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Electron drift and attachment in CHF_3 and its mixtures with argon

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Abstract

Measurements are reported of the electron drift velocity, w, in CHF_3 gas and in its mixtures with argon. The E/N dependence of w in the mixtures exhibits regions of distinct negative differential conductivity. A small electron attachment rate constant ($\sim 13 \times 10^{-14}$ cm^3 s^{-1} for density-reduced electric fields, $E/N < 50 \times 10^{-17}$ V cm^2) has been measured, which may be due to impurities. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Trifluoromethane (CHF_3) is a plasma-processing gas used in place of CF_4 in view of its lower global-warming potential and lifetime in the environment. In spite of this, there exist virtually no electron-transport data for this molecule [1]. In an effort to fill the need for data on electron interactions with CHF_3, we have measured electron drift velocities in CHF_3 and in mixtures of CHF_3 with Ar (the volume fraction of CHF_3 in argon was varied from 0.1% to 10%) over the electric field-to-gas density ratio, E/N, from 0.05×10^{-17} to 60×10^{-17} V cm^2 (0.05–60 Td). Measurements were also made of the electron attachment rate constant in CHF_3. Both the electron drift velocity and the electron attachment measurements are compared with limited data from other laboratories. The measurements of $w(E/N)$ for the mixtures of CHF_3 in argon can aid Boltzmann-transport-equation analyses aimed at calculating collision cross-section sets for CHF_3.

The experimental method employed is the pulsed Townsend technique [2], and the experimental apparatus is the same as used previously for similar measurements in CCl_2F_2 [3]. Electron swarms were photoelectrically produced at the cathode using a 5 ns, frequency-quadrupled (266 nm) Nd:YAG laser. The two electrodes of the parallel-plate drift arrangement employed are circular stainless steel disks of 6.2 cm diameter separated by a distance of 1.664 cm. The laser beam enters the chamber through a sapphire window and is focused by a converging lens through a small hole (0.6 mm diameter) in the center of the anode before striking the cathode. The induced current due to the motion of the electrons between the cathode and the anode is integrated by an RC ($R = 100$ GΩ and $C \approx 50$ 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

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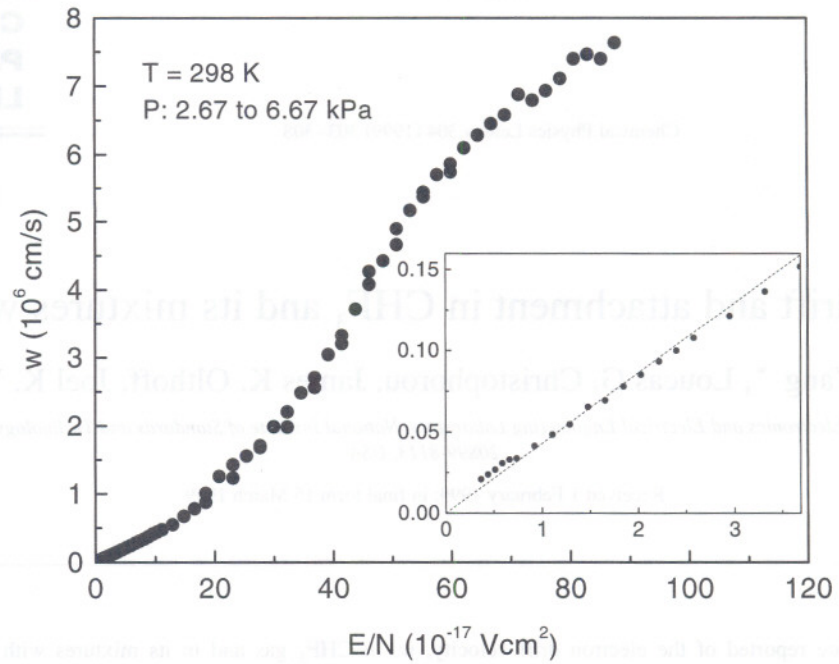

Fig. 1. Electron drift velocity, w, as a function of E/N for purified CHF_3. Inset: Comparison of the present measurements (●) with the w values reported earlier (Ref. [4]) for $E/N \leqslant 3.69 \times 10^{-17}$ V cm^2 (- - -).

