Fluoroanions and cations in the HF–SbF$_5$ superacid system. A ^{19}F and ^{1}H NMR study

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The ionic composition of the HF–SbF$_5$ superacid system has been investigated by ^{1}H and ^{19}F high field NMR. The anionic distribution over the whole composition range could be directly calculated from the ^{19}F NMR spectra. The cationic distribution was then estimated on the basis of charge balance. When the concentration of SbF$_5$ in HF was higher than 20 mol%, increasing amounts of nonassociated SbF$_5$ appeared. This change in composition can be linked to the change in reactivity of the superacid system in the activation process of small alkanes.

The awarding of the Nobel Prize in Chemistry to George Olah in 1994 acknowledged the important role of superacids as unusual reagents and solvents.[1,2] Liquid superacid media, which are generally a mixture of fluorinated Lewis acids such as SbF$_5$, TaF$_5$, AsF$_5$, *etc.* and fluorinated Broensted acids such as HF, HSO$_3$F, CF$_3$SO$_3$H, *etc.* are by definition[3] more acidic than 100% sulfuric acid ($H_0 \leqslant -12$). Acidities as high as $H_0 \sim -23$ have been measured for anhydrous hydrogen fluoride, fluorosulfonic acid and triflic acid containing 10, 30 and 40 mol% SbF$_5$, respectively;[4] further increasing the amount of SbF$_5$ is not accompanied by an increase in acidity. Since the first quantitative study by Kilpatrick and Lewis,[5] the ionic composition of the strongest superacid system, HF–SbF$_5$, has been investigated by various analytical techniques. The results obtained from electric conductivity,[5] cryoscopy[6] and vapor phase measurements,[7] as well as infra-red[8] and ^{19}F NMR spectroscopy,[9] all agree that SbF$_5$ is fully ionized in dilute HF solutions, first yielding the SbF$_6^-$ anion. With increasing concentration of SbF$_5$, increasing amounts of polymeric anions (Sb$_2$F$_{11}^-$, Sb$_3$F$_{16}^-$, *etc.*) are formed. According to an IR spectroscopic study,[8b] the predominant cationic species should be H$_3$F$_2^+$ for concentrations up to 40 mol% SbF$_5$, whereas at higher concentrations the H$_2$F$^+$ ion was observed. However, with the exception of this IR study and in contrast with NMR studies on weaker superacids,[10] most of the published work relates to dilute HF solutions and is more qualitative than quantitative in nature.

Due to its large chemical shift range, ^{19}F NMR has proven to be very useful as early as the late fifties, when Hoffmann and coworkers,[11] with a 56.7 MHz instrument, investigated liquid SbF$_5$ and assigned to it the polymeric *cis*-fluorine-bridged structure. The same instrumentation was used by Gillespie and Moss[9] to study the HF–SbF$_5$ system containing up to 40 mol% of SbF$_5$, in which they observed the SbF$_6^-$ and Sb$_2$F$_{11}^-$ anions. Later, with 94.1 MHz fluorine NMR, Gillespie's group described the structure of the polyanions Sb$_n$F$_{2n+1}^-$ and their adducts with various weak bases in a series of papers.[12]

With all these data available, it is surprising that, in contrast with other superacids such as fluoro and perfluoroalkylsulfonic acids, the anionic composition of the strongest superacid system available, HF–SbF$_5$, has not been reported in the literature. Considering that the limit of superacidity is already reached with less than 10 mol% SbF$_5$ in HF,[4] whereas the reactivity of this system towards alkanes increases steadily with increasing SbF$_5$ concentration,[13] we found it of interest to reinvestigate the ionic composition of the HF–SbF$_5$ system over the whole concentration range with the presently available high field 376 MHz^{19}F NMR spectroscopy.

Experimental

Anhydrous hydrogen fluoride (Matheson) was transferred into a 500 mL Kel-F flask from which it was distilled to the reactor as needed. Antimony pentafluoride from Allied Chemical was purified by triple distillation under dry nitrogen in a Pyrex apparatus in which it was stored until use. HF–SbF$_5$ solutions were obtained by distilling the pentafluoride into a weighed amount of HF in a Kel-F trap equipped with a Teflon valve and reweighing the trap. Sulfuryl fluorochloride (SO$_2$ClF) was prepared from ammonium fluoride and sulfuryl choride following ref. 14 and stored on P$_2$O$_5$ in a Pyrex flask.

