

«Original»

## Study of the Librational Motion of $H_2O$ Molecules in Hydrates by Neutron Inelastic Scattering

Huhn-Jun Kim and Byung-Gook Yoon

Nuclear Physics Department  
Korea Atomic Energy Research Institute, Seoul, Korea  
(Recd. Nov. 25, 1978)

### Abstract

Neutron inelastic scattering studies on polycrystalline hydrates,  $NaBr \cdot 2H_2O$  and  $BaCl_2 \cdot 2H_2O$  have been performed to observe librational modes. Assuming all observed peaks are from the  $H_2O$  librational origin, the weighted frequency distribution functions are obtained by eliminating the contributions from the higher order processes. All of theoretical frequencies obtained using FG matrix method are due to highly mixed modes, and therefore the modes identified as significant  $H_2O$  librational modes from their large potential energy distributions are assigned to the observed peaks. The H—bond interactions are estimated using a modified Lippincott-Schroeder potential function, and the applicability of the potential function to the H-bond with highly bent or bifurcated configuration is examined on the basis of the shape of  $H_2O$  librational potential energies. Some discussions are given on the usefulness of introducing O—H...Y bending terms in addition to the H...Y stretching in similar frequency calculation in order to obtain more information on the nature of H—bond. Also the purity and symmetry properties of the  $H_2O$  librational modes are discussed using group theoretical analyses.

### 요 약

수화물 결정에 있어서  $H_2O$  분자의 외부 각 운동을 조사하고자  $NaBr \cdot 2H_2O$  및  $BaCl_2 \cdot 2H_2O$  분말시료에 대한 중성자비탄성산란실험을 수행하였으며, 관측된 진동수를 모두 이 외부 각 운동에 의한 것으로 보고 다중 및 다준위산란효과를 제거하므로써 평균진동수 분포함수를 구하였다. FG 행렬법에 의해서 계산된 진동수의 이론 값들은 모두 복합 mode에 의한 것이었으며 따라서 그 중 포텐셜·에너지분포가 큰 mode로서 관측치에 대한 assignment를 하였다. 수소결합력은 Lippincott-Schroeder 포텐셜함수에서 추산하였으며, 절선형 및 분기형수소결합에 대한 이 함수의 유용성을  $H_2O$  외부 각 운동 포텐셜함수 모양에 의거하여 검토하였다. 수소결합력의 성질에 대하여 더욱 자세한 자료를 얻기 위해서는 진동수 계산에 H...Y 신축상호작용 뿐만 아니라 O—H...Y 변각상호작용의 도입이 필요함을 논의하였고 또  $H_2O$  외부 각 운동에 있어서 mode의 순수성 및 대칭성을 군론을 적용한 방법에 의거하여 논의하였다.

### 1. Introduction

\*This work was supported in part by the International Atomic Energy Agency, Vienna, Austria.

Neutrons are excellent probes to investigate the dynamics of hydrogenous compounds because

of the large incoherent cross-section of hydrogen. Measurements of neutron incoherent scattering spectra span modes of wide range of wavelengths (wave vector  $|q| = 10^{-3}$  to  $1 \text{ \AA}^{-1}$ ), whereas the optical spectra are restricted to long wavelength modes only ( $|q| \approx 0$ ). In addition, optical spectra are governed by certain selection rules. On the other hand, the neutron spectra, being free from constraints of such selection rules, exhibit all the modes in which hydrogen can take part. In neutron spectra, as a result, one may observe broad bands or even additional peaks due to large density of states at non-zero wave vector and the spectra, in fact, are related closely to the weighted frequency distribution function of the modes.

A number of inorganic hydrates have been investigated by neutron method to study the librational modes of  $\text{H}_2\text{O}$  molecules hydrogen-bonded in various crystalline environments<sup>1,2,3,4</sup>. The studies of this area are of wide interest in view of the facts, i) no definite assignment of the observed frequencies can be made easily except for some favourable cases<sup>4,5</sup> and, ii) very little is known quantitatively about the effects of hydrogen-bond (H-bond) interaction and metal-oxygen coordination involved on the dynamics of  $\text{H}_2\text{O}$  molecules, although it has been

observed by several workers that the H-bond is dominant interaction to govern the  $\text{H}_2\text{O}$  librational motions in some hydrates.

In the present work,  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  (sodium bromide dihydrate, SBD) and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (barium chloride dihydrate, BCD) have been studied as representative examples of A- and B- type crystal water molecules in Chidambaram's classification<sup>6</sup>. The tetra-molecular unit cells of SBD and BCD belong to space group  $P2_1/c$  and  $P2_1/n$  respectively and have two types of crystallographically non-equivalent water molecules,  $\text{H}_2\text{O}(\text{I})$  and  $\text{H}_2\text{O}(\text{II})$ . In the both hydrates, lone pairs of O atoms are approximately directed to metal ions and three of the four kinds of H atoms form approximately linear  $\text{O}-\text{H} \cdots \text{Y}$  bonds, Y being the H-bond acceptors, Br or Cl ion. But in SBD H(2) is weakly bound in a highly bent H-bond whereas in BCD H(4) is loosely shared between two Cl ions forming a bifurcated H-bond. The relevant crystallographic data for these hydrates are summarized in Table 1<sup>6,7</sup>.

Measurements were carried out using an inverted filter spectrometer with BeO as filter and the experimental remarks are described in Section 3. In section 4, the weighted frequency distribution function of the  $\text{H}_2\text{O}$  librational motions

**Table 1. Geometry of Hydrogen-bonds and Oxygen Coordinates of Water Molecules in  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$**

		M—O (Å)	M—O—M (deg)	Type	O—H (Å)	H—O—H (deg)	O...Y (Å)	H...Y (Å)	O—H...Y (deg)	Y—O—Y (deg)	
Na	O(1)	H(1) ... Br	2.48	101	A	0.99	104	3.37	2.38	177	81
Na		H(2) ... Br	2.42			1.02		3.58	2.80	133	
Na	O(2)	H(3) ... Br	2.37	96	A	0.98	105	3.37	2.41	169	104
Na		H(4) ... Br	2.41			1.01		3.32	2.32	167	
<hr/>											
Ba	O(1)	H(1) ... Cl(2)	2.84	123	B	0.97	106	3.18	2.24	165	111
Ba		H(2) ... Cl(2)	2.85			0.97		3.13	2.17	167	
Ba	O(2)	H(3) ... Cl(1)	2.87	117	B	0.97	103	3.18	2.22	171	125
Ba		H(4) ... Cl(2)	2.89			0.95		3.30	2.66	125	
								3.24	2.49	135	

are obtained from the observed spectra by eliminating contributions due to the higher order processes. The assignments of the observed peaks have been made by comparing with the theoretical frequencies calculated from FG matrix method in Section 5. For the estimation of the H-bond interactions between  $\text{H}_2\text{O}$  molecules and H-bond acceptors, we have resorted to a modified Lippincott-Schroeder potential function (LSPF). In order to look into the applicability of LSFF to the H-bond with highly bent or bifurcated configuration in some direct way, we have discussed the potential energies of  $\text{H}_2\text{O}$  librational modes on the basis of a simple model. Group theoretical analyses which provide informations on the purity and symmetry properties of the modes are also discussed here.

## 2. Experimental

The experiments were carried out at TRIGA Mark III reactor in Korea Atomic Energy Research Institute using an inverted filter spectrometer similar to those described in detail elsewhere<sup>9,10</sup>. Fig. 1 shows a schematic drawing of the experimental arrangement. Monoenergetic

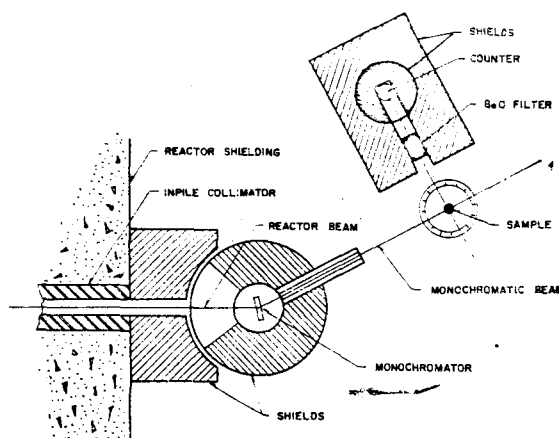


Fig. 1. Schematic view of the experimental arrangement (inverted filter spectrometer).

neutrons were selected from the pile spectrum by Bragg reflection using  $\text{Cu}(111)$  planes. These are then allowed to strike the sample and neutrons scattered therefrom were detected by a  $\text{BF}_3$  counter placed vertically behind a 10 cm long polycrystalline  $\text{BeO}$  filter. The cross section of  $\text{BeO}$  is such that only those neutrons with energy less than 3.7 meV are transmitted and therefore the filter-detector combination acts an energy analyzer of constant window.

To observe the inelastic spectrum, the incident neutron energy was varied by changing the

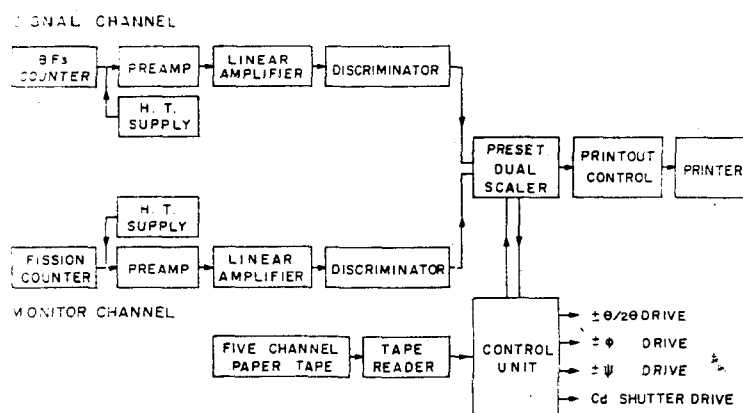


Fig. 2. Block diagram of counting and control electronics of the inverted filter spectrometer.

