DISCLAIMER

BINARY AND TERNARY GAS MIXTURES WITH TEMPERATURE ENHANCED DIFFUSE GLOW DISCHARGE CHARACTERISTICS FOR USE IN CLOSING SWITCHES

Inventors: Loucas G. Christophorou
121 Nebraska Avenue
Oak Ridge, Tennessee 37830
U. S. Citizen

Scott R. Hunter
105 Mason Lane
Oak Ridge, Tennessee 37830
Citizen of Australia

Field of the Invention

The present invention relates, in general, to the art of switches, and in particular, to the art of glow discharge switches. Specifically, the present invention relates to a gas mixture used in glow discharge closing switches used in capacitive energy storage circuits.

Background of the Invention

The present invention was developed during work on a contract No. DE-AC05-840R21400 with the Department of Energy, and therefore, the Government has rights in this invention.

In certain applications, such as high-power microwave sources, pulsed lasers, particle beam generators, nuclear event simulators, and directional energy weapons, and the like, it is necessary to store electrical energy for release in pulses having extremely fast rise times (e.g., $\lesssim 10$ nanoseconds) and short durations (100 nanoseconds to microseconds).

High current self-sustained diffuse glow discharges are suitable for use in high voltage pulsed power applications where fast closing, high repetition rate switching is required. A schematic showing the operation of a UV light triggered glow discharge closing switch in a capacitive energy storage circuit is shown in Figure 1. The major problems that have been encountered with this type of switch are the high impedance of the discharge and the instabilty of the glow discharge which leads to the formation of electrical arcs between the switch electrodes and consequently destroys the repetitive operation of the switch. The voltage waveform that appears across the switch

electrodes is shown schematically in Figure 2. The present disclosure describes gas mixtures which will lower the switch voltage V_s (i.e., increase the switch efficiency) by the use of temperature modified electron attachment processes while at the same time increasing the stability of the discharge.

Accordingly, there is need for a gas mixture for use in such switches that has the capability for conducting a large amount of energy between the electrodes of a diffuse-discharge switch when the switch is in a conducting mode with a high electrical efficiency and which has a high insulating capability when the switch is in a nonconducting mode.

The physio-chemical properties required of the gas mixture to achieve high efficiency, stable discharge operation were discussed in detail for the first time in S.R. Hunter, L.G. Christophorou, J.G. Carter and P.G. Datskos, "New Concepts for High Current Self-Sustained Diffuse Discharge Closing Switches" to be published in the Proceedings of the 6th IEEE Pulsed Power Conference, Arlington, VA, June 29-July 1, 1987 (the disclosure of which is incorporated herein by reference). The stability of the glow discharge is enhanced by tailoring the electron attachment coefficient (η/N) and the ionization coefficient (α/N) of the gas mixture in such a way that the rate of change in the electron production and loss is minimal during small perturbations of the applied electric field beyond the glow discharge operating voltage level V_s.

The invention disclosed in the co-pending application by the present inventors, the disclosure of which is fully

incorporated herein by reference thereto (L.G. Christophorou and S.R. Hunter, "Ternary Gas Mixtures for Diffuse Discharge Switch," U.S. Patent to be issued, DOE No. ESID 156-X), discusses the various gases which may be used to improve the switching stability and efficiency of room temperature diffuse discharge closing switches. The present invention is distinguished from that invention by utilizing the heat generated in the diffuse discharge to improve the efficiency of the closing switch. This is accomplished by utilizing different physio-chemical properties of the gas mixture in comparison with those described in S.R. Hunter and L.G. Christophorou, "Binary and Ternary Gas Mixtures for Use in Glow Discharge Closing Switches," U.S. Patent Application, DOE No. ESID 243-X, the disclosure of which is fully incorporated herein by reference thereto, namely the large decrease in electron attachment with increasing gas temperature that has been observed to occur in several electronegative gases disclosed in the present disclosure.

However, increased efficiency and stability during the diffuse glow discharge is still needed to further enhance the desirable characteristics of this type of switch.

Objects of the Invention

It is a main object of the present invention to provide an improved diffuse-discharge switch system for use in generating high-energy electrical pulses.

It is another object of the present invention to provide a diffuse-discharge switch having a gas mixture therein which

conducts a large amount of electrical energy when initiated by an ultraviolet light source but which serves as an effective insulator when not activated by the light source.

It is another object of the present invention to provide a gas mixture for use in a glow discharge switch which exhibits temperature enhanced diffuse glow discharge characteristics.

It is another object of the present invention to provide a gas mixture for use in a glow discharge closing switch that will increase the efficiency of such a diffuse glow discharge closing switch at elevated temperatures.

It is another object of the present invention to provide a gas mixture for use in a glow discharge closing switch that will improve the stability at elevated temperatures of the switch during the conducting stage of that switch.

It is another object of the present invention to provide a gas mixture for use in a glow discharge closing switch which inhibit arc formation at elevated temperatures.

It is another object of the present invention to provide a gas mixture for use in a glow discharge closing switch which exhibits low resistivity at elevated temperatures during the conducting stage of operation.

It is another object of the present invention to provide a gas mixture for use in a glow discharge closing switch that exhibits fast recovery characteristics at elevated temperatures during the opening stage of operation.

It is another object of the present invention to provide binary and ternary gas mixtures for use in a glow discharge

switch that exhibit temperature enhanced diffuse discharge characteristics.

Summary of the Invention

These, and other, objects are accomplished by the present invention which is embodied in various gas mixtures that have temperature enhanced diffuse discharge characteristics that lead to stable low impedance glow discharges, thereby improving the switching characteristics of the system.

Specifically the gas mixtures embodying the present invention exhibit decreasing electron attachment at elevated temperatures thereby resulting in increased conductivity of the glow discharge. Such gas mixtures increase the efficiency of diffuse glow discharge switches above that of the gases used in previous glow discharge closing switches.

Most specifically, the present invention is embodied in a gas mixture exhibiting decreasing electron attachment with increasing gas temperature for use in diffuse glow discharge closing switches. The present invention comprises two species, as follows:

A gas selected from the group consisting of He, Ne, Ar, Kr, and Xe, or a mixture thereof, in combination with a second compound selected from the group consisting of c-C_4F_8, c-C_4F_6, n-C_4F_{10}, l-C_3F_6, c-C_3F_6, C_3F_8, C_6F_6, or mixtures thereof; or

a gas selected from the group consisting of He, Ne, Ar, Kr, and Xe, or mixtures thereof, in combination with a second compound selected from the group consisting of N,N,N',N'-

tetramethyl-1,4-benzenediamine (TMPD); 1,1',3,3'-tetramethyl-2,2'bi(imidazolidine) (TMBI); [tetrakis-(dimethyl)-amino]-ethylene (TMAE); N,N,N',N'-tetramethyl-p-phenylenediamine (TMAB); triethylamine; methylaniline; diethylamine; aniline; Co-ocene; Ch-ocene; Ni-ocene; and Fe-ocene, or mixtures thereof, in combination with a third compound selected from the group consisting of n-C_4F_{10}, C_3F_8, c-C_3F_6 and i-C_4F_{10}.

Brief Description of the Figures

Figure 1 is a schematic representation of a self-sustained diffuse discharge closing switch in a capacitive energy storage circuit of the type in which the invention can be advantageously employed.

Figure 2 is a schematic representation of the voltage-time characteristics for the repetitively operated self-sustained switch shown in Figure 1. The voltage pulse is applied at t_0, and the discharge current becomes significant at t_1. At t_3 the temperature enhanced conductivity process becomes important.

Figure 3 is a schematic of the desirable electron attachment coefficient η/N and ionization coefficient α/N characteristics as a function of E/N at gas temperatures T=300K and 600K. The desirable $(E/N)_{lim}$ values at these temperatures are also indicated.