Caution. Handling anhydrous HF needs extreme caution to protect skin and eyes. It can cause severe burns, which may not be visible or painful for several hours.

NMR spectra were recorded on a Bruker AM400 spectrometer. The HF–SbF$_5$ solutions were analyzed at temperatures between −10 and −90 °C using quartz NMR tubes (5 mm OD). In order to compare all NMR spectra at the same temperature (−60 °C) we used SO$_2$ClF to keep the viscosity of the solution at a low enough level. ^{19}F chemical shifts were always measured using SO$_2$ClF as internal standard (99.1 ppm downfield from CFCl$_3$).

Results and discussion

The anions Sb$_n$F$_{5n+1}^-$

HF has a very small autoprotolysis constant of the order of 10^{-12} at 0 °C. As a consequence, a steep rise in acidity is noticed following the ionization reaction:[15]

$$\mathrm{SbF_5} + n\mathrm{HF} \rightarrow \mathrm{SbF_6^-} + \mathrm{H(HF)_{n-1}^+}$$

The cation has been written most often as H$_2$F$^+$ for simplicity but as we will see below, it is rather a polymeric, strongly

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hydrogen bonded species. The hexafluoroantimonate ion SbF_6^-, which is generated first, can be further complexed when more SbF_5 is added to the HF solution:

$$SbF_6^- + SbF_5 \rightarrow Sb_2F_{11}^-$$

$$Sb_2F_{11}^- + SbF_5 \rightarrow Sb_3F_{16}^-$$

$$Sb_3F_{16}^- + SbF_5 \rightarrow Sb_4F_{21}^-$$

All these ions have been previously identified[12] and their ^{19}F NMR lines have been assigned on the basis of homonuclear ^{19}F coupling constants with 94.1 MHz NMR, but the higher fields now available overcome the problem of overlapping and facilitate the quantitative analysis of the individual components.

The structure and the fluorine atom numbering of the fluoroantimonate ions and adducts are presented in Scheme 1. We use the numbering pattern originally suggested by Dean and Gillespie,[12b] which always starts from the terminal fluorine opposite to a fluorine bridge, or, if this is not present, opposite to a donor molecule and gives the same number to chemically equivalent fluorines. We have collected in Table 1 the chemical shifts of the various fluorine nuclei for each species.

Two characteristic 376 MHz ^{19}F NMR spectra are shown in Fig. 1. As can be seen, characteristic lines due to the strong magnetic field are available for quantitative measurements, even at high SbF_5 concentration when all four ions are present. The variation of the composition of the HF–SbF_5 system as a function of the concentration of SbF_5 is presented in Fig. 2. For SbF_5 concentrations lower then 10 mol%, SbF_6^- is practically the only anionic species present. In the concentration range of 10 to 22 mol% SbF_5 in HF the anions are essentially SbF_6^- and $Sb_2F_{11}^-$, which are in slow equilibrium on the NMR time scale:

$$SbF_5 + n\mathrm{HF} \rightarrow SbF_6^- \cdot H^+(HF)_{n-1}$$

$$SbF_5 + SbF_6^- \cdot H^+(HF)_{n-1} \rightleftharpoons Sb_2F_{11}^- \cdot H^+(HF)_{n-1}$$

The structure of $Sb_2F_{11}^-$ anions in fluoronium salts has been confirmed recently by X-ray structural analysis of two ionic adducts corresponding to $SbF_5 \cdot 1.5$ HF and $SbF_5 \cdot$ HF.[16] We notice that the formation of the polymeric ions $Sb_3F_{16}^-$ and $Sb_4F_{21}^-$ occurs for higher concentrations of the Lewis acid. These results are somewhat more precise than

