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Electron motion in the gases CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}

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The drift velocity w of electrons has been measured in the perfluoroalkanes n-C_NF_{2N+2} ($N=1-4$) over the density-reduced electric field (E/N) range $0.03\times10^{-17}\ \mathrm{V\,cm^2}\leq E/N\leq 500\times10^{-17}\ \mathrm{V\,cm^2}$ using a pulsed Townsend 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 nonequilibrium and boundary corrections to the measured electron swarm transit time. This is the first observation of a pressure dependence in the electron drift velocity in these gases and is believed to be due to changes in the electron energy distribution function $f(\varepsilon,E/N)$ with gas pressure resulting from increases in the density-normalized electron attachment coefficient η/N with gas 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. Possible mechanisms leading to the observation of NDC effects in these molecular gases are discussed.

I. INTRODUCTION

The perfluoroalkane series of molecules n-C_NF_{2N+2} ($N=1-4$) have previously been found by us to possess most interesting electron attaching properties.[1-6] The total electron attachment rate constants $k_a(\langle\varepsilon\rangle)$ for these molecules peak at mean electron energies $\langle\varepsilon\rangle$ well in excess of thermal energy (1 eV $\leq\langle\varepsilon\rangle\leq$ 5 eV). These molecules also possess thermal electron attachment rate constants $(k_a)_{\mathrm{th}}$ which are orders of magnitude lower than their peak values.[2,6] Electron attachment to CF_4 and C_2F_6 has been found to be purely dissociative with electron attachment cross sections $\sigma_a(\varepsilon)$ having thresholds at approximately 4 and 2.5 eV, respectively.[1,2] In contrast, both C_3F_8 and n-C_4F_{10} capture electrons, both dissociatively and nondissociatively.[2,4-6] The former processes dominate at energies $\gtrsim 2$ eV and the cross sections of the latter have thresholds at approximately 1.2 eV and 0.5 eV, respectively, and extend to energies of approximately 5 eV and 4 eV, respectively. Due to formation of parent anions in C_3F_8 and n-C_4F_{10}, the measured $k_a(\langle\varepsilon\rangle)$ (or density-normalized electron attachment coefficient η/N or density-normalized electron attachment collision frequency ν_a/N) were found to strongly depend both on the gas number density N and the gas temperature T. The formation of parent anions disappears in C_3F_8 at gas temperatures $T>450$ K (Ref. 4) and in n-C_4F_{10} at $T>500$ K (Ref. 5).

The low electron attachment rate constants for this series of molecules below $E/N\approx 20\times10^{-17}\ \mathrm{V\,cm^2}$ and the large k_a values at higher E/N values have made them serious candidates as constituents in gas mixtures for diffuse gas discharge switches which may find application in many pulsed power technologies.[7,8] The primary electron attachment characteristics of gases for this application are negligibly small electron attachment rate constants at low E/N values ($E/N\lesssim 3\times10^{-17}\ \mathrm{V\,cm^2}$) while the switch is conducting and large electron attachment rate constants at high E/N values ($50\times10^{-17}\ \mathrm{V\,cm^2}\lesssim E/N\lesssim 300\times10^{-17}\ \mathrm{V\,cm^2}$) when the switch opens and the electrical conductivity of the discharge rapidly decreases.[7,8] Mixtures containing small quantities of CF_4, C_2F_6, and C_3F_8 in either Ar or CH_4 buffer gases have been found to possess large drift velocity maxima at low E/N and, furthermore, to possess w values that decrease in magnitude with increasing E/N at higher E/N values.[7,8] Preliminary w measurements in pure CF_4, C_2F_6, and C_3F_8 have also shown pronounced maxima at comparatively low E/N ($20-40\times10^{-17}\ \mathrm{V\,cm^2}$) with decreasing w values at higher E/N.[8] This effect was shown to decrease with increasing molecular size. Such electron drift velocity characteristics are also very desirable in diffuse discharge opening switch applications.[7,8]

The large electron drift velocities ($w\geq 10^7\ \mathrm{cm\,s^{-1}}$) observed in pure CF_4 and CF_4 rare gas mixtures (where the rare gas was either He, Ar, or Xe) at comparatively low E/N values ($E/N<10\times10^{-17}\ \mathrm{V\,cm^2}$) has led to the suggestion that CF_4 may be used as a gas additive in ionizing radiation detectors.[9-11] 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. Further measurements of the electron transport parameters in this and the other perfluoroalkanes will undoubtedly aid in the development of these detectors.

A recent study[12] of the influence of pressure dependent, nonthermal electron attachment rate constants on the electron transport parameters in a Townsend discharge found that the electron transport parameters, particularly the electron drift velocity, could be significantly altered by changes in the magnitude and speed dependences of the electron attachment collision frequency $\nu_a(v)$, if $\nu_a(v)$ is significant in comparison with the electron energy exchange collision frequency $\nu_\varepsilon(v)$. We thought that the measurement of w in the perfluoroalkane series of molecules might be a good test of this finding as nonthermal pressure dependent η/N have been observed in C_3F_8 and n-C_4F_{10} but have not been observed in CF_4 and C_2F_6.[1–6] Consequently, we have measured the electron drift velocity in these four gases over the E/N range 0.03×10^{-17} V cm$^2 \le E/N \le 500\times10^{-17}$ V cm^2 using a pulsed Townsend (PT) experimental technique. 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. We have observed that w is indeed dependent on gas pressure in C_3F_8 and n-C_4F_{10} but independent of gas pressure in CF_4 and C_2F_6. The observed pressure dependence in w for C_3F_8 and n-C_4F_{10} is thought to be due to the increase with pressure of the density normalized electron attachment coefficients η/N which we have previously observed in these two molecules.[1–6] The mechanisms leading to the pressure dependence in w and the pronounced regions of negative differential conductivity (NDC) in CF_4, C_2F_6, C_3F_8, and n-C_4F_{10} are discussed in Sec. IV.

II. EXPERIMENTAL METHOD

The experimental technique and apparatus used to perform the present electron-drift-velocity measurements have been described in detail previously.[13] Briefly, the present experiments were performed using a PT experimental technique with the detection circuit operating in the voltage integrating mode.[6,13,14] The motion of the electrons and ions in the drift gap induces a charge on the anode and, hence, across the effective capacitance C of the input of the detection circuit preamplifier and thereby establishes an increasing potential $V(t)$ across the input resistance R of the preamplifier. The time constant of the preamplifier input ($\tau = RC \approx 1$ s) in the present experiments was much greater than those of the electron transit time ($T_e \approx 10^{-7}$–10^{-5} s) or positive or negative ion transit times ($T_+ \approx T_- \approx 10^{-4}$–$10^{-2}$ s). Since $T_e \ll T_+ \approx T_-$, the voltage drop across R due to the drift of the positive and negative ions is negligible during the electron swarm transit time. Consequently, a break will occur in the voltage transient allowing T_e and, hence, the experimentally measured electron drift velocity $w_m = d/T_e$ (where d is the electrode separation in the experimental chamber) to be obtained from the discontinuity in the waveform.

