NMR STUDIES OF

CARBONIUM IONS

IN SUPERACID MEDIA

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By

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SCOPE AND CONTENTS:

Proton and fluorine nmr have been used to study the formation of simple alkylcarbonium ions in SbF_5-containing media. The $Sb_2F_{11}^-$ ion and the previously unreported cis-$Sb_3F_{16}^-$ ion have been shown to be among the anions formed. The fluorine spectra of SbF_5 and cis-$Sb_3F_{16}^-$ have been analyzed in detail.

Evidence has been found that methyl and ethyl fluoride form donor-acceptor complexes $RSbF_6$ and RSb_2F_{11} which undergo very rapid exchange at the carbon-fluorine bond. The fluorine spectrum of such a complex cannot be distinguished from that of the corresponding anion.

Several reactions of alkanes in SbF_5-containing media have been investigated. It has been shown that protonated alkanes do not exist as a stable form in superacid solutions. It is also shown that SbF_5 is capable of hydride abstraction from an alkane.

Several new coupling constant values have been obtained from proton spectra of carbonium ions and other species. An attempt has been made to discuss these and some literature values in terms of molecular orbital theory.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

(1) GENERAL

This thesis describes the result of an investigation into the production of stable alkylcarbonium ions in solutions of very high acidity. The simple alkylcarbonium ions, $R-C^+\!\!\stackrel{R}{\underset{R}{\diagdown}}$, where alkyl groups or hydrogens are attached to a carbon with a formal positive charge are considered. Such ions have been known to exist in the gas phase and have been studied extensively by mass spectrometry[1], but were thought until recently to exist only as transient entities in solution, e. g. as in the well known $S_N 1$ reaction. In the last five years extensive research, starting with the initial paper of Olah and his colleagues[2] has shown many tertiary, and several secondary alkylcarbonium ions exist in superacid media containing antimony pentafluoride. Most of this work has been carried out with the aid of nuclear magnetic resonance spectroscopy, generally that of protons.

(2) NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY[3,4]

Nuclear magnetic resonance has its origin in the magnetic properties of the nucleus. Any nucleus having a non-zero spin I has an associated magnetic moment μ given by

$$\mu = \gamma I \hbar$$

where γ is a constant, called the magnetogyric ratio, for a given nucleus. When such a nucleus is placed in a static magnetic field of intensity H_0, the energy of interaction between the field and the nuclear moment is

$$E = -m \hbar \gamma H_0$$

where m is an integer having one of the $2I+1$ values I, I-1, ------, -I specifying the orientation of the nuclear moment with respect to the magnetic field. That is, there are $2I+1$

1

energy levels separated by $\hbar\gamma H_0$. Irradiation of the nuclear magnet situated in an applied magnetic field with electromagnetic radiation will therefore cause transitions between adjacent levels if the frequency of the irradiating field ν is such that $h\nu=\hbar\gamma H_0$, that is

$$\nu=\frac{\gamma H_0}{2\pi}$$

The resulting absorption of energy under such conditions is called nuclear magnetic resonance and the above expression for ν the resonance condition. The resonance frequency is seen to be proportional to both γ and H_0. For a 14.092 kilogauss field the proton resonance frequency is 60.000 MHz and that of ^{19}F is 56.445 MHz. At 23.487 kilogauss the corresponding frequencies are 100.000 and 94.077 MHz. Most commercial spectrometers presently in use operate at one of these field strengths. Protons and ^{19}F nuclei, the two most used isotopes in nmr, both have $I=1/2$, reducing the above picture to two energy levels corresponding to parallel and antiparallel orientations of the nuclear spin with respect to the applied magnetic field.

The magnetic fields experienced by nuclei of the same kind in chemically different environments in a molecule differ slightly from each other, and from the applied field H_0, as a result of small local magnetic fields arising from induced orbital motions of the electrons about the nuclei. These local magnetic fields are largely diamagnetic, that is oppose H_0, and are therefore said to shield the nucleus from H_0. Therefore in the nmr experiment as it is usually performed, in which the irradiating frequency is kept constant and the magnetic field is varied, each chemically different group of nuclei comes to resonance at a slightly different value of the applied field H_0. The displacement of an individual resonance is called the chemical shift, and is usually measured relative to the resonance of a standard compound, generally tetramethylsilane (TMS) for protons and trichlorofluoromethane ($CFCl_3$) for fluorine resonance.

Since the induced motion of the electrons, and hence the local magnetic field, is proportional to the applied field, the chemical shifts will also be proportional to the applied field. It is therefore convenient to express chemical shifts as the dimensionless quantity δ defined by

$$\delta = \frac{H - H_r}{H} \times 10^6$$

where δ is the chemical shift in parts per million (ppm), H is the resonance field and H_r is the resonance field for the reference compound. Different functional groups have chemical shifts which are characteristic of that group and vary over a limited range only. The area of each resonance peak turns out to be proportional to the number of resonating nuclei in the functional group giving rise to the resonance. Measurement of the positions and areas of nmr resonances can therefore be used to determine the number of functional groups and the number of nuclei in each environment. It should be noted that it is sometimes useful to express chemical shifts and chemical shift differences in units of frequency. This can be done by multiplying δ, in ppm, by the oscillator frequency ν_0, in MHz, to give $\nu_0\delta$, the chemical shift in Hz.

Under high resolution the spectra of most compounds show more lines than can be accounted for on the basis of chemical shift considerations alone, individual resonances being split into multiplets. It has been shown that this multiplet splitting arises from a field independent interaction between nuclear spins, generally those in different chemical environments. As an example, let us take the proton spectrum of isopropyl chloride, $(CH_3)_2CHCl$, shown in Fig. 1. Under low resolution two lines are seen, one 4.33 ppm below TMS and the second 1.66 ppm below TMS. The area of the latter is six times that of the former. Clearly the resonance at high field is that of the six equivalent methyl protons and the low field resonance is that of the single methine proton. Most of the 2.77 ppm shift between

the two resonances is due to the greater withdrawal by the electronegative chlorine of electrons from the vicinity of the methine proton, resulting in its deshielding. This deshielding generally occurs for protons on a carbon attached to an electronegative site. Under high resolution the methyl resonance is split into two lines separated by 6.5 Hz. This splitting has its origin in the two possible orientations of the methine proton spin. The methine spin interacts with the methyl spins through the spins of the electrons in the bonds between them. The energy of interaction between two spins is specified by the spin-spin coupling constant J, given in Hz. When $\nu_0 \delta >> J$, the so-called first order condition, it can be shown that the effect on one spin of coupling to a second spin in a different chemical environment is equivalent to an increase or decrease in the local magnetic field of $J/2$, depending on whether the second spin is parallel or anti-parallel to the applied magnetic field. Statistically the methine spin has an equal probability of either orientation, and so the methyl resonance is split into two peaks separated by J, which can be read directly from the spectrum. The resonance of the methine proton is a septet having the relative intensities 1:6:15:20:15:6:1, as the local fields from the six methyl protons add to give one of seven possible total values with the statistical weights shown. The splitting between adjacent peaks of the septet is also J. In general, coupling to a group of n nuclei having $I=1/2$ gives a multiplet of n+1 lines with relative intensities given by the coefficents in the binomial expansion for n. Coupling constants between protons separated by four or more single bonds are generally very small. ($\leqslant 0.5$Hz)

We may note that the above spectrum shows no coupling effects from carbon or chlorine. This is because ^{12}C has $I=0$ and both isotopes of chlorine have $I=3/2$. In the case $I>1/2$ a relaxation mechanism exists which rapidly relaxes

the nuclear spin, that is, causes frequent transitions between the different orientations of the nuclear magnet, unless it is situated in a very symmetrical environment. This results in any coupling to chlorine being averaged out. Another averaging process is chemical exchange, which can lead to an nmr spectrum simpler than that expected. Two separate signals will coalesce when an exchange process between the states involved occurs at a rate which is greater than the frequency which separates the signals. An example will be discussed in the following section.

Although ^{12}C has $I=0$, ^{13}C has $I=1/2$ and is present in 1.1% natural abundance. Coupling between protons and ^{13}C in natural abundance results in the so-called ^{13}C satellites in the proton spectrum. These are peaks of very low intensity situated $J_{CH}/2$ above and below the normal resonance and are simply another instance of spin-spin coupling.

(3) ALKYLCARBONIUM IONS IN SUPERACIDS

Stable, long-lived alkylcarbonium ions in solution were first observed by Olah and coworkers[2] who dissolved alkyl fluorides in excess antimony fluoride and in excess antimony fluoride/sulfur dioxide solutions and formulated the reactions

$$C_3H_7F + SbF_5 \longrightarrow (CH_3)_2C^+H + SbF_6^-$$
$$C_4H_9F + SbF_5 \longrightarrow (CH_3)_3C^+ + SbF_6^-$$
$$C_5H_{11}F + SbF_5 \longrightarrow (CH_3)_2C^+CH_2CH_3 + SbF_6^-$$
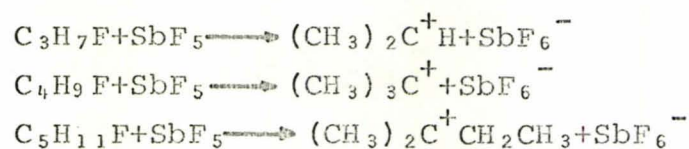
Considerable heat is evolved in these reactions. These three ions are known as the dimethylcarbonium, trimethylcarbonium, and dimethylethylcarbonium ions respectively in one nomenclature, and as the isopropyl, t-butyl and t-pentyl (t-amyl) ions in another. The evidence put forward by Olah for the existence of these ions as stable species consisted of some quite striking changes in chemical shifts and coupling constants in the proton spectrum after reaction had occured. Fig. 2 shows the proton spectrum of t-butyl fluoride, $(CH_3)_3CF$, neat and mixed with SbF_5, as obtained by Olah.

The spectrum of t-butyl fluoride itself consists of the resonance of the nine equivalent methyl protons at 1.30 ppm below TMS, split into a 20 Hz doublet by coupling with the fluorine. After reaction with SbF_5 the resonance shifts downfield to 4.35 ppm below TMS and becomes a single line, the H-F coupling disappearing. A reasonable interpretation of this is the removal of a fluoride ion by antimony pentafluoride to give the t-butyl ion, $(CH_3)_3C^+$. The 3.05 ppm low field shift of the methyl resonance then results from the withdrawal of electrons from the methyl group by the positively charged carbon, and the C-F bond being broken, no H-F coupling can occur. An alternate explanation, that of the formation of a rapidly exchanging donor-acceptor complex, will be discussed in section (4).

The isopropyl and t-pentyl ions are formed when propyl and pentyl fluorides are dissolved in SbF_5. Fig. 3 shows the proton spectrum of isopropyl fluoride, $(CH_3)_2CHF$, neat and dissolved in SbF_5. The spectrum of neat isopropyl fluoride is like that of isopropyl chloride (Fig. 1) already discussed, except that coupling to the fluorine (two bond H-F coupling to methine proton, $^2J_{HF}=48$ Hz, three bond coupling to methyl protons, $^3J_{HF}=23.5$ Hz) results in two septets and two doublets. On mixing with SbF_5, coupling is no longer observed and a septet and doublet are observed at -13.5 and -5.06 ppm respectively. Here the carbonium ion, $(CH_3)_2C^+H$ in this case, also appears to be produced, the proton attached to the positively charged carbon being greatly deshielded. Similar conclusions as to the formation of t-amyl ion can be drawn from the spectra of t-amyl fluoride, $(CH_3)_2CFCH_2CH_3$, and t-amyl fluoride - SbF_5 mixtures. It should be noted that Olah et al. found that all isomeric propyl, butyl and pentyl fluorides gave only the isopropyl, t-butyl and t-amyl ions, respectively. Apparently the propyl ion and the primary and secondary butyl and pentyl ions rapidly rearrange to the more stable forms, the expected order of stability being primary<secondary<tertiary. Very recently Saunders and

Hagen[5] have obtained the spectrum of the sec-butyl ion, $CH_3C^+HCH_2CH_3$, by ionizing 2-chlorobutane in SbF_5/SO_2ClF at $-110°$. It should be noted here that chlorides appear to ionize to carbonium ions in the same manner as the fluorides.

Olah et al[2] found that solutions of alkyl fluorides in SbF_5/SO_2 gave essentially the same proton spectra as discussed above, indicating that ionization to carbonium ions occurs in this system as well. The isopropyl ion was not stable in SbF_5/SO_2, apparently because the carbonium ion is unstable enough to deprotonate, the resulting olefin joining with another isopropyl ion to form t-hexyl or alkylcyclopentenyl ion. The resonances of the tertiary ions are at slightly higher field, about 0.5 ppm above those in SbF_5 solution, that is the amount of shielding is slightly less. As the freezing point of SbF_5 is 7°, the presence of SO_2, Fp $-72.7°$, makes low temperature studies possible, which is particularly useful in the case of the t-amyl ion which gives a broadened and partially collapsed spectrum at room temperature due to an exchange between the methyl groups, believed to take place by a series of 1,2-hydride and 1,2-methyl shifts as shown in the mechanism below[6-9]

$$(CH_3)_2C^+CH_2CH_3 \rightleftharpoons (CH_3)_2CHC^+HCH_3$$
$$CH_3CH_2C^+(CH_3)_2 \rightleftharpoons CH_3C^+HCH(CH_3)_2$$
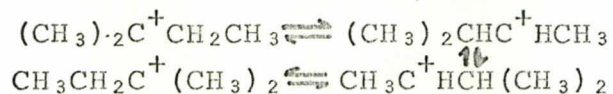
At $-30°$ in SO_2 the exchange is essentially stopped, giving the spectrum shown in Fig. 4. There are three resonances, that of the six protons in the α-methyl groups at -3.97, that of the three protons in the β-methyl group at -1.72 and that of the two α-methylene protons at -4.30. The methyl resonances are split into triplets, $J \approx 5$ Hz in both cases, by coupling to the methylene protons, which are themselves split into a ten-line multiplet. A 5 Hz coupling between α-methyl and α-methylene protons is quite surprising, since this involves four bonds where a very small coupling, ≤ 0.5 Hz, would normally be expected. Olah assumed this tenfold anomaly in $^4J_{HH}$ was in some way related to a planar

sp^2-hybridized structure for the carbonium ion. The interpretation of $^4J_{HH}$ will be discussed in detail in Chapter 6 of this work.

In the five years since the work in SbF_5 and SbF_5/SO_2 described above, various workers have extended the investigation of alkylcarbonium ions using other SbF_5-containing superacid media. Most of this work has been done by Olah and colleagues, and by various researchers at Royal Dutch/ Shell Laboratories, Amsterdam. The systems studied include HF/SbF_5,[7,8] HSO_3F/SbF_5,[10] $HSO_3F/SbF_5/SO_2$,[11] $HSO_3F/SbF_5/SO_2ClF$,[6] and SbF_5/SO_2ClF.[5,9,12] Most of these solvents are quite good for low temperature studies. A variety of reactions for the preparation of carbonium ions in these solvents exists[7,8,13]; in addition to the ionization of alkyl halides these include the protonation and cleaving of alcohols and ethers, the protonation of olefins, and acid-catylysed ring opening

$$ROH \xrightarrow{H^+} ROH_2^+ \xrightarrow{H^+} R^+ + H_3O^+$$

$$R_2O \xrightarrow{H^+} R_2OH^+ \xrightarrow{2H^+} 2R^+ + H_3O^+$$

$$(CH_3)_2C=CH_2 \xrightarrow{H^+} (CH_3)_3C^+$$

$$CH_3-\triangleleft \xrightarrow{H^+} (CH_3)_3C^+$$
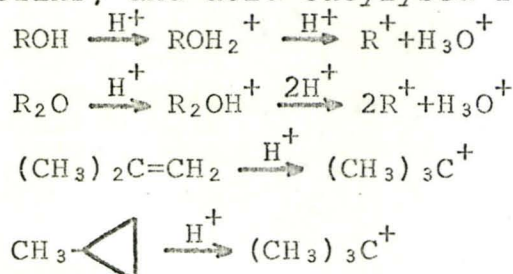
Perhaps the most interesting and one of the easiest methods of preparation is the reaction of isoalkanes with protonic media,[6-8,10] e.g.

$$(CH_3)_2CHCH_2CH_3 \xrightarrow{H^+} (CH_3)_2C^+CH_2CH_3 + H_2$$
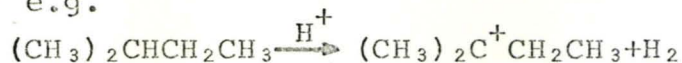
Except for the very low temperature ionization of 2-chlorobutane already mentioned[5], the ions produced are always in a tertiary form regardless of the isomer used as a starting material. The isopropyl ion, not susceptible to simple rearrangement, appears to be stable only in SbF_5 and SbF_5/SO_2ClF. No primary ions, and no secondary ions other than the isopropyl and sec-butyl ions, have as yet been reported.

The tertiary ions now known include hexyl, heptyl and octyl ions. The t-hexyl ion is stable at room temperature

and exists in all three isomeric forms, dimethylisopropyl-carbonium ion $(CH_3)_2C^+CH(CH_3)_2$, methyldiethylcarbonium ion, $CH_3C^+(CH_2CH_3)_2$, and dimethylpropylcarbonium ion, $(CH_3)_2C^+CH_2$ CH_2CH_3. At room temperature and at $-20°$ all three isomers are present in nearly equal amounts, indicating their relative stabilities differ only slightly. Olah and Lukas[6] have shown that reaction of the appropriate hexane in $HSO_3F/SbF_5/$ SO_2ClF at $-60°$ yields a single unrearranged t-hexyl ion. The dimethylisopropylcarbonium ion is particularly interesting because a rapid 1,2-hydride shift occurs at all temperatures, leading to the equivalence of all the methyl protons

$$(CH_3)_2C^+CH(CH_3)_2 \rightleftharpoons (CH_3)_2CHC^+(CH_3)_2$$

The methyl resonance of this ion is a doublet centred mid-way between the chemical shifts expected for α and β-methyl groups. The doublet splitting is the result of an averaged coupling to the equilibrating proton. An analogous equili-brium occurs for the t-heptyl ion $(CH_3)_2C^+C(CH_3)_3$, where a rapid 1,2-methyl shift causes one singlet methyl resonance. This and other t-heptyl ions are stable at $-60°$, but convert to t-butyl and t-hexyl ions at $0°$ or room temperature. Tertiary octyl ions are stable only at temperatures below $-80°$. Table I gives a summary of chemical shifts and coupling constants reported for the proton spectra in various media used to identify some of the ions discussed here.

(4) OBJECTS OF THE PRESENT WORK

Although the proton nmr data summarized in Table I is excellent evidence for the production of completely ionized alkylcarbonium ions in the systems so far studied, it is not, in fact, conclusive evidence. As the original workers themselves pointed out,[2,13] elimination of H-F coupling and considerable proton deshielding could also take place through a rapidly exchanging donor-acceptor complex, presum-ably as shown below.

$$F_5Sb \leftarrow F \overset{R}{\underset{R}{\rightleftharpoons}} F \rightarrow SbF_5 \rightleftharpoons F_5Sb \leftarrow F \overset{R}{\underset{R}{\rightleftharpoons}} F \rightarrow SbF_5$$

Definite identification of the anions produced by means of their ^{19}F resonance spectra would therefore be additional and quite necessary evidence for the carbonium ions themselves, and this study was undertaken with this view in mind. Alkyl fluorides and chlorides were studied in neat SbF_5, SbF_5/SO_2, and SbF_5/SO_2ClF by ^{1}H and ^{19}F mmr. In addition, preparation of the ethyl ion, $CH_3CH_2^+$, was attempted by low temperature ionization of ethyl fluoride.

The reaction of the alkanes with HSO_3F/SbF_5 and HF/SbF_5 has been discussed by Olah in a manner which implies that CH_5^+ and related protonated alkanes are formed in solution as relatively stable intermediates, rather than simply as transition states. We have therefore studied neopentane in $HSO_3F/SbF_5/SO_3$, an acid system believed to be the strongest protonic acid known,[14] in an attempt to find the spectrum of such an intermediate. The energetics of the formation of such a protonated intermediate can be helpfully considered using the approximate, all valence electron SCF molecular orbital treatment for small molecules developed by Pople, Santry and Segal.[15-17] Very recent work[18] indicates alkanes will react with SbF_5/SO_2ClF at $-30°$ to form a carbonium ion and an unknown precipitate, a surprising result in an aprotic solvent system. We have therefore examined solutions of isopentane, $(CH_3)_2CHCH_2CH_3$, in SbF_5/SO_2ClF and SbF_5/SO_2

No really satisfactory explanation of the anomalous four bond H-H coupling has as yet appeared in the literature. Some new values of this and other coupling constants were therefore measured and, together with literature values, considered in the light of molecular orbital theory and the coupling constant theory of Pople and Santry.[19]

TABLE I

Literature Values[1] for Chemical Shifts and Coupling Constants of Simple Alkylcarbonium Ions in Various Superacid Media

Ion	SbF$_5$[2]		SbF$_5$/SO$_2$ClF[3]		HSO$_3$F/SbF$_5$[4]		HSO$_3$F/SbF$_5$/SO$_2$ClF[5]		SbF$_5$/SO$_2$[6]		HF/SbF$_5$[7]	
	δ	J	δ	J	δ	J	δ	J	δ	J	δ	J
$(\overset{a}{CH_3})_2C^+\overset{b}{H}$ a	5.06	*	*	ab 5.0	Not Stable		Not Stable		Not Stable		Not Stable	
b	13.5		*									
$(CH_3)_3C^+$	4.35				4.50		4.20[8]		4.07		3.93	
$(\overset{a}{CH_3})_2C^+\overset{b}{CH_2}\overset{c}{CH_3}$ a	4.50	ab*	4.42	ab 4.7	4.42	ab 5.0	4.02	ab 4.7	3.97	ab 5	3.81	ab 4.5
b	4.93	bc*	4.75	bc 5.3	4.75	bc 5.6	4.42	bc 5.2	4.30	bc 5	4.23	bc 5.3
c	2.27		2.30		2.17		1.94		1.72		1.68	
$(\overset{a}{CH_3})_2\overset{+}{C}\overset{b}{CH}(\overset{c}{CH_3})_2$ a					3.32	ab 4.2	3.04	ab 4.2			2.76	ab 5
b					*		4.55				*	
$\overset{a}{CH_3}C^+(\overset{b}{CH_2}\overset{c}{CH_3})_2$ a					4.40	ab 4.8	4.16	ab 4.8			3.8	ab*
b					4.70	bc 4.8	4.44	bc 6.0			4.15	bc*
c					2.20		1.87				1.67	

Table I cont'd.

Ion	SbF$_5$ [2]		SbF$_5$/SO$_2$ClF [3]		HSO$_3$F/SbF$_5$ [4]		HSO$_3$F/SbF$_5$/SO$_2$ClF [5]		SbF$_5$/SO$_2$ [6]		HF/SbF$_5$ [7]	
	δ	J	δ	J	δ	J	δ	J	δ	J	δ	J
(CH$_3$)$_2$C$^+$CH$_2$CH$_2$CH$_3$ a					4.30	ab 4.8	4.05	ab 4.8			3.8	ab *
b					4.70	bc 4.8	4.40	bc 6.0			4.15	bc *
c					2.72		2.58	cd 7.0			2.17	cd 7.0
d					1.83		1.43				1.29	
(CH$_3$)$_2$C$^+$(CH$_3$)$_3$ a							2.86				2.58	

[1] Chemical shifts in ppm below TMS as external reference except for HF/SbF$_5$ where internal (CH$_3$)$_4$NSbF$_6$ was assumed to be δ=3.20. The two scales probably agree to 0.1 ppm. Coupling constant are in Hz.

[2] Ref. 2, starting material alkyl fluorides. Spectrum of t-amyl ion at 0°, others at ambient temperature.

[3] Ref. 9, and 12, starting material alkyl chlorides. Low temperature spectra.

[4] Ref. 10, starting material alkanes. Spectra at ambient temperature except for t-amyl ion, -30°

[5] Ref. 6, starting material alkanes. Low temperature spectra and sample preparation.

[6] Ref. 2, starting material alkyl fluorides. Spectrum of t-butyl ion at 0°, t-amyl ion at -30°.

[7] Ref. 8, various starting materials. Spectra at -20°.

[8] Ref. 11 gives δ=3.83 for (CH$_3$)$_3$C$^+$ produced from t-butanol in HSO$_3$F/SbF$_5$/SO$_2$.

*Indicates parameter not stated in reference cited, or difficult to measure under the experimental conditions. (line broadening, etc.)

