Infrared Absorption Spectra of Water of Crystallization in Sodium Sulfate Decahydrate Crystals

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Preceding papers[1] have examined the observed spectra of water of crystallization of various salts as they were affected by the coördination of the water molecule on the metal atom and by the hydrogen bonding between the water molecule and the anion.

For the present study, spectra of sodium sulfate decahydrate were investigated. Attempts were made to interpret the results by the effect of hydrogen bonding only, because no coördination exists between the water molecule and the sodium atom. The spectra suggest the existence of at least two kinds of water molecules in the unit cell of the crystal.

Experimental

Preparations.—Commercial sodium sulfate decahydrate of a guaranteed grade was recrystallized from water. Sodium sulfate, used for the reference spectra, was obtained by keeping this purified sodium sulfate decahydrate at 100°C for 30 min.[2]

Measurements.—Spectra were obtained by means of a Perkin-Elmer Infracord spectrophotometer with a rock-salt prism. For the hydrate, the use of the potassium bromide disk was unsuitable because a large amount of water escaped during the vacuum process, resulting in a considerable weakening of the water bands. Therefore, the Nujol and H.C.B. mull techniques were employed. For the anhydride, however, the potassium bromide disk technique was suitable.

Results

The spectra are given in Fig. 1. (For reference, the spectra of sodium sulfate are also given in the figure.) In the 3μ region, one strong band is observed at $3510\,\text{cm}^{-1}$. Is can be assigned to the O–H stretching mode of a water molecule affected by hydrogen bonding. A weak but relatively sharp band is observed at $2940\,\text{cm}^{-1}$. It disappears upon complete dehydration and therefore must be attributde to a water mode. Probably this is due to a stretching vibration much more strongly influenced by hydrogen bonding than that mentioned above. These two bands are too widely separated to be attributed to the antisymmetric and the symmetric O–H stretching mode respectively of one and the same water molecule. In the $5\,\mu$ region a very weak but clear band is observed at $2170\,\text{cm}^{-1}$. It also disappears upon dehydration and can be assigned to a combination of the bending and the wagging (probably) vibration of a restricted water molecule. A similar band is observed at 2080 cm^{-1}. It does not disappear by the same treatment and therefore can be attributed to a

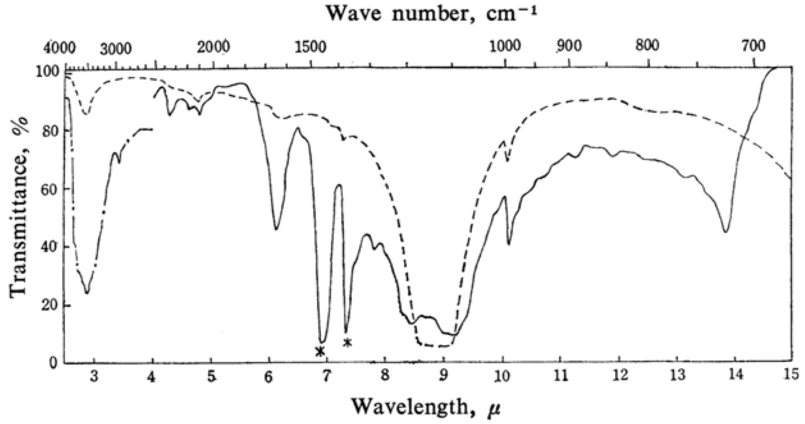

Fig. 1. Absorption bands of $Na_2SO_4\cdot10H_2O$ and Na_2SO_4.
—— $Na_2SO_4\cdot10H_2O$ (Nujol) –·–· $Na_2SO_4\cdot10H_2O$ (H. C. B.)
---- Na_2SO_4 (KBr disk) * Nujol bands

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[1] I. Gamo, This Bulletin, 34, 760, 764, 1430, 1433 (1961).

