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Studies on the Chemistry of Halogens and of Polyhalides. XXXI. Spectroscopic Studies of Acid–Base Equilibria in Liquid Bromine Trifluoride[1,2]

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Received April 23, 1970

The addition of strong acids and bases to liquid BrF_3 has been studied by Raman and infrared spectroscopic techniques. The separate bands in the Raman spectrum of liquid BrF_3 have been resolved and vibrational assignments were made. The fundamental vibration frequencies for the monomer in liquid BrF_3 are 236 (a_1), 265 (b_2), 341 (b_1), 531 (a_1), 613 (b_1), and 673 (a_1) cm^{-1}. The fundamental frequencies for the tetrafluorobromate(III) anion are 249 (b_{1g}), 302 (a_{2u}), 455 (b_{2g}), 528 (a_{1g}), and 570 (e_u) cm^{-1} in liquid BrF_3. The Raman spectrum of solid $KBrF_4$ had fundamental vibrational frequencies at 530 (a_{1g}), 455 (b_{2g}), and 242 (b_{1g}) cm^{-1}. This gives strong support for a square-planar (point group D_{4h}) configuration for the BrF_4^- anion in both liquid BrF_3 and solid $KBrF_4$. Data for the BrF_2^+ cation are not as clear. A Raman band at 625 cm^{-1} and an infrared band at 635 cm^{-1} have been observed and attributed to the cation in liquid BrF_3, but in BrF_2SbF_6 and other solid acid compounds, bands attributed to the cation occur above 700 cm^{-1}. Solvation is suggested as a factor in the difference between these spectra.

Introduction

Despite its high reactivity, bromine trifluoride has been fairly extensively studied as a medium for inorganic reactions. Pioneering work in this field was carried out by Emeleus and his coworkers.[3-7] Liquid bromine trifluoride has a high degree of self-ionization as evidenced by its high specific conductance of 8×10^{-3} ohm^{-1}.[6,8] It has been postulated that the self-ionization can be represented by $2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$. Consequently, it is possible to visualize acid–base reactions in this solvent of the type

$$KF + BrF_3 \longrightarrow K^+ + BrF_4^-$$

$$SbF_5 + BrF_3 \longrightarrow BrF_2^+ + SbF_6^-$$

$$K^+ + SbF_6^- \longrightarrow K^+SbF_6^-$$

It should be noted, however, that so far neither the structure nor even the presence of BrF_4^- and BrF_2^+ ions in liquid BrF_3 has been unambiguously demonstrated.

Spectroscopic studies on BrF_3 and on its solutions have been somewhat sparse. The Raman spectrum of the liquid and infrared spectrum of the gaseous compound were obtained by Claassen, *et al.*[9] The authors concluded that the molecule is "T" shaped with C_{2v} symmetry. An infrared spectrum of liquid BrF_3 in the overtone region was also reported by Haendler and coworkers.[10] After this work was concluded, Selig, *et al.*,[11] published the infrared and Raman spectra of BrF_3 vapor and further elucidated the fundamental vibrational frequencies for the BrF_3 molecule.

Some work has been done on the structure of solid addition compounds of BrF_3. Siegel[12] and Sly and Marsh[13] investigated the structure of potassium tetrafluorobromate(III), $KBrF_4$, by powder X-ray diffraction. The results were inconclusive. Recent neutron diffraction studies on this compound by Edwards and Jones[14] showed that the BrF_4^- ion has a square-planar configuration. These authors also carried out neutron diffraction studies[15] on difluorobromonium(III) hexafluoroantimonate(V) and found that the structure corresponds to the formulation $BrF_2^+SbF_6^-$ with the BrF_2^+ cation having a nonlinear configuration. The authors noted, however, that the fluorine atoms of the anion were close enough to the bromine atom to allow considerable interaction, and, therefore, the compound forms an endless chain through fluorine bridging. Brown, *et al.*,[16] reported that the infrared spectral studies of $(BrF_2)_2GeF_6$ were inconsistent with the proposed ionic structure of the compound.

The present study was undertaken in order to elucidate the nature of ionic species present in liquid bromine trifluoride solutions. In particular, this phase of work has been concerned with the species formed on self-ionization of the solvent itself.

