BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 690—697 (1970)

Far-Infrared Spectra and Lattice Vibrations of Barium Chloride Dihydrate

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(Received August 25, 1969)

The far-infrared spectra of barium chloride dihydrate and its deutero analog were measured in the region of 60—4000 cm^{-1}. The assignment of the infrared bands due to crystal water and crystal heavy water was made on the basis of the band frequency shift associated with deuteration. The optically-active lattice vibrations were calculated in order to assign the far-infrared bands and elucidate the nature of the vibrations.

There are many types of crystal water molecules in crystals from the point of view of their coordination to the surrounding ions and the electron-acceptor groups. Chidambaram has classified crystal water molecules on the basis of their coordination to ions and electron-acceptor groups.$^{1)}$

In the present study, barium chloride dihydrate (b.c.d.) was adopted as a representative of B-type crystal water molecules in Chidambaram's classification, and a spectroscopic investigation in the IR spectral region and a normal coordinate treatment of the crystal as a whole were made in order to elucidate the nature of the optically-active lattice vibrations and the potential in the crystal. As measurements of the IR spectra in the region of 300—4000 cm^{-1} had already been made by several investigators for b.c.d. and its deutero analog (b.c.d.-d),$^{2-5)}$ this paper will primarily present the results of the measurement of the far IR spectra in the 60—300 cm^{-1} region of these compounds.

Experimental

The sample for the measurements was obtained by the recrystallization of a special-grade b.c.d. of the Wako Pure Chemical Co., Ltd., from an aqueous solution. The IR spectra of the sample in Nujol mull were measured with a Perkin-Elmer Model 521 spectrophotometer and a Hitachi FIS-3 far-infrared spectrometer. The deuterated sample was made by the recrystallization of b.c.d. from a heavy water solution. The IR spectra of the deuterated sample in Nujol mull were also measured. The results of the measurements are shown in Figs. 1, 2, 3, and 4. The degree of deuteration is manifested in the relative intensities of the O–H stretching bands in the region of 3100—3400 cm^{-1} and of the O–D stretching bands in the region of 2200—2700 cm^{-1} in Fig. 3.

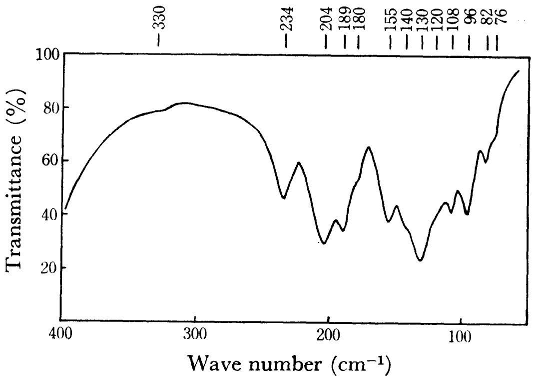

Fig. 1. Far infrared spectra of barium chloride dihydrate in Nujol mull.

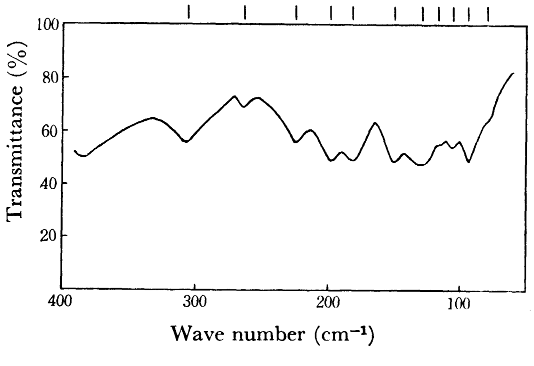

Fig. 2. Far infrared spectra of deuterated barium chloride dihydrate in Nujol mull.

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1) R. Chidambaram, A. Sequeira and S. K. Sikka, *J. Chem. Phys.*, **41**, 3616 (1964).

2) T. Noto, H. Sawada, Y. Sato, K. Kotera, M. Goto, N. Fukuba and T. Takahashi, *Tanabe Seiyaku Kenkyu Nempo*, **3**, 48 (1958).

3) O. Salvetti and D. Nobili, *Ann. Chim.* (Rome), **47**, 99 (1952).

4) F. A. Miller and C. H. Wilkins, *Anals. Chem.*, **24**, 1253 (1952).

5) J. Elsken and D. W. Robinson, *Spectrochim. Acta*, **17**, 1249 (1961).

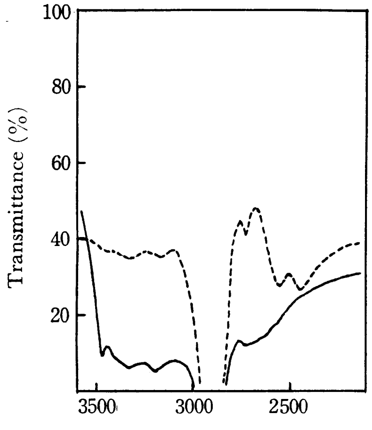

Fig. 3. Infrared spectra of barium chloride dihydrate in Nujol mull (solid line) and deuterated barium chloride dihydrate in Nujol mull (dotted line).

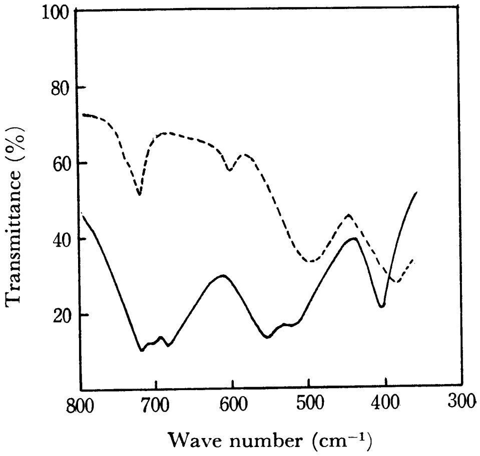

Fig. 4. Infrared spectra of barium chloride dihydrate in Nujol mull (solid line) and deuterated barium chloride dihydrate in Nujol mull (dotted line).

Assignment of IR Absorption Bands

The assignment of the IR absorption bands in the region of 800—4000 cm^{-1} have already been made by several investigators.[2-4] The shift of the IR-band frequencies on deuteration in the present study (3300 cm^{-1}, 3200 cm^{-1}, 1639 cm^{-1}, 1603 cm^{-1} →2545 cm^{-1} 2440 cm^{-1}, 1198 cm^{-1} 1173 cm^{-1}) confirms the assignment[2,3] of the bands at 3300 cm^{-1} and 3200 cm^{-1} to O–H stretching vibrations, and the bands at 1639 cm^{-1} and 1603 cm^{-1} to H_2O bending vibrations. In the region of 300—800 cm^{-1}, Elsken and Robinson found that the bands at 690 cm^{-1}, 560 cm^{-1}, and 520 cm^{-1} shift to lower frequencies on deuteration.[5] This fact was confirmed in the present study, in addition, it was found that the bands at 710 cm^{-1} and 405 cm^{-1} also shift to 500 cm^{-1} and 308 cm^{-1} respectively, as is shown in Figs. 2 and 4. The band at about 720 cm^{-1} in Fig. 4 is due to Nujol, and the weak band at 600 cm^{-1} is considered to be due to an overtone or to a combination band.

