

Infrared spectra of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and its deuterated analogue at 110 K in 1200-250 cm^{-1} region

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Abstract. IR absorption spectra of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and its deuterated analogue are reported in the region 1200-250 cm^{-1} at 110 K. The half-widths and relative integrated intensities of the bands are also reported. The study largely confirms the assignments for the ν_3 and ν_4 modes of SO_4^{2-} ion and the ν_3 mode of $\text{Be}(\text{aq})_4^{2+}$, complex as made by Diem *et al.* The assignments of the other modes of SO_4^{2-} and $\text{Be}(\text{aq})_4^{2+}$, and the librational modes of water are given a more solid footing as result of the present investigation.

Keywords. Infrared; hydrate; $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$; crystal water; SO_4^{2-} .

1. Introduction

The infrared spectrum of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in the region 1200-250 cm^{-1} is quite complex because, apart from the internal modes of SO_4^{2-} ion and the librations of water, a quasi molecule $\text{Be}(\text{H}_2\text{O})_4^{2+}$ occurring in this hydrate (Sikka and Chidambaram 1969) also gives its spectrum. Several IR, Raman and neutron inelastic scattering (NIS) studies are available on this salt (*e.g.*, Glemser and Hartert 1955; Diem *et al* 1968; Katiyar and Krishnamurthy 1969; Thaper *et al* 1969 and 1974). However, the assignments of the bands need reexamination, particularly those for the librations of water and the modes of $\text{Be}(\text{aq})_4^{2+}$, since they are of central importance in relation to the role of H-bonding and $\text{M}-\text{O}_w$ coordination, both of which are here amongst the strongest known for hydrates.

In the present work we report the IR absorption spectra of polycrystalline $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and its deuterated analogue at 110 K in the 1200-250 cm^{-1} region. While the work largely confirms the earlier assignments for the internal modes of SO_4^{2-} , fresh assignments are given for the internal modes of $\text{Be}(\text{aq})_4^{2+}$ and the librations of water.

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 normal salt in D_2O and evaporation in a vacuum system. Thin film technique (Jain *et al* 1973) on CsBr plate was used for recording

the spectra, but high deuteration spectra were checked using the nujol mull technique. The spectra were recorded on Perkin-Elmer 521 IR spectrophotometer. The frequency scale was calibrated against the peaks of polystyrene and indene. For sharp and isolated bands the accuracy is $\pm 2 \text{ cm}^{-1}$. The observed spectra were analysed giving Lorentzian shape to the components. Such analysis is justified when band widths are much larger compared to the instrumental slit width (Bartoli and Litovitz 1972). We used the principle of minimum number of components warranted by the observed curve and the most consistent intensity distribution as between repeated trials. The positions thus obtained may be accurate to $\pm 5 \text{ cm}^{-1}$ and intensities to $\pm 20\%$ in most cases.

For low temperature, liquid nitrogen was used as the coolant for a copper block which held the sample. The temperature at the sample was measured with a calibrated thermocouple.

3. Results

The spectrum of the hydrate at 110 K is given in figure 1 along with the Lorentzian analysis. The corresponding spectrum of the deuterate is given in figure 2. The band positions, half-widths, integrated intensities and assignments are given in table 1. The polarizations shown are those of the bands in corresponding positions observed by Diem *et al* (1968) in the polarised IR reflection spectra of the single crystals at 14 K.

