

## SPECTROSCOPIC AND CONDUCTIMETRIC STUDIES OF HALOGEN FLUORIDE COMPOUNDS IN ANHYDROUS HYDROGEN FLUORIDE\*

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### SUMMARY

Raman, infrared and electrical conductance studies have been undertaken on liquid mixtures of chlorine trifluoride and hydrogen fluoride and of bromine pentafluoride and hydrogen fluoride. The experimental data reveal the existence of a fluoride-ion transfer equilibrium,  $\text{ClF}_3 + \text{HF} \rightleftharpoons \text{ClF}_2^+ + \text{HF}_2^-$ , in the former case. No fluoride-ion transfer is observed in the HF/BrF<sub>5</sub> system. In addition, Raman studies have been undertaken on separate solutions of CsBrF<sub>4</sub>, CsClF<sub>4</sub>, CsBrF<sub>6</sub>, ClF<sub>2</sub>SbF<sub>6</sub>, BrF<sub>2</sub>SbF<sub>6</sub> and BrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub> in hydrogen fluoride. For the cesium salt solutions, experimental data reveal that the halogen fluoride anions act as Lewis bases in the reaction  $\text{ClF}_4^- + \text{HF} \rightleftharpoons \text{HF}_2 + \text{ClF}_3$ . Fluoride-ion transfer,  $\text{BrF}_4^+ + 2\text{HF} \rightleftharpoons \text{BrF}_5 + \text{H}_2\text{F}^+$ , is also observed for BrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub> in HF. The spectra of BrF<sub>2</sub><sup>+</sup> and ClF<sub>2</sub><sup>+</sup> in HF are similar to the spectra of these cations in their respective solid compounds. However, addition of excess halogen fluoride to these solutions lowers the frequencies attributed to the stretching vibrations of the cations. Approximate acidity function values have been determined for BrF<sub>3</sub>, ClF<sub>3</sub> and BrF<sub>5</sub> relative to hydrogen fluoride. Numerical values are based on the *H*<sub>0</sub> values previously reported for hydrogen fluoride solutions.

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### INTRODUCTION

There has been much interest in the properties of, and equilibria in, mixtures of various halogen fluorides and anhydrous hydrogen fluoride<sup>1-3</sup>. Recently, anhydrous hydrogen fluoride has proved of particular value in studying reactive fluorides, such as adducts of SF<sub>4</sub><sup>4</sup> and IF<sub>7</sub><sup>3-6</sup>, by means of Raman spectroscopy.

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Polarization measurements on the Raman scattering of these species in hydrogen fluoride may yield information about molecular vibrations and aid in their assignment. Such information is most easily obtainable from liquids and gases; for solids, it can only be obtained from orientated single crystals and matrix-isolated species. It was therefore of interest to obtain Raman data on HF solutions containing  $\text{BrF}_2^+$  and  $\text{BrF}_4^+$  cations whose assignments were in question<sup>6-8</sup>.

It further was of interest to obtain some semi-quantitative idea of the relative acidities of the halogen fluorides. The halogen fluoride systems have long been recognized as fluoride-ion analogues of proton-transfer acid-base systems. For solvents containing hydrogen, the acid strength is measured in logarithmic units, pH in aqueous systems,  $H_0$ , or some related quantity, in non-aqueous solvents. By studying solutions containing anhydrous hydrogen fluoride, the fluoride-ion transfer scale can be linked to the  $H_0$  scale, inasmuch as an  $H_0$  value of  $-11$  has been measured for HF<sup>9</sup>. It has already been shown that the Hammett acidity function can be applied to antimony pentafluoride dissolved in hydrogen fluoride<sup>10</sup>. Therefore, it was deemed advantageous to study the HF/ $\text{BrF}_3$ , HF/ $\text{ClF}_3$  and HF/ $\text{BrF}_5$  systems for the purpose of obtaining approximate Hammett acidity values for these species.

## EXPERIMENTAL

### *Reagents*

Bromine trifluoride used in this investigation was obtained from the Matheson Co. and purified as described previously<sup>7</sup>. Antimony pentafluoride, hydrogen fluoride, chlorine trifluoride and bromine pentafluoride were purified as described in previous publications<sup>7,8</sup>.

Potassium and cesium fluorides were of reagent grade quality.

