

MASS SPECTRA OF SOME FLUOROHYDROCARBONS

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(Received in USA 29 June 1967; accepted for publication 14 August 1967)

Abstract—The mass spectrometric cracking patterns of some representative fluorohydrocarbons are discussed. Most of the compounds exhibit spectra which are useful in structure determination. Fragmentations involving the loss of difluorocarbene are common. The limits of usefulness of the mass spectrometric method for these compounds is discussed.

THE mass spectra of organofluorine compounds are discussed only briefly in the modern textbooks;¹ compilations² with little interpretation and isolated examples³ have also appeared.

During research in organofluorine chemistry, we found mass spectrometry to be a highly useful tool for structure analysis. Organofluorine compounds, because of their high volatility and good stability, are excellent subjects of the mass spectrometer; also, because fluorine has only one stable isotope, ions may be assigned with reasonable certainty without exact mass measurements. Most compounds exhibited spectra which were easy to interpret and may be considered as "textbook examples". A few were unique and unexpected. We will limit this discussion to compounds which contain C, H and F. No attempt has been made to probe mechanistic details with labelling experiments.

The mass spectrum of (heptafluoroisopropyl)benzene (I)⁴ is shown in Fig. 1. The

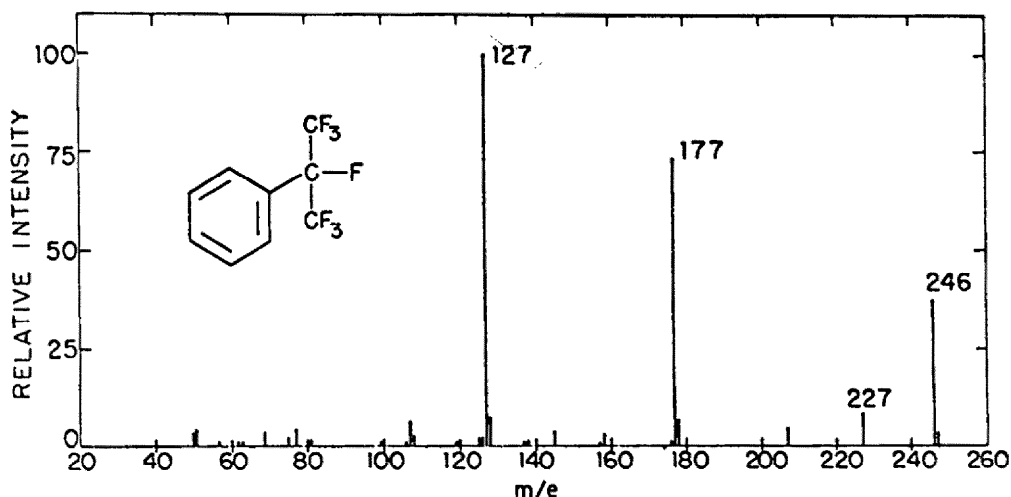
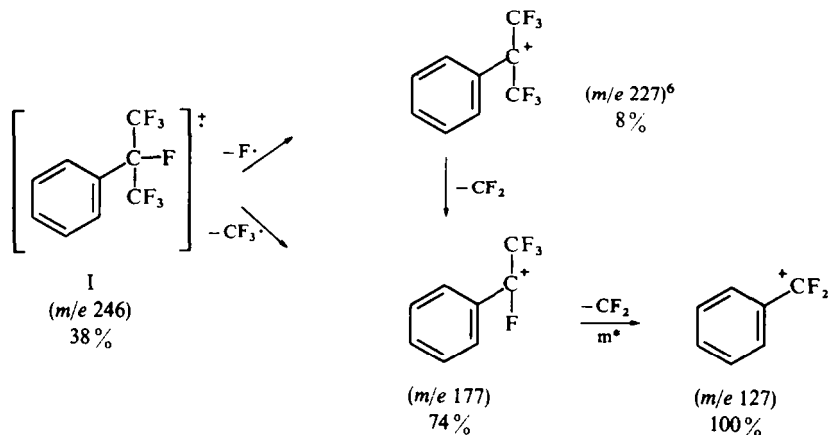


