

# MASTER

## THE ROLE OF ELECTRON SWARM STUDIES IN THE DEVELOPMENT OF GASEOUS DIELECTRICS<sup>1</sup>

L. G. Christophorou<sup>2</sup>

Atomic, Molecular and High Voltage Physics Group,  
Health and Safety Research Division, Oak Ridge National  
Laboratory, Oak Ridge, Tennessee 37830

### ABSTRACT

Recent knowledge provided by swarm studies allowing control of the number densities and energies of free electrons in electrically stressed gases is highlighted. This knowledge aided the discovery of new gas dielectrics and the tailoring of gas dielectric mixtures. The role of electron attachment in the choice of unitary gas dielectrics or "electronegative" components in dielectric gas mixtures, and the role of electron scattering at low energies in the choice of buffer gases for mixtures is outlined.

### KEYWORDS

Electron swarms; ion swarms; gas dielectrics.

### INTRODUCTION

Electron and ion swarm studies--along with electron and ion beam studies--have unravelled and quantified the basic processes connected with electron and ion interactions in gases which constitute the foundation of many technologies (Christophorou, 1980a). Based on these studies it is now possible to optimize in electrically stressed gases the electron and ion densities and their energies and to enhance or to inhibit the critical reaction(s) of importance for the particular application.

In this paper the role of electron (and ion) swarm studies in the development of high-voltage insulating gases is highlighted. There is a pressing need for gaseous dielectric materials to conserve energy and to meet the multiple needs of the power industry in energy transmission and distribution. Distinct advantages over overhead transmission lines (Christophorou *et al.*, 1981a,b; Christophorou, 1980b) and considerable energy savings (by increasing transmission line voltages to perhaps

<sup>1</sup>Research sponsored by the Division of Electric Energy Systems, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

<sup>2</sup>Also Department of Physics, The University of Tennessee, Knoxville, TN 37916.

≥1.5 MV) can be realized by using compressed gas insulated enclosed systems. Gaseous dielectrics can, of course, be used in virtually any application which requires electrical insulation (e.g., high-voltage power supplies, switch gear, Van de Graaff accelerators and other research equipment).

#### BASIC KNOWLEDGE PROVIDED BY ELECTRON SWARM STUDIES

The basic quantities measured in electron swarm studies are the electron transport coefficients  $w$  and  $D/\mu$  ( $D_T/\mu$  and  $D_L/\mu$ , perpendicular to and along the applied electric field, respectively) which are functions of  $E/N$ . From these coefficients, physical quantities are deduced which can serve as probes of the effects of molecular structure on the dielectric strength and can aid the choice and tailoring of gaseous dielectrics. Such quantities include the mean electron energy,  $\langle \epsilon \rangle$ , the mean fractional energy loss per collision, the mean electron relaxation time (all as functions of  $E/N$ ), and the mean scattering cross section at thermal energies. Momentum transfer cross sections,  $\sigma_m(\epsilon)$ , inelastic scattering cross sections, and electron energy distribution functions,  $f(\epsilon, E/N)$ , can be calculated from the transport coefficients and appropriate theory, but such knowledge is presently rather limited for polyatomic gases.

Additionally, electron swarm studies provide valuable information on the total electron attachment cross section,  $\sigma_a(\epsilon)$ , especially at subexcitation energies. And at high  $E/N$ , from measurement of the current growth preceding breakdown, the primary ionization coefficient,  $\alpha$ , and the effective electron attachment coefficient,  $\eta$ , can be determined as a function of  $E/N$ . These latter coefficients are related to the respective attachment,  $\sigma_a(\epsilon)$ , and ionization,  $\sigma_i(\epsilon)$ , cross sections and  $f(\epsilon, E/N)$  by

$$\alpha/N = (2/\pi)^{1/2} w^{-1} \int_I^{\infty} f(\epsilon, E/N) \epsilon^{1/2} \sigma_i(\epsilon) d\epsilon, \quad (1)$$

$$\eta/N_a = (2/\pi)^{1/2} w^{-1} \int_0^{\infty} f(\epsilon, E/N) \epsilon^{1/2} \sigma_a(\epsilon) d\epsilon, \quad (2)$$

where  $I$  is the ionization onset energy,  $N$  is the total number density, and  $N_a$  is the electron attaching gas number density.

Finally, electron and ion swarm studies provide valuable knowledge on the stability, energies, destruction mechanisms, and reaction pathways of negative, as well as of positive, ions in dielectric gases.

#### FROM BASIC RESEARCH TO APPLICATION

##### What Makes a Good Dielectric?

In a gas under an applied electric field, as the voltage is increased, the ever-present free electrons gain energy and their  $f(\epsilon, E/N)$  shifts to higher  $\epsilon$ . When a sufficient fraction of the electrons can induce ionization, gas breakdown occurs.

The most effective way to prevent electrons from initiating breakdown is the removal of the electrons from the dielectric. An effective way of achieving this is to attach the electrons to the gas molecules forming negative ions. The unattached electrons must be slowed down and be prevented from ionizing the gas and triggering breakdown.

The gas dielectric strength, therefore, can be optimized by effective control of the energies and number densities of the free electrons present, i.e., by maximizing the quantity

$$\int_0^{\infty} \sigma_a(\epsilon) f(\epsilon, E/N) d\epsilon, \quad (3)$$

and by minimizing the quantity

$$\int_1^{\infty} \sigma_i(\epsilon) f(\epsilon, E/N) d\epsilon. \quad (4)$$

To maximize (3)  $\sigma_a(\epsilon)$  should be as large as possible over as wide an energy range as possible, and since  $\sigma_a(\epsilon)$  increases with decreasing  $\epsilon$  (Christophorou, 1980a, 1978), to optimize (3)  $f(\epsilon, E/N)$  must be shifted to as low energies as possible. To minimize (4),  $\sigma_i(\epsilon)$  must be as small as possible, especially close to 1, which itself must be as high as possible. For a given  $\sigma_i(\epsilon)$ ,  $f(\epsilon, E/N)$  must again be shifted to low  $\epsilon$  to minimize (4). Thus the reduction of the electron energies is of paramount significance because a lower  $f(\epsilon, E/N)$  minimizes (4) but also maximizes (3). Such a reduction in electron energies requires large cross sections for elastic and inelastic electron scattering, especially in the subexcitation energy range.

### The Concept of the Multicomponent Gaseous Insulator; Tailoring Gas Dielectrics

From (3) and (4) it is apparent that the optimum gaseous dielectric is not a single (unitary) gas but rather a combination of gases (a multicomponent gas mixture) designed as to components to provide the best effective combination of *electron-attaching* and *electron-slowng-down* properties to optimize (3) and (4). The art of designing multicomponent gaseous insulators is complicated but also enriched by the many processes entering (3) and (4). Basic knowledge on these processes offers several ways to the *systematic* development of dielectric gas mixtures (Christophorou, 1978).

### Practical Requirements

The conditions employed to obtain the results in the following sections were carefully chosen to reflect the effects on breakdown of the intrinsic properties of the gas dielectric itself. Also, most of the emphasis is on the breakdown voltage,  $V_s$ , although in practice this is by no means the only important quantity. In engineering uses of gaseous dielectrics, conditions vary significantly, but many practical requirements such as response to nonuniform fields, space-charge effects, time-voltage characteristics, decomposition products and their reactions, etc., have their roots in basic electron and ion swarm studies in the low-energy regime (Christophorou *et al.*, 1981a,b; Christophorou, 1980b; Meek and Craggs, 1978; see also following sections).