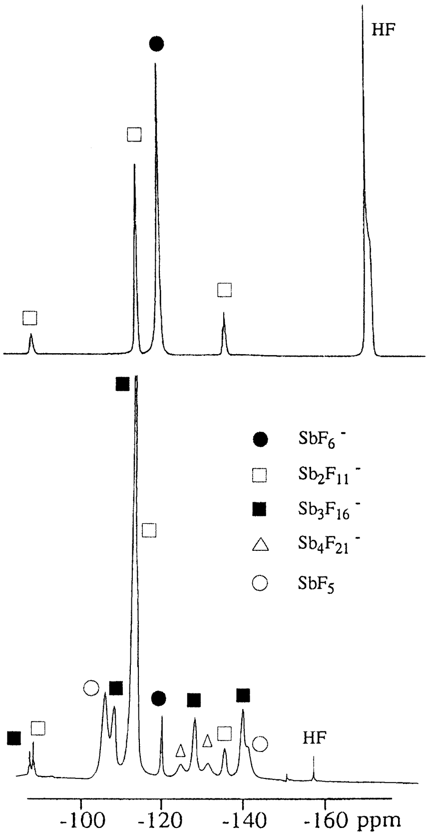
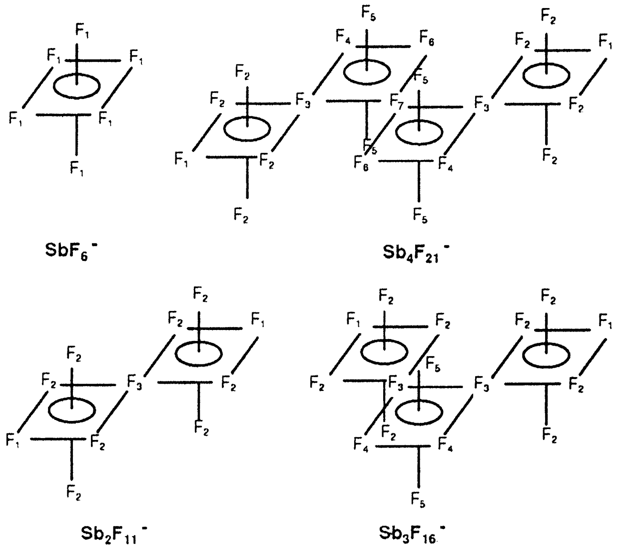


Fig. 1 Characteristic ^{19}F NMR spectra of the HF–SbF_5 system. Top: 17.3 mol% SbF_5; bottom: 77.1 mol% SbF_5.



Scheme 1

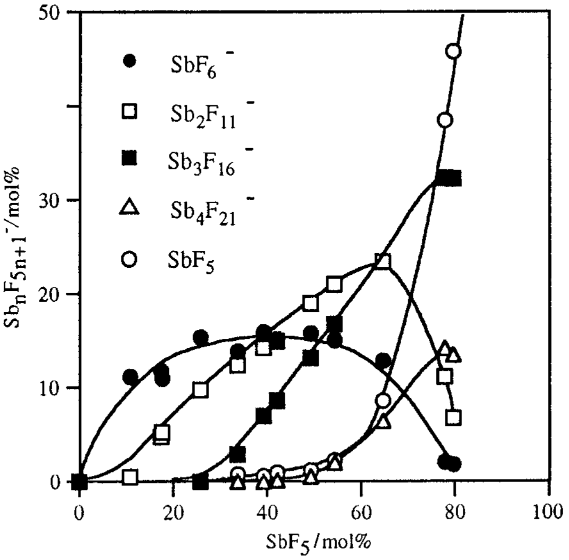


Fig. 2 The anionic composition of the HF–SbF_5 system.

Table 1 ^{19}F chemical shifts of fluoroantimonate ions (δ referenced to external $CFCl_3$)

	F_1	F_2	F_3	F_4	F_5	F_6	F_7
SbF_6^-	−122.3						
$Sb_2F_{11}^-$	−138.7	−116.7	−90.4				
$Sb_3F_{16}^-$	−139.7	−111.9	−88.3	−127.2	−107.1		
$Sb_4F_{21}^-$	−141.3	−111.5	−88.3	−123.9	−104.6	−119.3	−82.2

those of Bonnet *et al.*, who did not detect polymeric species larger than $Sb_2F_{11}^-$ when the concentration of SbF_5 in HF was below 40 mol%.[8b]

