

# THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

## Part II. Correlation with Crystal Structure

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### 1. INTRODUCTION

THE application of conventional methods of group theory for elucidating the features observed in the Raman and infra-red spectra of crystals is well known and is dealt with in detail by Bhagavantam and Venkatarayudu in their treatise on the Theory of Groups. The group theoretical methods give the total number of vibrations appearing under each of the different symmetry classes and in addition it is usually possible to resolve this number into translatory, rotatory and internal vibrations. It had been pointed out by Bhagavantam<sup>13</sup> in his discussion of the case of crystalline  $\text{Hg}_2\text{Cl}_2$  that in the case of crystals containing linear groups (like the hydroxyl ions figuring in our discussions) which possess only two degrees of rotational freedom, the usual formulæ used for resolving the total number of vibrations into the lattice and internal types of vibrations are inapplicable. However, since the symmetry properties and selection rules of the different irreducible representations of the various point groups have all been worked out and are readily available for reference (*vide e.g.*, *Molecular Vibrations* by Wilson *et al.*) it is possible from simple considerations of symmetry to picture the nature of the individual symmetry modes in simple cases. In the following we shall adopt this procedure of identification wherever feasible.

Crystal structure data naturally play an important role in the explanation of the observed facts. The relevant data are summarized in Table I. A list of references appears at the end of the paper and the numbers appearing in the first column of Table I refer to the concerned papers. In column 4 of the same table are shown the distances between the oxygens of the hydroxyl groups and in the case of the hydrates the figures marked with an asterisk denote the distances between the oxygens of the hydroxyls and the oxygens of the water molecules.

TABLE I  
Details of crystal structure

Substance	Crystal system	Space group and number of units in primitive cell	O-O distance in A.U.	Characteristic features of the structure
LiOH <sup>1</sup>	Tetra- gonal	D <sup>7</sup> <sub>4h</sub> (2)	3.6	Layer structure normal to <i>c</i> . Each Li is surrounded by four hydroxyls nearly tetrahedrally. Each hydroxyl has four Li neighbours on one side and four hydroxyls of the next layer on the other side. Hydroxyls are parallel to <i>c</i> -axis. Site symmetry of Li: D <sub>2d</sub> ; of OH: C <sub>4v</sub> .
LiOH · H <sub>2</sub> O <sup>2</sup>	Mono- clinic	C <sup>8</sup> <sub>2h</sub> (2)	2.99 3.14 to 3.34*	Chain structure. Each Li surrounded nearly tetrahedrally by two hydroxyls and two water molecules. Site symmetry of oxygens of OH: σ <sub>h</sub> ; of Li: C <sub>2</sub> ; of O (H <sub>2</sub> O): C <sub>2</sub> .
NaOH <sup>3-4</sup> KOH <sup>3</sup>	Ortho- rhombic	D <sup>17</sup> <sub>2h</sub> (2) do.	3.40 3.26	Layer structure normal to <i>c</i> . Each Na is surrounded by five OH groups. OH ions are parallel to <i>c</i> . Na and O approximately in the <i>ab</i> plane. Characteristic double layers of Na and OH normal to <i>c</i> . Site symmetry for both Na and OH: C <sub>2v</sub> . Similarly for KOH.
NaOH · H <sub>2</sub> O <sup>5</sup>	Ortho- rhombic	D <sup>15</sup> <sub>2h</sub> (8)	3.5 to 4.5 2.64 to 3.11*	Layer structure normal to <i>b</i> . No special positions of symmetry. Each Na surrounded by three hydroxyls and one H <sub>2</sub> O nearly tetrahedrally. Each OH surrounded by 3 Na's and 2 H <sub>2</sub> O's, and 3 OH's very much farther out than Na and H <sub>2</sub> O.

TABLE I (Contd.)

