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**OAK
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MASTER

**High Voltage Research
(Breakdown Strengths of
Gaseous and Liquid Insulators)
and Environmental Effects
of Dielectric Gases**

Semiannual Report
(April 1, 1979—September 30, 1979)

L. G. Christophorou

D. R. James
R. Y. Pai
R. A. Mathis
I. Sauers

L. Frees
M. O. Pace
D. W. Bouldin
C. C. Chan

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Health and Safety Research Division

Atomic, Molecular and High
Voltage Physics Group

HIGH VOLTAGE RESEARCH (BREAKDOWN STRENGTHS OF
GASEOUS AND LIQUID INSULATORS) AND ENVIRONMENTAL
EFFECTS OF DIELECTRIC GASES

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L. G. Christophorou

D. R. James
R. Y. Pai
R. A. Mathis
I. Sauers
L. Frees (Postdoctoral Fellow)
M. O. Pace (part time)
D. W. Bouldin (part time)
C. C. Chan (student)

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
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ABSTRACT

A number of gas mixtures are suggested for industrial-scale testing. Electron attachment rates were measured and unfolded to give attachment cross section functions for CCl_3F , CCl_2F_2 , and CClF_3 each in N_2 , and for CCl_3F in Ar. The results of this study led to conclusions relating these parameters to molecular structure. Electron attachment rates were measured also for $n\text{-C}_6\text{F}_{14}$ in both Ar and N_2 .

Recent work on the negative ion states of organic molecules was synthesized. The effects of molecular structure on energy, cross section, and lifetime of negative ion states of molecules were especially considered.

A study was made of the potential role of electron detachment in breakdown. The roles of several modes of detachment was assessed, especially for SF_6 and O_2 .

The role of dipolar scattering of electrons in inhibiting breakdown was investigated. The importance of large electron scattering cross sections at subexcitation energies was demonstrated, and means of realizing this with dipolar scattering were studied.

The nature of synergisms among constituents of a gas dielectric mixture is discussed. Examples are cited from recent breakdown measurements and discussed relative to fundamental electron-molecule interactions.

The systematic errors in our direct current breakdown measurements were assessed. They appear to be on the order of 3%.

Breakdown measurements in plane-plane geometry were made for CF_4 , 1,1,1- CH_3CF_3 , and CHF_3 . Similar measurements were conducted with binary mixtures containing one electron attaching component from the set

(α -C₄F₈, SF₆) and one dipolar electron scattering component from the set (CF₄, CH₂F₂, 1,1,1-CH₃CF₃, CH₂F₂). Of special interest in these results were the observed synergisms and the effect of dipole moment on the breakdown strengths of mixtures. Additionally, breakdown measurements in plane-plane geometry were made for mixtures of the two attaching gases α -C₄F₈ and SF₆, which are excellent candidates for mixtures in practical systems. Binary mixtures of each of these two gases with 1-C₃F₆ were also studied.

The initial fragmentation of 1,1,2-C₂Cl₃F₃ under electron impact was studied using a time-of-flight mass spectrometer. The fragments were identified and their dependence on electron energy measured.

Final decomposition products of sparked SF₆/2-C₄F₆ mixtures were identified and quantified with a gas chromatograph-mass spectrometer apparatus. Optimum mixture compositions for carbon inhibition were found, and a method for optimizing dielectric gases containing fluorocarbons were outlined.

The breakdown products of SF₆ were studied on the quadrupole mass spectrometer. Many positive and negative ions were identified under different experimental conditions of electrode material, sparking mode, and spacing from spark electrodes to aperture.

The impulse measurements concentrated on α -C₄F₈/SF₆ mixtures, which were found to be especially interesting under impulse conditions. Lightning and switching surges were used with a large point-plane gap as well as a sphere-sphere gap. Values of V_{50} , V_{NO} , and $V_{10\%}$ were obtained and evaluated.

In the practical conditions of cylindrical geometry with and without surface roughness, many multicomponent mixtures of the gases SF_6 , $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, N_2 , and $1,1,1\text{-CH}_3\text{CF}_3$ were tested, at both 1 and 4.4 atmospheres. The electric fields were calculated by computer for the end conditions of our cylinders, and the results provided comparison of the maximum E field at breakdown to the critical field of certain gases. The fluorocarbons and their mixtures were found to be less sensitive to nonuniform fields than SF_6 and its mixtures.

In the study of liquid dielectrics n -hexane and perfluoro- n -hexane were tested.

I. INTRODUCTION

As we have stressed in previous reports, the Oak Ridge Program on Gaseous Dielectrics is comprehensive. It embraces basic knowledge, applied testing, practical testing under laboratory conditions, and environmental effects studies. Also, we have made a systematic effort to interface with industry by means of continuous discussions with colleagues in industry; by serious inputs to their own programs on gas insulation, by frequent exchange of visits, by participation at and contribution to appropriate national and international meetings, by identification and solution of specific industrial problems in the use of gaseous dielectrics, and by organizing and hosting the First and Second International Symposium on Gaseous Dielectrics. Currently, efforts are underway to conduct larger scale testing jointly with industrial laboratories.

Additionally, based on results presented in this and earlier reports on synergistic effects, carbon inhibition, dc and impulse testing, vapor pressure and toxicity, a number of dielectric gas mixtures such as

are suggested for industrial testing. The data in this and in earlier reports can be used to determine the optimum compositions of such mixtures.

II. BASIC STUDIES OF GASEOUS DIELECTRICS

A. Electron Attachment to Chlorofluoromethanes

Measurements have been made[†] of the absolute rate of electron attachment as a function of the mean electron energy at room temperature ($\sim 298\text{K}$) for CCl_3F , CCl_2F_2 , and CClF_3 in mixtures with N_2 and for CCl_3F in mixtures with argon.¹ These are shown in Tables 1 and 2. The attachment rates in Table 1 are plotted in Fig. 1; for comparison earlier data from our laboratory on CCl_4 are also plotted in this figure. Using the data in Table 1 we¹ calculated — by employing the swarm-unfolding technique and a new set of electron energy distribution functions for N_2 (see ref. 1 for details) — the attachment cross sections tabulated in Table 3 and plotted in Fig. 1.

The present results on $\alpha\omega(E/P_{298})$ and $\sigma_a(\epsilon)$ for the chlorofluoromethanes support our earlier conclusions (e.g., refs. 3-5) about chlorofluorinated hydrocarbons and indicate that the magnitude of $\sigma_a(\epsilon)$ increases with increasing number of chlorine atoms in the molecule, that the $\sigma_a(\epsilon)$ for multiply chlorinated molecules are large, that electron attachment for these molecules proceeds through a multiplicity of negative ion states, and that the most predominate negative ion following electron impact at $\epsilon \lesssim 2\text{ eV}$ is Cl^- . The data presented in Fig. 1 also seem to indicate that the positions of the maxima in $\sigma_a(\epsilon)$ shift toward lower energy with increased chlorine substitution. Finally, the extensive fragmentation of these compounds upon electron impact at these low energies (see, for example, refs. 3 and 6) demonstrates their extreme fragility toward the presence of low-energy electrons, including those of thermal energy. It also indicates that multiply chlorinated compounds may be unstable as gaseous dielectrics.

[†]This work has been conducted in collaboration with Dr. D. L. McCorkle of the University of Tennessee.

Table 1. Electron Attachment Rate Constants for CCl_3F , CCl_2F_2 , and CClF_3 in N_2 ^a

E/P_{298} (V cm ⁻¹ torr ⁻¹)	$\langle \epsilon \rangle^b$ (eV)	CCl_3F^c		CCl_2F_2^d		CClF_3^e	
		$\alpha\omega$ (10 ⁸ sec ⁻¹ torr ⁻¹)	sd^f (10 ⁸ sec ⁻¹ torr ⁻¹)	$\alpha\omega$ (10 ⁷ sec ⁻¹ torr ⁻¹)	sd^f (10 ⁷ sec ⁻¹ torr ⁻¹)	$\alpha\omega$ (10 ⁵ sec ⁻¹ torr ⁻¹)	sd^f (10 ⁵ sec ⁻¹ torr ⁻¹)
0.01	0.040	3.88	0.41			0.08	0.01
0.02	0.046	3.95	0.37	4.64	0.23	0.06	0.02
0.03	0.055	3.80	0.30	5.86	0.16	0.06	0.02
0.05	0.076	3.90	0.32	6.19	0.20	0.05	0.02
0.07	0.099	4.18	0.29	6.06	0.13	0.04	0.02
0.10	0.133	4.79	0.30	5.74	0.15	0.04	0.04
0.15	0.184	5.65	0.30	5.30	0.11	0.03	0.03
0.20	0.231	6.20	0.38	5.05	0.12	0.05	0.03
0.30	0.327	6.97	0.43	5.11	0.14	0.19	0.05
0.40	0.417	7.31	0.43	5.60	0.16	0.44	0.07
0.50	0.493	7.37	0.50	5.99	0.14		
0.60	0.555	7.41	0.54	6.38	0.16	1.52	0.14
0.80	0.647	7.22	0.56	6.75	0.12	2.96	0.10
1.0	0.711	6.92	0.56	6.70	0.10	4.30	0.11
1.3	0.781	6.35	0.56	6.48	0.16	5.86	0.11
1.6	0.827	5.92	0.52	6.17	0.18	7.07	0.10
2.0	0.872	5.58	0.55	5.84	0.12	8.24	0.21
2.5	0.911	5.45	0.58			9.39	0.68

^a The pressures of N_2 used are 1500, 2000, 3000, and 4000 torr.

^b Using new $f(\epsilon, E/P_{298})$ for N_2 (see ref. 1).

^c The average of 42 independent measurements with CCl_3F pressures in the range 0.4 to 3.82×10^{-3} torr.

^d The average of 7 independent measurements with CCl_2F_2 pressures in the range 0.66 to 2.04×10^{-3} torr.

^e The average of 8 independent measurements with CClF_3 pressures in the range 0.52 to 1.0 torr.

^f Standard deviation

Table 2. Electron Attachment Rate Constants for CCl_3F in Ar^a

E/P_{298} (V cm ⁻¹ torr ⁻¹)	$\langle \epsilon \rangle^b$ (eV)	$\overline{\sigma}^c$ (10 ⁸ sec ⁻¹ torr ⁻¹)	sd ^d
0.05	0.935	5.72	0.30
0.06	1.01	5.12	0.27
0.07	1.09	4.69	0.27
0.08	1.16	4.31	0.23
0.10	1.29	3.74	0.23
0.15	1.56	2.84	0.20
0.20	1.80	2.28	0.19
0.25	2.01	1.94	0.13
0.30	2.20	1.69	0.13
0.40	2.53	1.36	0.11
0.50	2.81	1.20	0.07
0.70	3.28	1.01	0.08
1.00	3.87	0.90	0.09

^a The pressures of Ar used are 2000, 3000, and 4000 torr.

^b From ref. 2.

^c The average of 33 independent measurements with CCl_3F pressures in the range 0.13 to 0.96 x 10⁻³ torr.

^d Standard deviation.

Fig. 1. Electron attachment rate as a function of $\langle \epsilon \rangle$ and electron attachment cross section as a function of ϵ for chlorofluoromethanes (ref. 1).

Table 3. Total electron attachment cross sections for
 CCl_3F , CCl_2F_2 , and CClF_3

ϵ (eV)	$\sigma_a(\epsilon)$		
	CCl_3F (10^{-16}cm^2)	CCl_2F_2 (10^{-16}cm^2)	CClF_3 (10^{-18}cm^2)
0.04	13.6	0.66	
0.05	9.16	1.86	
0.06	6.46	3.13	
0.07	5.04	3.40	
0.08	4.27	2.87	
0.10	3.89	1.18	
0.12	4.24	0.64	
0.14	5.12	0.34	
0.16	6.34	0.24	
0.18	7.69	0.23	
0.20	9.26	0.32	
0.25	9.46	0.41	
0.30	8.55	0.55	
0.35	7.02	0.49	
0.40	5.87	0.35	
0.45	5.30	0.26	
0.50	5.19	0.22	
0.55	5.44	0.23	
0.60	5.83	0.26	
0.65	6.32	0.34	
0.70	6.67	0.44	
0.75	6.70	0.57	
0.80	6.47	0.70	
0.85	5.99	0.82	0.02
0.90	5.36	0.89	0.03
0.95	4.59	0.89	0.04
1.0	3.15	0.70	0.08
1.1	1.56	0.35	0.18
1.2	0.39	0.07	0.63
1.3	0.05		1.60
1.4			2.09
1.5			1.33
1.6			0.57
1.7			0.25
1.8			0.16

B. Electron Attachment to Perfluoro-*n*-hexane

Attachment rates of electrons to $n\text{-C}_6\text{F}_{16}$ (perfluoro-*n*-hexane) have been measured in nitrogen and argon as buffer gases for mean electron energies up to 2.8 eV. Figure 2 shows the measured attachment rate as a function of the mean electron energy $\langle \epsilon \rangle$ at 2000 torr total pressure.

The electron attachment rates for C_6F_{14} in N_2 as a function of $\langle \epsilon \rangle$ and total pressure, indicate that two different electron attachment processes occur, one which is independent of pressure and another which depends on pressure. For this reason these studies have been extended to much higher pressures (up to $\sim 14,000$ torr). The observed pressure dependence of the attachment rate is under investigation.

C. Negative Ion States of Polyatomic Molecules

The importance of negative ion states in gaseous dielectrics has been pointed out by us earlier^{7,8} and has been demonstrated repeatedly at our laboratory since. In view of this and the delicate dependence of the energies and the cross sections of such states on the details of molecular structure we have synthesized recent work on the negative ion states of organic molecules formed in the field of the ground electronic state via a *shape* or a *nuclear-excited Feshbach* resonance mechanism.⁸ Electron scattering and electron attachment data on three basic groups of polyatomic organic molecules (non-aromatic double-bonded structures, benzene and benzene derivatives, selected halocarbons) have been used to indicate the rather delicate and strong effects of molecular structure on the energy, cross section, and lifetime of the negative ion states of organic molecules. The fragility of anionic species toward (multiple) fragmentation has been shown also using recent data on perfluorinated

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Fig. 2. Electron attachment rate, αw , as a function of mean electron energy, $\langle \epsilon \rangle$, for $n\text{-C}_6\text{F}_{14}$ in N_2 and Ar as buffer gases.

and other halocarbons.

This work will be presented at a special American Chemical Society Symposium (Houston, Texas, March 23-28, 1980) and will be published in the Symposium Proceedings.

D. Electron Detachment⁹

In a gas discharge, in which electronegative molecules are present, the detachment of electrons from *stabilized* negative ions is a *possible* source of electrons which needs to be considered in the modelling of the discharge. For Townsend discharge studies, electron detachment can lead to a modification of the current growth equation.⁹

For discharges with high over voltages, dynamic studies¹⁰ indicate that a source of electrons may exist in some regions of the gas. One possible source is detached electrons from negative ions formed in an electron avalanche which has swept past that region leaving slower negative ions behind to contribute delayed electrons via detachment.

If electron detachment from negative ions is indeed a significant source of free electrons — thus warranting a detailed study — we need to examine the processes which could cause electron detachment in order to assess the contributions of each process. Possible processes are

- (a) Field-induced detachment,
- (b) Electron-impact-induced detachment,
- (c) Photodetachment,
- (d) Reactive detachment, and
- (e) Collisional detachment (ion-molecule collision).

Mechanisms a-c have been discussed in our previous reports.^{11, 12}

By reactive detachment we mean any detachment process in which the neutral molecule or the molecular structure of the negative ion changes character. The energy balance must then include the chemical energy of

⁹This work has been done in collaboration with Dr. H. W. Ellis of Eckerd College, St. Petersburg, Florida.

the reaction. Reactive detachment and collisional detachment are intertwined in a larger network of ion-molecule reactions (in which electrons may also be interchanged but not detached). The two processes can not be separated since the relative abundances of the species involved are interrelated. However, ion-molecule reactions are extremely complicated and not completely known, so reactive detachment will not be treated here.

Collisional detachment of electrons from negative ions has been studied in both swarm/avalanche experiments^{13,14} and in beam experiments.^{15,16} In two common electron attaching gases, namely O_2 and SF_6 , detachment rates and relative concentrations of ions at low gas-densities have been measured, and these data can be used to evaluate the magnitude of the effect of this electron detachment process.

In SF_6 , calculations based on measured ion mobilities and the electron affinity of SF_6 indicate that, under near-breakdown conditions, electron detachment from anions with relatively low-electron affinities such as SF_6^- is energetically possible. To evaluate the relative importance of SF_6 detachment one must also examine the cross section for such a process, and also determine whether SF_6^- ions are present in large numbers under the conditions in question.

The experimental data of O'Neill and Craggs¹³ can be used for the case of SF_6 . These workers derived the detachment rate coefficient, δ/N , for SF_6^- in SF_6 over a range of E/N around 430 Td ($1 \text{ Td} = 10^{-17} \text{ V-cm}^2$), which is above the uniform field breakdown ratio of electric field, E , to gas number density, N , for SF_6 . Extrapolation to $E/N = 330 \text{ Td}$ (the breakdown ratio) yields $\delta/N \sim 10^{-19} \text{ cm}^2$. Using an estimated value of $0.90 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ for the reduced mobility at 330 Td of the SF_6^- ions (which is an

extrapolation of the mobilities reported by Patterson¹⁷ and by Naidu and Prasad¹⁸ at lower E/N) we obtained a detachment frequency, f , of $2 \times 10^5 \text{ sec}^{-1}$ at atmospheric number density for SF_6 gas. For a negative ion density of $\sim 10^8 \text{ cm}^{-3}$ [§] the number of electrons created by detachment will be $n_i \times f = 10^8 \text{ cm}^{-3} \times 2 \times 10^5 \text{ sec}^{-1} = 2 \times 10^{13} \text{ cm}^{-3} \text{ sec}^{-1}$. And, thus, in a volume of $(1 \text{ mm})^3$ immediately behind a streamer head, about twenty electrons per nanosecond will be detached. The experimental data imply that detachment from SF_5^- and F^- is very small - an observation consistent with the electron affinities:¹⁹ 0.46 eV for SF_6^- ; 2.71 eV for SF_5^- and 3.4 eV and F^- . It should be pointed out that ion clusters have been observed in SF_6 (refs. 9 and 10) and identified as (SF_6^-) $(\text{SF}_6)_n$ with $n = 1, 2$ even at gas pressures below 1 torr at 300°K.

[§] The total number of negative ions created per centimeter, dN_T , by a classical streamer head of $\sim (1 \text{ mm})^3$ size and with 10^8 electrons, moving in SF_6 gas at 1 atm ($N = 2.7 \times 10^{19} \text{ molecules cm}^{-3}$) at an E/N value of 330 Td is

$$dN_T \approx N_e \frac{\eta}{N} N \approx 8.1 \times 10^{10} \text{ cm}^{-1},$$

where the attachment coefficient $\frac{\eta}{N}$ at $E/N = 330 \text{ Td}$ was taken equal to $3 \times 10^{-17} \text{ cm}^2$.¹³ One, then, under these conditions obtains for the number density of negative ions immediately behind the streamer head a value of $\sim 8 \times 10^{12} \text{ cm}^{-3}$. This number density is unlikely, however, since space charge effects seriously distort the local electric field for number densities of the order of 10^{11} cm^{-3} . This crude calculation, nonetheless, indicates that as high a density of negative ions as 10^8 cm^{-3} may not be unreasonable.

