# On the Structure of Complexes between Bromine Trifluoride and Lewis Acids

BY KARL O. CHRISTE* AND CARL J. SCHACK

The two known adducts $BrF_3 \cdot SbF_5$ and $2BrF_3 \cdot GeF_4$ and the new adduct $BrF_3 \cdot AsF_5$ were prepared and characterized by laser Raman and low-temperature infrared spectroscopy. It is shown for the $BrF_3 \cdot SbF_5$ adduct, the exact structure of which is known from single-crystal X-ray data, that vibrational spectra alone may often be insufficient to distinguish between predominantly ionic and covalent donor–acceptor complexes. Distortion of the $SbF_6^-$ anion results in a rather complex spectrum. However, based on frequency and relative intensity arguments and by comparison with the spectrum of $BrF_3 \cdot AsF_5$, the three fundamentals belonging to the $BrF_2^+$ cation could be assigned. Force constants were computed for $BrF_2^+$ and compare favorably with those previously reported for $ClF_2^+$ thus supporting the suggested assignments.

## Introduction

The existence of $BrF_3 \cdot$ Lewis acid adducts is well known and the literature until 1965 has been summarized in a review article[1] by Stein. More recently five papers dealing with $BrF_3 \cdot$ Lewis acid adducts have been published. Brown and coworkers investigated[2] the $2BrF_3 \cdot GeF_4$ adduct by low-temperature infrared spectroscopy and reached the conclusion that the adduct cannot be ionic. Toy and Cannon reported[3] the preparation of $BrF_2^+BF_4^-$; however, subsequently their claim was refuted.[4] In spite of much previous speculation as to $BrF_3$ and its adducts being either covalent or ionic, the first unambiguous report on the structure of one of the adducts was published only in 1967. Edwards and Jones showed[5] by single-crystal X-ray diffraction data that $BrF_3 \cdot SbF_5$ can be considered as being predominantly ionic with some contribution from weak covalent fluorine bridges. Furthermore, they showed that $BrF_2^+$ is bent having a bond angle of 95° and that the symmetry of the $SbF_6^-$ anion is lowered from $O_h$ to $C_{2v}$ by distortion due to weak cis fluorine bridging. No structural data were given in a recent paper[6] by Kemmit, *et al.*, dealing with $2BrF_3 \cdot PtF_4$. Since vibrational spectroscopy had proven[7–10] to be a powerful tool in the structural investigation of the analogous $ClF_3$ adducts, the method was also applied to these controversial $BrF_3$ adducts. In this paper we wish to present the vibrational spectra of the $BrF_3 \cdot SbF_5$, $BrF_3 \cdot AsF_5$, and $2BrF_3 \cdot GeF_4$ adducts, showing that the characteristic $BrF_2^+$ frequencies can be assigned in spite of complex spectra due to nonoctahedral anions.

* To whom correspondence should be addressed.

(1) L. Stein in "Halogen Chemistry," Vol. 1, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

(2) D. H. Brown, K. R. Dixon, and D. W. A. Sharp, *Chem. Commun.*, 654 (1966).

(3) M. S. Toy and W. A. Cannon, *J. Phys. Chem.*, **70**, 2241 (1966).

(4) K. O. Christe, *ibid.*, **73**, 2792 (1969).

(5) A. J. Edwards and G. R. Jones, *Chem. Commun.*, 1304 (1967); *J. Chem. Soc. A*, 1467 (1969).

(6) R. D. W. Kemmit, R. D. Peacock, and I. L. Wilson, *Chem. Commun.*, 772 (1968).

(7) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(8) R. J. Gillespie and M. J. Morton, *ibid.*, **9**, 616 (1970).

(9) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **357**, 125 (1968).

(10) K. O. Christe and W. Sawodny, *ibid.*, **374**, 306 (1970).

## Experimental Section

**Materials and Apparatus.**—The materials used in this work were manipulated in a well-passivated (with $ClF_3$) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise–Bourdon tube-type gauge (0–1500 mm ± 0.1%). Bromine trifluoride (from The Matheson Co.) was purified by fractional condensation, the material retained at −23° being used. It was nearly white as a solid and pale yellow as a liquid. Antimony pentafluoride (from Ozark Mahoning Co.) was purified by vacuum distillation at ambient temperature. Arsenic pentafluoride and $GeF_4$ (from Ozark Mahoning Co.) were purified by fractional condensation. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (~0.3- and ~0.5-mm o.d.).

