

# Infrared and Polarized Raman Spectra of Tetramethyl Ammonium Cerium(III) Bis(sulfate) Trihydrate

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Received February 29, 1996; in revised form July 15, 1996; accepted August 8, 1996

Infrared and polarized Raman spectra of  $(\text{CH}_3)_4\text{NCe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  are recorded and analyzed. Bands are assigned on the basis on  $(\text{CH}_3)_4\text{N}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}_2\text{O}$  vibrations. Methyl rotational modes and tetramethyl skeletal bending modes are not observed in the IR spectrum confirming the X-ray data that the tetramethyl ammonium ion retains its  $T_d$  symmetry in the crystal. Small splitting observed in the nondegenerate modes of  $\text{SO}_4^{2-}$  ions implies slight distortion of the anions in the crystal. The existence of two types of  $\text{SO}_4^{2-}$  ions cannot be confirmed. The shifting of the stretching and bending vibrations of the water molecules from the free state value confirms the formation of hydrogen bonds of varying strengths in the crystal.

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## INTRODUCTION

Double sulfates of rare earths and tetramethyl ammonium with empirical formula  $(\text{CH}_3)_4\text{NLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{and Dy}$ ) are synthesized and studied by different methods including TGA, DTA, DTG, and X-ray powder diffraction method by Jordanovska and Siftar (1). Several studies have reported on the vibrational spectral analysis of hydrated double sulfates of tetrahedral ammonium ions (2, 3). Though such double sulfates have been subjected to detailed vibrational analysis, studies on double sulfates of tetramethyl ammonium cation have not been reported so far. The tetramethyl ammonium (TMA) ion is of spectroscopic interest due to its high symmetry. Solid state IR spectra of  $(\text{CH}_3)_4\text{N}^+$  ions in different crystalline environments demonstrate the presence of hydrogen bonding between cation C–H bonds and anions such as halides, halates, and borates (4). Tempera-

ture dependent changes in the infrared and Raman spectra of TMA salts with complex inorganic anions have been used to demonstrate the existence of phase transitions in these compounds (5–7).

In this paper, the IR and polarized Raman spectra of single crystal of  $(\text{CH}_3)_4\text{NCe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  (hereafter referred as TAST) at room temperature are recorded and analyzed to understand the nature of vibrations of the TMA ion, the sulfate ion, and water molecules as a continuation of our work on sulfates.

## EXPERIMENTAL

Single crystals of the title compound were prepared by slow evaporation of an aqueous solution containing equivalent quantities of tetramethyl ammonium sulfate and cerium(III) sulfate (8). Colorless prismatic crystals with well developed faces were used for the study. A Spex Ramalog 1401 double monochromator equipped with the Spectra Physics model 165 Ar<sup>+</sup> laser was used to record the polarized Raman spectra for six polarization geometries in the Stokes region with a power of 100 mW on the 5145 Å line. IR spectra in the region 400–4000  $\text{cm}^{-1}$  were recorded as KBr pellets using a Nicolet 170 SX FT-IR spectrometer and the region below 400  $\text{cm}^{-1}$  as polyethylene pellets using Bruker IFS-66V FT-IR spectrometer.

## CRYSTAL STRUCTURE AND FACTOR GROUP ANALYSIS

X-ray studies show that the compound crystallizes in the orthorhombic system with space group  $Pca2_1$  having four formula units per unit cell (8). The Ce atom is coordinated by eight oxygen atoms, five belonging to sulfate groups

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TABLE 1  
Vibration Spectral Data (in  $\text{cm}^{-1}$ ) and Assignments of  $(\text{CH}_3)_4\text{NCe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$