Figure 4 is a graph of mean electron energy vs total electron attachment rate constant for c-C_4F_8 in N_2 for various gas temperatures T(K).

Figure 5 is a graph as in Figure 4 but for c-C_4F_6 in N_2.

Figure 6 is a graph as in Figure 4 but for 1-C_3F_6 in N_2.

Figure 7 is a graph as in Figure 4 but for $n\text{-}C_4F_{10}$ in N_2.

Figure 8 is a graph as in Figure 4 but for C_6F_6 in N_2.

Figure 9 is a graph as in Figure 4 but for C_3F_8 in N_2.

Figure 10 is a graph of temperature vs $(E/N)_{lim}$ curves for several gases.

Figure 11 is a graph as in Figure 4 also showing advantages of a ternary mixture in terms of (E/N) and $\langle \mathcal{E} \rangle$ vs k_1 and k_a.

Detailed Description of the Preferred Embodiments

In a fast closing switch of the present type, once the discharge has been triggered by an externally produced electron source, the discharge is self-sustained. That is, it does not require an external source of ionization to maintain the discharge, and will continue until the charge on the capacitor is depleted. This is in contrast to an externally sustained diffuse discharge opening switch which is used in an inductive energy storage circuit to extract pulses of energy from an inductor. This just-mentioned switch concept was the subject of two previous inventions by the present inventors and is described in the aforementioned patent application, DOE No. ESID 156-X and in U.S. Patent 4,063,130, the disclosures of which are incorporated herein by reference. Although both the self-sustained closing switch and the externally sustained opening switch rely on diffuse discharges, the operation, use and hence the physio-chemical properties required of the gas mixtures in the two switches are very different.

The basic requirements of a gaseous medium for use in a diffuse-discharge closing switch in a capacitive energy storage

type pulse generating system can best be understood by a consideration of the operation of the circuit illustrated in Figure 1. A storage capacitor 1 is charged from a high voltage source 2 through an isolating resistor 3. A switch 4 contains one of the subject mixtures and contains two electrodes 5 separated by a light path 6. The gap 6 is illuminated by a short burst of ultraviolet radiation from a laser of UV flash lamp 7, which produces a uniform photoionization of one or more of the gas components. A fast or slow rising pulse 10, Figure 2, is then applied across the electrodes at time t_0, which has the shape given by curves 10, 11, and 12, and is terminated at time t_3. After a given time interval t_f (the formative time lag required for the discharge to develop), a high current, uniform glow discharge is formed in the gap between the electrodes, starting at time t_1 and the voltage across the electrodes decreases (curve 13) and levels off at curve 14. At time t_3 the gas begins to heat up due to inelastic loss processes in the discharge, and the electron attachment coefficient η/N starts to decreases as shown schematically in Figure 3. The switch voltage V_S [or alternatively the switch electric field strength $(E/N)_{lim}$] similarly decreases as indicated in Figure 3, and follows curve 15 to a much lower value and levels off at time t_4 in Figure 2. The switch continues to conduct with much improved efficiency until the applied voltage pulse V_A is terminated at time t_5, opening the switch.

Several electronegative gases having the desired temperature dependence in the electron attachment process are

shown in Figures 4 - 9 where the electron attachment rate k_a ($=w(\eta/N)$; where w is the electron drift velocity and η/N is the electron attachment coefficient) is plotted as a function of the mean energy of the electrons $\langle\varepsilon\rangle$ in the discharge at several gas temperatures T. Temperature dependent $(E/N)_{lim}$ curves for several of these gases are shown in Figure 10. These measurements indicate that as the gas temperature is raised, the operating electric field strength in the switch $(E/N)_{lim}$ decreases.

The $(E/N)_{lim}$ measurements given in Figure 9 were performed for pure gases. It is noted that adding 1% to 50% (by volume) of these electronegative gases to a more abundant rare gas buffer gas will reduce the $(E/N)_{lim}$ of the room temperature gas mixtures within the switch, i.e., reduce the voltage drop across the switch at a given gas number density and hence improve the discharge efficiency. Also, the percentage change in the $(E/N)_{lim}$ as a function of gas temperature will be much larger. This is expected to be due to a more favorable overlap of the electron energy distribution function of the electrons in the discharge with the lower energy portion of the electron attachment cross section in the gas mixture than for the pure electron attaching gas.

It is also noted that the η/N values in the gas mixture are thus expected to experience a greater percentage decrease with increasing gas temperature near the $(E/N)_{lim}$ value than those of the pure gas, and consequently, $(E/N)_{lim}$ will similarly experience a greater percentage decrease with increasing gas temperature T. This leads to a more efficient switch than is

possible with gas temperature independent electron attachment processes.

The binary electron attaching gas mixtures are listed in descending order of preference in Table I below:

TABLE I

Binary Gas Mixtures

Electron Attaching Gases	Rare Gas Buffer Gases
$c\text{-}C_4F_8$	He
$c\text{-}C_4F_6$	Ne
$1\text{-}C_3F_6$	Kr
$n\text{-}C_4F_{10}$	Xe
C_6F_6	Ar
C_3F_8	
$c\text{-}C_3F_6$	

The concentration of the attaching gas in the buffer gas is 1% to 50% by volume. Combinations of all these attaching gases in any of the rare gases are possible.

For ternary gas mixtures, the electron attachment rate constants in $n\text{-}C_4F_{10}$ and C_3F_8 indicate that the electron attachment rate constant k_a [= $w(\eta/N)$] at room temperature ($\approx$300K) peaks at mean electron energies $\langle\varepsilon\rangle$=1 to 3 eV. In particular, the k_a values for $n\text{-}C_4F_{10}$ decrease by almost an order of magnitude over the gas temperature, T, range $350 \leq T \leq$

500 K with the peak in k_a moving from $\langle\varepsilon\rangle \approx 1.2$eV to $\gtrsim$2.2 eV at 500K. These specific properties of the electron attachment process in n-C_4F_{10} (and possibly C_3F_8, c-C_3F_6 and i-C_4F_{10}) in which (1) the room temperature k_a values peak at electron energies will in excess of thermal energies (i.e.,>1 eV), (2) the k_a values considerably decrease in magnitude with increasing gas temperature, and (3) the peak in the k_a measurements moves to higher mean electron energies (i.e., higher E/N values) with increasing gas temperature, can be used to achieve a much greater percentage reduction in $(E/N)_{lim}$ at the higher gas temperatures that can be achieved utilizing the binary gas mixtures.

The principle of the technique can be seen by examining the k_a measurements for n-C_4F_{10} which are replotted in Figure 11 along with the expected electron impact ionization rate constant k_i [= $w(\alpha/N)$] for n-C_4F_{10} plotted both as a function of $\langle\varepsilon\rangle$ and also on an approximate E/N scale.

Adding a low ionization threshold gas additive to a mixture of n-C_4F_{10} in a rare gas buffer gas will cause the k_i curve for the ternary mixture to move to lower $\langle\varepsilon\rangle$ (or E/N) values until, for a given concentration of each component the k_i (mixture) curve as a function of $\langle\varepsilon\rangle$ (or E/N) is obtained. The $(E/N)_{lim}$ of this mixture (defined when $\alpha/N = \eta/N$ or $k_i = k_a$) at room temperature is about 200 x 10^{-17} V cm^2. When the gas temperature is raised (i.e., during the operation of the gas discharge) the $(E/N)_{lim}$ will move to a much lower value; possibly as low as about 20 x 10^{-17} V cm^2 at about 500K as is shown schematically

in Figure 11. The $(E/N)_{lim}$ of this mixture will decrease by up to an order of magnitude; whereas, in the binary mixtures, the $(E/N)_{lim}$ will decrease by at most a factor of 2 to 5. The larger drop in $(E/N)_{lim}$ in the ternary mixture in comparison with that expected in the binary mixtures is due to the k_1 curve in the mixture shifting to the low E/N side of the k_a curve at the elevated gas temperatures. This phenomenon does not occur in the binary gas mixtures as the thresholds for ionization in the rare gas buffer gasses and the electron attaching gases are too high (<12 eV) for this effect to occur; the effect is due to the presence of the low ionization onset additive in the ternary gas mixture.