Bragg angle of the monochromator and the scattered neutron intensity at each position of the monochromator was recorded for a preset number of monitor counts of a thin fission counter placed on the incident beam. Discrete peaks associated with the various modes of motions in the system would be observed in the inelastic spectrum when the condition

$$E_0 - \langle E_A \rangle \equiv \varepsilon = h\nu_i \quad (1)$$

is satisfied; i. e. when the neutron after exciting  $i$ -th mode has just enough energy to get through the analyzer. Here  $E_0$  is the incident neutron energy,  $\varepsilon$  is the energy transfer in the scattering process,  $\nu_i$  is the frequency of the mode to which the neutron loses energy, and  $\langle E_A \rangle = 2.5$  meV is the average energy of BeO analyzer window.

The operation of the spectrometer is automatic. For a variety of experiments including the constant  $Q$  and  $E$  scans, the monochromator angle ( $\theta_M$ ), scattering angle ( $\phi$ ) and sample orientation ( $\psi$ ) can be changed nonlinearly by means of five channel paper tape on which instructions are perforated. For the present work with polycrystalline samples,  $\phi$  was kept at  $90^\circ$  for all measurements and  $\theta_M$  was changed in steps of  $0.1^\circ$ .

The samples were obtained by cooling aqueous solution in a sealed atmosphere. Similarly, deuterated sample of SBD, was prepared by dissolving the anhydrate in  $D_2O$  (99.89 mole %) and cooling. As the compounds become readily dehydrated in vacuum, the powder forms of samples were packed in the air-tight aluminium container of 50 mm diameter and 0.75 mm wall thickness, and held in half-angle transmission geometry in the liquid nitrogen cryostat which has provision to vary the sample temperature by adjusting the electric current through a heater fastened around the sample container. The sample temperature was continuously monitored by two thermocouples at-

ched to the top and bottom of the sample container and the temperature fluctuation was less than  $\pm 4^\circ K$  throughout the experiment. The neutron transmission through the samples were about 70%.

### 3. Observation

Measurements were performed mainly over the  $H_2O$  librational frequency region and the results are summarized in Figs. 3 and 4 after correcting for the background. The error bars are based on counting statistics alone. In Fig. 3 all spectra are shown on the same intensity scale by normalizing measurements for the same monitor counts.

The SBD spectrum at  $100^\circ K$  shows three distinct peaks at 403, 562,  $650\text{ cm}^{-1}$  and an indistinct peak around  $474\text{ cm}^{-1}$  as shoulder.

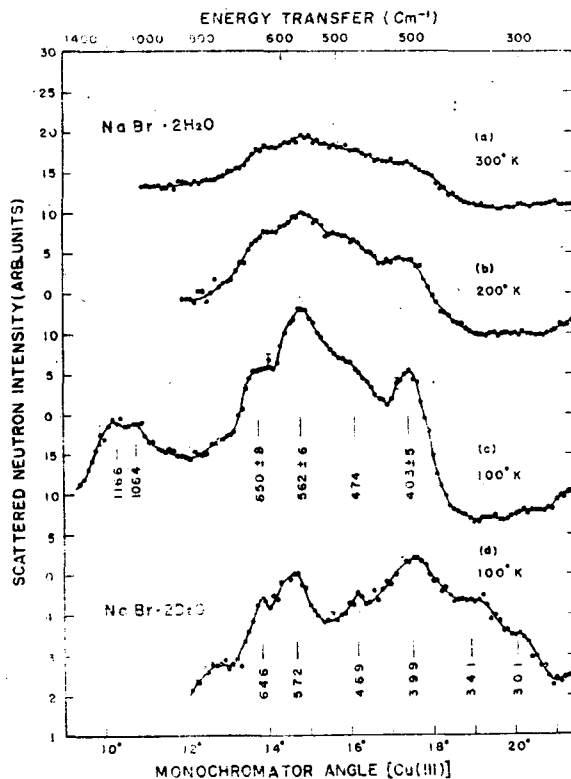


Fig. 3. The neutron inelastic scattering spectra of  $NaBr \cdot 2H_2O$  and  $NaBr \cdot 2D_2O$ .

Two peaks at 1,064 and 1,166  $\text{cm}^{-1}$  are considered mainly due to the multi-phonon process as discussed in detail in Section 4. With increasing temperature, rapid decrease of peak intensities are seen and RT data gives only a broad distribution barely showing the evidence of three peaks. As seen more clearly from 210°K spectrum, however, there is no remarkable change in the general feature of distribution and the position of peaks.

The NMR study of SBD showed a large drop of the second moment above 174°K and for the partial explanation of this Sarma<sup>11)</sup> suggested a model in which  $\text{H}_2\text{O}(\text{I})$  molecules execute free rotation about the line joining the linear  $\text{O}-\text{H}\cdots\text{Br}$  bond above the temperature. If  $\text{H}_2\text{O}$  molecules execute rotation with frequency comparable with those of the librational modes, one can expect that the peaks due to the librational modes will be all washed out in neutron inelastic spectrum<sup>12,13)</sup>. Persistence of similar feature of spectrum up to RT, as seen in Fig. 3, therefore suggests that (i)  $\text{H}_2\text{O}$  molecules are executing reorientational motions with frequencies much lower than librational frequencies, and (ii) SBD does not undergo any phase transition which could bring significant change of crystal structure and accordingly dynamics of  $\text{H}_2\text{O}$  molecules up to RT. The spectrum of the deuterate was obtained only for SBD to confirm the librational nature of peaks observed in the hydrate by isotopic shift. As compared in the same figure, all peaks are found to shift to lower frequencies with isotopic ratios of about  $\sqrt{2}$ . The intensities of two peaks which persist around 572 and 646  $\text{cm}^{-1}$  could be due to about 2% of hydrate impurity.

For BCD the neutron time-of-flight spectrum at RT was reported by Boutin<sup>1)</sup>. In the present work we have taken spectrum only at 100°K and four peaks at 423, 531, 601 and 717  $\text{cm}^{-1}$  and an indistinct peak around 568  $\text{cm}^{-1}$  are

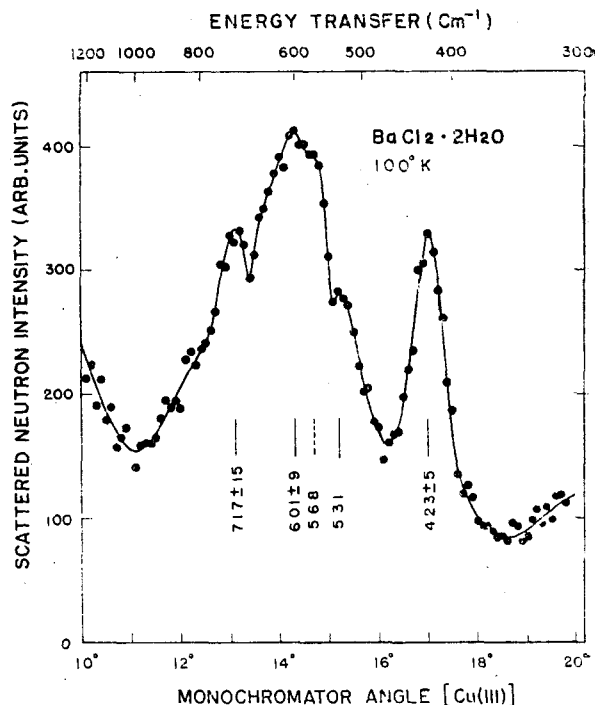


Fig. 4. The neutron inelastic scattering spectrum of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

observed as seen in Fig. 4. The peaks observed in the present experiment are summarized in Table 10 along with earlier results obtained by neutron<sup>1)</sup> and optical methods<sup>14,15)</sup>.

#### 4. Weighted frequency distribution function of $\text{H}_2\text{O}$ librational mode

The scattering of slow neutrons from hydrates are predominantly from proton and incoherent. Further, at low temperatures the inelastic scattering is almost entirely by the excitation or de-excitation of the external modes since the internal modes, which have large energies, can not be excited either thermally or by the neutrons. It is observed by several authors<sup>3,16)</sup> that the frequency distribution function can be extracted from the incoherent scattering data even for molecular solids in favourable cases. The main requirement for this is that the translational and

librational parts of the spectrum should be well separated, and we assumed this is the case with the present samples in view of the fact that for a large number of crystal hydrates the  $H_2O$  librational modes fall in  $300\sim 900\text{ cm}^{-1}$  range, while the translatory modes lie around or below  $300\text{ cm}^{-1}$  <sup>1,17</sup>.

The measured neutron spectrum includes invariably contributions from two kinds of higher order processes involving multiple number of phonon\*. One is referred as 'multi-phonon' process and the other as 'multipul-scattering' process.

