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. © 1988 Academic Press, Inc.

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 $(NH_4)_2 M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn) have been made to get a better understanding of the anions, the complex unit, and hydrogen bonding in these crystals.

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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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BRIEF COMMUNICATIONS

TABLE I

Vibrational Spectra Data (in cm $^{-1}$) and Assignments of $(NH_4)_2 M(SO_4)_2 \cdot 6H_2O \ (M$ = Zn, Mn)

RamanIRRamanIRAssignments3353 br3360 br3360 br ν_2 H ₂ O I3353 br3360 br3342 br ν_3 H ₂ O II3310 br3311 br ν_2 H ₂ O II3269 br3286 br ν_1 H ₂ O II3244 w3238 w ν_1 H ₂ O II3217 br3214 br ν_1 H ₂ O II3162 m3168 m3130 w ν_1^3 3143 w3166 w3130 w ν_2^3 3166 m3120 m3110 m3060 vw3060 vw3064 vw $\nu_2^2 + \nu_4^2$ 3036 vw3044 vw 200 vw $2\nu_1^2$ 200 vw2040 br $\nu_2^2 + \nu_4^2$ 2040 br2040 br $\nu_2^2 + \nu_4^2$ 1741 br1742 br $\nu_4^2 + \nu_6^2$ 1741 br1670 m1642 m1670-1610 br1690 s1637 s1400 m ν_4^2 164 br1470 m1462 br1400 m143 br1450 br1440 br1443 br1150-1080 br1133 m1120 m ν_3^2 105 m1034 vw $\nu_4^2 + \nu_4^2$ 980 w984 vs980 w988 br872 w ν_r H ₂ O II750 br764 br761 br105 m670-750 br724 m690 sh900 sh920 vw920 vw921 br<	$(\mathbf{NH}_4)_2 \mathbf{Zn}(\mathbf{SO}_4)_2 \cdot \mathbf{6H}_2\mathbf{O}$		$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$		
3353 br 3360 br ν_3 H ₂ O I 3332 br 3342 br ν_3 H ₂ O II 3310 br 3311 br ν_3 H ₂ O III 3310 br 3311 br ν_3 H ₂ O III 3269 br 3286 br $3500-3200$ br 3214 w 3238 w ν_1 H ₂ O III 3217 br 3214 br ν_1 H ₂ O III 3162 m 3168 m ν_1 H ₂ O III 3143 w 3146 w 3130 w ν_1^4 3060 vw 3064 vw $\nu_2^4 + \nu_4^4$ 3036 vw 3044 vw 3022 m 200 vw 2200 vw 2200 vw 2200 vw 2200 vw 2200 vw 2200 vw 2040 br $\nu_2^4 + \nu_6^4$ 1741 br 1742 br ν_4 H ₂ O III ν_2 H ₂ O III 1690 s 1693 s 1662 br 1671 br ν_2 H ₂ O III ν_2 H ₂ O III 1644 br 1470 m 1462 br 1400 m ν_4^4 ν_4^5 1105 m 1440 br 1104 m 1090 br 1131 m 120 m ν_5^4 1138 m 1150-1080 br 1133 m 1120 m ν_5 ν_4	Raman	IR	Raman	IR	Assignments
3332 br 3342 br ν_3 H ₂ O II 3310 br 3311 br ν_3 H ₂ O III 3310 br 3311 br ν_3 H ₂ O III 3269 br 3286 br ν_1 H ₂ O II 3244 w 3238 w ν_1 H ₂ O III 3217 br 3214 br ν_1 H ₂ O III 3120 m 3116 m 3120 m ν_1 H ₂ O III 3500-3000 br 3110 m ν_1 H ₂ O III ν_1 H ₂ O III 3143 w 3146 w 3130 w ν_1^a 3060 vw 3064 vw ν_1^a ν_1^a 3022 m 3019 m ν_1^a $\nu_2^a + \nu_1^a$ 3020 m 1741 br 1742 br $\nu_2^a + \nu_0^a$ 1741 br 1742 br $\nu_2^a + \nu_0^a$ ν_2^a 1690 s 1671 br $\nu_2^a + \mu_0^a$ $\nu_2^a + \nu_0^a$ 1690 s 1662 br 1400 m ν_4^a $\nu_4^a + \nu_0^a$ 1644 br 1470 m 1462 br 1400 m ν_4^a 1443 br 1450 br 1433 m 1120 m ν_3^a 1105 m 1034 vw $\nu_4^a + \nu_4^a$ ν_4^a	3353 br		3360 br		$\nu_3 H_2 O I$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3332 br		3342 br		$\nu_3 H_2 O II$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3310 br		3311 br		ν_3 H ₂ O III