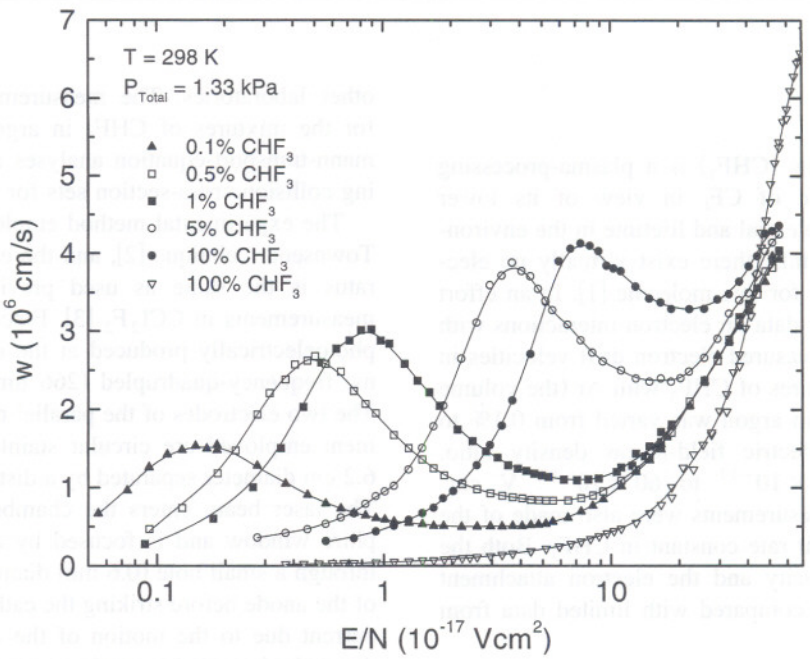

Fig. 2. Electron drift velocity, w, as a function of E/N for volume mixtures of CHF_3 and argon at the following compositions: 0.1% CHF_3 + 99.9% Ar (▲), 0.5% CHF_3 + 99.5% Ar (□), 1% CHF_3 + 99% Ar (■), 5% CHF_3 + 95% Ar (○), and 10% CHF_3 + 90% Ar (●). For comparison the drift velocities in 100% CHF_3 (▽) are also shown. The solid lines are weighted-least-squares fits to the data.

Table 1
Values of drift velocities (in units of 10^6 cm/s) in CHF_3 and in its mixtures with argon as a function of E/N determined from fits to the measured data shown in Fig. 2

