Infrared Spectra of Water of Crystallization in Some Inorganic Chlorides and Sulfates

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The infrared investigation of water of crystallization provides much information on its binding state in the crystal[1,2]. The frequency shifts of its characteristic bands from those of the water vapor seem to be caused mainly by the coördination of water oxygen with metal and by the hydrogen bonding with outer ions. In the present paper, the absorption bands are investigated from this standpoint.

Experimental

Preparation.—The samples were of commercial guaranteed grade. Most of them were recrystallized from water.

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[1] J. Lecomte, *J. Chim. Phys.*, **50**, C53 (1953).

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

Measurements.—The spectra were obtained by a Perkin-Elmer Infracord double beam spectrophotometer using a rock salt prism. The potassium bromide disk and the Nujol and H. C. B. mull techniques were employed.

Results and Discussion

The results are shown in Table I together with those hitherto obtained. In general our values are in good agreement with them within experimental error. As examples, absorption bands of nickel chloride hexahydrate and zinc sulfate heptahydrate are shown in Figs. 1 and 2, respectively. The error is estimated to be about 2.5 cm^{-1} in the 14 μ region, whereas it is 14 cm^{-1} and 57 cm^{-1}, respectively, in the 6 μ and the 3 μ region. As will be shown later, the 14 μ band is very sensitive to coördination and hydrogen bonding. The 6 μ and the 3 μ band are less sensitive. Furthermore the error is very small in the 14 μ band. For these two reasons attention shall be focussed on the 14 μ region in the following discussion, though they are less prominent.

The author may consider the M—OH$_2$ and the O—H···X(X=Cl or O) distance as a measure

TABLE I$^{a)}$. OBSERVED WAVE NUMBERS, cm^{-1} $^{b)}$

Substance	This research Region					Other researches	Lit.
	3 μ	5 μ	6 μ	14 μ	others		
$CaCl_2 \cdot 6H_2O$	3440 s	2170 w	1630 s	719 m		3432, 3417, 3387, 1663	1
						3440, 3298, 3250	2
$SrCl_2 \cdot 6H_2O$	3470 s	2130 w	1640 m	690 w		3438, 3418, 3383, 1663	1
						3611, 3436, 3391, 3221	3
						3437, 2915, 1629	4
$BaCl_2 \cdot 2H_2O$	3380 s	2060 w	1620 m	709 w		3455, 3324, 3237	5
						3456, 3376, 3345, 3285, 717	6
						3466, 3385, 3327, 3228	7
						3568, 3300, 3230	8
						3370, 1645, 1615, 700	9
$MgCl_2 \cdot 6H_2O$	3430 s	2250 w	1630 s	714 w		3387, 3227	5
						3497, 3352	10
$AlCl_3 \cdot 6H_2O$	3030 s, b	2420 m	1640 m	844 m	1950 w	3312, 3044	11
					1160 w, v. b	3272, 3057	10
						3410, 2915, 1625	4
$CoCl_2 \cdot 6H_2O$	3440 s		1620 m	781 w		3513, 3393, 3151	5
$NiCl_2 \cdot 6H_2O$	3370 s		1610 m	763 w		3513, 3424, 3163	5
						1481, 1089, 1018, 803	12
$Na_2SO_4 \cdot 10H_2O$	3550 s	2080 w	1650 m	719 m		3513, 3431, 3372, 3276	3
$MgSO_4 \cdot 7H_2O$	3290 s		1650 w	749 w		3300, 3214, 3078, 2125, 2044	5
						3393∼3506, 3179∼3346	10
$ZnSO_4 \cdot 7H_2O$	3230 s	2170 w	1590 w	758 w		3407, 3292∼3353	10
$Al_2(SO_4)_3 \cdot 18H_2O$	3330 s	2460 w	1640 w	704 w	2940 s	2957∼3528	10
$FeSO_4 \cdot 7H_2O$	3360 s		1630 m	712 w		3330, 1625, 611	9
$CoSO_4 \cdot 7H_2O$	3230 s		1620 w	755 w			
$NiSO_4 \cdot 7H_2O$	3280 s		1630 w	760 w		3279, 3208, 3091, 2078	5

