Infrared Absorption Spectra of Water of Crystallization in Aluminum Sulfate Octodecahydrate Crystals

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The study of the vibrational spectra of hydrated aluminum salts seems to be more attractive than that of most of the hydrated salts of other metals, because the water bands of the former present some peculiar features that are not observable in those of the latter. We meet in particular several bands that are not found in other salts. Among aluminum salts, aluminum chloride hexahydrate has already been subject to several fairly detailed infrared[1,2] and Raman[3] studies.

In the present paper the infrared absorption spectra of aluminum sulfate octodecahydrate are compared with those of aluminum chloride hexahydrate, and their characteristic features are analyzed. Attention is mainly focused on the water bands.

Experimental

Preparation.—Commercial aluminum sulfate octodecahydrate of a guaranteed grade was recrystallized from water.

Measurement.—Spectra were obtained by means of a Perkin-Elmer Infracord spectrophotometer with a rock-salt prism. The potassium bromide disk technique was employed.

Results

The spectra are shown in Fig. 1. In the 3μ region, two strong bands are observed at 3330 and 2940 cm^{-1}. The former can be assigned to the antisymmetric, while the latter can be assigned to the symmetric, O–H stretching mode of a water molecule affected by the aluminum-water coördination and by the hydrogen bonding O–H$\cdots$O[2]. It is interesting that in hydrated salts usually only one peak is observed in this region, while in the present case there are two clearly-separated bands. They seem to correspond to the one broad band which ranges from 3400 to 2900 cm^{-1} in aluminum chloride hexahydrate.

In the 4 μ region, one weak band is observed at 2460 cm^{-1}. This probably corresponds to the band at 2420 cm^{-1} in aluminum chloride hexahydrate and can be assigned to a combination of the bending and a restricted rotation mode of a ligand water molecule. In the 6μ region, the spectrum shows a band of medium intensity at 1640 cm^{-1}, attributable undoubtedly to the bending mode of water. In the 8$\sim$10 μ

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[1] E. Hartert and O. Glemser, *Z. Elektrochem.*, **60**, 746 (1956).

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

[3] A.-W. Marchand, Thesis (University of Paris). (1957), p. 17.

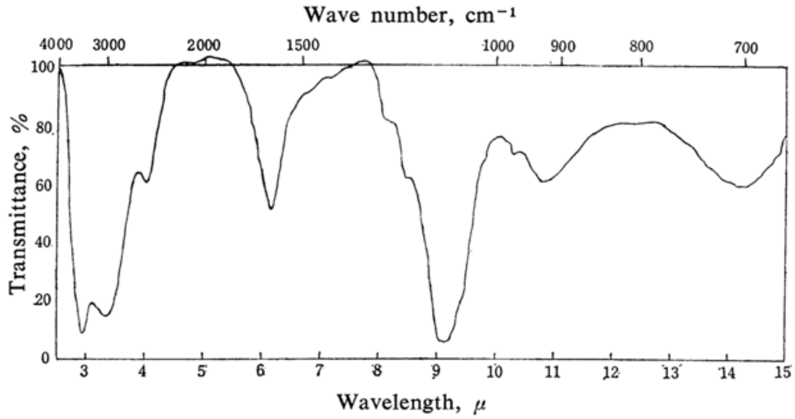

Fig. 1. Absorption bands of $Al_2(SO_4)_3\cdot 18H_2O$.

region, characteristic bands of inorganic sulfates[4] are observed at 1230, 1190, 1110 and 975 cm^{-1}, all attributable to the stretching vibrations of the sulfate ion and presumably resulting from a distortion of the tetrahedron of the ion caused by some perturbations from outside.

The weak broad band at 920 cm^{-1} can be assigned, from its position and shape, to a restricted rotation mode of water. It is probably due to the rotation of a water molecule about the axis of the smallest moment of inertia (wagging vibration). Similarly, the very broad band at 690 cm^{-1} can be assigned to another restricted rotation, that is, the twisting or the rocking vibration. Since the twisting band is too weak to be observed in ice and in other cases, it seems reasonable to attribute this band to the rocking vibration (rotation about the axis of the greatest moment of inertia). Of course, the difference between the binding states of the water molecules in aluminum salts and in ice must be taken into account; the latter is free from coördination. Judging from its very broad shape, one cannot assign this band to the bending vibration of the sulfate ion (613 cm^{-1} in solution[5]). The very weak band at 1390 cm^{-1} can be tentatively assigned to the first overtone of this band.

TABLE I. OBSERVED FREQUENCIES OF $Al_2(SO_4)_3\cdot 18H_2O$[a)]

Wave number, cm^{-1}		Assignment
3330	s	$\nu_3(H_2O)$ antisym. stretch.
2940	s	$\nu_1(H_2O)$ sym. stretch.
2460	w	$\nu_2+\nu_{R'}(H_2O)$
1640	m	$\nu_2(H_2O)$ bend.
1390	vw	$2\nu_{R''}(H_2O)$
1230	w shoulder	$\nu_3(SO_4)$ triply degenerate stretch.
1190	w shoulder	$\nu_3(SO_4)$ triply degenerate stretch.
1100	vs	$\nu_3(SO_4)$ triply degenerate stretch.
975	w	$\nu_1(SO_4)$ totally sym. stretch.
920	w, b	$\nu_{R'}(H_2O)$ wag.
690	m, vb	$\nu_{R''}(H_2O)$ rock.