E/N	CHF_3 concentration by volume					
(10^{-17} V cm^2)	0.1%	0.5%	1%	5%	10%	100%
0.06	0.75	–	–	–	–	–
0.07	0.92	–	–	–	–	–
0.08	1.08	–	–	–	–	–
0.09	1.22	–	0.259	–	–	–
0.10	1.33	0.527	0.311	–	–	–
0.12	1.45	0.716	0.412	–	–	–
0.14	1.51	0.878	0.501	–	–	–
0.16	1.52	1.03	0.594	–	–	–
0.18	1.51	1.17	0.683	–	–	–
0.20	1.49	1.34	0.780	–	–	–
0.23	1.41	1.58	0.918	–	–	–
0.26	1.31	1.82	1.07	–	–	–
0.30	1.21	2.08	1.28	0.374	–	–
0.34	1.12	2.30	1.49	0.400	–	–
0.40	1.01	2.50	1.83	0.434	–	0.022
0.44	0.941	2.60	2.06	0.457	–	0.024
0.50	0.863	2.63	2.36	0.498	–	0.027
0.60	0.764	2.52	2.72	0.575	0.321	0.031
0.70	0.699	2.34	2.88	0.654	0.358	0.035
0.80	0.653	2.14	2.97	0.753	0.392	0.038
0.90	0.618	1.97	2.97	0.859	0.427	0.042
1.0	0.589	1.83	2.87	0.945	0.469	0.046
1.2	0.557	1.59	2.63	1.13	0.554	0.054
1.4	0.536	1.42	2.39	1.40	0.636	0.061
1.6	0.519	1.29	2.20	1.70	0.730	0.070
1.8	0.508	1.19	2.01	2.00	0.837	0.077
2.0	0.503	1.12	1.85	2.32	0.946	0.085
2.3	0.499	1.04	1.67	2.77	1.12	0.097
2.6	0.500	0.981	1.55	3.15	1.31	0.110
3.0	0.502	0.927	1.43	3.55	1.59	0.127
3.4	0.504	0.895	1.33	3.76	1.90	0.144
4.0	0.509	0.864	1.24	3.79	2.40	0.170
4.4	0.517	0.849	1.20	3.69	2.74	0.188
5.0	0.536	0.838	1.16	3.46	3.21	0.213
6.0	0.594	0.840	1.11	3.16	3.83	0.254
7.0	0.667	0.860	1.10	2.97	4.08	0.297
8.0	0.749	0.895	1.11	2.78	4.09	0.343
9.0	0.838	0.952	1.13	2.65	3.97	0.386
10.0	0.935	1.02	1.18	2.56	3.84	0.432
12.0	1.12	1.17	1.32	2.45	3.66	0.528
14.0	1.30	1.33	1.45	2.39	3.50	0.648
16.0	1.48	1.51	1.60	2.38	3.39	0.786
18.0	1.72	1.68	1.75	2.38	3.33	0.942
20.0	1.91	1.86	1.90	2.41	3.30	1.11
23.0	2.15	2.16	2.16	2.53	3.30	1.36
26.0	2.40	2.39	2.39	2.69	3.34	1.60
30.0	2.69	2.67	2.69	2.97	3.42	1.95
34.0	2.92	2.95	2.96	3.25	3.55	2.36
40.0	3.27	3.28	3.35	3.52	3.79	3.14
44.0	3.49	3.50	3.55	3.75	4.00	3.75
50.0	3.79	3.78	3.84	4.08	4.24	4.68
60.0	–	–	–	–	–	5.84
70.0	–	–	–	–	–	6.70
80.0	–	–	–	–	–	7.25

amplifier is then digitized with a LeCroy 9420 [1] digital oscilloscope which has 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 line voltage. This synchronization scheme allows subtraction of the line noise and thus improves the overall performance of the pulsed Townsend method.

All $w(E/N)$ measurements were made at room temperature (~ 298 K) at pressures ranging from 1.33 to 6.67 kPa (10–50 Torr), and have an estimated uncertainty of $\pm 5\%$. The highest values of E/N at which measurements were made were limited by breakdown in our apparatus. The CHF_3 and the Ar gases were of research grade, but both were further purified by fractional distillation before use.

2. Electron drift velocity, w, as a function of E/N

Fig. 1 shows the present $w(E/N)$ measurements in CHF_3 taken at pressures ranging from 2.67 to 6.67 kPa. The low values of w for CHF_3 at low E/N, as compared to CF_4 [5], are due to the large scattering cross-section caused by the large permanent electric dipole moment (5.504×10^{-30} C m = 1.65 D) [6] of CHF_3. There are no other electron transport data with which to compare these measurements except an earlier value of the slope of w versus E/N line measured [4] at low E/N ($< 3.69 \times 10^{-17}$ V cm^2). At this low E/N, the electrons are in thermal equi-

[1] The identification of commercial equipment and their sources is made to foster understanding. In no case does this identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the instrument is the best available.

librium with the gas, and thus w varies linearly with E/N. This early measurement is shown by the broken line in the inset of Fig. 1 and is in good agreement with the present measurements.