Raman						IR	Assignments
<i>a(bb)c</i>	<i>a(cb)c</i>	<i>a(ba)c</i>	<i>a(ca)c</i>	<i>b(aa)c</i>	<i>a(cc)b</i>		
<i>A</i> <sub>1</sub>	<i>B</i> <sub>2</sub>	<i>A</i> <sub>2</sub>	<i>B</i> <sub>1</sub>	<i>A</i> <sub>1</sub>	<i>A</i> <sub>1</sub>		
1	2	3	4	5	6		
					3514vww	3649vw	
3358vw	3345vw	3438m	3370vww	3392vw			$\nu_3\text{H}_2\text{O}$
3305vw				3366vw		3349br	
				3334vw			
3168vw		3190vww	3218w	3199vw	3143vw		$\nu_1\text{H}_2\text{O}$
3118vw		3138vw		3144vw	3118w		
3058m	3051s	3054s	3062w	3052s	3046m	3048w	$\nu_{\text{as}}\text{CH}_3$
3040s	3038s	33040s	3039m	3040s	3035m	3019w	
2982sh	2985sh			2980sh	2978sh	2966vw	
2961s	2957m	2959m	2959m	2960s	2955vs	2946sh	$\nu_{\text{sy}}\text{CH}_3$
2919vw	2902brw		2917m	2908m			
2807w	2808w			2796w	2803m	2784vww	combination and
2720vww						2575vww	overtones
1640vw						1621m	$\nu_2\text{H}_2\text{O}$
1468vs	1468m	1470w	1468m	1475s	1471vs	1488vs	$\delta_{\text{as}}\text{CH}_3$
					1461sh		
1438vw							
1413vw		1413vw	1413vw	1413vww		1406m	$\delta_s\text{CH}_3$
1263vs	1263m	1264vw	1268vw	1264s	1258vw	1260m	
1188vw					1176w		$\nu_1\text{CH}_3$
1128w		1120vww	1087vww	1124w	1122vww	1227s	
						1125sh	$\nu_3\text{SO}_4$
1046w	1038w	1047s	1040m	1038w	1038m	1049vvs	
1001vvs	1001s	1000s	1001s	1001s	998vs	996w	
972vs	972s	970s	973m	972s	968vvs	968w	$\nu_1\text{SO}_4$
949w	948brm	948s	946m	948m	946m	947vs	$\nu_{\text{as}}\text{C}_4\text{N}$
755m	758m	755w	755m	756m	752vs	764w	$\nu_{\text{sy}}\text{C}_4\text{N}$ , $\nu_1\text{H}_2\text{O}$
600w	638vww	628vww	650vww	687vw	620vw	650s	$\nu_4\text{SO}_4$ , $\nu_1\text{H}_2\text{O}$
	600vw	600vw		598vww	587vw	610sh	
			524w			594s	
482w		484m	479vw	487w	483vw	529m	$\nu_w\text{H}_2\text{O}$
465w	463w	456m	459w	468m	457w	477m	$\nu_2\text{SO}_4$
428w	430vww		438vw	434w		453m	
				382m	387vs	424w	$\delta_{\text{as}}\text{C}_4\text{N}$
273w			295w	294vw	272vww		TMA sk. bend
182w	186w	180vw		184w			$\text{CH}_3$ rot.
						195vbr	$\delta_t\text{CH}_3$ ,
							$\nu\text{OH} \cdots \text{O}$
159w	154w			166w	158w	165vww	$\text{SO}_4$ rot,
							Ce–O stretch
						95vw	$\delta\text{OH} \cdots \text{O}$
82m	82m	80vw	89w	83s		81vww	$\text{SO}_4$ translation
						67vw	

and three belonging to the water molecules in the form of an irregular polyhedron so that all the water molecules are in the coordination sphere of Ce(III). The structure can be described as layers of  $\text{N}(\text{CH}_3)_4$  cations,  $\text{SO}_4$  anions, Ce, and water molecules. All the ions, molecules, and Ce atoms occupy the general sites in the crystal. The factor group analysis (9) predicts 309 modes at  $K = 0$  and they split into

$$\Gamma^{\text{TAST}} = 77A_1 + 78A_2 + 77B_1 + 77B_2.$$

## RESULTS AND DISCUSSION

The observed bands of the IR and Raman spectra of TAST with assignments of various vibrational modes are given in Table 1. The spectra are analyzed in terms of the vibrations of  $(\text{CH}_3)_4\text{N}^+$ ,  $(\text{SO}_4)^{2-}$ , and water molecules.