A fast waveform digitizer (Biomation Model 6500: 2 ns/channel, 6 bits vertical resolution) was used to record the voltage waveform during the electron drift velocity measurements. The digitized waveforms were transferred to a PDP/11 computer where multiple waveforms could be averaged, and the resultant waveform analyzed to determine w_m. In practice, a distinct break in the waveform only occurs at high gas pressures (and hence low E/N where T_e is long) and when electron attachment and ionization processes are small. Under other experimental conditions, the finite width of the uv laser pulse (in the present experiments the half width is approximately equal to 5 ns), electrical noise, electron diffusion, and the rounding of the electron voltage transient due to electron attachment and ionization reduce the accuracy with which T_e can be determined.[13,14] In these circumstances, T_e can be determined to a good approximation from the intersection of the linear extrapolation of the two voltage segments before and after significant rounding of the waveform due to diffusion has occurred.[14,15]

The measured electron drift velocity w_m (when electron diffusion to the cathode and anode is the only significant correction term) can be shown to be related to the center-of-mass electron drift velocity w by the following[15,16]

$$w_m = w\left[1 + C_1\left[\frac{ND_L}{w}\right]\left[\frac{1}{Nd}\right] + 2\left[\frac{\eta}{N} - \frac{\alpha}{N}\right]\left[\frac{ND_L}{w}\right] + \cdots\right], \tag{1}$$

where D_L is the longitudinal diffusion coefficient and C_1 is a constant which can be obtained for each gas under study from the variation in w_m with Nd at each E/N value. The first correction term to w_m in Eq. (1) is due to back diffusion to the cathode and to forward diffusion of the electron swarm as it is absorbed into the anode and is inversely proportional to Nd.[15] Consequently, performing the measurements as a function of Nd and finding the value of w_m when $1/Nd \to 0$ allows this term to be accounted for. Unfortunately, in the absence of a pressure dependence to η/N, the second correction term in Eq. (1) is independent of Nd, and values of $(\eta-\alpha)/N$ and $D_L/\mu = (ND_L/w)(E/N)$ ($\mu = w/E$ is the electron mobility) must be estimated in order to correct for these electron nonconservation processes as the swarm is absorbed into the anode.

The present technique for obtaining w_m has been checked by performing a series of w_m measurements in CH_4 (Ref. 13) and N_2 as a function of N. We have obtained the same variation in w_m with N for nitrogen as that found using Bradbury-Nielsen electrical shutter techniques (Ref. 15, p. 345) and the w values obtained from the w_m measurements in both N_2 and CH_4 are in excellent agreement with previous high accuracy measurements.[17,18] Consequently, we have assumed that the w_m values obtained using the present technique are similar to those obtained using electrical shutter methods.[15] The accuracy of w measurements obtained using electrical shutter techniques is usually higher than those obtained using the present technique except in the presence of electron attachment and at high E/N values. The experimental uncertainties involved in performing the present measurements have been discussed previously.[13] The estimated total uncertainty in the w_m measurements when electron attachment and ionization are negligible is ±2% and rises to a maximum of ±5% when either the ionization or the attachment coefficient is large due primarily to an increased uncertainty in determining the electron transit time from the break in the voltage waveform.

The gases CF_4 and C_2F_6 were obtained from Matheson Gas Products with a stated purity of 99.6%, C_3F_8 was obtained from Union Carbide Corporation, Linde Division, with a stated purity of 99%, and n-C_4F_{10} was obtained 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.[1,2] They 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 condensible impurities. All measurements were made at room temperature ($T \approx 300$ K).

III. RESULTS

A. CF_4 and C_2F_6

The electron drift velocity w_m has been measured in CF_4 over the E/N range 0.03×10^{-17} V cm$^2 \leq E/N \leq 300\times10^{-17}$ V cm^2 and in C_2F_6 over the E/N range 0.05×10^{-17} V cm$^2 \leq E/N \leq 400\times10^{-17}$ V cm^2 and has been found to be significantly dependent on the gas pressure at low E/N ($E/N < 40\times10^{-17}$ V cm^2 for CF_4 and $E/N < 70\times10^{-17}$ V cm^2 for C_2F_6) and to a lesser extent at high E/N values ($E/N > 80\times10^{-17}$ V cm^2 for CF_4 and $E/N > 150\times10^{-17}$ V cm^2 for C_2F_6). Typical examples of the measured electron drift velocities w_m as a function of the inverse of the gas pressure are given in Fig. 1 for CF_4. These measurements show that, in contrast to the expected increase in w_m with increasing $1/N$ (i.e., $1/P$) predicted from Eq. (1) and which we have observed in N_2, w_m decreases with increasing $1/P$ in CF_4 and C_2F_6. The observed dependence of w_m on P in CF_4 and C_2F_6 is most probably due to electrode boundary effects where the electron number density gradients are large, and to initial nonhydrodynamic equilibrium behavior of the electron swarm at low Nd values,[19] both of which diminish in importance at large Nd values. A similar dependence of w_m on $(1/P)$ has recently been observed by us[13] in CH_4 and may be associated with the electron scattering processes in these particular types of molecules. These three molecules are known to possess Ramsauer-Townsend–type minima in their total scattering cross sections along with large vibrational excitation cross sections at electron energies of a few tenths of an eV.[18,20] We have previously proposed that the apparent variation in η/N for CF_4 and C_2F_6 observed at small values of Nd ($< 5\times10^{17}$ cm^{-2}) is due to these nonequilibrium processes,[6] although this is mainly conjecture at this point.

Although the variation of w_m with Nd in CF_4 and C_2F_6 is complicated by a number of competing processes, it is clear that for a nonreacting electron swarm (i.e., when electron nonconservation processes due to electron attachment, detachment and ionization are negligible), then at large Nd, these processes become negligible (i.e., $w_m \rightarrow w$). Consequently, we have assumed that w_m can be expanded as follows:

$$w_m = w\left[1 + \sum_{i=1}^{\infty} C_i (N)^{-i}\right], \tag{2}$$

where the coefficients C_i are unknown functions of d and E/N and may be of either sign due to the competing processes which either increase or decrease w_m as a function of N. Most of the w_m measurements for CF_4 and C_2F_6 can be fitted to Eq. (2) by assuming a linear dependence of w_m on $1/P$, but in the E/N range $10\text{–}25\times10^{-17}$ V cm^2, the w_m measurements in CF_4 (Fig. 1) are nonlinearly dependent on N and higher-order terms in Eq. (2) are required to fit to the data. In all cases, the electron drift velocity w can be obtained by finding the value of w_m when the measurements are extrapolated to infinite gas pressure (i.e., $1/P \rightarrow 0$, Fig. 1). Using this analysis

