Infrared Spectra of CuSO$_4$·5H$_2$O and its Deuterated Analogue in 4000–300 cm$^{-1}$ Region

(A critical analysis of the internal and external mode vibrations of water and the internal mode vibrations of SO$_4^{2-}$ ion)

ABSTRACT

Infrared Spectra of CuSO$_4$·5H$_2$O and its deuterated analogue to different degrees have been recorded at 300K and 110K in the region 4000–300 cm$^{-1}$ using thin film and nujol mull techniques. The bands have been assigned to the internal modes of water, librational modes of water, internal modes of SO$_4^{2-}$ ion and a Cu–O$_w$ (water–oxygen) stretching mode. Half-widths and relative integrated intensities have been obtained for the bands in the uncoupled OH/OD stretching mode envelopes and for those in the region 1200–300 cm$^{-1}$.

The stretching mode envelope in the hydrate has a very poor resolution but the corresponding one in the deuterate shows a definite structure. Lowering of temperature slightly improves the resolution. Uncoupled OH/OD stretching mode bands have been obtained using highly deuterated (~90%) and a lowly deuterated (~30%) sample respectively*. As many as seven components are identified in each case. These have been attributed to seven out

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of the eight different H-bonds known in the crystal. No band has been observed corresponding to the longest O...O bond.

For bending mode of water only two bands are observed in both the hydrate and the deuterate. Their positions are well above the vapor phase value implying in general strong H-binding.

In the lower frequency region (1200-300 cm\(^{-1}\))\(^+\) eight bands have been observed for \(\text{SO}_4^{2-}\) in \(\text{CuSO}_4 \cdot 5\text{D}_2\text{O}\) and the ion is inferred to be at \(\text{C}_1\) site. Evidence for \(\nu_2\) band has been obtained for the first time from the deuterate spectrum. It does not appear in the hydrate spectrum. The ion is found to become more distorted on deuteration both linearly and angularly. Cooling also has a similar effect. For librational modes of water in all five bands appear in the hydrate and six in the deuterate. No component is attributed to the twisting mode. Tentative distinction is given between the wagging and the rocking modes. One band has been found corresponding to \(\text{Cu-O}_\text{W}\) stretching mode. Its position is quite high implying strong \(\text{Cu-O}_\text{W}\) bond.

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6.1 General: CuSO$_4$$\cdot$5H$_2$O is a unique system providing extremely asymmetric environment for water. The triclinic unit cell consists of two formula units, and the space group is C$_1$\_1. All of the five water molecules per formula unit are asymmetric and crystallographically inequivalent. While four H$_2$O act as 'coordinate water' linking to two H-bonds (with either a water oxygen O$_w$ or an oxygen from SO$_4$$^{2-}$ ion) and a Cu-O$_w$ bond each, the fifth water molecule acts as a lattice water associating in four H-bonds (playing the role of acceptor for two of these). The highly asymmetric situations would lead to several bands for the internal as well as external modes of water. Also the involved H-bonds are of largely different strengths so that the half-width and intensities of the pertaining bands would also vary. Further the SO$_4$$^{2-}$ ion tetrahedra are also distorted so that the forbidden mode fundamentals may appear and the degeneracies may be lifted. Thus the overall spectra are expected to be quite complex and hence interesting to interpret.

Although several infrared and Raman studies are available in literature on this hydrate, major attention has been on the SO$_4$$^{2-}$ ion vibrations and only a little understanding is available on the internal as well as external mode vibrations of water molecules. The recorded spectra pertain to room temperature (~300K) work and only the positions of the peaks separately resolved at this temperature are reported without any analysis about intensities and band-widths.

In the present work we have studied the IR spectra of CuSO$_4$$\cdot$5H$_2$O and its analogues deuterated to different degrees, at 300K (RT) and 110K (LT). In the region of the librational modes
Water and the internal modes of \( \text{SO}_4^{2-} \) ion all the bands have been assigned using the correlation of the bands in the hydrate and the deuterate. The observed band positions and the computed integrated intensities have been discussed in terms of the coordination effects. In the internal mode region of water partial deuteration has helped in obtaining uncoupled OH/OD stretching frequencies. These have been correlated with the known H-bonds. The relative integrated intensities of these have also been discussed in terms of the coordination effects.

6.12 Preparation and Stability of CuSO\(_4\).5H\(_2\)O: Copper sulfate apart from its anhydrous form, is known to occur as penta-, tri- and monohydrate. Of these the pentahydrate is the only one stable at room temperature and hence the most widely studied. Several studies have been performed on the crystallization and dehydration of this hydrate (1-3), and Mellor has given a good summary of its various physical and chemical properties (2). As regards dehydration of CuSO\(_4\).5H\(_2\)O, the first stage occurs not below 95\(^\circ\)C (2), and in aqueous solution CuSO\(_4\).5H\(_2\)O is stable below 60\(^\circ\)C.

6.13 Crystal Structure: The crystal structure of CuSO\(_4\).5H\(_2\)O has been studied using the asymmetric method for photographing (10,11), x-ray diffraction (12) and neutron diffraction (13). One study is also available on the deuterated analogue CuSO\(_4\).5D\(_2\)O for its lattice constants, using x-ray diffraction (14). All these studies confirmed the system to be triclinic one. While the other studies only give the six lattice parameters, neutron diffraction (13) could give the details of the various positional coordinates also.
As mentioned in Sec. 6.11 four of the five water molecules act as 'coordinate water' and the fifth one is a 'crystal' water. There are eight H-bonds for coordinate and four for crystal water molecules. Out of these twelve, there are eight different H-bond lengths. Further four oxygens of coordinate waters \( O_w \) together with two oxygens of \( SO_4^{2-} \) ion \( O_s \) form an octahedron with Cu in the centre and since there are two different Cu-O\(_w\) bond lengths there are two such octahedra of slightly different geometry. As regards the \( SO_4^{2-} \) tetrahedra these are both linearly and angularly distorted from the ideal tetrahedral geometry i.e. the four \( 8-O_s \) bond lengths are unequal and the \( O_s \)-8-O\(_s\) bond angles are unequal within themselves as also not equal to 109° as in an ideal tetrahedron.