a) Abbreviations: s, strong; m, medium; w, weak; b, broad; v. b, very broad
b) Observed frequencies attributable to SO_4^{2-} modes are omitted.
1) A. W. Marchand, *Compt. rend.*, **242**, 1791 (1956). R
2) G. P. Nayar, *Proc. Ind. Acad. Sci.*, **A8**, 419 (1938). R
3) E. Canals and Peyrot, *Compt. rend.* **207**, 224 (1938). R
4) P. J. Lucchesi and W. A. Glasson, *J. Am. Chem. Soc.*, **78**, 1347 (1956). IR
5) J. Lecomte, *J. Chim. Phys.*, **50**, C53 (1953). IR
6) A. Galy, *Compt. rend.*, **235**, 1504 (1952). R
7) O. Salvetti and D. Nobili, *Chem. Abstr.*, **51**, 12656b (1957). IR
8) C. Duval, *Anal. Chim. Acta*, **13**, 32 (1955). IR
9) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952). IR
10) O. Theimer, *Mh. Chem.*, **81**, 301 (1950). R
11) G. P. Nayar, *Proc. Ind. Acad. Sci.*, **A28**, 469 (1948). R
12) C. Duval, R. Duval and J. Lecomte, *Bull. soc. chim. France*, (V) **14**, 1048 (1947). IR

IR: observed in infrared spectra; R: observed in Raman spectra.

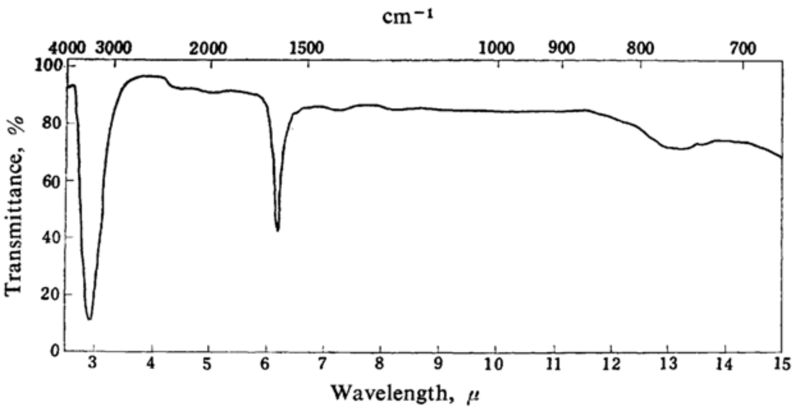

Fig. 1. Absorption bands of $NiCl_2 \cdot 6H_2O$.

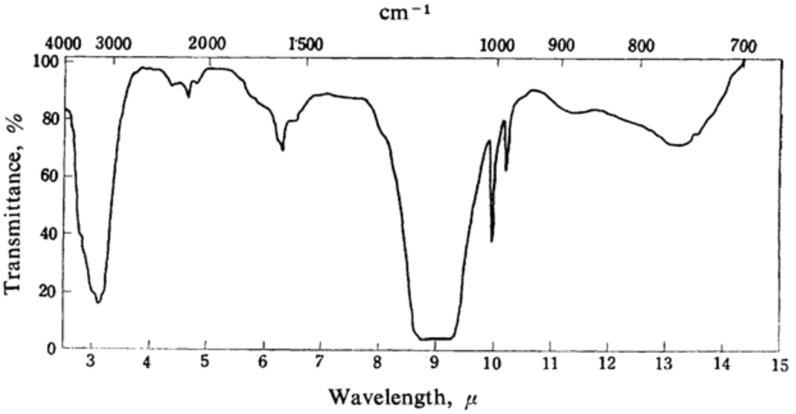

Fig. 2. Absorption bands of $ZnSO_4 \cdot 7H_2O$.

