

## IR and polarized Raman spectra of strontium tartrate trihydrate

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**Abstract.** The IR and polarized Raman spectra of  $\text{SrC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$  have been recorded and analysed. The factor group analysis of the divalent tartrate ion has been carried out on the basis of  $C_2$  symmetry. As the ion possesses lower symmetry in the crystal, splittings have been observed for the different vibrational modes. Separate bands in the bending region of water suggest the existence of three crystallographically different water molecules in the crystal, which is confirmed by deuterium substitution.

**Keywords.** Polarized Raman spectrum; infrared spectrum; crystal field effect.

### 1. Introduction

Metal tartrates form an interesting class of compounds as they exhibit ferroelectric and ferroelastic properties (Taylor *et al* 1984; Udagawa *et al* 1979). Vibrational spectra of certain tartrates in the microcrystalline form have been reported earlier (Bolard 1965; Kaneko *et al* 1984). Aleshin (1968) investigated the IR spectra of certain tartrate compounds at various temperatures and identified bands due to some of the vibrational modes of the tartrate ion,  $(\text{C}_4\text{H}_4\text{O}_6)^{2-}$ . Recently, Taylor *et al* (1984) reported the single crystal Raman spectra of  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  and  $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ . However, a complete assignment of the modes of the tartrate ion has not been done. In this paper a detailed IR and single crystal Raman study of strontium tartrate trihydrate is presented. The spectra of deuterated samples have also been investigated.

### 2. Experimental

Single crystals of  $\text{SrC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$  have been grown by the method suggested by Ambady (1968). For monoclinic systems  $Ag(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$  and  $\alpha_{xy})$  and  $Bg(\alpha_{xz}$  and  $\alpha_{yz})$  species give different spectra. However, for obtaining the complete information, all the six polarizations coming under  $Ag$  and  $Bg$  have been recorded. A SPEX RAMALOG 1401 double monochromator equipped with Spectra Physics model 165  $\text{Ar}^+$  laser has been employed to record the Raman spectra in the Stokes region of the blue line

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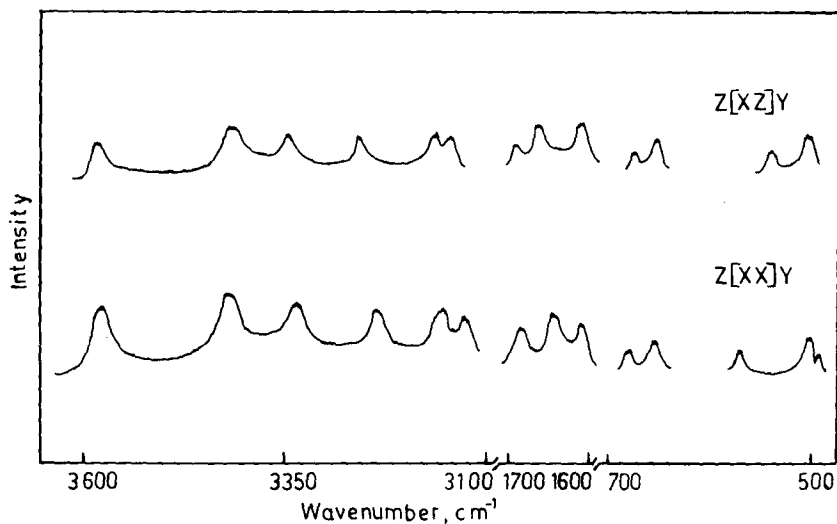


Figure 1. Raman spectrum of water of crystallization.

(488.0 nm). The accuracy of the data is expected to be  $\pm 2 \text{ cm}^{-1}$ . In figures 1 and 2, spectra of  $A_g[z(xx)y]$  and  $B_g[z(xz)y]$  are given. The IR spectra of the microcrystalline sample has been recorded on a PE 580 spectrophotometer using both nujol mull and KBr pellet techniques.

### 3. Results and discussion

$\text{SrC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$  crystallizes in the monoclinic system with space group  $P2_1(C_2^2)$ . There are two formula units per unit cell (Ambady 1968). The tartrate ion, water molecule and strontium atom are in general positions. The group theoretical analysis (table 1) gives 141 normal modes of vibrations,  $\Gamma = 71A + 70B$ , exclusive of 3 acoustical modes, which are active both in Raman and IR.

#### 3.1 Vibrations of the tartrate ion

The tartrate ion consists of two halves, each consisting of a carboxyl group, a tetrahedral carbon and a hydroxyl oxygen. The two halves are connected through C-C bonds so that the four carbon atoms are in a zig-zag planar configuration. This leads to the consideration of  $C_2$  symmetry for the free tartrate ion. Owing to the lower symmetry ( $C_1$ ) of the ion in the crystal, splitting of vibrational modes is expected.

