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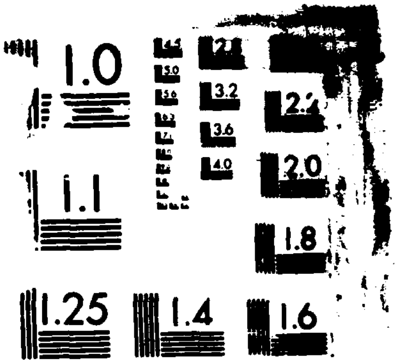

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BASIC STUDIES OF GASES FOR FAST SWITCHES

Annual Summary Report
October 1, 1985 to November 30, 1986

by

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BASIC STUDIES OF GASES FOR FAST SWITCHES

L. G. Christophorou and S. R. Hunter

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Oak Ridge National Laboratory

I. INTRODUCTION

This annual report contains a summary of the progress that we have made during the past year on the identification and optimization of fast gas mixtures for use in diffuse-discharge switches. Several papers describing our measurements of the key transport parameters and breakdown strength characteristics of gas mixtures which we have suggested for use in practical switching devices have been published[1-6] or have been submitted for publication[7-10] during the past year.

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During the present contractual period, we have performed measurements of the basic transport and rate coefficients [i.e., the electron drift velocity, w, the electron attachment and ionization coefficient, η/N and α/N, respectively, the gas ionizing W values, and the high voltage breakdown field strengths $(E/N)_{lim}$] of gas mixtures of potential practical interest as well as studied the behavior of these gas mixtures under more severe environmental conditions which are likely to occur in practical applications. In this connection, we have continued our studies of w, η/N, α/N, and k_a (the electron attachment rate constant) as a function of gas temperature T and have initiated a new project to study the effect of gas temperature on the $(E/N)_{lim}$ of selected gas mixtures. This information is crucial to the understanding of the mechanisms limiting the rapid recovery of the dielectric properties of the gas mixture after the switch has opened (i.e., the switch current has decreased to zero) and the high repetition rate operation of the switch at elevated gas temperatures.

The technical progress we have made on the identification of gas mixtures with desirable electron transport and rate coefficient properties for use in diffuse gas discharge switching applications and the effects of elevated gas temperature on these transport parameters and high voltage breakdown field strengths are given below.

II. TECHNICAL PROGRESS

The measurements that have been performed during this reporting period have allowed us to continue our studies on identifying attaching gas/buffer gas mixtures which have very desirable electron attaching and drift velocity characteristics for possible use in diffuse discharge opening switches. Our studies of the temperature dependence of the electron transport and rate coefficients have received increased emphasis during the past year, and our initial results from these studies have previously been published.[11,12] Important new W value measurements have been obtained in several gas mixtures in our continuing effort to optimize the electrical conductivity of the discharge when the switch is closed. These measurements and analyses have also recently been published.[2,6,13] We have submitted a patent application on these new Penning ionization gas mixtures because of their potential for greatly improving the efficiency (i.e., lowering the resistivity) of the switch during conduction.

A. Basic Data

We have measured the electron attachment and ionization coefficients and electron drift velocities in O_2, CH_4, CF_4, C_2F_6, C_3F_8, and n-C_4F_{10} gases using a new method of data analysis. The pressure dependence of the electron attachment coefficient in O_2, C_3F_8, and n-C_4F_{10} and of the electron drift velocity in C_3F_8 and n-C_4F_{10} have been reported and discussed. The accuracy and sensitivity of the present pulsed Townsend technique has been investigated by performing electron attachment coefficient measurements in pure O_2 over a wide range of E/N at selected O_2 pressures and by determining the electron attachment and ionization coefficients and electron drift velocity in CH_4 over a wide E/N range. Good agreement has been obtained between the present and the previously published electron attachment coefficients in O_2 and for the drift velocity measurements in CH_4. A paper describing these measurements and analyses has recently been published.[5]

Measurements of the electron attachment (η_T/N) and ionization (α_T/N) coefficients for the perfluoroalkanes n-C_NF_{2N+2}(N = 1 to 4) have been made over the density-reduced electric field (E/N) range 5×10^{-17}

$\leq E/N \leq 400 \times 10^{-17}$ V cm^2 using pulsed Townsend (PT) experimental techniques. The present η_T/N measurements are the first to be obtained for pure C_2F_6, C_3F_8, and n-C_4F_{10} at low E/N values. The η_T/N measurements in C_3F_8 and n-C_4F_{10} were dependent on gas pressure over a wide E/N range in agreement with previous high pressure electron attachment rate constant, k_a, measurements in these gases. The dissociative and nondissociative electron attachment processes for C_3F_8 and n-C_4F_{10} have been quantified from the pressure dependence of the measured electron attachment coefficients η_T/N as a function of E/N. The thermal electron attachment rate constants $(k_a)_{th}$ and the high voltage limiting electric field strengths $(E/N)_{\ell im}$ obtained from the present measurements are in good agreement with previous literature values. These measurements and analyses have been described in a paper which has been accepted for publication.[8]

The drift velocity, w, of electrons has been measured in the perfluoroalkanes n-C_NF_{2N+2} (N = 1 to 4) over the density-reduced electric field (E/N) range $0.03 \times 10^{-17} \leq E/N \leq 500 \times 10^{-17}$ V cm^2 using a pulsed Townsend (PT) experimental method. The present measurements of w are the first to be obtained for C_2F_6, C_3F_8 and n-C_4F_{10} at low E/N values. The electron drift velocity measurements in C_3F_8 and n-C_4F_{10} are dependent on gas pressure at high E/N values, even after allowing for diffusion corrections to the electron swarm transit time. This is the first observation of a pressure dependence in the w of these gases and is believed to be due to changes in the electron energy distribution function $f(\epsilon, E/N)$ with gas pressure. These changes in $f(\epsilon, E/N)$ are the result of increases in electron attachment with pressure. The perfluoroalkanes CF_4, C_2F_6, and C_3F_8 exhibit regions of pronounced negative differential conductivity (NDC) similar to but smaller in magnitude than that in CH_4. These measurements and the possible mechanisms leading to the observed NDC effects have been described in a paper which has been accepted for publication.[9]

The total electron attachment rate constant, $k_a(\langle\epsilon\rangle)$, for n-$C_4F_{10}$ has been measured using an electron swarm technique in the mean electron energy, $\langle\epsilon\rangle$, range 0.76 to 4.81 eV and over the temperature, T, range 300 to 750 K. The measured $k_a(\langle\epsilon\rangle, T)$ and the total electron attachment cross section,

$\sigma_a(\epsilon T)$, determined from these are reported. The $k_a(\langle\epsilon\rangle)$ first decrease slowly with T between 300 and 400 K, then decrease precipitously between 400 and ~500 K, and subsequently increases for T > 500 K. The overall variation of k_a with T depends on $\langle\epsilon\rangle$. From the measured dependence of $k_a(\langle\epsilon\rangle)$ on the total gas number density and T we determined the contribution of dissociative and nondissociative attachment to k_a at a function of $\langle\epsilon\rangle$; the contribution of nondissociative attachment decreases with T (due to increased autodetachment with increasing T), and the contribution of dissociative attachment increases with T (due to increased autodissociation into fragment anions with increasing T). The ratio, $R_{d/t}$, of the dissociative to the total electron attachment is small at low $\langle\epsilon\rangle$ and T, but it increases with both $\langle\epsilon\rangle$ and T and reaches unity for T > 500 K and $\langle\epsilon\rangle$ > 1.7 eV. These results have been discussed in relation to earlier work on C_2F_6 and C_3F_8 in a paper which has recently been accepted for publication.[10]

Measurements of $k_a(\langle\epsilon\rangle)$ have also been made in n-C_6F_{14} as a function of gas temperature T up to 675 K in argon buffer gas over the mean electron energy range $0.4 \lesssim \langle\epsilon\rangle \lesssim 4.8$ eV. These measurements are strongly dependent on gas temperatures, but in contrast to C_3F_8 and n-C_4F_{10} where $k_a(\langle\epsilon\rangle)$ initially decreases with increasing T up to T ≈ 500 K,[10,12] the $k_a(\langle\epsilon\rangle)$ measurements in n-C_6F_{14} initially increase with T up to T ≈ 400 K, decreases markedly with T up to T ≈ 550 K, and then finally increase with further increases in T in a manner similar to that observed for both C_3F_8 and n-C_4F_{10}. These measurments indicate that there is a complex interplay between the various electron attachment processes in n-C_6F_{14}. We have previously shown that parent anion formation processes decrease with increasing T, while dissociative attachment processes increase with increasing T, and it is the conpetition between these processes and their functional dependences on T which leads $k_a(\langle\epsilon\rangle)$ to either increase or decrease with increasing gas temperature. Analysis of these measurements is in progress.

We have recently performed a series of $k_a(\langle\epsilon\rangle)$ measurements in c-C_4F_8 and c-C_4F_6 as a function of gas temperature in nitrogen buffer gas over the mean electron energy range from thermal energy (≈0.038 eV) up to ≈1.0 eV.

Electron attachment to these two molecules over this $\langle\varepsilon\rangle$ range is almost exclusively by parent anion formation with the thresholds for dissociative electron attachment occurring at several eV. Consequently, we have observed that $k_a(\langle\varepsilon\rangle)$ decreases by up to two orders of magnitude over the temperature range $300 \lesssim T \lesssim 600$ K due to the drastic decrease in stable parent anion formation with increasing T. Analysis of the measurements in c-C_4F_8 has been completed and a journal paper will be submitted for publication.[14]

We have shown from the measurements described above that the electron attachment rate constant, k_a, for several gases can decrease or increase significantly with gas temperature, T, from room temperature to T > 750 K. We thus expect the limiting value, $(E/N)_{lim}$ of the density-reduced electric field, E/N, for such gases to be similarly affected by T. Measurements of the $(E/N)_{lim}$ have been made in the dielectric gases 1-C_3F_6, C_3F_8, c-C_4F_8, and n-C_4F_{10} over the T range ~300 to 600 K. For 1-C_3F_6, c-C_4F_8, and n-C_4F_{10} for which the k_a decreases as T increases, the $(E/N)_{lim}$ was found to decrease with T; its value at 600 K was ~5%, ~25%, and ~10% lower than at 300 K for 1-C_3F_6, c-C_4F_8, and n-C_4F_{10}, respectively. For C_3F_8, the $(E/N)_{lim}$ is initially independent of T up to ~450 K and then it decreases by ~3% at 600 K. This T dependence of the $(E/N)_{lim}$ for C_3F_8 is qualitatively in agreement with the T dependence of the k_a which was found to decrease with T only for $T \gtrsim 400$ K. These findings and those on C_2F_6 and CF_3Cl for which the k_a increases rather than decreases with T, have been analyzed and a journal paper describing these findings is in preparation.[15]

B. Publications

Several papers describing the measurements and analyses outlined above have been published[1-6] or submitted[7-10] for publication during the past contractual year. In particular, a paper has been published in which our electron drift velocity, attachment, and ionization measurements in several proposed switching gas mixtures have been summarized, and the relevance of these results to the design and optimization of gas mixtures for diffuse discharge switching applications has been outlined.[1] A paper has been published describing our initial W value measurements in C_2F_6 gas mixtures.[13]

These measurements, analyses, and implications for diffuse gas discharge switching applications have been discussed in a paper which was presented at the 5th IEEE Pulsed Power Conference.[2] A paper has also been recently published[6] in which the W-values of CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}, and several binary and ternary gas mixtures were measured. We found that the W-value decreased, and hence the electrical conductivity of the discharge increased when small percentages of C_2H_2 (0.5% to 5%) are added to several binary Ar/PFC (= CF_4, C_2F_6 and C_3F_8) gas mixtures.

An invited paper was presented at the 5th IEEE Pulsed Power Conference in which our measurements of the effect of gas temperature on the electron drift velocity and electron attaching and ionizing properties of gas molecules was discussed.[3] Our more recent measurements of the effect of elevated gas temperatures on the electron drift velocity and attachment and ionization coefficients in C_2F_6/Ar and C_2F_6/CH_4 gas mixtures have recently been discussed at two conferences.[16,17]

An invited paper describing the effects of elevated gas temperatures on the dissociative and nondissociative electron attachment properties of gas molecules, which have been observed under partial support by ONR, has been presented at the Joint Symposium on Swarm Studies and Inelastic Electron-Molecule Collisions.[4]

A paper describing our improved pulsed Townsend experimental technique for the measurement of electron transport and rate coefficients in gases has been published.[5] Measurements of the electron attachment coefficient in O_2 and the electron drift velocity and attachment and ionization coefficients CH_4 are given in comparison with previous literature values for these measurements.

A paper describing our electron attachment and ionization coefficient measurements in CF_4, C_2F_6, C_3F_8 and n-C_4F_{10} using this pulsed Townsend experimental technique has been accepted for publication (see Appendix A).[8]

The measurements of $k_a(\langle\epsilon\rangle)$ in n-C_4F_{10} as a function of gas temperature, and the analysis of the results to obtain the relative contributions of dissociative electron attachment and non-dissociative parent anion formation processes as a function of gas temperature have been described in a paper which has been accepted for publication (see Appendix B).[10]

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APPENDIX A

Electron attachment and ionization processes in CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}

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Measurements are reported of the electron attachment (η_T/N) and ionization (α_T/N) coefficients for the perfluoroalkanes n-C_NF_{2N+2} ($N = 1$ to 4) over the density-reduced electric field (E/N) range $5\times10^{-17} \leqslant E/N \leqslant 400\times10^{-17}$ V cm^2 using pulsed Townsend (PT) experimental techniques. The present η_T/N measurements are the first to be obtained for pure C_2F_6, C_3F_8, and n-C_4F_{10} at low E/N values. The η_T/N measurements in C_3F_8 and n-C_4F_{10} are dependent on gas pressure over a wide E/N range in agreement with previous high pressure electron attachment rate constant k_a measurements in these gases. The dissociative and nondissociative electron attachment processes for C_3F_8 and n-C_4F_{10} have been quantified from the pressure dependence of the measured electron attachment coefficients η_T/N as a function of E/N. The thermal electron attachment rate constants $(k_a)_{th}$ and the high voltage limiting electric field strengths $(E/N)_{lim}$ obtained from the present measurements are in good agreement with previous literature values.

I. INTRODUCTION

The perfluoroalkane series of molecules n-C_NF_{2N+2} ($N = 1$ to 4) are of considerable fundamental interest due to their unique electron attaching and scattering properties and their potential use in several applied areas.[1] These perfluorocarbons have been studied for many years as high voltage gaseous insulators due to their large electron attachment coefficients to high E/N (electric field E to gas number density N ratio) values, which gives C_2F_6, C_3F_8, and n-C_4F_{10} high voltage breakdown field strengths $(E/N)_{lim}$ comparable to or greater than that of SF_6. In addition, they possess good thermal and chemical stability, low toxicity, and relatively high vapor pressure.[1-6] Recently, interest has been renewed in these and other perfluorocarbons, in general, due to the desirability of finding gases and gas mixtures with breakdown field strengths greater than that of SF_6 for use in compressed gas insulated substations, switchgear, and transmission lines.[7-12] The $(E/N)_{lim}$ values for uniform electric fields in C_3F_8[10] and n-C_4F_{10}[13] have been found to be dependent on gas pressure P over the pressure range $15 < P < 400$ kPa in contrast to the usual behavior where at sufficiently large values of Pd (d is the electrode separation) the $(E/N)_{lim}$ of a gas is independent of P. This finding was anticipated[14] and shown[15] to result from the pressure dependent electron attachment rate constant in these two gases. The $(E/N)_{lim}$ of the gas mixture C_3F_8/SF_6 has also been found to exhibit a positive synergistic behavior[12] [i.e., the $(E/N)_{lim}$ of the mixture is greater than that of either of the component gases] which was interpreted[15] as resulting from the pressure dependent stabilization of the transient parent negative ions in the mixture.