H_0 (ppm below TMS) ⟶
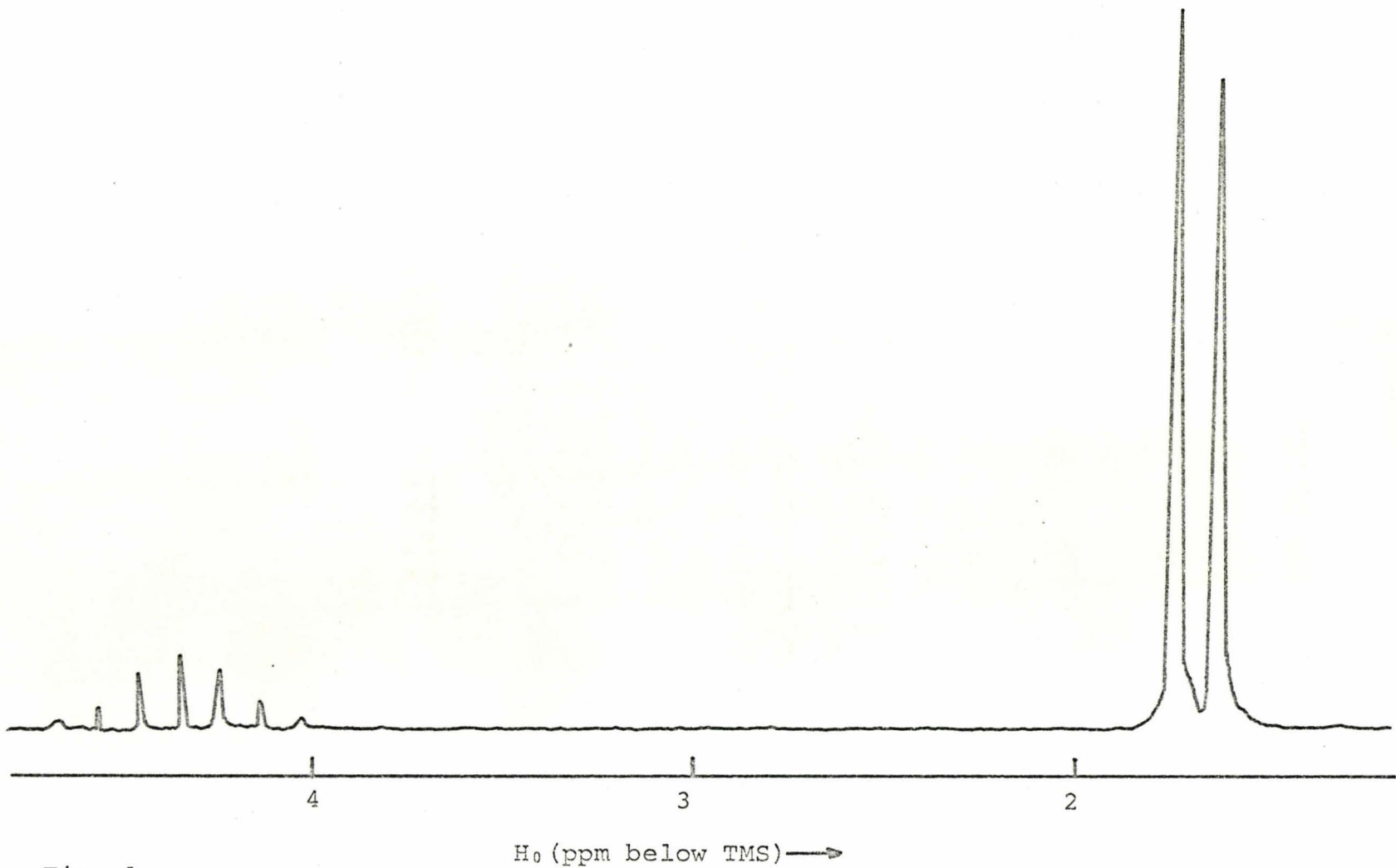
Fig. 1
Proton Spectrum of Isopropyl Chloride Showing Chemical Shift and Spin-Spin Splittings
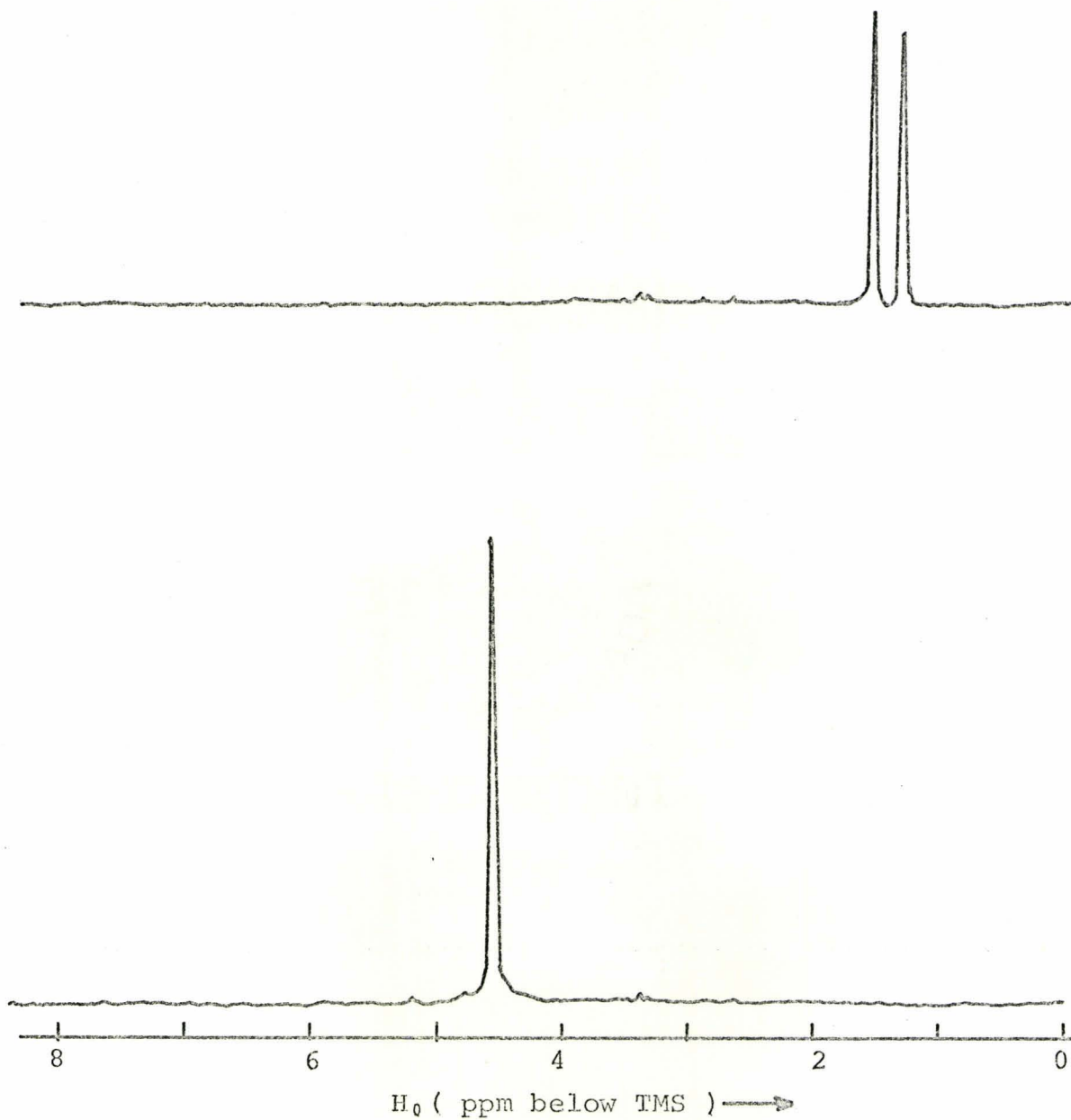
Fig. 2
Proton (60.000 MHz) Spectra of t-Butyl Fluoride (top)
and t-Butyl Fluoride/SbF$_5$ (bottom)

H_0 (ppm below TMS) ⟶
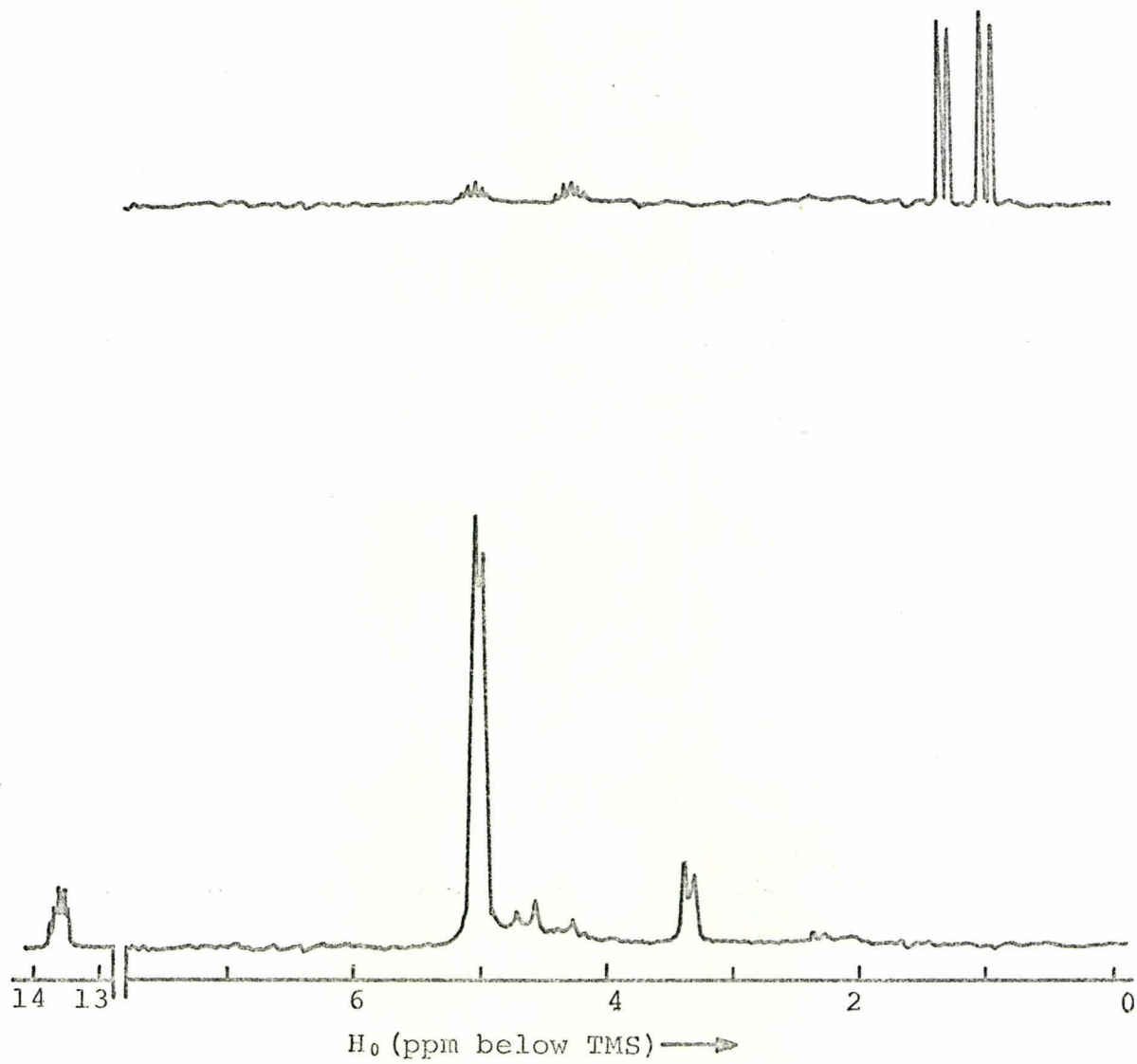
Fig. 3

Proton (60.000 MHz) Spectra of Isopropyl Fluoride (top)
and Isopropyl Fluoride/SbF$_5$ (bottom)
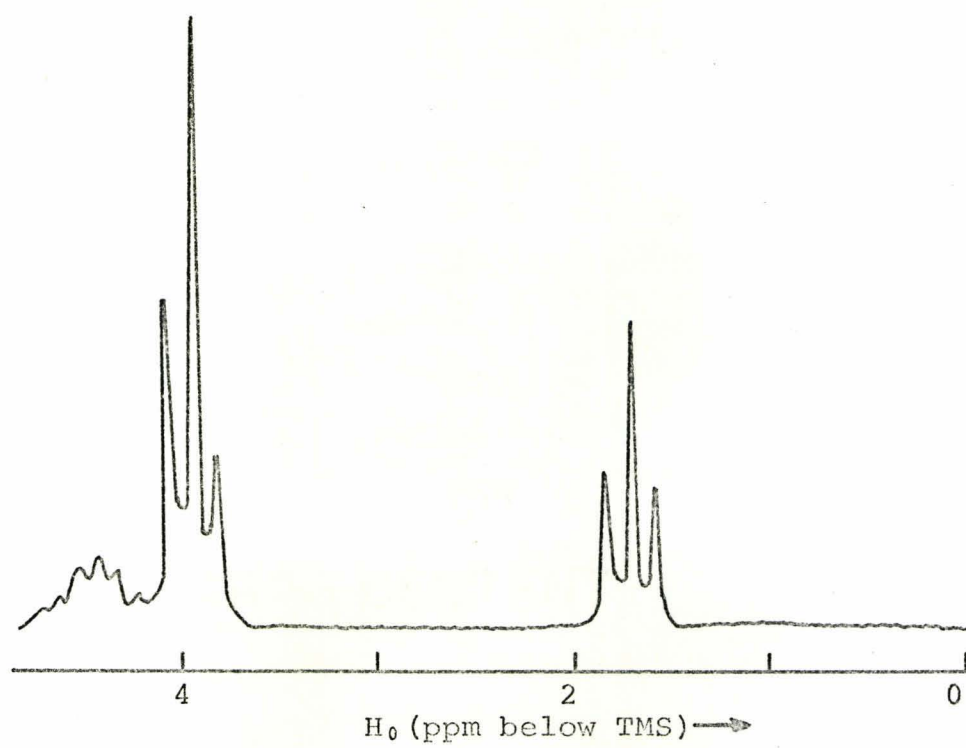
Fig. 4

Proton (60.000 MHz) Spectrum of t-Amyl Fluoride/SbF$_5$/SO$_2$ at $-30°$

EXPERIMENTAL

(1) PREPARATION AND PURIFICATION OF MATERIALS

ANTIMONY PENTAFLUORIDE

Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in pyrex glass apparatus in an atmosphere of dry air. Before use the still was rigorously dried by flaming out while a stream of dry air was slowly passed through the apparatus, and then leaving the still overnight while the dry air continued to run. The fraction boiling at 142-143° was collected and then generally redistilled at room temperature on the pyrex vacuum line used to make up the mmr samples.

DRY AIR

Compressed air was passed through a drying train consisting of a Dreschel bottle containing concentrated sulfuric acid, followed by two others containing molecular sieves, and a 3 ft. tube packed with phosphorous pentoxide supported on glass wool.

SULFUR DIOXIDE

Anhydrous sulfur dioxide (Matheson of Canada Ltd.) was stored as a gas over phosphorous pentoxide in a 3 litre gas bulb before use.

SULFURYL CHLOROFLUORIDE

Sulfuryl chlorofluoride, SO_2ClF, was prepared from KSO_2F and chlorine according to the method of Seel and Riehl.[20] In a typical preparation, a dry box was used to place 100 g. of finely powdered potassium fluoride in a 300 ml. stainless steel autoclave which was then attached to the vacuum line. 200 g. SO_2 was distilled in under vacuum, and the autoclave closed, removed from the vacuum line, and placed in a mechanical shaker. After five or more days under autogenous pressure,

the potassium fluoride was about 30% converted to potassium fluorosulfinate, KSO_2F. The KF/KSO_2F mixture was removed from the autoclave, ground to a fine powder, and placed in a pyrex tube equipped with a fritted glass disc at the bottom, using the dry box throughout. When a mixture of dry nitrogen and chlorine gases was passed through the fritted disc and up the column, sulfuryl chlorofluoride was produced according to the reaction

$$KSO_2F + Cl_2 \longrightarrow KCl + SO_2ClF$$

The product was condensed in a dry ice-acetone cooled u-tube at the top of the column and redistilled on the vacuum line. Any sulfur dioxide produced by the side reaction

$$2KSO_2F + Cl_2 \longrightarrow 2KCl + SO_2 + SO_2F_2$$

was removed by distilling the product onto about 5 g. of SbF_5 using the vacuum line and distilling the SO_2ClF back out of the resulting solution, the SO_2 remaining behind as the adduct $SbF_5 \cdot SO_2$. The purified SO_2ClF was then stored as a gas over phosphorous pentoxide in a 3 litre gas bulb.

FLUOROSULFURIC ACID

Technical grade fluorosulfuric acid (Baker and Adamson) was purified by double distillation in pyrex apparatus similar to that used for antimony pentafluoride. The still was dried using the same technique employed with the antimony penta-fluoride still. The pure acid distills at 163-164°.

SULFUR TRIOXIDE

Sulfur trioxide was distilled from Baker and Adamson "Sulfan" in a still protected from moisture by a potassium perchlorate drying tube.

ALKYL HALIDES

Commercially obtained t-butyl chloride was purified by fractional distillation. t-Butyl fluoride was prepared by the reaction[21] of t-butanol and 48% hydrofluoric acid at 60-70° in plastic apparatus. In a typical preparation 70 ml. (0.742 moles) t-butanol and 50 ml. (1.445 moles) 48% HF were

heated together for four hours, the gaseous product condensing in the ice-salt mixture cooled receiver. The crude product was then fractionally distilled into glass apparatus and treated with bromine to remove olefin impurities (see below). Isopropyl fluoride was prepared by the reaction of isopropyl p-toluenesulfonate (isopropyl tosylate) with potassium fluoride in diethylene glycol.[22] Isopropyl tosylate (167 g.) was first prepared by placing one mole each of p-toluene-sulfonyl chloride and isopropanol in a well stirred flask kept at 0° and adding two moles of pyridine over a three hour period. After a further eight hours of reaction time, the reaction was quenched with ice water, the product extracted with diethyl ether[22] dried over molecular sieves, and the ether removed by distillation under reflux. Small amounts (≈ 0.1 moles) of isopropyl fluoride were then prepared as required by reaction of an appropriate amount of the tosylate with a five-fold excess of potassium fluoride in diethylene glycol as solvent at 90° and 100-200 mm pressure. Isopropyl fluoride, t-butyl fluoride and t-butyl chloride all contain measurable amounts of olefin impurities produced during preparation or by elimination of hydrogen halide on standing. Before use each of these compounds was therefore treated by dropwise addition of liquid bromine while the halide was stirred at a temperature well below its boiling point, until the bromine added was no longer decolourized. The purified compound was then allowed to distill out of the bromination apparatus, collected, distilled on the vacuum line, and used immediately. Ethyl fluoride (Air Products and Chemicals, Inc.) and methyl fluoride (Peninsular Chemresearch, Inc.) were distilled twice on the vacuum line, collecting the middle fraction only, and then used immediately.

ALKANES

Neopentane (Matheson of Canada, Ltd.) was allowed to stand over phosphorous pentoxide for several hours and then distilled on the vacuum line. Isopentane was dried over

molecular sieves and distilled on the vacuum line.

ACETONE

Reagent grade acetone used for the protonation experiment was dried twice over anydrous magnesium sulfate and distilled on the vacuum line.

CARBONYL CHLOROFLUORIDE

Carbonyl chlorofluoride (Ozark Mahoning Co.) was distilled twice on the vacuum line.

(2) PREPARATION OF SAMPLES

All nmr samples used in the course of this work were sealed in 5 mm.o.d. precision pyrex glass tubes (NMR Specialties Type E). Although the required sample volume in such a tube is only approximately 0.4ml., the solutions themselves were made up in various types of 100 ml. flasks attached to the vacuum line, in quantities large enough (generally 2-10 ml.) to permit accurate measurement, by weight or volume, of the amount of each solution component present. In addition, the starting material (alkyl halide, alkane, etc.) was added, generally as the last component, by allowing it to distill under vacuum into the flask containing the acid medium over a considerable period of time, generally 30 minutes or more. In this way local overheating of the solution with possible subsequent decomposition reactions was avoided.

Mixtures of t-butyl fluoride, t-butyl chloride, and isopropyl fluoride with SbF_5 were made by placing several ml. of freshly distilled SbF_5 in a 100 ml. round bottomed flask equipped with a detachable glass tap using a glass syringe in the dry box. The flask, with tap, was then attached to the vacuum line, evacuated, and the alkyl halide allowed to evaporate very slowly into the SbF_5 flask and react at room temperature over the period of one hour. Small amounts of the resulting liquid were transferred from the reaction flask to nmr tubes equipped with detachable glass taps using the dry box once again. These tubes, with

taps, were then attached to the vacuum line and sealed. Some samples containing SO_2 were prepared, in which case the SO_2 was distilled in on the vacuum line before the tube was sealed off.

The remaining solutions in this work were prepared using flasks to which the nmr tubes had already been sealed. All of these solutions were made up at low temperatures, generally in the range -85 to -60°. This permitted the study of solutions before ionization to carbonium ions occured, as the flask containing the cold solution could be removed from the vacuum line, completely immersed, except for the top portion, in a large low temperature bath, and tilted so a suitable volume of solution entered the nmr tube sealed to it. Both flask and nmr tube were then frozen in liquid nitrogen and the tube sealed off, giving an nmr sample which had experienced no temperature above -60°.

The sample of acetone in HSO_3F/SbF_5 was prepared by first dissolving a known volume of HSO_3F in a known weight of SbF_5, using the dry box. A small portion of the HSO_3F/SbF_5 was then transferred to the 100 ml. flask, attached to the vacuum line, cooled, and an appropriate amount of acetone allowed to distill in. Samples in $HSO_3F/SbF_5/SO_3$ were prepared by adding a known amount of a solution of SO_3 in HSO_3F to HSO_3F/SbF_5 in the reaction flask and then distilling in the reactant under vacuum.

All solutions in SbF_5/SO_2ClF, and the SbF_5/SO_2 solutions of methyl fluoride, ethyl fluoride and isopentane were prepared by distilling first SbF_5 and then the solvent into the reaction flask. Appropriate weighings on a Mettler single pan balance gave the amount of solvent and SbF_5 to ±0.03 g. A known volume of reactant (methyl fluoride, etc.) was then allowed to evaporate into the reaction flask, which was kept at low temperature. Similar weighing and volumetric techniques were used for all the samples prepared.

In general, samples of the alkyl halides, alkanes, etc. were taken, degassed and sealed, and their nmr spectra taken to determine purity and to allow comparison of nmr parameters with those for the carbonium ions themselves.

(3) NUCLEAR MAGNETIC RESONANCE SPECTRA

Proton spectra were recorded at 60.000 and 100.000 MHz on Varian A-60 and HA-100 spectrometers, respectively. Fluorine spectra were obtained at 56.445 and 94.077 MHz using Varian DA-60 and HA-100 spectrometers, respectively. All three spectrometers were equipped with Varian variable temperature analytical probes and temperature controllers, which were used for recording the low temperature spectra. The field-frequency lock of the A-60 spectrometer uses an external water sample which is likely to freeze when the temperature of the sample whose spectrum is being recorded is maintained at or below -60° for long periods of time. The A-60 was therefore used for proton spectra only for runs where temperatures at or below -60° were not required, the HA-100 being used in the other cases. Most fluorine spectra were run on the DA-60, the HA-100 being used for fluorine mainly to check spectral assignments, notably in the case of the $Sb_3F_{16}^-$ ion. The field-frequency lock of the A-60 gives precalibrated spectra, but this calibration was checked repeatedly by generating audio sidebands with a Muirhead-Wigan D-890-A Decade Oscillator. The internal lock capabilities of the DA-60 and HA-100 spectrometers were not employed, mainly due to the difficulty of providing a suitable lock signal. Spectra were recorded in the HR centreband or sideband mode instead and calibrated by audio sidebands. Proton spectra were referenced with respect to tetramethylsilane (TMS) and fluorine spectra to $CFCl_3$, in both cases by sample interchange. Fluorine shifts were accurate to better than 1 ppm, while HA-100 proton shifts were accurate to about 0.1 ppm. Proton shifts obtained on the A-60 were slightly

more accurate. Coupling constants obtained on the A-60 were
accurate to 0.1 Hz. Where practicable and useful, coupling
constants measured on the other spectrometers were done so
10 or more times, and a statistical analysis done on the
results, giving coupling constants accurate to 0.3 Hz.

The use of an external TMS referencing system is
necessary because addition of TMS to the SbF_5-containing
solutions studied here, as is generally done in proton nmr,
would result in reaction and decomposition of the reference.
Olah and his coworkers have used external TMS referencing
throughout their work. Since most literature values for
organic compounds are given with respect to internal TMS,
chemical shift values for the majority of the compounds used
in this study were measured with respect to external TMS,
so that meaningful comparisons of chemical shifts before and
after solution in the superacid medium could be made. These
chemical shift values are used in discussing the results of
this work, although, in many cases, the nmr spectrum of the
alkyl halide, etc., may already be reported in the literature.

(4) COMPUTER CALCULATIONS

A copy of Bothner-By and Castellano's program LAOCN3
for calculating theoretical nmr spectra[23] was obtained from
the Mellon Institute and run on the IBM 7040 computer in the
McMaster Computation Centre after slight modifications. Most
of the spectra encountered in the course of this work were
first order, exceptions being the fluorine spectra of
SbF_5 and $Sb_3F_{16}^-$. The output of LAOCN3 in these two cases
consists of 128 lines. Many of these lines are separated
by less than the natural line width of the fluorine resonance,
necessitating some allowance for the overlapping of adjacent
lines. This was done by writing a computer program NMRPLT
which took the line positions and intensities as calculated
by LAOCN3 and calculated the line shape as the sum of

individual Lorentzian curves, given a value for the natural
line width. This summed line shape was plotted using a
Benson-Lehner off-line plotting system and compared with the
experimental spectra.

Molecular orbital calculations were done using a copy
of the program CNDO2 incorporating the Pople-Santry-Segal
approximate SCF treatment[15-17], which was obtained from
Prof. D. P. Santry and Mr. A. C. Blizzard of the Chemistry
Dept., McMaster University. This program was modified by
writing a subroutine JAB which took the energies and wave-
functions calculated by CNDO2 and calculated spin-spin
coupling constants using the Pople-Santry theory.[19] Sub-
routines were also written to calculate cartesian coordinates
for molecules and ions of interest. All CNDO2 programs were
run on the CDC 6400 computer in the McMaster Computation Centre.

CHAPTER 3.

^{19}F NMR OF SOLUTIONS OF t-BUTYL FLUORIDE, t-BUTYL CHLORIDE AND ISOPROPYL FLUORIDE IN SbF_5, SbF_5/SO_2 and SbF_5/SO_2ClF

(1) INTRODUCTION

In principle it would appear to be possible to determine ionization to a carbonium ion through the identification of the anion produced using fluorine nmr. If the reactions

$$RF + SbF_5 \longrightarrow R^+ + SbF_6^-$$
$$RCl + SbF_5 \longrightarrow R^+ + SbF_5Cl^-$$

formulated by Olah et al.[2] do in fact occur in solution, quite distinctive fluorine spectra for these ions would be expected. The SbF_6^- ion gives a single broad resonance about 111 ppm above $CFCl_3$[24]. The resonance is broad because antimony has two naturally occuring isotopes, both with I>1/2, [121]Sb, I=5/2 and [123]Sb, I=7/2. Since I>1/2, rapid transitions between the different orientations of the antimony spin occur through the well known quadrupole relaxation mechanism.[25-27] For the case of a chlorine nucleus in an alkyl chloride mentioned in Chapter 1, the transitions occur so rapidly that coupling between the chlorine and the other nuclei is averaged to zero. However the antimony nucleus in SbF_6^- is in an octahedral site and these transitions occur at a much slower rate. In fact, true octahedral symmetry at the nucleus would result in no transitions at all[25-27], but interaction with the solvent causes small distortions of the ion, giving rise to a slow rate of relaxation which results in only a partial collapse of the expected multiplet. The broad line which results can be as much as 10 KHz wide, or much narrower, depending on the amount of ion-solvent interaction. The spectrum of SbF_5Cl^- is not known, but should be similar to the spectra of a number of SbF_5X coordination complexes.