Fig. 2 shows the measured values of $w(E/N)$ in mixtures of CHF_3 with argon containing 0.1%, 0.5%, 1%, 5% and 10% of CHF_3 by volume. The data from Fig. 1 for 100% CHF_3 are also shown for comparison. The solid lines are fits to the data, and values from these curves are listed in Table 1. There has been a recent conference report [7] of measurements of $w(E/N)$ for a number of CHF_3 mixtures in argon with CHF_3 volume fractions below 2%. These measurements can be compared with our data for the two common mixture concentrations of 0.1% and 1% (Fig. 3). The measurements of Clark et al. [7] have a reported uncertainty of less than $\pm 5\%$. The two sets of measurements are in reasonable agreement for the 0.1% mixture, but they differ for the 1% mixture. The relative shift in the two measurements may reflect a difference in mixture composition.

The most distinct characteristic of the $w(E/N)$ data for the mixtures of CHF_3 in argon is the region of pronounced negative differential conductivity and its dependence on mixture composition. The minima in the w versus E/N dependence become shallower as the percentage of CHF_3 in argon is increased. The values of E/N at which the w exhibits a local maximum, $(E/N)_{max}$, vary considerably with mixture composition over the concentration range from 0.1% to 10% covered in the present measurements. Interestingly, for the low-concentration mixture compositions in this work, $(E/N)_{max}$ varies linearly with the percentage of CHF_3 in argon as can be seen in Fig. 4. If one assumes that the local drift velocity maxima are the result of electrons being 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) [8], the values of $(E/N)_{max}$ would represent the E/N value at which the mean electron energy for a given gas mixture is ~ 0.23 eV. Indeed, calculations have indicated [7] that the mean energy at which the drift velocity is maximum varies little with mixture composition (from 0.27 eV for 0.1% to 0.42 eV for 2%, the

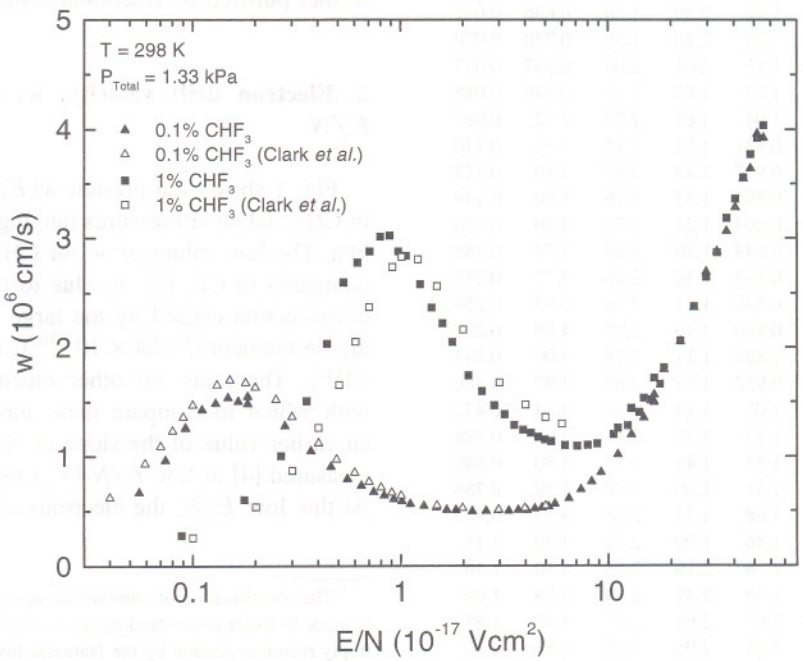

Fig. 3. Comparison of the electron drift velocity, w, in 0.1% CHF_3 + 99.9% Ar and 1% CHF_3 + 99% Ar as measured in the present study (▲, ■) and in the study by Clark et al. [7] (△, □). Typical uncertainties for each experiment are $\pm 5\%$.

