Infrared Absorption Spectra of Water of Crystallization in Ferrous Chloride Tetrahydrate Crystal

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The crystal structure of ferrous chloride tetrahydrate has been determined in detail by X-ray diffraction[1]. Therefore it is possible to correlate the infrared absorption spectra of the water of crystallization with the structure.

In the present study, the characteristic bands of the water of crystallization in the crystal were determined for this purpose. Like cobaltous chloride hexahydrate and dihydrate[2], the crystal has an advantage in that observed bands can be attributed to the vibrations of water molecules almost uniquely. The spectra have an interesting feature in the bending region that has not been observed in other cases in this series of studies[2-6].

Experimental

Preparation.—Commercial ferrous chloride tetrahydrate of guaranteed grade was recrystallized from water.

Measurement. — Spectra were recorded by a Kôken DS 301 infrared spectrophotometer equipped with a sodium chloride prism. The potassium bromide disk technique was employed.

Results

The spectra are given in Fig. 1. In the 3 μ region, one peak is observed at 3442 cm^{-1} and one shoulder at 3238 cm^{-1}. These are comparable to the peaks of various inorganic hydrated salts in this region, and can be assigned to the O–H stretching vibrations of water molecules affected by the interaction with an iron atom and by the hydrogen bonding with a chlorine atom. The overlapping of several stretching bands is probably responsible for the somewhat broad feature of the band. In the 5 μ region, a broad and very weak band is observed at 2301 cm^{-1}. It can be assigned to the combination of the bending and the wagging mode of a water molecule. It is somewhat overlapped by the carbon dioxide band at 2352 cm^{-1}. A similar band observed at 1740 cm^{-1} is probably due to an overtone of some restricted rotation mode or a combination of such modes. In the 6 μ region, two remarkably sharp peaks of medium intensity are observed at 1626 and 1603 cm^{-1}, the former being a little weaker than the latter. They are assigned to the bending vibrations of water molecules affected by the same effects as in the cases of streching modes. They are the sharpest bending bands that have been observed in this series of studies. Hitherto only one bending band was observed or in the case of two peaks at least one was not sharp[2,4]. This is not because the present instrument is better in resolving power than that used in most of the previous measurements. An infrared study of the crystal by the latter instrument gave two equally sharp bands in the same region. The shoulder at 1492 cm^{-1} is too low to be assigned to the bending mode and therefore should be attributed to the first overtone of the wagging mode (see below). Probably the weak band at 1229 cm^{-1} has its origin in a combination or an overtone. The 755 cm^{-1} band can be

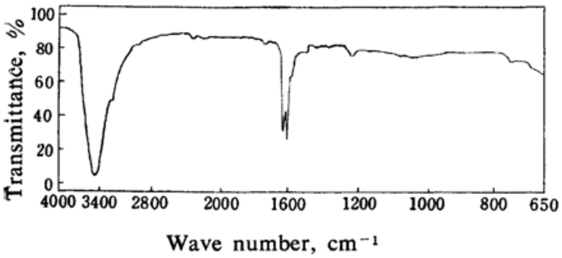

Fig. 1. Observed bands of $FeCl_2 \cdot 4H_2O$.

Table I. Observed frequencies of $FeCl_2 \cdot 4H_2O$

Wave number, cm^{-1}	Assignment
3442 v. s	$\nu(H_2O)$ stretch.
3238 m, shoulder	$\nu(H_2O)$ stretch.
2301 v. w, b	$\nu_2+\nu_R$ (H_2O) bend.+wag.
1740 v. w, b	
1626 m, v. sh	$\nu_2(H_2O)$ bend.
1603 m, v. sh	$\nu_2(H_2O)$ bend.
1492 w, shoulder	$2\nu_R(H_2O)$
1229 w, b	
755 w, b	$\nu_R(H_2O)$ wag.

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

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[1] B. R. Penford and J. A. Grigor, *Acta Cryst.*, 12, 850 (1959).

[2] I. Gamo, This Bulletin, 34, 1430 (1961).

[3] I. Gamo, ibid., 34, 760 (1961).

[4] I. Gamo, ibid., 34, 764 (1961).

[5] I. Gamo, ibid., to be published.

[6] I. Gamo, ibid., to be published.

assigned to the wagging mode of a water molecule because of its position and shape.

Table I summarizes these results.