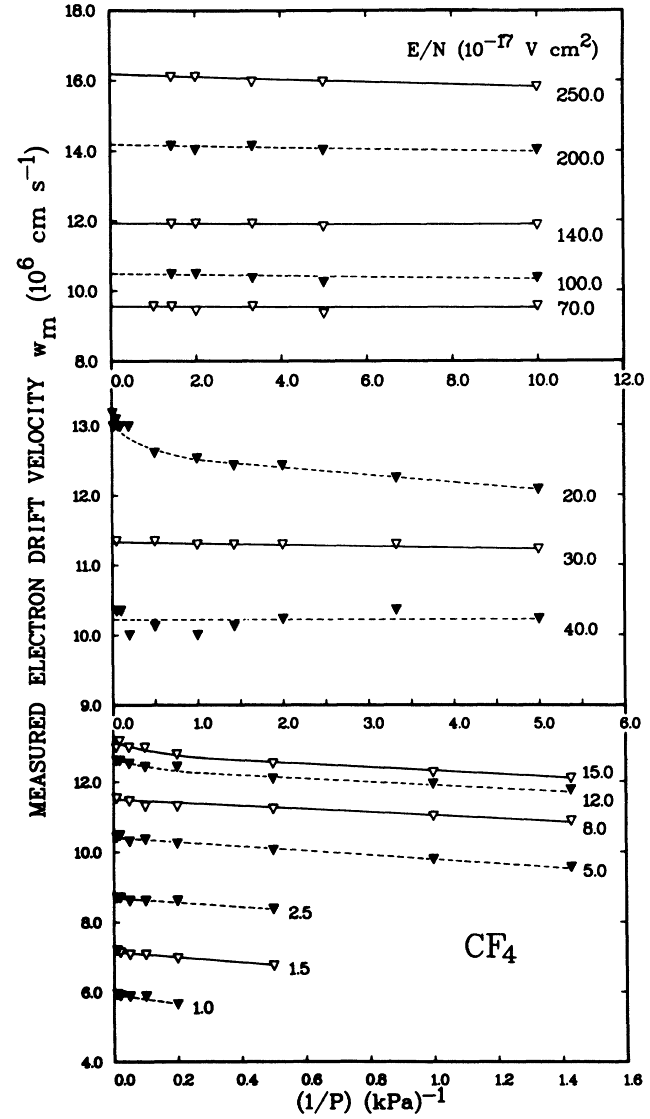

FIG. 1. Experimentally measured electron drift velocity w_m as a function of the inverse of the gas pressure in CF_4. The corrected electron drift velocity w is obtained by extrapolating these measurements to infinite gas pressure (i.e., $1/P \rightarrow 0$). w_m is independent of the gas pressure over the E/N range 40×10^{-17} V cm$^2 \leq E/N \leq 80\times10^{-17}$ V cm^2.

procedure, we have obtained w measurements[13] in CH_4 (which we have previously observed to possess a similar dependence of w_m on P) which are in excellent agreement with previous high accuracy measurements in this gas.[18]

At E/N values $\gtrsim 40\times10^{-17}$ V cm^2, electron attachment and ionization processes are significant for both CF_4 and C_2F_6,[6] and estimates must be made of the second correction term in Eq. (1) if the measured electron drift velocity is to be corrected for these electron nonconservation processes. Since electron attachment is purely dissociative in CF_4 and C_2F_6, this term is independent of gas pressure, and consequently, values for both $\bar{\alpha}/N(=\alpha/N-\eta/N)$ and D_L/μ must be used to find this correction. We have recently published values for α/N and η/N over this E/N range,[6] but unfortunately, no D_L/μ data have been published for the perfluoroalkanes. We have previously argued,[6] however, that at high E/N values above $(E/N)_{\text{lim}}$ [where $(E/N)_{\text{lim}}$ is defined as the limiting high voltage breakdown field strength of an electronegative gas and occurs when $\alpha/N=\eta/N$], $D_L/\mu\approx D_T/\mu$ for CF_4 and C_2F_6, where D_T/μ is the ratio of the transverse diffusion coefficient to electron mobility. In gases which posses regions of negative differential conductivity, as in the case for CF_4 and C_2F_6, Robson[21] has shown that $D_L/\mu \ll D_T/\mu$ over this E/N region, which is a result of a rapidly increasing momentum-transfer cross section combined with a decreasing inelastic scattering cross section at higher electron energies in this type molecule. Parker and Lowke[22] have also shown that a rapidly increasing momentum-transfer cross section leads to a small D_L/D_T ratio. Consequently, below $(E/N)_{\text{lim}}$ for both CF_4 and C_2F_6 we assume that $D_L/\mu \ll D_T/\mu$ and under these circumstances, the second correction term in Eq. (1) is negligibly small. At $(E/N)_{\text{lim}}$, $\bar{\alpha}/N=0$ and the electron nonconservation term in Eq. (1) vanishes.

Using the literature values for D_T/μ in CF_4 and C_2F_6 (Refs. 8, 23, and 24) and making the assumption that $D_L/\mu=D_T/\mu$ at E/N values above $(E/N)_{\text{lim}}$, the largest correction to w_m in CF_4 occurs at $E/N=300\times10^{-17}$ V cm^2 and is + 14%, and in C_2F_6 the largest correction occurs at $E/N=400\times10^{-17}$ V cm^2 and is + 6%. The $(E/N)_{\text{lim}}$ value where the electron nonconservation correction vanishes occurs in CF_4 and $E/N\approx140\times10^{-17}$ V cm^2 and in C_2F_6 at $E/N\approx275\times10^{-17}$ V cm^2. The measured electron drift velocity w_m obtained at $E/N>100\times10^{-17}$ V cm^2 from an extrapolation of the measured values to infinite pressure (i.e., $1/P\rightarrow0$) for CF_4 and C_2F_6 are plotted in Fig. 2 in comparison with the electron drift velocity w corrected for electron nonconservation diffusion processes at the electrode boundaries [i.e., the second correction term in Eq. (1), see Table I]. At E/N values below $(E/N)_{\text{lim}}$, if $D_L/\mu=D_T/\mu$, then the largest corrections to w_m would occur at the peak values[6] of η/N (i.e., at $E/N\approx100\times10^{-17}$ V cm^2 in CF_4 and at $E/N\approx140\times10^{-17}$ V cm^2 in C_2F_6) and are -3% for CF_4 and -5% for C_2F_6. The actual corrections are considerably less than this as D_L/μ is less than D_T/μ in this region.

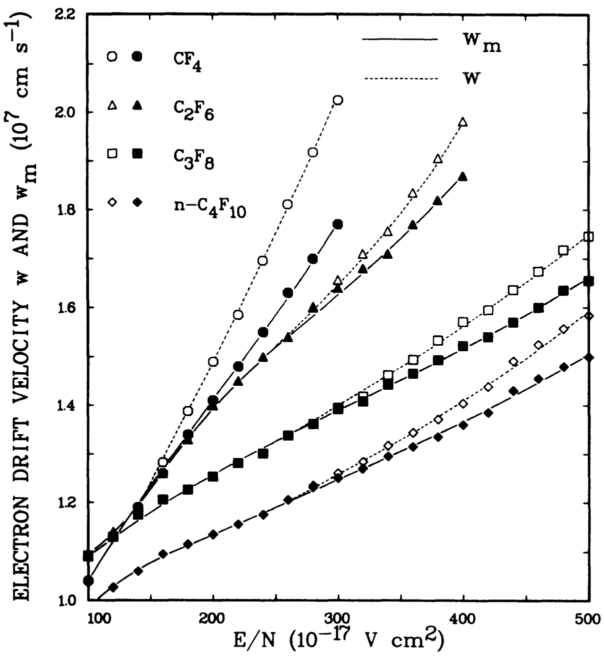

FIG. 2. Experimentally measured electron drift velocity w_m corrected for nonequilibrium and boundary processes and the electron drift velocity w obtained by further correction for electron nonconservation processes at high E/N values in CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}.

The size of the corrections to w_m, to obtain w especially at the highest E/N values at which measurements were performed (Fig. 2), adds additional uncertainties to w due primarily to possible errors in the measurement of D_T/μ and the accuracy of the assumption that $D_L/\mu\approx D_T/\mu$ for these gases. The estimated maximum error for the w measurements above $(E/N)_{\text{lim}}$ is $\pm5\%$, and below $(E/N)_{\text{lim}}$, the error decreases to $\pm2\%$ at low E/N values below the onset of electron attachment.