Substance	Crystal system	Space group and number of units in primitive cell	O-O distance in A.U.	Characteristic features of the structure
KOH·H <sub>2</sub> O <sup>6</sup>	.. Mono-clinic	C <sup>5</sup> <sub>2h</sub> (4)	2.63*	Layer structure parallel to (100). No special positions of symmetry. Oxygens (OH—OH <sub>2</sub> —OH) form zig-zag chains parallel to <i>c</i> .
Mg(OH) <sub>2</sub> <sup>7</sup> Ca(OH) <sub>2</sub> <sup>8-9</sup>	.. Trigonal do.	D <sup>3</sup> <sub>3d</sub> (1) do.	3.22 3.33	Layer structure normal to <i>c</i> . Hydroxyls parallel to <i>c</i> . Site symmetry of Mg: D <sub>3d</sub> ; of OH: C <sub>3v</sub> . Each Mg is surrounded by six hydroxyls. Each OH is surrounded by three Mg's on one side and on the other side by three OH's of the next layer. Similarly for Ca(OH) <sub>2</sub> .
Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O <sup>10</sup>	Tetra-gonal	D <sup>8</sup> <sub>4h</sub> (4)	2.9 2.7*	Site symmetry of Sr: D <sub>2</sub> ; of oxygens of OH: C <sub>4</sub> . The rest are in general positions. Each OH surrounded octahedrally by 4 H <sub>2</sub> O's and 2 OH's.
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O <sup>11</sup>	Mono-clinic	C <sup>5</sup> <sub>2h</sub> (4)		Atomic positions not determined. But all atoms are in general positions.
Al(OH) <sub>3</sub> <sup>12</sup>	.. Mono-clinic	C <sup>5</sup> <sub>2h</sub> (8)	2.75 to 3.46	All atoms in general positions. Distorted version of Mg(OH) <sub>2</sub> structure, the double layers of hydroxyls being parallel to (001). But only two-thirds of octahedral holes between hydroxyl layers are filled by Al. Owing to the distorted nature not all hydroxyls are parallel to <i>c</i> as in Mg(OH) <sub>2</sub> .

\* See text above for explanatory remarks.

## 2. THE HIGH FREQUENCY REGION OF THE SPECTRUM

The following facts regarding the crystal structures of the hydroxides enable us to readily account for the general features observed in the high frequency region of the spectrum. All the crystal structures shown in Table I belong to the centro-symmetric classes and the hydroxyl groups in the unit cell are separable into two halves related to each other by the centre of inversion. In many of the cases [*viz.*, LiOH, LiOH·H<sub>2</sub>O, NaOH, KOH, Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>] the unit cell contains only two hydroxyl groups which are on either side of the centre of inversion. As a consequence there arise two coupled hydroxyl stretching vibrations which are respectively symmetric and antisymmetric with respect to the centre of inversion. In particular, in the cases of LiOH, NaOH, KOH, Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> where the hydroxyl groups occupy special positions of symmetry their symmetric vibrations actually belong to the totally symmetric class. In the case of LiOH·H<sub>2</sub>O the positions of the hydrogens of the hydroxyls are not known. However, since it is remarked by Levy and Peterson<sup>14</sup> that the hydroxyl ion in LiOH·H<sub>2</sub>O does not take part in hydrogen bonding, it appears highly probable that the hydrogens of the hydroxyls are situated on the symmetry plane, and the symmetric vibrations of the hydroxyls in this case also can easily be seen to belong to the class A<sub>g</sub> of C<sub>2h</sub>. The symmetric vibrations in all these cases are active only in the Raman effect. The vibrations appearing in the infra-red are antisymmetric and Raman inactive. The observation of a single frequency shift in each one of the above cases is hence in accordance with theory, and these shifts are identified with the internal vibrations of the hydroxyls belonging to the totally symmetric class.

With regard to substances which contain more units in the primitive cell, the coupled internal vibrations of the hydroxyls can be divided into two groups of equal number of vibrations which are characterized by the fact of their being symmetric or antisymmetric with respect to the centre of inversion. With the exception of Sr(OH)<sub>2</sub>·8H<sub>2</sub>O, in all the remaining cases wherein the atoms are situated in general positions, *i.e.*, in the case of NaOH·H<sub>2</sub>O, KOH·H<sub>2</sub>O, Ba(OH)<sub>2</sub>·8H<sub>2</sub>O and Al(OH)<sub>3</sub>, all vibrations which are symmetric with respect to the centre of inversion are Raman active. Hence, the spectra of NaOH·H<sub>2</sub>O, KOH·H<sub>2</sub>O, Ba(OH)<sub>2</sub>·8H<sub>2</sub>O and Al(OH)<sub>3</sub> should according to theory exhibit respectively 4, 2, 4 and 12 components due to the internal vibrations of the hydroxyls. However, it is obvious that only the modes in which the internal vibrations of all the hydroxyls take place in identical phase (*i.e.*, totally symmetric class) would be intensely Raman active, the others being relatively weak. Also, if the hydroxyl groups are far removed from each other as in NaOH·H<sub>2</sub>O the coupling between the

hydroxyls will be too weak for the differences in the phases of adjacent groups to influence the frequency shift observably. In particular, in  $\text{NaOH}\cdot\text{H}_2\text{O}$  the eight units of the primitive cell are distributed equally in two adjacent layers which are quite far apart, the spacing being 5.9 A.U. In these circumstances, the appearance, in the spectra, of fewer components than that predicted by theory may be ascribed to either the low intensity of some of the components and (or) to their falling too close to the totally symmetric frequency to be resolved from it.