### *Preparation of solutions*

Solutions for spectral measurements were prepared in a manner previously described. Special precautions were taken for the solutions used for conductivity measurements. This procedure has also been described previously<sup>11</sup>.

### *Equipment*

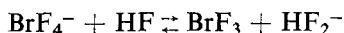
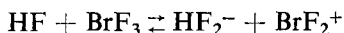
The vacuum line used for handling hydrogen fluorides and halogen fluorides as well as the conductivity cells have been described in previous publications<sup>10,11</sup>. The conductivity measurements were made with a Wayne Kerr autobalance precision bridge, Model B331. Overall conductivities are probably good to  $\pm 1\%$ . Raman spectra were excited as previously described<sup>12</sup>.

A DuPont curve resolver, Model 310, was employed when necessary to analyze the observed Raman spectra.

## RESULTS AND DISCUSSION

*The HF/BrF<sub>3</sub> system*

The following equilibria were examined:



where N.R. is no reaction.

Raman spectra were obtained for solutions of  $\text{BrF}_2\text{SbF}_6$  in HF (Fig. 1). The vibrational assignments are listed in Table 1 together with those for the solid. As seen, the higher frequency band is polarized and thus must be given the assignment for the symmetric stretching vibration. There seems to be very little interaction between cation and solvent HF since the location of the bands for the cation vary very little in going from the solid to solution. This is somewhat surprising as the band attributed to  $\nu_1$  for  $\text{BrF}_2^+$  in  $\text{BrF}_3$  occurs<sup>7</sup> at  $625 \text{ cm}^{-1}$ , a displacement of  $80 \text{ cm}^{-1}$  which shows a fairly large amount of cation-solvent interaction. The addition of  $\text{BrF}_3$  to a solution of  $\text{BrF}_2\text{SbF}_6$  in HF does indeed shift both stretching vibrations to lower frequencies, the extent of the shift increasing as the ratio of  $\text{BrF}_3$  to complex increases. At a 1:2 ratio of  $\text{BrF}_3$  to complex, the stretching vibrations occur at 700 and  $689 \text{ cm}^{-1}$  for  $\nu_1$  and  $\nu_3$ , respectively. For a 3:1 ratio of  $\text{BrF}_3$  to complex, the symmetric stretching vibration of  $\text{BrF}_2^+$  shifts to about  $680 \text{ cm}^{-1}$  and an additional band is formed at about  $625 \text{ cm}^{-1}$ . We have noted

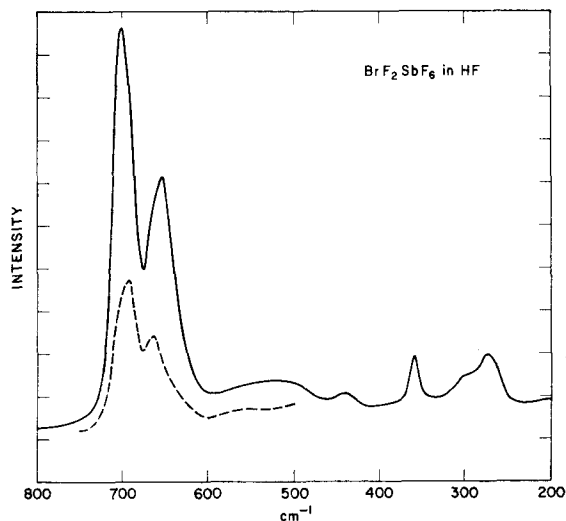


Fig. 1. Raman spectrum of  $\text{BrF}_2\text{SbF}_6$  in HF.

this latter band earlier and attributed it to the symmetric stretch of the solvated  $\text{BrF}_2^+$  cation in  $\text{BrF}_3$ .<sup>7</sup> It seems, therefore, that for  $\text{BrF}_2^+$  in excess  $\text{BrF}_3$  there is significant cation-parent molecule interaction which causes a decrease in the frequency of the stretching vibration of the cation.

TABLE 1  
RAMAN SPECTRUM OF THE DIFLUOROBROMONIUM(III) CATION

Assignment	$\text{BrF}_2^+$ in solid state <sup>a</sup>	1:2 ratio $\text{BrF}_3$ : $\text{BrF}_2^+\text{SbF}_6^-$ in HF	$\text{BrF}_2^+\text{SbF}_6^-$ in HF
$\nu_1$ ( $\text{BrF}_2^+$ )	705	700 (p)	707 (p)
$\nu_3$ ( $\text{BrF}_2^+$ )	702	689	695
$\nu_1$ ( $\text{SbF}_6^-$ )		660 (p)	658 (p)
$\nu_2$ ( $\text{SbF}_6^-$ )		550 (br)	550 (br)
$\nu_2$ ( $\text{BrF}_2^+$ )	362	362	361
$\nu_5$ ( $\text{SbF}_6^-$ )		{ 295 280	{ 295 278

<sup>a</sup> Ref. 6.