## EXAMPLES OF ELECTRON SWARM CONTRIBUTIONS

### The Coefficients $\alpha$ and $\eta$ and the Formulation of the Breakdown Criteria

The coefficients  $\alpha$  and  $\eta$  have been measured for a number of gas dielectrics (see Fig. 1) and have been used to predict the breakdown voltage of gases/mixtures in both uniform and nonuniform fields. In the uniform-field case the limiting,  $(E/N)_{lim}$ , value of  $E/N$  at which breakdown occurs is defined as that for which

$$\frac{\alpha - \eta}{N} \equiv \frac{\bar{\alpha}}{N} = 0. \quad (5)$$

Figure 2 illustrates this for  $SF_6$  (Kline *et al.*, 1978). The "net ionization coefficient,"  $\bar{\alpha}/N$ , is plotted against  $E/N$ ;  $(E/N)_{lim} = 3.62 \times 10^{-15} \text{ V cm}^2$ . Similar studies have been performed for other gases and gas mixtures (Christophorou, 1980b; Kline *et al.*, 1978).

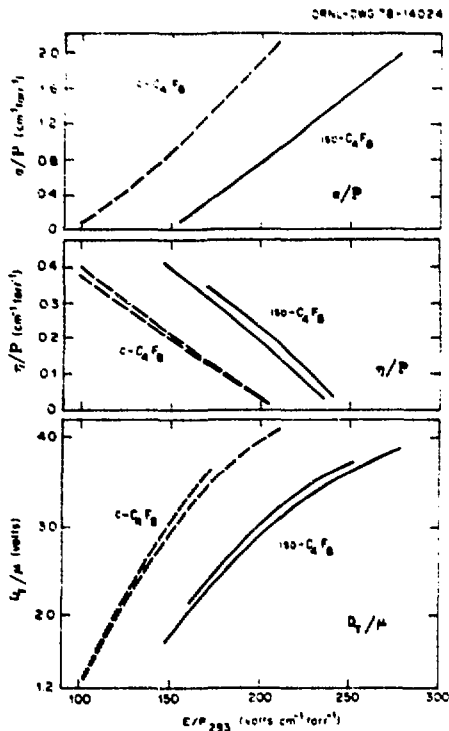


Fig. 1.  $\alpha/P$ ,  $\eta/P$ , and  $D_T/\mu$  vs  $E/P_{293}$  for electrons in  $c\text{-C}_4\text{F}_8$  and  $150\text{-C}_4\text{F}_8$  (Naidu and Prasad, 1972; Naidu *et al.*, 1972). The double lines in the  $\eta/P$  and  $D_T/\mu$  vs  $E/P_{293}$  data refer to different values of  $P$ .

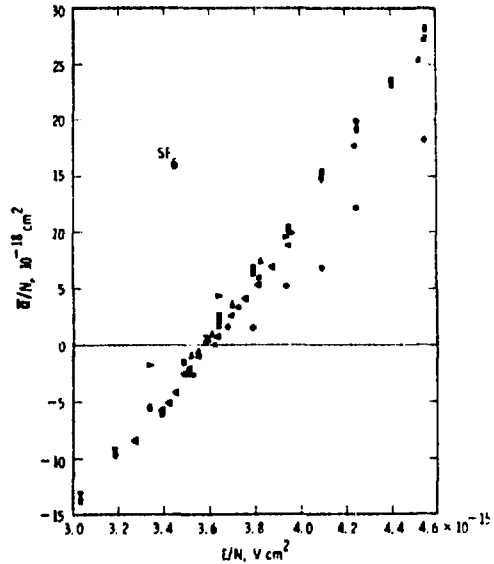


Fig. 2.  $\bar{\alpha}/N$  vs  $E/N$  for  $\text{SF}_6$  in uniform fields; data of Kline *et al.* (1978) and earlier investigators (Kline *et al.*, 1978) in the vicinity of  $(E/N)_{lim}$ .

For nonuniform fields,  $\bar{\alpha}$  is a function of the position between the electrodes, and the breakdown voltage can be calculated using the Townsend criterion for a self-sustaining avalanche or the Meek criterion for streamer growth (Waters, 1978); the latter can be expressed as

$$\int_0^{x_0} \bar{\alpha}(x) dx = k, \tag{6}$$

where  $x_0$  is the length at which the electron avalanche reaches a critical number of electrons in the avalanche tip to cause a streamer formation, and  $k$  is a constant characteristic of the gas.

The Electron Attachment Cross Section and the Choice of Unitary Gas Dielectrics or "Electronegative" Components of Mixtures

Swarm studies are the basic source of knowledge on electron attachment rate constants  $k_a(\langle \epsilon \rangle)$ , and cross sections,  $\sigma_a(\epsilon)$ , in gases. Though the role of "electronegative" gases in dielectrics has long been recognized (Meek and Craggs, 1978), it is only recently--and as a result of extensive swarm work--that the dominant effect of both the magnitude and energy dependence of  $\sigma_a(\epsilon)$  on the breakdown strength and other dielectric gas properties has been investigated and effectively used to develop new gaseous dielectric materials (Christophorou *et al.*, 1981b; Christophorou, 1978, 1980b).

The highest known dielectric strengths are exhibited by those gases (e.g.,  $\text{SF}_6$ , perfluorocarbons) which possess the largest electron attachment cross sections as

can be seen from the data in Table 1 and Fig. 3. For the perfluorocarbons in Table 1 (Groups A and B) which capture strongly thermal and near-thermal energy electrons forming long-lived ( $>10^{-5}$  s) parent negative ions, the DC uniform-field breakdown voltage,  $V_S$ , (relative to  $SF_6$  of 1), shows a general increase with the energy-integrated attachment cross section<sup>3</sup>

$$\int_{0.04 \text{ eV}}^x \sigma_a(\epsilon) d\epsilon = IA. \quad (7)$$

Table 1 Electron Attachment Data and Relative DC Uniform Field Breakdown Strengths of Some Gaseous Dielectrics\*