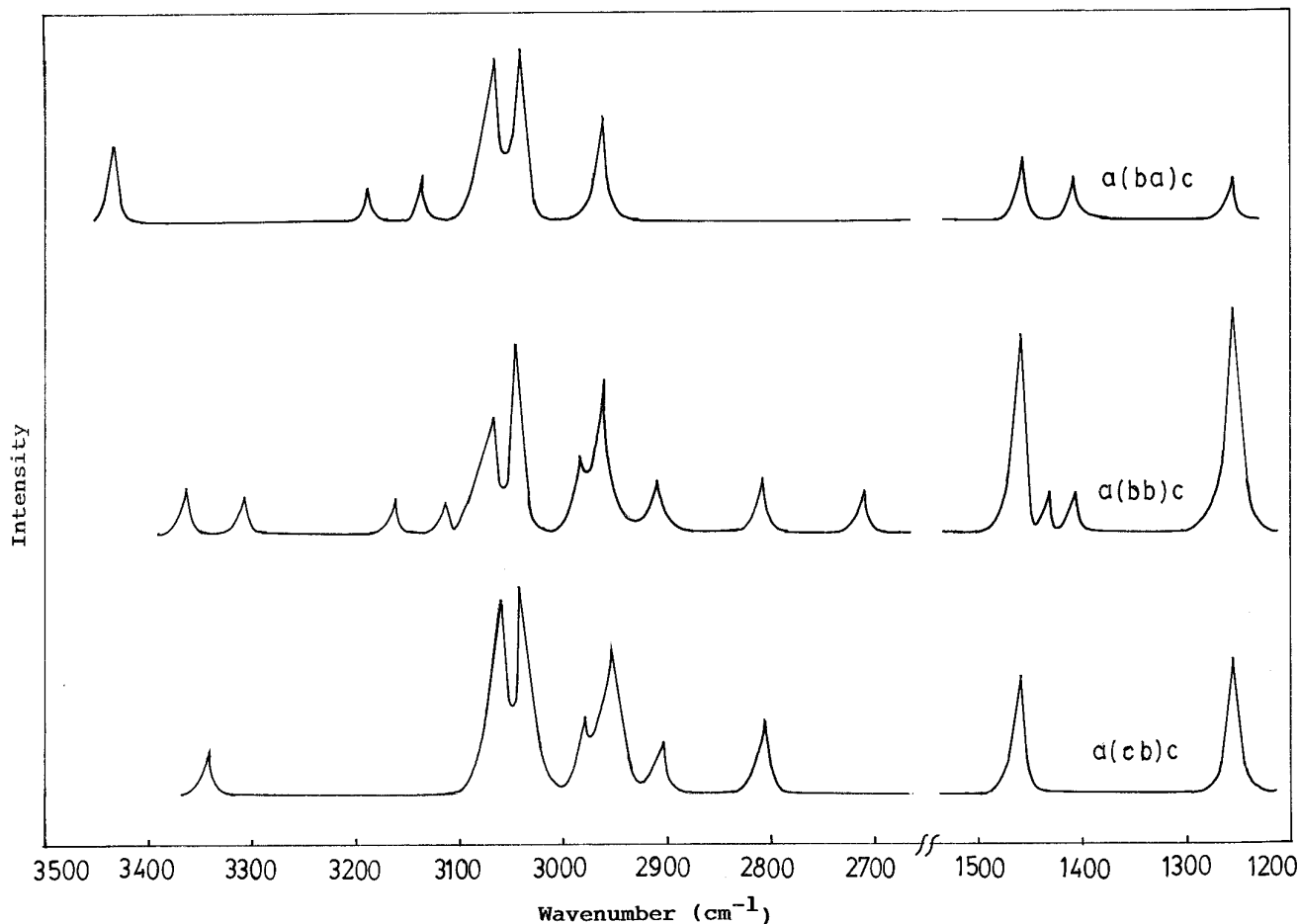


FIG. 1. Raman spectra of  $(\text{CH}_3)_4\text{N}\text{Ce}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in the  $1200\text{--}3500\text{ cm}^{-1}$  region for the  $a(ba)c$ ,  $a(bb)c$ , and  $a(cb)c$  orientations.

### Internal Modes

*$(\text{CH}_3)_4\text{N}^+$  vibrations.*  $\text{CH}_3$ ,  $\text{C}_4\text{N}$ , and skeletal modes contribute to the internal modes of the  $(\text{CH}_3)_4\text{N}$  cation. The tetramethyl ammonium group with  $T_d$  symmetry has 45 internal modes distributed as  $3A_1 + A_2 + 4E + 4F_1 + 7F_2$ . In the crystal all these modes are expected to give bands as it occupies a  $C_1$  symmetry.