The HF/ $\text{BrF}_3$  system has been studied previously by spectroscopic and conductimetric methods<sup>11</sup>. From data obtained from these studies it was possible to calculate approximate values for the Hammett acidity function for these solutions and from these calculations to extrapolate to pure  $\text{BrF}_3$ . Methods used for these calculations have been discussed previously<sup>8,10</sup>. These values are listed in Table 2. Admittedly these are approximate, but they give some idea of how the inherent acidity of bromine trifluoride is related to protonic systems.

TABLE 2  
FLUORIDE-ION TRANSFER EQUIVALENTS OF HAMMETT ACIDITY  
VALUES FOR HF/ $\text{BrF}_3$  SYSTEM

Solution	Ratio $\text{HF}_2^-$ : HF	$F_o$
Pure HF		-11 ( $H_o$ value <sup>10</sup> )
1 mol l <sup>-1</sup> $\text{HF}_2^-$ in HF	1:50	-8.3
1 mol l <sup>-1</sup> HF in $\text{BrF}_3$	1:10	-7.6*
10 mol l <sup>-1</sup> HF in $\text{BrF}_3$	1:30	-8.0*
Pure $\text{BrF}_3$		-7*

\* Estimated value.

A note should be added here regarding the acidity function being used. The Hammett acidity function,  $H_o$ , is based on the ratio of protonated indicator cation to neutral indicator molecule. Since no organic indicators are presently known

to be stable in these systems, the ratio  $\text{HF}_2^- : \text{HF}$  was used to calculate the acidity function or, more properly, the fluoride-ion transfer equivalent of the Hammett acidity function,  $F_0$ . For this to be correct, we must assume that  $[\text{H}_2\text{F}^+][\text{HF}_2^-] = K_1$  for HF. This assumption is incorrect, however, as the anions are solvated to form a variety of species of the general type  $\text{H}_n\text{F}_{n+1}^-$ . Thus all acidity values obtained for the systems which were studied are approximate.

Basic salts of  $\text{BrF}_3$ , such as  $\text{CsBrF}_4$  and  $\text{KBrF}_4$ , were also dissolved in HF. The resulting spectra were rather complex (see Fig. 2). Using a curve resolver, it was possible to separate this spectrum into its component bands. By assuming the band at  $537 \text{ cm}^{-1}$  was  $\nu_1$  for  $\text{BrF}_4^-$ , it was possible to calculate  $K_{\text{eq}}$  values for the reaction  $\text{BrF}_4^- + \text{HF} \rightleftharpoons \text{BrF}_3 + \text{HF}_2^-$ . These are listed in Table 3.

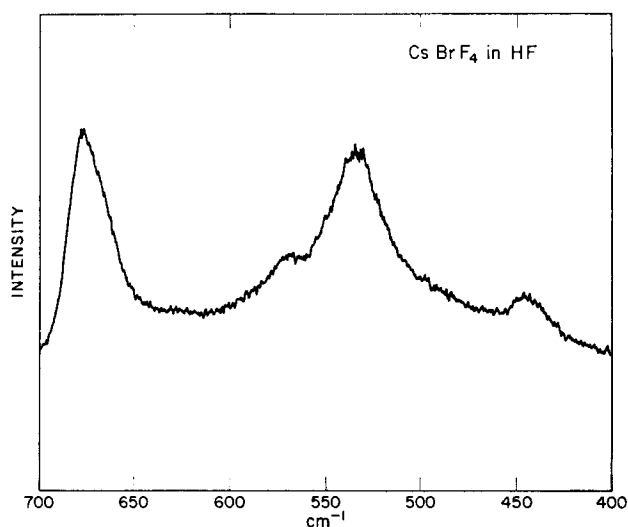


Fig. 2. Raman spectrum of  $\text{CsBrF}_4$  in HF.

