$

where the symbols have their usual meanings.

## 3. Experimental

Large single crystals of KZSH were grown by slow evaporation of the aqueous saturated solution of analar grade  $K_2SO_4$  and  $ZnSO_4 \cdot 7H_2O$  in equimolar ratios at room temperature ( $25^\circ C$ ). The indicatrix axes of the single crystal were examined under the polarizing microscope. Subsequently, the crystal was cut into a rectangular slab ( $8 \times 5 \times 3 \text{ mm}^3$ ) with its faces normal to the indicatrix axes. The faces were ground with 800 grade carborandum and then polished with aluminium oxide powder and finally with a soft cloth.

The Raman spectra were recorded in five different polarization geometries<sup>†</sup>, viz.,  $Z(XX)Y$ ,  $Z(YX)X$ ,  $X(ZZ)Y$ ,  $X(ZX)Y$ , and  $Z(YZ)X$  using  $90^\circ$  geometrical arrangement on Spex Ramalog model-4 Raman spectrometer attached with a Spex model 1401 double monochromator. The  $5145 \text{ \AA}$  line of the  $Ar^+$  laser was used to excite the spectra at a power of about 200 mW. The photon count and time constant were

\*The results have been repeated here because our elements of the transformed Raman tensor  $A_{ij}$  differ from those reported by Brenblut *et al* (1971).

†For the designation of different polarization geometries, we have used the standard notation given by Porto *et al* (1966).

kept at  $10^3$  and 2.5 sec, respectively. The infrared spectrum in the  $1500\text{--}250\text{ cm}^{-1}$  region was recorded on PE-521 IR spectrophotometer while in the  $400\text{--}50\text{ cm}^{-1}$  region on Polytec-FIR-30 spectrophotometer in the KBr and polyethylene matrices, respectively.

#### 4. The factor group analysis

The dynamics of KZSH crystal can be described in terms of 186 zone centre ( $q = 0$ ) phonon modes including 3 acoustical ones. These modes have been classified in table 1 in terms of internal and libratory modes of  $H_2O$  molecules,  $SO_4^{2-}$  ion and the  $Zn(H_2O)_6]^{2+}$  complex and of the translatory modes of last two units and  $K^+$  ion. The translatory modes of  $H_2O$  molecules and Zn-atoms have been accounted for by the modes of the complex. The notations  $t$ ,  $l$  and  $\nu$  have been used respectively for the translatory, libratory and internal modes. To distinguish the modes due to  $H_2O$  molecules,  $SO_4^{2-}$ ,  $K^+$  and  $[Zn(H_2O)_6]^{2+}$  complex, respectively, the superscripts  $w$ ,  $s$ ,  $k$  and  $c$  have been used.

#### 5. Results and discussion

##### 5.1 The observed spectra: the phonon frequencies

The observed Raman spectra of the single crystal of KZSH in  $Z(XX)Y$ ,  $Z(YY)X$ ,  $X(ZZ)Y$ ,  $X(ZX)Y$  and  $Z(YZ)X$  scattering geometries have been shown in figure 1. The IR spectra of polycrystalline KZSH in the regions  $250\text{--}1500\text{ cm}^{-1}$  and  $50\text{--}400\text{ cm}^{-1}$  have been depicted respectively in figures 2a and 2b. The observed Raman frequencies corresponding to  $A_{g-}$  and  $B_{g-}$  symmetries along with their visually estimated

Table 1. The factor group analysis of  $K_2Zn(SO_4)_2 \cdot 6H_2O$  crystal

		$A_g$	$B_g$	$A_u$	$B_u$	Total
Translatory Modes	$t^k$	3	3	3	3	12
	$t^s$	3	3	3	3	12
	$t^c$	0	0	3	3	6
Libratory Modes	$l^w$	9	9	6+3*	6+3*	36
	$l^s$	3*	3*	3*	3*	12
	$l^c$	3*	3*	0	0	6
Internal Modes	$\nu^w$	9	9	9	9	36
	$\nu^s$	9	9	9	9	36
	$\nu^c$	6	6	6+3*	6+3*	30
Total		45	45	48	48	186

Here the superscripts  $w$ ,  $s$ ,  $c$  and  $k$  refer to the modes of water,  $SO_4^{2-}$ , the complex  $[Zn(H_2O)_6]^{2+}$  and potassium ion respectively.