3269 br 3286 br ν_1 H ₂ O 1 3244 w 3238 w ν_1 H ₂ O II 3217 br 3214 br ν_1 H ₂ O III 3217 br 3214 br ν_1 H ₂ O III 3500-3000 br 3168 m ν_1 H ₂ O III 3110 m 3160 w 3130 w ν_1^2 3116 m 3120 m 3110 m $\nu_2^2 + \nu_4^2$ 3060 vw 3064 vw $\nu_2^2 + \nu_4^2$ ν_4^2 3022 m 3019 m ν_1^2 ν_2^2 200 vw 2200 vw 2040 br $\nu_2^2 + \nu_4^2$ 1741 br 1742 br $\nu_4^2 + \nu_6^2$ 1693 s 1662 br 1671 br ν_2 H ₂ O III 1644 br 1644 br 1470 m 1642 br 1400 m ν_4^2 1443 br 1450 br 1440 br ν_4 ν_5 105 m 1104 m 1090 br ν_5 ν_5 105 m 1104 m 1090 br ν_1 H ₂ O III ν_5 105 m 1104 m 1090 br ν_1 H ₂ O III ν_5 105 m 1104 m 1090 br <td< td=""><td></td><td></td><td></td><td>35003200 br</td><td></td></td<>				35003200 br	
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3214 br $\nu_1 H_2 O III$ 3500-3000 br 3162 m 3168 m 3164 m 3130 w ν_1^2 3164 m 3130 w ν_2^2 3162 m 3110 m 3164 w 3110 m $\nu_1^2 + \nu_4^2$ 3019 m ν_1^2 3019 m ν_1^2 3020 vw 2200 vw 2200 vw 3019 m $\nu_1^2 + \nu_4^2$ 1741 br 1742 br $\nu_2 H_2 O III 1642 br 1670 m 1642 m \nu_2 H_2 O III 1644 br 1470 m 1460 br \nu_2 H_2 O III 1644 br 1470 m 1462 br 1400 m \nu_2 H_2 O III 1644 br 1470 m 1462 br 1400 m \nu_2 H_2 O III 1470 m 1470 $	3244 w		3238 w		ν_1 H ₂ O II
$3500-3000 \text{ br}$ 3162 m 3168 m 3143 w 3146 w 3130 w ν_1^3 3116 m 3120 m 3110 m $\nu_2^2 + \nu_4^2$ 3060 vw 3064 vw $\nu_2^2 + \nu_4^2$ 3036 vw 3064 vw 2200 vw $2\nu_5^3$ 3022 m 3019 m ν_1^2 $\nu_2^4 + \nu_6^2$ 2200 vw 2200 vw 2200 vw $2\nu_5^2$ 2040 br 1742 br $\nu_4^2 + \nu_6^2$ 1590 s 1690 s 1671 br $\nu_2 \text{ H}_2 O \text{ II}$ 1690 s 1662 br 1670 m 1642 m $1670-1610 \text{ br}$ $\nu_2 \text{ H}_2 O \text{ II}$ 1434 br 1470 m 1462 br 1400 m ν_4^3 14350 br 1440 br 1400 m $\nu_2^4 + \nu_4^3$ 14350 m 1133 m 1120 m ν_5^3 1105 m 1440 br $\nu_1 \text{ H}_2 O \text{ II}$ $\nu_2 \text{ H}_2 0 \text{ II}$ 1313 w 1250 w 980 w 980 w	3217 br		3214 br		ν_1 H ₂ O III
3162 m 3168 m 3143 w 3146 w 3130 w ν_1^n 3116 m 3120 m 3110 m 310 w ν_2^n 3060 vw 3064 vw $\nu_2^2 + \nu_4^n$ 3036 vw 3044 vw 3022 m 3019 m ν_1^n 2200 vw $2\nu_2^*$ 2040 br 2040 br $\nu_2^n + \nu_6^n$ 1711 m $\nu_2^n + \nu_6^n$ 1741 br 1742 br $\nu_2^n + \nu_6^n$ 1715 m 1714 m ν_2^n 1690 s 1693 s 1662 br 1671 br ν_2 H ₂ O III 1664 br ν_2 H ₂ O II 1641 m 1670 m 1642 m 1670-1610 br ν_2 H ₂ O II 1444 br 1443 br 1450 br 1440 br 1440 m 1440 m 1440 m 1440 m 1133 m 1120 m ν_3^1 1105 m 1134 m 1090 br 1034 vw $\nu_2^1 + \nu_4^2$ ν_7^1 960 sh 960 sh 920 vw 920 vw $2\nu_2^1$ ν_4^1 888 br 872 w ν_7 H ₂ O III ν_7 ν_7 ν_7 750 w 670-750 br 724 m		3500-3000 br			