In Fig. 6.1 we depict the environment around the \( SO_4^{2-} \) ion. The data on the H-bond lengths and angles and on the geometry of water are given in Table 6.1 where the geometrical parameters of the \( SO_4^{2-} \) ion distorted tetrahedron are also noted.

### 6.14 Available IR/Raman Spectral Studies:

Among the several IR/Raman spectral studies on this salt \( (15, 37) \), the first is in the region >4300 cm\(^{-1}\) i.e. outside the region of the fundamental modes of vibration. Spectra were studied at different polarizations using a calcite polarizer. It was indicated that such studies might be able to yield information on the positions of water molecules in the crystal. Three studies \( (17, 21, 24) \) pertain to the internal mode region of water. All of these relate to room temperature (RT) spectra and none is extended to the deuterated analogue. In the stretching mode region the resolution is reported to be too poor to yield any useful information. While Mastumura \( (17) \) reported three...
bands, Gamo (21) and Ferraro and Walker (24) reported one band each in this region. In the bending mode region only one band has been reported in the two latter studies (21,24); Matsuura's spectra do not extend to bending mode region. These results are included in Table 6.3 along with the band positions in the hydrate and the deuterate as observed by us (cf. sec. 6.31).

The external mode bands of water molecules are covered by four studies (16,21,24,26). All these pertain to the spectra at RT only. Studies of Fujita et al (16) and Gamo (21) show a librational band around 875 cm\(^{-1}\). Ferraro and Walker (24) report bands both for the librational and the Cu–O\(_w\) stretching mode of water. The relevant results are included in Table 6.3. Brehet and Wancke (27) have studied only the translational modes of water and attribute bands at 322 and 182 cm\(^{-1}\) to this mode.

The SO\(_4^{2-}\) ion vibrations have received wide attention (16,19-26), but no convincing or consistent interpretation has been achieved. In fact even the experimental results of different workers do not match. For instance while Gamo (21) reported two bands for \(\nu_3\) and two for \(\nu_1\) mode of SO\(_4^{2-}\) ion, Ferraro and Walker (24) observed one each for \(\nu_3\), \(\nu_1\) and \(\nu_4\) modes.

6.2 Experimental: Analytical Grade CuSO\(_4\).5H\(_2\)O obtained from BDH was further purified by recrystallization from aqueous solution at room temperature (300K, hereafter referred to as RT). Deuteration was done to two different degrees (~30% and ~90%) using the process of repeated vacuum distillation (cf. sec. 2.5, Chapter II.). For this purpose a ~99.8% pure D\(_2\)O was used. Deuteration content was determined spectroscopically (cf. sec. 1.54, Chapter I) by comparing the integrated intensities of the stretching mode envelopes of H\(_2\)O and D\(_2\)O in the IR spectrum of the salt.
The IR spectra were recorded on Perkin-Elmer 521 machine using the technique of thin films. However, in the case of highly deuterated samples the nujol mull technique was employed in order to check the loss of deuteration. The system strongly reacted with CsBr windows but not with KRS-5 and hence, the latter were used. Also the KBr technique could not be employed because KBr shows some spurious reaction (28) with CuSO₄. The frequency scale of the instrument was calibrated against the standard sharp peaks of polystyrene and indane.

For low temperature work the Wagner-Hornig type cell was used with liquid nitrogen as the coolant. Temperature up to 110 K thereafter referred to as low temperature (LT) was achieved at the sample as measured with a thermocouple.

The spectra in the regions of the fundamental vibrations - internal modes of water, external modes of water and SO₄²⁻ vibrations - showed overlapping and hence they were subjected to Lorentzian analysis in order to obtain the band-width and integrated intensity parameters. The accuracy of the band positions may be placed at ± 1 cm⁻¹ for the isolated bands and ± 5 cm⁻¹ for the broad and overlapping bands. The reported half-width and integrated intensity parameters may generally be correct to within ± 5 cm⁻¹ and ±15% respectively.

6.3 Results and Discussion:

6.3.1 Internal mode Fundamentals of Water:

(i) Coupled H₂O and D₂O Bands: In Fig. 6.2 we give the spectra of CuSO₄·5H₂O and CuSO₄·5D₂O (∼90%) in the region 4000-1200 cm⁻¹ at LT. In this region fall the internal mode vibrations of water and various possible
combinations of these with low frequency modes as also the combinations of \( \text{SO}_4^{2-} \) mode vibrations and the librations of water. The combination bands may thus have several alternative assignments and for lack of information on polarization nature of bands, it is not possible to make a choice. For this reason we have listed and assigned in Table 6.2 bands only in the region of fundamental internal modes of water.

In Fig. 6.3 are shown the spectra in the OH stretching region for (A) the full hydrate (\( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \)), RT, (B) the full hydrate, LT and (C) the low hydrate (~90% deuterated sample), LT. The corresponding envelopes in the OD stretching region, we replot in Fig. 6.4 for (A) the "full" deuterate (~90%), RT, (B) the "full" deuterate, LT, and (C) the low deuterate (~30%), LT. Table 6.2 summarizes the band positions (including that of the bending mode of water) in the full hydrate and full deuterate at RT and LT. Here we also include the results of earlier workers for comparison.

First we take up the stretching mode region. It is seen that in the RT spectrum of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) (Fig. 6.3A), one can only locate two bulges at 3480 and 3400 cm\(^{-1}\) followed by a very broad absorption region (3350-3000 cm\(^{-1}\)). These positions match closely with those reported by Matsumura (cf. column 1). On cooling to 110K the resolution slightly improves. In particular the broad region (3350-3000 cm\(^{-1}\)) now shows a clear peak around 3220 cm\(^{-1}\) and the region below 3100 cm\(^{-1}\) becomes considerably weaker relative to the rest of the stretching mode region.