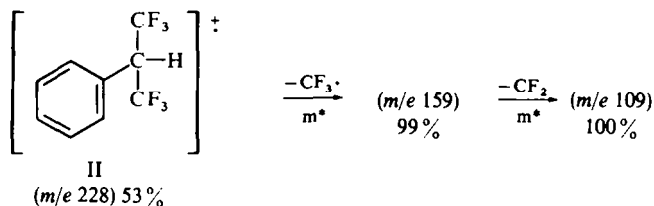
FIG. 1. Mass spectrum of (heptafluoroisopropyl)benzene (I).

most abundant ion is at m/e 127 and corresponds to $C_6H_5CF_2^+$. A reasonable path for its formation is shown below:



Of immediate interest is the suggested loss of CF_2 .^{3c} Such fragmentation is in sharp contrast to the analogous loss of CH_2 which does not occur in the hydrocarbon series. A possible explanation is the greater stability of difluorocarbene as compared to methylene.⁵ The benzyl carbonium ion* representations are used instead of the corresponding tropylium ion structures^{1, 3c} for simplicity.

The simple substitution of a hydrogen atom for the tertiary fluorine atom in I does not substantially alter the fragmentation process. Fig. 2 shows the mass spectrum of (hexafluoroisopropyl)benzene (II).⁶ The loss of $CF_3\cdot$ followed by the loss of CF_2 remains the major fragmentation path:



Figs 2b and 2c show the mass spectra of 7,7-bis-(trifluoromethyl)1,3,5-cycloheptatriene (III)⁶ and 2,2-bis-(trifluoromethyl)bicyclo[3.2.0]heptadiene (IV)⁶ which are isomeric with II. The spectra of II, III and IV show noticeable differences in fragment intensities. The observed decrease in relative abundance of the parent ions at m/e 228 as one goes from aromatic to triene to diene is consistent with other data.¹ The differences in II and III were shown to be reproducible at least on a semi-quantitative



* This ion may have the structure: $C_6H_5CF(CF_3)CF_2^+$.

basis by running several spectra of each at constant instrument conditions. The most important difference is the relative intensities of the m/e 109 peaks. Let us suppose that a good representation for the ion at m/e 159 (derived from each parent by loss of

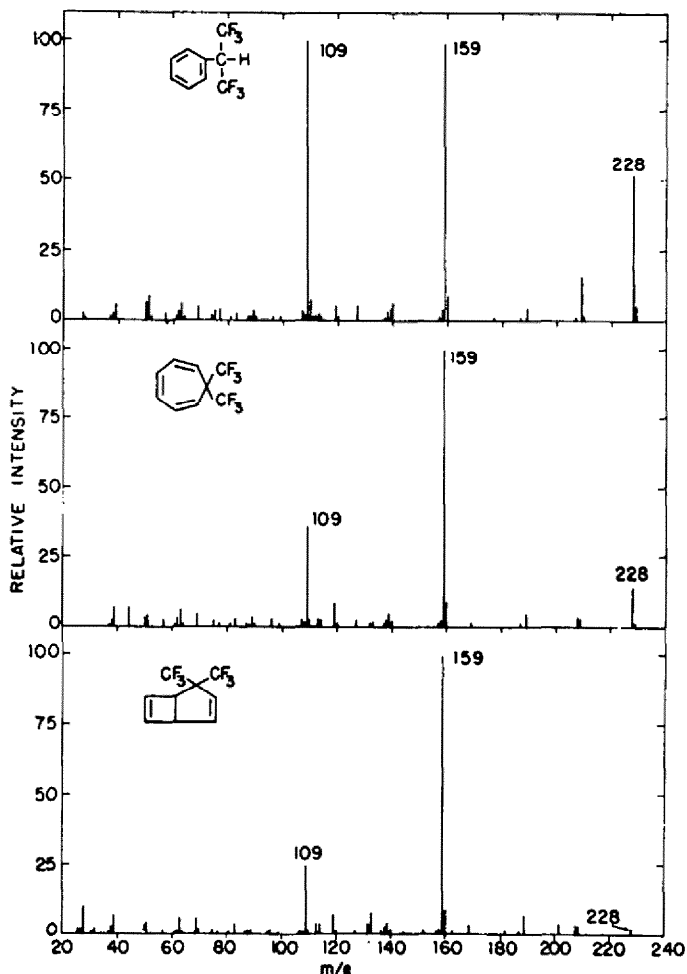
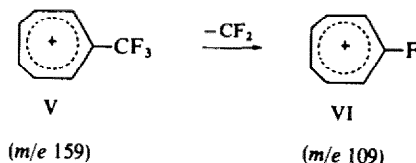