The specific characteristics required of each component of the ternary gas mixture are as follows:

1. Electron attaching gas: high energy electron attachment threshold, with $k_a(\langle\varepsilon\rangle)$ peaking at $\langle\varepsilon\rangle > 1$ eV; $k_a(\langle\varepsilon\rangle)$ strongly dependent on gas temperature; the peak in k_a moves to higher $\langle\varepsilon\rangle$ with increasing gas temperature. (these properties are manifested only for a small number of molecules which the inventors have discovered; namely, $n\text{-}C_4F_{10}$, C_3F_8, $c\text{-}C_3F_6$ and $i\text{-}C_4F_{10}$.) 2. Low ionization threshold gas additive (threshold <8 eV). The concentration of the additive in the electron attaching gas is such that the $(E/N)_{lim}$ of the mixture occurs at E/N values above the peak in the electron attachment coefficient at room temperature, but occurs below the peak in the electron attachment coefficient at gas temperatures $T \lesssim 500K$.

3. Rare gas buffer gas to control the mean energy of the

discharge (and hence the value of $(E/N)_{lim}$ at room temperature). The suggested gases are given in Table II below.

TERNARY GAS MIXTURES

1. Electron attaching gas with high energy ($\langle\varepsilon\rangle$ > 1 eV) electron attachment peak and strongly temperature dependent electron attachment process.

Examples - $n\text{-}C_4F_{10}$ (and possibly C_3F_8, $c\text{-}C_3F_6$, $i\text{-}C_4F_{10}$)

2. Low ionization threshold gas additive ($\lesssim$ 8 eV).

Examples - Amines

	TMAE $((CH_3)_2N)_4C_2$	TMBI $C_2H_4N_4(C_4H_8)_2$	TMAB $((CH_3)_2N)_4C_4H_2$	TMPD $C_6H_4(N(CH_3)_2)_2$
I.P. (eV)	5.4	5.4	5.6	6.2

	Triethylamine $(C_2H_5)_3N$	Methylaniline $(C_6H_5NHCH_3)$	Diethylamine $(C_2H_5)_2NH$	Aniline $(C_6H_5NH_2)$
I.P. (eV)	7.5	7.5	8.0	8.0

Ocenes

	Co-Ocene $(C_5H_5)_2Co$	Ch-Ocene $(C_5H_5)_2Ch$	Ni-Ocene $(C_5H_5)_2Ni$	Fe-Ocene $(C_5H_5)_2Fe$
I.P. (eV)	5.7	6.0	6.7	6.8

3. Rare gas buffer gas to determine the mean electron energy

He, Ne, Ar, Kr, Xe (preferably He, then Ne).

Approximate concentration of each component.

Electron attaching gas : 1 to 80%
Ionizing gas additive : 0.1 to 20%
Rare gas buffer gas : 0 to 99%

Other gas combinations with similar temperature dependent electron attachment processes are possible; i.e., gases in which the electron attachment process peaks at high mean electron energies (E/N) at room temperature, decreases in magnitude significantly with increasing gas temperature with the peak in the electron attachment rate constant moving to higher mean electron energies (or E/N) at the higher gas temperatures.

It is to be understood that while certain forms of the present invention have been illustrated and described herein, it is not to be limited to the specific forms or arrangement of parts described and shown.

BINARY AND TERNARY GAS MIXTURES WITH TEMPERATURE ENHANCED DIFFUSE GLOW DISCHARGE CHARACTERISTICS FOR USE IN CLOSING SWITCHES

ABSTRACT

An improvement to the gas mixture used in diffuse glow discharge closing switches is disclosed which includes binary and ternary gas mixtures which are formulated to exhibit decreasing electron attachment with increasing temperature. This increases the efficiency of the conductance of the glow discharge and further inhibits the formation of an arc.

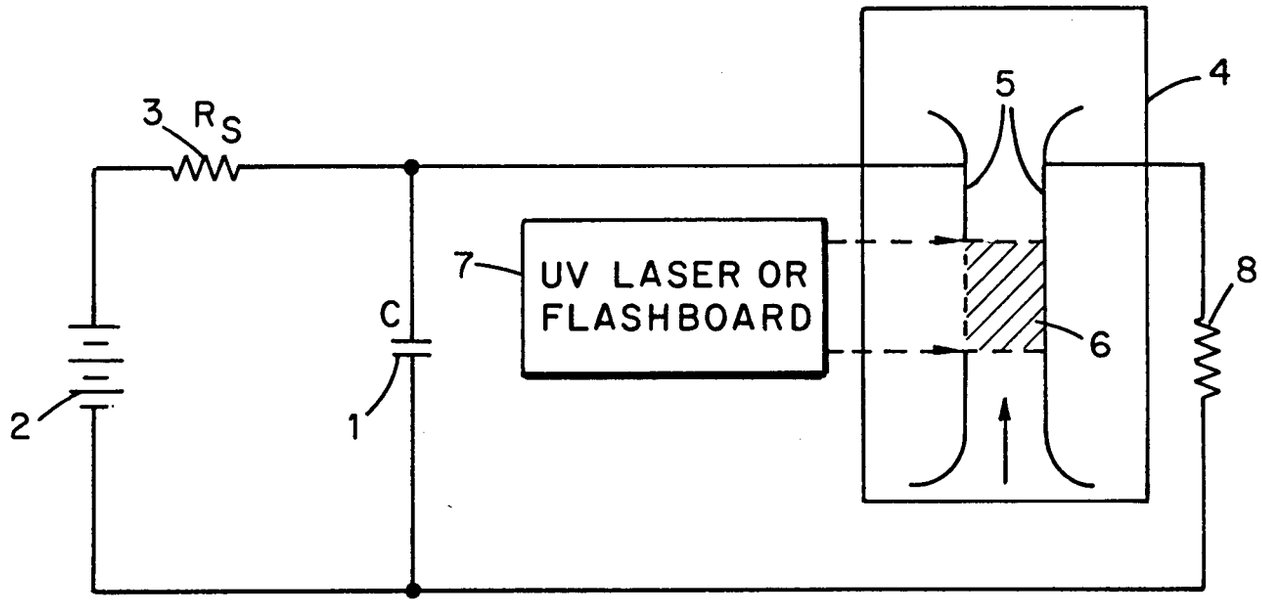
3 R_S
5
4
7
UV LASER OR
FLASHBOARD
C
8
6
2
1