The gas CF_4 has been suggested[16] and has recently found application[17] as an additive in gas mixtures for use in ionizing radiation detectors. High count rate, position sensitive detectors require gas mixtures with large electron drift velocities and low diffusion coefficients over a wide E/N range in order to detect the path of the ionizing radiation with good resolution. The gas mixtures CF_4/Ar[16] and CF_4/He[17] have been found to possess these desirable characteristics.

Another very recent application of the perfluoroalkanes is in the area of plasma etching using low pressure gas discharges. In this process, micron-sized features are etched onto substrates for use in a variety of semiconductor devices.[18] The molecules CF_4, C_2F_6, and C_3F_8 have been used in several experimental studies to determine their suitability as plasma etchants,[19] but considerably fewer studies have concentrated on understanding the underlying mechanisms governing the etching process in these gas discharges.[20,21] A recent study of the etching mechanisms in CF_4 has shown that the processes involved are very complex, and the magnitude of several of the negative and positive ion and neutral radical reaction rate constants are poorly known.[21]

A final area of practical importance where the perfluoroalkane molecules under study have been found to exhibit very desirable electron transport and attachment rate constant characteristics is in externally sustained diffuse gas discharge switches for pulsed power technology applications.[1,22] The primary requirements on a gas mixture in this application are (1) negligibly small (or zero) electron attachment rate constants and large electron drift velocities at low E/N values ($E/N \lesssim 3\times10^{-17}$ V cm^2), and (2) large electron attachment rate constants and, preferably, low electron drift velocities at high E/N values ($50\times10^{-17} \lesssim E/N \lesssim 300\times10^{-17}$ V cm^2). Gas mixtures composed of small percentages of the perfluoroalkanes (either CF_4, C_2F_6, or C_3F_8) in buffer gases of either Ar or CH_4 have been found to exhibit near-ideal electron drift velocity and attachment characteristics for use in diffuse discharge opening switches.[22-24] Recent measurements in small-scale externally sustained diffuse discharge opening switches have shown that switching times an order of magnitude faster than previously obtainable (i.e., opening times $\lesssim 20$ ns) have been achieved

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when small percentages ($\lesssim 2\%$) of either CF_4, C_2F_6, or C_3F_8 are added to high pressure ($P_T \gtrsim 100$ kPa) CH_4 acting as a buffer gas.[24] Studies of the operating parameters of self sustained diffuse discharge *closing* switches indicate that the electron attachment requirements on the gas mixture in these applications are similar to those for diffuse discharge *opening* switches.[25] The perfluoroalkanes CF_4, C_2F_6, and C_3F_8 in mixtures with high pressure Ar have also been used in experimental studies of this switching concept.[25,26]

Despite the large number and diverse nature of the applications for which these molecules are suited, surprisingly little is known about the electron scattering, electron attachment, and electron energy loss processes in these molecules.[1,27] The lack of knowledge of these processes hinders studies aimed at modeling the practical applications described above for these molecules. The information currently available concerning the electronic excitation and ionization processes in the lower members of the perfluoroalkane series has recently been summarized.[27] The total dissociation cross sections for CF_4, C_2F_6, and C_3F_8 at electron energies above 12 eV have been measured, and it was argued that excitation to all electronic and ionic states in these perfluoroalkane molecules results in fragmentation, and, consequently, the measured dissociation cross sections are the sum of the cross sections for all these processes.[27]

The measurement of the electron attachment and ionization coefficients for these perfluorocarbons has received considerably more attention although large inconsistencies exist between these measurements. The density-normalized Townsend electron attachment and ionization coefficients (η_T/N and α_T/N, respectively) have been measured at high E/N values in CF_4,[4,5,28-32] C_2F_6,[4,5,31,32] C_3F_8,[3,32] and n-C_4F_{10}.[6,32] The relative[33,34] and normalized[35] electron attachment cross sections have been measured for these molecules in electron beam studies, and the total electron attachment cross section $\sigma_a(\epsilon)$ has recently been determined using a high pressure electron swarm technique for all four molecules.[36] The effect of elevated gas temperatures on the dissociative electron attachment and parent negative ion formation processes in C_2F_6[37] and C_3F_8[38] have also been studied recently. Previous measurements of the electron drift velocity w and the ratio of the transverse diffusion coefficient to electron mobility D_T/μ (where $\mu = w/E$) have been reported in C_2F_6, C_3F_8, and n-C_4F_{10} over a limited range of E/N at high E/N values[32] and over a wider E/N range in CF_4.[28,29]

In this paper we report measurements of η_T/N and α_T/N for the perfluoroalkanes n-C_NF_{2N+2} ($N = 1$ to 4) over the E/N range $5 \times 10^{-17} < E/N < 400 \times 10^{-17}$ V cm^2 using a pulsed Townsend (PT) experimental technique.[19,40] The present measurements are the first to be obtained for C_2F_6, C_3F_8, and n-C_4F_{10} at low E/N values. We have observed that η_T/N is dependent on gas pressure in both C_3F_8 and n-C_4F_{10}. The mechanisms leading to these pressure dependences are discussed in Sec. IV.

II. EXPERIMENTAL METHOD

The experimental technique and apparatus used to measure the electron attachment and ionization coefficients have been described in detail previously.[40] Briefly, the present experiments were performed using a pulsed Townsend (PT) experimental technique with the detection circuit operating in the voltage integrating mode.[19,40]

The errors involved in performing these experiments have been discussed previously.[40] The estimated total uncertainty in the electron ionization or attachment coefficient measurements, when only ionization or attachment is present, varies between ±2 and ±5% depending on the magnitude of the process. When both electron ionization and electron attachment processes are present, the errors in determining α_T/N and η_T/N uniquely are considerably larger and are discussed more fully in Sec. III. The present technique has previously been checked by performing electron attachment coefficient measurements in O_2 and electron ionization coefficient and electron drift velocity measurements in CH_4.[40] In all cases, we have obtained excellent agreement with the most reliable previous measurements of these parameters. In addition, the electron attachment coefficient was also measured in CH_4, and these measurements have shown that the technique is capable of accurately measuring both the electron attachment and ionization coefficients, even when one of the coefficients is considerably smaller than the other.[40]

The gases CF_4 and C_2F_6 were obtained from Matheson Gas Products with a stated purity of 99.6%, C_3F_8 from Union Carbide Corporation, Linde Division, with a stated purity of 99%, and n-C_4F_{10} from Columbia Organic Chemicals Company with a stated purity of 95%. Previous analyses of these gases indicated that they were at least 99.9% pure.[36] These gases were subjected to several vacuum distillation cycles prior to any measurements in order to remove air from the samples. The vapor from each of these compounds was then extracted at temperatures just above their respective boiling points to remove water vapor and any other condensable impurities.

III. RESULTS

We have performed an extensive series of measurements of η_T/N and α_T/N in CF_4, C_2F_6, C_3F_8, and n-C_4F_{10} over a wide range of gas pressures ($0.03 \leqslant P \leqslant 100$ kPa). Examples of the waveforms obtained in CF_4 using this technique at low, moderate, and high rates of electron attachment are given in Fig. 1. The density-normalized electron attachment coefficient η/N, can be obtained from the ratio R_e of the total voltage to electron voltage in these waveforms when ionization and longitudinal diffusion are negligible from[40,41]

$$R_e = \left(\frac{\eta}{N}\right) \frac{(Nd)}{(1 - \exp[-(\eta/N)Nd])}, \qquad (1)$$

where d is the electrode separation.

The present measurements of η/N at low E/N in C_2F_6 are plotted in Fig. 2 as a function of Nd for a fixed drift distance ($d \simeq 2$ cm) using an analysis based on Eq. (1). At sufficiently low values of Nd, the apparent electron attachment coefficient is a function of Nd indicating that, in this Nd range, the electron swarm has not achieved equilibrium with the applied electric field (i.e., the hydrodynamic approximation fails for this gas under these conditions). Simi-

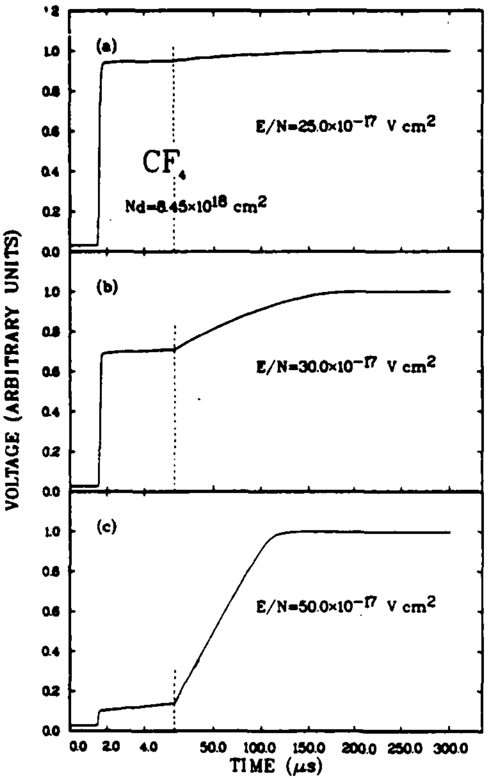

FIG. 1. Digitized voltage waveforms obtained in CF_4 at E/N values corresponding to (a) low, (b) moderate, and (c) high rates of electron attachment. The first segments of the waveforms were digitized at 10 ns/channel, and the second segments (occurring after the vertical dashed lines) were digitized at 200 ns/channel.

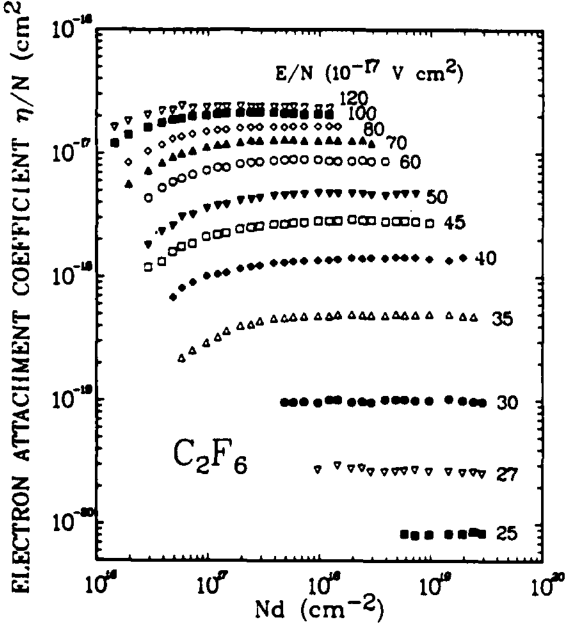

FIG. 2. Electron attachment coefficient η/N (uncorrected for diffusion) in C_2F_6 as a function of Nd (gas number density times electrode gap separation) at several E/N values below the onset of electron ionization.

lar, but larger, Nd dependences have also been observed in the present measurements of η/N in CF_4. Measurements of η/N in gases with a high electron attachment threshold energy (the threshold energy for electron attachment of CF_4 is 5 eV and for C_2F_6 is 2 eV[34,36]) appear to be sensitive probes of nonequilibrium conditions in the electron swarm and may possibly be useful in studying the influence of boundary conditions and higher-order diffusion processes on the attainment of equilibrium within the electron swarm.

At higher E/N values than those shown in Fig. 2, electron ionization processes become significant in addition to electron attachment for CF_4 and C_2F_6. Under these circumstances a different analysis procedure must be applied to the experimental voltage ratios to obtain unique values of the ionization coefficient α/N and η/N. In the presence of significant electron attachment, ionization, and diffusion, the voltage ratio has been shown by Blevin *et al.*[41] to be

$$R_v = \frac{[\eta d + 1 - (\overline{\alpha}/\overline{\alpha}_T) - \alpha d(2 - (\overline{\alpha}/\overline{\alpha}_T))\exp[\overline{\alpha}_T d\,]]}{[1 - (2 - (\overline{\alpha}_T/\overline{\alpha}))\exp(\overline{\alpha}_T d)]}, \tag{2}$$

where $\overline{\alpha} = (\alpha - \eta)$ is the unnormalized effective ionization coefficient, and $\overline{\alpha}_T = (\alpha_T - \eta_T)$ is the unnormalized effective Townsend ionization coefficient. The coefficients $\overline{\alpha}$ and $\overline{\alpha}_T$ are related by[42]

$$\frac{\overline{\alpha}_T}{N} = 2\frac{\overline{\alpha}}{N}\left(1 + \left[1 - 4\left(\frac{D_L}{\mu}\right)\left(\frac{E}{N}\right)^{-1}\left(\frac{\overline{\alpha}}{N}\right)\right]^{1/2}\right)^{-1}, \tag{3}$$

where $\overline{\alpha}_T/N$ and $\overline{\alpha}/N$ are the gas density normalized effective Townsend ionization and effective ionization coefficients, respectively, and D_L/μ is the longitudinal diffusion coefficient to electron mobility ratio.

Using the analysis procedure outlined in Ref. 40, Eq. (2) can be fitted to the experimental voltage ratios as a function of Nd to obtain unique values of α_T/N and η_T/N. Examples of the degree of fitting to the experimental voltage ratios in CF_4 are given in Fig. 3. An alternate analysis can also be used to obtain α/N and η/N (assuming that longitudinal diffusion is negligible) by noting that when $Nd \rightarrow 0$, both α and $\eta \rightarrow 0$ and the parameter $(\alpha + \eta)/N$ is then given by[43]

$$\frac{\alpha + \eta}{N} = \frac{(2R_v - 1)}{Nd}. \tag{4}$$

Equations (1) and (4) can also be used to obtain unique values of α/N and η/N as has been outlined in Ref. 40. The attachment and ionization coefficients determined in this manner have been substituted into Eq. (3) to find the ratio $\overline{\alpha}_T/\overline{\alpha}$ which was then used in Eq. (2) to determine the diffusion-corrected values of α_T/N and η_T/N uniquely using the experimental voltage ratios as a function of Nd. The degree of fitting obtained using this analysis procedure is shown in Fig. 4 for CF_4 and is considerably more sensitive to variations in either α/N or η/N than by fitting to the voltage ratio measurements as a function of Nd given in Fig. 3. From an analysis of the standard deviations of the derived coefficients and tests of uniqueness, we believe that the parameter $(\alpha + \eta)/N$ has an uncertainty of $\pm 5\%$, while the individual coefficients α/N and η/N have uncertainties of less than

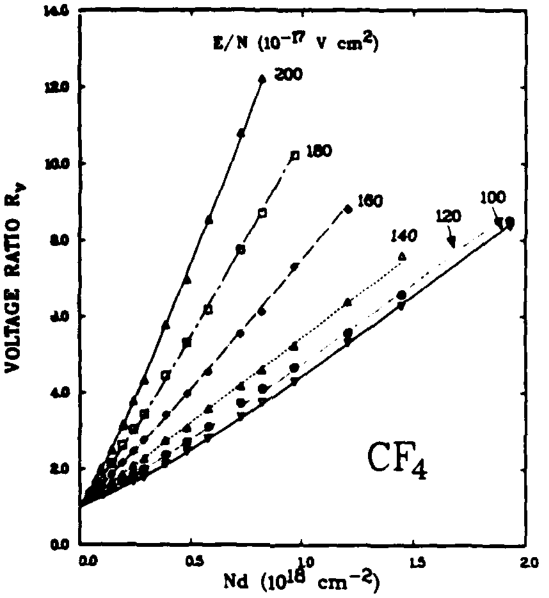

FIG. 3. Experimental voltage ratios R_v obtained in CF_4 as a function of Nd at several E/N values where both electron attachment and ionization processes are significant. The lines are calculated results obtained using the values of α_T/N and η_T/N determined by the analysis given in Eqs. (2) and (3).