TABLE 3

THE  $\text{F}^-/\text{BrF}_3/\text{HF}$  SYSTEM. EQUILIBRIUM CONSTANTS FOR  
 $\text{BrF}_4^- + \text{HF} \rightleftharpoons \text{HF}_2^- + \text{BrF}_3$

Type of system	$K_{\text{eq}}$
4.3 mol $\text{l}^{-1}$ $\text{CsBrF}_4$ in HF	0.45
Excess fluoride ion	0.27
4.0 mol $\text{l}^{-1}$ KF	
1.3 mol $\text{l}^{-1}$ $\text{BrF}_3$	
Excess $\text{BrF}_3$	0.12
3.1 mol $\text{l}^{-1}$ $\text{BrF}_3$	
0.7 mol $\text{l}^{-1}$ KF	

As seen, the concentrations of  $\text{BrF}_3$  and fluoride ion were varied in order to observe any possible effect this might have on  $K_{\text{eq}}$ . The values obtained agree fairly well considering the analytical problems involved in measurement. One interesting note, however, is the fact that the band attributed to  $\nu_1$  for  $\text{BrF}_4^-$  is not polarized. Hence it must be assumed that the anion is somehow distorted due to interaction with the solvent molecules and thus loses its center of symmetry. We are, however, not really satisfied with this explanation especially since the frequency at which this band occurs is not shifted appreciably from its position in the spectrum of the solid ( $530 \text{ cm}^{-1}$ ) or in  $\text{BrF}_3$  ( $528 \text{ cm}^{-1}$ ).

#### *The HF/BrF<sub>5</sub> system*

The following equilibria were examined:

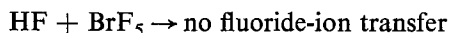
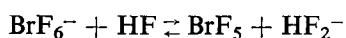
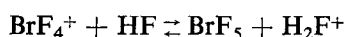


Table 4 lists the values of the conductivity of the HF/BrF<sub>5</sub> system vs. mole percentage of BrF<sub>5</sub>, while Table 5 lists a comparison of our values with previously published data<sup>13,14</sup>. Our values agree fairly well with those of Rogers and co-workers although the value they obtained for the solution containing the highest

TABLE 4

CONDUCTIVITY OF BROMINE PENTAFLUORIDE IN HYDROGEN FLUORIDE

BrF <sub>5</sub> (mol %)	Conductivity $\times 10^5$ ( $\Omega^{-1} \text{ cm}^{-1}$ )
0	1.76
1.1	2.32
1.8	2.65
3.8	4.97
7.0	8.87
8.3	12.12
9.4	13.71
10.8	15.28
14.3	12.22
17.7	10.92
19.5	10.05
26.9	9.48
42.6	6.45
51.0	5.19
58.8	4.27
81.8	2.65
91.0	0.444
100	0.010

TABLE 5

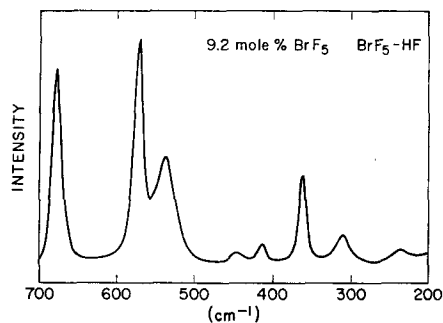
COMPARISON OF CONDUCTIVITIES OF HF/BrF<sub>5</sub> SYSTEM OBTAINED BY INDEPENDENT WORKERS

This work		Rogers <i>et al.</i> <sup>13</sup>		Quarterman <i>et al.</i> <sup>14</sup>	
BrF <sub>5</sub> (mol %)	10 <sup>5</sup> κ (Ω <sup>-1</sup> cm <sup>-1</sup> )	BrF <sub>5</sub> (mol %)	10 <sup>5</sup> κ (Ω <sup>-1</sup> cm <sup>-1</sup> )	BrF <sub>5</sub> (mol %)	10 <sup>5</sup> κ <sup>a</sup> (Ω <sup>-1</sup> cm <sup>-1</sup> )
100	0.010	100	0.010	—	—
91.0	0.444	90.5	0.45	90.4	33
81.8	2.65	81.4	1.90	—	—
58.8	4.27	61.4	12.50	—	—
42.6	6.45	—	—	46.5	100
26.9	9.48	—	—	28.0	1040
17.7	10.92	—	—	17.3	470

<sup>a</sup> At 10°.

concentration of HF is considerably greater than ours. The values obtained years ago in this laboratory are an order of magnitude higher, perhaps due to the ubiquitous contamination problem which often raises observed conductivities. Hydrogen fluoride is not a strong electrolyte in bromine pentafluoride solutions while bromine pentafluoride is only a slightly stronger electrolyte in anhydrous hydrogen fluoride solutions.