In multi-phonon process, we are concerned with the neutron exchanging energy (gain or loss) with a single nucleus in the sample system due to zero phonon, one phonon, two phonon etc. processes. Multiple scattering refers to contributions arising from more than one scattering process in the sample system, that is at more than one scattering nucleus, in each scattering of which, multi-phonon processes are allowed. Clearly the multiple scattering process depend on the number of nuclei present in the sample and therefore on the size and shape of the sample,

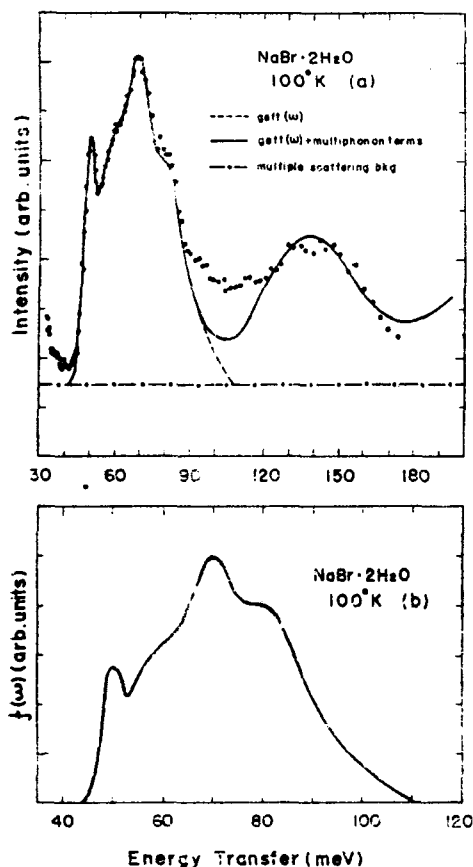


Fig. 5. (a) Spectrum from NaBr·2H<sub>2</sub>O is compared with the calculated cross-section, i.e., the effective librational spectrum,  $g_{eff}(\omega)$ , plus the contribution due to multi-phonon processes (see text). (b) Weighted frequency distribution function of H<sub>2</sub>O librational modes,  $f(\omega)$ , calculated from  $g_{eff}(\omega)$ .

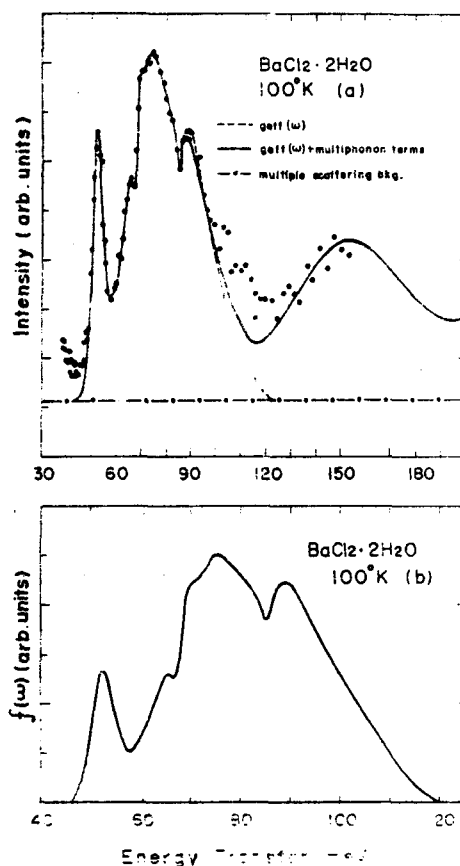


Fig. 6. (a) Spectrum from BaCl<sub>2</sub>·2H<sub>2</sub>O is compared with the calculated cross-section, i.e., the effective librational spectrum,  $g_{eff}(\omega)$ , plus the contribution due to multi-phonon processes (see text). (b) Weighted frequency distribution function of H<sub>2</sub>O librational modes,  $f(\omega)$ , calculated from  $g_{eff}(\omega)$ .

and many works were reported for the calculation of this contribution. With the inverted filter spectrometer, however, one has to consider the additional contribution arising from those neutrons which have energies greater than the filter cut-off energy but reach the detector after undergoing multiple or small angle scattering in the filter<sup>18)</sup>. Because of the complication involved in the detailed theoretical shape analysis of this contribution, we simply assumed that those contributions due to multiple and small angle scattering in the filter and multiple scattering in the sample are fairly smooth over the entire energy transfer range for incoherent scattering, and the background which appeared over and above the room background as shown by broken lines in Figs. 5-a and 6-a were subtracted before applying the multi-phonon corrections.

To evaluate corrections due to multi-phonon processes, we have adopted the scheme of Sjolander<sup>19)</sup> as this is easily amenable to numerical computation. We briefly discuss the relevant equations;

The total incoherent scattering cross section is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = \sum_j \frac{\sigma_{inc,j}}{4\pi} \frac{k}{k_0} e^{-2W_j} \times \sum_{n=0}^{\infty} \frac{(2W_j)^n}{n!} G_n(\omega - \omega_0) \quad (2)$$

where  $\hbar\omega$  and  $\hbar\omega_0$  are energies of scattered and incident neutrons,

$\sigma_{inc,j}$ ; the total incoherent scattering cross section of the  $j$ -th nucleus,

$k$  and  $k_0$ ; the scattered and incident neutron wave vector,

$e^{-2W_j}$ ; the Debye-Waller factor of the  $j$ -th nucleus,

$G_n(\omega - \omega_0)$  is defined by recursion relations;

\*In this discussion we use the term 'phonon' to denote both the translational and rotational excitation energy quanta.

$$G_0(\omega) = \delta(\omega)$$

$$G_1(\omega) = g(\omega) = g_{eff}(\omega)$$

$$G_2(\omega) = \int_{-\infty}^{\infty} g(\omega - \omega') G_1(\omega') d\omega' \quad (3)$$

.....

$$G_n(\omega) = \int_{-\infty}^{\infty} g(\omega - \omega') G_{n-1}(\omega') d\omega'$$

Here,  $g(\omega)$  is related to the effective frequency distribution,  $f(\omega)$ , as follows;

$$g(\omega) = \frac{f(\omega)}{2W} \frac{1}{2} \left\{ \coth\left(\frac{\hbar\omega}{2k_B T}\right) - 1, \right. \\ \left. \begin{array}{ll} |\omega| \leq \omega_m \\ = 0, & |\omega| > \omega_m \end{array} \right. \quad (4)$$

$$\text{with } f(\omega) = f_T(\omega) + \frac{3M}{2M_R} f_R(\omega). \quad (5)$$

Here,  $f_T(\omega)$  and  $f_R(\omega)$  are the respective translational and rotational frequency distribution function,  $M$  and  $M_R$  are the respective molecular and effective rotational mass and  $\omega_m$  the maximum vibrating frequency.

We observe two facts; (i) that the recursion relation helps in easy evaluation of contributions due to higher order processes, given  $g(\omega)$  and (ii)  $g(\omega)$  is directly proportional to once corrected  $d^2\sigma/d\Omega d\omega$  if higher order contribution is estimated intuitively. One can then evaluate the total  $G(\omega)$  starting from this  $g(\omega)$  and compare with experimental  $d^2\sigma/d\Omega d\omega$ . We have adopted this approach in the data analysis, neglecting the translational part in Eq. (5). However, the error involved in this simplification will not be considerable in view of the fact that the scattering due to the librational part is relatively enhanced by a large mass factor ( $3M/2M_R$ ) compared to the translational part.

The normalization of the related functions are as follows;

$$\int_{-\infty}^{\infty} g(\omega) d\omega = 1 \text{ and } \int_{-\infty}^{\infty} G_n(\omega) d\omega = 1,$$

$$\text{whereas } \int_0^{\infty} f(\omega) d\omega = 1.$$

$g(\omega)$  is not even function and  $g(-\omega)$  can be obtained from the relation  $f(\omega) = f(-\omega)$  and

Eq. (4).  $2W$  is calculated as function of  $Q$  using  $f(\omega)$  and the relation

$$2W = \frac{2m_H}{\hbar Q^2} \int_0^\infty \coth(\beta\omega) \frac{f(\omega)}{\omega} d\omega, \quad (6)$$

with  $\beta = \frac{\hbar}{2k_B T}$ ,  $k_B$  being the boltzmann constant,  $T$  the temperature of scattering sample,  $m_H$  the mass of hydrogen atom.

To start with,  $g_{eff}(\omega)$  was isolated intuitively from the spectrum, and this input spectrum was adjusted by trial and error so that the resulting total scattering cross section which contains up to 6th higher order contributions could represent the observed spectrum reasonably, as shown the results in Figs. 5-a and 6-a with individual spectrum  $g_{eff}(\omega)$  by dotted line and the total scattering cross section by full line. Although there are discrepancies between calculations and experimental data around 100~120 meV which may be due to lack of our knowledge of  $g_{eff}(\omega)$  below 40 meV, we believe that the agreement between calculated and measured distribution is reasonable. The effective frequency distribution extracted in the manner described above is shown in Figs. 5-b and 6-b. It may be remarked that these distributions are only "weighted" frequency distributions and related the frequency density function of the hydrate through polarization vectors associated with the various modes of librations. Out of all salient peaks of the frequency distribution functions only 423  $\text{cm}^{-1}$  peak in BCD can be isolated approximately and the width (HWHM)  $\sim 40 \text{ cm}^{-1}$  is found roughly to agree with instrumental resolution at the corresponding energy transfer, suggesting fairly small dispersion of the associated librational branch.

In the region of the librational frequencies the number of the second order neutrons in the incident beam was invariably less than 10% and no correction has been made for this contamination.

## 5. Theoretical analysis and discussion

To understand the dynamical nature of the external molecular motion of  $\text{H}_2\text{O}$  molecules in hydrates, one has to carry out theoretical analysis of  $g_{eff}(\omega)$ . There are two aspects to this problem: (i) to associate the effective frequency spectrum with various kinds of hydrogenic motions and (ii) to calculate the frequency distribution given a certain force field in the solid and compare with  $g_{eff}(\omega)$ . The first aspect can be studied by group-theoretical techniques and the latter by numerical methods. Calculation of theoretical  $g_{eff}(\omega)$  is quite a labourous problem. A better alternative is to calculate the eigenvalues and eigenvectors of the dynamical matrix starting from the force field if this is known and then make comparisons with frequencies and intensities of observed modes. Two approaches are possible using either the Born von Karman theory or Wilson FG matrix method. In both approaches there are two major difficulties namely (i) there is very little theoretical basis for choosing suitable force fields and (ii) there is no known general force field applicable to all cases even a priori.