In Fig. 3 we have plotted the amount of HF remaining after ionization and the total amount of anionic species as a function of SbF_5 concentration in HF. If we compare these curves with those published for the $FSO_3H–SbF_5$ and $CF_3SO_3H–SbF_5$ systems by Commeyras *et al.*[10b] we notice a striking difference. In both sulfonic acid based systems, complete ionization of the acids was observed when the concentration of SbF_5 reached 50 mol%. A steady increase of the concentration of the monoadduct $RSbF_5^-$ ($R = FSO_3$, CF_3SO_3) was observed with a maximum at 50 mol% SbF_5, the $RSb_2F_{10}^-$ species (diadduct) appeared only at SbF_5 concentrations higher than 50 mol%. In contrast, in the HF–SbF_5 system the ^{19}F NMR signal of the un-ionized HF can be observed up to 80 mol% SbF_5. According to Fig. 2 the diadduct $Sb_2F_{11}^-$ starts to appear at 10 mol% and the triadduct at 25 mol%. In this superacid SbF_5 prefers to complex the fluoroantimonate ions instead of ionizing more HF and the total concentration of the anionic species remains lower over the whole concentration range. The large difference in superacidity between the HF based and the fluorosulfonic acid based systems is probably also related to the difference in anionic composition, in addition to the presence of more basic oxygen lone pairs in the sulfonic superacids.

On the other hand, an interesting observation was the presence of an initially small but increasing amount of uncomplexed SbF_5 observed for concentrations above 20 mol% SbF_5 in HF. The presence of this un-ionized SbF_5 can help us to rationalize the concentration dependent selectivity observed when isobutane is reacted with the HF–SbF_5 system.[13a,b] The conversion of isobutane in liquid superacids (Scheme 2) can be monitored either by measuring the amount of hydrogen produced or by measuring the amount of pivalic ester obtained by trapping the ions with carbon monoxide followed by quenching with excess ethanol.[13c] It was reported[13] that for concentrations up to 20 mol% SbF_5, reaction (1) in Scheme 2 was purely protolytic as the amount of hydrogen produced was equivalent to the amount of ester. For concentrations higher than 25 mol% SbF_5, the hydrogen production decreased drastically whereas the production of ethyl pivalate continued to increase. The production of SbF_3, observable as a white precipitate, indicated that SbF_5 was reduced during isobutane conversion with production of HF (see Scheme 3), as earlier suggested by Olah *et al.*[17] We assume that this change in product distribution is related to the change in composition of the superacid as at higher concentrations in HF, SbF_5 becomes available for direct participation in the activation process.

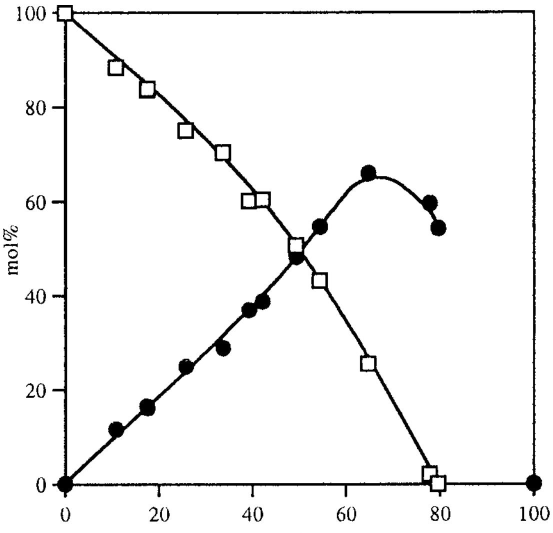
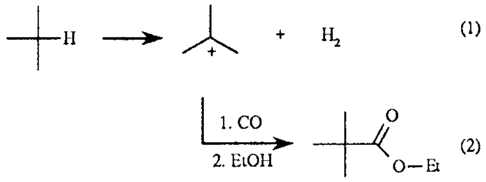
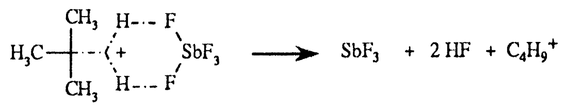


Fig. 3 Amount of HF remaining after ionization (□) and the total amount of anionic species (●) as a function of SbF_5 concentration in HF.



Scheme 2



Scheme 3

A related observation was made when HF was replaced by DF: at SbF_5 concentrations below 20 mol% a reversible protonation of the alkanes was observable *via* H/D exchange of the hydrogens of isobutane. This exchange is about 20 times faster than protolysis.[13] At higher concentrations the exchange process becomes negligible in comparison with ionization.[18]

On the other hand, we have also shown earlier[4] that the acidity of HF–SbF_5 is close to its limit ($H_0 \approx -23$) in the 15–20 mol% SbF_5 range. Thus, increasing the concentration of SbF_5 above 20 mol% should not result in an increase of the rate of protolysis.

