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ELECTRON COLLISIONS IN GAS SWITCHES\*

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I. INTRODUCTION

Many technologies rely on the conduction/insulation properties<sup>1</sup> of gaseous matter for their successful operation.<sup>2</sup> Many others (e.g., pulsed power technologies) rely on the rapid change (switching or modulation) of the properties of gaseous matter from an insulator to a conductor and vice versa.<sup>2</sup> Studies of electron collision processes in gases aided the development of pulsed power gas switches, and in this paper we shall briefly illustrate the kind of knowledge on electron collision processes which is needed to optimize the performance of such switching devices. To this end, we shall refer to three types of gas switches: (i) spark gap closing, (ii) self-sustained diffuse discharge closing, and (iii) externally-sustained diffuse discharge opening. The desirable properties and characteristics of these three types of switches are listed in Table 1, along with the required properties of the gaseous medium.

In efforts to optimize the performance of pulsed power gas switches by appropriate choice of the gaseous medium, knowledge is needed on those basic processes which crucially determine the number densities and energies of free electrons in electrically-stressed gases. Foremost among these are electron attachment, detachment, impact ionization, scattering and recombination. Photon interactions are also important in that they can affect the electron and the anion number densities, through, for example, the processes of photodetachment and photoionization and through photoenhanced electron collision processes.

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In this paper, we shall restrict ourselves to recent work on electron attachment, electron impact ionization, and electron drift velocities in switching gases. We shall, in particular, discuss recent results on electron attachment cross sections  $\sigma_a(\epsilon)$  and coefficients  $n/N_a(E/N)$ , electron impact ionization coefficients  $\alpha/N(E/N)$ , and electron drift velocities  $w(E/N)$  of switching gases/mixtures ( $\epsilon$  is the electron energy,  $N_a$  and  $N$  are, respectively, the attaching gas and the total gas number densities and  $E/N$  is the density-reduced electric field). We shall also discuss the effect of internal energy of excitation of the switch-gas molecules on electron collision processes. The significance of these quantities and processes and of the effective ionization

TABLE I DESIRABLE CHARACTERISTICS OF AND GAS PHYSICAL PROPERTIES/ PROCESSES FOR THREE TYPES OF GAS SWITCHES

Type of Switch	Switch Characteristics	Gas Physical Properties/Processes
A Spark Gap Closing	<ul style="list-style-type: none"> <li>High Power Efficiency Repetition Rate</li> <li>Fast Recovery Closing/Opening</li> <li>Control of Closing/Opening Time</li> </ul>	<ul style="list-style-type: none"> <li>Good insulator in hold-off stage and good conductor in closing stage [large <math>(E/N)_{lim}</math>; low <math>(E/N)_{conduction}</math>]</li> <li>Short formative time lag</li> <li>Large <math>k_a(\langle\epsilon\rangle)</math> which decreases with <math>T</math> (Gas is strongly electron attaching when cold (<math>\sim 300K</math>) and weakly attaching or nonattaching when warm)</li> <li>Steep increase of <math>\bar{\alpha}/N</math> with <math>E/N</math> around <math>(E/N)_{lim}</math></li> </ul>
B. Diffuse Discharge Closing (Self-Sustained)	<ul style="list-style-type: none"> <li>Optical Modification of Conduction/Insulation Properties</li> <li>Good Discharge Stability (to <math>\sim 100</math> ns) for II</li> </ul>	<ul style="list-style-type: none"> <li>Good insulator in hold-off stage and good conductor in closing stage [large <math>(E/N)_{lim}</math>; low <math>(E/N)_{conduction}</math>]</li> <li>Long diffuse discharge conduction time</li> <li><math>k_a(\langle\epsilon\rangle)</math> (large; high-energy onset; decreases with <math>T</math>)</li> <li>Slow-varying <math>\bar{\alpha}/N(E/N)</math> near <math>(E/N)_{lim}</math></li> <li>Delicate dependencies of <math>\alpha/N</math> and <math>n/N</math> on <math>E/N</math></li> </ul>
C. Diffuse Discharge Opening (Externally Sustained)		<ul style="list-style-type: none"> <li>Good conductor in closing stage (low <math>E/N</math>) and good insulator in opening stage (high <math>E/N</math>)</li> <li><math>k_a(E/N)</math> small at low <math>E/N</math> and large at high <math>E/N</math></li> <li><math>w</math> large for <math>(E/N)_{conduction}</math> and low at high <math>E/N</math> (negative differential conductivity)</li> <li>Optical modification of conduction/insulation</li> <li>High efficiency of electron production by external means</li> </ul>

coefficient  $\bar{\alpha}/N(E/N) = \alpha/N(E/N) - \eta/N_a(E/N)$  in optimizing the properties of gas switches, as well as of the optical modification of electron attachment in developing new techniques to actively control the switch opening and closing time will be elaborated upon. Examples of new switching concepts based on recent knowledge of electron collision processes in gases will be outlined.

## II. ELECTRON COLLISIONS IN SWITCHING GASES

### A. Electron Attachment

Dissociative and nondissociative electron attachment reactions depend strongly on the electron energy, the position of the negative ion state via which attachment occurs, and the internal energy of the electron attaching molecule.<sup>3,4</sup> With regard to the internal energy of the molecule, we can distinguish electron attachment to (i) ground state, (ii) vibrationally/rotationally-excited ("hot"), and (iii) electronically-excited molecules. Knowledge on such processes is indispensable for understanding the insulating/switching properties of gaseous matter. Examples of recent knowledge--mostly from the author's Laboratory--on (i)-(iii) for gases of direct interest to gas switches are given in this section.

#### (i) Electron attachment to ground-state molecules

Recently, detailed studies have been performed on electron attachment in a number of gases/mixtures of interest to gas switches over wide ranges of  $E/N$ ,  $N$ , and buffer gases (e.g., see Refs. 2-5). In Fig. 1 are shown our<sup>5d</sup> recent measurements on the electron attachment rate constant  $k_a$  for  $SF_6$  in the buffer gases  $N_2$ , Ar, and Xe over a wide range of  $E/N$  values. In Fig. 2, the same data are plotted as a function of the mean electron energy  $\langle \epsilon \rangle$  in the respective buffer gases determined from the corresponding electron energy distribution functions  $f(\epsilon, E/N)$ . The  $k_a(E/N)$  in Fig. 1 for  $SF_6$  in the three buffer gases have been used along with electron transport and electron scattering cross section data (see Ref. 5d) in a numerical two-term, spherical harmonic Boltzmann equation analysis, and the electron attachment cross sections  $\sigma_a(\epsilon)$  shown in Fig. 3 have been obtained. In these calculations a nondissociative attachment cross section for  $SF_6^-$  formation, a dissociative attachment cross section for  $SF_6^-$  formation, and a composite dissociative attachment cross section for  $F^-$ ,  $F_2^-$ , and  $SF_4^-$  formation were used; the cross section set of Klein et al.<sup>6</sup>--modified in accordance with recent cross-section shape measurements<sup>7</sup>--was used as the initial attachment cross section input.