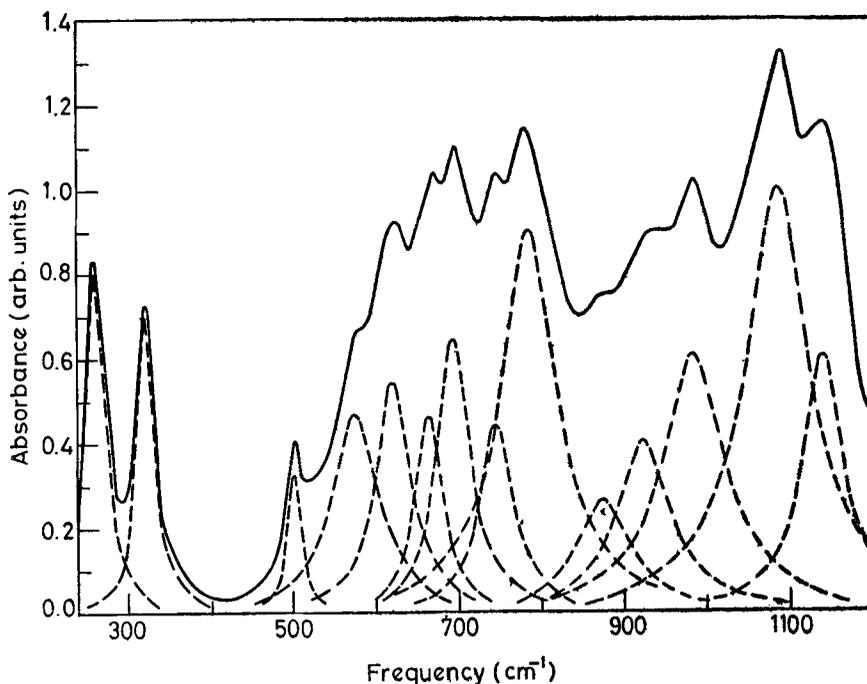


Figure 1. Infrared absorption spectrum of a thin film of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ at 110 K in $1200\text{--}250 \text{ cm}^{-1}$ region. Solid curve shows the observed spectrum while the broken curves show the Lorentzian components.

Table 1. IR absorption bands of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and its deuterate at 110 K in the region 1200–250 cm^{-1} along with their assignments. In paranthesis the first figure gives the half-width in cm^{-1} , the second gives the relative integrated intensity obtained as the product of half-width and peak intensity and normalized to 100 for the stronger component of $\nu_3(\text{SO}_4^{2-})$ mode.

ν_H (hydrate) (cm^{-1})	ν_D (deuterate) (cm^{-1})	ν_H/ν_D	Assignment ⁺
1143 (70, 50) \perp *	1135 (60,30) \perp	1.01	} ν_3^1 ν_3^2 SO_4^{2-}
1078 (95, 100) \perp, \parallel	1078 (100, 100) \perp, \parallel	1.00	
982 (90, 60) \perp	858 (70, 50) \perp	1.14	} ν_8^1 ν_8^2 $\text{Be}(\text{aq})_4^{2+}$ **
923 (80, 35) \parallel	900 (\sim 60, 10) \parallel	1.02	
878 (80, 20)	810 (\sim 60, 10)	1.08	} ν_4^1 ν_4^2 $\text{Be}(\text{aq})_4^{2+}$
784 (80, 75) \parallel	770 (90, 70) \parallel	1.02	
745 (50, 25) \perp	534 (25, 10) \perp	1.40	} Rock ($\text{H}_2\text{O}/\text{D}_2\text{O}$)
693 (50, 35) \perp	475 (30, 10) \perp	1.45	
663 (40, 20) \perp	673 (30, 25) \perp	0.99	} ν_4^1 ν_4^2 ν_4^3 SO_4^{2-}
618 (50, 30) \perp	618 (40, 20) \perp	1.00	
575 (\sim 70, 40) \parallel	592 (20, 15) \parallel	0.97	
$\sim 610^a$	442 (40, 30) \parallel	1.38	Wag ($\text{H}_2\text{O}/\text{D}_2\text{O}$)
502 (20, 5) \parallel	500 (30, 20) \parallel	1.00	ν_2 SO_4^{2-}
323 (25, 20) \parallel	311 (30, 30) \parallel	1.04	} $\nu(\text{Be}(\text{aq})_4^{2+} \cdots \text{SO}_4^{2-})$
266 (30, 25)	261 (20, 20)	1.03	

* Polarization data are taken from the work of Diem *et al* (see text). \perp and \parallel show polarization with respect to the z-axis of the crystal. Corresponding to $\nu_H = 1078 \text{ cm}^{-1}$ Diem *et al* observed two bands (one \perp , and one \parallel); $\nu_H = 878 \text{ cm}^{-1}$ and $\nu_D = 810 \text{ cm}^{-1}$ were not observed by Diem *et al*; and $\nu_H = 266 \text{ cm}^{-1}$ and $\nu_D = 261 \text{ cm}^{-1}$ fall outside the range of Diem *et al*'s study.