It has been observed for some hydrates<sup>3,14)</sup> that the  $\text{H}_2\text{O}$  librational motions are primarily sensitive to H-bond interactions. In order to examine the nature of H-bond on the librational motion more conveniently, we have preferred to calculate the frequencies associated with the long-wave modes only using FG method and make a comparison with the observed frequencies. This approach is supported partly by the fact that the dispersion of the librational branches of hydrates is generally not large due to weak  $\text{H}_2\text{O}-\text{H}_2\text{O}$  interactions.

For the H-bond interaction between  $\text{H}_2\text{O}$  molecule and the H-bond acceptors, we have adopted the Lippincott-Schroeder potential func-



tion (LSPF)<sup>20</sup> based on the semi-empirical model, and modified for non-linear configuration by Chidambaram and Sikka<sup>21</sup>. If H-bonds of  $\text{H}_2\text{O}$  molecules are of the longer and weaker type, as are the cases with the present samples, and if the librational amplitudes are not large, the H-bond P.E. in  $\text{O}\cdots\text{H}\cdots\text{Y}$  bond can be approximated by  $\text{H}\cdots\text{Y}$  interaction alone;

$$U(\text{H}\cdots\text{Y}) = -CD \exp[-n(r-r_0)^2/Cr]. \quad (7)$$

Here  $D$  is the dissociation energy of the  $\text{H}-\text{Y}$  bond and  $r_0$  is its equilibrium separation.  $r$  is interatomic distance of the  $\text{H}\cdots\text{Y}$  bond and  $C$  is a factor which takes into account the weakness of the  $\text{H}\cdots\text{Y}$  bond at the same separation and the quantity  $n$  is related to the stretching force constant  $k_0$  of the  $\text{H}-\text{Y}$  by the relation  $n = k_0 r_0 / D$ .

Before going into the theoretical analysis mentioned above, we have calculated the potential energies of the  $\text{H}_2\text{O}$  librational modes and their frequencies derived therefrom on the basis of a simple model with a view to examining the nature of LSPF on the H-bond with highly bent or bifurcated configuration in some direct way.

### (i) Simple model

In this approach, the  $\text{H}_2\text{O}$  molecule bounded into the crystal is assumed to be rigid and to have three independent librational modes about its three principal axes at its center of mass, viz, the wagging mode (about the A axis), the twisting mode (about the two-fold B axis) and the rocking mode (about the C axis perpendicular to the molecular plane). The potential for the librational motion of the  $\text{H}_2\text{O}$  molecule in each of the three modes has been calculated as a function of its amplitude by assuming that all the rest of atoms in the crystal to be fixed at their equilibrium positions.

The contribution from the H-bond between

$\text{H}_2\text{O}$  molecule and H-bond acceptor atoms has been obtained from Eq. (7) using the constants as given in Table 2. The quantity  $n$  has been obtained from the respective stretching force constant of  $\text{HBr}$  and  $\text{HCl}$ , 4.12 md/Å and 5.16 md/Å. A constant  $c=0.715$  was found by Lippincott and Schroeder to be suitable for all type of linear H-bonds and was also found to be satisfactory for non-linear  $\text{O}\cdots\text{H}\cdots\text{O}$  bonds by Chidambaram et al<sup>21</sup>. Hence this value is retained in the present calculation. The total energy of the bifurcated H-bond has been estimated by adding the constituent  $\text{H}\cdots\text{Y}_1$  and  $\text{H}\cdots\text{Y}_2$  interactions.

The contribution due to the electrostatic interaction of the  $\text{H}_2\text{O}$  molecule with the rest of the structure, excluding the H-bond acceptors,

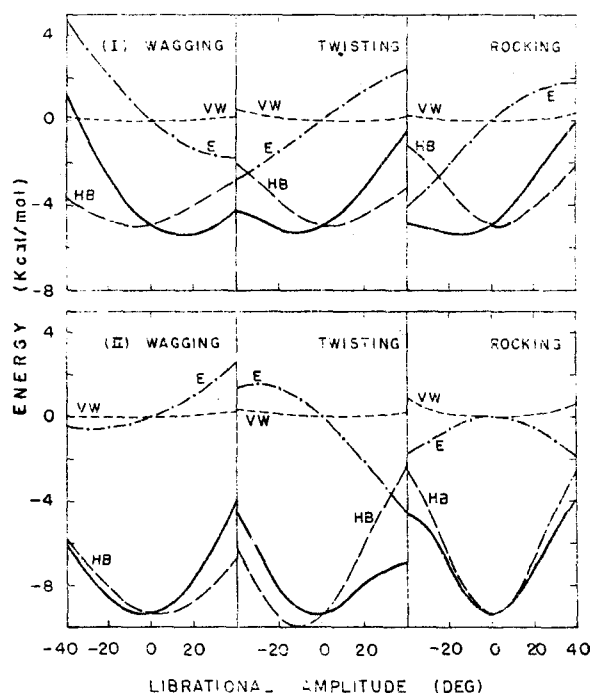


Fig. 7. Potential energy as a function of the librational amplitude of  $\text{H}_2\text{O}(\text{I})$  and  $\text{H}_2\text{O}(\text{II})$  in  $\text{NaBr}\cdot 2\text{H}_2\text{O}$ . E, electrostatic energy, VW, Van der Waals energy, HB, hydrogen-bond energy. The full line indicates the total energy.

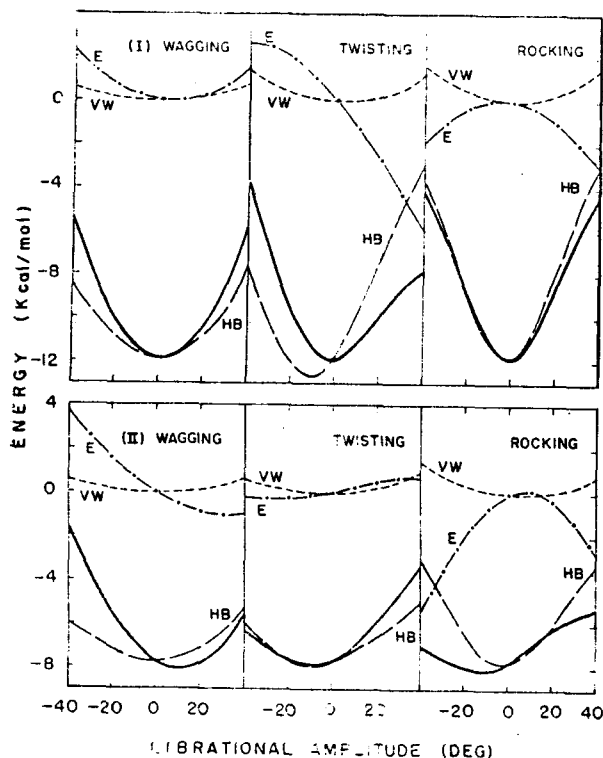


Fig. 8. Potential energy as a function of the librational amplitude of  $\text{H}_2\text{O(I)}$  and  $\text{H}_2\text{O(II)}$  in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . E, electrostatic energy, VW, Van der Waals energy, HB, hydrogen-bond energy. The full lines indicate the total energy.

has been estimated by assigning formal point charges to various atoms. The interactions with interatomic distances of more than  $24\text{\AA}$  has been neglected. For the  $\text{H}_2\text{O}$  molecule the effective charges on atoms has been deduced from the dipole moment of water,  $1.84(D)$ . A value of unity has been used for the dielectric constant. Similarly, the Van der Waals energy has been estimated from Kitaigorodskii's formula<sup>22)</sup> using the Van der Waals radii listed in Table 2.

The resulting individual and total potential energy curves of three librational modes for non-equivalent  $\text{H}_2\text{O}$  molecule are given in Figs. 7 and 8. For the  $\text{H}_2\text{O}$  molecule participated partly in highly bent or bifurcated configuration, much

Table 2. Constants used for the calculation of H-bond and non-bond potentials in the simple model.

	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
Force Constant and Parameters involved in $U(\text{H} \cdots \text{Y})$	$K(\text{H}-\text{Br}) = 4.12 \text{md/\AA}$ $r_0 = 1.41 \text{\AA}$ $D = 86.7 \text{ Kcal/mole}$ $n = 9.64 \text{\AA}^{-1}$ $C = 0.715$	$K(\text{H}-\text{Cl}) = 5.16 \text{md/\AA}$ $r_0 = 1.27 \text{\AA}$ $D = 103.2 \text{ Kcal/mole}$ $n = 9.14 \text{\AA}^{-1}$ $C = 0.715$
Charge(e)	Na : +1.0 Br : -1.0 H : +0.32 O : -0.64	Ba : +2.0 Cl : -1.0 H : +0.32 O : -0.64
Dielectric Constant	1.0	1.0
Van der Waals radii ( $\text{\AA}$ )	Na : 1.54 Br : 2.02 H : 1.20 O : 1.52	Ba : 2.16 Cl : 1.75 H : 1.20 O : 1.52

weaker H-bond potential energies are seen. As seen in Table 1,  $\text{H} \cdots \text{Y}$  distances are larger when they are involved in highly bent or bifurcated bond ranging from  $2.49$  to  $2.80\text{\AA}$ , compared with the cases of approximately linear bonds. For  $\text{H}_2\text{O}$  molecule in BCD, even the resulting energy of the bifurcated bond from  $\text{H(4)} \cdots \text{Cl(1)}$  and  $\text{H(4)} \cdots \text{Cl(2)}$  interactions is still weaker than that of  $\text{H(3)} \cdots \text{Cl(1)}$  interaction, since the shorter the bond, the shaper is the increase in  $U(\text{H} \cdots \text{Y})$  of Eq. (7).

