ELECTRON DRIFT VELOCITIES AND ELECTRON ATTACHMENT COEFFICIENTS IN PURE CHF_3 AND ITS MIXTURES WITH ARGON

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ABSTRACT

Measurements are reported of (*i*) the electron drift velocity in pure trifluoromethane (CHF_3) gas and in its mixtures with argon, and (*ii*) electron attachment in pure CHF_3. The electric field-to-gas density ratio (*E/N*) dependence of the electron drift velocity in the mixtures exhibits regions of distinct negative differential conductivity. The values of the electron attachment coefficients in pure CHF_3 are small and decrease with *E/N*. The measurements were made at room temperature and cover the *E/N* range from 0.05×10^{-17} V cm^2 to 60×10^{-17} V cm^2 (0.05 Td to 60 Td, 1 Td = 10^{-17} V cm^2). The electron attachment rate constant is virtually independent of *E/N* below about 50×10^{-17} V cm^2 and equal to ~ 13×10^{-14} cm^3 s^{-1}. This small attachment rate constant may be due to impurities.

INTRODUCTION

The CHF_3 molecule is polar, and its electric dipole moment is 5.504×10^{-30} C m (1.65 debye).[1] It has been studied in the past as a polar buffer gas in dielectric gas mixtures with electronegative components.[2] It is also used as a plasma processing gas in place of CF_4 in view of its lower global warming potential and lifetime in the atmosphere.[3] Very limited electron collision cross section and electron transport coefficient data are available for this gas,[3] although recently there has been a new report on measurement of the total electron scattering cross section[4] for CHF_3 and also another report on the electron transport coefficients in mixtures of CHF_3 with argon.[5]

In an effort to fill the need for data on electron interactions with CHF_3, we measured electron drift velocities in pure CHF_3 and in mixtures of CHF_3 with Ar (percentages of CHF_3 in argon ranged from 0.1 % to 10 %) for electric field-to-gas density ratios (*E/N*) ranging from ~ 0.05×10^{-17} V cm^2 to ~ 60×10^{-17} V cm^2. Measurements were also made of the electron

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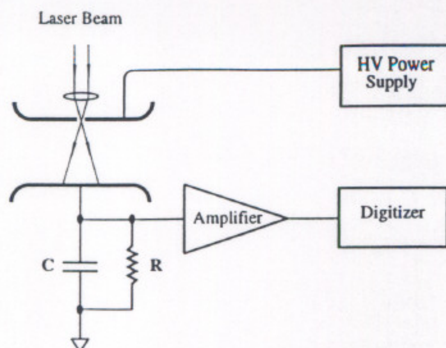

Fig. 1. Schematic diagram of the operating principle of the pulsed Townsend technique as employed in the present study.

attachment coefficient in pure CHF_3. The measurements with the gas mixtures can aid Boltzmann transport equation analyses aimed at calculating collision cross section sets for the CHF_3 molecule. They may also find use in particle radiation detectors.

EXPERIMENTAL METHOD

The experimental method employed is a pulsed Townsend technique with electron swarms photoelectrically produced using a 5 ns, frequency quadrupled (266 nm) Nd:YAG laser. A schematic diagram showing its operating principle is given in Fig. 1. The two parallel electrodes are circular stainless steel disks 6.2 cm in diameter. They are separated by a distance of 1.664 cm and are contained in a six-way cubic stainless steel chamber. The laser beam entering the chamber through a sapphire window is focused with a converging lens through a small hole (~0.6 mm diameter) at the center of the anode electrode before striking the cathode electrode. The induced current due to the motion of the electrons in the drift region is integrated by the RC (R = 100 GΩ and C ~50 pF) circuit in front of a high-impedance, unity-gain, buffer amplifier with a slew rate of 0.22 V/ns. The output voltage of the amplifier is then digitized by a digital oscilloscope with a resolution of 8 bits and a maximum sample rate of 10^8 samples/s. To minimize the influence of the AC line noise, laser pulses are synchronized with the zero-crossings of the AC line voltage. The synchronization scheme allows subtraction of the line noise and thus improves the overall performance of the pulsed Townsend method.

