

## 1212. *The Vibrational Spectra of the Tetrachloroborate and Tetrabromoborate Ions*

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All the fundamental vibration frequencies of the tetrachloroborate and tetrabromoborate ions have been obtained from Raman and infrared measurements on solutions. The frequencies and force constants are similar to those of the isoelectronic carbon tetrahalides.

PREVIOUS studies<sup>1-4</sup> of the infrared spectra of crystalline tetrahaloborates have yielded only  $\nu_3$ , the boron-halogen stretching frequency, for the ions  $\text{BCl}_4^-$ ,  $\text{BBr}_4^-$ , and  $\text{BI}_4^-$ . In many of the spectra reported earlier, moreover, the  $\nu_3$  band had a complicated structure owing to the removal of the degeneracy of this vibration by the crystal fields. A determination of all the fundamental vibration frequencies of  $\text{BCl}_4^-$  and  $\text{BBr}_4^-$  from the Raman and infrared spectra of tetra-alkylammonium tetrahaloborates in solution is now reported.

The tetrachloroborate ion was studied in solution in liquid sulphur dioxide. Burge *et al.*<sup>5</sup> have obtained evidence from conductivity studies which indicates the formation of a 1 : 1 complex between potassium chloride and boron trichloride in solution in liquid sulphur dioxide. In view of the subsequent isolation of tetrachloroborates from solutions of boron trichloride and alkylammonium chlorides in other inert solvents,<sup>1,2</sup> there seems little doubt that the complex ion in sulphur dioxide solution is the tetrachloroborate ( $\text{BCl}_4^-$ ) ion. The tetrabromoborate ion was examined in solution in methylene chloride as its ethyldi-isopropylammonium salt, since experiments showed that tetrabromoborates react rapidly with sulphur dioxide to form thionyl bromide and boric oxide.

### RESULTS AND DISCUSSION

In addition to the characteristic bands of sulphur dioxide and the strongest spectra features of the tetramethylammonium ion, the Raman spectra of the solution of tetramethylammonium tetrachloroborate contain four bands, which can with certainty be

<sup>1</sup> W. Kynaston, B. E. Larcombe, and H. S. Turner, *J.*, 1960, 1772.

<sup>2</sup> T. C. Waddington and F. Klanberg, *J.*, 1960, 2332, 2339.

<sup>3</sup> T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 1960, 85.

<sup>4</sup> T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 1960, 315.

<sup>5</sup> D. E. Burge, H. Freund, and T. H. Norris, *J. Phys. Chem.*, 1959, **63**, 1969.

assigned to the regular-tetrahedral tetrachloroborate ion. In the spectra of the tetrabromoborate solution, three bands entirely consistent with the tetrahedral tetrabromoborate ion were observed; the fourth tetrabromoborate band and the spectrum of the ethyldi-isopropylammonium cation were too weak to appear above the continuous spectral background, which was rather high in these spectra in the vicinity of Hg 5461 Å. The fourth frequency ( $\nu_3$ ) of tetrabromoborate was therefore obtained from the infrared spectrum of the solution of ethyldi-isopropylammonium tetrabromoborate, where it appeared as a strong band ( $605 \text{ cm.}^{-1}$ ) close to the weaker band ( $574 \text{ cm.}^{-1}$ ) of the ethyldi-isopropylammonium cation.

The observed frequencies and their assignment (point group  $T_d$ ) are given in Table 1. The frequencies, relative intensities, and the high degree of polarisation associated with the breathing frequency  $\nu_1$ , closely parallel those in the isoelectronic carbon tetrahalides, and leave no doubt of the assignment of the frequencies to the tetrahalogenoborate ions. The spectra show that other anionic species such as  $\text{ClSO}_2 \text{ BCl}_3^-$  postulated by Burg<sup>6</sup> as intermediates in the solvolysis of the tetrachloroborate ion in sulphur dioxide solution cannot be present in high concentrations.