Highly polarized bands observed between 2900 and 2985  $\text{cm}^{-1}$  are assigned to the symmetric stretching mode of  $\text{CH}_3$ . Corresponding to this mode a weak band at 2966  $\text{cm}^{-1}$  with a shoulder at 2946  $\text{cm}^{-1}$  is observed in the IR spectrum. The polarization effects on the Raman bands in the 3035–3060  $\text{cm}^{-1}$  region are less compared to the highly polarized bands in the 2900–3000  $\text{cm}^{-1}$  region. Hence, the bands in the 3015–3060  $\text{cm}^{-1}$  region are assigned to the asymmetric stretching mode of  $\text{CH}_3$ . The degeneracy of this mode is lifted in the crystal as the  $(\text{CH}_3)_4\text{N}$  ion occupies a site of lower symmetry,  $C_1$ . In compounds containing the TMA ion, bands arising due to the combinations and

overtone of deformation modes appear in the 2800–2500  $\text{cm}^{-1}$  region (10, 11). Therefore, the weak IR band at 2784  $\text{cm}^{-1}$  and the weak Raman bands in the 2700–2900  $\text{cm}^{-1}$  region (Fig. 1) are assigned to the nonfundamental modes.

In the bending mode region of  $\text{CH}_3$ , Raman spectra exhibits highly polarized bands around 1460  $\text{cm}^{-1}$  and depolarized weak bands at 1413  $\text{cm}^{-1}$ . Correspondingly a very intense band at 1488  $\text{cm}^{-1}$  and a medium intense band at 1406  $\text{cm}^{-1}$  are observed in the IR spectrum. Since the frequency of the methyl asymmetric bending motion is always found near 1450  $\text{cm}^{-1}$  independent of the molecule of which they are a part (12), the bands are assigned accordingly.

The strong polarized bands around 752  $\text{cm}^{-1}$  in the Raman spectra and the band at 764  $\text{cm}^{-1}$  in the IR spectrum are assigned to the symmetric stretching mode of  $\text{C}_4\text{N}$ . The asymmetric stretching mode appears around 948  $\text{cm}^{-1}$  in all orientations of the Raman spectra and as an intense band at 947  $\text{cm}^{-1}$  in the IR. The methyl rotational modes appear between 272 and 295  $\text{cm}^{-1}$  and the tetramethyl