A Raman spectrum of a dilute solution of BrF<sub>5</sub> in HF is shown in Figure 3. There seems to be no change in the spectrum of BrF<sub>5</sub> except that due to dilution. However, on closer analysis, it appears that the band at 535 cm<sup>-1</sup> ( $\nu_4$ ) decreases slightly in intensity with respect to the intensities of the other fundamental bands of BrF<sub>5</sub> as the dilution is increased. This is the only observable band which arises from a b<sub>1</sub> symmetry class vibration. Preliminary data show that this is even more pronounced in the HF/IF<sub>5</sub> system<sup>15</sup> and it may be a real phenomenon due to a specific interaction. However, no new bands were observed in the Raman or the infrared spectrum of this system. The diamond window cell used for these infrared

Fig. 3. Raman spectrum of 9.2 mol % BrF<sub>5</sub> in HF.

measurements has been described previously<sup>16</sup>. Since this seems to be the first reported infrared spectrum of liquid  $\text{BrF}_5$  it is shown in Figure 4 and compared with data for gaseous  $\text{BrF}_5$  in Table 6. No visible changes were noted in the bromine pentafluoride spectrum upon dilution.

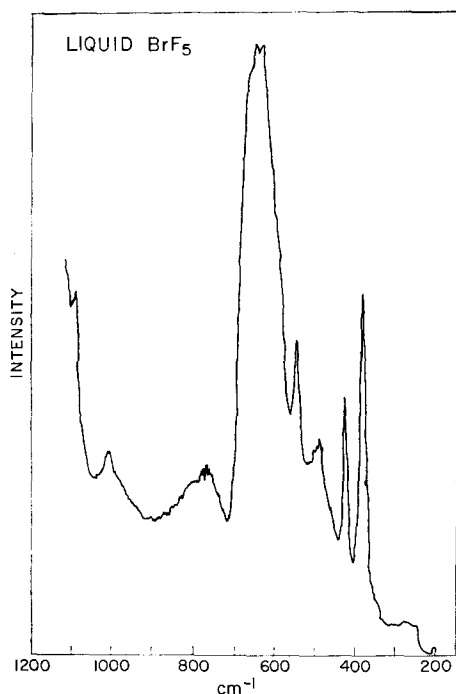


Fig. 4. Infrared spectrum of liquid  $\text{BrF}_5$ .

TABLE 6

INFRARED SPECTRUM OF  $\text{BrF}_5$

Species	IR (vapor <sup>a</sup> )	IR (liquid <sup>b</sup> )	Designation
$A_1$	683 (s)	672 (s)	$\nu_1$
$A_1$	587 (m)	n.o.	$\nu_2$
$A_1$	369 (s)	369 (s)	$\nu_3$
$B_1$	[547]	544 (m)	$\nu_4$
$B_1$		n.o.	$\nu_5$
$B_2$		n.o.	$\nu_6$
E	644 (v)	640 (s)	$\nu_7$
E	415 (m)	414 (m)	$\nu_8$
E		n.o.	$\nu_9$

<sup>a</sup> G. M. BEGUN, W. H. FLETCHER AND D. F. SMITH, *J. Chem. Phys.*, 42 (1965) 2236.

<sup>b</sup> This work.

n.o. = not observed.



It appears, therefore, that for the HF/BrF<sub>5</sub> system there is little or no fluoride-ion transfer on the optical or NMR time scale, although rather complete exchange within a few minutes has been reported in <sup>18</sup>F exchange studies in HF/BrF<sub>5</sub> solution.