Experimental Section

Reagents.—Bromine trifluoride used in this investigation was obtained from the Matheson Co. It was purified by two fractional distillations in a nickel still followed by pumping at room temperature to remove any remaining volatile impurities. The

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Abstracted in part from the Ph.D. thesis of T. Surles, Michigan State University, 1970.

(3) A. G. Sharpe and H. J. Emeleus, *J. Chem. Soc.*, 2135 (1948).

(4) H. J. Emeleus and A. A. Wolff, *ibid.*, 164 (1950).

(5) H. J. Emeleus and A. A. Wolff, *ibid.*, 1050 (1950).

(6) A. A. Banks, H. J. Emeleus, and A. A. Wolff, *ibid.*, 2861 (1949).

(7) A. A. Wolff and H. J. Emeleus, *ibid.*, 2865 (1949).

(8) L. A. Quarterman, H. H. Hyman, and J. J. Katz, *J. Phys. Chem.*, **61**, 912 (1957).

(9) H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, **28**, 285 (1955).

(10) H. M. Haendler, S. W. Bukata, and B. Millard, *ibid.*, **22**, 1939 (1954).

(11) H. Selig, H. H. Claassen, and J. H. Holloway, *ibid.*, **52**, 3517 (1970).

(12) S. Siegel, *Acta Crystallogr.*, **9**, 493 (1956).

(13) W. G. Sly and R. E. Marsh, *ibid.*, **10**, 378 (1957).

(14) A. J. Edwards and G. R. Jones, *J. Chem. Soc.*, 1936 (1969).

(15) A. J. Edwards and G. R. Jones, *ibid.*, 1467 (1969).

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

purified product had a melting point of 8.8° and was pale yellow. It was stored in polychlorotrifluoroethylene (Kel-F) containers.

Chlorine trifluoride, arsenic pentafluoride, and antimony pentafluoride were also obtained from the Matheson Co. The first two compounds were purified by vacuum distillation at low temperature. Antimony pentafluoride was stored overnight over anhydrous sodium fluoride in a Kel-F vessel. Following this treatment a vacuum was pulled on the system for 3 hr in order to remove volatile impurities and then the compound was distilled under vacuum at 60°.

Potassium, rubidium, and cesium fluorides were of reagent grade quality.

Preparation of Solutions.—Solutions of alkali metal fluorides in bromine trifluoride were prepared by condensing the appropriate amount of the solute in bromine trifluoride. Solutions of antimony pentafluoride and of arsenic pentafluoride were prepared by condensing required amounts of the solvent and the solute in a tared reaction vessel.

The densities of the solutions were determined with a Kel-F pycnometer. The concentrations of the solutions in terms of molalities, molarities, and mole fractions were calculated from the above data.

Preparation of Solid Compounds.—The solids were all prepared by vacuum line techniques. A drybox was used to minimize exposure to moisture during necessary transfer of nonvolatile solids. Potassium tetrafluorobromate(III), $KBrF_4$, was prepared by adding a slight excess of BrF_3 to anhydrous potassium fluoride in a Kel-F reaction vessel. The reaction was allowed to proceed at room temperature, and excess BrF_3 was removed under vacuum. The residue was a solid white, microcrystalline powder. The melting point was 332° (lit.[17] mp 330°).

Difluorobromonium(III) hexafluoroantimonate(V), BrF_2SbF_6, was prepared in the same manner. A light yellow, microcrystalline solid was obtained with a melting point of 128° (lit.[17] mp 130°). The yellow coloration was probably due to some BrF_3 which was absorbed on the solid and could not be pumped off. Difluorobromonium(III) hexafluoroarsenate(V) was prepared by slowly distilling arsenic pentafluoride into a Kel-F reaction vessel containing some BrF_3. An excess of AsF_5 was added and the reaction was allowed to go to completion. The excess AsF_5 was pumped off and a white solid remained, BrF_2AsF_6. *Anal.* Calcd for BrF_2AsF_6: Br, 25.2; As, 23.7. Found: Br, 25.3; As, 26.2.

