Infrared Absorption Spectra of Water of Crystallization in Copper Sulfate Penta- and Monohydrate Crystals

By Itaru GAMO

(Received September 20, 1960)

Infrared spectra of copper sulfate penta- and monohydrate have been separately subject to several investigations[1-3]. However, there has been no comparative study of these spectra in relation to their structural difference.

In the present paper, observed spectra were examined in relation to this difference, mainly to that of the binding state of the water molecules in them.

Experimental

Preparation.—Copper sulfate pentahydrate of commercial first grade was made free from iron according to Gmelin's handbook[4]. The sample was then twice recrystallized from water. Copper sulfate monohydrate was obtained by keeping this purified pentahydrate at 110°C for 3 hr. under reduced pressure in an Abderhalden apparatus[5].

Measurements.—Spectra were obtained by means of a Perkin-Elmer Infracord spectrophotometer with a rock salt prism. The Nujol mull technique was employed throughout. The potassium bromide disk technique was unsuitable for the pentahydrate, because the prepared disk became dark brown. A similar phenomenon was observed in the case of cupric chloride dihydrate.

Results

The spectra are given in Fig. 1. In the 3 μ region one peak is observed for the pentahydrate at 3420 cm^{-1}, and two peaks for the monohydrate at 3340 and 3190 cm^{-1}. These compare with the peak of various inorganic hydrated sulfates[6] in this region, and can be assigned to O-H stretching vibrations of water. Overlapping of the symmetric and the antisymmetric mode together with their splitting is probably responsible for the broadness of these three bands. In the 5 μ region the spectrum of the pentahydrate shows a weak band at 2120 cm^{-1}, attributable to a combination of the bending and the rocking mode of water or that of the totally symmetric and the triply degenerate stretching mode of sulfate ion. Of course there is a possibility of their overlapping. In the 6 μ region a band of medium intensity is observed at 1640 cm^{-1} for the pentahydrate. At the same position a broad weak band is observed for the monohydrate, with an additional band of medium intensity at 1510 cm^{-1}. These three can be assigned to the bending modes of water, the latter two resulting from splitting.

In the 8 μ region, characteristic bands of inorganic sulfates[7] are observed for the pentahydrate at 1200 and 1170 cm^{-1} and for the monohydrate at 1200 and 1120 cm^{-1}, attributable to the triply degenerate stretching vibrations of sulfate ion. The sharp 1000 and 966 cm^{-1} bands of the former and the 1020 cm^{-1} band of the latter can be assigned to the totally symmetric stretching vibrations that have become active in infrared by some perturbations. In this connection it is to be noticed that the intensities of the former two bands are considerably greater than in the usual cases of sulfates. The 875 cm^{-1} band of

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[1] J. Lecomte, *Compt. rend.*, **226**, 1088 (1948); *J. chim. Phys.*, **50**, C53 (1953).

[2] O. Matsumura, *Mem. Fac. Sci., Kyushu Univ., B*, **I**, 1 (1951).

[3] J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3963 (1956).

[4] "Gmelins Handbuch der anorganischen Chemie", part 60, Cu B1 (1958), p. 508.

[5] ibid., p. 523.

[6] I. Gamo, This Bulletin, **34**, 760 (1961).

[7] L. J. Bellamy, "Infrared Spectra of Complex Molecules", Methuen and Co., Ltd., London (1958), p. 345.

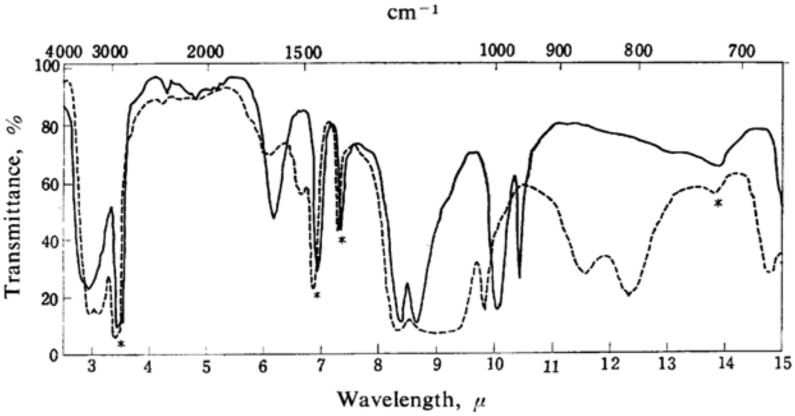

Fig. 1. Observed bands of $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot H_2O$.
——, $CuSO_4 \cdot 5H_2O$; ----, $CuSO_4 \cdot H_2O$
* Nujol bonds