A typical voltage waveform is shown in Fig. 2(a). It was acquired in a 1% CHF_3 + 99% Ar mixture with a gap voltage of 200 V and a total pressure of 1.33 kPa (10 Torr). The intersection between a line fitted to the rising signal and a line fitted in the plateau region gives the electron transit time, $t = 0.522\ \mu s$. The smooth transition is caused by the thermal diffusion of electrons. Figure 2(b) shows a waveform that was obtained at 100 V with the chamber under vacuum. It shows that the rise time of the electronic system is shorter than 20 ns. The estimated uncertainty for the measured electron transit time and the drift velocity is ±5%, due primarily to the uncertainty in determining the intersection points of the measured waveform.

All measurements were made at room temperature (about 298 K) at pressures ranging from 1.33 kPa to 66.7 kPa. Both the CHF_3 and the Ar gases were high purity (i.e., research grade). However, both gases had to be purified further by fractional distillation. This was found to be necessary as can be seen from the measurements on "pure" argon shown in Fig. 3.

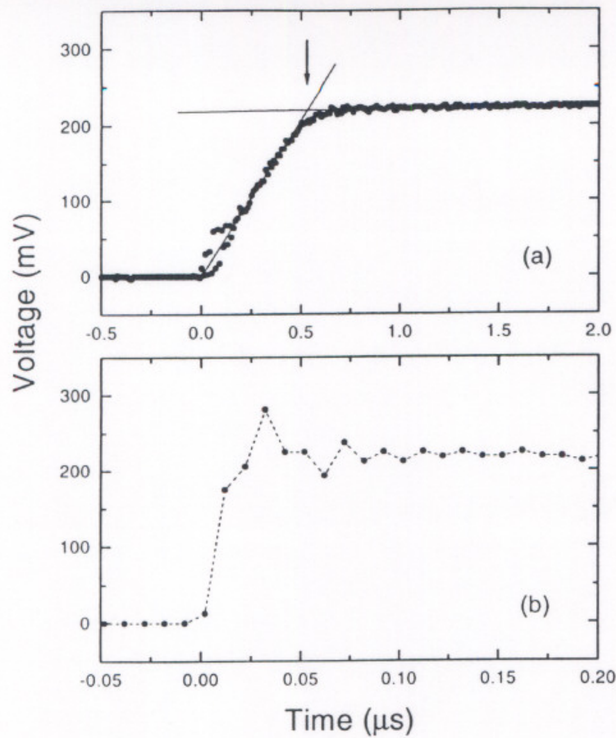

Fig. 2. (a) Typical voltage waveform ($E/N = 37 \times 10^{-17}$ V cm^2; P_{total} = 1.33 kPa; 1 % CHF_3 + 99 % Ar). (b) Waveform with the chamber under vacuum (applied voltage = 100 V).

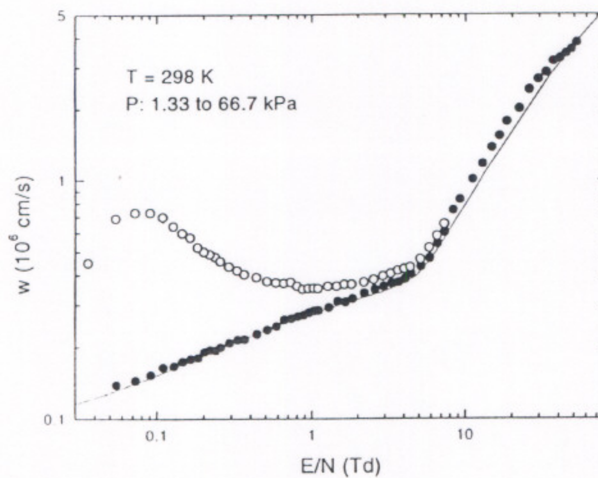

Fig. 3. Electron drift velocity, w, as a function of E/N in pure argon. ∘, "ultra high purity argon" (quoted purity 99.999 %) used as received; •, the same measurements after gas purification by several freeze-pump-thaw cycles; (—), average of values as given in Ref. 6.

