AFML-TR-70-38

MASS SPECTRA OF SOME SUBSTITUTED POLYFLUOROBENZENES

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JULY 1970

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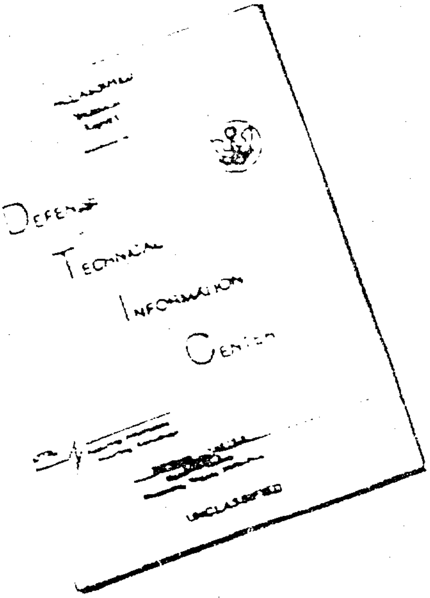

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FOREWORD

This report was prepared jointly by the Analytical Branch, Materials Physics Division, and the Polymer Branch, Nonmetallics Materials Division of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, and the University of Cincinnati, the latter under United States Air Force Contract No. F33615-67-C-1565. This work was initiated under Project No. 7360, "Chemical, Thermal, and Dynamic Properties of Materials," Task No. 736005, "Compositional, Atomic, and Molecular Analysis," with Lee D. Smithson as the Project Engineer. Mr. Freeman F. Bentley of the Analytical Branch, Air Force Materials Laboratory, was the Project Engineer of the University of Cincinnati contract under which part of this work was performed.

This report covers work performed between January 1969 and December 1969. The report was submitted by the authors in January 1970. A portion of this work was presented at the National American Chemical Society Meeting in New York 8 September 1969.

The authors wish to acknowledge the help of Mr. Kenneth M. Oates in obtaining the mass spectral data and in drawing the bar diagrams.

This technical report has been reviewed and is approved.

Freeman F. Bentley
FREEMAN F. BENTLEY
Chief, Analytical Branch
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ABSTRACT

The application of mass spectrometry, including precise mass measurements of molecular ions and selected fragment peaks, in determining the structure of various substituted polyfluorobenzenes is discussed. A high resolution CEC 21-110B mass spectrometer was used. It is shown that the nature of substituents, their size, position on the ring, and the completeness of fluorination are all vitally important in determining the fragmentation process. The rupture of the various carbon to halogens and carbon to hydrogen bonds are discussed. Interesting metastable peaks were found in some cases and their precursors were traced. For example, the following transition

$$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$$

was found where the metastable peak appears at m/e 81.97.

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SECTION I

INTRODUCTION

Despite the high cost and complexity of mass spectrometers, they have become widely used in the analysis of organic compounds. Mass spectrometry is especially useful in the study of highly fluorinated organic compounds because of the difficulty and uncertainty of analyzing these compounds for fluorine by microchemical methods.

Using high resolution mass spectrometers, the molecular ion, corresponding to the molecular weight of a compound, can be determined to four decimal places with an accuracy of better than 10 ppm, and from this data, a molecular formula can be calculated. Fragments in the mass spectrum can also be measured accurately and elemental compositions can be calculated, which allows a great deal of structural information to be obtained.

Using Carbon-12 as a standard, all other atoms have nonintegral masses. For example:

H = 1.007825
C = 12.000000
N = 14.003074
O = 15.994915
F = 18.998405
S = 31.972074

Many combinations of atoms have the same integral mass but there are significant differences in their nonintegral mass. For example, the following combinations of atoms have an integral mass of 28, but the differences in their nonintegral masses makes it possible to distinguish these combinations by high resolution mass spectrometry:

$$CO = 27.994914$$

$$N_2 = 28.006158$$

$$CH_2N = 28.018723$$

$$C_2H_4 = 28.031299$$

The resolving power necessary to separate all of these ions at mass 28 is that necessary to separate the two closest in mass. This would be the CO and N_2 where the difference in mass (Δ m) is 0.011244. The resolving power can then be calculated:

$$\frac{m}{\Delta m} = \frac{28}{0.011244} = 2491$$

It can be seen that if a similar cluster of peaks occurred at mass 280, the resolving power would have to be 24,910 to separate these peaks. High resolution mass spectrometers are generally thought of as those that have a resolution of 10,000 or more. The instrument used for these studies is a CEC 21-110B which has a resolution of 31,000.

The mass spectra in this report were recorded at an ionizing voltage of 70 eV and an ion accelerating voltage of 8 KV. The liquid samples were introduced into the mass spectrometer through the heated inlet system and the solids were introduced via the direct introduction probe.

Before discussing some of the mass spectra, the term "metastable" should be explained. A metastable ion is one that decomposes after nearly complete acceleration from the ion source but before complete mass analysis (lifetime of roughly 10^{-6} second). The product ion from such a decomposition gives rise to a somewhat diffuse peak in the spectrum below its actual m/e. Acceleration of the ion to a velocity determined by the higher mass followed by magnetic deflection at the lower mass results in collection at a still lower m/e, with kinetic energies of decomposition and variation of lifetimes causing a broad distribution of the m/e of focus. Such metastables are quite useful in elucidating ion decomposition pathways. Identification of a particular reaction pathway can provide valuable evidence as to the arrangement of atoms in a molecule.

The following equation relates the metastable (m*), daughter (m_2), and precursor (m_1) ions:

$$m^* = \frac{m_2^2}{m_1}$$

In bromopentafluorobenzene, the peak at mass 81.97 arises, for example, by the transition:

$$\underset{m/e\,=\,167}{C_6F_5^+} \longrightarrow \underset{m/e\,=\,117}{C_5F_3^+} + CF_2$$

In a CEC 21-110B mass spectrometer (see Figure 18), the metastables normally are formed in the second drift region between the electric and magnetic sectors. Metastables formed in the first drift region between the source and the electric sector are removed by the electric sector's energy filtering action. An "Electric Sector Decoupling Unit" was installed in the instrument which allows the accelerating voltage to be decoupled from the electric sector voltage which makes it possible to adjust the accelerating voltage to pass metastables but not normal peaks.

Majer (Reference 1) reported mass spectral results of some polyfluoro compounds and pointed out the unusual CF_3^+ obtained from hexafluorobenzene. The rearrangement peak due to CF_3^+ is generally a minor one, however, and happens to be a prominent peak only in the case of those fluoroaromatic compounds which possess a CF_3 unit. McLafferty (Reference 2) has shown that ring fluorinated alkyl benzenes are accompanied by only a very minor loss of fluorine or hydrogen fluoride, the major cleavage being β-fission of the side chain as in ordinary alkylbenzenes. Mass spectral studies of polyfluorinated aromatic and heterocyclic compounds containing a carbonyl group have been studied by a Russian group (Reference 3). They demonstrated that in the mass spectrum of pentafluorobenzaldehyde, $C_6F_5^+$ and $C_6F_4H^+$ ions decompose to produce $C_5F_3^+$ and $C_5F_2H^+$, respectively. In our present investigation, we have unequivocally established the above mechanism, based on the nature of the substituents.

SECTION II

RESULTS AND DISCUSSION

In the case of hexafluorobenzene (I), the molecular ion happens to be the most abundant peak as shown in Figure 1. The well known CF_3^+ peak, noticed in almost all aliphatic fluorinated compounds, is quite insignificant in this case. On the other hand, the CF_3 elimination peak, i.e., $C_5F_3^+$ is intense. This peak happens to be a very interesting peak in most of the substituted compounds discussed here. The rupture of the carbon-fluorine bond yields the $C_6F_5^+$ peak, whose intensity becomes larger when fluorine from the ring is replaced by other substituents. Other significant peaks are due to $C_3F_3^+$, $C_5F_5^+$, $C_5F_4^+$, $C_5F_2^+$, and CF^+, but these are not necessarily in order of their relative abundance. Several mass spectra of hexafluorobenzene from different sources were examined and the m/e 31 peak varied in intensity a great deal. The m/e 31 peak in the API spectrum (No. 1295) had a relative intensity of 61%; the ASTM E-14 spectrum (No. 1152) had a peak at m/e 31 which had a relative intensity of 30%; and a spectrum that we obtained on a sample of hexafluorobenzene that was repeatedly purified by gas chromatography to obtain a sample that was 99.9% pure gave a peak at m/e 31 which had a relative intensity of only 5.98%. We, therefore, concluded that as the purity of hexafluorobenzene increased, the m/e 31 peak due to CF^+ decreased.

When a fluorine from the ring (I) was replaced by bromine (II) or iodine (III), the mass spectra (Figures 2 and 3) incorporate $C_5F_3^+$ and $C_6F_5^+$ as the most intense peaks, presumably obtained from the rupture of the weaker carbon-bromine and carbon-iodine bonds. It was noticed that a metastable peak close to m/e of about 82 appeared in both cases. This peak could be assigned to the following transition:

$$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$$
$$m/e = 167 \quad m/e = 117$$

Therefore, the metastable peak should appear at $(117)^2/167 = 81.97$. This peak is observed in the mass spectra of bromopentafluorobenzene (II) and iodopentafluorobenzene (III). This substantiates the validity of the proposition of the above reaction. Other fragmentation peaks observed for (II) and (III) are CF^+, $C_3F_3^+$, $C_5F_2^+$, C_5F^+, $C_4F_2^+$, $C_3F_2^+$, and C_3F^+.

