Infra-red spectra and the solid state.
IV. Borofluorides

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The vibrational spectra of the solid crystalline borofluorides of ammonium, potassium and sodium have been measured between 2 and 25μ, both at room temperatures and at that of liquid air. The bands observed have been assigned to vibrational frequencies of the $(BF_4)^-$ and $(NH_4)^+$ ions. Some of the bands are found to split into two or more components, and this splitting has been considered in terms of isotopic species and in relation to the removal of vibrational degeneracy which may arise when the tetrahedral ions are situated in a crystal field of lower symmetry.

In part III measurements on the vibrational spectrum of solid potassium bifluoride were described, and the results were considered in relation to vibrational frequency assignment and to the crystal structure. This paper describes similar work with borofluorides of sodium, potassium and ammonium.

The main experimental procedure was as described previously. The salts were prepared by adding pure ammonia liquor, or Analar sodium or potassium carbonate to a solution of boric acid in Analar hydrogen fluoride. The solids were recrystallized twice from distilled water and dried *in vacuo*. Further recrystallization did not affect the spectrum.

Ammonium borofluoride was sublimed in air or under vacuum on to the plates of rock salt, potassium bromide or fluorite. The thin films thus obtained showed little scattering of radiation. The substance was also measured as a paste in paraffin or perfluorokerosene, particularly when thicker layers were needed to study the overtone and combination bands. The sodium and potassium salts could not be sublimed and were measured only as pastes. There was no evidence that the borofluoride ion attacked either paraffin or the plates of rock salt or potassium bromide. The variation of spectrum with change of temperature was found to be reversible.

Results and discussion

The spectra are shown in figures 1 and 2, the frequencies being listed in table 1. The spectra of sodium and potassium borofluorides were almost unaffected by change of temperature. It was necessary to use different thicknesses of solid in different spectral regions, and these correspond to the separate curves. All the substances showed intense absorption near 10μ, and it was impossible to obtain homogeneous layers thin enough to reduce the peak absorption to a level which might have led to better resolution. Duval & Lecomte (1947) previously reported this intense absorption at roughly the same position. At frequencies below 1400 cm.$^{-1}$ there is a definite parallelism between the spectra of all three borofluorides, each having

a group of strong absorption bands near 520 and 1050 cm.$^{-1}$, with weaker bands near 770 and 1300 cm.$^{-1}$. It is evident that these regions of absorption are connected with the $(BF_4)^-$ ion, and that the bands near 1430 and 3330 cm.$^{-1}$ found with the ammonium salt are associated with the $(NH_4)^+$ ion.

TABLE 1. VIBRATION BANDS (CM.$^{-1}$) OF BOROFLUORIDES

(n.m. = not measured)

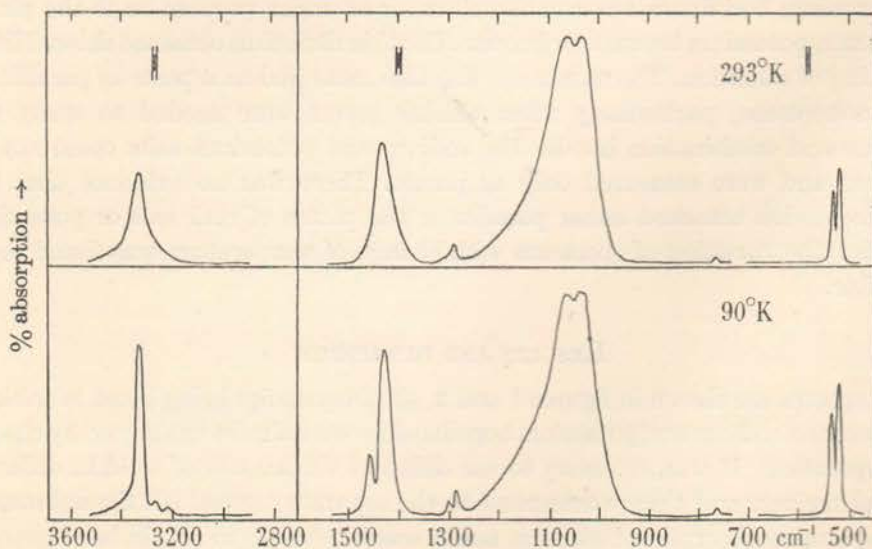| ammonium		potassium		sodium	
293° K	90° K	293° K	90° K	293° K	90° K
521	520	521	521	518	516
529	533	534	535	522	527
				551	553
766	766	771	772	770	768
				779	779
1030	1030	1032	1030	1036	1036
1063	1063	1058	1059	1076	1078
		1072	1075		
		—	1090		
1291	1289	1302	1298	1305	1305
—	1300	—	1305		
				1332	1335
		1784	n.m.	n.m.	1835
2100	2100	2148	n.m.	n.m.	2116
—	3239				
—	3274				
3332	3332				
1431	1430				
—	1456				