In view of the foregoing remarks the frequency shifts observed at  $3568\text{ cm.}^{-1}$  in  $\text{NaOH}\cdot\text{H}_2\text{O}$  and at  $3501$  in  $\text{KOH}\cdot\text{H}_2\text{O}$  may be assigned to the totally symmetric class. The appearance of two strong components well separated from each other at  $3481$  and  $3529\text{ cm.}^{-1}$  in the case of  $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$  is indicative of considerable coupling between the hydroxyls of the unit cell; the former which is more intense evidently belongs to the totally symmetric class. In the case of  $\text{Al}(\text{OH})_3$  five components, some of them rather broad, have been observed at  $3369$ ,  $3431$ ,  $3521$ ,  $3583$  and  $3602\text{ cm.}^{-1}$ . It is probable that some of them are unresolved groups of lines. The distribution of the observed frequencies over a considerable range is due to the large differences in the distances between the several hydroxyls in the unit cell and correspondingly varying degrees of interactions between them.

In the case of  $\text{Sr}(\text{OH})_2\cdot 8\text{H}_2\text{O}$  since there are eight hydroxyls per unit cell, there are, in all, four coupled internal vibrations symmetric with respect to the centre of inversion. Unlike the cases discussed above, the group  $D_{4h}$  to which  $\text{Sr}(\text{OH})_2\cdot 8\text{H}_2\text{O}$  belongs contains an irreducible representation  $A_{2g}$  symmetric with respect to the centre of inversion and which is Raman inactive. Since the positions of the hydrogen atoms are not known, it is not possible to determine the exact number of components active in the Raman effect. Three components have been observed at  $3488$ ,  $3536$  and  $3593\text{ cm.}^{-1}$ ; the intense line at  $3488\text{ cm.}^{-1}$  most probably belongs to the totally symmetric class.

In the case of hydrated hydroxides, the spectrum should in addition exhibit frequency shifts due to the water molecules. According to theory the Raman spectrum of water vapour should exhibit three frequency shifts. Only a single strong frequency shift (of the symmetric class) at  $3655\text{ cm.}^{-1}$  had been so far observed, the two other vibrations being presumably too weak (*vide Infra-red and Raman Spectra* by Herzberg). However, they have been observed in the infra-red spectrum at  $1595$  and  $3756\text{ cm.}^{-1}$ . Considerations similar to that put forward for the explanation of the hydroxyl

frequencies indicate that corresponding to the  $3655 \text{ cm.}^{-1}$  shift of water vapour, the spectra of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{NaOH}\cdot\text{H}_2\text{O}$ ,  $\text{KOH}\cdot\text{H}_2\text{O}$  and  $\text{Ba}(\text{OH})_2\cdot 8 \text{ H}_2\text{O}$  should exhibit respectively 1, 4, 2 and 16 components which arise due to the coupling of the vibrations and which take place symmetrically with respect to the centre of inversion. In the case of  $\text{Sr}(\text{OH})_2\cdot 8 \text{ H}_2\text{O}$ , 16 components are possible. But, the actual number that should be expected to appear in Raman effect cannot be determined in the absence of any data regarding the positions of the hydrogens. The fact that no shifts due to water are observed with  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{NaOH}\cdot\text{H}_2\text{O}$  and  $\text{KOH}\cdot\text{H}_2\text{O}$  is rather surprising and it requires further experimental study with clear and large crystals to observe them. The broad bands at 3302 and 3393 in  $\text{Sr}(\text{OH})_2\cdot 8 \text{ H}_2\text{O}$  and 3335  $\text{cm.}^{-1}$  in  $\text{Ba}(\text{OH})_2\cdot 8 \text{ H}_2\text{O}$  are evidently due to the large number of shifts appearing unresolved from each other. The explanation of the diminution of these frequencies from the value of  $3655 \text{ cm.}^{-1}$  for water vapour, we shall consider in the following section.

### 3. HYDROXYL BONDING EFFECTS

The large variations in the hydroxyl frequency shifts observed in the different cases are explicable as arising due to the interactions between the different hydroxyls (and the water molecules as well in the hydrates) which are contiguous to each other. Bernal and Megaw<sup>15</sup> have discussed in detail the nature of the interactions between hydroxyl groups—called by them the hydroxyl bond to distinguish it from the hydrogen bond. In the case of interactions between hydroxyl groups the distances between the groups are comparatively large (ranging from 2.75 to 3.6 A.U.). (In the case of hydrogen bonding, the oxygen atoms approach to within 2.55 A.U. of each other and the hydrogen linking them is not preferentially attached to either of them.)

