The Vibrational Spectra of Water of Crystallization in Barium Chlorate Monohydrate, Calcium Sulfate Dihydrate and Copper Chloride Dihydrate Crystals

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(Received October 22, 1971)

Infrared spectra of water of crystallization and heavy water of crystallization were mesasured for $Ba(ClO_3)_2 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $Ba(ClO_3)_2 \cdot D_2O$, $CaSO_4 \cdot 2D_2O$, and $CuCl_2 \cdot 2D_2O$, in which the divalent metal ion lies on the bisector line of H–O–H angle or D–O–D angle. From a comparison of the spectra, assignment of the infrared absorption bands was made for the rotational and the translational vibrations of the water of crystallization.

Water of crystallization is classified into several types by the mode of bonding with surrounding atoms and ions.[1] It was reported[2-4] that the optically active lattice vibration frequencies associated with water of crystallization change sensitively with the change of its state of bonding. In the present study, barium chlorate monohydrate. $Ba(ClO_3)_2 \cdot 2H_2O$, calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$, copper chloride dihydrate, $CuCl_2 \cdot 2H_2O$ (type D in Chidambaram's classification[1]) were chosen as representatives of the crystals in which water of crystallization coordinates with a divalent metal ion on the bisector line of H–O–H angle,[5-7] and their bands due to water of crystallization were measured and assigned on the basis of the spectral change on deuteration.

Experimental

The sample were obtained by recrystallization of a-$(ClO_3)_2 \cdot H_2O$ of guaranteed grade, Kanto Chemical Co., Inc., $CaSO_4.2H_2O$ of guaranteed grade, Wako Pure Chemical Industries Ltd., and $CuCl_2 \cdot 2H_2O$ of guaranteed grade, Kanto Chemical Co., Inc. from their aqueous solutions. The deuterates of $Ba(ClO_3)_2 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$ were prepared as residues obtained by vacuum distillation of their heavy water solutions. The duterate of $CuCl_2 \cdot 2H_2O$ was obtained by exposure of $CuCl_2$ to D_2O vapor overnight in a small sealed bottle.

IR spectra in the region 4000—400 cm^{-1} were measured with the Nujol mulls of $Ba(ClO_3)_2 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$, and their deuterates, and those of $CuCl_2 \cdot 2H_2O$ and its deuterate with the Nujol mulls placed between KBr plates covered with thin polyethylene sheets to avoid reaction of the samples with KBr plates. Far IR spectra (400—30 cm^{-1}) of $CaSO_4 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$ and their deuterates were measured with their Nujol mulls placed between two polyethylene plates of 2 mm thickness, while those of $Ba(ClO_3)_2 \cdot H_2O$ and its deuterate were measured with a solid paraffin-sample mixture prepared by dispersing the sample powder into molten paraffin and solidifying the mixture cast on a polyethylene plate. The spectra are shown in Figs. 1—6.

Infrared spectra of $CaSO_4 \cdot 2H_2O$ above 300 cm^{-1} have been reported by many investigators.[8-10] The spectra of $CaSO_4 \cdot 2H_2O$ above 300 cm^{-1} in Figs. 3 and 4 are given mainly for the sake of comparison with those of its deuterate. A Hitachi EPI-G3 Infrared Spectrophotometer and a FIS-3 Far Infrared Spectrometer were used.

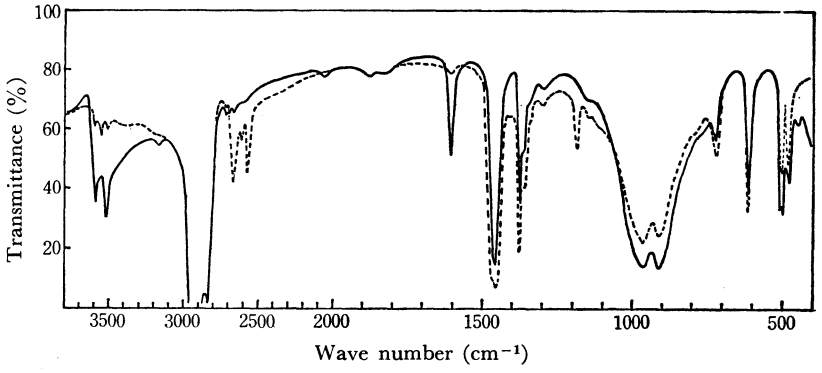

Fig. 1. Infrared spectra of barium chlorate monohydrate in Nujol mull (solid line) and its deuterate in Nujol mull (broken line).