Schmidt and Jungblut²⁰ reported pressure-dependent reduced mobilities for ions (at low E/N) at gas pressures from 0.1 to 10.0 bar. Thus, the ion population at atmospheric density may be radically different from that observed by O'Neill and Craggs,¹³ whose measurements were performed at a gas density of $1.62 \times 10^{16} \text{ cm}^{-3}$. The effect of the heavier cluster ion is not clear, since its electron affinity and detachment coefficients are not known. Presumably, its mobility is lower than that of SF_6^- (see refs. 9 and 10 for mobilities of singly and doubly clustered SF_6^-).

O'Neill and Craggs concluded that, for SF_6 at E/N values up to 30% above that of uniform field breakdown, the effect of detachment on electron densities is negligible compared to attachment. If clusters of SF_6^- (SF_6)_n are indeed formed at atmospheric pressure then the lower mobilities (and possibly higher electron affinities) of these clusters would reduce the detachment rate. Thus detachment as a term in the current growth equation can be neglected in SF_6 .

However, in a study of the dynamics of breakdown in SF_6 , Chalmers et al.²¹ have observed dramatic changes in the light emission regions of the early stages of an SF_6 discharge with relatively small changes in voltage. This complexity of the observed phenomena of SF_6 breakdown indicates that there are many processes occurring which influence the dynamics of SF_6 breakdown. Although the electron detachment coefficient is much smaller than the electron attachment coefficient in SF_6 , detachment can be a significant factor in the dynamics of breakdown in a region temporarily devoid of free electrons. The contribution of detachment would then be as a source of free electrons in that region

which then multiply and change the course of the breakdown. If the arguments on electron detachment discussed in this section are correct, the region behind a streamer head will not be devoid of free electrons. In the time scale of a few nanoseconds, detachment of electrons from SF_6^- will allow new avalanches to start immediately behind a streamer head.

Similarly to SF_6 , mean energy calculations and electron affinity data for O_2 show that detachment of electrons from the dominant negative ion species is energetically possible at the E/N value ($E/N = 150 \text{ Td}$) of uniform field breakdown. O'Neill and Craggs¹⁴ have measured the dominant negative ions and derived detachment rates for O_2 at low pressure and E/N values up to and beyond the uniform field breakdown value.

The primary negative ions found in O_2 are O^- , O_2^- , and O_3^- . At the pressures used (up to 60 torr) by Moruzzi⁹ the dominant sources for these ions are:

The electron affinities, EA, of O , O_2 , and O_3 are^{22, 23} 1.465, 0.44, and 1.96 eV, respectively.

Although the electron affinity of O_2 is much less than that of O , the dominant collisional detachment comes from O^- . This anomaly is due to two properties of the collision of O_2^- with O_2 . One is that resonant charge exchange can occur between O_2^- and O_2 . This process leads to high momentum transfer rates. Using drift velocity data from ref. 24

and appropriate formulae from ref. 25, the mean kinetic energy, $\langle \epsilon \rangle$ of O^- and O_2^- at 140 Td is:

$$\text{for } O^-, \langle E_{\text{kin}} \rangle = 0.89 \text{ eV}; \frac{\langle E_{\text{kin}} \rangle}{EA(O)} = 0.61$$

$$\text{for } O_2^-, \langle E_{\text{kin}} \rangle = 0.16 \text{ eV}; \frac{\langle E_{\text{kin}} \rangle}{EA(O_2)} = 0.36.$$

The second property is that the threshold for O_2^- detachment in O_2 measured in ion beam studies is ~ 7.0 eV,²⁶ probably due to the pseudo crossing of the $O_2^- + O_2$ and $O_2 + O_2 + e$ potential curves being high on these curves.

Price et al.²⁷ have measured the growth of current in O_2 as a function of gap separation for pressures from 10 to 400 torr. Attachment and detachment coefficients were derived from current growth measurements up to an E/N value of 150 Td. The fact that detachment coefficients were measured implicitly means that electron detachment is a contributing process in current growth in oxygen at $E/N = 150$ Td. Measurements of the dynamics of breakdown in oxygen by Chalmers et al.²¹ indicated that all breakdown in oxygen is through a streamer mechanism. Detachment of electrons could be a source of free electrons in the development of the streamer.

The situation in air is not clear. Moruzzi and Price²⁸ found no measurable attachment in air for E/N from 90 to 200 Td which they attributed to fast electron detachment involving N_2 . If attachment does occur it is smaller than would be expected from the concentration of oxygen in air.

In summary, electron detachment via collisions between negative ions and neutral gas molecules seems to occur at and above the E/N

values for breakdown in SF_6 and O_2 . In SF_6 , the rate for attachment of electrons is so much greater than for detachment that detachment can be neglected in current growth calculations. However, in the volume immediately behind a streamer virtually no electrons and primarily negative ions are present. In that region electron detachment can play a crucial role in breakdown development.

In O_2 , electron detachment seems to play a role in both current growth and discharge dynamics since at E/N for breakdown in O_2 the detachment coefficient is larger than the attachment coefficient.^{14,27} In air, ion-molecule reaction processes seem to play a dominant role.

E. Dielectric Gas Mixtures with Polar Components

As we have discussed in our last report,¹¹ the scattering cross section for thermal and epithermal electrons by dipolar molecules is a very strong function of the magnitude of the electric dipole moment. We have also shown in ref. 11 that the values of the electron-dipolar molecule scattering cross sections determined² at thermal and near thermal energies can be used to calculate such cross sections to higher energies (~ 6 eV). During this reporting period we explored further the role of electron-dipole scattering in V_g for multicomponent gaseous dielectrics containing a dipolar electron slowing down component and also a dipolar component in combination with a component which scatters subexcitation electrons efficiently via negative ion state(s).

It is important to note that the cross section for electron-dipole scattering at low energies can exceed by far that for indirect electron scattering via negative ion states (NISs). The former also is of a

nonresonant character as opposed to the latter, which is distinctly resonant. Dipole scattering however, is mostly elastic while indirect scattering via NISs can contain a large inelastic component. It should be noted nonetheless that although dipole scattering is mostly elastic, still a substantial fraction of the electrons can be scattered at large angles with respect to the direction of the drift and can thus be slowed down by the electric field to zero energy before reversing direction. They, then, can be removed efficiently by an abundant electron attaching additive possessing a large electron attachment cross section at thermal and near thermal energies.

Some of our findings on multicomponent gaseous dielectrics containing one dipolar component and one electron attaching component are presented and discussed in Section IV. In this section we draw attention to the results in Table 4 where the uniform field breakdown data for mixtures of 30% SF₆ with 70% of an additive X are compared with those of 30% SF₆ with 35% X + 35% N₂. The N₂ has a peak in its $\sigma_{sc}(\epsilon)$ at ~ 2.3 eV due to a NIS at this energy (see Fig. 3). The additives X are: CF₄, CHF₃, CH₂F₂, and 1,1,1-C₂H₃F₃ with electric dipole moments 0, 1.65, 1.97, and 2.32 debye, respectively. The scattering cross section, $\sigma_{sc}(\epsilon)$ for CF₄ should be lower than that for $\sigma_{D=1}$, in Fig. 3; the $\sigma_{sc}(\epsilon)$ for CH₂F₂ would be somewhat larger than the $\sigma_{D=1}$ (Fig. 3). For 1,1,1-C₂H₃F₃ $\sigma_{sc}(\epsilon)$ is expected to be larger than $\sigma_{D=1}$.[#] Values of the ratio $\langle R \rangle = V_s(30\% \text{ SF}_6 + 35\% \text{ X} + 35\% \text{ N}_2) / V_s(30\% \text{ SF}_6 + 70\% \text{ X})$ for the four additives are given in Table 4 and are seen to decrease in the order

$$\text{CF}_4 > \text{CHF}_3 > \text{CH}_2\text{F}_2 > 1,1,1\text{-C}_2\text{H}_3\text{F}_3$$

[#]The measurement of $\sigma_{sc}(\epsilon)$ for CHF₃, CH₂F₂ and 1,1,1-C₂H₃F₃ is in progress.

Table 4. V_g for the binary mixtures 30% SF_6 + 70% X and the ternary mixtures 30% SF_6 + 35% X + 35% N_2 (X = CF_4 , CHF_3 , CH_2F_2 , 1,1,1- $\text{C}_2\text{H}_3\text{F}_3$)

Percentage			V_g (kV) ^a d (inches)									$\langle R \rangle^b$	D_x (debye)
SF_6	N_2	X	0.075	0.125	0.175	0.225	0.275	0.325	0.425	0.525	0.625		
30		70	7.58	12.31	17.15	21.87	26.75	31.50	41.12	50.80	60.33	1.16	0 [X= CF_4]
30	35	35	8.75	14.47	19.87	25.37	30.97	36.55	47.70	58.90	69.98		
30		70	8.00	12.77	17.92	22.93	27.91	33.02	43.07	53.23	63.24	1.12	1.65 [X= CHF_3]
30	35	35	8.74	14.41	20.01	25.63	31.27	36.87	48.18	59.39	70.63		
30		70	7.65	12.46	17.27	22.15	27.01	31.89	41.61	51.39	61.15	1.11	1.97 [X= CH_2F_2]
30	35	35	8.43	13.84	19.35	24.62	30.22	35.52	46.47	57.38	68.42		
30		70	9.56	15.73	21.72	27.92	34.04	40.08	52.32	64.66	76.92	0.99	2.32 [X=1,1,1- $\text{C}_2\text{H}_3\text{F}_3$]
30	35	35	9.49	15.45	21.45	27.49	33.49	39.57	51.67	63.71	75.74		

^aTotal pressure: 500 torr; T = 296K; plane-plane electrode geometry.

^b $\bar{R} = V_g$ (30% SF_6 + 35% N_2 + 35% X) / V_g (30% SF_6 + 70% X) determined from the slopes of V_g versus d data for each mixture.

Fig. 3. Cross section vs electron energy. σ_a are attachment cross sections for the species indicated; σ_T is the total electron scattering cross section for N_2 and $\sigma_D = 1, 2, 3$, and 4 and the theoretical (see text and ref. 11) cross sections for electron-dipole scattering for dipolar molecules with electric dipole moments equal to 1, 2, 3, and 4 debye.

(i.e., with increasing dipole moment). This behavior is understood on the basis of the data in Fig. 3. When the $\sigma_{sc}(\epsilon)$ of N_2 exceeds that of X , the ratio $\langle R \rangle$ is >1 ; when, as in the cases of 1,1,1- $C_2H_3F_3$, the $\sigma_{sc}(\epsilon)$ of N_2 is lower than that of X , $R \lesssim 1$.

These findings demonstrate again the direct effect of large $\sigma_{sc}(\epsilon)$ at subexcitation energies of ν_s and also suggest that a careful combination of gases slowing-down electrons via dipole scattering and via NISs could be beneficial in effecting large values of ν_s . These investigations continue.

III. DESIRABLE SYNERGISMS IN DIELECTRIC GAS MIXTURES

In tailoring dielectric gas mixtures to effect high dielectric strengths and/or to reduce cost, or obtain systems with special properties or satisfy specific industrial needs, two general types of synergistic behavior seem desirable. These are depicted schematically in Fig. 4a, b.

In Fig. 4a, the breakdown voltage, $(V_s)_{\text{mix}}$, of the mixture is plotted as a function of the percentage of A in B . In this type of behavior the breakdown voltage $(V_s)_{\text{mix}}$ of the mixture can exceed that of either component alone for certain compositions. Mixtures exhibiting such properties can comprise two electron attaching components, one electron attaching, A , and one electron slowing down, SD , component or a combination of A 's and/or SD 's. Two examples, taken from our previous report,¹¹ are shown in Figs. 5 and 6. The $(V_s)_{\text{mix}}$ of a 40% SF_6 /60% 1- C_3F_6 mixture is (for $d = 0.325$ in.) ~20% higher than the weighted average V_0 while a 60% $\text{c-C}_4\text{F}_8$ /40% 1- C_3F_6 mixture is ~25% higher than the weighted average value of $(V_s)_{\text{mix}}$. The $\text{c-C}_4\text{F}_8$ /1- C_3F_6 mixtures show better synergism than do the SF_6 /1- C_3F_6 mixtures.

In Fig. 4b another type of synergistic behavior is illustrated schematically. Here one wishes to effect as high an increase in $(V_s)_{\text{mix}}$ as possible with as small an amount of A in B as possible. This kind of synergism has significant practical utility and is characteristic of dielectric gas mixtures made up of one electron attaching component A and one dipolar electron slowing-down component B (See Section IV C). The steeper the increase in $(V_s)_{\text{mix}}$ with the addition of small amounts

Fig. 4. Schematic illustration of two desirable kinds of synergism.

Fig. 5. Direct current breakdown voltage of mixtures of 1-C₃F₆ in c-C₄F₈ (the total pressure of 500 torr, temperature ~295 K, and the electrode geometry plane-plane).

Fig. 6. Direct current voltages of mixtures of 1-C₃F₆ in SF₆ (the total pressure was 500 torr, the temperature ~295 K and the electrode geometry plane-plane).

of A in B the better. As will be seen in Section IVC polar electron slowing down components are good in effecting a sharp increase in V_s with small percentages of A . From the practical point of view this is very advantageous since often excellent electron attaching components with high V_s are expensive, have low vapor pressures or are toxic. In such cases, then, it is desirable to use only a small amount of A and a large amount of an abundant and inexpensive component B .

Although in the two examples of desirable synergistic behaviors illustrated in Fig. 4a,b we used only binary mixtures with one A and one SD component, combinations of more than one A and/or more than one B components could be beneficial both in achieving increased values of $(V_s)_{mix}$ and in reducing breakdown decomposition products and/or inhibiting toxic or other undesirable products (see Section VB).

It is, finally, stressed that synergistic behaviors are not simply a matter of molecular weights or number densities (partial pressures) as has been implied by some authors although in cases of mixtures with similar components, the measured $(V_s)_{mix}$ can be quite close to the partial pressure weighted breakdown voltage. In general, however, the gas mixture simply is *not* the sum of its constituent gases. Some of the basic factors whose careful evaluation can effect desirable synergistic behavior by proper combination of gases are the optimal matching of electron attachment cross sections for maximum removal of electrons, the suitable combination of electron slowing down into energy regions where electron capture is most effective, the formation of secondary negative ions (via charge transfer or ion-molecule reactions) whose ionic stabilities (electron affinities) are larger (and, thus reduce electron detachment),

the reduction of effective ionization, and the avoidance of increased ionization (via Penning ionization processes).

IV. DIRECT CURRENT BREAKDOWN STRENGTHS OF GASES/MIXTURES

A. Unitary Gases

In connection with the work on dipolar gas mixtures, we measured the dc breakdown strengths of the unitary gases CF_4 , 1,1,1- CH_3CF_3 , and CHF_3 at 500 torr using plane-plane electrode geometry. The results are shown in Fig. 7. The breakdown strengths of these gases relative to SF_6 of 1 are 0.27, 0.39, and 0.41 for CHF_3 , CF_4 , and 1,1,1- CH_3CF_3 , respectively. They were found by comparing the slopes of the V_s vs d (P = fixed) for these compounds to that of SF_6 (see Fig. 7). These relative strengths differ somewhat from the ones listed in our previous report in which some of the data used were taken from the literature. Also our previously reported value of 1,1,1- CH_3CF_3 was obtained using data taken with 3/8 in. sphere-sphere electrodes which had a small linear region. The new values from the plane-plane measurements should be much improved over the earlier sphere-sphere data. The CH_2F_2 gas was not studied during this period due to a shortage of this compound. Our conclusions regarding the large synergisms observed in attaching gas/dipolar gas mixtures are unaffected by these changes in the relative breakdown strength data.

B. Comment on Error Analysis

A number of factors enter into the determination of the experimental error in our measurements of the breakdown voltage of a gas.

(1) *Pressure.* Wallace and Tiernan gauges have been used in all but a few very recent measurements to measure the gas pressure. In general there can be as much as ± 10 torr drift in the reading during a run (10-20 breakdowns) due to hysteresis in the gauge, to changes in the gas

Fig. 7. Uniform field dc breakdown voltages for the unitary gases SF_6 , $1,1,1\text{-CH}_3\text{CF}_3$, CF_4 , and CHF_3 . (500 torr; plane-plane electrode geometry.)

temperature caused either by changes in room temperature, or by sparking. In one apparatus we do not have provision for measuring the gas temperature accurately. Hence we do not calculate the number density N from $N = P/kT$, where k is Boltzmann's constant and T is the absolute gas temperature. We usually plot V_g versus d at a fixed P , or V_g versus the product Pd . Thus, there is a related error in V_g due to the uncertainty in P . For pressures of 500 torr this error amounts to $\pm 2\%$ for the worst possible case. The compressibility factor (z) of the gas should also be considered. For many gases at pressures ≥ 3 atm deviations from the ideal gas law can be several percent. For example, at 293°K and z for SF_6 at ~ 3 atm (~ 3 barr) is ²⁹ 0.96 and at ~ 10 atm z is 0.89. However, at 500 torr (~ 0.67 atm) the z is 0.992 which contributes relatively little error.

(2) *Gap Setting.* A varian micrometer feedthrough with a dial readout in thousandths of an inch is used to set the electrode gap. The zero is determined after the chamber has been filled to the test pressure to avoid discrepancies arising from bowing of Flanges, etc. The zero can be found to ± 0.001 in. which is one division on the micrometer dial. The gap itself can be read to within ± 0.0005 in. For an average gap of 0.200 in. these members represent an error of about $\pm 0.75\%$.

(3) *Voltage Measurement System.* A digital voltmeter (HP 3484) calibrated periodically to a National Bureau of Standards (NBS) secondary standard has a quoted accuracy of $\pm 0.01\%$, which is negligible for our purposes. However, the accuracy of the (built in) voltage divider for the 100 kV Spellman power supply is estimated to be $\pm 0.5\%$. The Delta Ray 300 kV power supply which we used on the high pressure, variable temperature apparatus has a quoted accuracy of $\pm 0.1\%$.

(4) *Other Sources.* The uncertainty in electrode alignment for plane-plane uniform field geometry is very difficult to estimate. We have one electrode on an adjustable type tripod arrangement, and we adjust the electrode in such a way that it appears aligned at viewing positions 90° apart. Alignment could be slightly different each time the electrode is installed. Another problem involves the surface roughness of the electrodes. Due to the stored energy in the high voltage (H.V.) power supply, some pitting of the electrode surface results when a spark occurs. The condition of the electrode surface therefore varies from gas to gas as the surface gradually becomes more pitted. When the scatter in the breakdown voltages begins to become noticeably worse, the electrodes are removed and polished.