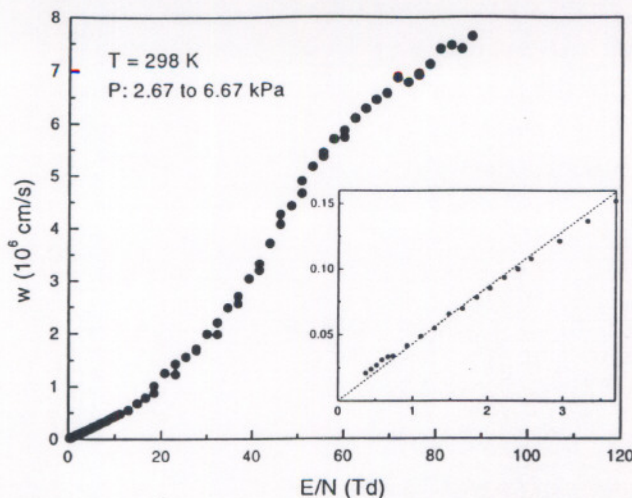

Fig. 4. Electron drift velocity, w, as a function of E/N for purified CHF_3. Inset: Comparison of the present measurements (●) with the w values reported earlier[2] for $E/N \leq 3.69 \times 10^{-17}$ V cm^2 (- - -).

The measurements on the ultra-high purity gas (quoted purity 99.999 %) used as provided by the manufacturer clearly show the effect of impurities. Upon purification by fractional distillation the measured electron drift velocities agreed with those reported in the literature.[6] The total pressures and the mixture ratios were measured using two temperature-controlled, high accuracy capacitance manometers. The estimated measurement uncertainty for the total pressure, the mixture ratio, and E/N is less than ±1%.

RESULTS AND DISCUSSION

Electron Drift Velocity, w, as a Function of E/N

In Fig. 4 are shown the present measurements of the electron drift velocity, w, in pure CHF_3 taken at pressures ranging from 2.67 kPa to 6.67 kPa. There are no other data to compare these measurements with besides an earlier value of the slope of the w versus E/N line measured[2] at low E/N ($<3.69 \times 10^{-17}$ V cm^2) where the electrons are in thermal equilibrium with the gas and w varies linearly with E/N. This is shown by the broken line in the inset of Fig. 4. It is in good agreement with the present measurements.

In Fig. 5 are shown the measured electron drift velocities in mixtures of CHF_3 with argon containing 0.1 %, 0.5 %, 1 %, 5 %, and 10 % of CHF_3. For comparison, the $w(E/N)$ for pure CHF_3 and for pure argon are also shown. The most distinct characteristic of the $w(E/N)$ data for the mixtures are the regions of pronounced negative differential conductivity and its dependence on mixture composition. The values, $(E/N)_{max}$, of E/N at which the w is maximum are plotted in Fig. 6 as a function of the percentage of the CHF_3 in the mixture. If one assumes that the drift velocity maxima are the result of electrons scattered by CHF_3 (principally through inelastic vibrational excitation of the CHF_3 molecules) into the energy region where the electron scattering cross section in argon has a minimum (~ 0.23 eV), the values of $(E/N)_{max}$ would represent the E/N value at which the average electron energy in the mixture is ~0.23 eV. Interestingly, this value increases linearly with the percentage of CHF_3 in Ar for the percentages used. If the linear dependence observed in Fig. 6 holds all the way to pure CHF_3,

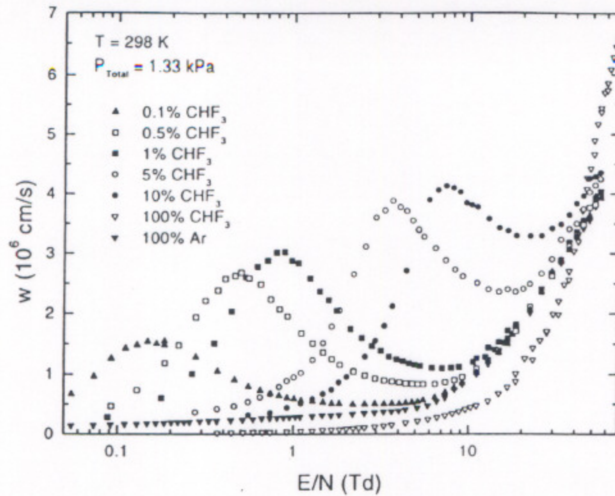

Fig. 5. Electron drift velocity, *w*, as a function of *E / N* for mixtures of CHF_3 and argon at the following compositions: 0.1 % CHF_3 +99.9 % Ar (▴), 0.5 % CHF_3 + 99.5 % Ar (□), 1 % CHF_3 + 99 % Ar (■), 5 % CHF_3 + 95 % Ar (○), and 10 % CHF_3 + 90 % Ar (●). For comparison the drift velocities in pure CHF_3 (▿) and pure argon (▾) are shown.

