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IR and Polarized Raman Spectra of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn)

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The IR and polarized Raman spectra of two isomorphous Tutton's salts $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn) have been recorded and analyzed. The degeneracies of the internal modes of the sulfate ion, the ammonium ion, and the complex unit have been lifted. The sulfate ion is more distorted in the manganese salt. Free rotation of the ammonium ion is not likely in the crystalline lattice. Separate bands for the three different water molecules have been observed. The hydrogen bond strength is stronger in water than in the ammonium group.

The vibrational study of a potassium Tutton salt (*1*) has shown that the symmetry of the sulfate ion is distorted considerably from tetrahedral and that the angular distortion is more than the linear one. The ammonium Tutton salt provides another interesting double sulfate isomorphous to the potassium one. From IR analysis of ammonium Tutton salts, Oxton and Knop (*2*) explained the hydrogen bonding in the ammonium ions and water molecules. In this communication, the IR and polarized Raman spectra of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn) have been made to get a better understanding of the anions, the complex unit, and hydrogen bonding in these crystals.

The single crystals used for the investigation were grown by slow evaporation of equimolar aqueous solutions of analar grade $(NH_4)_2SO_4$ and MSO_4 (M = Zn, Mn) at room temperature (*3, 4*). A Spex Ramalog 1401 double monochromator equipped with a Spectra Physics Model 165 Ar^+ laser (5145 Å) was used to record the Raman spectra for the six polarization geometrices. A PE283 spectrophotometer was employed to record the IR spectra using nujol mull technique.

$(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn) crystallize in monoclinic symmetry with the space group $P2_1/a(C_{2h}^5)$ and has $z = 2$ (*3, 4*). All the atoms except the metal cation are at C_1 symmetry. The six water oxygens form an octahedral coordination around the metal cation and each of them is hydrogen bonded to sulfate oxygens. The group theoretical analysis predicts 234 fundamentals,

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TABLE I

VIBRATIONAL SPECTRA DATA (IN cm^{-1}) AND ASSIGNMENTS OF $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn)

$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$		$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$		
Raman	IR	Raman	IR	Assignments
3353 br		3360 br		ν_3 H_2O I
3332 br		3342 br		ν_3 H_2O II
3310 br		3311 br		ν_3 H_2O III
			3500–3200 br	
3269 br		3286 br		ν_1 H_2O I
3244 w		3238 w		ν_1 H_2O II
3217 br		3214 br		ν_1 H_2O III
	3500–3000 br			
3162 m		3168 m		
3143 w		3146 w	3130 w	ν_3^a
3116 m		3120 m	3110 m	
3060 vw		3064 vw		$\nu_2^a + \nu_4^a$
3036 vw		3044 vw		
3022 m		3019 m		ν_1^a
	2200 vw		2200 vw	$2\nu_3^s$
	2040 br		2040 br	$\nu_2^a + \nu_6^a$
1741 br		1742 br		$\nu_4^a + \nu_6^a$
1715 m		1714 m		ν_2^a
1690 s		1693 s		
1662 br		1671 br		ν_2 H_2O III
1641 m	1670 m	1642 m	1670–1610 br	ν_2 H_2O II
1619 br		1616 br		ν_2 H_2O I
1464 br	1470 m	1462 br	1400 m	ν_4^a
1443 br	1450 br	1440 br		
1407 w		1416 w		
1159 m		1147 m		
1138 m	1150–1080 br	1133 m	1120 m	ν_3^s
1105 m		1104 m	1090 br	
1031 vw		1034 vw		$\nu_2^s + \nu_4^s$
984 vs	980 w	984 vs	980 w	ν_1^s
960 sh		960 sh		
920 vw		920 vw		$2\nu_2^s$
888 br		872 w		ν_r H_2O III
856 w		829 w		ν_r H_2O II
826 w		808 br		ν_r H_2O I
760 br		761 w		ν_t H_2O III
732 m	670–750 br	724 m	690–750 br	ν_t H_2O II
698 w		680 br		ν_t H_2O I
631 s		627 s		
623 sh	600 m	618 m	610 m	ν_4^s
615 m		612 sh	600 m	
575 w		586 w		ν_w H_2O III
563 w		562 w		ν_w H_2O II
541 br		540 br		ν_w H_2O I
460 w		455 vs		ν_2^s
457 vs		446 w		
402 s	400 w	404 s	410 w	ν_1^c
364 br		364 br		$\nu_6^{a a}$