Fig. 1

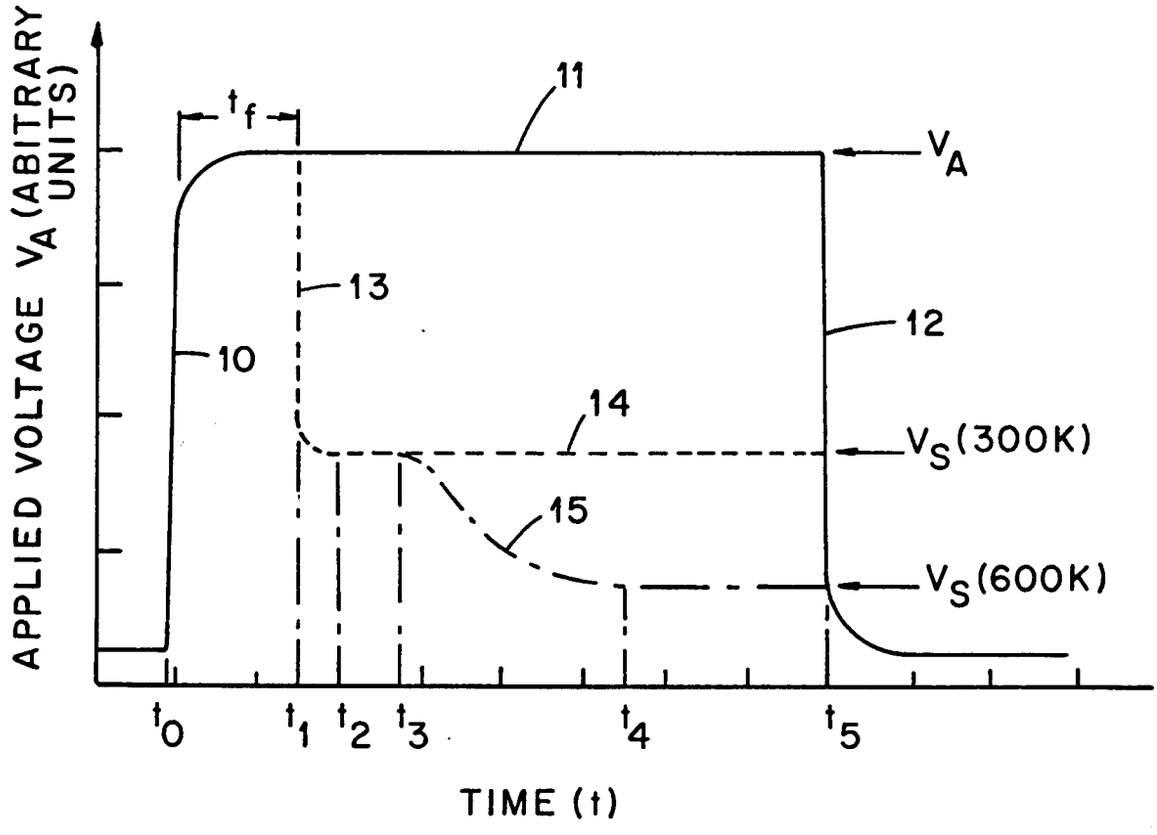
APPLIED VOLTAGE V_A (ABITRARY UNITS)
t_f
11
V_A
13
12
10
14
V_S(300K)
15
V_S(600K)
t_0
t_1
t_2
t_3
t_4
t_5
TIME (t)

Fig. 2

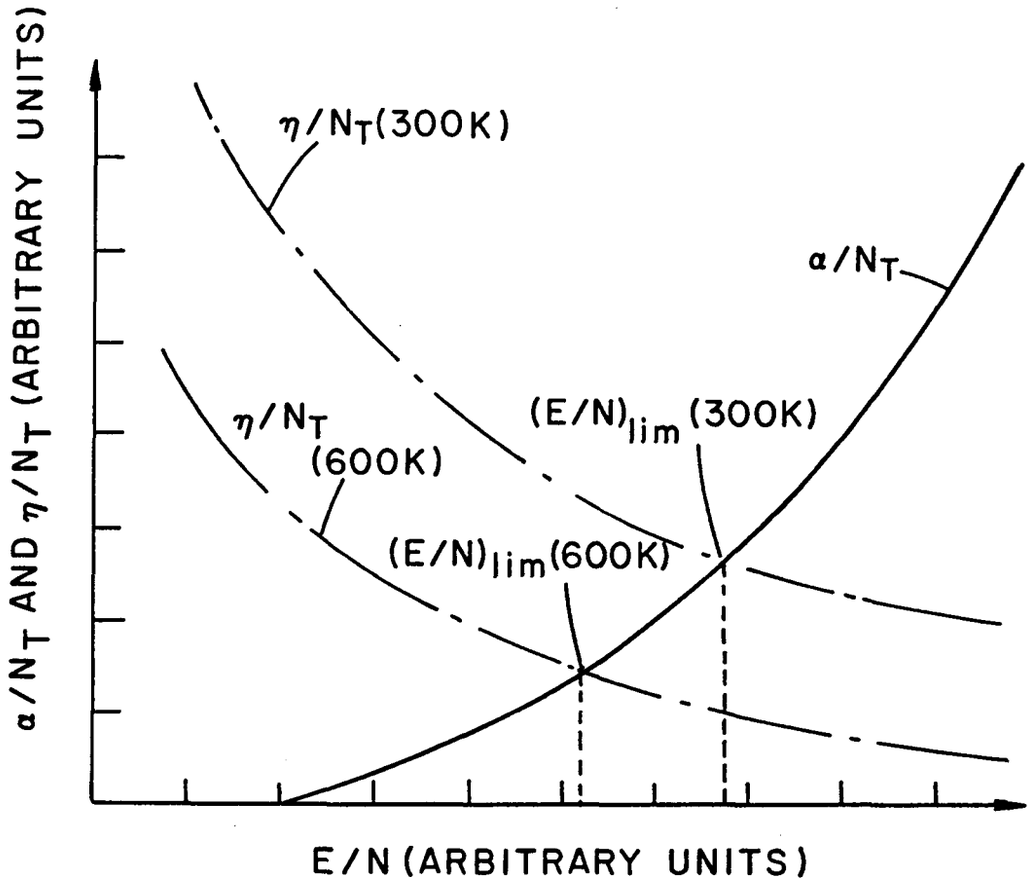
α/N_T AND η/N_T (ARBITRARY UNITS)
η/N_T(300K)
α/N_T
η/N_T
(600K)
(E/N)_lim (300K)
(E/N)_lim(600K)
E/N (ARBITRARY UNITS)

Fig. 3

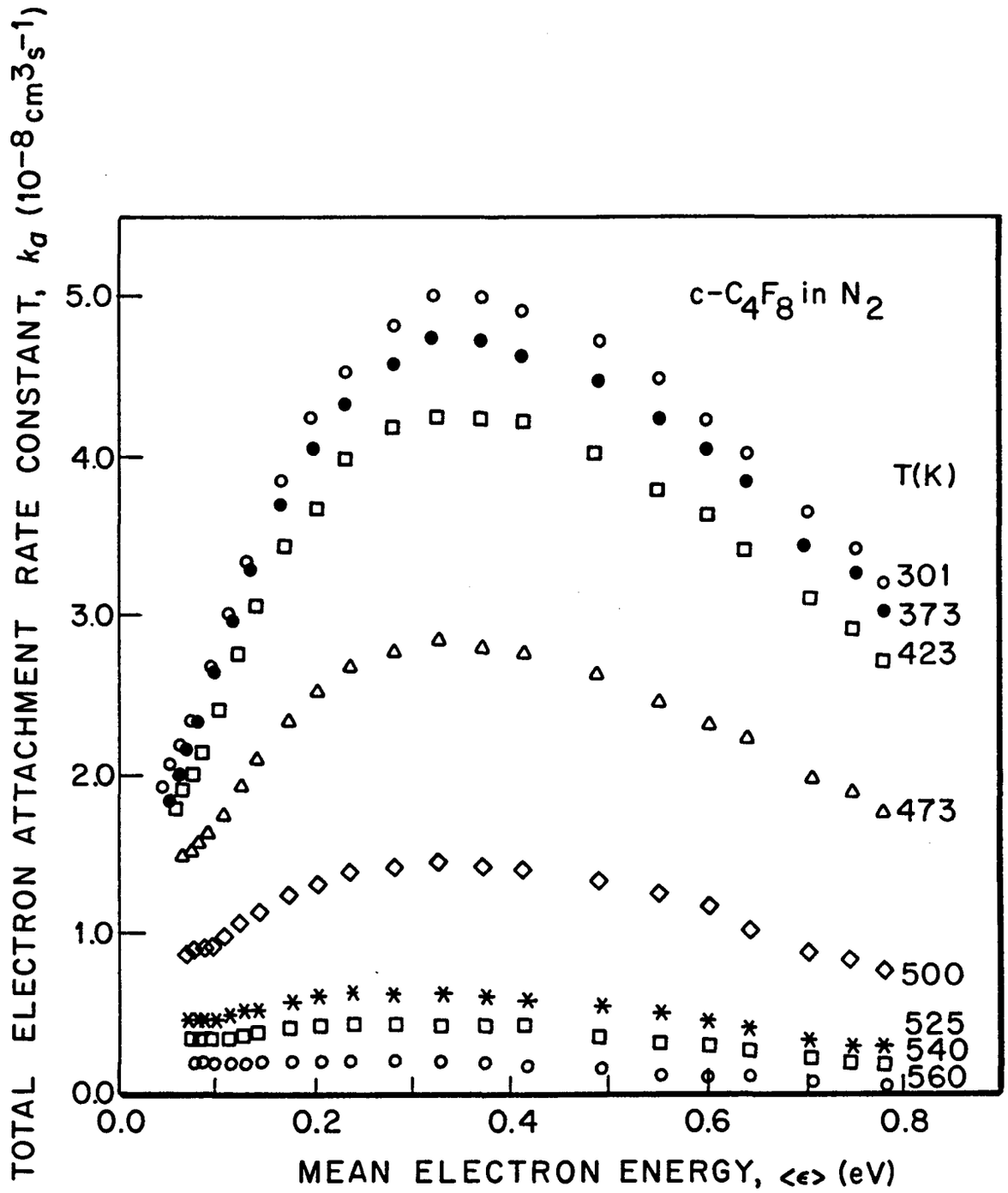
TOTAL ELECTRON ATTACHMENT RATE CONSTANT, k_a (10^{-8} $cm^3 s^{-1}$)
MEAN ELECTRON ENERGY, <ε> (eV)
c-C_4F_8 in N_2
T(K)
301
373
423
473
500
525
540
560
0.0
1.0
2.0
3.0
4.0
5.0
0.0
0.2
0.4
0.6
0.8