Spectral Measurements.—Raman spectra were obtained on a Cary Model 81 Raman spectrophotometer equipped with an He–Ne laser light source and (when a new instrument became available)[11] on an Ar ion laser spectrometer, which has been described elsewhere. Solutions were poured into the Raman cell through flexible Kel-F tubing without exposure to the atmosphere. The vacuum-tight cell consisted of a Kel-F body in which the windows were held in place by a metal frame and sealed with Teflon gaskets. The windows were obtained from Perkin-Elmer and were made of synthetic sapphire. Nonmetallic reflective coatings had been deposited on the windows to increase the number of light passages through the solution and thus increase the sensitivity. These coatings did not come into contact with the solutions being studied. Solid samples were prepared in place and sealed in Kel-F tubing.

Infrared spectra were obtained on a Beckman Model 12 infrared spectrophotometer which had been fitted with a beam condenser. Measurements were made on solutions in the 200–1000-cm^{-1} spectral regions in a cell[18] which used diamonds as window material. Irtran-2 was used as window material for solutions in the 1000–2000-cm^{-1} spectral region. It was found that Irtran-6 windows, which are transparent below 1000 cm^{-1}, reacted with bromine trifluoride and, therefore, could not be used.

Spectra in the ultraviolet and visible regions were obtained on a Cary Model 14 spectrophotometer. Synthetic sapphire was used as window material.

Resolution of spectral curves was carried out on a Du Pont Model 310 curve resolver. An effort was made to use as few curves as possible in resolving the liquid bromine trifluoride Raman spectra and the Raman spectra of its solutions. Perram[19] has pointed out that it is possible to resolve one Gaussian curve into two components when in fact these components are artificial. The resolved spectra contained the minimum number of bands possible while fulfilling chemical and spectral considerations.

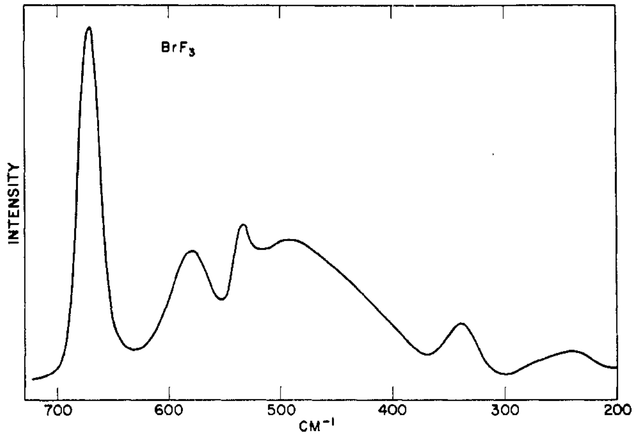

Figure 1.—Raman spectrum of liquid BrF_3.

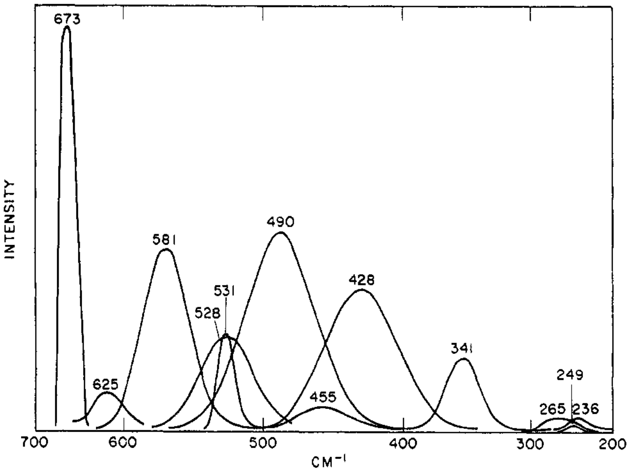

Figure 2.—Resolved Raman spectrum of liquid BrF_3.

Results and Discussion

Vibrational Spectrum of Bromine Trifluoride.—The Raman spectrum of bromine trifluoride is shown in Figure 1 and the resolved spectrum in Figure 2. The vibrational assignments are listed in Table I.