For  $\text{H}_2\text{O}$  molecules involved only in approximately linear bonds their total potential energy minima can be taken to represent the structural equilibrium positions satisfactory in the both samples, whereas for  $\text{H}_2\text{O(I)}$  in SBD and  $\text{H}_2\text{O(II)}$  in BCD these energy curves exhibit considerable asymmetric feature and their minima are deviated from the structural data\*.

The potential due to the non-bond interactions of O atom have been negligible and the same

remained even when the effect of its lone pair electrons has been taken into account by assuming the charge distribution according to Pople's model<sup>23</sup>. The librational frequencies estimated by fitting the harmonic potentials over the amplitude of  $\pm 15^\circ$ <sup>11</sup> for total P.E. curves and also for P.E. curves due to the H-bond interaction alone are compared with the observed frequencies in Table 10.

### (ii) Group theoretical analysis of dynamical modes of $\text{H}_2\text{O}$

The symmetry properties of normal modes of any crystal can be studied by using the formalism given by Maraudin and Vosko<sup>24</sup>. This method has been extended to external modes by Venkataraman et al.<sup>25</sup>. One can study by these methods several aspects of "an arbitrary crystal belonging to an arbitrary symmorphic or non-symmorphic space group". The power of group-theoretical analysis can be used for this problem because it is possible to construct a set of matrices in the  $3n$  dimensional space of eigenvectors corresponding to crystal symmetry operations, providing a matrix representation of the relevant group  $G_0(\mathbf{q})$  of the wave-vector  $\mathbf{q}$ . Without going into the details, it is sufficient for our purpose to mention the followings; If we restrict ourselves to those operations  $R_m [= \{R(\mathbf{v}(R) + \mathbf{x}(m))\}]$  of the space group  $G(\mathbf{q})$  of  $\mathbf{q}$ , the purely rotational elements (R) in this space group, form a point group  $G_0(\mathbf{q})$  called the group of the wave vector  $\mathbf{q}$ . We can associate with each element R of  $G_0(\mathbf{q})$  a matrix  $T(\mathbf{q}, R)$ , whose elements are given by

$$T^{ii'}_{\alpha\beta}(\mathbf{k}, \mathbf{k}', \mathbf{q}, R_m) = R_{\alpha\beta} C^i \delta_{ii'}$$

$$\cdot \delta(\mathbf{k}, F_0(\mathbf{k}', R)) \exp \{i\mathbf{q}[\mathbf{x}(\mathbf{k}) - R\mathbf{x}(\mathbf{k}')]\}. \quad (8)$$

Here  $R_m$  is an element of  $G(\mathbf{q})$ ,  $R_{\alpha\beta}$  is the  $(\alpha, \beta)$ th element in matrix representation R of the rotational part of  $R_m$ .  $i$  and  $i'$  comprehensively represent  $t$  and  $r$  signifying translation and rotation respectively.  $C^i(R)$  is given by

$$\begin{aligned} C^i(R) &= 1 & \text{if } i=t \\ &= \det(R) & \text{if } i=r; \\ &= 1 & \text{for proper rotations} \\ &= -1 & \text{for improper rotations} \end{aligned}$$

Table 3. Atomic interchanges by space group operations  $P2_1/m(C_{2h}^2)$  in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Atoms in the molecular unit  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  are labelled by number 1 to 9.

Mol/Atom	$E$ mol/atom	$C_2$ mol/atom	$i$ mol/atom	$\sigma_h$ mol/atom
1 1	1 1	2 1	3 1	4 1
2	2	2	2	2
3	3	3	3	3
4	4	4	4	4
5	5	5	5	5
6	6	6	6	6
7	7	7	7	7
8	8	8	8	8
9	9	9	9	9
2 1	2 1	1 1	4 1	3 1
2	2	2	2	2
3	3	3	3	3
4	4	4	4	4
5	5	5	5	5
6	6	6	6	6
7	7	7	7	7
8	8	8	8	8
9	9	9	9	9
3 1	3 1	4 1	1 1	2 1
2	2	2	2	2
3	3	3	3	3
4	4	4	4	4
5	5	5	5	5
6	6	6	6	6
7	7	7	7	7
8	8	8	8	8
9	9	9	9	9
4 1	4 1	3 1	2 1	3 1
2	2	2	2	2
3	3	3	3	3
4	4	4	4	4
5	5	5	5	5
6	6	6	6	6
7	7	7	7	7
8	8	8	8	8
9	9	9	9	9

\*For  $\text{H}_2\text{O}(\text{I})$  in SBD, there are considerable differences between hydrogen positions located by Van Meerssche et al. using PMR method and by Ladd using crystal energy calculation. In the present work, the structural data from the former has been adopted since total potential energy curves obtained therefrom showed somewhat more favorable shapes.

$$\begin{array}{l|cccc} T(0, E) = & A & 0 & 0 & 0 \\ & 0 & A & 0 & 0 \\ & 0 & 0 & A & 0 \\ & 0 & 0 & 0 & A \\ \\ T(0, i) = & 0 & 0 & C & 0 \\ & 0 & 0 & 0 & C \\ & C & 0 & 0 & 0 \\ & 0 & C & 0 & 0 \end{array} \quad \begin{array}{l|cccc} T(0, C_s) = & 0 & B & 0 & 0 \\ & B & 0 & 0 & 0 \\ & 0 & 0 & B & 0 \\ & 0 & 0 & 0 & B \\ \\ T(0, \sigma_h) = & 0 & 0 & 0 & D \\ & 0 & 0 & D & 0 \\ & 0 & D & 0 & 0 \\ & D & 0 & 0 & 0 \end{array}$$

(i) in the atomic model

[illegible]

A, B, C and D are given by

$$\begin{aligned}
 A &= \begin{vmatrix} R_1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & R_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & R_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & R_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & R_1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & R_1 \end{vmatrix} & B &= \begin{vmatrix} R_2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & R_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & R_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -R_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & R_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -R_2 \end{vmatrix} \\
 C &= \begin{vmatrix} R_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & R_3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & R_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -R_3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & R_3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -R_3 \end{vmatrix} & D &= \begin{vmatrix} R_4 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & R_4 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & R_4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & R_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & R_4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & R_4 \end{vmatrix}
 \end{aligned}$$

with

$$R_1 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad R_2 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad R_3 = \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \quad R_4 = \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

**Table 5. Irreducible Representation for  $G_0(0)$  in  $BaCl_2 \cdot 2H_2O$**

Repn.	$E$	Operations		
		$C_2$	$i$	$\sigma_h$
$A_g$	1	1	1	1
$A_u$	1	1	-1	-1
$B_g$	1	-1	-1	1
$B_u$	1	-1	1	-1

**Table 6. Symmetry Adopted Eigenvector Matrix for  $q=0$  in  $BaCl_2 \cdot 2H_2O$**

$$\tilde{U} = \begin{vmatrix} A & A & A & A \\ B & -B & B & -B \\ C & -C & -C & C \\ D & D & -D & -D \end{vmatrix}$$

A, B, C, D are defined in Table 4-(i)

The  $\delta$ -function,  $\delta(k, F_0(k', R))$  referring to interchange of sublattices if any, vanishes unless  $k$  corresponds to  $F_0(k', R)$  arrived at from the sublattice  $k'$  via  $R_n$  in which case the delta function is unity.  $x(k)$  and  $x(k')$  are coordinates of the sublattices  $k$  and  $k'$ .  $k$  and  $k'$  can be atomic or molecular units. If there are  $\mu$  atoms and  $\eta$  'molecules' in the unit cell,  $T(q, R)[R \in G_0(q)]$  provides a  $(3\mu + 6\eta)$  dimensional multiplier representation of  $G_0(q)$ . One can use the  $T(q, R)$  matrices to classify the eigenvalues and eigenvectors by using the reduction formula,

$$C_s = \frac{1}{h} \sum_{R \in G_0(q)} \chi^s(q, R) \chi(q, R) \quad (9)$$

where  $\chi^s(q, R)$  and  $\chi(q, R)$  are the characters of the irreducible and reducible multiplier representations of  $G_0(q)$ ,  $h$  its order.  $C_s$  indicate the number of times the irreducible multiplier representation (IMR)  $\tau^s(q)$  of dimensionality  $f_s$  occurs in the set  $T(q, R)$ . Correspondingly, there will be  $C_s$  eigenvalues each of which will be  $f_s$ -fold degenerate. The corresponding eigen-

vectors each can be labelled as

$$\{e(q, s, 1, 1) \cdots e(q, s, 1, f_s)\}, \\ \{e(q, s, 2, 1) \cdots e(q, s, 2, f_s)\}, \\ \cdots \{e(q, s, C_s, 1) \cdots e(q, s, C_s, f_s)\}.$$

One can project out  $C_s$  orthogonal symmetry adopted vectors

$$\xi(q, s, 1, \lambda) \cdots \xi(q, s, C_s, \lambda)$$

by using projection-operator technique. The eigenvectors  $e(q, s, a, \lambda)$  are linear combination of  $\xi(q, s, b, \lambda)$ . The purity of the modes is decided by this linear combination. If  $\xi(q, s, b, \lambda)$  is unique,  $e(q, s, a, \lambda)$  is unique and hence the associated mode is pure and not otherwise.