Total electron attachment rate constants  $k_a(\langle \epsilon \rangle)$  and cross sections  $\sigma_a(\epsilon)$  for a most interesting for switching purposes group of molecules--the perfluoroalkanes  $n-C_NF_{2N+2}$  ( $N = 1$  to 6)--are shown in Fig. 4. As the size of these molecules increases, the magnitude of  $k_a(\langle \epsilon \rangle)$  and  $\sigma_a(\epsilon)$  increases and the function  $k_a(\langle \epsilon \rangle)$  and  $\sigma_a(\epsilon)$  shifts progressively to lower energies. While for  $CF_4$  and  $C_2F_6$  electron attachment is entirely due to dissociative processes, as the molecular size increases beyond  $C_2F_6$ , increasingly a larger fraction of the measured  $k_a(\langle \epsilon \rangle)$  is

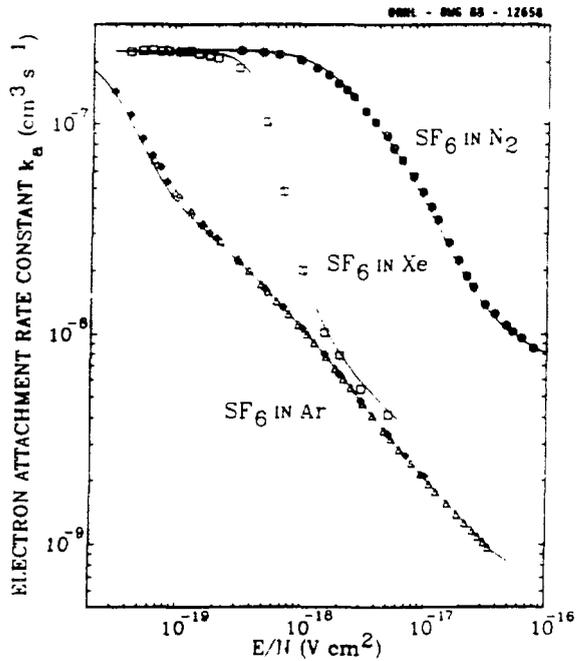


Fig. 1. Experimental (data points) and calculated (solid lines) electron attachment rate constants  $k_a(E/N)$  for SF<sub>6</sub> in the buffer gases N<sub>2</sub>, Ar, and Xe [From Ref. 5d].

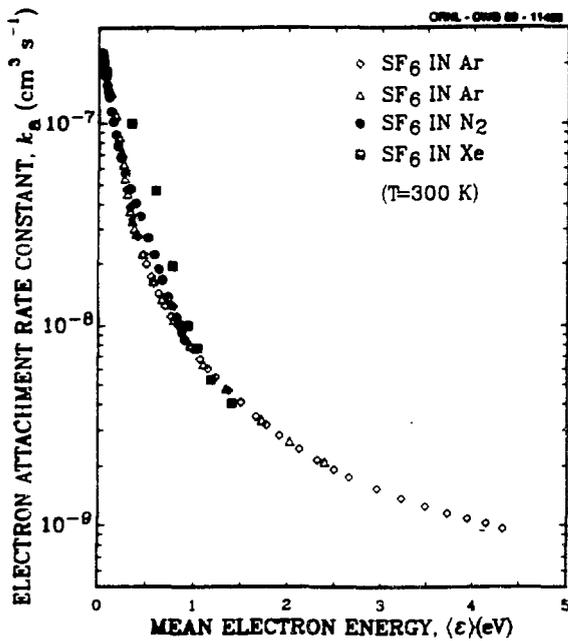


Fig. 2.  $k_a$  vs  $\langle \epsilon \rangle$  for SF<sub>6</sub> measured<sup>5d</sup> in mixtures with N<sub>2</sub>, Ar, and Xe.

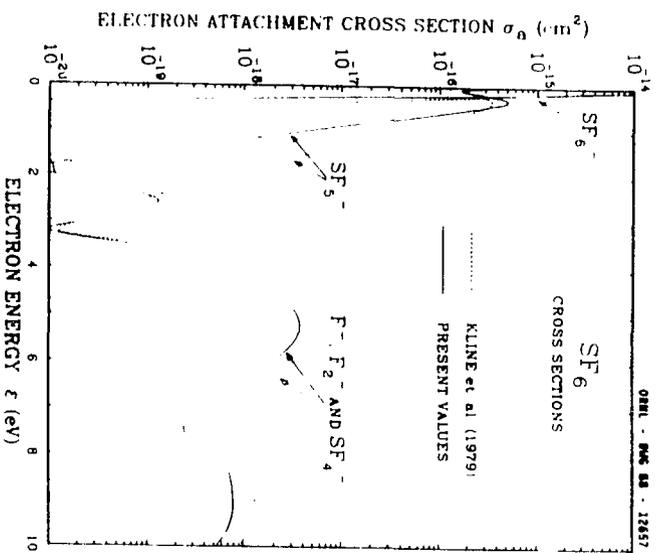


Fig. 3.  $\sigma_a(\epsilon)$  for  $\text{SF}_6^-$ ,  $\text{SF}_5^-$ , and  $\text{F}^- + \text{F}_2^- + \text{SF}_4^-$  (see the text and Ref. 5d).

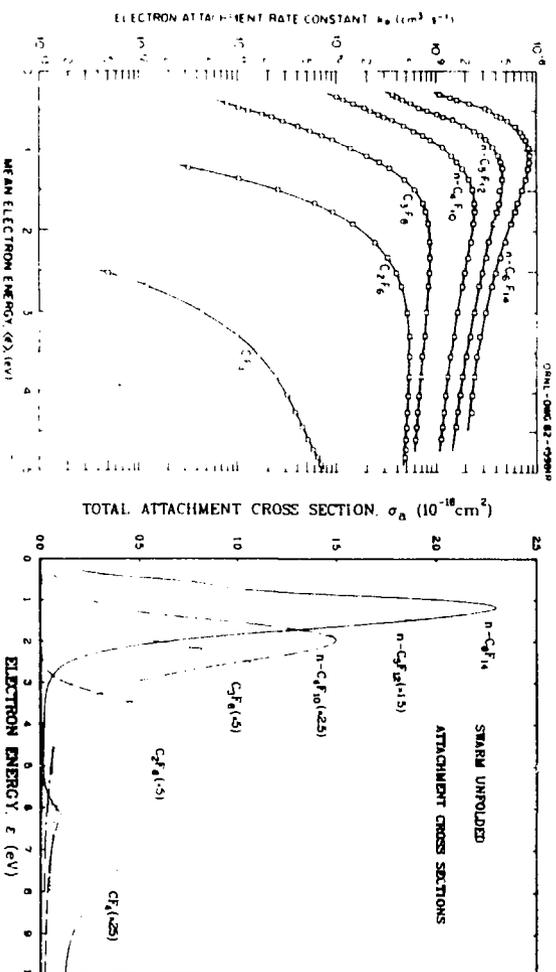


Fig. 4.  $k_a(\langle \epsilon \rangle)$  and  $\sigma_a(\epsilon)$  for the perfluoroalkane molecules  $n\text{-C}_N\text{F}_{2N+2}$  ( $N = 1$  to 6) (From Ref. 5b).

due to parent anions, whose rate of formation delicately depends on  $N$  and temperature  $T$  (Fig. 5; see Ref. 5c and later this section). The small values of  $k_a$  at low  $\langle \epsilon \rangle$  (low  $E/N$ ) and the large values of  $k_a$  at high  $\langle \epsilon \rangle$  (high  $E/N$ ) make this group of molecules serious candidates as constituents in gas mixtures for diffuse discharge switches.<sup>8</sup>

(ii) Electron attachment to vibrationally/rotationally-excited ("hot") molecules

Low energy ( $\lesssim 2$  eV) electron attachment processes can be extremely sensitive to gas temperature. As the internal energy of a gas molecule increases, delicate and often profound changes occur in its electron attaching properties which crucially depend on the molecule itself and the mode (dissociative or nondissociative) of electron attachment.<sup>4,5c,9-11</sup>

For dissociative electron attachment, the rate constant/cross section generally increases with increasing internal energy of the molecule, i.e., with increasing  $T$ . From the view point of gas switches, of particular interest is the reported<sup>4,5c,9-11</sup> sensitivity to  $T$  of the low-energy dissociative electron attachment processes in freons and halocarbons. In Fig. 6, are shown recent measurements<sup>10</sup> of  $\sigma_a(\epsilon, T)$  for the production of  $\text{Cl}^-$  from  $\text{C}_2\text{H}_3\text{Cl}$ . Especially interesting for switching purposes are molecules possessing very low-lying dissociative attachment resonances with a vertical onset behavior,<sup>4</sup> since these are expected to show a profound increase of the dissociative attachment cross section with small increases in  $T$  above ambient temperature. This is clearly shown by our<sup>11</sup> preliminary measurements of  $k_a(\langle \epsilon \rangle, T)$  for  $\text{CH}_3\text{Cl}$  (Fig. 7) (See also Ref. 12). Such a type of behavior would make such gases (or their mixtures with appropriate buffer gases) poorly electron attaching when cold ( $\lesssim 300\text{K}$ ) and strongly electron attaching when "warm". The profound changes with  $T$  for molecules such as those in Figs. 6 and 7 indicate possible infrared laser photoenhanced attachment for these species.