B. C_3F_8 and n-C_4F_{10}

In comparison with CF_4 and C_2F_6, the measured electron drift velocities in C_3F_8 and n-C_4F_{10} show larger dependences on gas pressure, particularly in n-C_4F_{10} at the higher E/N values (Fig. 3). The observed dependences of w_m on gas pressure at the lower E/N values (i.e., $E/N<50\times10^{-17}$ V cm^2 for C_3F_8 and $E/N<80\times10^{-17}$ V cm^2 for n-C_4F_{10}) for these two molecules are due to nonequilibrium and electron diffusion processes at the electrode boundaries similar to those observed in CF_4 and C_2F_6 and can be accounted for by extrapolating the measurements to infinite gas pressure (i.e., $1/P\rightarrow0$) as was done for CF_4 and C_2F_6. At $E/N>150\times10^{-17}$ V cm^2 for C_3F_8 and $E/N>100\times10^{-17}$ V cm^2 for n-C_4F_{10}, w_m decreases with increasing gas pressure, while at the lower E/N values (Fig. 3) w_m increases with gas pressure. This behavior is in contrast to CF_4 and C_2F_6 where, for all E/N values, w_m was either independent of P or increased with increasing P (Fig. 1).

The high E/N pressure-dependent w_m measurements are replotted in Figs. 4 and 5 as a function of E/N for C_3F_8 and n-C_4F_{10}, respectively. These results show that the largest pressure dependence in w_m occurs at E/N values near $(E/N)_{\mathrm{lim}}$ for both C_3F_8 and n-C_4F_{10} and the pressure dependence in w_m decreases at lower E/N values such that w_m becomes independent of gas pressure at $E/N < 150 \times 10^{-17}$ V cm^2 for C_3F_8 and at $E/N < 100 \times 10^{-17}$ V cm^2 for n-C_4F_{10} (Figs. 3–5). The observed pressure dependence in w_m is not a result of a variation of the second correction term in Eq. (1) with gas pressure near $(E/N)_{\mathrm{lim}}$, as by definition the term $(\eta-\alpha)/N$ vanishes. We consequently interpret the pressure dependence of w_m at high E/N for C_3F_8 and n-C_4F_{10} as being due not to the influence of boundaries and other nonequilibrium processes on the electron transit time T_e (as we have argued that these effects are small and should possess the opposite dependence on gas pressure) but to a real change in the electron drift velocity w due to a pressure-dependent change in the electron energy distri-

TABLE I. The electron drift velocity w in CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}. The electron drift velocity values in C_3F_8 and n-C_4F_{10} at high E/N values, where both electron attachment and ionization are significant, have been obtained by extrapolating the pressure-dependent w_m measurements to zero gas pressure as outlined in the text.

E/N (10^{-17} V cm^2)	CF_4 w (10^6 cm s^{-1})	C_2F_6 w (10^6 cm s^{-1})	C_3F_8 w (10^6 cm s^{-1})	n-C_4F_{10} w (10^6 cm s^{-1})
0.03	0.275			
0.04	0.36			
0.05	0.46	0.147		
0.06	0.55	0.176		
0.08	0.74	0.237		
0.10	0.93	0.295		
0.12	1.11			
0.15	1.40	0.435		
0.20	1.83	0.58		
0.30	2.61	0.87		
0.40	3.28	1.15	0.60	
0.50	3.85		0.75	
0.60	4.38	1.69	0.88	
0.80	5.22	2.23	1.14	
1.0	5.95	2.71	1.39	
1.2	6.53			
1.5	7.20	3.69	1.98	
2.0	8.05	4.54	2.57	
2.5	8.72			
3.0	9.10	5.68	3.57	
4.0	9.88	6.51	4.37	
5.0	10.5	7.13		4.10
6.0	10.8	7.62	5.57	4.45
8.0	11.6	8.36	6.49	5.08
10.0	12.0	8.92	7.14	5.46
12.0	12.6	9.3	7.92	5.85
15.0	13.0	9.9	8.45	6.38
17.0	13.2		8.80	
20.0	13.1	10.5	9.25	7.11
25.0	12.5	10.8	9.8	7.54
30.0	11.3	10.9	10.1	7.94
35.0	10.7	11.0	10.3	8.18
40.0	10.2	10.9	10.3	8.45
50.0	9.6	10.8	10.1	8.75
60.0	9.5	10.5	10.0	9.0
70.0	9.6	10.5	10.1	9.2
80.0	9.8	10.6	10.3	9.4
90.0	10.0		10.5	9.6
100.0	10.4	10.9	11.0	9.9
120.0	11.3	11.4	11.3	10.3
140.0	11.9	11.9	11.8	10.6
160.0	12.8	12.6	12.1	10.9
180.0	13.9	13.3	12.3	11.2

TABLE I. (*Continued*).

E/N (10^{-17} V cm^2)	CF_4 w (10^6 cm s^{-1})	C_2F_6 w (10^6 cm s^{-1})	C_3F_8 w (10^6 cm s^{-1})	n-C_4F_{10} w (10^6 cm s^{-1})
200.0	14.9	14.0	12.5	11.4
220.0	15.9	14.5	12.8	11.6
240.0	17.0	15.0	13.0	11.8
260.0	18.1	15.4	13.4	12.0
280.0	19.2	16.0	13.6	12.3
300.0	20.3	16.6	13.9	12.6
320.0		17.1	14.2	12.8
340.0		17.6	14.6	13.2
360.0		18.4	14.9	13.4
380.0		19.1	15.3	13.7
400.0		19.8	15.7	14.0
420.0			15.9	14.4
440.0			16.4	14.9
460.0			16.7	15.2
480.0			17.2	15.6
500.0			17.5	15.8

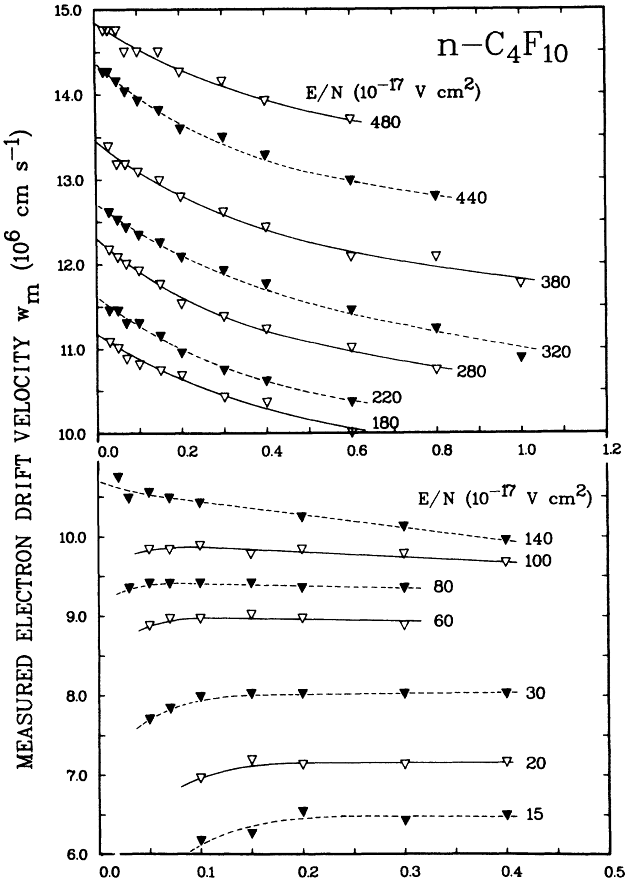

FIG. 3. Experimentally measured electron drift velocity w_m as a function of gas pressure P in n-C_4F_{10}. The w_m measurements are independent of gas pressure over a limited E/N range (90×10^{-17} V cm$^2 \lesssim E/N \lesssim 120\times10^{-17}$ V cm^2) and increase with P at low E/N and decrease with P at high E/N values ($E/N > 120\times10^{-17}$ V cm^2).

bution function $f(\varepsilon,E/N)$ caused by the nonlinear dependence of the attachment collision frequency $\bar{\nu}_a$ on N in these two gases. This phenomena is discussed more fully in Sec. IV.

