The Structures of Bromine Trifluoride Adducts

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BROMINE TRIFLUORIDE can act as a nonaqueous solvent system. Ionisation

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

is postulated, and bromine trifluoride adducts with alkali fluorides, *e.g.*, $KF,BrF_3(K^+BrF_4^-)$, are bases on this system and adducts with Lewis acids, *e.g.*, BrF_3,SbF_5, are postulated as acids containing the BrF_2^+ ion. Structural information on these latter adducts is not available.[1] Chlorine trifluoride forms adducts with Lewis acids and on the basis of infrared spectroscopy these have been postulated as containing the ClF_2^+ ion.[2,3]

New adducts $GeF_4,2BrF_3$, $2BF_3,BrF_3$ (stable to $-120°$), and BF_3,BrF_3 (stable to $-80°$) are prepared by direct combination of the constituent

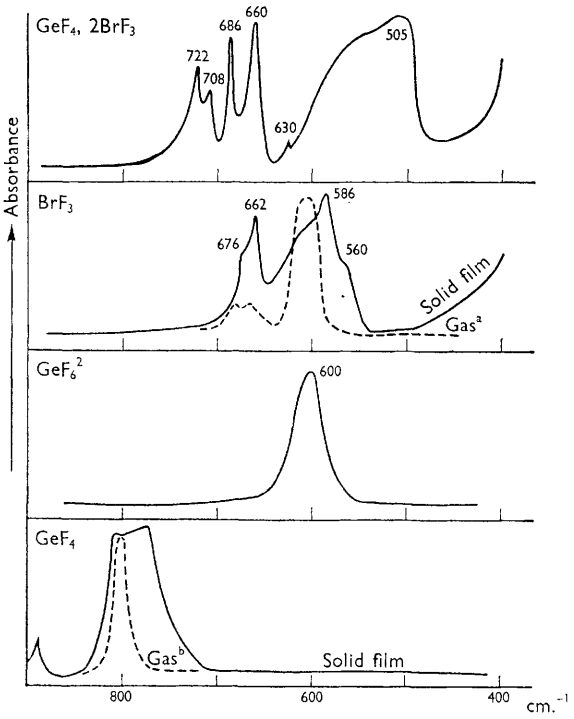

FIGURE. *Infrared spectrum of* $GeF_4,2BrF_3$.

(a) H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, 1958, **28**, 285.

(b) A. D. Caunt, L. N. Short, and L. A. Woodward, *Trans. Faraday Soc.*, 1952, **48**, 873.

fluorides. The first adduct sublimes slowly at 20° under vacuum and it has been possible to obtain a good infrared spectrum of a solid film of the material condensed on a silver chloride plate at low temperatures (see Figure). The hexafluorogermanate(IV) ion has a strong band[4] at 600 cm.$^{-1}$ and there is no such band present in the spectrum of $GeF_4,2BrF_3$ so that a structure such as $(BrF_2^+)_2$ (GeF_6^{2-}) must be ruled out. The spectrum of the adduct is completely distinct from those of the two components. Other possible structures would involve fluorine bridging or donation of electrons from the bromine to the germanium. The present evidence does not permit distinction between these two models. In addition to the bands shown in the Figure, $GeF_4,2BrF_3$ has a broad weak band at 1780 cm.$^{-1}$ and additional peaks due to HF_2^-, GeF_6^{2-}, and SiF_6^{2-} appeared if the sample was allowed to warm up to room temperature. These peaks presumably result from interaction with the materials of the cell. All infrared absorptions, except those due to attack on the window materials, could be removed by pumping.

The inference that the adduct $2BrF_3,GeF_4$ is not ionic would not preclude ionic behaviour in bromine trifluoride as solvent. An *X*-ray powder photograph suggests that the substance is orthorhombic, $a = 9{\cdot}07$, $b = 7{\cdot}59$, $c = 6{\cdot}78$ Å.

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