FIG. 2. Mass spectra of (a) (hexafluoroisopropyl)benzene (II); (b) 7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene (III); (c) 2,2-bis(trifluoromethyl)bicyclo(3.2.0)hepta-3,6-diene (IV)

CF_3^*) is the (trifluoromethyl)tropylium ion V. We make this assumption because, according to present evidence,^{1, 3c,†} this ion is likely to be formed from II on loss of CF_3 . Compound III already has the C_7 -ring system. Let us further assume that all the



* Some of the 159 intensity may be derived in two or more steps from the parent (e.g. $228 \xrightarrow{-\text{F}} 209 \xrightarrow{-\text{CF}_2} 159$).

† The mass spectra of cycloheptatriene and toluene are almost identical.^{7a}

m/e 109 intensity is derived from the m/e 159 ion (V) by loss of CF_2 . We would then predict that the intensity of the 109 peaks (relative to 159) should be the same in both cases because they are derived from a common intermediate. The intensities of the 109 peaks are not the same,* and, because no other source of the 109 peaks seems plausible, we must conclude that the 159 ions from the two sources are in some way different.

The mass spectrum of 7,7-bis(pentafluoroethyl)cycloheptatriene (VII) (Fig. 3) is

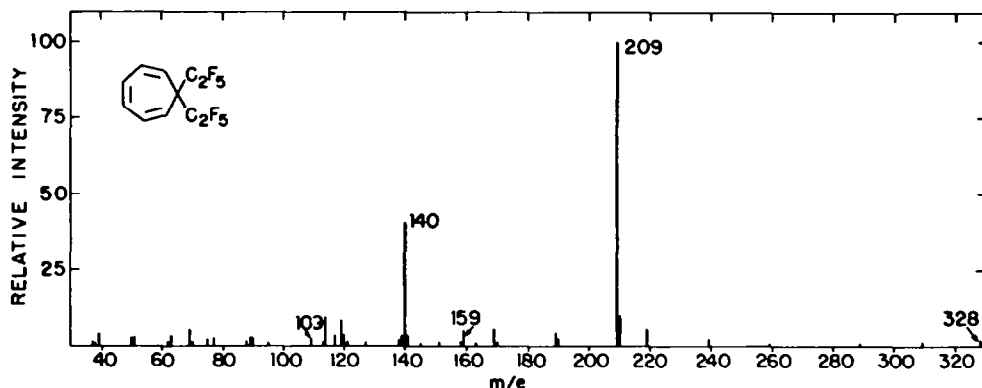
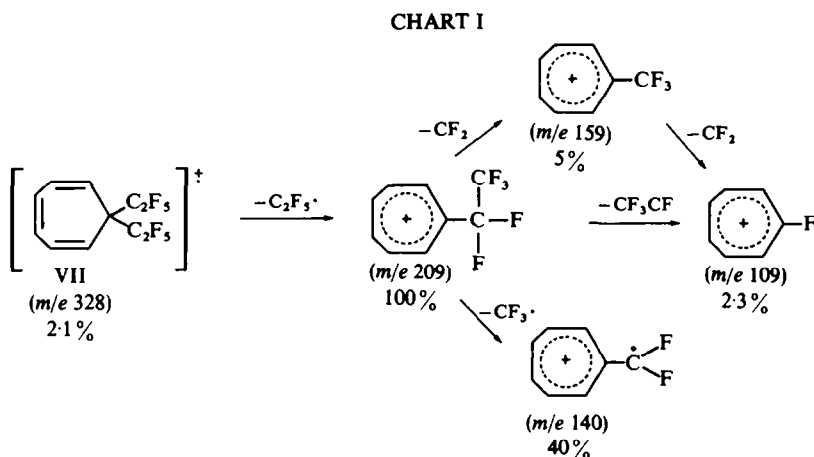


FIG. 3. Mass spectrum of 7,7-bis(pentafluoroethyl)1,3,5-cycloheptatriene (VII).

somewhat more complex than that of the bis(trifluoromethyl) analog III. A suggested scheme is given (Chart 1).



The major fragmentation process is the loss of the C_2F_5 radical to give an ion at m/e 209. The further loss of $CF_3 \cdot$ to give an ion-radical at m/e 140 is a surprisingly favorable process.

