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Vibrational Spectra of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ and $NH_4\mathit{Ln}(SO_4)_2 \cdot 2H_2O[\mathit{Ln} = \mathrm{Yb, Tm}]$

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The IR and Raman spectra of a single crystal $NH_4Sm(SO_4)_2 \cdot 4H_2O$ and that of two polycrystalline compounds $NH_4\mathit{Ln}(SO_4)_2 \cdot 2H_2O$ [Ln = Yb, Tm] have been recorded and analyzed. Two types of SO_4 groups predicted by the X-ray data of the samarium compound are not observed in the present study. However, the bands show two crystallographically distinct SO_4^{2-} ions in the other two compounds. The absence of free rotation and broadness of the bands in the internal mode region confirms that NH_4^+ ions form hydrogen bonds in the crystals under study. The observed stretching and bending bands show the presence of three distinct types of water molecules in $NH_4Sm(SO_4)_2 \cdot 4H_2O$. The water molecules form hydrogen bonds of medium strength in all three crystals. © 1996 Academic Press, Inc.

INTRODUCTION

The lanthanides form a number of hydrated double sulfates with tetrahedral ammonium ions. Several investigations have been carried out on this series of compounds using different techniques including X-ray diffraction and IR and Raman spectroscopy (1–6). The structural studies by Iyer and Natarajan have shown that $NH_4\mathit{Ln}(SO_4)_2 \cdot 2H_2O$ (Ln = Yb, Tm) forms an isomorphous series of double sulfates with ammonium and trivalent lanthanides (3). The crystal structure of a samarium compound $NH_4Sm(SO_4)_2 \cdot 4H_2O$ was reported by Eriksson *et al.* (4). Malhotra *et al.* have suggested two types of SO_4 groups in the isostructural $NH_4Ce(SO_4)_2 \cdot 4H_2O$ (5). However, from the IR and Raman spectral studies Xavier Mathew (6) has shown that no such splitting is observed for $NH_4Ce(SO_4)_2 \cdot 4H_2O$ and $NH_4La(SO_4)_2 \cdot 4H_2O$. A detailed vibrational study of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ and $NH_4\mathit{Ln}(SO_4)_2 \cdot 2H_2O$($\mathit{Ln}$ = Yb, Tm) is expected to provide a better understanding of the difference in the crystalline field perturbing the vibrating ions in these crystals. In this paper, the IR and Raman spectral studies of the title crystals have been reported.

EXPERIMENTAL

The crystals were prepared by the slow evaporation of an aqueous solution containing lanthanide sulfate and ammonium sulfate at room temperature (300 ± 3 K) (4, 5). Yb and Tm double sulfate crystals were provided by Dr. P. N. Iyer after X-ray diffraction studies. Raman spectra in the Stokes region were recorded using both a Spex 1401 double monochromator and a Dilor Z24 triple monochromator with a resolution better than 3 cm^{-1}. For excitation, the 488-nm line of a Spectra Physics model 165.08 argon laser with a power of 200 mW was used. Polarized Raman spectra of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ were obtained for the orientations $c(bb)a$, $c(bc)a$, $c(ab)a$, and $c(ac)a$. Because of the difficulty in obtaining single crystals of adequate size, only polycrystalline samples of $NH_4\mathit{Ln}(SO_4)_2 \cdot 2H_2O$ (Ln = Yb, Tm) were used for the study. Raman spectra were recorded for samples in a capillary tube. IR spectra were obtained by using a Perkin–Elmer 577 spectrophotometer with samples prepared as KBr pellets.

FACTOR GROUP ANALYSIS

The single crystal $NH_4Sm(SO_4)_2 \cdot 4H_2O$ (referred to as ASH) belongs to the monoclinic system with the space group $P2_1/c$ (C_{2h}^5) and possesses four formula units per unit cell (5). All atoms are at general positions. The samarium atom is coordinated to nine oxygen atoms, six belonging to four different sulfate ions and three belonging to three water molecules. The average Sm–O distance is approximately the same for samarium–sulfate oxygen distances and the samarium–water oxygen distances. The standard group theoretical analysis (7) has been carried out to find the active modes for each symmetry species of the factor group modes at $k = 0$. The expected 333 fundamentals excluding the acoustic modes split into (see Table 1)

$$\Gamma = 84A_g(\mathrm{R}) + 84B_g(\mathrm{R}) + 83A_u(\mathrm{IR}) + 82B_u(\mathrm{IR}).$$