The studies on the structure of  $\text{Al}(\text{OH})_3$  and other hydroxides have led Bernal and Megaw (*loc. cit.*) to conclude that there exists an attractive force between the hydroxyls. The hydroxyl ion can be pictured to be made up of an  $\text{O}^{--}$  and a proton  $\text{H}^+$  and as a result the negative charge of one oxygen can attract the positive charge of a neighbouring hydrogen to form the hydroxyl bond. It follows that the attraction will be greater at shorter O-O distances and will result in the displacement of the hydrogen atom from its normal position near the oxygen to which it belongs and as a consequence a diminution of the hydroxyl frequency would result. However, this is only a simplified picture of the actual state of affairs and, in general, the effects of all the surrounding neighbours will have to be taken into account. Especially in cases like  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  where the hydroxyl groups are far apart and are orientated parallel to each other and normal to

the layers, no large diminution of the frequency can be expected to occur. Even so, the fact that the hydroxyl frequency shifts in LiOH, NaOH and KOH (3664, 3632 and 3597  $\text{cm}^{-1}$ ) follow the same sequence as the O—O distances in them (3.6, 3.4 and 3.26 A. U.) is significant. In the case of Ca (OH)<sub>2</sub> and Mg (OH)<sub>2</sub> the O—O distances are respectively 3.33 and 3.22 A.U. Their respective hydroxyl shifts 3616 and 3651  $\text{cm}^{-1}$  fall in the region approximately near that of NaOH; however, it is surprising that the frequency shift in Mg (OH)<sub>2</sub> should be higher than that in the case of Ca (OH)<sub>2</sub>.

In the case of the hydrates additional interactions arise between the hydroxyl ions and the water molecules contiguous to them. The progressive diminution of the frequency shifts in LiOH·H<sub>2</sub>O, NaOH·H<sub>2</sub>O, KOH·H<sub>2</sub>O and Sr (OH)<sub>2</sub>·8 H<sub>2</sub>O is evidently due to the diminishing O—O distances in these cases and the correspondingly large interactions between the hydroxyls and the water molecules contiguous to each other. The diminution of the frequency shifts of the water bands in Sr (OH)<sub>2</sub>·8 H<sub>2</sub>O and Ba (OH)<sub>2</sub>·8 H<sub>2</sub>O (from the normal value of 3655  $\text{cm}^{-1}$  observed for water vapour) is also presumably due to analogous causes.

#### 4. THE LOW-FREQUENCY REGION OF THE SPECTRUM

In the present section, we shall discuss the cases for which lattice frequency shifts are reported.

(i) *Lithium hydroxide monohydrate*.—The total number of vibrations to be expected in the Raman effect according to theory is 18. Amongst these are included the single symmetric internal vibration of the hydroxyls and three others due to the water present in the structure. Hence, fourteen vibrations should appear in the low-frequency region. However, it should be remarked that since LiOH·H<sub>2</sub>O dehydrates easily to become LiOH when heated in an atmosphere of hydrogen below 140° C. (Partington, 1958),<sup>16</sup> the binding of the water molecules in the lattice is weak and the translational and rotational frequencies due to them will be rather low. It had not been possible to observe them. On the other hand, the binding between Li and OH should be quite strong as is evidenced by the high melting point of LiOH (450° C.). If we ignore the water molecules, there should appear in the Raman effect eight lattice frequency shifts, of which only five could be observed.

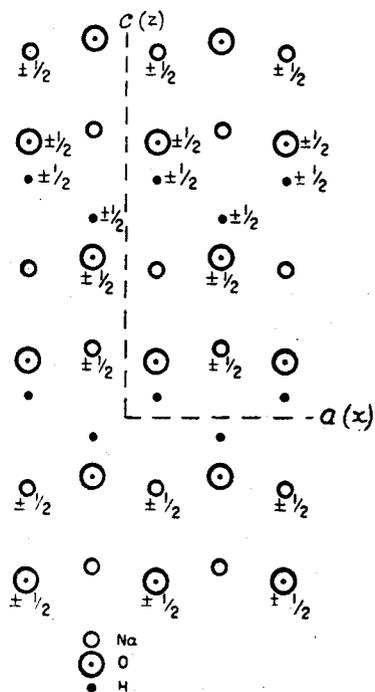
(ii) *Sodium hydroxide*.—The group characters and selection rules of the various irreducible representations of the group D<sub>2h</sub>, to which NaOH belongs, are reproduced in Table II following. Figure 1 in the text illustrates the structure of NaOH.