The CH stretching vibrations are generally observed as strong bands in the  $2800\text{--}3100 \text{ cm}^{-1}$  region (Colthup *et al* 1964). The two strong bands appearing in all polarization geometries with mean frequencies  $2894$  and  $2976 \text{ cm}^{-1}$  and the medium intensity band at  $2948 \text{ cm}^{-1}$  have been assigned to this mode. In IR this mode appeared at  $2880$  and  $2940 \text{ cm}^{-1}$ . In most of the settings two bands have been observed (three in  $\alpha_{xz}$ ) for the  $\text{CO}_2$  symmetric stretching mode indicating the existence of carboxylate ion in the crystal (Colthup *et al* 1964). The corresponding IR band

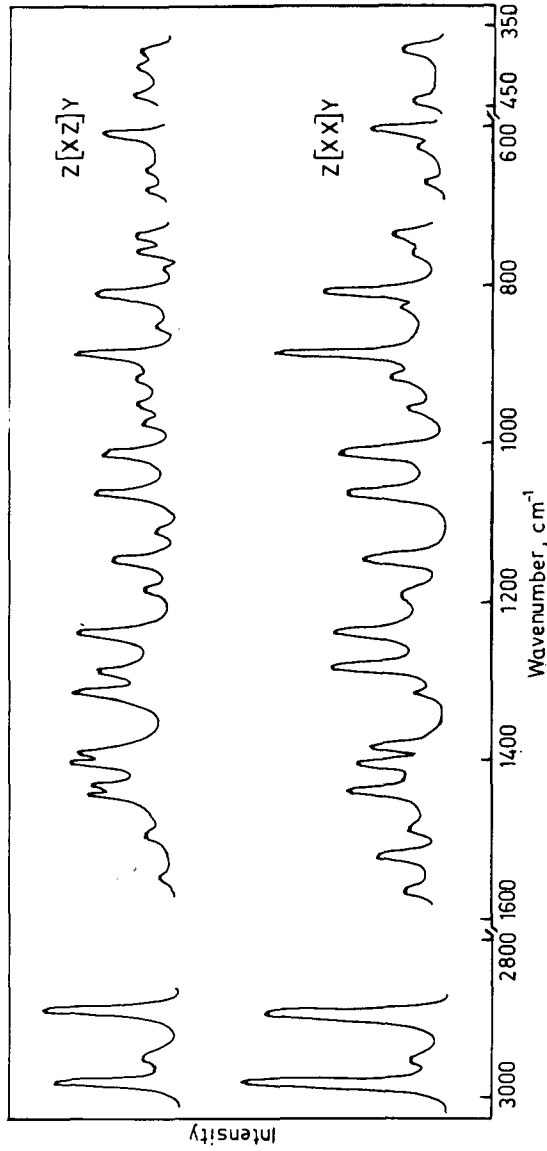


Figure 2. Raman spectrum of tartrate ion.

**Table 1.** Factor group analysis of  $\text{SrC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ .

	Symmetric species	
	A	B
Internal modes of		
$(\text{C}_4\text{H}_4\text{O}_6)^{2-}$	36	36
$\text{H}_2\text{O}$	9	9
Librational modes of		
$(\text{C}_4\text{H}_4\text{O}_6)^{2-}$	3	3
$\text{H}_2\text{O}$	9	9
Translational modes of		
$(\text{C}_4\text{H}_4\text{O}_6)^{2-}$	3	3
$\text{H}_2\text{O}$	9	9
Sr	3	3
	72	72

$$\Gamma_{141} = 71A(R, 1R) + 70B(R, 1R).$$

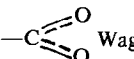
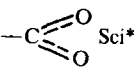
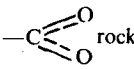
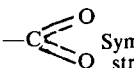
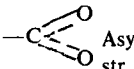
appeared as a weak one at  $1440\text{ cm}^{-1}$ . The assignments of  $\text{CO}_2$  deformation modes which are expected in the  $450\text{--}850\text{ cm}^{-1}$  region have been made on the basis of the normal coordinate calculations (Kaneko *et al* 1984) and intensity. The OH in-plane bending mode has appeared only in  $\alpha_{xx}$  and  $\alpha_{zz}$  at  $1384$  and  $1386\text{ cm}^{-1}$  respectively. But the out-of-plane bending mode is found to be active in all polarizations. As the hydroxyl possesses low polarizability the bands due to in-plane bending mode in other geometries may be too weak to be observed. It is difficult to assign the stretching modes of the hydroxyl group of the tartrate ion, as it overlaps with the stretching modes of water. Five bands have been identified in the CC stretching region (table 2). Winterfeldt (1980) from his investigations on Rochelle's salt assigned the band at  $890\text{ cm}^{-1}$  to the deformation modes of CH. However, following the calculated and observed frequencies on other tartrates; (Kaneko *et al* 1984) his assignment seems doubtful. This band can be assigned to the CC stretching mode.