In the region of 60—400 cm^{-1}, a comparison of the spectra of b.c.d. with those of b.c.d.–d (Figs. 1 and 2) leads to the following conclusions. The band of b.c.d., which corresponds to the band at 264 cm^{-1} of b.c.d.-d, is considered to be overlapped by the band 405 cm^{-1} of b.c.d., as the frequency ratio (264/405) is close to $1/\sqrt{2}$, which is a rough measure of the frequency ratio of deuteration, while the band at 264 cm^{-1} may be due to a rotational lattice vibration of crystal heavy water. The IR absorption bands in the region of 220—800 cm^{-1}, which are concluded to be due to the rotational lattice vibrations of crystal water and crystal heavy water, are shown in Table 1. Those frequencies in the table correspond to the peak frequencies in neutron-scattering spectra:[6] 710 cm^{-1} (664 ±40 cm^{-1}), 684 cm^{-1} (664±40 cm^{-1}), 555 cm^{-1}

TABLE 1. OBSERVED FUNDAMENTAL FREQUENCIES OF INFRARED ABSORPTION BANDS (4000—400 cm^{-1}) (in cm^{-1})*

$BaCl_2 \cdot 2H_2O$	$BaCl_2 \cdot 2D_2O$
3300 (m)	2545 (m)
3200 (m)	2440 (m)
1639 (s)	1198 (m)
1603 (s)	1173 (m)
710 (s)	500 (m)
684 (s)	488 (sh)
555 (s)	380 (m)
525 (s)	
405 (m)	308 (w)
330 (sh)	264 (w)

* Intensity description:
s, strong; m, medium; w, weak; sh, shoulder

TABLE 2. RESULT OF THE FACTOR GROUP ANALYSIS $BaCl_2 \cdot 2H\ O(C^2_{5h})$ OR $BaCl_2 \cdot 2D_2O$ (C^2_{5h})

	N	T	T'	R'	n
A_g	27	0	15	6	6
A_u	27	1	14	6	6
B_g	27	0	15	6	6
B_u	27	2	13	6	6

N number or the total freedom
T number of the translation
T' number of the translational lattice vibrations
R' number of the rotational lattice vibrations
n number of intramolecular vibrations of H_2O or D_2O

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6) H. Boutin, G. J. Safford and H. R. Danner, *J. Chem. Phys.*, **40**, 2670 (1964).

(536 +32cm^{-1}), 525 cm^{-1} (480±24 cm^{-1}), 405 cm^{-1} (384±16 cm^{-1}), 234 cm^{-1} (224±16 cm^{-1}). The figures in parentheses are the peak frequencies in neutron-scattering spectra and their errors.

The number of the observed bands is less than the number derived from a factor group analysis of b.c.d.

This may be interpreted as being due to small frequency differences between A_u and B_u vibrations or to the weak intensities of some bands.

Normal Coordinate Treatment

The crystal structure of b.c.d. was investigated by Jensen,[7] by Padmanabhan *et al.*,[8] and by Padmanabhan *et al.*,[9] the investigators concluded that the space group was $P2_1/n$ for the crystal. In the present study, on the basis of the investigation by Padmanabhan *et al.*,[9] which determined the locations of the hydrogen atoms of crystal water molecules by the neutron diffraction method, the optically-active vibrations were calculated. According to the investigations, b.c.d. is monoclinic and the lattice parameters are $a=6.738$ Å, $b=10.86$ Å, $c=7.136$ Å, and $\beta=90°57'$. The Bravais lattice of the crystal is a simple monoclinic lattice (P), in which four chemical units, 4($BaCl_2 \cdot 2H_2O$), belong to each lattice point.

The optically-active lattice vibrations were calculated according to the method developed by Shimanouchi *et al.*[10]

The optically-active cartesian and internal symmetry coordinate vectors, X_{op} and R_{op}, are expressed by the cartesian and internal symmetry coordinate vectors, $(X_s)^{i,j,k}_{Bravais}$ and $(R_s)^{i,j,k}_{Bravais}$ respectively, associated with the Bravais cell (i,j,k).

$$X_{op} = \lim\, (n_1n_2n_3)^{1/2} \sum_{i=0}^{n_1} \sum_{j=0}^{n_2} \sum_{k=0}^{n_3} (X_s)^{i,j,k}_{Bravais}$$

$$n_1,\ n_2,\ n_3 \to \infty$$

$$R_{op} = \lim\, (n_1n_2n_3)^{1/2} \sum_{i=0}^{n_1} \sum_{j=0}^{n_2} \sum_{k=0}^{n_3} (R_s)^{i,j,k}_{Bravais}$$

$$n_1,\ n_2,\ n_3 \to \infty$$

TABLE 3. CARTESIAN SYMMETRY COORDINATES (COMPONENTS OF THE VECTOR, $((X_s)^{i.j.k}_{Bravais})$*

$$\begin{array}{ll}
A_g & s_{ix} = \Delta(x_i^{I}+x_i^{II}-x_i^{III}-x_i^{IV})/2 \\
 & s_{iy} = \Delta(y_i^{I}+y_i^{II}-y_i^{III}-y_i^{IV})/2 \\
 & s_{iz} = \Delta(z_i^{I}-z_i^{II}-z_i^{III}+z_i^{IV})/2 \\
A_u & s_{ix} = \Delta(x_i^{I}-x_i^{II}+x_i^{III}-x_i^{IV})/2 \\
 & s_{iy} = \Delta(y_i^{I}-y_i^{II}+y_i^{III}-y_i^{IV})/2 \\
 & s_{iz} = \Delta(z_i^{I}+z_i^{II}+z_i^{III}+z_i^{IV})/2 \\
B_g & s_{ix} = \Delta(x_i^{I}-x_i^{II}-x_i^{III}+x_i^{IV})/2 \\
 & s_{iy} = \Delta(y_i^{I}-y_i^{II}-y_i^{III}+y_i^{IV})/2 \\
 & s_{iz} = \Delta(z_i^{I}+z_i^{II}-z_i^{III}-z_i^{IV})/2 \\
B_u & s_{ix} = \Delta(x_i^{I}+x_i^{II}+x_i^{III}+x_i^{IV})/2 \\
 & s_{iy} = \Delta(y_i^{I}+y_i^{II}+y_i^{III}+y_i^{IV})/2 \\
 & s_{iz} = \Delta(z_i^{I}-z_i^{II}+z_i^{III}-z_i^{IV})/2
\end{array}$$

* $i=1$ though 9; refer to Table 6.

TABLE 4. INTERNAL SYMMETRY COORDINATES (COMPOENTS OF THE VECTOR, $(R_s)^{i.j.k}_{Bravais}$)*

$$\begin{array}{ll}
A_g & \Delta R_{si} = \Delta(R_i^{I}+R_i^{II}+R_i^{III}+R_i^{IV})/2 \\
A_u & \Delta R_{st} = \Delta(R_i^{I}-R_i^{II}-R_i^{III}+R_i^{IV})/2 \\
B_g & \Delta R_{si} = \Delta(R_i^{I}-R_i^{II}+R_i^{III}-R_i^{IV})/2 \\
B_u & \Delta R\ _i = \Delta(R_i^{I}+R_i^{II}-R_i^{III}-R_i^{IV})/2
\end{array}$$

$i=1$ through 44

$$\begin{aligned}
\Delta R^{I}_{33} &= \Delta\alpha_{6(i,j-1,k)4(i,j-1,k)7(i,j,k)} \\
\Delta R^{I}_{34} &= \Delta\alpha_{8(i,j,k)5(i,j,k)9(i,j,k)} \\
\Delta R^{I}_{35} &= \Delta\alpha_{8(i,j,k)5(i,j,k)1(i,j,k)} \\
\Delta R^{I}_{36} &= \Delta\alpha_{8(i,j,k)5(i,j,k)1(i,j-1,k)} \\
\Delta R^{I}_{37} &= \Delta\alpha_{1(i,j,k)5(i,j,k)1(i,j-1,k)} \\
\Delta R^{I}_{38} &= \Delta\alpha_{1(i,j,k)5(i,j,k)9(i,j,k)} \\
\Delta R^{I}_{39} &= \Delta\alpha_{1(i,j-1,k)5(i,j,k)9(i,j,k)} \\
\Delta R^{I}_{40} &= \Delta\alpha_{6(i,j-1,k)4(i,j-1,k)1(i,j,k)} \\
\Delta R^{I}_{41} &= \Delta\alpha_{6(i,j,k)4(i,j,k)1(i,j,k)} \\
\Delta R^{I}_{42} &= \Delta\alpha_{1(i,j,k)4(i,j-1,k)1(i,j-1,k)} \\
\Delta R^{I}_{43} &= \Delta\alpha_{1(i,j,k)4(i,j-1,k)7(i,j,k)} \\
\Delta R^{I}_{44} &= \Delta\alpha_{1(i,j-1,k)4(i,j-1,k)7(i,j,k)}
\end{aligned}$$

$$\Delta R_i^{II} = \sigma(\Delta R_i^{I}),\ \Delta R_i^{III} = i(\Delta R_i^{I}),\ \Delta R_i^{IV} = C_2(\Delta R_i^{I})$$

* ΔR_i^{I} 's for $i=1$ through 32 correspond to R_i 's in Table 5. The symbols, **σ**, **i** and **C_2**, represent symmetry operations associated with glide plane, inversion and 2-fold screw axis.