\*The modes that have become active under the factor group analysis.

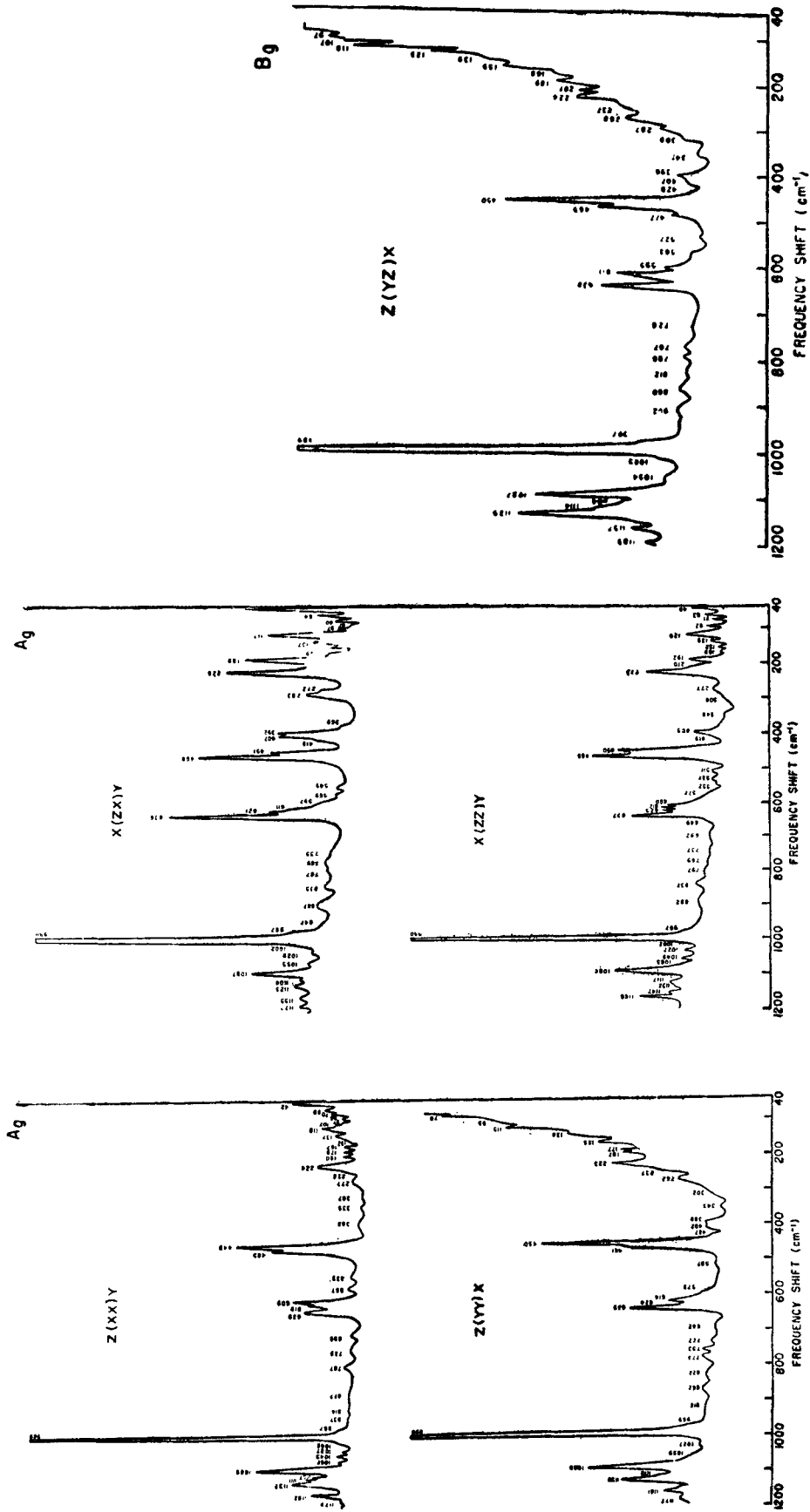


Figure 1. The Raman Spectra of the single crystal of  $K_2Zn(SO_4)_2 \cdot 6H_2O$  in  $Z(XX)Y$ ,  $Z(YY)X$ ,  $X(ZZ)Y$ ,  $X(ZX)X$  and  $Z(YZ)X$  polarizations.

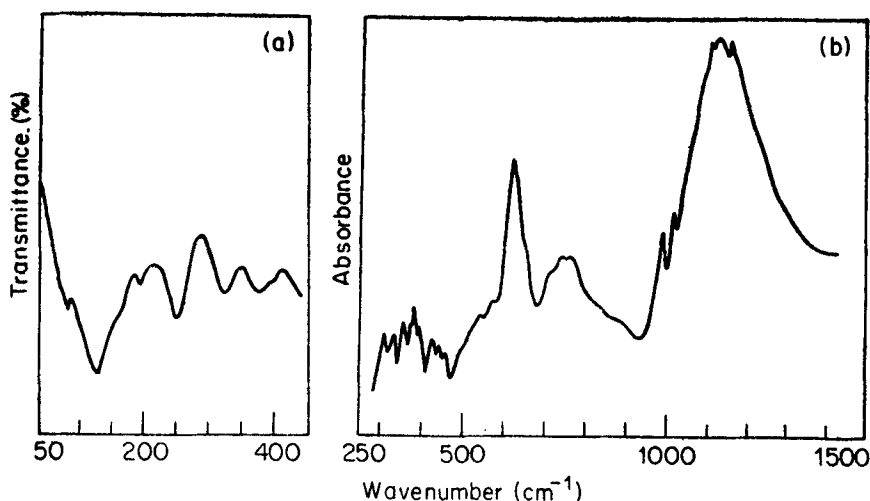


Figure 2. (a) The far-IR and (b) the IR spectra of micro crystalline sample of  $K_2Zn(SO_4)_2 \cdot 6H_2O$ .

relative intensities (in brackets) on an arbitrary scale and the infrared frequencies have been given in table 2 along with their assignments. The feeble bands have been marked by the symbol *f*. The Raman frequencies of sharp and well resolved bands are accurate upto  $\pm 1 \text{ cm}^{-1}$ , whereas those of weak, diffuse and unresolved bands upto  $\pm 10 \text{ cm}^{-1}$ . The running suffixes 1, 2, 3, ... have been used for the internal modes and *r*, *w* and *t* respectively for the rocking, wagging and twisting libratory modes of  $H_2O$  molecules. Other notations are given in § 4.

### 5.2 Internal modes of $SO_4^{2-}$

The  $SO_4^{2-}$  in KZSH occupies  $C_1$  site (Canterford and Ninio 1975). The consequences of the lowering of its site symmetry are two-fold: first, the IR inactive  $\nu_1^s (A_1)$  and  $\nu_2^s (E)$  modes become IR active and second, the degeneracies of the degenerate modes are lifted (table 1). The discussion that follows fully corroborates the above facts.

In the Raman spectrum, the  $\nu_1^s$  mode has appeared as the strongest band around  $990 \text{ cm}^{-1}$  in all the polarizations. It is, however, surprising to note that in IR, we have observed two weak and sharp bands at 983 and  $1008 \text{ cm}^{-1}$ . Following our previous (Singh *et al* 1980) and other related studies (Ananthanarayanan 1961, 1962), the  $983 \text{ cm}^{-1}$  band in IR may unambiguously be assigned to  $\nu_1^s$  mode. The other band may arise due to one of the three reasons, *viz.* (i) the correlation field splitting, (ii) the multiphonon mode and (iii) the presence of two types of  $SO_4^{2-}$  ions in the crystal. The structure and the intensity of the  $1008 \text{ cm}^{-1}$  band does not support the second possibility. A comparison of the infrared spectrum of KZSH with that of CuK-salt which possesses two types of  $SO_4^{2-}$  ions (Shashi Prabha and Khanna 1981) does not support the existence of two types of  $SO_4^{2-}$  ions in KZSH. Therefore, the only plausible explanation for the appearance of this band may be the correlation field splitting.