Cationic composition of the HF–SbF_5 system

Hydrogen fluoride plays a double role as acid and solvent. The presence of the Lewis acid favors the dissociation of the acid as the fluoride ion is complexed by SbF_5. In this way a mixture of larger anions is generated:

$$n\mathrm{SbF_5} + \mathrm{HF_{excess}} \rightarrow \mathrm{Sb}_n\mathrm{F}_{5n+1}^- + \mathrm{H^+(HF)}$$

Due to charge balance the formation of each anion, whatever its size, is accompanied by the generation of one proton.

The second role of HF is the solvation of these protons by its un-ionized fraction:

$$n\mathrm{HF} + \mathrm{H^+} \rightarrow \mathrm{H^+(HF)}_n$$

For this reason, the structure of these cationic species is also dependent on the molar ratio of Lewis acid to HF. Some of these fluorinated cations have been described in the literature.

At high dilution, the remaining HF molecules are organized as a polymeric structure associated by hydrogen bonding.[9]

^1H and ^{19}F chemical shifts of HF and $H^+(HF)_n$ cations. In both ^1H and ^{19}F spectra, even at temperatures as low as −120 °C, only one solvent signal was observed. The inter- and intramolecular exchange processes between the cationic species (H_2F^+, $H_3F_2^+$, …, $H_{n+1}F_n^+$) are indeed too fast, on the NMR time scale, to allow the observation of separate signals.

In Fig. 4, we present the variation of the ^1H chemical shift of the solvated proton $H^+(HF)_n$ as a function of the molar concentration of SbF_5 in the superacid medium. The signal appears at 8.1 ppm for pure HF and with higher concentrations of SbF_5 shifts to lower field, reaching 16 ppm when the concentration of SbF_5 is 80 mol% in HF–SbF_5. The deshielding observed with increasing concentration of SbF_5 has been rationalized by a progressive desolvation of the protons, inducing a concentration of the positive charge in smaller $H^+(HF)_n$

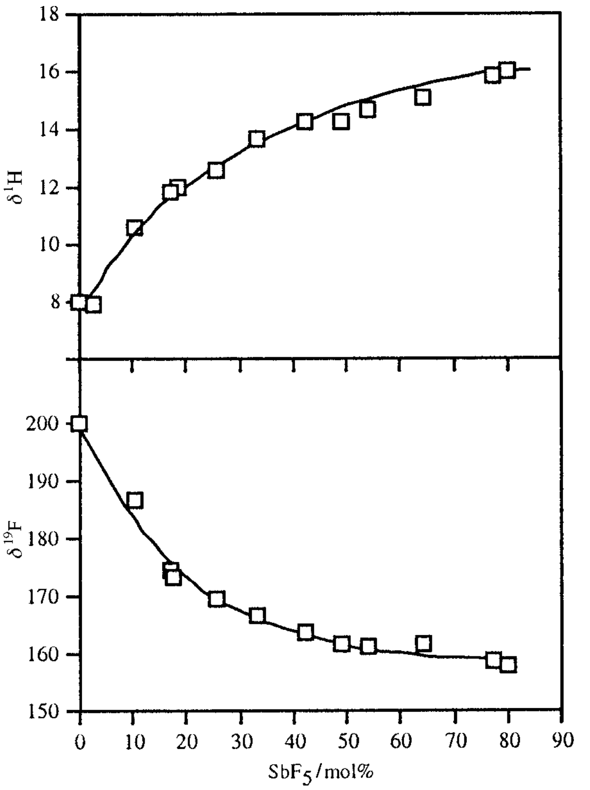
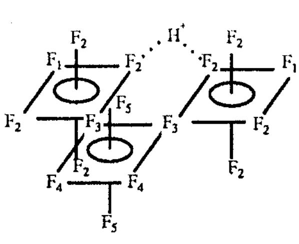


Fig. 4 Variation of the ^{1}H (top) and ^{19}F (bottom) chemical shifts of HF with SbF$_5$ concentration.

entities.[19] The variation of chemical shift is more pronounced in diluted solutions, in which each molecule of SbF$_5$ leading to SbF$_6{}^-$ creates a positive charge. When the concentration of Lewis acid increases, a higher number of SbF$_5$ molecules is needed to observe the same effect due to progressive polymerization of the anions (two molecules of SbF$_5$ when the dimeric Sb$_2$F$_{11}{}^-$ anion is formed, three molecules when an Sb$_3$F$_{16}{}^-$ anion is created, *etc.*).