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TABLE 1
Correlation Scheme for the Internal Modes of SO_4^{2-}, NH_4^+, and H_2O in $NH_4Sm(SO_4)_2 \cdot 4H_2O$

SO_4^{2-}

Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry C_{2h}
8 $A_1(\nu_1)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$		$(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy})$ A_g 18
16 $E(\nu_2)(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$	A	$(\alpha_{xz}, \alpha_{yz})$ B_g 18
48 $2F_2(\nu_3, \nu_4)(\alpha_{xy}, \alpha_{xz}, \alpha_{yz})$		A_u 18
		B_u 18

NH_4^+

Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry C_{2h}
4 $A_1(\nu_1)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$		$(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy})$ A_g 9
8 $E(\nu_2)(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$	A	$(\alpha_{xz}, \alpha_{yz})$ B_g 9
24 $2F_2(\nu_3, \nu_4)$ $(\alpha_{xy}, \alpha_{xz}, \alpha_{yz})$		A_u 9
		B_u 9

H_2O

Molecular symmetry C_{2v}	Site symmetry C_1	Factor group symmetry C_{2h}
32 $2A_1(\nu_1, \nu_2)(\alpha_{xx}, \alpha_{yy}, \alpha_{zz})$		$(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy})$ A_g 12
	A	$(\alpha_{xz}, \alpha_{yz})$ B_g 12
		A_u 12
16 B_1 (ν_3) (α_{xz})		B_u 12

$NH_4Ln(SO_4)_2 \cdot 2H_2O$ (Ln = Yb, Tm) crystallizes in the monoclinic system (referred to as AYH and ATH) with space group $P2_1/c$ (C_{2h}^5) and possesses four formula units per unit cell (4). The lanthanide metal ion is coordinated to eight oxygen atoms, six belonging to the sulfate ions and two belonging to water molecules. The expected 261 optical phonon modes ($k = 0$) have the irreducible representation as

$$\Gamma = 66A_g(\mathrm{R}) + 66B_g(\mathrm{R}) + 65A_u(\mathrm{IR}) + 64B_u(\mathrm{IR}).$$

RESULTS AND DISCUSSION

The spectral analysis has been carried out on the basis of the vibrations of the SO_4^{2-} and NH_4^+ ions, and the water molecules (see Table 2). The Raman and IR spectra of the three ammonium lanthanide sulfates are given in Figs. 1–3.

SO_4^{2-} Vibrations

The normal modes of vibration of a free tetrahedral SO_4^{2-} ion under T_d symmetry have average frequencies at 981, 451, 1104, and 614 cm^{-1} for $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ modes, respectively. All of these modes are Raman active, whereas the triply degenerate modes ν_3 and ν_4 are infrared active (8).

In all three crystals, the sulfate ion occupies a symmetry lower than its free ion symmetry (T_d), and therefore anisotropic crystal fields may remove degeneracies of normal modes and allow inactive modes to become active (see Table 1). Even though the compounds under study belong to the same factor group and possess same number of molecules per unit cell, there are some differences in the spectral features.

For ASH, the symmetric stretching vibration, which involves larger changes in polarizability, is observed as an intense band at 997 cm^{-1} in all orientations of the Raman spectra (see Fig. 1). However, this mode is split into two and they appear at higher wavenumbers in the other two compounds. For ATH, the ν_1 mode appears at 1001 and 1024 cm^{-1} and at 995 and 1019 cm^{-1} for AYH (see Table 2). In the IR spectrum of ASH, a weak band is observed in this region (see Fig. 3), indicating a small dipole moment

TABLE 2
Spectral Data and Band Assignments (cm^{-1})