+ Assignments of ν_3 and ν_4 modes of SO_4^{2-} and of ν_3^1 mode of $\text{Be}(\text{aq})_4^{2+}$ match well with those given by Diem *et al*.

** $\text{Be}(\text{aq})_4^{2+}$ is the tetrahedral aquo-complex quasi-molecule.

^a Taking cue from the strong band 610 cm^{-1} (\parallel) observed by Diem *et al* (see text). In our spectra this band would be obscured by the 618 cm^{-1} band. Part of the intensity shown for that band thus belongs to Wag ($\text{H}_2\text{O}/\text{D}_2\text{O}$).

4. Discussion

(i) Assignments: General and SO_4^{2-} modes

Our absorption spectra of powdered samples at 110 K match largely with those reported by Diem *et al* (1968) using reflection of polarized IR radiation from single crystals at 14 K. Hence their information about the polarization may be used for bands observed in corresponding positions by us. Among the notable differences (as expected from the different processes of study), two weak bands listed by them in deuterate spectrum at 923 and 410 cm^{-1} are not observed by us, and the bands observed by us at 900 and 810 cm^{-1} in the deuterate and at 878 cm^{-1} in the hydrate were not observed by them. Presumably our 900 cm^{-1} band corresponds to their band at 923 cm^{-1} . The region below 300 cm^{-1} was not covered by Diem *et al*. Intensitywise the only major departure is that a very strong band

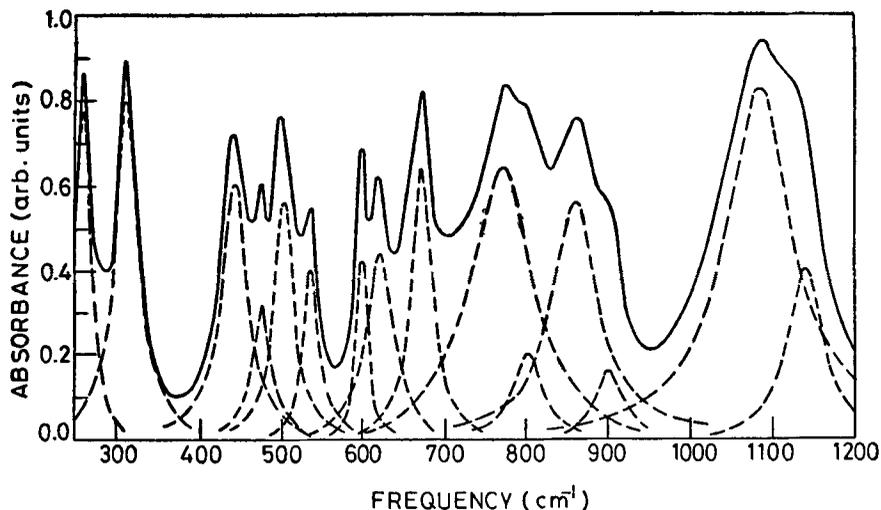


Figure 2. Infrared absorption spectrum of nujol mull of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (on CsBr plates) at 110 K in $1200\text{--}250\text{ cm}^{-1}$ region. Solid curve shows the observed spectrum while the broken curves show the Lorentzian components.

observed by them at $\sim 610\text{ cm}^{-1}$ (||) is not observed by us separately from the band at 618 cm^{-1} which has only medium intensity.

For assignments the three main criteria are: the ratio $\nu_{\text{H}}/\nu_{\text{D}}$ of a band position in the hydrate to that in the deuterate, the p. larization of bands and the intensity distribution. Assuming that no noticeable structural change occurs on deuteration, the SO_4^{2-} bands are sorted out by $\nu_{\text{H}}/\nu_{\text{D}} = 1.00$. Then the water librations and the internal modes of $\text{Be}(\text{aq})_4^{2+}$ complex are marked by $\nu_{\text{H}}/\nu_{\text{D}} \sim 1.4$ and ~ 1.05 respectively. Table 1 shows that all the bands observed in the hydrate and the deuterate can be correlated and sorted out for assignments on this basis. It is interesting that the correlation holds true as regards the polarization of the corresponding bands in the hydrate and the deuterate. Also it is found that the intensities of the bands in the spectra of the two isotropic analogues correlate satisfactorily. Minor departures are to be attributed to the shifts in coupling effects on deuteration (Berenblut *et al* 1973).