Multiplicity of the bands observed in the different vibrational modes of tartrate ion is due to the crystal field effect.

### 3.2 Vibrations of water

The  $\alpha_{xx}$ ,  $\alpha_{zz}$  and  $\alpha_{yz}$  spectra contain as much as six bands in the stretching region (table 2). But as the OH stretching modes of the tartrate ion also fall in this range, it is not possible to assign these bands to the  $\nu_1$  and  $\nu_3$  modes of the water of crystallization. The three well-resolved bands observed in all polarizations for the bending mode indicate the presence of three different water molecules in the crystal. In the deuterated spectrum (table 3) two bands ( $1203$  and  $1258\text{ cm}^{-1}$ ) have been observed. This third is expected around  $1230\text{ cm}^{-1}$ . As there is a very strong band in this region (CH bend) this could not be observed separately. The assignments are proposed on the basis of the O-H...O bond lengths,  $2.78\text{ \AA}$  ( $\text{H}_2\text{O}$  I),  $2.63\text{ \AA}$  ( $\text{H}_2\text{O}$  II) and  $2.45\text{ \AA}$  ( $\text{H}_2\text{O}$  III). As a result of the low polarizability of water molecules most of the bands are weak and broad.

Table 2. Observed frequencies and vibrational assignments.

Raman ( $\text{cm}^{-1}$ )						IR ( $\text{cm}^{-1}$ )	Assignments	
$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{xy}$	$\alpha_{xz}$	$\alpha_{yz}$			
68 s	66 s	67 s	66 s	66 s	68 s			
104 s	104 s	105 s	105 s	104 s	106 s			
119 s	119 s	122 m	119 s	119 s	119 vs			
136 s	136 s	136 s	136 s	136 br	136 m			
	176 m	171 br	166 m	174 s	177 s			
		191 br	203 br	189 br				
	223 w	222 m	223 w	221 w	223 br	250 br	External modes	
	238 w		270 br					
295 w	290 br	289 w	285 br	275 w	279 m			
372 w	336 w	358 m		302 w	327 br			
				320 w				
379 m	380 w	382 m	382 w	378 m	385 w	380 w	 Wag	
	396 w	398 w	399 w	398 m	397 m			
441 m	436 m	440 m	439 w	437 br	441 br	450 w		
492 w	493 w	488 w	495 w			510 w	$\nu_w \text{H}_2\text{O}$	
504 m	504 w	507 w	504 m	504 br	505 m			
589 br	574 w	541 w		550 w			$\nu_t \text{H}_2\text{O}$	
605 m	607 vs	607 vs	607 vs	607 vs	607 vs	600 sh		
625 vw	647 vw	648 w	648 w	651 vw	648 vw	650 br	 Sci*	
672 w	682 w	667 w		678 w				
695 w		696 w		696 w	692 wbr	697 w		
726 w			722 w			720 br	$\nu_r \text{H}_2\text{O}$	
738 w	738 w	738 w	738 w	738 w	738 w			
761 w	769 w	772 m	768 m	759 w	767 w		 rock	
				777 vw				
810 s	810 s	810 s	810 s	810 s	810 s	820 m	OH out-of-plane bend	
829 vw	831 vw			826 w		850 w		
888 s	888 s	888 s	888 s	888 vs	887 s	890 vw		
917 w	912 w	918 w	917 w	919 w	917 w	920 vw	CC stretch	
958 w	945 w	951 w	951 w	948 w	950 w	950 br		
	974 w			970 w	992 w	1020 w		
1011 m	1011 s	1010 s	1011 s	1011 s	1009 s			
1063 mbr	1063 m	1058 mbr	1063 m	1062 m	1061 m	1060 vs		
	1106 w	1103 w	1109 w	1107 w	1106 w		CO stretch	
1144 mbr	1144 m	1147 m	1144 mbr	1144 m	1144 m	1150 vs		
1194 w	1188 w	1184 w	1192 w	1177 w	1178 w		In-plane	
1236 s	1236 s	1242 s	1236 s	1236 s	1237 s	1250 w	} -CH bend	
1282 s	1282 s	1283 s	1281 s	1283 m	1283 s	1270 w		Out-of-plane
1315 w	1309 m	1312 s	1311 s	1311 s	1312 s	1300 vw		
1384 m				1386 m		1340 w	OH in-plane bend	
						1380 m		
1404 m	1396 m	1401 m	1398 m	1398 m	1401 m			
				1429 m			 Sym. str.	
1436 s	1443 m	1436 s	1436 s	1438 m	1436 m	1440 w		
1484 vw	1486 w	1485 w	1484 w	1489 w	1485 w	1470 m		
1518 m	1529 w	1541 w	1529 w	1544 w	1534 w	1540 sh	 Asy. str.	
1562 w								

(continued)

Table 2. (Contd.)