The doubly degenerate  $\nu_2^s$  and the triply degenerate  $\nu_4^s$  modes have been observed in the Raman as well as in the infrared spectrum with their degeneracies partially or completely removed. These observations confirm the fact that the symmetry of

**Table 2.** The frequencies and intensities (in brackets) of the bands observed in the Raman (five polarizations) and the IR spectra of  $K_2Zn(SO_4)_2 \cdot 6H_2O$  with their assignments.

$A_g$				Mean $A_g$	$B_g$	IR	Assignments
$Z(XX)Y$	$Z(YY)X$	$X(ZZ)Y$	$X(ZX)Y$		$Z(YZ)X$		
42(4)	—	45(2)	46(4)	44	—	—	$t^s$
58(4)	—	—	—	58	—	56	multiphonon modes
—	—	63(1)	64(2)	64	—	70	
70(1)	—	71(1)	—	71	—	78	
—	76(1)	—	80(1)	78	—	78	$l^s$
97(1)	99(2)	97(2)	97(f)	98	97(f)	88	$t^s$
118(5)	115(4)	120(4)	117(9)	118	118(1)	120	$t^s$
137(3)	134(3)	139(1)	137(4)	137	139(f)	133	$t^k$
152(1)	155(3)	152(1)	152(f)	153	159(2)	150	$l^s$
167(1)	—	165(f)	169(2)	167	168(f)	170	$l^s$
190(1)	187(1)	192(4)	189(7)	190	189(7)	—	$\nu_g^f$
—	—	—	—	—	—	196	$t^k$
—	—	210(2)	212(1)	211	207(1)	—	$\nu_g^f$
224(9)	223(6)	225(11)	225(15)	224	226(2)	—	$\nu_g^f/t^k$
—	—	—	—	—	—	255	$\nu_g^f$
—	262(7)	—	272(1)	267	268(2)	—	$\nu_g^f$
277(3)	—	277(4)	283(8)	279	287(1)	—	
—	—	—	—	—	—	326	$K^+ \dots O^-(SO_4^{2-})$
—	—	—	—	—	—	374	
—	—	—	—	—	—	384	
—	—	—	—	—	—	398	
382(2)	388(3)	—	392(7)	387	396(3)	—	$2\nu_g^f$
—	402(3)	405(6)	407(6)	405	407(3)	—	$\nu_g^f$
—	—	—	—	—	—	423	—
449(12)	450(15)	450(10)	451(6)	450	450(16)	445	$\nu_g^f$
463(8)	461(6)	465(10)	464(14)	463	465(6)	461	
—	507(f)	511(1)	—	509	477(2)	495	$l_r^w$ III
539(2)	—	537(1)	—	538	527(f)	538	$l_r^w$ III
567(2)	575(2)	577(2)	569(f)	572	563(1)	570	$l_r^w$ III
—	—	600(4)	597(4)	599	595(2)	—	$\nu_g^f + \nu_g^f$
609(6)	614(7)	612(4)	611(4)	612	611(5)	—	$\nu_g^f$
619(4)	624(3)	625(4)	621(6)	622	—	619	
639(7)	635(10)	637(10)	636(16)	637	638(7)	630	
699(1)	682(3)	692(3)	—	691	—	700	$l_r^w$ I/ $l_r^w$ II
739(3)	727(1)	737(f)	735(f)	735	726(f)	740	$l_r^w$ II
—	773(2)	769(f)	769(2)	770	767(1)	762	$l_r^w$ I
—	822(2)	837(1)	835(2)	831	820(f)	820	$l_r^w$ II
877(f)	862(2)	882(1)	887(4)	879	880(2)	870	$l_r^w$ I
989(20)	990(28)	990(24)	990(32)	990	989(30)	983	$\nu_g^f$
—	—	—	—	—	—	1008	
1027(1)	1027(1)	1027(1)	1029(1)	1028	—	—	$\nu_g^f + t^s$
1045(1)	—	1045(1)	—	1045	—	—	
1062(1)	1059(4)	1065(1)	1055(2)	1060	1054(2)	1072	$\nu_g^f + \nu_g^f$
1089(9)	1089(14)	1084(5)	1087(6)	1087	1087(6)	1092	$\nu_g^f$
1107(1)	—	—	—	—	1104(1)	—	$\nu_g^f + \nu_g^f$
1111(4)	1113(2)	1117(2)	—	1114	1114(2)	—	$\nu_g^f + t^s$
1132(6)	1133(6)	1132(2)	1123(2)	1130	1129(10)	1112	$\nu_g^f$
1162(3)	1161(2)	1166(3)	1155(2)	1161	1157(2)	1142	
1175(f)	1177(1)	—	1177(1)	1177	1185(1)	1165	