In the deuterated analogue (Fig. 6.4A) the corresponding spectrum has a better resolution at RT itself showing four peaks (2585, 2495, 2400, and 2310 cm\(^{-1}\)) and a possible shoulder (2620 cm\(^{-1}\)).
But in this case cooling does not improve the resolution much except that now the convolution around 2400 cm\(^{-1}\) clearly shows the existence of at least two component bands there. Also, the broad band with peak at 2316 cm\(^{-1}\) at RT appears now as a distinct band at ~30 cm\(^{-1}\), lower frequency (2280 cm\(^{-1}\)).

Poor resolution of the OH stretching envelopes, and its improved resolution on cooling may be explained as follows. For water in a crystal hydrate, apart from the normal intra-molecular coupling between the two OH bonds in a given water molecule, there are several other effects which may be superimposed on the OH stretching vibration (cf. sec.1.54, Chapter I.) like the inter-molecular coupling, tunneling of proton in the D.M. potential of H-bond, distortion from C\(_{3v}\) symmetry of water and crystallographically distinct sites. With H-bonds of eight different lengths and large asymmetry, all the above factors may lead to a multiplet structure of the stretching bands as also to their broadening. Poor resolution in the spectrum of the full hydrate (Fig.6.3A) is obviously a combined effect of these factors. On cooling the coupling and tunneling effects become less dominant, and also the anharmonic couplings (with low frequency lattice modes) become weak. These result in somewhat smaller half-widths of bands and hence a better resolution.

Improvement in resolution on deuteration would imply that in passing from hydrate to deuterate the half-widths of the stretching mode bands decrease by a factor somewhat larger than that by which the frequencies decrease.

Even from these diffuse spectra one can have an estimate of the range of H-bond lengths using the known spectroscopic correlation (cf. Chapter III) of the parameter 'effective overlap'
with the OH/OD stretching frequency shifts from the vapor state frequencies (3707 cm\(^{-1}\) for OH and 2727 cm\(^{-1}\) for OD).

In the case of H\(_2\)O (LT) the frequency shifts vary from ~230 to ~490 cm\(^{-1}\) (column 7, Table 6.2) leading to H-bond lengths varying from 2.85 to 2.72 Å.

In the bending mode region there appear just two bands, both in hydrate and deuterate spectra. These bands are of comparable intensities and hence both are attributed to the bending mode fundamentals. The frequencies are well above the vapor phase values (1595 cm\(^{-1}\) for H\(_2\)O and 1178 cm\(^{-1}\) for D\(_2\)O). Now H-bonding is well known to raise the \(\nu_2\) mode frequency, while M-O\(_w\) coordination has an opposite effect (sec. 1.52, Chapter I). The high frequencies here thus indicate relatively stronger effect of H-bonds. On cooling, these frequencies move slightly upwards, indicating further strengthening of H-bonds at lower temperatures—an inference in line with the one drawn from the behaviour of stretching frequencies with lowering of temperature.

Normally one would expect at least five \(\nu_2\) mode bands corresponding to five kinds of water molecules in the present case (cf. Table 6.1) whereas only two are observed. One explanation could be that the bands in the present case are relatively broader and hence all the components may not distinctly show up. Among the observed two bands at LT, the lower frequency band would then belong to the first two water molecules attached to Cu\(_1\) (Table 6.1) with relatively weaker H-bonds and the higher frequency band would belong to the two water molecules attached to Cu\(_2\) with relatively stronger H-bonds. The fifth water molecule (though linked through much weaker H-bonds) does not participate in Cu-O\(_w\) coordination and thus may have a \(\nu_2\) band.
coinciding with the position of one of the two bands observed here. The lower frequency band is relatively stronger and one may tenta-
vitively infer that it has a contribution from the fifth water molecule.

(i) Uncoupled Stretching Band Positions: Isotopic dilution is well
known as a technique for obtaining uncoupled stretching bands (cf. sec. 1.54, Chapter I).
In a highly deuterated sample there are a few OH oscillators
surrounded by a large number of OD oscillators; hence its
spectrum would yield uncoupled OH stretching bands. Similarly
a low deuterated sample yields uncoupled OD stretching bands.
The spectra shown in Figs. 6.3C and 6.4C, for ~90% deuteurate and
~30% deuteurate respectively, thus are dominantly suited to give
uncoupled OH and OD stretching bands. Applying the statistical
average distribution (cf. sec. 1.54, Chapter I) in the two
respective samples, relative content of the three isotopic
species comes out in the two cited samples in the proportion of
H₂O : HOD : D₂O = 0.01 : 0.18 : 0.81 and 0.49 : 0.42 : 0.09 respec-
tively. Thus in the 90% deuterated sample both of the intra-and
inter-molecular couplings for OH oscillators would be negligibly
weak. In the second sample (~30% deuterated) the intra-molecular
coupling for OD oscillators would be negligible but inter-
molecular coupling would make some contribution. However inter-
molecular coupling is known to contribute only to band widths
and is hardly able to manifest in the form of split components
(cf. sec. 1.54; Chapter I). Thus so far as band positions are
concerned all 30% deuterated sample would yield OD stretching
bands free of coupling effects. The observed consistency in the
OH and OD stretching frequencies in these partially deuterated
samples (cf. Table 6.3) is in conformity with this.

It is seen that the uncoupled OH stretching envelope (Fig. 6.3C) has clear evidence of six bands. A careful Lorentzian analysis (Fig. 6.5) further shows the broad asymmetric shape around 2220 cm\(^{-1}\) to comprise of two components. The uncoupled OD stretching envelope also has six distinct components and a Lorentzian analysis (not shown in the Figure) shows evidence of a seventh weak band around 2515 cm\(^{-1}\). The positions of the seven bands in each case are listed in Table 6.3, columns 3 and 4.