$\pm$ 10% except when one is considerably smaller than the other. Note that for CF_4, $\alpha/N \simeq \eta/N$ at $E/N = 140 \times 10^{-17}$ V cm^2 and under these circumstances, R_v is a linear function of Nd (Fig. 3), and the parameter $(2R_v - 1)/Nd$ is independent of Nd (Fig. 4). When $\alpha/N \simeq \eta/N$, then $\bar{\alpha} \simeq 0$ and under these circumstances the diffusion correction of $\bar{\alpha}_T/N$ is negligible (i.e., for CF_4 at $E/N \simeq 140 \times 10^{-17}$ V cm^2, $\alpha/N = \alpha_T/N \simeq \eta/N = \eta_T/N = 0.445 \times 10^{-17}$ cm^2).

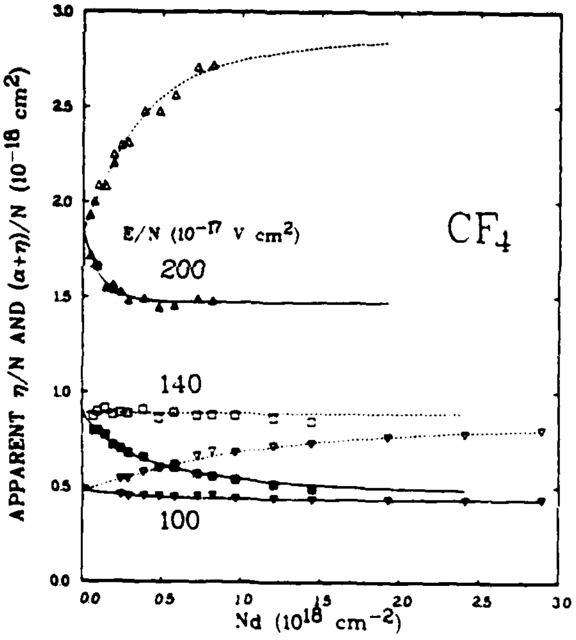

FIG. 4. Apparent values of the electron attachment coefficient η/N at $E/N = 100 \times 10^{-17}$ and 140×10^{-17} V cm^2 (solid symbols), the electron ionization coefficient α/N at $E/N = 200 \times 10^{-17}$ V cm^2 (solid symbols), and $(\alpha + \eta)/N$ at all E/N values (open symbols) for CF_4 calculated using Eqs. (1) and (4) in comparison with the experimental values obtained from the experimental voltage ratios using these equations.

A. CF_4 and C_2F_6

The present measurements of η_T/N and α_T/N in CF_4 and C_2F_6 obtained using this technique are given in Table I and in Figs. 5 and 6, respectively, in comparison with previous literature values using steady state Townsend techniques (SST) which measure α_T/N and η_T/N directly. Unlike the situation in CH_4,[40] no D_L/μ measurements have been published for the perfluoroalkanes under study, and estimates must be obtained for this parameter if the diffusion correction to the electron attachment and ionization coefficients are to be obtained. These perfluoroalkane molecules, particularly CF_4 and C_2F_6, possess electron drift velocities and transverse diffusion coefficients that have similar dependences on E/N to those of CH_4.[23,28,44–46] Consequently, we make the assumption that at high E/N values when $\alpha_T/N > \eta_T/N$, these molecules behave in a similar manner to CH_4 and that $D_L/D_T \simeq 1$. At lower E/N values where w is decreasing with increasing E/N (this is the region where the attachment coefficient peaks for all the perfluoroalkanes studied), we assume that $D_L/\mu \ll D_T/\mu$. This assumption has been approximately verified in drift velocity measurements in these gases.[47]

Using the literature values for D_T/μ in CF_4 and C_2F_6 [23,28,32] and making the assumption that $D_L/\mu = D_T/\mu$ at E/N values above $(E/N)_{\text{lim}}$ [i.e., the E/N value at which $\eta_T/N = \alpha_T/N$; $(E/N)_{\text{lim}} \simeq 140 \times 10^{-17}$ V cm^2 for CF_4 and $(E/N)_{\text{lim}} \simeq 275 \times 10^{-17}$ V cm^2 for C_2F_6], the largest correction to α_T/N in CF_4 occurs at $E/N = 200 \times 10^{-17}$ V cm^2 and is $+3\%$; in C_2F_6 it occurs at $E/N = 400 \times 10^{-17}$ V cm^2, and it is also $+3\%$. At E/N values below $(E/N)_{\text{lim}}$, if $D_L/\mu = D_T/\mu$, then the largest corrections to η_T/N occur at the peak values of η_T/N and are -2% for CF_4 and -3% for C_2F_6. The actual corrections are considerably less than this as D_L/μ will be much less than D_T/μ in this region. At E/N values near $(E/N)_{\text{lim}}$ the diffusion corrections to α_T/N and η_T/N are negligible.

In general there is good agreement between the present measurements and those obtained previously using both SST[29–32] and time-of-flight (TOF)[28] techniques, although we believe that the uncertainty in our results is considerably less than that obtained using conventional SST techniques. At E/N values $> 200 \times 10^{-17}$ V cm^2, our attachment measurements appear to be significantly higher than the previous measurements, especially for C_2F_6. We have observed significant secondary ionization processes at the larger Nd values for CF_4 at $E/N > 100 \times 10^{-17}$ V cm^2 and for C_2F_6 at $E/N > 200 \times 10^{-17}$ V cm^2. Secondary electron production was also observed at large E/N and Nd values in recent electron attachment and ionization coefficient measurements in CH_4,[40] but in contrast to that study where photoelectron production at the cathode was the predominant electron production mechanism, positive ion bombardment of the cathode appears to be the major mechanism in the present study. As we have noted earlier for CH_4,[40] the disagreement

TABLE I. Electron attachment and ionization coefficients in CF_4 and C_2F_6 as a function of E/N.

	CF_4			C_2F_6		
E/N (10^{-17} V cm^2)	η_T/N (10^{-18} cm^2)	α_T/N	Total uncertainty[a]	η_T/N (10^{-18} cm^2)	α_T/N	Total uncertainty[a]
20	0.0010		± 0.0001			
22	0.0027		± 0.0001	0.0009		± 0.000 04
25	0.0134		± 0.0003	0.0082		± 0.000 2
27				0.0264		± 0.000 8
30	0.093		± 0.003	0.099		± 0.004
35	0.306		± 0.012	0.49		± 0.01
40	0.636		± 0.015	1.40		± 0.04
45	1.05		± 0.03	2.82		± 0.06
50	1.48		± 0.03	4.61		± 0.08
55	1.92		± 0.04			
60	2.38		± 0.08	8.7		± 0.2
70	3.10		± 0.07	12.7		± 0.3
80	3.64	0.11	± 0.03	16.2		± 0.2
90	4.08	0.32	± 0.05	18.8		± 0.3
100	4.36	0.44	± 0.05	20.9		± 0.4
110	4.50	1.10	± 0.03			
120	4.52	2.08	± 0.05	23.6		± 0.3
140	4.45	4.45	± 0.05	24.5	0.6	± 0.4
160	4.23	7.37	± 0.06	24.3	1.0	± 0.4
180	4.11	10.7	± 0.05	23.3	3.2	± 0.4
200	3.77	14.7	± 0.08	22.0	5.7	± 0.4
225				19.9	9.9	± 0.4
250				18.1	13.6	± 0.4
275				17.5	17.5	± 0.8
300				16.4	21.1	± 0.7
325				16.0	25.0	± 0.7
350				15.6	29.4	± 0.7
375				15.0	35.0	± 0.9
400				13.6	40.4	± 0.9

[a] This is the uncertainty in each of the coefficients.

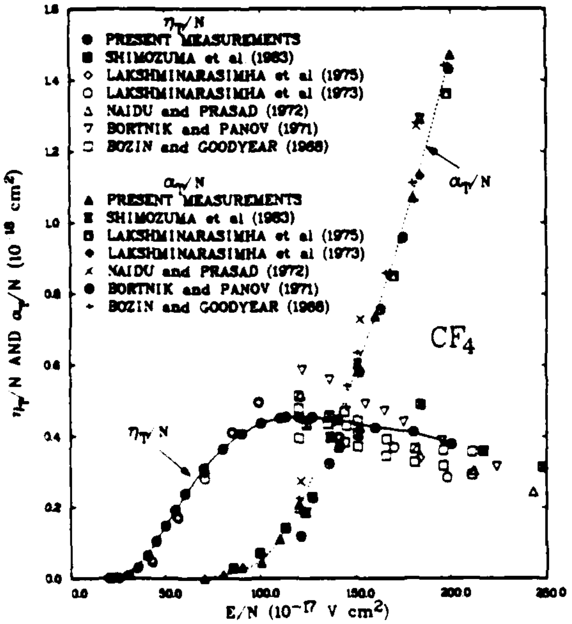

FIG 5 Present measurements of the diffusion-modified electron attachment coefficient η_T/N and diffusion-modified ionization coefficient α_T/N as a function of E/N for CF_4 in comparison with the measurements of Shimozuma *et al.* (Ref. 30), Lakshminarasimha *et al.* (Refs. 28 and 29), Naidu and Prasad (Ref. 32), Bortnik and Panov (Ref. 31), and Bozin and Goodyear (Ref. 5)

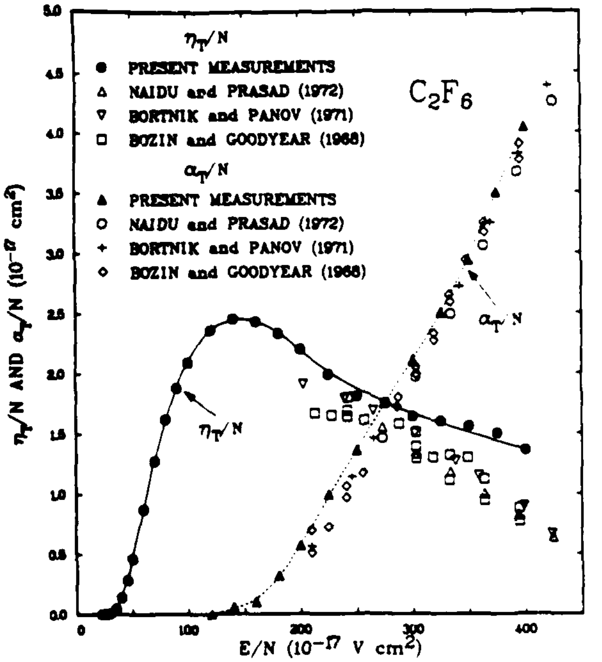

FIG. 6. Present measurements of the diffusion-modified electron attachment coefficient η_T/N and the diffusion-modified ionization coefficient α_T/N as a function of E/N for C_2F_6 in comparison with the measurements of Naidu and Prasad (Ref. 32), Bortnik and Panov (Ref. 31), and Bozin and Goodyear (Ref. 5).

between the present and the previous electron attachment measurements may be due to the neglect of this secondary electron production process in the analysis of the current growth curves in previous SST measurements of the electron attachment and ionization processes in these gases. The time resolution afforded by the present PT method enabled us to clearly identify and account for the primary positive and negative ion and secondary electron production mechanisms.

B. C_3F_8 and n-C_4F_{10}

In contrast to CF_4 and C_2F_6, the electron attachment coefficients for C_3F_8 and n-C_4F_{10} depend on gas pressure, particularly for n-C_4F_{10} (Figs. 7 and 8). We have previously shown that electron attachment to CF_4 and C_2F_6 is dissociative in nature (and, consequently, independent of gas pressure),[34,36,37] whereas at room temperature electron attachment to C_3F_8 and n-C_4F_{10} is largely due to nondissociative parent anion formation.[36,38] The autodetachment lifetimes of the parent anions are sufficiently short (10^{-11} to 10^{-8} s)[36,38] that the rate of stabilization of the parent anion is dependent on the gas pressure over the pressure range of the present measurements ($0.05<P<20$ kPa). Under these conditions we are unable to obtain unique values for α_T/N and η_T/N above the ionization threshold (below this threshold, the η_T/N measurements for C_3F_8 and n-C_4F_{10} are as accurate as those obtained for CF_4 and C_2F_6) because the present measurements were made in a chamber where the drift gap was fixed. We have used the α_T/N values of Naidu and Prasad[32] for C_3F_8 and n-C_4F_{10} (which we assume are independent of gas pressure) as initial estimates to fit to the experimental voltage ratios. The α_T/N measurements of Naidu and Prasad[32] for CF_4 and C_2F_6 are in good agreement with our present measurements (Figs. 5 and 6). The electron attachment and ionization coefficient measurements are not as unique as for CF_4 and C_2F_6 using this procedure, although a certain degree of confidence can be obtained for the measurements by noting that at high gas pressures, the experimental waveforms are nearly those for the dominant process as mentioned above [i.e., for η_T/N below $(E/N)_{\text{lim}}$ and for α_T/N above $(E/N)_{\text{lim}}$]. This can be shown from Eq. (2) assuming longitudinal diffusion is negligible; when $\eta/N>\alpha/N$, then at large values of Nd, $R_v \to \eta d$. Conversely, when $\alpha/N>\eta/N$, then as $Nd\to\infty$, $R_v\to\alpha d$. At low gas pressures the attachment measurements are very sensitive to the assumed E/N dependence of the electron ionization coefficient near the onset. The E/N dependence of the electron attachment coefficient can be established at high Nd values where $R_v \simeq \eta d$, and the electron ionization coefficient can be adjusted to give the correct E/N dependence to η/N at low gas pressures.

The diffusion correction to α_T/N using the literature values of D_T/μ for C_3F_8 and n-C_4F_{10}[32] is the largest at the highest E/N values (i.e., $E/N=400\times10^{-17}$ V cm^2), being $+2\%$ for both molecules at all gas pressures studied. The

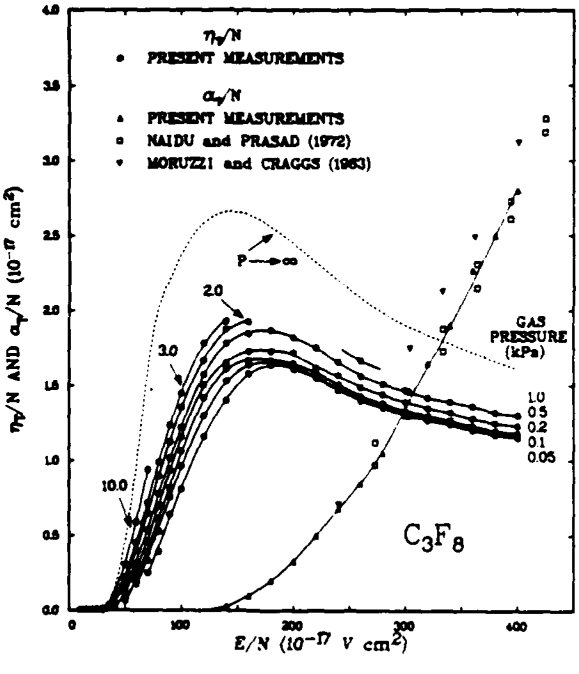

FIG. 7. Present measurements of the diffusion-modified electron attachment coefficient η_T/N and the diffusion-modified ionization coefficient α_T/N as a function of E/N and gas pressure for C_3F_8 in comparison with the measurements of Naidu and Prasad (Ref. 32) and Moruzzi and Craggs (Ref. 3). The dashed line is the resultant attachment coefficient when the present measurements are extrapolated to infinite gas pressure using the method of analysis given in the text.