3143 w 3146 w 3130 w ν_1^n 3116 m 3120 m 3110 m $\nu_2^n + \nu_4^n$ 3060 vw 3064 vw $\nu_2^n + \nu_4^n$ 3036 vw 3019 m ν_1^n 200 vw 200 vw $2\nu_3^1$ 2040 br 2040 br $\nu_2^1 + \nu_6^n$ 1741 br 1742 br $\nu_4^n + \nu_6^n$ 1715 m 1714 m ν_2^n 1600 s 1693 s 1662 br 1661 br ν_2 H ₂ O III 1641 m 1670 m 1642 m 1670 m 1642 br 1400 m ν_4^n 1434 br 1450 br 1440 br ν_4 1443 br 1450 br 1133 m 1120 m ν_3^3 1105 m 1104 m 1090 br 1031 vw ν_4 H ₂ O II 984 vs 980 w 984 vs 980 w ν_5^4 960 sh 920 vw $2\nu_2^5$ ν_5 888 br 872 w ν_7 H ₂ O II ν_7 H ₂ O II 732 m 670–750 br 724 m 690–750 br ν_1 H ₂ O II 631 s <td>3162 m</td> <td></td> <td>3168 m</td> <td></td> <td></td>	3162 m		3168 m		
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3060 vw 3064 vw $v_1^2 + v_4^2$ 3036 vw 3019 m v_1^2 3022 m 3019 m v_1^2 2200 vw 2200 vw $2v_5^2$ 2040 br 2040 br $v_2^2 + v_6^2$ 1741 br 1742 br $v_1^2 + v_6^2$ 1715 m 1742 br $v_1^2 + v_6^2$ 1690 s 1693 s 1693 s 1662 br 1671 br v_2 H ₂ O II 1644 m 1670 m 1642 m 1670-1610 br v_2 H ₂ O II 1644 br 1470 m 1462 br 1400 m v_4^2 1443 br 1450 br 1440 br 1470 m 1462 st 1138 m 1150-1080 br 1133 m 1120 m v_5^2 1031 vw 980 w 984 vs 980 w $v_5^2 + v_4^2$ 980 sh 960 sh 900 vw $2v_2^2$ 888 br 872 w v_r H ₂ O III 826 w 808 br v_r H ₂ O II 760 br 761 w v_r H ₂ O II 732 m 670-750 br 724 m 690-750 br v_t H ₂ O II <td>3116 m</td> <td></td> <td>3120 m</td> <td>3110 m</td> <td>5</td>	3116 m		3120 m	3110 m	5
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3022 m 3019 m ν_1^n 2200 vw 2200 vw $2\nu_2^5$ 2040 br 2040 br $\nu_2^n + \nu_6^n$ 1741 br 1742 br $\nu_4^n + \nu_6^n$ 1715 m 1714 m ν_2^2 1690 s 1693 s $\nu_2 \text{ H}_2 \text{O} \text{ III}$ 1690 s 1671 br $\nu_2 \text{ H}_2 \text{O} \text{ III}$ 1642 m 1670 m 1642 m 1671 br $\nu_2 \text{ H}_2 \text{O} \text{ II}$ 1644 br 1470 m 1464 br 1470 m 1435 br 1440 br 1443 br 1450 br 1447 m 1120 m 138 m $1150-1080 \text{ br}$ 1104 m 1090 br 1031 vw 980 w 984 vs 980 w 984 vs 980 w 920 vw $2\nu_2^t$ 888 br 872 w $\nu_r \text{ H}_2 \text{O} \text{ II}$ 826 w 808 br $\nu_r \text{ H}_2 \text{O} \text{ II}$ 761 w $\nu_r \text{ H}_2 \text{O} \text{ II}$ 698 w 680 br 613 s 627 s 623 sh 600 m 615 m 612 sh 600 m 562 w $\nu_w \text{ H}_2 \text{O} \text{ II}$ 53 w 562 w $\nu_w \text{ H}_2 \text{O} \text{ II}$ 540 br $\nu_w \text{ H}_2 \text{O} \text{ II}$ 540 br $\nu_w \text{ H}_2 \text{ O} \text{ II}$ 540 br $\nu_w \text{ m}^2$	3036 vw		3044 vw		~ .