The components of the vectors, $(X_s)^{i,j,k}_{Bravais}$ and $(R_s)^{i,j,k}_{Bravais}$, are shown in Tables 3 and 4. In the tables, for example, the superscript, I, of X_i^{I} or R_i^{I} represents the chemical unit number, and the underscript, i, of X_i^{I} represents the atom number in one chemical unit. The underscript of R_i^{I} represents simply the coordinate number. In Table 4, $\Delta\alpha_{l(i,j,k)m(i,j,k)n(i,j,k)}$ represents the change in the angle formed by the l atom in the Bravais cell (i,j,k), the m atom in the Bravais cell (i,j,k), and the n atom in the Bravais cell (i,j,k). (In the case of ion, the word "atom" must be replaced by "ion".) The optically-active B matrix, B_{op}, and the optically-active F matrix, F_{op}, are defined as follows:

$$R_{op} = B_{op}X_{op}$$

$$F_{op} = F_{000} + F_{100} + \tilde{F}_{100} + F_{010} + \tilde{F}_{010} + F_{001} + \tilde{F}_{001} + \cdots$$

Here, F_{000} is related to one Bravais cell, and F_{100}, F_{010}, F_{001}, $\cdots$ are interaction matrices between the Bravais cell and the surrounding Bravais cells.

The lattice vibration frequencies were calculated

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7) A. T. Jensen, *Mat. fys. Medd.*, **22**, 22 (1945).

8) V. M. Padmanabhan, V. S. Jakkal and J. Shanker, *Indian J. Pure Appl. Phys.*, **1**, 293 (1963).

9) V. M. Padmanabhan, W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **16**, 13 (1963).

10) T. Shimanouchi, M. Tsuboi and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1963).

by solving the secular equation, $|M^{-1}F_{xs}-\lambda E|=0$. M is diagonal matrix having diagonal elements of masses of atoms or ions, and $F_{xs}=B_{op}F_{op}B_{op}$. The following potential was assumed: $V=V_{H_2O}+V_{\text{inter}}$. V_{H_2O} is the Urey-Bradley force field[11] associated with crystal water molecules, and V_{inter} represents the interaction potential between crystal water molecules and ions, between ions, and also between water molecules.

$$\begin{aligned}
2V_{\text{inter}} = & \sum f_i(\text{Cl}^-\cdots\text{H})(\Delta q_i(\text{Cl}^-\cdots\text{H}))^2 \\
& + f_i(\text{Ba}^{2+}\cdots\text{O})(\Delta q_i(\text{Ba}^{2+}\cdots\text{O}))^2 \\
& + f_i(\text{Ba}^{2+}\cdots\text{Cl}^-)(\Delta q_i(\text{Ba}^{2+}\cdots\text{Cl}^-))^2 \\
& + f_i(\text{O}\cdots\text{O})(\Delta q_i(\text{O}\cdots\text{O}))^2 \\
& + \sum f_i(\text{O}\cdots\text{Cl}^-)(\Delta q_i(\text{O}\cdots\text{Cl}^-))^2 \\
& + \sum f_i(\text{Cl}^-\cdots\text{Cl}^-)(\Delta q_i(\text{Cl}^-\cdots\text{Cl}^-))^2 \\
& + \sum H_i(\text{H–O}\cdots\text{Ba}^{2+})r^i_{\text{O-H}}r^i_{\text{Ba}^{2+}\cdots\text{O}}(\Delta\alpha^i_{\text{HO}\cdots\text{Ba}^{2+}}))^2 \\
& + \sum H_i(\text{Ba}^{2+}\cdots\text{O}\cdots\text{Ba}^{2+})r^i_{\text{Ba}^{2+}\cdots\text{O}}r^i_{\text{Ba}^{2+}\cdots\text{O}} \\
& \quad \times\ (\Delta\alpha^i_{\text{Ba}^{2+}\cdots\text{O}\cdots\text{Ba}^{2+}}))^2 \\
& + 2a(\Delta\alpha^k_{\text{H-O}\cdots\text{Ba}^{2+}})(\Delta\alpha^l_{\text{H-O}\cdots\text{Ba}^{2+}}) \\
& + 2b(\Delta\alpha^m_{\text{Ba}^{2+}\cdots\text{O-H}})(\Delta\alpha^n_{\text{Ba}^{2+}\cdots\text{O-H}})
\end{aligned}$$

In the above equation, the Δq_i's and $\Delta\alpha_i$'s represent changes in the interatomic distances and in the bond angles respectively, and the r's represent equilibrium interatomic distances. The force constants, a and b, are the interaction force constant between two $\Delta\alpha_{\text{H-O}\cdots\text{B}}{}^{2+}$'s which share a O–H bond and that between two $\Delta\alpha_{\text{Ba}^{2+}\cdots\text{O-H}}$'s which share a $\text{Ba}^{2+}\cdots\text{O}$ bond respectively. The atom-atom, atom-ion, or ion-ion interactions with interatomic distances of more than 4.0 Å were neglected. The interactions taken into account are shown for the chemical unit, I, in Table 5.

The first-trial set of force constants are shown in Table 7 as set I. $K(\text{Cl}^-\cdots\text{Cl}^-)$ and $K(\text{O}\cdots\text{O})$ were calculated by the assumed formula: $K=A\exp(-Br)$, in which r represents the interatomic distance. The parameters, A and B, were determined from two values of $\text{Cl}^-\cdots\text{Cl}^-$ force constants (0.11 mdyn/Å, 0.15 mdyn/Å), corresponding to two values of interatomic distances (3.29 Å, 3.18 Å)[12] and from seven values of O···O force constants (5.14 mdyn/Å, 3.02 mdyn/Å, 3.03 mdyn/Å, 1.74 mdyn/Å, 1.05 mdyn/Å, 0.76 mdyn/Å, and 0.555 mdyn/Å) corresponding to seven values of interatomic distances (2.09 Å, 2.20 Å, 2.21 Å, 2.27 Å, 2.36 Å, 2.47 Å, and 2.48 Å).[13] The formula for $K(\text{Cl}^-\text{–Cl}^-)$ was used for the estimation of $K(\text{O}\cdots\text{Cl}^-)$. $K(\text{H}\cdots\text{Cl}^-)$ was estimated from the $K(\text{H}\cdots\text{Cl}^-)$ values in Ref. 14. $H(\text{H–O}\cdots\text{Ba}^{2+})$ and $H(\text{Ba}^{2+}\cdots\text{O}\cdots\text{Ba}^{2+})$ were taken from Ref. 13. $K(\text{Ba}^{2+}\cdots\text{O})$ and $K(\text{Ba}^{2+}\cdots\text{Cl}^-)$ were estimated to be twice the $K(\text{Cs}^+\cdots\text{O})$ and $K(\text{K}^+\cdots\text{Cl}^-)$ values in Ref. 14. The results of the calculation showed a good agreement of the calculated frequencies with the frequencies of the far IR bands in the region of 60—250 cm^{-1}. Therefore, only the force constants, K(O–H), H(H–O–H), $H_i(\text{H–O}\cdots\text{Ba}^{2+})$'s, $H_i(\text{Ba}^{2+}\cdots\text{O}\cdots\text{Ba}^{2+})$'s, a and b were adjusted by the method of least squares[15] in order to obtain the best fit of the observed frequencies with the calculated frequencies.