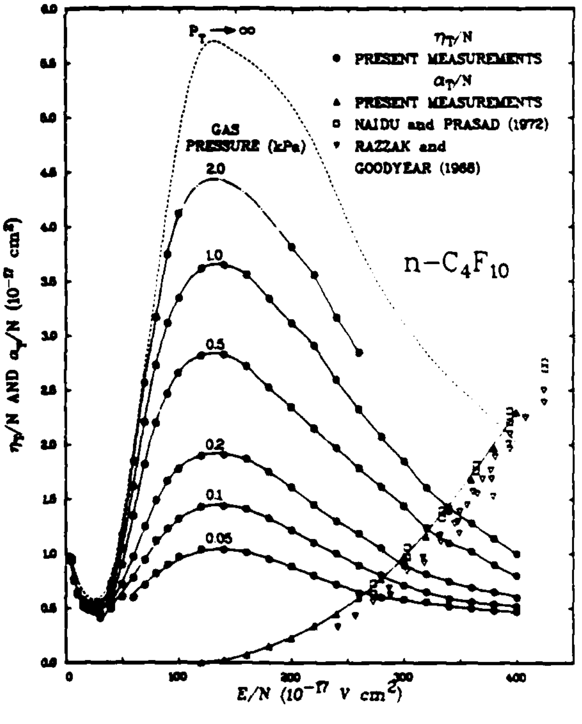

FIG. 8. Present measurements of the diffusion-modified electron attachment coefficient η_T/N and the diffusion-modified ionization coefficient α_T/N as a function of E/N and gas pressure for n-C_4F_{10} in comparison with the measurements of Naidu and Prasad (Ref. 32) and Razzak and Goodyear (Ref. 6). The dashed line is the resultant attachment coefficient when the present measurements are extrapolated to infinite gas pressure using the method of analysis given in the text.

correction is considerably smaller than this value at lower E/N values ($E/N < 360 \times 10^{-17}$ V cm^2) above $(E/N)_{\lim}$. At E/N values below $(E/N)_{\lim}$, assuming that $D_T/\mu = D_L/\mu$, the largest correction to η_T/N at the highest gas pressure used is -2% for C_3F_8 at $E/N = 140 \times 10^{-17}$ V cm^2 and -4% for n-C_4F_{10} at $E/N = 120 \times 10^{-17}$ V cm^2. The actual correction to η_T/N for these molecules will be smaller than these values for the same reasons outlined above.

IV. ANALYSIS AND DISCUSSION

A. Electron attachment reaction mechanisms

The pressure dependent electron attachment coefficient measurements for C_3F_8 and n-C_4F_{10} given in Figs. 7 and 8, respectively, can be explained by a reaction scheme where an electron can either be captured into an attractive negative ion state (with a positive electron affinity) which can lead to the formation of parent negative ions or into one or more repulsive negative ion states which can lead to the formation of fragment anions. The pressure independent electron attachment measurements for CF_4 and C_2F_6 (Figs. 1 and 2, respectively) are solely the result of dissociative electron attachment processes leading to fragment anion formation. If the bound and unbound negative ion states of the perfluoroalkane molecules do not internally convert, then the measured electron attachment coefficient $(\eta/N)_m$ can be expressed as[38]

$$\left(\frac{\eta}{N}\right)_m = \left(\frac{\eta}{N}\right)_d + \left(\frac{\eta}{N}\right)_n \frac{1}{[(\beta/N)+1]}, \quad (5)$$

where $(\eta/N)_d$ is the dissociative electron attachment component, $(\eta/N)_n$ is the nondissociative electron attachment component which is dependent on N, and $\beta = \nu_{2n}/k_{3n}$. The ratio ν_{2n}/k_{3n} is called the critical number density N_c,[36] where the rate of autodetachment of the excited negative ion is equal to the rate of collisional stabilization. From Eq. (5), when $N \rightarrow 0$, $(\eta/N)_m \rightarrow (\eta/N)_d$ (i.e., only dissociative electron attachment processes are observed). Conversely, when $N \rightarrow \infty$, $(\eta/N)_m \rightarrow (\eta/N)_d + (\eta/N)_n$ (i.e., all parent and fragment anions are observed assuming that collisional detachment of PFA^{-*} is negligible).

A nonlinear least squares fitting routine[48] has been applied to the electron attachment measurements as a function of N for C_3F_8 and n-C_4F_{10} to determine the linear coefficients $(\eta/N)_d$ and $(\eta/N)_n$ and the nonlinear parameter β in Eq. (5). The dissociative and nondissociative electron attachment coefficients calculated for C_3F_8 and n-C_4F_{10} using this method are shown in Fig. 9, and the total electron attachment coefficients [i.e., $(\eta/N)_d + (\eta/N)_n$] for C_3F_8 and n-C_4F_{10} are given by the dashed curves in Figs. 7 and 8, respectively.

For C_3F_8 at low E/N values ($E/N < 100 \times 10^{-17}$ V cm^2) [and hence low mean electron energies (< 2 eV[38])] parent anion formation is the predominant negative ion production mechanism, but it is rapidly eclipsed at higher E/N values by the dissociative electron attachment component. This observation is in agreement with our recent electron attachment rate constant measurements in C_3F_8 as a function of gas temperature.[38] These measurements indicated, however, that the magnitude of the dissociative and nondissociative electron attachment components were approximately equal at high mean electron energies ($\langle\epsilon\rangle > 3$ eV), whereas in the present study $(\eta/N)_d$ is considerably larger than $(\eta/N)_n$ at high E/N values [e.g., at $E/N = 400 \times 10^{-17}$ V cm^2, $(\eta/N)_d/(\eta/N)_n \simeq 3$]. The differences in the relative dissociative to nondissociative negative ion production ratios observed for these two types of experiment are due to differences in the pressure ranges over which the present and previous measurements have been performed.[34,36,38] In the extreme case of single collision negative ion production cross section measurements where very low gas pressures are employed ($P < 0.1$ Pa), only dissociative electron attachment fragment anions and long-lived ($\tau > 1$ μs) parent anions are observable.[34] The lifetimes of the parent anions of C_3F_8 are very much smaller than this ($\tau < 10^{-8}$ s[36,38]), and, consequently, no parent anions from C_3F_8 are detected in this type of experiment.[34] In contrast, the electron attachment rate constant measurements were performed in a high pressure buffer gas ($P \leqslant 1.3$ MPa), and nearly all the short-lived parent anions from C_3F_8 are stabilized in collisions with the buffer gas at these gas pressures.[36,38] The present measurements are performed over a pressure range intermediate between these two extremes ($0.05 \leqslant P \leqslant 20$ kPa), and only a small fraction (which becomes smaller the higher the E/N value since the autodetachment lifetime decreases with increasing electron energy) of the transient parent anions were stabilized.

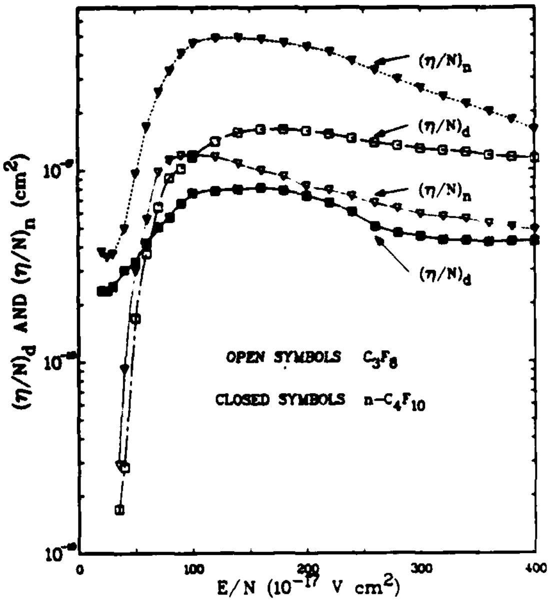

FIG. 9. The dissociative electron attachment coefficient $(\eta/N)_d$ and the nondissociative electron attachment coefficient $(\eta/N)_n$ for C_3F_8 and n-C_4F_{10} as a function of E/N obtained using the analysis given in the text.

Electron attachment to n-C_4F_{10} is predominantly by parent anion formation over the entire E/N range of the present measurements. These observations have also been verified in recent electron attachment rate constant measurements in n-C_4F_{10} where the rate constant for parent anion formation was observed to be approximately ten times greater than that for nondissociative electron attachment at room temperature.[49] The parent anion production rate constant has also been found to decrease, and the dissociative electron attachment rate constant has been found to increase with increasing gas temperature T above $T \simeq 400$ K.[49] Similar variations in the ratio of dissociative to nondissociative electron attachment with gas temperature were also observed in C_3F_8.[36]

B. Electron attachment rate constants

The dissociative electron attachment rate constants $k_a = (\eta/N)_d w$ [obtained from the present electron attachment coefficient measurements (given in Figs. 5 and 6) and using recent electron drift velocity measurements in these gases[47]] are plotted in Fig. 10 for CF_4 and C_2F_6 along with the total electron attachment rate constant measurements (k_a when $N \rightarrow \infty$) for C_3F_8 and n-C_4F_{10}. The magnitude of the peak in k_a for CF_4 is in good agreement with that obtained in the previous high pressure electron attachment rate constant study,[36] but that of the peaks in k_a of the larger PFA molecules fall significantly below those obtained in the previous study.[36] In addition to the problem mentioned above of the low stabilizing efficiency for the transient parent anions at the low gas pressures of the present experiments for C_3F_8 and n-C_4F_{10} (which is the reason why the k_a values for C_3F_8 are equal to or smaller than those for C_2F_6 in contrast to the high pressure rate constant measurements[36]), recent studies have shown that when the electron attachment process in a gas or gas mixture is large, then the electron energy distribution function $f(\epsilon, E/N)$ can be significantly altered by the loss of electrons due to the electron attaching process.[50,51] Physically, $f(\epsilon, E/N)$ can be depleted over a given energy range when the electron attachment collision frequency ν_a is comparable in magnitude to the electron energy transfer collision frequency ν_e.[50] In the high pressure electron attachment rate constant measurements,[36] the concentration of the attaching gas in the buffer gas is so low ($\lesssim 1$ part in 10^6) such that $\nu_a \ll \nu_e$ for all the PFA molecules, and $f(\epsilon, E/N)$ is unperturbed by the addition of the attaching gas. Under these circumstances, the $f(\epsilon, E/N)$ functions for the gas mixture can be calculated using a Boltzmann equation analysis enabling the mean electron energy $\langle \epsilon \rangle$ to be obtained as a function of E/N from the known elastic and inelastic scattering cross sections of the buffer gas. By applying a swarm unfolding procedure, the total electron attachment cross section can be uniquely obtained for the attaching gas using the known $f(\epsilon, E/N)$ functions of the buffer gas.[36–38]

In contrast, the present electron attachment measurements were performed with pure gas and for the larger PFA molecules, ν_a can become significant with respect to ν_e. Large reductions in $f(\epsilon, E/N)$ can occur over the energy range where the electron attachment cross sections $\sigma_a(\epsilon)$ are large under these circumstances.[50] This will then lead to significant reductions in the k_a values in the pure gas in comparison with those obtained in a high pressure buffer gas. This effect can be clearly seen in the k_a measurements for CF_4 and C_2F_6, where electron attachment to these molecules is purely dissociative and, consequently, unaffected by the gas pressure at which the measurements were performed. The electron attachment collision frequency for CF_4 is significantly smaller than for the other PFA molecules, and as a result, the k_a values measured by the two techniques are very similar. However, for C_2F_6, ν_a is large in comparison with ν_e, and the k_a values near the peak in the present measurements (i.e., at $E/N \simeq 200 \times 10^{-17}$ V cm^2) are $\simeq 60\%$ lower than those obtained in the high pressure swarm experiments[36,37] at mean electron energies near the peak in the k_a values (i.e., $\langle \epsilon \rangle \simeq 3.5$ eV). For the pure electron attaching molecules studied in the present work, the $f(\epsilon, E/N)$ functions are unknown, but the electron attachment and ionization coefficients measured in these experiments, in conjunction with the electron attachment and electron ionization cross sections determined from the high pressure electron attachment rate constant measurements and single collision electron ionization studies, can be used to determine the elastic and inelastic loss processes in these molecules. In this sense, the electron attachment measurements made in the pure gas and in the high pressure rate constant experiments are complementary by allowing further insights into the electron scattering processes in these gases than could be obtained from either experiment separately.

The thermal electron attachment rate constants $(k_a)_{th}$ (at gas temperature $T = 300$ K) have been estimated from the present measurements and are given in Table II in comparison with previous values.[16,52,53] For CF_4 and C_2F_6, the

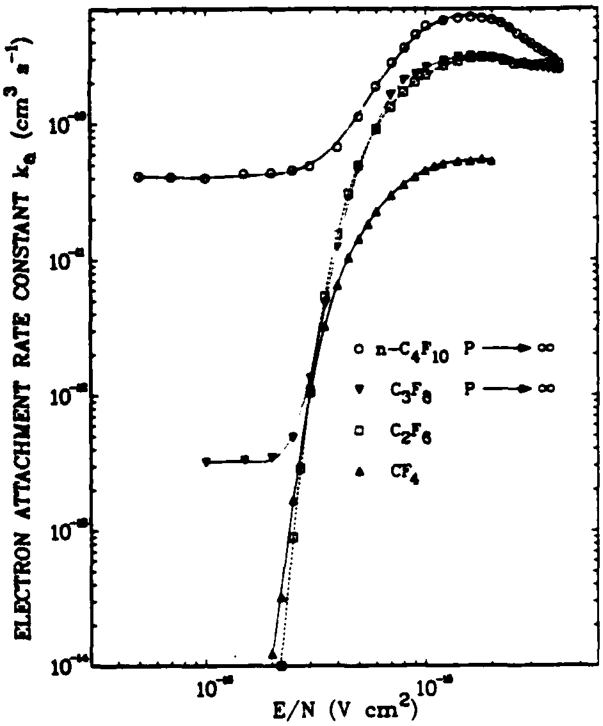

FIG. 10. The electron attachment rate constant k_a for CF_4, C_2F_6, C_3F_8, and n-C_4F_{10} plotted as a function of E/N, obtained from the present electron attachment coefficient measurements and the electron drift velocity values given in Ref. 47. The k_a values for C_3F_8 and n-C_4F_{10} have been obtained from the attachment coefficient measurements extrapolated to infinite gas pressure using the procedure outlined in the text.

TABLE II. Thermal electron attachment rate constants and limiting electric field strengths for the perfluoroalkanes CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}.

Perfluoroalkane molecule	Thermal attachment rate constant ($T = 300$ K) $(k_a)_{th}$ (cm^3 s^{-1}) Present values	Previous values	Limiting electric field strength $(E/N)_{lim}$ (10^{-17} V cm^2) Present values	Previous values
CF_4	$<10^{-16}$	$<10^{-13}$[a] $<10^{-16}$[g] $<3\times10^{-13}$[j]	140	137,[b] 138,[c] 149,[d] 143,[e] 140[f] 141,[h] 151[i]
C_2F_6	$<10^{-16}$	$<10^{-13}$[a] $<10^{-16}$[g] $<1.6\times10^{-13}$[j]	275	277,[b] 277,[c] 277[d] 275,[h] 285[i]
C_3F_8	$\lesssim 3\times10^{-13}$	1.8×10^{-12}[a] $<10^{-15}$[g] $<1.2\times10^{-12}$[j]	295–330[k]	302–313,[b] 308[l] 360,[h] 353,[i] 320–346[m] 331–353[n]
n-C_4F_{10}	4×10^{-11}	4×10^{-11}[a] 9.6×10^{-12}[g]	265–380[k]	327–332,[b] 346–393[o] 472,[h] 392–467[p]

[a] Reference 36.

[b] Reference 32. Obtained from low pressure electron attachment and ionization coefficient measurements.

[c] Reference 5. Obtained from low pressure electron attachment and ionization coefficient measurements.

[d] Reference 31. Obtained from low pressure electron attachment and ionization coefficient measurements.