Similar observations can be noted when the ^{19}F chemical shift of HF is plotted *versus* the concentration of SbF$_5$ (Fig. 4): the ^{19}F chemical shift varies gradually from 200 ppm (pure HF) to 158 ppm (80 mol% SbF$_5$).

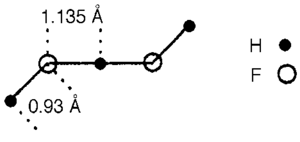
With increasing concentration of SbF$_5$, the relative area of the HF signal diminished, vanishing completely when the concentration reached 80 mol% SbF$_5$. At this point, when no HF is left in the solution, a proton signal is nevertheless observed at 16 ppm in ^{1}H NMR. To our knowledge, this is the first NMR assignment of such an acidic species in liquid solution. Up to now the cationic species described in the literature, on the basis of IR observation or direct X-ray structural analysis, involved at least one HF solvent molecule. As in the condensed phase the proton cannot be naked, we assume that at these concentrations where no free HF is present, the proton is directly solvated by the Sb$_3$F$_{16}{}^-$ anion. We suggest a structure (Scheme 4) in which the proton could be chelated between two fluorine atoms. In this structure the F–H–F distance (2.6 Å) is close to that measured for crystal structures of SbF$_5$ · HF adducts.[16]



Scheme 4

The cationic species. For many years the existence of positively charged H$^+$(HF)$_n$ species has been the subject of theoretical and experimental studies. In analogy with H$_3$O$^+$, the existence of the H$_2$F$^+$ ion has long been postulated, in order to rationalize the conductivity of superacid solutions such as HF–SbF$_5$ and HF–BF$_3$. The first observation of this ion has been reported by Van Huong *et al.*, based on IR observations.[8a] Leibovici, performing semi-empirical and *ab initio* calculations,[20] and Dierksen *et al.*,[21] with the SFC-LCAO-MO method, have calculated the structure of this cation. Bonnet and Mascherpa, using infrared spectroscopy,[8c] reported its observation for concentrations higher than 40 mol% SbF$_5$ in liquid HF–SbF$_5$ mixtures and claimed that it was the only cation observed at concentrations higher than 85 mol% SbF$_5$. This latter assumption is not in agreement with our NMR spectra, which show the disappearance of the HF signal in the ^{19}F NMR spectra when the concentration reaches 80 mol% SbF$_5$. More recently, Mootz and Bartmann[16] isolated crystals of H$_2$F$^+$ · Sb$_2$F$_{11}{}^-$, corresponding to the ionic adduct SbF$_5$ · HF. According to these studies, H$_2$F$^+$ is bent, presenting an elongated HF bond compared to HF.

The ion H$_3$F$_2{}^+$, resulting from the solvation of one proton by two molecules of HF, has been studied theoretically.[20,21] It was found that the *trans* C_2h structure with a central hydrogen (Scheme 5) was the most stable. Bonnet and Mascherpa[8c] observed the typical absorption bands of this ion in the liquid phase and concluded that between 0 and 20 mol% mol SbF$_5$ in HF–SbF$_5$, H$_3$F$_2{}^+$ solvated by HF molecules was the predominant species. In the range 20–40 mol% SbF$_5$, only H$_3$F$_2{}^+$ was observed. They postulated the existence of H$_3$F$_2{}^+$ · Sb$_2$F$_{11}{}^-$ and H$_3$F$_2{}^+$ · Sb$_3$F$_{16}{}^-$ adducts in this concentration range and suggested that for concentrations greater than 40 mol% SbF$_5$, H$_3$F$_2{}^+$ was progressively replaced by H$_2$F$^+$. In a recent study, this ion, associated with Sb$_2$F$_{11}{}^-$ in the ionic adduct SbF$_5$ · 1.5 HF, has also been characterized by X-ray diffraction.[16]



Scheme 5

The existence of larger H$_{n+1}$F$_n{}^+$ cationic species was suggested on the basis of the following observatiosn from DTA studies performed by Bonnet *et al.*:[8b] SbF$_5$ · 4HF, SbF$_5$ · 6HF and SbF$_5$ · 9HF.