The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Model 337 and 457 spectrophotometers in the range 4000–400 cm⁻¹. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectra were taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Screw-cap metal cells with AgCl windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to −25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or Kel-F or Teflon FEP capillaries were used as sample containers.

**Preparation of the Adducts.** $BrF_3 \cdot SbF_5$.—Antimony pentafluoride (28.08 mmol) and $BrF_3$ (69.99 mmol) were combined in a prepassivated 10-ml Monel cylinder. The contents of the cylinder were shaken at ambient temperature for several days. Unreacted $BrF_3$ (43.20 mmol) was removed *in vacuo* at 110°. Therefore, $SbF_5$ (28.08 mmol) had reacted with $BrF_3$ (26.79 mmol) in a mole ratio of 1:0.954 producing the adduct $BrF_3 \cdot SbF_5$. The cylinder was opened in the glove box and contained a white crystalline solid.

$BrF_3 \cdot AsF_5$.—Arsenic pentafluoride (45.38 mmol) and $BrF_3$ (41.34 mmol) were combined in a prepassivated 10-ml Monel

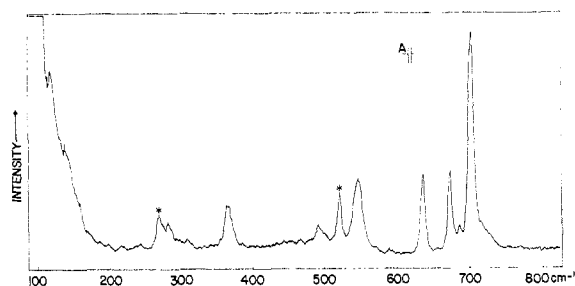Figure 1.—Raman spectrum of solid BrF₃·SbF₅. Sample container glass tube; transverse viewing—transverse excitation technique; A indicates spectral slit width. The bands marked by an asterisk are mainly due to scattering from the glass tube.

## Results and Discussion

**Synthesis and Properties.**—Our synthesis of the BrF₃·SbF₅ adduct was similar to that reported[11] by Sheft, *et al.*, and their observations were confirmed. The only difference was that our adduct was white and not canary yellow.[11] Only upon prolonged storage or exposure to glass surfaces a pink to red color developed. The X-ray powder diffraction pattern of our adduct could be easily indexed on the basis of the orthorhombic unit cell ($a$ = 10.12, $b$ = 5.81, and $c$ = 10.95 Å) reported by Edwards and Jones,[5] thus indicating that their and our products had identical structures. The BrF₃·AsF₅ adduct has not previously been described.



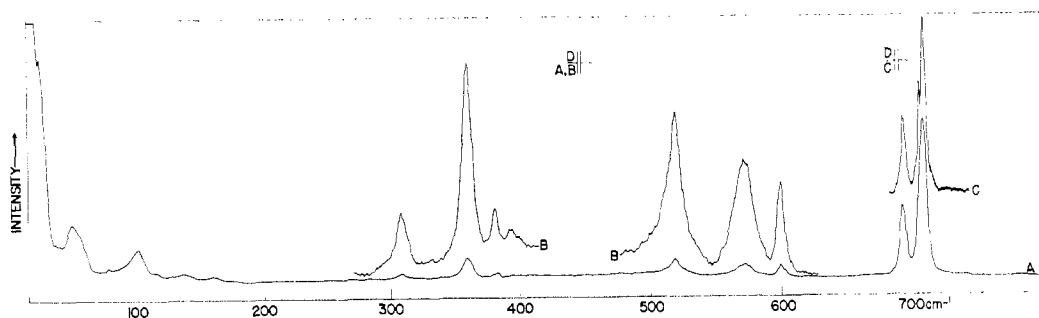Figure 2.—Raman spectrum of solid BrF₃·AsF₅. Sample container glass tube; axial viewing—transverse excitation technique; D indicates spectral slit width. Traces A and B were recorded at different recorder voltages; trace C was at higher resolution.
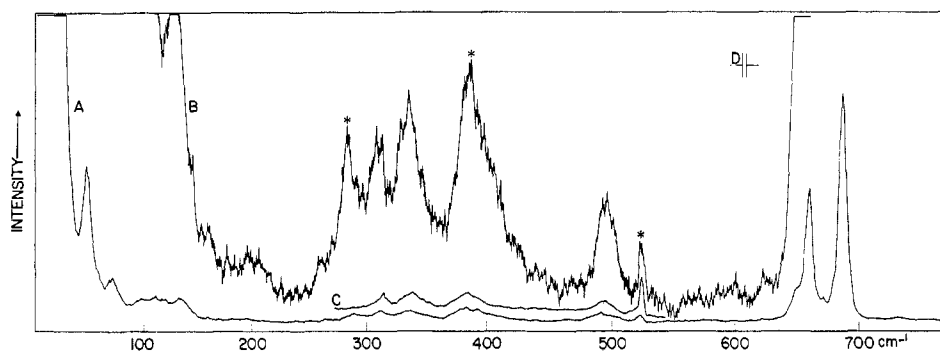