for the strength of coördination and that of hydrogen bonding respectively. The 14 μ band is attributable to either one of the wagging, twisting and rocking modes[2]. In the case of metal ammine complexes the rocking frequency of ammonia[3] seems to increase with increasing coördination and hydrogen bonding[4]. Assuming the additivity for these two effects in the case of water of crystallization also[2], and attributing tentatively our 14 μ band to the rocking mode, the wave number will decrease with increasing distance O—H···X, if the hydrogen bonding effect is predominant. Fig. 3 shows this to be inverse for strontium chloride hexahydrate and magnesium chloride hexahydrate. (The straight hydrogen bondings were assumed throughout, and in case there are more than two kinds of equivalent positions of water in one crystal, the nearest approaches were adopted for O—H···X and for M—OH_2, assuming that the observed band peaks correspond to them.). Therefore the coördination effect is larger in the magnesium-water bond than in that of the strontium-water. Correspondingly the former distance is considerably smaller than the latter.

The frequency of the rocking mode increases in the order, strontium chloride hexahydrate, cobaltous chloride hexahydrate and aluminum chloride hexahydrate. These three substances have a nearly equal O—H···Cl distance (3.10 Å), and the metal-water distance decreases in this order. Plotting the observed frequency against the metal-water distance, we obtain a straight line in Fig. 4. In the next place, magnesium chloride hexahydrate and nickel sulfate heptahydrate each occupies a position in the left side of this line corresponding to their metal-water distance. Also, the perpendicular distance between this point and the line is greater in the former than in the latter. This is understandable, since the weaker hydrogen bonding results in the lower frequency and O—H···Cl distances of the former and the latter are 3.21

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[3] S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, 23, 1367 (1955).

[4] J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, 78, 3295 (1956).

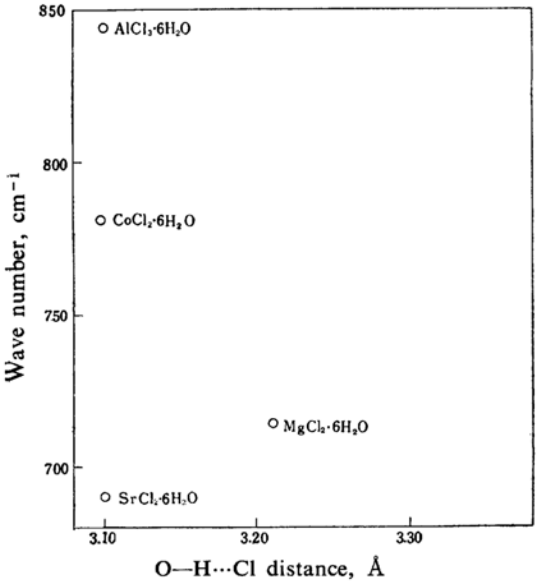

Fig. 3. Rocking frequency versus O—H···Cl distance. References for the interatomic distances :

$SrCl_2 \cdot 6H_2O$, A. T. Jensen, *Kgl. Danske. Videnskab. Selskab. Math-fys. Medd.*, **17**, No. 9 (1940).

$MgCl_2 \cdot 6H_2O$, K. R. Andress and J. Gundermann, *Z. Krist.*, **A87**, 345 (1934).

$CoCl_2 \cdot 6H_2O$, J. Mizuno, K. Ukei and T. Sugawara, *J. Phys. Soc. Japan*, **14**, 383 (1959).

$AlCl_3 \cdot 6H_2O$, K. R. Andress and C. Carpenter, *Z. Krist.*, **A87**, 446 (1934).

and 3.13 Å*, respectively. The structures of the other crystals are not yet completely determined. Among them, however, nickel chloride hexahydrate is completely isomorphous with cobaltous chloride hexahydrate⁶⁾. Therefore the periodic table suggests that nickel-water bond has nearly the same distance as cobalt-water. The position of nickel chloride hexahydrate in Fig. 4 seems to be valid on this assumption.