TABLE I—*Continued*

$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$		$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$		
Raman	IR	Raman	IR	Assignments
354 vw				$2\nu_5^c$
	270 w		270 w	ν_4^c
255 m		249 m		
223 w	230 vw	228 w	230 vw	ν_2^c
198 m		184 m		
185 sh		165 sh		ν_5^c
175 w		153 w		
124 br		124 br		$\nu_{N-H...O}$
104 br		102 br		$\nu_{O-H...O}$
90 s		90 s		Lattice modes
69 w		78 w		

Note. The values given are the mean frequencies of the six polarization settings α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{xz}, and α_{yz}. The superscripts *n*, *s*, and *c* refer to the modes of ammonium ion, sulfate ion, and the complex $[M(H_2O)_6]^{2+}$, respectively, whereas the subscripts r, w, and t refer to the rocking, wagging, and twisting modes of the water, respectively. The letters vs, s, vw, w, and br represent the very strong, strong, very weak, weak, and broad band intensities, respectively.

[a] ν_6^n represents the internal rotation of the ammonium ion.

at $K = 0$ (including three acoustic) which are distributed as:

$$\Gamma_{234} = 57A_g^{(R)} + 57B_g^{(R)} + 60A_u^{(IR)} + 60B_u^{(IR)}.$$

The stretching and bending frequencies of a free SO_4^{2-} ion occur in the regions 950–1200 cm^{-1} and 400–650 cm^{-1}, respectively (*5*). The splitting of the nondegenerate mode $\nu_1(A_1)$ in Raman (Table I) is due to resonance interaction between the vibrating ions. The complete splitting of the bending modes and the slight shifting of the stretching modes (Table I) from the free ion values (*5*) suggest that the angular distortion of the ion is greater than the linear distortion, consistent with the crystal structure data (3, 4). The ion is more distorted in the manganese crystal, as the splitting of the asymmetric modes of the ion is observed both in IR and Raman.

The assignments of the internal modes of the NH_4^+ ion are based on the free ion values (*5*) and the hydrogen bond strengths (*2*). The number of bands observed in the different orientations for different internal modes are consistent with the factor group analysis. As the observed frequencies lie close to the free ion values, it is evident that the ion makes weak hydrogen bonds. The appearance of combinations of bending modes (ν_2 and ν_4) with an internal rotation mode (ν_6) rules out the possibility of a freely rotating ion in the crystalline lattice (*6*, *7*).

The complex unit $M(H_2O)_6$ possesses the center of symmetry. The assignments are made based on the fact that the stretching modes (ν_1, ν_2, ν_5) should appear at higher frequencies with greater intensities than the bending modes (ν_3, ν_4, ν_6) and the data available in the literature (*8*). The appearance of IR inactive modes $\nu_1(A_{1g})$ and $\nu_2(E_g)$ and the lifting of degeneracy of $\nu_2(E_g)$ and $\nu_5(F_{2g})$ modes indicate that the complex is distorted considerably.

On the basis of the hydrogen bond strengths (*2*), the internal modes of water have been assigned. Broad bands with frequencies shifted considerably from the free state values have been observed in most of the polarization settings due to the effect of hydrogen bonding. The appearance of three bands each in the stretching and bending modes suggest that the unit cell contains three different water molecules. The large shifting of the bending modes observed reveals that the hydrogen bonding is considerable. The librational modes of water fall in the region 500–900 cm^{-1} (*9*). The assignments can be made by considering the hydrogen bond strengths and the fact that the rocking mode will have greater frequency than the wagging mode in inorganic salt hydrates with linear or in plane bend hydrogen bonds (*10*).

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