Comparing the total envelopes for the coupled and uncoupled OH stretching modes (Fig. 6.3B, 6.3 C), one notices that the absorption in the region below ~ 3100 cm\(^{-1}\) falls sharply in the latter. It appears that on removing the coupling the bands falling in this region become very much weaker, or possibly shift to the position 3140 cm\(^{-1}\). Similar examination of the OD stretching band gives clear evidence in favour of shift of the lowest frequency band by 30 cm\(^{-1}\) upward when the coupling is removed. Now uncoupled OH/OD bands, irrespective of the symmetries of the concerned water molecules, should have frequencies lying in between those of the corresponding coupled bands. In the present case some seven close-lying uncoupled bands are involved and hence the difference between the coupled and the uncoupled OH/OD stretching spectra should be observable only at the extreme ends of the envelope—an upward shift of the lowest frequency and a downward shift of the highest frequency. In the present spectra the effect is conspicuous at the low frequency end only, showing that the coupling effect is larger for the more tightly H-bonded OH/OD oscillators.
uncoupled OH/OD peaks observed have to be assigned. Since the intra- and inter- molecular coupling effects have been eliminated by the isotopic dilution technique, the observed bands would owe their presence to proton tunneling and/or asymmetric and crystallographically distinct water molecules. In case of proton tunneling in the DH potential the bands would shift by a factor much larger than $\sqrt{2}$ on deuteration (cf. sec.1.54, Chapter I). The observations show that all the OH bands shift to corresponding OD bands by a factor 1.34 - 1.35 (cf. Table 6.3) which is quite close to 1.37 as expected on the basis of inertia factor alone ($29,50$). The observed bands would thus belong to different OH bonds of the asymmetric and crystallographically distinct water molecules. In Table 6.3 we have given the correlation of the uncoupled OH/OD stretching frequencies with the OH bonds in different water molecules in the salt. In column 1 is given the nature of the bonds and in column 2 are listed the H-bond lengths taken from neutron diffraction work ($13$). In column 3 and 4 are given the OH and OD stretching frequencies respectively. In parantheses before these frequencies are the half-widths in cm$^{-1}$ and relative integrated intensities in arb. units (normalised to 100 for the strongest band in the two spectra) respectively, as obtained from Lorentzian analysis.

We note that while neutron diffraction studies showed the crystal structure of this hydrate to involve H-bonds of eight different strengths ($13$), the observed bands are only seven. From the known correlation curve (cf. Chapter III) for frequency shift $\Delta \nu$ versus effective overlap $r^0$, we find that
the fitting of all the seven bands is good and that it is the band corresponding to the smallest $r^0$ (longest $O\ldots O$ bond) which is not observed either due to want of resolution or because the eight $O\ldots O$ bond corresponds to a free OH bond. The correlation of the OD stretching bands is made on the same basis, and again it is the band corresponding to the smallest $r^0$ which is missing.

It will be noted from Table 6.3 column 2 that there are two H-bonds of length 2.76 Å and two of length 2.79 Å. In the first case the water of both is coordinated to Cu whereas in the second case one water is coordinated to Cu and the other acts as acceptor for two more H-bonds. One would therefore expect two slightly different frequencies corresponding to the H-bond length of 2.79 Å. We do not find evidence for this in these spectra; in fact the corresponding band is the weakest in both the OH and OD stretching envelopes. It is possible that the other component is merged with a neighbouring band.

(iv) Half-widths of and Intensity Distribution in Uncoupled Stretching Mode Bands: $\Delta v_{1/2}(OD)$ would be expected to be smaller than $\Delta v_{1/2}(OH)$ values by a factor $\sqrt{2}$. However in the present case (cf. Table 6.3) although $\Delta v_{1/2}$ for 'uncoupled' OD bands is generally smaller than $\Delta v_{1/2}$ for 'uncoupled' OH bands, the reduction factor is far less than $\sqrt{2}$. In this context we note that the 'low deuterate' (for uncoupled OD) refers to a sample with 30% deuteration whereas the 'low hydrate' (for uncoupled OH) refers to one with 10% hydration. As such some intermolecular coupling will be present in the case of $\nu(OH)$ band (cf. sec. 6.31(1)). It is this intermolecular coupling which is responsible for increased
large $\Delta \nu_{1/2}$(OD) and the amount that this coupling contributes to bandwidths, is interesting to note.

As regards the relative integrated intensities of the bands, they generally correlate well for the two isotopic analogues and thus support our assignments. It is seen that bands with the largest frequency shifts (strongest H-bonds) share the maximum intensity, which decreases as we pass to weaker H-bonds. For stronger H-bonds the transition moment will be larger because of greater rate of change of dipole moment ($\mu'$) for the vibration concerned. The band attributed to the H-bond of length 2.79 Å is the weakest in both the spectra. This has been discussed in the last section.

6.32 Overlapping region (1200–300 cm$^{-1}$) for the external Modes of Water and Internal Modes of $SO_4^{2-}$ ion: In Fig. 6.6 we compare the spectra of CuSO$_4$. $5H_2O$ at RT (broken curve) and LT (solid curve) in the region 1200–300 cm$^{-1}$. The bands as usual show a relatively better resolution at lower temperature. The corresponding spectra for the deuterated analogue are not shown in Figure. In Fig. 6.7 is shown the Lorentzian analysis of the LT spectrum. The analysis for the corresponding deuterate spectrum is not shown. The results are summarized in Table 6.4. In column 1 and 2 we give the band positions reported by earlier workers. The positions of the bands observed by us and their half-widths and relative integrated intensities are given in columns 3–5. In the last column are given the assignments for the observed bands. The results for the deuterated analogue are summarized in Table 6.5. Here column 1 gives the band positions and column 2 and 3 give the half-width and the intensity data.
respectively. For the purpose of comparison, intensities for the hydrate and the deuterate bands are normalized by attributing a value 100 to $v_3(SO_4^{2-})$ bands in the two spectra. These allowed mode bands unlike forbidden mode bands would not display an intensity modification even if the structure undergoes slight modification on deuteration.

(1) **Assignments:** The correlation of the bands in the region 1200–360 cm$^{-1}$ in the IR spectra of CuSO$_4$.5H$_2$O and CuSO$_4$.5D$_2$O, as assigned in Tables 6.4 and 6.5 respectively, is represented schematically in Fig. 6.8.

For assigning the bands the main criteria followed were the frequency shift ratios on deuteration and a comparison of the half-widths and intensities of the bands in the spectra of the two isotopic analogues. Thus the bands corresponding to the internal modes of $SO_4^{2-}$ ion should have $v_H/v_D$ quite close to 1 while those exhibiting an isotopic shift of ~1.35 would belong to the librational modes of water. The bands corresponding to the translational modes of water should have $v_H/v_D$ close to 1.05. Also in the case of $SO_4^{2-}$ ion vibrations the frequencies should fall close to the free state values. Our assignments follow this scheme closely (cf. last column, Table 6.5).