It is possible to obtain electron-drift-velocity values from the experimental measurements in C_3F_8 and n-C_4F_{10} at the high E/N values by extrapolating the measured

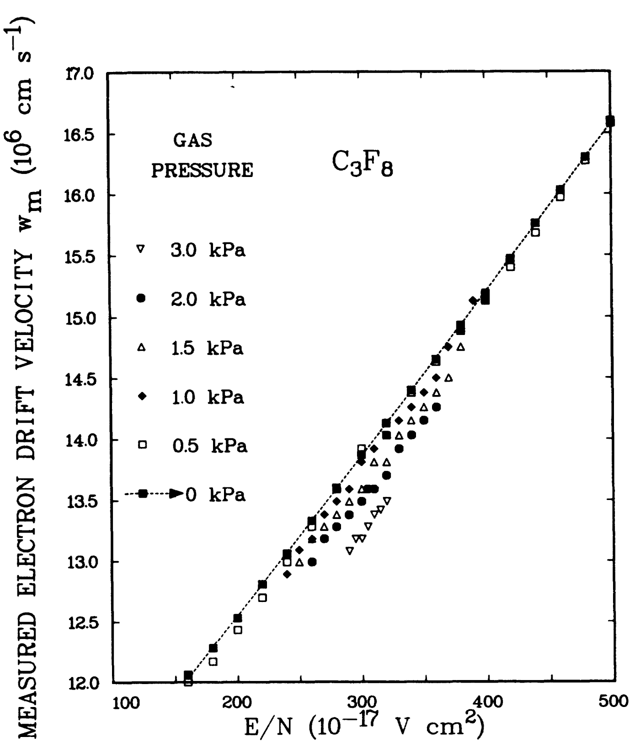

FIG. 4. Experimental w_m plotted as a function of E/N at selected gas pressures in C_3F_8. The dashed line represents the w_m values that have been obtained by extrapolating the measured values to zero gas pressure.

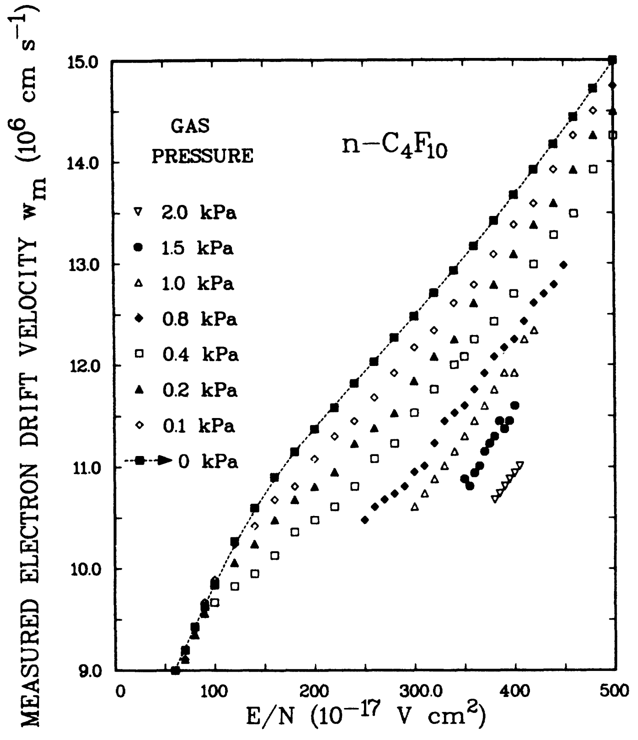

FIG. 5. Experimental w_m plotted as a function of E/N at selected gas pressures in n-C_4F_{10}. The dashed line represents the w_m values that have been obtained by extrapolating the measured values to zero gas pressure.

values to zero gas pressure (Fig. 3) and then correcting these values for electrode effects. These values will then not be affected by the pressure dependent nondissociative electron attachment processes in these two gases. Unfortunately, the pressure dependence in w_m due to nonequilibrium and boundary effects [Eq. (2)] are not accounted for by this procedure. At high E/N the w_m measurements for CF_4 and C_2F_6, which should possess similar dependences of w_m on P due to nonequilibrium and boundary effects since the electron scattering processes in all these molecules are similar, indicate that over the pressure range in which the measurements in C_3F_8 and n-C_4F_{10} were performed, extrapolating the w_m measurements in C_3F_8 and n-C_4F_{10} to zero gas pressure underestimates the true electron drift velocity by at most 3–5%. That is, the effect of nonequilibrium processes [Eq. (2)] is to increase w_m with increasing P while the pressure dependence in η/N leads to a decrease in w_m with increasing P. The values for the electron drift velocity w_m obtained by this procedure are given by the dashed lines in Figs. 2, 4, and 5. These w_m values for C_3F_8 and n-C_4F_{10} have been corrected for electron nonconservation processes [second correction term in Eq. (1)] using the same reasoning given above for CF_4 and C_2F_6 and are listed in Table I and plotted in Fig. 2 in comparison with the w measurements in CF_4 and C_2F_6. The electron nonconservation diffusion corrections to w_m, using the literature values[24] of D_T/μ and our previously measured α/N and η/N for C_3F_8 and n-C_4F_{10} values[6] are largest at $E/N=500\times10^{-17}$ V cm^2, being $\lesssim +6\%$ for both molecules. The corrections to w_m are considerably smaller at lower E/N values (Fig. 2) and are negligible at E/N values close to $(E/N)_{\mathrm{lim}}$. The $(E/N)_{\mathrm{lim}}$ values occur at $E/N\approx290\times10^{-17}$ V cm^2 for C_3F_8 and $E/N\approx280\times10^{-17}$ V cm^2 for n-C_4F_{10} at the gas pressure $P=0.05$ kPa.[6] At E/N values below $(E/N)_{\mathrm{lim}}$, assuming that $D_T/\mu=D_L/\mu$, the largest electron nonconservation diffusion correction to w_m at the highest gas pressures used is -4% for C_3F_8 at $E/N=140\times10^{-17}$ V cm^2 and -4% for n-C_4F_{10} at $E/N=120\times10^{-17}$ V cm^2. The actual corrections to w_m are considerably smaller for the same reasons outlined above for CF_4 and C_2F_6.

C. Comparison with previous measurements

The present electron-drift-velocity measurements in CF_4 are plotted in Fig. 6 in comparison with the previous literature values.[9,24,25] The present measurements in CF_4 are in excellent agreement with those of Snelson,[25] which were obtained using a modified time-of-flight experimental technique, over the E/N range 20×10^{-17} V cm^2 $<E/N<130\times10^{-17}$ V cm^2, but at lower E/N values the present results are significantly higher. Snelson's measurements were obtained over the limited gas pressure range 0.04 kPa $\lesssim P \lesssim 0.7$ kPa,[25] and the present measurements (Fig. 1) show that at $E/N\leq30\times10^{-17}$ V cm^2, w_m is dependent on gas pressure. Over the E/N range below the onset of electron at-