TABLE II

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	Activity
$A_g$ ..	1	1	1	1	1	1	1	1	R.E. only
$B_{1g}$ ..	1	1	-1	-1	1	1	-1	-1	R.E. only
$B_{2g}$ ..	1	-1	1	-1	1	-1	1	-1	R.E. only
$B_{3g}$ ..	1	-1	-1	1	1	-1	-1	1	R.E. only
$A_u$ ..	1	1	1	1	-1	-1	-1	-1	Inactive in both
$B_{1u}$ ..	1	1	-1	-1	-1	-1	1	1	I.R. only
$B_{2u}$ ..	1	-1	1	-1	-1	1	-1	1	I.R. only
$B_{3u}$ ..	1	-1	-1	1	-1	1	1	-1	I.R. only
$U_R$ ..	6	6	0	0	0	0	6	6	

$U_R$  = number of atoms invariant under the group operation.

$x, y, z$  correspond to the crystallographic axes  $a, b$  and  $c$  respectively.



TEXT-FIG. 1. Projection of the structure of NaOH in a plane normal to the  $b$ -axis.  $\pm \frac{1}{2}$  indicate that the atoms are at the levels  $\pm \frac{1}{2}b$ . The remaining atoms are in the plane passing through the origin.

TABLE III

Class	$n_i$	T	T'	R	$n_i'$	Activity
$A_g$ ..	3	0	2	0	1	R.E.
$B_{1g}$ ..	0	0	0	0	0	R.E.
$B_{2g}$ ..	3	0	2	1	0	R.E.
$B_{3g}$ ..	3	0	2	1	0	R.E.
$A_u$ ..	0	0	0	0	0	Inactive
$B_{1u}$ ..	3	1	1	0	1	I.R.
$B_{2u}$ ..	3	1	1	1	0	I.R.
$B_{3u}$ ..	3	1	1	1	0	I.R.

$n_i$  = Total number of vibrations; T = pure translations; T' = Translational oscillations; R = rotational oscillations;  $n_i'$  = number of hydroxyl vibrations.

Table III shows the distribution of the several frequencies under the various classes. Group theoretical analysis shows that there should appear in the Raman effect 9 vibrations, *i.e.*, three each under the classes  $A_g$ ,  $B_{2g}$ , and  $B_{3g}$ . We have already seen that the symmetric internal vibration of the hydroxyls belongs to class  $A_g$ . Since the three pure translations of the unit cell belong to the classes  $B_{1u}$ ,  $B_{2u}$  and  $B_{3u}$  and since no rotational oscillations can occur about the two-fold axis  $C_2(z)$  owing to the hydroxyl groups lying parallel to it, the remaining two vibrations under  $A_g$  should be of the translatory type. These can be described as arising from the translatory movements of the sodiums and hydroxyls along the  $z$ -axis and symmetrically with respect to the centre of inversion. Considerations analogous to the above show that there should be one rotational oscillation under each one of the classes  $B_{2g}$  and  $B_{3g}$ , the rotations of the hydroxyl groups being respectively about the  $y$  and  $x$ -axes. Also, there occur two oscillations under each one of the classes  $B_{2g}$  and  $B_{3g}$  due to the translatory movements (symmetrically with respect to the centre of inversion) of the Na's and OH's along the  $x$  and  $y$ -axes respectively.

Contrary to the theoretically expected number of eight, only five frequency shifts have been observed. However, a tentative explanation for the smaller number of observed shifts can be offered. The unit cell parameters determined by Ernst for NaOH show that for this orthorhombic

structure the lattice constants  $a$  and  $b$  are equal to each other within the limits of experimental error. Hence, each of the double layers possesses tetragonal symmetry, the four-fold axis (*i.e.*,  $c$ -axis) being shifted by  $a/2$  as we pass from one double layer to another. If we neglect the weak coupling between the double layers which are far apart, it may easily be seen that the translatory movements along  $x$  and  $y$  axes (and also the rotational oscillations about the  $x$  and  $y$ -axes) would be of nearly the same frequency. In other words, the corresponding frequencies coming under the classes  $B_{2g}$  and  $B_{3g}$  would fall too close to each other to be resolved and only five frequencies would be observed.