We shall designate a band in the hydrate spectrum as $v_H$ and the corresponding one in the deuterate spectrum as $v_D$. Now $v_D = 566$ cm$^{-1}$ does not have a corresponding $v_H$ possibly due to suppression by the neighbouring $v_L$ band (546 cm$^{-1}$) which shifts to 398 cm$^{-1}$ position in the deuterate spectrum. But positionwise the 566 cm$^{-1}$ band could only be attributed to the $v_4$ mode of $SO_4^{2-}$ ion. Intensitywise it is not so weak as to be attributed to a combination mode. Moreover our assignment is
also supported by the group theoretical considerations regarding
the site symmetry of $\text{SO}_4^{2-}$ ion in the unit cell of $\text{CuSO}_4\cdot5\text{H}_2\text{O}$.
This is discussed in the following section.

The bands at $\nu_D = 453$ and 445 cm$^{-1}$ are attributed to
the $\nu_2(\text{SO}_4^{2-})$ forbidden mode for two reasons. Firstly the posi-
tions are quite close to those observed in the free ion (31)
and secondly the bands have distinctly small half-widths—a
characteristic for forbidden mode bands. The corresponding $\nu_H$
bands do not show up and are masked by $\nu_H = 447$ cm$^{-1}$. This $\nu_H$
band is too broad (35 cm$^{-1}$) and strong to be attributed to a
forbidden mode band. Based on $\nu_H/\nu_D$ ratio (cf. Table 6.5) it
is attributed to $\text{Cu-O}_\text{W}$ stretching mode of water. The corres-
ponding $\nu_D$ is at 417 cm$^{-1}$ and is thus far away from $\nu_2(\text{SO}_4^{2-})$
mode positions.

$\nu_D = 617$ cm$^{-1}$ band is assigned as $\nu_4(\text{SO}_4^{2-})$ correspon-
ding to $\nu_H = 615$ cm$^{-1}$ and also as a librational band of water
corresponding to $\nu_H = 863$ cm$^{-1}$. It is worth noting that inten-
sity considerations support such kind of an arrangement. For
the $\nu_H$ bands at 863 and 615 cm$^{-1}$ attributed to $\nu_L^2$ and $\nu_4(\text{SO}_4^{2-})$
respectively, $I_t = 80$ and for the pertaining $\nu_D$ bands at 617 and
566 cm$^{-1}$, $I_t = 80$ (intensities in the two spectra are normalized
by attributing 100 arb. units to $\nu_3(\text{SO}_4^{2-})$ bands). Such intensity
considerations do not hold only in one case i.e. for the bands
attributed to the librational mode of water $\nu_L^3$. Reason for
this is not clear at present.

The band $\nu_D = 375$ cm$^{-1}$ could not be uniquely correlated.
Its intensity is not small and therefore the corresponding $\nu_H$
should have appeared at about the same position if it were some
translational or other lattice mode vibration. But no corres-
ponding $v_H$ is observed. $v_D = 375 \text{ cm}^{-1}$ could therefore be the result of the splitting of a librational mode in the deuterate (cf. in sub-section (iii) ahead).

Two bands at $v_H = 1035$ and $610 \text{ cm}^{-1}$ are attributed to some combination modes and are not plotted in Fig. 6.8. The bands $v_D = 1020$ and $810 \text{ cm}^{-1}$ are obviously the corresponding bands in the deuterate. Now, according to $v_H/v_D$ ratio these would not belong to librational modes of water. Also the positions of these bands are far off from those for the free state modes for $\text{SO}_4^{2-}$ ion, and are too high to attribute them to Cu-O_W stretching mode. Thus these must arise from some combination. Positionwise and group theoretically several alternative combinations can be considered, but the data are insufficient to enable us to choose amongst them.

(ii) **Internal Mode Vibrations of $\text{SO}_4^{2-}$ ion**: In this system of low symmetry, one finds that the forbidden mode bands are also appearing. The symmetric stretching $v_1$ shows up with a medium intensity in the spectra of both the isotopic analogues. Accordingly, the symmetric bending $v_2$ should also appear, though weakly. In fact in the hydrate spectrum the pertaining bands expected around $450 \text{ cm}^{-1}$ are possibly masked by the neighbouring Cu-O_W stretching at $447 \text{ cm}^{-1}$ (as discussed in the last section). But in the deuterate spectrum two components show up distinctly. Regarding the allowed mode bands, the degeneracy on $v_3$ is completely lifted and it appears as a triplet in the spectra. However, $v_4$ is observed only as a doublet in the deuterate spectrum and as a relatively stronger single band in that of the hydrate.
While $\nu_1$ was also identified by the earlier workers (cf. Table 6.6) evidence about $\nu_2$ band has been obtained for the first time, using the deuterate (Table 6.5). For $\nu_4$ Hezel and Ross (25) had observed three bands using the KBr pellet technique but only one broad single band in the nujol mull technique. However, a detailed examination has established (22) that the KBr pellet method gives spurious results in the case of CuSO$_4$•5H$_2$O. Hence one should rely only on the nujol mull spectrum. Thus our observations on the hydrate are in conformity with those of the earlier workers (24, 25).

Hezel and Ross (25) have attributed a $C_1$ site to the SO$_4^{2-}$ ion in the present hydrate. However this violates the rule that the site group must also be a subgroup of the point group ($T_d$, in the present case). Now the only other site available under the $C_1$ space group (32) is $C_1$ (effectively no symmetry), which obviously is also a subgroup of $T_d$. Thus the true site group for SO$_4^{2-}$ ion here is $C_1$ and not $C_1$. At the $C_1$ site all the nine internal mode vibrations of SO$_4^{2-}$ should appear. Out of those we have observed as many as eight in the spectrum of the deuterated salt at LT.