As regards the SO_4^{2-} mode vibrations, our assignments for the ν_3 and ν_4 modes agree with those of Diem *et al* (1968). The forbidden ν_2 mode, which is allowed at S_4 site in the present case, should be of small half-width. We therefore assign the bands at $\nu_{\text{H}} = 500\text{ cm}^{-1}$, $\nu_{\text{D}} = 502\text{ cm}^{-1}$ to this mode. The band at 982 cm^{-1} in the hydrate is close in position to the ν_1 mode of free SO_4^{2-} . But no corresponding band is observed in the deuterate and both the intensity and half-width of the band are much too large for a mode disallowed (Tayal *et al* 1974) at S_4 site. Hence the 982 cm^{-1} band is attributed to $\text{Be}(\text{aq})_4^{2+}$, in spite of the fact that $\nu_{\text{H}}/\nu_{\text{D}}$ ratio in this case is somewhat larger, being 1.14 compared with the expected ~ 1.05 .

(ii) *Internal modes of $\text{Be}(\text{aq})_4^{2+}$ complex tetrahedron*

In table 1 four of the observed bands are attributed to the $\text{Be}(\text{aq})_4^{2+}$ complex.

The crystal structure data (Sikka and Chidambaram 1969 show that the $\text{Be}(\text{aq})_4^{2+}$ tetrahedron has linear symmetry (S—O bond lengths are equal) and is only angularly distorted. Thus the ν_1 mode would not appear in infrared. The observed bands have thus to be attributed to ν_3 and ν_4 modes. In line with the general convention ($\nu_3 > \nu_4$) we have attributed the two higher frequency bands to ν_3 modes (consistent with Diem *et al*'s assignments in the hydrate) and the two lower frequency bands to ν_4 modes. Out of the available four sites (C_1 , C_2 , D_2 and S_4) under the group D_{2d} , S_4 is the nearest to satisfying the observed number of bands. At this site a component for ν_3 should also appear. In the present case this band may be too weak to distinctly show up.

The internal mode frequencies of $\text{Be}(\text{aq})_4^{2+}$ complex here observed ($\sim 900 \text{ cm}^{-1}$) are high compared with those in metal-aquo complexes reported so far (Ross, 1972). In $\text{Al}(\text{H}_2\text{O})_4$ complex, for example, the highest frequency is only 540 cm^{-1} (Ross 1972). The high frequency in $\text{Be}(\text{aq})_4^{2+}$ cannot be attributed to low Be mass alone, since in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ the Li—O_w stretching frequency is as low as 447 cm^{-1} (Meshitsuke *et al* 1971) in spite of the light Li atom. Thus the occurrence of very high frequencies in the present case indicates that the Be—O_w bond is exceptionally strong.

We note that the ν_3 and ν_4 mode bands of $\text{Be}(\text{aq})_4^{2+}$ fall much closer together than the corresponding ones of SO_4^{2-} . Also the intensities $I(\nu_3^1 + \nu_3^2)$ and $I(\nu_4^1 + \nu_4^2)$ are comparable (being 95 and 95 units in the hydrate; 60 and 80 units in the deuterate) whereas for SO_4^{2-} the ν_3 mode is far stronger than ν_4 mode. In this context we recall that although the complex $\text{Be}(\text{aq})_4^{2+}$ has the same geometry as the ion SO_4^{2-} , the bindings in the two cases are essentially different in nature. Amongst complexes close lying ν_3 , ν_4 values are not unusual; thus in ion KSbF_4 they fall at 747, 550 cm^{-1} respectively (Ross, 1972). Close lying ν_3 , ν_4 would contribute to strong mixing of the modes and would make the intensities comparable. In $\text{Be}(\text{aq})_4^{2+}$ the small mass of Be will further add to the mixing of the ν_3 and ν_4 modes.