[e] References 28 and 29. Obtained from low pressure electron attachment and ionization coefficient measurements.

[f] Reference 30. Obtained from low pressure electron attachment and ionization coefficient measurements.

[g] Reference 52.

[h] Reference 7. High voltage breakdown measurements, $P = 66.6$ kPa.

[i] Reference 8. High voltage breakdown measurements, $P = 150$ kPa.

[j] Reference 53.

[k] These were the values obtained over the limited pressure range ($0.05<P<2$ kPa) of the present measurements. If it were possible to measure α_T/N and η_T/N at higher gas pressures, then the present $(E/N)_{lim}$ values would have overlapped the experimental high voltage breakdown measurements.

[l] Reference 3. Obtained from low pressure electron attachment and ionization coefficient measurements.

[m] Reference 10. High voltage breakdown measurements, $P = 10$–210 kPa.

[n] Reference 13. High voltage breakdown measurements, $P = 27$–285 kPa.

[o] Reference 6. Obtained from low pressure electron attachment and ionization coefficient measurements

[p] Reference 13. High voltage breakdown measurements, $P = 3$–160 kPa.

$(k_a)_{th}$ values are negligibly small, and only upper limits of $<10^{-16}$ cm^3 s^{-1} can be placed on these coefficients using the present technique. These limits are consistent with our previous high pressure rate constant upper limits,[36] and with the previous literature values.[52,53] The true $(k_a)_{th}$ values for C_3F_8 and n-C_4F_{10} are very difficult to measure accurately due to the likely presence of thermal electron attaching impurities in these gases. An upper limit of $(k_a)_{th} \lesssim 3\times10^{-13}$ cm^3 s^{-1} for C_3F_8 has been obtained in the present measurements, which is significantly lower than our previous value[36] as we have used a "cleaner" gas sample for the present measurements. The present and previous[36] $(k_a)_{th}$ values for n-C_4F_{10} are in excellent agreement [$(k_a)_{th} = 4\times10^{-11}$ cm^3 s^{-1}], but our present values of $(k_a)_{th}$ for C_3F_8 and n-C_4F_{10} are significantly larger than a previous estimate of these coefficients.[52] It is possible that even after careful purifying and impurity analysis of these gases, our samples still contained traces of a strongly thermal electron attaching impurity. The possible presence of such impurities does not affect the electron attachment measurements at higher electron energies.

C. Effective ionization coefficients and high voltage breakdown field strengths

The electron attachment and ionization coefficient measurements given in Figs. 5 to 8 have been used to obtain the effective ionization coefficient ($\overline{\alpha}/N = \alpha/N - \eta/N$) for the PFA molecules over the E/N range above and below the E/N value when $\overline{\alpha}/N \simeq 0$, and these values are plotted in Fig. 11. The limiting E/N value of an electronegative gas $(E/N)_{lim}$ is defined as the E/N value when $\overline{\alpha}/N = 0$, and in the absence of significant secondary electron loss or gain processes (e.g., secondary ionization processes, collisional detachment, etc.). $(E/N)_{lim}$ can also be equated with the uniform field high voltage breakdown field strength of the gas.

The E/N values where $\overline{\alpha}/N = 0$ for CF_4 and C_2F_6 are given in Table II and are in excellent agreement with previous $(E/N)_{lim}$ values obtained from ionization and attachment coefficient measurements[5,28–32] and high voltage breakdown field strength measurements.[7,8,10] The electron attachment coefficients and, hence, $(E/N)_{lim}$ values for C_3F_8 and n-C_4F_{10} are dependent on gas pressure over the pressure range of the present measurements and cannot be directly compared with the high voltage breakdown measurements which are usually obtained at atmospheric gas pressures. The present $(E/N)_{lim}$ measurements for C_3F_8 and n-C_4F_{10} are in good agreement with the previous ionization and attachment coefficient determinations of $(E/N)_{lim}$, where these measurements have been performed over a similar gas pressure range.[3,6,13] The values of $(E/N)_{lim}$ obtained from the high voltage breakdown field strength measurements at the lower gas pressure also over-

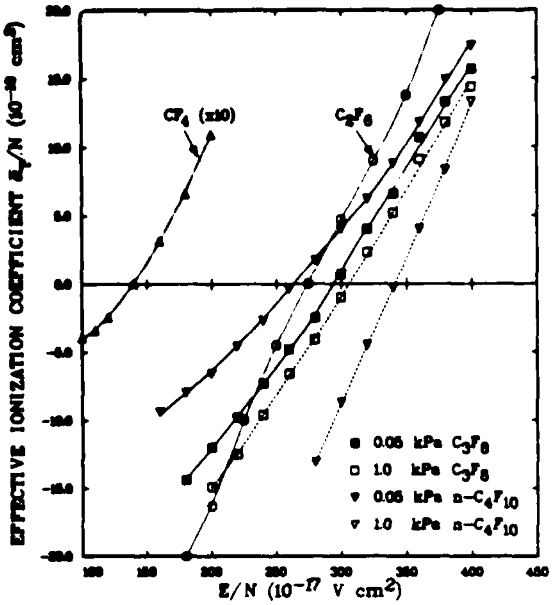

FIG. 11. The effective ionization coefficient $\bar{\alpha}/N = (\alpha - \eta)/N$ for CF$_4$, C$_2$F$_6$, C$_3$F$_8$, and n-C$_4$F$_{10}$ vs E/N. The limiting breakdown field strength $(E/N)_{\rm lim}$ is defined as the E/N value for which $\bar{\alpha}/N = 0$. The values of $(E/N)_{\rm lim}$ obtained from this figure are listed in Table II. Note the dependence of $(E/N)_{\rm lim}$ for C$_3$F$_8$ and n-C$_4$F$_{10}$ on gas pressure.

lap the present $(E/N)_{\rm lim}$ obtained at the higher gas pressures.[10,13] At higher gas pressures, however, the high voltage measurements give considerably higher $(E/N)_{\rm lim}$ values.[7,8,10,12,13] As we have demonstrated earlier,[14,15,36] the pressure dependence that has been observed in $(E/N)_{\rm lim}$ in high voltage breakdown field strength measurements is due to the pressure dependence of the electron attachment coefficient in these gases and represents a genuine violation of Paschen's law.[15]

The electron attachment and ionization coefficient measurements we have made in these perfluoroalkanes considerably enhance our understanding of the electron–molecule scattering processes in these gases, and, along with other studies,[23,36,47] are expected to lead to the determination of a consistent set of electron scattering cross sections in these gases which can then be used in modeling studies of these processes in gas discharges for several applications.

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APPENDIX B

Variation of the electron attachment to n-C_4F_{10} with temperature

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The total electron attachment rate constant $k_a(\langle\epsilon\rangle)$ for n-C_4F_{10} has been measured using an electron swarm technique in the mean electron energy, $\langle\epsilon\rangle$, range 0.76 to 4.81 eV and over the temperature, T, range 300 to 750 K. The measured $k_a(\langle\epsilon\rangle,T)$ and the total electron attachment cross section $\sigma_a(\epsilon,T)$ determined from these by unfolding are reported. The $k_a(\langle\epsilon\rangle)$ first decrease slowly with T between 300 and 400 K, then decrease precipitously between 400 and ~500 K, and subsequently increase for $T > 500$ K. The overall variation of k_a with T depends on $\langle\epsilon\rangle$. From the measured dependence of $k_a(\langle\epsilon\rangle)$ on the total gas number density and T we determined the contribution of dissociative and nondissociative attachment to k_a as a function of $\langle\epsilon\rangle$; the contribution of nondissociative attachment decreases with T and the contribution of dissociative attachment increases with T. The ratio $R_{d/t}$ of the dissociative to the total electron attachment is small at low $\langle\epsilon\rangle$ and T, but it increases with both $\langle\epsilon\rangle$ and T and reaches unity for $T > 500$ K and $\langle\epsilon\rangle > 1.7$ eV. These results are discussed in relation to similar earlier work on C_2F_6 and C_3F_8.

I. INTRODUCTION

The study of electron attachment to hot (vibrationally/rotationally excited) molecules is of practical, as well as basic, significance.[1] Vibrational and (to a lesser extent) rotational excitation affects the magnitude and the energy dependence of the cross section for electron attachment (see, for example, Refs. 2–10). As a rule[6,7] for molecules, AX, for which only dissociative attachment processes occur, the effect of T on the cross section $\sigma_{da} = \sigma_c' p'$ of the reaction

$$e + \mathrm{AX} \underset{\tau_a'^{-1}}{\overset{\sigma_c'}{\rightleftharpoons}} \mathrm{AX}^{-*} \xrightarrow{p'} \mathrm{A} + \mathrm{X}^- \tag{1}$$

is an increase in σ_{da}; in reaction (1) σ_c', $\tau_a'^{-1}$, and p' are, respectively, the capture cross section to produce AX^{-*}, the rate of autodetachment of AX^{-*}, and the probability of AX^{-*} to decay into $\mathrm{A} + \mathrm{X}^-$. The increase in σ_{da} with T results mainly from an increase in p' with T which itself results from a decrease with increasing T of the separation time of A and X^-. For molecules AX with purely nondissociative attachment, the effect of T is a decrease of $\sigma_{nd} = \sigma_c p$ with increasing T for the reaction

$$e + \mathrm{AX} \underset{\tau_a^{-1}}{\overset{\sigma_c}{\rightleftharpoons}} \mathrm{AX}^{-*} \xrightarrow{p} \mathrm{AX}^-, \tag{2}$$

which results from a decrease in p and/or σ_c as T increases. In those cases where dissociative and nondissociative electron attachment processes take place concurrently over a given energy range ϵ, the mode of electron attachment (dissociative or nondissociative) itself varies with both ϵ and T (see Refs. 7 and 8 and this work). It appears[7] that for both dissociative and nondissociative attachment the effect of T on σ_c or σ_c' is small, except in those cases where electron capture by the hot molecule is accompanied by geometrical changes.

In this paper we report the results of a high pressure electron swarm study on the variation of the dissociative and the nondissociative electron attachment to n-C_4F_{10} with temperature. The normal perfluoroalkanes with three or more carbon atoms have been found earlier[8,9,11–13] to attach electrons both dissociatively and nondissociatively, with both processes extending over a wide range, and with the latter process decreasing as ϵ increases. Electron beam studies[11,12] have shown that the parent anion of n-C_4F_{10} is formed at low energies (it has an onset at ~0.0 eV and a peak at ~0.6 eV) and is long lived (the "apparent" mean autodetachment lifetime at the peak of the resonance was found to be ~21 μs).[12] Fragment anions ($C_4F_9^-$, $C_3F_7^-$, $C_2F_5^-$, CF_3^-, and F^-) were detected whose relative cross sections exhibited maxima around 3.0 eV and thresholds ranging from ~1 to 2.2 eV; the predominant fragment anion was F^- with a cross section maximum at 2.65 eV and an onset at 1.6 eV.[12] On the other hand, electron swarm studies[13] have shown that both dissociative and nondissociative electron attachment processes are present and that the latter—while predominant at low energies (< 1 eV)—extends to $\langle\epsilon\rangle > 5.0$ eV. The parent anion contribution was found to be much larger than indicated by the electron beam studies. This is understood because in the swarm study transient anions with lifetimes in the range 10^{-6} to 10^{-11} s are stabilized and detected, while in the time-of-flight mass spectrometric study[11,12] transient anions with lifetimes shorter than 10^{-6} s go undetected.

Based on the above studies, therefore, n-C_4F_{10} has a bound low-lying negative ion state whose potential energy curve has a minimum below that of the neutral, a vertical attachment energy of ~0.6 eV, and rises rather steeply in the Franck–Condon region. In addition, n-C_4F_{10} possesses one or more repulsive negative ion states at higher energies

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which can lead to fragment anions. Both dissociative and nondissociative electron attachment processes occur over a common and wide energy range.

The present study demonstrates that the mode—dissociative or nondissociative—of electron attachment to n-C_4F_{10} is a function of T and ϵ. It also demonstrates—by comparing the results of the present study with those of similar earlier work on C_2F_6 and C_3F_8—that this dependence is a strong function of the molecular size for this series of compounds.

II. EXPERIMENTAL

The experimental procedure and apparatus employed in the present study have been previously described.[8] The experiments were performed using Ar as the buffer gas which was of Matheson ultrahigh purity (99.999%). Before use, the Ar gas was cooled to liquid nitrogen temperatures to freeze out condensible impurities. The vapor from this cold gas was extracted at temperatures just above the Ar boiling point. The n-C_4F_{10} sample used was obtained from PCR/SCM Specialty Chemicals with a stated purity of 99%. This gas was subjected to several vacuum distillation cycles prior to the measurements to remove air from the sample. The total gas number density, N_t, was in the range 2.25 to 12.88×10^{19} cm^{-3} and the N_a of the attaching gas was varied, depending on the temperature, from 4.25 to 13.52×10^{13} cm^{-3} at 300 K, where the magnitude of the attachment rate constant was the highest and from 4.69 to 98.12×10^{13} cm^{-3} at 500 K, where the magnitude of k_a was the lowest. The ratio N_a/N_t of the attaching gas number density to the total gas number density varied from 0.33 to 12.47×10^{-6}. At each T, measurements were made over a wide range of E/N (density-reduced electric field) corresponding to a mean electron energy $\langle \epsilon \rangle$, in the range 0.63 to 4.81 eV. The measured electron attachment rate constants $k_a(\langle \epsilon \rangle, T)$ and the buffer gas electron energy distribution functions $f(\epsilon, \langle \epsilon \rangle)$ were used to calculate[14] the total electron attachment cross section $\sigma_a(\epsilon, T)$. The $f(\epsilon, \langle \epsilon \rangle)$ and the electron drift velocity $w(E/N)$ for Ar at T above room temperature were assumed to be those at room temperature since for the E/N range employed, the preponderance of the electrons have energies far in excess of thermal.

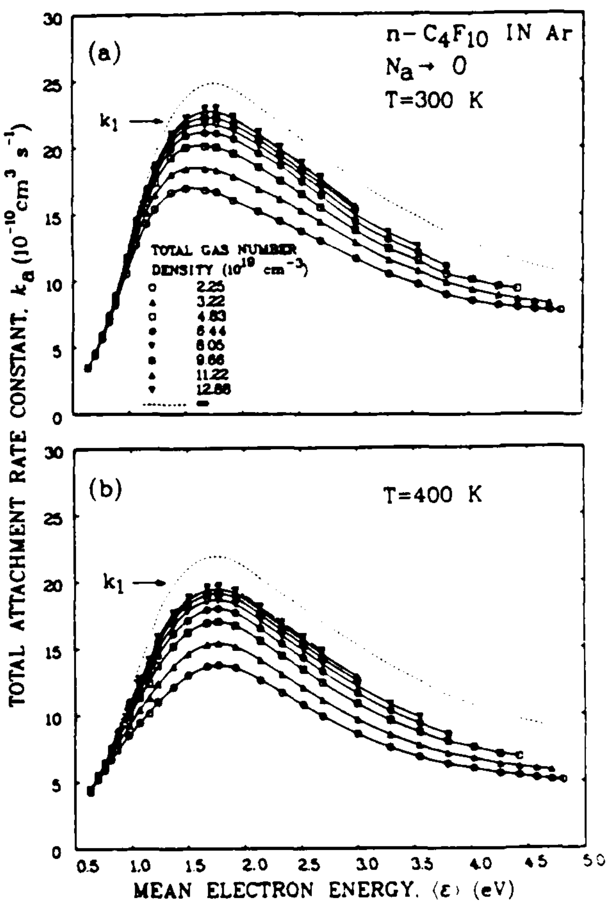


FIG. 2. Total electron attachment rate constant k_a (for $N_a \to 0$) for n-C_4F_{10} as a function of the mean electron energy $\langle \epsilon \rangle$ and total gas number density N_t at (a) $T = 300$ K and (b) $T = 400$ K. The broken curve shows the rate constant k_1 for $N_t \to 0$.