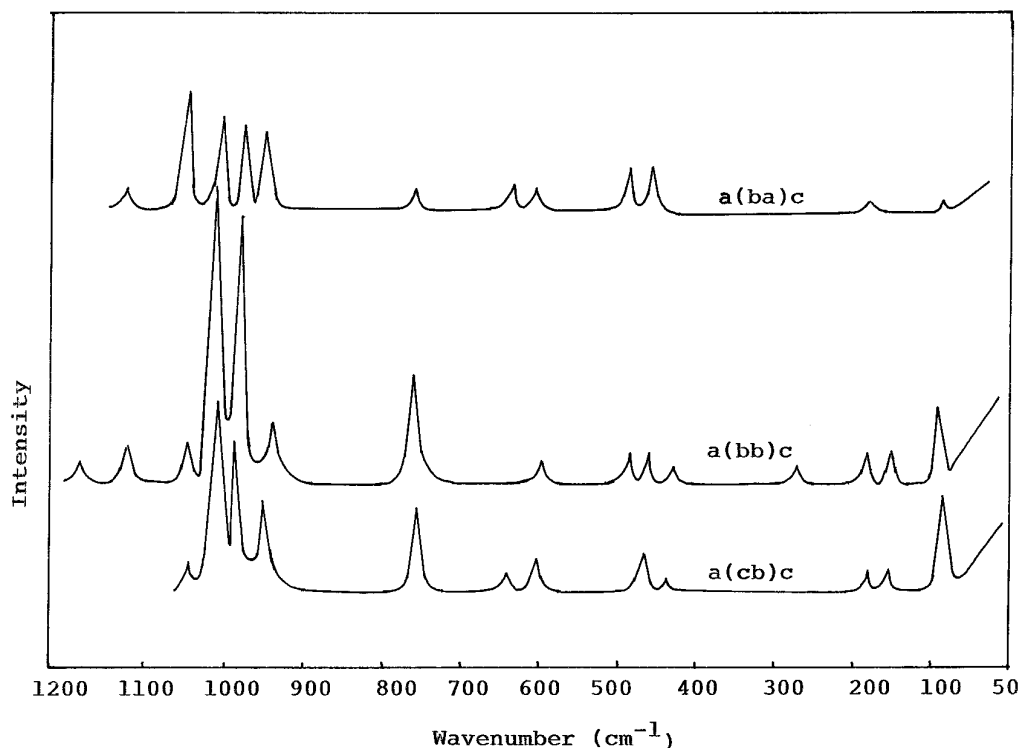


FIG. 2. Raman spectra of  $(\text{CH}_3)_4\text{Nce}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in the  $50\text{--}1200\text{ cm}^{-1}$  region for the  $a(ba)c$ ,  $a(bb)c$ , and  $a(cb)c$  orientations.

bending modes around  $387\text{ cm}^{-1}$  in the Raman spectra. Correspondingly no bands are observed in the IR.

Methyl rotational bands and tetramethyl skeletal bending bands are forbidden in the IR spectrum in  $(\text{CH}_3)_4\text{N}^+$  ions retaining  $T_d$  symmetry (13). The absence of these bands in the IR spectrum confirms the X-ray data that the TMA ion retains  $T_d$  symmetry in the crystal.

**$\text{SO}_4^{2-}$  vibrations.** The normal modes of vibration of free tetrahedral  $\text{SO}_4^{2-}$  ion under  $T_d$  symmetry have average frequencies at  $981$ ,  $451$ ,  $1104$ , and  $614\text{ cm}^{-1}$  for the  $\nu_1(A_1)$ ,  $\nu_2(E)$ ,  $\nu_3(F_2)$ , and  $\nu_4(F_2)$  modes, respectively. All these modes are Raman active, whereas the triply degenerate modes  $\nu_3$  and  $\nu_4$  are infrared active (14). In the crystal, the  $\text{SO}_4^{2-}$  ion occupies a lower site symmetry  $C_1$ . As a result the IR inactive  $\nu_1$  and  $\nu_2$  modes may become active and the degeneracies of  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  modes may be removed. The nondegenerate  $\nu_1$  mode of the ion is found to be split into two components in the Raman spectra appearing around  $970$  and  $1001\text{ cm}^{-1}$ . Correspondingly two medium bands are observed at  $968$  and  $996\text{ cm}^{-1}$  in the IR spectrum. Appearance of this IR inactive mode can be due to the lowering of symmetry of the sulfate ion from  $T_d$  to  $C_1$ .

The polarizability tensor components  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$  of  $\nu_1(\text{SO}_4)$  with  $T_d$  symmetry belong to the  $A_1$  species of the  $C_{2v}$  factor group. Therefore this mode appears in these

polarizations of the crystal without any distortion of the  $\text{SO}_4$  ion (15). But the distortion of the ion from  $T_d$  to the site symmetry  $C_1$  leads to the appearance of this mode in the  $\alpha_{xy}$ ,  $\alpha_{xz}$ , and  $\alpha_{yz}$  orientations of the crystal as observed in the spectra (Fig. 2). The symmetric deformation mode  $\nu_2$  appears as two bands in the  $440\text{--}490\text{ cm}^{-1}$  region in both IR and Raman spectra with the lifting of degeneracy in all the polarizations except in  $a(cb)c$ .  $\nu_3$  and  $\nu_4$  have polarizability tensor components  $\alpha_{xy}$ ,  $\alpha_{xz}$ , and  $\alpha_{yz}$  belonging to the  $A_2$  and  $B_2$  species, respectively. But these modes appear in all the orientations of the Raman spectra. The  $\nu_3$  mode appears as a broad intense band with peaks at  $1227$ ,  $1225$ , and  $1049\text{ cm}^{-1}$  in the IR while this mode gives two bands only in five polarizations of the Raman spectra. The  $\nu_4$  mode appears as two intense bands at  $594$  and  $650\text{ cm}^{-1}$  with a shoulder at  $610\text{ cm}^{-1}$  in the IR. The large intensity observed for these bands in the IR may be due to the presence of the librational modes of water in the same region.