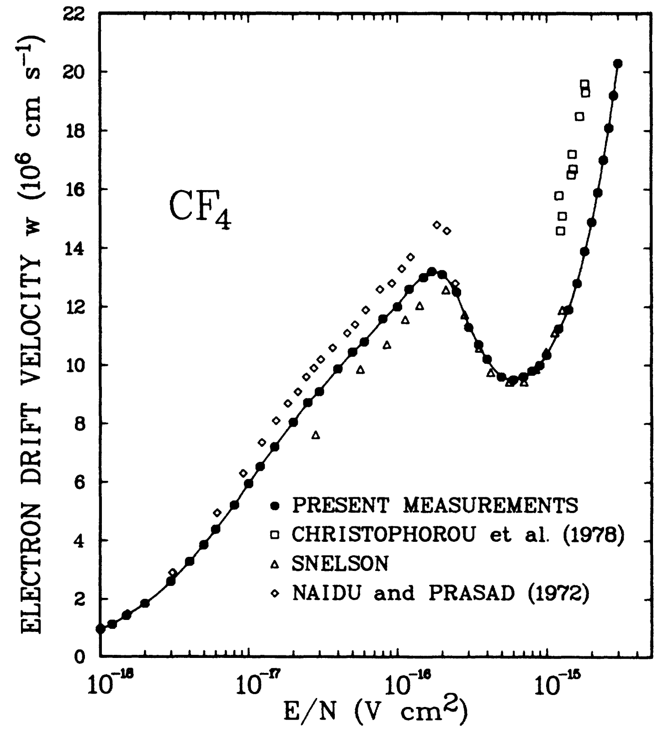

FIG. 6. Present electron drift velocity w in CF_4 plotted as a function of E/N in comparison with the previous measurements of Naidu and Prasad (Ref. 24), Snelson (Ref. 25), and Christophorou *et al.* (Ref. 9).

tachment ($E/N < 20\times10^{-17}$ V cm^2), the present measurements were performed at gas pressures up to 100 kPa, to overcome the influence of nonequilibrium and boundary effects on the drift velocity measurements. Measurements taken at similar gas pressures to those used by Snelson[25] give w_m values in very good agreement with his results over this E/N range. The measurements of Christophorou *et al.*[9] (which were obtained using a PT method similar in principle to the present technique) were determined from photographs of an oscilloscope trace of the voltage transient.

Large differences are observed between the present results and those obtained by Naidu and Prasad[24] for CF_4 (Fig. 6), and to a lesser but still significant extent for C_2F_6, C_3F_8, and n-C_4F_{10}. These differences are approximately equal to 50% for CF_4 at $E/N = 300\times10^{-17}$ V cm^2. The difference in the measurements is even greater than this as Naidu and Prasad did not apply the boundary diffusion correction at the drift tube shutters due to the electron nonconservation processes [second term in Eq. (1)].[24,26] The most likely reason for the differences in the results of Naidu and Prasad[24,26] and the present measurements is errors in the experimental technique of Naidu and Prasad which may be large at high E/N values. The major sources of error in that experiment were the measurements of the swarm transit time using oscilloscope tracings when the transit time was <0.5 μs (i.e., $w > 10^7$ cm s^{-1}), the finite width of the pulsed light source (half width approximately equal to 350 ns and rise time approximately equal to 250 ns) and high background ion currents (ion to electron current ratios as low as 1:1.03) which became worse at high E/N values.[26]

The low field ($E/N \leq 10\times10^{-17}$ V cm^2) density-normalized electron mobility $\mu N = w/(E/N)$ values for all four perfluoroalkanes are given in Fig. 7 in comparison with our recent μN measurements in CH_4.[13] The electron mobility measurements in the present study were performed at sufficiently low values of E/N ($E/N < 10^{-17}$ V cm^2) such that the electron swarms were in thermal equilibrium with the surrounding gas for CF_4 and C_2F_6 (and possibly C_3F_8). The density-normalized thermal electron mobility $(\mu N)_{\mathrm{th}}$ is constant under these conditions (Fig. 7), and the present values of $(\mu N)_{\mathrm{th}}$ for CF_4, C_2F_6, and C_3F_8 are listed in Table II.

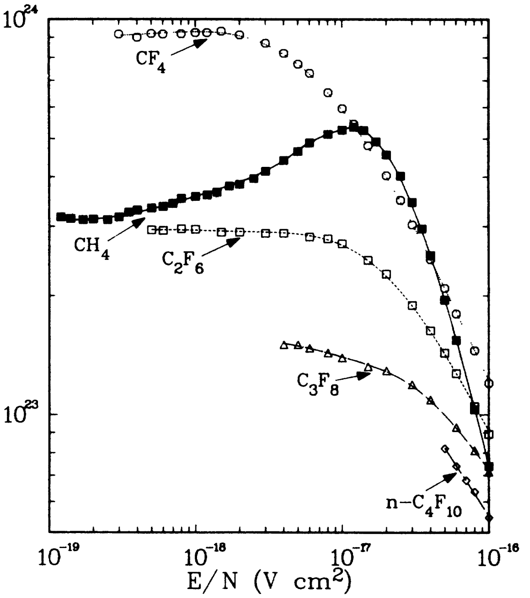

FIG. 7. Density-normalized electron mobility μN for CF_4, C_2F_6, C_3F_8, and n-C_4F_{10} plotted at low E/N values in comparison with the μN measurements in CH_4 obtained in a previous study (Ref. 13).

TABLE II. Density-normalized thermal electron mobility in CF_4, C_2F_6, C_3F_8, and n-C_4F_{10}. The value for CH_4 is taken from Ref. 13.

Molecule	Density-normalized thermal electron mobility μN (T=300 K) (10^{23} V^{-1}cm^{-1}s^{-1})
CF_4	9.2±(0.2)
C_2F_6	2.92±(0.05)
C_3F_8	$\geq$1.5±(0.1)
CH_4	3.12±(0.03)

The electrons are in thermal equilibrium with the surrounding gas at progressively higher E/N values, and the $(\mu N)_{\mathrm{th}}$ values decrease in magnitude with increasing molecular size for these perfluoroalkanes due primarily to an increase in the inelastic loss processes for these molecular at near-thermal electron energies.[20] It is interesting to note that both CF_4 and C_2F_6 have large μN values at $E/N \lesssim 10^{-17}$ V cm^2, comparable in magnitude to those of CH_4 (Fig. 7). Mixtures containing small percentages of either CF_4 or C_2F_6 in CH_4 are also expected to have high μN values near $E/N \approx 10^{-17}$ V cm^2 and, consequently, will have high electrical conductivities at these E/N values. At higher E/N values ($E/N > 2\times10^{-17}$ V cm^2), μN rapidly decreases with increasing E/N for all these molecules (Fig. 7). These characteristics are very desirable for the electron conduction and opening characteristics of the externally sustained diffuse discharge opening switches mentioned in Sec. I.[7,8]

IV. DISCUSSION

The most important features observed in the present electron-drift-velocity measurements for these four perfluoroalkane gases are the pronounced dependences of the measured electron drift velocities on the gas pressure and the NDC effects which have been observed in CF_4, C_2F_6, and to a lesser extent in C_3F_8. The origin of these effects are discussed below.

A. Pressure dependence in w_m

1. Boundary and nonequilibrium processes

The observed pressure dependence in w_m for all the perfluoroalkane gases at low E/N below the drift velocity maximum (i.e., $E/N < 50\times10^{-17}$ V cm^2 for CF_4, C_2F_6, and C_3F_8, and $<100\times10^{-17}$ V cm^2 for n-C_4F_{10} which does not possess a low E/N drift velocity maximum) and at high $E/N(>80\times10^{-17}$ V cm^2) for CF_4 and C_2F_6 is the result of nonequilibrium diffusion processes within the swarm and at the electrode boundaries of the drift chamber. The electron drift velocity w has been obtained in this situation using the analysis procedure outlined in Sec. III.