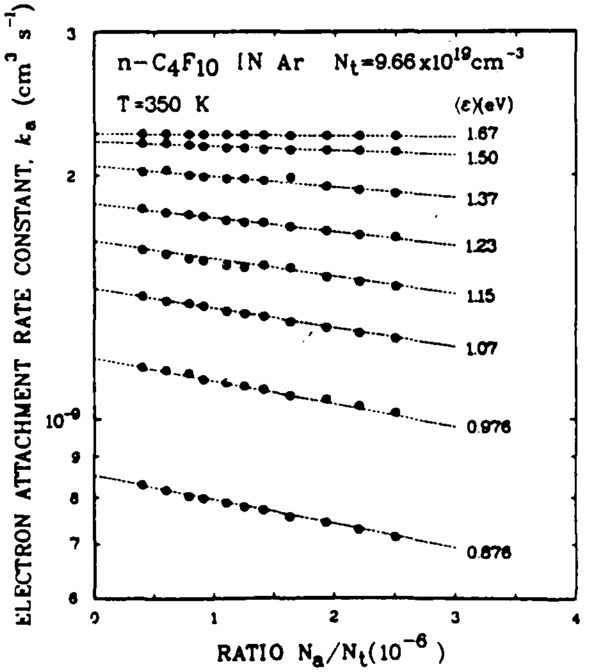


FIG. 1. Total electron attachment rate constant k_a for n-C_4F_{10} as a function of the ratio of the attaching gas number density N_a to the total gas number density N_t for several values of the mean electron energy $\langle \epsilon \rangle$ ($T = 350$ K and $N_t = 9.66 \times 10^{19}$ cm^{-3}).

The possible sources of error in the measurement of the $k_a(\langle \epsilon \rangle)$ have been discussed in Ref. 13. The total uncertainty in the measurement of $k_a(\langle \epsilon \rangle)$ at 300 K was estimated[13] to be 5% to 7%. At higher temperatures it is somewhat larger ($\sim$6% to 8%)[8] due to the uncertainty in determining the temperature. [Chromel–alumel-type KX thermocouples were used[8] which were accurate within 2.2 °C ($\pm$0.75%).] The uncertainty in $k_a(\langle \epsilon \rangle)$, however, is larger in the T range where the $k_a(\langle \epsilon \rangle)$ decreases precipitously with T (see results in Sec. III).

III. RESULTS

A. Electron attachment rate constants $k_a(\langle\epsilon\rangle,T)$ as a function of $\langle\epsilon\rangle$ and T

The total electron attachment rate constant, $k_a(E/N)$ or $k_a(\langle\epsilon\rangle)$, for n-C$_4F_{10}$ has been measured at 300, 350, 400, 450, 500, 600, 675, and 750 K. Although the number density N_a of n-C$_4$F$_{10}$ is $\sim 10^6$ times smaller than the total gas number density N_t, it was felt that even this small a quantity of n-C$_4$F$_{10}$ in Ar could change the $f(\epsilon,\langle\epsilon\rangle)$ for the mixture compared with those for the pure buffer gas. For this reason, at each value of T and $\langle\epsilon\rangle$, the k_a was measured at a fixed N_t as a function of N_a. From a plot of $k_a(\langle\epsilon\rangle,T)$ vs N_a/N_t the values of $k_a(\langle\epsilon\rangle,T)$ for $N_a\to 0$ were determined by extrapolation. These are considered to be the rates that would be measured had $f(\epsilon,\langle\epsilon\rangle)$ been characteristic of pure Ar and are the values used in subsequent discussions and analyses. A typical set of k_a vs N_a/N_t plots is shown in Fig. 1 for $T=350$ K, $N_t=9.66\times10^{19}$ cm^{-3}, and $\langle\epsilon\rangle$ in the range 0.876 to 1.67 eV; the lower the $\langle\epsilon\rangle$ (the closer the electron energies are to the Ramsauer–Townsend minimum of Ar), the larger the effect.

As a previous *room* temperature study has shown,[13] the $k_a(\langle\epsilon\rangle)$ for n-C$_4$F$_{10}$ increases with N_t. In the present study we found that $k_a(\langle\epsilon\rangle)$ increases with N_t for $T\lesssim 450$ K. At 500 K, the $k_a(\langle\epsilon\rangle)$ was found to increase with N_t only for $\langle\epsilon\rangle\lesssim 1.5$ eV and to be independent of N_t at higher values of $\langle\epsilon\rangle$. For $T>500$ K, $k_a(\langle\epsilon\rangle)$ was independent of N_t. These findings (see later this section) reflect the fact that as T increases the measured $k_a(\langle\epsilon\rangle)$ is increasingly dominated by the contribution of the dissociative attachment processes which is N_t independent. However, in the T region where there is a large contribution from the nondissociative attachment process, the effect of N_t on $k_a(\langle\epsilon\rangle)$ is large; it is larger the higher the $\langle\epsilon\rangle$ and T because the lifetimes of the transient anions decrease with both $\langle\epsilon\rangle$ and T (see Refs. 6, 9, 13, and Sec. IV). This is clearly seen from the data in Fig. 2. At low $\langle\epsilon\rangle$, the $k_a(\langle\epsilon\rangle)$ is almost independent of N_t because the lower the $\langle\epsilon\rangle$, the longer lived the parent negative ions are; at 0.6 eV the parent anions were found to have an apparent mean autodetachment lifetime of ~ 21 μs.[12] Thus, the absence of a density dependence of k_a is not suggestive of an absence of parent anions but rather that the anions produced are longer lived so that for the N_t used they are completely stabilized.

From sets of data such as in Fig. 2, the value $k_1(\langle\epsilon\rangle)$ of $k_a(\langle\epsilon\rangle)$ for $N_t\to\infty$ were determined at each T. These values are shown in Fig. 2 by the broken curves and are listed in Table I. They are also plotted in Fig. 3(a) for $T=300$, 350, 400, 450, and 500 K. In Fig. 3(b) the $k_1(\langle\epsilon\rangle)$ for $T=600$, 675, and 750 K are plotted, but since at these temperatures the attachment is entirely dissociative, these rate constants are equal to the measured $k_a(\langle\epsilon\rangle)$ at any N_t. The broken curves in Fig. 3(b) for 300, 400, and 500 K are only the dissociative attachment component of the rate constant at these temperatures. Clearly, the total attachment rate con-

TABLE I. Total electron attachment rate constants k_1 for n-C$_4$F$_{10}$ in Ar.

E/N (10^{-18} V cm^2)	$\langle\epsilon\rangle$ $T=300$ K (eV)	w $T=300$ K (10^5 cm s^{-1})	k_1 (10^{-10} cm^3 s^{-1}) T (K) 300	350	400	450	500	600	675	750
0.621	0.634	1.44	3.50	3.60	4.55		0.30			
0.777	0.702	1.53	4.60	4.70	5.61	1.40	0.46			
0.932	0.764	1.61	6.00	6.09	6.60	1.95	0.62			
1.09	0.822	1.68	7.50	7.58	7.80	2.35	0.74	0.90	1.57	2.75
1.24	0.876	1.75	9.05	9.14	9.11	2.90	0.88	1.10	2.00	3.60
1.55	0.976	1.87	12.10	12.30	11.70	3.92	1.22	1.75	3.05	5.20
1.86	1.068	1.95	15.00	15.10	13.80	4.97	1.54	2.40	3.90	6.50
2.17	1.15	2.03	17.65	17.60	15.50	5.85	1.89	2.95	4.85	7.80
2.49	1.23	2.10	19.60	19.60	17.60	6.71	2.29	3.50	5.60	8.60
3.11	1.37	2.22	22.30	22.30	19.70	8.01	2.82	4.30	6.75	10.00
3.73	1.50	2.33	23.72	23.50	21.00	9.01	3.41	5.10	7.59	11.00
4.66	1.67	2.46	24.75	24.40	21.81	9.82	3.97	5.90	8.30	11.70
5.28	1.77	2.54	24.80	24.45	21.88	10.01	4.20	6.25	8.60	11.95
6.21	1.92	2.64	24.30	23.99	21.51	9.98	4.40	6.65	8.85	12.05
7.77	2.14	2.79	23.00	22.55	20.25	9.25	4.54	6.80	8.90	11.85
9.32	2.33	2.92	21.75	21.25	19.03	8.57	4.56	6.75	8.75	11.50
10.97	2.52	3.04	20.55	20.19	18.00	7.96	4.53	6.55	8.40	11.00
12.4	2.69	3.14	19.46	19.08	16.95	7.48	4.44	6.31	8.07	10.55
15.5	3.00	3.33	17.50	17.21	15.25	6.61	4.20	5.90	7.45	9.80
18.6	3.29	3.49	15.95	15.55	13.70	5.98	3.94	5.50	6.95	9.08
21.7	3.55	3.63	14.80	14.31	12.53	5.45	3.91	5.20	6.50	8.50
24.9	3.80	3.76	13.69	13.30	11.41	5.01	3.49	4.90	6.10	8.00
27.9	4.03	3.88	12.88	12.48	10.71	4.75	3.33	4.65	5.80	
31.1	4.26	3.99	12.00	11.65	10.01	4.51	3.16	4.45	5.50	
34.2	4.43	4.18	11.52	11.16	9.60	4.35	3.07	4.30	5.30	
37.3	4.58	4.38	11.11	10.71	9.30	4.25	2.99	4.20	5.18	
40.4	4.71	4.62	10.83	10.52	9.00	4.15	2.94	4.12	5.10	
43.5	4.81	4.90	10.71	10.38	8.88	4.10	2.92	4.08		

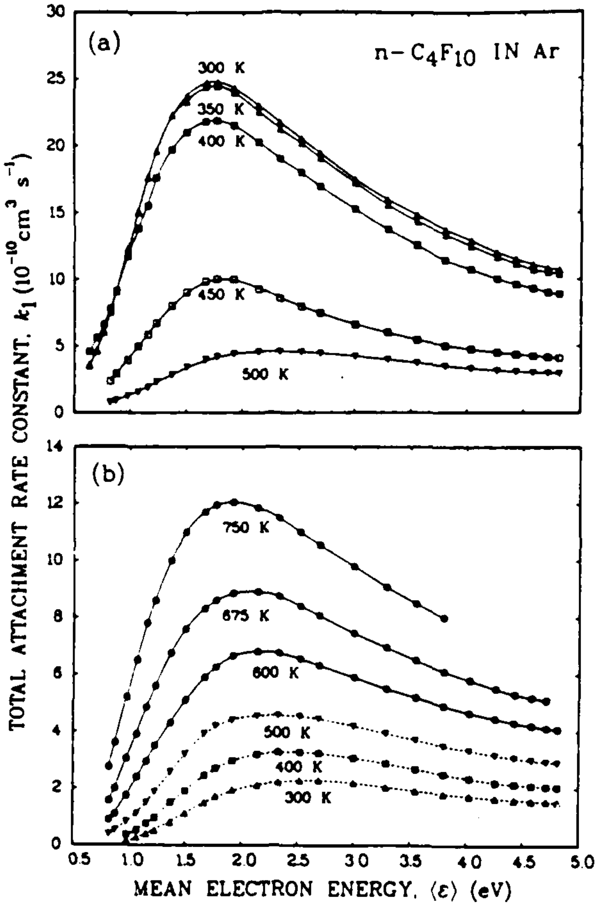


FIG. 3. The total electron attachment rate constant k_1 (for $N_a \to 0$, $N_t \to \infty$) for n-C$_4$F$_{10}$ as a function of mean electron energies ⟨ε⟩ at (a) 300, 350, 400, 450, and 500 K and (b) 600, 675, and 750 K. The 300, 400, and 500 K curves in (b) are the dissociative attachment components $(k_a)_d$ of the total rate constant k_1 at these temperatures.

stant initially decreases with T above ambient temperatures and then increases. As was found earlier[9] for C$_3$F$_8$ (see discussion in Sec. IV), the decrease of $k_1(\langle\epsilon\rangle)$ with T is due to the decrease with T of the nondissociative part of the attachment, and the increase with T is due to the increase with T of the dissociative attachment component; the contribution of the latter process increases with increasing T and dominates for $T \gtrsim 500$ K. As a result of the delicate temperature dependencies of the dissociative and nondissociative contributions to the total attachment rate constant, the position of the maximum of $k_1(\langle\epsilon\rangle)$ changes little with increases in T as long as the nondissociative contribution is large, and it shifts to lower energy with increasing T when the dissociative attachment contribution predominates (see Fig. 3).

These delicate effects of T on $k_1(\langle\epsilon\rangle)$ and the relative contribution to $k_1(\langle\epsilon\rangle)$ of the dissociative and the nondissociative processes are further illustrated by the data in Fig. 4, where k_1 is plotted as a function of T for four values of ⟨ε⟩. At high T ($\gtrsim 500$ K) the logarithm of $k_1(\langle\epsilon\rangle)$ increases linearly with T and is N_t independent. These findings, coupled with earlier knowledge[2-9] on the effect of T on dissociative attachment, show that the linearly rising portion of $\log k_1$ for $T \gtrsim 500$ K is due to dissociative attachment processes. The data on $\log k_1(\langle\epsilon\rangle)$ for $T > 500$ K in plots such as in Fig. 4 were fitted to a straight line and extrapolated to 300 K. In this way the dissociative $(k_a)_d$ and the nondissociative $(k_a)_{nd}$ (shaded areas in Fig. 4), components of k_1 at each ⟨ε⟩ and T were determined [see Sec. IV for another way to determine $(k_a)_d$ and $(k_a)_{nd}$ which gave results con-

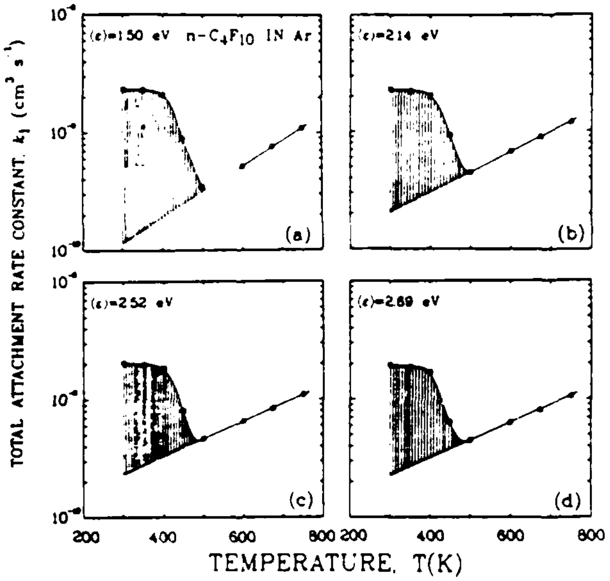


FIG. 4. Total electron attachment rate constant k_1 (for $N_a \to 0$, $N_t \to \infty$) for n-C$_4$F$_{10}$ as a function of temperature T and the mean electron energies ⟨ε⟩, 1.50, 2.14, 2.52, and 2.69 eV.

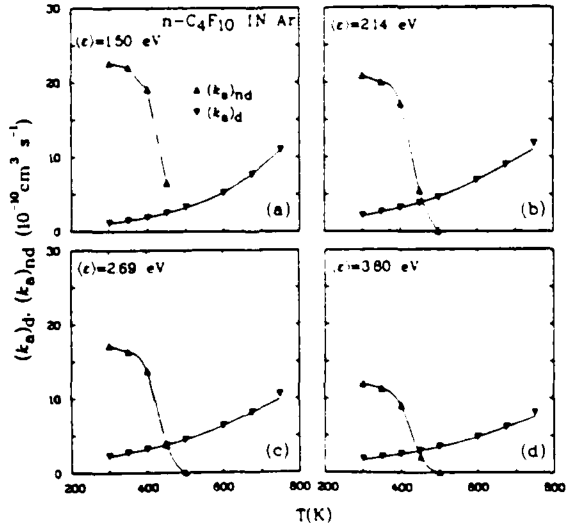


FIG. 5. The electron attachment rate constants $(k_a)_d$ and $(k_a)_{nd}$ of n-C$_4$F$_{10}$ due, respectively, to dissociative and nondissociative electron attachment as a function of the temperature T at the mean electron energies ⟨ε⟩, 1.50, 2.14, 2.69, and 3.80 eV.

