THE CONSTITUTION OF SOME BORIC OXIDE COMPOUNDS.

JAMES H. HIBBEN.

ABSTRACT.

The chemical constitution and spacial configuration of boric acid, sodium metaborate, and borax have been investigated by means of the Raman effect. The Raman spectra of these compounds as crystals and in aqueous solution were determined and compared with the spectra from boric oxide and borax glasses.

These results show that, although a ring structure for boric acid is not entirely excluded, in solution the more probable structure corresponds to a plane equilateral triangle, the oxygen atoms being located at the corners and the boron atom at the center. Sodium metaborate is not a linear molecule but slightly bent, and has the symmetry C_{2v}. Borax, or sodium tetraborate, appears to be a chain molecule in the crystalline state, but in solution dissociates into boric acid and sodium metaborate. The addition of hydrochloric acid to a borax solution converts all the borax to boric acid. When sodium hydroxide is added to boric acid, in solution, the acid neutralized is converted immediately to sodium metaborate. The spectrum from borax glass bears some resemblance to that of the crystalline tetraborate, but differs quite appreciably from that of boric oxide.

Boric oxide, like silica, may exist in both the crystalline and amorphous states. The boric oxides, also like silica, may combine with the alkalis to produce a variety of crystalline or amorphous compounds and solutions. Although silica has been investigated by both spectrographic and diffraction pattern methods, boric oxide, boric acid, and boric acid salts have been examined by Raman spectra methods only recently.

Silica, as is well known, does not correspond to the triatomic molecule having the formula SiO_2, but rather exists in the crystalline and amorphous states as a tetrahedral molecule having the symmetry T_d and the effective constitution corresponding to SiO_4. A molecule of this type should give rise to four Raman lines, of which one is polarized and corresponds to a symmetrical vibration, and three are depolarized. These four frequencies occur near $\Delta\tilde{\nu}$500, 600, 800, and 1000-1100 cm.$^{-1}$, where $\Delta\tilde{\nu}$ represents the difference between the frequency of the Raman line and the exciting radiation expressed in wave numbers per centimeter. Actually, some of these frequency shifts are broken up into more than one component, probably because of a lack of completely regular tetrahedral symmetry.

With the boric oxide compounds the situation is quite different. Here it is possible to have a molecule of the type ABA representing the metaborate ion, which in the linear form would have the symmetry $C_{\infty h}$ and give rise to but a single Raman line. On the other hand, the molecule may be bent, in which case the symmetry would be C_{2v} and there should appear three Raman frequencies corresponding to the ν_π, ν_σ, and δ_π types of oscillation. For boric acid the most probable arrangement would be a molecule of the type AB_3 having the symmetry D_{3h} in which a" three B groups would lie at the corners of a plane triangle with the A atom in the center. This is similar to the arrangement of the NO_3 group in the nitrate ion and the CO_3 group in the carbonate ion. This configuration would give rise to three Raman lines, two of which would be doubly degenerate, and one would correspond to the symmetrical expansion and contraction of the molecule.

Recently, Ananthakrishnan[1] observed for boric acid in solution only one line at 855(3),[2] and for the crystalline H_3BO_3 two additional frequencies near 3180(3) and 3256(1). In the crystalline boric acid, Nielsen[3] has observed other frequencies, $\Delta\tilde{\nu}$ 503 (4), 1065 (0), and 1155 (0). Of these frequencies, those in the 3000-3600 region are connected solely with the O$\leftrightarrow$H oscillation. These results, together with the new observations of the writer and all other Raman spectra data on boric acid and its derivatives, are shown in the table.

Ananthakrishnan attempts to correlate the largest pair of frequencies observed by him with a "hydroxyl bond" in contradistinction to a "hydrogen bond." The evidence for this distinction is not well founded, first, because the O-H frequency is present, presumably in acids supposed to exhibit hydrogen bonding, and second, because the diminishing of the O-H frequency in the alkali hydroxides from $\Delta\tilde{\nu}$ 3600 to 3300, or less, does not seem to be significant of any hydroxyl bonding. The same reduction in the typical O-H shift occurs in most crystal hydrates.