The appearance potential of $C_6F_6^+$ from electron impact studies is of the order of 9.9 ±0.2 eV (Reference 4). The appearance potential of all other peaks are much higher than the ionization potential of the molecular ion. It is possible to estimate the value of the carbon-fluorine bond by making some simple assumptions. The values of the appearance potential for $C_5F_3^+$ or the corresponding $C_5X_3^+$ for the partially substituted fluorobenzenes vary only slightly. The latter types of compounds include 1,2,4,5-tetrafluorobenzene (IV) and 1,2,3,5-tetrafluorobenzene (V) whose mass spectra are recorded in Figures 4 and 5, respectively. It can, therefore, be argued that the stabilization of the molecular ion was achieved due to the inductive effects of fluorine atoms and their transfer to the ring via the $C_6F_6^+$ structure.

Accordingly, it has been noticed that the molecular ion happens to be the base peak obtained by the electron bombardment of (IV) and (V).

As mentioned earlier, corresponding $C_5X_3^+$ peaks were obtained analogous to the $C_5F_3^+$ from (I). In both (IV) and (V), it is equivalent to m/e = 81, i.e., $C_5FH_2^+$ (X containing the maximum possible number of hydrogens). Other significant peaks are due to $C_5F_3H_2^+$, $C_3F_2H^+$, CF^+, $C_6F_3H_2^+$, $C_6F_2H^+$, and $C_5F_2H^+$. No significant difference was noticed between these two mass spectra and, hence, it can be concluded that the positions of hydrogen on the ring has no effect on the resultant mass spectra.

Analogous to the loss of a hydrogen from the methyl group in toluene, producing a tropylium ion, the most prominent peak in the spectrum of methylpentafluorobenzene (Figure 6) is due to $(M-H)^+$. The molecular ion peak due to this compound, methylpentafluorobenzene (VI), was also quite substantial. The mass spectrum had a large peak corresponding to CF^+ and several other fragmentation peaks due to $C_7F_4H_3^+$, $C_6F_3H_3^+$, $C_7F_4H^+$, $C_5F_3^+$, $C_6F_2H_2^+$, $C_3F_2H^+$, $C_3F_3^+$, and $C_5F_2H^+$. It can be concluded, therefore, that the introduction of hydrogens in the side chain tends to yield more fragments. This is in agreement with the earlier argument about the inductive effect.

When a methyl group is a substitutent on the ring of a partially fluorinated benzene, like tetrafluorobenzene, a similar $(M-H)^+$ peak is the most intense peak (Figure 7). The only other prominent contribution in the mass spectrum of 1-methyl-2,3,4,5-tetrafluorobenzene (VII), was due to the process of the elimination of one fluorine from the ring. Other smaller peaks correspond to $C_3F_3^+$, $C_3F_2H^+$, and $C_5F_2H^+$. Thus, the incorporation of hydrogen in the side chain in the form of a methyl group in a partially fluorinated benzene does not yield too many prominent fragmentation peaks.

The substitution of an ethyl group on the ring of (I) yielded a large peak corresponding to a loss of a methyl group along with a smaller molecular ion peak (Figure 8) for ethylpentafluorobenzene (VIII). No other significant peaks were observed. This points out that the position of smaller alkyl groups is an important determining factor in the mass spectra of substituted polyfluorobenzenes.

The aforementioned observation is seen only for smaller alkyl groups, like methyl and ethyl. When higher groups like n-butyl were considered, they played a bigger role and asserted their presence in every way. A look at the mass spectrum of 1,2,4-trifluoro-3-butylbenzene (Figure 9) revealed a prominent peak due to $C_3H_7^+$ and equally big peaks corresponding to the loss of C_3H_7 and C_3H_8. The molecular ion peak was also quite marked. Thus, the butyl portion of the above compound, 1,2,4-trifluoro-3-butylbenzene (IX), exercised its full influence. Another peak of (IX) was due to $C_3H_5^+$, which probably was formed from $C_3H_7^+$ by a H_2^- transfer process. Therefore, the bigger alkyl substitutions in partially fluorinated benzenes exhibit their own fragmentation pattern.

The case of the substitution of a carboxylic group is also equally interesting. Figure 10 represents the mass spectrum of pentafluorobenzoic acid (X), where the principal peak is again due to $C_5F_3^+$. In addition, prominent peaks due to CF^+ and CO_2H^+ as well as those due to the loss of OH and CO_2H from the molecular ion were observed. Some other peaks corresponded to C_5F^+, $C_4F_2^+$, $C_6F_4^+$ and $C_3F_2^+$. It can be concluded that monosubstituted polyfluorobenzenes give a prominent peak corresponding to $C_5F_3^+$.

The similarity of ionic behavior of benzene and hexafluorobenzene has been mentioned by earlier workers (Reference 5). A similar analogy can, therefore, be expected also for toluene and octafluorotoluene. The mass spectrum of octafluorotoluene (XI), as shown in Figure 11, is in agreement with the above view. The principal peak was due to $C_7F_7^+$, which was then followed by peaks due to $C_5F_3^+$, $C_6F_6^+$, $C_7F_8^+$, (i.e., the molecular ion), CF^+, CF_3^+, $C_3F_3^+$ and C_5F^+. This compound seems to be highly stable as a small doubly charged peak corresponding to $C_7F_7^+$ at m/e 108.5 was noticed. However, if a trifluoromethyl group is substituted in a partially fluorinated benzene like 1,2,4,5-tetrafluoro-3-trifluoromethylbenzene (XII), then the molecular ion happens to be the most prominent peak (Figure 12). Equally prominent peaks were obtained due to the loss of a fluorine atom and that of CF_2 from the molecular ion, the former process being slightly more favorable. Other contributing peaks were due to $C_6F_4H^+$, $C_5F_2H^+$, C_5FH^+, CF^+ and $C_3F_3^+$. It can be concluded that the tendency for the carbon-fluorine bond to break is greater than that of the carbon-hydrogen bond in partially fluorinated aromatic compounds.

When bulky groups are substituted on the ring (I), the fragmentation pattern is rather limited to that group. Some of the results are enumerated as follows:

1. 1,2,3,4-TETRAFLUORO METHYLBENZOATE (XIII)

The mass spectrum (Figure 13) showed a prominent peak due to $(M-OCH_3)^+$ and then those due to M^+ and $(M - COOCH_3)^+$, where M represents the molecular ion. A small rearrangement peak also appeared for $C_5F_2H^+$.

2. 1,2,3,4-TETRAFLUORO DIMETHYLPHTHALATE (XIV)

The mass spectrum (Figure 14) had a prominent peak due to M^+ and $\left[M - 2(COOCH_3) \right]^+$. Some metastable peaks also occurred possibly corresponding to the following transition:

$$\underset{m/e = 266}{(CH_3COO)_2C_6F_4^+} \longrightarrow \underset{m/e = 235}{(CH_3COO)(CO)C_6F_4^+} + OCH_3$$

so that the metastable peak should appear at $(235)^2/266 = 207.61$.

3. 1,3-DIBROMO-2,4,5,6-TETRAFLUOROBENZENE (XV)

The mass spectrum (Figure 15) showed a prominent pattern for the molecular ion consisting of two bromines with their proper isotopic abundance. As expected, another cluster for $(M\text{-}Br)^+$ with equal contributions from the ^{79}Br and ^{81}Br isotope was obtained together with a large peak due to $(M\text{-}Br_2)^+$. The commonly occurring $C_5F_3^+$, C_5F^+ and CF^+ were also present.

Partially fluorinated pyridine, like 2,3,5,6-tetrafluoropyridine (XVI) was found to be a rather stable compound yielding principally a prominent molecular ion and also a doubly charged molecular ion (Figure 16). Only smaller contributions were obtained due to the loss of CFN from the molecular ion and those of $C_3F_2H^+$, CF_3^+, and CF^+. It has thus been repeatedly shown that hydrogens are retained in the fragmentation peaks of partially fluorinated benzene. However, if the hydrogen in the 4-position of (XVI) is replaced by bromine, then the resulting compound 4-bromo-2,3,5,6-tetrafluoropyridine (XVII) yields many fragmentation peaks (Figure 17), a prominent molecular ion peak with its proper isotopic abundance for bromine, and also, peaks due to $(M\text{-}Br)^+$, $C_4F_3^+$, $C_4F_2N^+$, $C_4F_2^+$, $C_3F_2^+$ and CF^+. Here, also, metastable peaks appeared between m/e 97 and 98. This has been attributed to the following transition:

$$C_5F_4{}^{79}BrN^+ \longrightarrow C_5F_4N^+ + {}^{79}Br$$
$$m/e = 229 \qquad m/e = 150$$

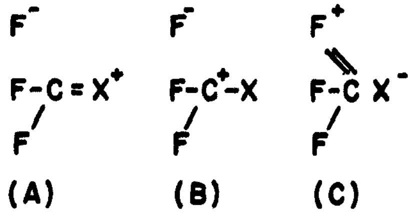
with a metastable peak at $(150)^2/229 = 98.25$. The other similar one is due to the transition of the other isotopic form

$$C_5F_4{}^{81}BrN^+ \longrightarrow C_5F_4N^+ + {}^{81}Br$$
$$m/e = 231 \qquad m/e = 150$$

with a metastable peak at $(150)^2/231 = 97.40$.