The assignments of the individual frequency shifts to specific symmetry modes are arrived at from the following considerations. Even though each Na is surrounded by five hydroxyls, it is the hydroxyl nearest to it (along the  $z$ -axis) which can be identified as forming the NaOH group, the other group in the unit cell being related to it by the centre of inversion. (For the sake of convenience we shall describe here only the movements of the atoms in one group, the movements in the other being such that the vibration is symmetric with respect to the centre of inversion.) The translatory oscillations of Na and OH ions can actually be divided into (i) the movements of the Na and the hydroxyl against each other and (ii) the movement of the NaOH group as a whole. The former would be of high frequencies and amongst them the movement of the Na against the OH along the  $z$ -axis would be of highest frequency and hence the shift at  $380 \text{ cm.}^{-1}$  is identified with this mode ( $A_g$ ). Similar translatory oscillations of the Na's and OH's of the unit cell with their displacements parallel to the  $x$  and  $y$  axes would be of lower frequency and the frequency shift at  $291 \text{ cm.}^{-1}$  therefore represents these modes ( $B_{2g}$  and  $B_{3g}$ ). The translatory movements of the NaOH group as a whole parallel to the  $x$ ,  $y$  and  $z$  axes would be of low frequencies and are to be identified with the shifts  $98$  and  $114 \text{ cm.}^{-1}$ . Amongst these, the more intense line at  $98 \text{ cm.}^{-1}$  conceivably arises due to the overlap of the modes  $B_{2g}$  and  $B_{3g}$  involving movements parallel to  $x$  and  $y$  axes and the other shift at  $114 \text{ cm.}^{-1}$  due to movements normal to the layer ( $A_g$ ). The rather strong shift at  $215 \text{ cm.}^{-1}$  is identified with the rotational oscillations about the  $y$  and  $x$ -axes (*i.e.*, classes  $B_{2g}$  and  $B_{3g}$ ) since rotational oscillations of anisotropic groups usually give rise to strong Raman shifts. The appearance of the translatory oscillations with adequate intensity is due to the coupling generally present between translatory and rotatory symmetry modes.

Sodium hydroxide undergoes a structural transformation at about  $300^\circ \text{ C}$ . The crystal structure of the high temperature form is not known. Whether the exceptionally large widths of the lines  $215 \text{ cm.}^{-1}$  and  $380 \text{ cm.}^{-1}$

are connected with this transformation (as in the case of the  $206\text{ cm.}^{-1}$  Raman line in  $\alpha$ -quartz) is not quite clear.

(iii) *The monohydrates of sodium and potassium hydroxides.*—As a result of the numerous groups present in the unit cells of these two crystals, the number of lattice vibrations theoretically Raman active in the case of  $\text{NaOH}\cdot\text{H}_2\text{O}$  and  $\text{KOH}\cdot\text{H}_2\text{O}$  is quite large, being respectively 56 and 28. Nine lattice frequencies have been observed in  $\text{NaOH}\cdot\text{H}_2\text{O}$  and eight in  $\text{KOH}\cdot\text{H}_2\text{O}$ . The following are plausible reasons for the small number of shifts observed. (i) Several of the allowed lines may be inherently weak. (ii) The large separation between the groups as in the case of the layered structure of  $\text{NaOH}\cdot\text{H}_2\text{O}$  indicates that the number of actual units that are responsible for the observed frequencies might be fewer than that rigorously considered. (iii) As is evident from the fact of the low transition points of the hydrates, the water molecules are feebly bound to the structure and their translatory and rotatory movements would be of very low frequencies and weak intensities. From a comparison of the spectrum of  $\text{NaOH}\cdot\text{H}_2\text{O}$  with that of  $\text{NaOH}$  it may be seen that there exists a correspondence between some of the frequencies. In particular, the intensities of the shifts  $240\text{ cm.}^{-1}$  in  $\text{NaOH}\cdot\text{H}_2\text{O}$  and  $220, 232\text{ cm.}^{-1}$  in  $\text{KOH}\cdot\text{H}_2\text{O}$  and their correspondence to the strong  $215\text{ cm.}^{-1}$  shift in  $\text{NaOH}$  indicate that they also arise most probably due to the rotational oscillations of the hydroxyls. The shifts at  $213$  and  $243\text{ cm.}^{-1}$  observed in  $\text{LiOH}\cdot\text{H}_2\text{O}$  may also be due to the rotational oscillations of the hydroxyls.

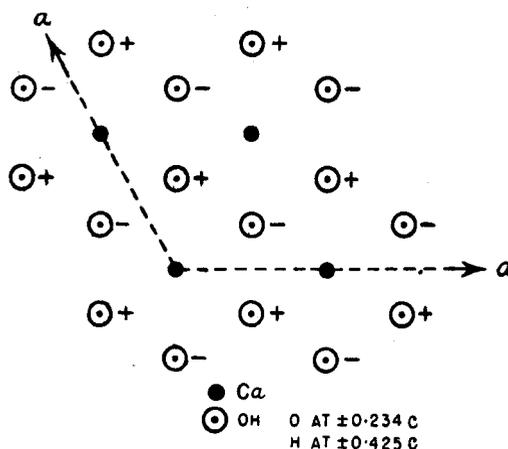
(iv) *Calcium hydroxide.*—In view of the fact that  $\text{Ca}(\text{OH})_2$  figures in our discussions in Part III also, the group characters and selection rules of the irreducible representations of the group  $D_{3d}$  to which it belongs are reproduced in Table IV. In it are also shown the number of vibrations under the different classes and their resolution into the translatory, rotatory and internal oscillations. Figure 2 in the text illustrates the structure of  $\text{Ca}(\text{OH})_2$ .

