

## COPPER SULFATE MONOHYDRATE : CENTROSYMMETRIC OR NON-CENTROSYMMETRIC?

Bojan Šoptrajanov and Mira Trpkovska

Institut za hemija, PMF, Univerzitet "Kiril i Metodij",  
P.O. Box 162, 91001 Skopje, Macedonia

The presence, in the infrared spectra of the title compound, of at least three intense bands which are undoubtedly due to water librations made us suspect that, contrary to the results of the crystal structure determination, the crystals of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  are not centrosymmetric and two of the librational bands (relatively close to each other) originate from modes of two different types of water molecules.

### 1. INTRODUCTION

A long time ago [1], one of us was involved in the study of crystalline hydrates with very low HOH bending frequencies and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  came to his attention, this compound apparently being the first hydrate in the spectrum of which this phenomenon was observed [2]. Very low  $\delta(\text{HOH})$  frequencies were later found in the spectra of a number of hydrates with the general formula  $\text{MXO}_4 \cdot \text{H}_2\text{O}$  (where  $\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$  or  $\text{Zn}$ ;  $\text{X} = \text{S}$  or  $\text{Se}$ ) which belong to the so-called *kieserite family* [3-6], *kieserite* being the mineralogical name for  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . Even lower values for the  $\delta(\text{HOH})$  frequencies were found in some other cases [1,7] and tentative explanations for the possible origin of the phenomenon were offered [1,7,8]. The low water bending frequencies, however, are not the point we would like to discuss presently.

The main concern of the present communication is the spectroscopic verification (or rejection) of the

crystallographic conclusions [9] that  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  crystallizes in the centrosymmetric space group  $P\bar{1}$ . Šoptrajanov [1], namely, paid attention to the fact that *three* intense bands attributable to water librations exist in the spectrum of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , whereas in the spectra of the structurally related compounds of the *kieserite family* only two such bands are strong. One of the possible explanations for the observed differences was that copper sulfate monohydrate is not centrosymmetric and that two non-equivalent (but structurally similar) water molecules exist in the unit cell. At that time the crystal structure was not yet determined.

Despite the fact that in the meantime the structure of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  was solved and very satisfactorily refined [9], we decided to reinvestigate the infrared spectra (and record the Raman spectra as well) in order to be certain (on spectroscopic grounds) that the space group was properly chosen.

If the space group is indeed  $\bar{P}1$ , then the two water molecules would be equivalent and under the factor-group selection rules each mode of an isolated water molecule or sulfate ion would give rise to only one infrared active and one Raman active band with non-coincident frequencies. If, on the other hand, the space group is the non-centrosymmetric  $P1$  one, the polyatomic structural units would belong to two different types (one molecule or anion of each type per unit cell) and every mode would give rise to two bands, coincident in the infrared and Raman spectra.

## 2. EXPERIMENTAL

The monohydrate of copper sulfate was prepared by dehydration of the corresponding pentahydrate [10].

The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer equipped with a RIIC (London) variable-temperature cell. The Raman spectra were obtained on a Spex Ramalog 5M System, using a Spectra Physics argon-ion laser. The facilities of the Department of Physics of King's College in London (UK) were used to record the Raman spectra as a part of the cooperation (under the auspices of British Council) between our Institute and King's College.

## 3. RESULTS AND DISCUSSION

The 1300-400  $\text{cm}^{-1}$  region of the infrared spectra of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) are shown in Fig. 1 whereas the RT Raman spectrum is given in Fig. 2. For our present purposes

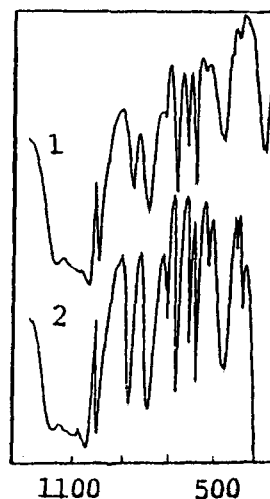


Fig. 1. Infrared spectra of copper sulfate monohydrate recorded at room temperature (1) and at liquid-nitrogen temperature (2)

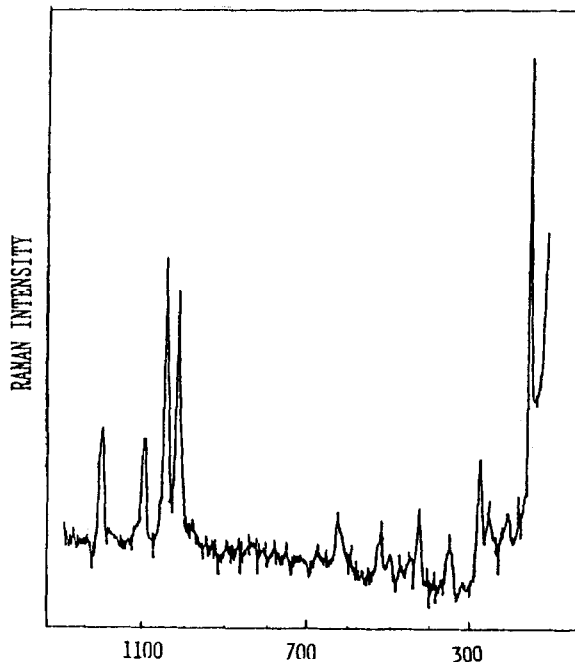


Fig. 2. RT Raman spectrum of copper sulfate monohydrate

this region is the most relevant one since all sulfate modes and the water librations give rise to bands in the above-mentioned region.