Fig.4

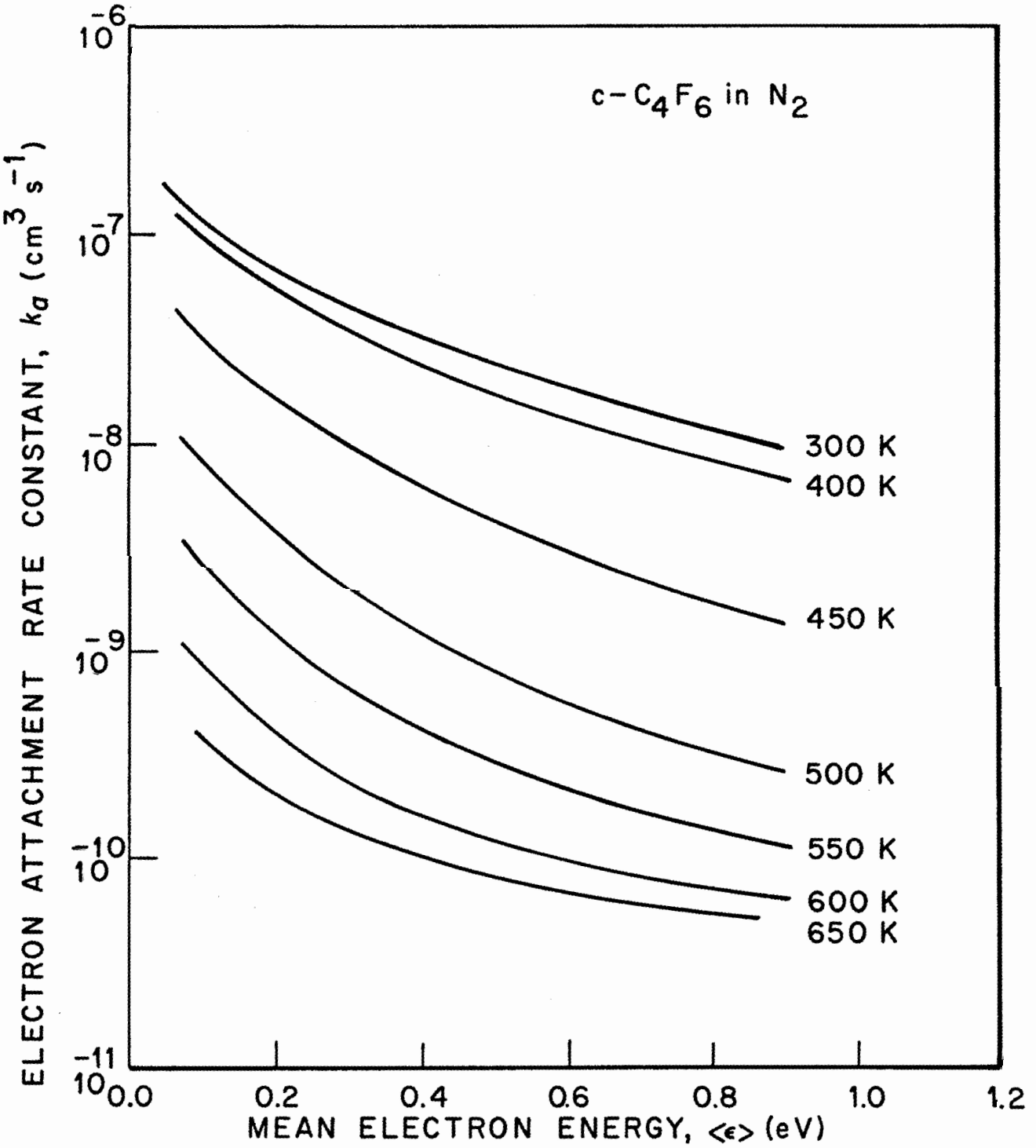
$c-C_4F_6$ in N_2
300 K
400 K
450 K
500 K
550 K
600 K
650 K
ELECTRON ATTACHMENT RATE CONSTANT, k_a ($cm^3 s^{-1}$)
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
0.0
0.2
0.4
0.6
0.8
1.0
1.2
MEAN ELECTRON ENERGY, <ε> (eV)