A good example is the spectrum of $SbF_5 \cdot SO_2$, which has been reported as a doublet and quintet at 105 and 137 ppm relative to $CFCl_3$, respectively, with J_{FF}=100 Hz.[28] For SbF_5X compounds the antimony spin is not a complicating factor, since the lower symmetry gives rise to very rapid transitions and the coupling to antimony is averaged out, leaving lines which are only 20 to 40 Hz wide.

(2) ALKYL FLUORIDE ^{19}F RESONANCE SPECTRA

The fluorine resonance of t-butyl fluoride consists of a ten-line multiplet 132.7 ppm above $CFCl_3$. This multiplet has $^3J_{HF}$=20.2 Hz. The spectrum of isopropyl fluoride consists of two overlapping septets, that is, a doublet further split into septets, the peak separations giving $^2J_{HF}$=48.4 and $^3J_{HF}$=22.9 Hz, at 167.9 ppm above $CFCl_3$. The fluorine spectra of ethyl fluoride and methyl fluoride, used in the solutions of Chapter 4, were also obtained during the course of this work. The fluorine chemical shifts and proton-fluorine coupling constants obtained for all four fluorides are shown in Table II. They are in general agreement with values previously reported[4], but are probably more accurate.

(3) t-BUTYL HALIDE/SbF₅ SOLUTIONS IN SO₂

When t-butyl fluoride vapour was allowed to react with neat antimony pentafluoride on the vacuum line, a coloured liquid of composition t-BuF/SbF₅=1/3.8 was obtained. Under the experimental conditions used, this was the largest t-BuF/SbF₅ ratio obtained, the reaction occurring with the evolution of heat in the presence of excess SbF₅. Slightly larger amounts of SbF₅ can be used, but when t-BuF/SbF₅=1/5, an almost colourless layer separates out, as previously reported.[2] This colourless layer appears to be almost entirely SbF₅, as the ^{19}F resonance at low temperatures shows only the SbF₅ spectrum,[29] while the room temperature ^1H spectrum shows a very weak single line resonance in the

$(CH_3)_3C^+$ region. Hence t-butyl fluoride and SbF_5 are miscible in the range $3.8 < SbF_5/t-BuF < 5$ only, and any further addition of SbF_5 causes an SbF_5 layer containing a very small amount of carbonium ion to separate out. The SbF_5 layer is slightly less viscous than purified SbF_5, while the coloured layer is much less viscous. The coloured layer, neat or dissolved in liquid SO_2, gives the same room temperature proton spectrum as that reported by Olah et al.,[2] namely the strong single resonance assigned to $(CH_3)_3C^+$.

When the $t-BuF/3.8SbF_5$ mixture was dissolved in SO_2, the ^{19}F spectrum shown at the top of Fig. 5 was obtained at $-80°$. Of the five resonances in the spectrum, those at 90.3, 110.2 and 132.2 are clearly those of the $Sb_2\overline{F}_{11}$ ion, shown below.
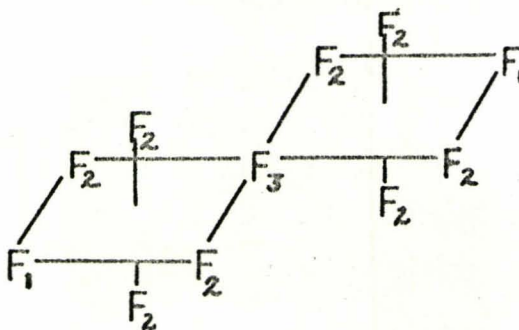
The spectrum of this ion was first reported by Gillespie and Moss[30] for solutions of SbF_5 in HF. There are three chemically different sets of fluorine atoms in this ion, giving rise to three resonances of relative areas 1/8/2. Gillespie and Moss found the resonance of the terminal fluorines F_1 to occur at high field, split into a quintet ($J_{12}=100$ Hz) by coupling to four of the equivalent fluorines F_2. The resonance of the F_2 fluorines is split into four lines, first by the 100 Hz coupling to one of the terminal fluorines and then by a smaller coupling ($J_{23}=53$ Hz) to the bridging fluorine. This resonance is often called a "doublet of doublets". The resonance of the bridging fluorine occurs at low field and is split into a nine-line multiplet (separation 53 Hz) by the coupling to F_2. There appears to be no

coupling between F_1 and F_3. For t-BuF/3.8SbF$_5$ dissolved in SO$_2$ therefore, Sb$_2$F$_{11}^-$ is clearly present and the resonances at 90.3, 110.2 and 132.2 ppm are assigned to F_3, F_2 and F_1, respectively. The two lines in the middle of the doublet of doublets overlap. The doublet (J=100) at 101.0 ppm in the spectrum of Fig. 5 appears to arise from SbF$_5 \cdot$SO$_2$. The quintet resonance of SbF$_5 \cdot$SO$_2$ is not seen, but probably lies under the right hand side of the Sb$_2$F$_{11}^-$ quintet at 132.2 ppm. Dean and Gillespie[31] find the SbF$_5 \cdot$SO$_2$ shifts in SO$_2$ to be 100.9 and 133.7, in good agreement with the above assignment, and not 105 and 137 ppm as previously reported[28]. The areas in the spectrum of Fig. 5 correspond to Sb$_2$F$_{11}^-$/SbF$_5 \cdot$SO$_2$=1/1.4. The stoichiometry would imply Sb$_2$F$_{11}^-$/SbF$_5 \cdot$SO$_2$=1/1.8, assuming all the SbF$_5$ in excess of the composition t-BuF/2SbF$_5$ reacts with the solvent to form SbF$_5 \cdot$SO$_2$, but a small amount of SbF$_5$.SO$_2$ appears to separate out of solution. The remaining resonance in the spectrum, the single peak at 106.6 ppm is rather more difficult to assign. It can probably be attributed to some fluorine-containing species of antimony (III) such as SbF$_3$ complexed with SbF$_5$. A slight charring of the solutions was noted with time, hence some of the carbonium ion may be oxidized by SbF$_5$, accounting for the presence of antimony(III).

When t-butyl chloride vapour is allowed to react with SbF$_5$ on the vacuum line, slightly more SbF$_5$ is absorbed than in the t-butyl fluoride case. The low temperature fluorine spectrum of a t-BuCl/5.5SbF$_5$ mixture dissolved in SO$_2$, shown at the bottom of Fig. 5, has the same five resonances discussed above, showing that the anion is Sb$_2$F$_{11}^-$ again, and not the previously suggested SbF$_5$Cl$^-$. The chlorine is presumably present in some other species, which may precipitate out of solution. Careful comparison of the fluorine spectra of SO$_2$ solutions of t-BuCl/SbF$_5$ with those of t-BuF/SbF$_5$ shows two small resonances to the low field side of the bridging fluorine in the chloride case which are not present in the case of the fluoride. These new peaks are broad singlets,

width $\approx$ 120 Hz, with chemical shifts of 71.8 and 79.9 ppm. Replacement of fluoride ions by chloride ions in fluoro-complexes generally causes a downfield shift in the resonance or resonances of the remaining fluorines.[32] This would suggest that the chlorine is present in some species such as $SbF_4Cl \cdot SO_2$. Whatever the species, the areas of the peaks indicate most of it has precipitated out of solution.

Dean and Gillespie[31] have shown that mixtures of Et_4NSbF_6 and SbF_5 in SO_2 also give the $Sb_2F_{11}^-$ ion and $SbF_5 \cdot SO_2$. Their results, together with the results of this section on t-butyl halide/SbF_5 solutions in SO_2, are summarized in Table III.

(4) ALKYL HALIDE/SbF_5 SYSTEMS

The fluorine spectra of t-BuF/3.8SbF_5, t-BuCl/5.5SbF_5 and isopropyl fluoride/4.4SbF_5 were all obtained in the absence of SO_2 solvent as a function of temperature. The low temperature spectrum of the neat t-BuF/3.8SbF_5 mixture shown in Fig. 6 is typical. This spectrum consists of a very broad line 110 ppm above $CFCl_3$, which has superimposed upon it the spectrum of SbF_5[29]. As the temperature is lowered, the broad peak increases in width ($\approx$ 2000 Hz at $-40°$) and the area of the SbF_5 peaks increases, but at no time exceeds 10% of the main spectrum. Dean and Gillespie[31] found essentially the same spectrum for solutions of Et_4NSbF_6 in SbF_5. They noted that the small SbF_5 peaks were seen only at low temperatures, when the solution was turbid, implying that a small amount of SbF_5 is present as a suspension in the remaining liquid.

If neat alkyl fluoride/SbF_5 mixtures are in fact solutions of $R^+Sb_2F_{11}^-$ in SbF_5 it is difficult to see why SbF_5 should separate out at high SbF_5 concentrations or at low temperature as is observed here. The results are more consistent with all the SbF_5 in the homeogenous liquid being incorporated into a polynuclear anion $Sb_nF_{5n+1}^-$ which

disproportionates with increasing length or decreasing temperature into a smaller anion and polymeric SbF_5. In this interpretation t-BuF/3.8SbF_5 would be regarded as a mixture of $(CH_3)_3C^+Sb_3F_{16}^-$, $(CH_3)_3C^+Sb_4F_{21}^-$, and possibly $(CH_3)_3C^+Sb_5F_{26}^-$. The proposed long, unstable anion might be expected to break up and reform readily, giving the broad temperature dependent line observed and the decomposition of such an anion by the SO_2 solvent is not surprising. The liquids may, therefore, be regarded as room temperature fused salts.

(5) THE SbF_5 SPECTRUM

When t-butyl fluoride was distilled into SbF_5/SO_2ClF on the vacuum line, a solution of composition t-BuF/SbF_5/SO_2ClF =1/2.5/2.2 was obtained. After warming to 0°, the proton spectrum showed the strong singlet resonance of $(CH_3)_3C^+$, indicating ionization. New fluorine resonances were found in the fluorine on antimony region for this sample, and these are shown in the next section to arise from the previously unreported ion cis-$Sb_3F_{16}^-$. The analysis of this spectrum, which is rather complicated, was undertaken after a detailed analysis of the SbF_5 spectrum had been done as part of this work. There are a number of similarities in the two spectra and their analyses. The spectrum of SbF_5 will be discussed first, in this section, and that of the $Sb_3F_{16}^-$ ion in the following section.

Hoffman, Holder and Jolly[29] found the fluorine spectrum of purified liquid SbF_5 to consist of three peaks of relative areas 1/2/2, and therefore proposed the cis-fluorine bridged polymeric structure for the liquid shown below.
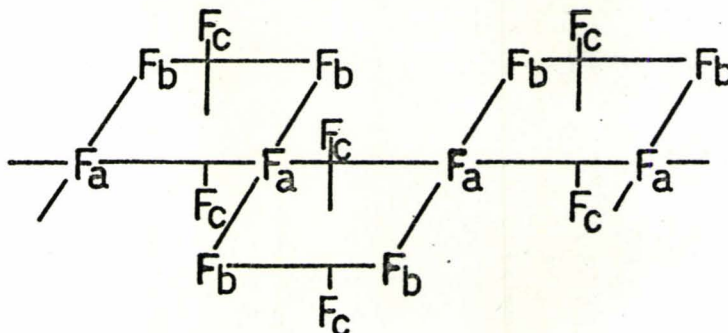
This structure should give rise to three chemically shifted
resonances with the relative areas observed, and is also
in accord with the extremely high viscosity of SbF_5, which
suggests a polymer of considerable length. The spectrum
observed by these authors, shown at the top of Fig. 7, showed
fine structure in two of the resonances, that at high field
being split into a triplet (J=130 ± 15 Hz) and that in mid-
spectrum appearing to be a septet(J=70 ± 10 Hz). The authors
took the high field resonance to be that of the two fluorines
(F_c) which are each cis to both of the bridging fluorines,
split by coupling to the two fluorines (F_b) which are each
trans to one bridging fluorine and cis to the other. In this
interpretation, the resonance of the F_b flourines, split
into a triplet by the coupling to the two F_c fluorines, is
further split by the smaller coupling to the bridging fluorines
(F_a). Since $J_{bc} \approx 2J_{ab}$, the resulting triplet of triplets
appears as a septet. The authors assumed $J_{ac} \leqslant 30$ Hz. First
order theoretical spectra for this interpretation are shown
below the experimental spectrum in Fig. 7.

Gillespie and Rothenbury[33] found that dilution of pure
SbF_5 with Freon-114, $CF_2Cl \cdot CF_2Cl$, increased the resolution
in the fluorine spectrum markedly, presumably through a
decrease in the polymer chain length and in the viscosity,
narrowing the natural width of the individual lines. Their
spectrum for a solution having SbF_5/Freon = 1/0.4, recorded
at -56°, the temperature of best resolution, is shown at the
top of Fig. 8. The septet is quite well resolved, and two
of the lines in the triplet at the high field end of the
spectrum are split into doublets. Gillespie and Rothenbury
were unable to explain this further splitting, and this work
remained unpublished. Recently similar spectra have been
obtained for SbF_5 diluted with AsF_5[34] and C_4F_8[35] No explan-
ation of the doublet splitting has been given.

During this work, it became apparent that these spectra
of diluted SbF_5 could be satisfactorily interpreted by

reassigning the chemical shifts and considering the effects of magnetic inequivalence. The value of 130 Hz for J_{bc} reported by Hoffman et al.[29] compares very favourably with literature values for J_{FF} in other cis-SbF_4X_2 species, e.g. for the cis-polymer of SbF_4SO_3F, J= 125-128 Hz[36] and for the cis-$SbF_4(SO_3F)_2^-$ ion, J = 122-126 Hz[37]. However $J_{ac} \leqslant 30$ Hz is somewhat surprizing, since in $Sb_2F_{11}^-$ the coupling between the bridging fluorine and fluorines cis to it is 53 Hz.[30] Trans couplings to the bridging fluorine in $Sb_2F_{11}^-$ are very small, perhaps $\leqslant 10$ Hz, yet Hoffman et al. report $J_{ab} \approx 70$ Hz for SbF_5. Clearly these authors have interchanged the identities of F_b and F_c and the fluorines in the polymer should in fact be labelled as shown below.

$$J_{ab} = 70$$
$$J_{bc} = 130$$
$$J_{ac} < 30$$
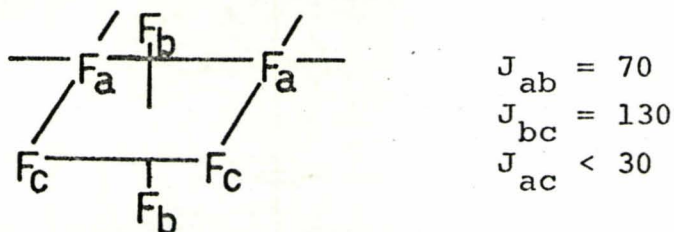
Such a reassignment makes no difference to the first order spectrum, and the first order coupling constants are then consistent with the values observed for $Sb_2F_{11}^-$.

If we now examine the SbF_6 unit in the polymer as relabelled, we see that all four of the coupling constants J_{ab} are equal to each other, as are the four coupling constants J_{bc}. The coupling between F_a and F_c cannot be described by a single value, however, since the cis-coupling, J_{ac}, would be expected to be much larger than the trans-coupling, $J_{ac'}$, by comparison with the $Sb_2F_{11}^-$ ion once again. This situation is known as "magnetic non-equivalence" and generally results in spectra of more complexity than expected from first order considerations. An excellent example is the proton or fluorine spectrum of 1,1-difluoroethylene, $CF_2=CH_2$. From first order rules a simple 1:2:1 triplet would be expected. However, since the molecule is planar, there are two unequal H-F coupling constants,

J_{cis} and J_{trans}.   It can be shown that the first order rules break down in such a situation owing to changes in the selection rules and small changes in the positions of the energy levels corresponding to the various spin states.   In the $CF_2=CH_2$ spectrum, the outer lines of the expected triplet are seen, but the centre line is split into 8 lines, the spacings and intensities depending on J_{cis}, J_{trans}, and the two geminal coupling constants J_{HH} and J_{FF}.   The quantum mechanical treatment for the case of $CF_2=CH_2$ has been very well summarized by Roberts.[38]

Since the four spins labelled F_a and F_c represent a case of magnetic inequivalence, by analogy with the $CF_2=CH_2$ case we might expect the spectrum of SbF_5 to depend on J_{ac}, $J_{ac'}$, J_{aa} and $J_{cc'}$ as well as J_{ab} and J_{bc}.   We might also expect the resonance of the F_c fluorines to show splittings which cannot be explained using the first order rules.   (The resonance of the F_a fluorines is a single broad resonance showing no multiplet splitting, presumably due to coupling with the fluorine nuclei of the adjacent SbF_6 units.)   As we have seen above, the splitting of two of the lines in the triplet resonance of the F_c fluorines has yet to be explained. Trial six-spin spectra were calculated for SbF_5 with a single SbF_6 unit as model, using the LAOCN3/NMRPLT program.   Initially the values

$$J_{ab}=70 \qquad J_{ac}=53$$
$$J_{bc}=130 \qquad J_{ac'}=10$$
$$J_{aa}=25 \qquad J_{cc}=100$$

were used, together with appropriate chemical shift vlaues and an estimate of 30 Hz for the line width. J_{ab} and J_{bc} were varied until the splittings observed in the septet were reproduced.   The other four coupling constants were then varied.   When

$$J_{ab}=85.6 \qquad J_{ac}=61.5$$
$$J_{bc}=144.3 \qquad J_{ac'}=-8.5$$
$$J_{aa}=25 \qquad J_{cc}=85$$

and a 32 Hz line width is assumed, the spectrum shown at the
bottom of Fig. 8 is obtained. It is an excellent fit for
the experimental spectrum. The same two lines of the triplet
are split into doublets in both spectra, and the magnitude
of these splittings and those in the septet are well
reproduced (largest deviation 1.8 Hz, average deviation
1.4Hz). The calculated line shape for the triplet resonance
is shown in greater detail in Fig. 9, together with the
individual lines making up the multiplet.

The coupling constants for SbF_5 obtained above are
all reasonable values. The only trans-coupling constant
obtained, J_{ac}, is less than 10 Hz as expected by analogy with
the $Sb_2F_{11}^-$ ion. (The only other trans coupling constant in
the SbF_6 unit, J_{bb}, has no effect on the spectrum, and there-
fore cannot be measured.) All the remaining coupling constants
involve fluorines which are cis to one another, and are in
the order $J_{bc} > J_{ab} \approx J_{cc} > J_{ac} > J_{aa}$. The reason for this
order is not clear, but it is interesting to note that the
cis coupling between any given fluorine and a bridging
fluorine is always less than that between the same fluorine
and a fluorine which is not bridging. The same relationship
holds in the $Sb_2F_{11}^-$ ion, that is $J_{12} > J_{23}$. Presumably
the observed order is related to the electronic mechanism
involved in forming the fluorine bridge. However, the cal-
culation of the theoretical spectrum is of interest, for the
moment, chiefly because of the splitting of the F_c resonance
due to magnetic inequivalence. The successful calculation
of this splitting confirms the reassignment of chemical shifts
proposed here and gives us a new method for understanding
the fluorine spectra of species with two fluorine bridges
cis to one another, as will be seen in the next section.

(6) t-BUTYL FLUORIDE in SbF_5/SO_2ClF SOLUTION

When a solution having $t\text{-BuF}/SbF_5/SO_2ClF=1/2.5/2.2$
was prepared and allowed to ionize to the t-butyl ion, the

56.445 MHz spectrum shown in Fig. 10 was obtained at -95°.
Given t-BuF/SbF$_5$=1/2.5, we might reasonably expect the sol-
ution to contain either equimolar amounts of the Sb$_2$F$_{11}^-$ and
Sb$_3$F$_{16}^-$ ions or Sb$_2$F$_{11}^-$ and SbF$_5$ coordinated with the solvent.
When the SO$_2$ is the solvent, it is the later which occurs,
as was shown in section (3) . Dean and Gillespie[39] have
done an extensive nmr study on solutions of SbF$_5$ in SO$_2$ClF,
both with and without the addition of weak bases such as
SO$_2$ and SOF$_2$. Their work shows SO$_2$FCl to be a much weaker
base towards SbF$_5$ than SO$_2$ is, and so the Sb$_3$F$_{16}^-$ ion might well
be stable in SO$_2$ClF. The spectrum of Fig. 10 shows seven
resonances. Resonance a, a broad signal 89.8 ppm above CFCl$_3$,
is in the bridging fluorine region. Resonance c at 112.3 ppm
is close to the resonance position found for the eight
equivalent fluorines of Sb$_2$F$_{11}^-$ in SO$_2$ solution (see above),
and appears to be a doublet of doublets. Resonances f and
g are simple quintets (J=100 ± 2 Hz) at 136.3 and 144.1 ppm,
the upper lines of one overlapping the lower lines of the
other. Resonances b and e are multiplets at 108.3 and 127.8
ppm, and the remaining resonance, d, is a broad peak at
117.9 ppm. We may first of all assign the quintet f and
resonances a and c to the Sb$_2$F$_{11}^-$ ion. Peak d appears to be
the resonance of SbF$_6^-$; for solutions of SbF$_5$ in HF[30] the
resonance of SbF$_6^-$ lies 5-6 ppm above that of the eight
equivalent fluorines in the Sb$_2$F$_{11}^-$ ion, in good agreement with
the 5.6 ppm shift between peaks c and d. The quintet g and
multiplets b and e remain to be assigned.

Let us now consider the structure for cis-Sb$_3$F$_{16}^-$
shown below
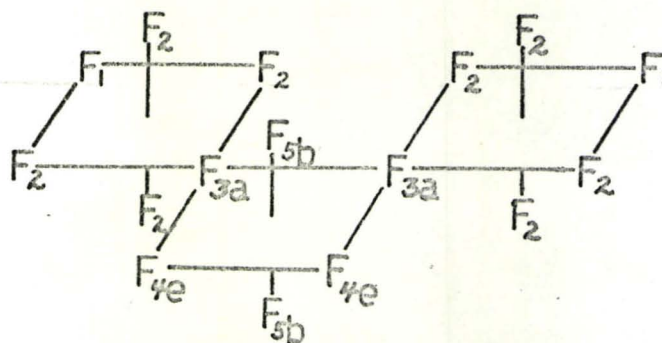
Assuming free rotation about the fluorine bridges, it can be seen there would be five groups of chemically different fluorines in such an ion. If trans couplings are small, as is the case in the $Sb_2F_{11}^-$ ion[30] and SbF_5 (this work), the resonance of the F_1 fluorines should be a quintet with $J \approx 100$ Hz. The quintet resonance g can therefore be assigned to these fluorines. SbF_5SO_2ClF would also give rise to a quintet with $J \approx 100$ Hz in the same region, but the strong doublet resonance of SbF_5SO_2ClF expected at 105.1 ppm[39] is not seen in the spectrum of Fig. 10, and therefore little or no SbF_5SO_2ClF is present. The resonance of the F_2 fluorines in cis-$Sb_3F_{16}^-$ should be a doublet of doublets, for the same reasons as in $Sb_2F_{11}^-$, and the bridging fluorines F_3 would give rise to a broad, very complicated multiplet, since each F_3 will be coupled strongly ($J = 50-80$Hz) to four F_2 fluorines, both F_5 fluorines, and one of the F_4 fluorines. If we assume that fluorines F_3 and F_2 of $Sb_3F_{16}^-$ make up part of resonances a and c, already assigned to the analogous fluorine atoms in the $Sb_2F_{11}^-$ ion present in this solution, then multiplets b and e can be assigned to fluorines F_5 and F_4 of the $Sb_3F_{16}^-$ ion. We may note that e, assigned to F_4, is a triplet showing the same doublet splitting as seen in the triplet at high field in the spectrum of SbF_5 (see above), and that multiplet b could be a septet with its three upper lines overlapped by resonance c. The splittings in multiplets b and e are of the same order of magnitude as in SbF_5 , but slightly different, as would be expected for a different species. We see therefore that the experimental spectrum can be interpreted on the basis of the spectrum of the $Sb_2F_{11}^-$ ion, already known, plus the spectrum of a new ion cis-$Sb_3F_{16}^-$, the spectrum of this ion having some of the features of the spectra of both the $Sb_2F_{11}^-$ ion and SbF_5. Since relative areas $F_1/F_2/F_3 = 2/8/1$ are expected for the $Sb_2F_{11}^-$ ion, and relative areas $F_1/F_2/F_3/F_4/F_5 = 2/8/2/2/2$ for

cis-$Sb_3F_{16}^-$ ion, equimolar amounts of the two ions should give
relative areas a/b+c/e/f+g=3/18/2/4 in excellent agreement
with the observed experimental areas 2.8/18.4/2/4.2. The
spectral areas appear to confirm the proposed assignment,
therefore.

94.077 MHz fluorine spectra of the solution were
recorded in order to spread out the spectrum and separate
resonance b from resonance c. In the spectrum obtained at
-75°, shown in Fig. 11, all of multiplet b but the highest
peak is seen. The overlap between quintets f and g is
reduced, although resonance a is essentially unchanged.
Resonance c has now split into five peaks. It would appear
from this that c is made up of two overlapping doublets of
doublets at 112.4 and 113.2 ppm, one arising from $Sb_2F_{11}^-$ and
one from $Sb_3F_{16}^-$, as postulated above. Multiplet e now shows
a doublet splitting on all three peaks. (We expect some small
changes in the shape of the spectrum when the operating
frequency is changed from 56.445 to 94.077 MHz because the
first order condition $\nu_0\delta \gg J$ is true only to a first
approximation in these fluorine spectra.) Since the 94.077
MHz spectrum shows more of multiplet b and gives three
doublet splittings in the triplet, LAOCN3/NMRPLT calculations
for cis-$Sb_3F_{16}^-$ were first done on this spectrum, and not the
56.445 MHz spectrum. Reference to the structural diagram
for $Sb_3F_{16}^-$ given above shows that the centre SbF_6 unit of this
ion should give rise to a spectrum similar to that of SbF_5,
as is observed, and that the spectrum of the F_4 and F_5 fluorines
should depend on the same six coupling constants. A trial
spectrum was calculated using values of J_{ab} and J_{be} estimated
from multiplet b and the final values obtained for the other
four coupling constants in SbF_5, that is

$$J_{ab}=91.5 \qquad J_{ae}=61.5$$
$$J_{be}=131.1 \qquad J_{ae'}=-8.5$$
$$J_{aa}=25 \qquad J_{ee}=85$$

The parameters were varied until the splittings in the
spectra were well reproduced, with the largest deviation
1.7 Hz and the average deviation 0.9 Hz. The final set
of coupling constants is

$$J_{ab}=85.6 \qquad J_{ae}=79.3$$
$$J_{be}=135.7 \qquad J_{ae'}=-11.1$$
$$J_{aa}=27.5 \qquad J_{ee}=112.5$$

The spectrum for multiplets b and e calculated with these
parameters is shown by a dashed line in Fig. 11. The doublet
splittings in the experimental spectrum (49.9, 45.0, 32.2 Hz,
from low to high field) are particularly well reproduced in
the calculated spectrum (50.1, 44.7, 31.9). The final set
of coupling constants were also used to calculated a theore-
tical 56.445 MHz spectrum, shown by a dashed line in Fig. 10,
for comparison with the theoretical spectrum. It is also
an excellent fit.