FIGURE 1. Ammonium borofluoride: spectrum at 293 and 90° K.

The $(BF_4)^-$ ion can be regarded as tetrahedral, and the nine normal modes will include a single vibration ν_1 (class A_1), one twofold degenerate vibration ν_2 (class E)

and two threefold degenerate vibrations ν_3 and ν_4 (class F_2). ν_1 is the symmetrical breathing vibration of B—F links, and ν_3 the degenerate B—F stretching oscillation. ν_2 and ν_4 are deformational motions. In the case of such gaseous compounds as carbon tetrafluoride and silicon tetrafluoride, which also have tetrahedral structures, the four frequencies have magnitudes which differ from compound to compound roughly as might be expected from the change in mass of the central atom and of the force constants, but the increase in value along the series $\nu_2, \nu_4, \nu_1, \nu_3$ seems to be
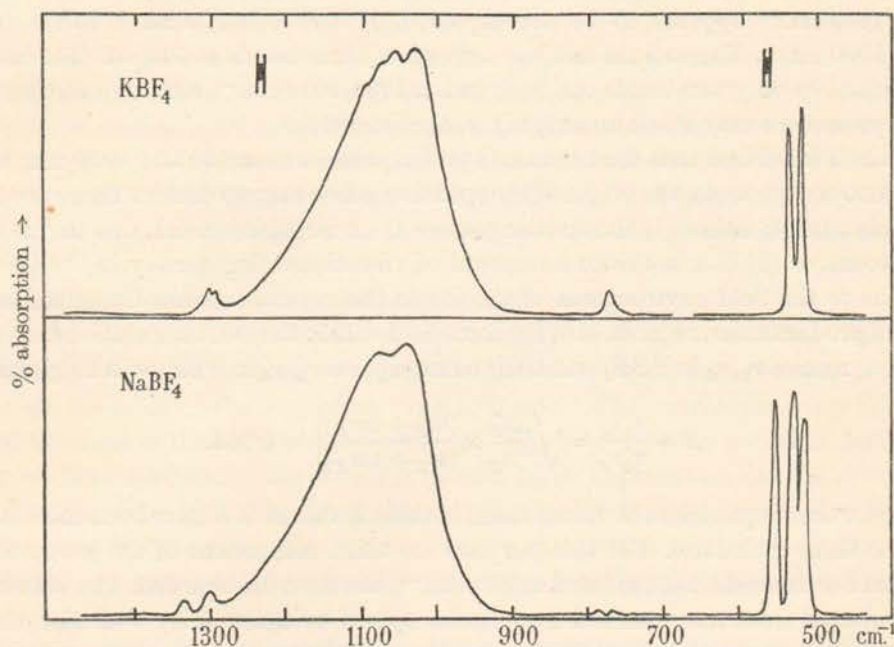

FIGURE 2. Sodium and potassium borofluorides: spectra measured at 90° K.

TABLE 2. FREQUENCIES IN CM.$^{-1}$

	ν_2	ν_4	ν_1	ν_3	
CF$_4$	437	635	904	1265	Bailey, Hale & Thompson (1938)
SiF$_4$	268	390	800	1010	Yost (1938), Jones, Kirby-Smith, Woltz & Nielsen (1951)

preserved, as shown in table 2. The strong bands of the borofluorides near 520 and 1050 cm.$^{-1}$ can be assigned to ν_4 and ν_3, which would be the only permitted fundamental vibrations for tetrahedral T_d symmetry. We might then expect ν_1 and ν_2 to have values of about 750 and 300 cm.$^{-1}$ respectively. The lower values of ν_4 and ν_3 as compared with the corresponding vibrations of CF$_4$, in spite of the lower mass of the boron atom, must arise from a smaller value of the force constant of the B—F link in the (BF$_4$)$^-$ ion.