Fig. 5

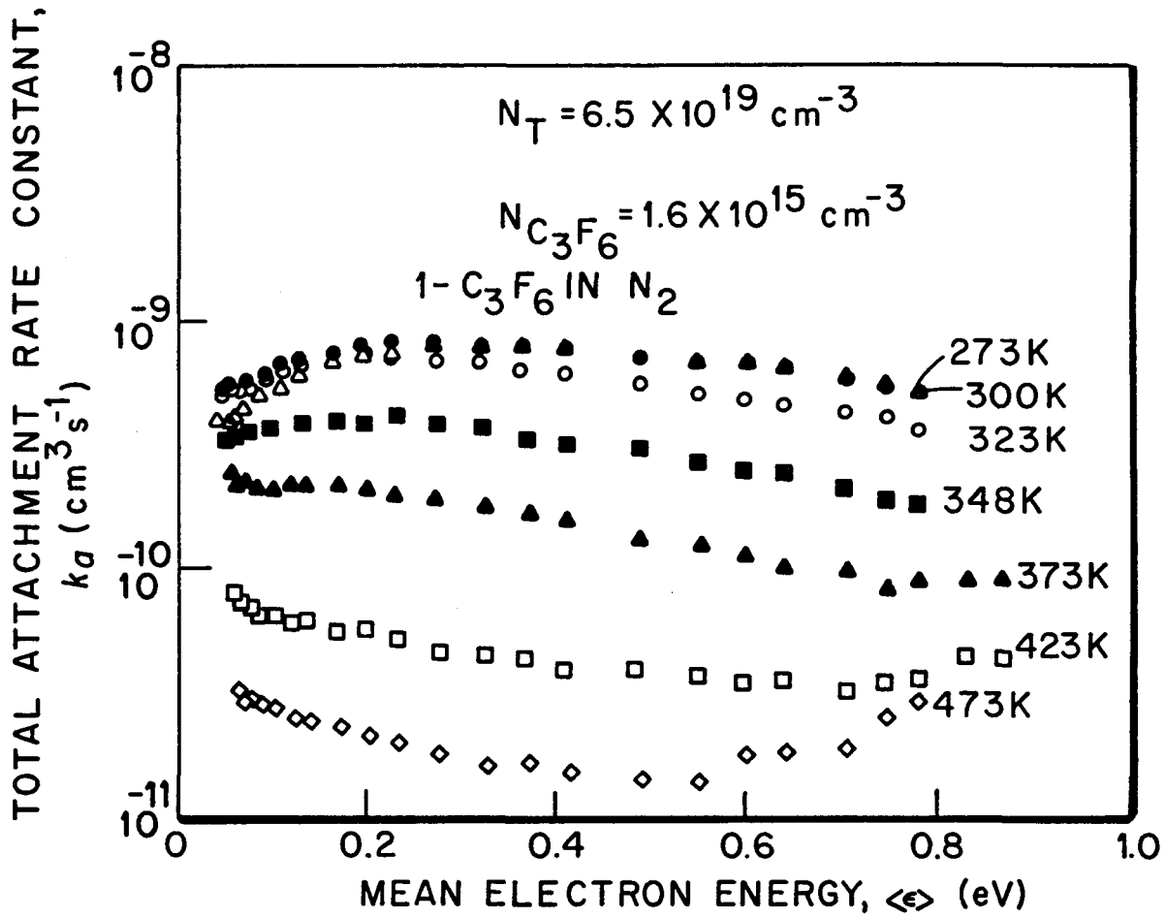
TOTAL ATTACHMENT RATE CONSTANT, k_a ($cm^3 s^{-1}$)
10^{-8}
10^{-9}
10^{-10}
10^{-11}
$N_T = 6.5 \times 10^{19}\ cm^{-3}$
$N_{C_3F_6} = 1.6 \times 10^{15}\ cm^{-3}$
$1\text{-}C_3F_6$ IN N_2
273K
300K
323K
348K
373K
423K
473K
0
0.2
0.4
0.6
0.8
1.0
MEAN ELECTRON ENERGY, <ε> (eV)

Fig. 6

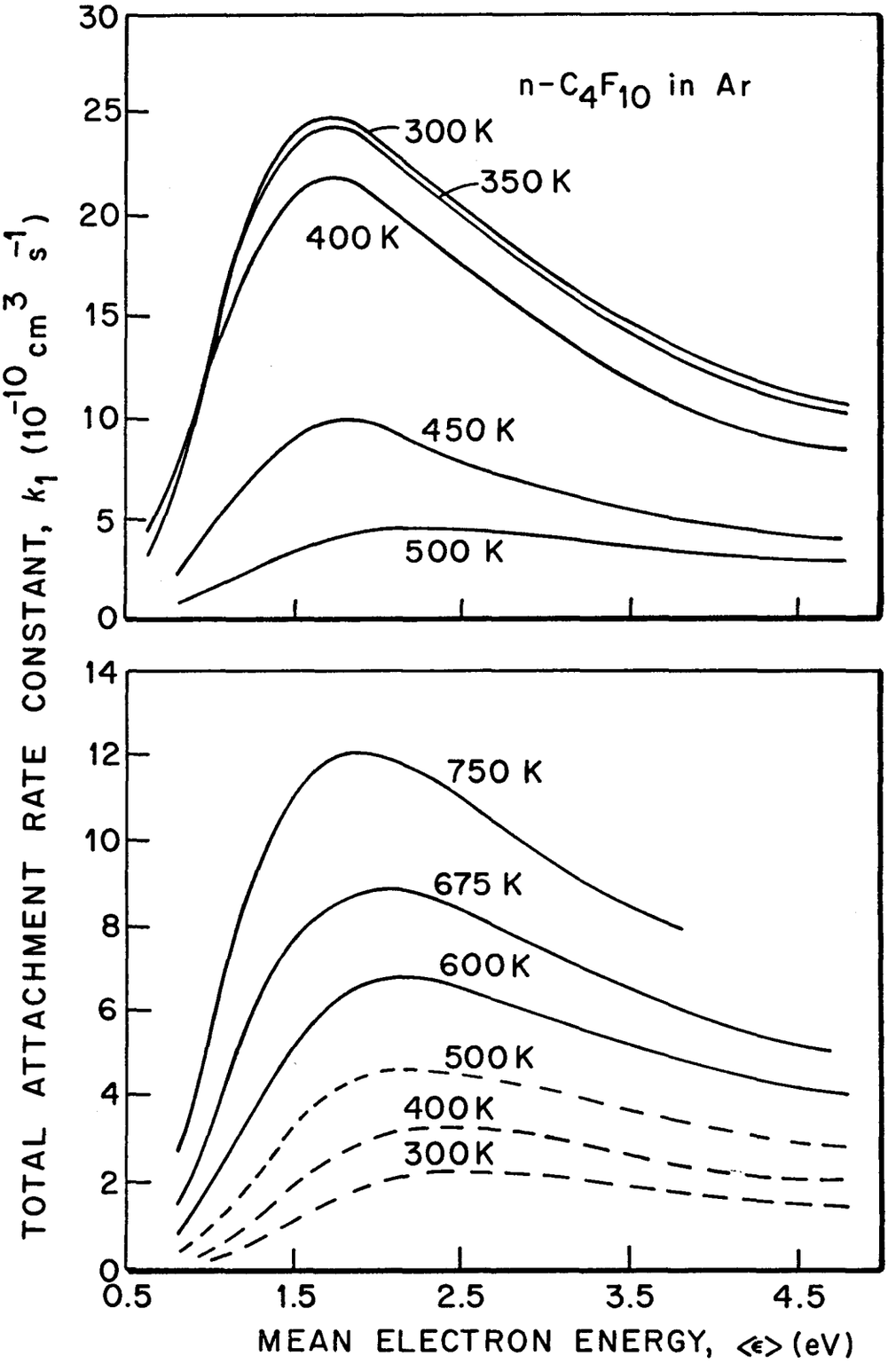
n-C4F10 in Ar
300 K
350 K
400 K
450 K
500 K
750 K
675 K
600 K
500 K
400 K
300 K
TOTAL ATTACHMENT RATE CONSTANT, k1 (10^-10 cm^3 s^-1)
MEAN ELECTRON ENERGY, <ε> (eV)
0
5
10
15
20
25
30
2
4
6
8
12
14
0.5
1.5
2.5
3.5
4.5