In view of the stability of cyclopropenyl cations, it is not surprising that the major

* Another interesting difference was found in the intensities of the "metastable peaks" marking the 159 to 109 fragmentations: $m^* = 75.0$ (calc. 74.7) for II had 0.4 relative abundance, while $m^* = 75.0$ for III had 0.2 relative abundance.

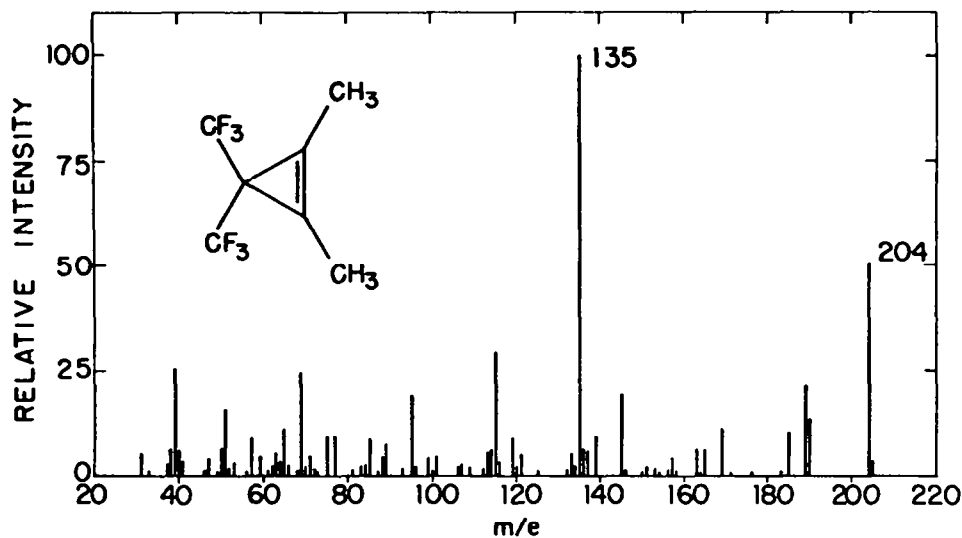
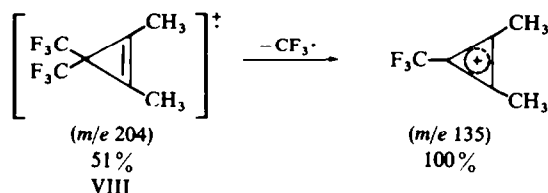


FIG. 4. Mass spectrum of 1,3-dimethyl-2,3-bis(trifluoromethyl)cyclopropene (VIII).

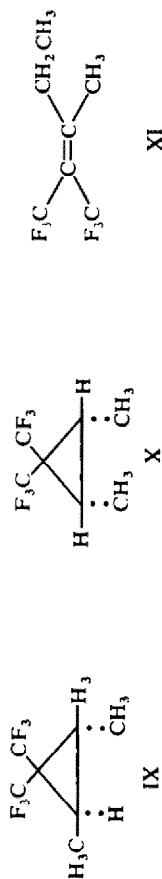
peak in fragmentation of cyclopropene VIII (Fig. 4) is due to the loss of $\text{CF}_3\cdot$ from the parent.



Thus far we have discussed the spectra of fluorohydrocarbons which can ionize on electron impact to give unusually stable ions by some simple fragmentation process. When no simple path is available, the spectrum becomes difficult to interpret and is reminiscent of the situation found for simple paraffins, i.e., gross rearrangements become dominant. The next few examples will illustrate the limits of usefulness of the mass spectrometric method for fluorohydrocarbons.

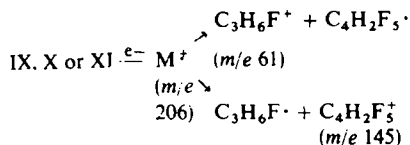
Table 1 lists the relative intensities of the major fragments obtained from three isomeric fluorohydrocarbons ($\text{C}_7\text{H}_8\text{F}_6$; parent at m/e 206) measured at various ionization potentials. At 70 ev, the three spectra are very similar, and one could not *a priori* make assignments of structure. Fortunately, NMR studies were sufficient to distinguish these three isomers.⁶ At lower ionization potentials, differences appear, but because the *base peak throughout* at m/e 61 is not an obvious fragment from any of the isomers, structural assignments would be dangerous. The peak at m/e 61 must be due to $\text{C}_3\text{H}_6\text{F}^+$. The isotope abundance at m/e 62 excludes C_3H^+ , the only other way 61 mass units can be arrived at from compounds containing only C, H and F. Exact mass measurements of the m/e 61 region of X and XI confirm $\text{C}_3\text{H}_6\text{F}^+$

