

## Infrared spectra of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and its deuterated analogue in 4000-1200 $\text{cm}^{-1}$ region

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**Abstract.** IR spectra of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and its deuterated analogue at  $\sim 300$  K and  $\sim 110$  K are reported in the region 4000-1200  $\text{cm}^{-1}$  using thin film and nujol mull techniques. The observed bands have been assigned as the internal modes of the water and the overtones and combinations of various modes using the recently revised assignments of  $\text{SO}_4^{2-}$  and  $\text{Be}(\text{aq})_4$  fundamentals in the region 1200-250  $\text{cm}^{-1}$  (Srivastava *et al* 1976). The splitting of the internal modes of water has been discussed in the light of the effects of deuteration and cooling and it is shown that all the water molecules in a unit cell are asymmetric but crystallographically equivalent.

**Keywords.** IR; hydrate;  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ; crystal water,  $\text{SO}_4^{2-}$ .

### 1. Introduction

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  occupies a special position among the crystal hydrates because hydrogen bonds (H-bonds) here are the strongest amongst the known hydrates; besides, the metal-oxygen ( $\text{M}-\text{O}_w$ ) coordination is so strong here that the four water molecules around the  $\text{Be}^{2+}$  cation are tightly bound, so much so that a quasi-tetrahedral molecule  $\text{Be}(\text{aq})_4$  ( $\text{aq} = \text{H}_2\text{O}$ ) is formed (Sikka and Chidambaram 1969). Though infrared and Raman studies are available on this salt in 4000-1200  $\text{cm}^{-1}$  region (Glemser and Hartert 1955; Diem *et al* 1968; Katiyar and Krishnamurthy 1969), assignments are so far primarily limited to the fundamental bands of water only. This may be due to the fact that the spectrum in the region 1200-250  $\text{cm}^{-1}$  did not have satisfactory assignment so far (Srivastava *et al* 1976) so that the overtones of and combinations with modes falling in that region were difficult to place.

The present work is part of a comprehensive study on assigning the full spectrum of the salt in the region 4000-250  $\text{cm}^{-1}$  using the partial deuteration technique. The analysis in the lower frequency region 1200-250  $\text{cm}^{-1}$  using isotopic shift ratios, and intensities and polarization of the bands, has changed some of the existing assignments for  $\text{Be}(\text{aq})_4$  complex modes and water librations (Srivastava *et al* 1976). In the present paper we report the IR absorption spectrum of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and

its deuterate in the region  $4000\text{--}1200\text{ cm}^{-1}$  at room and low temperatures. All the observed bands have been assigned, involving various fundamental modes, overtones and combination bands. The positions of the fundamental modes of water and their splittings have been correlated with the known environment. The effects of deuteration and of lowering the temperature on the band positions have also been discussed.

## 2. Experimental

Analar grade  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  was purified by recrystallization from its aqueous solution at room temperature (Mellor 1957). The deuterate was prepared by repeated dissolution of the salt in  $\text{D}_2\text{O}$  (99.8%) and evaporation in a vacuum system. Spectra of samples at two stages of deuteration were studied. Thin film (on CsBr plates) technique (Jain *et al* 1973) was used for recording the spectra to avoid nujol interference in the stretching band of  $\text{H}_2\text{O}$ . The spectra of highly deuterated samples were also checked in nujol mull. The spectra were recorded on Perkin-Elmer 521 IR spectrophotometer. The frequency scale was calibrated against the peak of polystyrene and indene. For sharp and isolated bands the accuracy is  $\pm 2\text{ cm}^{-1}$ , for others  $\pm 5\text{ cm}^{-1}$ . For studies at low temperature a modified Hornig type cell was used with liquid nitrogen as the coolant. The temperature at the sample was measured with a calibrated thermocouple and was  $\sim 110\text{ K}$ , hereafter called low temperature (LT).