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

Table I summarizes these results.

Discussion

The results obtained above supply some insight into the binding states of the water molecules in the crystal. As in the previous studies[6], the water frequencies will be assumed to be influenced by the coördination and the hydrogen bonding.

The deviations of the two stretching frequencies from the values of the vapor state (3755.8 and 3651.7 cm^{-1}) are reasonable as compared with the usual cases of hydrated salts. It suggests that at least some of the water molecules are coördinated with an aluminum atom, like the six water molecules in aluminum chloride hexahydrate, and that at the same time they form hydrogen bonds with oxygen atoms of other water molecules or sulfate ions. The clear separation of the symmetric stretching band from the antisymmetric one is probably due to its sharpness and strong intensity. The combination band at 2460 cm^{-1} is also much stronger than usual.

The position of the bending band is the same as in aluminum chloride hexahydrate within the range of experimental error. This indicates that in this mode the total effect of aluminum-water coördination and hydrogen

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

[5] K. W. F. Kohlrausch, "Ramanspektren. Hand- und Jahrbuch der chemischen Physik", 9, Part 6 (1943), p. 399.

[6] I. Gamo, This Bulletin, 34, 760, 764 (1961).

bonding O–H···O is of the same order as in aluminum chloride hexahydrate.

The 920 cm^{-1} wagging frequency is, on the contrary, about 80 cm^{-1} higher than the corresponding one in aluminum chloride hexahydrate. (In a previous paper[2] the bands in the 11∼14 μ region were tentatively assigned to the rocking mode, but it seems better to assign them to the wagging vibration for reasons stated in the preceding section.) Therefore, the total effect mentioned above is somewhat greater in aluminum sulfate octodecahydrate. Furthermore, the value, 920 cm^{-1}, is much higher than in the usual cases of inorganic hydrated salts[2]. This leads one to expect a very high frequency also for the rocking mode, since the two modes are likely to be influenced in a similar manner by the two effects. This seems to provide another reason for the assignment which was proposed in the preceding section for the band at 690 cm^{-1}. The rocking frequency is usually under 650 cm^{-1}.

The discussion hitherto has been based on the assignments described in the preceding section. As an alternative, an assumption of the existence of two kinds of water molecules is possible if the bands at 920 and 690 cm^{-1} are assigned to wagging vibrations, and if the bands at 2940 and 3330 cm^{-1} are regarded as due to the corresponding stretching modes. However, the following discussion suggests the invalidity of such an assumption. First, it will be reasonable in this case to suppose that water molecules of the first kind are coördinated with the aluminum atom, while those of the second kind are almost free from such coördination, since coördination lowers the stretching and increases the wagging frequency. On these suppositions one may try to apply to the 3330 cm^{-1} band the relationship proposed by Glemser[7] between the O–H···O distance and the stretching frequency in inorganic hydrated salts. This relationship seems to be correctly applicable to cases where only the hydrogen bonding effect dominates the frequency. In the present case, the 3330 cm^{-1} band is supposed to be due to the stretching mode affected only by this effect. Hence, the application is suitable, giving 2.66 Å for the O–H···O distance. Then, from the band at 690 cm^{-1}, one may try to estimate this distance by applying the relationship obtained in a previous study[2]. It shows the dependence of the wagging frequency* upon the hydrogen bond distance and the metal-water distance[2]. The aluminum-water distance in the present case must be far greater than 1.88 Å (the value in aluminum chloride hexahydrate[8]), because the water molecules are supposed to be almost free from coördination and 1.88 Å is abnormally short, even for coördination distance. Correspondingly, a value far less than 2.66 Å is obtained for the O–H···O distance by the above-mentioned relationship. After all, the two values estimated from the stretching and from the wagging frequency conflict with each other, while in the original assignments they can be reconciled by proper adjustment. These circumstances seem to favor the original assignments.

Lastly, we have been able to observe an overtone and a very strong combination band of water, just as we observed several in the case of aluminum chloride hexahydrate, because of their great intensity. It may be that some connection exists between this fact and the aluminum-water coördination, because the coördination distance in aluminum chloride hexahydrate (1.88 Å) is anomalously shorter than usual.

Summary

The observed spectra of water of crystallization were compared with those of aluminum chloride hexahydrate and interpreted on the basis of the effects of aluminum-water coördination and hydrogen bonding O–H···O. The wagging and the rocking frequency were both much higher than is usual in water of crystallization. It was proposed that this result, together with other peculiarities, may have some connection with the coördination strength between aluminum and water.

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

* Described as the rocking frequency in Ref. 2.

[8] K. R. Andress and C. Carpenter, *Z. Krist.*, **A87**, 446 (1934).