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3) K. Fukushima and H. Kataiwa, *ibid.*, **43**, 690 (1970).
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Discussion

The relative intensities of O—H stretching and H–O–H bending bands are much weaker than those of O–D stretching and D–O–D bending bands as shown in Figs. 1, 3, and 5. This indicates that the major component of each deuterate is $Ba(ClO_3)_2 \cdot D_2O$ $CaSO_4 \cdot 2D_2O$, or $CuCl_2 \cdot 2D_2O$.

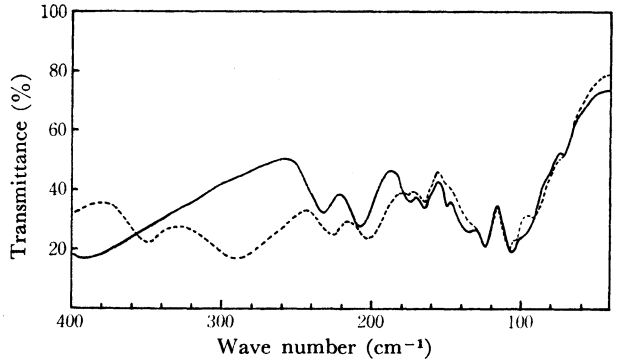

Fig. 2. Far infrared spectra of barium chlorate monohydrate dispersed into solid paraffin (solid line) and its deuterate dispersed into solid paraffin (broken line).

As shown in Fig. 6, the band of deuterated copper chloride dihydrate at 223 cm^{-1} corresponds to that of $CuCl_2 \cdot 2H_2O$ at 243 cm^{-1}. The asymmetrical band of $CuCl_2 \cdot 2H_2O$ at 298 cm^{-1} is interpreted to be composed of two overlapped bands at about 310 cm^{-1} and at 298 cm^{-1} from the fact that two bands appear at 295 cm^{-1} and 255 cm^{-1} for the deuterate and from a comparison of 310/255 value with the ν_H/ν_D values in Table 2. Similarly, the band of $CaSO_4 \cdot 2H_2O$ at 306 cm^{-1} corresponds to that of the deuterate at 259 cm^{-1}.

Comparing the spectra of the crystals with those of their deuterates, a correspondence can be set up between the observed frequencies of the former and of the latter as shown in Table 1. For $Ba(ClO_3)_2.2H_2O$,

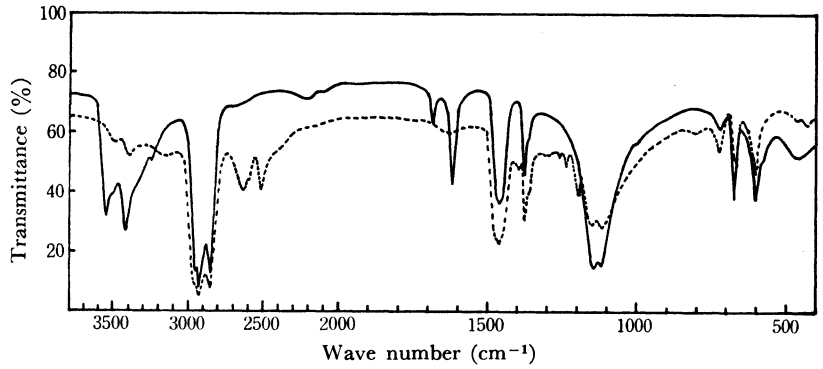

Fig. 3. Infrared spectra of calcium sulfate dihydrate in Nujol mull (solid line) and its deuterate in Nujol mull (broken line).

Table 1. Frequencies in cm^{-1} of IR bands of water of crystallization

$Ba(ClO_3)_2 \cdot H_2O$ ν_H	$Ba(ClO_3)_2 \cdot D_2O$ ν_D	ν_H/ν_D	$CaSO_4 \cdot 2H_2O$ ν_H	$CaSO_4 \cdot 2D_2O$ ν_D	ν_H/ν_D	$CuCl_2 \cdot 2H_2O$ ν_H	$CuCl_2 \cdot 2D_2O$ ν_D	ν_H/ν_D
451	350	1.29	576	432	1.33	*	360	
390	290	1.34	460	345	1.33	430	315	1.36
*	*		306	259	1.18	310	255	1.22
			271	212	1.28	243	223	1.09
233	226	1.03						
207	203	1.02						

* Not observed because of weak intensity and overlapping with other bands.