The nmr spectra, area measurements and calculated
spectra given above clearly show the existence of the $Sb_3F_{16}^-$
ion in SO_2ClF. The observation of the effects of magnetic
inequivalence on the triplet resonance at 127.8 ppm shows
that the fluorine bridges in the $Sb_3F_{16}^-$ ion are cis to one
another, as is the case for SbF_5. Edwards et al.[40] studied
crystalline $Br_2^+Sb_3F_{16}^-$ by X-ray diffraction and found trans-
fluorine bridging for the anion. If $Sb_3F_{16}^-$ were trans-bridged
in the solutions studied, the four non-bridging fluorines
in the centre SbF_6 unit would be chemically equivalent, and
give a single resonance split into a triplet by coupling to
the two bridging fluorines, rather than the two multiplets
observed experimentally.

Table IV summarizes the nmr parameters obtained for
the various anions in SO_2 and SO_2ClF. Shifts are also given
for $Sb_2F_{11}^-$ and SbF_6^- in HF. It can be seen there is a
considerable solvent effect on the chemical shift, in the
direction $HF > SO_2ClF > SO_2$.

TABLE II

Chemical Shifts and Coupling Constants Obtained from the

Fluorine Spectra of the Alkyl Fluorides[1]

Compound	$\emptyset$ (ppm)	$^2J_{HF}$ (Hz)	$^3J_{HF}$ (Hz)
$(CH_3)_3CF$	132.7		20.2
$(CH_3)_2CHF$	167.9	48.4	22.9
CH_3CH_2F	217.3	47.3	25.8
CH_3F	273.1	46.3	

[1] $\emptyset$ is used to indicate chemical shift relative to the resonance of $CFCl_3$. The coupling constants are accurate to 0.3 Hz.

TABLE III

Fluorine Chemical Shifts[1] for Various Mixtures in Liquid SO_2

Mixture	Resonance				
	a	b	c	d	e
t-BuF/3.8SbF$_5$	90.3	110.2	132.2	101.0	106.6
t-BuCl/5.5SbF$_5$	90.1	110.2	132.2	101.0	106.7
Et$_4$NSbF$_6$/4.6SbF$_5$	90.5	110.9	134.3	101.5	105.4
Et$_4$NSbF$_6$/7.9SbF$_5$	91.2	110.9	135.1	101.3	−

[1] ppm relative to CFCl$_3$

TABLE IV

NMR Data[1] for $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ in Several Solvents

Solvent	Ion	Chemical Shifts				
		F_1	F_2	F_3	F_4	F_5
SO_2	$Sb_2F_{11}^-$	132.2	110.2	90.3		
SO_2ClF [2]	$Sb_2F_{11}^-$	136.4	113.2	89.7		
	$Sb_3F_{16}^-$	141.1	112.4	89.7	127.8	108.3
HF [3]	$Sb_2F_{11}^-$	141.8	120.1	93.0		

[1] Chemical shifts in ppm relative to $CFCl_3$. Fluorines are numbered as in the text. All nmr data taken from this chapter, except for HF as solvent, which is taken from ref. 41

[2] SbF_6^- in SO_2ClF, 118 ppm. For $Sb_3F_{16}^-$, $J_{12}=99$, $J_{13}=54$, six other coupling constants are given in the text.

[3] SbF_6^- in HF, 125 ppm.
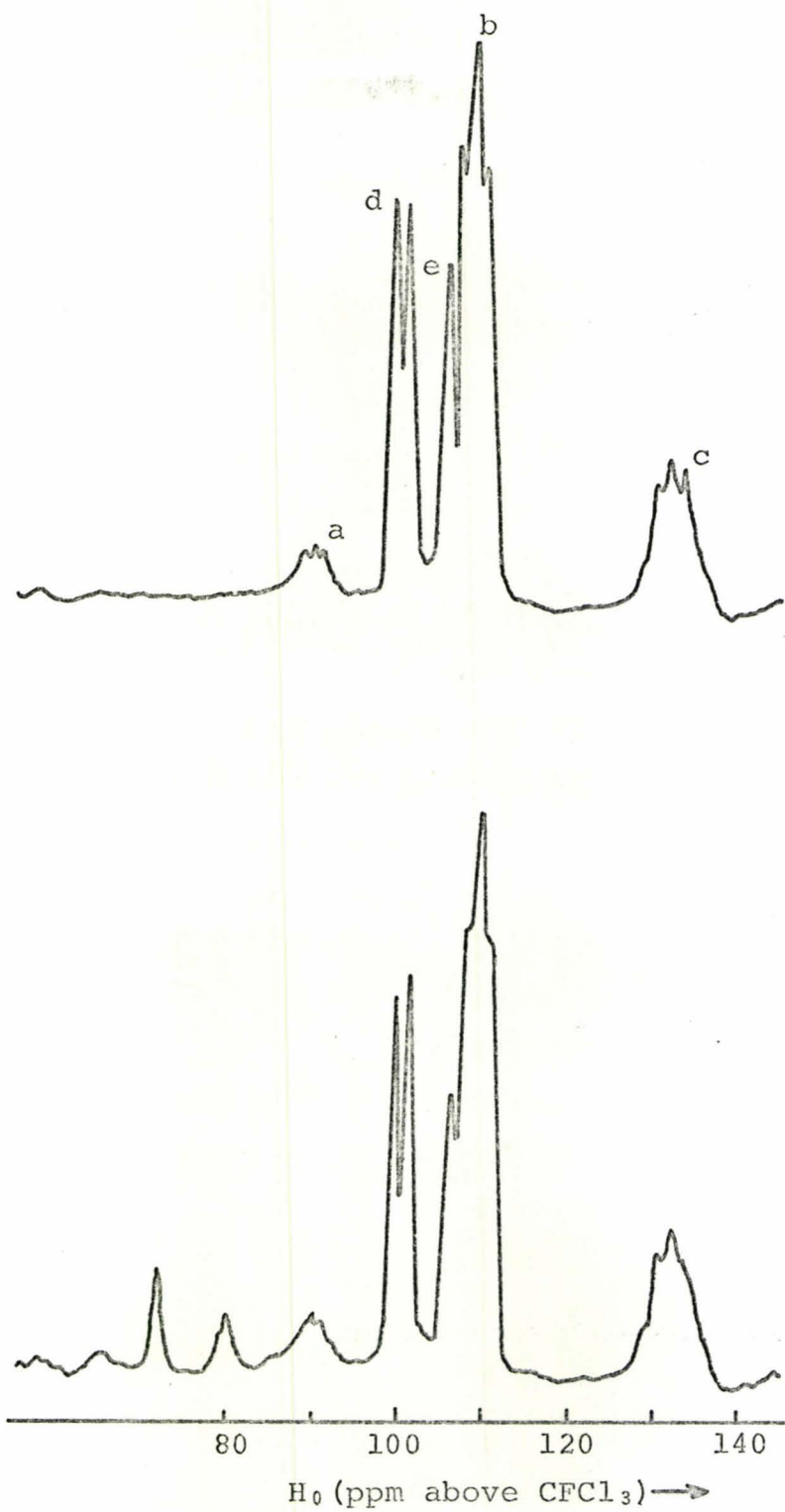
<u>Fig. 5</u>

Fluorine (56.445 MHz) Spectra of t-Butyl Fluoride/3.8SbF$_5$ in SO$_2$ (top) and t-Butyl Chloride/5.5SbF$_5$ in SO$_2$ (bottom), both at -80°
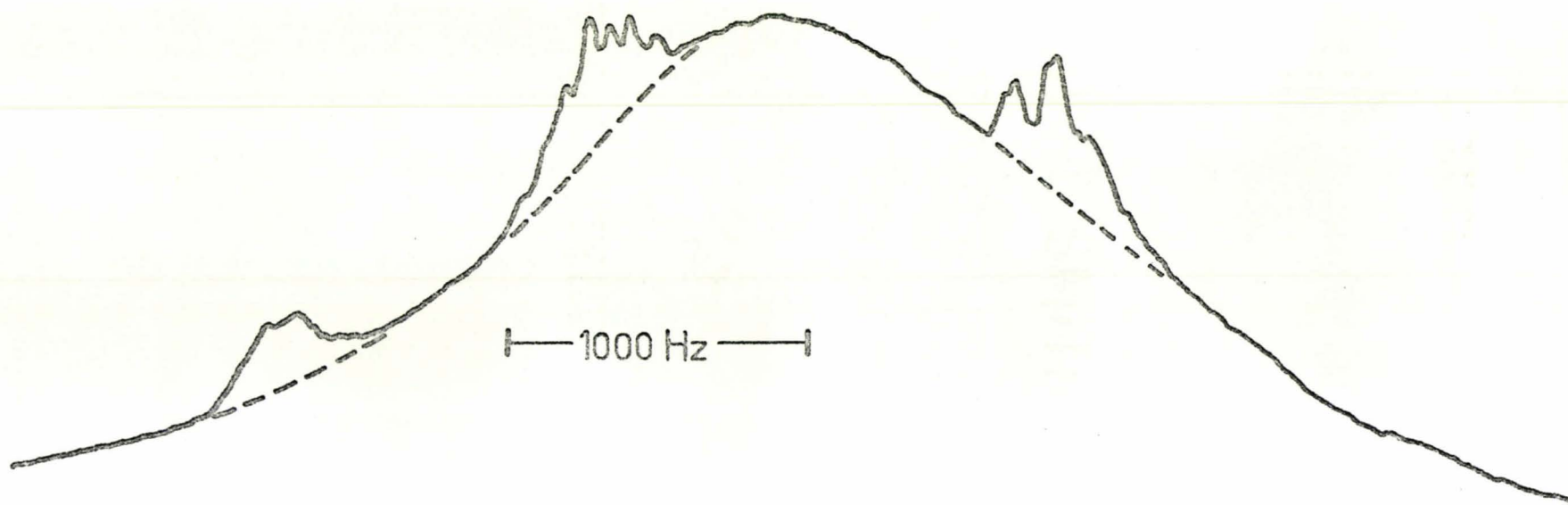
Fig. 6

Fluorine (56.445 MHz) Spectrum of t-BuF/3.8SbF$_5$ at $-40°$
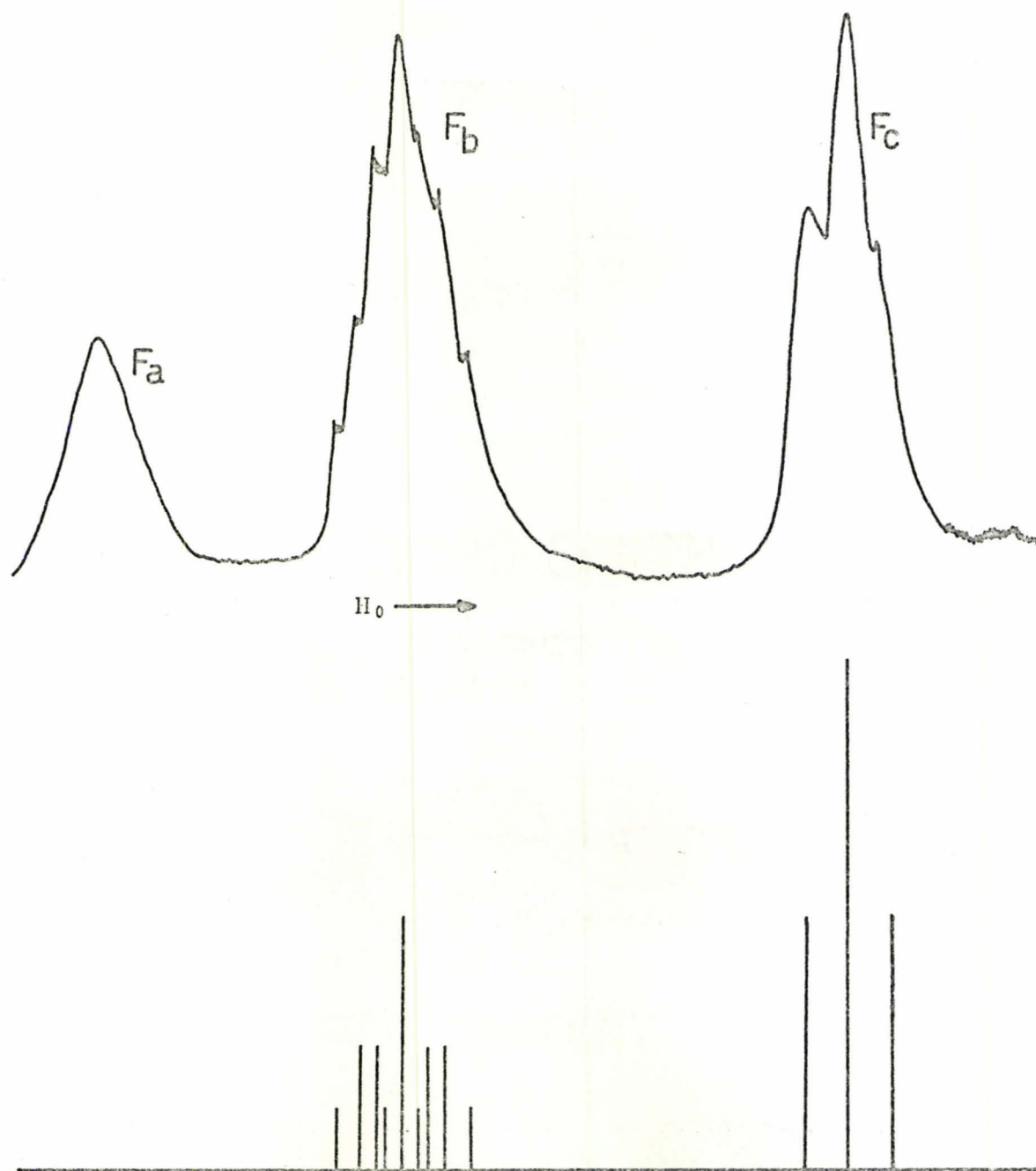
Fig. 7

Fluorine (40 MHz) Spectrum of Purified Liquid SbF₅
          as obtained by Hoffman, Holder and Jolly[29].
The first order theoretical spectrum is shown below.
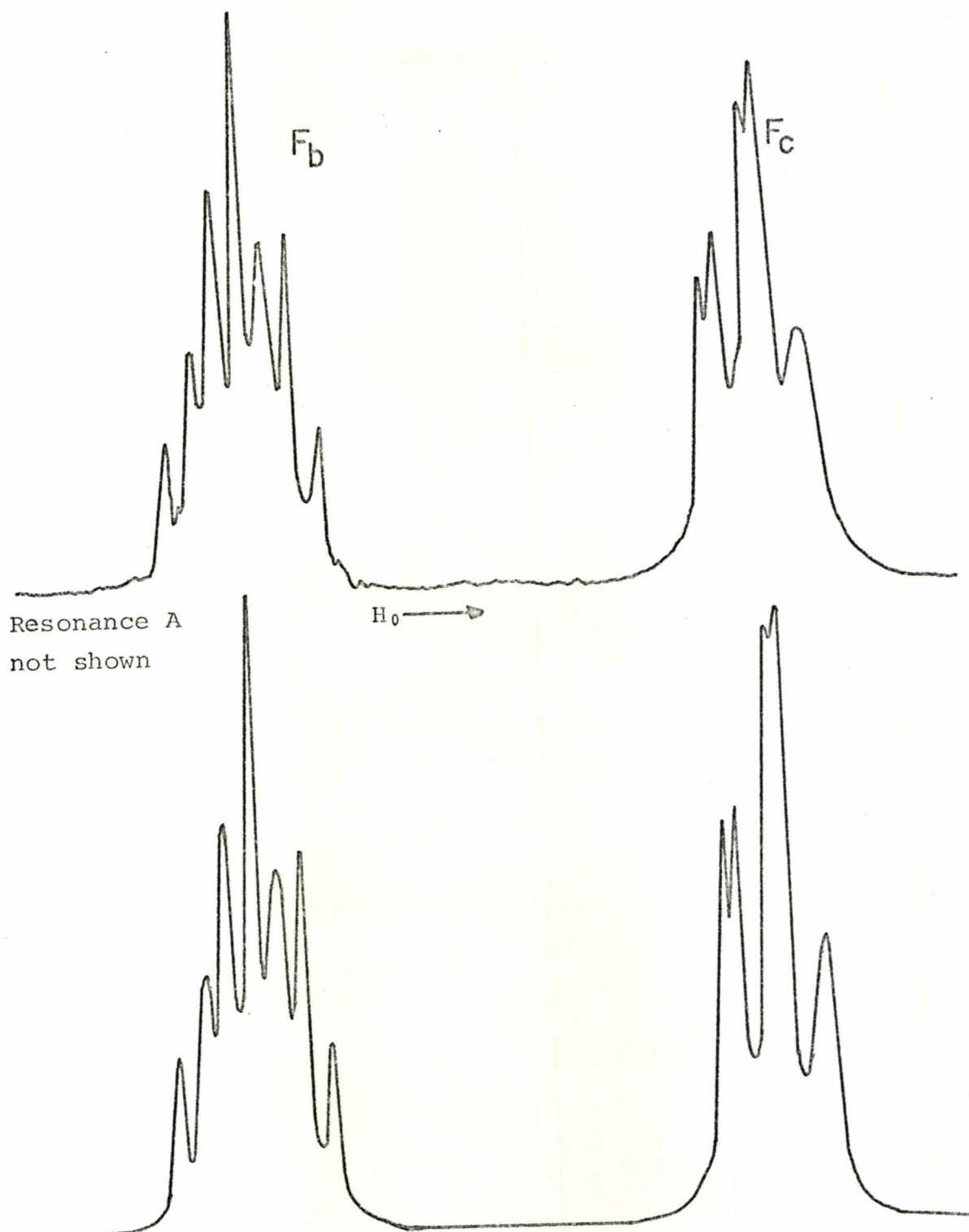
Fig. 8

Fluorine (56.445 MHz) Spectrum of SbF₅/0.4 Freon-114 as obtained by Gillespie and Rothenbury[33]. The theoretical spectrum calculated by LAOCN3/NMRPLT (this work) is shown below.
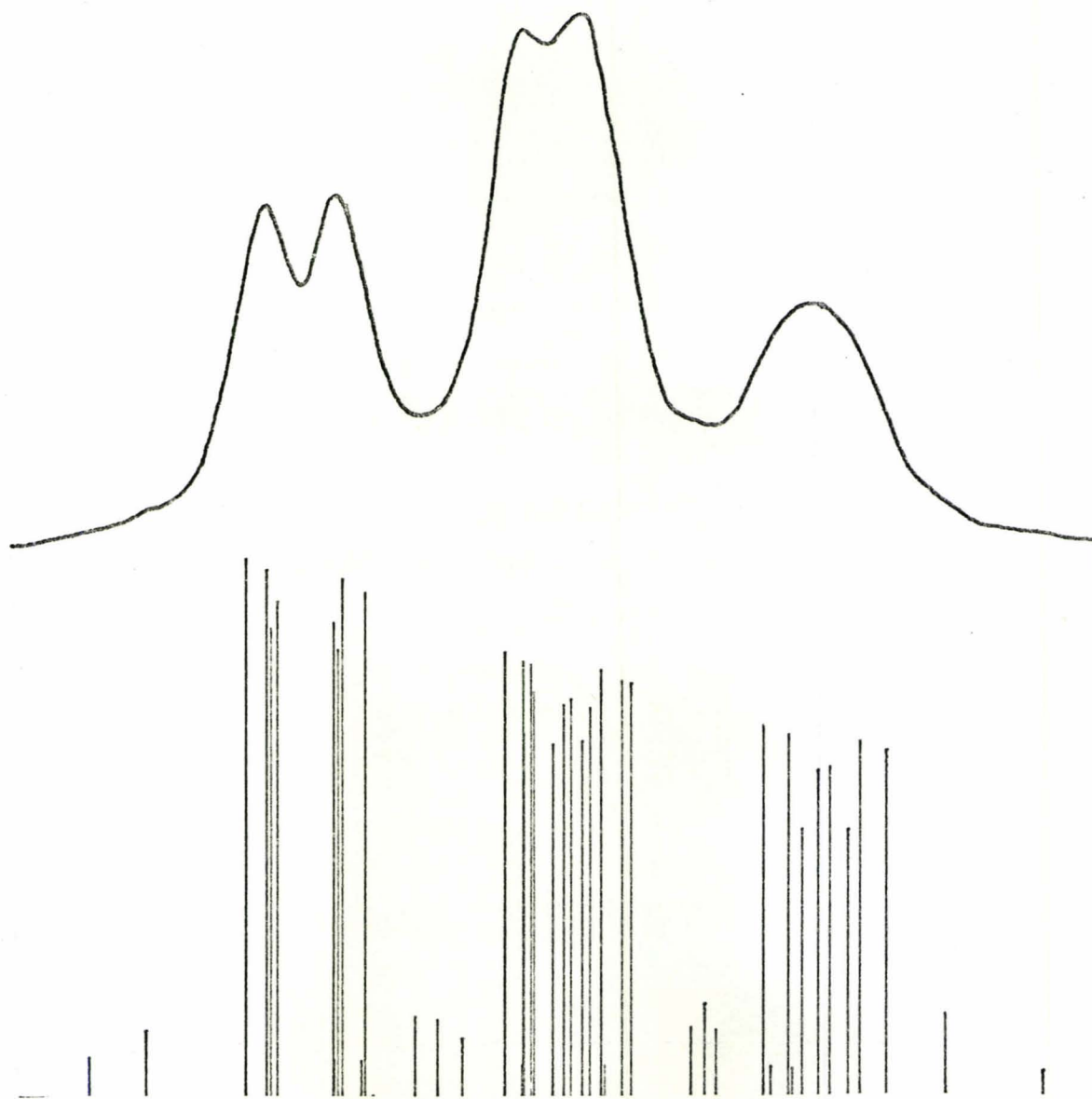
Fig. 9

Calculated Line Shape and Individual Lines for the High
Field Triplet in the Fluorine Resonance of SbF_5/0.4 Freon-114
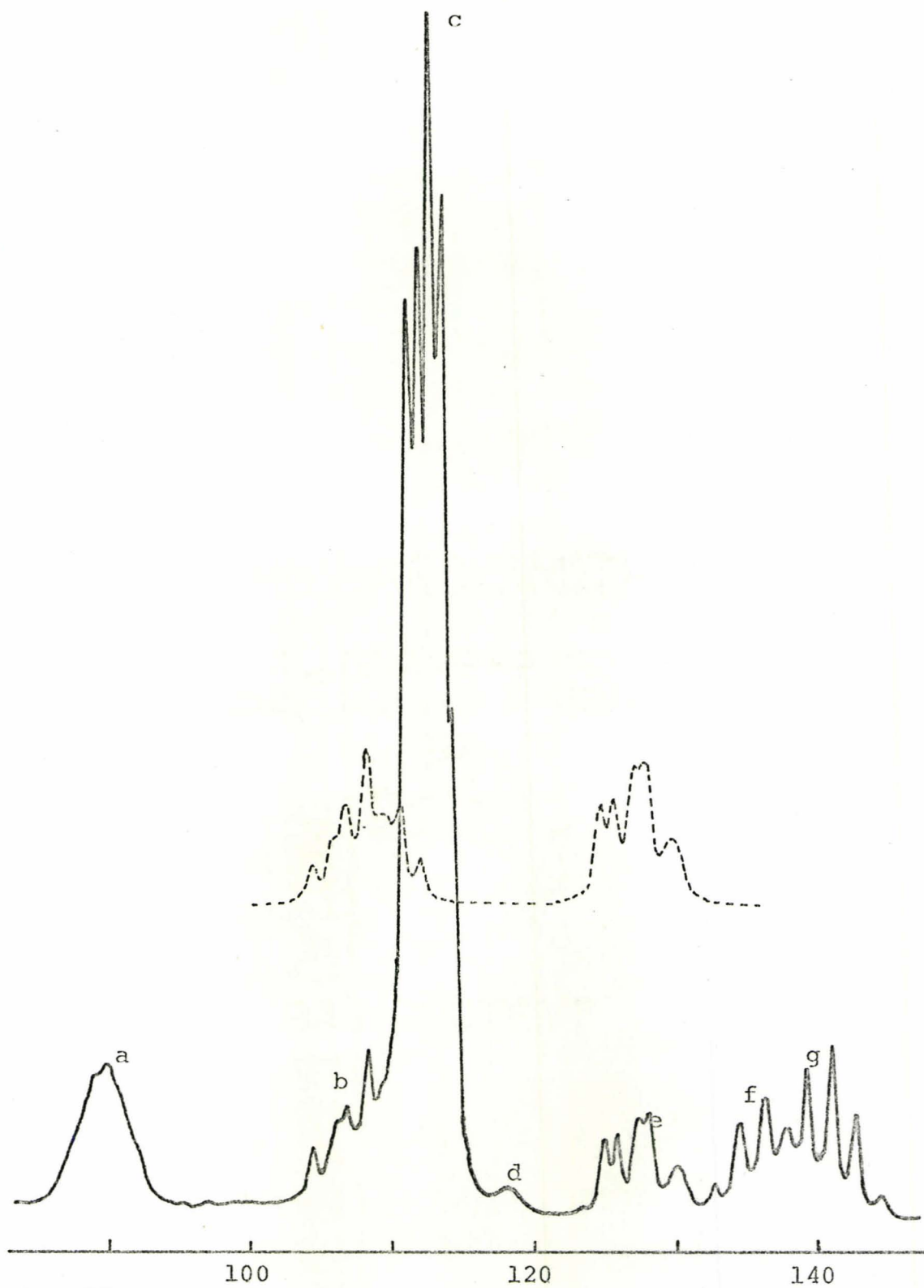
Fig. 10