In addition to the intense line at $\Delta\tilde{\nu}$ 875 in an aqueous solution of boric acid, Hibben[4] has observed also two other lines of fair intensity at $\Delta\tilde{\nu}$ 506(2) and 1420(1). These two fre-

[1] Ananthakrishnan, R.: Proc. Indian Acad. Sci., 5, 285, 1937.
[2] Any whole digit in parenthesis following a number represents the relative intensity of this line on the basis of ten.
[3] Nielsen, J. Rud: Personal communication.
[4] Hibben, J. H.: Reported in this communication.

quencies are broad and diffuse. There occur, furthermore, two lines—or possibly one band—at $\Delta\tilde{\nu}$ 1060 and 1130. If this were a single band the intensity center would be near $\Delta\tilde{\nu}$ 1100. These two bands (or band) are exceedingly weak and probably correspond to the equivalent frequencies seen in the crystals, where they appear as reasonably sharp lines, although with intensities that are very feeble.

It is to be noted, therefore, that the spectrum obtained from boric acid solutions is approximately identical with that observed in the crystals with the exception of the line attributable to the O-H oscillations which are naturally masked in aqueous solutions by the O-H vibrations of the water molecule. From this similarity one may reasonably draw the conclusion that boric acid in solution contains the O-H group attached to the boron atom and that there is no possibility of the existence of a molecule having the form H_3BO_3. This is substantiated further by the lack of any B-H line corresponding to the P-H line found in H_3PO_3. There exist, then, three frequencies for boric acid which are beyond dispute, namely, $\Delta\tilde{\nu}$ 506, 873, and 1420. This last frequency shift differs too widely from a combination of $\Delta\tilde{\nu}$ 873 with 506 to be a combination frequency. The relative grouping and intensity of these three lines are reminiscent of the three Raman shifts at $\Delta\tilde{\nu}$ 710, 1050, and 1340 observed in the nitrate ion.

Consider next the simplest salt of boric acid, sodium metaborate. In solution this was originally supposed to yield 253(1) and 1403(4) by Ghosh and Das,[5] while Nielsen and Ward[6] reported $\Delta\tilde{\nu}$ 749. More recently, Nielsen[3] has observed an additional line at $\Delta\tilde{\nu}$ 950(1). Hibben[4] also finds $\Delta\tilde{\nu}$ 747(6), but in addition, the broad band extending from $\Delta\tilde{\nu}$ 1132 to 1276 which may be made up of two separate diffused lines. The band reported from $\Delta\tilde{\nu}$ 400 to 500 in the table is undoubtedly the hindered rotational band observed in water. Crystalline sodium metaborate tetrahydrate, according to Nielsen,[3] yields $\Delta\tilde{\nu}$ 741(5) and two frequencies at $\Delta\tilde{\nu}$ 3190(1) and 3555(1). These last two frequencies are connected with the hydroxyl group in the hydrated crystals, while no other frequencies were observed between $\Delta\tilde{\nu}$ 741 and 3190. They are probably in existence, but are too difficult to discern when small crystals are used.

[5] Ghosh, J. C., and Das, S. K.: J. Phys. Chem., 36, 586, 1932.
[6] Nielsen, J. Rud, and Ward, N. E.: J. Chem. Phys., 5, 201, 1937.

TABLE I.

Raman Spectra of Some Boric Oxide Compounds.