TABLE 5. ATOM–ATOM AND ATOM–ION INTERACTIONS

	Interacting pair		Distance (Å)
R_1	$1(i,j,k)4(i,j-1,k)$	$\text{Ba}^{2+}\cdots\text{O}$	2.747
R_2	$1(i,j,k)5(i,j,k)$	$\text{Ba}^{2+}\cdots\text{O}$	2.865
R_3	$1(i,j,k)2(i-1,j-1,k)$	$\text{Ba}^{2+}\cdots\text{Cl}^-$	3.178
R_4	$1(i,j,k)3(i-1,j,k)$	$\text{Ba}^{2+}\cdots\text{Cl}^-$	3.168
R_5	$1(i,j,k)5(i-1,j-1,k)$	$\text{Ba}^{2+}\cdots\text{O}$	2.874
R_6	$1(i,j,k)5(i-1,j-1,k)$	$\text{Ba}^{2+}\cdots\text{O}$	2.940
R_7	$1(i,j,k)2(i-1,j-1,k)$	$\text{Ba}^{2+}\cdots\text{Cl}^-$	3.210
R_8	$1(i,j,k)3(i-1,j-1,k)$	$\text{Ba}^{2+}\cdots\text{Cl}^-$	3.199
R_9	$4(i,j,k)6(i,j,k)$	O–H	0.967
R_{10}	$4(i,j,k)7(i,j+1,k)$	O–H	1.057
R_{11}	$4(i,j,k)5(i+1,j+1,k)$	$\text{O}\cdots\text{O}$	3.236
R_{12}	$5(i,j,k)8(i,j,k)$	O–H	0.965
R_{13}	$5(i,j,k)9(i,j,k)$	O–H	0.953
R_{14}	$6(i,j,k)3(i+1,j+1,k)$	$\text{H}\cdots\text{Cl}^-$	2.242
R_{15}	$7(i,j,k)3(i,j,k)$	$\text{H}\cdots\text{Cl}^-$	2.172
R_{16}	$2(i,j,k)8(i+1,j,k)$	$\text{H}\cdots\text{Cl}^-$	2.222
R_{17}	$9(i,j,k)2(i+1,j+1,k)$	$\text{H}\cdots\text{Cl}^-$	2.631
R_{18}	$9(i,j,k)3(i+1,j+1,k)$	$\text{H}\cdots\text{Cl}^-$	2.529
R_{19}	$4(i,j,k)2(i-1,j,k)$	$\text{O}\cdots\text{Cl}^-$	3.665
R_{20}	$4(i,j,k)2(i,j,k)$	$\text{O}\cdots\text{Cl}^-$	3.508
R_{21}	$4(i,j,k)2(i-1,j,k)$	$\text{O}\cdots\text{Cl}^-$	3.936
R_{22}	$4(i,j,k)3(i-1,j,k)$	$\text{O}\cdots\text{Cl}^-$	3.302
R_{23}	$4(i,j,k)2(i+1,j+2,k)$	$\text{O}\cdots\text{Cl}^-$	3.372
R_{24}	$5(i,j,k)3(i,j,k)$	$\text{O}\cdots\text{Cl}^-$	3.365
R_{25}	$5(i,j,k)2(i-1,j-1,k)$	$\text{O}\cdots\text{Cl}^-$	3.475
R_{26}	$5(i,j,k)3(i,j+1,k)$	$\text{O}\cdots\text{Cl}^-$	3.439
R_{27}	$2(i,j,k)3(i,j,k)$	$\text{Cl}^-\cdots\text{Cl}^-$	3.922
R_{28}	$2(i,j,k)2(i+2,j+2,k)$	$\text{Cl}^-\cdots\text{Cl}^-$	3.986
R_{29}	$2(i,j,k)3(i+1,j+1,k)$	$\text{Cl}^-\cdots\text{Cl}^-$	3.905
R_{30}	$2(i,j,k)3(i,j+1,k)$	$\text{Cl}^-\cdots\text{Cl}^-$	3.901
R_{31}	$3(i,j,k)3(i+1,j+1,k)$	$\text{Cl}^-\cdots\text{Cl}^-$	4.075
R_{32}	$3(i,j,k)2(i+2,j+1,k)$	$\text{Cl}^-\cdots\text{Cl}^-$	4.072

The computations were carried out making use of the Computation Center, University of Tokyo. The programs, BGLZ and LSMB, were constructed at the Shimanouchi Lab., Department of Chemistry, Faculty of Science, University of Tokyo, while the other programs made by one of the authors, Dr. Fukushima.

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11) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

12) J. Hiraishi and T. Shimanouchi, *Spectrochim. Acta*, **22**, 1483 (1966).

13) T. Shimanouchi, *Pure Appl. Chem.*, **7**., 131 (1963).

14) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 1707 (1966).

15) D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano, *J. Chem. Phys.*, **27**, 43 (1957).

The cartesian coordinate values of the atoms and ions in the chemical unit, I, are shown in Table 6. The coordinate axes, X, Y, and Z, are chosen in such a way that the symmetry elements of the factor group, $\mathbf{C}_2$ and $\boldsymbol{\sigma}$, coincide with the Z axis and the XY plane respectively. Therefore, the cartesian coordinate values of the atoms and ions in other chemical units, II, III, and IV, can be obtained by the operation of $\boldsymbol{\sigma}$, $\mathbf{i}$ and $\mathbf{C}_2$ respectively on the coordinates of the chemical unit, I. Here, $\boldsymbol{\sigma}$, $\mathbf{i}$ and $\mathbf{C}_2$ mean (translation, $(\boldsymbol{a}+\boldsymbol{c})/2$)+(reflection with respect to the XY plane), inversion, and (translation, $\boldsymbol{b}/2$)+(rotation of 180°) respectively.

TABLE 6. CARTESIAN COORDINATES OF ATOMS AND IONS IN THE CHEMICAL UNIT, I (in Å)

No.	Atom or Ion	X	Y	Z
1	Ba^{2+}	−1.424	−0.742	−0.363
2	Cl^-(1)	4.034	3.884	−1.833
3	Cl^-(2)	2.606	0.369	−1.575
4	O (1)	0.748	4.930	−1.188
5	O (2)	−0.393	1.824	−1.113
6	H (1)	0.592	4.512	−2.046
7	H (2)	1.515	−1.497	−1.352
8	H (3)	−1.097	2.473	−1.229
9	H (4)	−0.081	1.696	−2.005

TABLE 7. FORCE CONSTANTS (in mdyn/Å)

	Set I	Set II	*
$f(Ba^{2+}\cdots O)$	0.250	0.250	
$f(Ba^{2+}\cdots Cl^-)$	0.200	0.200	
K(OH)	5.640	5.830	
$f(O\cdots O)$	0.009	0.009	
$f^1(H\cdots Cl^-)$	0.150	0.150	ΔR_{14}, ΔR_{15}, ΔR_{16}
$f^2(H\cdots Cl^-)$	0.100	0.100	ΔR_{17}, ΔR_{18}
$f(O\cdots Cl^-)$	$\ln f=7.070-2.820\,r$		
$f(Cl^-\cdots Cl^-)$	$\ln f=7.070-2.820\,r$		
H^1(H–O–H)	0.640	0.763	ΔR_{33}
H^2(H–O–H)	0.640	0.735	ΔR_{34}
$F(H\cdots H)$	−0.100	−0.100	
$H^1(H–O\cdots Ba^{2+})$	0.040	0.0405	ΔR_{35}, ΔR_{36}
$H^2(H–O\cdots Ba^{2+})$	0.040	0.0400	ΔR_{38}
$H^3(H–O\cdots Ba^{2+})$	0.040	0.0600	ΔR_{39}
$H^4(H–O\cdots Ba^{2+})$	0.040	0.0570	ΔR_{40}, ΔR_{41}
$H^5(H–O\cdots Ba^{2+})$	0.040	0.0375	ΔR_{43}, ΔR_{44}
$H(Ba^{2+}\cdots O\cdots Ba^{2+})$	0.040	0.0400	
a	0.000	0.019**	
b	0.000	−0.019**	

* coordinates representing change of bonds and bond angles for which the force constant was used.