We had made a tentative assignment for the spectrum of the BrF<sub>4</sub><sup>+</sup> cation in BrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub><sup>8</sup> and more recently a study of the crystal structure of BrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub> by Lind and Christie found that there was fluorine bridging between the anion and the cation but that the ionic formulation was essentially correct<sup>17</sup>. We have now obtained the Raman spectrum of BrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub> dissolved in HF (Fig. 5). The spectrum shows that the interaction between the solvent and the cation, BrF<sub>4</sub><sup>+</sup> + HF ⇌ BrF<sub>5</sub> + H<sub>2</sub>F<sup>+</sup>, lies far to the right. BrF<sub>5</sub> is a poor base and only in the reaction with SbF<sub>5</sub> has it been shown to form the BrF<sub>4</sub><sup>+</sup> cation. It is not surprising, therefore, that the BrF<sub>4</sub><sup>+</sup> cation acts as an acid in anhydrous hydrogen fluoride by accepting a fluoride ion from an HF solvent molecule which acts as the base. All the bands in the Raman spectrum are due to the BrF<sub>5</sub> molecular species, except for the bands at 726 and 606 cm<sup>-1</sup> which are due to Br-F symmetric stretching vibrations in BrF<sub>4</sub><sup>+</sup> and are thus the most intense Raman bands for this species. This also illustrates why there is little or no fluoride-ion transfer between HF and BrF<sub>5</sub> since they are comparable in their acidic strength.

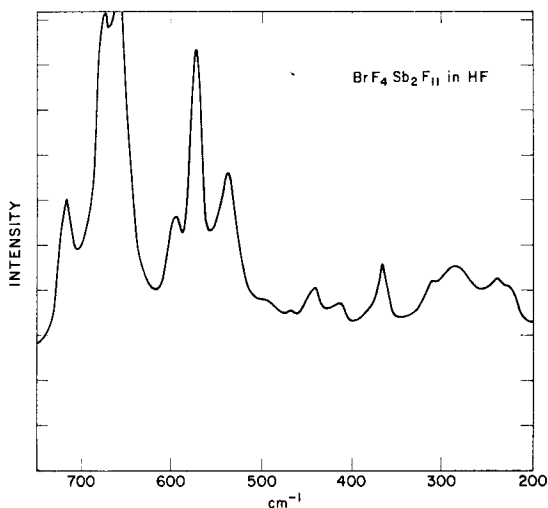


Fig. 5. Raman spectrum of BrF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub> in HF.

CsBrF<sub>6</sub> was also dissolved in HF. Here HF acts as an acid because the only bands which were observed in the Raman spectrum of the solution are those of the BrF<sub>5</sub> molecule. Varying the conditions as in the F<sup>-</sup>/BrF<sub>3</sub>/HF system produced results identical to that for the solution of CsBrF<sub>6</sub> in HF. Thus while BrF<sub>5</sub>

appears to be a strong acid, it appears to exist preferentially as a molecular species rather than any ionized form, as is supported by its low conductivity of  $9 \times 10^{-8} \Omega^{-1} \text{ cm}^{-113}$ .

*The HF/ClF<sub>3</sub> system*

The following equilibria were studied:

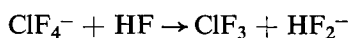
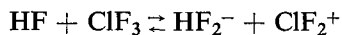


Table 7 lists the values for the conductivity of the HF/ClF<sub>3</sub> system and the molar conductivity of ClF<sub>3</sub> as a solute. Our values for the ClF<sub>3</sub>-rich region agree well with those of Rogers *et al.*<sup>18</sup>. These values show significant ionization which we interpret in terms of incomplete fluoride-ion transfer from ClF<sub>3</sub> to HF, *i.e.* ClF<sub>3</sub> is a weak base in HF while HF is a weak acid in ClF<sub>3</sub>. That the acid-base interaction in the direction postulated is confirmed by the Raman studies.

TABLE 7

CONDUCTIVITIES IN THE HF/ClF<sub>3</sub> SYSTEM

ClF <sub>3</sub> (%)	Conductivity $\times 10^4$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	Molar conductivity $\times 10^2$ ( $\text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$ )
0	0.455	—
1.9	1.41	14.2
4.1	2.31	12.3
7.9	2.69	7.87
11.2	2.98	6.33
13.4	2.98	5.64
16.7	2.87	4.54
19.0	2.78	3.85
24.0	2.52	2.93
29.0	2.69	2.74
33.7	2.31	2.12
39.2	1.81	1.52
48.4	1.57	1.15
56.3	1.41	0.96
63.2	0.387	0.246
72.0	0.104	0.0622
83.8	0.0354	0.0198
93.1	0.00052	0.00028
100	0.000045	0.000024