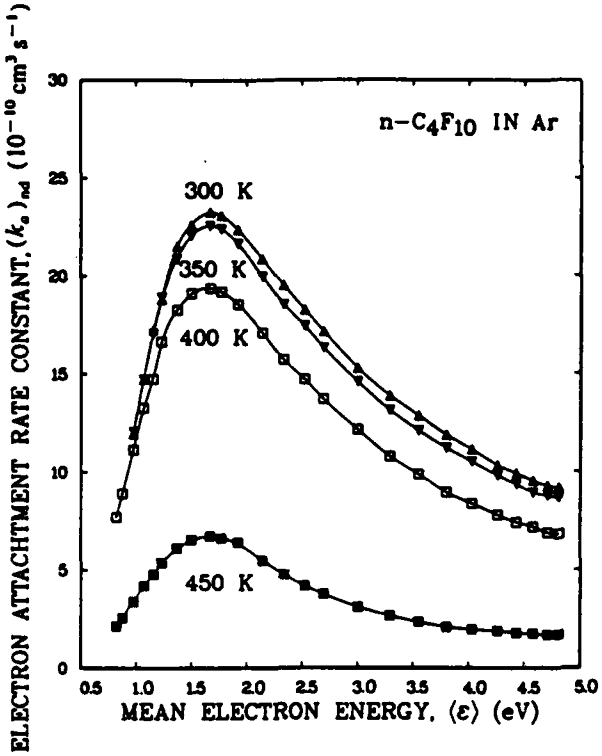


FIG. 6. Electron attachment rate constant $(k_a)_{nd}$ for n-C_4F_{10} due to nondissociative attachment as a function of the mean electron energy at 300, 350, 400, and 450 K.

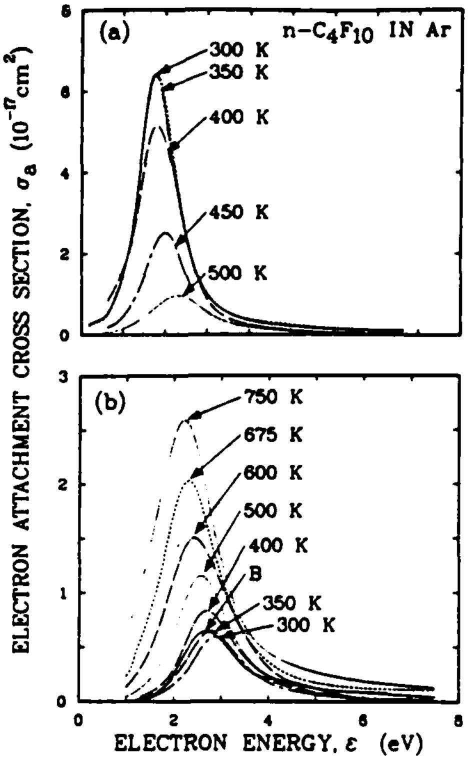


FIG. 7. The swarm unfolded total electron attachment cross sections $\sigma_a(\epsilon)$ for n-C_4F_{10} obtained using the $k_1(\langle\epsilon\rangle)$ in Ar shown in Fig. 3 at (a) 300, 350, 400, 450, and 500 K and (b) 600, 675, and 750 K. The 300, 350, 400, and 500 K curves (b) are the dissociative attachment cross sections $(\sigma_a)_d(\epsilon)$ at these temperatures. In Fig. 7(b) is plotted also the total relative cross section measured in an electron beam experiment (Ref. 12) (curve B) which has been normalized to the peak of the $(\sigma_a)_d(\epsilon)$ at 350 K (see the text).

sistent with the extrapolation method]. Examples of the variation of $(k_a)_d$ and $(k_a)_{nd}$ with T determined in this way are shown in Fig. 5 for four values of $\langle\epsilon\rangle$. In Fig. 6, the $(k_a)_{nd}$ is shown for 300, 350, 400, and 450 K. The dramatic decrease of $(k_a)_{nd}(\langle\epsilon\rangle)$ with T is but apparent.

B. Swarm unfolded cross sections

The total electron attachment rate constants $k_1(\langle\epsilon\rangle)$ in Fig. 3(a) ($300<T<500$ K) were unfolded, and the total electron attachment cross sections $\sigma_a(\epsilon,T)$ obtained are shown in Fig. 7(a). They decrease in magnitude with increasing T because in this temperature range, $\sigma_a(\epsilon,T)$ contains a large contribution (which decreases as T increases) from a nondissociative attachment process. Very interestingly, however, the $\sigma_a(\epsilon,T)$ peaks at progressively higher $\langle\epsilon\rangle$ in this temperature range reflecting the depletion of the parent and the preponderance of the fragment anions as T increases.

The total $k_1(\langle\epsilon\rangle)$ for 600, 675, and 750 K in Fig. 3(b) were similarly unfolded, and the resultant cross sections are shown in Fig. 7(b). Clearly, at these temperatures the attachment cross section increases with T and—as is indicated by the data in Fig. 4—it is entirely due to dissociative attachment. Also shown in Fig. 7(b) are the dissociative attachment cross sections $(\sigma_a)_d(\epsilon)$ for 300, 400, and 500 K which were obtained by unfolding only the $(k_a)_d(\langle\epsilon\rangle)$ component of $k_1(\langle\epsilon\rangle)$. The behavior of $(\sigma_a)_d(\epsilon,T)$ for n-C_4F_{10} is consistent with that of the $(\sigma_a)_d(\epsilon,T)$ of other molecules with

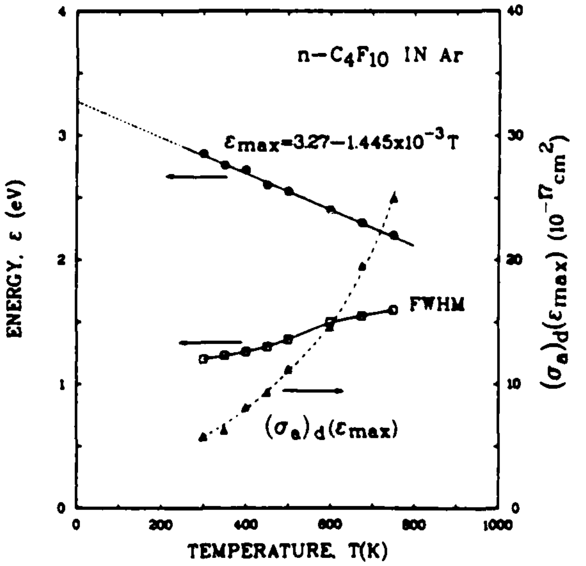


FIG. 8. Variation of the peak energy ϵ_{max} full width at half-maximum, FWHM, and peak value $(\sigma_a)_d(\epsilon_{max})$ of the total dissociative electron attachment cross section of n-C_4F_{10} with temperature.

TABLE II. Values of FWHM, ϵ_{max}, and $(\sigma_a)_d(\epsilon_{max})$ for the $(\sigma_a)_d(\epsilon)$ of n-C_4F_{10}.

T (K)	FWHM (eV)	ϵ_{max} (eV)	$(\sigma_a)_d(\epsilon_{max})$ (10^{-17} cm^2)
300	1.20	2.85	6.00
350	1.23	2.76	6.50
400	1.26	2.72	8.44
450	1.30	2.60	9.70
500	1.36	2.55	11.65
600	1.50	2.40	15.20
675	1.55	2.30	20.32
750	1.60	2.20	26.00

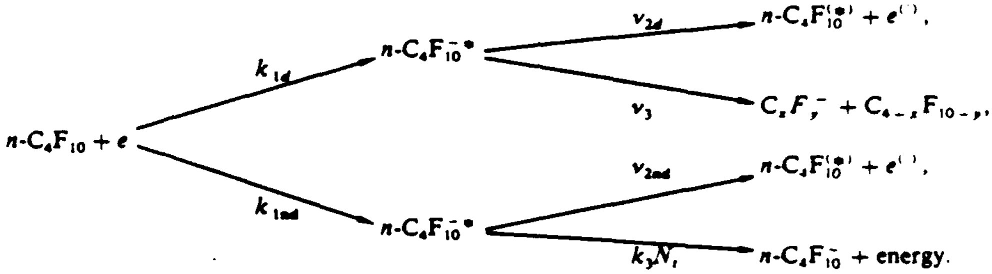
purely dissociative attachment processes[2-7]: its magnitude and width increase and its peak energy position ϵ_{max} and onset shift to lower energies with increasing T. In Fig. 8 (see also Table II) are shown the observed dependencies of the full width at half-maximum, the peak energy position (ϵ_{max}), and the magnitude of $(\sigma_a)_d(\epsilon,T)$ at ϵ_{max} on temperature.

The curve B in Fig. 7(b) is the total (for all fragment anions) $(\sigma_a)_d(\epsilon)$ for n-C_4F_{10} as measured in a single collision beam experiment[12] normalized to the swarm unfolded $(\sigma_a)_d(\epsilon)$ at $T = 350$ K.

IV. DISCUSSION

A. Variation of the dissociative and nondissociative electron attachment processes in n-C_4F_{10} with electron energy and temperature

As discussed in Sec. I, earlier electron swarm and electron beam studies indicated that low-energy electron attachment to n-C_4F_{10} can be described by electron attachment to an attractive negative ion state leading to parent anions and to repulsive higher-lying negative ion states leading to fragment anions, viz.,



(3a)

(3b)

(3c)

(3d)

The n-$C_4F_{10}^{-*}$ produced by electron capture into dissociative negative ion state(s) (NISs) with a rate constant k_{1d} decays by autodetachment [process (3a)] with a rate constant ν_{2d} or dissociates with a rate constant ν_3 to form negative ion and neutral fragments. The n-$C_4F_{10}^{-*}$ produced by electron capture into the nondissociative (bound) NIS with a rate constant, k_{1nd}, either decays by autodetachment with a rate constant, ν_{2nd} (average lifetime, τ_a) or is stabilized by collision with another species (in the present experiment in collision with an Ar atom) with a rate constant, k_3N_t to form a stable parent anion, n-$C_4F_{10}^-$ [process (3d)]. If the bound and unbound NISs do *not* internally convert to each other, the measured total $k_a(\langle\epsilon\rangle)$ can be expressed—on the basis of processes (3a) to (3d)—by

$$k_a = k_{1d}\frac{\nu_3}{\nu_{2d}+\nu_3} + k_{1nd}\frac{k_3N_t}{\nu_{2nd}+k_3N_t}. \qquad (4)$$

If the contribution to k_a from dissociative attachment is negligible, $1/k_a\,[=1/(k_a)_{nd}]$ would vary linearly with $1/N_t$, viz.,

$$\frac{1}{(k_a)_{nd}} = \frac{1}{k_{1nd}} + \frac{\nu_{2nd}}{k_{1nd}k_3}\frac{1}{N_t}. \qquad (5)$$

This relationship is indeed obeyed [Fig. 9(a)] for $T = 300$ K and $\langle\epsilon\rangle \lesssim 1.50$ eV (i.e., under conditions for which nondissociative electron attachment predominates). However, as $\langle\epsilon\rangle$ increases, the contribution of dissociative attachment processes increases, and $1/k_a$ vs $1/N_t$ is no longer linear. As expected, this latter type of behavior becomes more pronounced the higher the value of T [compare data in Figs. 9(a) and 9(b)], since the dissociative attachment contribution increases with T. If at a given value of T the rate constant $(k_a)_d$ due to the dissociative attachment is subtracted from the measured total attachment rate constant k_a and the inverse of the resultant nondissociative rate constant $(k_a)_{nd}$ is plotted as a function of $1/N_t$, a linear relationship is indeed obtained. This is clearly seen from Fig. 10, where the $(k_a)_{nd}^{-1}$ values for 450 K [determined from the respective $1/k_a$ data in Fig. 9(b)] are plotted as a function of $1/N_t$.

It should be pointed out that the $(k_a)_d$ and $(k_a)_{nd}$ components of k_a can be obtained—as in an earlier study[9]—by applying a nonlinear least squares fit to Eq. (4) (see Fig. 11, curve for 450 K). Furthermore, when $N_t \to \infty$ (i.e., when all parent and fragment anions are detected), Eq. (4) leads to

$$k_a \to k_{1d}\frac{\nu_3}{\nu_3+\nu_{2d}} + k_{1nd} \equiv k_1, \qquad (6)$$

and when $N_t \to 0$ (i.e., when only the dissociative attachment fragment anions are detected), it leads to

$$k_a \to k_{1d}\frac{\nu_3}{\nu_3+\nu_{2d}} \equiv (k_a)_d. \qquad (7)$$

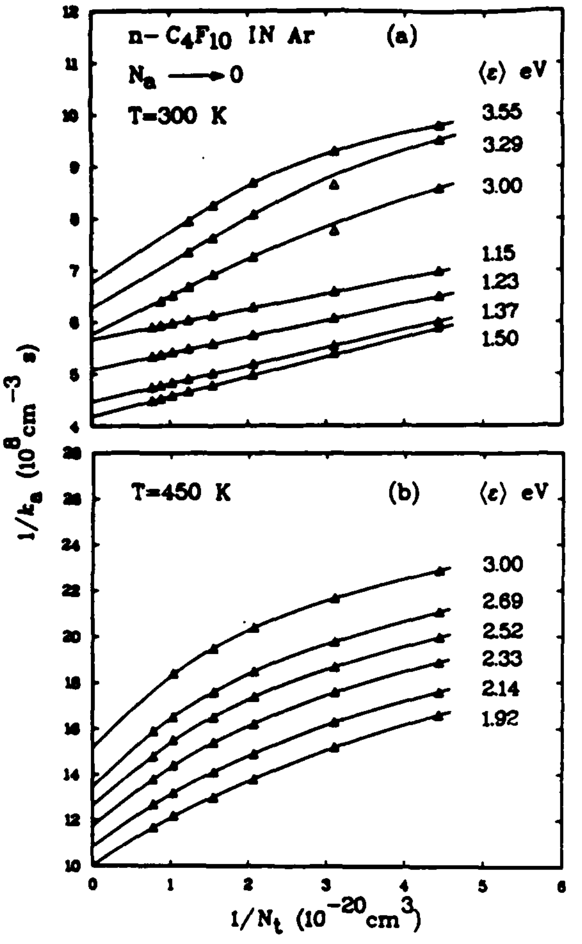


FIG. 9. $1/k_a$ vs $1/N_t$ for n-C_4F_{10} in Ar at (a) 300 K and (b) 450 K (see the text).

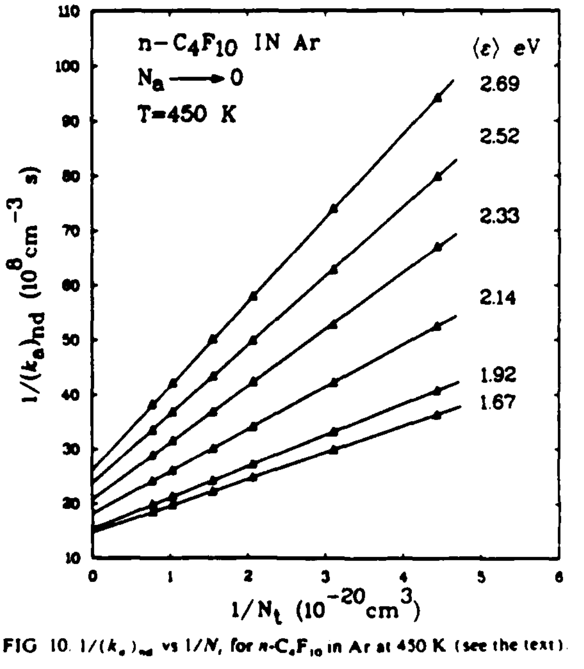


FIG. 10. $1/(k_a)_{nd}$ vs $1/N_t$ for n-C_4F_{10} in Ar at 450 K (see the text).