If we add up the estimated error from all sources (1)-(3) we have [not including (4)] a total error of $\pm 3.25\%$. To assess the effect of the uncertainties discussed in (4), we examined four sets of data on SF_6 at 500 torr on plane-plane geometry. These data were taken under identical conditions over a period of 20 months (from February 1978 to October 1979). During this time the electrodes had been in different stages of surface roughness and had been removed, polished, and aligned several times. These measurements effectively provide for an experimental determination of the error due to all sources. Table 5 gives the results for SF_6

The average slope corresponds to a limiting E/P value of 117.6 V/cm-torr which compares favorably with the value of 117.9 V/cm-torr of Boyd and Crichton.³⁰ We are using our value of 8.94 kV/atm-mm for SF_6 throughout this report and in future work. This usage will prevent small discrepancies that arise from using slightly different values for SF_6

Table 5. SF_6 dc breakdown data taken under identical conditions at 500 torr and with plane-plane electrodes

Run identification	Date	Slope ^{α} (kV/atm-mm)	Intercept kV
A321-A325	2/78	8.898	-0.341
A926-A937	11/78	9.206	0.182
1251-1262	6/79	8.763	0.204
1819-1825	10/79	8.884	0.182

^{α} Average slope 8.94 ± 0.27 kV/atm-mm.

which we measure periodically. The error ± 0.27 kV/atm-mm brackets the slopes and represents a 3.0% error. The good agreement with other published data indicates that the systematic error is probably small. In comparing the two methods of error analysis, we can conclude that our error in a measurement of the breakdown voltage or in the slope of V_s versus Pd is ~ 3 to 3.25%.

C. Gas Mixtures

(i) Binary mixtures with one electron attaching and one dipolar component.

The investigations on the role of dipole scattering in the breakdown voltages of gases has progressed well during this reporting period. A discussion of the physics of electron scattering by dipolar gases appears in Section IIE (see also ref. 11).

A systematic study of the breakdown voltages of mixtures of CF_4 , CHF_3 , and 1,1,1- CH_3CF_3 with SF_6 and $c-C_4F_8$ is nearing completion. Some of our recent data are listed in Table 6 and are plotted in Figs. 9-13. The mixtures with CF_4 , which has a dipole moment of zero, show relatively little synergism with either SF_6 or $c-C_4F_8$ as demonstrated by the nearly linear behavior seen in Figs. 8 and 9. This behavior may be contrasted with that shown in Figs. 10-13 for the dipolar gases. Each of the latter systems show marked synergism with behavior similar to that shown in Fig. 4b of Section III.

The CHF_3 and 1,1,1- CH_3CF_3 are especially sensitive to the addition of $c-C_4F_8$; $\sim 20\%$ $c-C_4F_8$ increases the breakdown voltage by at least a factor of 2 over that of the pure dipolar gas.

Table 6. V_s for binary mixtures of SF_6 and $\text{c-C}_4\text{F}_8$ each with CF_4 , CHF_3 and $1,1,1\text{-CH}_3\text{CF}_3$ [500 torr; plane-plane geometry]

A	SD		(V_s) (kV)							d (inches)
Electron Attaching Compound	Dipolar Compound	Dipole Moment (debye)	A: SD:	0% 100%	20% 80%	40% 60%	60% 40%	80% 20%	100% 0%	
SF_6	CF_4	0.00	5.13	6.92	8.11	9.38	10.30	11.39	0.075	
			8.08	11.09	13.19	15.26	17.01	18.86	0.125	
			10.97	15.33	18.26	21.04	23.53	26.33	0.175	
			13.92	19.58	23.37	27.08	30.29	33.79	0.225	
			16.89	23.75	28.49	32.95	36.97	41.26	0.275	
			19.81	28.05	33.61	38.97	43.71	48.73	0.325	
$\text{c-C}_4\text{F}_8$	CF_4	0.00	22.71	32.21	38.81	44.81	50.38	56.20	0.375	
			5.13	7.60	10.09	11.85	14.17	15.96	0.075	
			8.08	12.38	16.25	19.23	22.96	26.28	0.125	
			10.97	17.12	22.08	26.21	31.05	35.66	0.175	
			13.92	21.63	27.86	32.97	39.36	44.93	0.225	
			16.89	26.22	33.56	39.92	47.39	54.08	0.275	
SF_6	CHF_3	1.65	19.81	30.77	39.38	46.88	55.48	63.39	0.325	
			22.71	35.32	45.10	53.68	63.45	72.37	0.375	
			4.70	7.17	8.19	9.30	10.09	11.39	0.075	
			6.90	11.31	13.24	15.19	16.63	18.86	0.125	
			8.97	15.65	18.42	21.24	23.19	26.33	0.175	
			10.89	19.96	23.61	27.31	29.99	33.79	0.225	
$\text{c-C}_4\text{F}_8$	CHF_3	1.65	12.84	24.15	28.86	33.36	36.63	41.26	0.275	
			14.81	28.47	34.09	39.41	43.23	48.73	0.325	
			16.66	32.75	39.38	45.49	50.00	56.20	0.375	
			4.70	9.01	11.46	13.26	14.94	15.96	0.075	
			6.90	14.59	18.86	21.91	24.43	26.28	0.125	
			8.97	20.10	26.42	30.52	33.95	35.66	0.175	
SF_6	$1,1,1\text{-CH}_3\text{CF}_3$	2.32	10.89	25.69	33.81	39.25	43.17	44.93	0.225	
			12.84	31.19	41.43	47.72	52.49	54.08	0.275	
			14.81	36.77	49.00	56.62	62.22	63.39	0.325	
			16.66	42.35	56.49	65.41	71.77	72.37	0.375	
			6.30	8.90	9.80	9.89	10.84	11.39	0.075	
			9.59	14.44	15.96	16.53	17.85	18.86	0.125	
$\text{c-C}_4\text{F}_8$	$1,1,1\text{-CH}_3\text{CF}_3$	2.32	12.60	19.90	21.99	23.13	24.79	26.33	0.175	
			15.74	25.34	28.09	29.90	31.78	33.79	0.225	
			18.66	30.67	34.38	36.50	38.74	41.26	0.275	
			21.51	35.85	40.29	43.14	45.79	48.73	0.325	
			24.45	41.58	46.82	49.83	52.75	56.20	0.375	
			6.30	10.84	12.98	14.15	15.31	15.96	0.075	
SF_6	$1,1,1\text{-CH}_3\text{CF}_3$	2.32	9.59	18.11	22.05	23.55	25.36	26.28	0.125	
			12.60	25.25	30.81	32.48	34.58	35.66	0.175	
			15.74	32.39	39.77	41.86	43.62	44.93	0.225	
			18.66	39.50	48.59	51.08	52.62	54.08	0.275	
			21.51	46.79	57.54	60.53	61.71	63.39	0.325	
			24.45	53.71	66.25	69.52	70.36	72.37	0.375	

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Fig. 8. Direct current breakdown voltages V_s for mixtures of SF_6 and CF_4 ($D = 0$) as functions of percentage of SF_6 by volume, and electrode gap. (500 torr; plane-plane geometry).

Fig. 9. Direct current breakdown voltages V_s for mixtures of $c\text{-C}_4\text{F}_8$ and CF_4 ($D=0$) as functions of percentage of $c\text{-C}_4\text{F}_8$ in CF_4 by volume and electrode gap. (500 torr, plane-plane geometry).

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Fig. 10. Direct current breakdown voltages V_s for mixtures of SF_6 and CHF_3 ($D = 1.65$ debye) as functions of percentage of SF_6 in CHF_3 by volume and electrode gap. (500 torr; plane-plane geometry).

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Fig. 11. Direct current breakdown voltages V_b for mixtures of $c\text{-C}_4\text{F}_8$ and CHF_3 ($D = 1.65$ debye) as functions of percentage of $c\text{-C}_4\text{F}_8$ in CHF_3 by volume and electrode gap (500 torr; plane-plane geometry).

Fig. 12. Direct current breakdown voltages V_s for mixtures of SF_6 and 1,1,1- CH_3CF_3 ($D = 2.32$ debye) as functions of percentage of SF_6 in 1,1,1- CH_3CF_3 by volume and electrode gap (500 torr, plane-plane geometry).

Fig. 13. Direct current breakdown voltages V for mixtures of $c\text{-C}_4\text{F}_8$ and 1,1,1- CH_3CF_3 ($D = 2.32$ debye) as functions of percentage of $c\text{-C}_4\text{F}_8$ in 1,1,1- CH_3CF_3 by volume and electrode gap (500 torr, plane-plane geometry).

The dipolar gas CH_2F_2 ($D = 1.97$ debye) has not been studied systematically as yet due to difficulty in buying the compound. The large synergism observed in previous measurements,¹¹ however, warrant further investigation of this gas.

(ii) Binary mixtures with two electron attaching gas components

Mixtures of $\alpha\text{-C}_4\text{F}_8$ and SF_6 , both strongly electron attaching gases, have been studied systematically and their breakdown voltages are shown in Fig. 14. We see very little, if any, synergism with these two compounds.

We have also measured the uniform field dc breakdown voltages for a 20% $\alpha\text{-C}_4\text{F}_8$ /80% SF_6 mixture for gaps from 0.075 to 0.800 in. Figure 15 compares this data with that for pure SF_6 and pure $\alpha\text{-C}_4\text{F}_8$, both of which have been extrapolated above 0.325 in. The breakdown voltage of the mixture remains linear with gap up to 0.800 in. at which point it begins to fall slightly below the straight line.

(iii) Binary mixtures of one electron attaching and one electron thermalizing gas.

In our previous report¹¹ we reported on the synergism between the double bonded electron thermalizer gas $1\text{-C}_3\text{F}_6$ and two electron attaching gases, namely SF_6 and $\alpha\text{-C}_4\text{F}_8$. These synergisms were the first in which we observed the breakdown voltage of the mixture to be higher than that of either individual component alone. It was reported and indicated in Fig. 20 of ref. 11 that synergism appears to be much larger at the larger gap spacings and that the maximum synergism for the $\alpha\text{-C}_4\text{F}_8$ mixture occurs at 60% $\alpha\text{-C}_4\text{F}_8$ /40% $1\text{-C}_3\text{F}_6$. These conclusions appear to be questionable due to the fact that the analysis was based on ratios of the V_s values at particular values of the electrode gap, d , rather than on ratios

Fig. 14. Direct current breakdown voltages as functions of percentage of $c-C_4F_8$ in SF_6 by volume and electrode gap (500 torr, plane-plane geometry).

Fig. 15. Direct current uniform field breakdown voltage for 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 mixture compared to pure $c\text{-C}_4\text{F}_8$ and pure SF_6 at electrode gaps from 0.075 to 0.800 in. (500 torr, plane-plane geometry).

of the slopes of the V_s vs d lines. The slopes are preferable when comparing gases to avoid situations in which the intercept is not negligible at the lower breakdown voltages. Figure 16 shows the synergistic behavior for mixtures of 1-C₃F₆ with *c*-C₄F₈ and SF₆. The slope of the measured V_s vs d lines for each mixture was calculated along with the partial pressure-weighted average slope which was determined by using the measured slopes for the pure gases. The ratio of the measured slope to the weighted average slope characterizes the amount of synergism for the mixture. We see that the maximum synergism occurs at ~40% of the attaching gases for both SF₆ and *c*-C₄F₈. The dielectric strength of the 40% *c*-C₄F₈/60% 1-C₃F₆ is 31% higher than that of the weighted average. The synergism is not a function of the electrode gap. There is decidedly a higher synergistic effect for the *c*-C₄F₈ mixtures than for the SF₆ mixtures.

D. Direct Current Breakdown Voltages for Gas Mixtures in Nonuniform Fields

Breakdown voltages for 100% SF₆ and 20% *c*-C₄F₈/80% SF₆ mixtures have been measured on point-plane geometry (1 mm radius point, 14 cm diameter flat plane) for pressures of 760, 1520, and 2280 torr. Figures 17 and 18 give the V_s vs d for pure SF₆ and the mixture for negative point polarity. For pure SF₆ there is a region in which the 1520 torr data is approximately equal to that at 2280 torr. The increase at the lower pressure may be due to corona stabilization. However, a detailed study of corona onset was not made for these measurements. Figure 18 is a similar plot for the mixture 20% *c*-C₄F₈/80% SF₆. In Fig. 19, the data for pure SF₆ and 20% *c*-C₄F₈/80% SF₆ are compared

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Fig. 16. Synergism in 1-C₃F₆. Ratio of the measured slope for the mixture to the partial-pressure-weighted average slope for the component gases for different percentage mixtures of c-C₄F₈ and SF₆ in 1-C₃F₆ (500 torr, plane-plane geometry).

Fig. 17. Direct current breakdown voltages for SF_6 in point-plane geometry as functions of electrode separation and pressure; negative point polarity.

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Fig. 18. Direct current breakdown voltages for 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 in point-plane geometry as functions of electrode separation and pressure; negative point polarity.

Fig. 19. Comparison of breakdown voltages for SF_6 and 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 in point-plane geometry as a function of electrode separation; negative point polarity.

at 1, 2, and 3 atm pressure. In general, the breakdown voltages increase with gap separation. The 3-atm mixture shows considerable improvement over pure SF_6 . Plans are being made to increase further the gap separation for these studies.

Figures 20, 21, and 22 show V_g data for pure SF_6 and for 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 for point-plane geometry but for both negative and positive polarities. For negative polarity, the mixture is superior to SF_6 with the substantial improvement occurring at the highest pressure (2280 torr). For positive polarity the mixture is roughly equal to pure SF_6 for 760 and 1520 torr. At 2280 torr the mixture, though lower than SF_6 at small gaps, approaches SF_6 and may exceed SF_6 at larger gaps. Modifications are under way to extend the measurements to higher gaps. These measurements on dc breakdown complement those on impulse studies discussed in Section VI using the same geometry.

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Fig. 20. Comparison of dc breakdown voltage for SF_6 and 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 in point-plane geometry for positive and negative polarities (760 torr total pressure).

Fig. 21. Comparison of dc breakdown voltage for SF_6 and 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 in point-plane geometry for positive and negative polarities (1520 torr total pressure).

Fig. 22. Comparison of dc breakdown voltage for SF_6 and 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 in point-plane geometry for positive and negative polarities (2280 torr total pressure).

V. ENVIRONMENTAL EFFECTS STUDIES AND DECOMPOSITION ANALYSES

A. Initial Decomposition of Gaseous Dielectrics under Electron Impact

Time-of-flight data were taken for electron-impact-induced fragmentation of the chlorofluorocarbon 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$. The intensity of negative ion fragments as a function of electron energy is shown in Fig. 23. The most abundant ion is Cl^- formed at ~ 0.0 eV. It is compared with the shape of the SF_6^{-*} resonance from SF_6 . Since the shape of the SF_6^{-*} resonance is extremely narrow, the observed shape of the $\text{SF}_6^{-*}/\text{SF}_6$ resonance is instrumental due to the finite spread of electron energies in the beam. The difference between the sharp fall-off of SF_6^{-*} compared to Cl^- indicates the presence of other negative ion resonances in the 0-1 eV electron energy range. These resonances, however, could not be resolved. Nevertheless, this finding is compatible with the results of electron attachment rate data determined from swarm experiments reported earlier.¹¹ The total electron attachment cross section for 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$ showed¹¹ resonance maxima at ~ 0.0 , 0.25, and 0.73 eV. These maxima found in the cross section function are apparently all due to dissociative electron attachment leading to formation of Cl^- .

The data on 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$ is similar to that on 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ presented in our previous report.¹¹ Both compounds yield strong Cl^- ions and weak (by a factor ≥ 1000) F^- and Cl_2^- ions. The ion CCl_3^- which was observed for 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ was not detected for the 1,1,2 isomer. The energy dependence of the yield for $\text{F}^-/1,1,2\text{-C}_2\text{Cl}_3\text{F}_3$ shows two resonances which were shifted to higher energy by ~ 0.8 eV compared to the $\text{F}^-/1,1,1\text{-C}_2\text{Cl}_3\text{F}_3$ data.

Fig. 23. Negative ion intensity versus electron impact energy for fragment ions formed from 1,1,2-C₂Cl₃F₃.

In comparison with work done on a similar molecule 1,1,2C₂Cl₃H₃ (fluorine atoms are replaced with hydrogen atoms) by Johnson et al.,³¹ the Cl₂⁻ intensity relative to Cl⁻ is ~1000 times smaller in the fluorocarbon than in the hydrocarbon. A summary of the negative ion data for the fluorine and hydrogen containing isomers is given in Table 7. Johnson et al.³¹ found that the Cl₂⁻ intensity (relative to Cl⁻) decreased by a factor of ~30 when all three chlorine atoms are bonded to a single carbon atom in the case of hydrocarbons. This was attributed to a smaller net energy resulting from dissociating a chlorine atom from two carbon atoms and subsequent formation of a π bond from the two unshared electrons. Apparently the Cl₂⁻ intensity for the fluorocarbons does not seem to follow this rule.

B. Studies of Final Decomposition Products

Work on the carbon inhibiting mixture 2C₄F₆/SF₆ was completed with quantitative measurements complementing the qualitative results discussed in the previous report.¹¹ To restate the problem, the compound 2C₄F₆ was selected as an example of a perfluorocarbon with high dielectric strength but with the "drawback" of producing carbon deposits when arced. It had been observed in the last report, however, that the addition of SF₆ substantially reduced carbon formation. It has also been brought to our attention recently that Mears and Orfeo³² described several other systems for which carbon inhibition had been observed. In most cases SF₆ was used as an additive to a fluoro or chloro-fluorocarbon for carbon suppression. However, the work of these authors was restricted to visual observation with

Table 7. Fragment negative ion intensities relative to Cl^- (given a value of 1000) for 1,1,1- $\text{C}_2\text{Cl}_3\text{H}_3$, 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$, 1,1,2- $\text{C}_2\text{Cl}_3\text{H}_3$ and 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$

Compound	Fragment negative ion intensity			
	Cl^-	Cl_2^-	F^-	CCl_3^-
$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{Cl} \quad \text{H} \end{array}$	1000 ^a	0.5 ^a		
$\begin{array}{c} \text{Cl} \quad \text{F} \\ \quad \\ \text{Cl} - \text{C} - \text{C} - \text{F} \\ \quad \\ \text{Cl} \quad \text{F} \end{array}$	1000	0.05	0.58	0.015
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{Cl} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	1000 ^a	15.0 ^a		
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{Cl} - \text{C} - \text{C} - \text{F} \\ \quad \\ \text{F} \quad \text{F} \end{array}$	1000	<0.02	0.36	

^aData taken from ref. 31.

no supporting data for the type and quantity of decomposition products formed. Our interests are in determining the role of SF_6 in carbon suppression and in determining the decomposition products formed. Thus the results of qualitative analyses performed by gas chromatography/mass spectrometry (GC/MS) indicated the primary product to be perfluoromethane, CF_4 , and to less degrees other saturated perfluorocarbons, C_2F_6 , C_3F_8 , C_4F_{10} , etc.; and that the CF_4 product increased with increased SF_6 component in the mixture. Since those analyses we acquired a gas chromatograph with thermal conductivity detector and we conducted quantitative studies on 2- C_4F_6 with SF_6 and N_2 additives.