For nondissociative electron attachment, the  $k_a(\langle \epsilon \rangle, T)$  generally decreases with increasing internal energy of the molecule, i.e., with increasing  $T$ .<sup>9</sup> Figure 8 shows examples of this type of behavior for  $\text{c-C}_4\text{F}_6$  and  $\text{c-C}_4\text{F}_8$  which are of interest as electronegative additives in gas switching mixtures.<sup>2</sup> The decrease in  $k_a(\langle \epsilon \rangle, T)$  with increasing  $T$  can be due to a decrease in the cross section for formation and/or an increase in the autodetachment rate of the transient anions of these molecules. The precipitous decrease of electron attachment with increasing  $T$  affects (decreases) the dielectric strength of such gases and is potentially useful for pulsed power switching (see Refs. 2, 9g, and Section III).

When dissociative and nondissociative electron attachment processes occur concomitantly, over a common energy range, then  $k_a(\langle \epsilon \rangle, T)$  and  $\sigma_a(\epsilon, T)$  can increase or decrease with increasing  $T$  depending on the relative significance of the two processes.<sup>4,9</sup> An example of this type of behavior is shown in Fig. 5c,d. The total attachment cross section deduced from these measurements are shown in Fig. 9a; they decrease with increasing  $T$  due to the depletion of the parent anions. If, however, the dissociative component of the measured rate constant is separated<sup>5c</sup> from

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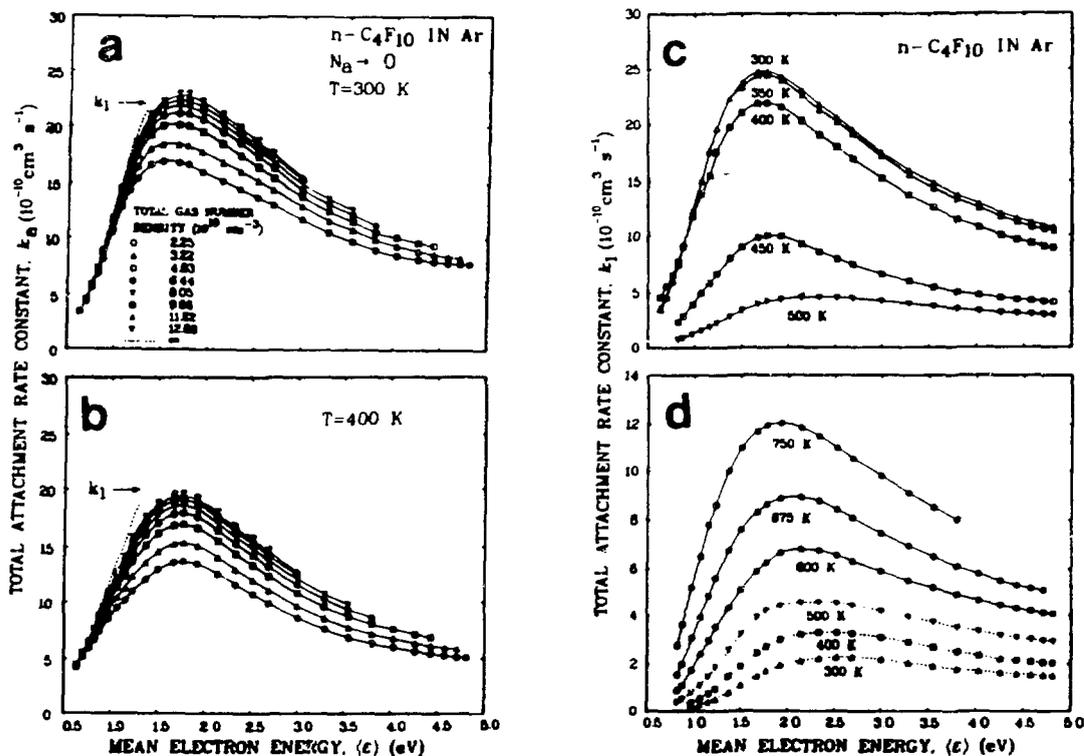


Fig. 5. Total electron attachment rate constant,  $k_a$  (for  $N_a \rightarrow 0$ ), for  $n\text{-C}_4\text{F}_{10}$  in Ar buffer gas versus mean electron energy,  $\langle \epsilon \rangle$ , at the indicated total gas number densities,  $N_t$ , for  $T = 300 \text{ K}$  (Fig. 5a) and  $T = 400 \text{ K}$  (Fig. 5b). The broken curves are the rate constants,  $k_1$ , for  $N_t \rightarrow \infty$ . The  $k_1(\langle \epsilon \rangle)$  at 300, 350, 400, 450, and 500 K, are shown in Fig. 5c, and the  $k_1(\langle \epsilon \rangle)$  for 600, 675, and 750 K in Fig. 5d. The 300, 400, and 500 K curves in Fig. 5d are the dissociative attachment components of the total rate constant  $k_1$  at these temperatures [From Ref. 5c].

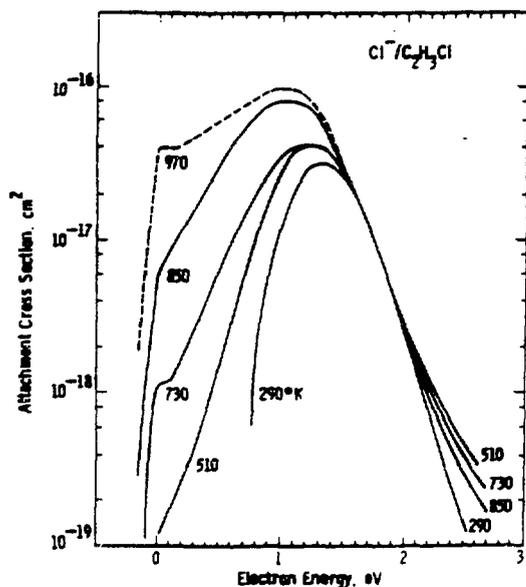


Fig. 6.  $\sigma_a(\epsilon, T)$  for  $\text{C}_2\text{H}_3\text{Cl}$ . The data at 970 K are uncertain due to thermal dissociation of the molecule [From Ref. 10].

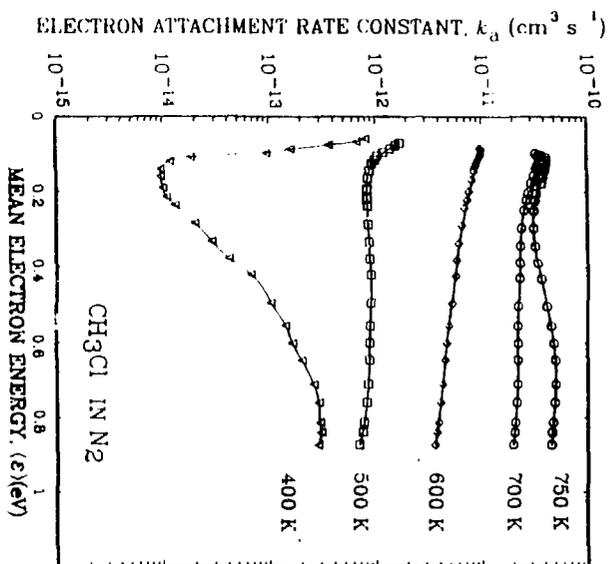


Fig. 7.  $k_a(\langle\epsilon\rangle, T)$  for  $\text{CH}_3\text{Cl}$  [Ref. 11].