Group theoretical analysis shows that the Raman spectrum should exhibit four frequency shifts, two each under the classes  $A_{1g}$  and  $E_g$ . We have already identified the internal vibrations of the hydroxyls symmetrically with respect to the centre of inversion as belonging to  $A_{1g}$ . The remaining frequency under  $A_{1g}$  represents the translatory movements, along the  $c$ -axis, of the hydroxyls symmetrically with respect to the centre of inversion. Similar symmetric translational oscillations of the hydroxyls in the plane perpendicular to the  $c$ -axis fall under the doubly degenerate class  $E_g$ . The rotational oscillations of the hydroxyls about any axis lying in the plane

TABLE IV

$D_{3d}$	E	$2C_3$	$3C_2$	$i$	$2S_6$	$3\sigma_d$	$n_i$	T	T'	R	$n_i'$	Activity
$A_{1g}$ ..	1	1	1	1	1	1	2	0	1	0	1	R.E. only
$A_{2g}$ ..	1	1	-1	1	1	-1	0	0	0	0	0	Inactive in both
$E_g$ ..	2	-1	0	2	-1	0	2	0	1	1	0	R.E. only
$A_{1u}$ ..	1	1	1	-1	-1	-1	0	0	0	0	0	i.a. both
$A_{2u}$ ..	1	1	-1	-1	-1	1	3	1	1	0	1	I.R. only
$E_u$ ..	2	-1	0	-2	1	0	3	1	1	1	0	I.R. only
$U_R$ ..	5	5	1	1	1	5						

R.E. = Raman effect; I.R. = infra-red; i.a. = inactive.



TEXT-FIG. 2. Projection of the structure of  $\text{Ca}(\text{OH})_2$  in a plane normal to the  $c$ -axis. + and - indicate the levels of the atoms. The hydroxyl groups are parallel to  $c$ . The Ca atoms are in the plane passing through the origin.

perpendicular to the  $c$ -axis belong to the class  $E_g$ . The calciums do not take part in any of the Raman active vibrations owing to their being located at the centres of inversion.

As indicated by theory, in the case of  $\text{Ca}(\text{OH})_2$  three lattice frequency shifts are observed at 247, 282 and 359  $\text{cm}^{-1}$ . The observed shifts, however, fall within too limited a range of frequencies to permit their identification with specific symmetry modes.

(v) *Octahydrated hydroxides of strontium and barium.*—Since the lattice spectra of  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  and  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  exhibit respectively only eight and nine frequency shifts (which are far fewer than would be indicated by the presence of the large number of groups in the unit cell) and also since the positions of the hydrogen atoms have not been determined, no attempt is made here to enumerate the frequencies theoretically. The reasons advanced in the cases of  $\text{NaOH} \cdot \text{H}_2\text{O}$  and  $\text{KOH} \cdot \text{H}_2\text{O}$  for the meagreness of the results observed in this region of the spectrum apply equally well to these cases also.

The unit cell parameters of  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  are given by  $a = 9.35$ ;  $b = 9.28$ ;  $c = 11.87 \text{ A.U.}$ , and  $\beta = 99^\circ$ . The substance exhibits a small optic axial angle of  $8^\circ 33'$ . The unit cell dimensions of  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  are  $a = 9.00$ ;  $c = 11.58 \text{ A.U.}$  and are comparable to that of  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ . It appears highly likely that the structure of  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  is only a slightly distorted version of  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  and hence a comparison of their spectra is of interest.