Experimental Method

Gases were mixed in an experimental chamber which was pumped out to a base pressure of $\sim 2 \times 10^{-6}$ torr. The mixing time was ~ 20 min, and the data was found to be independent of the order of mixing. A small ($\sim 250 \text{ cm}^3$) spark cell was filled with the gas mixture to a total pressure of 1000 torr as measured on a 3 atm Wallace and Tiernan gauge.

The spark cell was a Varian 2 3/4 in. cross in which two spherical stainless steel electrodes were set, via an externally controlled linear motion feedthrough, to 0.5 mm gap for all the data reported here. Each discharge was produced by the charging of a capacitor up to breakdown. A run consisted of 2000 sparks which were counted by detecting pulses from a photodiode placed in front of a sapphire window on the spark cell. The sparked gas was subsequently transferred to a stainless steel storage cell and filled to greater than 1 atm pressure with helium in order to facilitate injection into the gas chromatograph (GC) and to minimize leakages of air into the sparked sample.

The sample gas was released into the carrier gas (helium) stream which flowed through a silica gel column in the GC. Several standards were injected to establish retention times for identification. Table 8 lists the gases and their retention times under the conditions noted. Because of the inability to separate the compounds C_2F_4 and C_2F_6 from SF_6 no quantitative data could be obtained when SF_6 was used as the additive. Perfluoropropane ($n-C_3F_8$) could be separated, however. For each mixture that was run, a standard was prepared which contained approximately the same quantities of SF_6 and $2-C_4F_6$ as in the sparked run but with a small known admixture (2-3%) of CF_4 . By checking the response of the GC to the standard, a calibration factor was determined which was then applied to the sample gas to determine the quantity of CF_4 produced in the discharge cell. Since the GC response can vary, a standard was run for each mixture of sparked sample.

Results for $2-C_4F_6/SF_6$

The percentage of CF_4 formed in breakdowns of $2-C_4F_6/SF_6$ mixtures as a function of SF_6 concentration is shown in Fig. 24. At 0%, corresponding to 100% $2-C_4F_6$, a small amount ($\sim 0.24\%$) of CF_4 was measured. This product is attributed to the decomposition of $2-C_4F_6$. As the concentration of SF_6 is increased from 20 to 70%, CF_4 content increased to 2.74% in spite of the fact that the perfluorocarbon component ($2-C_4F_6$) is decreasing from 80 to 30%. The inference is that in this range of mixture compositions carbon is being converted to CF_4 through the addition of SF_6 . From 0 to 20% there is virtually no change in CF_4 content which is probably due to the fact that the amount of CF_4 produced directly from $2-C_4F_6$ has decreased (since $2-C_4F_6$ concentration has decreased).

Table 8. Retention times for compounds in this work. Column was silica gel at 373 K with thermal conductivity detector

Compound	Retention time (min)
CF ₄	0.85
C ₂ F ₆	2.1
SF ₆	2.15
C ₂ F ₄	2.5
C ₃ F ₈	5.5
2-C ₄ F ₆	10.8

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Fig. 24. Concentration of CF_4 (%) formed in sparked mixtures of 2- C_4F_6 with SF_6 (denoted by $\square$) and with N_2 (denoted by $\bullet$) as a function of the concentration of the additive.

slightly while some CF_4 is being created through conversion of free carbon. This point will be demonstrated in the following section in the results on $2\text{-C}_4\text{F}_6/\text{N}_2$ mixtures. Beyond 70% SF_6 , the CF_4 content decreases (see Fig. 24). At its maximum, the CF_4 product increased in concentration by an order of magnitude greater than the amount formed in pure $2\text{-C}_4\text{F}_6$ decomposition. This 30%/70% mixture of $2\text{-C}_4\text{F}_6/\text{SF}_6$ corresponds nicely to the visual observation of the disappearance of deposits, suggesting that this is the optimum carbon inhibiting mixture for this system.

Results for $2\text{-C}_4\text{F}_6/\text{N}_2$

In Fig. 24 are shown the percentages of CF_4 produced for $2\text{-C}_4\text{F}_6$ mixtures in which N_2 replaced SF_6 as the additive. Perfluoromethane is seen to be in very small amounts and to decrease linearly as N_2 concentration is increased, indicating that the CF_4 production (from direct decomposition of $2\text{-C}_4\text{F}_6$) is proportional to the $2\text{-C}_4\text{F}_6$ concentration. The CG/MS analyses of two mixtures, 80% N_2 /20% $2\text{-C}_4\text{F}_6$ and 40% N_2 /60% $2\text{-C}_4\text{F}_6$ (see Fig. 25) showed no difference in the type of products formed in mixtures of N_2 and $2\text{-C}_4\text{F}_6$ from those formed in pure $2\text{-C}_4\text{F}_6$.

By subtracting the N_2 data from the SF_6 data, an estimate of the CF_4 content due to carbon conversion is determined. This is shown in Fig. 26.

Effect of SF_4

One of the products which we have observed in SF_6 decomposition is SF_4 . However, the amount that we detected depended largely on the time elapsed between sparking of the sample and the analysis. This is due to the highly reactive behavior of SF_4 in contact with chamber walls

Fig. 25. Ion chromatograms ($m/e = 69$) of sparked mixtures of (a) 20% $2\text{-C}_4\text{F}_6$ in SF_6 and N_2 and (b) 40% $2\text{-C}_4\text{F}_6$ in SF_6 and N_2 under the same conditions as given in Fig. 24.

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Fig. 26. Percent of CF_4 from carbon conversion as a function of SF_6 concentration in $2\text{-C}_4\text{F}_6$. Inset shows extrapolated carbon content in percent.

and creates a serious uncertainty in the determination of the amount of SF_4 produced. Since SF_4 is a major product of sparked SF_6 and is highly reactive, it was considered a possible candidate as a carbon scavenger in $2\text{-C}_4\text{F}_6/\text{SF}_6$ breakdown. Even so, because most ($\geq 95\%$) of the original SF_6 was not decomposed only a few percent of SF_4 (or some other reactive product) would be responsible for carbon scavenging. Mixtures of 2% $\text{SF}_4/98\%$ $2\text{-C}_4\text{F}_6$ and 10% $\text{SF}_4/90\%$ $2\text{-C}_4\text{F}_6$ were sparked under the same conditions as the $\text{SF}_6/2\text{-C}_4\text{F}_6$ and $\text{N}_2/2\text{-C}_4\text{F}_6$ mixtures. No noticeable reduction of carbon formation was observed, however; the CF_4 content was negligible. This negative result indicates that SF_4 is not the perfluorinating agent in carbon suppression in the present study.

Effect of energy input

The data which has been presented thus far is for energy inputs of 5J/spark (as determined by the discharge of the 0.1 μF capacitor) or 10 kJ total energy (2,000 sparks). A check of the voltage and current waveforms on a storage oscilloscope confirmed the calculated value. The number of sparks was varied for the mixture of $2\text{-C}_4\text{F}_6/\text{SF}_6$ for which CF_4 production was a maximum (i.e., 30% $2\text{-C}_4\text{F}_6$ in SF_6); the percent CF_4 varied linearly with the number of sparks up to 2000 sparks.

A smaller discharge capacitor ($c = 0.01 \mu\text{F}$) was installed and the CF_4 concentration was measured and found to be, within the error limits, proportional to the 5J/spark data.

Concluding Remarks

The results reported in this section suggest that perfluorination of elemental carbon by SF_6 [or SF_6 by-product(s)] is responsible for formation of CF_4 which essentially removes carbon into the gas phase.

In addition, the CF_4 product is chemically inactive (Its $\text{dc } V_s$ is $0.395 V_s(\text{SF}_6)$, see Section IVA). From the $2\text{-C}_4\text{F}_6/\text{N}_2$ data it appears that the direct CF_4 product is proportional to the $2\text{-C}_4\text{F}_6$ starting component in the sample. If it is assumed that the carbon product behaves in a similar manner, then it appears from the data in Fig. 26 that from 70% SF_6 in $2\text{-C}_4\text{F}_6$ and higher concentrations, all available carbon is scavenged; this amount decreased to 0 (for 100% SF_6) linearly. The inset in Fig. 26 repeats the same data points, but with the linear portion extrapolated back to pure $2\text{-C}_4\text{F}_6$, giving an indication of the initial degree of carbonization (i.e., for 100% $2\text{-C}_4\text{F}_6$). The data also suggests that measurement of perfluoromethane may provide a diagnostic tool in SF_6 / perfluorocarbon mixtures for evaluating the carbonization in the system and optimizing the composition of the mixture for carbon inhibition.

C. Quadrupole Mass Spectrometric Studies of Sparked SF₆[#]

It is the purpose of this part of the program to provide an understanding of the mechanism of the decomposition of sulfur hexafluoride (SF₆) in an electrical discharge. This breaks down into four sub-categories: what ions are produced, where are they produced, how are they transported to the sampling aperture of the mass spectrometer, and how varying the experimental parameters affects the kind of ions detected and their intensities.

Some parameters which might have an effect on the observed ions are the nature of the arc (three different sparking modes will be described in the following pages along with the associated variables such as the spark current and voltage, spark duration, and spark repetition rate), the electrode gap, the electrode-to-aperture distance, the aperture diameter, the gas pressure, and the ion source temperature. It must be emphasized that these parameters are not all independently variable, particularly those directly associated with the spark itself.

With the present configuration of the instrument, the electrode gap can be set from 0.1 to ~4.0 mm, the electrode-to-aperture distance may be varied from ~0.5 to 10 mm, the aperture diameter may be chosen as 25, 19, or 10 μ m, the gas pressure may be varied from 0 to 100 kPa (~760 torr), and the ion source temperature may be varied from ambient to 150°C.

Photographs and functional drawings for the mass spectrometer and the spark ion source appeared in the previous semi-annual report.¹¹

[#]Part of this work was done in collaboration with Dr. H. W. Ellis of Eckerd College, St. Petersburg, Florida, on an ORAU Summer Faculty appointment.

Choice of Electrode Material

Various electrode materials have been tried including tungsten, tungsten carbide, tantalum, molybdenum, stainless steel, iridium, copper, and aluminum. There was slight but noticeable wear of the positive electrode for all these materials, probably due to electrode bombardment from the plasma. The negative electrodes of stainless steel, copper, iridium, and tungsten carbide showed very little sign of wear but, unfortunately, they all caused a white to yellow solid deposit to form which blocked the aperture after several hours of operation. In addition, the copper and iridium formed black deposits where exposed to the spark. The aluminum electrodes resulted in rapid (after 15 min) blocking of the aperture with sputtered aluminum from the cathode. The gap distance for tantalum and molybdenum increased from 0.1 to 1.5 mm after several hours of operation because of severe erosion of the negative electrode. In addition white to yellow deposits were produced which eventually blocked the aperture. Tungsten electrodes showed significant cathode erosion after several hours of operation, but did not produce any solid deposits on the aperture. The electrode erosion rate increased with increasing spark energy. All the data included in this report were taken with electrodes made of either tungsten or tungsten carbide.

It was necessary to bake the ion source under vacuum before operation. Solid deposits form both on the aperture and the electrodes, rapidly blocking the aperture and sometimes bridging the electrode gap when the source was not baked. This seems to be due to desorption of moisture adsorbed on the walls of the ion source.

The possible effect of electrode material on the ions produced in the discharge must be considered. For instance, it has been reported by Boudene et al.³³ that the presence of oxygen in tungsten alloy electrodes is a major contributor to the production of SOF_2 in sparked SF_6 . The oxygen and moisture content of the gas has varying effects on the quantities of SOF_4 , SOF_2 , and SO_2F_2 produced depending on the electrode material used.

In addition to reactant species being produced from the electrode material, it is possible that this material might affect such arc parameters as peak current, or, equally important, it could affect the current density at the places on the cathode responsible for the electron emission. This in turn could affect the plasma temperature profiles which might have an effect on the ions observed. Further details about using resistive electrode materials to prevent hot spot formation can be found in a recent paper by Willis et al.³⁴ An interesting discussion on spark formation is contained in a paper by Barreto.³⁵

Ion source operating modes

Three modes of operation for the spark ion source were used. Spark current and voltage vs time characteristics for two of these modes are shown in Fig. 27. In all cases, high voltage was applied to one electrode, with the other remaining at or near ground potential. The aperture was also grounded.

The first mode indicated is a high voltage pulse breakdown. Figure 27a shows the voltage applied to the electrodes, where no breakdown occurs. This waveform was produced using a transistorized automobile ignition system. The pulse polarity could be reversed by

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Fig. 27. Discharge current and voltage characteristics: (a) negative high voltage pulse, no breakdown; (b) negative high voltage pulse with breakdown; (c) current waveform associated with negative high voltage pulse breakdown; (d) voltage applied in positive polarity capacitance discharge showing several breakdowns; (e) voltage during breakdown for positive polarity capacitance discharge; (f) current waveform during breakdown for positive polarity capacitance discharge.

reversing the connections to the primary side of the high voltage coil. The pulse width and rise time were fixed. Figure 27b shows the voltage waveform where breakdown has occurred. The voltage rises normally to -8 kV, where the gap breaks down. The voltage then stabilizes at -600 V for the duration of the pulse. Figure 27c shows the corresponding current waveform. The current rises sharply from zero to a peak of approximately 20 A coincident with the drop in voltage from -8 kV to -600 V. It then proceeds to decay approximately exponentially, reaching zero at the end of the pulse. The magnitude of this current could be lowered by inserting resistors in series with the gap. A resistance of one megohm ($1\text{ M}\Omega$) was typically used in order to increase the useful lifetime of the electrodes.

The second sparking mode used was a simple capacitance discharge circuit. A variable high voltage dc power supply was connected to the electrodes with a high value resistor (10 to $100\text{ M}\Omega$) in series with the high voltage lead. The inherent capacitance of the shielded cables and the spark gap itself (measured to be approximately 40 pF) was charged through the resistor until the gap breakdown voltage was reached, whereupon the capacitor discharged into the gap. The voltage waveform over the course of several breakdowns is shown in Fig. 27d. Figures 27e and 27f show the voltage and current waveforms for a single breakdown on a much faster scale. The current pulse duration is less than 500 nanoseconds. Again, the current onset corresponds to the sharp drop in voltage. The average spark repetition rate was determined by the time constant of the circuit ($R \times C$), although sometimes there was considerable variation (as much as a factor of 2) in the time between breakdowns. Either polarity of voltage could be used.

In the third mode, the set up was the same as for the capacitance discharge mode. When the applied high voltage was negative in polarity, and the electrode gap ≥ 1.0 mm, there existed a range of electrode-to-aperture distances, d , depending on gas pressure, over which no visible spark was observed, although copious quantities of ions could be detected. This is shown graphically in Fig. 28. At small d , bright sparks between the high voltage electrode and the aperture were observed (region B). At much larger distances, bright sparks between the two electrodes could be seen (region A). At SF_6 pressures above 150 torr for intermediate distances, no sparking was observed (region C). This range of distances increased markedly with pressure. Below 150 torr, the sparking underwent an abrupt transition from electrode-to-electrode to electrode-to-aperture sparking. Mass spectra were recorded for regions A and C, but not for B, since the electrode to aperture sparking could cause permanent aperture damage. The voltage across the electrode for region C, which seems to be a corona-type discharge, remained at 2.5 kV, and the current was 2.3 μA dc with a 1 μA peak-to-peak sinusoidal ac component with a period of approximately 20 nsec. This phenomenon was observed only for negative polarity high voltage.

Ions Observed for Various Sparking Modes

Table 9 shows the positive and negative ions observed under five different ionization conditions, the last being the standard electron impact technique, given here only for comparison.

For the negative high voltage pulses both positive and negative ions were observed. Adding a dc bias potential of ± 300 V to the previously grounded electrode had no effect on either the positive

Fig. 28. Plot of electrode to aperture distance versus SF_6 pressure showing three different breakdown regions: (A) visible spark between electrodes (gap of 0.5mm); (B) visible spark between high voltage electrode and the aperture disc; (C) no visible spark. The ions observed in regions A and C are listed; no mass spectra were taken for region B since this condition damages the aperture disc and causes electrical interference with the detection electronics.

or the negative ions observed. A crude time-of-flight spectrum was obtained by monitoring the output of the detector preamp with a storage oscilloscope, using the spark current onset as the trigger. The simple ionic fragments of SF_6 arrived in narrow bundles according to mass, the time width of which was considerably less (by more than one order of magnitude) than the spark duration. A plot of the arrival time of each ionic species *vs* the square root of the mass of the ion resulted in a straight line with a *y*-intercept of $<10^{-6}$ sec. Ion arrival times were not affected by varying *d* over the range of 0.5 to 25 mm, nor by varying the pressure over the range of 25 to 250 torr. Taken together, these results seem to indicate that the transit time of ions through the ion source is very small compared to the transit time through the quadrupole mass spectrometer and that these ions originate within a microsecond of the spark current onset.

For a positive high voltage pulse, only positive ions were observed. Biasing the previously grounded electrode positive by 300 V had no effect on the ion intensity, while a negative 300 V bias significantly decreased the positive ion intensity. Time-of-flight spectra for each of the positive ions showed an initial narrow pulse of ions, as in the negative high voltage pulse case, followed by a spread of ion arrival times equal to the spark pulse duration.

The mass spectra for the negative high voltage pulse yielded simple ionic fragments of SF_6 , such as F^- , F_2^- , SF_5^- , SF_5^+ , etc.; ions due to contaminants in the gas or the ion source, such as Cl^- , NO_3^- , NO^+ , and NO_2^+ , as well as various sulfur oxyfluoride ions, such as SO_2F^- , SO_3F^- , SOF_3^- ,

Table 9. Comparison of ions observed under different ionization conditions

Ion mass	Negative HV pulse		Neg. C.D. Neg. ions	Pos. C.D. Pos. ions	Negative HV corona		Electron impact	
	Neg. ions	Pos. ions			Neg. ions	Pos. ions	Neg. ions ^a	Pos. ions ^b
19	F ⁻		F ⁻		F ⁻		F ⁻	
30		NO ⁺		NO ⁺				
32						S ⁺		S ⁺
35	Cl ⁻		Cl ⁻					
38	F ₂ ⁻		F ₂ ⁻		F ₂ ⁻		F ₂ ⁻	
46		NO ₂ ⁺		NO ₂ ⁺				
51		SF ₂ ⁺				SF ⁺		SF ⁺
62	NO ₃ ⁻		NO ₃ ⁻					
67		SOF ₂ ⁺		SOF ₂ ⁺				
70		SF ₂ ⁺		SF ₂ ⁺		SF ₂ ⁺		SF ₂ ⁺
83	SO ₂ F ⁻							
89		SF ₃ ⁺		SF ₃ ⁺		SF ₃ ⁺		SF ₃ ⁺
99	SO ₃ F ⁻		SO ₃ F ⁻					
105	SO ₃ F ⁻	SOF ₃ ⁺		SOF ₃ ⁺				
108		SF ₄ ⁺				SF ₄ ⁺		SF ₄ ⁺
123	SOF ₃ ·H ₂ O ⁻		SOF ₃ ·H ₂ O ⁻					
124			SOF ₄ ⁻					
127	SF ₅ ⁻	SF ₅ ⁺	SF ₅ ⁻	SF ₅ ⁺	SF ₅ ⁻	SF ₅ ⁺	SF ₅ ⁻	SF ₅ ⁺
143	SOF ₅ ⁻		SOF ₅ ⁻					
146	SF ₆ ⁻		SF ₆ ⁻		SF ₆ ⁻		SF ₆ ⁻	SF ₆ ⁺

^aA. J. Ahearn and N. B. Hannay, *J. Chem. Phys.* **21**, 119 (1953).