## 3. Results

The spectra of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and a partial deuterate ( $\sim 60\%$ ) in the region  $4000\text{--}1200\text{ cm}^{-1}$  are shown in figure 1. The positions of all the observed bands in the hydrate and the partial deuterate are given in columns 1 and 3 of table 1. Their assignments are given in column 5. For the assignments the frequencies of

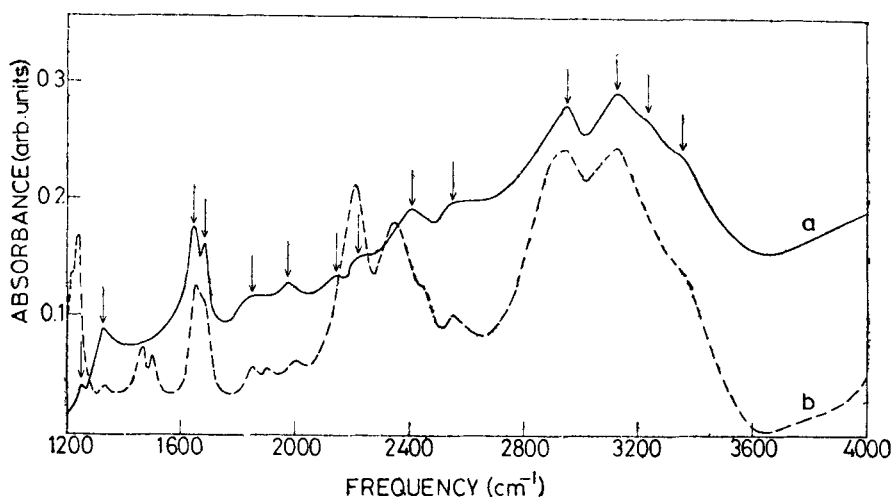


Figure 1. Infrared spectra of thin films of (a)  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (continuous curve) and (b) its partial deuterate (broken curve) at  $110\text{ K}$  in  $4000\text{--}1200\text{ cm}^{-1}$  region. The arrows over curve (a) denote the positions of the bands noted in table 1.

**Table 1.** Infrared absorption spectrum of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and its partial deuterate at 110 K in the region 4000–1200  $\text{cm}^{-1}$ 

Hydrate		Partial deuterate <sup>a</sup>		Assignments*	$\nu_{\text{cal}}$ ( $\text{cm}^{-1}$ )
Band position ( $\text{cm}^{-1}$ )	Intensity	Band position ( $\text{cm}^{-1}$ )	Intensity		
1	2	3	4	5	6
3340	m	3340	w	$2\nu_2/2\nu'_2(\text{H}_2\text{O})$	3360/3300
3210	vw	..		?	
3110	vs	3100	s	$\nu_{\text{OH}}$	Fund.
2925	vs	2925	s	$\nu'_{\text{OH}}$	Fund.
2550	vw	2560	vw	$2\nu_3^1(\text{SO}_4^{2-}) + \nu''_L$	2542
2405	vw	..		$2\nu_3^2(\text{SO}_4^{2-}) + \nu''_L$	2420
..		2445	vw	$2\nu_2/2\nu'_2(\text{D}_2\text{O})$	2472/2436
..		2350	vs	$\nu_{\text{OD}}$	Fund.
2225	vw	..		$2\nu_3^1(\text{aq})_H + \nu''_L$	2228
..		2205	vs	$\nu'_{\text{OD}}$	Fund.
2155	vw	Obscured by $\nu'_{\text{OD}}$		$2\nu_2^2(\text{aq})_H + \nu'_L$	2163)
				$2\nu_3^2(\text{SO}_4^{2-})$	2156)
		2000	vw	$2\nu_3^1(\text{aq})_D + \nu'_L$	2033
1975	vw	..		$2\nu_3^1(\text{aq})_H$	1964
..		1900	vw	$2\nu_4^1(\text{aq})_D + \nu'_L$	1937
..		1850	vw	$2\nu_4^2(\text{aq})_D + \nu'_L$	1857
1830	vw	..		$\nu_3^1(\text{aq})_H + \nu_4^1(\text{aq})_H$	1860
1680	s	1680	m	$\nu_2(\text{H}_2\text{O})$	Fund.
1650	s	1650	m	$\nu'_2(\text{H}_2\text{O})$	Fund.
..		1500	w	$\nu_2(\text{HOD})$	Fund.
..		1460	w	$\nu'_2(\text{HOD})$	Fund.
1335	w	1345	vw	$\nu_3^2(\text{SO}_4^{2-}) + \nu''_L$	1342
1256	w	Obscured by $\nu_2(\text{D}_2\text{O})$		$\nu_4^1(\text{SO}_4^{2-}) + \nu_4^2(\text{SO}_4^{2-})$	1286
..		1236	s	$\nu_2(\text{D}_2\text{O})$	Fund.
..		1218	s	$\nu'_2(\text{D}_2\text{O})$	Fund.