The foregoing results demonstrate the behavior of carbon-fluorine bonds in a variety of substituted polyfluorobenzenes. It is well known that as fluorine atoms successively displace hydrogen atoms attached to the same carbon atom, the strength of the carbon-fluorine bond increases (Reference 6). In other words, as fluorine is replaced by hydrogen in partially fluorinated compounds, the bond strength decreases and allows more fragmentation. This has been very well illustrated by our experimental results.

Electron impact studies aid in calculating the bond dissociation energies and other relevant thermochemical data. Dibeler, Reese, and Mohler (Reference 5) have estimated the carbon-fluorine dissociation energy in hexafluorobenzene to be 145 kcal. A substantial increase in the strength of the carbon-fluorine bond takes place as the fluorine content of an organic molecule is increased. This increase in strength is accompanied by a contraction in the length of these bonds. Pauling (Reference 7) has ascribed different resonant structures, as follows, to account for the increasing stability of the carbon halogen bond with more substitutions:



Clearly, when X is F, structures (A) and (C) will contribute equally. The possible resonance structures of these types will change in number and, therefore, in importance as the fluorine content is changed. It, thus, gives a partial double bond character to the carbon-fluorine bonds. The identity of X will definitely determine the importance of these resonance contributors.

SECTION III

CONCLUSIONS

1. In the case of monosubstituted polyfluorobenzenes, a prominent peak corresponds to that of $C_5F_3^+$.

2. In partially fluorinated aromatic hydrocarbons, a prominent peak corresponds to $C_5X_3^+$, where X contains the maximum number of hydrogens.

3. The following transition has been established on the basis of metastable studies:

$$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$$

4. The position of hydrogens in the case of incomplete fluorination of benzene has hardly any effect on the resultant mass spectra.

5. The substitution of any bulky group in the side chain exhibits its own fragmentation.

6. Several mass spectra of hexafluorobenzene from different sources were examined and the m/e 31 peak varied in intensity a great deal. It was found that the intensity of the m/e 31 peak due to CF^+ decreased as the purity of the compound increased.

7. The introduction of hydrogens in the side chain tends to yield more fragments because of the inductive effect.

8. The position of small alkyl groups is an important factor in determining the fragmentation path.

9. There is a great deal of similarity between these fluorinated compounds and the corresponding hydrogenated compounds.

10. Bromine and iodine substituted compounds have a remarkable tendency to lose the halogens very easily.

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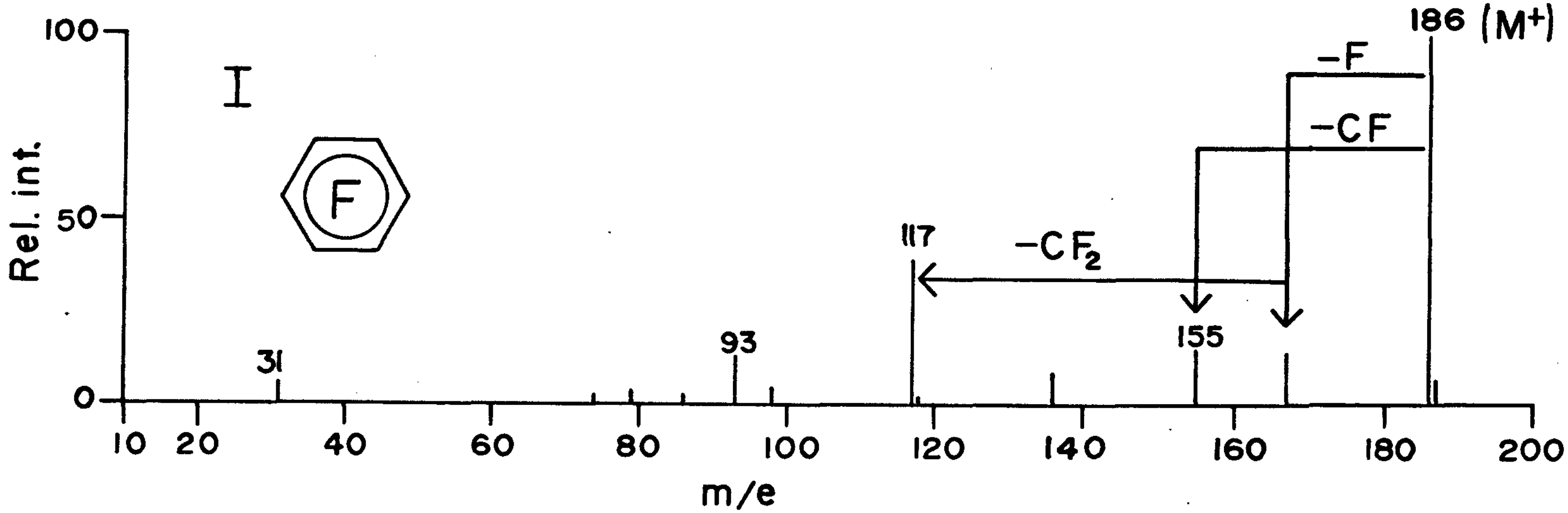