Gas	$\int_{0.04}^{2.5 \text{ eV}} \sigma_a(\epsilon) d\epsilon = IA$ ( $10^{-16} \text{ cm}^2 \text{ eV}$ )	$k_{th}^+$ ( $10^{-8} \text{ cm}^3 \text{ s}^{-1}$ )	EA (eV)	$V_S^R$	Comments
$SF_6$	11.1	24.9	$\geq 0.46$	1	
1-C <sub>2</sub> F <sub>2</sub>	4.4	0.38		1.2	<u>Group A:</u> Anions mostly parent at low energies and long lived ( $\tau_a > 10^{-5}$ s); (IA) = $6.6 \times 10^{-16} \text{ cm}^2 \text{ eV}$ .
c-C <sub>2</sub> F <sub>2</sub>	5.1	14.3		1.7	
2-C <sub>2</sub> F <sub>2</sub>	7.2	4.7	$\geq 0.7$	1.7	
c-C <sub>3</sub> F <sub>2</sub>	9.7	1.3	$\geq 0.4$	1.2-1.3	
1,3-C <sub>3</sub> F <sub>2</sub>	10.5	12.6		$\approx 1.5$	
2-C <sub>4</sub> F <sub>2</sub>	12.9	5.4	0.7-1.45	2.2-2.4	<u>Group B:</u> Anions mostly parent at low energies and long lived ( $\tau_a > 10^{-5}$ s); (IA) = $19 \times 10^{-16} \text{ cm}^2 \text{ eV}$ .
c-C <sub>4</sub> F <sub>2</sub>	17.4	7.4		$\approx 2.4$	
c-C <sub>5</sub> F <sub>2</sub>	18.1	38.9		$\approx 2.1-2.2$	
c-C <sub>6</sub> F <sub>2</sub>	18.1	15.0		2.3-2.4	
c-C <sub>7</sub> F <sub>2</sub>	19.1	39.2		1.9-2.2	
C <sub>7</sub> F <sub>8</sub>	20.3	27.4	$\geq 1.7$	$\approx 2.4$	
c-C <sub>7</sub> F <sub>2</sub>	26.6	3.2		2.1	
1,1,1-C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>	13.5	28.0		2.47	<u>Group C:</u> Anions are dissociative attachment fragments; mostly Cl <sup>-</sup> . The electron affinity of Cl is 3.61 eV.
1,1,2-C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>	5.94	1.1		2.41	
1,1-C <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub>	3.23	0.5		1.68	
1,2-C <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub>	1.85	0.07		1.63	
1,1,1-C <sub>2</sub> Cl <sub>2</sub> H <sub>2</sub>	1.74	1.5		1.62	
1,1,2-C <sub>2</sub> Cl <sub>2</sub> H <sub>2</sub>	1.02	0.02 <sup>†</sup>		1.50	
1,1-C <sub>2</sub> Cl <sub>2</sub> H <sub>2</sub>	0.23	0.002 <sup>‡</sup>		1.01	
1,2-C <sub>2</sub> Cl <sub>2</sub> H <sub>2</sub>	0.07	0.003 <sup>‡</sup>		$\approx 1(?)$	
CCl <sub>4</sub>	24.9	23.7 <sup>‡</sup>		2.36	
CCl <sub>3</sub> F	6.4	1.2 <sup>‡</sup>		1.84	
CCl <sub>2</sub> H	4.4	0.38 <sup>‡</sup>		1.77	
CCl <sub>2</sub> F <sub>2</sub>	0.66	0.012		1.08	
CF <sub>4</sub>	$\infty$			0.39	<u>Group D:</u> Weak dissociative attachment.
C <sub>2</sub> F <sub>4</sub>	$\infty$			0.80	
C <sub>3</sub> F <sub>8</sub>	$\infty$			0.90	
CO	$\infty$			0.40	
CO <sub>2</sub>	$\infty$			0.30	
N <sub>2</sub> O	$\infty$			0.44	
Ne	$\infty$			0.006	<u>Group E:</u> Nonelectron attaching.
Ar	$\infty$			0.07	
H <sub>2</sub>	$\infty$			0.18	
N <sub>2</sub>	$\infty$			0.36	

\*All data from Christophorou et al. (1981c) unless otherwise indicated. See Christophorou et al. (1981c) for references to original data.

<sup>†</sup>Thermal electron attachment rate constant.

<sup>‡</sup>IA upper limit = 1.8 eV.

<sup>3</sup>From Christophorou et al. (1981a).

<sup>3</sup>Due to the general lack of knowledge of  $f(\epsilon, E/N)$  for polyatomic gas dielectrics, determination of (3) is not possible, and use is made of (7).

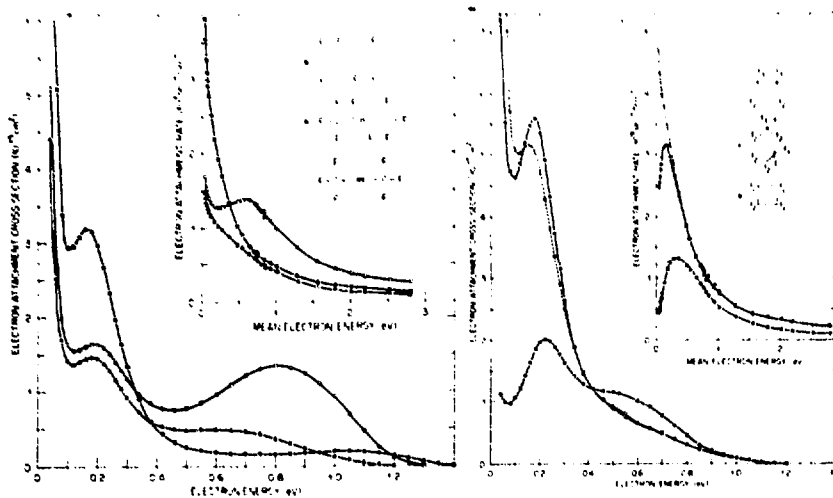


Fig. 3. Total electron attachment cross section as a function of  $\epsilon$  and total electron attachment rate as a function of  $\langle \epsilon \rangle$  for six perfluorocarbon dielectric gases (data of Christodoulides *et al.*, 1979; Pai *et al.*, 1979).

A one-to-one correspondence between  $V_S$  and IA is rather difficult to expect since other factors (Christophorou *et al.*, 1981c) which change from one compound to another also affect  $V_S$ . When the variation of the unknowns from one gas to another is minimized--as in the case of the haloethanes in Table 1 (Group C) (these freons capture slow electrons dissociatively forming principally  $Cl^-$  whose large [ $\approx 3.61$  eV] electron affinity precludes appreciable detachment) a rather quantitative relationship between  $V_S$  and IA is observed (Fig. 4 and Christophorou *et al.*, 1981c). Interestingly, the data in Table 1 (see also Christophorou *et al.*, 1981c) indicate that as IA increases,  $V_S$  saturates, suggesting an upper limit to  $V_S^R$  of  $\approx 2.5$ . Additionally, studies by Christophorou and co-workers suggest that the higher the energy range over which  $\sigma_a(\epsilon)$  is large, the higher is  $V_S$ . Extension of  $\sigma_a(\epsilon)$  to high energies can increase considerably (3) since it allows for a larger overlap between  $\sigma_a(\epsilon)$  and  $f(\epsilon, E/N)$ .

Weakly electron attaching or nonelectron attaching gases (Table 1) have low  $V_S$ . Some weakly electron attaching *polyatomic* gases, however, have reasonably high  $V_S$  compared to, say, the rare gases and this reflects the role of electron scattering processes on  $V_S$ .

Certain perfluorocarbons in Table 1,  $SF_6$ , and mixtures of these are suitable for industrial use. Of great practical potential, also, are mixtures of the strongly electron attaching gases in Table 1 with abundant, inert, and cheap buffer gases (e.g.,  $N_2$ ) with which they act synergistically, the buffer gas scattering electrons into the region where the electronegative gas captures electrons most efficiently. It is also essential to recognize the role of electron swarm work in understanding and in quantifying the density dependence of the electron attachment processes and the role of swarm and beam studies in understanding the decomposition of gaseous dielectrics under electron impact. These latter studies have shown that (multiple) molecular fragmentation--via the process of dissociative attachment--can occur very efficiently (depending on the details of molecular structure) even with "zero" energy electrons. Extensive decomposition can render an otherwise excellent gas dielectric unacceptable because of loss of its long-term stability. Identification and quantification of the decomposition products under electron impact aids the

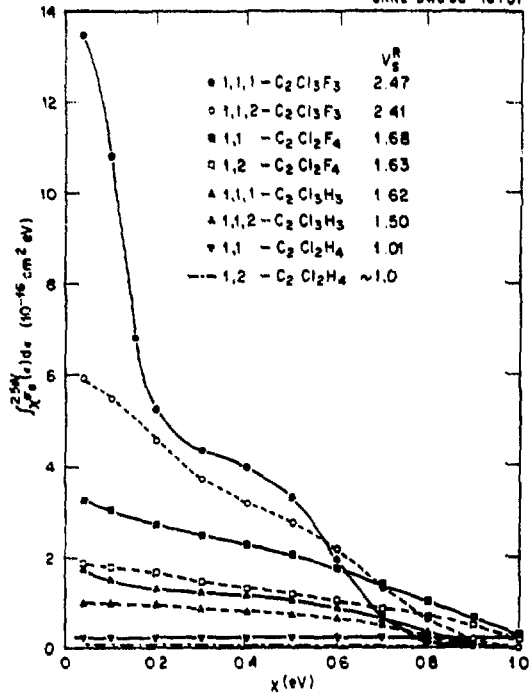


Fig. 4.  $\int_{\chi}^{2.5 \text{ eV}} \sigma_a(\epsilon) d\epsilon$  vs  $\chi$  for chlorofluoro and hydrochloroethanes (Christophorou *et al.*, 1981c).

characterization of the precursors of the final products (which may be of environmental concern) in stressed or sparked dielectric gases.