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2040 br2040 br $\nu_2^0 + \nu_3^e$ 1741 br1742 br $\nu_4^4 + \nu_6^e$ 1715 m1714 m ν_2^d 1690 s1693 s1662 br1671 br ν_2 H ₂ O III1641 m1670 m1642 m1670 m1642 m1670-1610 br1646 br1470 m1462 br1464 br1470 m1462 br1464 br1470 m1462 br1464 br1470 m1477 w1416 w1195 m1104 m1090 br1034 vw984 vs980 w980 w984 vs980 w980 w984 vs980 w980 w920 vw920 vw921 vw920 vw922 vw ν_r H ₂ O II838 br872 w94 vs980 w956 sh90-750 br971 m711 m722 m670-750 br724 m690-750 br75 w586 w75 w586 w75 vs460 br75 vs446 w400 w455 vs452 vs ν_2^a 454 br		2200 vw		2200 vw	$2\nu_1^s$
1741 br 1742 br $\nu_4^4 + \nu_6^c$ 1715 m 1714 m ν_2^4 1690 s 1693 s 1662 br 1671 br ν_2 H ₂ O III 1641 m 1670 m 1642 m 1670-1610 br ν_2 H ₂ O II 1645 br 1470 m 1462 br 1400 m ν_4^4 1443 br 1450 br 1440 br 1440 m 1440 m 1443 br 1450 br 1440 br 1440 m 1990 br 105 m 1104 m 1090 br 1031 vw $\nu_2^4 + \nu_4^5$ 984 vs 980 w 984 vs 980 w ν_2^4 984 vs 980 w 980 w ν_1^4 960 sh 960 sh 960 sh 960 sh 920 vw 920 vw 2 ν_2^5 888 br κ_72 w ν_r H ₂ O III 856 w 829 w ν_r H ₂ O III 1631 s 627 s 623 sh 600 m 613 s 627 s 600 m 512 sh 600 m 528 w ν_2 H ₂ O III 633 w 562 w ν_w H ₂ O II ν_w H ₂ O I 140 m ν_2 H ₂ O		2040 br		2040 br	$\nu_{2}^{n} + \nu_{6}^{n}$
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1600 s1693 s1693 s1662 br1671 br ν_2 H ₂ O III1641 m1670 m1642 m1670-1610 br ν_2 H ₂ O II1619 br1616 br ν_2 H ₂ O I1464 br1470 m1462 br1400 m ν_4^a 1443 br1450 br1440 br1416 w1407 w1416 w1133 m1120 m ν_5^a 1105 m1104 m1090 br1034 vw $\nu_2^c + \nu_4^s$ 984 vs980 w984 vs980 w ν_1^c 960 sh960 sh920 vw $2\nu_2^c$ 888 br872 w ν_r H ₂ O II856 w829 w ν_r H ₂ O II760 br761 w ν_r H ₂ O II732 m670-750 br724 m690-750 br ν_r H ₂ O II631 s627 s623 sh600 m618 m575 w586 w ν_w H ₂ O II563 w562 w ν_w H ₂ O II575 v586 w ν_w H ₂ O II563 w562 w ν_w H ₂ O II564 br540 br ν_s^f 364 br364 br ν_s^f	1715 m		1714 m		ν ^η
1662 br1671 br $\nu_2 H_2 O III$ 1641 m1670 m1642 m1670-1610 br $\nu_2 H_2 O II$ 1619 br1616 br $\nu_2 H_2 O I$ 1464 br1470 m1462 br1400 m ν_4^4 1443 br1450 br1440 br1407 w1416 w1159 m1147 m1138 m1150-1080 br1133 m1120 m ν_5^5 105 m1034 vw $\nu_2^5 + \nu_4^5$ 984 vs980 w984 vs980 w ν_1^5 960 sh960 sh960 sh $\nu_r H_2 O III$ 826 w829 w $\nu_r H_2 O III$ 826 w808 br $\nu_r H_2 O II$ 760 br761 w $\nu_r H_2 O II$ 760 br761 w $\nu_r H_2 O II$ 760 br761 w $\nu_r H_2 O II$ 631 s627 s623 sh600 m615 m612 sh600 m615 m563 w562 w $\nu_w H_2 O II$ 563 w562 w $\nu_w H_2 O II$ 564 br540 br $\nu_w H_2 O I$ 563 w562 w $\nu_w H_2 O II$ 564 br540 br $\nu_w H_2 O II$	1690 s		1693 s		. 2