Fig. 7

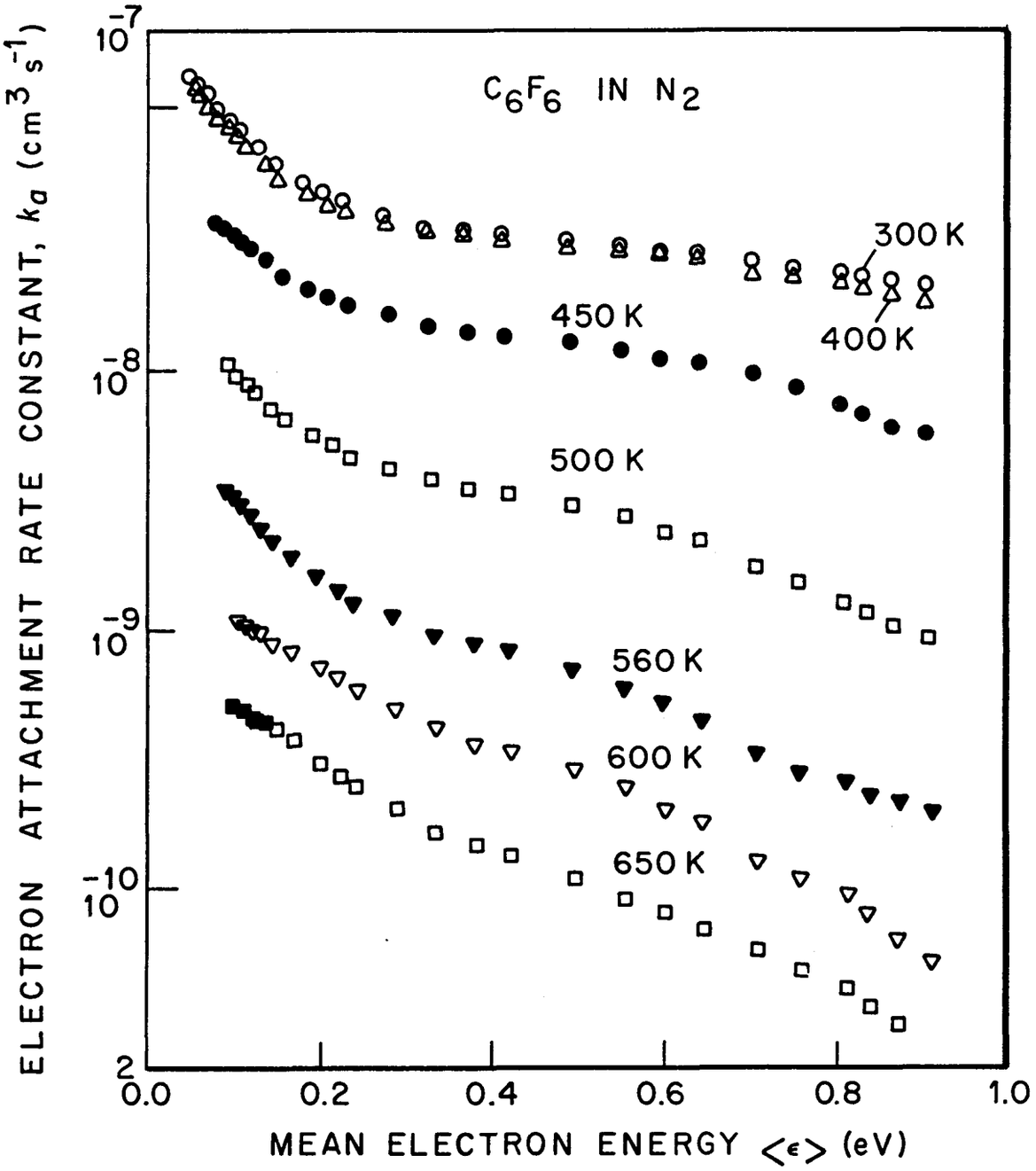
C_6F_6 IN N_2
300 K
400 K
450 K
500 K
560 K
600 K
650 K
ELECTRON ATTACHMENT RATE CONSTANT, k_a ($cm^3 s^{-1}$)
10^{-7}
10^{-8}
10^{-9}
10^{-10}
2
0.0
0.2
0.4
0.6
0.8
1.0
MEAN ELECTRON ENERGY $\langle \epsilon \rangle$ (eV)

Fig. 8

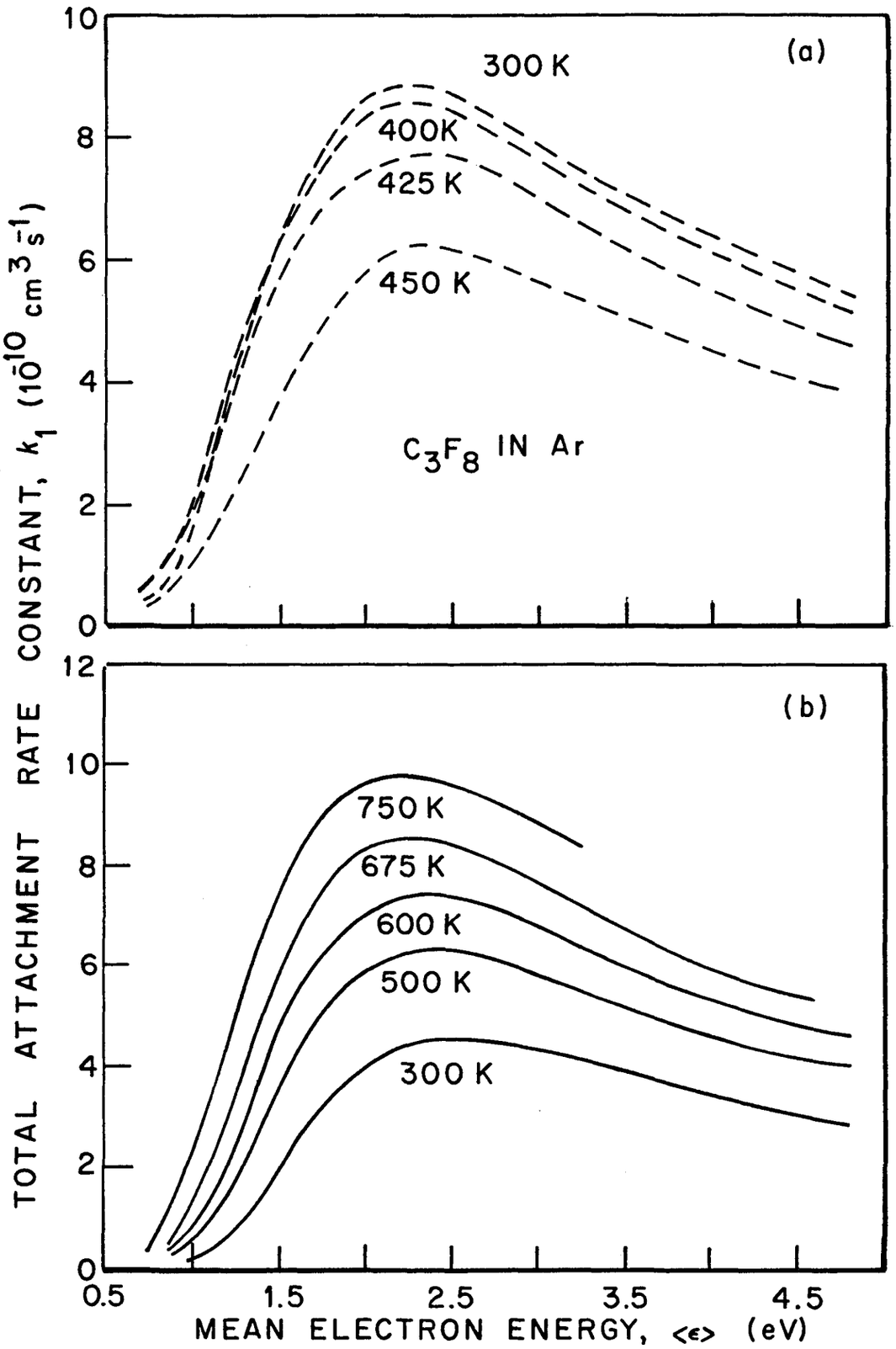
(a)
300 K
400K
425 K
450 K
C_3F_8 IN Ar
(b)
750 K
675 K
600 K
500 K
300 K
TOTAL ATTACHMENT RATE CONSTANT, k_1 (10^{10} cm^3 s^{-1})
MEAN ELECTRON ENERGY, <ε> (eV)
0
2
4
6
8
10
12
0.5
1.5
2.5
3.5
4.5