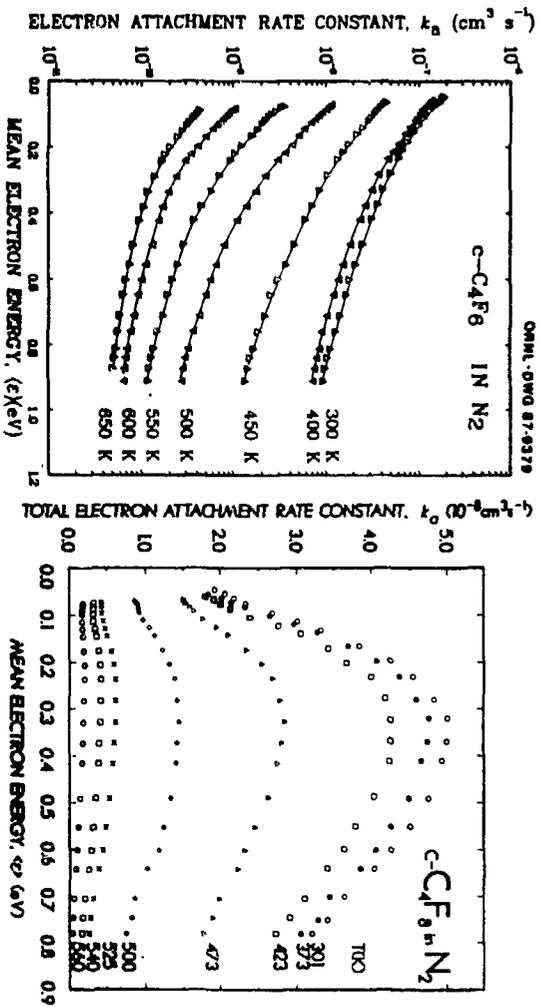


Fig. 8.  $k_a(\langle\epsilon\rangle, T)$  for  $c\text{-C}_4\text{F}_6$  [Ref. 9h] and  $c\text{-C}_4\text{F}_6$  [Ref. 9c].

the nondissociative component, and the resultant rate constant due to dissociative attachment is used to unfold the dissociative attachment cross section as a function of  $T$ ,  $\sigma_{da}(\epsilon, T)$ , these increase monotonically - as expected - with increasing  $T$  (Fig. 9b).

In the aforementioned examples the internal excitation of the molecules is nonselective. Direct or indirect laser-induced selective vibrational excitation of parent or fragment species leading to (optically) enhanced electron attachment has been observed in a number of cases (e.g., Ref. 13) and is useful in gas switching schemes.

### (iii) Electron Attachment to Electronically-Excited Molecules

Electron capture in the field of an excited electronic state for very short times ( $\lesssim 10^{-14}$  s) has long been known to occur as resonances in electron scattering and in dissociative electron attachment reactions.<sup>4</sup> It has, also, been reported<sup>14</sup> that long-lived (auto-detachment lifetimes  $> 10^{-6}$  s) anions of the p-benzoquinone molecule can be formed in collisions with slow ( $\sim 2-3$  eV) electrons whereby the initial kinetic energy of the colliding electron is almost entirely expended in exciting the molecule to its lowest excited (triplet) state with the resultant thermal electron being concomitantly captured by the so-produced electronically-excited molecule. The first example of dissociative electron attachment to pre-prepared electronically-excited molecules is that for  $O_2^*$  ( $a^1\Delta_g$ ) produced in a microwave discharge.<sup>15</sup> Electron attachment to electronically-excited molecules produced indirectly by laser irradiation has also been reported recently.<sup>16</sup> In Fig. 10 are shown the observed large enhancements in the electron attachment coefficient  $\eta/N_a$  for thiophenol ( $C_6H_5SH$ ) effected by UV excimer laser irradiation.<sup>16a</sup> Curves 1 and 2 are the  $\eta/N_a$  for dissociative attachment to ground state molecules and curve 3 is the  $\eta/N_a$  for dissociative attachment to thiophenol molecules excited to their lowest triplet state populated indirectly by internal conversion from higher excited singlet states originally reached by laser light absorption. Curves 4 - 7 show the measured  $\eta/N_a$  for a double laser pulse experiment where the gas was excited by a laser pulse and electron attachment was measured 12 ms later when the attaching electrons were produced by a second similar laser pulse. This "delayed" photoenhanced electron attachment process occurred at times  $> 100 \mu s$  after the first laser pulse and is much stronger than that for a single pulse.<sup>16</sup> The single pulse attachment is due to dissociative electron attachment to thiophenol molecules in their lowest triplet state and occurs within a few  $\mu s$  of laser irradiation, while the "delayed" photoenhanced attachment is believed<sup>16b</sup> to be due to electron attachment to diphenyl disulfide ( $C_6H_5SSC_6H_5$ ) produced by the interaction of thiophenoxy radicals ( $C_6H_5S^\cdot$ ) formed directly or indirectly via laser irradiation.

The limited knowledge to date in this area clearly shows that the cross sections for electron scattering by and electron attachment to electronically excited molecules far exceed those of the corresponding ground state molecules. The importance of such processes in pulsed power gas switches can not be overstated. Optical enhancement of electron attachment can, for example, form the basis for fast switching (or modulation) of the impedance (electronic conduction/insulation) properties of gaseous matter in the  $\mu s$  to the ns range.<sup>2,16</sup> In this

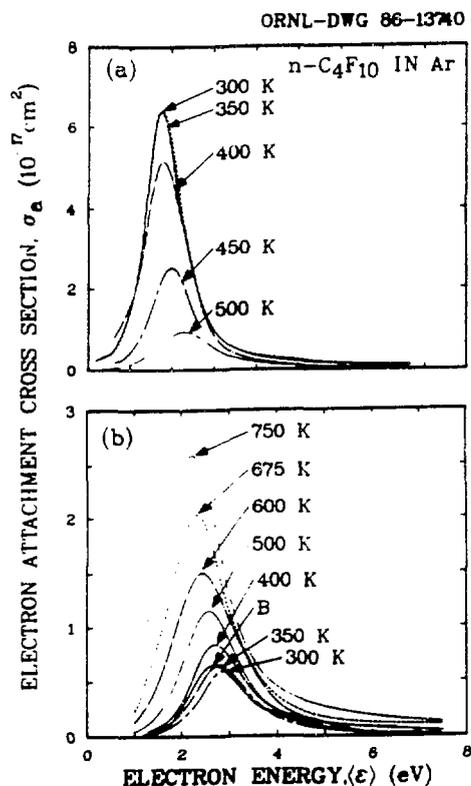


Fig. 9. The swarm unfolded total electron attachment cross sections  $\sigma_a(\epsilon, T)$  for n-C<sub>4</sub>F<sub>10</sub> at (a) 300, 350, 400, 450, and 500K and (b) 600, 675, and 750K. The 300, 350, 400, and 500K curves (b) are the dissociative attachment cross sections at these temperatures [From Ref. 5c].