Fluorine (56.445 MHz) Spectrum of t-Butyl Fluoride/2.5SbF$_5$/
2.2SO$_2$ClF at -95°. The theoretical spectrum for multiplets b
and e calculated by LAOCN3/NMRPLT is also shown (dashed line)
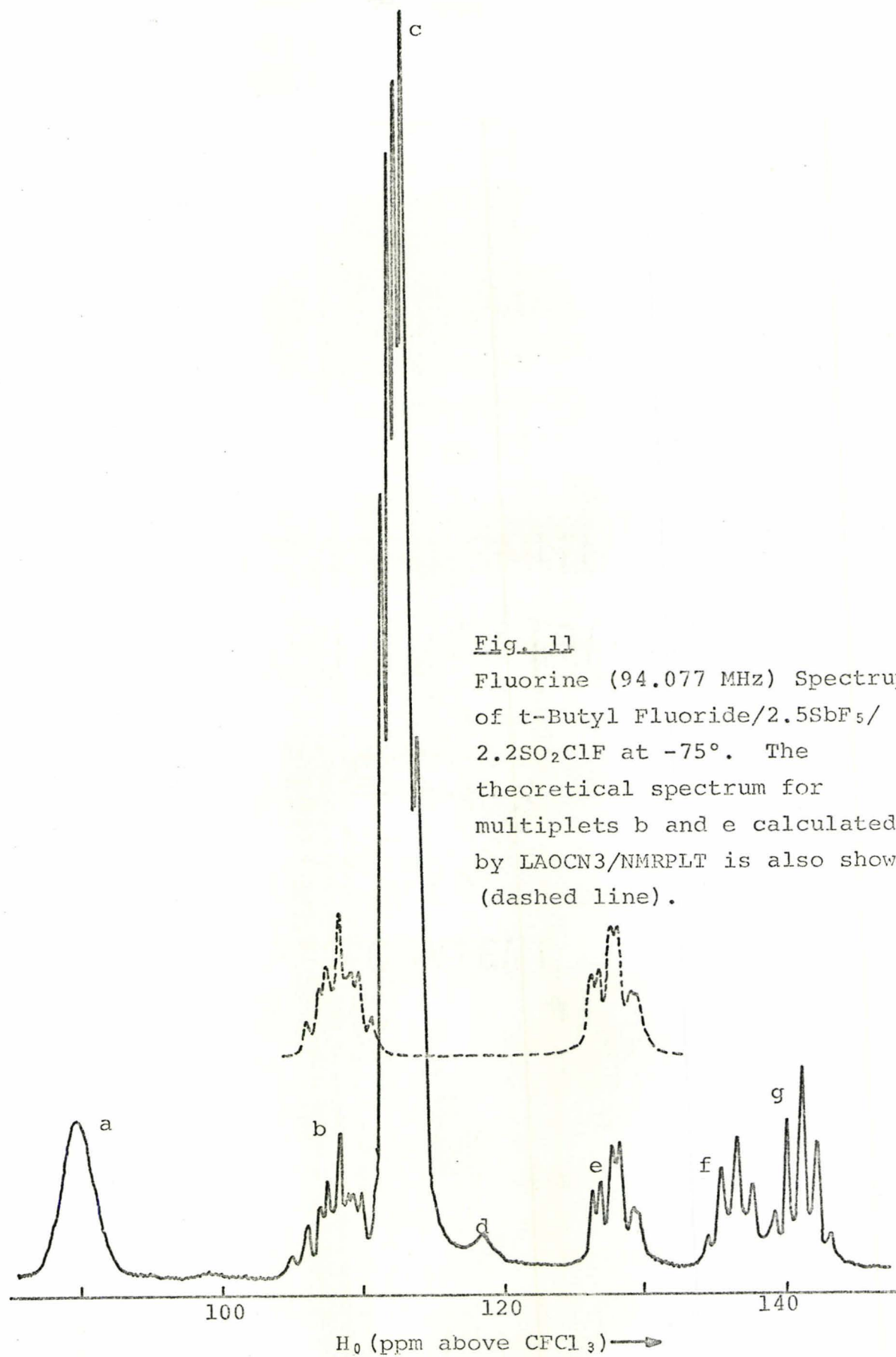
Fig. 11

Fluorine (94.077 MHz) Spectrum of t-Butyl Fluoride/2.5SbF$_5$/ 2.2SO$_2$ClF at −75°. The theoretical spectrum for multiplets b and e calculated by LAOCN3/NMRPLT is also shown (dashed line).

H$_0$ (ppm above CFCl$_3$) ⟶

CHAPTER 4

PROTON AND FLUORINE NMR OF SOLUTIONS OF METHYL FLUORIDE, ETHYL FLUORIDE, AND CARBONYL CHLOROFLUORIDE IN SbF_5/SO_2 and SbF_5/SO_2ClF

(1) INTRODUCTION

In the preceding chapter it was seen that the $Sb_2F_{11}^-$ anion is produced when t-butyl halide/SbF_5 mixtures are dissolved in SO_2 and that the $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ anions are produced when t-butyl fluoride ionizes to the carbonium ion in SbF_5/SO_2ClF. It would now be tempting to say that these results give a method for characterizing the ionization of a compound to a carbonium ion, that is that fluorine spectra like those in Fig. 5 and 10 indicate the production of a carbonium ion from the compound initially dissolved in the SbF_5-containing medium in all cases. However, it is conceivable that the fluorine spectrum of an exchanging donor-acceptor complex might be the same as, or very similar to, that of the free anion. Olah et al.[42] have recently claimed that methyl fluoride forms an exchanging donor-acceptor complex with SbF_5 in SO_2 solution. These authors did not obtain the fluorine spectrum of this system. The proton spectrum obtained showed a sharp singlet 5.56 ppm below external TMS. Since the proton resonance of methyl fluoride in SO_2 in the absence of SbF_5 is a doublet (J=45.8 Hz) 4.00 ppm below TMS, the authors concluded that methyl fluoride dissolved in SbF_5/SO_2 is present in the form of the donor acceptor-complex $CH_3F{\rightarrow}SbF_5$, the 1.56 ppm deshielding resulting from the withdrawal of electrons by the SbF_5 group. A much larger deshielding, about 10 ppm, would be expected for the methyl ion, which in any case is expected to be too unstable to exist in the solution. Since the proton resonance assigned to the donor-acceptor complex

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shows no proton-fluorine coupling, it must be assumed that the donor-acceptor complex is exchanging in some way which involves the breaking and reforming of the C-F bond. Olah et al. formulated this exchange as occuring through the structure shown below
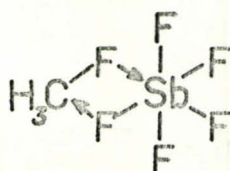
It is not clear whether Olah et al. regard this as the transition state for exchange or the structure of the donor-acceptor complex itself. In any case, the fluorine spectrum of such a complex would serve to both identify the complex and to show whether or not its fluorine spectrum can be distinguished from the spectra of the anions studied in this work. It is also possible that ethyl fluoride might form a similar complex. As part of this work, therefore, solutions containing methyl fluoride and ethyl fluoride were prepared. Solutions of COFCl in SbF_5/SO_2ClF were also prepared, as COFCl could ionize to COF^+ (isoelectronic with CO_2), ionize to $COCl^+$ (isoelectronic with COS), or form a donor-acceptor complex through either oxygen or fluorine.

(2) ETHYL FLUORIDE IN SbF_5/SO_2 SOLUTION

A solution having $EtF/SbF_5/SO_2=1/5.0/75$ was prepared on the vacuum line and an nmr sample sealed off, all at low temperature. The SbF_5/SO_2 ratio used corresponds to approximately 1.35 M in SbF_5. The proton spectrum of this sample at $-80°$ shows an ethyl group spectrum, that is a methylene quartet at 6.53 and a methyl triplet at 2.29, both ppm below external TMS. The fluorine couplings ($^3J_{HF}=25.8$, $^2J_{HF}=47.3$ Hz) to the methyl and methylene protons seen in the proton and fluorine spectra of neat ethyl fluoride do not appear in this spectrum. The proton spectrum of neat ethyl fluoride, done

as part of this work, gives chemical shift values of 4.17 and 1.03 ppm below external TMS for the methylene and methyl resonances, respectively. We see therefore that a 2.36 ppm deshielding of the methylene resonance and a 1.26 ppm deshielding of the methyl resonance have taken place, as well as the elimination of proton-fluorine coupling.

The fluorine spectrum of $EtF/5.0SbF_5/75SO_2$ at $-85°$ is shown in Fig. 12. It consists of four resonances, and would appear at first sight to be that of a mixture of $Sb_2F_{11}^-$ and $SbF_5 \cdot SO_2$, by comparison with Fig. 5, for example. The chemical shifts, a=92.3, b=111.5, c=134.4 and d=102.4, are only ≈ 1.5 ppm to high field of those given in Table III for t-butyl halides in SbF_5/SO_2, a difference which is of the same order of magnitude as the experimental error. A small solvent effect is also a possibility. The areas are in the ratio a/b/c/d=1.3/8/4.6/10.9. For $Sb_2F_{11}^-/SbF_5 \cdot SO_2 = 1/2.7$ the ratio 1/8/4.7/10.8 would be expected. If $Sb_2F_{11}^-$ were produced by ionization of the ethyl fluoride to the ethyl ion

$$CH_3CH_2F + 2SbF_5 \xrightarrow{SO_2} CH_3CH_2^+ + Sb_2F_{11}^-$$
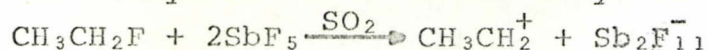
then, since $EtF/SbF_5=1/5$, we would expect $Sb_2F_{11}^-/SbF_5 \cdot SO_2=1/3$, since $Sb_2F_{11}^-$ is the longest polyanion which can exist in SO_2 and any SbF_5 in excess of the amount necessary to produce $Sb_2F_{11}^-$ will combine with the solvent, giving $SbF_5 \cdot SO_2$. It cannot be said, however, that the ethyl ion is produced, as we should expect a methylene resonance at ≈ 14 ppm and a methyl resonance at ≈ 4 ppm, by comparison with the isopropyl ion (see Table I, for instance) The observed shifts, given above, are 6.53 and 2.29 ppm. Some other explanation for the fluorine spectrum must therefore be found. Another possible ionization reaction is that to the ethylhalonium ion, shown below

$$2CH_3CH_2F + 2SbF_5 \longrightarrow (CH_3CH_2)_2F^+ + Sb_2F_{11}^-$$
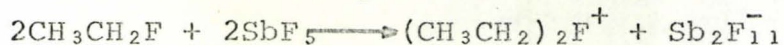
The ions $(CH_3CH_2)_2Cl^+$, $(CH_3CH_2)_2Br^+$ and $(CH_3CH_2)_2I^+$ have been reported by Olah and DeMember[43]. In the above reaction, one SbF_5 per mole of ethyl fluoride added is ionized to one-half mole of $Sb_2F_{11}^-$, leading to $Sb_2F_{11}^-/SbF_5 \cdot SO_2=1/8$. This is not in

accord with the spectral areas, which suggest $Sb_2F_{11}^-/SbF_5 \cdot SO_2$ =1/2.7, as discussed above. The discrepancy could be accounted for only if large amounts of $SbF_5 \cdot SO_2$ were precipitated at -85°. When the nmr sample was kept at -85° for an hour, only a very small amount of precipitate was observed. It appears, therefore, that ionization to the ethylfluoronium ion can also be ruled out.

The only plausible explanation for the experimental spectrum would appear to be that a donor-acceptor complex is formed, as already suggested by Olah et al.[42] for methyl fluoride in SbF_5/SO_2. Two possible structures for a 1:1 donor-acceptor complex are shown below.

The first structure would give rise to three resonances of equal intensity. If we recall that $J_{cis} \approx 50-80$ Hz when one of the fluorines involved is in a bridging position and 100-145 Hz otherwise, we see that the resonances of F_a and F_c should each be split into triplets, while that of F_c should be split into a triplet of triplets. Clearly this structure can be ruled out immediately, by comparison with the experimental spectrum. The second structure would give rise to three resonances of relative areas 1/4/1, split into two quintets (F_a, F_c) and a doublet of doublets (F_b). This is superficially similar to the spectrum of the $Sb_2F_{11}^-$ ion, assuming similar chemical shifts, except that the bridging fluorine is a quintet and has twice the relative area that the bridging fluorine has in the $Sb_2F_{11}^-$ ion. The structure is unsatisfactory in that it does not explain the disappearance of proton-fluorine coupling. It can also be ruled out on the basis of areas, since formation of a 1:1 complex implies $EtFSbF_5/SbF_5 \cdot SO_2$ =1/4. The relative areas observed, already given above,

correspond to $EtFSbF_5/SbF_5 \cdot SO_2 = 1/1.35$, for which $a/b/c/d = 2/8/4.7/10.8$. The stoichiometry, however, would imply $EtFSbF_5/SbF_5 \cdot SO_2 = 1/4$. The discrepancy is much too large.

Let us now consider the 1:2 complex as shown below.
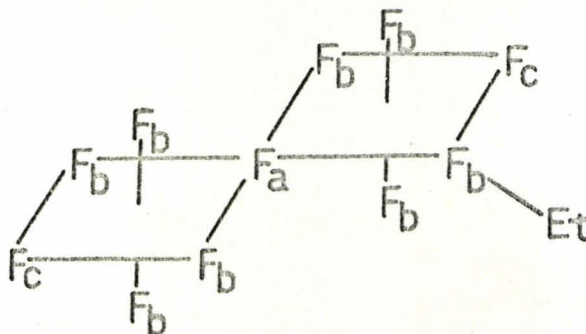
If we assume that the ethyl group undergoes rapid exchange between fluorines, we account for both the lack of proton-fluorine coupling and the fact that only three fluorine resonances are observed. The presence of such an exchange implies a rather novel donor-acceptor complex, in that the C-F bond in the C-F-Sb linkage formed must be weaker than the F-Sb bond. As far as the effects on the proton and fluorine spectra are concerned, the exchange can be intramolecular or intermolecular, and may involve only the F_b fluorines or the F_c fluorines or both. Since fluorine bridges are generally cis to one another, the exchange of the ethyl group between F_b fluorines alone would seem to be the most likely situation. If a 1:2 complex is formed, we expect $EtSb_2F_{11}/SbF_5 \cdot SO_2 = 1/3$. The observed areas give 1/2.7 for this ratio. The small discrepancy can be explained by the small amount of white solid in the nmr sample at low temperatures. Of all the possibilities considered, the exchanging 1:2 complex appears to be the only satisfactory one. An exchanging 1:1 complex would, of course, give a single fluorine resonance.

The $-80°$ proton spectrum showed the donor-acceptor complex to be 96% unreacted, that is, little decomposition to carbonium ions (C_4, C_5, C_6 etc.) had occured. Small amounts of t-butyl, t-amyl and t-hexyl ions corresponding to 4% reaction were present in the spectrum. There were also two small singlet

resonances. One, at 5.76 ppm below external TMS is probably that of the methyl fluoride-SbF_5 donor-acceptor complex (5.56 expected) as the neat ethyl fluoride sample appears to contain a small amount (1%) of methyl fluoride as an impurity. The other singlet in the -80° proton spectrum of $EtSb_2F_{11}$ occured at 1.23 ppm and is not identified, although it is probably an alkane. In any case, at -80° well over 90% of the area of the proton spectrum corresponds to $EtSb_2F_{11}$. When the sample was warmed to -60°, a very slow reaction to t-butyl ions occurred, presumably as shown below.

$$CH_3CH_2Sb_2F_{11} \longrightarrow CH_3CH_2^+ + Sb_2F_{11}^-$$

$$2CH_3CH_2^+ \longrightarrow (CH_3)_3C^+ + H^+$$
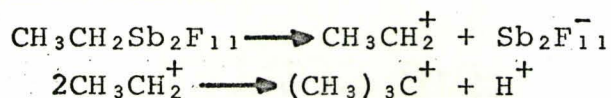
After 75 minutes at -35°, this reaction was 60% complete. The signal from the acid proton, presumably present as H_2F^+, $HSbF_6$ or HSb_2F_{11}, was seen at 10.6 ppm below external TMS. Clearly the ethyl ion is not stable even at -60°. After a total of 150 minutes at -35°, the fluorine spectrum was run again, and found to be the same as before reaction, showing that the fluorine spectrum of the donor-acceptor complex is indistinguishable from that of the $Sb_2F_{11}^-$ ion, present after essentially complete reaction to t-butyl ion and Sb_2F_{11}.

Samples having $EtF/SbF_5=1/1.3$ and $1/0.78$ were also prepared, by distilling ethyl fluoride into a cold SbF_5/SO_2 solution which was about 1.5 M in SbF_5. The low temperature proton spectra of both of these samples consist of the ethyl group resonance showing deshielding and no coupling to fluorine as already discussed above. The fluorine spectrum of the $EtF/1.3SbF_5/SO_2$ sample at -90° is shown at the bottom of Fig. 12. It is similar to the spectrum for $EtF/5.0SbF_5/SO_2$ already discussed above, except that the resolution is a great deal better and that little or no $SbF_5 \cdot SO_2$ is present. The spectrum would appear to be that of the 1:2 complex, $EtSb_2F_{11}$, once again, this time uncomplicated by the presence of $SbF_5 \cdot SO_2$. The composition of the solution would suggest that considerable amounts of either the 1:1 complex, $EtSbF_6$, or free ethyl fluoride

should be present. Free ethyl fluoride is not seen in the proton spectrum of this sample. Only one deshielded ethyl resonance appears in the proton spectrum, so if both $EtSbF_6$ and $EtSb_2F_{11}$ are present, either the postulated ethyl group exchange mechanism is intermolecular to some extent or the proton chemical shifts are the same in the 1:1 and 1:2 complexes. We may note that the fluorine resonance of $EtSbF_6$ might well be a broad line owing to a partially collapsed multiplet structure which would arise if the antimony spins undergo quadrupole relaxation at a relatively slow rate, in which case the fluorine-antimony coupling is not completely averaged out, as discussed in section (1) of Chapter 3. Such a broad line might be difficult to observe at all but the highest concentrations of $EtSbF_6$. When the spectrum of the $EtF/0.78SbF_5/SO_2$ sample was obtained at -90°, it was found to consist of just such a broad resonance, ≈ 2000 Hz wide, in the fluorine on antimony region of the spectrum, which had superimposed on it the spectrum found for the $EtF/SbF_5/SO_2$ sample, already discussed. The width of the broad resonance decreases as the temperature is lowered, which is to be expected if this resonance is a partially collapsed multiplet, the rate of quadrupole relaxation, and hence the degree of collapse towards a sharp line, increasing as the temperature is lowered[27]. The broad resonance makes up about 90% of the total area. Here we appear to have mainly $EtSbF_6$ with some $EtSb_2F_{11}$ present, although strictly speaking the stoichiometry implies $EtSbF_6$ with some free ethyl fluoride. As no free ethyl fluoride is seen in the proton spectrum, it appears that some ethyl fluoride is consumed in a way other than donor-acceptor complex formation. Some reaction to a yellow solid which is partially soluble in SO_2 appears to have occured, particularly in the samples which are more concentrated in ethyl fluoride. Most of the ethyl fluoride in the above samples, however, appears to form the novel donor-acceptor complexes $EtSbF_6$ and $EtSb_2F_{11}$ in which the carbon-fluorine

bond is considerably weaker than all the other bonds in the complex. It should be noted that the observation of a partially collapsed multiplet due to residual fluorine-antimony coupling for fluorine containing species of antimony has previously been noted only for SbF_6^-, all other species giving essentially complete collapse of the multiplet due to Sb-F coupling to a relatively narrow line. Very rapid exchange of the weakly bonded ethyl group in the postulated $EtSbF_6$ complex would appear to give rise to an averaging effect which can be regarded as providing an effectively octahedral symmetry about the antimony.

(3) METHYL FLUORIDE IN SbF_5/SO_2 SOLUTION

Samples having $MeF/SbF_5=1/2.0$ and $1/0.9$ were prepared on the vacuum line by distilling methyl fluoride into a cold SbF_5/SO_2 solution which was about 1.5M in SbF_5. The proton spectrum of the first sample at $-60°$ shows a singlet only, at 5.33 ppm below external TMS. The second sample shows a singlet at 5.29 ppm and the methyl fluoride doublet. In the latter case, the area of the doublet is 15% of that of the singlet peak, suggesting that the ratio of free methyl fluoride to complexed methyl fluoride is 0.15. The fluorine spectrum for the $MeF/2.0SbF_5/SO_2$ sample obtained at $-90°$, shown in Fig. 13, consists of the resonance of a small amount of $SbF_5 \cdot SO_2$ and the same $Sb_2F_{11}^-$-like spectrum found for the $EtF/1.3SbF_5/SO_2$ sample and identified as that of a 1:2 donor-acceptor complex. Since the singlet found in the proton resonance of this sample is only slightly deshielded, we can make similar assignment here, that of $MeSb_2F_{11}$. The spectrum is quite well resolved. The fluorine spectrum of the $MeF/0.91SbF_5/SO_2$ sample at $-90°$ shows a broad single resonance having the spectrum of a 1:2 complex superimposed upon it. The broad peak is presumably the resonance of a 1:1 complex, as in the case of the $EtF/0.78SbF_5/SO_2$ sample. From the areas in the spectrum, we obtain $MeSb_2F_{11}/MeSbF_6=0.08$. We may note

that some $MeSb_2F_{11}$ is formed even though methyl fluoride is
present in slight excess. It would appear that, in the pre-
sence of one mole of methyl fluoride, 0.91 moles of SbF_5 form
about 0.79 moles of $MeSbF_6$ and 0.06 moles of $MeSb_2F_{11}$, leaving
0.15 moles of free methyl fluoride. These amounts give
$MeSb_2F_{11}/MeSbF_6 = 0.08$, already found from the fluorine spectrum,
and free methyl fluoride/complexed methyl fluoride=0.18, com-
pared with the value of 0.15 already deduced for this ratio from
the proton spectrum. Virtually all of the methyl fluoride in
solution is therefore accounted for, and the stoichiometry
would appear to confirm the spectral assignments. Solutions
of methyl fluoride were colourless, as reported by Olah et
al.[42], in contrast to the ethyl fluoride solutions. As only
one singlet peak appears in the proton spectrum, even when
both 1:1 and 1:2 complexes are present, either at least some
of the exchange of the methyl groups is taking place by an
intermolecular mechanism or the proton chemical shifts for
the 1:1 and 1:2 complexes are the same.

(4) CARBONYL CHLOROFLUORIDE IN SbF_5/SO_2ClF

A sample having $COFCl/SbF_5/SO_2ClF=1/2.9/3.1$ was pre-
pared on the vacuum line by allowing COFCl to distill into a
cold solution of SbF_5/SO_2ClF. A great deal of white solid
formed immediately. Much of this solid could not be re-
dissolved, even when the temperature was raised to $-23°$.
Samples of the liquid layer in the flask were sealed off. The
low temperature fluorine spectrum of such a sample gave no
resonance in the region where neat COFCl resonates ($\emptyset=-57.7$)
and no new peak which might be the resonance of the COF^+
ion could be found. Spectra were recorded at both 56.445 and
94.077 MHz, the latter frequency being used to spread out the
spectrum in the fluorine on antimony region, thereby simpli-
fying the interpretation. The 94.077 MHz spectrum of the
fluorine on antimony region obtained at $-80°$ is shown in
Fig. 14 and consists of eight resonances. Resonance h

consists of at least three overlapping quintets. The three lines labelled b and c are two overlapping doublets whose chemical shifts differ by approximately 100 Hz at 94.077 MHz. Since the splitting on each doublet is also approximately 100 Hz, they give the appearance of a triplet, but the 56.455 MHz spectrum shows them to be two doublets. Reference to Fig. 11 of this work, and to the work of Dean and Gillespie[39] on complexes of SbF_5 with SO_2 and SO_2ClF shows that in Fig. 14 the spectra of $SbF_5 \cdot SO_2$ (b, part of h), SbF_5SO_2ClF (e, part of h), Sb_3F_{16} (part of a and h, and d,e,g) and Sb_2F_{11} (part of a and h, f) are all present. The negative signs on Sb_3F_{16} and Sb_2F_{11} have been deliberately omitted, in order to indicate that either ions, as in the results of Chapter 3, or exchanging donor-acceptor complexes, as in the results of the preceding sections of this chapter, may be formed. The areas in the spectrum correspond to $Sb_3F_{16}/Sb_2F_{11}/SbF_5SO_2ClF/SbF_5SO_2$ =1/0.22/0.38/0.38. The SbF_5SO_2ClF arises when the solvent coordinates with some of the SbF_6 in solution. The $SbF_5 \cdot SO_2$ is the result of SO_2 impurities in the first SO_2ClF made. A small amount of $Sb_2F_{10}SO_2ClF$ is also present, one of its resonances[39] appearing between a and b in the spectrum of Fig. 14. For the sake of completeness, it should be mentioned here that SbF_5SO_2ClF and $Sb_2F_{10}SO_2ClF$ are donor-acceptor complexes, coordination to SbF_5 taking place through the oxygen of the SO_2ClF. The 1:2 complex, $Sb_2F_{10}SO_2ClF$, consists of two SbF_5 molecules joined by a fluorine bridge, the coordination of the oxygen of SO_2ClF taking place in a cis-position as shown below.
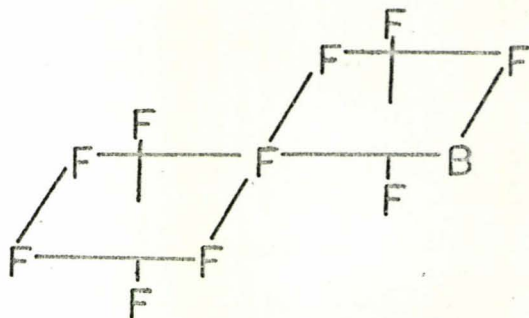
$B = SO_2ClF$

Dean and Gillespie[39] deduced these structures from the
fluorine nmr spectra of solutions of SbF_5 in SO_2ClF.