The values of  $\nu_3$  in Table 1 agree with the published infrared spectral data<sup>1</sup> on crystalline potassium tetrachloroborate and ammonium tetrabromoborate, in which crystal-field splitting of the  $\nu_3$  band is not observed. The doublet in the spectrum of the tetrachloroborate ion is now with certainty attributed to Fermi resonance between  $\nu_3$  and  $\nu_1 + \nu_4$ , as suggested by Waddington and Klanberg,<sup>2</sup> who observed this doublet ( $664, 692 \text{ cm.}^{-1}$ ) in the infrared spectra of several tetrachloroborates. The values of  $\nu_1$  and  $\nu_4$  reported

TABLE 1

Vibration frequencies of tetrahalogenoborate ions			
$\text{BCl}_4^-$		$\text{BBr}_4^-$	
Cm. <sup>-1</sup>	Assignment	Cm. <sup>-1</sup>	Assignment
190s, dp	$\nu_3(e)$	117s, dp	$\nu_3(e)$
274s, dp	$\nu_4(t_2)$	166s, dp	$\nu_4(t_2)$
405s, p	$\nu_1(a_1)$	243s, p	$\nu_1(a_1)$
670w	$\left. \begin{array}{l} \nu_3(t_2) \\ \nu_1 + \nu_4(t_2) = 679 \end{array} \right\}$	605(ir)	$\nu_3(t_2)$
707w			

s = Strong, w = weak, p = polarised, dp = depolarised in the Raman spectra, ir = observed only in infrared spectra.

here for the tetrabromoborate ion preclude such resonance, and Waddington and White<sup>3</sup> found a single band ( $593 \text{ cm.}^{-1}$ ) in the infrared spectra of crystalline tetrabromoborates, close to the value for the solution given here.

The complete force field for a molecule  $\text{XY}_4$  of  $T_d$  symmetry requires five free constants, whereas there are only four frequencies. The possibility arises in the tetrahalogenoborates of obtaining the fifth quantity required for the determination of the complete force field from the splitting of  $\nu_3$  or  $\nu_4$  due to the presence of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes. An estimated splitting of  $\nu_3$  of tetrabromoborate is roughly  $10 \text{ cm.}^{-1}$ , but in the infrared spectrum of the tetrabromoborate ion in solution in methylene chloride, the  $\nu_3$  band was too broad ( $\Delta\nu_3^a \sim 65 \text{ cm.}^{-1}$ ) for the isotope splitting to be detected. The infrared spectrum of tetraethylammonium tetrachloroborate in methylene bromide solution also shows no evidence of isotope splitting in the Fermi doublet of  $\text{BCl}_4^-$  at 667 and 697  $\text{cm.}^{-1}$ . A shoulder found at 724  $\text{cm.}^{-1}$  is too weak to be attributed to  $^{10}\text{BCl}_4^-$ ; it probably arises from the cation, since weak bands at 737 and 726  $\text{cm.}^{-1}$  are found in the infrared spectrum of solid tetraethylammonium chloride, though not of the iodide. Assumptions concerning the force field which reduce the number of force constants must therefore be made, and in Table 2 are given the values of force constants calculated for a Urey-Bradley force field. This

<sup>6</sup> A. B. Burg and E. R. Birnbaum, *J. Inorg. Nuclear Chem.*, 1958, **7**, 146.

type of field has been found satisfactory in its application to tetrahedral molecules,<sup>7</sup> and equations which relate the frequencies to the X-Y stretching and Y-X-Y bending-force constants  $K$  and  $H$ , and to the non-bonded atom interaction constants  $F$  and  $F'$  have been given by Simanouti.<sup>8</sup>

Included in Table 2 are the Urey-Bradley force constants for the isoelectronic carbon tetrahalides.<sup>8</sup> It is evident from the values of the force constants that, as expected, the bonding in the tetrahalogenoborates is essentially the same as that in the carbon tetrahalides. The values in Table 2 illustrate the characteristic increase in force constant with