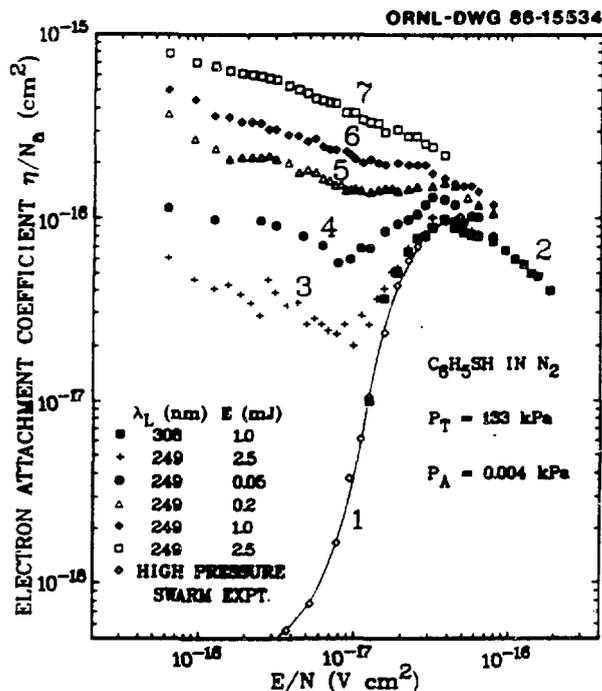


Fig. 10. Electron attachment coefficient,  $\eta/N_a$  vs  $E/N$  for C<sub>6</sub>H<sub>5</sub>SH in N<sub>2</sub> for the ground-state (curves 1 and 2) and the electronically excited (curves 3-7; curve 3 is for a single laser pulse, and curves 4-7 are for the double laser pulses) C<sub>6</sub>H<sub>5</sub>SH molecules. The values of the photoenhanced attachment are at least 100 times larger than shown since the number of excited attaching gas molecules is < 1% of those in the ground state, N<sub>a</sub> [From Ref. 16a].

connection, the observation of photoenhanced electron attachment to short-lived electronic species (e.g., TMAE and TEA)<sup>16c</sup> is most significant.

### B. Electron Impact Ionization

The understanding and modeling of the gas discharge processes in gas switches requires knowledge not just on the electron loss, but also on the electron gain processes occurring in the discharge. In this regard, the physical quantities most commonly measured are the density-normalized electron impact ionization  $\alpha/N$  and effective ionization  $\bar{\alpha}/N = \alpha/N - \eta/N_a$  coefficients, measured as a function of  $E/N$ . In general,  $\alpha/N$  does not depend strongly on either  $N$  or  $T$ , and the variation of  $\bar{\alpha}/N$  with  $N$  and  $T$  normally reflects the variation of  $\eta/N_a$  with  $N$  and  $T$  (e.g., see Fig. 11).

Both  $\alpha/N$  and  $\bar{\alpha}/N$ , however, depend rather strongly and delicately on  $E/N$  and knowledge of the magnitude and  $E/N$  dependence of these coefficients aid the tailoring of gaseous media for the various types of gas switches (Table 1) (e.g., see Refs. 2 and 8).

Two recent examples of  $\alpha/N$  ( $E/N$ ) and  $\eta/N$  ( $E/N$ ) measurements<sup>17,18</sup> are shown in Fig. 12 for  $\text{BF}_3$  and  $\text{SiF}_4$ . These two molecules possess dissociative electron attachment processes which have high energy onsets ( $\gtrsim 10.0$  eV)<sup>17</sup> and also relatively low  $(E/N)_{\text{lim}}$  values ( $123 \times 10^{-17}$  V cm<sup>2</sup> for  $\text{BF}_3$  and  $121 \times 10^{-17}$  V cm<sup>2</sup> for  $\text{SiF}_4$ ); the latter can be further lowered by small concentrations of low ionization onset (IO) additives (e.g., triethylamine, TEA; IO  $\approx 7.5$  eV) (see Fig. 12). Such gases and gas mixtures possessing low  $(E/N)_{\text{lim}}$  values and  $\bar{\alpha}/N$  which varies slowly with  $E/N$  near  $(E/N)_{\text{lim}}$  (i.e., mixtures in which the rate of change of electron production and loss is minimal during small perturbations in  $E$  beyond  $(E/N)_{\text{lim}}$ ) are ideal for use in new self-sustained diffuse discharge closing switching concepts<sup>2,18</sup> since they can enhance the efficiency and the stability of the discharge.

### C. Electron Drift Velocities/Scattering

The speed with which free electrons drift in a gas under an applied electric field affects the gas conductivity and the rates of electron gain and loss. The size of the electron drift velocity  $w$  is determined by the elastic and inelastic electron scattering properties of the gas and varies with  $E/N$ ,  $T$ , and  $N$  (e.g., see Refs. 3a, 4a, 8, 17, and 19-21). Many investigations studied the dependencies of  $w$  on  $E/N$ ,  $T$ , and  $N$  over broad ranges of values for a number of switch gases/mixtures.<sup>2,4,8</sup> For the gas pressures (a few atmospheres or less) normally employed in gas switches, the collision mean free path  $\ell$  is much larger than the electron de Broglie wavelength  $\lambda$  and hence the well-known<sup>4a,19</sup> effects of  $N$  on  $w$  which occur--especially at low  $E/N$ --when  $\ell \lesssim \lambda$  do not manifest themselves. However,  $w$  can vary with  $N$  at low  $N$  when electron gain and loss processes are significant. Such changes have been reported<sup>21b</sup> for  $\text{C}_3\text{F}_8$  and  $n\text{-C}_4\text{F}_{10}$  for  $E/N$  regions where  $\eta/N$  becomes density dependent due to the formation of parent--along with fragment--negative ions in these gases.

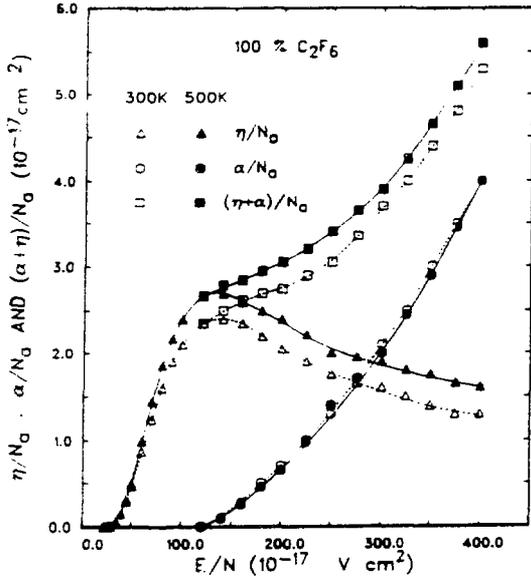


Fig. 11. Electron attachment coefficient  $\eta/N_a$ , electron impact ionization coefficient  $\alpha/N_a$  and total ion production coefficient  $(\alpha+\eta)/N_a$  of pure C<sub>2</sub>F<sub>6</sub> at 300 and 500K as a function of E/N.

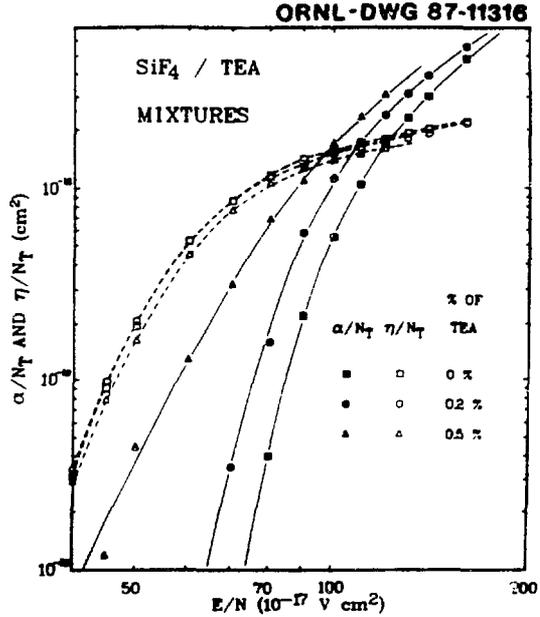
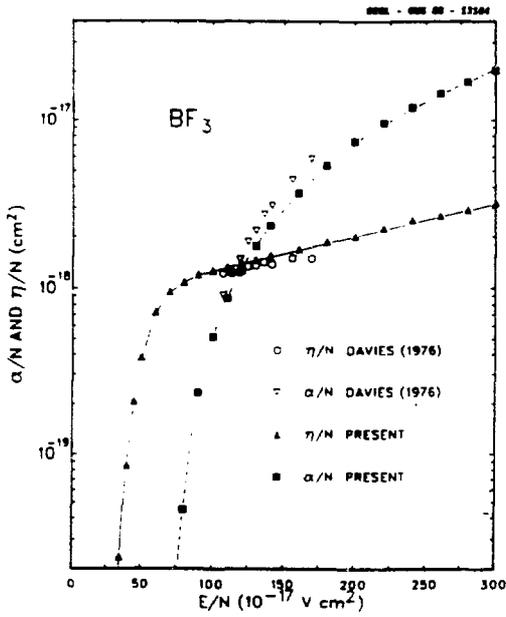


Fig. 12.  $\alpha/N(E/N)$  and  $\eta/N(E/N)$  for BF<sub>3</sub> [Ref. 17] and SiF<sub>4</sub> and SiF<sub>4</sub>/TEA mixtures [Ref. 18].