the pentahydrate found by Fujita et al.[3] was observed in our study only when the spectrum in this region was recorded immediately after the mull preparation. In the 12μ region of the monohydrate spectrum, strong but broad peaks are observed at 866 and 813 cm⁻¹, in rough accord with Lecomte's values[1], 850 and 796 cm⁻¹, respectively. They are tentatively assigned to the rocking modes of water. The 676 cm⁻¹ band of the monohydrate are assigned to the triply degenerate bending vibration of sulfate ion.

Tables I and II summarize these results.

TABLE I. OBSERVED FREQUENCIES OF $CuSO_4 \cdot 5H_2O$

Wave number, cm⁻¹	Assignment
3420 s	ν (H_2O) stretch.
2120 w	$\nu_3+\nu_1$ (SO_4) and/or $\nu_R+\nu_2$ (H_2O)
1640 m	ν_2 (H_2O) bend.
1200 s	ν_3 (SO_4) stretch.
1170 s	ν_3 (SO_4) stretch.
1000 s	ν_1 (SO_4) stretch.
966 s	ν_1 (SO_4) stretch.
875 s [a]	ν_R (H_2O) rock.

a, Observed by Fujita et al. (See Ref. 3.)

TABLE II. OBSERVED FREQUENCIES OF $CuSO_4 \cdot H_2O$

Wave number, cm⁻¹	Assignment
3340 s	ν (H_2O) stretch.
3190 s	ν (H_2O) stretch.
1640 w	ν_2 (H_2O) bend.
1510 w	ν_2 (H_2O) bend.
1200 s	ν_3 (SO_4) stretch.
1120 s	ν_3 (SO_4) stretch.
1020 s	ν_1 (SO_4) stretch.
866 m	ν_R (H_2O) rock.
813 m	ν_R (H_2O) rock.
676 m	ν_4 (SO_4) bend.

Discussion

According to X-ray analysis[8], four of the water molecules in copper sulfate pentahydrate crystal are closely coördinated with a copper atom by fairly covalent bonds, making a square with the copper atom at the center. The fifth occupies a hole in the structure, and hardly differs from the free water molecule.

Although the interatomic distances in copper sulfate pentahydrate crystal are determined well by the X-ray analysis, those in the monohydrate crystal are completely unknown. Nevertheless comparison of the unit cell parameters (see Table III) shows that the structure of the latter is quite different from that of the former, corresponding to a considerable rearrangement of atoms upon partial dehydration. In the following, we shall confine our discussion mainly to water bands.

Since copper sulfate pentahydrate belongs to the symmetry class C_i^1 [8], we can expect theoretically many water bands, due mainly to the splitting of the bands of the free molecule. Actually, only two peaks were observed in our study that are attributable to water. The resolving power of the instrument, which becomes rapidly small with increasing wave number, seems to be partly responsible for this poor observation. Nevertheless some interesting results are obtained.

The author assume tentatively the 3420 cm⁻¹ band to be due to the antisymmetric stretching vibration affected by the coördination of copper-water and by the hydrogen bonding between the water molecule and the outer oxygen atom of sulfate ion. Its deviation from the vapor

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8) C. A. Beevers and H. Lipson, *Proc. Roy. Soc.*, **A146**, 570 (1934).

9) F. Hammel, *Ann. Chim.*, (11) **11**, 247 (1939).