TABLE 2  
Urey-Bradley force constants ( $10^5$  dynes/cm.) of  $XY_4$  species

	$K$	$H$	$F$	$F'$		$K$	$H$	$F$	$F'$
$BCl_4^-$ ...	1.31	0.054	0.529	-0.063	$CCl_4$ .....	1.76	0.080	0.656	-0.097
$BBr_4^-$ ...	1.14	0.067	0.411	-0.035	$CBr_4$ ...	1.43	0.045	0.493	-0.078

atomic number in an isoelectronic series,<sup>9</sup> and the characteristic decrease in passing from tetrachloride to tetrabromide. Only in the bending constants  $H$  are departures from these trends found;  $H$  decreases in passing from tetrabromoborate ion to carbon tetrabromide and increases from tetrachloro- to tetrabromo-borate. Attention has been drawn<sup>10</sup> to a similar increase in  $H$  in passing from carbon tetrabromide to carbon tetraiodide.

#### EXPERIMENTAL

*Preparation of Solutions.*—Sulphur dioxide was transferred at low pressure on to dry tetramethylammonium chloride (0.018 mole) to give a 1.5M-solution. Addition of boron trichloride (0.015 mole) at  $-80^\circ$  caused precipitation of a white solid which completely dissolved at  $0^\circ$ . The solution was filtered directly into a Raman cell at room temperature within a sealed system. The solution appeared to be quite stable during the Raman exposures, but after two days an appreciable deposit of boric oxide gel had formed on the walls of the Raman cell.

Ethyl-di-isopropylammonium bromide was prepared from the tertiary amine and aqueous hydrobromic acid, and was recrystallised twice from a mixture of methylene chloride and carbon tetrachloride. Reagent-grade methylene chloride was freed from ethanol by standard procedures, and was freshly distilled before use. The bromoborate solutions were prepared by the addition of boron tribromide (0.0069 mole) to a 0.65M-solution of ethyl-di-isopropylammonium bromide (0.0072 mole) in methylene chloride.

*Raman Spectra.*—Spectra were excited by a 1 kw Toronto-arc source and recorded on Kodak Scientific Oa-G plates, with a Hilger E612 spectrograph fitted with a camera of f5.7 aperture. For Hg 4358 Å excitation, a saturated aqueous potassium nitrite solution was used as a pre-filter. This was replaced by a saturated solution of neodymium chloride and a Kodak Wratten type 12 gelatin filter for excitation by Hg 5461 Å. Frequencies are estimated to be accurate to  $\pm 2$   $cm^{-1}$ , except for  $\nu_3$  of tetrachloroborate, which was a broad band with estimated limits of error of  $\pm 5$   $cm^{-1}$ . Qualitative polarisation data were obtained by the polarised incident light method<sup>11</sup> by using cylinders of Polaroid film.

*Infrared spectra.*—The absorption spectrum of the 0.6M-solution of ethyl-di-isopropylammonium tetrabromoborate in methylene chloride in the range 375—800  $cm^{-1}$  was obtained with a Unicam S.P. 100 double-beams spectrometer. The spectrum of ethyl-di-isopropylammonium chloride was measured to determine the frequencies of the ethyl-di-isopropylammonium cation.

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<sup>7</sup> T. Simanouti, *Pure Appl. Chem.*, 1963, **7**, 131.

<sup>8</sup> T. Simanouti, *J. Chem. Phys.*, 1949, **17**, 245.

<sup>9</sup> L. A. Woodward, *Trans. Faraday Soc.*, 1958, **54**, 1271.

<sup>10</sup> H. Stammreich, Y. Tavares, and D. Bassi, *Spectrochim. Acta*, 1961, **17**, 661.

<sup>11</sup> D. H. Rank and R. E. Kagarise, *J. Opt. Soc. Amer.*, 1950, **40**, 89.