TABLE I

RAMAN SPECTRUM OF LIQUID BROMINE TRIFLUORIDE

Band location, cm^{-1}	Assignment	Band location, cm^{-1}	Assignment
673	ν_1 (a_1) BrF_3	455	ν_5 (b_{2g}) BrF_4^-
625	ν_1 (A_1) BrF_2^+	428	Polymer band
581	Polymer band	341	ν_5 (a_1) BrF_3
531	ν_2 (a_1) BrF_3	265	ν_6 (b_2) BrF_3
528	ν_1 (a_{1g}) BrF_4^-	249	ν_3 (b_{1g}) BrF_4^-
490	Possible dimer	236	ν_3 (a_1) BrF_3

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

(18) H. H. Hyman, T. Surles, L. A. Quarterman, and A. I. Popov, *Appl. Spectry.*, **24**, 464 (1970).

(19) J. W. Perram, *J. Chem. Phys.*, **49**, 4245 (1968).

The Raman-active fundamental vibrations of bromine trifluoride occur at 673 (ν_1), 531 (ν_2), 341 (ν_5), 265 (ν_6), and 236 cm^{-1} (ν_3). These observations and assignments are in good agreement with those of Selig, *et al.*[11] The bands at 428 and 581 cm^{-1} appear to be due to polymers formed in the liquid bromine trifluoride, since their intensities decrease upon the addition of either acid or base to the system. Selig[20] has also observed that the intensities of the bands at 428 and 581 cm^{-1} decrease with increasing temperature which would be consistent with the explanation that these are polymer bands. The band at 490 cm^{-1} also decreases in intensity upon addition of an acid or a base to the solvent, but in contrast to the 428- and 581-cm^{-1} bands, its intensity increases with increasing temperature. It seems reasonable to assume, therefore, that this band may be due to a bromine trifluoride dimer or, in any case, a lower polymer than those represented by the 428- and 581-cm^{-1} bands.

The infrared spectrum of bromine trifluoride is shown in Figure 3 and the vibrational assignments are listed in Table II. Comparison is made with the Raman spectrum of the compound as well as with the spectrum of gaseous bromine trifluoride observed by Selig, *et al.*[11] The spectrum obtained in the overtone region agrees with the results of Haendler, *et al.*[10]

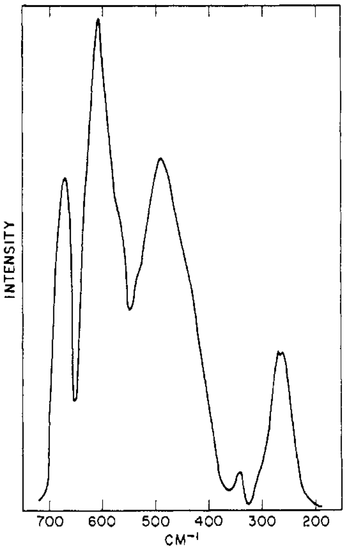

Figure 3.—Infrared spectrum of liquid BrF_3.

TABLE II

VIBRATIONAL SPECTRA OF BROMINE TRIFLUORIDE (CM^{-1})

Liquid BrF_3		Gaseous BrF_3[a]		Assignment
Infrared	Raman	Infrared	Raman	
674 s	673 p, s	668, 682 s	675 p, s	ν_1
614 vs	Not obsd	604, 614, 621 vs	612 vvw	ν_4
528 vw	531 p, m	547, 557 w	552 p, s	ν_2
344 w	341 m	342, 350, 359 w	Not obsd	ν_5
269 m	265 w	242 m	Not obsd	ν_6
Not obsd	235 p, w	242 m	Not obsd	ν_3

[a] Reference 11.

There is a strong band at 490 cm^{-1} in the infrared spectrum of BrF_3. While this has not been followed as a function of temperature, it decreases with the addition of acid or base and is probably due to the same species that has a band at 490 cm^{-1} in the Raman spectrum. This suggests the presence of a dimer without a center of symmetry and a fundamental vibration at 490 cm^{-1} in both the Raman and infrared spectra.

Spectrum of the Tetrafluorobromate(III) Anion.—The Raman spectrum of a 2.1 *M* solution of potassium fluoride in bromine trifluoride is shown in Figure 4.