If COFCl forms a donor-acceptor complex to SbF_5 through
the carbonyl oxygen, a COF resonance should still appear in
the fluorine spectrum, possibly displaced somewhat from the
resonance of free COFCl. Ionization to COF^+ should give rise
to a new resonance in the fluorine spectrum, perhaps greatly
displaced from that of COFCl. Both of these resonances
were searched for carefully, and neither was found. The
other two possibilities in this system are ionization to $COCl^+$
giving the $Sb_3F_{16}^-$ ion, and some $Sb_2F_{11}^-$ depending on the
amount of SbF_5 present, and on whether the solvent coordinates
to any of the SbF_5, or formation of a fluorine-bridged donor-
acceptor complex, $COClSb_3F_{16}$ (and possibly some $COClSb_2F_{11}$)
with rapid exchange of the COCl group, a situation analogous
to that discussed in the sections above for methyl and ethyl
fluoride in SbF_5/SO_2. Exchange of the COCl group is necessary
to account for the presence of only five chemically different
groups of fluorine nuclei in the Sb_3F_{16} part, if such a donor-
acceptor complex does in fact occur. On the basis of the
fluorine resonance alone, it would appear to be impossible to
distinguish between ionization to $COCl^+$ and formation of a
fluorine-bridged donor-acceptor complex, since we might
expect RSb_3F_{16} and $Sb_3F_{16}^-$ to give essentially the same fluorine
spectra, just as RSb_2F_{11} and $Sb_2F_{11}^-$ give similar spectra,
as discussed in the preceeding sections.

The presence of a precipitate during the making up of
the $COFCl/2.9SbF_5/3.1SO_2ClF$ sample made it impossible to
know the composition of the liquid layer with any degree of
exactness. An attempt was made to repeat the above experiment
at concentrations where no solid precipitated out. A solution
having $COClF/SbF_5/SO_2ClF=1/2.0/27$ was prepared. This amount
of SO_2ClF was the minimum required for complete solution. The
fluorine spectrum of this sample at $-95°$ consists of two
doublet-quintet spectra of the same intensity in the fluorine

on antimony region. The first of these with the doublet at
105.1 ppm and the quintet at 141.0, clearly arises from
SbF_5SO_2ClF, for which shifts of 105.1 and 141.8 are already
known[39]. The other doublet-quintet spectrum, with chemical
shifts 110.0 and 142.5 ppm, cannot be due to $SbF_5 \cdot SO_2$, which
might arise from SO_2 impurities in the solvent, and has
chemical shifts of 102.0 and 136.6 in SO_2ClF [39]. It would
appear instead to arise from a new donor-acceptor complex,
$SbF_5 \cdot COFCl$, since a previously unobserved singlet resonance
is now seen at -59.0 ppm, and this may reasonably be assigned
to coordinated COFCl, since a neat sample of COFCl resonates
at -57.7 ppm. Coordination clearly takes place through the
oxygen and not the fluorine in this case. Since $COFCl/SbF_5 =$
1/2.0 in this sample, the areas in the fluorine on antimony
region of the spectrum agree with the assignment, one mole of
SbF_5 complexing with COFCl and the other with the solvent.
The differing behaviour with concentration is most interesting,
the 1/2.9/3.1 sample providing evidence which suggests
ionization to $COCl^+$ or a fluorine-bridged complex, while all
the COFCl in the dilute sample, just discussed, is present as
the oxygen-bridged complex.

(5) DISCUSSION

The results of this chapter indicate that methyl and
ethyl fluoride dissolved in SbF_5/SO_2 form fluorine-bridged
donor-acceptor complexes with SbF_5 which may be written for
convenience as $RSbF_6$ and RSb_2F_{11}, the presence of rapid ethyl
and methyl group exchange implying that the C-F bond is much
weaker than the F-Sb bonds. This exchange occurs down to the
lowest temperature attainable in the SbF_5/SO_2 solvent system,
-90°. The rate of exchange may be very rapid indeed, as the
effective symmetry about the antimony nucleus in both $MeSbF_6$
and $EtSbF_6$ appears to approach that in the SbF_6^- ion itself,
since the very broad lines in the fluorine resonances of
these two complexes can reasonably be attributed to a partially

collapsed multiplet arising from fluorine-antimony coupling which is not completely averaged out. This exchange appears to be intramolecular. A careful reexamination of the proton spectra of section (2) and (3) shows no change in shift (to 0.03 ppm) with changing alkyl fluoride concentration if the SbF_5 concentration is constant. Since the relative amounts of $MeSbF_6$ and $MeSb_2F_{11}$ (or $EtSbF_6$ and $EtSb_2F_{11}$) change with alkyl fluoride concentration, this implies $RSbF_6$ and RSb_2F_{11} have the same chemical shift, accounting for the single proton resonance observed. We should perhaps regard the four complexes, $MeSbF_6$, $MeSb_2F_{11}$, $EtSbF_6$ and $EtSb_2F_{11}$, formed in SbF_5/SO_2 solution as members of a new class of what Cotton[44] calls "fluxional molecules".

Although the methyl and ethyl group exchange appears to be quite rapid, each half of the complex appears to retain a stereochemically rigid structure similar to that found in more conventional environments. The fluorine spectrum of RSb_2F_{11} is so similar to that of $Sb_2F_{11}^-$ that the two structures cannot be distinguished on the basis of fluorine spectra alone. Also, the proton-proton coupling constant in the ethyl group of $EtSbF_6$ and $EtSb_2F_{11}$ is 7.0 Hz, quite normal for an ethyl group, suggesting no gross change in the structure of the ethyl group. We should note that in RSb_2F_{11} the exchange must involve both ends of the Sb_2F_{11} group, since they are chemically equivalent.

It is quite possible that other such fluxional donor-acceptor complexes exist in suitable solvent systems, for example, in SO_2ClF we might expect to find $MeSb_3F_{16}$ and $EtSb_3F_{16}$. It may be that the $COFCl/2.9SbF_5/3.1SO_2ClF$ sample discussed in section (4) is an example of such a donor-acceptor complex where the "incipient cation" as we might term it, is something other than an ethyl or methyl group. The further study of this system is difficult, as there is no proton resonance to serve as an indication as to whether

ionization has occurred or not. One possible indicator might be ^{13}C shift measurements. Olah et al.[42] find the ^{13}C resonance in methyl fluoride only 1.1 ppm deshielded after solution in SbF_5/SO_2. We may compare this to the 273 ppm deshielding observed[2] for $(CH_3)_3{}^{13}CCl$ upon ionization to the t-butyl ion in SbF_5. Vibrational spectroscopy might also prove useful in distinguishing between a cation and an incipient cation.
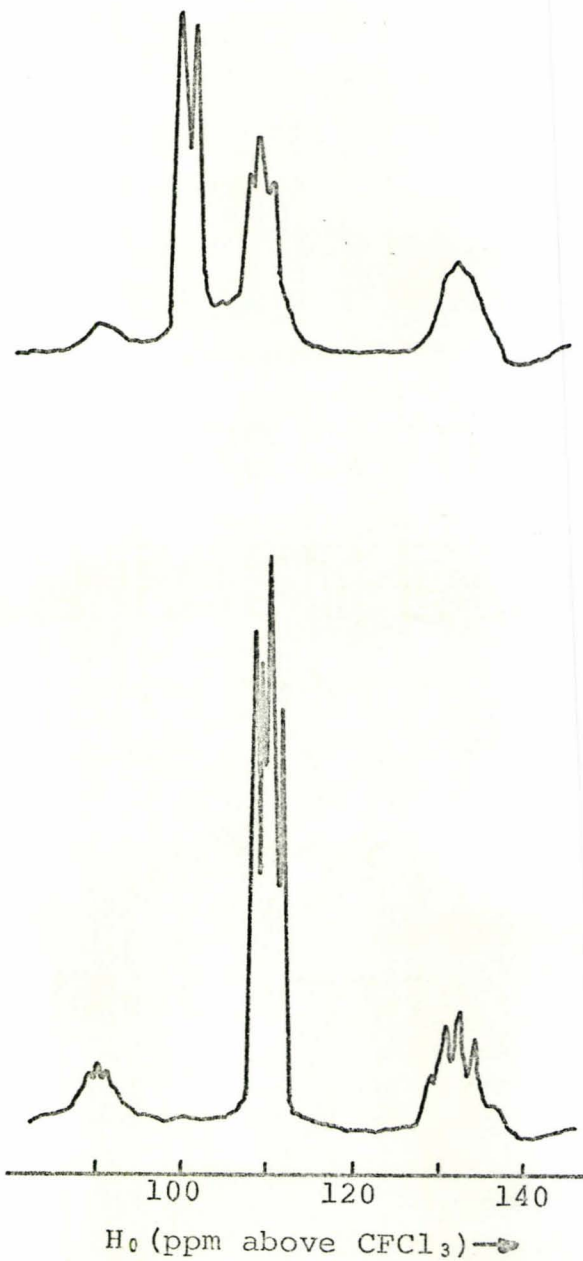
Fig. 12

Fluorine (56.445 MHz) Spectrum of Ethyl Fluoride/5.0SbF$_5$/75SO$_2$
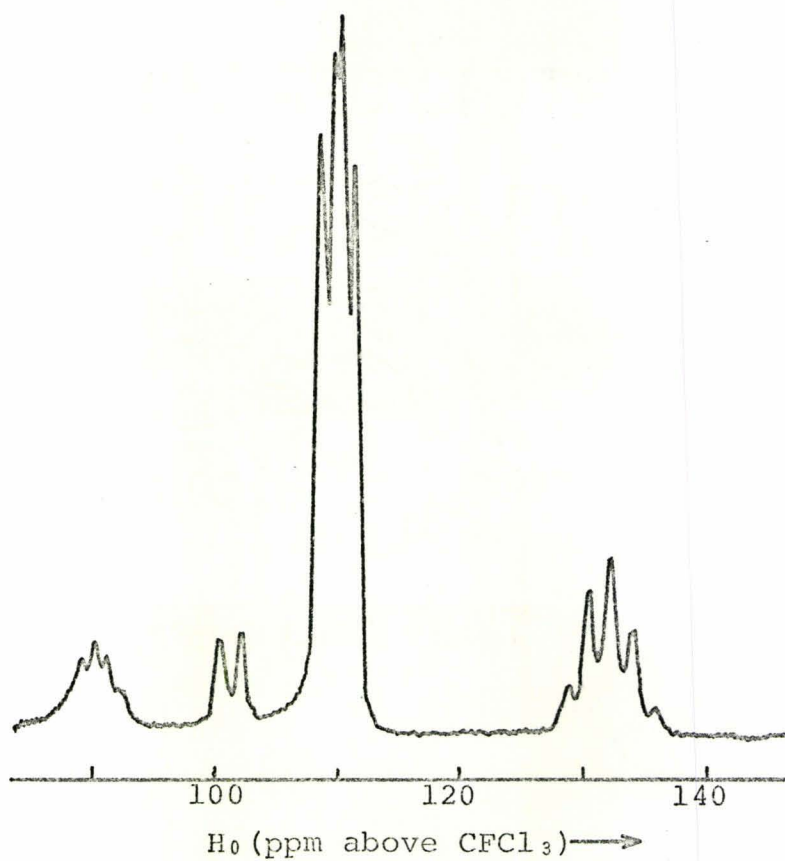at -85° (top). Fluorine Spectrum of Ethyl Fluoride/1.3SbF$_5$/SO$_2$
at -90° (bottom).

<u>Fig. 13</u>

Fluorine (56.445 MHz) Spectrum of Methyl Fluoride/2.0SbF$_5$/ SO$_2$ at -90°.
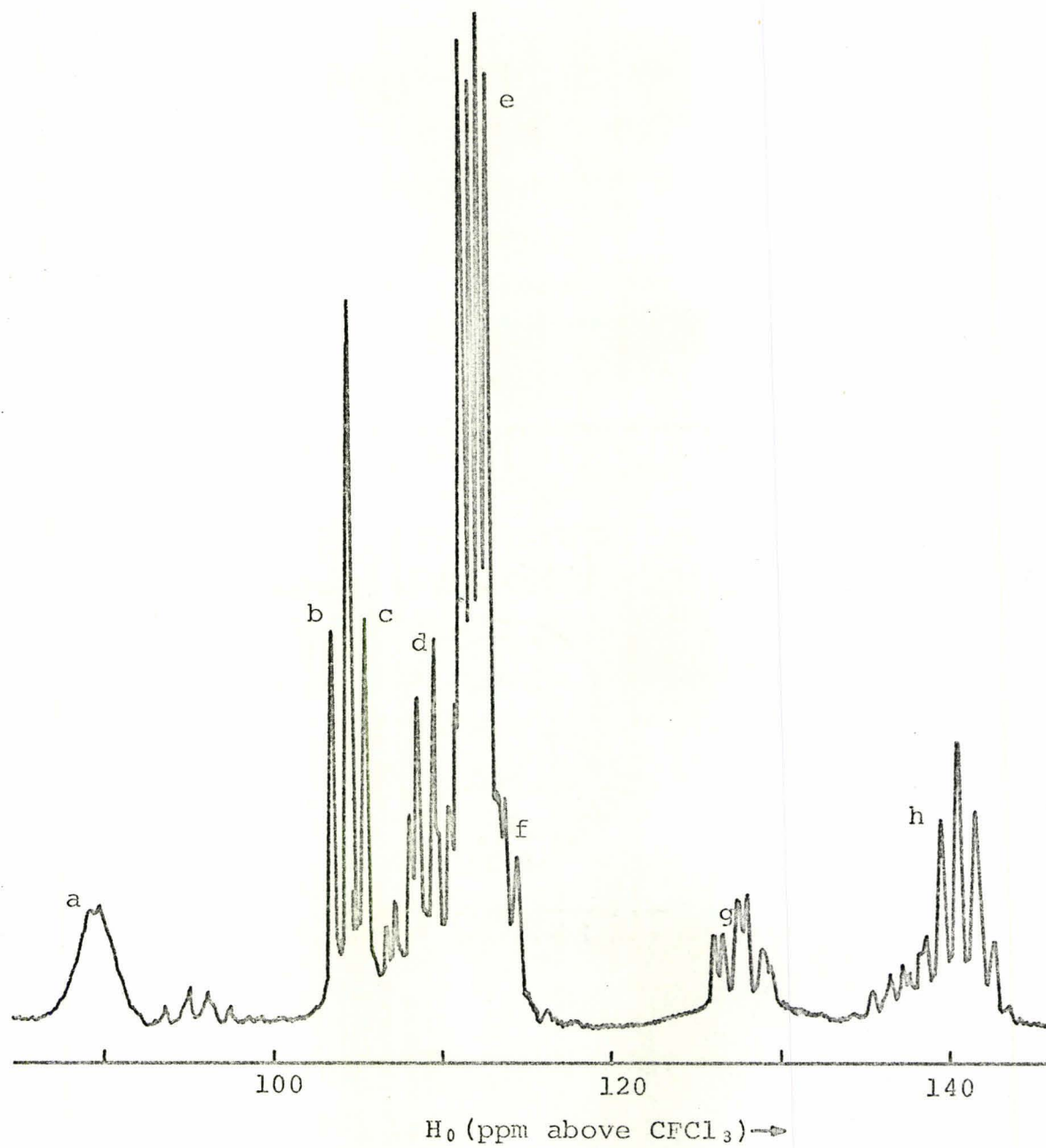
Fig. 14

Fluorine (94.077 MHz) Spectrum of Carbonyl Chlorofluoride/
2.9SbF₅/3.1SO₂ClF at -80°

CHAPTER 5

THE IONIZATION OF ALKANES TO CARBONIUM IONS IN SUPERACIDS

(1) INTRODUCTION

The production of carbonium ions by the reaction of alkanes with superacids was first reported, very briefly, by Brouwer and Mackor[7] in a short note. These authors reported that solutions of iosparaffins in HF/SbF_5 gave the corresponding tertiary carbonium ions. Extensive work by Olah and coworkers[6,10] has shown that the alkanes ionize in HSO_3F/SbF_5 and $HSO_3F/SbF_5/SO_2ClF$, e.g.

$$(CH_3)_3CH \xrightarrow{\ H^+\ } (CH_3)_3C^+ + H_2$$
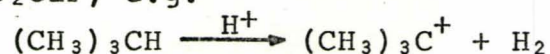
In the case of the isoparaffins the ionization can occur at temperatures down to $-100°$. Primary hydrogens will ionize only at higher temperatures, with subsequent rearrangement of the resulting carbonium ion. An excellent example is the reaction of neopentane in $HSO_3F/SbF_5/SO_2ClF$ at $-20°$, shown below.

$$(CH_3)_4C \xrightarrow{\ H^+\ } [(CH_3)_3CCH_2^+] \longrightarrow (CH_3)_2C^+CH_2CH_3$$
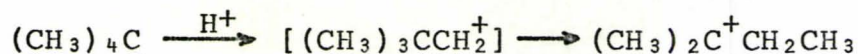
Olah et al. have also shown that neopentane reacts at room temperature in HSO_3F/SbF_5 to give the t-butyl ion and methane.

$$(CH_3)_4C \xrightarrow{\ H^+\ } (CH_3)_3C^+ + CH_4$$
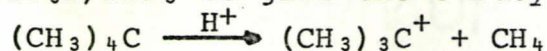
The mechanism of the hydride and alkide abstraction reactions is the subject of considerable speculation and experimentation, particularly since neopentane reacts in two different ways depending on temperature and solvent. Hogeveen and Bickel[45] have found that neopentane in HF/SbF_5 at room temperature also gives the t-butyl ion and methane, and have studied the kinetics of the reaction. Hogeveen and various coworkers[46,47] have also studied the kinetics of both the hydride abstraction from isobutane, and the reverse reaction between t-butyl ion and hydrogen, shown below, all in HF/SbF_5.

66

$$(CH_3)_3C^+ + H_2 \longrightarrow (CH_3)_3CH + H^+$$

Olah et al.[48] have recently reported kinetics for both neo-
pentane reactions. A number of deuterium exchange reactions
have been done, notably between neopentane and HF/SbF_5[45],
methane and HF/SbF_5[49], methane and HSO_3F/SbF_5[50], neopentane
and HSO_3F/SbF_5[50], and neopentane and $HSO_3F/SbF_5/SO_2ClF$[48].
The experiments with methane are particularly interesting,
since no measurable reaction to a carbonium ion occurs,
implying that the exchange takes place through CH_5^+, a species
having possible five-coordination about carbon. It has been
suggested that a similar five-coordinated structure occurs
during the course of the reaction of alkanes to carbonium
ions. Hogeveen[51] refers to this as a transition state, but
Olah appears to regard it as an intermediate, like the pro-
tonated alcohols sometimes used as a source of carbonium ions.

$$(CH_3)_3COH \xrightarrow{H^+} (CH_3)_3COH_2^+ \xrightarrow{H^+} (CH_3)_3C^+ + H_3O^+$$

$$(CH_3)_3CCH_3 \xrightarrow{H^+} (CH_3)_3CCH_4^+ \longrightarrow (CH_3)_3C^+ + CH_4$$
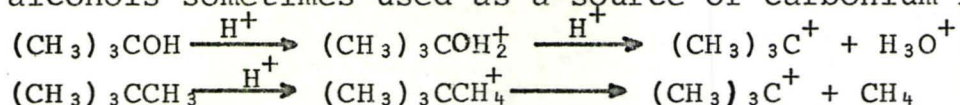
It is difficult to choose between the two possibilities,
transitions state vs. intermediate, as all the experiments to
date have studied the end products only, the carbonium ions
themselves. Clearly an nmr experiment starting with a sample
in which no reaction has yet occured would be useful, as
the spectrum recorded before reaction occurs should show if
a stable protonated intermediate is really present. The
results of such an experiment are reported in the next section.

(2) NEOPENTANE IN $HSO_3F/SbF_5/SO_3$ SOLUTION

The system $HSO_3F/SbF_5/SO_3$ is believed to be the strong-
est protonic acid system known.[14] This very high acidity
is due to the formation of the strong acid $HSbF_2(SO_3F)_4$
when the ratio $SO_3/SbF_5 > 3$.[37] A solution having $HSO_3F/SbF_5/SO_3 =$
1.1/1/4.0 was made up at low temperature and neopentane
distilled in on the vacuum line. After stirring at -50° to
dissolve the neopentane an nmr sample was sealed off. The
neopentane—acid mixture remaining was diluted with HSO_3F to

the composition $HSO_3F/SbF_5/SO_3$ = 11.9/1/4.0, stirred, and a second sample sealed off. At no time was either sample allowed to warm up above -50°. Two different samples were taken because the acidity when the concentration of $HSbF_2(SO_3F)_4$ is high is not too well known, and it was felt the acidity might possibly decrease when little HSO_3F is present. The concentrations of neopentane in the two samples were different, probably due to solubility effects, incomplete stirring, or some of the neopentane freezing before it could go into solution. The sample having $HSO_3F/SbF_5/SO_3$ =1.1/1/4.0 had 2.4×10^{-3} moles of neopentane per mole of SbF_5, and the 11.9/1/4.0 sample 8.2×10^{-2} moles of neopentane per mole of SbF_5. These neopentane concentrations were determined from the peak areas in the nmr spectra later recorded.

At temperatures below -40° the nmr spectra of both samples consists of two singlet peaks, the acid peak 14 ppm below TMS and the resonance of neopentane 1.44 ppm below TMS. Table 10.1 of reference 4 gives 0.94 ppm below TMS for the neopentane chemical shift, but this is with reference to TMS in solution. As a check on the effect of susceptibility differences[52] samples of neat and dilute TMS were run on the A-60. The sample of neat TMS was found to resonate 0.44 ppm above a dilute sample of TMS in chloroform. The literature value for neopentane must therefore be corrected by adding 0.44 to give 1.38 ppm below external TMS, in good agreement with the value of 1.44 found for neopentane dissolved in $HSO_3F/SbF_5/SO_3$. When the 1.1/1/4.0 sample was warmed to -33° in the nmr probe, the neopentane signal gradually decreased in intensity and the spectrum of the t-amyl ion appeared, showing the reaction

$$(CH_3)_4C \xrightarrow{H^+} (CH_3)_2\overset{+}{C}CH_2CH_3 + H_2$$
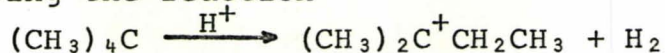
which also occurs in $HSO_3F/SbF_5/SO_2ClF$. The neopentane was 85% converted to t-amyl ion after 45 min at -33°. When the neopentane-acid solution left on the vacuum line after the nmr samples were sealed off was allowed to warm up gradually,

manometer readings showed the evolution of a gas around -30°. This gas appeared to be non-condensable at liquid nitrogen temperature (-196°), suggesting hydrogen (Bp -253°). The second sample did not react at -33°. At -3° it reacted to produce t-amyl ion, once again. After 2 hours at -3°, 65% of the neopentane had reacted, but the resulting t-amyl ion was about 30% decomposed to t-butyl and t-hexyl ion. The nmr shifts in the 1.1/1/4.0 sample are 4.71 (α-methylene), 4.22 (α-methyl) and 2.09 (β-methyl), all in ppm below TMS. These are similar to the values found by Olah and Lukas[6,10] for t-amyl ion in HSO_3F/SbF_5 and $HSO_3F/SbF_5/SO_2ClF$. The spin-spin splitting is not resolved in the 1.1/1/4.0 sample, as the lines are broad due to the high viscosity of the solution, but the spin-spin splitting is seen in the second, less viscous, sample. The 1.1/1/4.0 sample appears to be higher in acidity, since reaction takes place at a lower temperature.

If the protonated intermediate, $(CH_3)_3CCH_4^+$ were present in the above solutions, it would give rise to a distinctive nmr spectrum. The three methyl groups of such a species would be β to a carbon bearing positive charge, and so we might expect their resonance to occur near that of the β-methyl group in the t-amyl ion, that is about 2 ppm below TMS. The four protons at the protonation site should give rise to one or more resonances, depending on the symmetry at this site, all at very low field, say in the region of the 13.5 ppm shift reported for the methine proton in $(CH_3)_2C^+H$. At no temperature from -60° to that at which reaction to the t-amyl ion occurs is such a spectrum found, all the unreacted neopentane existing as the neutral molecule, since a singlet resonance only is found, at 1.44 ppm below TMS, as reported above. No new resonances were found at the very low fields expected for $-CH_4^+$. It is not impossible that the $-CH_4^+$ resonance might lie under the acid peak. In this case a singlet at the high field end of the spectrum could be the

resonance of the methyl protons of $(CH_3)_3CCH_4^+$, but in the
experimental spectrum the chemical shift of the singlet
observed, 1.44 ppm, allows it to be identified as neopentane
(1.38 ppm expected) and not the methyl groups of the inter-
mediate (2 ppm expected). Any other possible explanations
for a singlet resonance, such as an exchange process, would
lead to a resonance even further downfield, e.g. if all the
protons in $(CH_3)_3CCH_4^+$ were exchanging, an averaged chemical
shift of (4 x 13.5 + 9 x 2)/13=5.5 ppm below TMS would be
expected. The above results therefore indicate that CH_5^+
and other "alkanonium ions"[48] do not exist in superacid
solutions as intermediates, but merely as transition states.

   Hogeveen[49,51] has suggested three possibilities for
the transition state, having D_{3h}, C_{4v} and C_s symmetries, as
shown below for CH_5^+.
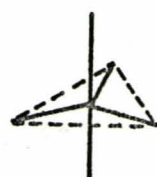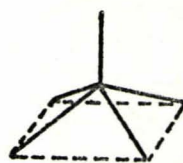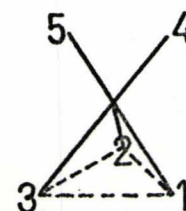
| D_{3h} | C_{4v} | C_s |

Recent CNDO2 molecular orbital calculations[53] on CH_5^+ show
that the configuration having C_s symmetry is the most stable,
lying about 10 kcal/mole below the trigonal bipyramidal (D_{3h})
configuration. The energy for the C_{4v} configuration lies
midway between those of the other two configurations. Essent-
ially the same conclusion as to the relative stabilities of
the D_{3h} and C_s configurations in CH_5^+ was reached by Olah,
Klopman and Schlosberg[48] using a different molecular orbital
method and somewhat arbitrary geometries. The C_s configura-
tion is the "front-side" protonation proposed by Olah[48] to
explain the observed reaction of neopentane to t-amyl ion in
$DSO_3F/SbF_5/SO_2ClF$ without the incorporation of deuterium
into the carbonium ion.

$$(CH_3)_4C \xrightarrow{D^+} [(CH_3)_3CCH_2\!\!\begin{smallmatrix}D\\H\end{smallmatrix}]^+ \longrightarrow [(CH_3)_3CCH_2^+] + HD$$
$$(CH_3)_2\overset{+}{C}CH_2CH_3$$
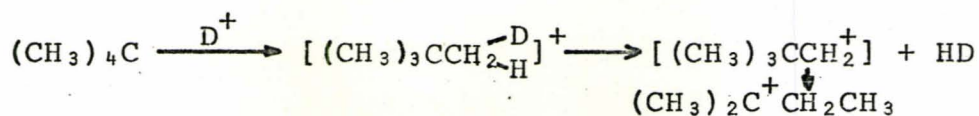
This reaction scheme is supported by the CNDO2 calculations[53] on CH_5^+. The authors minimized the energy of the C_s configuration by varying bond lengths and angles, assuming the three hydrogens labelled H_1, H_2 and H_3 (see above) had the same C-H bond length and that the three H-C-H bond lengths were equal. The other two hydrogens were assumed to lie above the carbon at equal distances from the ternary axis of the $H_1H_2H_3C$ pyramid. There were therefore two bond angles and two bond distances to be varied. The authors found $H_4-C-H_5=50°$, $H_1-C-H_2=110°$ at the energy minimum. The C-H_1 bond length found, 1.14Å, is only 0.016Å longer than that found for methane itself by Wiberg[54] in a CNDO2 calculation using the same parameters. The C-H_4 bond length, however, is rather longer, 1.21Å, an increase of 0.086Å from that calculated for methane. In other words, the $H_1H_2H_3C$ pyramid has the geometry of a methyl group, while H_4 and H_5 lie farther away from the carbon than the other three hydrogens and rather close to one another. H_4 and H_5 can therefore readily leave the C_s configuration, producing molecular hydrogen and the carbonium ion. In the case of neopentane in $DSO_3F/SbF_5/SO_2ClF$ we may therefore assume the C_s transition state as shown for CH_5^+, with H_1 replaced by a t-butyl group and the D^+ from the acid in the H_5 position. HD then cleaves off, leaving the unstable neopentyl cation which immediately rearranges to the t-amyl ion.