$SO_4^{2-}$  has been lowered. In the  $\nu_3^s$  mode region of Raman spectrum, Brown and Ross (1970) have reported only two bands lying very close to each other at 1083 and 1086  $cm^{-1}$  whereas Ananthanarayanan (1968) had observed four bands. But we have observed as many as six bands in each of the  $A_g^-$  and  $B_g^-$  polarizations. All the bands in almost all the polarizations are sharp and well resolved.

Since, the crystal under study is centro-symmetric, the observed splitting of  $\nu_3^s$  mode in the Raman spectrum could neither be accounted for due to the perturbation by the radiation field nor due to the contribution of electro-optic effect (Turrell 1972). However, on the basis of infrared spectrum in which we have observed three strong bands at 1092, 1112 and 1142  $cm^{-1}$ , we may assign the bands with mean frequencies of 1087, 1114 and 1130  $cm^{-1}$  in the  $A_g^-$  polarization and of 1087, 1114 and 1129  $cm^{-1}$  in the  $B_g^-$  polarization of the Raman spectrum to the  $\nu_3^s$  mode. But the band at 1114  $cm^{-1}$  in all the polarizations has appeared with an intensity which is incompatible with a fundamental band. Instead the band at 1161  $cm^{-1}$  ( $A_g^-$ ) and 1157  $cm^{-1}$  ( $B_g^-$ ) has appeared with quite an appreciable intensity in all but one polarizations. Thus the bands at 1087 (1087), 1130 (1129) and 1161 (1157)  $cm^{-1}$  in the  $A_g^-$  ( $B_g^-$ ) polarization of the Raman spectrum have been associated with the  $\nu_3^s$  fundamental mode.

### 5.3 Internal modes of $[Zn(H_2O)_6]^{2+}$

In KZSH, the complex  $[Zn(H_2O)_6]^{2+}$  occupies  $C_i$  site. Accordingly, the degeneracies of  $\nu_2^c$  ( $E_g$ ),  $\nu_3^c$  ( $F_{1u}$ ),  $\nu_4^c$  ( $F_{1u}$ ) and  $\nu_5^c$  ( $F_{2g}$ ) degenerate modes have been lifted and the IR as well as Raman inactive  $\nu_6^c$  ( $F_{2u}$ ) mode has been made infrared active (Singh *et al* 1980). The non-degenerate  $\nu_1^c$  mode falls around 400  $cm^{-1}$  (Ananthanarayanan 1963; Brown and Ross 1970; Nakagawa and Shimanouchi 1964) in the Raman spectrum. In our Raman spectrum, we have observed two bands of moderate intensities in most of the polarizations. But, according to the factor group analysis (Singh *et al* 1980) only one band could be associated with each of the  $A_g^-$  and  $B_g^-$  polarizations. Therefore, the band with mean frequency of 405  $cm^{-1}$  in the  $A_g^-$  polarization and of 407  $cm^{-1}$  in the  $B_g^-$  polarization has been associated with the  $\nu_1^c$  mode (table 2). Ananthanarayanan had also assigned only one band at 399  $cm^{-1}$  to the  $\nu_1^c$  mode in his unpolarized data. The remaining band in our observed spectra with mean frequency of 387  $cm^{-1}$  and 396  $cm^{-1}$  in the respective polarizations might be due to the first overtone of  $\nu_6^c$  mode or due to some other multiphonon mode.