** in mdyn·Å

Discussion

The calculated frequencies and the significant terms of the potential energy distributions for the set II force constants in Table 7 are shown in Tables 8, 9, 10, and 11, along with the observed frequencies. For the vibrations primarily associated with rotational lattice vibrations of crystal water and crystal heavy water, the following coordinates were used for the expression of the potential energy distributions.

$$\Delta R'_{s35} = (\Delta R_{s35}+\Delta R_{s36}+\Delta R_{s38}+\Delta R_{s39})/2$$
$$\Delta R'_{s36} = (\Delta R_{s35}-\Delta R_{s36}+\Delta R_{s38}-\Delta R_{s39})/2$$
$$\Delta R'_{s38} = (\Delta R_{s35}-\Delta R_{s36}-\Delta R_{s38}+\Delta R_{s39})/2$$
$$\Delta R'_{s39} = (\Delta R_{s35}+\Delta R_{s36}-\Delta R_{s38}-\Delta R_{s39})/2$$
$$\Delta R'_{s40} = (\Delta R_{s40}+\Delta R_{s41}+\Delta R_{s43}+\Delta R_{s44})/2$$
$$\Delta R'_{s41} = (\Delta R_{s40}-\Delta R_{s41}+\Delta R_{s43}-\Delta R_{s44})/2$$
$$\Delta R'_{s43} = (\Delta R_{s40}-\Delta R_{s41}-\Delta R_{s43}+\Delta R_{s44})/2$$
$$\Delta R'_{s44} = (\Delta R_{s40}+\Delta R_{s41}-\Delta R_{s43}-\Delta R_{s44})/2$$

$\Delta R'_{s36}$ and $\Delta R'_{s41}$, $\Delta R'_{s38}$ and $\Delta R'_{s43}$, and $\Delta R'_{s39}$ and $\Delta R'_{s44}$ represent H_2O (or D_2O) wagging, H_2O (or D_2O) twisting, and H_2O (or D_2O) rocking motions respectively. As is shown in the potential energy distributions, the IR bands at 710 cm^{-1}, 684 cm^{-1}, 555 cm^{-1}, and 525 cm^{-1} of $BaCl_2\cdot 2H_2O$ are due to the coupled vibrations of H_2O wagging and H_2O twisting vibrations, while the bands at 405 cm^{-1} and 330 cm^{-1} are due to H_2O rocking vibrations. The corresponding bands of the coupled D_2O wagging and D_2O twisting vibrations of $BaCl_2\cdot 2D_2O$ appear at 500 cm^{-1}, 488 cm^{-1}, and 380 cm^{-1}, while the bands due to D_2O rocking vibrations appear at 308 cm^{-1} and 264 cm^{-1}, as shown is in Tables 8 and 9. The frequency, 330 cm^{-1}, of the very weak band of $BaCl_2\cdot 2H_2O$ and the frequency shifts of the Raman lines listed in the Tables 10 and 11[16] were not used for the adjustment of the force constants.

There are two crystal water molecules per chemical unit, $BaCl_2\cdot 2H_2O$; these molecules differ in the type of bonding to the surrounding ions. In order to ascertain the bound state of the crystal water molecules, the force constants for rotation around the principal axes of the moment of inertia, k_A, k_B, and k_C, were calculated as follows. The following symbols were used:

atoms, H, O, H : i, j, k

F : Potential energy matrix having the coordinates which change by the displacement of the i, j, and k atoms as its bases

B : Matrix transforming the displacements of the i, j, and k atoms to the coordinates forming bases of F.

$\Delta\theta_m$ (m=A, B, C) : Angle of rotation around the principal axis, m.

The potential energy change, ΔV_m, due to the displacements of the i, j, and k atoms, ρ_{mn} (m=

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[16] A. Galy, *Compt. Rend.*, **235**, 1504 (1952).

A,B,C; $n=i,j,k$), is shown as:

$$2\Delta V_m = \sum_n \tilde{\rho}_{mn}\tilde{B}FB\rho_{mn} = k_m(\Delta\theta_m)^2$$

$$\rho_{An} = Y_n\Delta\theta_A e, \quad \rho_{Bn} = X_n\Delta\theta_B e \quad (n=i,j,k)$$

$$e = (r_{ji}\times r_{jk})/(|r_{ji}||r_{jk}|\sin\alpha_{ijk})$$

$$\rho_{Ci} = \sqrt{X_i^2+Y_i^2}\, e_1$$

$$e_1 = ((r_{gi}/|r_{gi}|)\cos\alpha_{igj} - (r_{gj}/|r_{gj}|))/\sin\alpha_{igj}$$

$$\rho_{Cj} = \sqrt{X_j^2+Y_j^2}\, e_2$$

$$e_2 = ((r_{gi}/|r_{gj}|)\cos\alpha_{jgk} - (r_{gk}/|r_{gk}|))/\sin\alpha_{jgk}$$

$$\rho_{Ck} = \sqrt{X_k^2+Y_k^2}\, e_3$$

$$e_3 = ((r_{gk}/|r_{gk}|)\cos\alpha_{igk} - (r_{gi}/|r_{gi}|))/\sin\alpha_{igk}$$

TABLE 8. CALCULATED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (A_u species)

$BaCl_2\cdot 2H_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
3300	3291	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0\ 47)$
	3282	$\Delta R_{s12}(0.59)$, $\Delta R_{s13}(0.39)$
3200	3211	$\Delta R_{s13}(0\ 60)$, $\Delta R_{s12}(0.39)$
	3210	$\Delta R_{s10}(0.50)$, $\Delta R_{s9}(0.48)$
1639	1638	$\Delta R_{s33}(0.97)$
1603	1607	$\Delta R_{s34}(0.96)$
710	725	$\Delta R'_{s38}(0.47)$, $\Delta R'_{s36}(0.17)$, $\Delta R_{s17}(0.19)$
684	688	$\Delta R'_{s43}(0.54)$, $\Delta R'_{s41}(0.26)$
555	557	$\Delta R'_{s36}(0.69)$, $\Delta R'_{s38}(0.41)$
525	516	$\Delta R'_{s41}(0.68)$, $\Delta R'_{s43}(0.43)$
405	398	$\Delta R'_{s39}(0.77)$, $\Delta R_{s18}(0.12)$
330	328	$\Delta R'_{s44}(0.94)$
234	235	$\Delta R_{s16}(0.15,)$, $\Delta R_{s37}(0.13)$, $\Delta R_{s6}(0.13)$
	232	$\Delta R_{s1}(0.36)$, $\Delta R_{s14}(0.18)$, $\Delta R_{s22}(0.11)$
···	224	$\Delta R_{s5}(0.33)$
204	212	$\Delta R_{s6}(0.35)$, $\Delta R_{s2}(0.33)$, $\Delta R_{s17}(0.12)$
···	168	$\Delta R_{s15}(0.31)$, $\Delta R_{s8}(0.14)$, $\Delta R_{s14}(0.14)$
155	153	$\Delta R_{s24}(0.20)$, $\Delta R_{s17}(0.15)$, $\Delta R_{s3}(0.14)$
140	137	$\Delta R_{s4}(0.45)$, $\Delta R_{s7}(0.14)$, $\Delta R_{s24}(0.10)$
130	129	$\Delta R_{s3}(0.26)$, $\Delta R_{s8}(0.12)$, $\Delta R_{s26}(0.11)$
120	124	$\Delta R_{s7}(0.55)$
108	106	$\Delta R_{s16}(0.23)$, $\Delta R_{s15}(0.13)$
96	96	$\Delta R_{s8}(0.26)$, $\Delta R_{s26}(0.18)$, $\Delta R_{s3}(0.15)$
82	78	$\Delta R_{s1}(0.24)$, $\Delta R_{s5}(0.17)$
76	70	$\Delta R_{s6}(0.26)$, $\Delta R_{s25}(0.17)$, $\Delta R_{s2}(0.11)$
···	62	$\Delta R_{s22}(0.16)$, $\Delta R_{\ 18}(0.12)$