Two  $\text{SO}_4^{2-}$  groups in the compound have the average S–O distances of  $1.470$  and  $1.479\text{ \AA}$ , respectively. Even though the  $\nu_1$  mode is split into two bands, the splitting cannot be due to the presence of two  $\text{SO}_4$  ions alone in the crystal as the difference between the two bands is only  $30\text{ cm}^{-1}$  in the Raman spectra. The splitting of the order

of 30 cm<sup>-1</sup> can also be due to the correlation field effect as there are eight SO<sub>4</sub> units in the crystal (16). Apart from the lifting of degeneracies no further splitting is observed in the  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  modes. Therefore the existence of two types of SO<sub>4</sub> ions cannot be confirmed. Further, it also implies only a small distortion of SO<sub>4</sub> ions in the crystal as obtained from the X-ray data.

*H<sub>2</sub>O vibrations.* The vibrating frequencies of a free water molecule usually occur at 3756( $\nu_3$ ), 3652( $\nu_1$ ), and 1595( $\nu_2$ ) cm<sup>-1</sup>. Depending upon the strength of the hydrogen bonding, the stretching modes will shift to lower wavenumbers and the bending mode to higher wavenumbers (17). The coordination of the water oxygen with the cerium atom is expected to distort the structure of the water molecules.

A broad band extending from 3138 to 3700 cm<sup>-1</sup> is observed in the IR spectrum in the region of symmetric and asymmetric stretching modes of H<sub>2</sub>O and CH<sub>3</sub>. CH<sub>3</sub> modes have been identified by the peaks observed in the broad band. Two peaks observed at 3649 and 3349 cm<sup>-1</sup> are assigned to the  $\nu_1$  and  $\nu_3$  modes of H<sub>2</sub>O vibration. In the Raman spectra, several weak bands are observed in the 3120–3520 cm<sup>-1</sup> region corresponding to these modes. In the bending mode ( $\nu_2$ ) region only a weak band at 1640 cm<sup>-1</sup> is obtained in the *a(bb)c* polarization. In the IR, a band with medium intensity is seen at 1621 cm<sup>-1</sup> in this region.

The librational modes of water fall in the range of 500–900 cm<sup>-1</sup> (18). These modes are more sensitive to interactions involving hydrogen bonds and less sensitive to those involving metal oxygen coordination. The low polarizability of water molecules makes these bands appear weak. In inorganic salt hydrates having linear hydrogen bonds, the rocking mode ( $\nu_r$ ) will appear at higher frequencies than the wagging modes ( $\nu_w$ ) (19). These modes are in the order  $\nu_r > \nu_t > \nu_w$ . Of these, the twisting mode ( $\nu_t$ ) and the rocking mode ( $\nu_r$ ) appear in the region of the  $\nu_4$  mode of the SO<sub>4</sub> ion and the C–N stretching mode of the TMA ion, respectively. The wagging mode is assigned around 525 cm<sup>-1</sup> in both IR and Raman spectra. This type of coupling between internal modes of anions and the librational modes of water molecules has been reported earlier (20). Even though the bending modes appear at frequencies shifted in higher wavenumber region in both the spectra, the appearance of the  $\nu_3$  mode up to 3649 cm<sup>-1</sup> in the IR suggests that the water molecules form hydrogen bonds of varying strengths in the crystal.

### External Modes

External modes appear below 295 cm<sup>-1</sup> which includes lattice modes of water, external modes of SO<sub>4</sub><sup>2-</sup> and CH<sub>3</sub>, and Ce–O stretching modes.

The bands of medium intensity around 82 cm<sup>-1</sup> in the Raman spectra and the weak band at 81 cm<sup>-1</sup> in the IR are assigned to the translatory modes of SO<sub>4</sub>. A very broad band in the 150–240 cm<sup>-1</sup> region observed in the IR spectra belongs to the region of CH<sub>3</sub> twisting and (OH)···O stretching modes. Correspondingly weak bands are observed in the Raman spectra around 182 cm<sup>-1</sup> in four orientations. The (OH)···O bending mode is observed in the IR only as a very weak band at 95 cm<sup>-1</sup>. Since the SO<sub>4</sub> rotatory modes and Ce–O stretching modes lie in the same wavenumber region, a strict assignment of these modes is very difficult.

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