1011641 m1670 m1642 m1670-1610 br ν_2 H ₂ O II1641 m1670 m1616 br ν_2 H ₂ O II1619 br1470 m1462 br1400 m ν_4° 1443 br1450 br1440 br1400 m ν_4° 1443 br1450 br1440 br1416 w1159 m1147 m1133 m1120 m ν_5° 105 m1104 m1090 br1031 vw $\nu_2 + \nu_4^{\circ}$ 984 vs980 w984 vs980 w ν_1° 960 sh960 sh960 sh920 vw $2\nu_2^{\circ}$ 888 br872 w ν_r H ₂ O II826 w808 br ν_r H ₂ O II760 br761 w ν_r H ₂ O II760 br761 w ν_r H ₂ O II670-750 br724 m690-750 br ν_t H ₂ O II688 w680 br ν_r H ₂ O II673 s627 s623 sh600 m615 m612 sh600 m575 w586 w ν_w H ₂ O II563 w562 w ν_w H ₂ O II564 br540 br ν_w H ₂ O I653 w562 w ν_w H ₂ O I654 br364 br ν_n°	1662 br		1671 br		ν2 H2O III
1619116161 ν_2 μ_2 OI16441470m1462br1400m ν_4^2 1443br1450br1440br11443br1450br1440br1407w1416w11159m1147m11138m1150–1080br1133m1120m ν_5^3 105m1104m1090br11031vw034vw $\nu_2^5 + \nu_4^5$ 980w ν_1^5 960sh960sh960sh920vw $2\nu_2^5$ 888br872w ν_r H ₂ O III826w808br ν_r H ₂ O III826w808br ν_r H ₂ O III760br761w ν_r H ₂ O III732m670–750br724m690–750br745m612sh600m575w586w ν_w H ₂ O III631s627s600m562w ν_w H ₂ O III563w562w ν_w H ₂ O II540br ν_w H ₂ O II541br540br ν_w H ₂ O I1460w455vs ν_2^5 457vs446w410w <td>1641 m</td> <td>1670 m</td> <td>1642 m</td> <td>1670–1610 br</td> <td>ν₂ H₂O II</td>	1641 m	1670 m	1642 m	1670–1610 br	ν ₂ H ₂ O II
1464 br1470 m1462 br1400 m ν_4^a 1443 br1450 br1440 br1416 w1407 w1416 w1159 m1147 m1138 m1150–1080 br1133 m1105 m1104 m1090 br1031 vw1034 vw $\nu_2^5 + \nu_4^5$ 984 vs980 w984 vs960 sh960 sh920 vw920 vw $2\nu_2^5$ 888 br872 w ν_r H ₂ O III826 w808 br ν_r H ₂ O I760 br761 w ν_r H ₂ O I760 br761 w ν_r H ₂ O I760 br761 w ν_r H ₂ O I670–750 br724 m690–750 br615 m612 sh600 m575 w586 w ν_w H ₂ O II563 w562 w ν_w H ₂ O II563 w562 w ν_w H ₂ O II564 br ν_5^a 446 w400 w455 vs457 vs446 w402 s400 w404 s410 w ν_1^c	1619 br		1616 br		ν_2 H ₂ O I
1443 br1450 br1440 br1407 w1416 w1159 m1147 m1138 m1150–1080 br1105 m1104 m1031 vw1034 vw984 vs980 w984 vs980 w960 sh960 sh920 vw920 vw9	1464 br	1470 m	1462 br	1400 m	ν_{4}^{n}
1407 w1416 w1159 m1147 m1138 m1150–1080 br1138 m1150–1080 br1105 m1104 m1090 br1031 vw1034 vw984 vs980 w984 vs980 w960 sh960 sh920 vw920 vw931	1443 br	1450 br	1440 br		
1159 m1147 m1138 m1150–1080 br1133 m1120 m v_3^5 1105 m1104 m1090 br1031 vw $v_2^5 + v_4^5$ 1031 vw1034 vw $v_2^5 + v_4^5$ 984 vs980 w980 w v_1^5 960 sh960 sh920 vw $2v_2^5$ 888 br872 w v_r H ₂ O III856 w829 w v_r H ₂ O I826 w761 w v_r H ₂ O I760 br761 w v_t H ₂ O II760 br761 w v_t H ₂ O II670–750 br724 m690–750 br613 s627 s623 sh600 m618 m610 m575 w586 w v_w H ₂ O II563 w562 w v_w H ₂ O II563 w562 w v_w H ₂ O I563 w562 w v_w H ₂ O I564 br540 br v_s^4	1407 w		1416 w		