Figure 3.—Raman spectrum of solid 2BrF₃·GeF₄. Trace A: container Teflon FEP capillary, transverse viewing—transverse excitation technique. Trace B: same conditions as for A but different recorder voltage. Trace C: container glass capillary, transverse viewing—transverse excitation. D indicates spectral slit width. Bands marked by an asterisk are mainly due to scattering from the sample containers.

cylinder. The contents of the cylinder were shaken at ambient temperature for 7 days. Unreacted AsF₅ (3.68 mmol) was removed *in vacuo* at 0°. Therefore, AsF₅ (41.70 mmol) had reacted with BrF₃ (41.34 mmol) in a mole ratio of 1:0.991 producing the adduct BrF₃·AsF₅. The cylinder was opened in the glove box and contained a white, crystalline solid. This adduct had a dissociation pressure of about 2 mm at 23°.

**2BrF₃·GeF₄.**—Liquid BrF₃ (29.50 mmol) was exposed to excess gaseous GeF₄ (18.12 mmol) in a Teflon FEP U trap at ambient temperature. The GeF₄ was slowly admitted into the trap and the contents of the trap were continuously shaken. An exothermic reaction occurred and a white, crystalline solid formed. Unreacted GeF₄ (2.88 mmol) was removed *in vacuo* at −23°. Therefore, BrF₃ (29.50 mmol) had reacted with GeF₄ (15.24 mmol) in a mole ratio of 2:1.03 producing the adduct 2BrF₃·GeF₄. This adduct has no detectable dissociation pressure at −23°, but at 23.6° its dissociation pressure amounts to about 4 mm.

It is of marginal stability at ambient temperature. For its synthesis the use of excess AsF₅ is advantageous owing to the latter's relatively high volatility and low tendency to form stable di- or polymeric anions. The synthesis and properties of the 2BrF₃·GeF₄ adduct were in good agreement with those previously reported by Brown, *et al.*[2] It was found easy to grow single crystals of the latter adduct by slow sublimation at ambient temperature.

**Vibrational Spectra.**—Figures 1–3 show the Raman spectra of solid BrF₃·SbF₅, BrF₃·AsF₅, and 2BrF₃·GeF₄, respectively. Figures 4 and 5 show the infrared spectra of BrF₃·SbF₅ and BrF₃·AsF₅, respectively.

(11) I. Sheft, A. F. Martin, and J. J. Katz, *J. Amer. Chem. Soc.*, **78**, 1557 (1956).

TABLE I

VIBRATIONAL SPECTRA (cm$^{-1}$) of BrF$_3$·SbF$_5$, BrF$_3$·AsF$_5$, AND 2BrF$_3$·GeF$_4$[a]