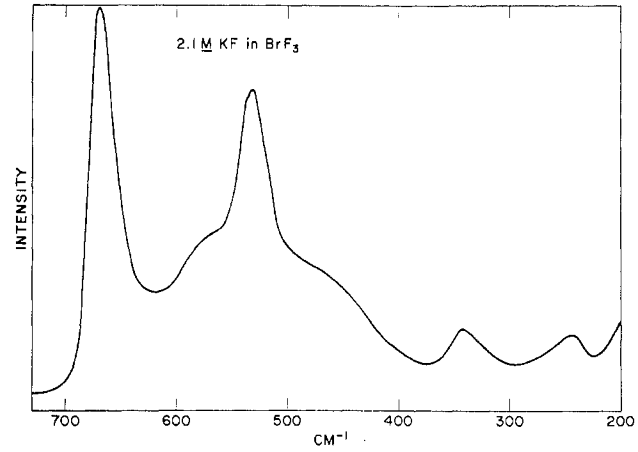

Figure 4.—Raman spectrum of 2.1 *M* KF in BrF_3.

The addition of KF to BrF_3 results in a sharp increase in intensity of the 528- and 455-cm^{-1} bands as well as in the intensity of the much weaker 249-cm^{-1} band. The Raman spectrum of solid $KBrF_4$ is shown in Figure 5.

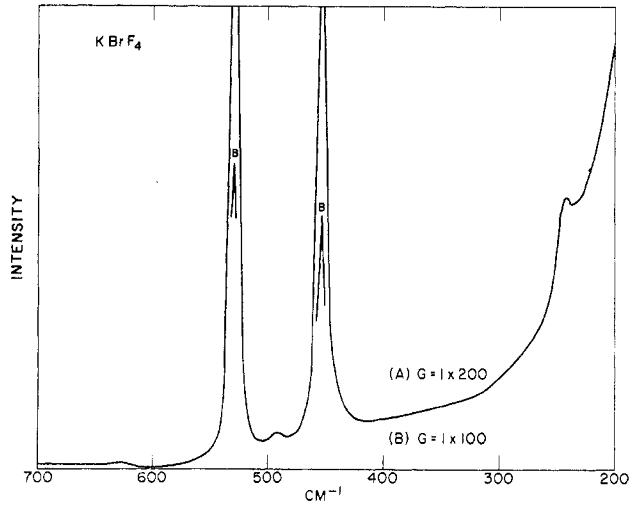

Figure 5.—Raman spectrum of solid $KBrF_4$.

After the completion of this work Shamir and Yaroslavsky[21] published the Raman spectrum of solid cesium tetrafluorobromate(III). As shown in Table III the spectrum of the ion is essentially the same in both solids.

Three Raman-active fundamentals are observed, two stretching modes and a single bending mode, as expected for a square-planar ion. A tetrahedral, T_d, configura-

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(20) H. Selig, private communication.

(21) J. Shamir and I. Yaroslavsky, *Israel J. Chem.*, **7**, 495 (1969).

Table III
Vibrational Spectra of Tetrafluorobromate(III) Anion (cm^{-1})

Assignment	Where obsd	BrF_4^- in liquid BrF_3[a]	BrF_4^- in solid $KBrF_4$[a]	BrF_4^- in solid $CsBrF_4$[b]	Solid XeF_4[c]
ν_1	R	528	530	530	543
ν_2	Ir	302			291
ν_3	R	249	242	242	235
ν_4	Inactive				
ν_5	R	455	455	453	502
ν_6	Ir	570			
ν_7	Ir	Not obsd			

[a] This work. [b] Reference 21. [c] H. H. Claassen, C. L. Chernick, and J. G. Malm, *J. Amer. Chem. Soc.*, **85**, 1927 (1963).

tion should show an additional bending mode and, therefore, four Raman-active fundamentals.

Infrared spectra were also obtained for potassium fluoride solutions in BrF_3. There is a strong increase in the intensity of the 570-cm^{-1} band which corresponds to the ν_6 infrared-active stretching vibration of the BrF_4^- anion. The increase in intensity corresponded to the increased concentration of potassium fluoride. A band was also observed at 302 cm^{-1}, presumably due to the ν_2 fundamental bending mode for a square-planar BrF_4^-. The infrared-active fundamental ν_7, a bending mode for the square-planar molecule, was not observed. However, our measurements did not go below 200 cm^{-1} and it is quite possible that this vibration occurs in this region. The infrared spectrum of solid $KBrF_4$ corresponds well to that found for the BrF_4^- anion in liquid BrF_3. Solutions of cesium and rubidium fluorides in liquid BrF_3 gave exactly the same spectra as potassium fluoride solutions.