That the bands near 520 and 1050 cm.$^{-1}$ with borofluorides appear in almost the same position for the ammonium salt as for the sodium and potassium compounds suggests that hydrogen bonding in the crystal between the ammonium ion and

fluorine atoms cannot much affect the B—F links. This confirms a previous result from X-ray measurements by Hoard & Blair (1935) who found that the B—F bond length is unaffected by replacement of rubidium by ammonium ion in the crystal lattice of the borofluorides.

The more precise interpretation of the absorption bands requires closer consideration. With ammonium borofluoride, the bands near 520 cm.$^{-1}$ form a pair about 10 cm.$^{-1}$ apart, and there are similarly two bands at 1030/1060 cm.$^{-1}$. With the potassium salt there is a pair at 521/535 cm.$^{-1}$, but the strong pair at 1030/1059 cm.$^{-1}$ appears to be accompanied by two other weaker bands near 1075/1090 cm.$^{-1}$. The sodium salt has a group of three bands at 516/527/553 cm.$^{-1}$, and near 10μ only two bands can be found at 1036/1076 cm.$^{-1}$, although the intense absorption here may mask underlying weaker structure.

While it is evident that the fundamental frequencies near 520 and 1050 cm.$^{-1}$ are split into components, the origin of the splitting is less easy to decide. There are two possible causes: either (1) the splitting arises from isotopic species, due to ^{11}B and ^{10}B atoms, or (2) it arises from a removal of vibrational degeneracy in the $(BF_4)^-$ ion due to the field environment of the ion in the crystal lattice. Using the well-known product rules, regardless of the force field within the ion, the relation between the frequencies ν_3, ν_4 in $^{11}BF_4$ and their counterparts ν_3', ν_4' in $^{10}BF_4$ will be given by

$$R = \frac{\nu_3 \nu_4}{\nu_3' \nu_4'} = \sqrt{\left\{ \frac{m_B'}{m_B} \times \frac{(m_B + 4m_F)}{(m_B' + 4m_F)} \right\}} = 0 \cdot 960.$$

Using for the frequencies the values listed in table 3, values of R have been calculated for the three molecules. For this purpose the third component of the group with sodium borofluoride, i.e. the band at 553 cm.$^{-1}$, has been disregarded. The values of R computed from the observed frequencies appear to agree fairly well with those calculated from the mass formula, but it is impossible to say whether this agreement is genuine or accidental. The computed values of R show remarkable constancy in the different molecules. Further, a difference from that obtained using the mass formula might well arise as a result of anharmonic vibrations. Small alterations in the values adopted for the measured frequencies, which in fact vary a little at different temperatures and cannot be fixed with high precision, could even lead to closer agreement. However, the abundance ratio of ^{11}B and ^{10}B is about 4 : 1, whereas the intensities of the components in all cases seem more nearly equal, and the bands near 520 cm.$^{-1}$ at any rate seem sufficiently well resolved to make their apparent intensities a good guide. A further difficulty in any interpretation based upon isotope doubling would be the occurrence with sodium borofluoride of the third component in the group near 520 cm.$^{-1}$, and also of the two weak additional bands to the pair 1030/1059 cm.$^{-1}$ in the case of the potassium salt.

TABLE 3

borofluoride	ν_3	ν_4	ν_3'	ν_4'	R
ammonium	520	533	1030	1063	0·948
potassium	521	535	1030	1059	0·948
sodium	516	527	1036	1078	0·942