vs = very strong; s = strong; m = medium; vw = very weak; Fund. = fundamental.

a: Deuteration D:H  $\approx$  3:2, deduced from stretching mode intensities after accounting for the combination mode contribution and applying weight factor 2:1 for OD:OH intensities.

\* For assignments of the combination modes the fundamentals in 1200–250  $\text{cm}^{-1}$  region are taken from our unpublished work (Srivastava *et al* 1976). The values are  $\nu_3^1(\text{aq})_H = 982$ ,  $\nu_3^2(\text{aq})_H = 923$ ,  $\nu_4^1(\text{aq})_H = 878$ ,  $\nu_4^2(\text{aq})_H = 784$ ,  $\nu_3^1(\text{aq})_D = 858$ ,  $\nu_3^2(\text{aq})_D = 900$ ,  $\nu_4^1(\text{aq})_D = 810$ ,  $\nu_4^2(\text{aq})_D = 770 \text{ cm}^{-1}$ . For  $\text{SO}_5^{2-}$  and the lattice modes the mean of corresponding positions in the hydrate and deuterate are used. The values for  $\text{SO}_4^{2-}$  are  $\nu_3^1 = 1139$ ,  $\nu_3^2 = 1078$ ,  $\nu_4^1 = 668$  and  $\nu_4^2 = 618 \text{ cm}^{-1}$ ; for the lattice modes,  $\nu'_L = 317$  and  $\nu''_L = 264 \text{ cm}^{-1}$ .

the internal modes of  $\text{SO}_4^{2-}$ ,  $\text{Be}(\text{H}_2\text{O})_4$  and  $\text{Be}(\text{D}_2\text{O})_4$ , and of two lattice modes are taken from our work (Srivastava *et al* 1976) in the region 1200–250  $\text{cm}^{-1}$ ; these frequencies are given in the footnote to table 1.

Figures 2 and 3 show the effect of reducing temperature on the bands assigned to the stretching and bending modes of water respectively in  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ . Figure 4 shows the effect of deuteration on the bending mode of  $\text{H}_2\text{O}$ .

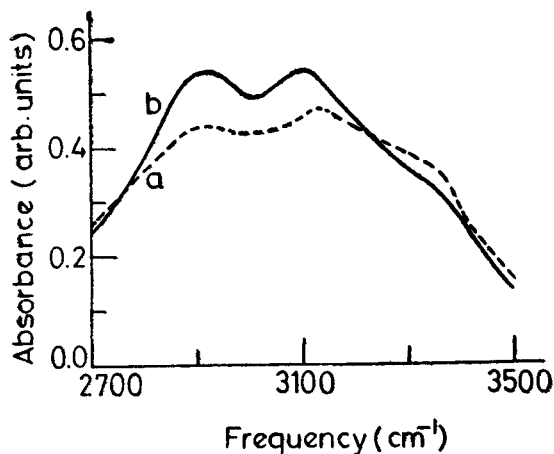


Figure 2. Stretching mode bands of  $\text{H}_2\text{O}$  in a partially deuterated  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  ( $\text{D}:\text{H} \approx 3:2$ ): (a) at 300 K and (b) at 110 K.