TABLE I. RELATIVE ABUNDANCES OF THE MAIN FRAGMENTS FROM COMPOUNDS IX, X AND XI

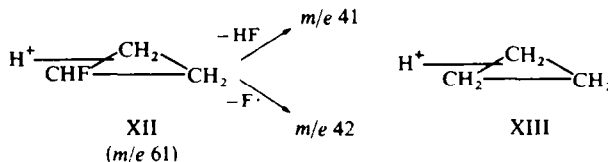
Relative abundance at various ionization potentials (± 2 ev)

<i>m/e</i>	10 ev	15 ev	41 ev	70 ev	10 ev	15 ev	41 ev	70 ev	10 ev	15 ev	41 ev	70 ev
206	11.7	4.5	3.7	2.3	—	—	—	1.1	14.1	5.2	5.4	8.5
171	—	4.7	13.5	14.2	—	5.84	13.4	16.7	—	7.2	19.1	23.3
159	—	13.7	27.2	28.2	—	17.2	30.1	36.0	—	14.5	38.4	45.1
145	—	6.5	62.7	68.1	—	8.2	64.4	83.3	—	7.3	77.9	97.0
137	9.65	15.1	23.7	24.4	11.6	17.9	24.9	30.0	—	17.6	34.0	41.3
121	—	1.0	11.3	12.0	—	—	11.6	15.2	—	1.2	17.6	22.0
69	—	—	11.1	16.6	—	—	11.1	21.3	—	—	15.5	28.7
61	100	100	100	100	100	100	100	100	100	100	100	100
55	—	8.4	19.6	14.6	—	4.7	10.5	20.3	—	12.4	21.6	35.6
47	—	2.3	16.0	16.4	—	2.5	16.2	17.4	—	—	16.7	17.5
42	7.61	22.6	45.6	43.3	8.3	21.9	46.5	55.3	6.0	28.0	54.6	62.1
41	—	2.4	18.1	19.1	—	1.8	15.5	23.4	—	2.9	18.5	26.5
39	—	—	17.6	22.8	—	—	17.2	28.4	—	—	20.4	31.5
29	—	4.5	32.1	30.7	—	4.8	34.0	33.9	—	4.8	43.3	27.6
28	—	4.9	27.8	36.0	—	6.5	40.4	46.7	—	3.6	27.3	30.0
27	—	—	36.4	38.0	—	—	36.2	44.9	—	—	33.5	38.6
15	—	—	4.3	5.8	—	—	4.2	8.6	—	—	10.4	17.8

and show <1% C_5H^+ . The 70 ev spectra are also unusual in that the next most abundant fragment is found in all three spectra at m/e 145 (99% $C_4H_2F_3^+$ by exact mass measurements on X and XI) and $61 + 145 = 206$, the parent mass! One might explain the data at 70 ev by assuming that the molecules of IX, X and XI, which are excited on electron impact, have no simple fragmentation path to a stable ion. The peak at m/e 61 may be XII by analogy with $C_3H_7^+$ (XIII)^{7b} in hydrocarbon frag-



mentations. The peaks at m/e 42 and 41 would then be 61-F and 61-HF, respectively. This mechanism does not, however, explain all of the peaks. An ion such as XII is



not formed from all compounds of the formula $C_7H_8F_6$. Compound XIV,⁷ $C_7H_8F_6$, has its base peak at m/e 55 with only small peaks at m/e 61 and 145 (Fig. 5). The ion at m/e 55 is resonance stabilized. The reason that olefin XI does not undergo a