Figure 1. Mass Spectrum of Hexafluorobenzene

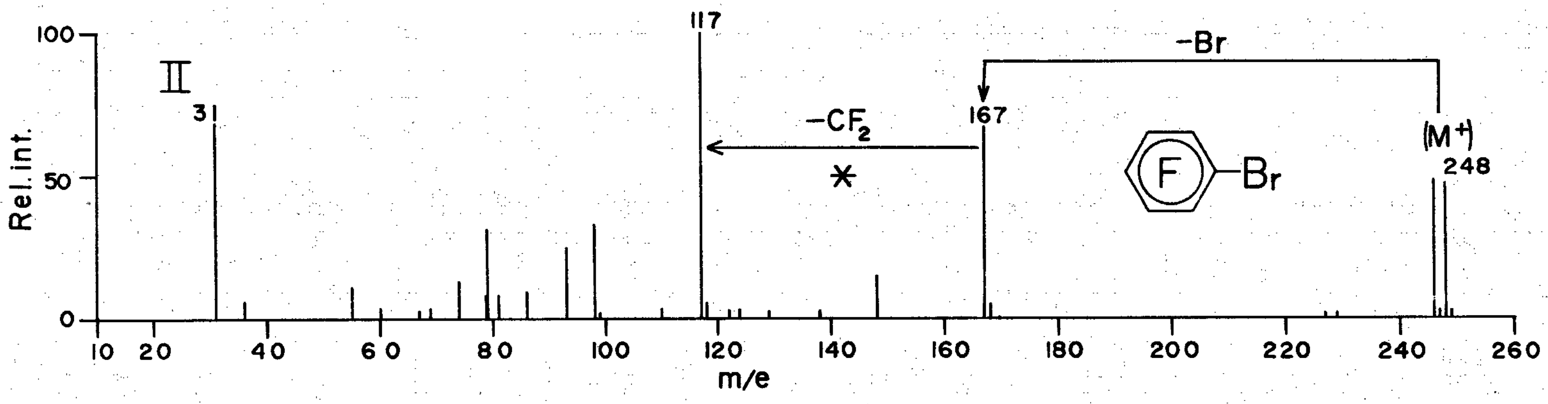

Figure 2. Mass Spectrum of Bromopentafluorobenzene

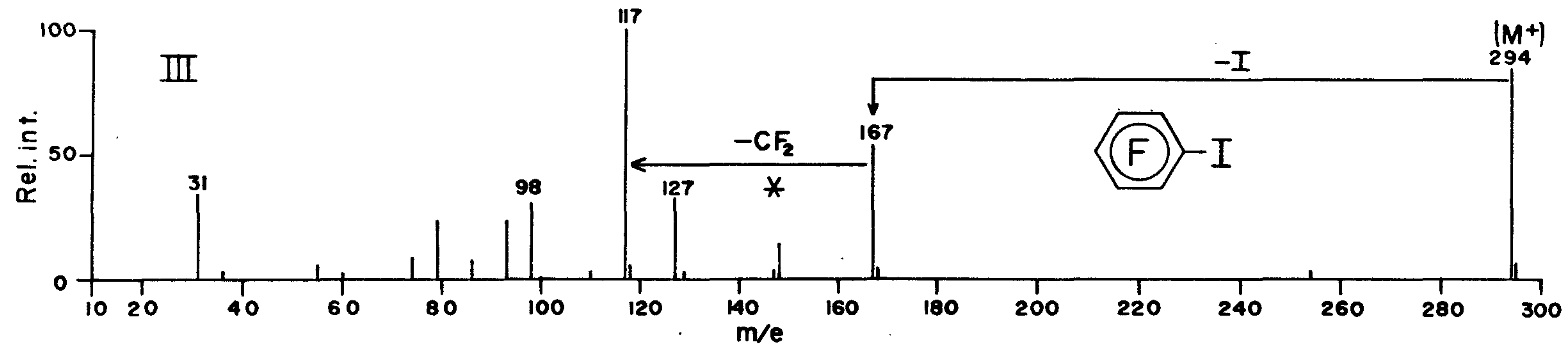

Figure 3. Mass Spectrum of Iodopentafluorobenzene

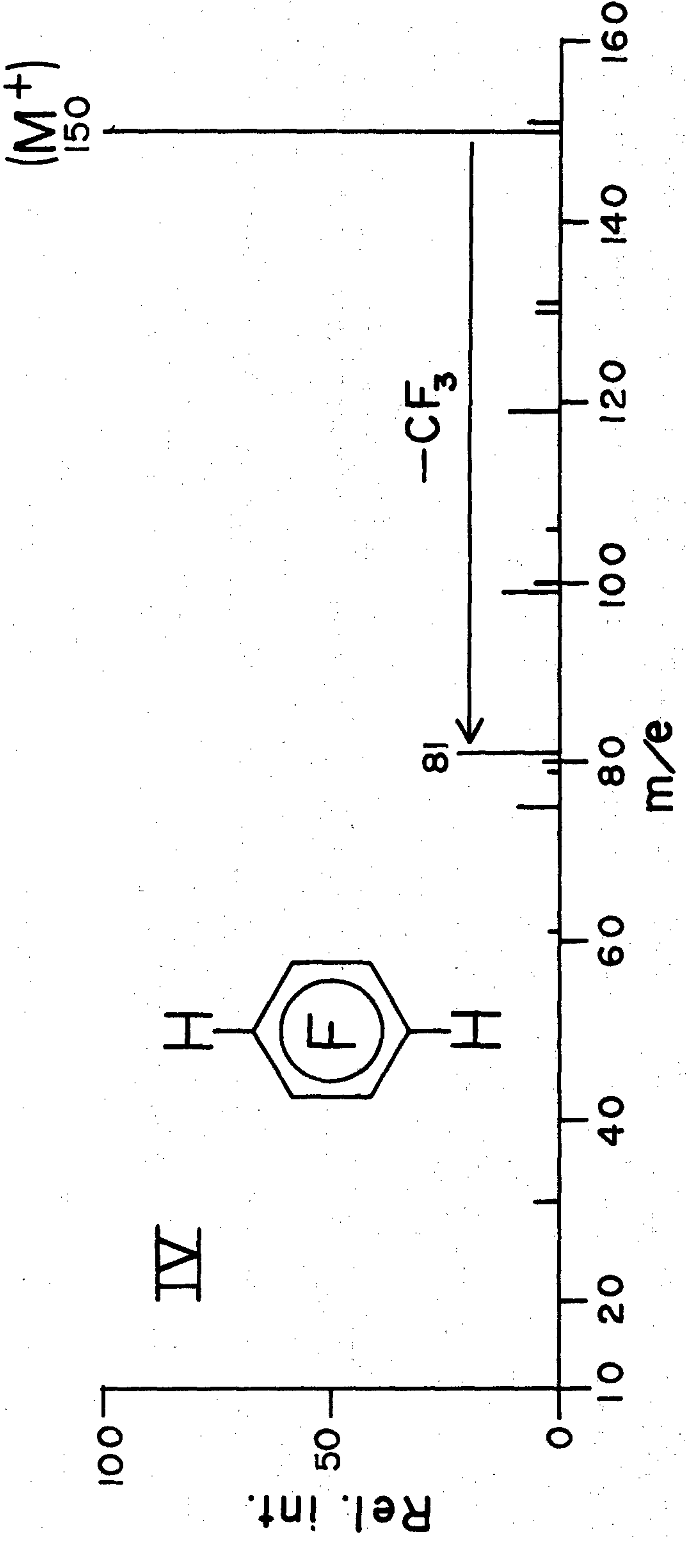

Figure 4. Mass Spectrum of 1,2,4,5-Tetrafluorobenzene

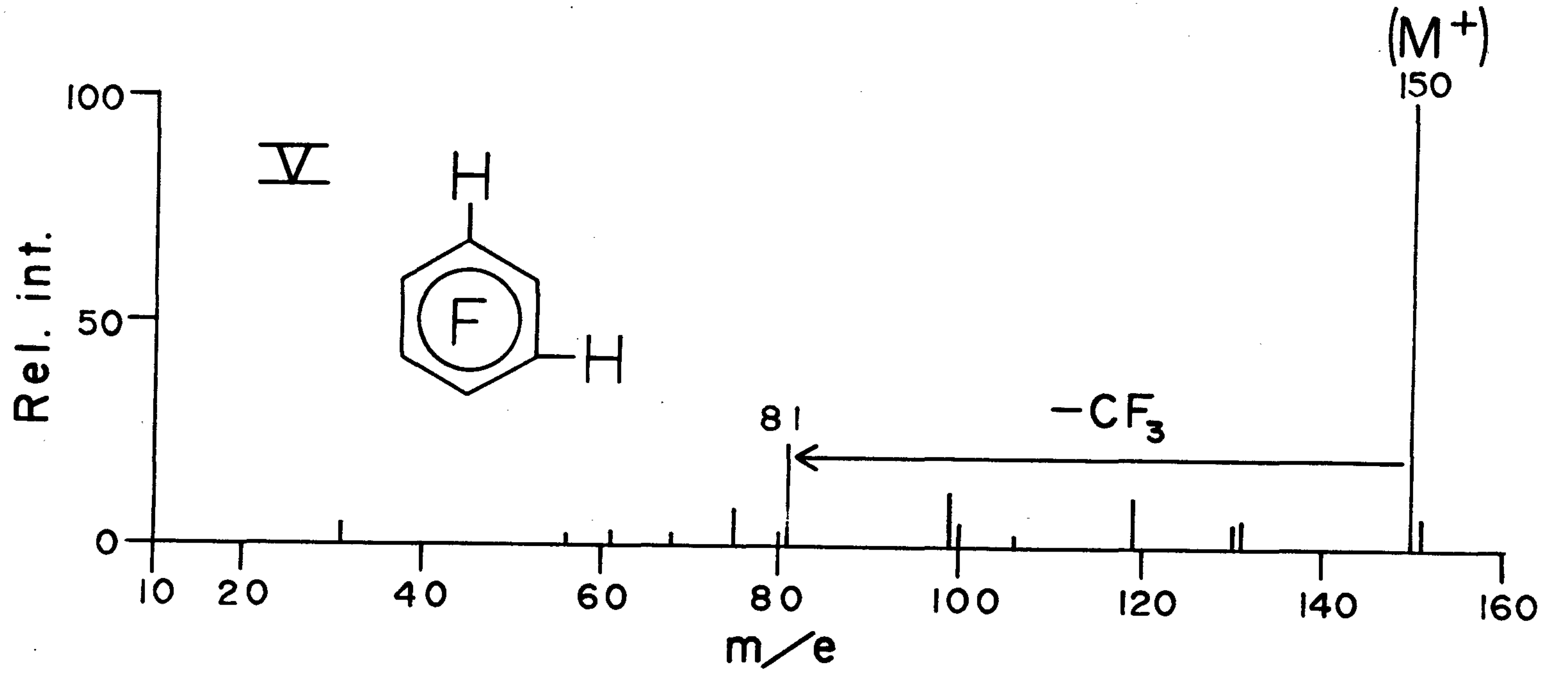

Figure 5. Mass Spectrum of 1,2,3,5-Tetrafluorobenzene

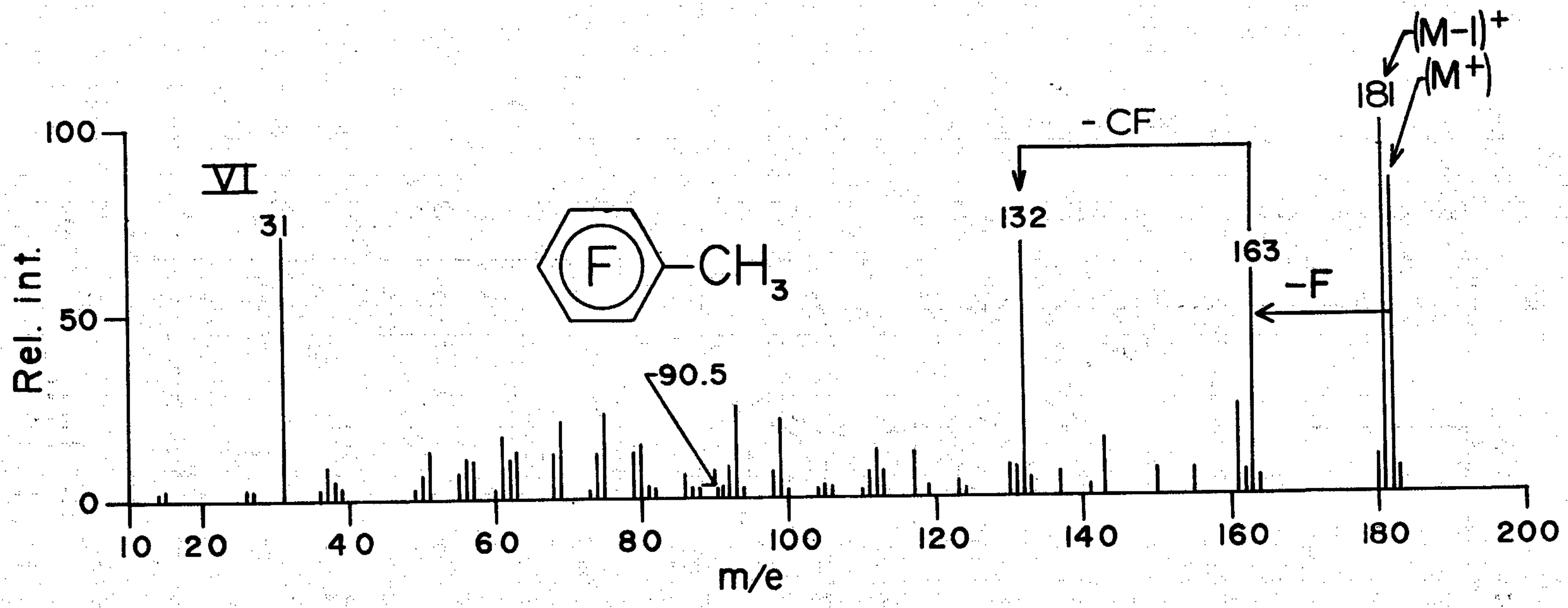

Figure 6. Mass Spectrum of Methylpentafluorobenzene

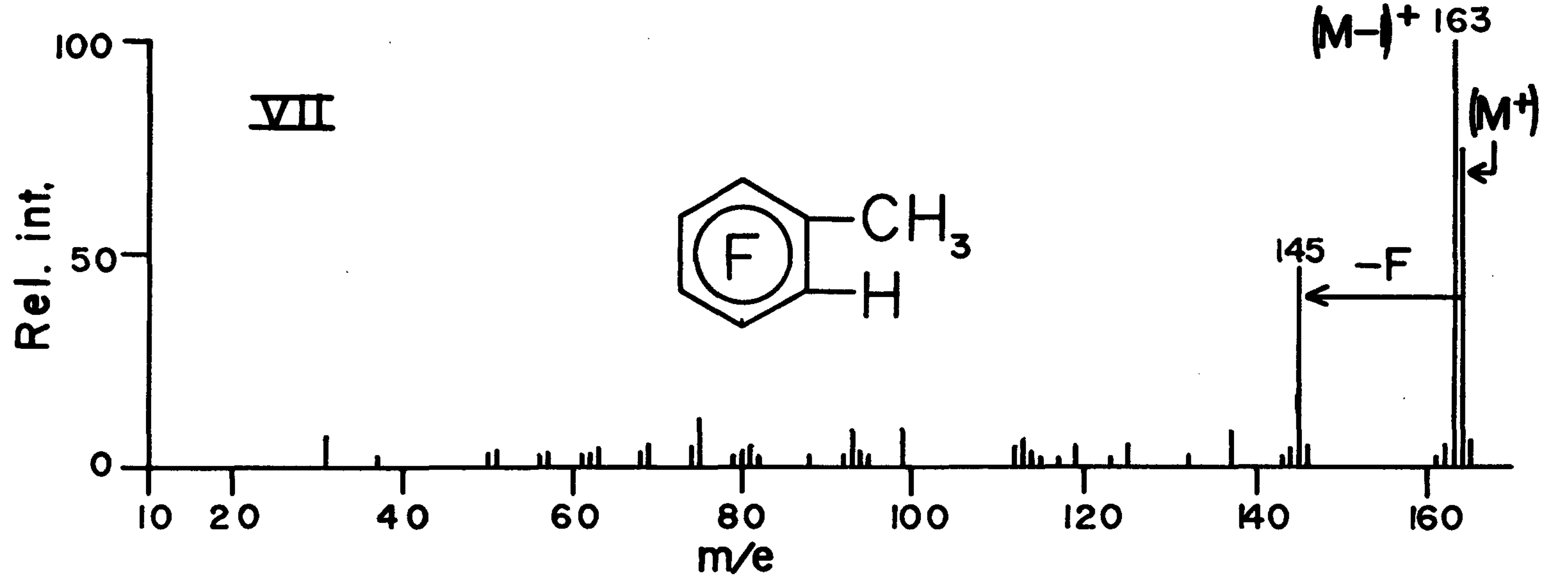

Figure 7. Mass Spectrum of 1-Methyl-2,3,4,5-tetrafluorobenzene

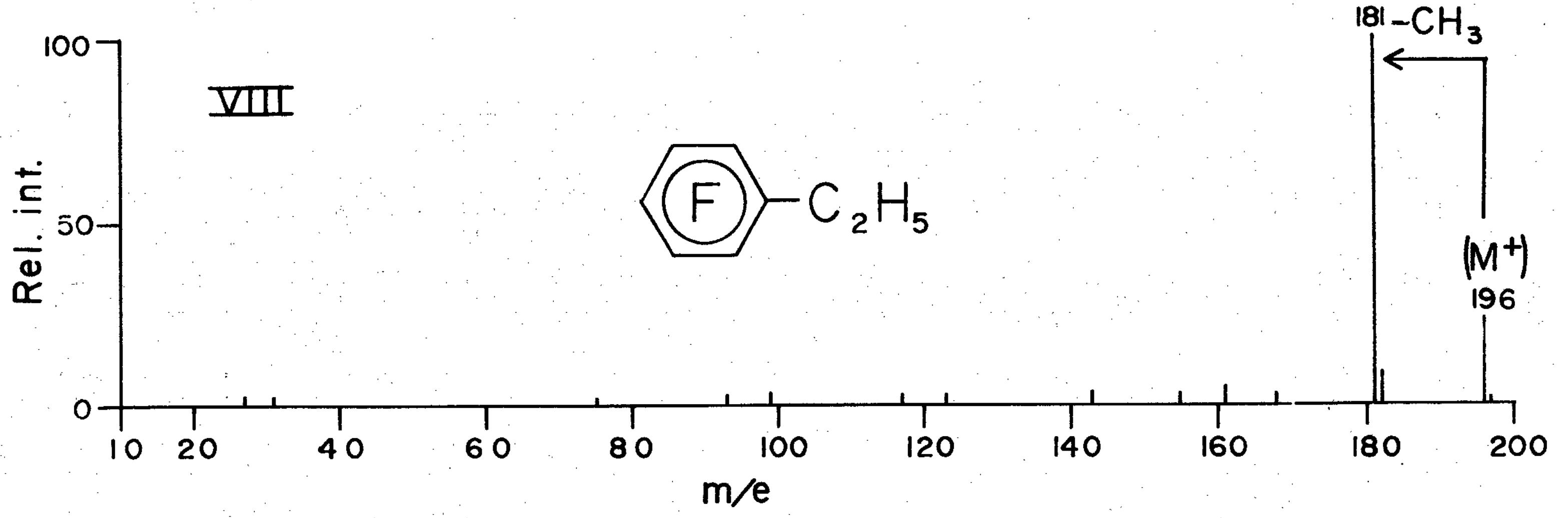

Figure 8. Mass Spectrum of Ethylpentafluorobenzene