$BaCl_2\cdot 2D_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
2545	2410	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.48)$
	2401	$\Delta R_{s12}(0.55)$, $\Delta R_{s13}(0.42)$
2440	2329	$\Delta R_{s13}(0.56)$, $\Delta R_{s12}(0.42)$
	2325	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.49)$
1198	1194	$\Delta R_{s33}(0.96)$
1173	1168	$\Delta R_{s34}(0.95)$
500	520	$\Delta R'_{s38}(0\ 39)$, $\Delta R'_{s36}(0.24)$, $\Delta R_{s17}(0.19)$
488	504	$\Delta R'_{s43}(0.40)$, $\Delta R'_{s41}(0.37)$
380	416	$\Delta R'_{s36}(0.61)$, $\Delta R'_{s38}(0.46)$
	385	$\Delta R'_{s43}(0.56)$, $\Delta R'_{s41}(0.51)$
308	310	$\Delta R'_{s39}(0.70)$, $\Delta R_{s18}(0.13)$
264	263	$\Delta R'_{s44}(0.74)$, $\Delta R_{s14}(0.13)$
226	224	$\Delta R_{s16}(0.14)$, $\Delta R_{s37}(0.13)$, $\Delta R_{s6}(0.13)$
···	216	$\Delta R_{s22}(0.15)$, $\Delta R_{s14}(0.10)$, $\Delta R_{s42}(0.10)$
···	210	$\Delta R_{s5}(0.35)$, $\Delta R_{s1}(0.11)$, $\Delta R_{s15}(0.12)$, $\Delta R_{s23}(0.11)$
198	200	$\Delta R_{s6}(0.33)$, $\Delta R_{s2}(0.30)$, $\Delta R_{s17}(0.15)$
151	157	$\Delta R_{s8}(0.22)$, $\Delta R_{s15}(0.20)$, $\Delta R_{s14}(0.11)$
	145	$\Delta R_{s3}(0.22)$, $\Delta R_{s24}(0.15)$, $\Delta R_{s17}(0.14)$
129	136	$\Delta R_{s4}(0.45)$, $\Delta R_{s7}(0.14)$
	126	$\Delta R_{s3}(0.15)$, $\Delta R_{s26}(0.15)$
118	124	$\Delta R_{s7}(0.50)$, $\Delta R_{s3}(0.13)$
106	104	$\Delta R_{s16}(0.23)$, $\Delta R_{s15}(0.11)$
94	90	$\Delta R_{s8}(0.28)$, $\Delta R_{s26}(0.19)$, $\Delta R_{s3}(0.13)$
82	77	$\Delta R_{s1}(0.24)$, $\Delta R_{s5}(0.18)$, $\Delta R_{s22}(0.10)$
···	70	$\Delta R_{s6}(0.26)$, $\Delta R_{s25}(0.17)$, $\Delta R_{s2}(0.10)$
···	59	$\Delta R_{s22}(0.15)$, $\Delta R_{s18}(0.12)$

TABLE 9. CALCULAED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTONS (B_u species)

$BaCl_2\cdot 2H_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
3300	3291	$\Delta R_{s9}(0.50)$, $\Delta R_{s10}(0.47)$
	3282	$\Delta R_{s12}(0.58)$, $\Delta R_{s13}(0.39)$
3200	3211	$\Delta R_{s13}(0.60)$, $\Delta R_{s12}(0.39)$
	3210	$\Delta R_{s10}(0.50)$, $\Delta R_{s9}(0.48)$
1639	1638	$\Delta R_{s33}(0.97)$
1603	1607	$\Delta R_{s34}(0.96)$
710	725	$\Delta R'_{s38}(0.47)$, $\Delta R'_{s36}(0.17)$, $\Delta R_{s17}(0.19)$
684	688	$\Delta R'_{s43}(0.54)$, $\Delta R'_{s41}(0.26)$
555	557	$\Delta R'_{s36}(0.69)$, $\Delta R'_{s38}(0.41)$
525	516	$\Delta R'_{s41}(0.69)$, $\Delta R'_{s43}(0.42)$
405	401	$\Delta R'_{s39}(0.75)$, $\Delta R_{s18}(0.13)$
330	334	$\Delta R'_{s44}(0.84)$
···	261	$\Delta R_{s1}(0.27)$, $\Delta R_{s5}(0.23)$
···	256	$\Delta R_{s2}(0.28)$, $\Delta R_{s6}(0.14)$, $\Delta R_{s16}(0.11)$, $\Delta R_{s37}(0.10)$
204	203	$\Delta R_{s15}(0.30)$, $\Delta R_{s22}(0.21)$, $\Delta R_{s8}(0.11)$
189	187	$\Delta R_{s6}(0.25)$, $\Delta R_{s16}(0.19)$, $\Delta R_{s24}(0.19)$
180	173	$\Delta R_{s4}(0.17)$, $\Delta R_{s23}(0.16)$, $\Delta R_{s8}(0.15)$
155	163	$\Delta R_{s7}(0.35)$, $\Delta R_{s3}(0.32)$
140	137	$\Delta R_{s23}(0.21)$, $\Delta R_{s4}(0.16)$, $\Delta R_{s20}(0.10)$,
130	130	$\Delta R_{s17}(0.46)$
108	112	$\Delta R_{s24}(0.22)$
96	90	$\Delta R_{s22}(0.16)$, $\Delta R_{s15}(0.11)$, $\Delta R_{s18}(0.11)$
82	84	$\Delta R_{s18}(0.16)$, $\Delta R_{s8}(0.16)$
···	67	$\Delta R_{s25}(0.27)$, $\Delta R_{s1}(0.12)$
···	48	$\Delta R_{s42}(0.13)$, $\Delta R_{s14}(0.13)$, $\Delta R_{s5}(0.10)$

TABLE 9. (Continued)