Substance	*Raman shifts*							
1. $B(OH)_3$ (Cryst.)			503(4)				880(6)	
2. $B(OH)_3$ (Sol.)			506(2)				873(6)	
3. $NaBO_2$ (Sol.)	253(1)							
4. $NaBO_2$ (Sol.)		400-500			747(6)			
5. $Na_2B_2O_4$ (Sol.)					743(5)			950(1)
6. $Na_2B_2O_4.4H_2O$					741(5)			
7. $Na_2B_4O_7.4H_2O$			500(2)	575(0)	735(3)	850(0)		934(6)
8. $Na_2B_4O_7.10H_2O$				578(1)		853(1)	891(1)	942(1)
9. $(NH_4)_2B_4O_7$ (Cryst.)		420(1)	525(1)		714(5)			
10. $Na_2B_4O_7$ (Sol.)		492-517		570(0)	747(6)		875(6)	950-1000(0)
11. $H_3BO_3 + NaOH$, 4:1					747(1)		875(6)	
12. $H_3BO_3 + NaOH$, 2:1				575(0)	747(2)		875(4)	
13. $H_3BO_3 + NaOH$, 1¼:1		400-500(0)		575(0)	746(4)		875(3)	
14. $H_3BO_3 + NaOH$, 1:2					747(5)			949(0)
15. $H_3BO_3 + NaOH$, 1:3					744(5)			
16. $Na_2B_4O_7 + 4HCl$							873(10)	
17. $Na_2B_4O_7$ (Glass)		430-535(0)			760(5)			950-1000(0)
18. B_2O_3 (Glass)						803(8)		
19. B_2O_3 (Glass)				602(1)		806(5)		
20. BO_3 (Ion)					700			915

TABLE I (continued).

Substance	*Raman shifts*								*References*
1. $B(OH)_3$ (Cryst.)	1065(0)		1155(0)			3180(3)	3256(1)	3574(3)	1, 3
2. $B(OH)_3$ (Sol.)	1060(0)	1130(0)			1420(1)				1, 4
3. $NaBO_2$ (Sol.)					1403(4)				5
4. $NaBO_2$ (Sol.)			1132(0)	1276(0)					4
5. $Na_2B_2O_4$ (Sol.)									3, 6
6. $Na_2B_2O_4.4H_2O$						3190(1)		3555(1)	3
7. $Na_2B_4O_7.4H_2O$		1100?					3269(2)	3343(3) 3425(2) 3552(10)	4
8. $Na_2B_4O_7.10H_2O$								3340(1) 3455(1) 3574(1)	3
9. $(NH_4)_2B_4O_7$ (Cryst.)		1100(2)							7
10. $Na_2B_4O_7$ (Sol.)		1132(0)	1161(0)		1420(0)				4
11. $H_3BO_3 + NaOH$, 4 : 1	1060(0)	1132(0)			1420				4
12. $H_3BO_3 + NaOH$, 2 : 1									4
13. $H_3BO_3 + NaOH$, 1¼ : 1 ..									4
14. $H_3BO_3 + NaOH$, 1 : 2			1150(0)	1220(0)					4
15. $H_3BO_3 + NaOH$, 1 : 3			1160(0)	1219(0)					4
16. $Na_2B_4O_7 + 4HCl$					1420(0)				4
17. $Na_2B_4O_7$ (Glass)	1077-1127(0)				1310-1520(0)				10
18. B_2O_3 (Glass)				1261(0)				3594(1)? 4983(1)?	8
19. B_2O_3 (Glass)	1030(1)		1120(1)	1257(0)					9, 10, 11
20. BO_3 (Ion)					1445				8

The principal and probably the symmetrical vibration, therefore, of the metaborate ions occurs at $\Delta\tilde{\nu}$ 747. This is present not only in solution but also in crystals, although in the latter it is reduced by a few wave numbers. This same frequency also occurs in sodium tetraborate, whose spectrum will be discussed shortly. It is obvious that the spectrum of sodium metaborate differs widely from that observed in boric acid. It was supposed originally that the BO_2 ion represented a linear grouping of a molecule of the type ABA. The appearance of additional Raman lines, however, would make this an impossibility for the reasons already mentioned in discussing molecules having the symmetry C_{2v} and a bent structure. An example of this type of molecule is SO_2, which shows three principal Raman lines at $\Delta\tilde{\nu}$ 525, 1144, and 1334, of which the middle frequency is the most intense. Zachariasen, from X-ray measurements, has concluded that the anhydrous metaborate exists in a ring formation somewhat similar to the benzene ring with alternating boron and oxygen atoms. If this structure persisted in solution it would exist as a B_3O_6 ion. The principal objection to such an hypothesis is a dearth of Raman lines. Such a structure could have twenty-one possible different frequency shifts. The symmetry conditions would undoubtedly reduce this number by a considerable amount, but it seems probable in this case that the number would exceed one or two Raman lines.