$NH_4Sm(SO_4)_2 \cdot 4H_2O$					$NH_4Tm(SO_4)_2 \cdot 2H_2O$		$NH_4Yb(SO_4)_2 \cdot 2H_2O$		
Raman									
$c(bb)a$ 1	$c(bc)a$ 2	$c(ab)a$ 3	$c(ac)a$ 4	IR 5	Raman 6	IR 7	Raman 8	IR 9	Assignments 10
		56 *w*	58 *w*				52 *m*		
65 *w*					63 *s*		64 *m*		SO_4 translations
78 *w*	77 *w*		71 *m*		82 *m*		72 *m*		
	88 *m*	105 *vw*	89 *w*		99 *m*				
	115 *w*		119 *w*		115 *vw*				SO_4 rotations and
164 *w*		136 *w*			151 *m*				Ln–O stretching
208 *w*	240 *vw*	175 *w*	198 *w*		186 *w*				
			211 *wbr*	218 *m*				205 *w*	
					235 *w*	225 *m*	221 *w*	226 *m*	NH_4 translations
	298 *vw*			285 *w*		247 *m*	299 *vw*	245 *m*	
312 *vw*		323 *vw*	328 *vw*		325 *w*		311 *w*		
					367 *vw*		353 *vw*	360 *w*	H_2O lattice modes
							407 *sh*	392 *w*	
						395 *m*			
427 *m*	428 *m*	426 *m*	429 *m*		428 *sh*		413 *m*		
				445 *m*	467 *m*	439 *w*	442 *sh*		ν_2 SO_4^{2-} and Ln–OH_2
						458 *m*	450 *w*		stretching and
							474 *w*		wagging
500 *mbr*	491 *mbr*	492 *wbr*	490 *m*	498 *w*	489 *m*	475 *m*	498 *m*	470 *m*	
518 *w*	518 *w*	507 *vw*	512 *w*	530 *w*	517 *m*				
				552 *w*		548 *w*	551 *vw*	550 *w*	ν_W H_2O
592 *vw*				590 *s*	577 *w*	589 *m*		589 *m*	
	608 *w*	605 *w*	611 *m*		618 *m*		603 *m*		
	626 *w*			625 *w*	622 *sh*		614 *sh*		$\nu_4 SO_4^{2-}$, $\nu_t H_2O$
644 *mbr*	642 *w*	644 *w*	638 *m*					651 *m*	
670 *w*		651 *vw*	654 *w*			651 *m*	666 *w*	659 *sh*	
					680 *m*	680 *w*			
				745 *w*	780 *vw*	720 *m*		715 *w*	ν_r H_2O
996 *vs*	998 *vs*	999 *vs*	996 *vs*	975 *w*	1001 *vs*	981 *sh*	995 *vs*	981 *sh*	ν_1 SO_4^{2-}
					1024 *s*	1006 *s*	1019 *s*	1001 *s*	
1020 *w*	1018 *vw*	1005 *w*	1025 *vw*						$(\nu_2 + \nu_4)$ SO_4^{2-}
1061 *w*	1071 *w*	1038 *vw*	1080 *w*	1045 *vs*	1074 *s*	1059 *vs*	1069 *s*		
1072 *w*	1111 *m*	1072 *w*	1120 *mbr*	1076 *s*	1095 *m*	1085 *m*	1092 *m*		ν_3 SO_4^{2-}
1104 *s*	1148 *w*	1112 *m*	1175 *wbr*	1110 *s*	1116 *m*	1142 *m*	1112 *m*	1030–	
1138 *w*					1183 *wbr*	1171 *s*	1181 *vw*	1230 *vsbr*	
1408 *w*	1435 *w*	1455 *w*	1425 *w*	1418 *s*		1429 *s*	1436 *w*	1424 *s*	ν_4 NH_4^+
1445 *w*	1452 *vw*	1474 *w*	1448 *w*	1478 *w*	1442 *w*				
1598 *mbr*	1598 *mbr*	1598 *mbr*	1600 *sbr*	1600 *m*		1621 *m*		1624 *s*	
1620 *mbr*	1610 *sbr*	1618 *mbr*	1620 *mbr*	1620 *mbr*					ν_2 H_2O
1645 *w*	1625 *s*	1635 *m*	1630 *w*	1650 *m*	1644 *w*	1645 *sh*	1648 *w*		