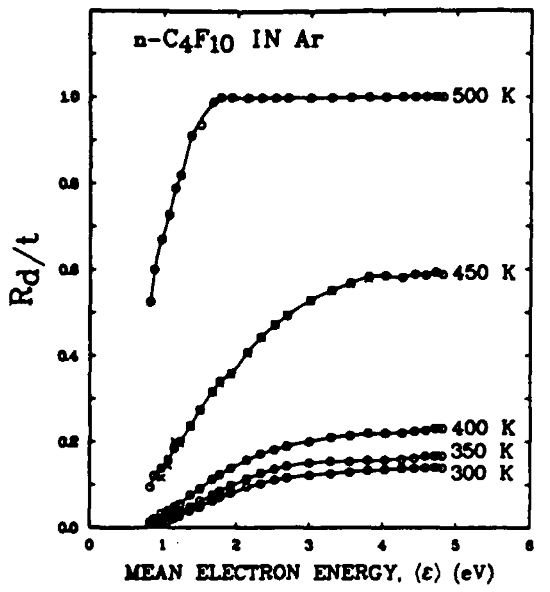


FIG. 11. The ratio $R_{d/t}$ of the dissociative to the total electron attachment rate constant for n-C_4F_{10} as a function of the mean electron energy $\langle\epsilon\rangle$ at 300, 350, 400, 450, and 500 K. The data points × for the 450 K are the values of $R_{d/t}(\langle\epsilon\rangle)$ calculated by a nonlinear least squares fit to Eq. (4).

The ratio of Eqs. (7) and (6) give the ratio $R_{d/t}$ of the dissociative to the total attachment rate constant. In Fig. 11 $R_{d/t}$ is plotted as a function of $\langle\epsilon\rangle$ for 300, 350, 400, 450, and 500 K; at low $\langle\epsilon\rangle$ and T the contribution of dissociative attachment to the total is small, but it rapidly increases as both $\langle\epsilon\rangle$ and T increase. This type of behavior is both a result of the $\langle\epsilon\rangle$ dependencies of $(k_a)_d$ and $(k_a)_{nd}$ and of

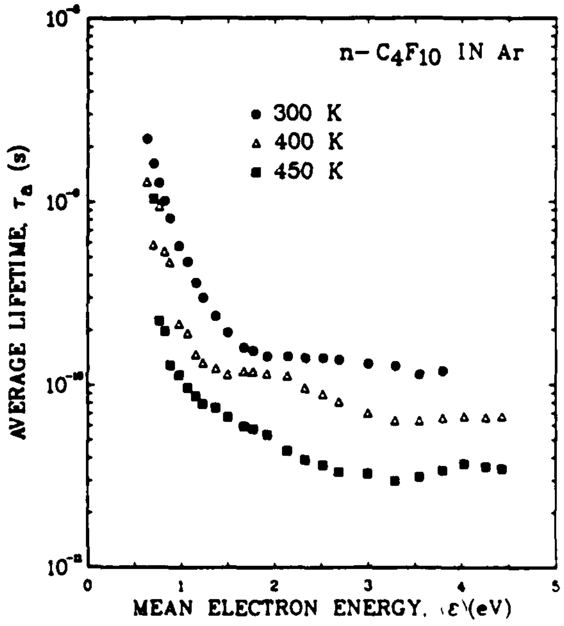


FIG. 12. Lower limits to the average apparent autodetachment lifetime τ_a of n-$C_4F_{10}^{-*}$ in the lowest bound negative ion state as a function of the mean electron energy $\langle\epsilon\rangle$ in Ar at 300, 400, and 450 K.

the opposite effect of T on $(k_a)_d$ (increasing with T) and $(k_a)_{nd}$ (decreasing with T).

B. Estimates of the "autodetachment" lifetime of n-C$_4$F$_{10}^{-*}$ in the lowest (bound) NIS

The observed linear dependence of $[(k_a)_{nd}(\langle\epsilon\rangle,T)]^{-1}$ on N_t^{-1} allows an estimate of the autodetachment lifetime τ_a of n-C$_4$F$_{10}^{-*}$ produced via the lowest (bound) NIS as a function of $\langle\epsilon\rangle$ and T. From Eq. (5) and linear plots such as in Fig. 10 we obtained $1/k_{1nd}$ and $\nu_{2nd}/k_{1nd}\,k_3$ at various values of $\langle\epsilon\rangle$ and T.

As discussed earlier,[9,13,15] the ratio ν_{2nd}/k_3 gives the gas number density N_c at which the rate of autodetachment of n-C$_4$F$_{10}^{-*}$ is equal to the rate of stabilization of n-C$_4$F$_{10}^{-*}$ by collision with Ar, i.e.,

$$\nu_{2nd}\,(=\tau_a^{-1}) = k_3N_c. \tag{8}$$

An estimate of k_3N_c can be obtained from[9,13,15]

$$\tau_s\,[=(k_3N_c)^{-1}] = \frac{\tau_c}{p} = \frac{1}{2\pi pN_c}\left(\frac{M_r}{e^2\alpha}\right)^{1/2} > \frac{1.948\times 10^9}{N_c}, \tag{9}$$

where τ_s is the stabilization time, α the static polarizability of Ar ($=1.64\times 10^{-24}$ cm^3),[16] and p the probability of stabilization of n-C$_4$F$_{10}^{-*}$ in each collision with an Ar atom which is assumed to be independent of the capture electron's energy; Eq. (9) was derived on the assumption that the cross section for the collision between C$_4$F$_{10}^{-*}$ and Ar is given by the classical Langevin expression.[17]

Using Eq. (9) and the slopes and intercepts we obtained from a linear least squares fit to Eq. (5), we estimated lower limits for τ_a at 300, 400, and 450 K. These are plotted in Fig. 12 as a function of $\langle\epsilon\rangle$. While the meaning of these "lifetimes" is unclear [at each value of $\langle\epsilon\rangle$ due to the broad $f(\epsilon,\langle\epsilon\rangle)$ one probes parent anions with a wide range of τ_a], they, nonetheless, demonstrate the increase in autodetachment probability with increasing $\langle\epsilon\rangle$ (and T). Since, however, the values of τ_a (see Fig. 12) at $\sim$0.5 eV are $<10^{-8}$ s while electron beam experiments indicated τ_a values $>10^{-5}$ s at this energy,[12] it seems that in the latter experiments only a small fraction of the parent anions formed is detected, perhaps only those formed at lower (near zero) energies whose τ_a is longer. Consistent with this is the fact that in the swarm experiments at $\langle\epsilon\rangle<1$ eV the parent anion intensity far exceeds that of the fragments, while the opposite is true in the electron beam study.

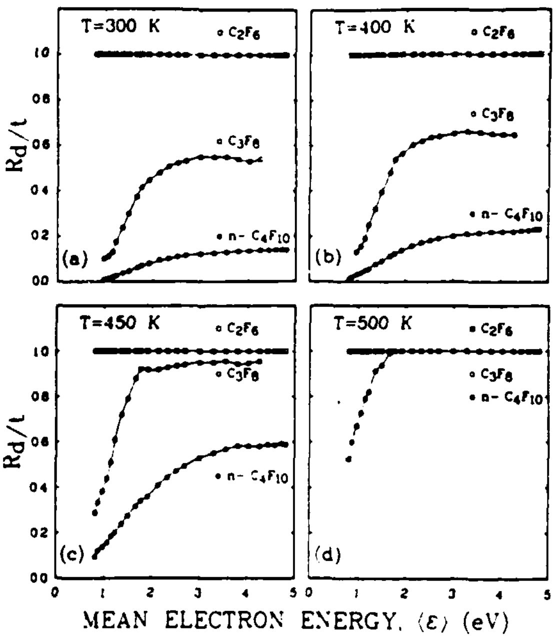


FIG. 14. Comparison of the ratio $R_{d/t}$ of the dissociative to the total attachment rate constant for C$_2$F$_6$, C$_3$F$_8$, and n-C$_4$F$_{10}$ as a function of the mean electron energy $\langle\epsilon\rangle$, at 300, 400, 450, and 500 K.

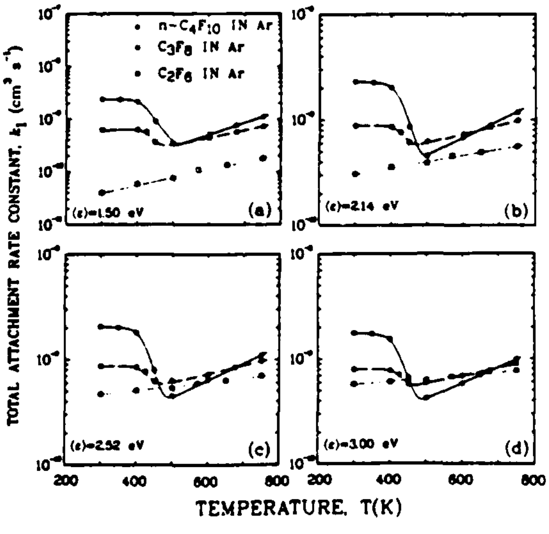


FIG. 13. *Comparison of the electron attachment rate constants* k_t *(for* $N_a \to 0$, $N_t \to \infty$) for C$_2$F$_6$, C$_3$F$_8$, and n-C$_4$F$_{10}$ as a function of the temperature T at the mean electron energies $\langle\epsilon\rangle$, 1.50, 2.14, 2.52, and 300 eV.

C. Effect of temperature on the nondissociative and dissociative electron attachment to n-C$_4$F$_{10}$

Both the nondissociative and the dissociative electron attachment to n-C$_4$F$_{10}$ are affected by T. The rate constant $(k_a)_{nd}$ decreases and the $(k_a)_d$ increases with T. The decrease of $(k_a)_{nd}$ with T observed in this study of n-C$_4$F$_{10}$ is attributed to the increase with T of the autodetachment rate[6,7,9] constant, ν_{2nd}, as is indicated by the data in Fig. 12 and also to the decrease in σ_c with T as is indicated by the decrease of k_{1nd} (see Figs. 9 and 10) with increasing T. The increase in $(k_a)_d$ with T is attributed (as in earlier studies[2-9]), to mainly the increase in the rate constant ν_3 for vibrationally excited n-C$_4$F$_{10}$ molecules.

D. Effect of temperature on the electron attachment to the perfluoroalkanes C$_2$F$_6$, C$_3$F$_8$, and n-C$_4$F$_{10}$

The present measurements on $k_1(T)$ for n-C$_4$F$_{10}$ are compared in Fig. 13 with those for C$_2$F$_6$ (Ref. 8) and C$_3$F$_8$ (Ref. 9) for four values of $\langle\epsilon\rangle$. The delicate dependence of k_1

on both T and $\langle \epsilon \rangle$ depends on the size of the molecules, which apparently determines the relative contributions of the dissociative and nondissociative processes. Thus, for C$_2$F$_6$ for which only dissociative attachment occurs, the $\log k_1$ increases monotonically (actually linearly) with T at any $\langle \epsilon \rangle$. For C$_3$F$_8$ for which both dissociative and nondissociative attachment processes occur, $\log[k_1(\langle \epsilon \rangle)]$ first decreases slowly and then precipitously with increasing T up to a minimum value around ~ 450 K and then increases linearly with T beyond ~ 500 K. This dependence varies with $\langle \epsilon \rangle$ and reflects the variation of $(k_a)_{nd}$ and $(k_a)_d$ with both $\langle \epsilon \rangle$ and T. For n-C$_4$F$_{10}$ for which the nondissociative attachment is larger, a behavior similar to that just described for C$_3$F$_8$ is observed but is more pronounced.

Finally, in Fig. 14 the ratio $R_{d/t}$ is plotted as a function of $\langle \epsilon \rangle$ for all three molecules and for four values of T. The ratio $R_{d/t}$ is small at low $\langle \epsilon \rangle$ and T, but it increases with both $\langle \epsilon \rangle$ and T and reaches unity for $T > 500$ K and $\langle \epsilon \rangle > 1.7$ eV.

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

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BASIC STUDIES OF GASES FOR FAST SWITCHES

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Papers Submitted to Refereed Journals
(Not Yet Published)

S. R. Hunter, J. G. Carter, and L. G. Christophorou
Electron Attachment and Ionization processes in CF_4, C_2F_6, C_3F_8, and $n\text{-}C_4F_{10}$
J. Chem. Phys. (in press)

S. R. Hunter
Comment on "Shortening of Electron Conduction Pulses by Electron Attachers O_2, N_2O, and CF_4"
J. Appl. Phys. (in press)

S. R. Hunter, J. G. Carter, and L. G. Christophorou
Electron Motion in CF_4, C_2F_6, C_3F_8, and $n\text{-}C_4F_{10}$
Phys. Rev. A (submitted)

P. G. Datskos and L. G. Christophorou
Variation of the Electron Attachment to $n\text{-}C_4F_{10}$ with Temperature
J. Chem. Phys. (in press)

Papers Published in Refereed Journals

S. R. Hunter, J. G. Carter, and L. G. Christophorou
Electron Transport Studies of Gas Mixtures for Use in e-Beam Controlled Diffuse Discharge Switches
J. Appl. Phys. **58**, 3001-3015 (1985)

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Studies of Total Ionization in Gases/Mixtures of Interest to Pulsed Power Applications
J. Appl. Phys. **60**, 499-308 (1986)

Patents Filed

L. G. Christophorou and S. R. Hunter
Penning Ionization Ternary Gas Mixtures for Diffuse-Discharge Switch

L. G. Christophorou, D. L. McCorkle, and S. R. Hunter
Gas Mixtures for Spark Gap Closing Switches

S. R. Hunter and L. G. Christophorou
Binary Gas Mixtures for Diffuse Glow Discharge Closing Switches

S. R. Hunter and L. G. Christophorou
Ternary Gas Mixtures for Diffuse Glow Discharge Closing Switches

Patents Granted

Books (and Sections Thereof) Submitted for Publication

Books (and Sections Thereof) Published

K. Nakanishi, L. G. Christophorou, J. G. Carter, and S. R. Hunter
Penning Ionization Ternary Gas Mixtures for Diffuse Discharge Switching Applications
In *Proceedings of the 5th IEEE Pulsed Power Conference* (M. F. Rose and P. J. Turchi, Eds.), IEEE, New York, 1986, pp. 40-43

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Effect of Termerature on Dissociative and Nondissociative Electron Attachment
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S. R. Hunter, J. G. Carter, and L. G. Christophorou
Electron Drift Velocity and Attachment and Ionization Coefficients in CH_4, CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}
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Electron Drift Velocity and Attachment and Ionization Coefficients in C_2F_6/Ar and C_2F_6/CH_4 Gas Mixtures at Elevated Gas Temperatures
38th Annual Gaseous Electronics Conference, Monterey, California, October 15-18, 1985

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Electron Attachment to NF_3 Revisited
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P. G. Datskos and L. G. Christophorou
Variation with Temperature of the Dissociative and Nondissociative Electron Attachment to $n\text{-}C_4F_{10}$
Thirty-ninth Annual Gaseous Electronics Conference, Madison, Wisconsin, October 7-10, 1986

Honors/Awards/Prizes

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