it would indicate that the maximum in the *w(E/N)* for pure CHF_3 should be at an *E/N* value of about 75×10^{-17} V cm^2. This value is not inconsistent with the measurements in Fig. 5. However, the drift velocity maximum in pure CHF_3 may not be as distinct as those in the low-concentration mixtures because the data indicate that the minima in the *w* versus *E/N* dependence become shallower as the percentage of CHF_3 in Ar is increased. The data in Fig. 5 can be useful in Boltzmann code analyses, as studies of other gases have indicated.[7,8]

Electron Attachment in Pure CHF_3

In Fig. 7 are shown preliminary measurements of the electron attachment coefficient, η/N, in pure CHF_3 as a function of *E/N* for a number of CHF_3 pressures. These are the average of three runs. The *w(E/N)* data for pure CHF_3 in Fig. 4 and the data on η/N *(E/N)* in pure CHF_3 in Fig. 7 have been used to determine the electron attachment rate constant

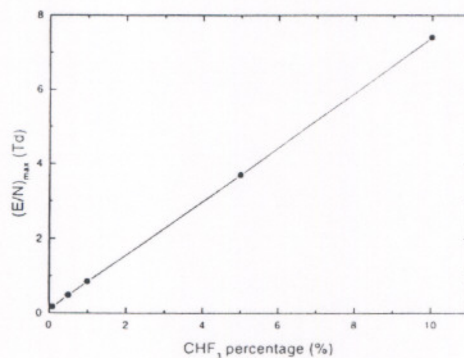

Fig. 6. $(E/N)_{max}$ versus CHF_3 volume fraction (in percent).

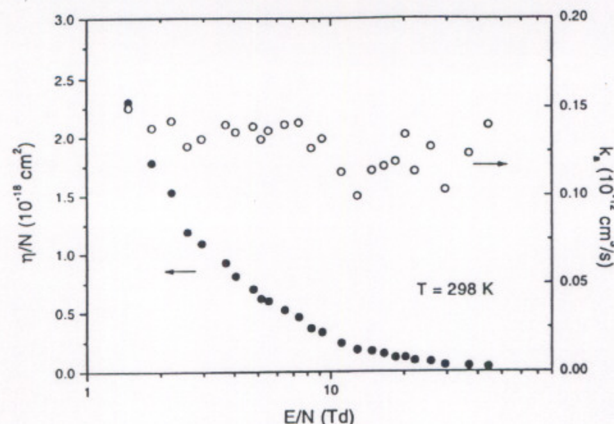

Fig. 7. Electron attachment coefficient, η/N, (●) and electron attachment rate constant, k_a, (○) as a function of *E/N* for pure CHF_3 measured at T = 298 K. Average values at three pressures (3.34 kPa, 6.67 kPa, and 13.3 kPa).

$$k_a(E/N) = \eta/N\,(E/N) \times w(E/N)$$

as a function of *E/N*. These are shown in Fig. 7 by the open circles. The values of k_a are virtually independent of *E/N* at about $13 \times 10^{-14}\ cm^3 s^{-1}$. Earlier electron swarm studies at only thermal energies showed that the thermal electron attachment rate constant for CHF_3 is less than about $6 \times 10^{-14}\ cm^3\ s^{-1}$ (see Ref. 3). Although efforts have been made to purify the gas by fractional distillation, it is not certain that the observed attachment is due to the CHF_3 molecule itself or due to possible residual traces of strongly electron attaching impurities. The CHF_3 molecule has not been reported to have a positive electron affinity. Its lowest negative ion state is at ~4.5 eV above the ground state of the neutral molecule, that is, the lowest vertical electron affinity of the CHF_3 molecule is about −4.5 eV. Earlier electron beam studies discussed in Ref. 3 showed that negative ions (mostly F^-) are produced by dissociative electron attachment and begin at about 2.2 eV. These are much higher energies than those expected in the present swarm study. It is highly unlikely that the observed attachment is due to dissociative electron attachment to the CHF_3 molecule. Clearly, electron attachment to CHF_3 is very weak or absent below about $50 \times 10^{-17}\ V\ cm^2$.

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