In the following relevant representations and discussions are given for BCD Table 3 indicates interchange of sublattices as a result of space group operations. If we consider long wave modes only ( $q=0$ ), the exponent  $q \cdot (x(k) - x(k'))$  is zero. One can easily write down the  $T(q, R)$  matrices. They are given in Table 4. At  $q=0$ , the IMR are the same as the irreducible representation for  $G_0(0)$  which is given in Table 5. Table 6 gives the symmetry adopted eigenvectors belonging to various representations. An inspection of Table 6 is quite informative; The eigenvectors being linear combination of symmetry adopted vectors, we conclude the following from the table;

i) the rotational modes *can* all be mixed in character and there need not be purely rocking or wagging or twisting modes,

ii) the two  $H_2O$  molecules in  $BaCl_2 \cdot 2H_2O$  unit possess in-phase motion always,

iii)  $H_2O$  molecules in different  $BaCl_2 \cdot 2H_2O$  units can have in-phase and out-phase motion,

iv) the coherence effects due to ii) and iii) can affect the spectra in a deuterated sample, whereas this has no relevance in hydrogenous

Table 7. Summary of Factor Group Analysis of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ 

Representation	$E$	$C_2$	$i$	$\sigma_h$	Total	Acoustic	Trans. opt	Rotatory	External	Internal	
$A_g$	1	1	1	1	27	0	15	6	21	6	Raman
$A_u$	1	1	-1	-1	27	1	14	6	21	6	IR
$B_g$	1	-1	-1	1	27	2	13	6	21	6	IR
$B_u$	1	-1	1	-1	27	0	15	6	21	6	Raman
Total $\chi(n)$	108	0	0	0	$N_R(\pm 1 + 2 \cos \theta)$						
Acoustic $\chi_A$	3	-1	1	-3	$\pm 1 + 2 \cos \theta$						
Optic trans $\chi_{op}$	57	1	-1	3	$(N_R(s) - 1)(\pm 1 + 2 \cos \theta)$						
Rotational $\chi_R$	24	0	0	0	$(N_R(s - m))\chi(p)$						

Notes:  $N_R$ ; No. of atoms remaining invariant under point group operation  $R$ .

$N_R(s)$ ; No. of structural groups left in variant by  $R$ .

$N_R(s - m)$ ; No. of poly-atomic groups remaining invariant under  $R$ .

+ and - for proper and improper operations respectively.

$\chi(P) = 1 + 2 \cos \theta$  for nonlinear molecules,  $= +2 \cos \theta$  for linear except for  $C_h$  and  $\sigma_v$ .

compounds due to the preponderant incoherent cross section of hydrogen.

Before we conclude this section, for the sake of completeness we have given the results of factor group analysis of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in Table 7. This analysis is useful in classifying the external modes into various categories of translational and rotational modes in infrared and Raman activities

### (iii) FG method

For the optically active lattice vibrations the motion of all the Bravais cells take place in phase, and the F and G matrices for lattice vibrations are obtained by adding F and G matrices for one Bravais lattice (i. e., the smallest unit in which no two groups of atoms become equivalent as the result of a simple translation) to the sum of all matrices representing interactions between that Bravais cell and its neighbours. The matrices may be set up in terms of either internal or Cartesian coordinates. The treatment given below is essentially same as the Shimanouchi and Fukushima et. al.'s<sup>26,27</sup> approach but with Cartesian coordinates.

Let the matrices relating to optically active vibrations be  $G_{opt}$  and  $F_{opt}$ . If the Bravais cell is denoted by  $(i, j, k)$ , we have

$$G_{opt} = N \sum_{i'j'k'} G_{(i,j,k);(i',j',k')} \quad (10)$$

$$F_{opt} = N \sum_{i'j'k'} F_{(i,j,k);(i',j',k')} \quad (11)$$

where  $N$  is normalization factor. It is possible to determine  $G_{opt}$  elements more readily by using Cartesian rather than internal coordinates, since  $G_{opt}$  is diagonal in Cartesian coordinates,

$$G_{opt(c)} = G_{(c)(c)(i,j,k);(i',j',k')} \quad (12)$$

its elements being the reciprocal masses of the atoms in the Bravais cell.

$F_{opt(c)}$  is related to  $F_{opt}$  as follows. There is a transformation matrix  $B$  such that  $R = BX$  where  $R$  and  $X$  are internal and Cartesian coordinates respectively. Then

$$F_{opt(c)} = \tilde{B}_{opt} F_{opt} B_{opt} \quad (13)$$

Analogous to  $R_{opt} = N \sum R_{(i,j,k)}$  in internal coordinates, we can define  $X_{opt} = N \sum X_{(i,j,k)}$  as the Cartesian coordinates, representing  $X$  optically active vibrations. Then

$$B_{opt} = \sum_{i'j'k'} B_{(i,j,k);(i',j',k')} \quad (14)$$

This can also put as,

$$B_{opt} = \sum_{ijk} B_{(i,j,k);(i',j',k')} \quad (15)$$

The matrix elements  $B_{opt}$  are calculated only for the internal coordinates in terms of which the potential energy of the crystal is calculated.

**Table 8.** Interactions and force constants taken into account in the potential of the first molecular unit ( $NaBr \cdot 2H_2O$ )<sup>†</sup>. The Bravais cells of the interacting pair are indicated in reference to the atom (or ion) of the first molecular unit located in  $(i, j, k)$  cell.

Interaction			Distance		Force Const. (md/Å)	
			Å	Å		
R 1	$(i, j, k)$	$(i-1, j, k)$	Na . . . O(1)	2.419	0.21	
R 2	$(i, j, k)$	$(i-1, j, k)$	Na . . . O(1)	2.482	0.19	
R 3	$(i, j, k)$	$(i, j-1, k)$	Na . . . O(2)	2.372	0.22	
R 4	$(i, j, k)$	$(i, j, k)$	Na . . . O(2)	2.405	0.21	
R 5	$(i, j, k)$	$(i-1, j, k)$	Br . . . O(1)	3.810	0.05	
R 6	$(i, j, k)$	$(i, j, k)$	Br . . . O(1)	3.910	0.05	
R 7	$(i, j, k)$	$(i+1, j-1, k)$	Br . . . O(1)	3.366	0.08	
R 8	$(i, j, k)$	$(i, j, k)$	Br . . . O(1)	3.576	0.07	
R 9	$(i, j, k)$	$(i-1, j, k-1)$	Br . . . O(1)	3.887	0.05	
R10	$(i, j, k)$	$(i, j, k)$	Br . . . O(2)	3.912	0.05	
R11	$(i, j, k)$	$(i, j-1, k)$	Br . . . O(2)	3.814	0.05	
R12	$(i, j, k)$	$(i+1, j-1, k)$	Br . . . O(2)	3.319	0.08	
R13	$(i, j, k)$	$(i, j, k)$	Br . . . O(2)	3.860	0.05	
R14	$(i, j, k)$	$(i, j, k-1)$	Br . . . O(2)	3.370	0.08	
R15	$(i, j, k)$	$(i, j, k+1)$	Na . . . Na	3.552	0.10	
R16	$(i, j, k)$	$(i, j, k)$	Na . . . Na	3.794	0.08	
R17	$(i, j, k)$	$(i, j, k-1)$	Na . . . Na	3.794	0.08	
R18	$(i, j, k)$	$(i, j, k)$	Na . . . Br	2.982	0.17	
R19	$(i, j, k)$	$(i, j, k)$	Na . . . Br	2.955	0.18	
R20	$(i, j, k)$	$(i+1, j, k)$	H(1) . . Br	2.380	0.63	
R21	$(i, j, k)$	$(i, j, k-1)$	H(2) . . Br	2.797	0.11	
R22	$(i, j, k)$	$(i, j, k)$	H(3) . . Br	2.406	0.58	
R23	$(i, j, k)$	$(i+1, j, k)$	H(4) . . Br	2.323	0.78	
R24	$(i, j, k)$	$(i, j, k)$	H(1)—O(1)	0.979	5.85	
R25	$(i, j, k)$	$(i, j, k)$	H(2)—O(1)	1.022	5.85	
R26	$(i, j, k)$	$(i, j, k)$	H(3)—O(2)	0.977	5.85	
R27	$(i, j, k)$	$(i, j, k)$	H(4)—O(2)	1.013	5.85	
R28	$(i+1, j, k)$	$(i, j, k)$	Na—O(1)—Na	2.419	2.482	0.04
R29	$(i+1, j, k)$	$(i, j, k)$	Na—O(1)—H(1)	2.419	0.988	0.048
R30	$(i+1, j, k)$	$(i, j, k)$	Na—O(1)—H(2)	2.419	1.022	0.048
R31	$(i+1, j, k-1)$	$(i, j, k)$	Na—O(1)—H(1)	2.482	0.988	0.048
R32	$(i+1, j, k-1)$	$(i, j, k)$	Na—O(1)—H(2)	2.482	1.022	0.044
R33	$(i, j, k)$	$(i, j, k)$	H(1)—O(1)—H(2)	0.988	1.022	0.750
R34	$(i, j, k)$	$(i, j, k)$	Na—O(2)—Na	2.372	2.405	0.05
R35	$(i, j, k)$	$(i, j, k)$	Na—O(2)—H(3)	2.372	0.977	0.06
R36	$(i, j, k)$	$(i, j, k)$	Na—O(2)—H(4)	2.372	1.013	0.06
R37	$(i, j, k-1)$	$(i, j, k)$	Na—O(2)—H(3)	2.405	0.977	0.06
R38	$(i, j, k-1)$	$(i, j, k)$	Na—O(2)—H(4)	2.405	1.013	0.06
R39	$(i, j, k)$	$(i, j, k)$	H(3)—O(2)—H(4)	0.977	1.013	0.75

**Table 9.** Interactions and force constants taken into account in the potential of the first molecular unit ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ )<sup>1</sup>. The Bravais cells of the interacting pair are indicated in reference to the atom (or ion) of the first molecular unit located in  $(i, j, k)$  cell.