| BrF$_3$·SbF$_5$ | | BrF$_3$·AsF$_5$ | | 2BrF$_3$·GeF$_4$ | |
| Raman | Ir | Raman | Ir | Raman | Ir |
|---|---|---|---|---|---|
| 705 (10) | 705 s | | 758 sh | | |
| 702 sh | | | 742 vs | | 723 s |
| 686 (0.9) | 692 vs | 706 (10) | 713 s | 690 (10) | 710 m |
| 678 (4.3) | 680 mw | 703 (3) | 698 vs | 657 (6.5) | 688 s |
| 661 (0+) | 657 vs | 691 (4.4) | 688 sh | 644 sh | 661 vs |
| 638 (4.1) | 640 vw, sh | | 649 w | | |
| | 598 w | 600 (0.8) | 609 sh | | 535 sh |
| 547 (3.5) | | | 590 s | 489 (0.4) | 504 vs |
| 492 (0.9) | 493 m | 572 (1.0) | | 391 (0.6) | |
| 362 (2.0) | | | 542 m | 344 (0.5) | |
| 281 (0.7) | | 519 (1.5) | | 315 (0.4) | |
| 270 (1.6) | | | 400 s | | |
| | | 382 (0.3) | | | |
| | | 360 (1.8) | | | |
| | | 308 (0.5) | | | |

[a] For comparison, the octahedral anions show the following frequencies (cm$^{-1}$): SbF$_6^-$: ir, $\nu_3(F_{1u})$ 650–690, $\nu_4(F_{1u})$ 270–290; Raman, ($\nu_1 A_{1g}$) 650–670, $\nu_2(E_g)$ 560–580, $\nu_5(F_{2g})$ 270–290;[12,13] AsF$_6^-$: ir, $\nu_3(F_{1u})$ 690–710, $\nu_4(F_{1u})$ 380–400; Raman, $\nu_1(A_{1g})$ 680–695, $\nu_2(E_g)$ 570–590, $\nu_5(F_{2g})$ 370–390;[14] GeF$_6^{2-}$: ir, $\nu_3(F_{1u})$ 598, $\nu_4(F_{1u})$ 349; Raman, $\nu_1(A_{1g})$ 627, $\nu_2(E_g)$ 454, $\nu_5(F_{2g})$ 318.[15]
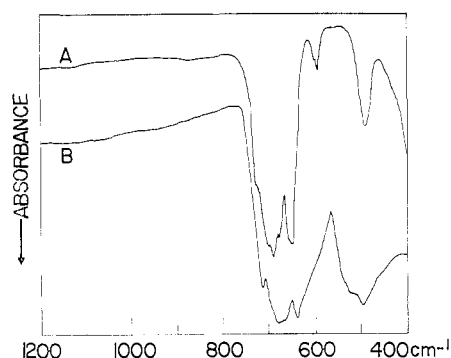


Figure 4.—Infrared spectrum of solid BrF$_3$·SbF$_5$. Trace A, crystalline film at low temperature; trace B, dry powder at 23°.
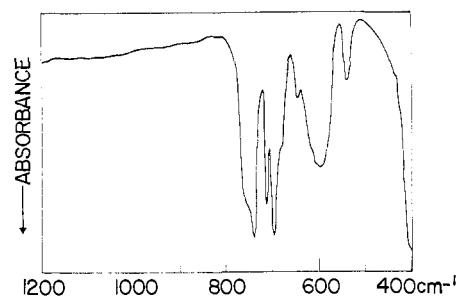


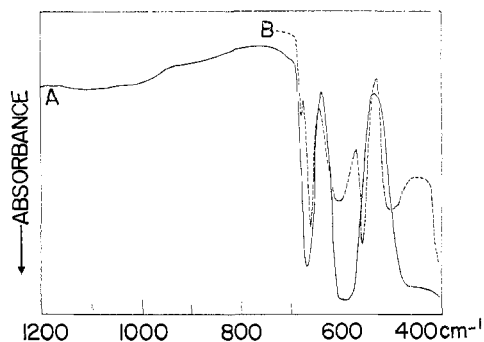Figure 5.—Low-temperature infrared spectrum of solid BrF$_3$·AsF$_5$.



Figure 6.—Low-temperature infrared spectrum of solid BrF$_3$. Trace A, glassy deposit; trace B, crystalline deposit.

The observed frequencies are listed in Table I. The low-temperature infrared spectrum of 2BrF$_3$·GeF$_4$ has also been recorded. It was in good agreement with that previously reported[2] and, hence, is not shown. The low-temperature infrared spectrum of solid BrF$_3$ is depicted in Figure 6. Two different spectra could reproducibly be obtained for BrF$_3$ depending on the experimental conditions during sample deposition. Fast plating out produced a glassy deposit (curve A), whereas slow deposition or resublimation produced a snowlike, crystalline film (curve B). The spectrum previously reported[2] for solid BrF$_3$ appears to be a mixture of the two components shown in Figure 6.