TABLE 2—*Continued*

1	2	3	4	5	6	7	8	9	10
1672 *w*	1655 *w*	1663 *w*	1655 *w*	1685 *w*	1682 *w*	1675 *w*	1685 *w*		ν_2 NH_4^+
1692 *w*	1666 *w*	1698 *w*	1678 *w*	1730 *w*		1691 *w*		1705 *w*	
1870 *vw*	1960 *w*	1940 *vw*	1865 *w*		2060 *vw*	1815 *w*		2010 *w*	$\nu_4 + \nu_6$ NH_4^+ and
2050 *w*	2105 *w*	2010 *w*	2040 *w*		2120 *vw*	2001 *w*	2115 *w*	2055 *w*	$\nu_2 + \nu_6$ NH_4^+
3065 *m*	3042 *w*	3048 *w*	3020 *w*		2880 *vw*	2880 *w*	3070 *w*	2840 *w*	ν_1 NH_4^+
					3064 *w*	3070 *m*		3075 *w*	
3142 *w*	3168 *w*	3156 *w*	3174 *w*		3136 *m*		3140 *w*	3150 *sbr*	ν_3 NH_4^+
3265 *w*	3251 *w*	3200 *vw*	3191 *w*		3266 *w*	3191 *s*	3191 *m*	3219 *sbr*	
3295 *vw*	3290 *w*	3255 *w*	3300 *w*	3000–	3385 *m*	3360 *s*	3388 *m*	3361 *s*	ν_1 H_2O
3326 *w*	3328 *w*	3332 *w*	3318 *vs*	3500 *sbr*					
3372 *m*	3352 *w*	3376 *w*	3349 *vw*						
3401 *w*	3395 *w*	3398 *w*	3401 *w*						
3427 *w*	3430 *w*	3424 *vw*	3432 *vw*		3467 *m*	3438 *s*	3436 *w*	3439 *s*	ν_3 H_2O
3453 *w*	3441 *w*	3480 *w*	3474 *w*				3464 *w*		
							3510 *m*		

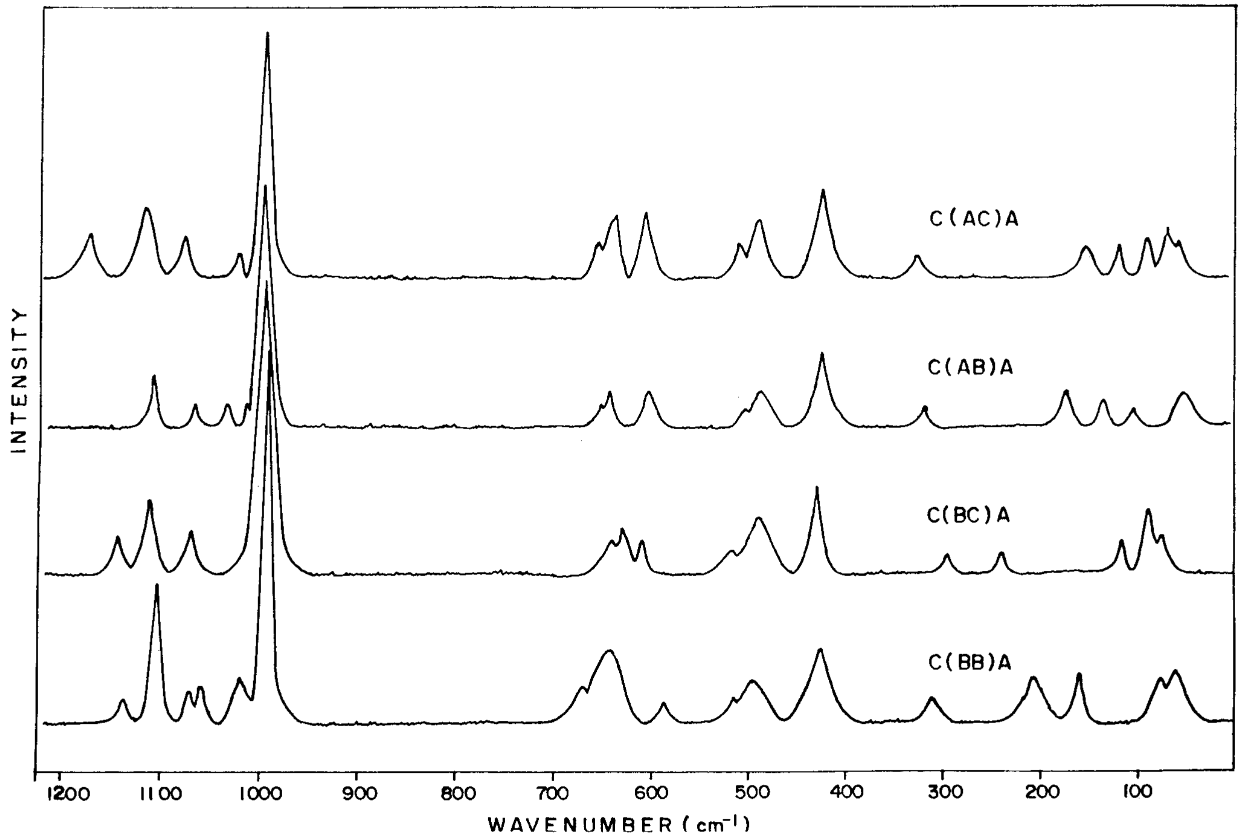

FIG. 1. Raman spectra of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ in the 50–1200 cm−1 region for the *c*(*bb*)*a*, *c*(*bc*)*a*, *c*(*ab*)*a*, and *c*(*ac*)*a* orientations.