If, however, the splitting due to isotopy is assumed, we could explain other bands in the spectra as follows. With ammonium borofluoride, the feeble band at 766 cm.$^{-1}$ must be regarded as ν_1, which although forbidden in a strictly tetrahedral ion, must be excited as a result of the lack of tetrahedral symmetry in the field around the ion. ν_1 will be a single (non-degenerate) frequency, as it indeed appears. According to the X-ray analysis of Hoard & Blair (1935) the field symmetry around both $(BF_4)^-$ and $(NH_4)^+$ ions is C_s, and if the field influences the ions sufficiently, all fundamental frequencies should become active in infra-red absorption. The intensities of frequencies which would be forbidden under T_d symmetry will be determined by the extent of the influence by the field. The pair of weak bands with ammonium borofluoride at 1289/1300 cm.$^{-1}$ will then be interpreted as $(\nu_1 + \nu_4)$, the pair arising because of isotope split in ν_4. The calculated values would be $(766 + 520) = 1286$, and $(766 + 533) = 1299$ cm.$^{-1}$. This pair is not satisfactorily explained as a combination of ν_3 with ν_2, since the isotope splitting of ν_3 is much greater than that found between the pair at 1300 cm.$^{-1}$. In the same way, the interpretation of the band at 766 cm.$^{-1}$ as a combination $(\nu_4 + \nu_3)$, rather than as the fundamental ν_1, is unlikely, since it should then show isotope splitting.

The interpretation of the bands with potassium borofluoride is similar. The band at 772 cm.$^{-1}$ will be assigned to ν_1, and the pair at 1298/1305 cm.$^{-1}$ to $(\nu_1 + \nu_4)$ and $(\nu_1 + \nu_4')$, the calculated values being 1293/1307 cm.$^{-1}$. The crystal symmetry appears to be the same as that of the ammonium salt. The only difficulty concerns the feeble pair at 1075/1090 cm.$^{-1}$, for which no satisfactory explanation can be provided, and in any case it is surprising that similar bands are not observed with the ammonium borofluoride. The intense and broad nature of the absorption near 1050 cm.$^{-1}$ in both cases may lead to certain weak components becoming masked, but this is not very convincing.

In the case of sodium borofluoride, the situation is slightly more complicated. The band at 779 cm.$^{-1}$ would be assigned again to ν_1, and the combination $(\nu_1 + \nu_4)$ would give two bands at $(779 + 516) = 1295$ cm.$^{-1}$, and $(779 + 527) = 1306$ cm.$^{-1}$. Only one band is found, at 1305 cm.$^{-1}$, although the second component may not be quite resolved. The band at 553 cm.$^{-1}$ would have to be interpreted as $2\nu_2$, giving ν_2 a value of about 280 to 300 cm.$^{-1}$ if allowance is made for anharmonicity. The band at 1335 cm.$^{-1}$ would then be assigned to

$$(\nu_1 + 2\nu_2) = (779 + 553) = 1332 \text{ cm.}^{-1},$$

and a very weak band near 768 cm.$^{-1}$ might be explained as $3\nu_2$, although the numerical agreement here is not very satisfactory.

Arguments were given above against the interpretation of the splitting of the bands near 530 and 1050 cm.$^{-1}$ as isotopic doubling. The alternative hypothesis would be to suppose that the degeneracy of the vibrations ν_4 and ν_3 is removed by the effect of the crystal field. The difference near 550 and 1335 cm.$^{-1}$ between the sodium salt on the one hand, and those of potassium and ammonium on the other might support this idea. The crystal structure of ammonium and potassium borofluorides has been found by Hoard & Blair (1935) to be D_{2h}^{16}. Some measurements on sodium borofluoride by Klinkenberg (1937) suggest that it falls in the class D_{2h}^{17}.

Also, by analogy with other compounds, it is very probable that the sodium salt will fall in a different symmetry class from the other two salts. For example, while the perchlorates of ammonium, potassium and rubidium all have the barium sulphate structure, sodium perchlorate is like calcium sulphate (anhydrite). The difference with the sodium salt seems to be a general effect due to its smaller ion. Thus, the site symmetry of the $(BF_4)^-$ ion in sodium borofluoride may be different from that in the other salts, being C_{2v} as in anhydrite.

Bhagavantam (1938) and Couture (1948) have drawn attention to the splitting of frequencies of the $(SO_4)^-$ ion in the Raman spectrum of anhydrite, and Couture (1946) and Narayanaswamy (1948) have shown that the splitting in the case of barium sulphate is similar except that ν_3 is split further, as shown in table 4. The degeneracy is fully removed although the intensities of the different components of the split fundamentals are widely different. Some authors have suggested that the splitting in barium sulphate in excess of the normal degeneracy may be due to other factors involving the whole crystal structure. The Raman spectra of other ions in crystals show similar effects, although the number of components and their relative intensity seems to be determined by the particular crystal field and its strength in each individual case.