#### Electron Scattering at Low Energies and the Choice of Buffer Gases

Although the role of  $f(\epsilon, E/N)$  is crucial in efforts to understand and to tailor gas dielectrics, there is, in spite of recent progress, a general lack of knowledge of  $f(\epsilon, E/N)$  for practical situations. Independently of the state of our knowledge of  $f(\epsilon, E/N)$ , however, a larger scattering cross section,  $\sigma_{sc}(\epsilon)$ , shifts  $f(\epsilon, E/N)$  to lower  $\epsilon$  and causes fast electron relaxation. In this way the number of electrons in the electrically stressed dielectric can be substantially reduced even by narrow but strong low-lying electron attachment resonances.

Examples of the use of basic knowledge--largely provided by electron swarm studies--to assess the effects of molecular structure and electron energy-loss processes on  $V_s$  are given below.

Effect of  $\sigma_{sc}(\epsilon)$  on  $V_s$ . Dielectric strength measurements on four gases (Ne, Ar, N<sub>2</sub>, and SF<sub>6</sub>) for which  $\sigma_{sc}(\epsilon)$  and  $\sigma_1(\epsilon)$  are known (Fig. 5) demonstrated the significance of efficient electron scattering at subexcitation energies--a region well suited for swarm studies--on  $V_s$ . The  $V_s$  data (Table 2) show that Ar as a unitary gas or as a buffer gas is generally superior to Ne, although  $I_{Ar} < I_{Ne}$  and  $(\sigma_1)_{Ar} \gg (\sigma_1)_{Ne}$  (Fig. 5). This is due to the larger  $\sigma_{sc}(\epsilon)$  for Ar which shifts  $f(\epsilon, E/N)$  to lower energies (Christophorou *et al.*, 1979) compared to Ne, resulting in a lower value of (4).

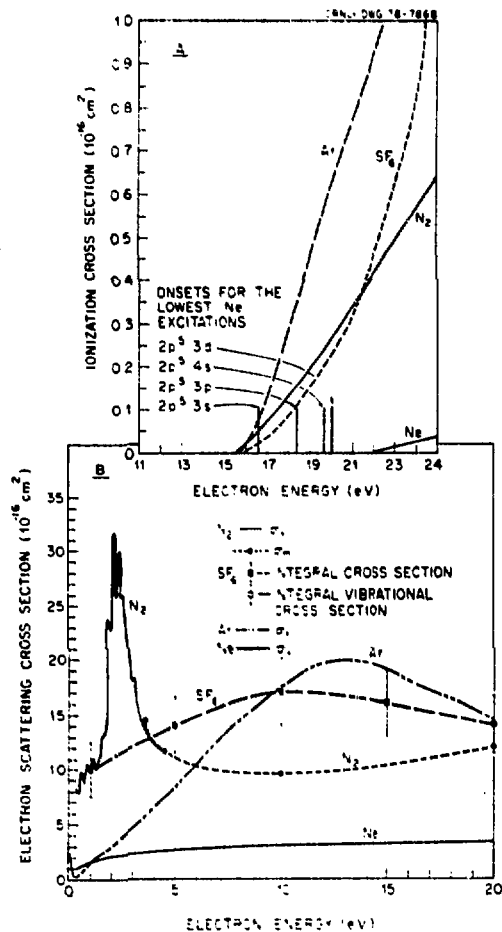


Fig. 5. A.  $\sigma_i(\epsilon)$  for Ne, Ar, N<sub>2</sub>, and SF<sub>6</sub>. B. Electron scattering cross sections for Ne, Ar, N<sub>2</sub>, and SF<sub>6</sub>: for N<sub>2</sub> ( $\sigma_t$ ,  $\sigma_m$ ); for SF<sub>6</sub> ( $\sigma_t$ ,  $\sigma_m$ ); for Ar ( $\sigma_t$ ); for Ne ( $\sigma_t$ ) (Christophorou *et al.*, 1979; see this reference for sources to original data).

The results on the binary and tertiary mixtures are consistent with the above rationale: When N<sub>2</sub>, for which  $\sigma_{SC}(\epsilon)$  is large (Fig. 5) is added to either Ne or Ar,  $V_S$  increases substantially, but, as expected (Christophorou *et al.*, 1979), proportionately more so for Ne than for Ar. Similarly, the  $V_S$  increases dramatically when SF<sub>6</sub> is added to either Ne or Ar due to both the large  $\sigma_{SC}(\epsilon)$  and  $\sigma_a(\epsilon)$  for SF<sub>6</sub>. In agreement with the above, when N<sub>2</sub> is added to the (SF<sub>6</sub> + Ne) mixture, the  $V_S$  improves much more than when it is added to the (SF<sub>6</sub> + Ar) mixture.

These, and other findings (see this section and Christophorou *et al.*, 1979), indicate that at least for uniform and quasi-uniform electric fields, large  $\sigma_{SC}(\epsilon)$  in the subexcitation ( $\epsilon < \text{energy of lowest excited electronic state}$ ) and subionization ( $\epsilon < I$ ) energy range are more important in effecting a high  $V_S$  than are  $\sigma_i(\epsilon)$ . The relative significance of  $\sigma_{SC}(\epsilon)$  and  $\sigma_i(\epsilon)$  in highly nonuniform fields needs investigation.



Table 3. Approximate Relative DC Breakdown Voltages,  $V_S^R$ , for Ne, Ar, N<sub>2</sub>, and SF<sub>6</sub> and Their Mixtures (Christophorou *et al.*, 1979)<sup>a</sup>

Ne	Percentage			$V_S^R$	$(V_S^R)_{Ne} / (V_S^R)_{Ar}$
	Ar	N <sub>2</sub>	SF <sub>6</sub>		
100				2	
	100			12	0.17
		100		40	
			100	100	
80		20		17	
	80	20		25	0.68
80			20	38	
	80		20	47	0.81
40		40	20	57	
	40	40	20	64	0.89

<sup>a</sup>These values are for sphere-on-sphere-sphere geometry and differ from Table 1 for Ne and Ar.

**Effect of Negative Ion Resonances (NIRs).** Negative ion resonances play two important roles in the dielectric strength of gases. For those gases--such as N<sub>2</sub>, H<sub>2</sub>, etc.--which do not have positive electron affinities, NIRs are efficient mechanisms for reducing the kinetic energy of the electrons. For those compounds with positive electron affinities--such as the perfluorocarbons in Table 1--NIRs allow the efficient capture of electrons, especially below  $\sim 1.5$  eV. The number and positions of such resonances are strong functions of molecular structure, and their respective cross sections can be very large compared to direct electron-scattering processes (Christophorou, 1978, 1980a).