Olah[48] postulates that the reaction of neopentane to the t-butyl ion and methane in HSO_3F/SbF_5 proceeds through a trigonal bipyramidal configuration, in order to explain the isotope exchange observed when neopentane-d_{12} is reacted with HSO_3F/SbF_5 at room temperature. Both the t-butyl and the methane produced contain ordinary hydrogen. However a critical examination of this scheme, shown below

$$(CD_3)_4C \xrightarrow{\ H^+\ } [(CD_3)_3C-\overset{D}{\underset{D}{\overset{D}{C}}}-H]^+ \longrightarrow \text{methane} + \text{t-butyl ion}$$
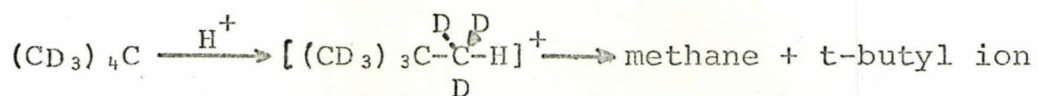
should clearly lead one to expect that only $(CD_3)_3C^+$ and CHD_3 would be produced by this mechanism, the same as would occur with a C_s configuration in the transition state. The isotope scrambling, which is actually quite small in extent (6% after 5 hours) must occur through protonation to the transition state, of whatever configuration, followed by elimination of a deuteron, this proceeding at the same time as the reaction to methane and t-butyl ion. The molecular orbital calculations of Olah et al.[48] give the same energy for the D_{3h} and C_s configurations of $(CH_3)_3CCH_4^+$, but this may be a consequence of the bond lengths and bond angles assumed. Hogeveen and Bickel[51] have observed that $(CH_3)_3C^+$ does not exchange deuterium with $(CH_3)_3CCH_2D$, that is, the reaction

$$(CH_3)_3C^+ + (CH_3)_3CCH_2D \longrightarrow (CH_3)_4C + (CH_3)_2C^+CH_2D$$

does not occur, and attribute this to a C_s transition state, which is expected to be more hindered than the trigonal bipyramidal configuration, shown below.

$$\left[(CH_3)_3C - \overset{H}{\underset{H}{C}} - C(CH_3)_3 \right]^+$$
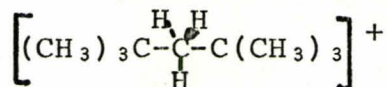
In all cases the molecular orbital calculations of Olah et al.[48] give substantial proton affinities for the alkanes, about 5-6 eV for the more stable configurations. This does not imply stable protonated intermediates, however, as the proton is present in superacid as the cation H_2A^+ or some similar species[30,37], e.g.

$$2HF + SbF_5 \xrightarrow{HF} H_2F^+ + SbF_6^-$$

$$2HSO_3F + SbF_5 \xrightarrow{HSO_3F} H_2SO_3F^+ + SbF_5SO_3F^-$$
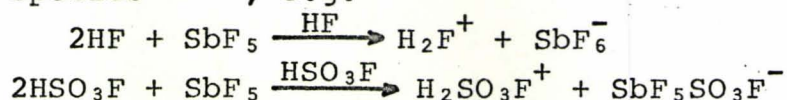
We must therefore consider the energy of the reaction

$$R + H_2A^+ \longrightarrow RH^+ + HA$$

and not merely

$$R + H^+ \longrightarrow RH^+$$
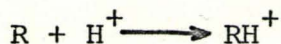
The simplest case relating to a superacid medium is that of H_2F^+, present in HF/SbF$_5$[30]. As discussed above, alkanes react with HF/SbF$_5$, and a CNDO2 calculation on H_2F^+ was done

as part of this work (see Chapter 6 for details). The reaction

$$H_2F^+ \longrightarrow HF + H^+$$

was considered and found to be 8.35 eV (193 kcal/mole) endo-thermic. This value is probably not too accurate, as HF and H_2F^+ are both stabilized in solution by hydrogen-bonding with other HF molecules, but it is probably of the right order of magnitude, that is, as large as the proton affinity of alkanes. Stable protonated alkanes are therefore not necessar-ily to be expected in the superacid media presently known. In this connection, it is interesting to note that the production of the carbonium ions themselves appears to be slightly unfavourable energetically. Hogeveen and Bickel[46] report that the reaction

$$(CH_3)_3C^+ + H_2 \longrightarrow (CH_3)_3CH + H^+$$

has an equilibrium constant of 10.7 at 0°. The driving force in the reactions observed may well be the removal of hydrogen (or methane, as the case may be) from solution as it is prduced.

(3) ISOPENTANE IN SbF_5/SO_2ClF AND SbF_5/SO_2 SOLUTION

In a private communication, G. A. Kramer reports that the addition of isopentane to a 2 M SbF_5/SO_2ClF solution at -30° produces a white precipitate, and that the nmr spectrum of the liquid remaining shows the presence of the t-amyl ion, indicating that the reaction

$$(CH_3)_2CHCH_2CH_3 \xrightarrow{-H^-} (CH_3)_2C^+CH_2CH_3$$
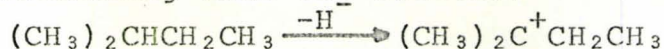
has occured. Such a reaction in an aprotic medium is quite unexpected. Since Kramer has obtained no fluorine spectra for these solutions, a sample of isopentane in SbF_5/SO_2ClF having isopentane/SbF_5/SO_2ClF = 1/3.0/11.8 was prepared at low temperature on the vacuum line and an unreacted nmr sample sealed off. (The SbF_5/SO_2ClF ratio used corresponds to approximately 2.8M.) The proton spectrum of a sample of neat isopentane shows a complicated spectrum in the region 0.6-1.7 ppm

below external TMS. Most alkanes resonate in this region. The spectrum is complex because the chemical shifts and coupling constants in isopentane do not obey the first order condition, $\nu_0 \delta >> J$. An attempt was made to obtain the proton spectrum of unreacted isopentane in SbF_5/SO_2ClF, but the supply of cooling nitrogen to the low temperature probe failed at this point and allowed the sample to warm up enough so that reaction did occur. The nmr tube then contained a good deal of white solid, but enough liquid remained for an nmr sample to be taken. The resonances of the t-amyl ion were found, α-methylene at 4.35, α-methyl at 3.91, and β-methyl at 1.79, all ppm below external TMS. There are four other peaks in the spectrum, two singlets at 1.14 and 9.66, a doublet (J=12.9) at 8.95 and a triplet (J=12.9) at 10.68 ppm below TMS. None of these peaks appears to be present in the spectrum of neat isopentane or in the spectrum of 2.8 M SbF_5/SO_2ClF which was run as a purity check. They are possibly due to the products of some side reaction. In any case, they account for only 7% of the area of the experimental spectrum. Clearly the liquid layer contains t-amyl ion in high concentration. When the solution remaining on the vacuum line after the nmr sample was taken was allowed to warm up gradually, a great deal of white precipitate formed suddenly at -20° and a non-condensable gas was evolved, suggesting the formation of molecular hydrogen.

The fluorine spectrum obtained at -85° for the nmr sample after reaction to t-amyl ion, shown in Fig. 15, consists of eight resonances. Resonances a and b, at 84.4 and 89.0 ppm, lie in the bridging fluorine region. Resonances d and e, at 107.3 and 111.9 ppm, are both doublets of doublets. There are two quintet resonances, g and h, at 134.2 and 140.7 ppm. Resonance f, at 128.2 ppm, is a triplet showing doublet splittings, partially overlapped by resonance g. Resonance c, at 104.2 ppm appears to be a singlet. Resonances a, d and g may be assigned to fluorines F_3, F_2 and F_1, respectively,

in the $Sb_2F_{11}^-$ ion, and resonances b, e, f and h to fluorines F_3, F_2, F_4 and F_1, respectively, in the $Sb_3F_{16}^-$ ion, using the numbering scheme of Chapter 3. Resonances a, d and g clearly belong to the same ion, as the splittings in d give $J_{12}=103$, $J_{23}=64$ Hz and the splittings in resonances g and a are 105 and 62 Hz, respectively. Similarly the splittings in e give $J_{12}=95$, $J_{12}=49$ Hz and the splittings in resonances h and b are 98 and 48 Hz respectively. Resonance f is clearly that of the F_4 fluorines in $Sb_3F_{16}^-$ and the resonance of the F_5 fluorine appears to lie under d. This is essentially the same assignment as made for the t-BuF/SbF$_5$/SO$_2$ClF sample in Chapter 3, except that the $Sb_2F_{11}^-$ resonances are shifted downfield by as much as 5 ppm. This is presumably a solvent effect, there being five times as much SO$_2$ClF in the isopentane sample. The experimental areas are in the ratio a/b/d/d/f/g+h=1.4/2.1/15.0/8/1.8/5.2. With the assignment given, $Sb_2F_{11}^-/Sb_2F_{16}^-$ =1.6 would require that the areas be in the ratio 1.6/2.0/14.8/8/2.0/5.2. The agreement is excellent. The reason for this ratio of the two ions will be discussed below. The peak at 104.2 ppm remains unassigned. This peak is most probably either the low field half of the doublet resonance of a small amount of SbF$_5$SO$_2$ClF present in the solution, the high field peak lying under d, or that of a fluorine-containing species of antimony (III). The peak in the fluorine spectrum of t-BuF/SbF$_5$/SO$_2$ assigned as a fluoro-complex of antimony (III) in Chapter 3 also lies just below the F_2 resonance of $Sb_2F_{11}^-$.

We may now consider possible reactions leading to the production of t-amyl ion, hydrogen, and the polyanions $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$. Abstraction of a hydride ion and its conversion to molecular hydrogen requires an oxidizing agent. Clearly either SbF$_5$ or SO$_2$ClF must be reduced, as shown in the half reactions below.

$$SbF_5 + 2e \longrightarrow SbF_3 + 2F^-$$
$$SO_2ClF + 2e \longrightarrow SO_2 + Cl^- + F^-$$
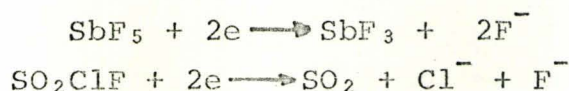
Recalling that $RH/SbF_5 = 1/3$ in the present case, the most likely overall reactions in the two cases would appear to be

$$2RH + 6SbF_5 + SO_2ClF \longrightarrow 2R^+ + H_2 + SbF_4Cl \cdot SO_2 + Sb_2F_{11}^- +$$
$$Sb_3F_{16}^-$$

$$2RH + 6SbF_5 \longrightarrow 2R^+ + H_2 + SbF_3 + Sb_2F_{11}^- + Sb_3F_{16}^-$$
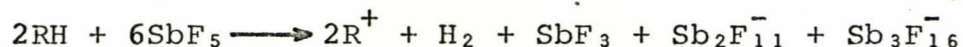
If it is the second reaction which occurs, alkanes might react to form carbonium ions in SbF_5/SO_2 solutions too. This possibility was tested by obtaining proton and fluorine spectra for an isopentane/SbF_5/SO_2 sample, as discussed below.

A sample of isopentane in SbF_5/SO_2 was prepared at low temperature on the vacuum line and an unreacted nmr sample sealed off. Enough isopentane was added to give $RH/SbF_5 = 1/2.9$ but apparently not all of this went into solution. The actual composition of the nmr sample is estimated as isopentane/SbF_5/ $SO_2 = 1/11/170$. The SbF_5/SO_2 ratio corresponds to approximately 1.3M. The proton spectrum at $-35°$ showed the spectrum of unreacted isopentane. After the sample had been kept at room temperature for 30 minutes, the $-35°$ proton spectrum showed the spectrum of the t-amyl ion, indicating that reaction also occurs in SbF_5/SO_2. The signal to noise ratio in the proton spectrum is fairly low, owing to the low initial concentration of isopentane, making it difficult to see the resonance of the α-methylene protons, but well resolved triplets due to the α-methyl and β-methyl protons can be seen at 3.65 and 1.43 ppm below external TMS.

The fluorine spectrum of the isopentane/SbF_5/SO_2 sample at $-85°$ is shown in Fig. 16. Resonances b and e, a doublet and a quintet at 102.1 and 134.3 ppm are assigned to $SbF_5 \cdot SO_2$. Resonance a and the doublet of doublets d at 91 and 111.5 ppm are assigned to fluorines F_3 and F_2, respectively, in the $Sb_2F_{11}^-$ ion. The resonance of fluorine F_1 in $Sb_2F_{11}^-$ appears to lie under the $SbF_5 \cdot SO_2$ quintet at 134.3, as in the t-BuF/SbF_5/SO_2 case. The remaining resonance, a singlet at 106.9 ppm, appears to arise from the reduction product of SbF_5. In the case of this particular sample there is no precipitate

or other solid in the sample at temperatures above $-90°$. We therefore have, in the spectrum of Fig. 16, the fluorine resonances of all the products of the ionization reaction. SbF_3 in aqueous solution resonates at 55 ppm above $CFCl_3$[24] well below the region characteristic of $Sb(V)$, but any SbF_3 in the nmr sample may be complexed with SbF_5. When the area of resonance d is taken as 8 fluorines, the area of c is equivalent to 3.5 ± 1.3 fluorines. The reaction

$$2RH + 5SbF_5 \longrightarrow 2R^+ + H_2 + SbF_3 + 2Sb_2F_{11}^-$$
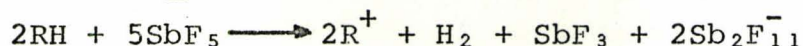
produces one mole of SbF_3 for every two of $Sb_2F_{11}^-$. Hence if $SbF_3 \cdot SbF_5$ occurs in solution, the total area corresponding to the amount present would be 4 fluorines when resonance d is taken as 8. It is not clear why $SbF_3 \cdot SbF_5$ should give rise to only one signal.

In the case of isopentane/SbF_5/SO_2ClF the reaction

$$2RH + 6SbF_5 \longrightarrow 2R^+ + H_2 + SbF_3 + Sb_2F_{11}^- + Sb_3F_{16}^-$$

would be expected, all of the SbF_5 being incorporated into the polyanions. In fact, equimolar amounts of $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ are not found from the fluorine spectrum, as the ratio $Sb_2F_{11}^-/Sb_3F_{16}^- =1.6$. This could come about if an error was made in measuring the amount of isopentane added to solution, but seems more likely to result from the incorporation of SbF_5 into the precipitate. If the precipitate were $SbF_3 \cdot SbF_5$, only $Sb_2F_{11}^-$ would appear in the fluorine spectrum of the liquid layer. Precipitation of $(SbF_3)_2SbF_5$ would result in $Sb_2F_{11}^-/Sb_3F_{16}^- =2$. Ruff and Plato[55] reported that SbF_3 and SbF_5 form compounds over the range $(SbF_3)_2SbF_5$ to $(SbF_3)_5SbF_5$, although this result has been questioned.[56] The precipitate could also contain considerable carbonium ion and $Sb_nF_{5n+1}^-$ precipitated out as a salt. It is most interesting to note that Olah and Lukas[6,10] report precipitates from solutions of alkanes in HSO_3F/SbF_5/SO_2 and HSO_3F/SbF_5/SO_2ClF which when redissolved in SO_2 or SO_2ClF give the proton spectra for the carbonium ions. Although hydride abstraction by H^+ appears to occur much more readily than that by SbF_5/SO_2ClF or SbF_5/SO_2

(-100° vs -20° and ambient temperature), it is not impossible that some of the reaction to carbonium ion in the work of Olah and Lukas is the result of hydride abstraction by SbF_5, particularly in the cases where reactions were done at room temperature or temperatures close to room temperature. In this case, these precipitates would probably be mixtures of carbonium ion salts and SbF_3 or an SbF_3-SbF_5 coordination compound.

The hydride abstraction in SbF_5 could proceed by the following series of reactions.

$$RH + SbF_5 \longrightarrow R^+ + SbF_5H^-$$

$$SbF_5H^- + SbF_5 \longrightarrow HF + SbF_3 + SbF_6^-$$
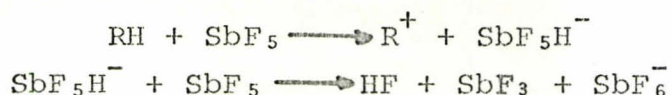
A similar scheme has already been proposed[58] for hydride abstraction from cycloheptatriene, triphenylmethane, and 9,10-dihydroanthracene by $SbCl_5$, where the overall reaction

$$RH + 2SbCl_5 \longrightarrow R^+ + SbCl_6^- + SbCl_3 + HCl$$
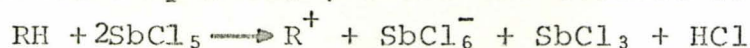
appears to occur. In the isopentane/SbF_5/SO_2ClF and isopentane/SbF_5/SO_2 solutions studied here, the presence of excess SbF_5 would give rise to a third stage in the reaction where a second molecule of alkane reacts with H^+

$$RH + HSbF_6 \longrightarrow R^+ + H_2 + SbF_6^-$$

giving the overall reaction proposed above, the SbF_6^- forming polyanions with any remaining excess SbF_5. SbF_5/SO_2ClF probably reacts at a lower temperature because SbF_5SO_2ClF and $(SbF_5)_2SO_2ClF$, the species in SO_2ClF solution[39] before the alkane is added, have their SbF_5 less strongly coordinated to a solvent molecule than does $SbF_5 \cdot SO_2$, the species in SO_2 solution,[28] SO_2 being a stronger base towards SbF_5 than SO_2ClF[39]. SbF_5/SO_2ClF is also a more useful solvent system in that it is difficult to prepare SbF_5/SO_2 solutions with the SbF_5 concentration in excess of 1.5M, owing to the low solubility of $SbF_5 \cdot SO_2$, whereas SbF_5 and SO_2ClF are miscible in all proportions[39].
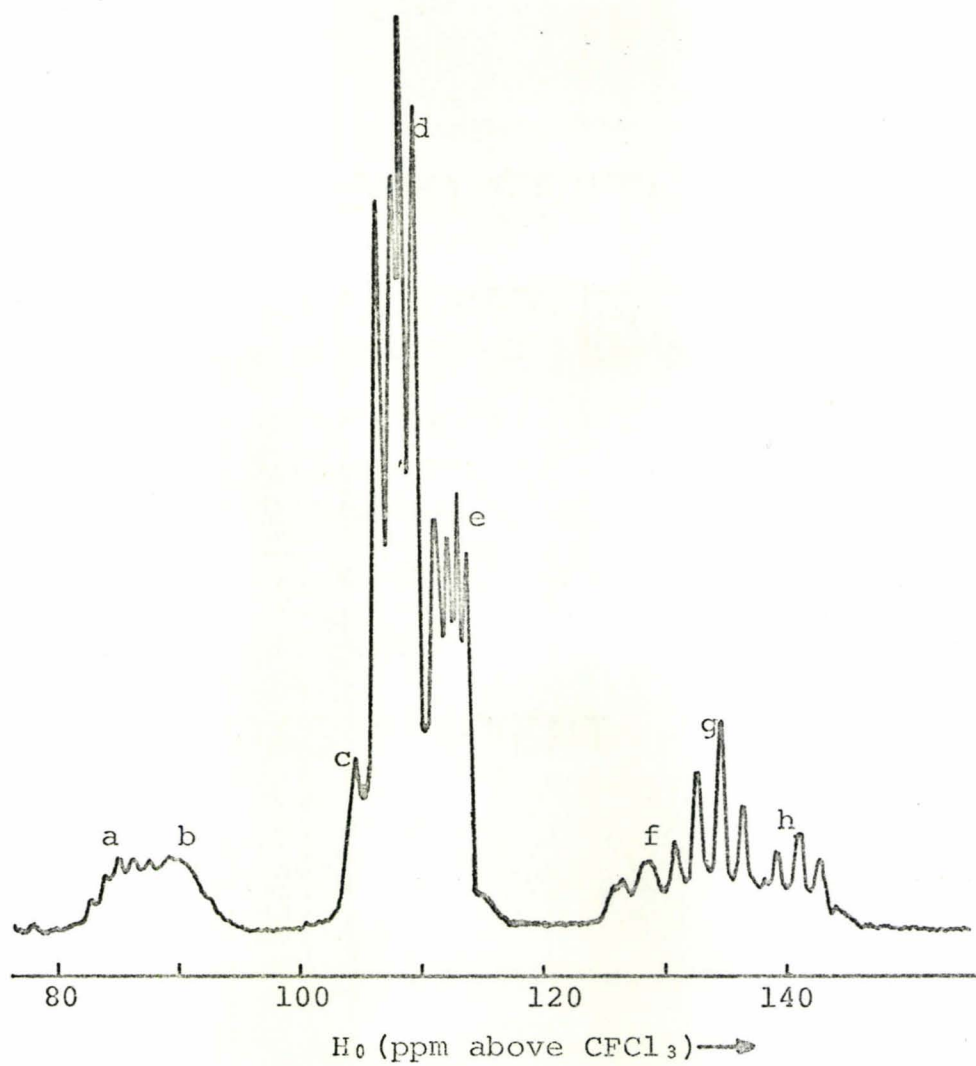
Fig. 15

Fluorine (56.445 MHz) Spectrum of Isopentane/3.0SbF$_5$/11.8SO$_2$ClF
at −95°
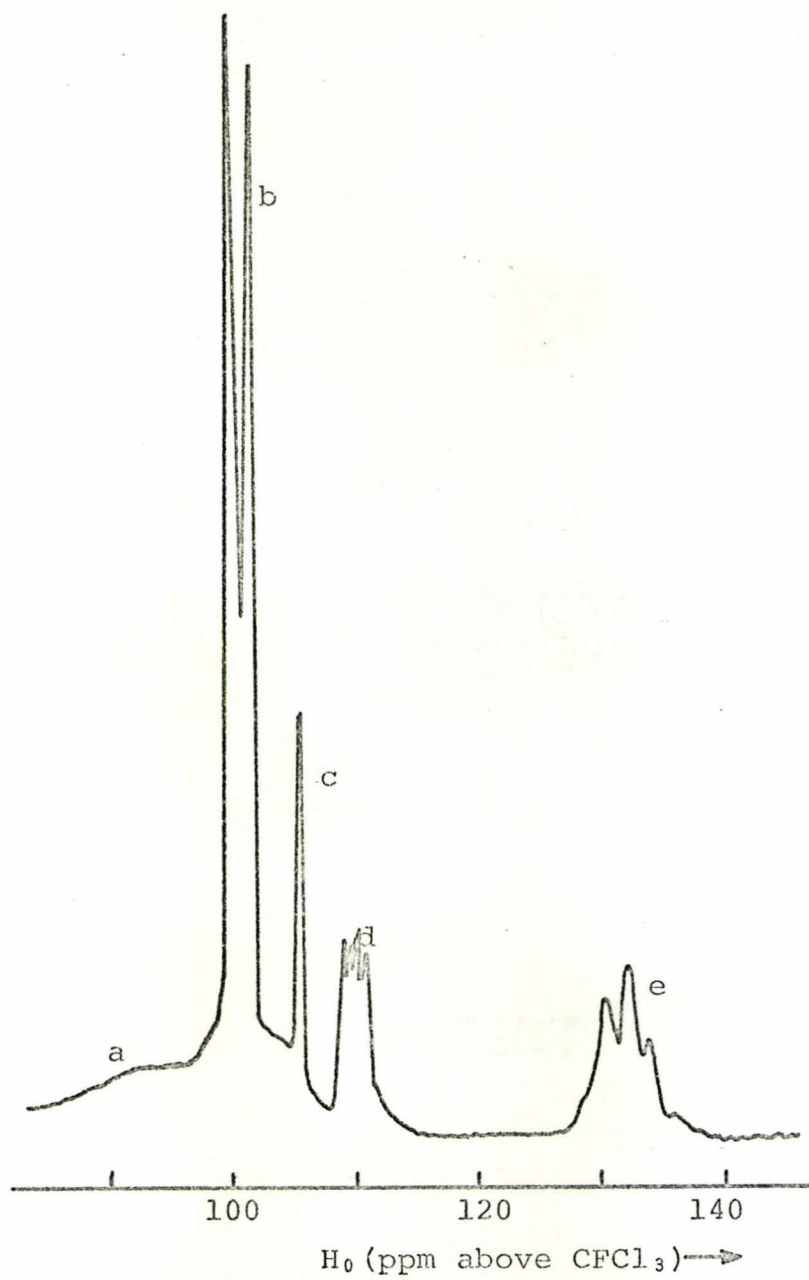
Fig. 16

Fluorine (56.445 MHz) Spectrum of Isopentane/SbF₅/SO₂at −85°.