^bS. Heller and G. Milne, *EPA/NIH Mass Spectral Data Base*, NSRDS-NBS63 (1978).

$\text{SOF}_3 \cdot \text{H}_2\text{O}^{-\#}$, SOF_5^- , SOF^+ , and SOF_3^+ . Establishing exact relative intensities for these ions is not yet possible since quantitative reproducibility is as yet not satisfactory, though this problem is being intensively studied.

A negative high voltage capacitance discharge spark yielded only negative ions; similarly, the positive high voltage set-up yielded only positive ions. The ion arrival times were not so closely bunched around the discharge current onset, as in the case of the high voltage pulse discharge. Exact comparisons are difficult, however, due to the much shorter current pulse duration and the finite resolving time of the mass spectrometer system. The mass spectra were very similar, indicating again the presence of sulfur oxyfluoride ions.

The mass spectra for the negative high voltage corona mode were quite distinct, however. Both positive and negative ions were detected. These ions were all simple ionic fragments of SF_6 ; no sulfur oxyfluoride ions were observed. The positive and negative ions observed were the same as those found in the standard 70 eV electron impact mass spectra,[†] although the relative intensities were not quite the same.

The Effect of Electrode-to-Aperture Distance on Ion Intensities

Figure 29 shows very preliminary data on the intensities of various negative ions as functions of d for the negative high voltage capacitance discharge mode, using tungsten carbide electrodes and with an SF_6 pressure of 75 torr. It is stressed that this data is very preliminary and not intended to be interpreted as quantitative. They represent averages of several measurements with considerable scatter. Its purpose is to

[#]This identification is not as yet certain, as no other such cluster has yet been identified in these studies.

[†]See Table 9 for references.

show, qualitatively the different dependences on d among the simple ionic fragments of SF_6 (in this case, F^- , SF_5^- , and SF_6^-) and the sulfur oxyfluoride ions ($\text{SOF}_3 \cdot \text{H}_2\text{O}^-$, SOF_4^- , and SOF_5^-). The simple SF_6 fragments fall off rapidly with distance whereas the oxyfluorides fall off much more gradually. This could be interpreted as indicating that the simple fragments are primary products of the breakdown, whereas the oxyfluorides are the products of secondary reactions between the primary products and the gas occurring between the spark channel and the aperture.

Figure 30 is similar to Fig. 29, but for the case of the negative high voltage corona, with tungsten carbide electrodes and a gas pressure of 300 torr, the same warnings apply to this graph as to the graph of Fig. 29. As can be seen, the negative ion intensities do not fall off very rapidly with increasing distance. Also, the F^- intensity is considerable at a distance of 2 mm, whereas in the previous graph no F^- was detected at 1.75 mm. The positive ion intensities, however, drop off very rapidly with distance.

Conclusions

The negative ion behavior from these last two different sparking modes is quite different. In the case of the capacitance discharge, it might be assumed that the ions are produced in the spark channel and then drift to the aperture due to diffusion and the electric fields present. The observations using the capacitance discharge are compatible with this hypothesis since only positive (negative) ions are observed for a positive (negative) high voltage. The positive high voltage pulse data also fits into this scheme. The detection of positive ions from the negative high voltage pulse and corona discharges does not fit into

Fig. 29. Ion intensity versus electrode to aperture distance for a negative high voltage capacitance discharge in SF_6 at a pressure of 75 torr with tungsten carbide electrodes (preliminary data).

Fig. 30. Ion intensity as a function of electrode to aperture distance for negative high voltage corona in SF₆ at a pressure of 300 torr with tungsten carbide electrodes (preliminary data).

this scheme, however. Since a negative 300 V bias was capable of significantly decreasing the observed positive ion intensity from a positive high voltage pulse discharge, the pressure reduced electric field should be sufficient (as much as $40 \text{ V/cm-torr}^{-1}$) to prevent positive ions from the region between the electrodes from reaching the aperture. It is possible therefore, that these ions are being produced outside the arc region by electrons emitted from the negative high voltage electrode.

The effect of the nature of the arc on the nature of the ions observed is also quite marked. As was stated previously, sulfur oxyfluoride ions are only seen in the case of high current sparks, such as the capacitance discharge and high voltage pulse modes. A possible explanation is that these species are formed from oxygen contained in the electrodes, liberated as the electrode surface is eroded. These are not produced in the corona case since there is very little electrode erosion. Again, these oxyfluoride ions could be primary or secondary products, depending on whether or not they are produced directly in the spark or in the region between the spark and the aperture from collisions with oxygen, or oxygen-containing species such as H_2O . This data must still be reconciled with the ion intensity *vs* d results for the various ions observed.

A new high voltage pulse power supply has been purchased which will provide exact control over the sparking parameters, which was not possible with our previous arrangements. It will be possible to vary the pulse

voltage, current, duration, and repetition rate over a wide range. This will greatly facilitate the quantitative observation of the effects of d and the SF_6 pressure on ion intensity. Further details about this power supply are contained in the apparatus section of this report.

Studies of the effects of the amount of O_2 or H_2O in SF_6 will also be undertaken. The effects of other electrode materials, including graphite, will be investigated.

D. Toxicity of $\alpha\text{-C}_4\text{F}_6$

Inhalation tests conducted on mice by Dr. H. Witschi of the ORNL Biology Division indicate that $\alpha\text{-C}_4\text{F}_6$ is toxic at a concentration of 1000 ppm.

VI. IMPULSE STUDIES

In this reporting period we have concentrated on measurements on the gas mixture 20% α -C₄F₈/80% SF₆. In addition to the lightning impulse, point-plane geometry measurements previously reported,¹¹ we have (i) extended the electrode gap to 1.50 in., (ii) measured lightning impulses with 1.5 in. diam sphere-sphere electrodes, and (iii) measured switching surge breakdown for both electrode geometries.

These measurements, along with the dc data with plane-plane and point-plane geometries, show the superior dielectric strength of the mixture compared to pure SF₆.

In Tables 10-13 are listed the V_{50} , V_{NO} and V_{10X} values for the geometries, gaps, pressures, and polarities tested. Figure 31 shows the V_{50} values of pure SF₆ and 20% α -C₄F₈/80% SF₆ for point-plane geometry, 3 atm total pressure, and 1.2/50 μ s waveform. Note the decided superiority of the mixture over pure SF₆ for negative polarity. At larger gaps, the positive polarity SF₆ and mixture V_{50} values are almost the same.

Figure 32 shows the switching surge waveform (200/2000 μ s), point-plane, positive and negative polarity V_{50} values for pure SF₆ and the mixture. Again the mixture is superior.

The sphere-sphere electrode geometry data (representing less non-uniform fields) are difficult to evaluate. Due to the high V_{50} values at 2 and 3 atm total pressure one or two gaps were all that could be measured. With the higher voltages available from our new impulse generator we hope to be able to extend the gap range over which data can be taken.

#The assistance of A. Fatheddin, a graduate student from the University of Tennessee, in these measurements, is acknowledged.

Table 10. V_{50} , V_{NO} and V_{10X} for sphere-sphere electrodes for waveforms of $1.2 \mu\text{s}$ rise and $50 \mu\text{s}$ decay times.

(Pressure in torr) Gas/Gas mixture	Gap (in.)	V_{50} (kV)	V_{NO} (kV)	V_{10X} (kV)	Polarity
760 SF_6	0.250	13.75 ± 0.5	7.5	15.5	Pos.
	0.375	18.0	11.5	20.0	
760 SF_6	0.250	9.0	8.0	12.0	Neg.
	0.375	11.0	9.0	14.0	
	0.500	14.5	10.0	17.0	
	0.625	16.0	11.5	18.0	
	0.750	17.2	12.0	18.0	
	0.875	18.7	13.0	18.5	
152 $\text{c-C}_4\text{F}_8$ 608 SF_6	0.250	9.5	7.5	11.0	Neg.
	0.375	12.2	10.0	14.5	
	0.500	14.0	12.0	16.0	
	0.625	14.5	12.0	17.5	
	0.750	15.0	12.5	17.5	
	0.875	15.5	13.0	16.5	
152 $\text{c-C}_4\text{F}_8$ 608 SF_6	0.250	9.0	7.5	10.5	Pos.
	0.375	13.0	8.0	15.5	
	0.500	17 ± 1	9.0	20.5	

Table 11. V_{50} , V_{NO} and V_{10X} for sphere-sphere electrodes for waveform with 200 μ s rise and 2000 μ s decay times

(Pressure in torr) Gas/Gas mixture	Gap (in.)	V_{50} (kV)	V_{NO} (kV)	V_{10X} (kV)	Polarity
760 SF ₆	0.250	12.2	8.0	14.5	Neg.
	0.375	15.5	10.5	17.5	
	0.500	18.0	13.0	>20.5	
760 SF ₆	0.250	16.0	8.0	20.0	Pos.
	0.375	18.0	14.0	20.0	
152 <i>c</i> -C ₄ F ₈	0.250	12.7	8.0	15.5	Pos.
608 SF ₆	0.375	18.0	11.0	20.0	
152 <i>c</i> -C ₄ F ₈	0.250	12.0	8.0	14.5	Neg.
608 SF ₆	0.375	15.5	12.0	18.0	
	0.500	17.5 $\pm$ 1	15.0	19.5	

Table 12. V_{50} , V_{NO} and V_{10X} for point-plane electrode geometry for waveforms with 200 μ s rise and 2000 μ s decay times

(Pressure in torr) Gas/Gas mixture	Gap (in.)	V_{50} (kV)	V_{NO} (kV)	V_{10X} (kV)	Polarity
2280 SF ₆	0.250	9.0	7.5	9.5	Neg.
	0.375	13.25	9.5	14.0	
	0.500	16.75	14.0	18.0	
2280 SF ₆	0.250	10.0	8.0	11.5	Pos.
	0.375	10.25	8.5	12.5	
	0.500	10.25	8.5	12.5	
	0.625	10.75	9.0	12.5	
	0.750	10.75	8.5	13.5	
	0.875	11.0	8.5	12.0	
1520 SF ₆	0.250	8.5	<7.0	10.0	Pos.
	0.375	8.75	<8.0	10.5	
	0.500	9.25	<8.0	11.0	
	0.625	8.75	7.0	10.5	
	0.750	9.5	7.0	12.0	
	0.875	9.25	7.0	10.5	
1520 SF ₆	0.250	7.0	<6.5	7.5	Neg.
	0.375	10.25	7.5	11.0	
	0.500	13.5	8.0	14.5	
	0.625	16.25	9.0	17.0	
	0.750	19.25	12.0	21.0	
456 <i>c</i> -C ₄ F ₈ 1824 SF ₆	0.250	10.5	7.5	11.5	Neg.
	0.375	14.75	10.0	16.0	
	0.500	19.5	14.0	>20.0	
456 <i>c</i> -C ₄ F ₀ 1824 SF ₆	0.250	9.75	7.0	11.0	Pos.
	0.375	10.5	8.0	11.5	
	0.500	11.25	9.0	12.0	
	0.625	12.0	9.5	14.5	
	0.750	12.75	10.5	15.0	
	0.875	12.75	11.0	16.0	
304 <i>c</i> -C ₄ F ₈ 1216 SF ₆	0.250	8.5	<7.0	10.0	Pos.
	0.375	11.0	7.5	12.0	
	0.625	16.25	10.0	17.5	
304 <i>c</i> -C ₄ F ₈ 1216 SF ₆	0.250	8.0	7.0	8.5	Neg.
	0.500	15.25	9.0	16.0	
	0.625	19.25	13.0	21.0	

Table 13. V_{50} , V_{NO} and V_{10X} for point-plane electrodes for a waveform with 1.2 μ s rise and 50 μ s decay times.

(Pressure in torr) Gas/Gas mixture	Gap (in.)	V_{50} (kV)	V_{NO} (kV)	V_{10X} (kV)	Polarity
2280 SF ₆	0.750	12.25	8.0	14.0	Pos.
	1.00	12.75	10.5	15.0	
	1.250	13.5	<11.0	15.0	
	1.50	13.5	11.5	15.0	
2280 SF ₆	0.750	17.2	12.5	19.0	Neg.
	1.00	19.7	16.0	21.0	
1520 SF ₆	0.875	16.2	15.0	18.0	Neg
	1.00	18.3	16.0	19.5	
	1.25	20.5	17.5	22.0	
1520 SF ₆	0.875	12.5	10.0	13.5	Pos.
	1.00	12.5	10.5	14.5	
	1.25	12.0	<11.0	13.0	
	1.50	12.2	9.0	14.0	
456 <i>c</i> -C ₄ F ₈	0.750	11.5	9.0	12.5	Pos. ^a
1824 SF ₆	1.00	11.25	9.5	12.5	
	1.25	11.75	9.5	13.0	
	1.50	12.25	10.0	14.0	
304 <i>c</i> -C ₄ F ₈	0.875	11.7	10.0	14.0	Pos. ^a
1216 SF ₆	1.0	13.2	11.0	14.5	
	1.25	14.2	12.5	16.5	
	1.5	15.5	13.0	18.5	

^aData with negative polarity was not taken because it was out of range of the impulse generator.

Fig. 31. V_{50} vs electrode spacing for pure SF_6 and 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 and 2280 torr total pressure. The impulse waveform has 1.2 μ s rise and 50 μ s decay time (point-plane electrodes). All negative polarity data for the mixture and positive polarity mixture data for 0.250 to 0.875 inch gap are from ref 11 (p. 82). Negative polarity SF_6 data for 0.250 to 0.625 in. gap and positive polarity SF_6 data for 0.250 to 0.875 in. gap are from ref. 12 (p. 36). All other data are from Table 13.

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Fig. 32. V_{50} vs electrode spacing for 2280 torr (3 atm) total pressure pure SF_6 and 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 . The waveform has 200 μ s rise and 2000 μ s decay time (point-plane electrodes).

VII. APPLIED STUDIES

In the last report,¹¹ a new moderating gas (1,1,1- $\text{C}_2\text{F}_3\text{H}_3$) was reported which shows "synergism" with electron attaching fluorocarbons. During this period, the breakdown strengths of electron attaching gases in binary mixtures with 1,1,1- $\text{C}_2\text{F}_3\text{H}_3$ have been tested at a total pressure of one atmosphere in concentric cylinder geometry. Additionally, breakdown studies have begun at higher total pressures (e.g., 4.4 atm) with the new high pressure chamber. The breakdown tests at 4.4 atm are mostly for multicomponent mixtures consisting of approximately 50% electron attaching gas and 50% electron moderating gas. Also, the effect of surface roughness of the inner electrode on V_g has been investigated.

A. Concentric Cylinder Geometry Breakdown Tests with

1,1,1- $\text{C}_2\text{F}_3\text{H}_3$ as the Moderating Gas at a Total Pressure of 1 atm

The breakdown voltages of $\text{SF}_6/1,1,1\text{-C}_2\text{F}_3\text{H}_3$, $\text{C}_2\text{F}_6/1,1,1\text{-C}_2\text{F}_3\text{H}_3$, and $2\text{-C}_4\text{F}_8/1,1,1\text{-C}_2\text{F}_3\text{H}_3$ mixtures with a 0.75-cm smooth inner cylindrical electrode at negative polarity are shown in Fig. 33. In all breakdown data in this section, each point is the mean of at least ten breakdowns with random scatter (standard deviation $\div$ mean) of less than 3%. These curves are characterized by their "synergistic" shapes. The breakdown strengths of the mixtures decrease in the order $2\text{-C}_4\text{F}_8/1,1,1\text{-C}_2\text{F}_3\text{H}_3$, $\text{C}_2\text{F}_6/1,1,1\text{-C}_2\text{F}_3\text{H}_3$, and $\text{SF}_6/1,1,1\text{-C}_2\text{F}_3\text{H}_3$. The "synergism" of fluorocarbon/1,1,1- $\text{C}_2\text{F}_3\text{H}_3$ mixtures makes them superior to fluorocarbon/ N_2 mixtures. The breakdown strengths of $\text{SF}_6/1,1,1\text{-C}_2\text{F}_3\text{H}_3$ are about the same as those of SF_6/N_2 .

The effect of surface roughness has also been studied with these mixtures. Figure 34 presents the breakdown voltages of $\text{SF}_6/1,1,1\text{-C}_2\text{F}_3\text{H}_3$

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Fig. 33. Breakdown voltages for three attaching gas/1,1,1-C₂F₃H₃ mixtures with negative polarity on the 0.75-cm-radius inner electrode.

c-C₄F₈/1,1,1-C₂F₃H₃ and 2-C₄F₈/1,1,1-C₂F₃H₃ mixtures on a 0.75-cm inner electrode which has a 2-in.-long center section with spiral grooves 0.020-in. deep. It can be seen that the breakdown strengths of all the mixtures have been reduced substantially by this degree of surface roughness. However, the SF₆/1,1,1-C₂F₃H₃ mixtures show a distinct characteristic: as the percentage of SF₆ increases, the breakdown strength of the mixture increases, reaching a maximum beyond which it declines again. For example, the breakdown strength of the 40% SF₆/60% 1,1,1-C₂F₃H₃ mixture is about the same as that of pure SF₆, and that of 80% SF₆/20% 1,1,1-C₂F₃H₃ mixture is about 5% higher than for pure SF₆. This implies that SF₆/1,1,1-C₂F₃H₃ mixtures are less sensitive to surface roughness than pure SF₆ and that some of the mixtures are superior to pure SF₆.

B. Concentric Cylinder Geometry Breakdown Tests with 1,1,1-C₂F₃H₃ and N₂ as Moderating Gases at a Total Pressure of 4.4 atm

The breakdown voltages of multicomponent mixtures with N₂ and 1,1,1-C₂F₃H₃ as moderating gases are presented in Table 14 for both smooth and rough inner electrodes. These multicomponent mixtures can be divided into two groups: those with N₂ alone as the electron moderating gas and those with both N₂ and 1,1,1-C₂F₃H₃, as the moderating gases. The breakdown voltage of pure SF₆ and 50% SF₆/50% N₂ are also given for comparison. For a smooth electrode, the data in Table 14 shows that the breakdown voltage of pure SF₆ is higher than that of most of the mixtures with a few exceptions (see Table 14).

With the introduction of inner electrode surface roughness the breakdown voltages dropped substantially. However, the breakdown strengths of multicomponent mixtures did not decrease so much as that

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Fig. 34. Breakdown voltages for three attaching gas/1,1,1-C₂F₃H₃ mixtures with negative polarity on the 0.75-cm-radius inner electrode. Inner electrode has 2-in.-long center section with spiral grooves 0.02-in. deep.