In the IR spectrum, two strong bands at 374 and 384  $cm^{-1}$  have been associated with the triply degenerate  $\nu_3^c$  mode. The partial lifting of its degeneracy reveals that the complex in this crystal has a symmetry lower than  $O_h$ .

The triply degenerate  $\nu_4^c$  mode ( $F_{1u}$ ) has been assigned by Ananthanarayanan (1963, 1970) at 272  $cm^{-1}$  whereas by Brown and Ross (1970) at 264  $cm^{-1}$ . But no band could be observed in our IR spectrum in between 260–275  $cm^{-1}$ . So the strong band observed at 255  $cm^{-1}$  in our IR spectrum may be associated with the  $\nu_4^c$  mode.

Actually, the main ambiguity is over the assignments of  $\nu_2^c$  and  $\nu_5^c$  modes. Ananthanarayanan (1961) and Ananthanarayanan and Danti (1966) has assigned  $\nu_5^c$  at a frequency higher than that of  $\nu_2^c$  whereas Brown and Ross (1970) have done it in the reverse way. Lafont (1959) observed  $\nu_2^c$  mode only. These authors have supported their data by their own theoretical calculations. However, it is a well established fact that the stretching modes always fall at frequencies higher than those of the bending ones and moreover the former, in general, appear stronger than the latter ones.

Therefore,  $\nu_1^c$ ,  $\nu_2^c$  and  $\nu_3^c$  (stretching modes) should appear at frequencies higher than those of  $\nu_4^c$ ,  $\nu_5^c$  and  $\nu_6^c$  (angular deformation) modes and also with greater intensities.

As  $\nu_4^c$  mode has already been assigned at  $255\text{ cm}^{-1}$ , the  $\nu_2^c$  mode must have a frequency higher than  $255\text{ cm}^{-1}$  and also  $\nu_5^c < \nu_2^c$  in contradiction to Ananthanarayanan's assignment to it around  $200\text{ cm}^{-1}$ . Following the above criteria and the empirical relation  $\nu_5^c = 2/3(\nu_1^c - \nu_2^c)$  given by Yost *et al* (1934), we have attributed the bands with mean frequencies of  $267$  and  $279\text{ cm}^{-1}$  in the  $A_{g-}$  polarization and of  $268$  and  $287\text{ cm}^{-1}$  in the  $B_{g-}$  polarization to the  $\nu_2^c$  mode whereas with mean frequencies of  $190$ ,  $211$  and  $224\text{ cm}^{-1}$  and  $189$ ,  $207$  and  $226\text{ cm}^{-1}$  in the respective polarizations to the  $\nu_5^c$  mode.

The  $\nu_6^c$  mode ( $F_{2u}$ ) which is allowed *via* the factor group selection rules in IR, may appear as a weak band in the spectrum. Brown and Ross (1970) have assigned it around  $114\text{ cm}^{-1}$  whereas Ananthanarayanan (1963) has located it around  $150\text{ cm}^{-1}$ . But in our IR spectrum, the band corresponding to this mode has most likely been masked by a very strong and broad absorption band spreading from  $100\text{ cm}^{-1}$  to  $170\text{ cm}^{-1}$ .