A shoulder at  $785 \text{ cm}^{-1}$  is observed in the Raman spectrum of a dilute solution of ClF<sub>3</sub> in anhydrous hydrogen fluoride. This band may be attributed to the ClF<sub>2</sub><sup>+</sup> cation discussed below. From separate measurements of the intensities

of the bands due to the  $\text{ClF}_3$  molecular species and the  $\text{ClF}_2^+$  cation and from the initial concentrations of HF and  $\text{ClF}_3$ , it is possible to determine an equilibrium constant for the reaction  $\text{ClF}_3 + \text{HF} \rightleftharpoons \text{HF}_2^- + \text{ClF}_2^+$  assuming that the concentration of  $\text{HF}_2^-$  is equal to that of the  $\text{ClF}_2^+$  cation.

The equilibrium lies largely to the left but, in contrast to the HF/ $\text{BrF}_5$  system, the cation band is observable in the Raman spectra of the system. We have discussed previously the difficulties in observing a band associated with the  $\text{HF}_2^-$  species [which is perhaps better described as  $(\text{HF})_n\text{F}$ ]<sup>12</sup>. The equilibrium concentrations and equilibrium constants are listed in Table 8, although the precision of the measured concentrations does not justify any attempt to explain variations in the value of the constant.

TABLE 8

EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN CHLORINE TRIFLUORIDE/HYDROGEN FLUORIDE MIXTURES

Mol fraction $\text{ClF}_3$	$\text{ClF}_3$ (mol l <sup>-1</sup> )	HF (mol l <sup>-1</sup> )	$\text{ClF}_2^+ = \text{HF}_2^-$ (mol l <sup>-1</sup> )	$10^4 K_{\text{eq}}^a$
0.63	15.6	8.8	0.1	0.7
0.50	13.8	13.3	0.2	2.2
0.36	11.2	19.7	0.2	1.8
0.17	6.4	31.9	0.22	2.4
0.10	4.3	37.7	0.17	1.8
0.036	2.2	43.3	0.10	4.4

<sup>a</sup> For the assumed equilibrium  $\text{ClF}_3 + \text{HF} \rightleftharpoons \text{ClF}_2^+ + \text{HF}_2^-$ .

Since it was necessary to know the position of the  $\text{ClF}_2^+$  bands in HF and to measure their intensity in relation to concentration,  $\text{ClF}_2\text{SbF}_6$  was dissolved in HF and the Raman spectrum shown in Figure 6 obtained (the asterisk in the spectrum signifies a Kel-F band). It is seen that the symmetric stretching vibration,  $\nu_1$ , occurs at 810  $\text{cm}^{-1}$ , while the asymmetric stretch,  $\nu_3$ , is not observed. Whilst  $\nu_3$  may have been shifted into accidental coincidence with  $\nu_1$ , the frequency shift or the lowered intensity must be attributed to some not readily interpreted interaction with the solvent.

When excess  $\text{ClF}_3$  is added to the solution of  $\text{ClF}_2\text{SbF}_6$  in HF the two stretching fundamentals may be distinguished and, as in the case of the  $\text{BrF}_3/\text{BrF}_2^+$  system, there is definite cation-parent molecule interaction which causes the stretching vibrations to occur at a lower frequency. Polarization measurements have been made which show that, as in the solid, the  $\nu_1$  symmetric stretching vibration occurs at a lower frequency than the  $\nu_3$  asymmetric stretching vibration. Table 9 summarizes the solid and solution spectra. Since it had been observed previously that the symmetric stretching vibration for  $\text{ClF}_2^+$  in  $\text{ClF}_3$  occurs at

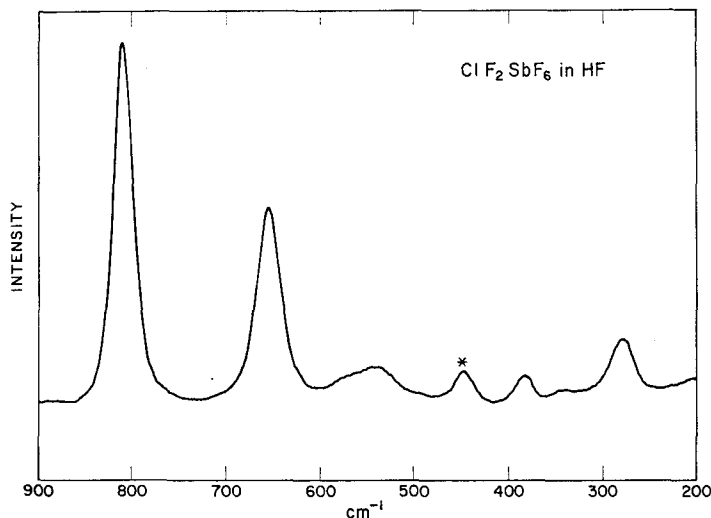


Fig. 6. Raman spectrum of  $\text{ClF}_2\text{SbF}_6$  in HF.