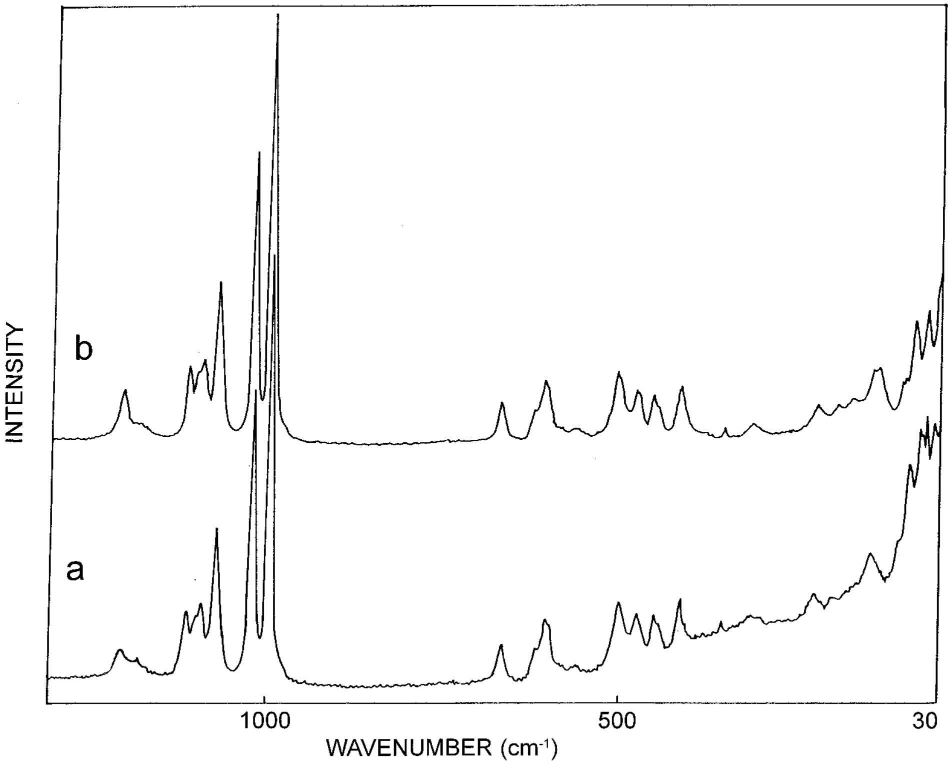

FIG. 2. Raman spectra of (a) $NH_4Yb(SO_4)_2 \cdot 2H_2O$ and (b) $NH_4Tm(SO_4)_2 \cdot 2H_2O$ in the 30–1200 cm^{-1} region.