TABLE III. COMPARISON OF UNIT CELL PARAMETERS

	Type	Symmetry	a	b	c	β	M	Lit.
$CuSO_4 \cdot 5H_2O$	$H_{4_{10}}$	C_i^1	6.12 Å	10.70 Å	5.97 Å	107.4°	2	8
$CuSO_4 \cdot H_2O$	—	m k l	6.80	7.90	12.6	~90	—	9

frequency (3756.5 cm^{-1}) is reasonable as compared with those of other hydrated salts. The fairly large covalent character of the copper-water bond (distance 1.98 Å), together with the strong hydrogen bond of 2.75 Å, is sufficient to explain this order of magnitude. In the next place, both the 3340 and the 3190 cm^{-1} band of the monohydrate can be reasonably assigned either to antisymmetric or to symmetric vibration. The observed doublings of the bending and the rocking vibration (see later) together with the nearly equal intensity of the two bands, seem to support this assignment strongly. The main cause of this doubling is probably a rather strong coupling of two neighboring water molecules through hydrogen bonding to the same oxygen atom of sulfate ion. The values of the two frequencies suggest that in this crystal, the binding strength between one water molecule and the neighboring sulfate ion is considerably greater than in the pentahydrate crystal. The magnitude of the change in the bending frequency of the pentahydrate is reasonable as compared with the values of other salts. In the monohydrate one of the two frequencies is reasonably higher than that in the vapor state (1595.5 cm^{-1}). The other is lower and therefore rather exceptional for this mode. Both bands are broader than in the usual cases of sulfates. This suggests stronger interaction. In these two respects, the bending modes of the water molecule in this crystal deserve to be noticed.

The shapes and the frequency values of the two rocking bands of the monohydrate are the same as usual. The great value of the splitting (53 cm^{-1}) as well as the value in the case of the bending mode (130 cm^{-1}) seems to support the above assumption of hydrogen bonding. An intensity consideration in the two modes (see Fig. 1) suggests that the two hydrogen bonds are not completely equivalent. This is understandable, since the numerical ratio of water molecules to sulfate ions in the crystal is 1 : 1, preventing the two water molecules from occupying a position equivalent to the same oxygen atom. We can roughly estimate the mean value of the two O–H···O distances by using the relation obtained in the preceding paper. The two water molecules are assumed to make covalent bonds of equal length (1.98 Å, value in the ligand water molecule of the pentahydrate) with two different copper atoms respectively. In Fig. 4 of that paper the O–H···O distance is thus estimated to be somewhat smaller than 2.61 Å using the mean value of the two rocking frequencies and the covalent bond length 1.98 Å.

The author could not observe the band peaks expected from the fifth almost free water molecule in the pentahydrate crystal. Probably they are weak and hidden in other bands.

The author shall now proceed to a brief discussion of the sulfate ion bands. For the pentahydrate, the observed two frequencies of ν_3 are higher than that in solution (1104 cm^{-1} 10)). For ν_1, however, one component is higher and the other, lower than ν_1 in solution (981 cm^{-1} 10)). According to X-ray analysis8), the four sulfate oxygen atoms in this crystal are all making different contacts with other atoms or molecules. Probably this is responsible for these splittings. For the monohydrate, the bands are fairly broader than in the pentahydrate. It is very interesting that one component of the doublet band ν_1 (966 cm^{-1} of the pentahydrate) disappears upon the partial dehydration.

Summary

The observed spectra of water in the penta- and monohydrate crystals were interpreted by the effects of coördination copper-water and hydrogen bonding O–H···O. The whole difference in the spectra of the two crystals were explained in relation to the escape of the four ligand water molecules and the resulting rearrangement of atoms. The stretching, bending and rocking modes, which are single in the case of the pentahydrate, split into doublets in the monohydrate. This result was explained by a single assumption of strong coupling of two neighboring water molecules in the latter.

The author is indebted to Professor Takehiko Shimanouchi of the University of Tokyo for his helpful guidance.

Chemical Laboratory
Department of General Education
Faculty of Science and Engineering
Waseda University
Shinjuku-ku, Tokyo

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10) K. W. F. Kohlrausch, " Ramanspektren. Hand- und Jahrbuch der chemischen Physik ", 9, part 6 (1943), p. 399.