Now while intensities of the allowed mode bands would show only small variations if some structural change occurs following a change of state (say deuteration), those of the forbidden mode bands could vary considerably and thus work as pointers for distortions from ideal symmetries. In the present case on deuteration the forbidden $\nu_1$ mode band enhances in intensity by a factor of ~2 (cf. column 5, Table 6.4, and Column 3, Table 6.5). Similarly the forbidden $\nu_2$ mode bands which are very weak in the hydrate spectrum, gain much in intensity on
deuteration. Since \( \nu_1 \) is symmetric stretching its intensity would depend on the linear distortion in \( T_d \) symmetry (differences in \( S-O_2 \) bond lengths); in contrast \( \nu_2 \) being symmetric bending its intensity would depend on the angular distortion (differences in \( O_5-S-O_2 \) bond angles). Thus the distinct enhancement in the intensities of both \( \nu_1 \) and \( \nu_2 \) mode bands on deuteration is evidence for the \( SO_4^{2-} \) ion being more asymmetric in CuSO\(_4\).5D\(_2\)O than in CuSO\(_4\).5H\(_2\)O. Increase of intensities may also arise from a favourable shift of coupling from neighbouring bands; but Table 6.5 shows that on deuteration no band falls too close either to \( \nu_1 \) or to \( \nu_2 \) mode band of \( SO_4^{2-} \) to contribute in this manner.

As regards the effect of temperature we note that the \( \nu_1 \) mode band in CuSO\(_4\).5D\(_2\)O enhances in intensity by a factor of \( \approx 2 \) as we pass from 300 K to 110 K (cf. Fig. 6.9), showing that \( S-O_2 \) bond lengths become more unequal on cooling (possibly a result of unequal shortening of \( H \)-bond lengths on lowering the temperature). The effect is comparatively less pronounced in the hydrate.

(iii) Librational Mode Bands of Water: Same considerations apply in the site symmetry of water as to that of \( SO_4^{2-} \) ion. Among the two sites available under \( C_1 \) space group, only \( C_1 \) is contained in the point group \( C_{2v} \) of water. At this site the forbidden twisting mode also becomes allowed. Thus all of the three modes Rocking (R), Wagg- ging (W) and Twisting (T) should show their corresponding bands in the present hydrate. Further, because of five crystallographically distinct environments for the water molecules, one could ideally expect in all 15 librational bands to appear. However, neither \( I_A \) nor \( I_B \) nor
the corresponding potential constant would vary by large amount
for the different water molecules and their environment. Hence
the frequency spread for the five expected components for each
mode (R, W and T) is bound to be not too large compared with the
half-width of the bands. For this reason as many as 15 librati-
onal bands would not distinctly appear. In fact in the earlier
studies (24) only one band at \(-870 \text{ cm}^{-1}\) (RT) was attributed to
a librational mode in \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\). In the present work in the LT
(110K) spectra we have been able to observe as many as five
librational bands in the hydrate and six in the deuterate; at RT
the situation is not distinct due to expected weak and broad
nature of the bands.

Regarding the separate assignments to R, W and T modes
we note that none of the observed bands is very weak as compared
to others. This would exclude the possibility of assigning any
of them to a T mode. Any further unique distinction between R
and W modes is not possible because of the water molecules
being linked with several kinds of bond lengths. The ratio \(\nu_H/\nu_D\)
is often used to choose between R and W modes (cf. sec.1.61,
Chapter 7) but in the present case the \(\nu_H/\nu_D\) ratios are nearly
equal for all of the five observed bands common to the hydrate
and the deuterate.

It is to be noted that the intensities of the librational
mode bands of water are more sensitive to changes in the sample
temperature than are the frequencies as brought out in Chap-
ter VII. Now, the 686 cm\(^{-1}\) librational band is the strongest in
the hydrate and also gains much in intensity on deuteration.
Using Miyazawa's criterion of \(T_{W/R} > 0.33\) we may attribute this
band to the W mode. Although this criterion is not unique,
it is found to hold in other transition metal hydrates also (cf. Chapter VII). The \( \nu_H \) bands at 893 and 863 cm\(^{-1}\), far off from the 686 cm\(^{-1}\) one, are then to be attributed to the R mode. This is in line with \( \nu_W \) falling lower than \( \nu_R \) in other transition metal hydrates (cf. Chapter VII). In the remaining two bands the one at lower frequency may again belong to \( W \) mode and the other to \( R \) mode. The bands in the deuterate are assigned to \( W \) and \( R \) using the \( \nu_H/\nu_D \) ratio correlation. The sixth band in the deuterate (375 cm\(^{-1}\)) is tentatively assigned as the second component with \( \nu_D = 350 \) cm\(^{-1}\).

(iv) \( \text{Cu-O}_W \) stretching band: One may ideally expect four bands for \( \text{Cu-O}_W \) stretching because of four 'coordinate' water molecules in different environments. But since the two \( \text{Cu-O}_W \) bonds are of nearly equal length (cf. Table 6.1) and H-bonding will have but small influence on the position of these bands, the four expected positions may be too close to separately appear. In the observed spectrum of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \), only one band (447 cm\(^{-1}\)) could be attributed to \( \text{Cu-O}_W \) stretching. The frequency is not unusual as compared to other \( M-O_W \) stretchings reported for aquo-complexes (34) but is certainly in the high range, indicating a rather strong \( \text{Cu-O}_W \) bond.
REFERENCES

Table 6.1:
Lengths of O-H bond of water, H-bond and Cu-OW bond in Angstrom units) in CuSO₄·5H₂O. Water bond angle and H-bond angle (in degrees) are also given.