In the spectra observed from sodium tetraborate (borax), $Na_2B_4O_7.10H_2O$, Nielsen[3] has found about four lines of equal intensity, in addition to the group of three attributable to the water molecule in the crystal hydrate. Hibben[4] likewise has observed a group of similar lines in kernite, $Na_2B_4O_7.4H_2O$, with the exception of $\Delta\tilde{\nu}$ 891 and inclusive of a strong line at $\Delta\tilde{\nu}$ 735 which was not noted by Nielsen. This shift is slightly reduced from the value near $\Delta\tilde{\nu}$ 747 in the solution of sodium tetraborate. Curiously enough, this shift was reported by Joglekar and Thatte[7] for ammonium tetraborate in the crystalline form at $\Delta\tilde{\nu}$ 714. At the same time, however, no shift was noted by them at $\Delta\tilde{\nu}$ 934. From the intensity observed for this line it apparently is the type of vibration equivalent to that which occurs near $\Delta\tilde{\nu}$ 875 but is displaced to a higher frequency in the crystals. The spectrum obtained from the saturated solution agrees fairly well with that observed in the crystals

[7] Joglekar, M. S., and Thatte, V. N.: Z. Physik, 98, 692, 1936.

with the exception of the possible splitting of $\Delta\tilde{\nu}$ 875 into several components. There is also a weak band which may be made up of a pair of lines near $\Delta\tilde{\nu}$ 1000 and 1130. The actual magnitude of these shifts can be only estimated, as these bands are too feeble and too diffused to measure with accuracy.

The question may be raised why such a strong pair of lines at $\Delta\tilde{\nu}$ 747 and 875 should appear from an aqueous solution of sodium tetraborate when the metaborate possesses only one

Fig. 1. Microphotometer tracing of the spectrum of O-H bands in $Na_2B_4O_7.4H_2O$.

strong line, and boric acid similarly has only one. Furthermore, the second strong line in the tetraborate coincides with that observed from boric acid. In fact, the entire spectrum of sodium tetraborate resembles, or is identical with, the combined spectrum of boric acid and sodium metaborate. Another peculiarity is the extreme intensity of the line at $\Delta\tilde{\nu}$ 3552 in the tetrahydrate. This line is much stronger than the usual lines that may be attributed to water of crystallization, and appears near the observed shift for the OH group in boric acid. This would seem to indicate the possibility of an actual hydroxyl group of constitution being present in the crystalline

tetraborate. This is shown in the microphotometer tracing in Fig. 1.

In an attempt to throw some light on this subject, Hibben[4] initiated a series of studies of solutions of boric acid containing variable amounts of sodium hydroxide. The results of these experiments are indicated in Figs. 2 and 3, which show not