From the point of view of gas switches, knowledge and control of the magnitude and  $E/N$  dependence of  $w$  are most significant. For example, in the case of externally-sustained diffuse discharge opening switches an electron drift velocity is required which maximizes at the  $(E/N)$  conduction and which then falls off for higher  $E/N$  values. Studies

of electron motion in gases have shown<sup>2,4,8,21</sup> that knowledge of the cross sections for elastic and inelastic processes in gases can be employed to identify gaseous media with enhanced drift velocities and/or specific  $w(E/N)$  dependencies. For example, it has been shown that for a number of molecular gases<sup>17</sup> and gas mixtures<sup>8,21a</sup> (e.g., Ar-CF<sub>4</sub>, Ar-C<sub>2</sub>F<sub>6</sub>, Ar-C<sub>3</sub>F<sub>8</sub>, CH<sub>4</sub>-CF<sub>4</sub>),  $w$  can be enhanced and a rapidly increasing  $w$  with increasing  $E/N$  at relatively low  $E/N$  can be followed by a region of higher  $E/N$  values where  $w$  actually decreases with increasing  $E/N$ . The latter phenomenon--where  $w$  decreases with increasing  $E/N$  ( $\partial w/\partial(E/N) < 0$ )--has been termed negative differential conductivity (NDC) and roughly occurs when<sup>22</sup>

$$\frac{\partial w}{\partial(E/N)} = \frac{A\epsilon_i}{2mw} \frac{\langle v_i \rangle}{\langle v_m \rangle} \left[ \frac{1}{\langle v_i \rangle} \frac{\partial \langle v_i \rangle}{\partial(E/N)} - \frac{1}{\langle v_m \rangle} \frac{\partial \langle v_m \rangle}{\partial(E/N)} \right]$$

Here,  $v_i$  is the inelastic and  $v_m(v) (= Nv\sigma_m(v))$  the momentum transfer collision frequency,  $\epsilon_i$  is the energy loss for the inelastic process, and  $A$  is a slowly varying constant as a function of  $E/N$  with a value near unity. From the above approximate expression it is seen that an NDC effect will be observed when  $\langle v_m \rangle$  rapidly increases and  $\langle v_i \rangle$  rapidly decreases with increasing  $E/N$ .

In Fig. 13a, are shown examples of gases with distinct maxima in  $w(E/N)$ , very high values of  $w$ , and an NDC effect,<sup>8,21</sup> and in Fig. 13b are shown mixtures of C<sub>2</sub>F<sub>6</sub> in Ar exhibiting similar behavior. The latter measurements (see, also, Refs. 2 and 8) show that the maximum in  $w(E/N)$  can be moved along the  $E/N$  axis by changing the concentration of the additive in Ar thus allowing flexibility in the tailoring of switching gas mixtures. The molecules CH<sub>4</sub>, CF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub> are known to possess--as does Ar--Ramsauer-Townsend-type minima in their total electron scattering cross sections along with large vibrational excitation cross sections at electron energies of a few tenths of an eV.<sup>23</sup> The SiF<sub>4</sub> and BF<sub>3</sub> molecules may exhibit a similar cross section behavior<sup>17</sup> in view of the  $w(E/N)$  data in Fig. 13a.

### III. EXAMPLES OF NEW GAS SWITCHING CONCEPTS BASED ON RECENT KNOWLEDGE OF ELECTRON COLLISIONS IN GASES

The specific, delicate, and frequently strong dependencies of  $\eta/N$ ,  $\alpha/N$ , and  $w$  on  $E/N$ , and of electron attachment on the internal energy content of switch gas molecules has recently led to a number of promising new switching concepts. Thus, the dependencies of  $k_a$  and  $w$  on  $E/N$  of a number of gases/mixtures which have the desirable properties listed in Table 1 for C (Column 3) has led to the identification of excellent gaseous media for externally-sustained diffuse discharge opening switches (Table 2, Column 3, Refs. 2 and 8). Similarly, since optically-enhanced

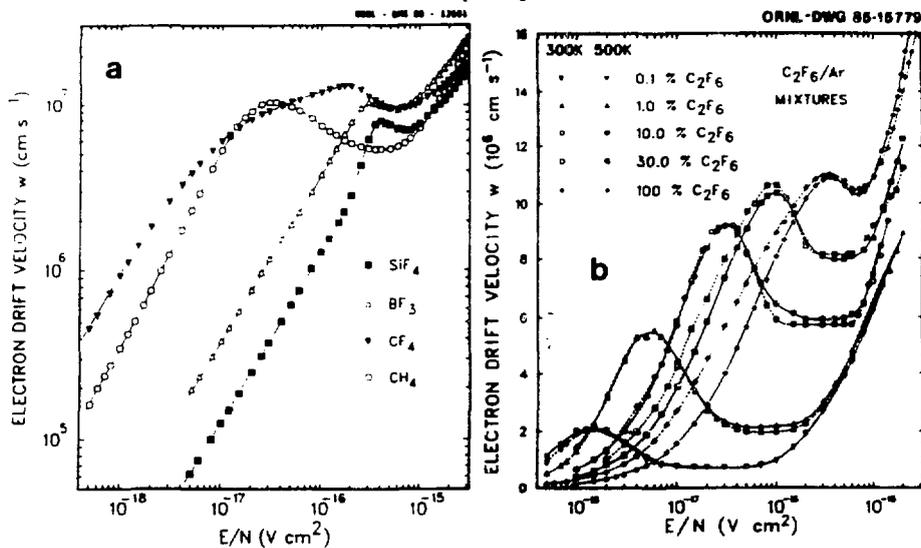


Fig. 13. (a)  $w(E/N)$  for  $\text{SiF}_4$ ,  $\text{BF}_3$ ,  $\text{CF}_4$ , and  $\text{CH}_4$  ( $T \approx 300\text{K}$ ; Ref. 17). (b)  $w(E/N)$  for  $\text{C}_2\text{F}_6$  and  $\text{C}_2\text{F}_6/\text{Ar}$  mixtures at 300 and 500K.

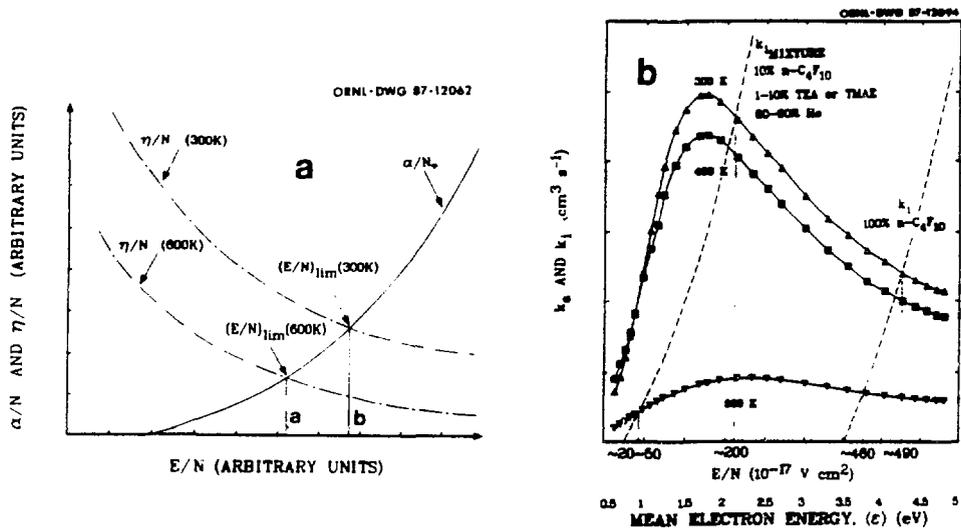


Fig. 14: (a) Schematic of the desirable  $\eta/N$  ( $E/N$ ) and  $\alpha/N$  ( $E/N$ ) characteristics at 300 and 600K. The desirable  $(E/N)_{lim}$  values at these temperatures are also indicated. (b) The approximate dependence of the rate constant  $k_a$  for attachment and  $k_i$  for ionization on  $\langle \epsilon \rangle$  and  $E/N$  in pure  $n\text{-C}_4\text{F}_{10}$  and in a gas mixture composed of  $\sim 10\%$   $n\text{-C}_4\text{F}_{10}$ , 1-10% TEA or TMAE and the balance He [9h,18].