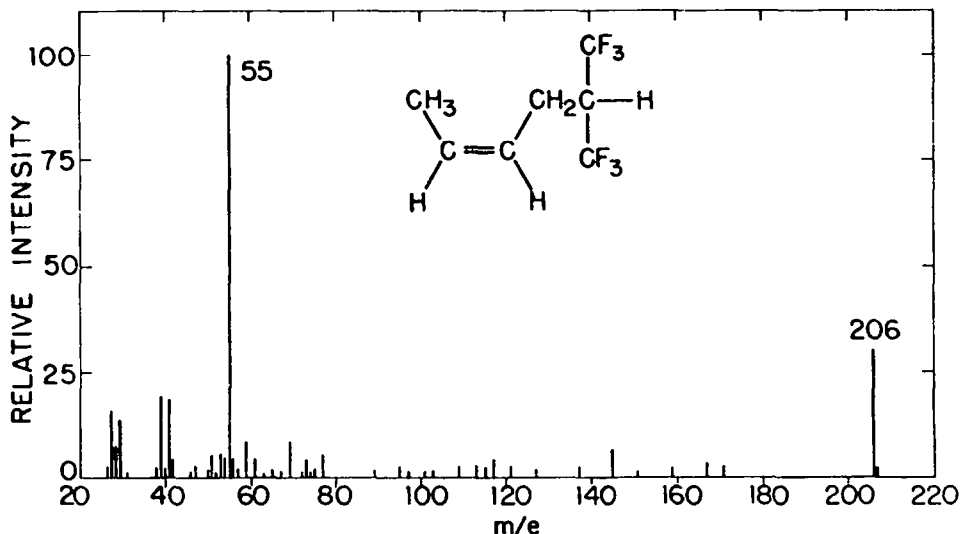
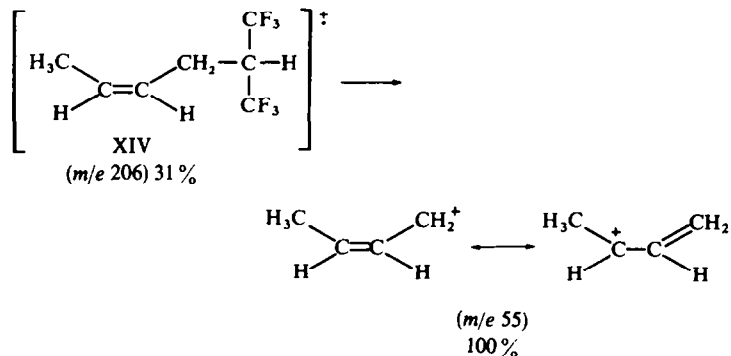
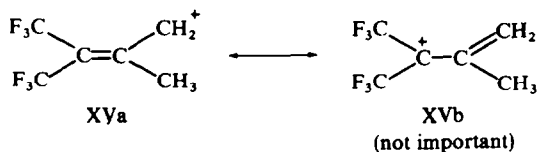


FIG. 5. Mass spectrum of *cis*-5-trifluoromethyl-6,6,6-trifluoro-2-hexene (XIV).

similar fragmentation to give an allylic carbonium ion XV (m/e 191) may be because canonical form XVb which would require a positive charge on a carbon atom bearing



two electronegative $-\text{CF}_3$ groups, does not contribute much to the stabilization;



in addition, the methyl radical, which would be formed along with XVI, is not particularly stable.

EXPERIMENTAL

Mass spectra were run at 70, 41, 15, or 10 ev (70 ev unless noted otherwise) on a CEC 21-103C instrument equipped with an inlet system at 150°. Exact mass measurements were taken on a CEC 21-110B instrument; Table 2 summarizes the data.

TABLE 2. ION IDENTIFICATION BY EXACT MASS MATCHING

Elemental composition	Calculated mass (a.m.u.)	Measured mass (a.m.u.) for	
		X	XI
$\text{C}_3\text{H}_6\text{F}^+$	61.0453	61.0451	61.0452
$^{13}\text{C}^{12}\text{C}_2\text{H}_6\text{F}^+$	62.0487	62.0487	62.0488
$\text{C}_4\text{H}_2\text{F}_3^+$	145.0077	145.0078	145.0075
$^{13}\text{C}^{12}\text{C}_3\text{H}_2\text{F}_3^+$	146.0110	146.0110	146.0104
$\text{C}_7\text{H}_8\text{F}_6^+$	206.0530	206.0537	206.0531

Acknowledgements—We are indebted to Mr. W. B. Askew for exact mass measurements and other experimental assistance, to Prof. D. C. DeJongh for helpful discussion, and to Drs. W. J. Middleton and W. A. Sheppard for samples.

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