The effect of NIRs on  $V_S$  is indicated by the data in Fig. 6, where  $D_T/\mu$  (E/P<sub>300</sub>) and  $\sigma_m(\epsilon)$  derived from these are shown for H<sub>2</sub>, N<sub>2</sub>, CO, and CO<sub>2</sub>. The relative  $V_S$  of CO, N<sub>2</sub>, and H<sub>2</sub> and the mixtures of these with one electron attaching gas (2-C<sub>4</sub>F<sub>6</sub> or SF<sub>6</sub>) are also given (James *et al.*, 1978) in Fig. 6 and are seen to decrease as the effectiveness in slowing-down electrons via their respective low-lying NIRs decreases [the  $\sigma_a(\epsilon)$  of CO, N<sub>2</sub>, and H<sub>2</sub> are exceedingly small or zero,  $I_{CO} < I_{N_2} \sim I_{H_2}$  and close to 1,  $\sigma_1(CO) > \sigma_1(H_2) \sim \sigma_1(N_2)$ ].

Each of the gases CO, N<sub>2</sub>, and H<sub>2</sub> when mixed with SF<sub>6</sub> shows synergism<sup>4</sup> (Fig. 7). Similar behavior is exhibited (Fig. 7) by COS and CO<sub>2</sub> both of which attach electrons weakly and possess NIRs at subexcitation energies; COS at  $\sim 1.3$  eV (Szmytkowski and Zubek, 1978) and CO<sub>2</sub> at  $\sim 4$  eV (see inset of Fig. 6). The cross section for COS is rather high (at the peak of the resonance at  $\sim 1.3$  eV,  $\sim 1.6 \times 10^{-14}$  cm<sup>2</sup>) (Szmytkowski and Zubek, 1978). The synergistic effects and the values of the  $V_S$  of the unitary gases increase in the order of increasing scattering cross section via the respective low-lying NIRs (i.e., COS > CO > N<sub>2</sub> > CO<sub>2</sub> > H<sub>2</sub>). Interestingly, the SF<sub>6</sub>/COS mixtures have breakdown strengths higher than either single component alone.

#### Electron-Electric Dipole Scattering and the $V_S$ of Mixtures Containing Polar Gases.

At subexcitation energies the electron scattering cross sections for polar molecules are large (Fig. 8). At thermal energies they increase roughly as the square of the electric dipole moment, D; they are expected to decrease as  $\epsilon^{-1}$ . The cross sections for electron-electric dipole scattering at low energies can exceed considerably

<sup>4</sup>Defined here as the difference between the measured  $V_S$  of the mixture and the sum of the partial-pressure-weighted  $V_S$  of the mixture components.

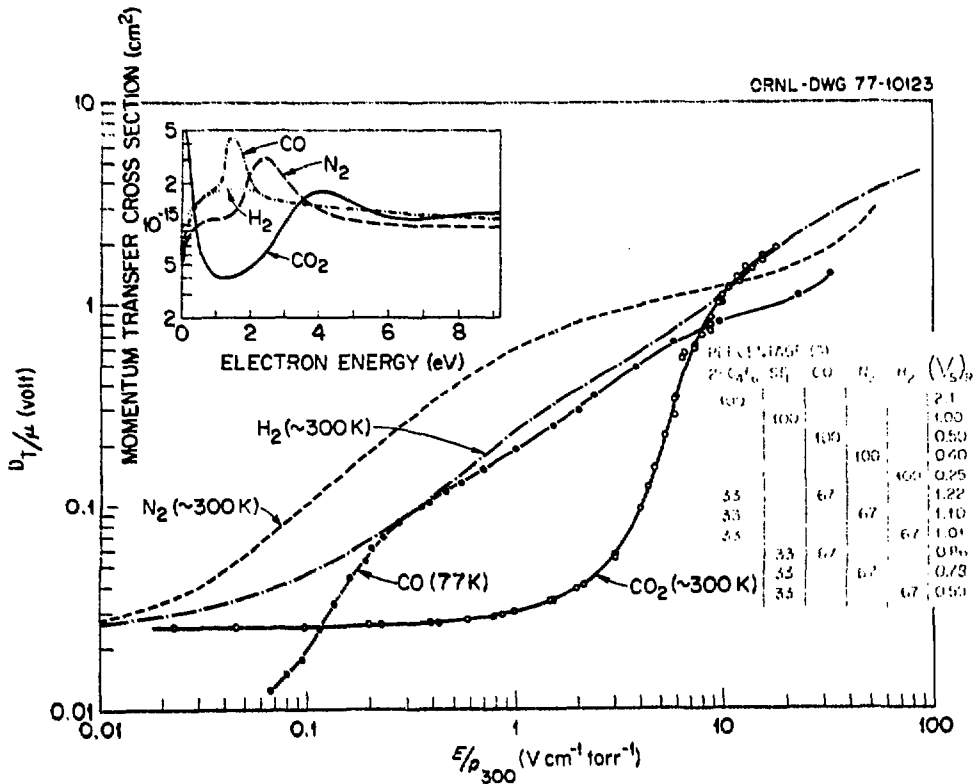


Fig. 6.  $D_T/\mu$  vs  $E/P_{300}$  and  $\sigma_m(\epsilon)$  for electrons in  $H_2$ ,  $N_2$ , CO, and  $CO_2$  (Christophorou, 1978; see this reference for sources to original data; breakdown data are from James *et al.*, 1978).

those for direct electron scattering and for indirect electron scattering via NIRs. They are of a nonresonant character as opposed to the cross sections for NIRs which are distinctly resonant.

It has been found (Christophorou *et al.*, 1981d) that polar electron slowing-down components effect a sharp increase in the  $V_s$  of mixtures with small percentages of electron attaching additives. This is seen from the data in Fig. 9, where mixtures of the polar buffer gases  $CHF_3$  ( $D = 1.65$  debye) and 1,1,1- $CH_3CF_3$  ( $D = 2.32$  debye) with the electron attaching gas  $c-C_4F_8$  exhibit strong synergism while the nonpolar gas  $CF_4$  ( $D = 0$ ) shows no such synergism. Stronger synergism was observed in mixtures of  $c-C_4F_8$  with the highly polar  $CH_3CN$  ( $D = 3.92$  debye) (see Christophorou *et al.*, 1981d, for more details and a complete discussion).

These and other findings (Christophorou *et al.*, 1981b) suggest that a careful combination of electron attaching gases with gases slowing down electrons via dipole scattering and via NIRs can effect large  $V_s$ . They indicate that a number of dielectric gas mixtures containing one or two electron attaching components from  $c-C_4F_8$ ,  $2-C_4F_6$ ,  $SF_6$ , and a dipolar component from  $CHF_3$ ,  $CH_2F_2$ , 1,1,1- $CH_3CF_3$  with or without  $N_2$  are excellent candidates for large-scale testing for possible eventual industrial adoption. Especially since recent studies (Sauers *et al.*, 1980; Christophorou *et al.*, 1981a) show that proper tailoring of dielectric gas mixtures containing fluoro-carbon(s) and  $SF_6$  can alleviate (or greatly reduce) both the problems of carbonization and  $SF_6$  toxic product formation.

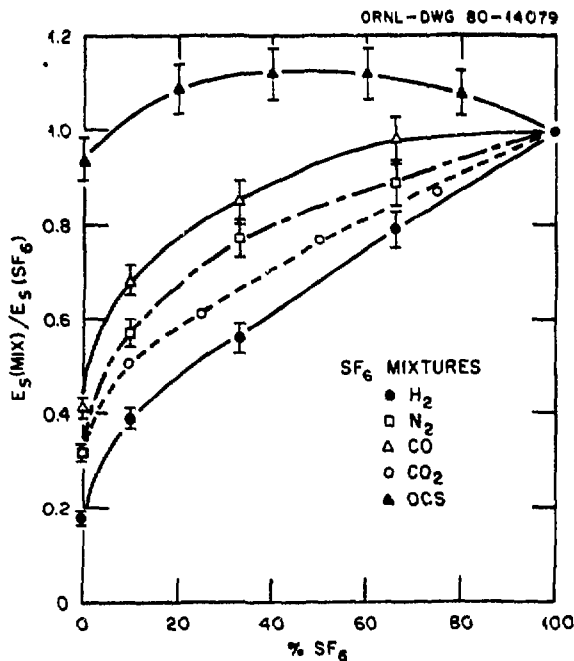


Fig. 7.  $E_S(\text{Mix})/E_S(\text{SF}_6)$  for mixtures of  $\text{SF}_6$  with: (●)  $\text{H}_2$ , (□)  $\text{N}_2$ , (△)  $\text{CO}$ , (○)  $\text{CO}_2$ , and (▲)  $\text{OCS}$  (Christophorou 1981b; see this reference for sources to original data).