TABLE 4. RAMAN FREQUENCIES OF THE $(SO_4)^-$ ION (CM.$^{-1}$)

state	ν_1	ν_2	ν_3	ν_4
solution	982 (12)	460 (6)	1106 (2)	617 (2)
CaSO$_4$ crystal	1018 (15)	415 (1)	1108 (2)	609 (2)
		499 (5)	1128 (10)	628 (2)
			1160 (5)	674 (8)
BaSO$_4$ crystal	988 (18)	453 (1·5)	1084 (0·2)	622 (1)
		462 (4)	1105 (0·1)	630 (0·3)
			1138 (1)	647 (0·6)
			1145 (0·1)	
			1167 (0·6)	

If this general interpretation applies to the borofluorides, the vibrational assignment would be essentially the same as that already given. The bands near 530 cm.$^{-1}$ would be associated with ν_4, those near 1050 cm.$^{-1}$ with ν_3, those near 770 cm.$^{-1}$ with ν_1, and those near 1300 cm.$^{-1}$ with $(\nu_1 + \nu_4)$. Some minor difficulties would remain such as the explanation of the very weak band of the sodium salt at 768 cm.$^{-1}$ and the abnormal splitting of the group near 1050 cm.$^{-1}$ with the potassium salt. It is also peculiar that on this interpretation the isotopic molecule frequencies are absent. The latter would only be expected with ν_4 and ν_3, and may be submerged beneath the bands actually observed, although this again seems unlikely. It therefore seems impossible to decide between the two alternative interpretations of the bands due to the borofluoride ions.

The only other spectral features are weak bands near 2100 and 1700 cm.$^{-1}$. These might be explained respectively as the first overtone of ν_4 and the combination $(\nu_1 + \nu_4)$. It was not possible to examine the salts at thicknesses sufficient to bring out the full details of structure in these bands, since the scattering of radiation by such thicker layers was too great.

As regards vibrations of the $(NH_4)^+$ ion in ammonium borofluoride, it is clear that the bands at 1431 and 3332 cm.$^{-1}$ are two fundamentals. At low temperatures the former is split into two components at 1430/1456 cm.$^{-1}$, and two weak satellites of the latter appear at 3239, 3274 cm.$^{-1}$. This dependence upon temperature is more marked than with the bands due to the $(BF_4)^-$ ion. For a tetrahedral ion with T_d symmetry, as explained above, there will be two active vibrations ν_3, ν_4, and these can be assigned to 3332 and 1431 cm.$^{-1}$ respectively. In the case of ammonium chloride the corresponding bands occur at 3086 and 1402 cm.$^{-1}$ (Wagner & Hornig 1950a). It is interesting that the values differ in this way, for whilst the known interatomic distances in ammonium halides and borofluorides suggest that in the latter there is greater hydrogen bonding which will lead to a rise in the deformational frequency ν_4, there should then be a fall in the value of ν_3, but the opposite is found. The significance of the two weak bands at 3239 and 3274 cm.$^{-1}$ is uncertain. They could be components arising from splitting of the fundamental ν_3, but their relative intensity is very low. The two bands at 1430 and 1456 cm.$^{-1}$, however, are satisfactorily explained as two components of the degenerate mode ν_4 under the influence of the crystal field. The fundamental ν_2 which by analogy with ammonium chloride would be expected near 1700 cm.$^{-1}$ does not appear to be excited.

From their studies on the spectra of ammonium halides Wagner & Hornig (1950a, b) have concluded that with the chloride and bromide, certain bands appear due to a combination of molecular modes with a torsional vibration lattice mode of frequency about 300 cm.$^{-1}$. These bands sharpened considerably at low temperatures. Such bands could not be detected in the spectrum of ammonium borofluoride, but in this case the increased strength of hydrogen bonding may prevent their occurrence, and indirectly this may support the suggestion that they exist in the other cases.

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