A similar consideration leads to the determination of other points. (Zinc sulfate heptahydrate and magnesium sulfate heptahydrate are isomorphous with nickel sulfate heptahydrate⁵⁾, and calcium chloride hexahydrate with strontium chloride hexahydrate⁷⁾. Cobaltous sulfate heptahydrate and ferrous sulfate heptahydrate are mutually isomorphous⁸⁾.)

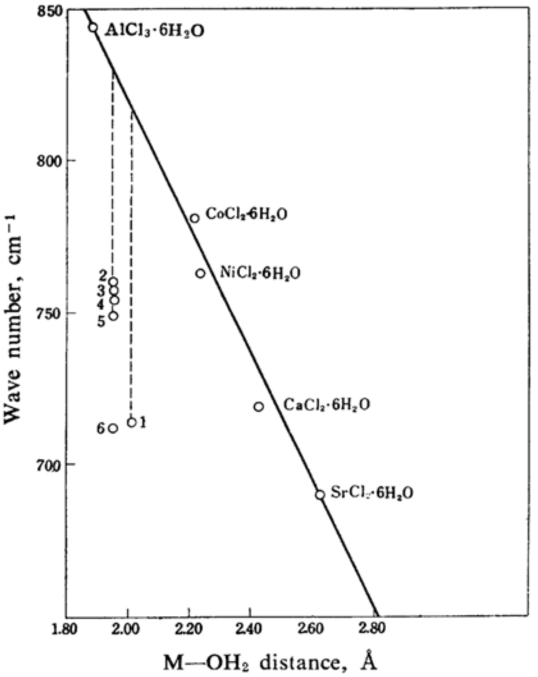

Fig. 4. Rocking frequency versus M—OH_2 distance.

1, $MgCl_2 \cdot 6H_2O$	4, $CoSO_4 \cdot 7H_2O$
2, $NiSO_4 \cdot 7H_2O$	5, $MgSO_4 \cdot 7H_2O$
3, $ZnSO_4 \cdot 7H_2O$	6, $FeSO_4 \cdot 7H_2O$

As a whole, the coördination seems to have a considerably greater effect upon this mode than the hydrogen bonding.

These relationships are less definite for the 6 μ (bending¹⁾) and the 3 μ (stretching¹⁾) mode. A more exact measurement will permit an analogous treatment.

The 5 μ band of the chlorides seems to be attributable to the combination of the bending and the rocking mode, as in the case of 2222 cm^{-1} band in ice¹,⁹⁾, although there remains a possibility of assigning it to the stretching mode strongly affected by the two effects, as Fujita et al. did for the weak band at 2270 cm^{-1} in nickel glycinate dihydrate²⁾. For the sulfates, this combination band may probably be overlapped with that of the totally symmetric and the triply degenerate stretching mode of sulfate ion.

Summary

The characteristic bands of water of crystallization in various chlorides and sulfates were determined in the rock salt region. The results were classified and explained inclusively

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* This 3.13 Å is obtained by subtracting the radius of oxygen atom 1.32 Å from the observed O—H···O distance⁵⁾, and adding the radius of chlorine atom 1.81 Å.

5) C. A. Beevers and C. M. Schwartz, *Z. Krist.*, **A91**, 157 (1935).

6) J. Mizuno, K. Ukei and T. Sugawara, *J. Phys. Soc. Japan*, **14**, 383 (1959).

7) A. T. Jensen, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*.**17**, No. 9 (1940).

8) I. Ness, *Naturwiss.*, **28**, 78 (1940).

9) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.*, **A174**, 234 (1940).

by the effects of coödination and hydrogen bonding.

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