#### 5.4 The libratory modes of $H_2O$ molecules

The objections raised over the assignments of weak Raman bands falling in the region  $400\text{--}900\text{ cm}^{-1}$  to the multiphonon modes by Ananthanarayanan (1963) have been discussed in our earlier communication (Singh *et al* 1980). After a careful study of the Raman spectrum of this region and comparing it with the corresponding region of infrared spectrum which is quite intense and also on the basis of our earlier study (Singh *et al* 1980) on  $NH_4$ -tutton salts, we have assigned the bands lying in this region to the libratory modes of  $H_2O$  molecules. These assignments are further supported from studies carried on other tutton salts (Campbell *et al* 1970) as well as on other hydrated sulphates, *viz.*  $NiSO_4 \cdot 6H_2O$  (Jain 1976),  $CuSO_4 \cdot 5H_2O$  (Berger 1976),  $NiSO_4 \cdot 7H_2O$  (Gupta 1979). The bands in the Raman spectra have appeared with weak intensities due to the low scattering power of  $H_2O$  molecules and also due to the coordination of  $H_2O$  molecules with Zn atom.

As  $H_2O$  I,  $H_2O$  II and  $H_2O$  III are arranged in the decreasing order of their H-bond strengths, the bands belonging to them in the above order will fall in the decreasing order of the frequencies (Jain 1976).

#### 5.5 Low frequency vibrations: the external lattice modes

In the region below  $200\text{ cm}^{-1}$ , we have observed very sharp and well resolved bands. The spectrum in this region is very rich in the sense that it contains bands belonging to the translatory motions of the  $SO_4^{2-}$ , the  $[Zn(H_2O)_6]^{2+}$  and the  $K^+$  ions as well as due to rotations of the first two units and also due to the H-bond vibrations (Ananthanarayanan and Danti 1966). Under the perfect symmetries of the polyatomic units in the crystal, the rotatory modes are forbidden in the Raman as well as in the infrared spectra (Herzberg 1960). But due to lowering of site symmetries of these units, the rotations of the complex have become active only in the Raman spectra whereas those of  $SO_4^{2-}$  in the Raman and IR spectra simultaneously (table 1).

For the assignments of the libratory and translatory modes of different units, we have used the simple criteria that the translatory modes are strongly mass dependent



while the rotatory modes, on the contrary, are less dependent or almost independent of mass (Takahashi *et al* 1975). The translatory modes are generally weak in the Raman spectra, strong in the IR spectra and broad in the reflection spectra while the libratory modes, on the other hand, are strong in the Raman and weak in the IR spectra provided they (libratory and translatory) are active in both IR and Raman. But in the present case, the libratory modes of  $SO_4^{2-}$  are allowed only through the site group coupling and may thus be observed with very weak intensities in both IR and Raman spectra. The translatory modes which are active in both the spectra, will be observed with appreciable intensity (being more strong in IR) as compared to their libratory counterparts.

The complex is a heavy quasi-molecule, its translatory as well as libratory modes are likely to fall beyond our spectral range and therefore have not been considered in our discussion. Only the translatory modes of  $K^+$  and  $SO_4^{2-}$  alongwith the libratory modes of latter will be discussed below.

In the Raman spectrum, the bands at 78, 153 and 167  $cm^{-1}$  in the  $A_g$ -symmetry and at 159 and 168  $cm^{-1}$  in the  $B_g$  symmetry are weak in intensity. The corresponding bands in the IR spectrum have appeared as weak shoulders at 78, 150 and 170  $cm^{-1}$ . In the IR spectra of the corresponding tutton salts of Mg and Cu, these bands have appeared as weak shoulders at 75, 140 and 184  $cm^{-1}$  and at 80, 146 and 182  $cm^{-1}$ , respectively. The same positions and features of the corresponding bands are also observed in the IR spectra of  $NH_4$ - and Cs-tutton salts of Zn, Cu and Mg. These observations indicate that these bands are weakly dependent on the mass of the cation. Their weak intensities show that they belong to some forbidden transitions. We have, therefore, assigned them to the libratory modes of  $SO_4^{2-}$  ion.