Table 14. Breakdown voltages^a of multicomponent mixtures with N₂ and 1,1,1-C₂F₃H₃ as moderating gases at a total pressure of 3344 torr (4.4 atm)

Percent by pressure						V_{SM}^b (kV)	V_R^c (kV)	$\frac{V_{SM}^d}{V_{SM}(SF_6)}$	$\frac{V_R^e}{V_R(SF_6)}$	$\frac{V_R/V_R(SF_6)}{V_{SM}/V_{SM}(SF_6)}$
SF ₆	c-C ₄ F ₃	2-C ₄ F ₈	2-C ₄ F ₆	N ₂	1,1,1-C ₂ F ₃ H ₃					
100						241.48	161.87	1.00	1.00	1.00
50				50		207.90	135.47	0.86	0.84	0.98
40	10			50		204.82	153.77	0.85	0.95	1.12
40		10		50		205.55	159.22	0.85	0.98	1.15
40			10	50		220.17	168.88	0.91	1.04	1.14
30	10	10		50		223.15	160.74	0.92	0.99	1.08
30		10	10	50		235.37	181.26	0.97	1.12	1.15
30	10		10	50		212.41	166.32	0.88	1.03	1.17
20	10	10	10	50		258.28	187.65	1.07	1.16	1.08
40	10			40	10	215.34	160.55	0.89	0.99	1.11
40		10		40	10	226.03	163.77	0.94	1.01	1.07
40			10	40	10	243.16	168.95	1.01	1.04	1.03
30	10	10		30	20	238.33	175.80	0.99	1.09	1.10
30		10	10	30	20	257.00	184.55	1.06	1.14	1.08
30	10		10	30	20	239.79	180.11	0.99	1.11	1.12
20	10	10	10	20	30	247.80	192.77	1.03	1.19	1.16

^aAll voltages measured with negative polarity at inner electrode.

^bBreakdown voltages with smooth inner electrode, V_{SM} .

^cBreakdown voltages with a groove depth of 0.02 in., V_R .

^d $V_{SM}(SF_6) = 241.48$ kV.

^e $V_R(SF_6) = 161.87$ kV.

of pure SF_6 . As a result, the breakdown voltages of all the multi-component mixtures are either comparable to or higher than that of SF_6 . This is clearly seen from the values of the ratios $V_R/V_{R(\text{SF}_6)}/V_{SM}/V_{SM(\text{SF}_6)}$ in Table 14. These ratios compare the effect of roughness on each mixture to the effect of roughness on SF_6 . Every fluorocarbon mixture has a ratio greater than one, which implies that it is less sensitive to surface roughness than pure SF_6 and SF_6/N_2 binary mixtures. Also, from Table 14, those mixtures containing both N_2 and $1,1,1\text{-C}_2\text{F}_3\text{H}_3$ have slightly higher breakdown voltages than those mixtures containing only N_2 .

C. Correlation of Calculated Maximum E -Fields with Observed Breakdown Voltages

An existing computer program³⁶ has been used to calculate the E field in the concentric cylinder gap with the end conditions of our experiment, especially the maximum field, on the central surface of the inner electrode. These results can be compared to the theoretical values assuming infinitely long cylinders (hence no end field fringing) and it can be shown that fringing at the ends of the electrodes reduced the maximum E field by 3.3, 5.5, and 9.0% for the inner electrodes of respective radii 1.4, 0.75, and 0.4 cm.

It is interesting to use these actual maximum E fields to predict, for a given gas, the ratio of measured breakdown voltage on two different inner electrodes. If we assume for the moment that each breakdown occurs for maximum E field equal to the critical field of the gas, then for two electrodes the ratio of maximum E fields should be inverse to the ratio of observed breakdown voltages. This comparison is made in

Table 15 for three electrodes and three gases, e.g., the above assumption would indicate that for each gas

$$\frac{E_{\max}(0.75)}{E_{\max}(0.4)} = \frac{V_s(0.4)}{V_s(0.75)} \quad .$$

However, from the streamer theory of breakdown applied to a cylindrical electrode it is expected that the breakdown voltage V_s would increase above the value where $E_{\max} = E_{\text{critical}}$, and this increment would be greater for more electrode curvature and would be less with greater slope of effective gas ionization coefficient $\bar{\alpha}$ vs E field. The "% of difference" in Table 15 does indeed show the expected sign in 8 of the 9 cases; however, the fluorocarbons show much greater increments than does SF_6 . This indicates that the fluorocarbons have values of $\bar{\alpha}$ less sensitive to E than does SF_6 , which is consistent with our earlier observations on the attachment cross sections of these gases, and which also suggests that the fluorocarbons will be superior to SF_6 in practical systems.

D. Diverter Studies

The trigatron gap previously used to divert energy in gas breakdown tests has been used to study triggered breakdown in air.³⁷ This trigatron was formed by two brass electrodes, each 60% of a 5-in.-diam sphere. Each has a 5/16-in.-diam central hole, the hole in the grounded electrode containing the 1/8-in.-diam tungsten trigger rod, which is insulated inside a quartz tube. The trigger pulse is provided by the Accel automobile ignition system.

The Sorenson HVDC power supply³⁸ used previously for applied testing provides the main gap voltage. It was reinstalled and

Table 15. Correlations between calculated maximum E -fields and observed breakdown voltages at a pressure of one atm

Calculated ratios ^a	$\frac{E_{\max}(0.75)}{E_{\max}(0.4)}:$	$\frac{E_{\max}(1.4)}{E_{\max}(0.75)}:$	$\frac{E_{\max}(1.4)}{E_{\max}(0.4)}:$
	0.8573	1.6066	1.3774
Observed ratios	$V_s(0.40):$ $V_s(0.75)$	$V_s(0.75):$ $V_s(1.4)$	$V_s(0.4):$ $V_s(1.4)$
SF ₆	0.9237	1.5103	1.3951
% difference ^b	+7.75	-5.99	+1.29
c-C ₄ F ₈	0.9774	1.6650	1.6274
% difference	+11.24	+3.64	+18.15
2-C ₄ F ₈	0.9669	1.7223	1.6654
% difference	+12.79	+7.20	+20.91

^aFor equal applied voltages. Ratios determined by a computer calculation of the field assuming the same applied voltage between center conductor and ground electrode for each radius of the center conductor.

$$\text{b } \% \text{ difference} = \frac{\text{observed ratio} - \text{calculated ratio}}{\text{calculated ratio}}$$

recalibrated, with the finding that the nonlinearity in its overall calibration curve was due to the resistor internal to the Sorenson, and not due to the auxiliary external resistor.

For a 1-in. gap with polarities for trigger and high voltage electrode (relative to the grounded electrode) of minus and plus respectively, Table 16 gives typical observed delay times. With the opposite polarities (trigger and high voltage electrode polarities plus and minus, respectively), much shorter times were observed and require more investigation, as is discussed below.

Reliability of triggering was tested for the 1-in. air gap and the two polarity combinations in Tables 17 and 18.

The triggered gap operated well in both cases, but the triggered range was especially wide for respective trigger and gap polarities of positive and negative.

The triggering is under further investigation for negative trigger and positive gap. In this case, it is observed that the main gap breaks down earlier (when triggered) than the formation of the trigger spark itself in the absence of the main gap voltage. This is seen by monitoring the current to the trigger electrode.

The image converter camera has been used to photograph some triggered breakdowns, and a typical result is shown in Fig. 35. Two streamers, one from each electrode, appear to merge just prior to intense breakdown. The main spark contacts the quartz insulator and spills over to the main ground electrode, avoiding the trigger electrode.

The image intensifier is expected soon, and it should help to reveal better the faint streamer activity which produces the triggered spark.

Table 16. Delay times of 1-in. triggered air gap for negative trigger voltage and positive gap voltage

Gap voltage (kV)	Delay between trigger and main sparks (μ s)	Standard deviation (μ s)
40	1800	163
50	398	85
55	140	28
60	4.2	1.8

Table 17. Triggering reliability for a 1-in. air gap with negative trigger and positive gap voltages

Gap voltage (kV)	Probability of triggered breakdown ^a (%)
34	13
35	25
36	35
38	75
40	94
42	100

(Untriggered gap breakdown at 79.08 kV; standard deviation 4kV)

^aFor 100 triggers.

Table 18. Triggering reliability of a 1-in. air gap with positive trigger and negative gap voltages

Gap voltage (kV)	Probability of triggered breakdown ^a (%)
21	5
22	4
24	40
26	91

(Untriggered gap breakdown at 81.3 kV, standard deviation 386 V.)

^aOut of 100 triggers.

This information would lead to better understanding of triggered gap operation. Meanwhile, a chamber is being prepared to house the trigatron for tests in gases other than air.

Fig. 35. Photograph at 2×10^7 frames per second for positive trigger, negative main gap voltage. (Sequence is left lower, left upper, #2 lower, #2 upper, etc.)

VIII. LIQUID DIELECTRICS[#]

Refinement of the experimental procedures used in testing liquids as dielectrics continued during this period. A systematic investigation was considered essential due to the diversity of the results reported in the literature. Specifically, a review monograph³⁹ states:

"During the past fifty years many aspects of breakdown in dielectric liquids have been extensively investigated and there now exists a large amount of published data on the subject. However the measurements of many independent workers show large variations and often appear to be in complete disagreement. As a result there is a diversity of opinion on the breakdown process and several theories are currently in vogue, each offering different explanations for the mechanism of breakdown."

In view of the lack of understanding of the breakdown phenomena in liquids and our desire to obtain consistent, reproducible results, we investigated numerous parameters which affect breakdown measurements.

One of the most important parameters affecting breakdown is the presence of impurities or contaminating particles. To remove these, a thorough procedure for cleaning the electrodes and test cell has been developed. First, the electrodes are buffered using a high-speed polisher. Then the test cell, its connecting flanges, and the electrodes are placed in an ultrasonic bath of distilled water for 30 min.

[#]This work was carried out in collaboration with J. G. Carter and D. Maughan, a graduate student from the University of Tennessee.

This step is followed by a sequence of rinses: tap water, distilled water, acetone, distilled water filtered to 15μ , distilled water filtered to 5μ , and then alcohol filtered to 5μ . Finally, these items are assembled and placed in a vacuum oven heated to $\sim 150^{\circ}\text{C}$ for 1 hr. The test cell and electrodes are then connected to the experimental apparatus which is heated at $\sim 150^{\circ}\text{C}$ and pumped to a pressure of 10^{-7} torr using a diffusion pump. Since this procedure has been adopted and 0.5μ in-line filters installed, no solid particles were observed in the test cell during breakdown experiments.

Two changes were made in our apparatus to ensure the accuracy of the data. First, a new high voltage power supply was calibrated with a precision electrostatic voltmeter. This action confirmed that our previous and present voltage measurements are accurate. Secondly, a new digital voltmeter was installed to exploit the capability of our electronic controller to automatically hold the voltage reading on breakdown. This change did, however, permit radio frequency interference between the spark and the digital circuitry of the voltmeter. To eliminate this problem, better grounding straps were used and feedthroughs were added to the shielding surrounding the electronic units.

Conditioning of the electrodes was apparent in these studies since generally lower breakdown values with much scatter (standard deviation/mean) were evident for the first 20-30 breakdowns. Then a series of consistent data was obtained until 200 or more breakdowns occurred when the readings dropped, probably due to a deterioration of the electrodes or an accumulation of by-products.

One variable of particular interest which affects the breakdown is the rate of rise of the applied voltage. For *n*-hexane ($n\text{-C}_6\text{H}_{14}$) at a gap of 0.10 mm, very slow rates (1.7 kV/min) produced breakdown values with a mean field of 0.76 MV/cm and a scatter of 13.5%. This scatter was 13.2% at a mean field of 0.75 MV/cm when the rate was increased to 4.5 kV/min. At 20 kV/min, a mean field of 0.77 MV/cm and a scatter of 11.9% were observed. Perhaps the slower rates permit thermal activity to dominate the breakdown process and allow greater scatter in the data. Further investigation using 1.7 kV/min is planned at a later date, but the 20 kV/min rise rate is presently being utilized for experiments to provide consistent data with a minimum of scatter. Rates much higher than 20 kV/min approach the pulse technique discussed in our previous report.¹¹

The effect of electrode separation of the spheres was investigated for *n*-hexane. Table 19 shows a slight decrease in breakdown strength as the separation is increased with a leveling off at 0.20 mm. These findings are in agreement with Maksiejewski and Tropper⁴⁰ except our readings are generally 0.2 MV/cm higher. The readings at a gap of 0.10 mm are also higher than those obtained by us during the rise rate studies but we attribute this in both cases to a more thorough degassing of the liquid during the separation studies.

Comparative data on perfluoro-*n*-hexane ($n\text{-C}_6\text{F}_{14}$) has been obtained under the identical conditions as the electrode separation experiments and are shown in Table 20.

Table 19. Breakdown strength vs electrode separation for $n\text{-C}_6\text{H}_{14}$

Separation (mm)	0.05	0.10	0.15	0.20	0.30
Mean (MV/cm)	1.05	1.00	0.92	0.82	0.82
Scatter (%)	8.6	11.1	8.2	10.2	10.9

Table 20. Breakdown strength vs electrode separation for $n\text{-C}_6\text{F}_{14}$

Separation (mm)	0.05	0.10	0.15	0.20
Mean (MV/cm)	0.96	0.91	0.85	0.78
Scatter (%)	9.0	9.8	10.1	10.4

As in the case of n -hexane, a decrease in breakdown strength occurs as the electrode separation is increased. For all gaps, the mean values for $n\text{-C}_6\text{F}_{14}$ averaged 8% lower than those for n -hexane. This finding is in contrast with that obtained under different conditions in our preliminary experiments reported previously in which the $n\text{-C}_6\text{F}_{14}$ strength was slightly higher (0.59 vs 0.54 MV/cm). Evidently the excellent scavenging characteristics of fluorocarbon gases are not sufficiently manifest in the gas bubbles formed just prior to breakdown to inhibit the process. However, the gas by-products of the process surely affect breakdown.

Unless additional data on perfluoro- n -hexane exhibits a much higher breakdown strength, it is unlikely that a dramatic difference between it and n -hexane exists.

IX. APPARATUS

New Impulse Generator

The new 400 kV, 4 kJ impulse generator made by Haefely was received in this period. In conjunction with the installation of this generator a Pet microprocessor by Commodore was ordered to automate the data acquisition, the ultimate goal being to have the entire impulse generator-recording system fully automated.

High Power Pulse Generator

A new high power pulse generator has been purchased for the spark ion source of the atmospheric pressure ionization quadrupole mass spectrometer. The Model 605P pulse generator, from Cober Electronics, Inc., is capable of peak pulse powers in the order of 24 kW. The basic unit is capable of putting out 0 to 2.2 kV pulses, at up to 11 A current, with pulse widths from 50 ns to 10 ms, at repetition rates from dc to one million pulses per second, with a duty factor maximum of 1.5%. The output voltage range may be increased to 10 kV by plug-in step-up transformers, at reduced current capacity. The pulse may be of either polarity, and the output may be biased by as much as 5 kV dc from ground potential.

This pulse generator makes it possible to bias both electrodes with respect to ground, which the present pulse generator does not permit. The pulse width is also variable, making it possible to study the effects of arc duration on the ions observed.

X. SECOND INTERNATIONAL SYMPOSIUM ON GASEOUS DIELECTRICS

Plans for the Symposium to be held in Knoxville, Tennessee, on March 9-13, 1980, have proceeded well. Response to the call for papers issued in February resulted in the acceptance of 52 abstracts from 15 countries. Authors were notified in September of the selection of these papers by the international organizing committee. The final program and abstracts booklet will be drafted in October for mailing early in December.

During September, ORNL successfully arranged for Pergamon Press to publish the Symposium Proceedings in hardback form. Working copies of all papers will be distributed at the conference. These papers, including discussion, will then be printed by Pergamon Press following the conference and mailed to all participants.

XI. PAPERS FOR THE SECOND INTERNATIONAL SYMPOSIUM ON
GASEOUS DIELECTRICS

The following five papers will be presented at the forthcoming
Second International Symposium on Gaseous Dielectrics:

1. H. C. Schweinler and L. G. Christophorou, "Calculation of the Electric Field Detachment Rate of Electrons from Mononegative Ions "
2. D. R. James, L. G. Christophorou, and R. A. Mathis, "New Unitary[†] and Multicomponent Gaseous Dielectrics "
3. R. Y. Pai and L. G. Christophorou, "Impulse Breakdown of $c\text{-C}_4\text{F}_8$ + SF_6 and $c\text{-C}_4\text{F}_8$ + SF_6 + N_2 ."
4. C. C. Chan, M. O. Pace, and L. G. Christophorou, "DC Breakdown Strengths of Some Multicomponent Gas Mixtures in Concentric Cylinder Geometries."
5. I. Sauers, L. G. Christophorou, L. C. Frees, and H. W. Ellis, "Aspects of Environmental Effects of Dielectric Gases."

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Appendix

Electron Attachment to Perfluorocarbon Compounds III.
Fragmentation of aliphatic perfluorocarbons of interest to gaseous
dielectrics

I. Sauers, L. G. Christophorou, and J. G. Carter

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Electron attachment to perfluorocarbon compounds. III. Fragmentation of aliphatic perfluorocarbons of interest to gaseous dielectrics^{a)}

I. Sauers, L. G. Christophorou,^{b)} and J. G. Carter

Atomic, Molecular, and High Voltage Physics Group, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 4 April 1979; accepted 26 June 1979)

Resonance nondissociative and dissociative attachment of slow electrons (0–12 eV) to the perfluorocarbons 2-C₄F₆, c-C₄F₆, 1,3-C₄F₆, c-C₄F₈ and 2-C₄F₈ have been studied using a time-of-flight mass spectrometer. All five compounds capture thermal energy electrons and form long-lived parent negative ions with autodetachment lifetimes, τ_a , equal to 6, 7, 9, 6, and 10×10^{-6} sec for c-C₄F₆^{-*}, 1,3-C₄F₆^{-*}, 2-C₄F₆^{-*}, c-C₄F₈^{-*}, and 2-C₄F₈^{-*}, respectively. Except for 1,3-C₄F₆, the yield for the parent negative ions of these perfluorocarbons was more than a factor of 10 larger than that of the fragment ions. The following fragment negative ions were detected: 2-C₄F₆: F⁻, CF₃⁻, C₃F₅⁻; c-C₄F₆: F⁻, C₃F₅⁻, C₄F₇⁻; 1,3-C₄F₆: F⁻, CF₃⁻, C₃F₅⁻, C₄F₇⁻; c-C₄F₈: F⁻, CF₃⁻, C₃F₅⁻, C₄F₇⁻; and 2-C₄F₈: F⁻, CF₃⁻, C₃F₅⁻, C₄F₇⁻, C₄F₉^{-*}, C₄F₇^{-*} (where the asterisk indicates that these fragment ions were found to be long-lived metastables with τ_a values equal to 70, 17, and 7×10^{-6} sec, respectively). Groups of negative ion resonance peaks were found in the 0–2 eV and 4–6 eV electron impact energy range. Fragmentation patterns indicate that multiple decomposition proceeds via common negative ion states of C₄F_x^{-*} (x = 6 or 8). Fragment ions resulting from multiple bond cleavage and molecular rearrangement in the C₄F_x^{-*} systems were observed as well as ions resulting from direct cleavage. From the appearance onsets of some of the fragment ions we determined $\Delta H_f(C_3F_5^-) = -4.4$ eV, $\Delta H_f(2-C_4F_6) = -9.8$ eV, E.A. (C₃F₅) ≥ 1.6 eV, E.A. (C₃F₅) ~ 3.0 eV and other thermochemical data. The relevance of this work to the decomposition of dielectric gases is discussed.