Thus, the components of the antisymmetric and symmetric sulfate stretches (3+1 for one type of  $\text{SO}_4^{2-}$  ions), and of the two bending modes (3+2 for a single type of sulfate anions) are expected to appear, in addition to the bands due to water librations. Of these, for one type of water molecules, two are expected to be sufficiently strong since for a water molecule with a  $C_{2v}$  symmetry the twisting mode is inactive.

As seen, the number of infrared bands (especially at LNT) by far exceeds the expected one.

This is especially true for the bands originating from water librations. On the basis of their position and temperature sensitivity, three *strong* bands (those at 880, 795 and 480  $\text{cm}^{-1}$ ) can be attributed, beyond doubt, to water librational modes. The band around 480  $\text{cm}^{-1}$  shows slight splitting and this would increase to four the number of such bands.

The assignment is supported by the study of the partially deuterated analogues (we failed to prepare a completely deuterated compound) as seen in Fig. 3.

Taken all together, in the spectrum of the protiated  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  three (or four) bands with appreciable intensity should be attributed to modes with librational character. This is exactly what one expects if two (rather than one) structurally similar types of water molecules are present in the structure and the twisting modes does not appear in

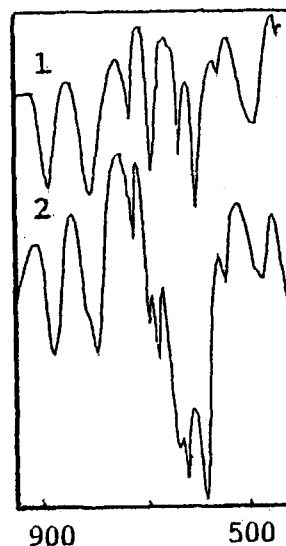


Fig. 3. The low-frequency region of the infrared spectra of protiated (1) and partially deuterated (2) copper sulfate monohydrate

the infrared spectrum. If this is so, then the space group can not be centrosymmetric.

An alternative explanation would evoke the complete mixing of two water librations, the out-of-plane modes (wagging and twisting) being the most reasonable candidates. In fact, according to the model calculations of Eriksson and Lindgren [11], for tetrahedrally coordinated water molecules (such as those which are present in the structure of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ) the wagging and twisting librations are expected to have higher frequencies than the rocking one.

However, the results of the partial deuteration do not support such a conclusion. As seen in Fig. 3, namely, marked changes occur in the 700-600  $\text{cm}^{-1}$  region where, obviously, two of the sulfate bending modes take part in vibrational interac-

tions with the HDO analogues of the water librations giving rise to the 880 and 795  $\text{cm}^{-1}$  bands. In the model developed in [11], namely, only the rocking HDO librations should have a form essentially similar to that of the  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ) counterparts whereas the mixed wagging and twisting  $\text{H}_2\text{O}$  modes would give rise to the so-called "H-motion" and "D-motion" respectively. It should be mentioned that in the spectra of the compounds from the kieserite family only *one strong* band is present around 800  $\text{cm}^{-1}$  and it has been assigned [1] to the rocking  $\text{H}_2\text{O}$  libration.

The presence of *two* rocking bands and of potential candidates for two wagging ones (the slightly separated doublet around 480  $\text{cm}^{-1}$ ) seems to be a sufficient evidence that the space group can not be centrosymmetric.

The region of the  $\text{SO}_4^{2-}$  stretching vibrations in the infrared spectrum may seem to corroborate the above conclusion since the number of maxima and shoulders there exceeds four. A closer look at the spectra indicates that this might not be so since the deep absorption window around 1030  $\text{cm}^{-1}$  is almost certainly an Evans hole originating from an interaction of one of the sulfate modes and a second-order transition (the combination of two sulfate bending vibrations).

The number and frequencies of the Raman bands can not be taken as an additional proof for the conclusion that the unit cell is not centrosymmetric. Thus, the number of bands in the  $\text{SO}_4^{2-}$  stretching region hardly exceeds four whereas their frequencies are only marginally different from those of the infrared ones.

The general conclusion would be that the unit cell of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  is most likely non-centrosymmetric but only the water molecules deviate slightly (but not negligibly) from the positions they would have occupied in the case of a centrosymmetric unit cell. This would explain the number of sulfate bands and the low *R* value obtained during the refinement of the crystal structure.

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