In the lattice frequency region and in the high frequency region as well, a fair agreement between the frequency shifts of  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  and  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  may be noticed to exist. An explanation for the correspondence between the two spectra is possible since the unit cell parameters in the two cases are comparable and also since the monoclinic group  $C_{2h}$  to which  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  belongs is a subgroup of the tetragonal group  $D_{4h}$  of  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ . From the point of view of Raman effect studies, only the following correlations existing between the five symmetric representations of  $D_{4h}$  and the two symmetric representations of  $C_{2h}$  are of interest. They are: (1)  $A_{1g} \rightarrow A_g$ ; (2)  $A_{2g} \rightarrow B_g$ ; (3)  $B_{1g} \rightarrow A_g$ ; (4)  $B_{2g} \rightarrow B_g$ ; (5)  $E_g \rightarrow A_g + B_g$ . In the group  $D_{4h}$  only the four symmetric classes  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$  and  $E_g$  are Raman active,  $A_{2g}$  being inactive. In  $C_{2h}$  both  $A_g$  and  $B_g$  are Raman active. Hence, as a result of the lowering of the symmetry from  $D_{4h}$  to  $C_{2h}$  the inactive vibrations corresponding to  $A_{2g}$  of  $D_{4h}$  become active and the doubly degenerate vibrations ( $E_g$ ) split into two. The lines under the totally symmetric class are often observed to be of considerable intensity. The transformation of  $B_{1g}$  of  $D_{4h}$  into  $A_g$  of  $C_{2h}$  might hence mean that the corresponding line observed with the substance of lower symmetry would appear with enhanced intensity. The appearance of the hydroxyl frequency at  $3529 \text{ cm.}^{-1}$  rather strongly in  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  in contrast to its weak counterpart at  $3536 \text{ cm.}^{-1}$  in  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  is therefore intelligible. The appearance of doublets in the lattice spectrum of  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  corresponding to single frequencies observed in  $\text{Sr}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$  (e.g.,  $230 \rightarrow 205-220$ ;  $297 \rightarrow 276 \text{ to } 287$ ) is obviously due to the splitting arising from the

removal of degeneracy. Here again, the two frequencies 205 and 220  $\text{cm.}^{-1}$  (corresponding to the line 215  $\text{cm.}^{-1}$  due to rotational oscillations of the hydroxyls in NaOH) represent the rotational oscillations of the hydroxyls, the former which is more intense belonging to the class  $A_g$  and the latter to  $B_g$ . The frequency shifts 230 and 297  $\text{cm.}^{-1}$  belong to the doubly degenerate class  $E_g$  of  $D_{4h}$ . It is evident that these corresponding frequencies represent predominantly the translatory and rotatory oscillations of the hydroxyls since the vibrations in which the bariums and strontiums participate would be of different frequencies owing to the large difference in their atomic masses.

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## 5. SUMMARY

The paper discusses the results reported in Part I in relation to the crystal structures of the substances. From a comparison of the facts with the theoretically expected picture of the spectrum, the salient features exhibited by the spectra have been explained, in addition to identification and assignment of the frequencies wherever feasible. The progressive variations in the hydroxyl shifts exhibited by the different hydroxides and their hydrates are explicable as due to the interactions of the hydroxyls with each other and also with their neighbouring water molecules in the case of the hydrates.

## 6. REFERENCES

1. Ernst, T. .. *Zeit. Physik. Chem.*, 1933, **20 B**, 65.
2. Pepinsky, R. .. *Phys. Rev.*, 1939, **55**, 1115. (See also *Strukturbericht*, Band VII, 1939, pp. 4 *et seq.*).
3. Ernst, T. .. *Angew. Chem.*, 1948, **60 A**, 77.
4. Busing, W. R. .. *J. Chem. Phys.*, 1955, **23**, 933.
5. Wunderlich, J. A. .. *Bull. Soc. Fran. Miner., Crist.*, 1958, **81**, 287.
6. Clastre, J. .. *Acta Cryst.*, 1954, **7**, 638.
7. Bragg, W. L. .. *Atomic Structure of Minerals*, Oxford University Press (1937), pp. 108.
8. Busing, W. R. and Levy, H. A. .. *J. Chem. Phys.*, 1957, **26**, 563.
9. Petch, H. E. .. *Canad. Jour. Phys.*, 1957, **35**, 983.
10. Smith, H. G. .. *Acta Cryst.*, 1953, **6**, 604.
11. Ramaseshan, S. .. Private communication.
12. Megaw, H. D. .. *Zeit. Krist.*, 1934, **87**, 185.
13. Bhagavantam, S. .. *Proc. Ind. Acad. Sci.*, 1941, **13 A**, 543.

14. Levy, H. A. and Peterson, S. W. *Rev. Mod. Phys.*, 1958, **30**, 101.
15. Bernal, J. D. and Megaw, H. D. *Proc. Roy. Soc.*, 1935, **151 A**, 384.
16. Partington, J. R. .. *General and Inorganic Chemistry*, McMillan & Co., London, 1958, pp. 322.
17. Krishnamurti, D. .. *Proc. Ind. Acad. Sci.*, 1959, **50 A**, 223.
18. Wilson, E. B., *et al.* .. *Molecular Vibrations*, McGraw-Hill Book Co., 1955.
19. Herzberg, G. .. *Infra-red and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., Inc., 1945, pp. 280 *et seq.*
20. Bhagavantam, S. and Venkatarayudu, T. *Theory of Groups and Its Application to Physical Problems*, Andhra University, Waltair, 1948.