Interaction			Distance		Force Const. (mb/Å)
			Å	Å	
R 1	$(i, j, k)$ $(i, j, k-1)$	Ba · · · O(1)	2.841		0.26
R 2	$(i, j, k)$ $(i-1, j, k-1)$	Ba · · · O(1)	2.851		0.26
R 3	$(i, j, k)$ $(i, j, k)$	Ba · · · O(2)	2.865		0.25
R 4	$(i, j, k)$ $(i-1, j, k-1)$	Ba · · · O(2)	2.894		0.25
R 5	$(i, j, k)$ $(i-1, j, k-1)$	Ba · · · Cl(1)	3.132		0.20
R 6	$(i, j, k)$ $(i-1, j, k-1)$	Ba · · · Cl(1)	3.249		0.20
R 7	$(i, j, k)$ $(i+1, j, k+1)$	Ba · · · Cl(1)	3.324		0.20
R 8	$(i, j, k)$ $(i-1, j, k)$	Ba · · · Cl(2)	3.168		0.20
R 9	$(i, j, k)$ $(i-1, j, k-1)$	Ba · · · Cl(2)	3.211		0.20
R10	$(i, j, k)$ $(i+1, j, k)$	Cl(1) · · O(1)	3.665		0.04
R11	$(i, j, k)$ $(i, j, k)$	Cl(1) · · O(1)	3.508		0.06
R12	$(i, j, k)$ $(i+1, j, k+2)$	Cl(1) · · O(1)	3.477		0.07
R13	$(i, j, k)$ $(i+1, j, k)$	Cl(1) · · O(2)	3.179		0.15
R14	$(i, j, k)$ $(i, j, k)$	Cl(1) · · O(2)	3.493		0.06
R15	$(i, j, k)$ $(i+1, j, k+1)$	Cl(1) · · O(2)	3.302		0.11
R16	$(i, j, k)$ $(i, j, k-1)$	Cl(2) · · O(1)	3.130		0.17
R17	$(i, j, k)$ $(i, j, k-1)$	Cl(2) · · O(1)	3.330		0.10
R18	$(i, j, k)$ $(i+1, j, k+1)$	Cl(2) · · O(1)	3.182		0.15
R19	$(i, j, k)$ $(i, j, k)$	Cl(2) · · O(2)	3.365		0.09
R20	$(i, j, k)$ $(i, j, k-1)$	Cl(2) · · O(2)	3.445		0.07
R21	$(i, j, k)$ $(i+1, j, k+1)$	Cl(2) · · O(2)	3.238		0.13
R22	$(i, j, k)$ $(i+1, j, k+1)$	H(1) · · Cl(2)	2.236		0.15
R23	$(i, j, k)$ $(i, j, k)$	H(2) · · Cl(2)	2.172		0.15
R24	$(i, j, k)$ $(i-1, j, k)$	H(3) · · Cl(1)	2.222		0.15
R25	$(i, j, k)$ $(i+1, j, k+1)$	H(4) · · Cl(1)	2.601		0.10
R26	$(i, j, k)$ $(i+1, j, k+1)$	H(4) · · Cl(2)	2.492		0.10
R27	$(i, j, k)$ $(i, j, k)$	H(1)—O(1)	0.967		5.83
R28	$(i, j, k)$ $(i, j, k-1)$	H(2)—O(1)	0.974		5.83
R29	$(i, j, k)$ $(i, j, k)$	H(3)—O(2)	0.965		5.83
R30	$(i, j, k)$ $(i, j, k)$	H(4)—O(2)	0.953		5.83
R31	$(i, j, k+1)$ $(i, j, k)$ $(i, j, k)$	Ba—O(1)—Ba	2.841	2.851	0.04
R32	$(i, j, k)$ $(i, j, k)$ $(i, j, k)$	Ba—O(2)—Ba	2.865	2.894	0.04
R33	$(i, j, k)$ $(i, j, k)$ $(i, j, k+1)$	H(1)—O(1)—H(2)	0.967	0.974	0.75
R34	$(i, j, k)$ $(i, j, k)$ $(i, j, k)$	H(3)—O(2)—H(4)	0.965	0.953	0.75
R35	$(i, j, k+1)$ $(i, j, k)$ $(i, j, k)$	Ba—O(1)—H(1)	2.841	0.967	0.038
R36	$(i, j, k+1)$ $(i, j, k)$ $(i, j, k+1)$	Ba—O(1)—H(2)	2.841	0.974	0.03
R37	$(i, j, k)$ $(i, j, k)$ $(i, j, k)$	Ba—O(1)—H(1)	2.851	0.967	0.038
R38	$(i, j, k)$ $(i, j, k)$ $(i, j, k+1)$	Ba—O(1)—H(2)	2.851	0.974	0.03
R39	$(i, j, k)$ $(i, j, k)$ $(i, j, k)$	Ba—O(2)—H(3)	2.865	0.965	0.03
R40	$(i, j, k)$ $(i, j, k)$ $(i, j, k)$	Ba—O(2)—H(4)	2.865	0.953	0.025
R41	$(i, j, k)$ $(i, j, k)$	Ba—O(2)—H(3)	2.894	0.965	0.03
R42	$(i, j, k)$ $(i, j, k)$ $(i, j, k)$	Ba—O(2)—H(4)	2.894	0.953	0.025



One  $B_{opt}^I$  corresponding to the first molecular unit,  $I$ , is constructed,  $B_{opt}$  corresponding to the other molecular units can be obtained by symmetry operations. For BCD, for example, it is

$$B_{opt}^{II} = R_2 B_{opt}^I; B_{opt}^{III} = R_3 B_{opt}^I$$

and  $B_{opt}^{IV} = R_4 B_{opt}^I$ .

$B_{opt}$  is diagonal in internal coordinates, if the potential energy can be set up without cross terms between any two internal coordinates.

One can obtain the lattice frequencies and their eigenvectors representation by transforming  $G_{(c)}$  and  $F_{(c)}$  (from here we drop the subscript 'opt', but it is always implied) using the relation,

$$G'_{(c)} = U G_{(c)} \tilde{U} \quad (16)$$

$$F'_{(c)} = U F_{(c)} \tilde{U} \quad (17)$$

where  $\tilde{U}$  indicates the conjugate transposed symmetry adopted eigenvector matrix derived by the group-theoretical approach. To summarize, diagonalization of  $G'_{(c)} \cdot F'_{(c)}$  results in obtaining the frequencies of optical vibrations of a crystalline lattice. The dimension of various matrices are  $G_{(c)}$ :  $3n \times 3n$ ,  $F$ :  $NR \times NR$ ,  $B_{opt}$ :  $NR \times 3n$  and  $U$ :  $3n \times 3n$ .  $NR$  is the number of interactions.

The potential energy of the crystal is assumed to be made up of two parts,

$$U = U_{H_2O} + U_{inter} \quad (18)$$

where  $U_{H_2O}$  is the Urey-Bradley force field associated with the crystal  $H_2O$  molecules, and  $U_{inter}$  represents the interaction potential between crystal water molecules and ions, between ions, and also between water molecules. For SBD,  $U_{inter}$  is assumed to be

$$2U_{inter} = \sum \{ f_{iNa-O} \Delta R_{iNa-O}^2 + f_{iBF-O} \Delta R_{iBF-O}^2 + f_{iNa-Na} \Delta R_{iNa-Na}^2 + f_{iNa-BF} \Delta R_{iNa-BF}^2 + f_{iH-BF} \Delta R_{iH-BF}^2 + H_{iNa-O-Na} r_{iNa-O}^2 \Delta \alpha_{iNa-O-Na}^2 + H_{iNa-O-H} r_{iNa-O}^2 r_{iH-O}^2 \Delta \alpha_{iNa-O-H}^2 \}$$

by neglecting some trivial interactions and,

similarly for BCD

$$2U_{inter} = \sum \{ f_{iCl-H} \Delta R_{iCl-H}^2 + f_{iBa^+-O} \Delta R_{iBa^+-O}^2 + f_{iBa^+-Cl} \Delta R_{iBa^+-Cl}^2 + f_{iO-O} \Delta R_{iO-O}^2 + f_{iO-Cl} \Delta R_{iO-Cl}^2 + f_{iCl-Cl} \Delta R_{iCl-Cl}^2 + H_{iH-O-Ba^+} r_{iO-H}^2 r_{iBa^+-O}^2 \Delta \alpha_{iH-O-Ba^+}^2 + H_{iBa^+-O-Ba^+} r_{iBa^+-O}^2 \Delta \alpha_{iBa^+-O-Ba^+}^2 \} \quad (20)$$

In the above equations, the  $\Delta R_i$ 's and  $\Delta \alpha_i$ 's represent interatomic displacements in distances and in bond angles respectively and the  $r_i$ 's represent equilibrium interatomic distances.