Effect of Double Bonds on  $V_S$ . Electron swarm studies have shown (e.g., see Fig. 13 in Christophorou, 1978) that the electron scattering cross section increases significantly and, for a fixed  $E/N$ , the  $\langle \epsilon \rangle$  is appreciably lower for compounds with double bonds. Although these data are for the low-energy range ( $\lesssim 2$  eV), they suggest that one would expect double-bonded compounds to slow down electrons efficiently in gas mixtures. The compounds  $\text{F}_2\text{C} = \text{CF}-\text{CF}_3$  and  $\text{F}_2\text{C} = \text{CFCl}$  (neither of which is expected to attach electrons significantly) when mixed with strongly electron attaching gases were found (Christophorou *et al.*, 1981b; Fig. 10) to show significant synergism in uniform fields.

Possible Effect of Scattered Electron Angular Distributions on the  $V_S$  of Mixtures. Basic to the proper combination of electron attaching and electron slowing-down gases is the finding by Christophorou *et al.*, 1981c, that in uniform fields  $\text{N}_2$  shows excellent synergism with electron attaching additives whose  $\sigma_a(\epsilon)$  are large at thermal energies, while polar gases are better with electron attaching additives whose  $\sigma_a(\epsilon)$  are large to energies well in excess of thermal. The observed synergism between  $\text{N}_2$  and electron attaching additives with large "zero-peaking" electron attachment cross sections implies that  $\text{N}_2$  scatters electrons into the "zero" energy region more efficiently than do the polar gases. It is possible that this property of  $\text{N}_2$  is related to the angular distribution of the scattered electrons from the 2.3 eV negative ion resonance, which has a strong backward component (Lane, 1980). If these electrons are scattered in a direction opposite to the drift direction, they would have to almost come to rest before reversing direction, and they, then, can be captured very efficiently at these extremely low energies. In contrast to  $\text{N}_2$ , the angular distribution of electrons scattered by a permanent electric dipole moment are distinctly peaking in the forward direction (Lane, 1980).

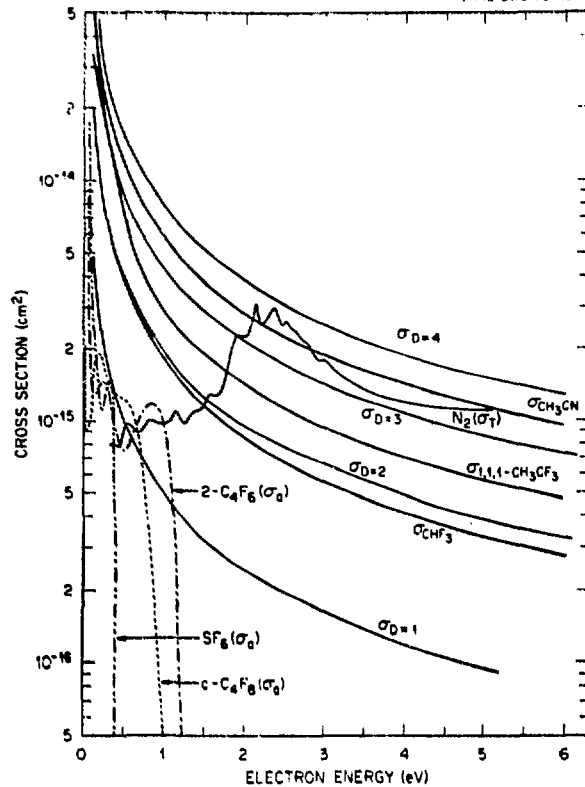


Fig. 8.  $SF_6$  ( $\sigma_a$ ),  $2-C_4F_6$  ( $\sigma_a$ ), and  $c-C_4F_8$  ( $\sigma_a$ ): total electron attachment cross sections for  $SF_6$ ,  $2-C_4F_6$ , and  $c-C_4F_8$ , respectively.  $N_2$  ( $\sigma_T$ ): total electron scattering cross section for  $N_2$ .  $\sigma_{D=1}$ ,  $\sigma_{D=2}$ ,  $\sigma_{D=3}$ , and  $\sigma_{D=4}$ : electron-electric dipole scattering cross section assuming  $\sigma_m(v) = 1.72 D^2/v^2$  for  $D = 1, 2, 3,$  and  $4$  debye, respectively.  $\sigma_{CH_3CN}$ ,  $\sigma_{1,1,1-CH_3CF_3}$ , and  $\sigma_{CHF_3}$ : scattering cross sections determined from  $A/v^2$  using experimental values of  $A$  given in Christophorou *et al.* (1981d); see this reference for detailed sources of data.

The Role of Electron Impact Ionization Cross Section. The results in the preceding sections and the work of Christophorou *et al.* (1979) indicate that for uniform fields the effect on  $V_s$  of  $\sigma_1(\epsilon)$  is relatively unimportant compared to that of  $\sigma_{sc}(\epsilon)$  and  $\sigma_a(\epsilon)$ . Apparently in (4), the crucial quantity is  $f(\epsilon, E/N)$  rather than  $\sigma_1(\epsilon)$ , but further investigations are necessary on nonuniform fields.

#### OTHER EXAMPLES OF SWARM CONTRIBUTIONS

##### Electron Affinity, Detachment, and Transfer

For the electron attachment process to be effective, the attached electron must be prevented from being detached. Swarm and beam studies provided basic needed knowledge on electron affinities, electron detachment processes, and electron transfer reactions, although much is still to be desired.

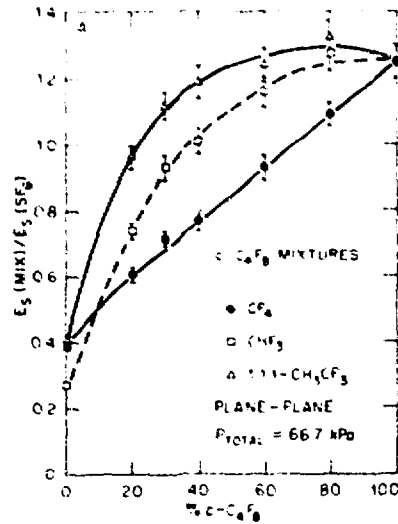


Fig. 9.  $E_S(\text{MIX})/E_S(\text{SF}_6)$  vs percent of  $c\text{-C}_4\text{F}_8$  in  $\text{CF}_4$ ,  $\text{CHF}_3$ , 1,1,1- $\text{CH}_3\text{CF}_3$  (Christophorou *et al.*, 1981b).