$BaCl_2 \cdot 2D_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
2545	2410	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.48)$
	2401	$\Delta R_{s12}(0.55)$, $\Delta R_{s13}(0.42)$
2440	2329	$\Delta R_{s13}(0.56)$, $\Delta R_{s12}(0.42)$
	2325	$\Delta R_{s10}(0.50)$, $\Delta R_{s9}(0.48)$
1198	1194	$\Delta R_{s33}(0.96)$
1173	1168	$\Delta R_{s34}(0.95)$
500	520	$\Delta R'_{s38}(0.39)$, $\Delta R'_{s36}(0.24)$, $\Delta R_{s17}(0.19)$
488	502	$\Delta R'_{s43}(0.42)$, $\Delta ER'_{s41}(\mathrm{C}.37)$
380	416	$\Delta R'_{s36}(0.61)$, $\Delta R'_{s38}(0.46)$
	385	$\Delta R'_{s43}(0.54)$, $\Delta R'_{s41}(0.51)$
308	316	$\Delta R'_{s39}(0.64)$, $\Delta R_{s18}(0.15)$
264	281	$\Delta R'_{s44}(0.46)$, $\Delta R_{s5}(0.18)$, $\Delta R_{s14}(0.16)$
…	242	$\Delta R_{s2}(0.27)$, $\Delta R_{s16}(0.16)$, $\Delta R_{s37}(0.12)$
226	229	$\Delta R_{s43}(0.24)$, $\Delta R_{s1}(0.20)$, $\Delta R_{s5}(0.11)$
198	194	$\Delta R_{s15}(0.23)$, $\Delta R_{s22}(0.17)$, $\Delta R_{s8}(0.15)$
182	174	$\Delta R_{s4}(0.13)$, $\Delta R_{s24}(0.10)$
…	165	$\Delta R_{s6}(0.18)$, $\Delta R_{s16}(0.14)$
…	161	$\Delta R_{s7}(0.29)$, $\Delta R_{s3}(0.26)$
129	130	$\Delta R_{s23}(0.20)$, $\Delta R_{s4}(0.13)$
118	121	$\Delta R_{s17}(0.44)$
106	111	$\Delta R_{s24}(0.24)$
94	89	$\Delta R_{s18}(0.16)$, $\Delta R_{s22}(0.14)$, $\Delta R_{s15}(0.12)$
82	80	$\Delta R_{s8}(0.14)$, $\Delta R_{s18}(0.10)$
…	65	$\Delta R_{s25}(0.27)$, $\Delta R_{s1}(0.13)$
…	47	$\Delta R_{s42}(0.13)$, $\Delta R_{s14}(0.12)$, $\Delta R_{s5}(0.10)$

TABLE 10. CALCULATED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (A_g species)*

$BaCl_2 \cdot 2H_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
3345	3291	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.47)$
	3282	$\Delta R_{s12}(0.59)$, $\Delta R_{s13}(0.39)$
3285	3211	$\Delta R_{s12}(0.39)$, $\Delta R_{s13}(0.60)$
	3210	$\Delta R_{s9}(0.48)$, $\Delta R_{s10}(0.50)$
…	1638	$\Delta R_{s33}(0.97)$
…	1607	$\Delta R_{s34}(0.96)$
717	725	$\Delta R'_{s38}(0.47)$, $\Delta R'_{s36}(0.17)$, $\Delta R_{s17}(0.19)$
	688	$\Delta R'_{s43}(0.54)$, $\Delta R'_{s41}(0.26)$
560	557	$\Delta R'_{s36}(0.69)$, $\Delta R'_{s38}(0.41)$
…	516	$\Delta R'_{s41}(0.68)$, $\Delta R'_{s43}(0.43)$
405	398	$\Delta R'_{s39}(0.77)$, $\Delta R_{s18}(0.12)$
…	328	$\Delta R'_{s44}(0.94)$
250	235	$\Delta R_{s1}(0.33)$, $\Delta R_{s14}(0.11)$
…	231	$\Delta R_{s5}(0.36)$, $\Delta R_{s15}(0.14)$, $\Delta R_{s23}(0.14)$, $\Delta R_{s22}(0.12)$
…	229	$\Delta R_{s16}(0.17)$, $\Delta R_{s37}(0.15)$, $\Delta R_{s2}(0.12)$
…	221	$\Delta R_{s6}(0.37)$, $\Delta R_{s2}(0.35)$, $\Delta R_{s17}(0.11)$
167	167	$\Delta R_{s4}(0.21)$, $\Delta R_{s24}(0.20)$, $\Delta R_{s8}(0.13)$
…	156	$\Delta R_{s15}(0.26)$, $\Delta R_{s7}(0.14)$, $\Delta R_{s14}(0.12)$
135	136	$\Delta R_{s3}(0.28)$, $\Delta R_{s8}(0.20)$
125	128	$\Delta R_{s7}(0.21)$, $\Delta R_{s4}(0.13)$, $\Delta R_{s25}(0.11)$
	125	$\Delta R_{s15}(0.19)$, $\Delta R_{s8}(0.17)$, $\Delta R_{s7}(0.12)$
…	111	$\Delta R_{s16}(0.21)$, $\Delta R_{s20}(0.15)$, $\Delta R_{s3}(0.13)$
98	94	$\Delta R_{s4}(0.22)$, $\Delta R_{s26}(0.15)$
77	78	$\Delta R_{s18}(0.13)$, $\Delta R_{s24}(0.11)$
…	53	$\Delta R_{s5}(0.15)$, $\Delta R_{s42}(0.12)$
46	48	$\Delta R_{s24}(0.13)$, $\Delta R_{s23}(0.13)$
33	33	$\Delta R_{s29}(0.21)$, $\Delta R_{s32}(0.13)$, $\Delta R_{s23}(0.10)$, $\Delta R_{s28}(0.10)$

$BaCl_2 \cdot 2D_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
…	2410	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.48)$
…	2401	$\Delta R_{s12}(0.55)$, $\Delta R_{s13}(0.42)$
…	2329	$\Delta R_{s13}(0.56)$, $\Delta R_{s12}(0.42)$
…	2325	$\Delta R_{s10}(0.49)$, $\Delta R_{s9}(0.49)$
…	1194	$\Delta R_{s33}(0.96)$
…	1168	$\Delta R_{s34}(0.95)$
…	520	$\Delta R'_{s38}(0.39)$, $\Delta R'_{s36}(0.24)$, $\Delta R_{s17}(0.19)$
…	504	$\Delta R'_{s43}(0.40)$, $\Delta R'_{s41}(0.37)$
…	417	$\Delta R'_{s38}(0.46)$, $\Delta R'_{s36}(0.61)$
…	386	$\Delta R'_{s43}(0.55)$, $\Delta R'_{s41}(0.50)$
…	310	$\Delta R'_{s39}(0.70)$, $\Delta R_{s18}(0.13)$
…	261	$\Delta R'_{s44}(0.77)$, $\Delta R_{s14}(0.12)$
…	222	$\Delta R_{s22}(0.14)$
…	219	$\Delta R_{s2}(0.11)$, $\Delta R_{s5}(0.11)$, $\Delta R_{s16}(0.10)$, $\Delta R_{s37}(0.12)$
…	214	$\Delta R_{s1}(0.30)$, $\Delta R_{s5}(0.25)$
…	209	$\Delta R_{s6}(0.34)$, $\Delta R_{s2}(0.31)$, $\Delta R_{s17}(0.14)$
…	162	$\Delta R_{s4}(0.24)$, $\Delta R_{s8}(0.16)$, $\Delta R_{s24}(0.16)$
…	146	$\Delta R_{s7}(0.23)$, $\Delta R_{s15}(0.16)$
…	133	$\Delta R_{s3}(0.22)$, $\Delta R_{s8}(0.20)$
…	126	$\Delta R_{s4}(0.16)$, $\Delta R_{s3}(0.10)$
…	119	$\Delta R_{s15}(0.24)$, $\Delta R_{s7}(0.21)$
…	108	$\Delta R_{s16}(0.20)$, $\Delta R_{s20}(0.13)$
…	89	$\Delta R_{s4}(0.21)$, $\Delta R_{s26}(0.18)$
…	75	$\Delta R_{s18}(0.12)$, $\Delta R_{s14}(0.11)$, $\Delta R_{s24}(0.11)$
…	53	$\Delta R_{s5}(0.15)$, $\Delta R_{s42}(0.12)$
…	48	$\Delta R_{s24}(0.14)$, $\Delta R_{s23}(0.13)$
…	33	$\Delta R_{s29}(0.21)$, $\Delta R_{s32}(0.13)$, $\Delta R_{s23}(0.10)$, $\Delta R_{s28}(0.10)$

* Observed frequencies were taken from Ref. 16.