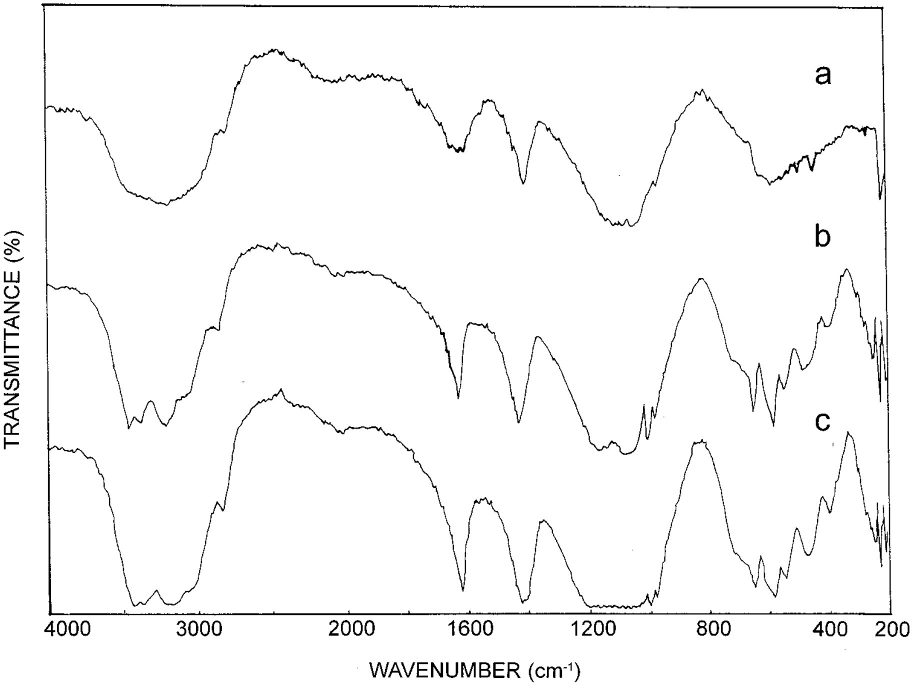

FIG. 3. Infrared spectra of (a) $NH_4Sm(SO_4)_2 \cdot 4H_2O$, (b) $NH_4Tm(SO_4)_2 \cdot 2H_2O$, and (c) $NH_4Yb(SO_4)_2 \cdot 2H_2O$ in the 200–4000 cm^{-1} region.

change associated with this IR inactive mode. But this mode appears as a strong doublet at 1006 and 981 cm^{-1} for ATH and at 1001 and 981 cm^{-1} for AYH.

In the triply degenerate asymmetric stretching (ν_3) mode region, Malhotra *et al.* have observed four bands in the 1050–1190 cm^{-1} region in the IR spectrum of $NH_4Ce(SO_4)_2 \cdot 4H_2O$ (5). In the present study, three well resolved bands are obtained in the Raman spectra whereas a broad band covering the 1020–1160 cm^{-1} region, with distinct peaks at 1045, 1076, and 1110 cm^{-1}, is observed in the IR spectra for ASH. The additional band observed by Malhotra *et al.* can be due to factor group splitting. In the other two crystals, four bands each are obtained in the 1060–1205 cm^{-1} region in the Raman spectra with complete lifting of degeneracy. The corresponding IR spectra give four bands for ATH whereas a very intense broad (unresolved) band is obtained for AYH in the 1030–1230 cm^{-1} region.

The doubly degenerate symmetric bending (ν_2) mode appears in the 395–500 cm^{-1} region in ASH (see Figs. 1–3) with the degeneracy lifted. Additional splitting is observed in the IR and Raman spectra of ATH and in the Raman spectrum of AYH for this mode. The bands obtained in the 577–680 cm^{-1} region of the Raman spectra are assigned to the asymmetric S–O bending (ν_4) vibrations of SO_4^{2-} ions, and the degeneracy is lifted in all the three crystals.

Since there are eight SO_4 units in the Bravais cell, 18 bands each can appear in all the orientations giving A_g and B_g species (see Table 1) in the internal mode region. However, only nine bands are observed for B_g species and ten bands for A_g species. If two types of anions, as suggested in the crystal structure (4), are present in ASH, one can expect a doubling of bands for both degenerate and nondegenerate vibrations. Only one band is observed for the nondegenerate symmetric stretching ν_1 mode. In the case of the degenerate modes ν_2, ν_3, and ν_4 no splitting other than the lifting of degeneracy is observed.

X-ray data show two average S–O distances for the two crystallographically nonequivalent SO_4 groups (1.465 and 1.477 Å, respectively) in ASH. However, this is not observed in the IR and polarized Raman spectra. For ATH and AYH, the nondegenerate symmetric stretching mode is found to be split in the IR and Raman spectra. The triply degenerate asymmetric stretching mode gives four bands each in the Raman spectra of both the crystals. The order of splitting is around 110 cm^{-1} in both of them. Therefore the splitting observed in both degenerate (ν_2, ν_3 and ν_4) and nondegenerate (ν_1) modes confirm the presence of two crystallographically different SO_4 groups in ATH and AYH (9, 10). The observed higher wavenumbers for the ν_1 mode for ATH and AYH crystals indicate the presence of stronger S–O bonds in these crystals.

NH_4^+ *Vibrations*

The internal modes of vibration of a free NH_4^+ ion with T_d symmetry have average frequencies at 3033, 1685, 3134, and 1397 cm^{-1} for $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ modes, respectively (8). The coordination of hydrogen atoms of the ammonium ion with oxygen atoms of the sulfate group is expected to distort the structure of the NH_4^+ ion.