electron attachment processes can allow a gas which is a conductor when it is not irradiated by a laser become an insulator when it is irradiated by a laser, and, conversely, since photodetachment of pre-formed negative ions can allow a gas which is an insulator when it is not irradiated by a laser to become a conductor when it is irradiated by a laser, the possibility exists of developing an optical switch whereby the electrical insulation/conduction properties of the gas are switched optically at ns times. While, in principle, these two mechanisms--optically-enhanced attachment and photodetachment--can be employed as discharge control mechanisms, more basic studies are required before an optical switch is realized.<sup>2, 16, 18, 24</sup>

Dielectric gases/mixtures (see Table 2, first column) which are excellent insulators when cold ( $\sim 300\text{K}$ ) due largely to their large  $k_a$  at these  $T$ , and which become poorly electron attaching when warm (e.g., see Fig. 8) can be used to improve the efficiency of spark gap closing switches.<sup>9g</sup> The efficiency of such devices is increased when the ratio  $V_c/V_s$  of the voltage  $V_c$  between the switch electrodes during the conducting stage and  $V_s$  during the insulating stage is reduced. The gases  $c\text{-C}_4\text{F}_8$  and  $c\text{-C}_4\text{F}_{10}$  are especially good additives in binary and ternary mixtures because at room temperature their  $V_s$  is high and because their  $k_a(\langle\epsilon\rangle)$  are small at low  $E/N$  and high  $T$ .

The recent knowledge on  $k_a(\langle\epsilon\rangle, T, E/N)$ ,  $\eta/N_a(T, E/N)$ , and  $\alpha/N(E/N)$  on a number of gases/mixtures can possibly be used<sup>2, 18</sup> to increase the efficiency of self-sustained diffuse discharge closing switches (i.e., lower the voltage drop across the switch) and the stability of the discharge (i.e., increase the conduction time of the discharge to  $\sim 100$  ns) during switch conduction. Two ways through which this can be done are depicted in Fig. 14a,b. The example in Fig. 14a refers to a gaseous medium (e.g.,  $c\text{-C}_4\text{F}_8$  in He) whose  $k_a(\langle\epsilon\rangle)$  or  $\eta/N_a(E/N)$  peaks at thermal energies ( $T \approx 300\text{K}$ ) and decreases with increasing  $T$  above ambient. During the opening stage of the switch the gas is cold ( $\approx 300\text{K}$ ) and the  $(E/N)_{\text{lim}}$  is high (represented by  $b$  in Fig. 14a). During the conducting stage of the switch the energy dissipated in the gas can increase the internal energy of the attaching gas molecules, i.e., warm up the gas. This will decrease  $\eta/N_a$ , but it will not affect  $\alpha/N$  and consequently the self-sustaining electric field of the discharge will decrease (dropping, say, to a value  $a$  as shown in Fig. 14a). Hence, the impedance of the discharge will be lowered and the switch efficiency increased.

Figure 14b depicts the principle of a second concept whereby a three-component system is employed: a rare gas buffer (e.g., He), a low-ionization onset ( $\lesssim 8\text{ eV}$ ) additive (e.g., TEA or TMAE), and an electronegative gas (e.g.,  $n\text{-C}_4\text{F}_{10}$ ) whose  $k_a$  at room temperature peaks at  $\epsilon \gtrsim 1\text{ eV}$ , decreases considerably with increasing  $T$ , and its peak shifts to lower  $E/N$  as  $T$  increases. In Fig. 14b the  $k_a$  for  $n\text{-C}_4\text{F}_{10}$  is plotted versus  $E/N$  (and  $\langle\epsilon\rangle$ ; see also Fig. 5) along with the expected<sup>18</sup> electron impact ionization rate constant  $k_i(E/N)$  for  $n\text{-C}_4\text{F}_{10}$ . Addition of TEA or TMAE to a mixture of  $n\text{-C}_4\text{F}_{10}$  in He will cause the  $k_i(E/N)$  curve for the

ternary mixture to move to lower  $E/N$  until for the appropriate concentrations of the components shown in Fig. 14b, the  $k_i(E/N)$  for the mixture resembles that shown in the figure. The  $(E/N)_{lim}$  for this mixture (Fig. 14b) is reduced from  $\sim 200 \times 10^{-17} \text{ V cm}^2$  at  $T \approx 300\text{K}$  to  $\sim 20 \times 10^{-17} \text{ V cm}^2$  at  $T = 500\text{K}$ . If such an increase in  $T$  is manifested during the operation of the gas discharge, the switch efficiency would be enhanced.

Table 2: Examples of Candidate Gases for Three Types of Gas Switches  
(See the text and cited literature.)

Spark Gap Closing	Diffuse Discharge Closing (Self-Sustained)	Diffuse Discharge Opening (Externally-Sustained)
c-C <sub>4</sub> F <sub>8</sub> or n-C <sub>4</sub> F <sub>10</sub> or C <sub>3</sub> F <sub>8</sub> in Ar or He or N <sub>2</sub> or Ar + C <sub>2</sub> H <sub>2</sub> <sup>†</sup> or He + C <sub>2</sub> H <sub>2</sub> <sup>†</sup>	c-C <sub>4</sub> F <sub>8</sub> + He n-C <sub>4</sub> F <sub>10</sub> + He + TEA <sup>†</sup> SiF <sub>4</sub> or BF <sub>3</sub> in He or Ne or Ar or He, Ne, Ar. + TMAE <sup>†</sup>	C <sub>2</sub> F <sub>6</sub> or C <sub>3</sub> F <sub>8</sub> in Ar or CH <sub>4</sub> or Ar + C <sub>2</sub> H <sub>2</sub> <sup>†</sup> or Ar + c-C <sub>4</sub> H <sub>8</sub> <sup>†</sup>

<sup>†</sup>Or other low ionization onset additive.

Finally, specific  $E/N$  dependencies of  $\alpha/N$  and  $\eta/N_a$  can be employed<sup>2, 18</sup>--in several ways--to improve the efficiency and stability of high current self-sustained diffuse gas discharges. Thus, the use of electronegative gases in which the  $\bar{\alpha}/N$  near the  $(E/N)_{lim}$  of the gas is minimal will enhance the stability of the discharge while the addition of a rare gas to the mixture will lower  $(E/N)_{lim}$  and thus increase the switch efficiency. Also, it may be possible to tailor the  $\alpha/N(E/N)$  and  $\eta/N_a(E/N)$  of a gas mixture such that the gas is ionized and conducts at low  $E/N$  and is an insulator at higher  $E/N$  (see Fig. 15 and Refs. 2 and 18).

#### IV. CONCLUSION

Significant basic new knowledge on electron-molecule--especially on electron-excited molecule--collisions in switch gases has been methodically acquired recently, and is being successfully used to modify, control and/or modulate the insulation/conduction properties of gaseous matter and the development of pulsed power gas switches.

#### V. REFERENCES

1. Crudely speaking, a gas is a good conductor when the free electrons present in it remain free and have large drift velocities  $w$ , and it is a good insulator when  $w$  is small and virtually all the electrons present are attached forming negative ions. Thus, switching or modulating the conduction/insulation properties of gaseous matter largely involves switching or modulating the relative numbers of free and attached electrons.