I. INTRODUCTION

A systematic study has been made of parent and fragment negative ions produced by direct electron impact on five perfluorinated four-carbon molecules C₄F_x (x = 6 or 8), namely: perfluoro-2-butene (2-C₄F₆), perfluorocyclobutene (c-C₄F₆), 1,3-perfluorobutadiene (1,3-C₄F₆), perfluorobutene-2 (2-C₄F₈), and perfluorocyclobutane (c-C₄F₈). Because of the high dielectric strengths^{1,2} of these molecules, due primarily to their large electron attachment cross sections at near thermal energies,³ interest has been generated in this laboratory to understand their decomposition patterns in impacts with low energy (0–12 eV) electrons. The potential usage of these perfluorocarbons as gaseous insulation (especially as additives in multicomponent gas mixtures^{1,2,4}), in underground high voltage power transmission lines, switchgear, and substations requires not only knowledge of how efficiently slow electrons are captured by them, but also knowledge of the kind and extent of initial fragment negative ions formed, since extensive dissociative attachment may render the usage of such gases as effective insulants impractical.

The interaction of low energy electrons with the C₄F_x (x = 6, 8) molecules may be envisioned as

where the asterisk indicates excess internal energy.

The parentheses indicate that the system may or may not have excess internal energy and the (') that the scattered electron may have different kinetic energy than the incident one. Channel (1) is indirect elastic and inelastic electron scattering, channel (2) is parent negative ion formation, channel (3a) is (multiple) dissociative attachment, and channel (3b) is dissociative attachment leading to long-lived metastable fragment ions which undergo autodetachment. Of these, Reactions (2) and (3a) and (3b) were experimentally accessible in the present study where we employed a time-of-flight mass spectrometric technique. In addition autodetachment lifetimes of the transient parent ions C₄F_x^{-*} of all compounds were measured.

Of the molecules studied in this work, only for c-C₄F₈ has the fragmentation induced by low-energy electrons been investigated previously.^{5–8} There is also one report⁹ on dissociative attachment to 2-C₄F₈. The three C₄F₆ isomers have not been previously investigated in electron beam work to our knowledge.

In part I³ of this series the results of a swarm study of these molecules on the (total) electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy have been presented and discussed. The magnitudes of $\sigma_a(\epsilon)$ and the resonances observed in their energy dependences were related to their respective molecular structures. It will be seen from the present work that isomers of a given compound fragment differently, thereby giving some insight into the effect of structural dependences of the dissociative attachment process. In some cases,

particularly in the cyclic molecules, negative ion fragments are produced which result from extensive rearrangement.

II. EXPERIMENTAL

The time-of-flight mass spectrometer (TOFMS) used in the present work has been described elsewhere.^{9,10} The electron energy was ramped and the digital output signal, proportional to the negative ion intensity, was stored on a digital signal analyzer. In general, aside from the parent negative ion signals, the fragment negative ion intensities were too weak to allow application of the retarding potential difference (RPD) method, although for some fragment negative ions, it was possible to employ the RPD technique (see Sec. III).

We calibrated the energy scale by comparison of the SF_5^- resonance from SF_6 (at 0.37 eV)¹¹ and the Cl^- resonance from HCl (at 0.8 eV)¹² with the ion of interest.

The gases, 2- C_4F_6 , c - C_4F_6 , and 2- C_4F_6 were obtained from Columbia Organic Chemicals Company, Inc., with purity claimed to be $\geq 95\%$. The c - C_4F_6 and 1,3- C_4F_6 compounds were purchased from PCR Research Chemicals, Inc., with quoted purity of 97% to 99%. In general the negative ion spectra were "clean" with all masses identifiable with specific fragments, except for a small amount of Cl^- impurity ion.

The autodetachment lifetimes of the long-lived ($\geq 10^{-6}$ sec) parent and fragment negative ions were measured, as reported previously.^{9,10} Metastable ions decay into a neutral species plus an electron so that for a specific metastable ion group exiting the collision chamber, the particles reaching the detector are negative ions and neutrals. At some point in the flight tube of the TOFMS the charged component of the beam was swept by deflector plates. The undecayed negative ion signal, N^+ , was determined from the difference of total signal, N^+ , and neutral signal N^0 . Assuming an exponential decay law for the metastable negative ion, τ_a was determined from the relation

$$\tau_a = -t / \ln(N^+/N^T), \quad (4)$$

where t is the time required for the metastable ion to travel from the acceleration grid at the entrance of the flight tube to the deflector plates. An average value of τ_a was determined from the slope of a plot of $-\ln(N^+/N^T)$ vs ion accelerating voltages, i.e., for varying times of flight, t (see Sec. III).

The pressure in the collision chamber was low enough to ensure single collision conditions. The maximum pressure was $\sim 4 \times 10^{-5}$ Torr and the typical operating pressure was $\sim 5 \times 10^{-6}$ Torr. The source temperature was not monitored during these experiments. However, in previous tests, the temperature of the collision chamber was found to be $\sim 60^\circ C$, which is due primarily to the hot filament.¹³ Heating tape maintained the entire TOFMS at an elevated temperature.

FIG. 1. Negative ion intensity as a function of electron impact energy on 2- C_4F_6 . (Note the multiplication factors for the various ions.)

III. RESULTS

A. C_4F_6 isomers

1. 2- C_4F_6

In Fig. 1 the negative ion intensity as a function of electron energy is plotted for each of the negative ions observed for 2- C_4F_6 . The parent ion $C_4F_6^-$ is formed at ~ 0.0 eV and is the most abundant ion below ~ 0.5 eV. The shape of the $C_4F_6^-$ resonance is instrumental. From ~ 0.5 to ~ 8.0 eV the ions $C_3F_3^-$, CF_3^- , and F^- were observed. These fragment ions are weaker by a factor of over 200 relative to the parent ion $C_4F_6^-$. The energy dependence of the yield of all three fragment ions shows a maximum between 5 to 6 eV. This may indicate the formation of a common transient negative ion at ~ 5 eV which decays by multiple dissociative attachment channels [process (3a)].

The four-carbon atoms of the triple bonded 2- C_4F_6 molecules are linear with freely rotating CF_3 groups.¹⁴ Consistent with this structural arrangement is the observed dissociative attachment fragmentation pattern which exhibits simple bond breakage at either a C-F or a C-C bond. Ions resulting from rearrangement are not observed and their absence tends to support a "rigid" structure for the transient negative ion prior to decomposition. It may be possible that the negative ion state at ~ 5 eV is associated with an electronically excited state, i.e., it is an electron-excited Feshbach (core excited) resonance.¹⁵

2. c - C_4F_6

The fragmentation pattern of the cyclic isomer of C_4F_6 is shown in Fig. 2. Also shown in Fig. 2 is the parent negative ion yield which, as for the butyne isomer, is very intense with a resonance maximum at ~ 0.0 eV.

The negative ion fragments include F^- , $C_3F_3^-$, and $C_4F_5^-$. Although the complementary ions F^- and $C_4F_5^-$ can be produced by simple bond breakage, $C_3F_3^-$ requires both multiple fragmentation and reorganization since

FIG. 2. Negative ion intensity as a function of electron impact energy on $c\text{-C}_4\text{F}_6$. (Note the multiplication factors for the various ions.)

$c\text{-C}_4\text{F}_6$ is a cyclic and planar structure¹⁶ in its ground state. If we compare the fragmentation pattern of $c\text{-C}_4\text{F}_6$ with that of $2\text{-C}_4\text{F}_6$, two features are evident: C_4F_5^- is observed in electron attachment to $c\text{-C}_4\text{F}_6$ but it is absent in the case of electron attachment to $2\text{-C}_4\text{F}_6$, while the reverse is true for the CF_3^- fragment ion.

The absence of CF_3^- production from electron collisions with $c\text{-C}_4\text{F}_6$ is not so surprising since no single carbon atom possesses three fluorine atoms, and the production of CF_3^- would require, in addition to the severing of two C-C bonds, the intramolecular transfer of a fluorine atom to a CF_2 radical.

The yields in the negative ion current for all the fragment ions exhibit several maxima which nearly coincide in the vicinity of 4 and 7 eV, which indicates common parent ion intermediates at these energies. Below ~2 eV, C_3F_3^- is the most abundant fragment, just as it is for dissociative attachment to $2\text{-C}_4\text{F}_6$. Above this energy the F^- ion predominates.

3. 1,3- C_4F_6

In striking contrast to the fragmentation patterns of the rest of the perfluorinated molecules studied in the

FIG. 3. Negative ion intensity as a function of electron impact energy on 1,3- C_4F_6 . (Note the multiplication factors for the various ions.)

present investigation, the yield of the dissociative attachment products far exceeds that of the parent negative ion for 1,3- C_4F_6 . Figure 3 shows the parent and fragment ion yields for 1,3- C_4F_6 in the energy range 0–9 eV. Fragment ions which appear in the 0.5–2.5 eV range are C_3F_3^- , F^- , and C_4F_4^- in decreasing order of abundance. Another group of dissociative attachment resonances peaks at ~6 eV and includes the ions C_3F_3^- , F^- , and CF_3^- . It is not clear why the fragment ion C_3F_3^- is more abundant than the parent ion. Structurally 1,3- C_4F_6 is nonplanar¹⁴ with the two ethylene groups lying in different planes. In view of this, a comparison of 1,3- C_4F_6 with perfluoroethylene (C_2F_4) might be informative. Thynne and MacNeill¹⁷ also investigated electron impact on perfluoroethylene and observed no C_2F_4^- ions. Also, they did not observe C_3F_6^- ions from perfluoropropylene at low electron energy. This, along with the low intensity of the parent C_4F_6^- ion in the present study, suggests that in general for the smaller (C_2 and C_3) perfluorocarbon molecules parent negative ion formation is negligible (or entirely absent) and for the larger perfluorocarbon molecules (C_4 and greater) parent negative ion formation becomes the dominant attachment process. It is possible that for the smaller perfluorocarbons the electron affinity is negative. Table I summarizes the

TABLE I. Negative ions for C_4F_6 isomers.

Molecule	C_4F_6^-	C_4F_5^-	C_4F_4^-	C_3F_3^-	CF_3^-	F^-
$2\text{-C}_4\text{F}_6$	~0.0 ^a (96.3) ^b	...	...	1.5 (2.5) 5.0	5.9 (1.1)	5.3 (0.1)
$c\text{-C}_4\text{F}_6$	~0.0 (98.6)	4.8 (0.3) 7.0	...	1.85 (0.9) 4.0 7.0	...	4.1 (0.1) 6.0 6.7 7.6 8.3
1,3- C_4F_6	~0.0 (1.9)	...	0.8 (1.1)	1.45 (64.5) 5.9	5.8 (0.2)	1.6 (32.2) 5.6

^aEnergy of resonance maxima in eV.

^bNumbers in parentheses give the percent of total negative ion production in the 0–12 eV energy range.

FIG. 4. Negative ion intensity as a function of electron impact energy on $c\text{-C}_4\text{F}_8$. (Note the multiplication factors for the various ions.)

results of our study on electron attachment to the three C_4F_8 isomers.

B. C_4F_8 isomers

1. $c\text{-C}_4\text{F}_8$

The negative ions produced by electron impact on $c\text{-C}_4\text{F}_8$ are shown in Fig. 4. The parent ion C_4F_8^- is the only ion observed below ~ 2 eV and its peak intensity is a factor of 10 greater than the most intense fragment ion F^- which has its primary resonance peak at ~ 4.5 eV. The CF_3^- and C_2F_3^- ions have resonance maxima at nearly the same electron impact energy, while the C_3F_5^- ion maximizes at slightly lower energy (~ 4 eV). The F^- yield exhibits a multiplicity of resonances, which is similar to that for $c\text{-C}_4\text{F}_6$. In Table II we compare the present results on $c\text{-C}_4\text{F}_8$ with those of other authors. Although there is some variance in the absolute energies of the peak positions there is a general qualitative

TABLE II. Positions of maxima of negative ions from $c\text{-C}_4\text{F}_8$ (as obtained by various authors).

Ion	Positions of negative ion maximum intensity (eV)				
	Present work	Harland & Thynne ^a	Lifshitz & Grajower ^b	Bibbey & Carter ^c	Kurepa <i>et al.</i> ^d
F^-	4.8	4.95	4.3	4.3	4.5
	6.5	7.4	6.75	6.8	6.9
	7.9	8.6	8.2	8.0	8.1
	10.2	10.8	10.6	9.6	10.4
CF_3^-	4.8	4.95	4.35	5.0	5.0
C_2F_3^-	4.9	4.4	...	...	...
C_3F_5^-	4.1	4.05	4.35	...	...
C_4F_8^-	...	...	...	not measurable	...

^aReference 7, these authors observed the parent ion peak at 0.45 eV.

^bReference 8, these workers used the $\text{SF}_6^-/\text{SF}_6$ resonance at ~ 0.0 eV for energy scale calibration.

^cReference 5.

^dReference 6; this was a total attachment experiment with no mass analysis of the specific ion.

agreement in the energy dependence and the number of peaks in the F^- yield.

The formation of C_3F_5^- , CF_3^- , and C_2F_3^- from a cyclic structure requires multiple bond cleavage plus rearrangement. Clustering of the fragment ion maxima at ~ 4.4 eV indicates the formation of a common negative ion state which multiply fragments. It is also seen that the C_2F_3^- resonance peak at ~ 8 eV coincides with one of the F^- resonance maxima at this energy, indicating a common precursor of these ions which is most likely a core-excited resonance.

2. $2\text{-C}_4\text{F}_8$

Seven (C_4F_7^- , C_4F_6^- , C_3F_5^- , C_3F_3^- , C_2F_3^- , CF_3^- , and F^-) fragment ions were detected when slow electrons (≤ 8 eV) impacted on $2\text{-C}_4\text{F}_8$. The asterisk indicates that the fragment ion was found to be a long-lived ($> 10^{-6}$ sec) metastable (see Sec. III C). This is the only perfluorocarbon molecule we studied for which fragment ions were found to be long-lived metastables.

In Fig. 5 is shown the energy dependence of the fragment ion yields as well as that of the parent negative ion, C_4F_8^- . Of particular interest is the appearance of the fragment ion peaks of C_4F_7^- and C_4F_6^- at ~ 0.0 eV. The very presence of a free electron close to this molecule is sufficient to initiate decomposition. Lifshitz and Grajower⁸ also detected a C_4F_7^- fragment at ~ 0.0 eV. However; they apparently did not observe the C_4F_6^- fragment ion. The F^- resonance maximum found in the present work is approximately 1 eV above that found by Lifshitz and Grajower. However in their measurement of F^- from $2\text{-C}_4\text{F}_8$ no mention is made of the manner in which the energy scale was calibrated.

The ions C_3F_5^- , CF_3^- , C_2F_3^- , and F^- were detected from both C_4F_8 isomers. However C_3F_5^- , CF_3^- , and F^- can be produced from $2\text{-C}_4\text{F}_8$ by simple bond cleavage. Formation of C_3F_3^- and C_2F_3^- on the other hand requires multiple fragmentation and rearrangement. Since the yield

FIG. 5. Negative ion intensity as a function of electron impact energy on $2\text{-C}_4\text{F}_8$. (Note the multiplication factors for the various ions.)

TABLE III. Negative ions for C_4F_8 isomers.

Molecule	Negative ion							
	$C_4F_8^{+*}$	$C_4F_7^{+*}$	$C_4F_6^{+*}$	$C_3F_5^{+*}$	$C_3F_3^-$	$C_2F_3^-$	CF_3^-	F^-
2- C_4F_8	$\sim 0.0^a$ (83.4) ^b	~ 0.0 (1.5)	~ 0.0 (0.4) 0.7	2.3 (0.9) 4.2	5.1 (0.4)	5.4 (0.2)	5.3 (0.6)	5.2 (12.7)
c- C_4F_8	~ 0.0 (56.3)	...	...	4.1 (0.6)	...	4.9 (0.4) 7.9	4.8 (1.1)	4.8 (41.6) 6.5 7.9 10.2

^aEnergy of resonance maxima in eV.^bNumbers in parentheses give the percent of total negative ion production in the 0–12 eV energy range.

of $C_3F_3^-$, CF_3^- , and $C_2F_3^-$ increases while that of $C_3F_5^{+*}$ decreases the possibility exists that at least part of the $C_3F_3^-$, CF_3^- , and $C_2F_3^-$ ions are produced in a secondary dissociation process, i.e., via the decomposition of $C_3F_5^{+*}$. This would require $C_3F_5^{+*}$ to be metastable both with respect to autodetachment and autodecomposition.

The negative ion data for the C_4F_8 isomers are summarized in Table III.

C. Autodetachment lifetimes of long-lived parent and fragment negative ions of C_4F_x ($x = 6$ or 8) molecules

In Fig. 6 are plots of $-\ln(N^+/N^T)$ vs the times-of-flight, t , for the parent negative ions of the C_4F_6 and C_4F_8 isomers, respectively. In Fig. 7 are similar plots for the parent $C_4F_8^{+*}$ and the fragments $C_4F_7^{+*}$ and $C_4F_6^{+*}$ from 2- C_4F_8 . From the slopes of the lines the autodetachment lifetimes for the respective ions were determined and are listed in Table IV.¹⁸ Due to low signal levels the $C_3F_5^{+*}$ lifetime was determined from an average of several $-\ln(N^+/N^T)$ measurements rather than by the slope method used for the other metastable negative ions.

Interestingly the lifetime of the fragment $C_4F_6^{+*}$ ion

FIG. 6. $-\ln(N^+/N^T)$ vs time, t , for M^{+*} formed by $e + M \rightarrow M^{+*}$, where M is (a) $c\text{-}C_4F_6$, $1,3\text{-}C_4F_6$, or $2\text{-}C_4F_6$ and (b) $c\text{-}C_4F_8$ or $2\text{-}C_4F_8$. The numbers in parentheses are the lifetimes in μsec .

from 2- C_4F_8 is twice that of $C_4F_6^{+*}$ produced from direct electron attachment to the three C_4F_6 isomers studied in the present work. The longer lifetime of the fragment $C_4F_6^{+*}$ may be indicative that the fragment $C_4F_6^{+*}$ is formed with a lower state of internal excitation compared with the parent ions formed from the three C_4F_6 isomers studied. The τ_a is known to decrease with increasing internal energy of the metastable negative ion.¹⁹ An alternative interpretation could of course be that the $C_4F_6^{+*}/2\text{-}C_4F_8$ is structurally different from the $C_4F_6^{+*}$ parent negative ions.