In the polarized Raman spectra of ASH, the symmetric stretching (ν_1) mode appears as a single band in all orientations of the crystal. The triply degenerate asymmetric stretching (ν_3) and asymmetric bending (ν_4) modes show partial lifting of degeneracies. The out-of-plane deformation $\nu_2(E)$ mode appears as two bands with degeneracy lifted in both IR and Raman spectra. The nondegenerate symmetric stretching (ν_1) mode is observed at 2880 and 3064 cm^{-1} in Raman and at 2880 and 3070 cm^{-1} in the IR for ATH. For AYH, this mode appears at 3070 cm^{-1} in Raman and at 2840 and 3075 cm^{-1} in IR. The asymmetric stretching (ν_3) vibrations are observed in the 3130–3300 cm^{-1} region for both the compounds. The bands in the 1675–1705 cm^{-1} region are assigned to the out-of-plane deformation mode (ν_2). A retention of degeneracy is observed for the asymmetric bending (ν_4) mode for both ATH and AYH compounds. The bands due to torsional oscillation of the ammonium ion (ν_6) are observed around the 200–300 cm^{-1} region (11).

A tetrahedral NH_4^+ ion can rotate about one of the threefold axes. If its rotation is prevented, the degeneracy is expected to be lifted in the crystal lattice. Such a locked NH_4^+ ion gives the presence of librational mode (ν_6) and its combination with deformation modes, $\nu_2 + \nu_6$ and $\nu_4 + \nu_6$ (12). These bands are observed for all three compounds, and therefore NH_4^+ ions in the crystals are not rotating freely. The absence of free rotation and the broadness of the NH_4 bands show that the ammonium ions form hydrogen bonds in the crystals (13). Splitting observed in the symmetric stretching (ν_1) mode of AYH and ATH confirms the formation of hydrogen bonds by ammonium ions.

In the Raman spectra, the symmetric stretching (ν_1) mode is expected to be the most intense band. But in AYH and ATH the asymmetric stretching (ν_3) band is more intense than the ν_1 mode. This indicates the possibility of intensity enhancement through Fermi resonance of ν_1 and ν_3 modes with the combination ($\nu_2 + \nu_4$) bands in both the compounds (14). Strong fluorescence bands are observed in the Raman spectrum ca. 2100 cm^{-1} in AYH and ca. 2600 cm^{-1} in ASH.

Water Vibrations

The vibrational frequencies of a free water molecule are at 3756 (ν_3), 3652 (ν_1), and 1595 (ν_2) cm^{-1} (15). Depending on the strength of hydrogen bonding, the stretching modes will shift to lower wavenumbers and the bending mode to a higher wavenumber.

The bands observed in the 3315–3510 cm^{-1} region in the IR and Raman spectra are assigned to the symmetric and asymmetric stretching modes of water molecules. In the IR spectrum of ASH, the stretching vibrations of the NH_4^+ ion and the water molecule together give rise to a strong broad band extending from 3000–3500 cm^{-1}.

The dynamic coupling of the HOH bending vibrations of the neighboring water molecules give rise to three medium intense bands at 1600, 1620, and 1650 cm^{-1} for ASH in the IR spectrum. This mode is observed at 1621 cm^{-1} with a shoulder at 1645 cm^{-1} for ATH and at 1624 cm^{-1} for AYH in the IR spectrum.

The significant decrease in the frequencies of the stretching modes and the increase in frequencies of the bending modes from the free state values show that water molecules form hydrogen bonds of medium strength in all the three crystals (16). The observed bands in the stretching and bending regions show the presence of three crystallographically distinct water molecules in ASH, as in $NH_4Ce(SO_4)_2 \cdot 4H_2O$ and $NH_4La(SO_4)_2 \cdot 4H_2O$. In AYH and ATH only one type of water molecule is observed. Librational modes of water are assigned on the basis of the intensity in the order wagging > rocking > twisting and the frequency in the sequence rocking > twisting > wagging (17).

External Modes

The external modes are assigned by considering the fact that the translatory and libratory modes of the NH_4^+ ion occur at higher wavenumbers than those of the SO_4^{2-} ions. The bands observed below 150 cm^{-1} are assigned to the translations and librations of the SO_4^{2-} ion. The librations of both NH_4^+ and SO_4^{2-} ions are found to be weaker in intensity than the corresponding translational modes (18).

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