The agreement between the vibrational spectra for solid $KBrF_4$ and the bands in solution which grow in intensity with the addition of a base to BrF_3 offers strong evidence for the presence of a BrF_4^- ion with an identical structure in both phases. The neutron diffraction pictures for the solid and the spectral assignments are both consistent with the square-planar, D_{4h}, symmetries for the BrF_4^- anion.

The much studied square-planar XeF_4,[22] quasi-isoelectronic with the halogen tetrafluoride anions, has a vibrational spectrum very similar to that for the BrF_4^- anion (Table III) and we conclude rather safely that this anion has basically a square-planar structure in both solid compounds and bromine trifluoride solutions.

Spectra of AsF_5 and SbF_5 Solutions in Bromine Trifluoride.—Raman spectra of arsenic pentafluoride and antimony pentafluoride solutions in bromine trifluoride (Figure 6) show a sharp increase in the intensity of the 625-cm^{-1} band and a decrease in intensity at 530 cm^{-1}. The infrared spectra of these acid solutions show an increase in the intensity of the 635-cm^{-1} band as well as a slight intensity increase of the 292-cm^{-1} band (Table IV). None of these bands can be identified with specific bands observed in the solids BrF_2AsF_6 and BrF_2SbF_6.

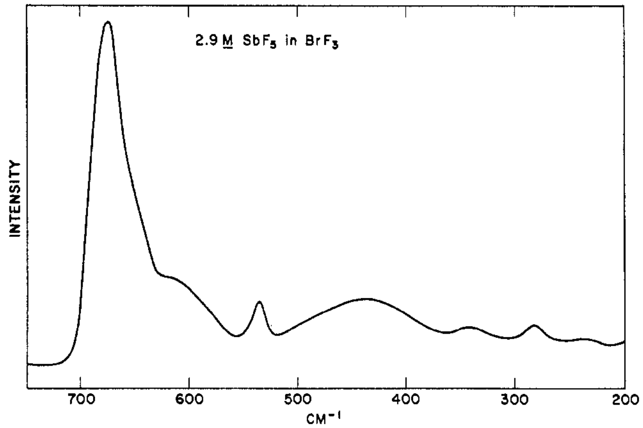

Figure 6.—Raman spectrum of 2.9 *M* SbF_5 in BrF_3.

Table IV
Vibrational Spectra of Liquid Bromine Trifluoride Containing Acid Solutes (cm^{-1})

AsF_5 soln	AsF_6^- in ClO_2AsF_6[a]	SbF_5 soln	SbF_6^- in $LiSbF_6$[b]	BrF_2^+	Where obsd
722 s	ν_3 (725)				Ir
685	ν_1 (684)				R
		680 s	ν_3 (669)		Ir
		652	ν_1 (668)		R
635 ms		635 ms		X[c]	Ir
625		625		X	R
Not obsd	ν_2 (572)	Not obsd	ν_2 (558)		R
404 m	ν_4 (382)				Ir
		350 w	ν_4 (350)		Ir
382	ν_5 (379)				R
		280	ν_5 (294)		R
292 vw		292 mw		X	Ir

[a] A. Carter, W. M. Johnson, and F. Aubke, *Can. J. Chem.*, **47**, (1969). [b] G. H. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967). [c] Vibrations of BrF_2^+.

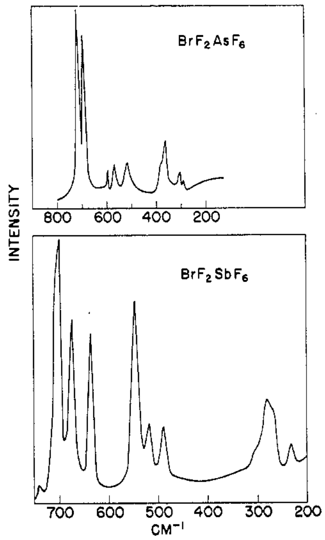

Figure 7.—Raman spectra of (top) solid BrF_2AsF_6 and (bottom) BrF_2SbF_6.