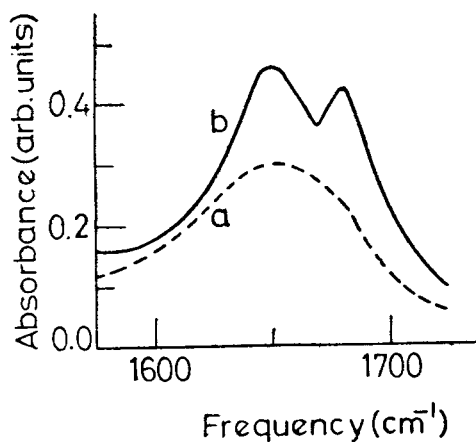


Figure 3. Bending mode bands of water in  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (a) at 300 K and (b) at 110 K.

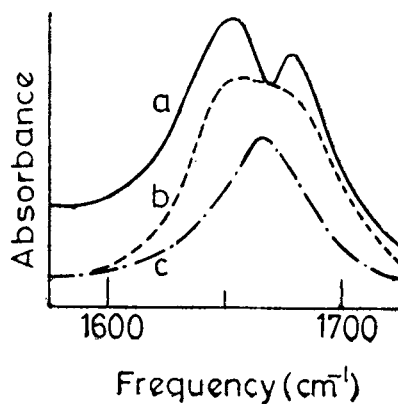


Figure 4. Bending mode bands of  $\text{H}_2\text{O}$  in  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  at 110 K with varying degree of deuteration.  $\text{D}:\text{H} \approx 0$  for (a) 3/2 for (b), 3/1 for (c).

## 4. Discussion

### 4.1. The stretching mode of water

The intense band in the region  $3150\text{--}2900\text{ cm}^{-1}$  represents the OH stretching mode, with peaks at  $3110$  and  $2925\text{ cm}^{-1}$ . In free water this doubling arises from intramolecular coupling and nomenclature  $\nu_1$  (symm.) and  $\nu_3$  (antisymm.) is valid. However, in hydrates effects like intermolecular coupling, proton tunnelling in the double minimum potential of the H-bond, crystallographically distinct sites of water and distortion of  $C_{2v}$  symmetry are superposed. Hence the separate nomenclature is not valid. The origin of the  $\nu$  (OH) doubling of  $185\text{ cm}^{-1}$  observed here could neither be inter- nor intramolecular coupling, since in either case the coupling would get weaker with increasing deuteration and the bands would tend to merge into one (Schiffer and Hornig 1969), which is not observed. Intramolecular coupling is also known to become stronger in the deuterate, so much so that the splitting  $\Delta\nu$  (OD) may even exceed  $\Delta\nu$  (OH) (Fifer and Schiffer 1969). But in the present case the ratio  $\Delta\nu$  (OD)/ $\Delta\nu$  (OH) is  $1.28$  (table 1), which is only slightly different from  $1.37$  expected (Kling and Schiffer 1969) on the basis of inertia factor alone.