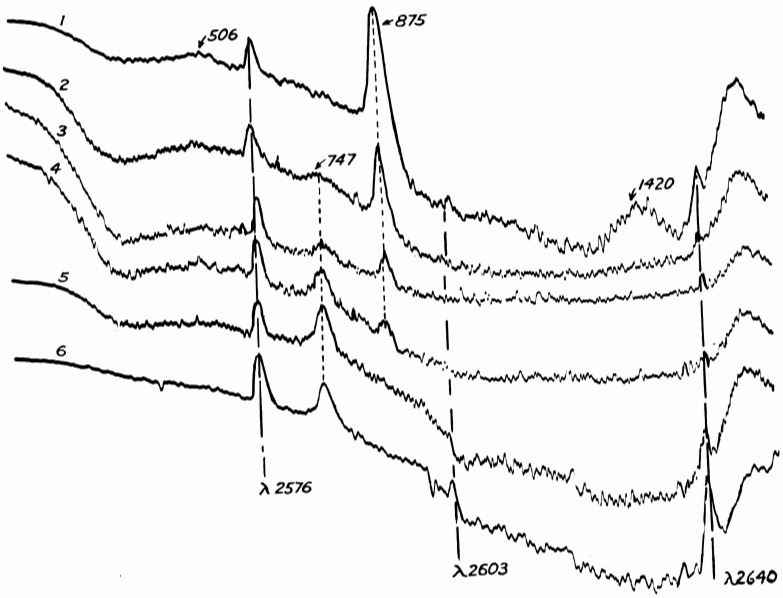


Fig. 2. Microphotometer tracings of the Raman spectra obtained from a solution of boric acid containing varying amounts of sodium hydroxide. Curve 1 represents the spectrum from a solution of pure boric acid; curves 2 to 6 are from a 0.18 molal boric acid solution to which has been added sodium hydroxide to yield the following ratios of boric acid to sodium hydroxide respectively: 4:1; 2:1; 1¼:1; 1:2; 1:3.

only the effect of the addition of sodium hydroxide to boric acid, but also give a comparison spectrum of the crystalline tetraborate and metaborate. In Fig. 2, line one represents the spectrum of aqueous boric acid solution. This microphotometer tracing shows the three strongest lines. The weakest ones were too feeble to register on the microphotometer but are visible on the original plates. The addition of a small quantity of sodium hydroxide to these solutions immediately produces a

broad band whose maximum is at $\Delta\tilde{\nu}$ 747 and a diminution in intensity of $\Delta\tilde{\nu}$ 875. As sodium hydroxide is added, the $\Delta\tilde{\nu}$ 875 progressively decreases and the 747 becomes less broad and increases in intensity. When the ratio of the boric acid mole-

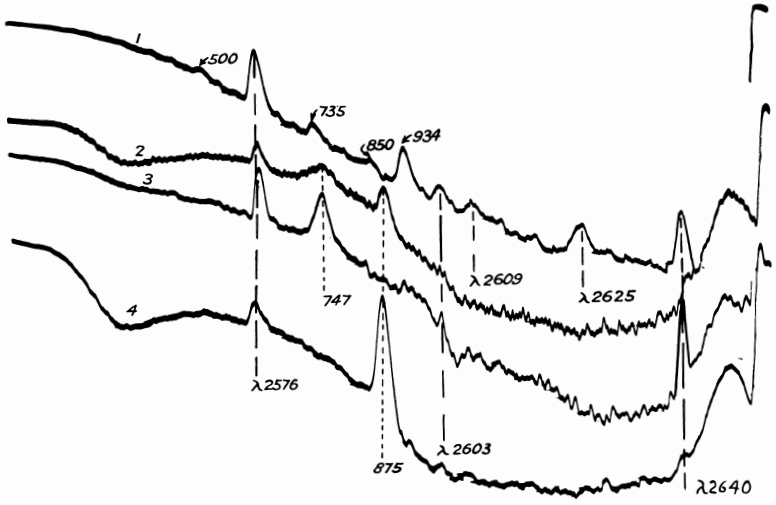


Fig. 3. Microphotometer tracings of the Raman spectra obtained from some salts of boric acid. Curve 1 represents the spectrum from $Na_2B_4O_7 \cdot 4H_2O$; curve 2 is from an aqueous solution of sodium tetraborate; curve 3 is from an aqueous solution of sodium metaborate; and curve 4 is from an aqueous solution of sodium tetraborate to which has been added a molecular excess of hydrochloric acid.

cules to sodium hydroxide molecules has the value of 2:1, or sufficient sodium hydroxide is added to convert all the boric acid to sodium tetraborate, according to the equation,

$$2NaOH + 4H_3BO_3 \longrightarrow Na_2B_4O_7 + 7H_2O,$$

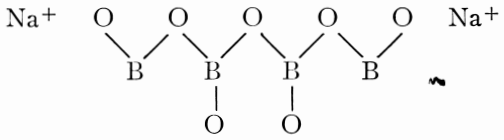
then the intensities of these two lines are nearly equal, giving a spectrum which is comparable with that observed for the tetraborate. When the molecular ratios are 1 : 1, and sodium hydroxide has been added to form $NaBO_2$, according to the equation,