Discussion

According to X-ray analysis[1], the crystal is monoclinic and belongs to space group $P2_1/c$ with a=5.91, b=7.17, c=8.44 Å and $\beta=112°10'$. The structure consists of discrete groups, two per unit cell. Each group contains one iron atom, four water molecules, and two chlorine atoms. It is a distorted octahedron. There are two iron-oxygen distances: 2.09 and 2.59 Å. Hereafter the corresponding oxygen atoms will be called oxygen I and II, and the corresponding water molecules will be called type I and type II, respectively. The distance 2.59 Å is considerably greater than the sum of the ionic radii of iron and oxygen (2.16 Å). Therefore oxygen II is very weakly held in the group. The analysis suggests that oxygen I forms a pair of hydrogen bonds with two chlorine atoms in the manner shown in Fig. 2, and in oxygen II two hydrogen atoms are used to form three hydrogen bonds (Fig. 3). Therefore they are likely to be more or less bifurcated.

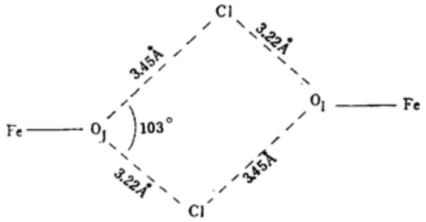

Fig. 2. Suggested hydrogen bonds for O_I. The error in each bond length is ±0.04 Å.

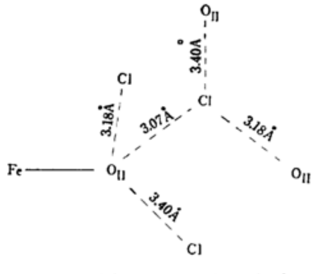

Fig. 3. Suggested hydrogen bonds for O_{II}. The error in each bond length is ±0.025 Å.

As in the previous studies[2-5], it will be assumed that the water frequencies are influenced by coördination and hydrogen bonding.

Figure 2 may suggest, at first sight, couplings between vibrations of two water molecules of type I due to hydrogen bonding. But it is unlikely because of the considerable difference between the distances of the two hydrogen bonds connected by the same chlorine atom. The situation is similar in the case of type II (Fig. 3). Therefore the observed two stretching frequencies are not due to splitting by hydrogen bonding. Further, there is a considerable difference between two O–H distances in each molecule because the corresponding hydrogen bonds are different in length. This suggests that the observed bands are not due to the symmetric and the antisymmetric vibration respectively.

The stretching frequency of water is in general likely to decrease by the effect of coördination, as suggested by comparison of the frequency of the ammonium ion with that of the ammonia molecule[7]. Hydrogen bonding of course lowers the frequency; therefore the two effects will be additive.

From this standpoint, it will first be assumed that the observed two bands at 3442 and 3238 cm^{-1} are both due to water of type II. Since the metal-to-oxygen bond is almost purely electrostatic in this case, we have only to take into account the hydrogen bonding effect. Then, from Glemser's relationship[8] between the stretching frequency and the hydrogen bond length, the corresponding O–H···Cl distances are estimated to be 3.32 and 3.11 Å, respectively. Both values seem to be compatible with the above-mentioned suggestion concerning hydrogen bonding for oxygen II, indicating the validity of the assumption. Bands due to water of type I should appear in a lower region because the coördination effect is fairly large (distance 2.09 Å). Probably they escape detection due to their weak intensity.

The two effects influence the bending frequency also. Hydrogen bonding increases the frequency as seen in the case of ice. The observed two frequencies 1626 and 1603 cm^{-1} are lower than the value 1644 cm^{-1} in ice, which is free from coördination. This suggests that coördination lowers the bending frequency. The situation may be similar to that in the case of the degenerate deformation frequency of the ammonia molecule in a metal ammine complex[9], which is somewhat lower than the corresponding value of the vapor state. Probably in the case of water in general the effect of coördination should cancel partly the effect of hydrogen bonding. This seems to be responsible for the relatively small change in the bending frequency by the two effects, as compared with that in the stretching frequency.

From the above-mentioned standpoint, the stronger coördination results in the lower

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[7] I. Gamo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 594 (1952).

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

[9] G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957).

bending frequency. Thus the observed bands at 1626 and 1603 cm^{-1} can be reasonably attributed to water molecules of type II and of type I, respectively, since the coördination is considerably weaker in the former and the hydrogen bonding effects are approximately equal in the two cases. For the present, their remarkable sharpness cannot be correlated with the crystal structure.

Experimental results[3,5] show that either of the two effects increases the wagging frequency. The band at 755 cm^{-1} is reasonably attributed to the wagging mode of water of type I, the metal-oxygen distance being 2.09 Å. The wagging band due to type II should appear in a lower region, because in this case the coördination effect is very small (distance 2.59 Å) and the hydrogen bond strength is of the same order as in ice, which is free from coördination and has a wagging band near 600 cm^{-1}.

Summary

The observed spectra of the water of crystallization were correlated with the crystal structure determined by X-rays. They were interpreted as affected by coördination and hydrogen bonding. The coördination was concluded to lower the bending frequency of water in general. Two remarkably sharp bending bands were found.

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