Table 2. Calculated moments of inertia of H_2O and D_2O molecules in $CaSO_4 \cdot 2H_2O$ and $CuCl_2 \cdot 2H_2O$ and their deuterates[a] (in 10^{-40} g·cm²)

	I_A	I_B	I_C	$\sqrt{I_{A,D_2O}/I_{A,H_2O}}$	$\sqrt{I_{B,D_2O}/I_{B,H_2O}}$	$\sqrt{I_{C,D_2O}/I_{C,H_2O}}$
$CaSO_4 \cdot 2H_2O$	1.067	2.089	3.157	1.34	1.41	1.39
$CaSO_4 \cdot 2D_2O$	1.919	4.174	6.093			
$CuCl_2 \cdot 2H_2O$	0.922	1.970	2.892	1.34	1.41	1.39
$CuCl_2 \cdot 2D_2O$	1.658	3.936	5.594			

a) The moments of inertia in the table were calculated using the bond length and bond angle of water of crystallization.[5,6] The same bond length and bond angle as H_2O molecule in the crystals were assumed for D_2O molecule in the deuterate crystals.

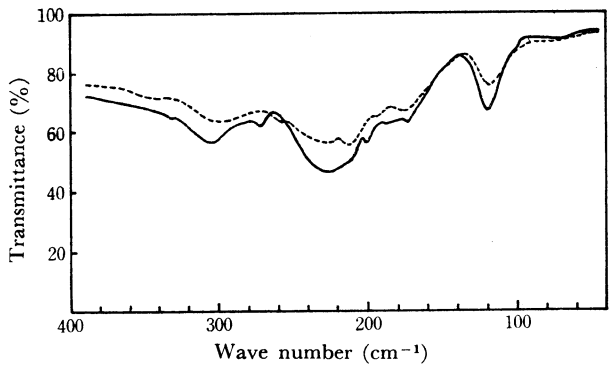

Fig. 4. Far infrared spectra of calcium sulfate dihydrate in Nujol mull (solid line) and its deuterate in Nujol mull (broken line).

Prask and Boutin observed[11] neutron scattering peak frequencies of 458 cm^{-1}, 390 cm^{-1}, 318 cm^{-1}, 238 cm^{-1}, 212 cm^{-1}, 149 cm^{-1}, 81 cm^{-1}, and 67 cm^{-1} as those due to water of crystallization. The observed IR band frquencies, which were found to shift on deuteration, correspond to the frequencies observed by Prask and Boutin except for the frequencies 318 cm^{-1}, 81 cm^{-1}, and 67 cm^{-1}. As shown in Table 1, the ν_H/ν_D values of 1.29 and 1.34 for the bands at 451 cm^{-1} and 390 cm^{-1}, respectively, lead to an assignment of the bands to the rotational vibrations of crystallization, while those of 1.03 and 1.02 for the bands at 233 cm^{-1} and 207 cm^{-1}, respectively, lead to an assignment of the bands to the translational vibartions of water of crystallization.

In the case of $CaSO_4 \cdot 2H_2O$ and $CuCl_2 \cdot 2H_2O$, the

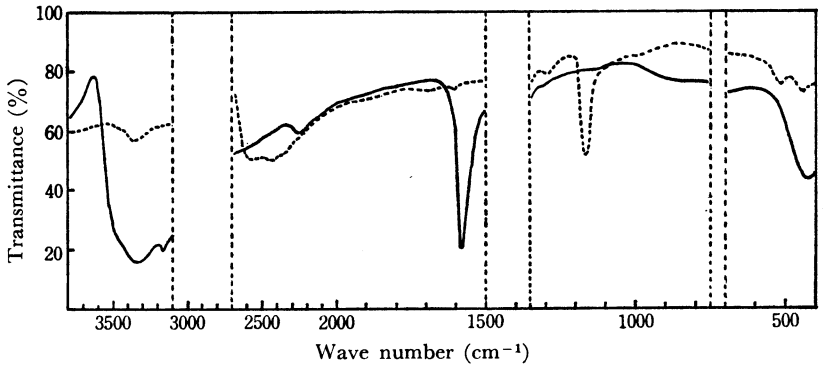

Fig. 5. Infrared spectra of copper chloride dihydrate in Nujol mull (solid line) and its deuterate in Nujol mull (broken line).