Somorjai and Hornig (1962) have discussed how the relative intensity of the two components should vary with temperature and with deuteration if the origin of doubling is a double minimum potential in the H-bond. But no such variations are observed in the present case. The fact that HOD bending mode also shows doubling (table 1) would show that there may be distortion of  $C_{2v}$  symmetry or there may be crystallographically different water molecules. But the latter is ruled out by the fact that on high deuteration the bending mode doublet for  $\text{H}_2\text{O}$  merges into a single peak (figure 4). Thus we get spectroscopic evidence that all the water molecules per unit cell are equivalent but are distorted from  $C_{2v}$  symmetry. This is in agreement with the crystallographic evidence (Sikka and Chidambaram 1969). Possibly the water molecules have  $C_s$  symmetry with the molecular plane as the plane of symmetry. They occupy a site  $C_1$  in the space group  $D_{2d}^{10}$ . Neutron diffraction studies (Sikka and Chidambaram 1969) show that the OH bond lengths are unequal in this salt. But the reported difference ( $0.003\text{ \AA}$ ) is too small to account for a splitting as large as  $185\text{ cm}^{-1}$ . In a typical case of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  the  $r$  (OH) difference is  $0.021\text{ \AA}$  (Atoji and Rundel 1958) accounting for a frequency split of  $83\text{ cm}^{-1}$  (Kling and Schiffer 1969). Therefore the distortion from  $C_{2v}$  symmetry in the present salt is not adequately reflected in the geometrical inequality of the two OH bonds of water, but largely involves dynamical inequality of the two bonds. At lower temperature the splitting  $\Delta\nu$  decreases (figure 2), showing that the asymmetry decreases.

### 4.2. The bending mode of water

The strong bands at  $1680$  and  $1650\text{ cm}^{-1}$  in the hydrate and  $1236$  and  $1218\text{ cm}^{-1}$  in the deuterate belong to the bending mode ( $\nu_2$ ) of water. For HOD the corresponding bands are at  $1500$  and  $1460\text{ cm}^{-1}$ . Since all the water molecules per unit cell are equivalent, the splitting of the  $\nu_2$  mode must arise from the correlation field interaction in the unit cell. Its value  $30\text{ cm}^{-1}$  is quite high, showing that this interaction is strong. Its change to  $18\text{ cm}^{-1}$  in  $\text{D}_2\text{O}$  is accounted almost wholly by the inertia factor alone. For the HOD case the splitting arises from asymmetry

(Seidle *et al.* 1969) and the high value ( $40\text{ cm}^{-1}$ ) indicates strong asymmetry. The intensity in the bending mode doublet for  $\text{D}_2\text{O}$  is reversed compared to  $\text{H}_2\text{O}$ , the origin of which is not clear.

The uncoupled  $\nu_2$  frequency for  $\text{H}_2\text{O}$  was obtained from  $\sim 75\%$  deuterated sample, and falls at  $1665\text{ cm}^{-1}$ . Compared with the free water position of the  $\nu_2$  mode ( $1595\text{ cm}^{-1}$ ) the uncoupled  $\nu_2$  mode in this salt shows an upward shift of  $70\text{ cm}^{-1}$ , which is among the highest observed in the hydrates. It is known that  $\nu_2$  frequency is enhanced by H-bonding and lowered by  $\text{M}-\text{O}_w$  coordination (Oswald 1965). The existence of the aquo-complex  $\text{Be}(\text{aq})_4$  is evidence for strong  $\text{M}-\text{O}_w$  coordination in this salt. Yet the influence of H-bonding on  $\nu_2$  mode position has the dominant effect.

#### 4.3. Overtone and Combination Bands

From the low frequency spectra ( $1200\text{--}250\text{ cm}^{-1}$ ) it has been inferred that both  $\text{SO}_4^{2-}$  ion and the  $\text{Be}(\text{aq})_4$  complex sit on  $\text{S}_4$  sites in the space group  $\text{D}_{2d}^{10}$  of the crystal (Srivastava *et al.* 1976). Thus some of the fundamentals of these groups, as also of water which occupies a site  $\text{C}_1$ , will be expected to show overtones and combinations. Besides these there are two bands at  $323$  and  $266\text{ cm}^{-1}$  in the hydrate ( $311$  and  $261\text{ cm}^{-1}$  in the deuterate), which are attributed to the lattice mode  $[\text{Be}(\text{aq})_4^{2+} \dots \text{SO}_4^{2-}]$ . These are also allowed by selection rules to combine with the internal modes of  $\text{Be}(\text{aq})_4$  and  $\text{SO}_4^{2-}$ . Among the allowed modes, not all are observed due to weak intensity, and some are obscured by other bands in the neighbourhood. The assignments on this basis are given in column 5 of table 1.