The Raman spectra of the solid compounds BrF_2SbF_6 and BrF_2AsF_6 are shown in Figure 7 and reasonable band assignments are listed in Table V. The infrared absorption spectrum in the 400–800-cm^{-1} region was obtained for BrF_2AsF_6. It was not obtained for the antimony compound, primarily because of difficulties aris-

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(22) H. H. Claassen, C. L. Chernick, and J. G. Malm, *J. Amer. Chem. Soc.*, **85**, 1927 (1963).

TABLE V

RAMAN SPECTRA OF SOLIDS CONTAINING THE DIFLUOROBROMONIUM(III) CATION (cm^{-1})

Solid BrF_2AsF_6	Solid BrF_2SbF_6	BrF_2^+
	734 (6)	
709	704 (100)	X
694	677 (75)	
598	637 (68)	
573	550 (78)	
520	520 (24)	
381	490 (22)	
363		
307 294	308 (9)	X
	280 (19)	
	273 (13)	
	234 (7)	

ing in transferring the sample to a suitable cell. Both infrared and Raman spectra are rather complicated and the presence of partial hydrolysis products may introduce further complications. An analysis of the spectra of these solid compounds is not as straightforward as might be expected. Christe and Sawodny[23] first studied the solids ClF_2AsF_6 and ClF_2SbF_6 and assumed that the only bands not due to the ClF_2^+ cation would correspond to the octahedral anion. Gillespie and Morton[24] pointed out that the lattice distortion might increase the number of vibrations associated with each anion and suggested a different set of assignments. Christe has concurred and with Schack[25] has now studied the solid bromine trifluoride complexes with arsenic pentafluoride and antimony pentafluoride. They noted that the anions found in the resulting salts are distorted octahedra and have several vibrational bands. For a possible limit, a species with C_{2v} symmetry might be expected, having a total of 15 fundamental vibrations, all Raman active.

The observations summarized in Table V are similar to, but not identical with, those of Christe and Schack.[25] The only assignment that seems certain for the BrF_2^+ cation is that for a symmetric stretching vibration at 704 and 709 cm^{-1} in the antimony and arsenic complexes, respectively. A tentative assignment, however, is also given in Table VI for a bending mode, at 308 cm^{-1}.

TABLE VI

VIBRATIONAL SPECTRA OF DIFLUOROBROMONIUM(III) CATION (cm^{-1})

BrF_2^+ in BrF_2SbF_6	BrF_2^+ in liquid BrF_3	ClF_2^+ in ClF_2SbF_6[a]	ClF_2^+ in liquid ClF_3
704 R	625 R	805, 809 R	782 R
705 ir[b]	635 ir		
308 R		387 R	
		830 R	

[a] Reference 24. [b] This work; BrF_2^+ in BrF_2AsF_6.

Thus, while the square-planar BrF_4^- anion is found unequivocally in both solid and solutions, the nature of the BrF_2^+ cation in solution and the solids cannot be inferred from the spectroscopic data, although X-ray evidence supports a C_{2v} symmetry for the cation in BrF_2SbF_6.[15] The nature of the cation in acid bromine trifluoride solutions is not spectroscopically similar to the species found in solid complexes. This is probably due to the fact that the BrF_2^+ cation is strongly solvated in solution. With solvation, the Br–F band distance would increase and the force constant would decrease, perhaps accounting for an observed frequency decrease for the Raman-active stretching vibration from ~700 to ~625 cm^{-1}. Preliminary work on the spectra of AsF_5 solutions in ClF_3 has shown that the stretching vibration for ClF_2^+ is observed at 782 cm^{-1} which is about 25 cm^{-1} below where it is observed in the solid ClF_2AsF_6.[24] In bromine trifluoride a stronger solvating effect might cause the stretching vibration to be decreased by about 80 cm^{-1} from where it occurs in the solid.

Acknowledgment.—T. S. appreciates the support received from an Associated Midwest Universities–Argonne National Laboratory predoctoral fellowship.

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

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

(25) K. O. Christe and C. J. Schack, private communication.