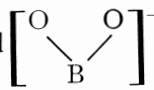
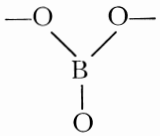
$$NaOH + H_3BO_3 \longrightarrow NaBO_2 + 2H_2O.$$

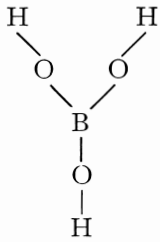
the line at $\Delta\tilde{\nu}$ 875 completely disappears. The addition of greater quantities of sodium hydroxide causes no further change in the principal line of the spectrum. The addition of an excess quantity of hydrochloric acid to a solution of sodium tetraborate causes the disappearance of $\Delta\tilde{\nu}$ 747, as shown in Fig. 3, and the strengthening of 875, or in short, the reversion to boric acid.

These results are best explained on the assumption that sodium metaborate, $NaBO_2$, is produced initially by the addition of sodium hydroxide to boric acid. Consequently there is a mixture of boric acid and the metaborate always present until one molecule of the base has been added for each molecule of the acid, at which time the conversion is complete. When sodium tetraborate is dissolved in water, it dissociates into $2NaBO_2 + 2B(OH)_3$, where the $NaBO_2$ is ionized into Na^+ and BO_2^- ions. According to this conception, the tetraborate is completely, or nearly completely dissociated in solution.

If the crystalline sodium tetraborate has the following chain formation:



then the two end  groups would have a vibration similar to sodium metaborate, and the intermediate  groups should have a vibration resembling the

 group.

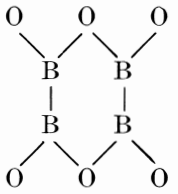
M. K. Sen and A. K. Sen Gupta have investigated the infra-red absorption spectra of the borates of lithium, potassium, calcium, magnesium, copper, and lead. These authors conclude that the borate ion has a plane configuration and somewhat resembles that of the NO_3 and CO_3 ions. It is presumed from this analogy that they refer to the existence of a BO_3 ion. The origin of a BO_3 ion from the $R_2B_4O_7$ is not entirely clear. The nearest approach is the BO_3 group in the chain of the crystalline tetraborate as indicated above. The absorption frequencies observed by them in the infra-red correspond to $\Delta\tilde{\nu}$ 709, 917, and 1315. The fourth frequency calculated by them to be the inactive vibration, so far as infra-red absorption is concerned, would fall at $\Delta\tilde{\nu}$ 1111. This vibration should correspond to the ν_1 type of oscillation or the symmetrical polarized frequency which appears most strongly in the Raman effect. This is obviously at $\Delta\tilde{\nu}$ 934, and it is difficult to correlate this result with the calculated $\Delta\tilde{\nu}$ 1111.

On taking up next the question of boric oxide as found in boric oxide glass, it can be seen that the observations of different observers are none too concordant. In the table referred to, item 18 gives the observations of Langenberg.[8] Item 19 includes the results of Avramenko,[9] Gross and Vuks,[10] and Kujumzelis.[11] Of these frequency shifts, only $\Delta\tilde{\nu}$ 806 and 1260 were obtained by all the workers. Gross and Vuks record $\Delta\tilde{\nu}$ 1120 while Avramenko adds $\Delta\tilde{\nu}$ 602 and 1030. The only lines which may be ascribed to boric oxide with absolute certainty are, therefore, $\Delta\tilde{\nu}$ 806 and 1260. Item 20 refers to what Langenberg is pleased to call the BO_3 ion in glasses.