As can be seen from Table I, the spectra observed for BrF$_3$·SbF$_5$, BrF$_3$·AsF$_5$, and 2BrF$_3$·GeF$_4$ do not exhibit the absorptions characteristic for octahedral SbF$_6^-$,[12,13] AsF$_6^-$,[14] and GeF$_6^{2-}$,[15] respectively. The absence of these characteristic bands in the spectra of adducts has frequently been used in the past as an argument against their possible ionic structure. Thus, Brown, *et al.*,[2] have based their conclusion that 2BrF$_3$·GeF$_4$ is not ionic on the absence of the 600-cm$^{-1}$ band of octahedral GeF$_6^{2-}$ in the infrared spectrum of 2BrF$_3$·GeF$_4$. The possibility of ionic structures containing anions of lower symmetry has in most cases not been considered. The BrF$_3$·SbF$_5$ adduct has according to single-crystal X-ray data[5] essentially the ionic structure BrF$_2^+$SbF$_6^-$, with distorted SbF$_6^-$ anions of symmetry $C_{2v}$. Therefore, it should be interesting to inspect its vibrational spectrum more closely. One should expect the spectrum to be that of the two discrete ions, *i.e.*, BrF$_2^+$ and SbF$_6^-$, because there is a very pronounced difference in bond length. For example, the Br–F bond length in BrF$_2^+$ is 0.60 Å shorter than the distance to the second nearest fluorine atoms, *i.e.*, "fluorine bridge" atoms, whereas the distance of these "bridge" atoms from the Sb cen-

(12) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967).
(13) K. O. Christe and W. Sawodny, to be submitted for publication.
(14) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969), and references cited therein.
(15) J. E. Griffiths and D. E. Irish, *ibid.*, **3**, 1134 (1964).

tral atom is only 0.08 Å longer than that of the non-bridging fluorine atoms.

Unfortunately, no spectroscopic data are available on distorted octahedral ions. Assuming symmetry $C_{2v}$ for SbF$_6^-$ as suggested by Edwards and Jones,[5] a total of 15 fundamental vibrations is expected for this ion. These are classified as 6 A$_1$ + 2 A$_2$ + 3 B$_1$ + 4 B$_2$. With the exception of the 2 torsional modes in species A$_2$ which should be only Raman active, all modes should be active in both the infrared and Raman spectra. Of the 15 vibrations 6 are stretching modes, 3 symmetric ones in species A$_1$ which should be of high relative intensity in the Raman spectrum and 3 antisymmetric ones (B$_1$ + 2 B$_2$) which should give rise to strong infrared bands. The bent BrF$_2^+$ cation should have symmetry $C_{2v}$ and exhibit 3 normal modes (2 A$_1$ + B$_1$). Of these, the 2 stretching modes (A$_1$ + B$_1$) are expected to have similar frequency values for reasons previously discussed[7] for the ClF$_2^+$ cation. The BrF$_2^+$ stretching modes should be of high relative intensity in both the infrared and Raman spectra, should have frequencies in the neighborhood of 700 cm$^{-1}$ ($\nu_{as}$(BrF$_2$) in BrF$_3$ is 613 cm$^{-1}$), and should occur in both the BrF$_2^+$SbF$_6^-$ and BrF$_2^+$-AsF$_6^-$ spectra. As can be seen from Table I, only the Raman band at 705 cm$^{-1}$ meets all these requirements and, hence, values of 705 and 702 cm$^{-1}$ are assigned to $\nu_1$(A$_1$) and $\nu_3$(B$_1$), respectively, of BrF$_2^+$. The BrF$_2^+$ deformation mode is expected to have a frequency between 300 and 400 cm$^{-1}$ and based on similar arguments is assigned to the 362-cm$^{-1}$ Raman line. The remaining bands should be due to the anions. In the range of the SbF$_6^-$ stretching vibrations (700–500 cm$^{-1}$), three intense Raman bands were observed at 678, 638, and 547 cm$^{-1}$, respectively, which might tentatively be assigned to the three symmetric stretching modes. The three infrared bands at 692, 657, and 493 cm$^{-1}$ might represent the remaining three antisymmetric Sb–F stretching modes. The fact that most of these bands assigned to SbF$_6^-$ modes are active in both the infrared and Raman spectra excludes (for SbF$_6^-$) structures having a symmetry center, thus agreeing with the X-ray data of Edwards and Jones.[5] If the weak "fluorine bridges" which probably are the main cause for the distortion of the SbF$_6^-$ octahedron would involve two fluorine atoms in trans position instead of two in cis position, one might expect conservation of the symmetry center for SbF$_6^-$, *i.e.*, a symmetry such as $D_{4h}$ or possibly $D_{2h}$. In the region of the SbF$_6^-$ deformation vibrations (300–200 cm$^{-1}$)[13] fewer bands were observed than theoretically expected for $C_{2v}$. This might be due to low relative intensities and partial coincidences.