IV. DISCUSSION AND CONCLUSIONS

A. Thermochemical data

1. Onsets for the appearance of CF_3^-

In general, for a reaction of the form

the heat of reaction, ΔH_{react} , is given by

$$\Delta H_{\text{react}} = \Delta H_f(X^-) + \Delta H_f(A) - \Delta H_f(AX) + E_{\text{int}}, \quad (6)$$

where $\Delta H_f(X^-)$, $\Delta H_f(A)$, and $\Delta H_f(AX)$ are, respectively, the heats of formation of X^- , A , and AX , and E_{int} is the internal energy of A . The threshold energy or as it is customarily called, the appearance potential (or, to be more precise, the appearance onset, AO) of the ion X^- is determined from the heat of reaction by $AO = \Delta H_{\text{react}} + E_{\text{trans}}$, where E_{trans} is the total kinetic energy of the fragments. Therefore, without adequate knowledge of E_{trans} , E_{int} , $\Delta H_f(AX)$, $\Delta H_f(X^-)$ and $\Delta H_f(A)$, the reaction

FIG. 7. $-\ln(N^+/N^T)$ vs time, t , for metastable negative ions $C_4F_7^{+*}$, $C_4F_8^{+*}$, and $C_4F_6^{+*}$ from electron impact on 2- C_4F_8 . The numbers in parentheses are the lifetimes in μsec .

TABLE IV. Lifetimes of metastable negative ions formed from C_4F_x ($x = 6$ or 8) molecules.

Metastable ion	Parent molecule	τ_a (10^{-6} sec)
$C_4F_6^{+*}$	$c-C_4F_6$	6
$C_4F_6^{+*}$	$2-C_4F_6$	9
$C_4F_6^{+*}$	$1,3-C_4F_6$	7
$C_4F_8^{+*}$	$c-C_4F_8$	10
$C_4F_8^{+*}$	$2-C_4F_8$	6
$C_4F_7^{+*}$	$2-C_4F_8$	7
$C_4F_6^{+*}$	$2-C_4F_8$	17
$C_3F_5^{+*}$	$2-C_4F_8$	70 ^a

^aSlope method not used (see text).

mechanism responsible for producing the detected X^- fragment ion cannot be unambiguously determined. To our knowledge no data exists on E_{int} and the only available information on E_{trans} , are measurements made by Harland and Franklin²⁰ on the translational energies of F^- and CF_3^- from dissociative electron attachment to CF_4 , C_2F_6 , C_3F_8 , and $c-C_4F_8$. Even so, they could not determine uniquely the reaction responsible for F^- formation from $c-C_4F_8$, for example. An additional complication is that the heats of formation of the negative ions require knowledge of the electron affinities of those ions and the electron affinities are often values obtained from other electron impact work and hence serve only as lower bounds.

Translational energies of fragment ions have been reported by Harland and Franklin²⁰ on $c-C_4F_8$. If we take the value of Harland and Franklin²⁰ of 2.6 eV for the E_{trans} of the CF_3^- ion via the reaction

the value of 3.4 eV for the appearance onset of CF_3^- from the present work, and the values -15.7²¹ and -7.0 eV²² for the heats of formation of $c-C_4F_8$ and CF_3^- , respectively, we obtain for the heat of formation of C_3F_5 the value of -7.9 eV. This value of $\Delta H_f(C_3F_5)$ depends of course on the assumptions that (1) the products CF_3^- and C_3F_5 are formed in their lowest electronic and vibrational state, and (2) that Reaction (7) is truly the reaction responsible for CF_3^- production.

We now apply this result to the dissociative attachment process

for which CF_3^- onsets at 3.7 eV. If we take $\Delta H_f(2-C_4F_8) = -16.6$ eV²¹ we obtain for the heat of the reaction $\Delta H_{react} = \Delta H_f(CF_3^-) + \Delta H_f(C_3F_5) - \Delta H_f(2-C_4F_8) = 1.7$ eV. This suggests that the kinetic energy of the fragments E_{trans} , is $AO - \Delta H_{react} = 2.0$ eV. This value is subject to the validity of the assumptions made for the case of $c-C_4F_8$ and also to the assumption that C_3F_5 in Reaction (8) is isomerically identical to C_3F_5 in Reaction (7), (i.e., that their heats of formation are equal).

2. Onsets for the appearance of F^-

In Table V is a list of the appearance onsets of F^- for the perfluorocarbons studied as determined by extrapolation of the linear portions of the first F^- resonance peaks for each of the five perfluorocarbons studied here. The appearance onsets show a wide range 0.5–3.75 eV. For F^- formation we consider reactions of the form

The appearance onset may be expressed in terms of the dissociation energy, $D(F - [M - F])$, the electron affinity of fluorine, $E.A.(F) = 3.75$ eV²⁴ and the excess energy, $E = E_{trans} + E_{int}$, as $AO = D - E.A. + E$. The dissociation energies under consideration are in fact the C–F bond energies which may vary from molecule to molecule depending on the geometry. However, reported values of $D(C-F)$ for a number of perfluorocarbons suggest that the bond energy does not vary greatly and a value of ~5 eV is rather typical.²⁵ The implication, therefore, is that excess energy >2 eV is generated in the reactions involving the production of F^- from $c-C_4F_8$, $2-C_4F_8$, and $2-C_4F_6$. This certainly is not unusual since Harland and Franklin²⁰ determined that over 3 eV of kinetic energy was imparted to the fragments of the reaction

In the $c-C_4F_8$ reaction Harland and Franklin²⁰ found that the excess translational energy was zero, implying that the excess energy went into internal energy of the $c-C_4F_7$ radical.²⁶

TABLE V. Energy onsets for the appearance of F^- from various perfluorocarbons.

Molecule	Perfluorocarbon structure	Onset (eV)
1,3- C_4F_6	<pre> F F F F C=C-C=C F F </pre>	0.5
$c-C_4F_6$	<pre> F F F-C-C-F C=C F F </pre>	2.7
$c-C_4F_8$	<pre> F F F-C-C-F F-C-C-F F F </pre>	3.45
2- C_4F_8	<pre> F F F F F-C-C=C-C-F F F </pre>	3.65
2- C_4F_8	<pre> F F F-C-C≡C-C-F F F </pre>	3.75

Without proper knowledge of the excess energy, E , only an upper bound on the dissociation energy can be obtained from

$$D \leq AO + E. A. \quad (10)$$

Thus using 0.5 eV for the appearance onset for F^- from 1,3- C_4F_6 we obtain a bond energy ≤ 4 eV which is quite low, although thermochemical values as low as 4.3 eV²⁵ have been documented for the C-F bond energy in CCl_3F . Bibby and Carter²⁷ cite a value of 93 kcal/mol (= 4.0 eV) for the C-F bond energy in CF_2-F .

3. Onsets for the appearance of $C_3F_3^-$

The $C_3F_3^-$ fragment ion was produced in electron impacts with each of the C_4F_6 isomers and 2- C_4F_6 . The energy dependence of $C_3F_3^-$ for each of the three C_4F_6 isomers indicated two prominent resonances with maxima in the 1.5–2.0 and 4–6 eV range. A gradual rise in the $C_4F_6^-$ yield in the 2.5–3.5 eV range for c - C_4F_6 and 2- C_4F_6 suggests a third resonance process in this region.

We shall assume that production of $C_3F_3^-$ is through the reaction $e + (2-, c-, \text{ or } 1,3-)C_4F_6 \rightarrow C_3F_3^- + CF_3$, and since nothing is known of the kinetic energy of the fragments we shall assume that it is zero. Using onsets of 0.4 and 0.8 eV for $C_3F_3^-/1,3-C_4F_6$ and $C_3F_3^-/c-C_4F_6$, respectively, and the heats of formation, $\Delta H_f(1,3-C_4F_6) = -9.7$ eV,²¹ $\Delta H_f(c-C_4F_6) = -10.1$ eV,²¹ and $\Delta H_f(CF_3) = -4.9$ eV,²³ we obtain for the heat of formation of $C_3F_3^-$,

$$\Delta H_f(C_3F_3^-) = -4.4 \text{ eV (from } 1,3-C_4F_6) \quad (11)$$

and

$$\Delta H_f(C_3F_3^-) = -4.4 \text{ eV (from } c-C_4F_6) \quad (12)$$

Given an onset of 0.5 eV for $C_3F_3^-/2-C_4F_6$ the heat of formation of 2- C_4F_6 is found to be

$$\Delta H_f(2-C_4F_6) = \Delta H_f(C_3F_3^-) + \Delta H_f(CF_3) - \Delta H_{\text{react}} = -9.8 \text{ eV}.$$

It should be emphasized that in these calculations it has been assumed that the $C_3F_3^-$ ion is structurally the same in each process and that the complementary CF_3 radical is not fragmented.

The $C_3F_3^-$ ion is also produced from 2- C_4F_6 . However, since the remaining neutrals include one carbon atom and five fluorine atoms, the process leading to the production of $C_3F_3^-$ should involve at least three fragments,

etc. The heats of reaction of Reactions (13), (14), and (15) are calculated to be 3.4, 7.3, and 11.2 eV, respectively, given $\Delta H_f(2-C_4F_6) = -16.6$ eV,²¹ $\Delta H_f(CF_4) = -9.6$ eV,²⁸ $\Delta H_f(F) = +0.8$ eV,²⁸ $\Delta H_f(F_2) = 0$ eV,²⁸ and $\Delta H_f(C_3F_3^-) = -4.4$ eV which we determined in the present work. Reaction (13) therefore appears to be responsible for $C_3F_3^-$ formation which exhibits an onset of 3.8 eV.

4. Onsets for the appearance of $C_2F_3^-$

Dissociative electron attachment to both C_4F_6 isomers studied produces $C_2F_3^-$. The proposed two-fragment reaction is:

The appearance onsets of $C_2F_3^-/2-C_4F_6$ and $C_2F_3^-/c-C_4F_6$ are 3.8 and 3.5 eV, respectively. The electron affinity of $C_2F_3^-$ must satisfy the inequality,

$$E. A. (C_2F_3^-) \geq \Delta H_f(C_2F_3) + \Delta H_f(C_2F_5) - \Delta H_f(C_4F_6) - A. O. (C_2F_3^-) \quad (17)$$

given $\Delta H_f(C_2F_3) = -2.0$ eV²³ and $\Delta H_f(C_2F_5) = -9.2$ eV.²³ The minimum electron affinity calculated from Reaction (17) is 1.6 and 1.9 eV using the 2- C_4F_6 and c - C_4F_6 data, respectively. These E. A. values for $C_2F_3^-$ agree fairly well with those reported by MacNeil and Thynne²⁹ (2.0 ± 0.2 eV) and Lifshitz and Grajower⁸ (2.0 ± 0.4 eV).

5. Onsets for the appearance of $C_3F_5^-$

The $C_3F_5^-$ fragment was detected from c - C_4F_6 and 2- C_4F_6 with appearance onsets of 3.0 and 0.8 eV, respectively. In addition, a higher energy peak in $C_3F_5^-/2-C_4F_6$ has an apparent onset at 3.0 eV. The low energy side of the $C_3F_5^-/c-C_4F_6$ resonance is quite broad, possibly indicating a resonance in the same energy region as for 2- C_4F_6 .

If one considers the reaction responsible for production of $C_3F_5^-$ ions to be $e + (2- \text{ or } c-)C_4F_6 \rightarrow C_3F_5^- + CF_3$, then the heat of formation of $C_3F_5^-$ is predicted to be -10.9 eV using the value determined in Sec. IV A 1 for $\Delta H_f(C_3F_5)$. This implies an electron affinity of $C_3F_5^-$ of 3.0 eV which is somewhat higher than other determinations (2.5 ± 0.3 ,³⁰ 2.6 ± 0.4 ,⁸ and 2.7 ± 0.2 eV³¹).

6. Onsets for the appearance of $C_4F_5^-$

The fragment, $C_4F_5^-$, has only been detected in electron impact with c - C_4F_6 . The reaction $e + c-C_4F_6 \rightarrow C_4F_5^- + F$, yields a heat of formation of $C_4F_5^-$ of -7.1 eV, assuming zero kinetic energy in the fragments.

B. Comparison with swarm data

The strong parent negative ion resonances at ~ 0.0 eV observed in the present study for all five molecules investigated are consistent with the large attachment cross sections for thermal and near thermal energies reported in the swarm study of Ref. 3. The poor energy resolution of the present experiment at low energies does not allow a direct comparison of the present data with the swarm-unfolded cross sections of Ref. 3, which showed three resonances below 1 eV, the first one at ~ 0.0 eV.

The swarm-unfolded cross sections³ are total cross sections, i.e., for all ions, parent or fragment, formed. The present work shows that at thermal and near thermal energies the swarm-unfolded cross sections for 2- C_4F_6 , c - C_4F_6 , c - C_4F_6 , and 2- C_4F_6 are principally due to parent negative ions. Those for 1,3- C_4F_6 , however, may contain (Fig. 3) a rather large contribution from fragment negative ions even at thermal ener-

gies. At higher energies, the swarm-unfolded cross sections³ contain varied degrees of contributions from dissociative attachment processes especially for 1,3-C₄F₆ and 2-C₄F₆.

C. Relevance to gaseous dielectrics

Considering the relatively high dielectric strength^{1,2,32} of the five perfluorocarbons studied, their effectiveness in practical electrical systems would depend largely on the extent and nature of their decomposition, resulting from breakdown and/or long periods of high electrical stress. Deterioration of the dielectric by electron impact is certainly an important aspect of gaseous dielectrics since reactions leading to final decomposition products are often initiated by electron-impact produced species which are the precursors of such reactions. The relative abundances of these precursors are a function of the electron energy and recent work^{1,2,4,32} indicates that the energy range of significance is that in the sub-excitation energy region.

The results of the present study are most relevant to gaseous dielectrics. They indicate that *c*-C₄F₆, 2-C₄F₆, and *c*-C₄F₈ are not easily decomposed by electrons having energies similar to those expected under practical gas dielectric conditions. These gases effectively remove electrons via *parent* negative ion formation.

The ultimate test of these and other perfluorocarbon gases is, of course, the analysis of the final stable decomposition products resulting from breakdown or from long periods of high electrical stresses. Analyses of decomposition products for 2-C₄F₆ following repeated breakdowns showed^{2,32} that this molecule is a relatively stable dielectric. Concerning the exposure of insulating gases to long periods of electrical stresses, gases which attach electrons dissociatively in the low energy region (≤ 1 eV) may decompose extensively, particularly when the average electron energy is raised sufficiently to enhance the dissociative attachment processes. The present work on 2-C₄F₆ which shows that this molecule attaches near thermal energy electrons dissociatively to form C₄F₅⁻ and C₄F₆⁻ fragments would indicate that this compound may not retain its integrity under prolonged electrical stress conditions. Similar arguments may apply to 1,3-C₄F₆.

D. Conclusions

Certain general observations can be made from the present work. With the exception of 1,3-C₄F₆, the *parent* negative ion for all perfluorocarbons studied is by far the most abundant. In all cases the *parent* negative ion is formed at ~ 0.0 eV electron impact energy and its lifetime against autodetachment at this energy is on the order of 10^{-5} sec. Peaks of negative ion fragments are grouped at 0–2 and 4–6 eV, indicating common negative ion resonances in these energy ranges. In the noncyclic compounds, fragments resulting from direct cleavage dissociated preferentially at the single bonds rather than at the multiple (double and triple) bonds. For cyclic compounds where fragments (other than F⁻) require the severing of at least two bonds, rearrangement processes occur.

TABLE VI. Summary of thermochemical data deduced in this work.

Reaction	Thermochemical results
$e + c\text{-C}_4\text{F}_8 \rightarrow \text{CF}_3^- + \text{C}_3\text{F}_5$	$\Delta H_f(\text{C}_3\text{F}_5) = -7.9$ eV
$e + 2\text{-C}_4\text{F}_8 \rightarrow \text{CF}_3^- + \text{C}_3\text{F}_5$	Excess energy of fragments: ~ 2.0 eV
$e + 1,3\text{-C}_4\text{F}_6 \rightarrow \text{F}^- + \text{C}_4\text{F}_5$	$D(\text{C}-\text{F}) \sim 4$ eV
$\{e + c\text{-C}_4\text{F}_6 \rightarrow \text{C}_3\text{F}_3^- + \text{CF}_3\}$ $\{e + 1,3\text{-C}_4\text{F}_6 \rightarrow \text{C}_3\text{F}_3^- + \text{CF}_3\}$	$\Delta H_f(\text{C}_3\text{F}_3) = -4.4$ eV
$e + 2\text{-C}_4\text{F}_6 \rightarrow \text{C}_3\text{F}_3^- + \text{CF}_3$	$\Delta H_f(2\text{-C}_4\text{F}_6) = -9.8$ eV
$e + 2\text{-C}_4\text{F}_8 \rightarrow \text{C}_3\text{F}_3^- + \text{CF}_4 + \text{F}$	$\Delta H_{\text{react}} = 3.8$ eV
$e + 2\text{-C}_4\text{F}_8 \rightarrow \text{C}_2\text{F}_3^- + \text{C}_2\text{F}_5$	E. A. (C ₂ F ₃) ≈ 1.6 eV
$e + c\text{-C}_4\text{F}_8 \rightarrow \text{C}_2\text{F}_3^- + \text{C}_2\text{F}_5$	E. A. (C ₂ F ₃) ≈ 1.0 eV
$e + 2\text{-C}_4\text{F}_8 \rightarrow \text{C}_3\text{F}_3^- + \text{CF}_3$	E. A. (C ₃ F ₃) = 3.0 eV
$e + c\text{-C}_4\text{F}_8 \rightarrow \text{C}_4\text{F}_5^- + \text{F}$	$\Delta H_f(\text{C}_4\text{F}_5) = -7.1$ eV

Although F⁻ and [M-F]⁻ ions are weak for the molecules studied, they are by far the most abundant (especially F⁻) for saturated perfluorocarbons.

The yield and multiplicity of fragment ions depend very strongly on molecular geometry. The linear and coplanar molecules exhibit less fragmentation than the cyclic and twisted molecules, which is an indication of the pronounced effects of geometrical configuration. The double-bonded systems which we studied undergo more fragmentation at low energies compared with cyclic and triple-bonded systems.

The negative ions F⁻ and [M-CF₃]⁻ were observed for all five perfluorocarbons studied. In all but one case (*c*-C₄F₈), the [M-CF₃]⁻ ion yield exhibited two distinct maxima, with the low energy maxima lying in the 1.5–2.5 eV range and the high energy maxima in the 4–6 eV range. Multiple peaks in the F⁻ ion yield were found for the two cyclic molecules (*c*-C₄F₆ and *c*-C₄F₈). Although their energy dependences differ, they both show an F⁻ yield maximizing in the 4–5 eV region and exhibit lower local maxima at increasing electron energy.

The presence of a number of ions such as C₃F₃⁻/*c*-C₄F₆, CF₃⁻/1,3-C₄F₆, and CF₃⁻/*c*-C₄F₈ implies that the decay of the C₄F₈⁻ ion follows reorganization.

Thermochemical values calculated from appearance onsets of selected fragment ions are summarized in Table VI.

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^bAlso Department of Physics, University of Tennessee, Knoxville, TN, 37916.

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