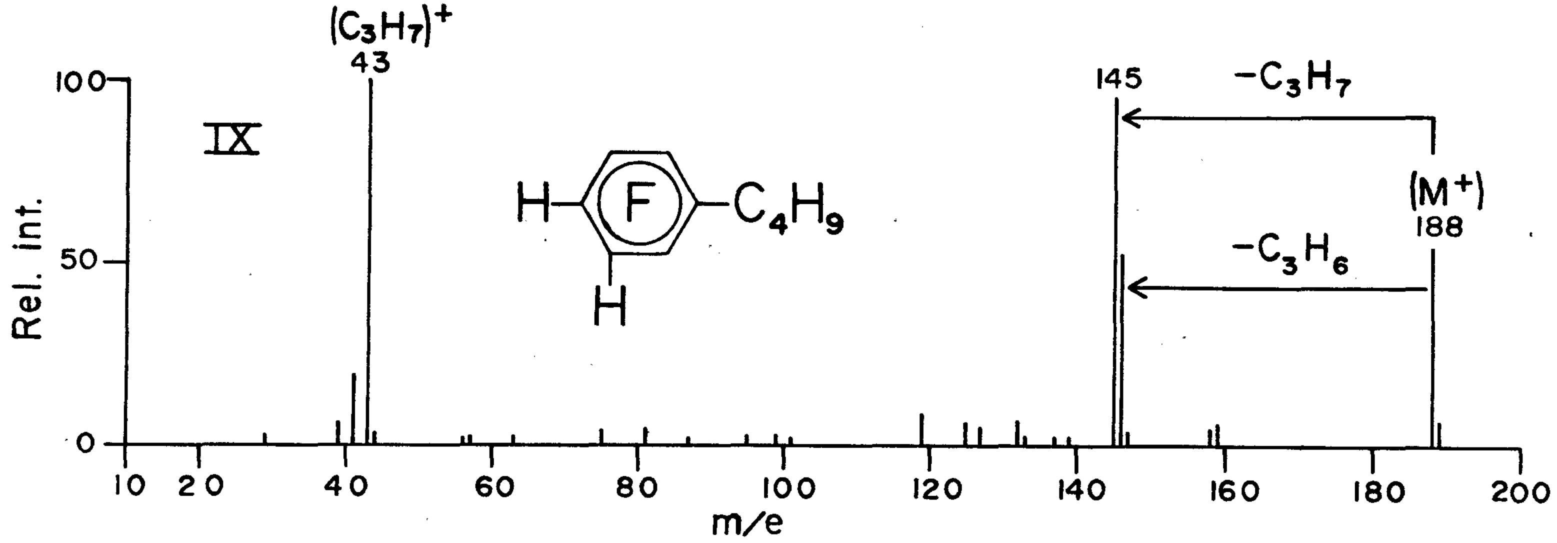

Figure 9. Mass Spectrum of 1,2,4-Trifluoro-3-butylbenzene

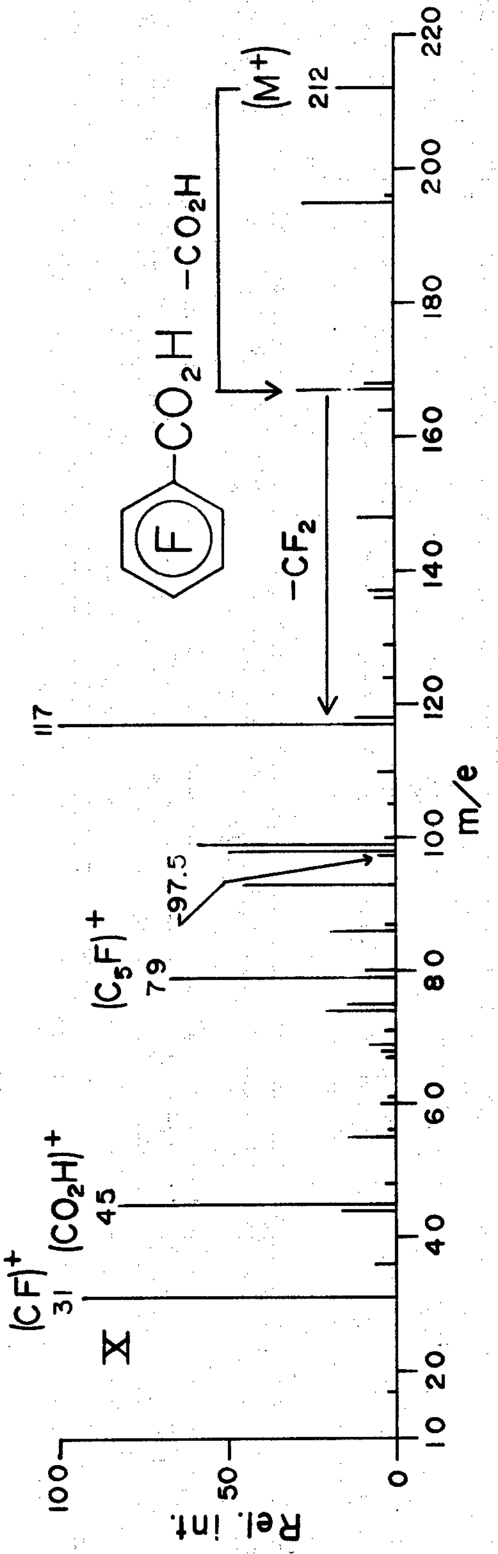

Figure 10. Mass Spectrum of Pentafluorobenzoic Acid

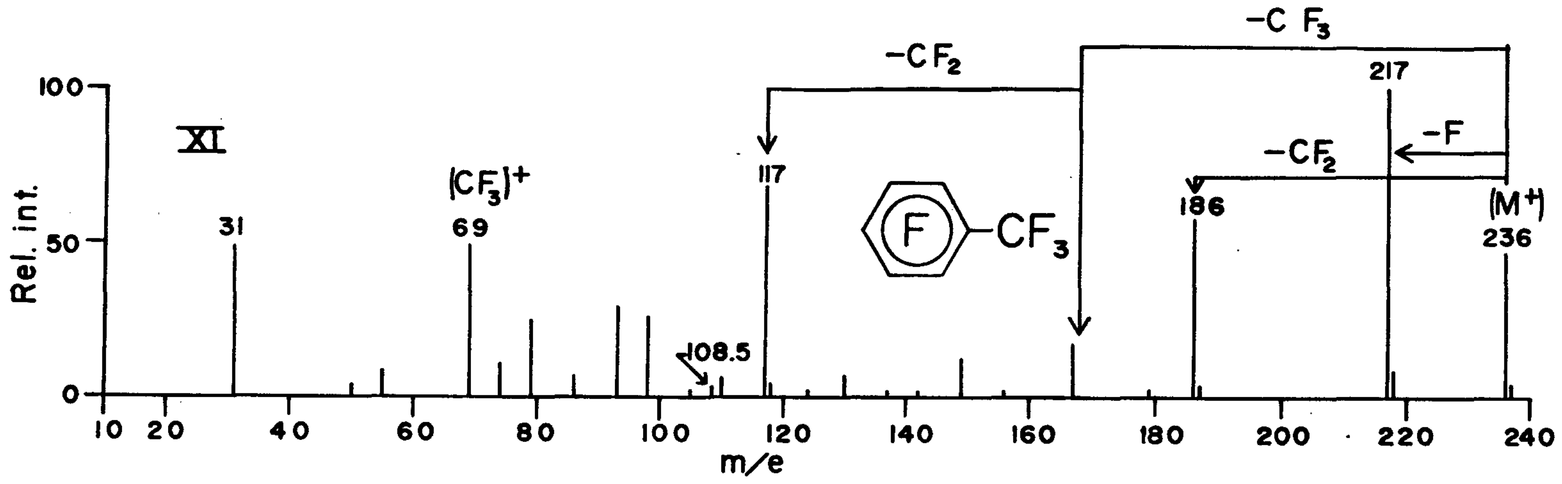

Figure 11. Mass Spectrum of Octafluorotoluene

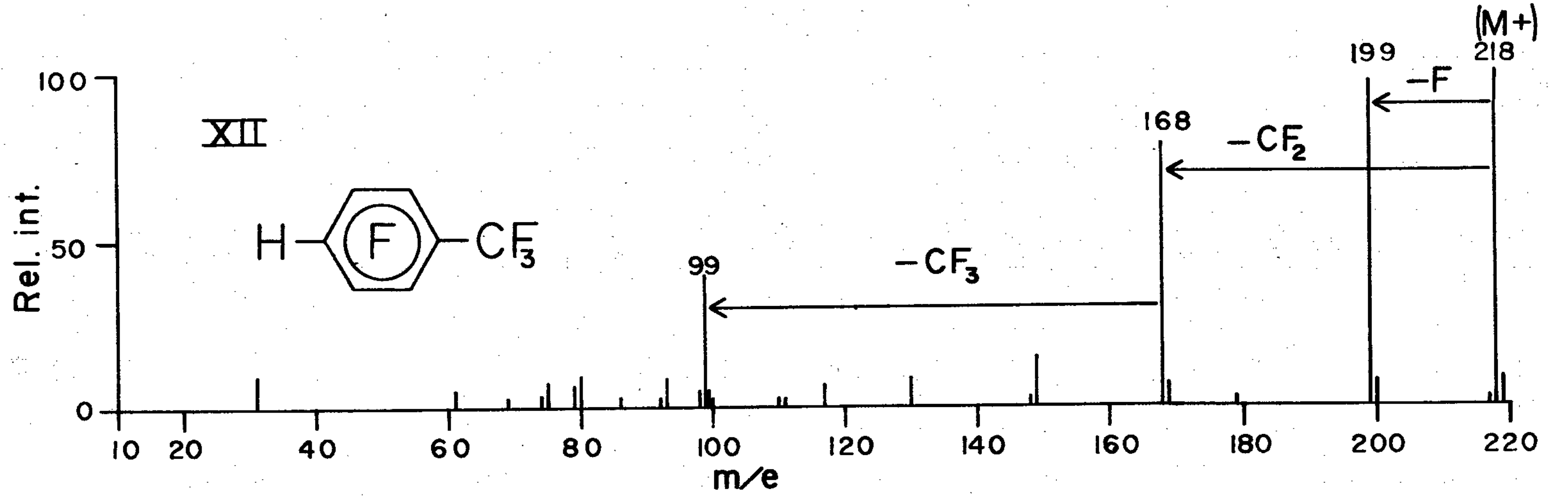

Figure 12. Mass Spectrum of 1,2,4,5-Tetrafluoro-3-trifluoromethylbenzene

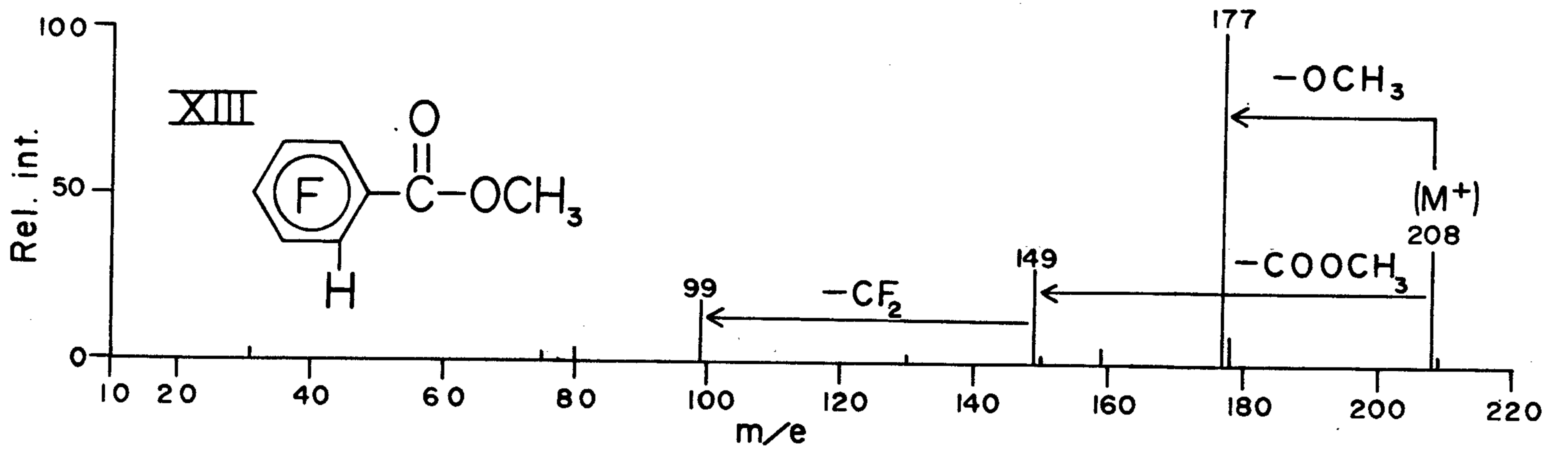

Figure 13. Mass Spectrum of 1,2,3,4-Tetrafluoro methylbenzoate

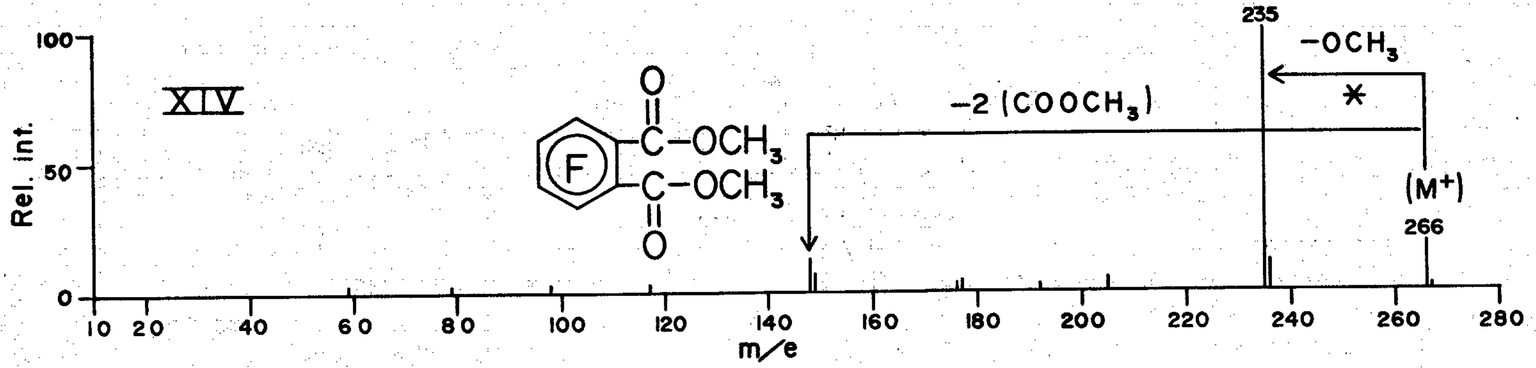

Figure 14. Mass Spectrum of 1,2,3,4-Tetrafluoro dimethylphthalate

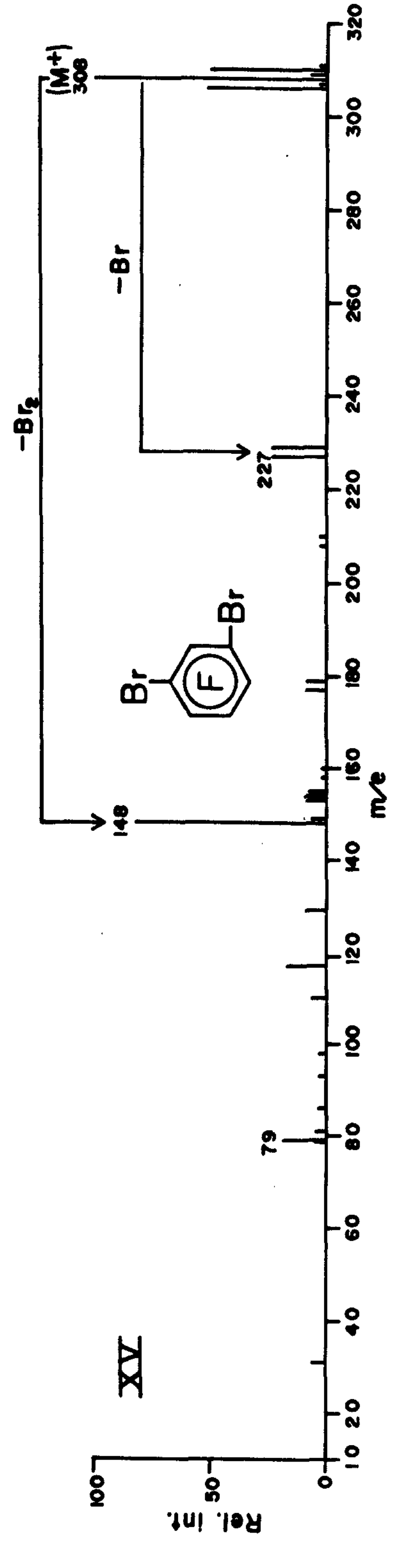

Figure 15. Mass Spectrum of 1,3-Dibromo-2,4,5,6-tetrafluorobenzene