At high E/N values when electron nonconservation processes (i.e., electron attachment and ionization processes in the present measurements) are significant, a further correction to w_m has been made for all the perfluoroalkane gases due to the diffusion processes at the electrodes which are influenced by the nonconservation of electrons in the swarm [i.e., the second correction term in Eq. (1)].

2. *Pressure dependence in η/N*

A recent study by Blevin *et al.*[12] of the influence of nonthermal electron attachment processes on the electron transport parameters in a model gas identified two mechanisms by which pressure-dependent η/N coefficients can lead to pressure dependences in the electron transport coefficients in the gas. Although they discussed these mechanisms for a highly idealized gas where inelastic scattering processes were not considered and the momentum-transfer collision frequency $\nu_m(v)$ was assumed to possess only one of two functional dependences on the electron speed v [namely, $\nu_m(v)$ independent of v and $\nu_m(v)\propto v$, whereas in a real gas $\nu_m(v)$ will possess a considerably more complex dependence on v], these mechanisms are thought to be responsible for the observed pressure dependence in w_m at $E/N>100\times10^{-17}$ V cm^2 for both C_3F_8 and n-C_4F_{10} (Figs. 3–5). To aid in this discussion, the w_m measurements at the high ($P=3$ kPa for C_3F_8 and $P=2$ kPa for n-C_4F_{10}) and low ($P\rightarrow0$ kPa) gas pressures are plotted for C_3F_8 and n-C_4F_{10} in Figs. 8 and 9, respectively, in comparison with the ionization coefficients α/N and high and low pressure electron attachment coefficients η/N for these two molecules.[6]

(a) Magnitude of $\nu_a(v)$. Blevin *et al.*[12] have shown that the electron transport parameters (in particular, w and $\langle\varepsilon\rangle$) may be significantly affected by the size of the ratio of the electron attachment collision frequency $\nu_a(v)$ to the energy transfer collision frequency $\nu_\varepsilon(v)$ and the speed dependences of the momentum transfer $\nu_m(v)$ and attaching collision frequencies. This is particularly true for electronegative gases possessing nonthermal electron attachment processes such as the perfluoroalkanes studied in the present work.[1-6] In particular, they found that when $\nu_a(v)[=Nv\sigma_a(v)]$ peaked at energies below $\langle\varepsilon\rangle$ for both of the dependences of $\nu_m(v)$ on v studied in their work, low-energy electrons were preferentially re-

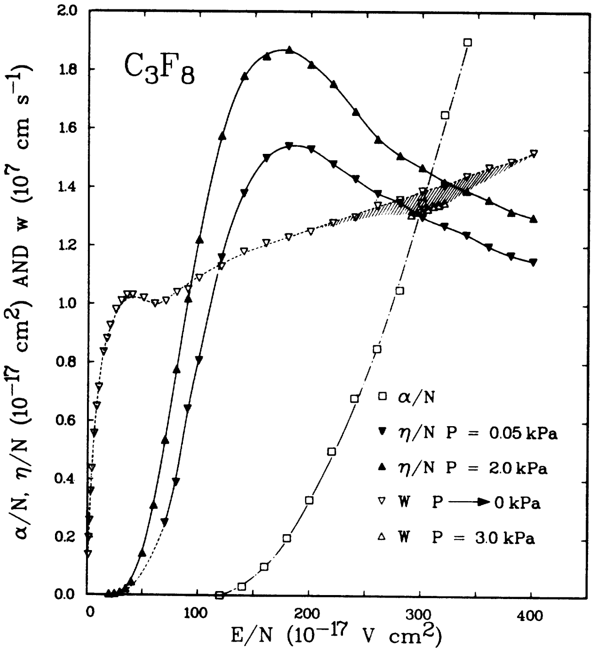

FIG. 8. Electron ionization coefficient α/N, high and low pressure electron attachment coefficient η/N, and high and low pressure electron drift velocity w in C_3F_8. The shaded region is the area over which pressure-dependent electron drift velocities have been observed.

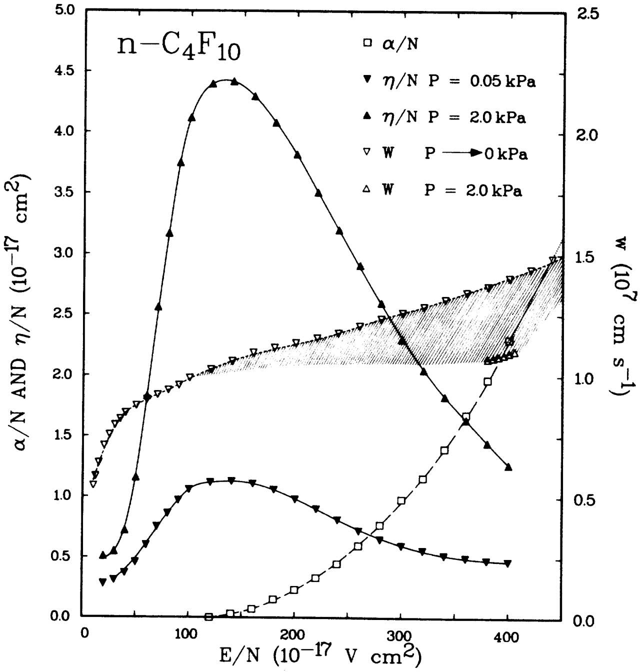

FIG. 9. Electron ionization coefficient α/N, high and low pressure electron attachment coefficient η/N, and high and low pressure electron drift velocity w in n-C_4F_{10}. The shaded region is the area over which pressure-dependent electron drift velocities have been observed.

moved from $f(\varepsilon, E/N)$, and $\langle \varepsilon \rangle$ increased when the magnitude of $\nu_a(v)$ increased. In the model calculations where $\nu_m(v) \propto v$, and $\nu_a(v)$ were comparable to $\nu_\varepsilon(v)$ [approximately equal to $(m/M)\nu_m(v)$ for this model], the electron drift velocity decreased with increasing $\nu_a(v)$. Although these calculations were performed for small $\nu_\varepsilon(v)$ (due to the neglect of inelastic scattering processes), nevertheless, the η/N coefficients of C_3F_8 and n-C_4F_{10} are large and the pressure dependence in η/N coefficients (Figs. 8 and 9) may affect the magnitude of w_m as a function of gas pressure due to this mechanism.

(b) Spatial variation in $\bar{\nu}_a(x)$. Belvin *et al.*[12] have also shown that the electron transport parameters in a gas can be substantially modified when spatial gradients in $\langle \varepsilon \rangle$ occur across the electron swarm in the direction (x) of the applied electric field. In these circumstances, the electron attachment and ionization collision frequencies [$\bar{\nu}_a(x)$ and $\bar{\nu}_i(x)$, respectively] are also spatially dependent within the electron swarm. These gradients in $\langle \varepsilon(x) \rangle$ can be significant even after the swarm has achieved equilibrium and the swarm-averaged transport and rate coefficients are independent of space and time.[27,28] When ionization processes are significant, the average ionization collision frequency $\bar{\nu}_i(x)$ (averaged over all electron speeds) has been shown to be highly spatially dependent within the swarm and can lead to an increase in the electron swarm drift velocity.[27–29] It thus seems likely that in an attaching gas, spatial gradients in $\langle \varepsilon \rangle$ for the electron swarm will lead to spatial dependences in $\bar{\nu}_a(x)$ (averaged over all electron speeds v) even though $\langle \bar{\nu}_a \rangle$ averaged over the whole swarm is constant. This, in turn, will displace the swarm centroid and hence will modify w and the other swarm transport parameters.[28] These modifications to the electron drift velocity are experimentally observable through a pressure dependence in either η/N or α/N.