Raman ( $\text{cm}^{-1}$ )						IR ( $\text{cm}^{-1}$ )	Assignments	
$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{xy}$	$\alpha_{xz}$	$\alpha_{yz}$			
1608 <i>br</i>	1604 <i>br</i>	1608 <i>br</i>	1609 <i>br</i>	1608 <i>mbr</i>	1609 <i>mbr</i>	1600 <i>br</i>	H <sub>2</sub> O I	
1644 <i>m</i>	1655 <i>w</i>	1667 <i>m</i>	1659 <i>w</i>	1656 <i>w</i>	1654 <i>w</i>		$\nu_2$	H <sub>2</sub> O II
1683 <i>w</i>	1687 <i>br</i>	1684 <i>br</i>	1686 <i>w</i>	1689 <i>w</i>	1687 <i>w</i>			H <sub>2</sub> O III
				2338 <i>w</i>	2335 <i>w</i>			
	2394 <i>w</i>	2343 <i>w</i>	2398 <i>w</i>	2390 <i>w</i>				
2455 <i>w</i>		2467 <i>w</i>	2458 <i>w</i>		2463 <i>w</i>			
2605 <i>w</i>	2610 <i>w</i>	2614 <i>w</i>	2602 <i>w</i>	2607 <i>w</i>		2600 <i>m</i>	Combinations	
2674 <i>w</i>	2723 <i>w</i>	2676 <i>w</i>	2730 <i>w</i>		2715 <i>w</i>	2740 <i>w</i>		
2763 <i>w</i>			2757 <i>w</i>	2788 <i>w</i>				
2896 <i>vvs</i>	2893 <i>vvs</i>	2898 <i>vvs</i>	2891 <i>vvs</i>	2893 <i>vvs</i>	2893 <i>vvs</i>	2880 <i>s</i>	CH str.	
2949 <i>m</i>	2947 <i>m</i>	2950 <i>m</i>		2945 <i>m</i>	2950 <i>m</i>			
2976 <i>vvs</i>	2976 <i>vvs</i>	2976 <i>vvs</i>	2976 <i>vvs</i>	2976 <i>vvs</i>	2976 <i>vvs</i>	2940 <i>s</i>		
3127 <i>br</i>	3135 <i>br</i>	3148 <i>br</i>	3122 <i>br</i>	3145 <i>w</i>	3148 <i>w</i>			
3156 <i>br</i>		3177 <i>w</i>		3162 <i>w</i>				
3238 <i>br</i>	3264 <i>br</i>	3286 <i>br</i>		3257 <i>br</i>	3250 <i>w</i>	3220 <i>br</i>	OH str.	
3332 <i>br</i>	3345 <i>br</i>	3366 <i>w</i>	3330 <i>w</i>	3345 <i>br</i>	3362 <i>w</i>	3400 <i>w</i>		
3420 <i>br</i>	3414 <i>br</i>	3439 <i>br</i>	3414 <i>w</i>	3415 <i>br</i>	3411 <i>br</i>		$\nu_1, \nu_3$ (H <sub>2</sub> O)	
					3574 <i>w</i>	3570 <i>w</i>		
3578 <i>br</i>		3481 <i>br</i>	3581 <i>br</i>	3580 <i>w</i>				

Note: The letters *vs*, *s*, *m*, *w*, *vw* and *br* stand for very strong, strong, medium, weak, very weak and broad band intensities respectively. Whereas the subscripts *w*, *t* and *r* refer to the wagging, twisting and rocking modes of water respectively.

\* Sci – scissoring; str. – stretch.

Table 3. Deuterated spectral data\*.

Raman		IR	
H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O
581	450		475
1385	1048	1380	1040
1607	1203		
		1600	1220
1686	1258		
3137	2370		
3259	2426		
		3400	2480
3346	2498		
3418	2544		

\* Only the shifted bands are given.

Librational modes of water fall in the range of 500–900  $\text{cm}^{-1}$  (Nakagawa and Shimanouchi 1964). The assignments are made by considering the fact that the rocking mode will have a greater frequency than the wagging mode (Singh *et al* 1980). Water bands are also distinguished from the deformation modes of CO<sub>2</sub> by

considering the band shape, deuterium substitution and intensity. The proposed assignments are given in table 2.

#### 4. Conclusions

- (i) Splittings observed for the vibrational modes of CH, CO<sub>2</sub>, CO and CC groups are due to the crystal field.
- (ii) The presence of separate bands in the bending region of water indicates that the three water molecules in the unit cell are distinct.

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