We have written a software for calculating the eigenfunctions and eigenvectors given  $G_o$ ,  $F'$ ,  $B_{opt}$  and  $U$  matrices. The interactions with interatomic distances of more than  $4\text{\AA}$  ( $3.8\text{\AA}$  in the case of BCD) have been neglected in Eqs. (19) and (20) and those interactions taken into account are shown for the first respective molecular unit in Tables 8 and 9 along with force constants adopted. The force constants in  $U_{H_2O}$  have been taken from Ref. (27) and the stretching force constants associated with non-bond pairs have been determined from the second derivatives of the electrostatic potentials at equilibrium interatomic distances using the point charges assigned in Table 2. Similarly the  $f_i(H \cdots Y)$ 's have been determined from the second derivatives of  $U(H \cdots Y)$ , and  $H_i(O-H \cdots M)$ 's,  $M$  being the metal ion, have been adjusted so as to obtain reasonable agreement of the calculated librational frequencies with observed frequencies. The results for  $A_u$  species are given in Table 10 along with the observed frequencies. It is seen that all of the calculated frequencies other than those from  $H_2O$  internal modes are due to highly mixed modes as expected from the discussion in 5-(ii). Therefore, only those modes identified as significant  $H_2O$  librational modes from their large potential energy distribution in  $A_u$  species are assigned to the frequencies. The results from  $A_g$ ,  $B_u$ , and  $B_g$

**Table 10. Comparison of the observed H<sub>2</sub>O librational frequencies with the theoretical values (in cm<sup>-1</sup>).**

NaBr · 2H <sub>2</sub> O						
Experimental		Theoretical				
IR <sup>14)</sup>	Neutron(100°K)	GF method	Simple model			
			Total P. E.		H-bond P. E.	
	650±8	658 W(2) R(2)	660 W(2)			
625		614 T(2) W(2)				
590		590 R(1) W(1)			599 T(2)	
	562±6	558 R(1) T(1)			566 R(2)	
			523 W(1)		539 W(2)	
470	474	478 R(2)	519 R(1)		440 W(1)	
405	403±5	393 R(1) T(1)	473 T(2)		389 R(1)	
			385 T(1)		366 T(1)	
BaCl <sub>2</sub> · 2H <sub>2</sub> O						
Experimental				Theoretical		
IR <sup>15)</sup>	Raman <sup>15)</sup>	T-O-F <sup>1)</sup> (300°K)	Neutron (100°K)	GF method	Simple model	
					Tabal P. E.	H-bond P. E.
715	714	660±40	717±15	740 R(2) W(2)	751 W(1)	
686				651 W(1)	646 W(2)	638 R(1)
						635 T(1)
592	611		601±9	585 T(1)	619 R(1)	596 W(1)
					600 T(1)	
561		536±32	568( ? )			
536	490	480±24	531	539 R(2) T(2)		477 W(2)
420	407	384±16	423±5	420 R(2) W(2)	425 T(2)	432 R(2)
411						
330				360 R(1)	308 R(2)	359 T(2)

species are almost same as A<sub>u</sub> species as far as the H<sub>2</sub>O librations are concerned. Similar calculation was also carried out for BCD earlier by Fukushima et al<sup>27)</sup>. Due to some differences in adopting relevant force constants, there is no detailed agreement between two works.

As already pointed out, the shapes of the librational potential energy curves based on the simple model can not represent the structure data satisfactorily for the H<sub>2</sub>O molecule involved either in highly bent or bifurcated H-bond. In fact, the possibility of extending LSPF to these H-bond configurations remains to be studied in further detail. As can be seen in Table 10, however, the agreement between experimental and theoretical frequencies obtained from FG method may be considered fair with all simplification

of estimating the non-linear H-bond interactions. This might be partly due to the parametrization of H<sub>i</sub>(O-H...M)'s.

As mentioned earlier, both methods, neutron and optical, do not observe exactly the same one. Without either detailed coherent neutron inelastic scattering measurements or calculation of complete lattice dynamics, it is difficult to say whether the disagreements in the observed frequencies by neutron and optical method are due to the dispersion of the librational branches or difference in the selection rule of both methods. Although neutron method is free from selection rules, some peaks may not be seen because of unfavorable polarization conditions. Considering these facts it is interesting to note that the observations from neutron and optical methods

hold agreements complementally to the theoretical frequencies obtained from FG method in both samples.

It is remarkable that the  $H_2O$  librational frequencies are found to be more sensitive to  $H_i(H-O\cdots M)$ 's, namely bending interactions between the metal ions and the lone pair orbitals of O atoms, than  $f_i(H\cdots Y)$ 's in FG method in contrast to the dominant contribution of H-bond in the simple model. This may be due to ignoring of  $O-H\cdots Y$  bendings in Eqs. (19) and (20). In other words, the H-bond interaction based on  $U(H\cdots Y)$  is the pure central force field and accordingly produces less bending component on the non-rigid  $H_2O$  librators, compared with the case of simple model. In the absence of reliable  $H_i(H-O\cdots M)$ 's we think that it does not provide much informations to include  $H_i(O-H\cdots Y)$ 's terms in Eqs. (19) and (20) and parametrize the values in the framework of the present approach. However, in view of the fact that the frequencies from the H-bond interaction alone are able to predict roughly the magnitude of the observed values in the simple model, the above discussion may be led to that the effect of  $O-H\cdots Y$  bending interactions are merged implicitly in  $H_i(H-O\cdots M)$ 's parametrized in FG method. Further detailed study of this problem in various crystal hydrates, will provide more understanding of the nature of H-bonds and the role of metal-oxygen coordinations in  $H_2O$  librations.

#### Acknowledgements

The authors are greatly indebted to Dr. K. R. Rao for many valuable discussions and detailed comments on theoretical treatments. Acknowledgements are also made to Drs. R. A. Chidambaram and S. K. Sikka for useful discussions on hydrogen bond interaction and calculation of crystal energy. We also wish to thank Dr. Moon Kyu Chung and Dr. Hae-Ill Bak for their constant

interest and encouragement throughout this work.

Thanks are also due to Mr. Han-Giu Kim who had joined to this work at the stage of construction of the inverted filter spectrometer. Valuable technical assistance has been provided by Mr. Byung Chil Chun.

#### References

1. H. Boutin et al., *J. Chem. Phys.* **40**, 2670 (1974); H. Prask and H. Boutin, *J. Chem. Phys.* **45**, 699 (1966); **45**, 1685 (1966)
2. A. Bajorek et al., *Neutron Inelastic Scattering*, **2**, 143, IAEA, Vienna (1968)
3. C. L. Taper et al., *Phys. Stat. Sol.* **34**, 279 (1969)
4. C. L. Taper et al., *Solid State Comm.* **7**, 496 (1970)
5. K. Ichida et al., *Spectrochimica* **28A**, 2433 (1972)
6. R. Chidambaram, A. Sequeira and S. K. Sikka, *J. Chem. Phys.* **41**, 3616 (1964)
7. J. P. Culot, P. Piret & M. V. Meerseche, *Bull. Soc. Franc. Miner. Crist.* **85**, 282 (1962); **85**, 290 (1962); M. F. C. Ladd, *Z. Krist.* **126**, 147 (1968)
8. V. M. Podmanabhan, W. R. Busing and H. A. Levy, *Acta Cryst.* **16** A26 (1963); W. H. Baur, *Acta Cryst.* **19**, 909 (1965)
9. Woods, A. D. B., Brockhouse, B. N., Sakamoto, M. and Sinclair, R. N., *Inelastic Scattering of Neutrons in Solids and Liquids*, IAEA, Vienna, 487 (1961)
10. H. J. Kim, H. K. Kim and B. G. Yoon, in the AERI Proceeding of a Study Group Meeting on Research Reactor Utilization, IAEA-147, 301, (1972) The design, construction and our experiences on the improvement of the performance of the inverted filter spectrometer will be published separately.
11. J. S. Sarma, *J. Chem. Phys.* **52**, 377 (1970)
12. H. J. Kim, P. S. Goyal, G. Venkataraman, B. A. Dasanncharya and C. L. Taper *Solid State*

- Comm. **8**, 889 (1970)
13. H.J. Kim, *J. Kor. Nucl. Soc.*, **4**, 306 (1972)
14. J. Van der Elsken and D.W. Robinson, *Spectrochim. Acta* **17**, 1249 (1961)
15. Y.S. Jain, V.K. Kapoor and H.D. Dist, *Appl. Spectroscopy* **30**, 440 (1976)
16. H. Hahn, *Inelastic Scattering of Neutron Scattering*, IAEA, Vienna, **2**, 279 (1965); H. Prask, H. Boutin and S. Yip, *J. Chem. Phys.* **48**, 3367 (1968)
17. Y.S. Jain, *Solid State Comm.* **17**, 650 (1975)
18. Thaper, C.L., Dasannacharya, B.A., Iyengar, P.K. and Srinivasan, T., *B.A.R.C. Report BARC 501* **61** (1970)
19. A. Sjölander, *Arkiv for Fysik* **14**, 315 (1958)
20. E.R. Lippincott and R. Schroeder, *J. Chem. Phys.* **23**, 1099 (1955)
21. R. Chidambaram and S.K. Sikka, *Chem. Phys. Letters*, **2**, 162 (1968); R. Balasubramanian, R. Chidambaram and G.N. Ramachandran, *Biochim. Biophys. Acta* **221**, 182 (1970); **221**, 196 (1970)
22. A.I. Kitaigorodskii, *Acta Cryst. B* **27**, 868 (1971)
23. J.A. Pople, *Proc. Roy. Soc.* **202A**, 323 (1950)
24. A.A. Maradudin and S.H. Vosko, *Rev. Mod. Phys.* **40**, 1 (1968)
25. G. Venkataraman and V.C. Saqni, *Rev. Mod. Phys.* **42**, 409 (1970)
26. T. Shimanouchi, M. Tsuboi and T. Miyazawa, *J. Chem. Phys.* **35**, 1597 (1961)
27. K. Fukushima and H. Kataiwa, *Chem. Soc. Japan*, **43**, 690 (1970)
-