1138 m1150-1080 br1133 m1120 m v_3^5 1105 m1104 m1090 br1031 vw vw $v_2^5 + v_4^5$ 984 vs980 w984 vs980 w v_1^5 960 sh960 sh960 sh920 vw $2v_2^5$ 988 br872 w v_r H ₂ O III856 w829 w v_r H ₂ O I826 w761 w v_r H ₂ O I760 br761 w v_t H ₂ O II760 br761 w v_t H ₂ O I670-750 br724 m690-750 br v_t H ₂ O I698 w680 br v_t H ₂ O I631 s627 s623 sh600 m618 m610 m v_4^5 615 m612 sh600 m575 w586 w v_w H ₂ O II563 w562 w v_w H ₂ O I564 br v_5^5 v_5^5 457 vs446 w410 w v_1^c 364 br364 br v_8^{aa}	1159 m		1147 m		
1105 m1104 m1090 br1031 vw1034 vw $v_2^{5} + v_4^{5}$ 984 vs980 w984 vs980 w960 sh960 sh960 sh920 vw920 vw $2v_2^{5}$ 888 br872 w v_r H ₂ O III856 w829 w v_r H ₂ O I826 w761 w v_r H ₂ O I760 br761 w v_t H ₂ O II732 m670-750 br724 m690-750 br724 m690-750 br680 br v_t H ₂ O I631 s627 s623 sh600 m615 m612 sh600 m575 w586 w v_w H ₂ O II563 w562 w562 w v_w H ₂ O I563 w562 w575 vs540 br540 br v_w H ₂ O I541 br540 br446 w402 s400 w404 s410 w425 vs426 br v_n^{6a}	1138 m	1150–1080 br	1133 m	1120 m	ν_1^s
1031 vw 1034 vw $\nu_2^{5} + \nu_4^{5}$ 984 vs 980 w 984 vs 980 w ν_1^{5} 960 sh 960 sh 920 vw $2\nu_2^{5}$ 888 br 872 w ν_r H ₂ O III 856 w 829 w ν_r H ₂ O I 826 w 808 br ν_r H ₂ O I 760 br 761 w ν_r H ₂ O II 760 br 761 w ν_t H ₂ O II 780 w 670–750 br 724 m 690–750 br ν_t H ₂ O II 698 w 680 br ν_t H ₂ O I 1631 s 627 s 623 sh 600 m 618 m 610 m ν_4^{5} 615 m 612 sh 600 m 575 w 586 w ν_w H ₂ O II 563 w 562 w ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 564 w 455 vs ν_5^{5} 446 w 400 s 410 w ν_1^{c} 364 br 364 br ν_6^{a} 364 br ν_6^{a}	1105 m		1104 m	1090 br	- ,
984 vs980 w984 vs980 w ν_1^s 960 sh960 sh960 sh920 vw $2\nu_2^s$ 888 br872 w ν_r H ₂ O III856 w829 w ν_r H ₂ O I826 w808 br ν_r H ₂ O I760 br761 w ν_r H ₂ O II732 m670–750 br724 m690–750 br724 m690–750 br680 br ν_t H ₂ O II631 s627 s623 sh600 m615 m612 sh600 m575 w586 w ν_w H ₂ O II563 w562 w562 w ν_w H ₂ O I563 w562 w564 br ν_s^s 457 vs446 w402 s400 w404 s410 w92 s400 w404 s410 w93 s960 sh94 br $\nu_n^{a_a}$	1031 vw		1034 vw		$\nu_{2}^{s} + \nu_{4}^{s}$
960 sh960 sh960 sh920 vw920 vw $2\nu_{5}^{5}$ 888 br872 w ν_{r} H ₂ O III856 w829 w ν_{r} H ₂ O I826 w808 br ν_{r} H ₂ O I760 br761 w ν_{t} H ₂ O III732 m670–750 br724 m690–750 br724 m690 w680 br ν_{t} H ₂ O I631 s627 s623 sh600 m615 m612 sh600 m575 w586 w ν_{w} H ₂ O III563 w562 w562 w ν_{w} H ₂ O I563 w562 w564 br ν_{s}^{4}	984 vs	980 w	984 vs	980 w	ν_1^s