$782\text{ cm}^{-120}$ , the  $785\text{ cm}^{-1}$  band was used to determine the concentration of  $\text{ClF}_2^+$  in HF/ $\text{ClF}_3$  mixtures.

TABLE 9

THE RAMAN SPECTRUM OF THE DIFLUOROCHLORINIUM(III) CATION

Assignment	$\text{ClF}_2^+\text{SbF}_6^-$ in solid state <sup>a</sup>	$\text{ClF}_2^+\text{SbF}_6^-$ in HF	$\text{ClF}_2^+\text{SbF}_6^-$ in HF with excess $\text{ClF}_3$
$\nu_3$ ( $\text{ClF}_2^+$ )	830	(810) (?)	802
$\nu_1$ ( $\text{ClF}_2^+$ )	{ 809 805	810 (p)	785 (p)
$\nu_1$ ( $\text{SbF}_6^-$ )	662	658 (p)	653 (p)
$\nu_2$ ( $\text{SbF}_6^-$ )	{ 596 543 532	550 (br)	550 (br)
$\nu_2$ ( $\text{ClF}_2^+$ )	387	384	384
$\nu_5$ ( $\text{SbF}_6^-$ )	{ 291 277	278	280

<sup>a</sup> Ref. 19.

$\text{CsClF}_4$  was also dissolved in anhydrous hydrogen fluoride when only  $\text{ClF}_3$  bands were observed in the Raman spectrum of the solution indicating, as expected, that  $\text{ClF}_4^-$  like  $\text{BrF}_6^-$  acts as a base in HF. Varying the concentrations of  $\text{ClF}_3$  and of the fluoride ion produced the same spectrum as that of  $\text{CsClF}_4$  in HF.

In a similar manner as for the  $\text{BrF}_3/\text{HF}$  system, the fluoride-ion transfer equivalents of the Hammett acidity values for the  $\text{HF}/\text{ClF}_3$  system have been calculated. These are listed in Table 10. The acidity value for  $\text{ClF}_3$  is slightly less than that for  $\text{BrF}_3$ . We have observed previously<sup>20</sup> that the equilibrium involved in  $\text{BrF}_3/\text{ClF}_3$  mixtures is of the type  $\text{BrF}_3 + \text{ClF}_3 \rightleftharpoons \text{ClF}_2^+ + \text{BrF}_4^-$ . Thus chlorine trifluoride acts as a very weak base in  $\text{BrF}_3$  and as a slightly stronger one in  $\text{HF}$ . We have therefore assigned an  $F_0$  value of  $-6$  for  $\text{ClF}_3$ .

TABLE 10

FLUORIDE-ION TRANSFER EQUIVALENTS OF HAMMETT ACIDITY VALUES FOR THE  $\text{HF}/\text{ClF}_3$  SYSTEM

Solution	Ratio $\text{HF}_2^-$ : HF	$F_0$
Pure HF		$-11$ ( $H_0$ value <sup>9</sup> )
20 mol $\text{l}^{-1}$ HF in $\text{ClF}_3$	1:100	$-8.6^*$
10 mol $\text{l}^{-1}$ HF in $\text{ClF}_3$	1:40	$-8.2^*$
Pure $\text{ClF}_3$		$-6^*$

\* Estimated value.

A number of systems have been examined and from the accumulated data we have been able to calculate the approximate values of the fluoride-ion transfer equivalents of the Hammett acidity functions,  $F_0$ , for  $\text{BrF}_3$ ,  $\text{ClF}_3$  and  $\text{BrF}_5$ . These were  $-7$ ,  $-6$  and  $-11$ , respectively. Whilst approximate, they provide semi-quantitative values for studies in media in which the main consideration is that of fluoride-ion transfer. Until now, little more than qualitative observations have been made.

Work is at present proceeding on the  $\text{HF}/\text{IF}_5$  system which appears to be more complex than first imagined.

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