Recently, Mootz and Bartmann, studying the melting diagram of the HF · SbF$_5$ system, found a new low-melting adduct SbF$_5$ · 7HF described as a fluoronium salt, (H$_7$F$_6$)SbF$_6$.[16b] They concluded that the novel H$_7$F$_6{}^+$ cation is formed as an unbranched chain by very strong hydrogen bonds between the respective F atoms, which become weaker from the center to the end.

The contribution of NMR to the study of the cationic species. Due to fast proton exchange the NMR technique cannot bring direct information about the cationic composition of the medium; however, if we make some assumptions, it is possible to estimate the nature of the different cationic species. If, assuming that only the three species observed by IR (H$_3$F$_2{}^+$, H$_2$F$^+$ and HF) do exist in the liquid phase in the 0–40 mol% SbF$_5$ range, we can calculate the ^{19}F chemical shift variation on the basis of the chemical shifts measured for HF and H$_2$F$^+$. We obtain the curve shown beside the experimental one in Fig. 5. It is obvious that the observed discrepancy is due to the presence of other H$_{n+1}$F$_n{}^+$ species. It is clear that if we take into account the presence of even heavier cationic

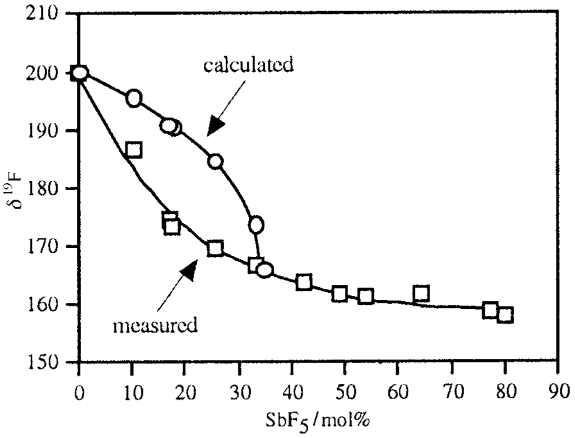


Fig. 5 Comparison of experimental (□) and calculated (○) ^{19}F chemical shifts for the $HF–H_2F^+–H_3F_2^+$ system.

Table 2 Calculated concentration limits for the existence of various cations in HF

Species	mol% SbF_5
$H^+ \leftrightarrow H_2F^+$	80
$H_2F^+ \leftrightarrow H_3F_2^+$	35
$H_3F_2^+ \leftrightarrow H_4F_3^+$	27.5
$H_4F_3^+ \leftrightarrow H_5F_4^+$	22.5
$H_5F_4^+ \leftrightarrow H_6F_5^+$	18.5
$H_6F_5^+ \leftrightarrow H_7F_6^+$	16
$H_7F_6^+ \leftrightarrow H_8F_7^+$	14
⋮	⋮

species, the fit between calculated and theoretical chemical shifts will be even better. In fact, the continuous variation in chemical shifts does not support the existence of only two or three cationic species but is in good accord with a continuous variation of solvation of the proton by as many HF molecules as available.

As it is apparent from the NMR spectra that the proton exchange between the different cations $H_{n+1}F_n^+$ is fast ($k \gg 10^{-3}$ at −60 °C), we assume that on average the solvation of the proton is always at a maximum and that the probability of the coexistence of the species $H^+(HF)_n$ and $H^+(HF)_{n+2}$ can be neglected. On this basis, the concentration of protons being equal to the concentration of the anions, the protons will be solvated by as much HF as is available after ionization. Thus the theoretical concentration limits of the different positive species can be estimated as reported in Table 2.

Conclusion

376 MHz ^{19}F NMR has been used to measure the concentration dependent anionic composition of the $HF–SbF_5$ superacid system. In comparison with other superacids, the ionization of the HF requires larger amounts of Lewis acid. From the anionic composition and on the basis of charge balance we tried to estimate the cationic composition of this medium. However, on the NMR time scale no definite concentration zone could be detected in which only one of the $H^+(HF)_n$ species exists independently and it appears that the change in solvation *via* strong hydrogen bonding is a continuum. The presence of increasing amounts of un-ionized SbF_5 at concentrations higher than 20 mol% in HF rationalizes the change in selectivity in small alkane activation by the superacid system.

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