920 vw 920 vw $2\nu_{5}^{5}$ 888 br 872 w ν_{r} H ₂ O III 856 w 829 w ν_{r} H ₂ O I 826 w 808 br ν_{r} H ₂ O I 760 br 761 w ν_{t} H ₂ O III 732 m 670–750 br 724 m 690–750 br ν_{t} H ₂ O II 698 w 680 br ν_{t} H ₂ O I 698 w 680 br ν_{t} H ₂ O I 631 s 627 s 623 sh 600 m 618 m 610 m ν_{4}^{4} 615 m 612 sh 600 m 575 w 586 w ν_{w} H ₂ O III 563 w 562 w ν_{w} H ₂ O II 541 br 540 br ν_{w} H ₂ O I 540 w 455 vs ν_{5}^{4} 457 vs 446 w 402 s 400 w 404 s 410 w ν_{1}^{c} 364 br 364 br ν_{6}^{a} ν_{6}^{a}	960 sh		960 sh		
888 br 872 w v_r H ₂ O III 856 w 829 w v_r H ₂ O II 826 w 808 br v_r H ₂ O I 760 br 761 w v_r H ₂ O III 732 m 670–750 br 724 m 690–750 br v_t H ₂ O II 698 w 680 br v_t H ₂ O I 690–750 br v_t H ₂ O II 631 s 627 s 623 sh 600 m 618 m 610 m v_s^4 615 m 612 sh 600 m 575 w 586 w v_w H ₂ O III 563 w 562 w v_w H ₂ O II 564 br 540 br v_w H ₂ O I 11 540 br v_w H ₂ O I 564 br 446 w 410 w v_1^c 364 br v_n^e	920 vw		920 vw		2µ5
856 w 829 w v_r H ₂ O II 826 w 808 br v_r H ₂ O I 760 br 761 w v_t H ₂ O III 732 m 670–750 br 724 m 690–750 br v_t H ₂ O II 732 m 670–750 br 724 m 690–750 br v_t H ₂ O II 698 w 680 br v_t H ₂ O I 631 s 627 s 623 sh 600 m 618 m 610 m v_s^4 615 m 612 sh 600 m 575 w 586 w v_w H ₂ O III 563 w 562 w v_w H ₂ O II 563 w 562 w v_w H ₂ O II 564 br 540 br v_w H ₂ O I 1460 w 455 vs v_s^5 457 vs 446 w 410 w v_1^c 364 br v_n^a	888 br		872 w		v. H ₂ O III
826 w 808 br ν_r H ₂ O I 760 br 761 w ν_t H ₂ O III 732 m 670–750 br 724 m 690–750 br ν_t H ₂ O II 698 w 680 br ν_t H ₂ O I 690–750 br ν_t H ₂ O I 631 s 627 s 623 sh 600 m 618 m 610 m ν_s^4 615 m 612 sh 600 m 575 w 586 w ν_w H ₂ O II 563 w 562 w ν_w H ₂ O II 1 563 w 562 w ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 460 w 455 vs ν_s^2 457 vs 446 w 410 w ν_1^c 364 br 364 br $\nu_n^{a_u}$	856 w		829 w		$\nu_{\rm r}$ H ₂ O II
760 br 761 w v_t H ₂ O III 732 m 670–750 br 724 m 690–750 br v_t H ₂ O III 698 w 680 br v_t H ₂ O I 690–750 br v_t H ₂ O I 698 w 680 br v_t H ₂ O I 690–750 br v_t H ₂ O I 631 s 627 s 623 sh 600 m 618 m 610 m v_s^4 615 m 612 sh 600 m 575 w 586 w v_w H ₂ O III 563 w 562 w v_w H ₂ O II 1 563 w 562 w v_w H ₂ O I 1 563 w 562 w v_w H ₂ O I 1 563 w 562 w v_w H ₂ O I 1 563 w 540 br v_w H ₂ O I 1 540 w 455 vs v_2^5 457 vs 446 w 402 s 400 w 404 s 410 w v_1^6 364 br 364 br v_8^6 v_8^6	826 w		808 br		ν. H ₂ Ο Ι
732 m $670-750$ br 724 m $690-750$ br ν_t H ₂ O II 698 w 680 br ν_t H ₂ O I 631 s 627 s 623 sh 600 m 618 m 610 m ν_s^s 615 m 612 sh 600 m 575 w 586 w ν_w H ₂ O III 563 w 562 w ν_w H ₂ O II ν_w H ₂ O II 563 w 562 w ν_w H ₂ O I ν_w H ₂ O I 563 w 562 w ν_w H ₂ O I ν_w H ₂ O I 563 w 562 w ν_w H ₂ O I ν_w H ₂ O I 563 w 540 br ν_w H ₂ O I ν_w H ₂ O I 460 w 455 vs ν_2^s 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br $\nu_n^{n_a}$	760 br		761 w		v. H ₂ O III