Fig. 9

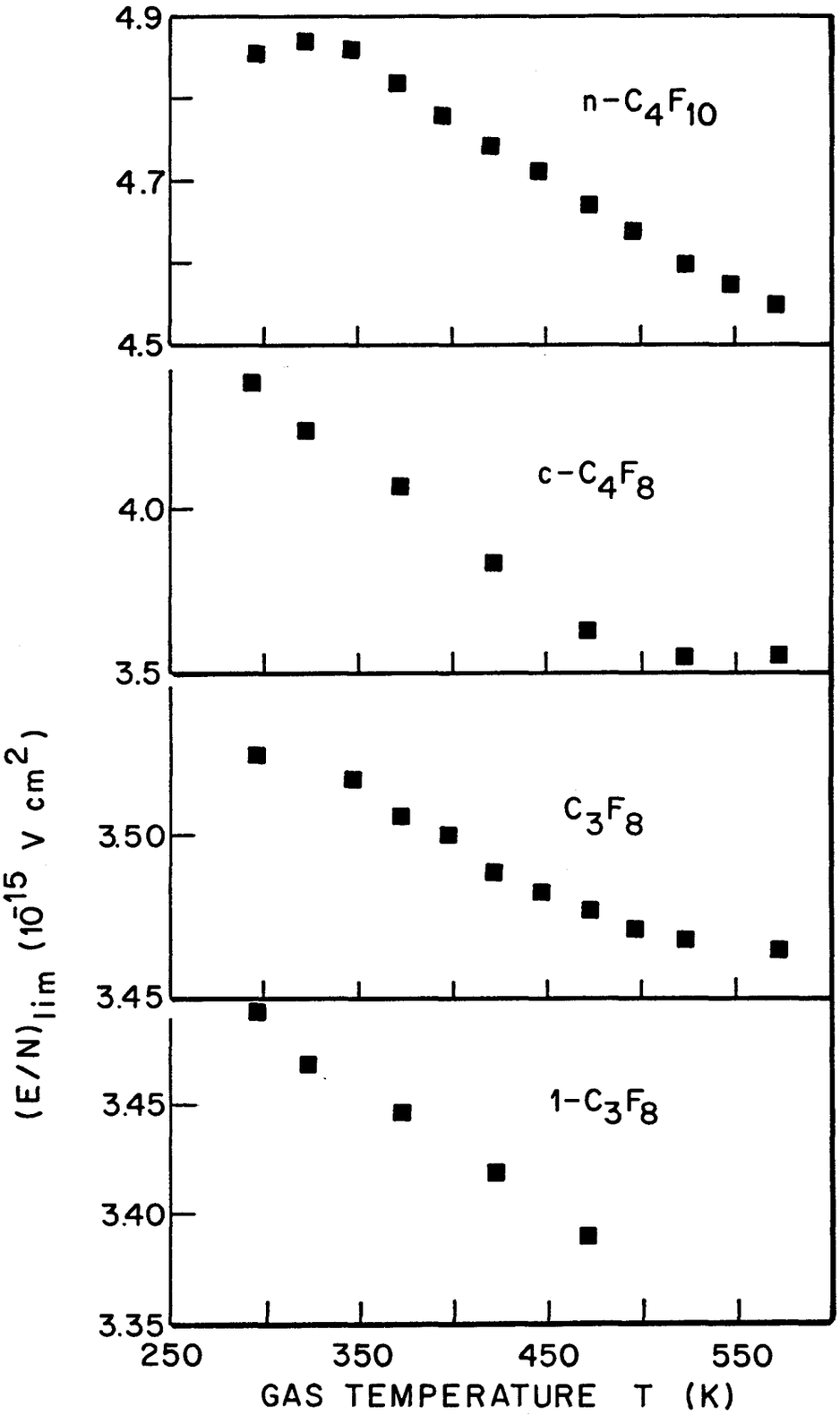
4.9
4.7
4.5
n-C4F10
4.0
3.5
c-C4F8
3.50
3.45
C3F8
3.45
3.40
3.35
1-C3F8
250
350
450
550
GAS TEMPERATURE T (K)
(E/N)lim (10-15 V cm2)

Fig.10

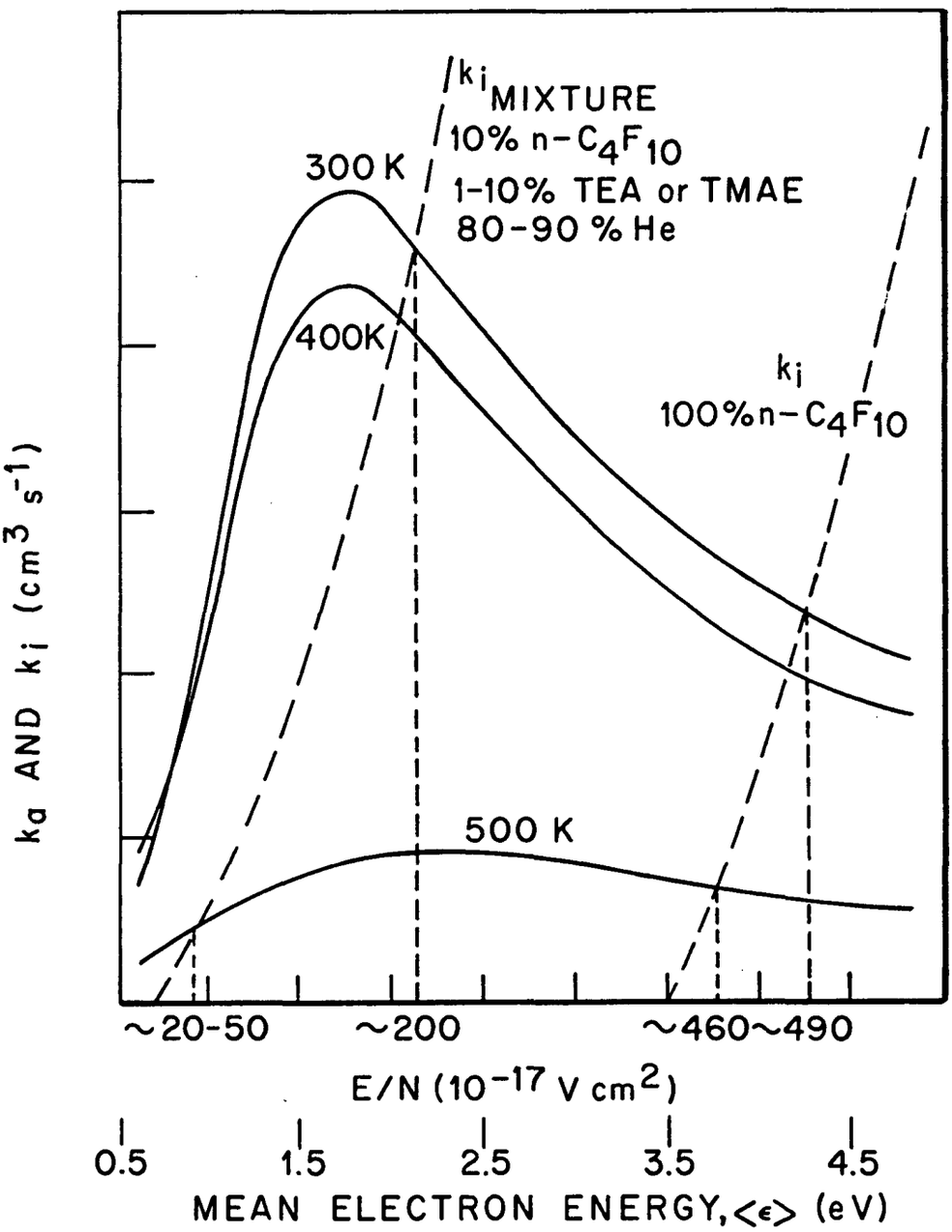
k_i MIXTURE
10% n-C_4F_{10}
1-10% TEA or TMAE
80-90 % He
300 K
400K
500 K
k_i
100%n-C_4F_{10}
k_a AND k_i ($cm^3\ s^{-1}$)
~20-50
~200
~460~490
E/N (10^{-17} V cm^2)
0.5
1.5
2.5
3.5
4.5
MEAN ELECTRON ENERGY, <ε> (eV)

Fig. 11