Corresponding to a medium intense band observed around 118  $cm^{-1}$  in the present Raman spectra, a weak band has appeared as a shoulder in the IR spectrum around 120  $cm^{-1}$  and at 122 and 114  $cm^{-1}$  respectively in the  $NH_4$ - and Cs-tutton salts. This band has been assigned by Ananthanarayanan and Danti (1966) to the H-bond bridging vibration. But we do not agree with their assignment because a band having almost the same position has also been observed at 115, 122 and 127  $cm^{-1}$  in the infrared spectra of  $Li_2SO_4$  (Takahashi *et al* 1975),  $K_2SO_4$  (Takahashi *et al* 1975) and  $KAl(SO_4)_2$  (Couchot *et al* 1978) respectively which have no H-bonding. These authors have assigned this band to the oscillations of  $SO_4^{2-}$  ion. Based on the above arguments and accounting for the intensities of observed bands, we are inclined to believe that bands at 118  $cm^{-1}$  in  $A_g$  and  $B_g$  polarizations and at 120  $cm^{-1}$  in the IR are due to a translatory mode of  $SO_4^{2-}$  ion. In the infrared spectrum, the weak intensity of the band may be due to it being masked by the strong translatory mode of  $K^+$  ion which falls close to it.

The other translatory modes of  $SO_4^{2-}$  have been associated with the strong bands observed at 44  $cm^{-1}$  and 98  $cm^{-1}$  in the  $A_g$ - polarization and at 97  $cm^{-1}$  in the  $B_g$ - polarization of the Raman spectra and at 88  $cm^{-1}$  in the infrared spectrum. These assignments are in agreement with the results of the previous studies on sulphates (Takahashi *et al* 1975; Berger 1976; Venkateswarlu *et al* 1975).

A medium intense band at 196  $cm^{-1}$  has appeared in the IR spectrum of  $KZnS$  and a corresponding band at 170  $cm^{-1}$  in the Cs- salt (Singh *et al*—unpublished data). The mass dependence of this band leads us to associate it with the translatory mode of  $K^+$  ion. The strong band observed at 133  $cm^{-1}$  in IR and comparatively weaker bands at 137 and 139  $cm^{-1}$ , respectively in the  $A_g$ - and  $B_g$ -symmetries of the Raman spectra

may also be assigned reasonably to a translatory mode of  $K^+$  ion. In the infrared spectrum, a very strong band has been observed at  $326\text{ cm}^{-1}$  but no corresponding band could be observed in any of the polarizations in the Raman spectra. In the IR spectrum of Cs-tutton salts of Zn, the same band has appeared around  $322\text{ cm}^{-1}$ . Brown and Ross (1970) have also reported a band in their IR spectrum at  $326\text{ cm}^{-1}$  and on the basis of their normal coordinate analysis, they have assigned it to the  $\nu_1^c$  mode. But  $\nu_1^c$  mode is forbidden in IR and active in Raman only and moreover, no corresponding band has been observed in the Raman spectra. Therefore, this band may not be assigned to the  $\nu_1^c$  mode which has already been identified at  $405\text{ cm}^{-1}$  in  $A_g^-$  polarization and at  $407\text{ cm}^{-1}$  in  $B_g^-$  polarization. The band at such low frequency may also not be assigned to the libratory modes of  $H_2O$  molecules. The only possibility is that it may belong to  $K^+ \dots O'$  (where  $O'$  is the oxygen atom of  $SO_4^{2-}$  ion) asymmetric stretching type of vibration. This assignment also gets support from the IR study of Belyaeva *et al* (1975) on  $M_2SO_4$  (where  $M = K, Rb$  or  $Cs$ ) in matrices of inert gases. They have assigned the band due to  $K \dots O$  stretch at  $298.6\text{ cm}^{-1}$  in  $K_2SO_4$ . The shift in our case to  $326\text{ cm}^{-1}$  might have been due to the change in the matrix and the crystalline environment.

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