Now the first overtones of  $\nu_2$  and  $\nu'_2$  modes of  $\text{H}_2\text{O}$  are expected around  $3360$  and  $3300\text{ cm}^{-1}$  respectively. The medium intensity band at  $3340\text{ cm}^{-1}$  is obviously the overlap of these. Similarly the band at  $2445\text{ cm}^{-1}$  in the deuterate spectrum is the overlap of  $2\nu_2$  and  $2\nu'_2$  of  $\text{D}_2\text{O}$ .

As regards the overtones of  $\text{SO}_4^{2-}$  fundamentals, those of  $\nu_1$  and  $\nu_2$  are not allowed. The positions of  $\nu_3$  and  $\nu_4$  which are permitted to show their overtone fall at  $1139$  ( $\nu_3^1$ ),  $1078$  ( $\nu_3^2$ ),  $668$  ( $\nu_4^1$ ) and  $618$  ( $\nu_4^2$ )  $\text{cm}^{-1}$  (footnote to table 1). However none of the overtones shows up clearly. Near the position of  $2 \times 1078\text{ cm}^{-1}$  there occurs a band at  $2155\text{ cm}^{-1}$  in the hydrate, but this could have an alternative assignment too. In two cases ( $2550$ ,  $2405\text{ cm}^{-1}$ ) the overtones occur in combination with the lattice mode  $\nu''_L$ , in one case ( $1335\text{ cm}^{-1}$ ) a fundamental mode of  $\text{SO}_4^{2-}$  combines with  $\nu''_L$ , and in one case ( $1256\text{ cm}^{-1}$ ) two fundamentals of  $\text{SO}_4^{2-}$  combine with one another.

The aquo-complex has the symmetry similar to  $\text{SO}_4^{2-}$  and hence the pertaining selection rules should be identical.  $\text{Be}(\text{H}_2\text{O})_4$  has fundamentals at  $982$  ( $\nu_3^1$ ),  $923$  ( $\nu_3^2$ ),  $878$  ( $\nu_4^1$ ) and  $784$  ( $\nu_4^2$ )  $\text{cm}^{-1}$ . The weak band at  $1925\text{ cm}^{-1}$  is assigned to  $2\nu_3^1$ . Positionwise  $1830\text{ cm}^{-1}$  band could be attributed to overtone of  $\nu_3^2$  but, as inferred from the polarized nature of this fundamental, its overtone is disallowed and hence the band is attributed to an alternative combination. In the deuterate spectrum the corresponding bands are obviously obscured by the other relatively strong bands at  $1680$  and  $1650\text{ cm}^{-1}$ . The overtones of the two  $\nu_4$  modes do not appear even weakly, which would mean that the involved anharmonicity for this mode is small. However they appear as combinations with  $\nu''_L$  in

the deuterate spectrum. Also in one case in the hydrate spectrum  $\nu_4^1(\text{aq})_H$  combines with  $\nu_3^1(\text{aq})_H$ . As regards the combinations of the overtones of  $\nu_3$  mode bands in the hydrate spectrum,  $2\nu_3^1(\text{aq})_H$  combines with  $\nu''_L$  while  $2\nu_3^2(\text{aq})_H$  combines with  $\nu'_L$ ; in the deuterate spectrum  $2\nu_3^2(\text{aq})_D$  shows a combination with  $\nu'_L$ .

As is clear from the foregoing discussion and table 1, both the lattice modes  $\nu'_L$  and  $\nu''_L$  combine with the overtones belonging to different symmetry species. This would mean that the lattice modes are of mixed character. Only one band ( $3210\text{ cm}^{-1}$ ) in the spectra could not be fitted into the scheme of such combinations. Positionwise it could be attributed to the combination  $\nu'_{OH} + \nu_L$  but since similar combinations are not observed with other OH/OD stretching modes this assignment is not included.

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