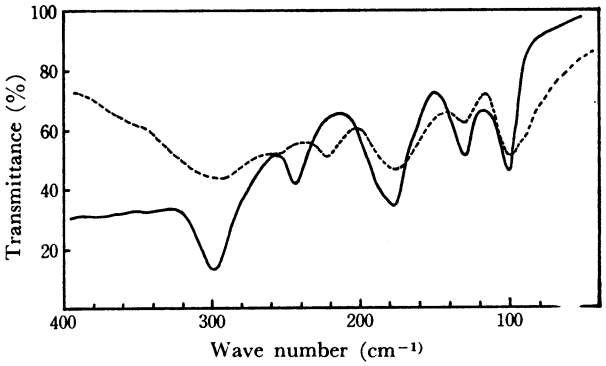

Fig. 6. Far infrared spectra of copper chloride dihydrate in Nujol mull (solid line) and its deuterate in Nujol mull (broken line).

bands at 576 cm^{-1} 460 cm^{-1}, and 430 cm^{-1}, are assigned to the rotational vibrations of water of crystallization on the basis of ν_H/ν_D values of 1.33, 1.33, and 1.36, respectively. The values are in accordance with the calculated values of $\sqrt{I_{A,D_2O}/I_{A,H_2O}}$ and $\sqrt{I_{C,D_2O}/I_{C,H_2O}}$ in Table 2. It is expected that ν_H/ν_D values of the translational vibrations of water of crystal lization in $CaSO_4 \cdot 2H_2O$ and $CuCl_2 \cdot 2H_2O$ crystals differ from those of $Ba(ClO_3)_2 \cdot H_2O$ crystal since the reduced masses of $Ca^{2+} \cdots OH_2$ and $Cu^{2+} \cdots OH_2$ systems differ from the mass of $Ba^{2+} \cdots OH_2$ system which is close to that of H_2O molecule. Thus, the bands at 271 cm^{-1} and 243 cm^{-1}, which have different ν_H/ν_D values higher than those of the bands at 233 cm^{-1} and 207 cm^{-1} of $Ba(ClO_3)_2 \cdot H_2O$ can be assigned to the translational vibrations of water of crystallization. The bands at 306 cm^{-1} and 310 cm^{-1} have very close ν_H/ν_D values. This indicates that these bands can be assigned to the rotational rather than the translational vibrations.

It has been reported that the spectra of the rotational vibrations of water of crystallization change remarkable with the change of bound state of water of crystallization.[2-4] Our results show that the spectra of water of crystallization having a coordinated divalent metal ion on the bisector line of H–O–H angle has a characteristic pattern, that is, the spectra consist of a broad band with medium intensity having two weaker bands on both sides, the characteristic spectra showing the difference corresponding to the different bound states of water of crystallization in the crystals. Interatomic distances in the crystals differ with the crystals. ($Ba(ClO_3)_2 \cdot H_2O$, $O_w \cdots Ba^{2+}$ 2.60 Å, $H_w \cdots O(ClO_3)$ 2.77 Å; $CuCl_2 \cdot 2H_2O$, $O_w \cdots Cu^{2+}$ 1.925 Å, $H_w \cdots Cl^-$ 2.258 Å; $CaSO_4 \cdot 2H_2O$, $O_w \cdots Ca^{2+}$ 2.34 Å and 2.35 Å, $H_w \cdots O(SO_4^{2-})$ 2.816 Å and 2.824 Å). These distances suggest that the water of crystallization of $CuCl_2 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$ is more strongly bound than that of $Ba(ClO_3)_2 \cdot H_2O$. This seems to cause the shift of frequencies of the weak band and the broad band having higher freuqncies than the other weak band.

11) H. J. Prask and H. Boutin, *J. Chem. Phys.*, **45**, 699 (1966).