From the standpoint of infra-red absorption, one may consider, then, that there are two bands which have their counterpart in the Raman effect near $\Delta\tilde{\nu}$ 700 and 915, but that $\Delta\tilde{\nu}$ 1315, observed in infra-red, has no shift in the Raman effect near this region except 1261 or 1445. So far as considering a BO_3 group in B_2O_3 as analogous to the NO_3 one, it should be pointed out that boric acid possesses the nearest known counterpart to a BO_3 group, and that this acid has no Raman lines which correspond to those observed from the boric oxide glass.

[8] Langenberg, R.: Ann. Physik, 28, 104, 1937.
[9] Avramenko, E. I.: J. Phys. Chem. (U. S. S. R.), 7, 339, 1936.
[10] Gross, von E., and Vuks, M.: Compt. rend. acad. sci. U. S. S. R., 1, 214, 1935.
[11] Kujumzelis, G.: Z. Physik, 100, 221, 1936.

Of course, several formulas may be set up to depict the structure of B_2O_3. Among these is the following:



etc.

This has the objection, already raised, of probably yielding a Raman spectrum more complicated than the one observed. Other structures such as an asymmetric tetrahedron similar to that of phosphorus oxychloride would give rise to six Raman lines, while a linear one of the type A-B-A-B-A would yield but three frequency shifts. In the absence of polarization and accurate intensity data, it is impossible to assign accurately any specific structural configuration for boric oxide in boric oxide glass from the Raman spectra information. It can be shown, nevertheless, that a number of possible configurations are improbable.

In borax glass there is observed by Gross and Vuks[10] a diffuse band from $\Delta\tilde{\nu}$ 430-535, a very strong line at $\Delta\tilde{\nu}$ 760, and three bands extending from 950-1000, 1077-1127, and 1310-1520. The maxima of these lines are in reasonable agreement with the results obtained from the crystalline sodium tetraborate, with the possible exception of the frequency at $\Delta\tilde{\nu}$ 934 which is much stronger than the one reported by Gross and Vuks for the same displacement. The lack of a frequency equivalent to $\Delta\tilde{\nu}$ 875 as observed in solutions of boric acid containing sodium hydroxide, and the closer approach to the crystalline results, would apparently indicate a nearer relationship of the glass to crystalline borax than to the products formed in an aqueous solution of sodium tetraborate.

SUMMARY.

The results of these investigations indicate that boric acid is a molecule of the type AB_3 having the symmetry D_{3h} in which all the B groups lie at the corners of a plane triangle with the boron atom in the center. Crystalline boric acid has a spectrum which shows the presence of O-H linkages and the complete absence of any B-H linkage.

It had been supposed previously that the BO_2 ion in sodium metaborate corresponded to a linear group of the type A-B-A which would result in the appearance of only one Raman line. Since at least two lines have been observed, it would seem reasonable to conclude that the ion has a bent structure with the symmetry C_{2v}. There are no lines present in the solution of this compound which would correspond to a Na$\leftrightarrow$B vibration, thus indicating complete ionization. Proposed structures of this molecule, based on a polymerized model or on a configuration resembling a benzene ring, are rejected on the ground that the simplicity of the Raman spectrum is not in accord with such an interpretation.

The spectrum from sodium tetraborate indicates a dissociation of this compound into sodium metaborate and boric acid on solution. The addition of sodium hydroxide to boric acid apparently produces sodium metaborate in equilibrium with boric acid, and there is no compound comparable to crystalline sodium tetraborate in an aqueous solution. The addition of hydrochloric acid to a solution of sodium tetraborate results in the formation of boric acid. The stepwise conversion of boric acid to sodium metaborate in equilibrium with boric acid or the complete conversion to the metaborate, is demonstrable by means of Raman spectra.

The spectrum of crystalline sodium tetraborate indicates that it is apparently nearly a composite of the spectra obtainable from BO_2 ions and from BO_3 groups. This is reasonably consistent with the supposition that sodium tetraborate is made up of long chains both in the crystalline and amorphous forms.

Several formulae have been proposed to depict the structure of B_2O_3 in glasses. From the data at hand it is not possible to designate which of the structures is correct, but it is possible to indicate that some of them are incorrect.