(iii) Librational modes of water molecules

All the bands assigned to water librations in the hydrate (745, 693 and $\sim 610 \text{ cm}^{-1}$) have their counterparts in the deuterate with consistent frequency ratios, intensities and half-widths. Thaper *et al* (1974) have also assigned a single broad band at 710 cm^{-1} in their NIS spectra to water librations in this crystal. As for separate assignments for rocking, wagging and twisting modes, we note that the twisting mode is normally IR forbidden. In the present case C_1 site symmetry (Srivastava *et al* 1976) could make it appear weakly. But none of the three observed bands is much weaker than the rest, and possibly this mode is absent. Among the observed bands, the close frequency shift ratios and comparable intensities of 745 and 693 cm^{-1} bands would link them to one mode, leaving the 610 cm^{-1} band to the other. For nearly harmonic potential the frequency shift ratios on deuteration are expected to be 1.32 for the wagging mode and 1.43 for the rocking mode (Van der Elksen and Robinson 1961). The observed ratios therefore suggest the assignment of 610 cm^{-1} to wagging and the other two to rocking. According to Miyazawa (1961) wagging band should be more intense than rocking. This

supports the above assignments in the case of deuterate spectra, but in the hydrate the situation is obscure because of overlapping of the H₂O wagging with the 618 cm⁻¹ band of SO₄²⁻.

(iv) *The bands at 323 and 266 cm⁻¹*

Both these bands are temperature sensitive and gain in intensity on cooling. Translations of water are already covered in the internal modes of Be(aq)₄²⁺ complex; also librations of SO₄²⁻ or of Be(aq)₄²⁺ complex are IR forbidden in T_a symmetry and would at best appear only weakly at S₄ site. Further, Be...O (SO₄²⁻) stretching is a third particle interaction and it will be difficult to define this mode free of mixing. Thus we are left with Be(aq)₄²⁺...SO₄²⁻ stretching as the possible origin for these bands. Here both the groups involved have large masses, but due to two electronic charges on each of them the interaction could be strong enough to give frequencies around 300 cm⁻¹.

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References

- Bartoli F J and Litovitz T A 1972 *J. Chem. Phys.* **56** 405
 Berenblut B J, Dawson P and Wilkinson G R 1973 *Spectrochim. Acta* **29A** 29
 Diem P, Hellwege K H, Jager J, Schaack G and Schedewie F J 1968 *Phys. Kondens. Mater.* **7** 52
 Glemser O and Hartert E 1955 *Naturwiss.* **42** 534
 Jain Y S, Bist H D and Upreti G C 1973 *Chem. Phys. Lett.* **22** 372
 Katiyar R S and Krishnamurthy N 1969 *Indian J. Pure Appl. Phys.* **7** 95
 Mellor J W 1957 *A Comprehensive Treatise on Theoretical and Inorganic Chemistry* Vol. IV (London: Longmans Green and Co.) p. 237
 Meshitsuke S, Takahashi H and Higasi K 1971 *Bull. Chem. Soc. Jpn.* **44** 3255
 Miyazawa T 1961 *Bull. Chem. Soc. Jpn.* **34** 202
 Ross S D 1972 *Inorganic Infrared and Raman Spectra* (London: McGraw-Hill Book Co.) p. 253
 Sikka S K and Chidambaram R 1969 *Acta Crystallogr.* **B25** 310
 Srivastava B K, Khandelwal D P and Bist H D 1976 *Pramāṇa* **7** 49
 Tayal V P, Khandelwal D P and Bist H D 1974 *Proc. Nucl. Phys. Solid State Phys. Symp. BARC* **17C** 263
 Thaper C L, Sequeira A, Dasannacharya B A and Iyengar P K 1969 *Phys. Stat. Solidi* **34** 279
 Thaper C L, Srinivasan T and Iyengar P K 1974 *Proc. Nucl. Phys. Solid State Phys. Symp. BARC* **17C** 205
 Van der Elsken J and Robinson D W 1961 *Spectrochim. Acta* **17A** 1249