<table>
<thead>
<tr>
<th>Bond Nature</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₁-O₅</td>
<td>0.96</td>
<td>109</td>
<td>2.76</td>
<td>154</td>
<td>1.98₃</td>
<td></td>
</tr>
<tr>
<td>Cu₁-O₆</td>
<td>1.00</td>
<td>2.76</td>
<td>172</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂-O₇</td>
<td>0.97</td>
<td>2.70</td>
<td>176</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂-O₈</td>
<td>0.96</td>
<td>2.68</td>
<td>173</td>
<td>1.94₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.97</td>
<td>106</td>
<td>2.79</td>
<td>167</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.96</td>
<td>2.99</td>
<td>161</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bond lengths in SO₄²⁻ tetrahedron (in Angstrom units)

\[ O₁ \quad O₂ \quad O₃ \quad O₄ \quad O₅ \]

1.47₈ 1.49₀ 1.46₇ 1.50₁

O₁ to O₄ represent SO₄²⁻ oxygens and O₅ to O₉ are water oxygens. Data are based on neutron diffraction study from reference 13.
Table 6.2: Band positions (in cm⁻¹ units) in the internal mode region of water in CuSO₄·5H₂O and CuSO₄·5D₂O at 300K and 110K (for comparison the positions reported by other workers are also given).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Matsumura (17)</th>
<th>Gamo (21)</th>
<th>Ferraro and Walker (24)</th>
<th>Present work LT(300K)</th>
<th>Present work LT(110K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂O</td>
<td>D₂O</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Stretching mode</td>
<td>3490</td>
<td>3376</td>
<td>3210</td>
<td>3480</td>
<td>2620sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3420</td>
<td>3250</td>
<td>3400</td>
<td>2585</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3350</td>
<td>2495</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2400</td>
<td>3220</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bending mode</td>
<td>-</td>
<td>1640</td>
<td>1650</td>
<td>1650</td>
<td>1210</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1675</td>
<td>1232</td>
</tr>
</tbody>
</table>

sh= shoulder.
Table 6.3: Correlation of the uncoupled $\text{OH}$ and $\text{OD}$ stretching frequencies in the partially deuterated analogues of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with the H-bond lengths

<table>
<thead>
<tr>
<th>Bond Nature$^a$</th>
<th>H-bond lengths$^a$ (Å)</th>
<th>$\nu_{\text{OH}}^b$ (cm$^{-1}$)</th>
<th>$\nu_{\text{OD}}^c$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$\text{Cu}_1\cdot\text{O}_5\cdot\text{H}\ldots\text{O}_9$</td>
<td>2.83</td>
<td>3475(50,50)*</td>
<td>2565(40,70)*</td>
</tr>
<tr>
<td>$\text{Cu}_1\cdot\text{O}_6\cdot\text{H}\ldots\text{O}_9$</td>
<td>3.76</td>
<td>3350(60,80)</td>
<td>2495(60,80)</td>
</tr>
<tr>
<td>$\text{Cu}_1\cdot\text{O}_6\cdot\text{H}\ldots\text{O}_9$</td>
<td>2.79</td>
<td>3395(60,60)</td>
<td>2515(50,30)</td>
</tr>
<tr>
<td>$\text{Cu}_1\cdot\text{O}_6\cdot\text{H}\ldots\text{O}_9$</td>
<td>2.76</td>
<td>3350(60,80)</td>
<td>2495(60,80)</td>
</tr>
<tr>
<td>$\text{Cu}_2\cdot\text{O}_7\cdot\text{H}\ldots\text{O}_3$</td>
<td>2.75</td>
<td>3300(60,70)</td>
<td>2440(50,70)</td>
</tr>
<tr>
<td>$\text{Cu}_2\cdot\text{O}_7\cdot\text{H}\ldots\text{O}_3$</td>
<td>2.70</td>
<td>3210(60,100)</td>
<td>2380(50,80)</td>
</tr>
<tr>
<td>$\text{Cu}_2\cdot\text{O}_8\cdot\text{H}\ldots\text{O}_3$</td>
<td>2.68</td>
<td>3140(70,90)</td>
<td>2320(60,100)</td>
</tr>
<tr>
<td>$\text{Cu}_2\cdot\text{O}_8\cdot\text{H}\ldots\text{O}_3$</td>
<td>2.72</td>
<td>3250(60,90)</td>
<td>2405(50,80)</td>
</tr>
<tr>
<td>$\text{O}_5\cdot\text{H}\ldots\text{O}_1$</td>
<td>2.79</td>
<td>3395(60,60)</td>
<td>2515(50,30)</td>
</tr>
<tr>
<td>$\text{O}_6\cdot\text{H}\ldots\text{O}_2$</td>
<td>2.99</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ The nature and the lengths of the bonds are taken from reference (13). $\text{Cu}_1$ and $\text{Cu}_2$ refer to copper atoms with two different $\text{Cu-O}_\text{W}$ distances; $\text{O}_1$ to $\text{O}_4$ represent oxygens on $\text{SO}_4^{2-}$ ions; and $\text{O}_5$ to $\text{O}_9$ are water oxygens.

$^b$ Taken from a ~ 90% deuterated sample.

$^c$ Taken from a ~ 30% deuterated sample.

* In parentheses the first figure gives the half-width of the band in cm$^{-1}$ and the second figure gives relative integrated intensity of the same in arb. units.
Table 6.3: Observed bands in 1200-300 cm\(^{-1}\) region in the IR spectrum of Cu\(\text{SO}_4\) \(5\text{H}_2\text{O}\) at 170 K (for comparison the band positions reported by two of the earlier workers are also given).

<table>
<thead>
<tr>
<th>Earlier workers</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>v (\text{(cm}^{-1}\text{)})</td>
<td>v (\text{(cm}^{-1}\text{)}), (\Delta v_{1/2}) (\text{(cm}^{-1}\text{)}), (I_t) (\text{(cm}^{-2}\text{)})</td>
</tr>
<tr>
<td>Ferraro and Walker ((24))</td>
<td>Hezel and Ross ((25))</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>2</td>
</tr>
<tr>
<td>1080</td>
<td>1130</td>
</tr>
<tr>
<td></td>
<td>1099</td>
</tr>
<tr>
<td>1081</td>
<td>1070</td>
</tr>
<tr>
<td>975</td>
<td>975</td>
</tr>
<tr>
<td>870</td>
<td>892</td>
</tr>
<tr>
<td></td>
<td>865</td>
</tr>
<tr>
<td></td>
<td>910</td>
</tr>
<tr>
<td></td>
<td>686</td>
</tr>
<tr>
<td>625</td>
<td>650-672</td>
</tr>
<tr>
<td></td>
<td>546</td>
</tr>
<tr>
<td></td>
<td>477</td>
</tr>
<tr>
<td>442</td>
<td>447</td>
</tr>
</tbody>
</table>

\(v\) : band position, \(\Delta v_{1/2}\) : band-width at half the maximum intensity

\(I_t\) : relative integrated intensity;

*total \(I_t\) for \(\nu_3\) \((\text{SO}_4^{2-}\text{)}\) bands is taken as 100, as also in the deuterate spectrum. This is done for the purpose of comparison of the band intensities in the spectra of the two isotopic analogues. \(\nu_3\) being a allowed band, its intensity would not display a major change even if the crystal structure undergoes slight modification on deuteration.