TABLE 11. CALCULATED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (B_g species)*

$BaCl_2 \cdot 2H_2O$

ν_{obsd}	ν_{calcd}	Significant terms of P.E.D.
3345	3291	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.47)$
	3282	$\Delta R_{s12}(0.59)$, $\Delta R_{s13}(0.39)$
3285	3211	$\Delta R_{s13}(0.60)$, $\Delta R_{s12}(0.39)$
	3210	$\Delta R_{s10}(0.50)$, $\Delta R_{s9}(0.48)$
…	1638	$\Delta R_{s33}(0.97)$
…	1607	$\Delta R_{s34}(0.96)$
717	725	$\Delta R'_{s38}(0.47)$, $\Delta R'_{s36}(0.17)$, $\Delta R_{s17}(0.19)$
	688	$\Delta R'_{s43}(0.54)$, $\Delta R'_{s41}(0.26)$
560	557	$\Delta R'_{s36}(0.69)$, $\Delta R'_{s38}(0.41)$
…	516	$\Delta R'_{s41}(0.68)$, $\Delta R'_{s43}(0.43)$
405	398	$\Delta R'_{s39}(0.77)$, $\Delta R_{s18}(0.12)$
…	328	$\Delta R'_{s44}(0.94)$
250	234	$\Delta R_{s16}(0.17)$, $\Delta R_{s2}(0.17)$, $\Delta R_{s37}(0.15)$
…	227	$\Delta R_{s5}(0.19)$, $\Delta R_{s42}(0.18)$, $\Delta R_{s22}(0.14)$, $\Delta R_{s6}(0.11)$
…	224	$\Delta R_{s1}(0.39)$, $\Delta R_{s5}(0.16)$
205	212	$\Delta R_{s6}(0.34)$, $\Delta R_{s2}(0.26)$, $\Delta R_{s17}(0.11)$
…	157	$\Delta R_{s14}(0.25)$, $\Delta R_{s8}(0.23)$
144	149	$\Delta R_{s15}(0.18)$, $\Delta R_{s4}(0.18)$, $\Delta R_{s8}(0.14)$, $\Delta R_{s22}(0.11)$
	147	$\Delta R_{s15}(0.18)$, $\Delta R_{s4}(0.14)$, $\Delta R_{s3}(0.11)$
135	130	$\Delta R_{s3}(0.33)$, $\Delta R_{s7}(0.15)$
125	128	$\Delta R_{s7}(0.36)$, $\Delta R_{s16}(0.10)$, $\Delta R_{s25}(0.10)$
	123	$\Delta R_{s26}(0.17)$, $\Delta R_{s4}(0.14)$
98	103	$\Delta R_{s24}(0.18)$, $\Delta R_{s26}(0.14)$, $\Delta R_{s23}(0.13)$, $\Delta R_{s20}(0.10)$
77	75	$\Delta R_{s18}(0.16)$
…	71	$\Delta R_{s2}(0.22)$, $\Delta R_{s6}(0.15)$, $\Delta R_{s18}(0.11)$
62	68	$\Delta R_{s25}(0.15)$, $\Delta R_{s22}(0.11)$
…	55	$\Delta R_{s23}(0.13)$, $\Delta R_{s8}(0.12)$, $\Delta R_{s14}(0.10)$

$BaCl_2 \cdot 2D_2O$

ν_{obsd}	ν_{balcd}	Significant terms of P.E.D.
…	2410	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.48)$
…	2401	$\Delta R_{s12}(0.55)$, $\Delta R_{s13}(0.42)$
…	2329	$\Delta R_{s13}(0.56)$, $\Delta R_{s12}(0.42)$
…	2325	$\Delta R_{s9}(0.49)$, $\Delta R_{s10}(0.49)$
…	1194	$\Delta R_{s33}(0.95)$
…	1168	$\Delta R_{s34}(0.95)$
…	520	$\Delta R'_{s38}(0.39)$, $\Delta R'_{s36}(0.24)$, $\Delta R_{s17}(0.19)$
…	504	$\Delta R'_{s43}(0.41)$, $\Delta R'_{s41}(0.37)$
…	416	$\Delta R'_{s38}(0.46)$, $\Delta R'_{s36}(0.61)$
…	386	$\Delta R'_{s43}(0.55)$, $\Delta R'_{s41}(0.51)$
…	309	$\Delta R'_{s39}(0.72)$, $\Delta R_{s18}(0.13)$
…	260	$\Delta R'_{s44}(0.81)$, $\Delta R_{s14}(0.11)$
…	222	$\Delta R_{s2}(0.19)$, $\Delta R_{s16}(0.17)$, $\Delta R_{s37}(0.15)$, $\Delta R_{s18}(0.11)$
…	217	$\Delta R_{s42}(0.17)$, $\Delta R_{s5}(0.16)$, $\Delta R_{s22}(0.14)$, $\Delta R_{s6}(0.11)$
…	206	$\Delta R_{s1}(0.35)$, $\Delta R_{s5}(0.18)$
…	200	$\Delta R_{s6}(0.32)$, $\Delta R_{s2}(0.23)$, $\Delta R_{s17}(0.13)$
…	153	$\Delta R_{s8}(0.41)$, $\Delta R_{s14}(0.18)$, $\Delta R_{s22}(0.13)$
…	147	$\Delta R_{s4}(0.33)$, $\Delta R_{s3}(0.17)$
…	140	$\Delta R_{s15}(0.21)$, $\Delta R_{s7}(0.18)$
…	129	$\Delta R_{s3}(0.32)$, $\Delta R_{s4}(0.14)$, $\Delta R_{s7}(0.11)$
…	125	$\Delta R_{s7}(0.33)$
…	116	$\Delta R_{s16}(0.21)$, $\Delta R_{s23}(0.14)$, $\Delta R_{s15}(0.14)$
…	99	$\Delta R_{s24}(0.22)$, $\Delta R_{s26}(0.20)$
…	73	$\Delta R_{s22}(0.15)$, $\Delta R_{s1}(0.14)$, $\Delta R_{s5}(0.11)$, $\Delta R_{s4}(0.11)$
…	70	$\Delta R_{s2}(0.22)$, $\Delta R_{s18}(0.16)$, $\Delta R_{s6}(0.14)$, $\Delta R_{s25}(0.12)$
…	67	$\Delta R_{s25}(0.11)$, $\Delta R_{s22}(0.10)$
…	55	$\Delta R_{s23}(0.14)$, $\Delta R_{s8}(0.12)$

* Observed frequencies were taken from Ref. 16.

In the above formulae, g represents the center of gravity of the H_2O molecule, and X_n and Y_n ($n=i, j, k$) represent the cartesian coordinates of the i, j, and k atoms with respect to the cartesian coordinate system, X–Y–Z, having its origin at the center of gravity and the coordinate axes coinciding with the principal axes of the moment of inertia. The vector, from i to j, is expressed by r_{ij}.

Using the above formulae and the force constants in Set II in Table 7, the following values were obtained for k_A, k_B, and k_C:

$k_A = 0.138$ mdyn·Å, $k_B = 0.283$ mdyn·Å,

$k_C = 0.115$ mdyn·Å

for H_2O I $(6(i,j-1,k)4(i,j-1,k)7(i,j,k))$

$k_A = 0.138$ mdyn·Å, $k_B = 0.307$ mdyn·Å,

$k_C = 0.165$ mdyn·Å

for H_2O II $(8(i,j,k)5(i,j,k)9(i,j,k))$

From these values, it can be concluded that both the crystal water molecules, H_2O I and H_2O II, are more strongly bound around the principal axis, B, than around the principal axes, A and C.

The authors express their gratitude to Professor T. Miyazawa of Osaka University for allowing them to use FIS-3 Far Infrared Spectrometer and Perkin-Elmer 521 spectrophotometer and to Dr. T. Kitagawa and Miss M. Tsuchida of Professor Miyazawa's laboratory for their kind assistance during the measurements of IR spectra.

Their thanks are also due to Professor T. Shimanouchi of The University of Tokyo for allowing them to use the programs, BGLZ and LSMA, and to Dr. I. Suzuki of Professor Shimanouchi's laboratory for his kind instruction of use of the programs and also to Professor S. Shibata of our Department for allowing them to use IBM key punch.