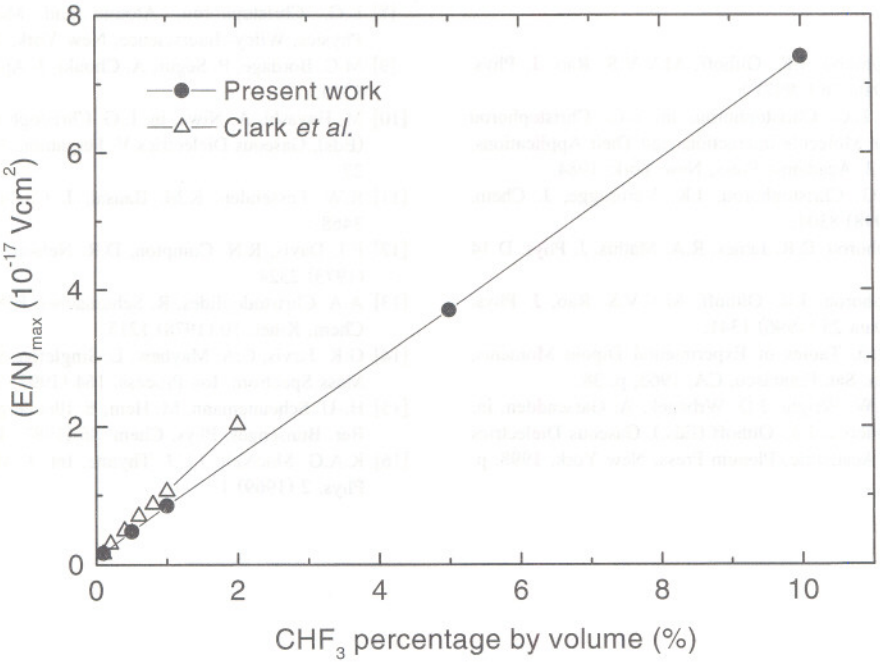

Fig. 4. $(E/N)_{max}$ versus CHF_3 volume percentage (see text): (●), present work; (△), Clark et al. [7].

corresponding values of $(E/N)_{max}$ at these mixture compositions being 0.16×10^{-17} V cm^2 and 2.03×10^{-17} V cm^2, respectively). The CHF_3 data in Table 1 can be useful in Boltzmann code analyses as studies of this [7] and other gases [9,10] have indicated.

3. Electron attachment in CHF_3

We have measured an electron attachment rate constant $k_a(E/N)$ for 100% CHF_3 equal to about 13×10^{-14} cm^3 s^{-1}, which is virtually independent of E/N for E/N values between 1.5×10^{-17} and 50×10^{-17} V cm^2. Earlier electron-swarm studies at only thermal energies [11–13] have shown that the thermal electron attachment rate constant for CHF_3 is less than 6×10^{-14} cm^3 s^{-1} (see Ref. [1]). Similarly, a recent electron-swarm mass spectrometric study [14] indicated a small value for the density-normalized electron attachment coefficient ($< 10^{-18}$ cm^2). In contrast to these measurements, the measurements of Clark et al. [7] indicate values of $k_a(E/N)$ for this molecule more than 10 times higher. In the present study, although efforts were made to purify the gas by fractional distillation, it is not certain whether the observed small electron attachment is due to the CHF_3 molecule itself or possibly to 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 [1,15,16] showed that negative ions (mostly F^-) are produced by dissociative electron attachment processes having energy thresholds in excess of 2.2 eV (values of 2.2 ± 0.3 eV [15] and 2.9 eV [16] have been reported). These are much higher electron energies than those observed in either the present swarm study, or the swarm study of Clark et al. [7]. Therefore we conclude that electron attachment to CHF_3 is very weak or absent for $E/N < 60 \times 10^{-17}$ V cm^2, and is certainly much less than indicated by the study of Clark et al. [7].

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