2. See, for example, articles in: (a) L. G. Christophorou and M. O. Pace (Eds), Caseous Dielectrics IV, Pergamon (New York, 1984), Chapter 5; (b) L. G. Christophorou and D. W. Bouldin (Eds), Caseous Dielectrics V, Pergamon (New York, 1987), Chapter 7; (c) A. Guenther,

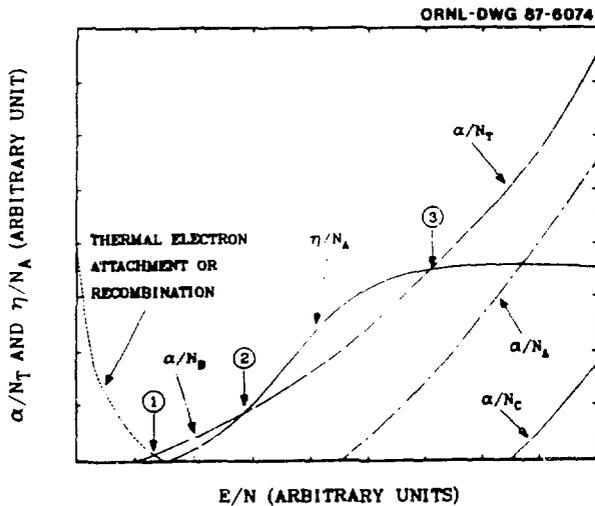


Fig. 15. The desirable  $\eta/N_A$  and  $\alpha/N_T$  ( $N_T$  = total gas number density) characteristics of gas mixtures for efficient self-sustained diffuse discharge closing switches:  $\alpha/N_A$ ,  $\alpha/N_B$ , and  $\alpha/N_C$ , refer respectively to the ionization coefficient of the electron attaching, low IO additive and high IO buffer gases. Between regions 1 and 2 the total ionization coefficient  $\alpha/N_T$  is larger than the attachment coefficient  $\eta/N_A$  while between regions 2 and 3  $\eta/N_A$  is larger than  $\alpha/N_T$ .  $\alpha/N_T = 0$  at  $E/N$  values denoted by 1, 2, and 3 [From Ref. 18].

M. Kristiansen, and T. Martin (Eds), Opening Switches, Plenum (New York, 1987); (d) P. J. Turchi and B. H. Bernstein (Eds), Proceedings of the 6th IEEE Pulsed Power Conference, Arlington, Virginia, IEEE Catalog Number 87CH2522-1, (1988).

3. See, for example, (a) L. G. Christophorou, Atomic and Molecular Radiation Physics, Wiley-Interscience, New York, 1971; (b) H. S. W. Massey, Negative Ions, Cambridge University Press, London, 1976; (c) B. M. Smirnov, Negative Ions, McGraw-Hill, New York, 1982.
4. (a) L. G. Christophorou (Ed), Electron-Molecule Interactions and Their Applications, Academic Press, New York, 1984, Volumes 1 and 2; (b) L. G. Christophorou, Plasma Physics 27, 237 (1987).
5. (a) S. M. Spyrou, I. Sauers, and L. G. Christophorou, J. Chem. Phys. 78, 7200 (1983); (b) S. R. Hunter and L. G. Christophorou, J. Chem. Phys. 80, 6150 (1984); (c) P. G. Datskos and L. G. Christophorou, J. Chem. Phys. 86, 1982 (1987); (d) S. R. Hunter, J. G. Carter, and L. G. Christophorou, J. Chem. Phys. 90, 4879 (1989).
6. L. E. Kline, D. K. Davies, C. L. Chen, and P. J. Chantry, J. Appl. Phys. 50, 6789 (1979).
7. A. Chutjian and S. H. Alajajian, Phys. Rev. A 31, 2885 (1985).
8. L. G. Christophorou, S. R. Hunter, J. G. Carter, and R. A. Mathis, Appl. Phys. Lett. 41, 147 (1982); S. R. Hunter, J. G. Carter, and L. G. Christophorou, J. Appl. Phys. 58, 3001 (1985).
9. (a) Ref. 4; (b) S. M. Spyrou, and L. G. Christophorou, J. Chem. Phys. 82, 1048 (1985); (c) A. A. Christodoulides, L. G.

- Christophorou, and D. L. McCorkle, *Chem. Phys. Lett.* 139, 350 (1987); (d) P. G. Datskos and L. G. Christophorou, *J. Chem. Phys.* 90, 2626 (1989); (e) S. M. Spyrou and L. G. Christophorou, *J. Chem. Phys.* 82, 2620 (1985); (f) S. M. Spyrou and L. G. Christophorou, *J. Chem. Phys.* 83, 2829 (1985); (g) L. G. Christophorou, R. A. Mathis, S. R. Hunter, and J. G. Carter, *J. Appl. Phys.* 63, 52 (1988); (h) L. G. Christophorou, S. R. Hunter, L. A. Pinnaduwege, P. G. Datskos, and J. G. Carter, *Proc. IXth Intern. Conf. Gas Discharges and Their Applications*, Venice, 19-23 Sept. 1988, p. 657.
10. P. J. Chantry and C. L. Chen, *J. Chem. Phys.* 90, 2585 (1989).
  11. P. G. Datskos, L. G. Christophorou, and J. G. Carter (unpublished).
  12. Z. Lj. Petrovic, W. C. Wang, and L. C. Lee, *J. Chem. Phys.* 90, 3145 (1989).
  13. C. L. Chen and P. J. Chantry, *J. Chem. Phys.* 71, 3897 (1979); I. M. Beterov and N. V. Fateyev, *J. Phys. (Paris) Colloq.* C7-447 (1983); M. W. McGeorch and R. E. Schlier, *Phys. Rev. A* 33, 1708 (1986); M. J. Rossi, H. Helm, and D. C. Lorents, *Appl. Phys. Lett.* 47, 576 (1985).
  14. L. G. Christophorou, J. G. Carter, and A. A. Christodoulides, *Chem. Phys. Lett.* 3, 237 (1969); 4, 646 (1970).
  15. P. D. Burrow, *J. Chem. Phys.* 59, 4922 (1973).
  16. (a) L. G. Christophorou, S. R. Hunter, L. A. Pinnaduwege, J. G. Carter, A. A. Christodoulides, and S. M. Spyrou, *Phys. Rev. Lett.* 58, 1316 (1987); (b) L. A. Pinnaduwege, L. G. Christophorou, and S. R. Hunter, *J. Chem. Phys.* 90, 6275 (1989); (c) Ref. 2d, p. 81.
  17. S. R. Hunter, J. G. Carter, and L. G. Christophorou, *J. Appl. Phys.* 65, 1858 (1989).
  18. S. R. Hunter, L. G. Christophorou, J. G. Carter, and P. G. Datskos, in Ref. 2d, pp. 1-8.
  19. L. G. Christophorou, in The Liquid State and Its Electrical Properties, E. E. Kunhardt, L. G. Christophorou, and L. H. Luessen (Eds), Plenum Press, New York, 1988, p. 283.
  20. S. R. Hunter, J. G. Carter, and L. G. Christophorou, *J. Chem. Phys.* 86, 693 (1987).
  21. (a) L. G. Christophorou, D. L. McCorkle, D. V. Maxey, and J. G. Carter, *Nucl. Instr. Meth.* 163, 141 (1979); (b) S. R. Hunter, J. G. Carter, and L. G. Christophorou, *Phys. Rev. A* 38, 58 (1988).
  22. Z. Lj. Petrovic, R. W. Crompton, and G. N. Haddad, *Austr. J. Phys.* 37, 23 (1984).
  23. G. N. Haddad, *Austr. J. Phys.* 38, 677 (1985); M. Hayashi and A. Niwa in 2b, p. 27.
  24. G. Schaefer and K. H. Schoenbach, *IEEE Trans. Plasma Sci.* PS-14, 561 (1986).