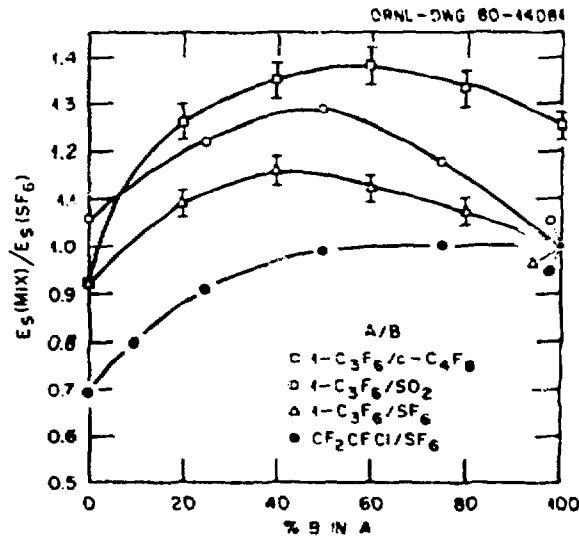


Fig. 10.  $E_S(\text{MIX})/E_S(\text{SF}_6)$  for mixtures containing double-bonded compounds  
 ( $\square$ ) 1- $\text{C}_3\text{F}_6/c\text{-C}_4\text{F}_8$  (James *et al.*, 1980);  
 ( $\circ$ ) 1- $\text{C}_3\text{F}_6/\text{SO}_2$  (Wootton *et al.*, 1980);  
 ( $\Delta$ ) 1- $\text{C}_3\text{F}_6/\text{SF}_6$  (James *et al.*, 1980);  
 ( $\bullet$ )  $\text{CF}_2\text{CFCl}/\text{SF}_6$  (Wootton *et al.*, 1980).  
 From Christophorou *et al.* (1981b).

The electron affinity of certain good perfluorocarbon dielectrics which form predominantly parent anions at low energies is  $\approx 1$  eV. For these, there is some evidence (Christophorou, 1981c) that electron detachment occurs, in contrast to those dielectrics (e.g., freons) whose negative ions (predominantly atomic halogen anion) are strongly bound.

Of the many electron detachment processes, collisional detachment seems to be the most important (Schweinler and Christophorou, 1980). Its role has been indicated in many studies. Thus, collisional detachment occurs (O'Neill and Craggs, 1973; Chalmers *et al.*, 1972; Price *et al.*, 1973) at and above the E/N values for uniform-field breakdown in both SF<sub>6</sub> (the most commonly used dielectric to date) and O<sub>2</sub> (one of the most notorious impurities in gas dielectrics). In SF<sub>6</sub> collisional detachment involves SF<sub>6</sub><sup>-</sup> (and not SF<sub>5</sub><sup>-</sup> or F<sup>-</sup>) and in O<sub>2</sub> it involves O<sup>-</sup> (rather than O<sub>2</sub><sup>-</sup> and O<sub>3</sub><sup>-</sup>) (see discussion in Christophorou *et al.*, 1980).

Evidence for the involvement of all three quantities above (electron affinity, detachment, and transfer) in the V<sub>S</sub> of gases/mixtures has been obtained by Dutton *et al.* (1973, 1974, 1975) in their work on N<sub>2</sub>O and N<sub>2</sub>O + O<sub>2</sub>. In pure N<sub>2</sub>O, the production of O<sup>-</sup> via dissociative attachment (e + N<sub>2</sub>O → N<sub>2</sub> + O<sup>-</sup>) undergoes an ion-molecule reaction (O<sup>-</sup> + N<sub>2</sub>O → NO + NO<sup>-</sup>) with N<sub>2</sub>O producing NO<sup>-</sup> which can be collisionally destroyed in the process NO<sup>-</sup> + N<sub>2</sub>O → N<sub>2</sub>O + NO + e. Dutton and co-workers found that a reduction in the rate of the last reaction by the electron transfer process NO<sup>-</sup> + O<sub>2</sub> → NO + O<sub>2</sub><sup>-</sup>, increased the breakdown voltage V<sub>S</sub> even though O<sub>2</sub> itself has a lower dielectric strength than N<sub>2</sub>O [EA(O<sub>2</sub>) = 0.44 eV > EA(NO) = 0.024 eV].

#### Identification of Spark and Ic Molecule Reaction Products

Basic studies concerned with the identification of spark products of dielectric gases, the reactions the initial products undergo with their gaseous environments, and the final products of such reactions are essential in the development of gaseous dielectrics. Such studies focused principally on SF<sub>6</sub>. A recent example is the work of Frees *et al.* (1981) who identified the positive (and negative) ions formed in sparked SF<sub>6</sub> over the pressure range 13-67 kPa. They found that the positive ion species produced in the spark depend strongly on the purity of SF<sub>6</sub>. Few parts per million of N<sub>2</sub> or O<sub>2</sub> complicated enormously the observed mass spectra. For extremely pure SF<sub>6</sub>, Frees *et al.* obtained only ions comprised solely of S and F atoms which were of the form S<sub>x</sub>F<sub>y</sub><sup>+</sup>, where x ranged from 2 to 16 and y was either zero or an odd integer. As the pressure of purified SF<sub>6</sub> increased from 13 to 67 kPa, only relatively few long-lived species remained (Fig. 11), notably S<sub>2</sub>F<sub>7</sub><sup>+</sup> (mass 197 u). These findings would indicate that the S<sub>2</sub>F<sub>7</sub><sup>+</sup> ion is an important precursor of reactions involving impurities.

Reactions involving SF<sub>6</sub> and its negative ions reacting with a variety of neutrals at 300 K were reported by Fehsenfeld (1971) and binary ionic recombination of SF<sub>5</sub><sup>-</sup> and SF<sub>6</sub><sup>-</sup> at 300 K by Church and Smith (1977). A number of ion-molecule reactions and ion mobility studies in SF<sub>6</sub> have also been undertaken (McGeehan *et al.*, 1975; Schmidt *et al.*, 1980); work in this area is expected to increase and to embrace new gas dielectrics/mixtures.

#### Ion Mobility, Energy, and Recombination

The role of these quantities in both the formation of the plasma and corona, as well as in gas decomposition, is yet to be fully assessed. Future contributions from these and other areas--such as electron attachment studies to hot gases, clustering, etc.--are anticipated.