For C_3F_8 and n-C_4F_{10} the greatest pressure dependence in w_m occurs at E/N values near $(E/N)_{\rm lim}$ and is not observed when α/N is negligibly small. The magnitude of the change in w_m with pressure correlates with the magnitude of the change in η/N with gas pressure for these two molecules. The experimental w_m values decrease significantly in n-C_4F_{10} (where there is a large increase in η/N) with increasing gas pressure, whereas a much smaller reduction in w_m is observed in C_3F_8 (which possesses a much smaller pressure dependence in η/N) with increasing gas pressure (Figs. 8 and 9). The molecules CF_4 and C_2F_6 possess only dissociative electron attachment processes and as a result η/N and $\bar{\nu}_a/N$ are independent of gas pressure.[2,6] Consequently, we have not observed a similar decrease in w_m with increasing gas pressure for these two molecules (in fact, w_m increases with increasing P for these molecules due to nonequilibrium processes in the electron swarm and diffusion corrections at the electrode boundaries; see Fig. 1). We interpret the decrease in w_m with increasing gas pressure in C_3F_8 and n-C_4F_{10} to be due to changes in $f(\varepsilon, E/N)$ with increasing gas pressure brought about by the effective increase in $\nu_a(v)$ with increasing P due to one or both of the mechanisms described above. The coefficients η/N and $\bar{\nu}_a/N$ are dependent on gas pressure for these two molecules due to the pressure-dependent parent anion formation processes mentioned in Sec. I.

Similar variations in w_m with gas pressure have recently been observed in 1-C_3F_6,[30] where w_m was found to possess an even larger dependence on P than has been observed in the present w_m measurements in C_3F_8 and n-C_4F_{10}. The molecule 1-C_3F_6 is also known to possess very strongly pressure-dependent parent anion formation processes over this pressure range.[31] The dependence of w_m on gas pressure in 1-C_3F_6 may, however, be complicated by the presence of short-lived dimeric species which could also cause w_m to decrease with increasing gas pressure.[30–32]

B. Origin of the observed NDC effects

1. Electron scattering processes

The most notable feature of the w measurements in these four perfluoroalkanes is the region of pronounced negative differential conductivity in CF_4 (Fig. 6) and to a lesser extent in C_2F_6 and C_3F_8. Negative differential conductivity may be defined to occur when $\partial w/\partial(E/N) < 0$, and recent studies of this phenomenon have quantified some of the conditions under which this effect may occur.[21,33]

A region of NDC will occur over a range of E/N values in a molecular gas when the gas possesses a large inelastic loss process which peaks at energies just above the threshold and then either remains constant or decreases with increasing electron energy. A second condition which will enhance the NDC effect is when $\sigma_m(v)$ is a rapidly increasing function of the electron speed v (or the electron energy ε). Consequently, NDC effects will be observed when the average momentum-transfer collision frequency $\langle \nu_m \rangle$ rapidly increases and the average inelastic collision frequency $\langle \nu_{\rm in} \rangle$ rapidly decreases with increasing E/N.

The molecule CF_4 is known to possess a Ramsauer-Townsend minimum in $\sigma_m(\varepsilon)$ at electron energies near 0.16 eV and a steeply rising $\sigma_m(\varepsilon)$ to the high-energy side of the minimum,[34–36] similar in shape but smaller in magnitude to that which has previously been observed in CH_4. Studies have also shown that CF_4 possesses large vibrational inelastic cross sections with thresholds approximately equal to 0.11 and 0.16 eV which decrease, or at least remain constant, at higher energies.[34–38] Recent Boltzmann equation calculations[20] of the electron motion in CF_4 and C_2F_6 have also demonstrated that both CF_4 and C_2F_6 possess a Ramsauer-Townsend minimum in their $\sigma_m(\varepsilon)$ scattering cross sections at low electron energies and large vibrational excitation cross sections which rapidly diminish in size at electron energies higher than that of the peak in the vibrational cross section (i.e., $\varepsilon > 0.3$ eV).[20] The similarity of the electron scattering processes in CH_4, CF_4, C_2F_6, and the other perfluoroalkanes in this study at high electron energies, and the electron transport and rate coefficients at lower electron energies, would indicate that C_3F_8 and possibly n-C_4F_{10} also possess similar, but smaller, Ramsauer-Townsend minima in $\sigma_m(\varepsilon)$ and large vibrational excitation cross sections at low electron energies leading to the NDC effects which we have observed in this series of molecules.

2. Magnitude of speed dependence of $\nu_a(v)$

Another possible mechanism which may at least partially account for the NDC effects which have been observed in these molecules is the influence of the electron attachment and ionization processes on the electron energy distribution function $f(\varepsilon,E/N)$ for these molecules. The study of Blevin *et al.*[12] has shown that for a nonthermal electron attachment process, when $\nu_a(v)$ is comparable to $\nu_\varepsilon(v)$, the electron drift velocity will be reduced by the presence of the electron attachment process, while previous studies[27–29] have shown that w will be increased when electron impact ionization is significant. Although the study by Belvin *et al.* considered only elastic electron scattering [i.e., $\nu_\varepsilon(v)$ was small compared with $\nu_m(v)$ in that study, while for the perfluoroalkanes in the present study, $\nu_\varepsilon(v)$ will be considerably larger due to the presence of large inelastic scattering processes], nevertheless, the magnitude of the electron attachment processes in C_3F_8 and n-C_4F_{10} are large enough to lead to significant changes in w_m due to the increase in η/N with gas pressure. Consequently, w_m may be reduced in all four perfluoroalkane gases due to the presence of the electron attachment process when electron impact ionization is absent, while at higher E/N when ionization is significant, w_m may be increased.

Further work is required to demonstrate the relative significance of these processes in influencing the magnitude and E/N dependence of the electron drift velocities in the four perfluoroalkane gases studied in the present work.

V. CONCLUSION

The electron-drift-velocity measurements reported in this paper have aided our understanding of the electron scattering processes in the perfluoroalkane series of molecules in several ways. Firstly, they have helped to elucidate the low-energy electron scattering processes in these molecules and indicate the existence of low-energy Ramsauer-Townsend minima in the momentum-transfer cross sections for CF_4, C_2F_6, C_3F_8, and possibly n-C_4F_{10}, along with large vibrational excitation processes near the minimum in σ_m of these molecules. These measurements have also highlighted the intricate effects that electron nonconservation processes can have on the electron energy distribution function and, consequently, on the electron transport parameters in these gases. Boltzmann equation analyses of the electron motion in gases, in which nonconservation processes and pressure-dependent-ion–molecule reactions occur, such as those outlined here and in other studies,[1–6,27–32,39] must be performed carefully if accurate electron scattering cross sections are to be deduced from electron transport and rate coefficient data. Significant errors can occur in these calculations unless proper account is taken of the effect on the electron energy distribution function $f(\varepsilon,E/N)$ of the loss or gain of electrons in the electron swarm.

Pressure-dependent electron drift velocities have been observed in C_3F_8 and n-C_4F_{10} for the first time at gas pressures ($P < 5$ kPa) well below those required for the observation of the effects of multiple scattering on w.[32] The dependence of w on gas pressure in these gases is interpreted as resulting from the strong pressure-dependent electron attachment coefficients η/N we have previously observed in C_3F_8 and n-C_4F_{10} but which are absent in CF_4 and C_2F_6.[1–6] These measurements will aid the ongoing effort to model the electron energy gain and loss processes in these gases which are interesting from a fundamental standpoint and also for the understanding of the gas discharge processes in several applied studies.

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