698 w 680 br ν_1 H ₂ O 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 ₂ O III 563 w 562 w ν_w H ₂ O II 111 563 w 562 w ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 460 w 455 vs ν_2^s 457 vs 446 w 410 w ν_1^c 364 br 364 br $\nu_n^{a_u}$	732 m	670–750 br	724 m	690–750 br	ν_1 H ₂ O II
631 s 627 s 633 s 600 m 618 m 610 m 615 m 612 sh 615 m 612 sh 600 m 575 w 586 w ν_w H ₂ O III 563 w 562 w 563 w 562 w 540 br ν_w H ₂ O II 540 w 455 vs 457 vs 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br $\nu_n^{a_u}$	698 w		680 br		ν_1 H ₂ O I
623 sh 600 m 618 m 610 m ν_4^5 615 m 612 sh 600 m 575 w 586 w ν_w H ₂ O III 563 w 562 w ν_w H ₂ O II 540 br ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 1460 w 455 vs ν_5^5 457 vs 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_6^{a} ν_6^{a} ν_6^{a}	631 s		627 s		
615 m 612 sh 600 m 575 w 586 w ν_w H ₂ O III 563 w 562 w ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 460 w 455 vs ν_z^5 457 vs 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_a^{6a}	623 sh	600 m	618 m	610 m	ν_{A}^{s}
575 w 586 w ν_w H ₂ O III 563 w 562 w ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 460 w 455 vs ν_z^5 457 vs 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_a^{6a} ν_a^{6a} ν_a^{6a}	615 m		612 sh	600 m	
563 w 562 w ν_w H ₂ O II 541 br 540 br ν_w H ₂ O I 460 w 455 vs ν_z^s 457 vs 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_a^{na}	575 w		586 w		ν _w H ₂ O III
541 br 540 br ν_w H ₂ O I 460 w 455 vs ν_s^2 457 vs 446 w 402 s 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_n^{aa}	563 w		562 w		$\nu_{\rm w}$ H ₂ O II
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 $\nu_6^{n_a}$	541 br		540 br		$\nu_{\rm w}$ H ₂ O I
457 vs 446 w 402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_6^{na}	460 w		455 vs		ν_2^s
402 s 400 w 404 s 410 w ν_1^c 364 br 364 br ν_6^{na}	457 vs		446 w		-
364 br 364 br ν_6^{na}	402 s	400 w	404 s	410 w	ν_1^c
	364 br		364 br		ν_6^{na}

$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$		$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$		
Raman	IR	Raman	IR	Assignments
354 vw				22
	270 w		270 w	ν_4^c
255 m		249 m		
223 w	230 vw	228 w	230 vw	ν ^c
198 m		184 m		•
185 sh		165 sh		ν_5^c
175 w		153 w		5
124 br		124 br		$\nu_{\rm N-H0}$
104 br		102 br		νo-H0
90 s		90 s		Lattice modes
69 w		78 w		

TABLE I-Continued

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 val-

ues (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 $\text{cm}^{-1}(9)$. 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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