\(\nu_L\) are librational bands of water.
<table>
<thead>
<tr>
<th>ν (cm⁻¹)</th>
<th>Δν₁/₂ (cm⁻¹)</th>
<th>Iₜ*</th>
<th>Assignment</th>
<th>ν_H/ν_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1135</td>
<td>70</td>
<td>39</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>1095</td>
<td>60</td>
<td>23</td>
<td>v₃(SO₄²⁻)</td>
<td>1.00</td>
</tr>
<tr>
<td>1065</td>
<td>70</td>
<td>38</td>
<td></td>
<td>1.01</td>
</tr>
<tr>
<td>1020</td>
<td>50</td>
<td>11</td>
<td>Combination</td>
<td></td>
</tr>
<tr>
<td>975</td>
<td>10</td>
<td>4</td>
<td>v₁(SO₄²⁻)</td>
<td>1.00</td>
</tr>
<tr>
<td>810</td>
<td>?</td>
<td></td>
<td>Combination</td>
<td></td>
</tr>
<tr>
<td>663</td>
<td>50</td>
<td>17</td>
<td>v₄¹</td>
<td>1.35</td>
</tr>
<tr>
<td>617</td>
<td>50</td>
<td>50</td>
<td>v₄²(SO₄²⁻)</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>v₂</td>
<td>1.36</td>
</tr>
<tr>
<td>566</td>
<td>70</td>
<td>23</td>
<td>v₄²(SO₄²⁻)</td>
<td></td>
</tr>
<tr>
<td>512</td>
<td>70</td>
<td>95</td>
<td>v₃</td>
<td>1.34</td>
</tr>
<tr>
<td>455</td>
<td>~15</td>
<td>~10</td>
<td>v₂(SO₄²⁻)</td>
<td></td>
</tr>
<tr>
<td>446</td>
<td>~10</td>
<td>~15</td>
<td>v₃(Cu-O₁)</td>
<td>1.07</td>
</tr>
<tr>
<td>417</td>
<td>30</td>
<td>34</td>
<td>v₄</td>
<td>1.41</td>
</tr>
<tr>
<td>395</td>
<td>25</td>
<td>34</td>
<td>v₅</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>30</td>
<td>34</td>
<td>v₆(cf.text)</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>30</td>
<td>34</td>
<td>v₅</td>
<td>1.36</td>
</tr>
</tbody>
</table>

ν : band position, Δν₁/₂ : band-width at half the maximum intensity
Iₜ : relative integrated intensity;

* total Iₜ for ν₃(SO₄²⁻) bands is taken as 100, as also in the hydrate spectrum. This is done for the purpose of comparison of the band intensity in the spectra of the two isotopic analogues. ν₃ being a allowed band, its intensity would not display a major change even if the crystal structure undergoes slight modification on deuteration.

v₄ and v₅ : are librational bands of water.
Fig. 6.1: Coordination of Cu in CuSO₄·5H₂O. 
H-bonds are formed from water to water and from water to sulfate oxygen. There seems to be no significant difference between the two types (Hamilton and Ibers, Hydrogen Bonding in Solids, p.24).
Fig. 6.2: Infrared absorption spectra of CuSO$_4$·5H$_2$O and CuSO$_4$·5D$_2$O (90%), both at 110 K, in the frequency range 4000–1200 cm$^{-1}$. The first of these is recorded as thin film on NaCl plate and the latter one is recorded using nujol mull technique over KRS-5 windows.
Fig. 6.3: OH stretching mode envelope of water in Copper
sulfate pentahydrate: (A) full hydrate, 500 K,
(B) full hydrate, 110 K, (C) low hydrate (30% deuterated),
110 K. Spectra A and B are with thin films on NaCl plate;
C is with nujol mull between KRS-5 plates (see text).
Fig. 6.4: OD stretching mode envelope of deuterated water in copper sulfate pentahydrate in nujol mulls: (A) "full" deuterate (90%), 300 K, (B) "full" deuterate, 110 K, (C) low deuterate (30%), 110 K.
Fig. 6.5: Lorentzian analysis of the uncoupled OH stretching mode envelope of water in the IR spectra of a thin film (on NaCl plate) of 90% deuterated CuSO$_4$·5H$_2$O at 110 K. The solid line curve is taken from the observed spectrum and the broken line curves show the analysed components.
Fig. 6.6: Infrared absorption spectra of CuSO₄·5H₂O at RT (300 K) and LT (110 K) in the frequency range 1200 - 300 cm⁻¹. Spectra were recorded using nujol mull technique over KRS-5 windows.
Fig. 6.7: Lorentzian analysis of the IR absorption spectrum of nujol mull (on KRS-5 windows) of CuSO$_4$·5H$_2$O at 110 K, in the overlapping region 1200 - 300 cm$^{-1}$. The solid line curve is taken from the observed spectrum and the broken line curves show the analysed components.
Fig. 6.3: Schematic diagram showing the correlation of the bands observed in the IR spectra of CuSO$_4\cdot5$H$_2$O and CuSO$_4\cdot5$D$_2$O at 110 K in the region 1200 - 300 cm$^{-1}$.
Fig. 6.9: $\nu_3$ and $\nu_1$ mode bands envelope of $\text{SO}_4^{2-}$ in CuSO$_4$·5D$_2$O at 300 K (solid line) and 110 K (broken line) showing an increase in the intensity of $\nu_1$ mode band on lowering of temperature.