[2] L. Gmelin, "Handbuch der anorganischen Chemie", Verlag Chemie, Berlin (1928), No. 21, p. 559.

combination of the triply degenerate and the totally symmetric stretching mode of the sulfate ion. In the 6 μ region the spectrum shows a band of medium intensity at 1650 cm^{-1}, attributable undoubtedly to the bending mode of a water molecule. The band of medium intensity at 1290 cm^{-1} disappears upon dehydration. Therefore, it must be attributed to a water mode even though its origin cannot be decided at present. Probably it is due to an overtone of some deformation mode or to a combination of deformation modes. The bands at 1180, 1090 and 988 cm^{-1} can be assigned to the stretching vibrations of the sulfate ion, as in the usual cases of sulfates[3]. The band at 720 cm^{-1} overlaps a Nujol band to some extent. It can be assigned from its position to the wagging vibration[1] of that water molecule which is responsible for the 2940 cm^{-1} stretching band. (The reason is explained later).

Table I summarizes these results.

TABLE I. OBSERVED FREQUENCIES OF $Na_2SO_4 \cdot 10H_2O$[a]

Wave number, cm^{-1}		Assignment[b]	
3510	s	$\nu(H_2O)$	stretch. of H_2O (I)
2940	w	$\nu(H_2O)$	stretch. of H_2O (II)
2170	vw	$\nu_2+\nu_R(H_2O)$	
2080	vw	$\nu_3+\nu_1(SO_4)$	
1650	m	$\nu_2(H_2O)$	bend.
1290	m	(H_2O)	
1180	s	$\nu_3(SO_4)$	antisym. stretch.
1090	vs, b	$\nu_3(SO_4)$	antisym. stretch.
988	m, sh	$\nu_1(SO_4)$	sym. stretch.
720	m	$\nu_R(H_2O)$	wag. of H_2O (II)

a) Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, sharp.

b) H_2O (I) and H_2O (II) denote two different kinds of water molecules in the unit cell respectively.

Discussion

The results obtained in the preceding section supply some insight into the binding states of water molecules in the crystal. Since the water molecules in this crystal do not seem to be affected by the coördination, only the influence of hydrogen bonding will be considered. From this standpoint, at least some of the water molecules must form hydrogen bonds with the oxygen atoms of other water molecules or of sulfate ions. Otherwise, it is impossible to explain the observed deviations in the water stretching frequencies from the values of the vapor state.

The 3510 cm^{-1} stretching frequency, which is considerably higher than the values for the water of crystallization in the usual inorganic salts[1], must be due to water molecules which are relatively free. Water molecules which are much more strongly influenced by hydrogen bonding are probably responsible for the band at 2940 cm^{-1}, since, in general, hydrogen bonding lowers the stretching frequency. By an application of Glemser's relationship between the stretching frequency and the O–H···O distance[4], 3.01 and 2.58 Å are obtained for the first and the second water molecule respectively. These values are comparable with those for ice (2.76 Å[5]) and gypsum (2.82 Å[6]), in both of which the water molecules are also free from coördination.

By the aid of the values thus obtained, the origin of the wagging band at 720 cm^{-1} can be deduced as follows. To begin with, this band may tentatively be assumed to be due to that water molecule which is responsible for the stretching band at 3510 cm^{-1}, the corresponding O–H···O distance being 3.01 Å. A previous study[7] shows roughly the dependence of the wagging frequency upon the metal-water distance and the hydrogen bond distance. It follows from this relationship that in the present case the metal-water distance is far less than 1.80 Å. But the distance cannot be less than 2.27 Å, the sum of the ionic radii of sodium and oxygen, since no water molecule seems to be coördinated with the metal atom, the interaction between them being purely electrostatic. The distance is estimated to be about 2.80 Å when this band is correlated with the stretching band at 2940 cm^{-1}. These circumstances seem to favor the assignment of this band described in the preceding section.

Summary

The observed spectra of water of crystallization were interpreted on the basis of the effect of hydrogen bonding. It was proposed that at least two kinds of water molecules exist in the unit cell of the crystal. The corresponding two O–H···O distances were roughly estimated to be 3.01 and 2.58 Å respectively by the use of Glemser's relationship between the stretching frequency and the hydrogen bond distance.

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

[4] O. Glemser and E. Hartert, *Naturwiss.*, **42**, 534 (1955).

[5] W. H. Barnes, *Proc. Roy. Soc.*, **A125**, 670 (1929).

[6] M. Atoji and R. E. Rundle, *J. Chem. Phys.*, **29**, 1306 (1958).

[7] I. Gamo, This Bulletin, **34**, 760 (1961). See also the preceding paper as regards the change of assignment from the rocking to the wagging mode.