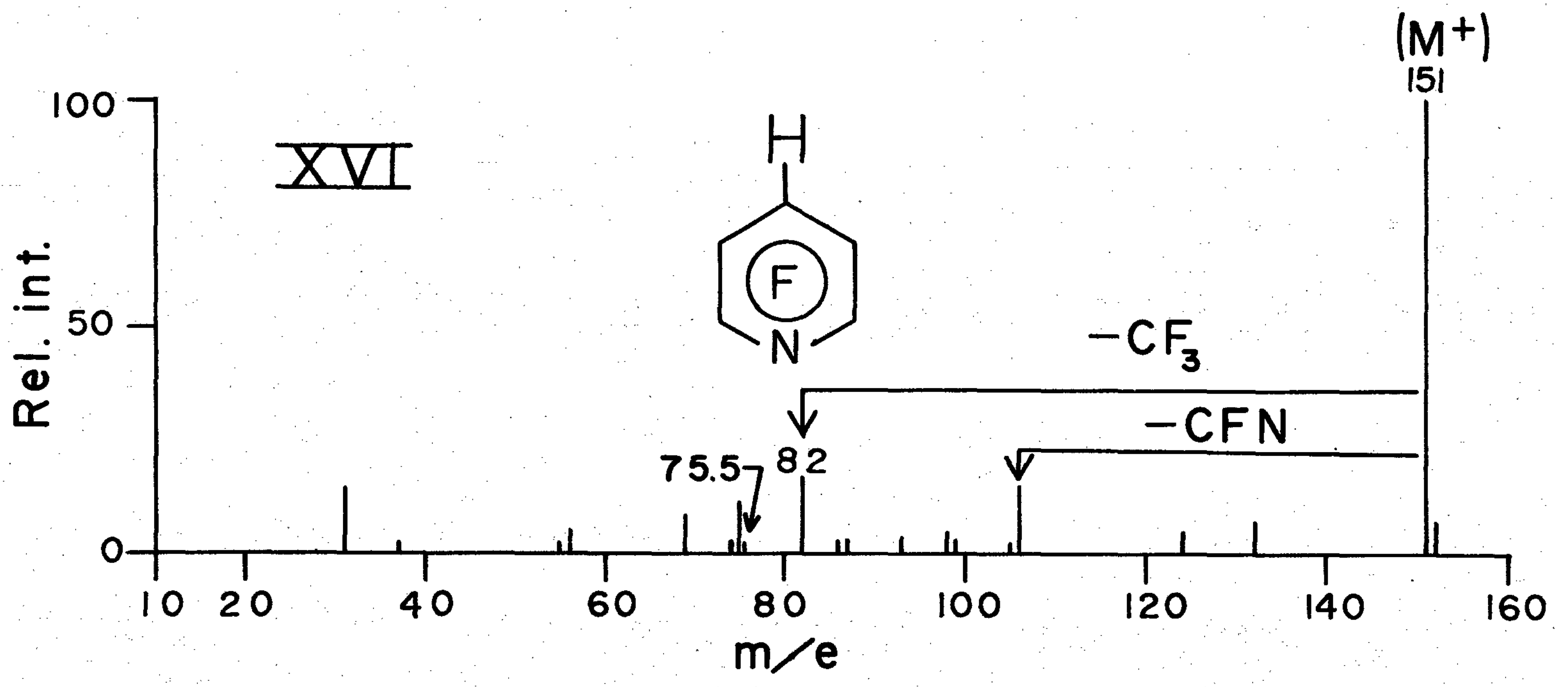

Figure 16. Mass Spectrum of 2,3,5,6-Tetrafluoropyridine

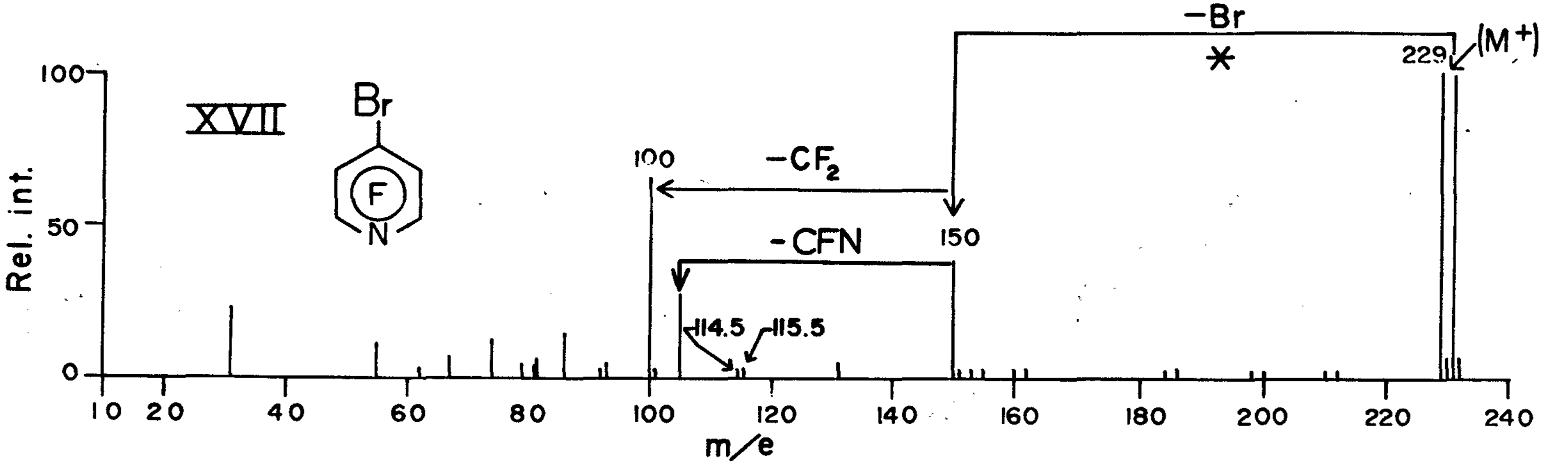

Figure 17. Mass Spectrum of 4-Bromo-2,3,5,6-tetrafluoropyridine

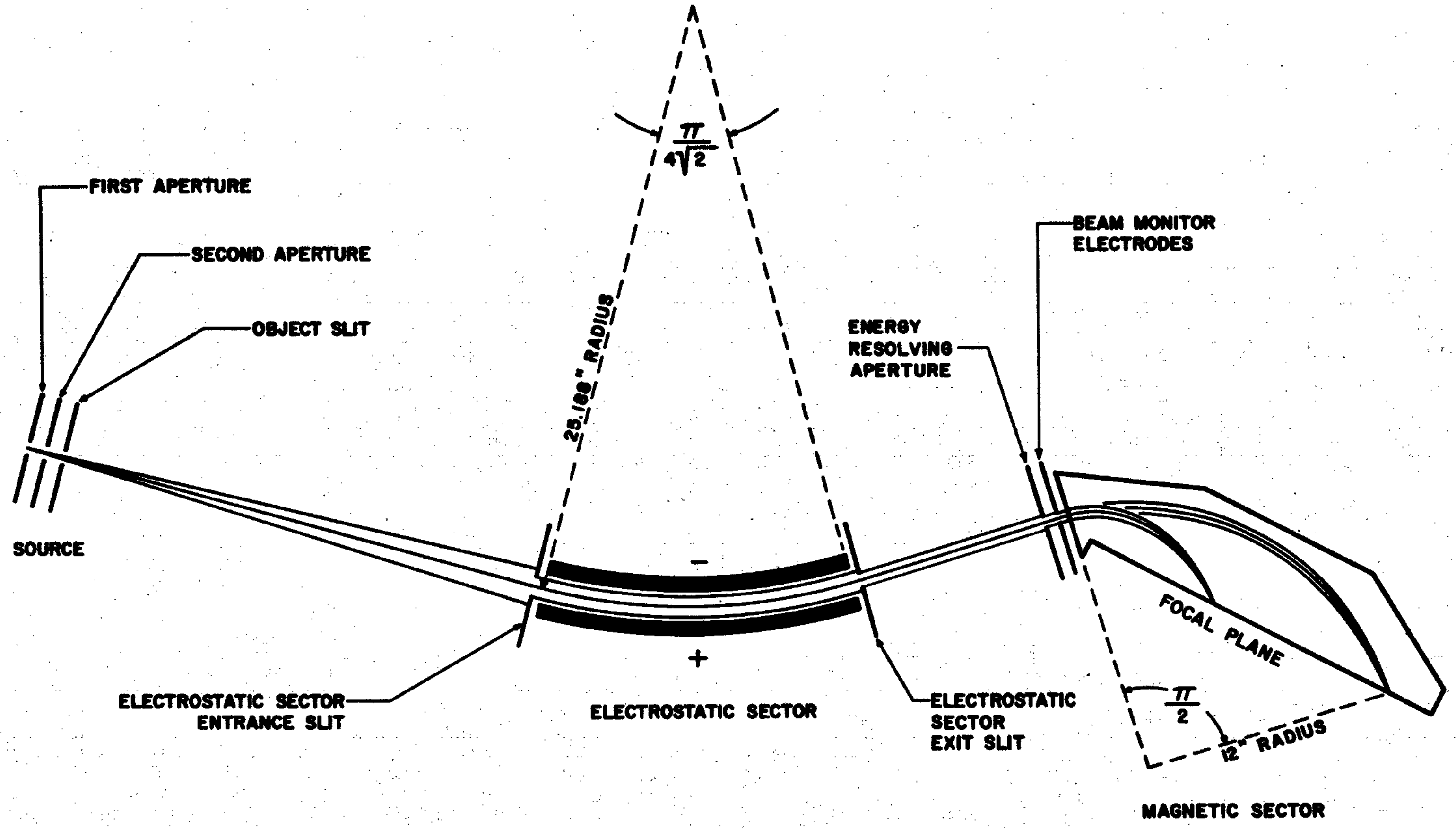

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Figure 18. Schematic of the Ion Beam Path of a CEC 21-110B Mass Spectrometer

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio 45433

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
MASS SPECTRA OF SOME SUBSTITUTED POLYFLUOROBENZENES

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
January - December 1969

5. AUTHOR(S) *(First name, middle initial, last name)*
Lee D. Smithson
Arun K. Bhattacharya
Christ Tamborski

6. REPORT DATE
June 1970

7a. TOTAL NO. OF PAGES
40

7b. NO. OF REFS
10

8a. CONTRACT OR GRANT NO.
F33615-67-C-1565

b. PROJECT NO. 7360

c. Task No. 736005

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
AFML-TR-70-38

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT
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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Air Force Materials Laboratory
Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

The application of mass spectrometry, including precise mass measurements of molecular ions and selected fragment peaks, in determining the structure of various substituted polyfluorobenzenes is discussed. A high resolution CEC 21-110B mass spectrometer was used. It is shown that the nature of substituents, their size, position on the ring, and the completeness of fluorination are all vitally important in determining the fragmentation process. The rupture of the various carbon to halogens and carbon to hydrogen bonds are discussed. Interesting metastable peaks were found in some cases and their precursors were traced. For example, the following transition

$$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$$

was found where the metastable peak appears at m/e 81.97.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluoroaromatic hydrocarbons						
Mass Spectrometry						
Mass spectra						
Organic compounds						
Analysis						