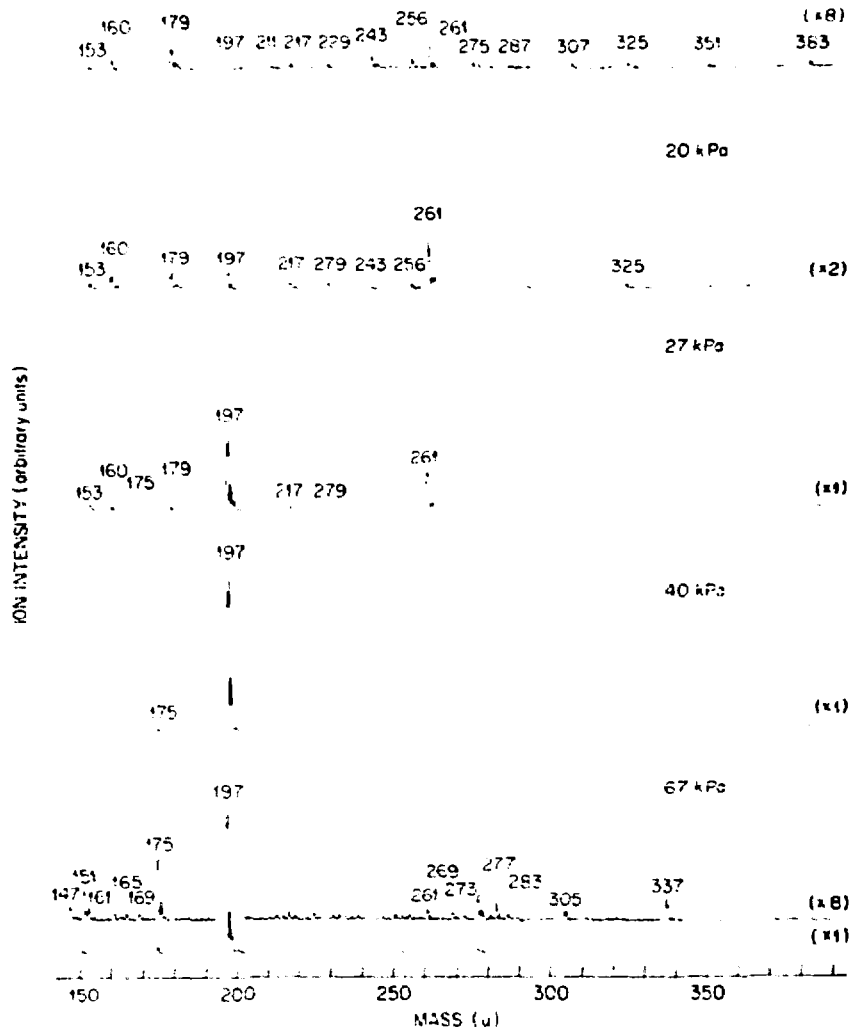
PURIFIED SF<sub>6</sub>  
13 kPa

Fig. 11. Mass spectra of positive ions in sparked purified SF<sub>6</sub> for P = 13, 20, 27, 40, and 67 kPa (mass 197 corresponds to S<sub>2</sub>F<sub>7</sub><sup>+</sup> (from Frees *et al.*, 1981)).

#### CONCLUDING REMARK

Though much basic swarm research is still necessary, swarm studies contributed fundamentally to the development of gaseous dielectrics. Through applied research, they led to significant new technological innovations, the full potential of which is yet to be realized.

#### REFERENCES

- Chalmers, I. D., H. Duffy, and D. J. Tedford (1972). *Proc. Roy. Soc. (London)*, **A282**, 171-191.
- Christodoulides, A. A., L. G. Christophorou, R. Y. Pai, and C. N. Tung (1979). *J. Chem. Phys.*, **70**, 1156-1168.

- Christophorou, L. G. (1978). *Proceedings Ninth International Conference on Phenomena in Ionized Gases*, Berlin (Leipzig: VEB Export-Import), pp. 51-72.
- Christophorou, L. G. (1980a). *Environ. Health Perspect.*, **36**, 3-32.
- Christophorou, L. G. (Ed.) (1980b). *Gaseous Dielectrics II*, Pergamon Press, New York.
- Christophorou, L. G., D. R. James, and R. A. Mathis (1979). *J. Phys. D: Appl. Phys.*, **12**, 1223-1236.
- Christophorou, L. G., D. R. James, and R. A. Mathis (1981d). *J. Phys. D: Appl. Phys.*, **14**, 675-692.
- Christophorou, L. G., D. R. James, and R. Y. Pai (1981b). In H.S.W. Massey, E. W. McDaniel, and B. Bederson (Eds.), *Applied Atomic Collision Physics*, Vol. II, Academic Press, New York (in press).
- Christophorou, L. G., D. R. James, R. Y. Pai, R. A. Mathis, I. Sauers, L. C. Frees, M. O. Pace, D. W. Bouldin, and C. C. Chan (1980). *Oak Ridge National Laboratory Report ORNL/TM-7173*.
- Christophorou, L. G., D. R. James, R. Y. Pai, R. A. Mathis, I. Sauers, D. H. Smith, L. C. Frees, M. O. Pace, D. W. Bouldin, C. C. Chan, A. Fatheddin, and S. R. Hunter (1981a). *Oak Ridge National Laboratory Report ORNL/TM-7624*.
- Christophorou, L. G., R. A. Mathis, D. R. James, and D. L. McCorkle (1981c). *J. Phys. D: Appl. Phys.* (in press).
- Church, M. J. and D. Smith (1977). *Int. J. Mass Spectr. Ion Phys.*, **23**, 137-145.
- Dutton, J., F. M. Harris, and D. B. Hughes (1973). *Proc. IEE*, **120**, 941-944.
- Dutton, J., F. M. Harris, and D. B. Hughes (1974). *Proc. IEE*, **121**, 223-226.
- Dutton, J., F. M. Harris, and D. B. Hughes (1975). *J. Phys. D: Appl. Phys.*, **8**, 1640-1646.
- Fehsenfeld, F. C. (1971). *J. Chem. Phys.*, **54**, 438-439.
- Frees, L. C., I. Sauers, H. W. Ellis, and L. G. Christophorou (1981). *J. Phys. D: Appl. Phys.* (in press).
- James, D. R., L. G. Christophorou, and R. A. Mathis (1980). In L. G. Christophorou (Ed.), *Gaseous Dielectrics II* (Proceedings of the Second International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 9-13, 1980), Pergamon Press, New York, pp. 115-127.
- James, D. R., L. G. Christophorou, R. Y. Pai, M. O. Pace, R. A. Mathis, I. Sauers, and C. C. Chan (1978). In L. G. Christophorou (Ed.), *Gaseous Dielectrics* (Proceedings of the First International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 6-8, 1978), Oak Ridge National Laboratory Report CONF-780301, pp. 224-251.
- Kline, L. E., D. K. Davies, C. L. Chen, and P. J. Chantry (1978). In L. G. Christophorou (Ed.), *Gaseous Dielectrics* (Proceedings of the First International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 6-8, 1978), Oak Ridge National Laboratory Report CONF-780301, pp. 258-272.
- Lane, N. F. (1980). *Revs. Mod. Phys.*, **52**, 29-119.
- McGeehan, J. P., B. C. O'Neill, A. N. Prasad, and J. D. Craggs (1975). *J. Phys. D: Appl. Phys.*, **8**, 153-160.
- Meek, J. M. and J. D. Craggs (Eds.) (1978). *Electrical Breakdown in Gases*, John Wiley and Sons, Chichester, England.
- Naidu, M. S. and A. N. Prasad (1972). *J. Phys. F: Appl. Phys.*, **5**, 983-993; 1090-1095.
- Naidu, M. S., A. N. Prasad, and J. D. Craggs (1972). *J. Phys. D: Appl. Phys.*, **5**, 741-746.
- O'Neill, B. C. and J. D. Craggs (1973). *J. Phys. B: Atom. Molec. Phys.*, **6**, 2625-2633.
- Pai, R. Y., L. G. Christophorou, and A. A. Christodoulides (1979). *J. Chem. Phys.*, **70**, 1169-1176.
- Price, D. A., J. Lucas, and J. L. Moruzzi (1973). *J. Phys. D: Appl. Phys.*, **6**, 1514-1524.



- Sauers, I., L. G. Christophorou, L. C. Frees, and H. W. Ellis (1980). In L. G. Christophorou (Ed.), *Gaseous Dielectrics II* (Proceedings of the Second International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 9-13, 1980), Pergamon Press, New York, pp. 429-437.
- Schmidt, W. F., H. Jungblut, D. Hansen, and H. Tagashira (1980). In L. G. Christophorou (Ed.), *Gaseous Dielectrics II* (Proceedings of the Second International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 9-13, 1980), Pergamon Press, New York, pp. 1-10.
- Schweinler, H. C. and L. G. Christophorou (1980). In L. G. Christophorou (Ed.), *Gaseous Dielectrics II* (Proceedings of the Second International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 9-13, 1980), Pergamon Press, New York, pp. 12-23.
- Szmytkowski, C. and M. Zubek (1978). *Chem. Phys. Lett.*, 57, 105-108.
- Waters, R. T. (1978). In Meek and Craggs (1978), pp. 392-403.
- Wootton, R. E., S. J. Dale, and N. J. Zimmerman (1980). In L. G. Christophorou (Ed.), *Gaseous Dielectrics II* (Proceedings of the Second International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 9-13, 1980), Pergamon Press, New York, pp. 137-148.