The vibrational spectrum of BrF$_2^+$AsF$_6^-$ will not be discussed at length owing to the absence of supporting X-ray data. However, the general appearance of the spectrum and the good frequency agreement for the bands attributed to BrF$_2^+$ with those in BrF$_2^+$SbF$_6^-$ suggests a structure similar to that of BrF$_2^+$SbF$_6^-$.

For the 2BrF$_3$·GeF$_4$ adduct an ionic structure of the type (BrF$_2^+$)$_2$GeF$_6^{2-}$ containing a distorted GeF$_6^{2-}$ octahedron cannot be ruled out. The Raman bands at 690 and 344 cm$^{-1}$ might well be due to the BrF$_2^+$ cation. The slight decrease in frequency when compared to the corresponding SbF$_6^-$ and AsF$_6^-$ salts would not be surprising. A similar frequency decrease has been observed for ClF$_2^+$ in the series ClF$_2^+$SbF$_6^-$, ClF$_2^+$AsF$_6^-$, and ClF$_2^+$BF$_4^-$.[8] Furthermore, the difference in composition (2:1 *vs.* 1:1 adduct) may result in significant structural changes. Consequently, additional data such as X-ray studies are required before conclusions about the actual nature of the 2BrF$_3$·GeF$_4$ adduct can be reached.

**Force Constants.**—In order to test the soundness of the assignments made above for BrF$_2^+$, a modified valence force field was calculated assuming $F_{12}$, *i.e.*, $f_{r\alpha}$, to equal zero. This assumption seems justified since in ClF$_2^+$ $f_{r\alpha}$ is quite small[7] and in BrF$_2^+$ the larger mass of the central atom should reduce this value further. For the computation an F–Br–F bond angle of 95° was used.[5] The internal force constants thus obtained are listed in Table II and compared to those of

TABLE II

INTERNAL FORCE CONSTANTS (MDYN/Å) OF BrF$_2^+$ AND ClF$_2^+$

|  | BrF$_2^+$ | ClF$_2^+$ I$^c$ | ClF$_2^+$ II$^d$ |
|---|---|---|---|
| $f_r$ | 4.60 | 4.74 | 4.88 |
| $f_{rr}$ | 0.21 | 0.14 | [0]$^a$ |
| $f_\alpha$ | 0.47 | 0.60 | 0.63 |
| $f_{r\alpha}$ | [0]$^a$ | 0.04 | [0]$^a$ |
| $\alpha$ | [95°]$^b$ | [100°]$^a$ | 95° |

$^a$ Assumed values. $^b$ Value taken from ref 5. $^c$ W. Sawodny, private communication; modified valence force field using the frequency values of ref 8. $^d$ Simple valence force field of ref 8 used to calculate two force constants and bond angle.

ClF$_2^+$. As can be seen, the principal force constants of BrF$_2^+$ favorably compare with those obtained for ClF$_2^+$, thus lending support to the assignments made for BrF$_2^+$. The slight increase of the value of the stretch–stretch interaction constant, $f_{rr}$, from ClF$_2^+$ to BrF$_2^+$ is unexpected. However, it should be kept in mind that the value of $f_{rr}$ depends strongly upon the bond angle[7] (which is unknown for ClF$_2^+$) and upon the frequency difference between $\nu_1$ and $\nu_3$ which is somewhat uncertain.

In summary, the vibrational spectrum of solid BrF$_3$·SbF$_5$ is best interpreted in terms of discrete BrF$_2^+$ and SbF$_6^-$ ions. It is shown that the absence of the characteristic vibrations of a normally highly symmetric ion should not be used as an argument against the ionic nature of an adduct.