CHAPTER 6

COUPLING CONSTANTS IN THE PROTON SPECTRA OF CARBONIUM IONS.
MOLECULAR ORBITAL CALCULATIONS

(1) INTRODUCTION

We have seen in Chapter 4 of this work that it may be impossible to distinguish between an ionized "carbonium ion salt" $R^+ Sb_n F_{5n+1}^-$ in solution and the corresponding donor-acceptor complex $RSb_n F_{5n+1}$ from the fluorine spectrum alone. The species studied in Chapters 3 and 5 can all be said to be ionic, because the proton spectra give the characteristic deshieldings (≈ 3 ppm for α-methyl and α-methylene protons, less for β-protons) and in the case of the t-amyl ion, the anomalous four bond coupling constant, $^4J_{HH} \approx 5$ Hz, both associated with carbonium ions. On the other hand, the donor acceptor complexes of Chapter 4 give smaller deshieldings then would occur if ionization took place, for example $CH_3CH_2Sb_2F_{11}$ at $-80°$ gives resonances at 6.53 and 2.29 ppm below external TMS, whereas $CH_3CH_2^+$ might be expected to give chemical shifts of 14 and 4 ppm for the methylene and methyl resonances. It is therefore the proton resonances which aid in the interpretation of the fluorine spectra, and not vice versa, as it was thought would be the case when this work was begun. The fluorine spectra can be seen to be quite useful in that they indicate which donor-acceptor complex is formed in Chapter 4 and which ionization pathway is followed in the last section of Chapter 5, but they are, in themselves, ambiguous. The chemical shifts and coupling constants in the proton spectrum are therefore most important.

It is interesting to consider the four bond coupling constant in some detail. In the t-amyl ion $^4J_{HH}$ is clearly of the same sign as $^3J_{HH}$ in the ethyl group of this ion, that

is, most probably positive, since the splittings in the methylene resonance remain unchanged when the intramolecular exchange of methyl groups occur[8,9]. $^3J_{HH}$ and $^4J_{HH}$ have almost the same magnitude in the t-amyl ion. If the coupling constants were of opposite sign, the exchange of methyl groups would result in an averaged coupling constant much smaller in magnitude than the orignal values found for $^3J_{HH}$ and $^4J_{HH}$ at low temperature. In neopentane and acetone $^4J_{HH}$, the coupling constant between the protons of one methyl group and those of another, is +0.35 and +0.53 Hz, respectively[58]. The much larger value in the t-amyl ion is the tenfold anomaly mentioned in Chapter 1. In protonated ketones, an intermediate situation is found. Olah and Calin[59] found a 1.0 Hz coupling between the methyl and methylene protons in diprotonated acetylacetone. We might expect the protonated ketones to bear some slight resemblance to the carbonium ions, since there should be some contribution from the resonance structure having a positive charge on the carbonyl carbon, as shown below.

$$H_3C\!\!-\!\!\underset{H_3C}{\overset{}{C}}\!\!=\!\!OH^+ \longleftrightarrow H_3C\!\!-\!\!\underset{H_3C}{\overset{}{C}}^{\pm}\!\!OH$$
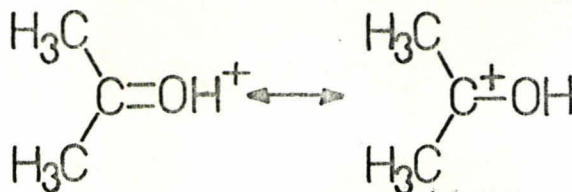
In the next section, some new values are reported for $^4J_{HH}$ and other constants in t-butyl halides, t-butyl ion, acetone and protonated acetone. These were obtained using the ^{13}C satellite technique of Cohen, Sheppard and Turner[60]. The values for $^4J_{HH}$ in t-butyl ion and protonated acetone are of particular interest, since few such values are known for charged species.

(2) PROTON COUPLING CONSTANTS AND CHEMICAL SHIFTS

Normally the spin-spin coupling between nuclei having the same chemical shift has no affect on the observed spectrum. One exception to this rule is the case of magnetic inequivalence,

briefly discussed in Chapter 3. A second case sometimes
arises for the ^{13}C satellites in proton spectra. As already
mentioned, the presence of ^{13}C in a molecule results in
resonances of low intensity situated $J_{CH}/2$ above and below the
normal proton resonance. The effect of the ^{13}C spin on the
spectrum is equivalent to a chemical shift of $\pm J_{CH}/2$, depend-
ing on the orientation of the ^{13}C spin. In the case of the
isopropyl group, the t-butyl group, acetone, or any other
molecule or ion containing the linkage CH_3CCH_3, the presence
of ^{13}C in one methyl group shifts the resonance of that group
by 60 or more Hz. The resonance of the second methyl group
is not shifted very much at all, because $^3J_{CH}$ is quite small,
generally $\leqslant$5 Hz. The net effect of the ^{13}C spin is therefore
to introduce an effective chemical shift between the methyl
groups. This results in the ^{13}C satellites being split by
$^4J_{HH}$, the methyl-methyl coupling. Recording the ^{13}C satellites
therefore enables us to determine $^4J_{HH}$, as well as $^1J_{CH}$.

Values of chemical shifts and the coupling constants
$^4J_{HH}$ and $^1J_{CH}$ obtained from the proton spectra of neat samples
of t-butyl fluoride and t-butyl chloride during the course of
this work are shown at the top of Table V. The values 0.52 and
0.41 Hz were obtained for $^4J_{HH}$ in t-butyl fluoride and t-
butyl chloride, respectively. These values are similar to
those for neopentane and acetone[58]. Samples of t-butyl
fluoride/SbF_5 and t-butyl chloride/SbF_5, both in the absence
and presence of SO_2 as solvent, were also studied. The ^{13}C
satellites in the case of these samples were much too faint
to be seen in a single sweep, the signal to noise ratio being
much lower than with the neat t-butyl halides. It was there-
fore necessary to accumulate spectra using a Varian C1024
Time Averaging Computer to improve the signal to noise ratio.
After 100 sweeps were stored, the low field ^{13}C satellites in
the neat t-butyl halide/SbF_5 samples could be seen quite
clearly. Only five peaks of the expected seven due to coupling
with six other methyl protons could be seen, however, the two
very small outer lines of the septet still lying under the

noise, apparently. For samples diluted with SO_2, accumulation of 200-300 spectra was required for an adequate signal to noise ratio. The values of chemical shifts and coupling constants obtained for these samples are shown in Table V. It can be seen that $^4J_{HH}=3.4$ Hz for $(CH_3)_3C^+$ in the absence of SO_2 solvent, but increases slightly on dilution with SO_2, at the same time as the proton resonance moves upfield. Olah has suggested[6] that an upfield shift in carbonium ion resonances implies a decrease in solvent acidity, which would in fact be expected when SO_2 is added. Whatever the merit of this suggestion, we may note that the anomalous value of $^4J_{HH}$, generally taken as an indication of the formation of the planar, sp^2-hybridized carbonium ion, increases slightly when SO_2 is added, implying that the solvent does not distort the ion very much. The literature values for $^4J_{HH}$ in t-amyl ion in a number of different solvent systems also vary only slightly, over the range 4.5-5.0 Hz.

Values for acetone and protonated acetone are shown at the bottom of Table V. The sample used for the study of protonated acetone had acetone/HSO_3F/$SbF_5=0.28/1/1.29$, and was made up at low temperature on the vacuum line. Best resolution of the nmr spectrum was obtained at 10°. After 100 sweeps were accumulated, a broad ^{13}C satellite was found which gave $^4J_{HH}=1.3$ Hz. The values of $^4J_{HH}$ obtained in this section will be considered in detail in the next section.

(3) CNDO2 CALCULATIONS

The complete neglect of differential overlap (CNDO) method for calculating molecular orbitals[15-17] is an all valence electron, semi-empirical, self-consistent-field (SCF), linear combination of atomic orbitals (LCAO) approach. As is the case in all LCAO calculations, each molecular orbital ψ_i is taken to be a linear combination of the various atomic orbitals in the basis set, that is

$$\psi_i = \sum_\nu \phi_\nu c_{\nu i}$$

In the CNDO case, all the valence electrons are considered, meaning ϕ_ν is a 1s orbital for a hydrogen and 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals for lithium through fluorine. The electronic energy is minimized by varying the coefficients in the molecular orbital, using the well-known Roothaan equations[61] which include the electronic interaction effects, e.g. interelectronic repulsions. Since the interaction between electrons depends on the molecular orbitals themselves, it becomes necessary to solve these equations by a series of iterations, until the electronic energy reaches a constant value. This is the so-called self-consistent-field approach. In the CNDO method, all overlap and exchange integrals are neglected. This is the complete neglect of differential overlap which gives the method its name. The coulomb integrals are approximated by a set of mean integrals which depend only on the separation and identity of the pair of atoms being considered. The elements of the Hamiltonian matrix are calculated empirically using data from atomic spectra and the results of detailed SCF calculations on small molecules. Since the CNDO method takes some account of the effects of interelectronic repulsion, reasonable bond lengths and angles can be found for molecules of chemical interest by calculating and minimizing the total energy of the molecule (given by the sum of the electronic energy and the repulsion energy between atomic cores) as a function of molecular geometry. The coefficients in the LCAO molecular orbitals are then used to calculate bond orders and charge densities.

During the course of this work, CNDO calculations were done on H_2, HF, H_2F^+, methane, methyl ion, t-butyl ion, isopropyl ion, propane, acetone and protonated acetone. Except in the cases of propane and protonated acetone, the energy was minimized by systematic variation of all the bond lengths and bond angles. For propane, C-C=1.540 $\overset{\circ}{A}$, C-H=1.114$\overset{\circ}{A}$, $\angle$C-C-C=112° and the tetrahedral H-C-H angles were assumed.

For protonated acetone the bond lengths and angles in the CH_3CCH_3 fragment were assumed to be between those calculated in acetone and the carbonium ions, and only C-O, O-H and ∠C-O-H varied to minimize the energy. Table VI shows the calculated energies, and for the first five species the equilibrium geometry and the charge distribution as well. The geometries of the larger molecules are discussed in detail later.

Let us now consider some reactions of interest, using the energy values given in Table VI. Since the proton affinities of molecules are generally measured in electron volts, this unit of energy will be used in the discussion. The reaction

$$H_2F^+ \longrightarrow HF + H^+$$

involves an energy change of $-28.43697-(-28.74377)=0.30680$ atomic energy units (a.u.) or 8.348 eV. This value has already been used in the preceding chapter to discuss the possibility of protonating alkanes in superacids. From the energy values for acetone and protonated acetone in Table VI it can be seen that the reaction

$$(CH_3)_2C=O + H^+ \longrightarrow (CH_3)_2C=OH^+$$
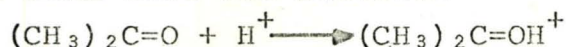
should be 14.186 eV exothermic, so the overall reaction

$$(CH_3)_2C=O + H_2F^+ \longrightarrow (CH_3)_2C=OH^+ + HF$$

is predicted to be 5.838 eV exothermic, that is acetone dissolved in HF/SbF$_5$ or other superacid should be protonated. This is in fact observed to occur, for instance, in $HSO_3F/SbF_5/SO_2$ solution[62]. Another reaction we might consider is the hydride abstraction reaction between protonic media and alkanes. For methane and propane, the only alkanes of Table VI, the reaction,

$$RH + H_2F^+ \longrightarrow HF + R^+ + H_2$$

is endothermic, by 7.522 eV in the case of methane and by 1.549 eV when propane is considered. In fact while methane reacts with alkanes only at elevated temperatures[48], propane does so at room temperature[10]. However, it does not appear to be the isopropyl ion, which is produced, but mixtures of

t-butyl and t-hexyl ions, and the extra stability of these
ions may be the driving force for reaction in the case of
propane. The important thing to note is that the energies
obtained from the CNDO calculation do appear to give some
indication as to the ease of reaction to be expected in the
only cases of interest which can be considered using the
energies in Table VI. Acetone is predicted to protonate,
while alkanes are expected not to, in agreement with experi-
ment in both cases. Extension of these calculations to other
reactions in carbonium ion chemistry, for example a whole
series of alkanes undergoing hydride or alkide abstraction by
protons, might prove interesting and worthwhile. Some
consideration might well be given to the transition state
in these reactions, as well, a really adequate calculation
having been done only on CH_5^+.

The molecular orbital calculations discussed in this
chapter were originally undertaken with the idea that an
explanation of the anomalous values of $^4J_{HH}$ in carbonium
ions in terms of structure might be found. Clearly the
sp^2-hybridization expected at the positively charged carbon is
not solely responsible, since $^4J_{HH}$ in acetone is only +0.53
Hz, not much greater than the value of +0.35 Hz found in
neopentane[58]. In a carbonium ion, the positively charged
carbon is stabilized by electron withdrawal from the attached
methyl groups, possibly through both inductive and hypercon-
jugative mechanisms, accounting for the observed order of
stability, tertiary>secondary>primary. This electron with-
drawal is expected to result in a deshielding of the methyl
group resonance in the proton nmr, as is observed. This
movement of electrons away from the methyl group might
reasonably be assumed to also be the cause of the anomalous
increase in $^4J_{HH}$ observed.

Pople and Santry[19] have considered the calculation
of spin-spin coupling constants from LCAO molecular orbital
wave functions in considerable detail. Their theory gives

$$J_{AB} = -\frac{128\Pi}{9} \beta^2 \hbar \gamma_A \gamma_B s_A^2(0) s_B^2(0) \sum_i^{occ.} \sum_j^{unocc.} \frac{c_{Ai} c_{Bi} c_{Aj} c_{Bj}}{^3\Delta E_{j \leftarrow i}}$$

where β is the Bohr magneton and γ_A, γ_B are the magneto-gyric ratios of nuclei A and B. $s_A^2(0)$ and $s_B^2(0)$ are the squares of the values of the s atomic orbitals on atoms A and B at the nuclei, and are taken as constant for a particular atom. The symbols c_{Ai} and c_{Bi} are the coefficients of the s atomic orbitals on atoms A and B in the ith (occupied) molecular orbital, while c_{Aj} and c_{Bj} are those in the jth (unoccupied) molecular orbital. $^3\Delta E_{j \leftarrow i}$ is the triplet state excitation energy for excitation of one electron from the ith to the jth molecular orbital. The mechanism for spin-spin coupling represented by this equation corresponds to a small perturbation which mixes the ground state with small contributions from the triplet excited states. Only the contact contribution to J_{AB}, that which arises from the Fermi contact interaction between nuclei and spins in s-orbitals, is considered in the above equation. Pople and Santry also considered the spin-dipolar and the orbital contributions to spin-spin coupling, and concluded the effect of these two mechanisms in most cases to be very much smaller than that of the contact interaction. When $s_A^2(0)$, $s_B^2(0)$ and the triplet state excitation energies are expressed in atomic units, and all other quantities in c.g.s. units, the above equation reduces to

$$J_{AB} = -4.23311 \times 10^{-6} \gamma_A \gamma_B s_A^2(0) s_B^2(0) \sum_i^{occ.} \sum_j^{unocc.} \frac{c_{Ai} c_{Bi} c_{Aj} c_{Bj}}{^3\Delta E_{j \leftarrow i}}$$

Pople and Santry suggest the value 0.5500 for $s_H^2(0)$. Since $\gamma_H = 2.67519 \times 10^4$ rad/sec/gauss, we finally obtain

$$J_{HH} = -916.42 \sum_i^{occ.} \sum_i^{unocc.} \frac{c_{Ai} c_{Bi} c_{Aj} c_{Bj}}{^3\Delta E_{j \leftarrow i}}$$

In the present work, the coefficients c_{Ai}, etc. were obtained from the CNDO2 calculation. The triplet excitation energies were calculated using the ground state geometry and the virtual orbital approximation of Kroto and

Santry[63] which gives

$$^3\Delta E_{j\leftarrow i} = \varepsilon_j - \varepsilon_i - J_{ij}$$

where ε_i, ε_j are the one electron molecular orbital energies calculated and J_{ij} is the molecular coulomb integral, given by

$$J_{ij} = \sum_A \sum_B D_i^A D_j^B \gamma_{AB}$$

where the summations are over all atoms A and B and

$$D_i^A = \sum_\mu^A c_{\mu i}^2$$

this summation taking place over all the atomic orbitals centred on atoms A, $c_{\mu i}$ being the coefficient of atomic orbital μ in the ith molecular orbital. γ_{AB} is the mean Coulomb integral for all atomic orbitals centred on atoms A and B and is part of the main CNDO calculation itself. (We may note a possible difficulty with symbols here: J_{AB} is a coupling constant while J_{ij} is a molecular coulomb integral, and γ_A is a magnetogyric ratio while γ_{AB} is an interatomic coulomb integral.) In the present work, a subroutine JAB was written which took the molecular orbital coefficients and interatomic Coulomb integrals found in the main CNDO program and calculated the molecular Coulomb integral and triplet state excitation energies for all possible ground state-triplet state excitations, using the above expressions. The summation term in the equation for the coupling constant given by Pople and Santry was then evaluated for the nuclei of interest, using these calculated excitation energies.

The majority of the coupling constants calculated by CNDO2/JAB are summarized in Table VII to IX, which also include bond lengths and angles, and the calculated charge distributions. The energy depends slightly on the conformation of the methyl groups in each case. The lowest energy conformer found is indicated in each table by a small drawing, indicating which hydrogens lie in the plane defined by the carbon atoms. In Table VII we see that five of the nine methyl-methyl coupling constants calculated in the case of the t-butyl ion are quite small, but the other four, those involving the out of plane hydrogens, are almost 5 Hz in size,

resulting in an averaged $^4J_{HH}=+2.10$ Hz. It is the out of plane hydrogens which should be involved in any hyperconjugative electron donation. In protonated acetone (Table VIII), we find an averaged $^4J_{HH}=+0.59$ Hz. The coupling between the proton on the oxygen and the protons of cis and trans-methyl groups in protonated acetone is calculated to be $J_{cis}=-0.25$, $J_{trans}=+0.61$ Hz. The experimental values for these coupling constants are t-butyl ion, $^4J_{HH}=3.4$ Hz (this work), protonated acetone, $^4J_{HH}=1.3$ Hz (this work), and $J_{trans}\approx 0$, $J_{cis}=1.0$ Hz[62]. The calculation of values of $^4J_{HH}$ for the t-butyl ion and protonated acetone which are in the right order and only a factor of two in error is encouraging, considering the many approximations involved in the method. However the couplings through oxygen calculated in protonated acetone are in the reverse order to those known from experiment, giving us good reason to doubt the method.

Table IX summarizes the calculations for the isopropyl ion. A value for $^4J_{HH}$ has not been determined experimentally. (This could be done by the ^{13}C satellite method.) The value of $^3J_{HH}$ calculated, 10.5 Hz, is twice that found by Saunders and Hagen[12]. When the calculations for acetone and propane (not shown in Tables VII to IX) are considered, we see just how unreliable the method is. Values of -2.6 and -1.5 Hz are calculated for $^4J_{HH}$ in acetone and propane, while experimentally $^4J_{HH}=+0.53$ in acetone[58] and is probably about the same value in propane. Interestingly enough, the value of $^4J_{HH}$ calculated for propane, 6.88 Hz, lies in the range 6.1-7.0 Hz found experimentally for this coupling in the isopropyl group.[64] The lowest energy conformation found for both propane and acetone is that shown diagramatically below.

$$\underset{H}{\overset{C}{\diagdown}}\underset{C}{\diagup}\underset{H}{\overset{C}{\diagdown}}$$
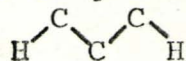
The equilibrium geometry calculated for acetone is

$$C-C = 1.4548 \text{ Å} \qquad \angle CCC = 119.46°$$
$$C-H = 1.1188 \qquad \angle CCH = 111.67$$
$$C-O = 1.2747$$

This is a somewhat shorter C-C and longer C-O bond than expected for acetone[65].

Clearly the object of this section, the calculation of values of $^4J_{HH}$ which reproduce or at least parallel those found in the neutral molecules and the carbonium ions discussed here, has not been attained. This may be due to the approximate nature of the wave functions calculated or to the coupling constant theory itself. Since the Pople-Santry theory is only a first order perturbation approach, too much accuracy is not to be expected. A new and more accurate approach to the calculation of coupling constants, the finite perturbation method[66,67] has recently been developed, and is just now coming into general use. Since there is little direct evidence for the sp^2-hybridized planar structure assumed for carbonium ions, such a finite perturbation calculation on the experimental coupling constants discussed here might be useful, as it could tie the couplings to the structure, as was unsuccessfully attempted in this section.

TABLE V

Chemical Shifts and Coupling Constants from the Proton Spectra

of Interest

Sample	δ ppm[1]	$^4J_{HH}$ Hz [3]	$^1J_{CH}$ Hz
t-BuF (neat)	1.30	0.52	125.76
t-BuCl (neat)	1.73	0.41	127.33
t-BuF/3.8SbF$_5$	4.48	3.4	130.5
t-BuF/3.8SbF$_5$/19SO$_2$	3.96	3.6	131.2
t-BuCl/5.5SbF$_5$	4.56	3.4	131.1
t-BuCl/5.5SbF$_5$/30SO$_2$	3.99	3.6	131.2
t-BuCl/5.5SbF$_5$/72SO$_2$	3.85	3.6	131.8
Acetone	1.88	0.52	126.77
Acetone/HSO$_3$F/SbF$_5$	3.70[2]	1.3	133

[1] Below external TMS.

[2] Methyl resonance. OH resonance occurs at 14.23

[3] Probably all positive, by comparison with t-amyl ion[8,9]. $^4J_{HH}$ is known to be positive in acetone.[58]

TABLE VI

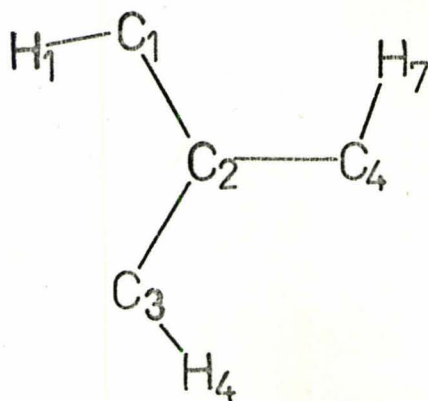### CNDO Calculated Energies, Equilibrium
Geometries and Charge Distributions

Species	Energy (a.u.[1])	Geometry	Charges	
H_2	-1.47483	H–H=0.7459Å		
HF	-28.43697	H–F=0.9998	+0.226	(H)
			-0.226	(F)
H_2F^+	-28.74377	H–F=1.0357	+0.509	(H)
		HFH=120.74°	-0.018	(F)
CH_4	-10.11707	C–H=1.1135	+0.011	(H)
			-0.044	(C)
CH_3^+	-8.67261	C–H=1.1167	+0.194	(H)
			+0.419	(C)
$(CH_3)_3C^+$	-35.02783			
$(CH_3)_2C^+H$	-26.28421			
$(CH_3)_2CH_2$	-27.50915	Arbitrary		
$(CH_3)_2C=0$	-44.27270			
$(CH_3)_2C=OH^+$	-44.79407	C–O=1.3228		
		O–H=1.0355		
		COH=113.49°		
		Remainder arbitrary		
H^+	Zero of energy scale			

[1]
$$\text{Atomic energy unit (a.u.)} = 27.210 \text{ eV}$$
$$= 627.46 \text{ kcal/mole}$$
$$1\text{eV} = 23.06 \text{ kcal/mole}$$

TABLE VII

Equilibrium Geometry, Charge Distribution and
Proton Coupling Constants Calculated for t-Butyl Ion.

C-C = 1.4319 Å
C-H = 1.1206
CCH = 111.30°

Charges

+0.061 (H_1)
+0.123 (H_2, H_3)
-0.089 (C_1)
+0.344 (C_2)

$J_{14} = -0.079$ Hz
$J_{15} = J_{16} = -0.043$
$J_{24} = J_{34} = +0.357$
$J_{25} = J_{36} = +4.775$
$J_{26} = J_{35} = +4.398$

Mean J $= +2.099$ Hz

H_2 above, H_3 below the plane at C_1
H_5 above, H_6 below the plane at C_2
H_8 above, H_9 below the plane at C_3

TABLE VIII

Geometry[1], Charge Distribution and Proton Coupling
Constants Calculated for Protonated Acetone
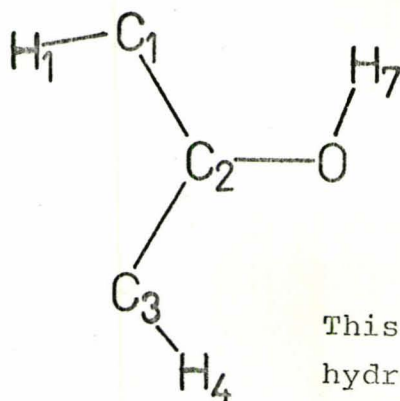
$C-C = 1.4400$ Å $CCC = 122.00°$
$C-H = 1.1190$ $CCH = 111.30$
$C-O = 1.3228$ $COH = 113.49$
$O-H = 1.0355$

This conformation assumed, out of plane hydrogens as in t-butyl ion.

Charges

+0.085 (H_1)

+0.125 (H_2, H_3)

−0.121 (C_1)

+0.090 (H_4)

+0.129 (H_5, H_6)

−0.107 (C_3)

+0.445 (C_2)

−0.144 (O)

+0.245 (H_7)

$J_{14} = +0.487$ Hz
$J_{15} = J_{16} = -0.456$
$J_{24} = J_{34} = -0.231$
$J_{25} = J_{36} = +9.518$
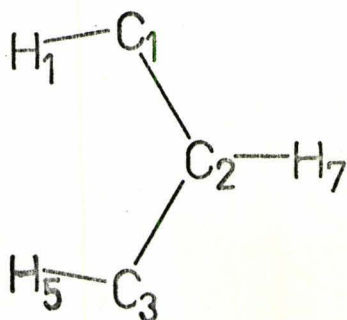$J_{26} = J_{35} = +2.570$

Mean $J = +0.588$ Hz

Methyl–hydroxyl coupling

$J_{cis} = -0.246$ Hz

$J_{trans} = +0.611$

[1] Only C-O, O-H and COH varied during calculation, other bond lengths and angles assumed.

TABLE IX

Equilibrium Geometry, Charge Distribution and
Proton Coupling Constants Calculated for Isopropyl Ion

C-C = 1.4114 Å
C-H = 1.1216 (methyl)
C-H = 1.1229 (methine)
CCC = 129.86°
CCH = 110.60

Charges

+0.082 (H$_1$)
+0.154 (H$_2$,H$_3$)
-0.098 (C$_1$)
+0.349 (C$_2$)
+0.067 (H$_7$)

J_{14}=J_{16}=J_{25}=J_{35}=-0.291 Hz
J_{15}=-4.253
J_{24}=J_{36}=+11.567
J_{26}=J_{34}=+5.774

Mean J =+3.252 Hz

Mean $^3J_{HH}$ =+10.517 Hz

H$_2$ above, H$_3$ below the plane at C$_1$
H$_4$ above, H$_6$ below the plane at C$_2$

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